

HRMAS NMR Analysis in Neat Ionic Liquids: a Powerful Tool to Investigate Complex Organic Molecules and Monitor Chemical Reactions

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Experimental

Compounds **1**, **2** and **3** were purchased from Acros Organics; compounds **4** and **5** were synthesized starting from commercial *p*-methoxy-benzyl alcohol and methyl- α -D-glucopyranoside according to standard procedures. The concentration of the samples, dissolved in deuterated solvents or in neat ILs, was always 0.2 M.

All NMR experiments were carried out on a Bruker Avance 500 MHz: experiments with the multinuclear 5-mm QNP probe were performed both with internal and external (coaxial capillary) deuterium lock; experiments with the HRMAS probe (50 μ L ZrO₂ rotor, maximum MAS rotation of 15 KHz) were performed with internal lock, using the 6% of deuterated solvent (d6-acetone).

Reference for the ¹H spectra was taken from TMS signal, that resulted always consistent with the central peak of the lock solvent.

All the experiments were performed at 303 K, while an increment of 1 K per KHz was considered working with HRMAS probe.

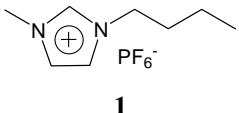
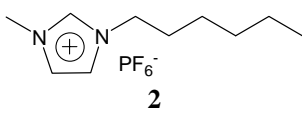
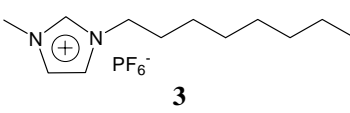
The monitoring of the chemical reaction through HRMAS technique was performed as follow:

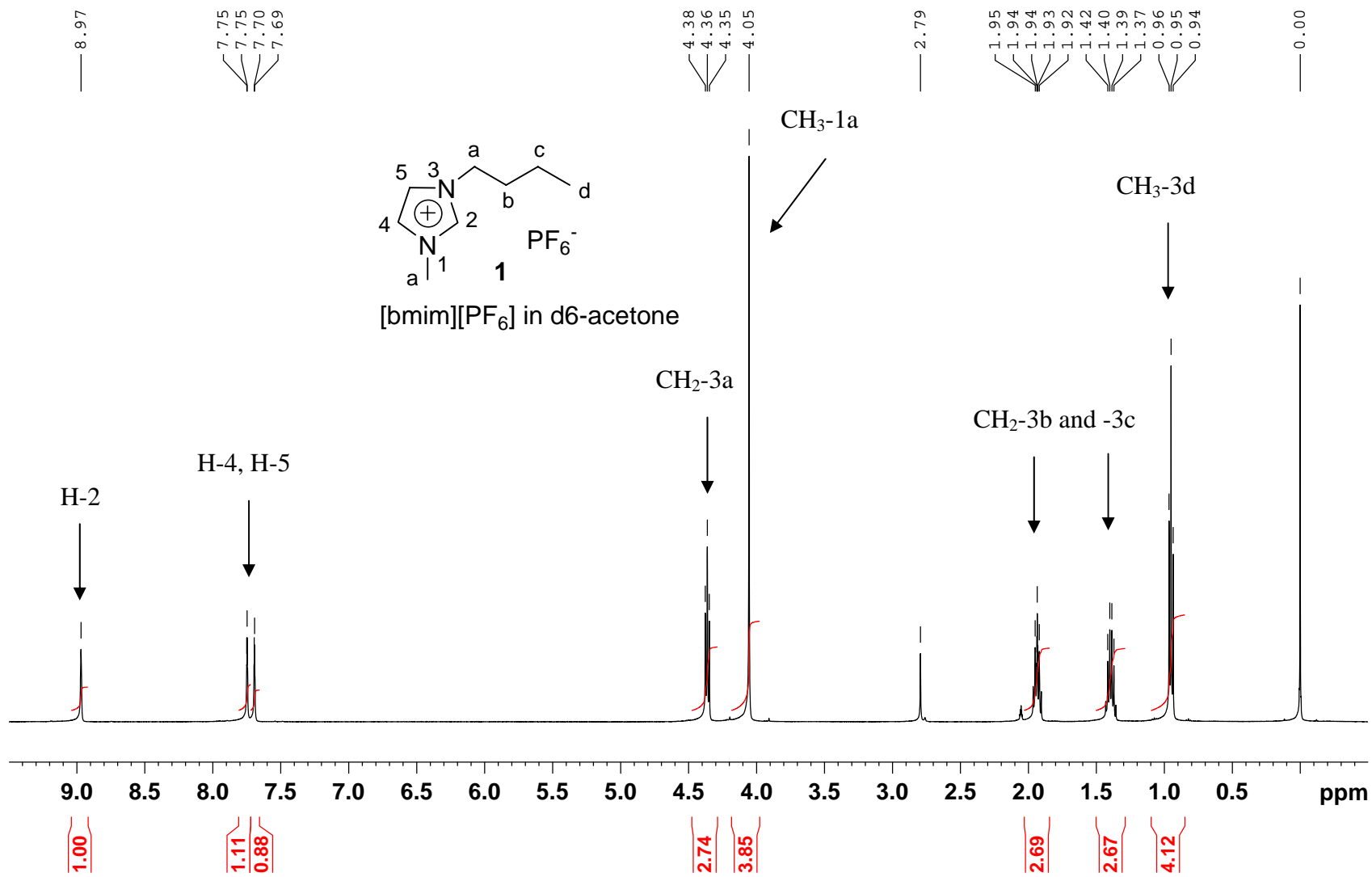
- 1) The optimal technical conditions were previously matched by registering the HRMAS spectrum of compound **6** (4 mg) in neat IL **2**.
- 2) Compound **6** (4 mg, 28.9 μ mol) was inserted on the bottom of the rotor. The subsequent additions were performed in the following order: a) 40 μ L of IL **2**, together with 6% of d6-acetone; b) Ac₂O (4.5 mg, 43.4 μ mol). In this way a physical separation between reagents was achieved.
- 3) As the MAS rotation of 15 KHz was steadily reached, a set of spectra were recorded at regular intervals of time up to the end of the reaction.

Marked differences in the chemical shifts were observed by recording the spectra of ILs in different conditions (see supplementary information). (1) ILs dissolved in different concentrations in a deuterated solvent; (2) neat ILs introduced in a 5-mm NMR tube with a coaxial capillary filled with a deuterated solvent and/or another reference solution; (3) neat ILs directly introduced into an coaxial insert of a 5-mm tube, surrounded by a deuterated solvent; These differences are mainly due to the different bulk magnetic susceptibility among the sample, the solvent and the reference. For the evidence of some of these chemical shift differences see the spectra reported in the supplementary material. Examples of these differences in the choice of the reference are found in: Bonhote, P.; Dias, A. P.; Papageorgiou, N.; Kalyanasundaram, K.; Gratzel, M. *Inorg. Chem.* **1996**, 35(5), 1168. Mele, A.; Tran, C. D.; De Paoli Lacerda, S. H. *Angew. Chem. Int. Ed.* **2003**, 42, 4364. Lycka, A.;

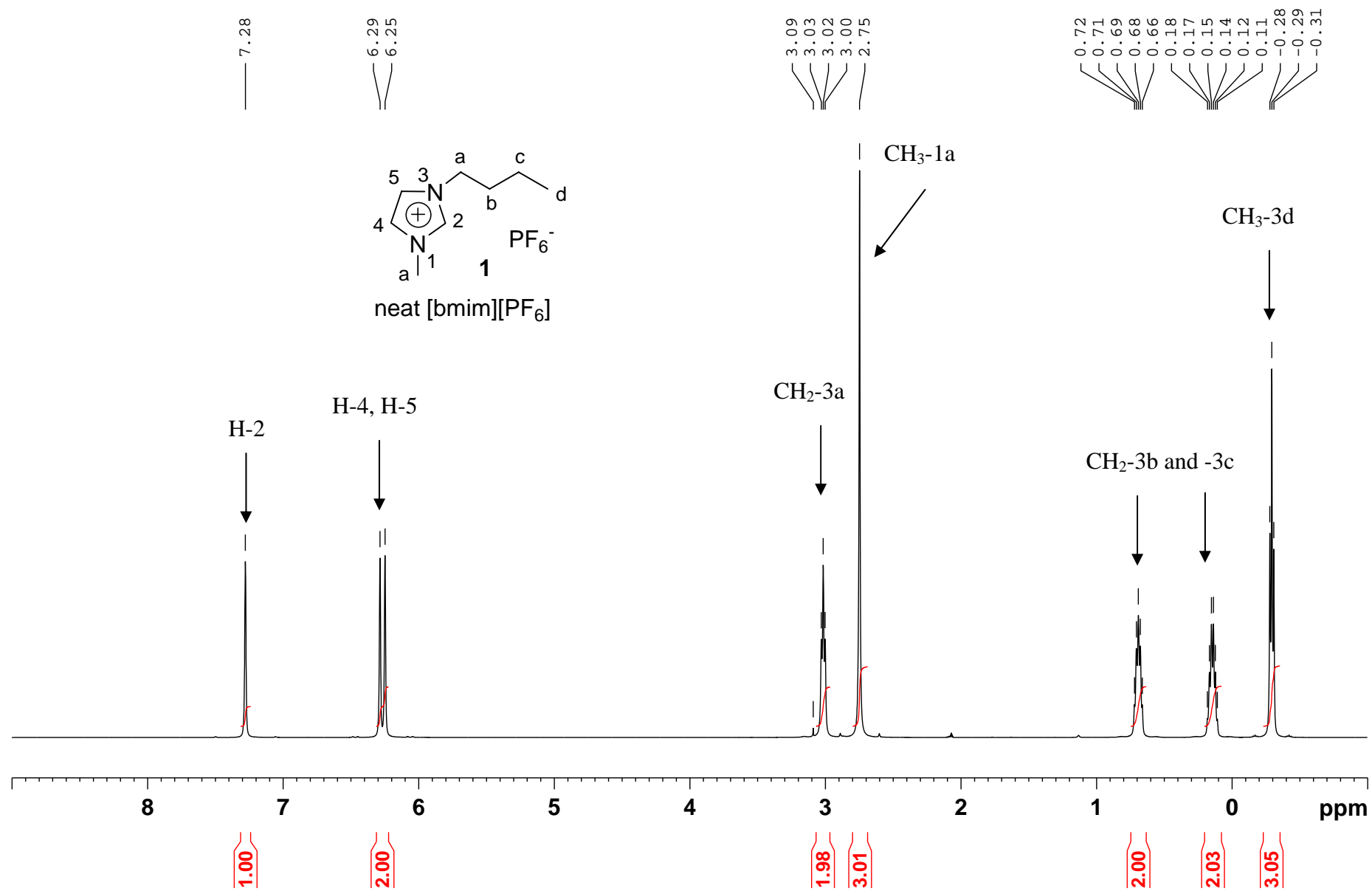
Dolecek, R.; Simůnek, P.; Macháček, V. *Magn. Res. Chem.* **2006**, *44*(5), 521. Heimer, N. E.; Wilkes, J. S.; Wahlbeck, P. G.; Carper, W. R. *J. Phys. Chem. A* **2006**, *110*(3), 868. Mele, A.; Romanò, G.; Giannone, M.; Ragg, E.; Fronza, G.; Raos, G.; Marcon, V. *Angew. Chem. Int. Ed.* **2006**, *45*, 1123; and in refs. 5 and 7.

Table: Structures and chemical shifts of ILs **1-3**

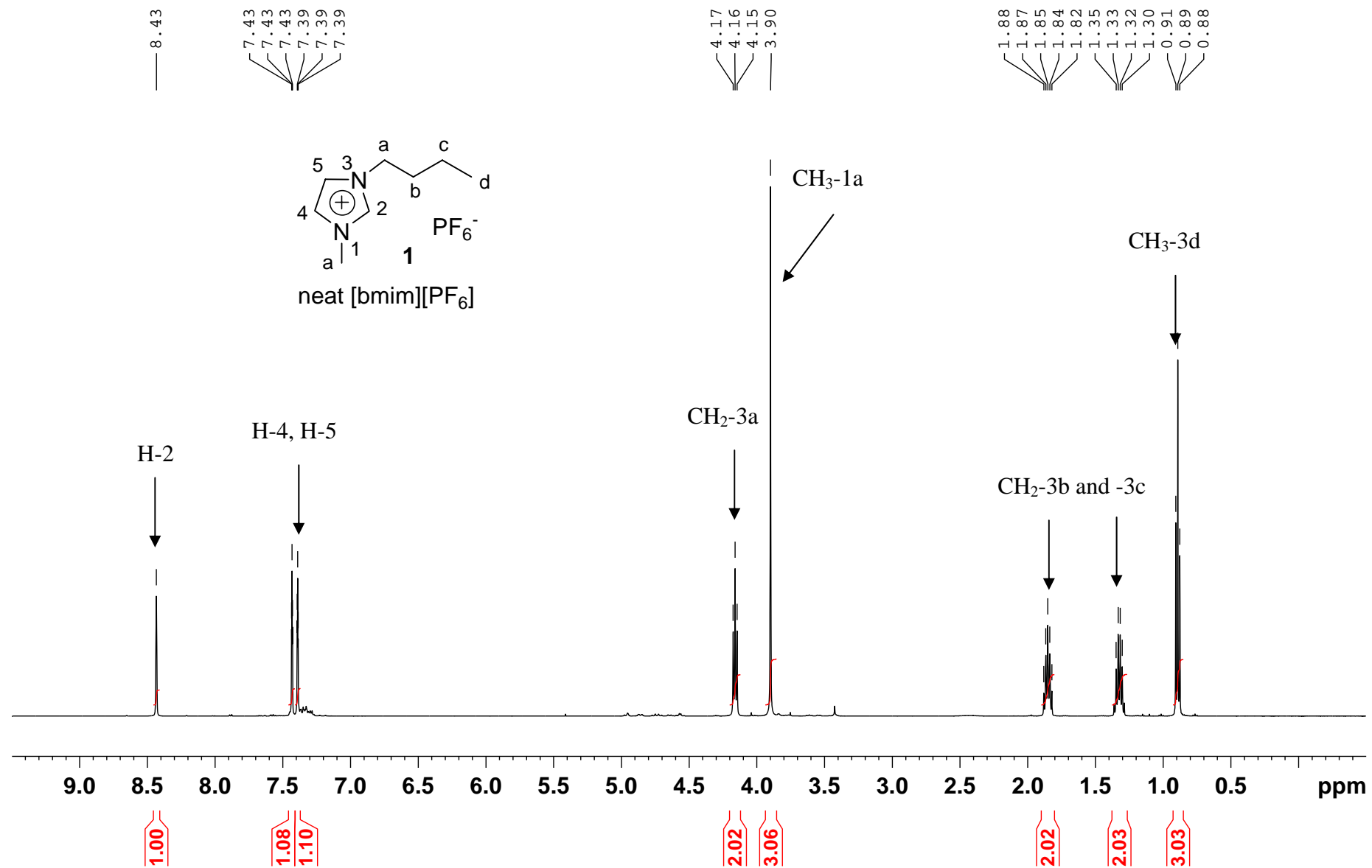
	$\delta(\text{H-2})$, ppm	$\delta(\text{H-2})$, ppm	$\delta(\text{H-2})$, ppm
Chemical structure of ILs	 1	 2	 3
IL in CDCl₃	8.79	8.75	8.51
IL in d₆-acetone	8.97	9.0	9.0
neat IL Conventional probe, coaxial capillary, ext. lock: d₆-acetone	7.28	7.36	7.41
Neat IL + 6% d₆- acetone, HRMAS	8.43	8.47	8.47

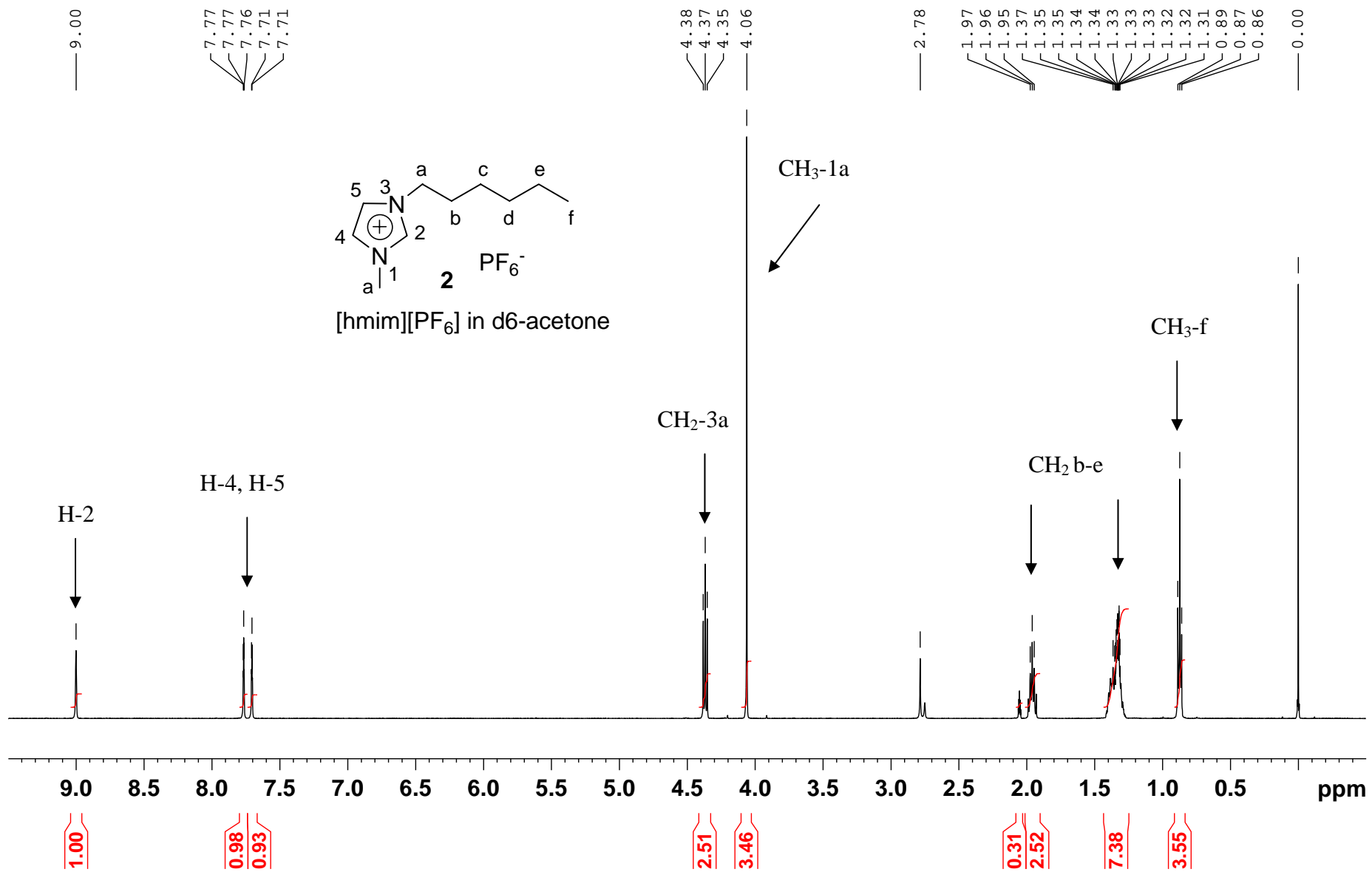


Neat [bmim][PF₆] with conventional probe, 5-mm coaxial capillary, external lock: d6-acetone

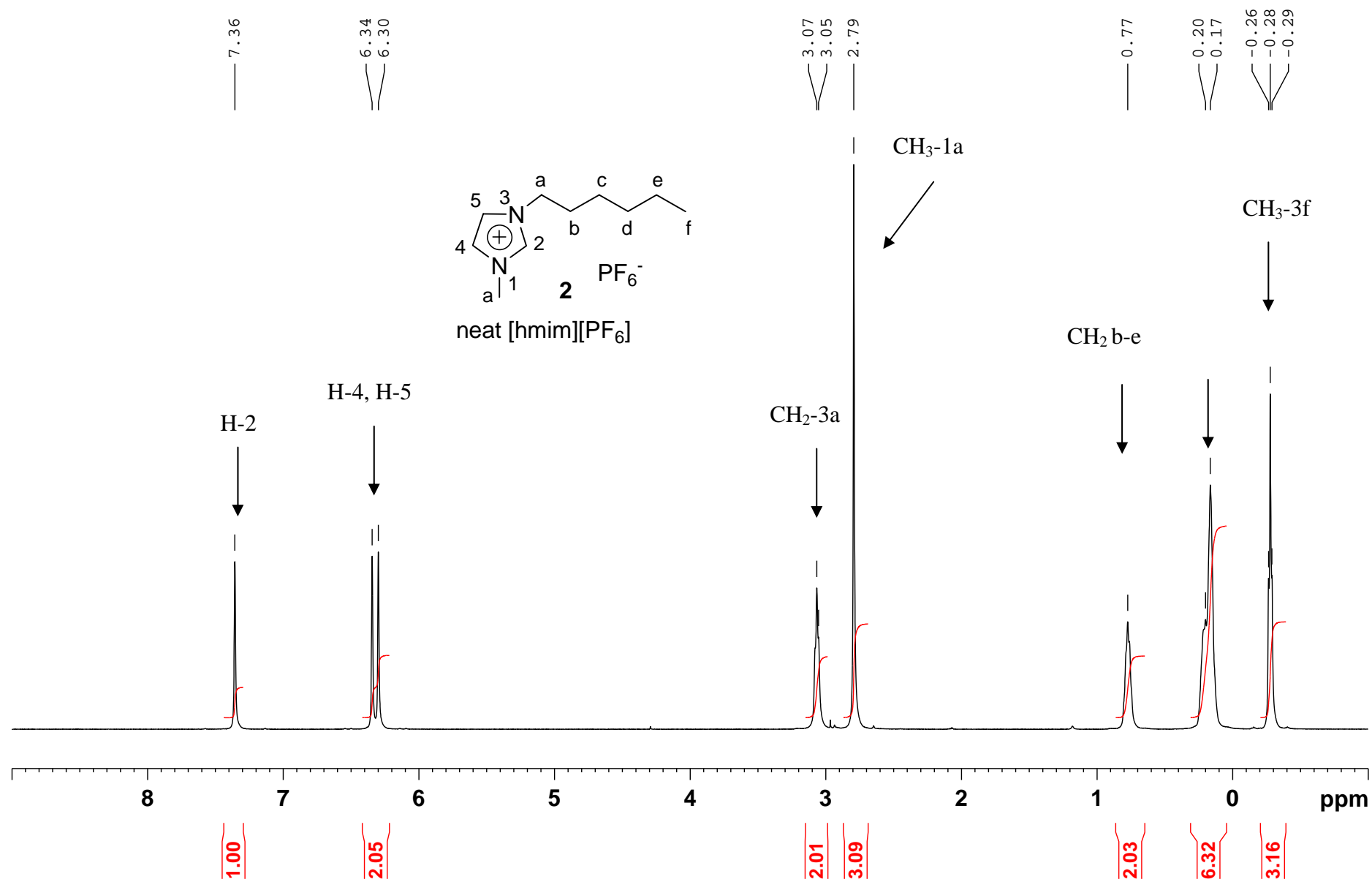


Neat [bmim][PF₆] + 6% d₆-acetone in HRMAS

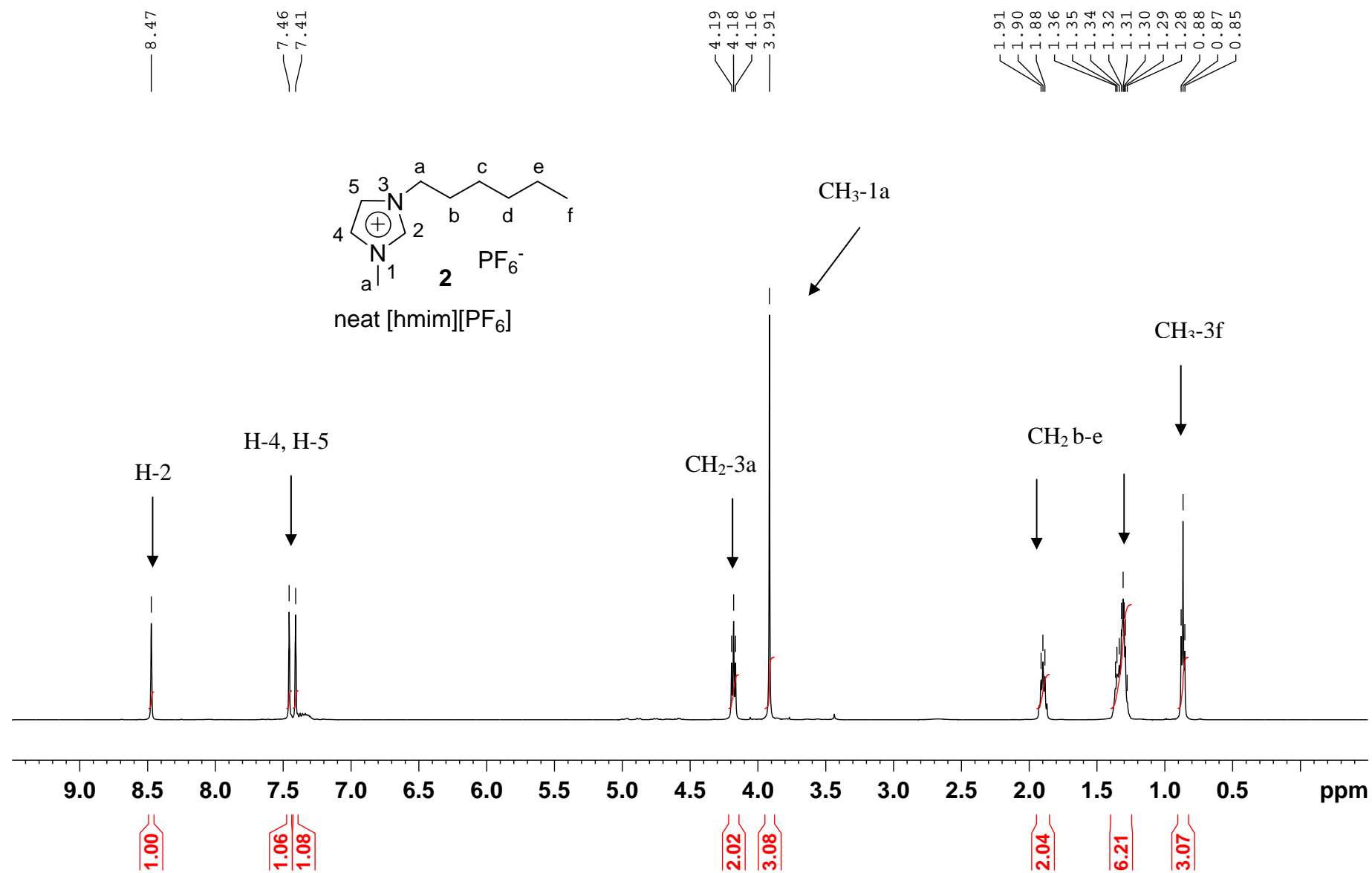


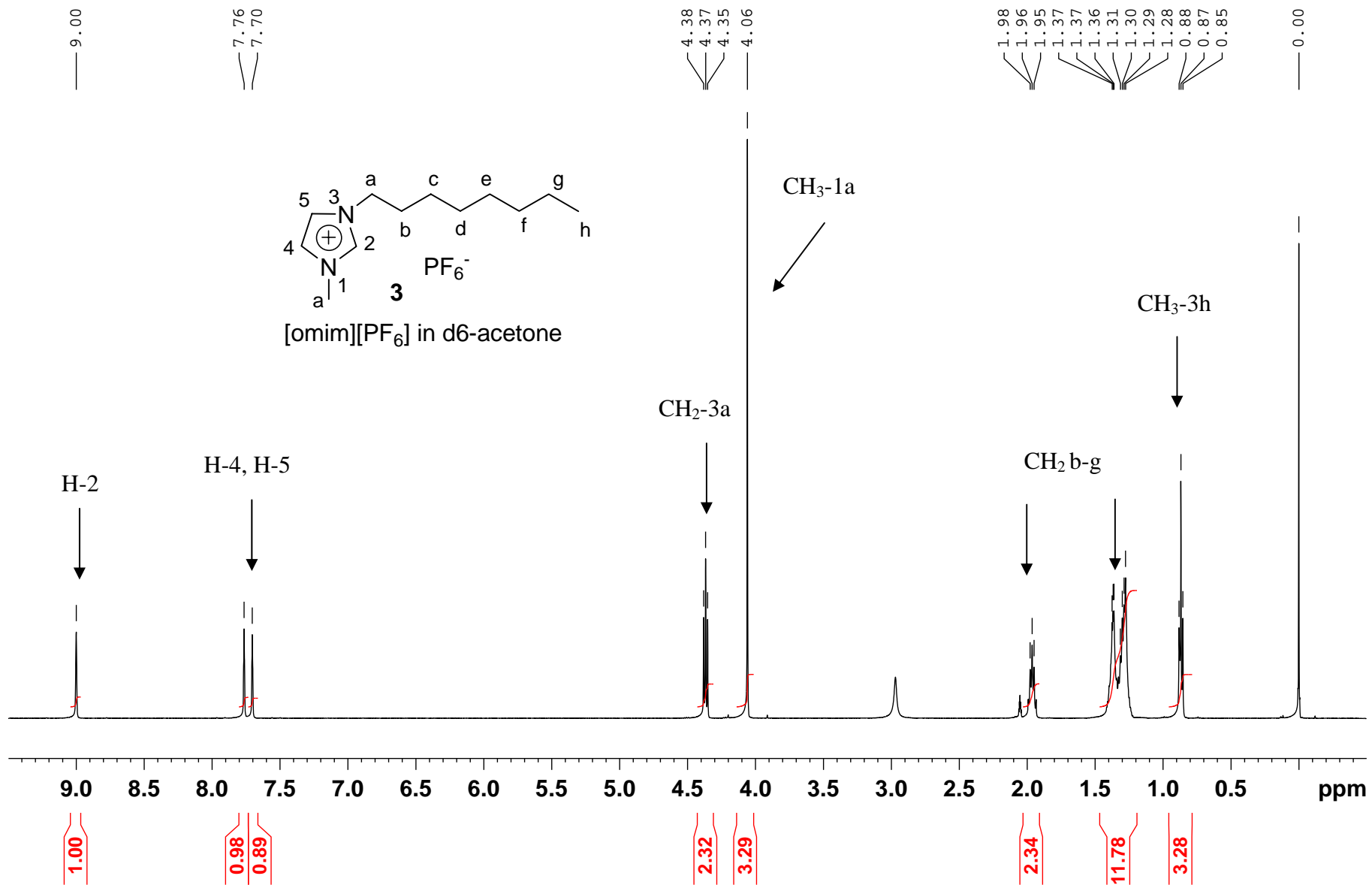


Neat [hmim][PF₆] with conventional probe, 5-mm coaxial capillary, external lock: d6-acetone

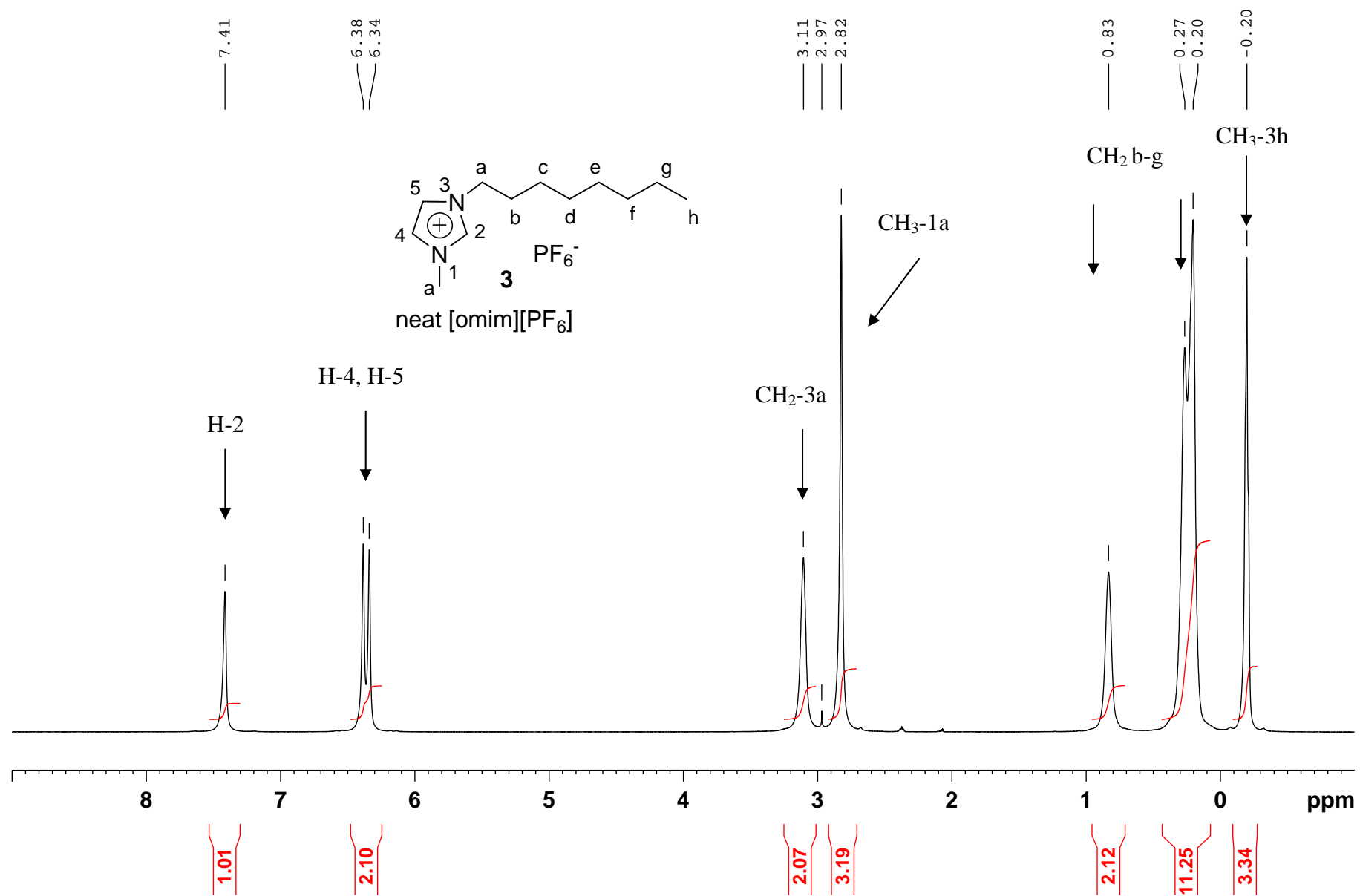


Neat [hmim][PF₆] + 6% d₆-acetone in HRMAS

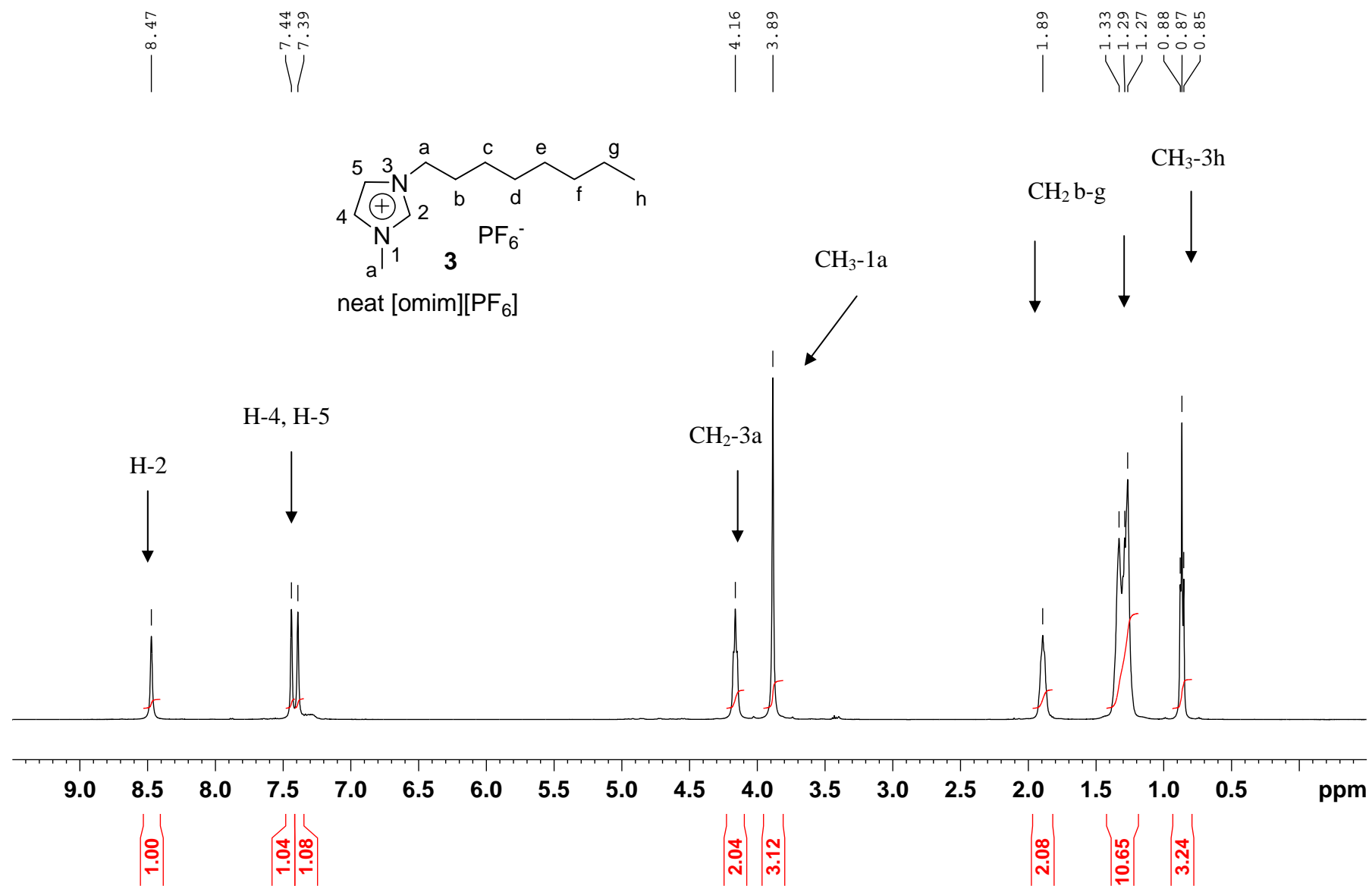




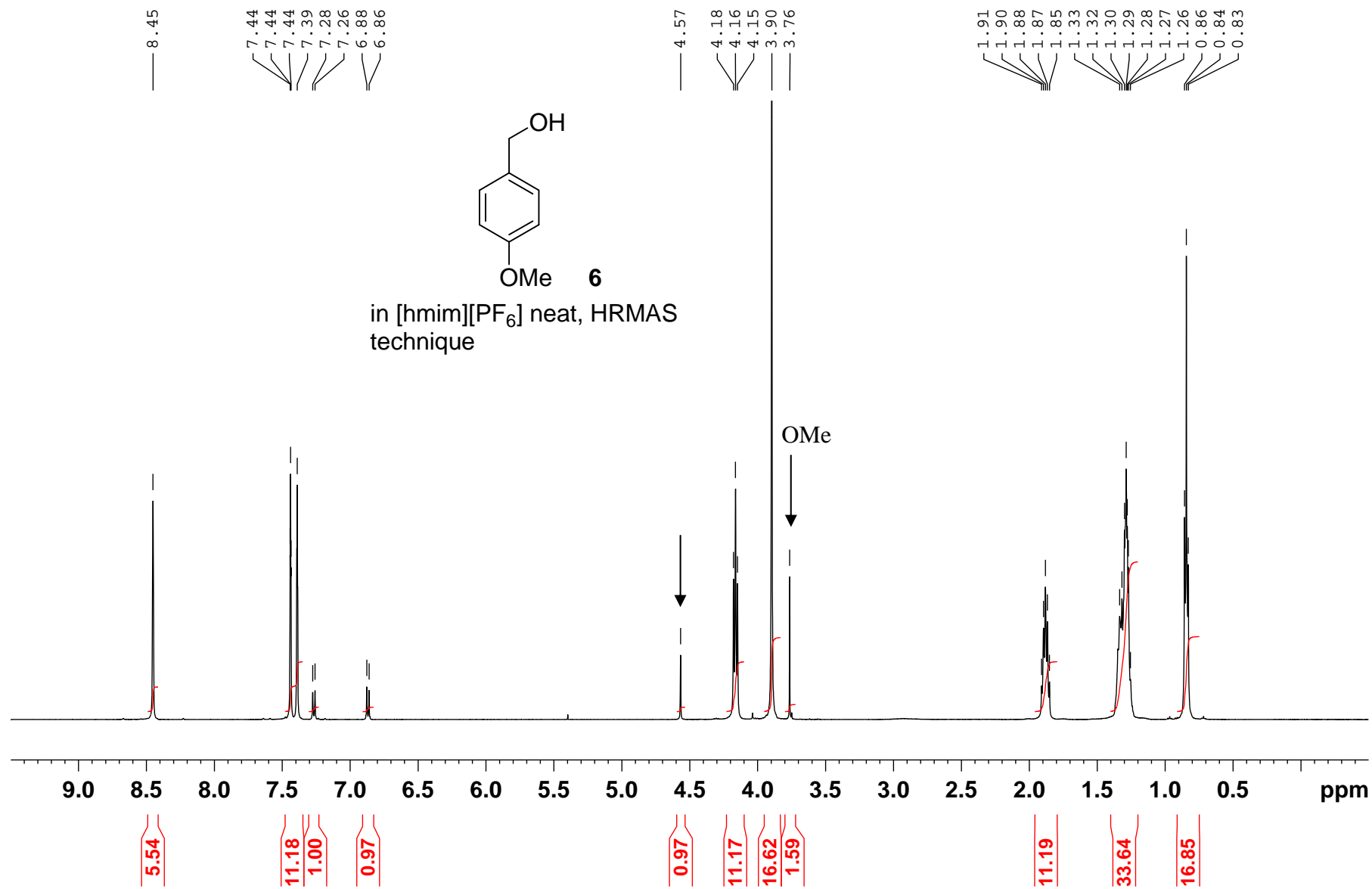
Neat [omim][PF₆] with conventional probe, 5-mm coaxial capillary, external lock: d6-acetone



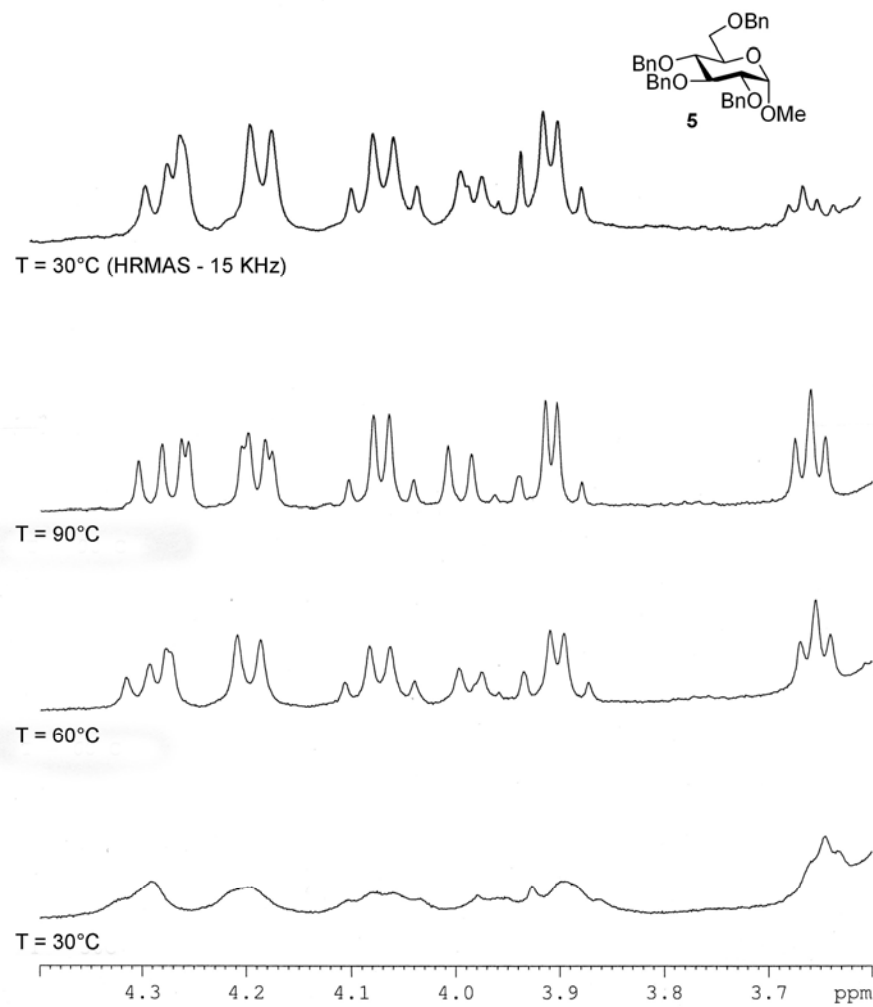
Neat [omim][PF₆] + 6% d₆-acetone in HRMAS



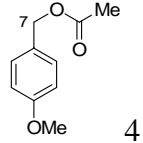
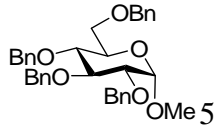
HRMAS 1H; 15KHz; "PMBOH" in HMIM PF6 neat + 6% acetone-d6.



Spectra of **5** in neat IL **1** recorded with external lock (d6-DMSO) at 30, 60 and 90°C and in HRMAS rotor at 30°C.

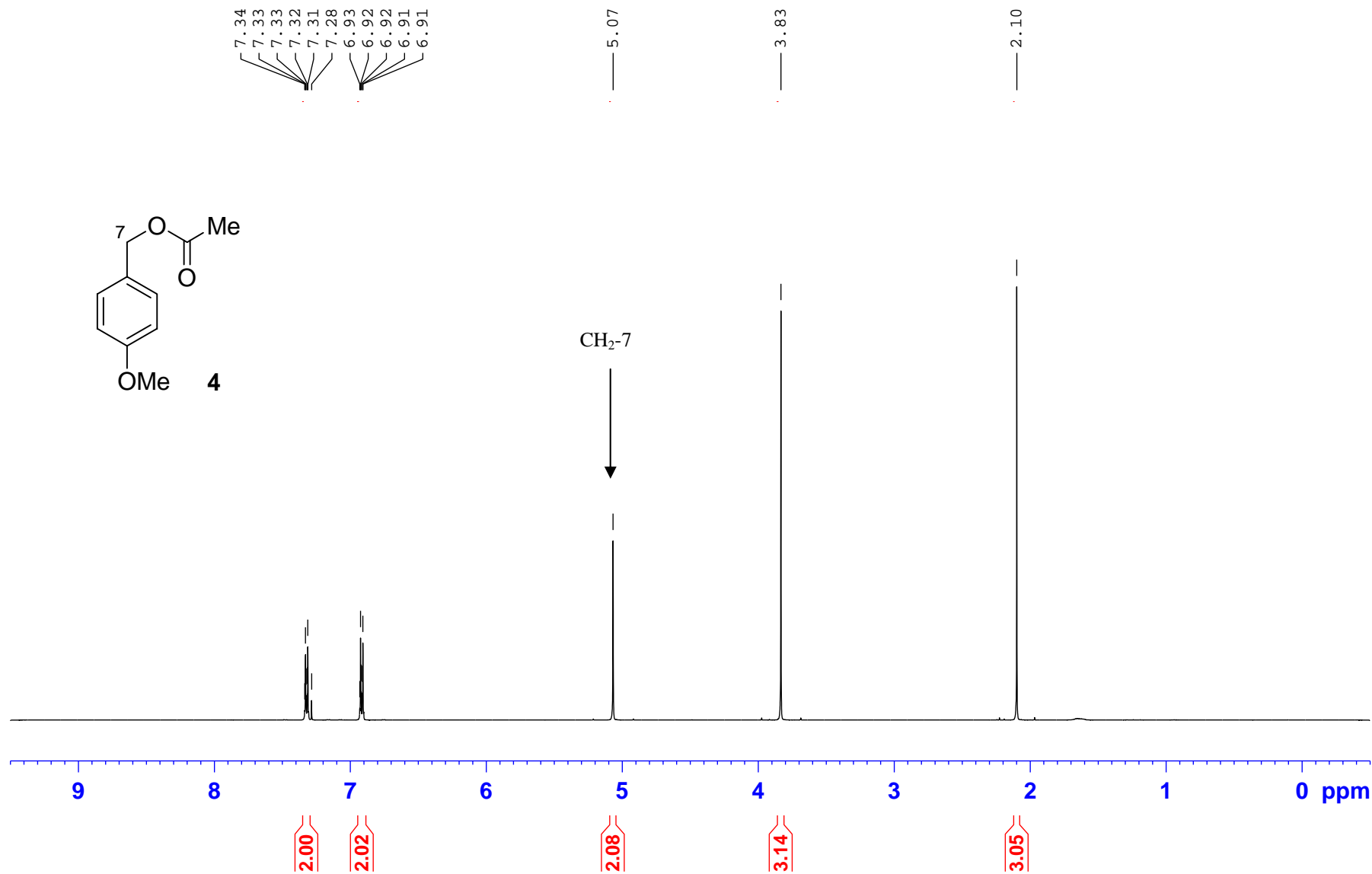


**Chemical Shifts of compounds 4 and 5 in neat ILs 1-3
(Conventional probe and HRMAS)**

Solvent	 4	 5
	δ (CH ₂ -7), ppm	δ (benzylic H), ppm
CDCl₃ T = 303 K	5.07	4.97
neat BMIM external ref: d6-acetone T = 303 K	3.83	3.79
neat HMIM external ref: d6-acetone T = 303 K	3.91	3.86
neat OMIM external ref: d6-acetone T = 303 K	3.95	3.87
neat BMIM + 6% d6-acetone (HRMAS)	5.03	4.96 (15KHz MAS – T = 313K)
neat HMIM + 6% d6-acetone (HRMAS)	5.02	4.98 (15KHz MAS – T = 313K)
neat OMIM + 6% d6-acetone (HRMAS)	5.01	4.96 (15KHz MAS – T = 313K)

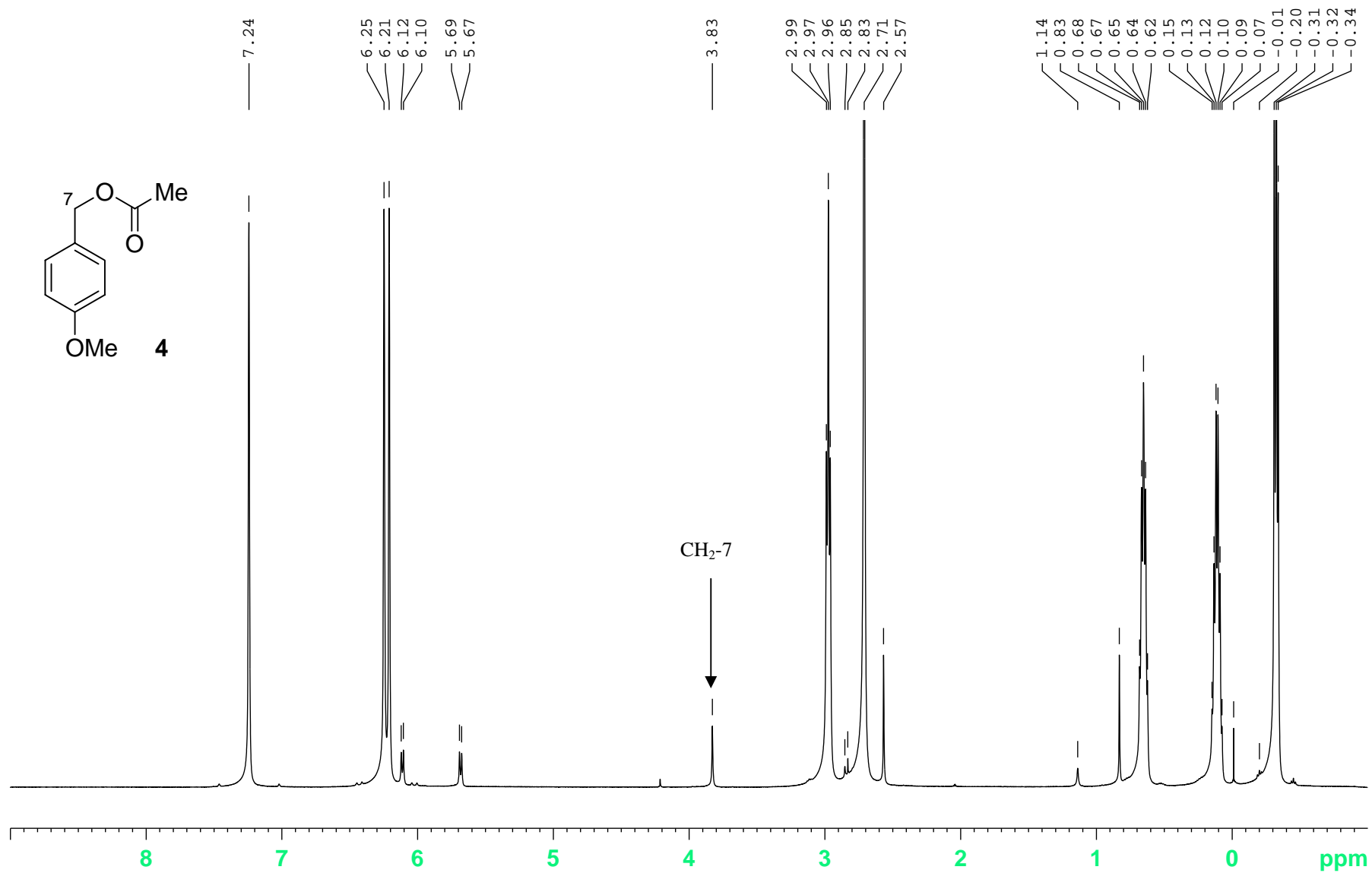
Compound **4** in CDCl₃

"PMBA in CDCl₃"; T = 303K; 1H; probe QNP.



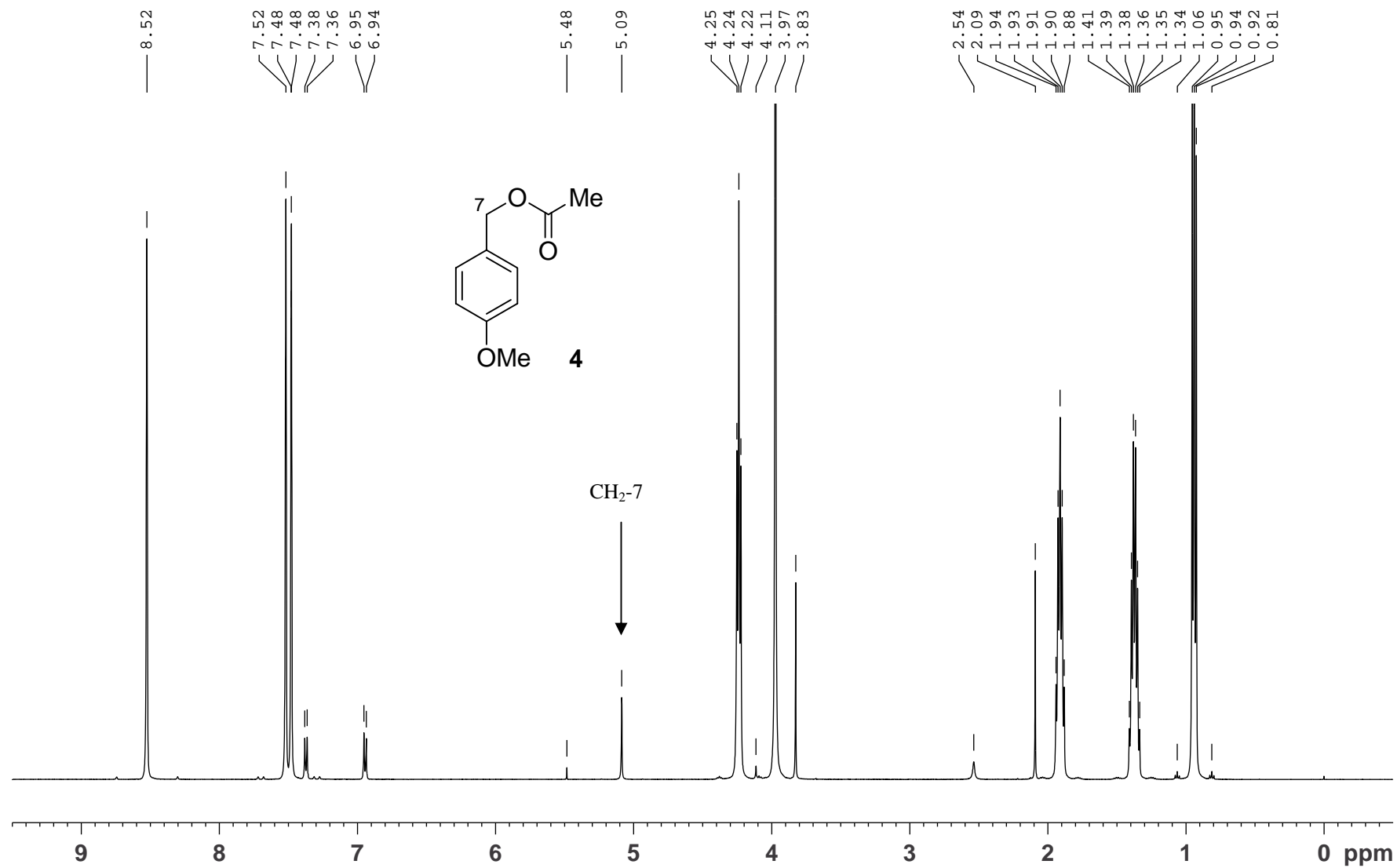
Compound 4 in neat IL 1

¹H "PMBA" in BMIM PF6 neat; lock ext. con Acetone-d6; T = 303 K.



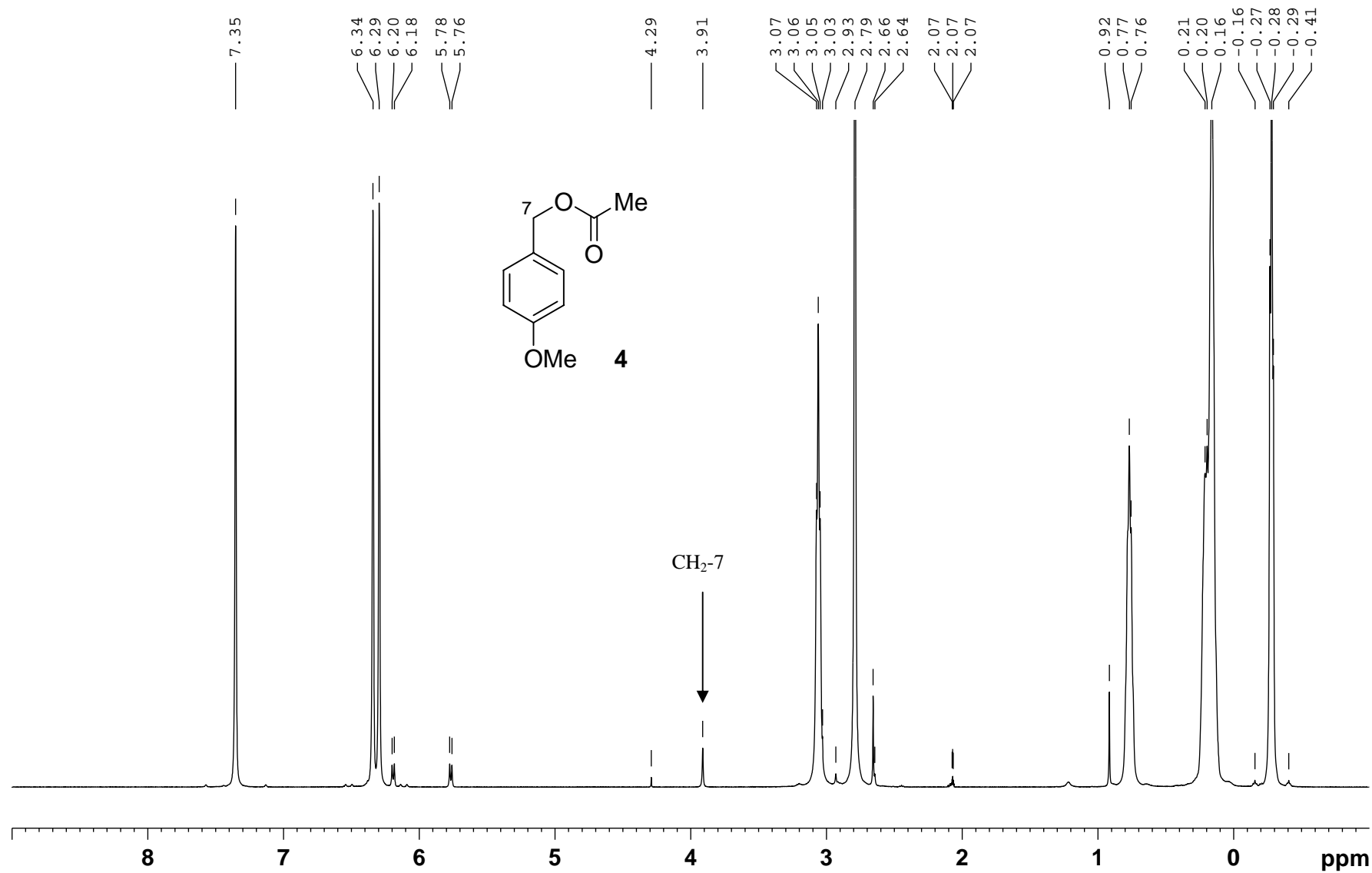
Compound **4** in neat IL **1** recorded with HRMAS NMR technique

HRMAS 1H; 5KHz; T=303K; +TMS; "PMBA" in BMIM PF6; Acetone-d6 (6% vol.).



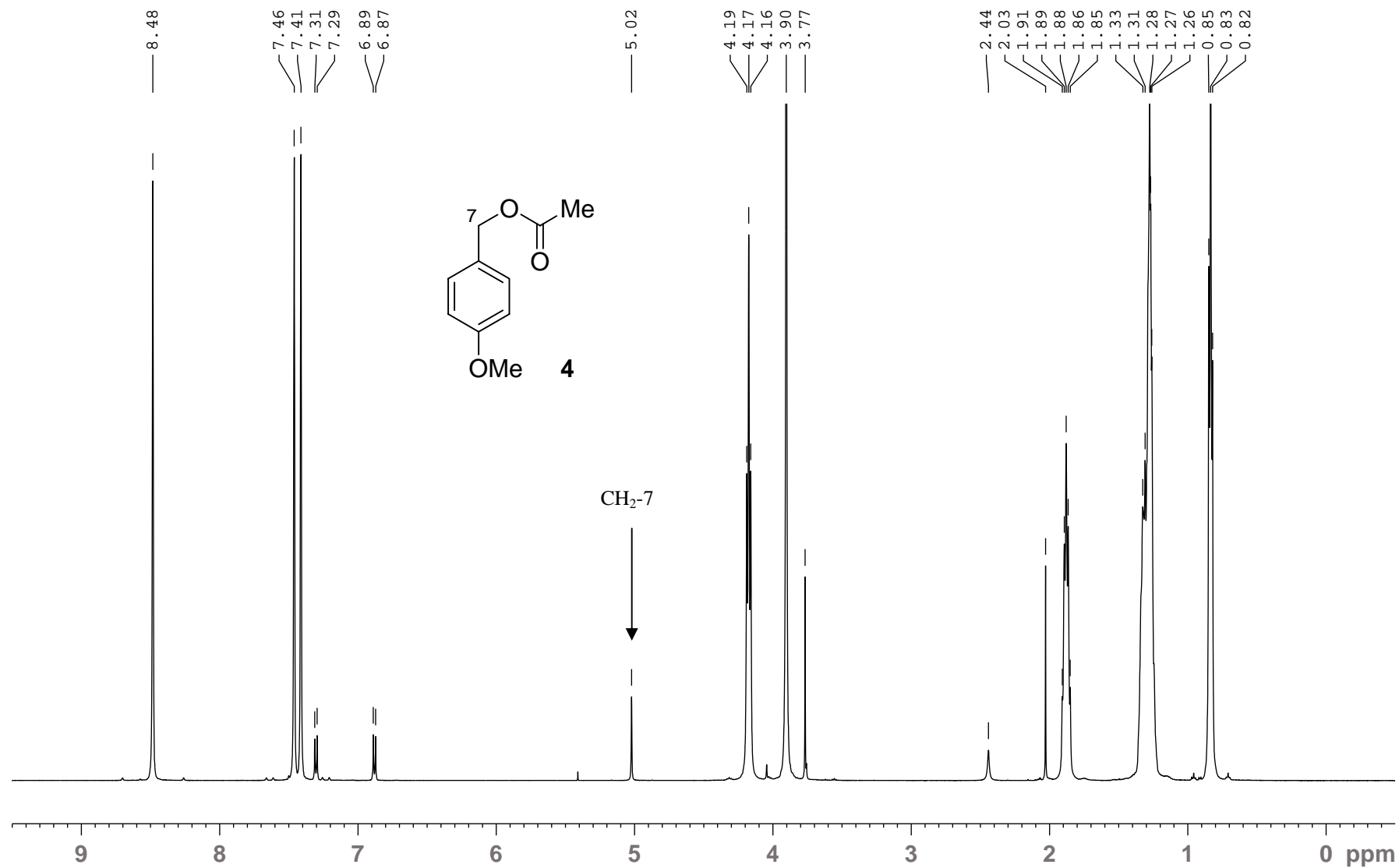
Compound 4 in neat IL 2

¹H "PMBA" in HMIM PF6; T = 303K; lock ext. con Acetone-d6.



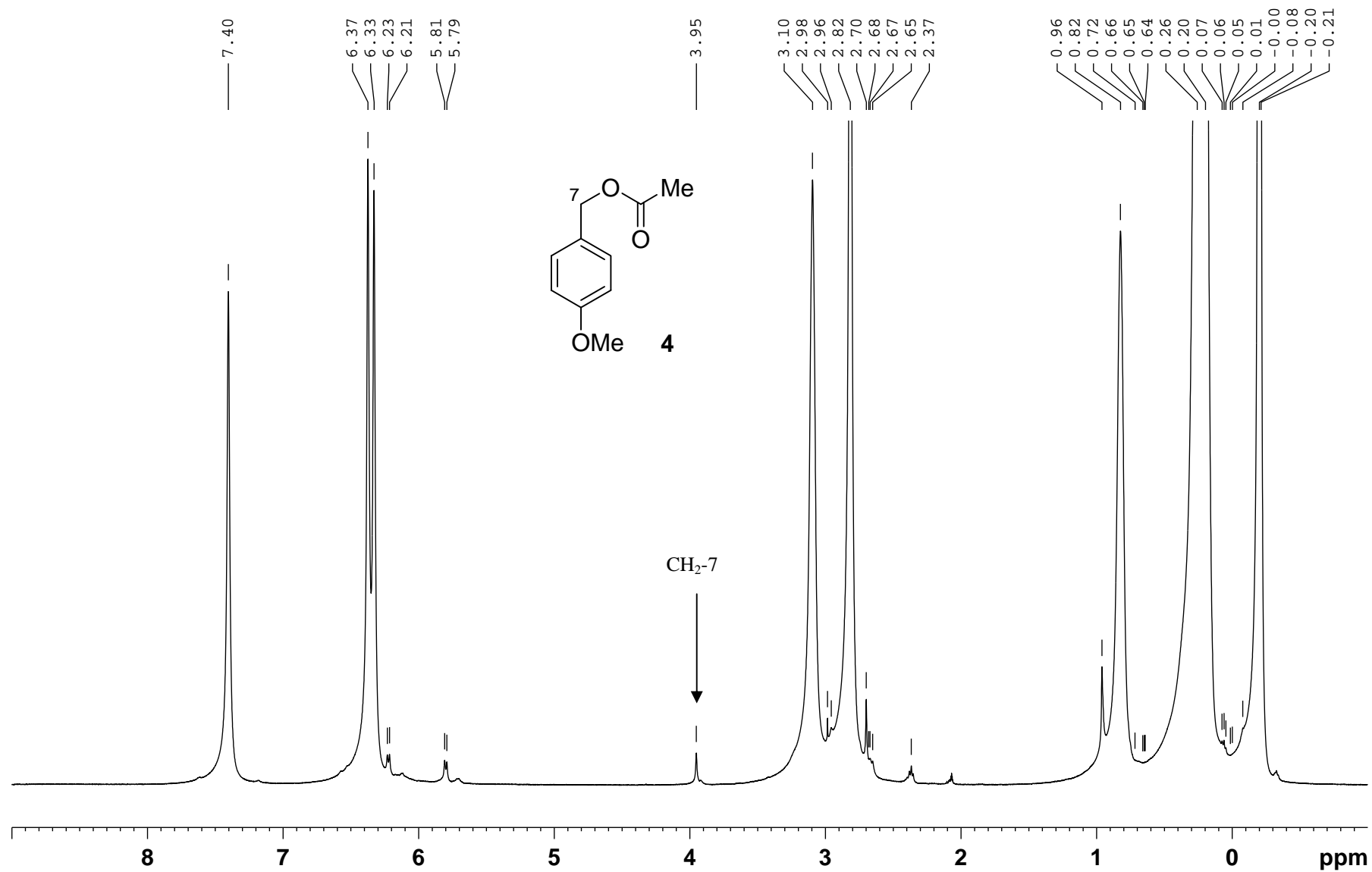
Compound **4** in neat IL **2** recorded with HRMAS NMR technique

HRMAS ^1H ; 5KHz rotaz.; "PMBA" in HMIM PF₆; T = 303K; Acetone-d₆.



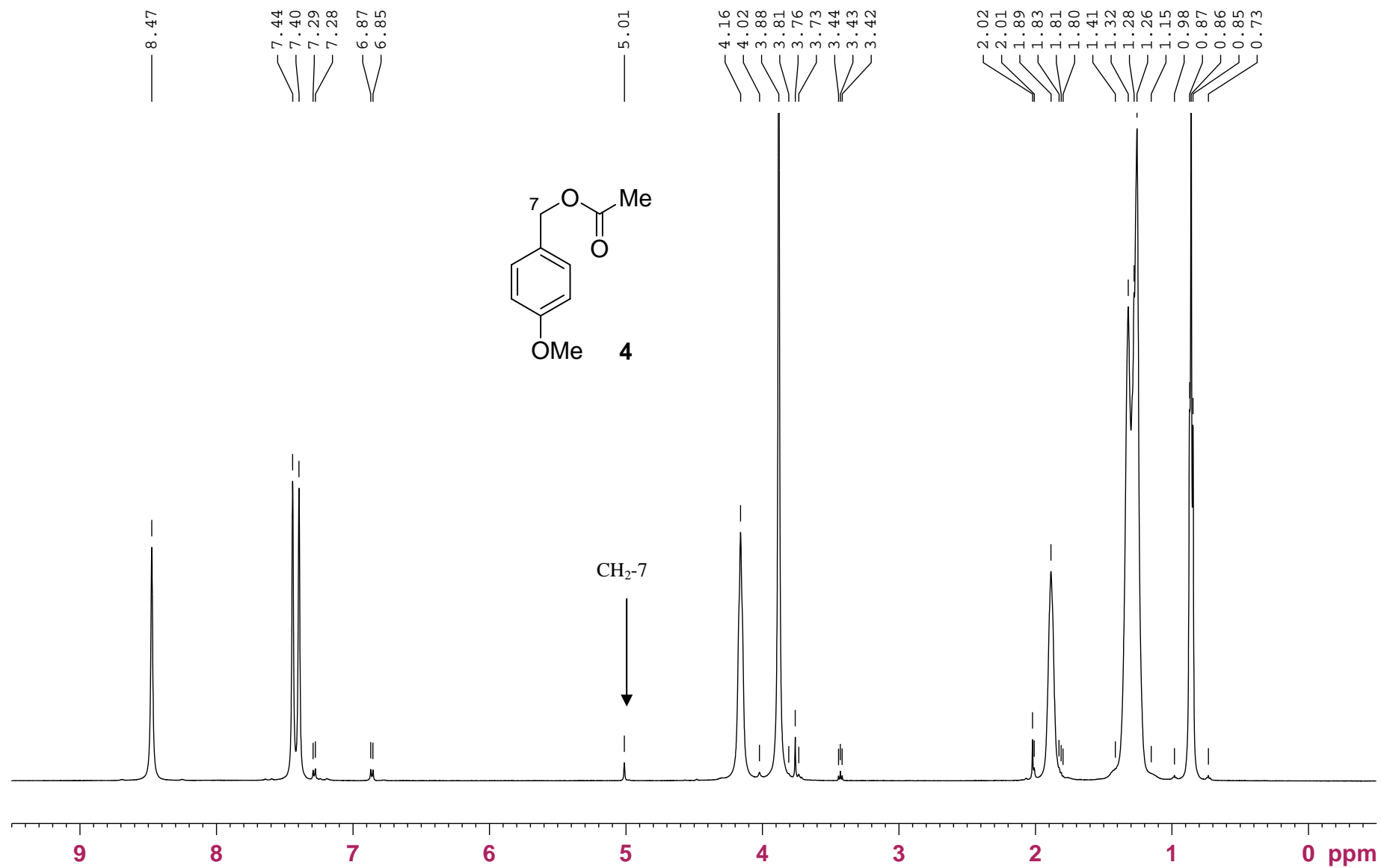
Compound 4 in neat IL 3

"PMBA" 10mg in OMIM PF6; T=303K; lock ext. con Acetone-d6.



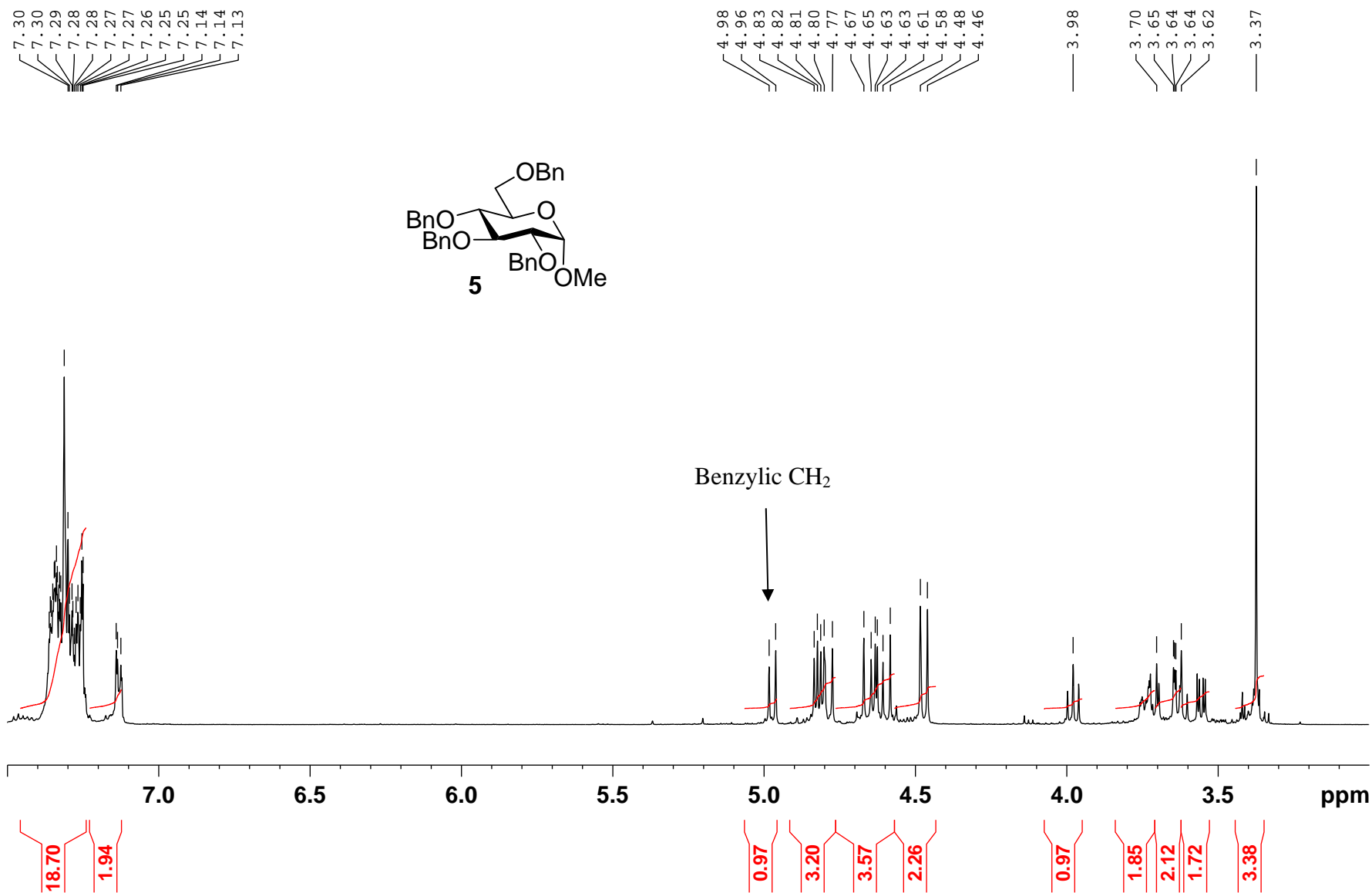
Compound **4** in neat IL **3** recorded with HRMAS NMR technique

HRMAS 1H; 5KHz rotaz.; "PMBA" in OMIM PF6; T = 303K; Acetone-d6.



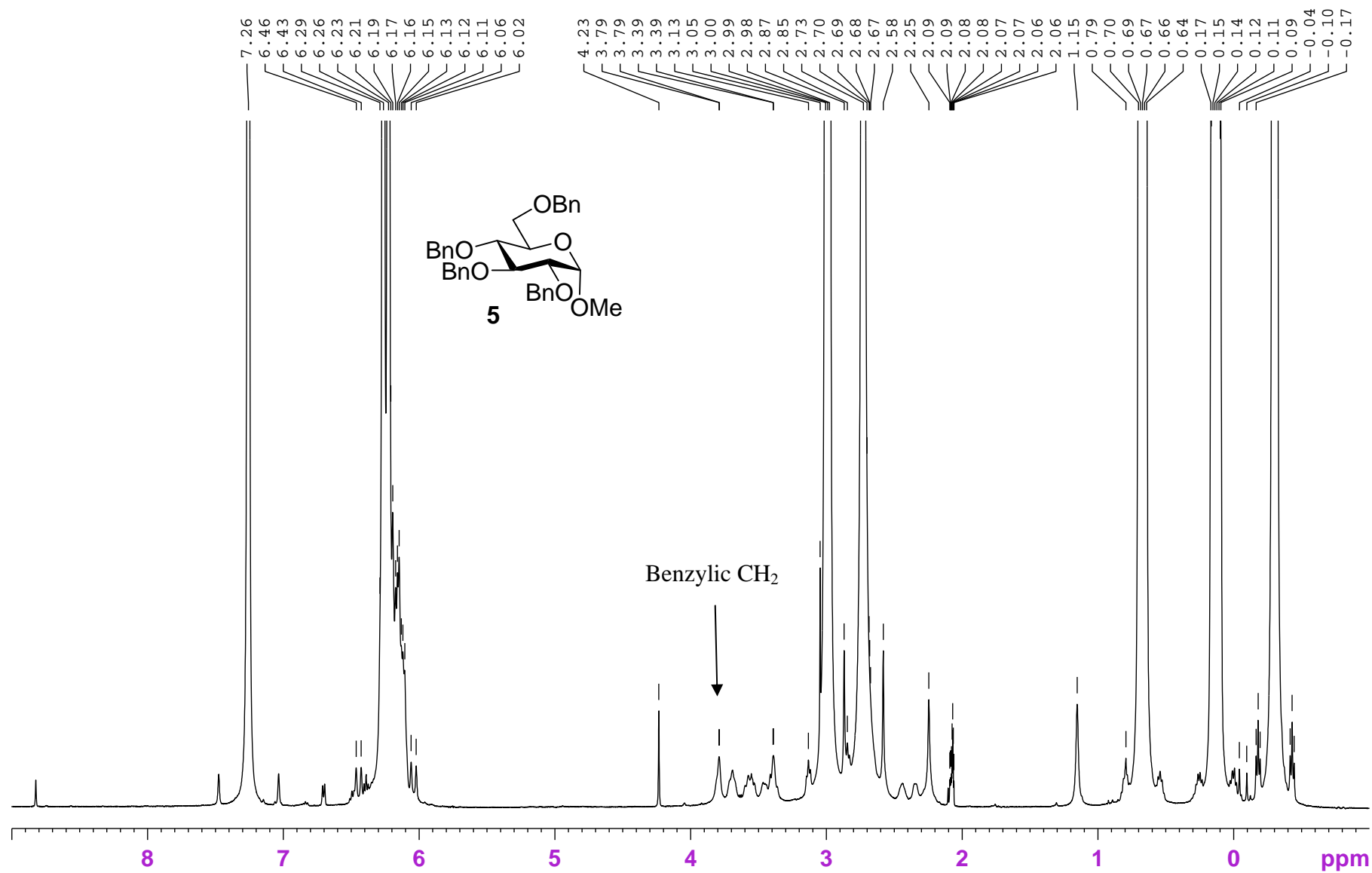
Compound **5** in CDCl₃

¹H "Gluc_OBz" in CDCl₃; T = 303 K.



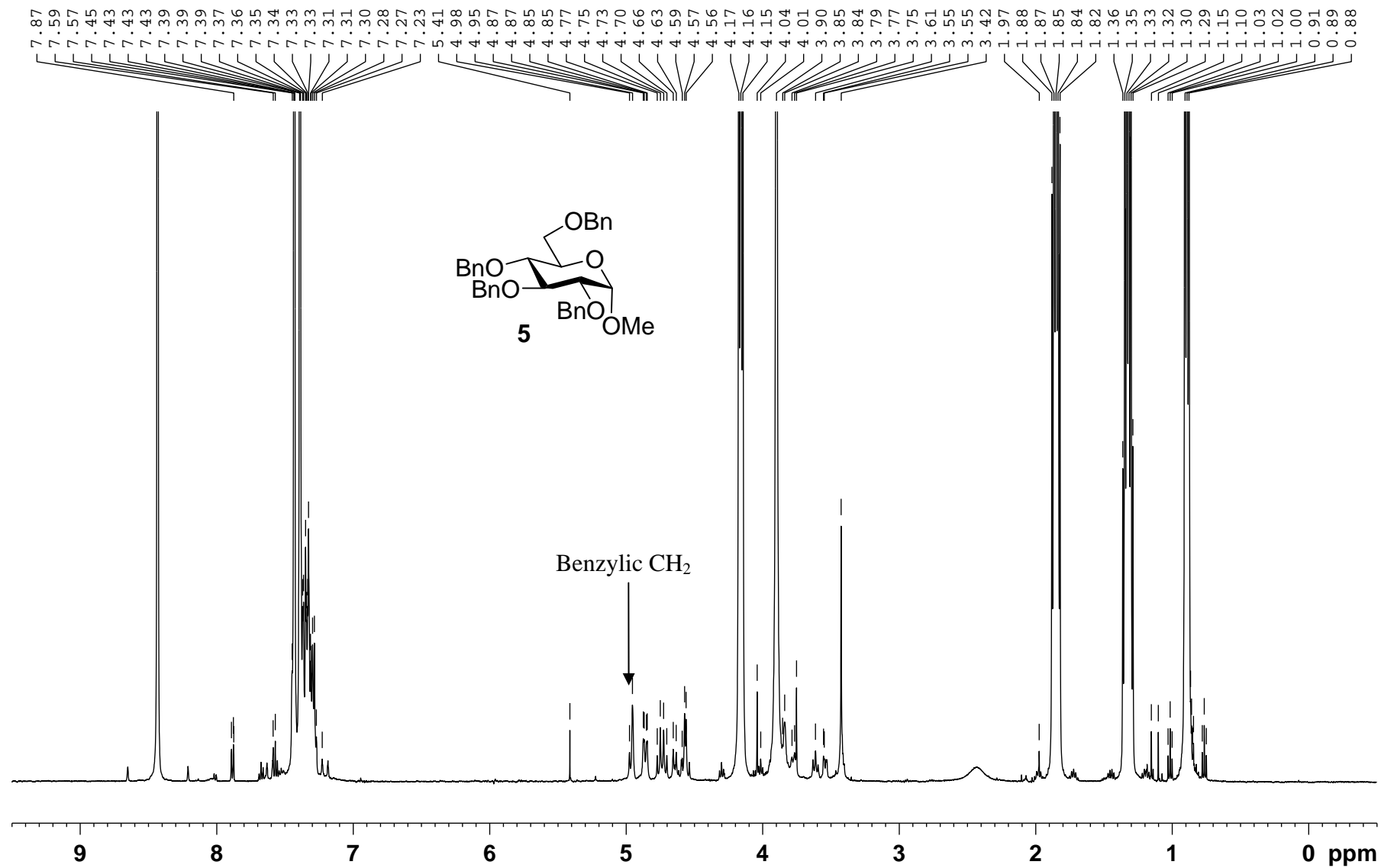
Compound **5** in neat IL **1**

¹H "Gluc_OBz" in BMIM PF₆; T = 303K; lock ext. con Acetone-d₆.



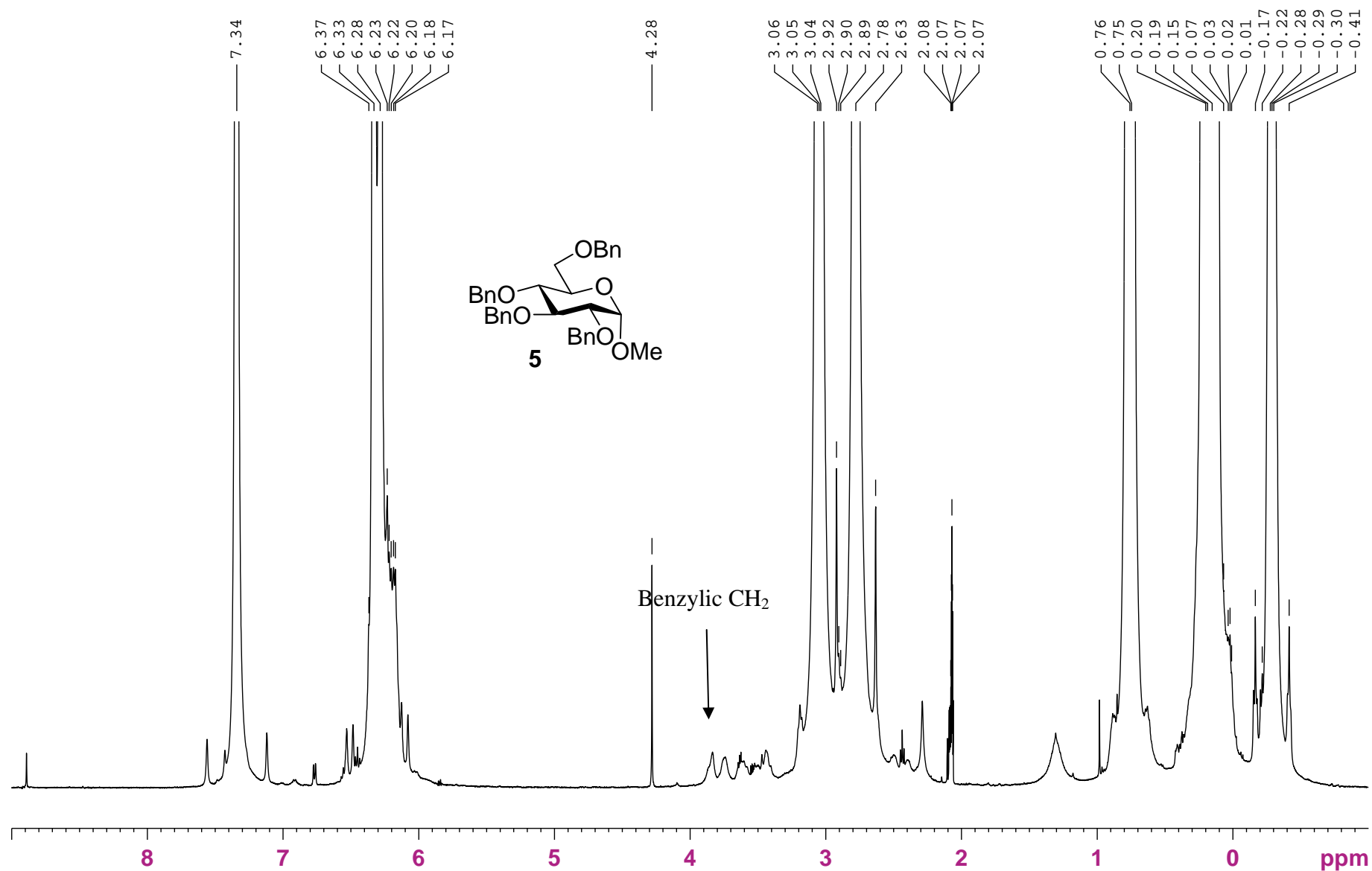
Compound **5** in neat IL **1** recorded with HRMAS NMR technique

HRMAS 1H; 15KHz; T = 313K; "Gluc_OBz" in BMIM PF6; Acetone-d6.



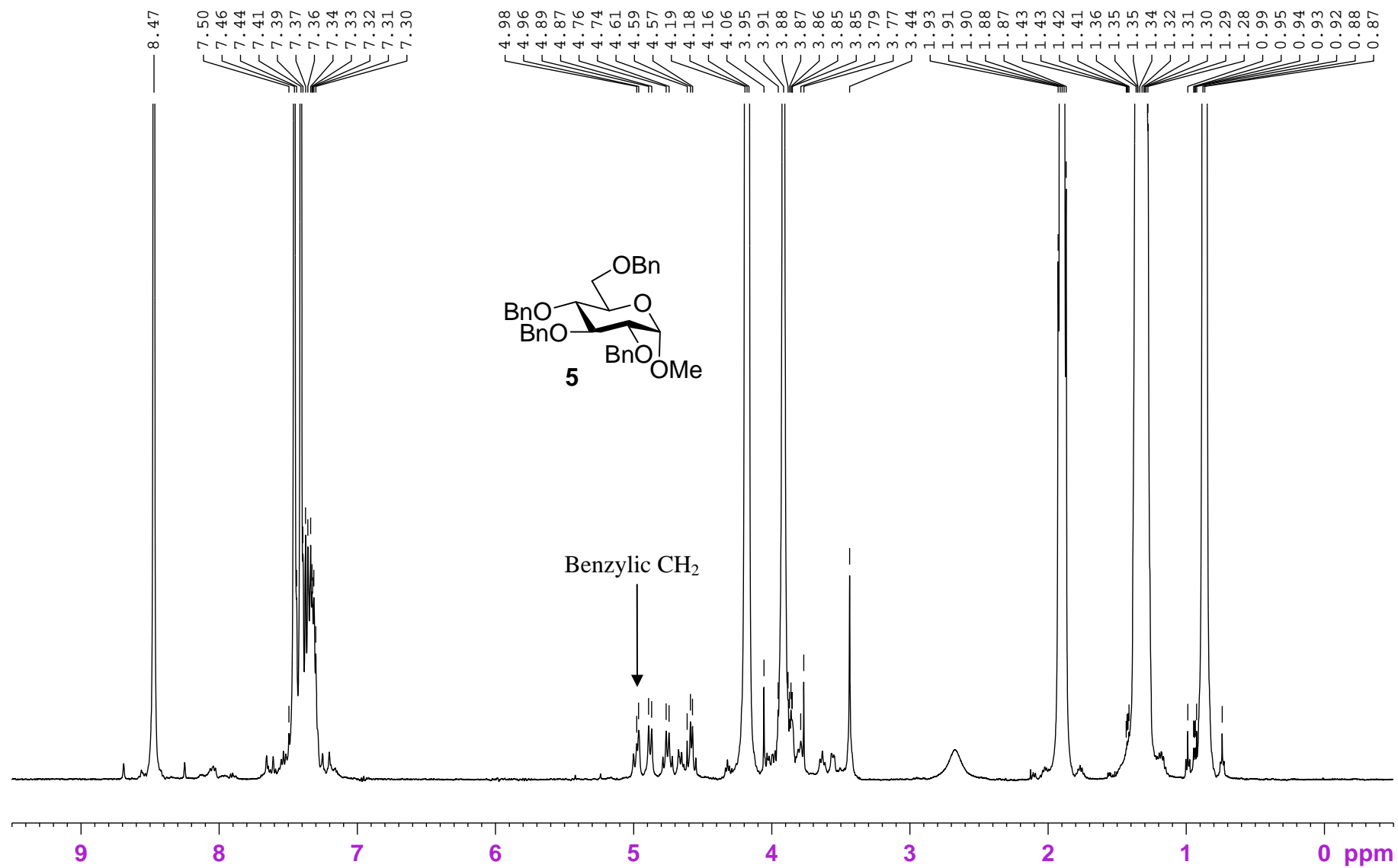
Compound **5** in neat IL **2**

^1H "Gluc_OBz" in HMIM PF₆; T = 303K; lock ext. con Acetone-d₆.



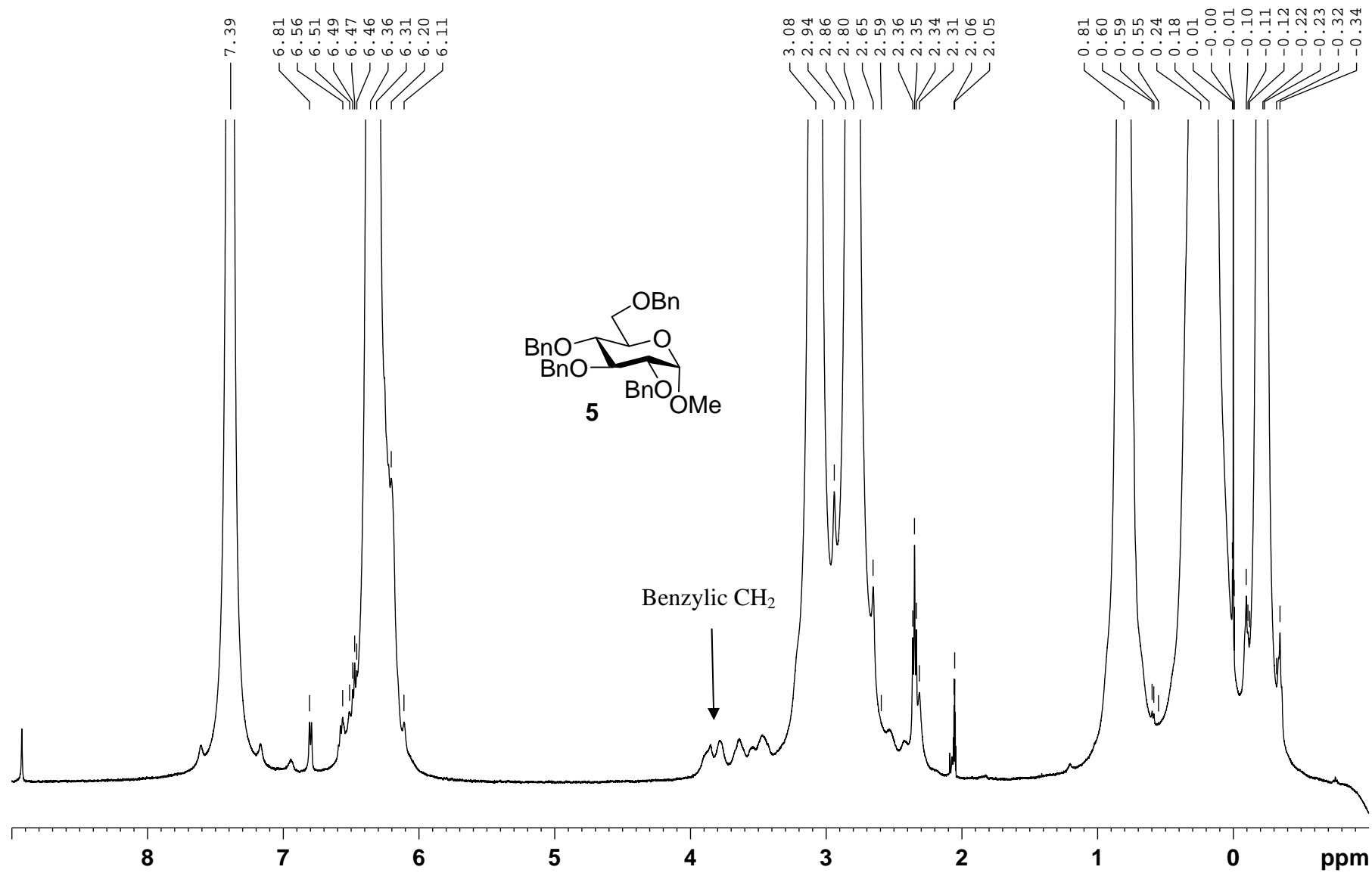
Compound **5** in neat IL **2** recorded with HRMAS NMR technique

HRMAS 1H; 15KHz rotaz.; "Gluc_OBz" in HMIM PF6 + TMS; T = 313K; Acetone-d6 (6% vol.).



Compound **5** in neat IL **3**

¹H "Gluc_Obz" in OMIM PF6 neat; lock ext. con Acetone-d₆; T = 303 K



Compound **5** in neat IL **2** recorded with HRMAS NMR technique

HRMAS 1H; 15KHz rotaz.; "Gluc_OBz" in OMIM PF6 + TMS; T = 313K; Acetone-d6 (6% vo

