Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supporting information

Insights into the recombination of radical pair in hexaarylbiimidazoles

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1. Experimental set-up

NMR spectra were recorded on Avance 500 spectrometer (^{1}H, 500 MHz, ^{13}C, 125 MHz) equipped with TXI probe, using standard sequences. Data sets were processed using Bruker Topspin 3.2 software.

Samples are dissolved in toluene-d_8 (*ca* 5 mM) in Shigemi NMR tubes.

When required, NMR experiments were carried at various low temperatures using a N_2 cooling setup connected to the spectrometer.

Irradiation was performed *in situ* using a pulsed Nd/YAG laser (4-6 ns pulses, 10Hz repetition rate), delivering laser pulses at 1064, 532 and 355 nm (3.5 mJ). SSP beam splitter enables to select the 355 nm beam. The laser is coupled to an optical fiber that transmits light to the sample into the spectrometer, through the transparent insert of the tube.

2. Computational details

Theoretical calculations were based on Density Functional Theory (DFT) and have been performed with the ORCA program package.[1] Full geometry optimizations were carried out for all systems using the hybrid functional B3LYP [2,3] in combination with the TZV/P [4] basis set for all atoms and by taking advantage of the resolution of the identity (RI) approximation in the Split-RI-J variant [5] with the appropriate Coulomb fitting sets. [6] The structure optimizations of all dimers were initiated from the X-ray structure of 1-2'dimer of o-Cl-HABI [7]. Increased integration grids (Grid4 in ORCA convention) and tight SCF convergence criteria were used. For all molecular property calculations, solvent effects were accounted for according to the experimental conditions. For that purpose, we used the DMF (ε=2.40) solvent within the framework of the conductor like screening (COSMO) dielectric continuum approach.[8]The chemical shift tensors were obtained from additional single-point calculations using the EPR/NMR module and the IGLO procedure as implemented in the ORCA program package. The B3LYP functional and an IGLO-II [9,10] basis set were employed for the calculation of NMR parameters. The calculated shielding tensors were transformed to relative chemical shifts δ by subtracting the calculated chemical shift of TMS.

[1]. Neese, F. Wiley Interdiscip. Rev. Comput. Mol. Sci. 2012, 2, 73.

[2]. Becke, A. D. J. Chem. Phys. 1993, 98, 1372.

[3]. Lee, C. T.; Yang, W. T.; Parr, R. G. Phys. Rev. B 1988, 37, 785.

[4]. Schäfer, A.; Huber, C.; Ahlrichs, R. J. Chem. Phys. 1994, 100, 5829.

[5]. Neese, F. J. Comput. Chem. 2003, 24, 1740.

[6]. Weigend, F. PhysChemChemPhys 2006, 8, 1057.

[7]. Kawano, M.; Sano, T.; Abe, J.; Ohashi, Y. J. Am. Chem. Soc. 1999, 121, 8106-8107

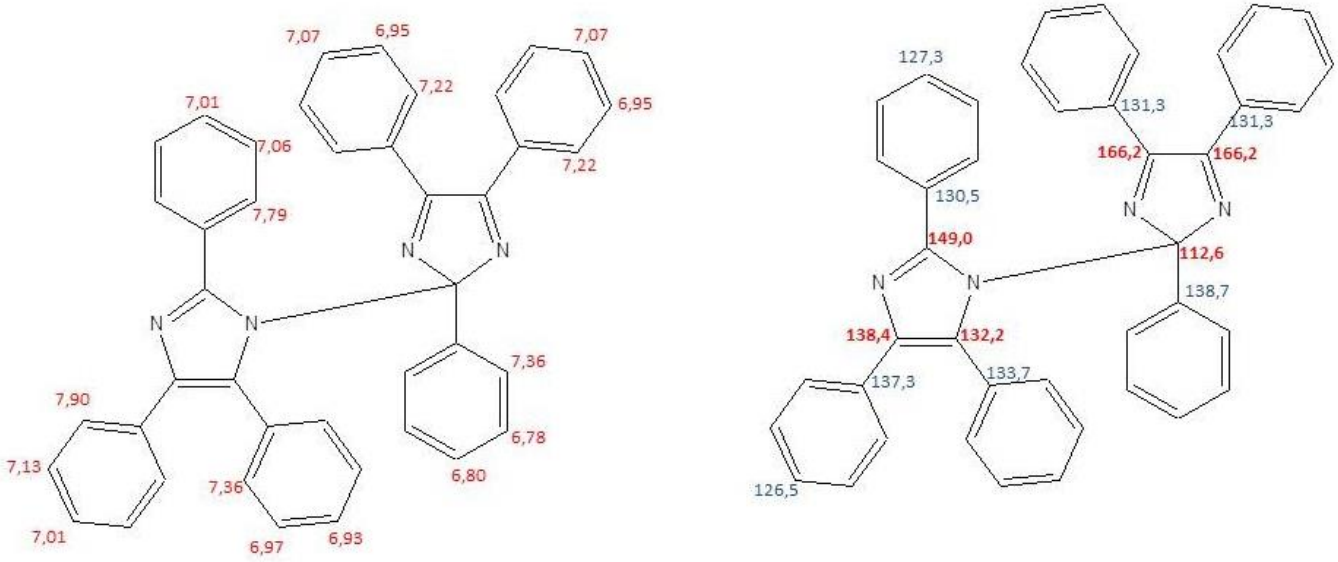
[8]. Klamt, A.; Schürmann, G. J. Chem. Soc., Perkin Trans. 2 1993, 799.

[9]. Kutzelnigg, W.; Fleischer, U.; Schindler, M.; Springer-Verlag: Heidelberg, Germany, 1990; Vol. 23.

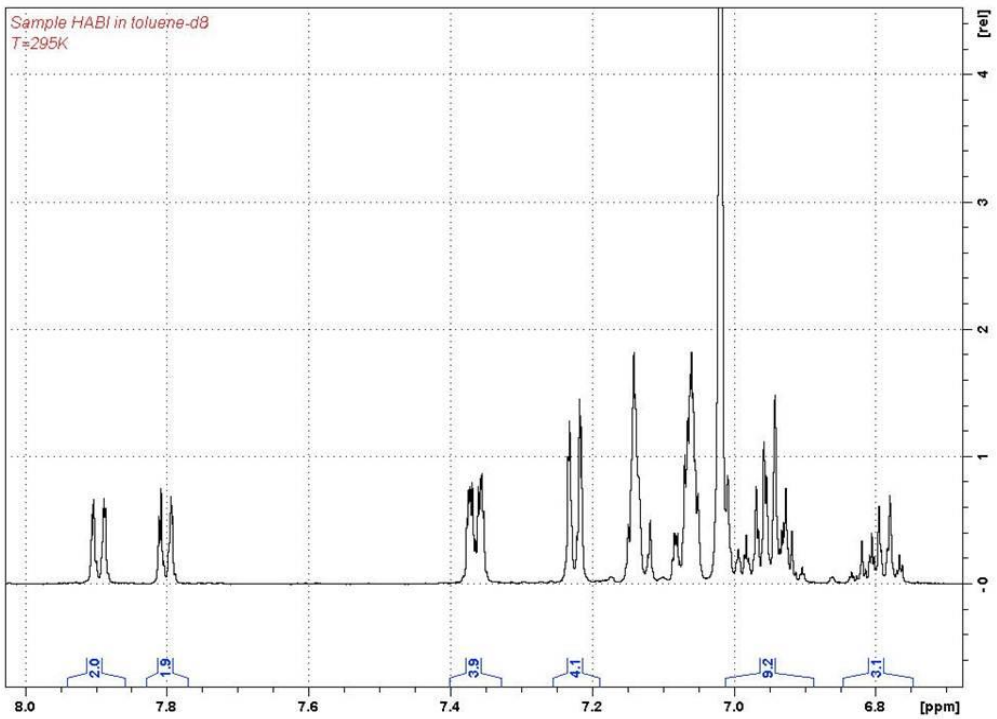
[10]. Huzinaga, S. J. Chem. Phys. 1965, 42, 1293−1302.

3. NMR characterization of 1,2'-dimer of HABI

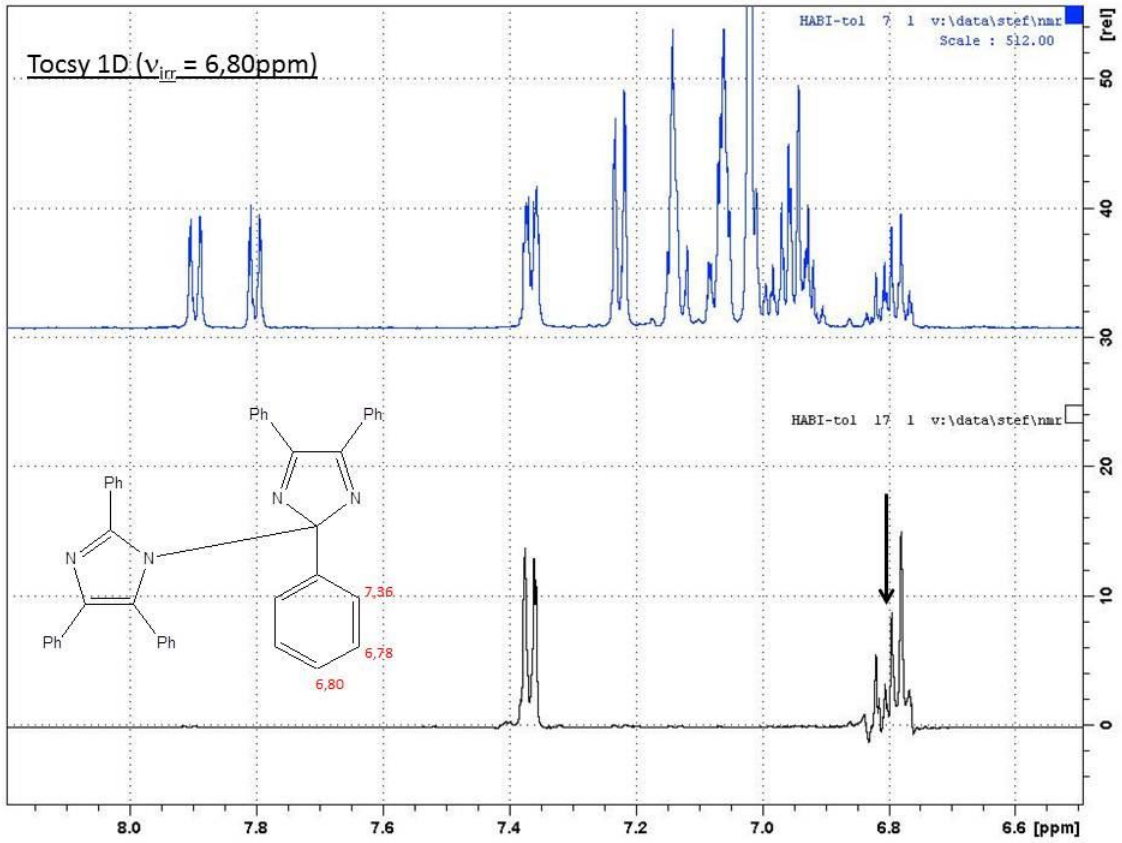
a) ^{1}H and ^{13}C chemical shifts of 1,2'-HABI in toluene-d_8 at rt

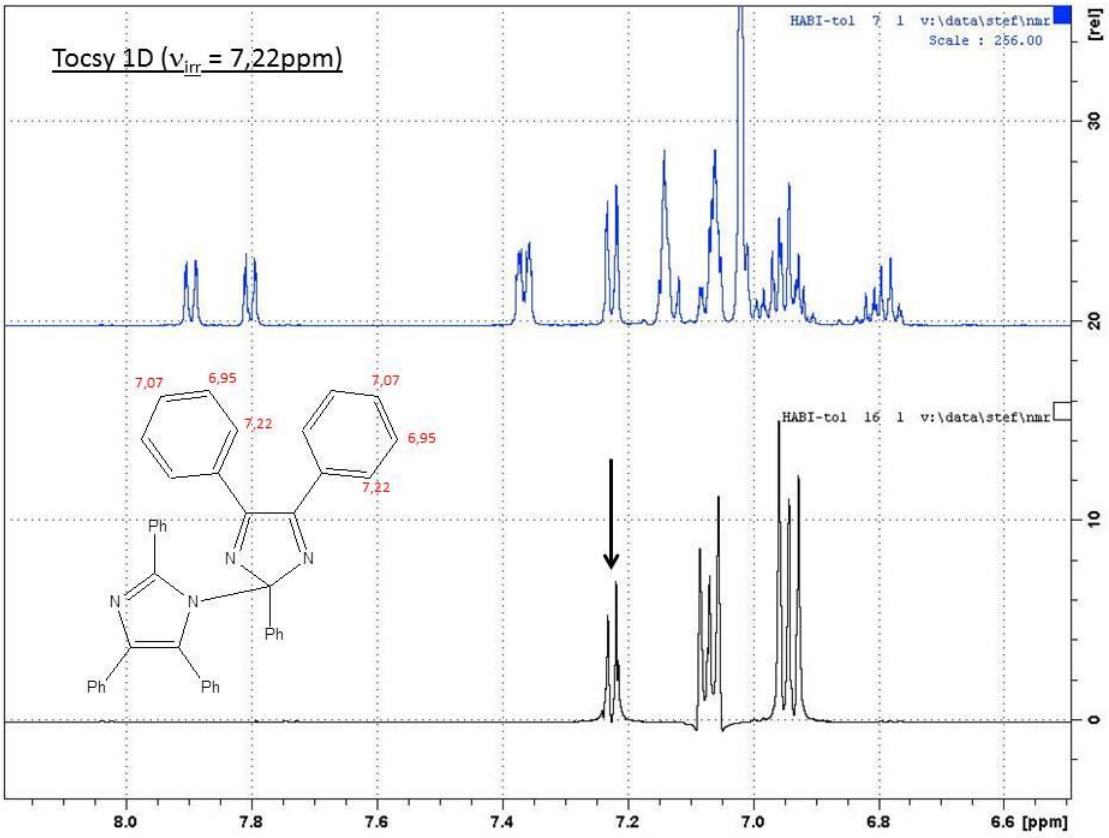


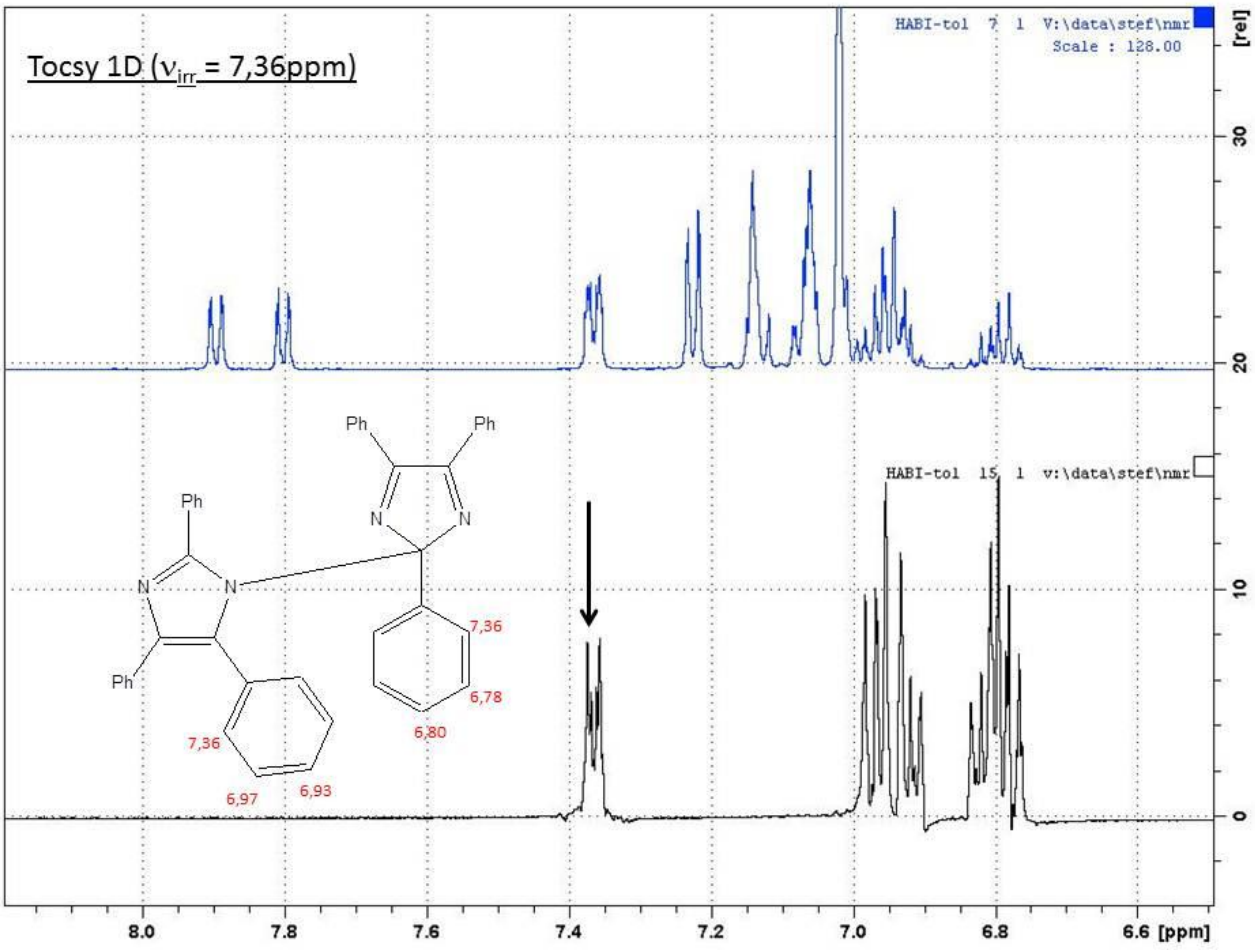
b) ^{1}H NMR spectrum of 1,2'-HABI in toluene-d_8 at rt

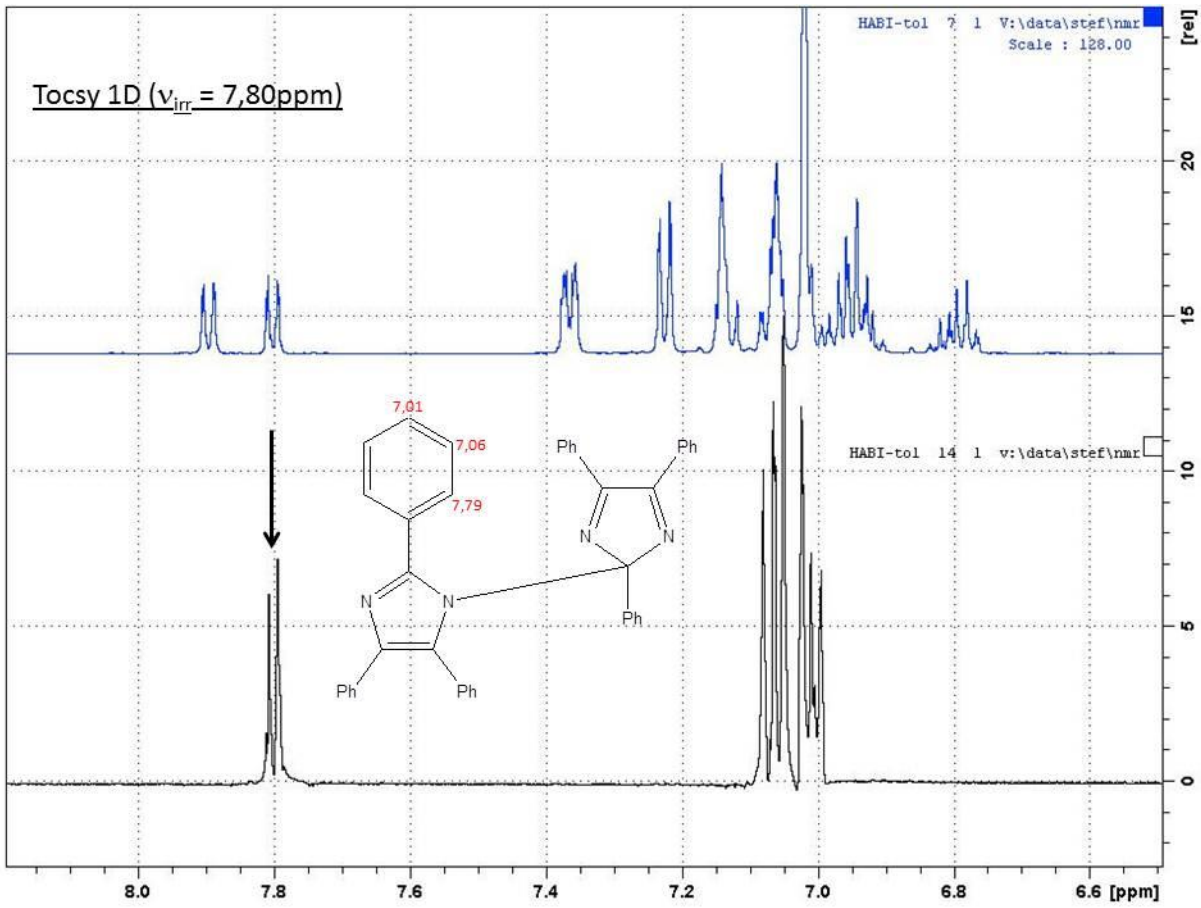


c) Tocsy NMR spectra of 1,2'-HABI in toluene-d_8 at rt






Tocsy 1D (ν_{irr} = 7,36ppm)
HABI-tol 7 1 V:\data\stef\nmr
Scale : 128.00
HABI-tol 15 1 v:\data\stef\nmr
Ph
Ph
N
N
Ph
N
N
Ph
7,36
6,78
6,80
7,36
6,97
6,93
[rel]
30
20
10
0
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6 [ppm]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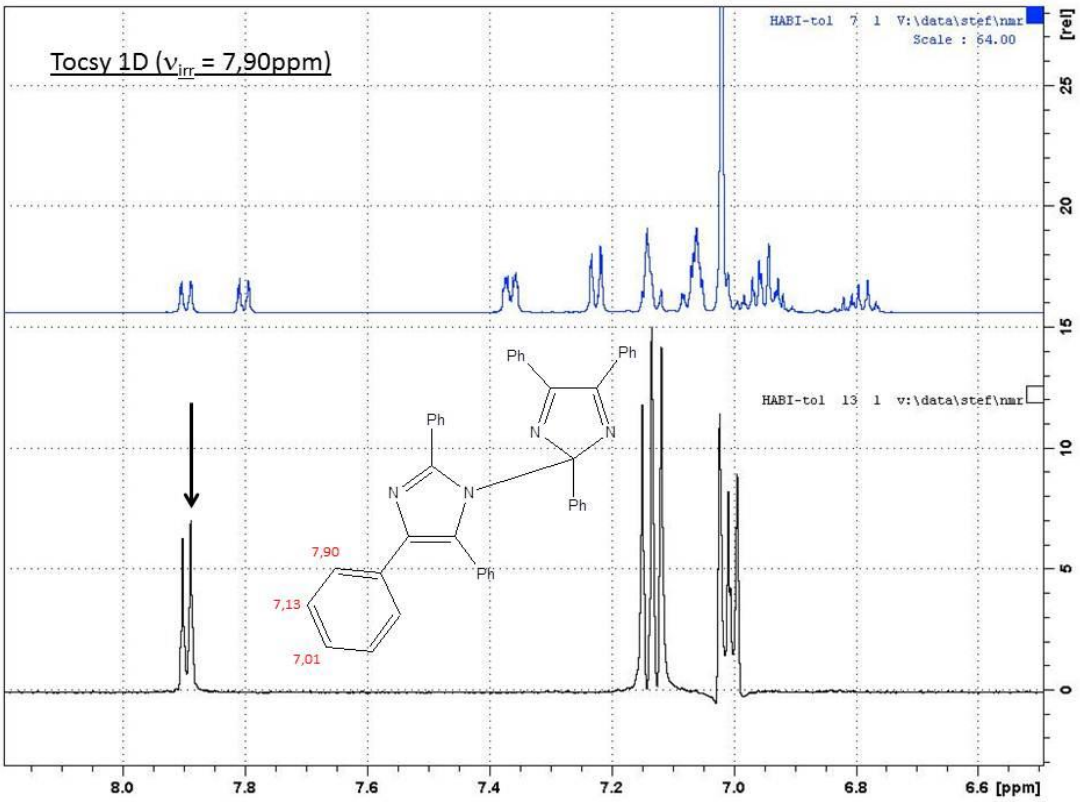
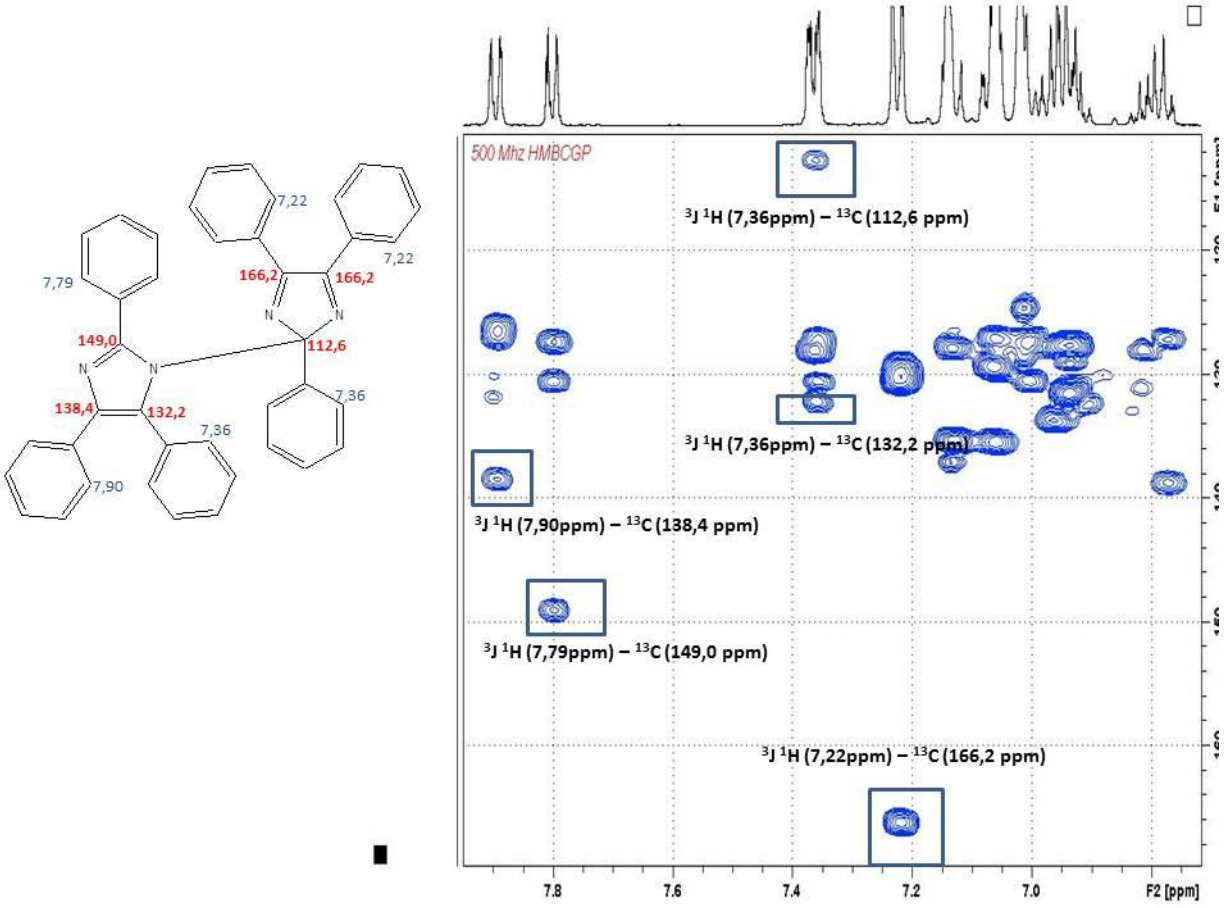
Scale : 128.00
HABI-tol 14 1 v:\data\stef\nmr
7,01
7,06
7,79
Ph
Ph
N
N
Ph
N
N
Ph
Ph
[rel]
20
15
10
5
0
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6 [ppm]

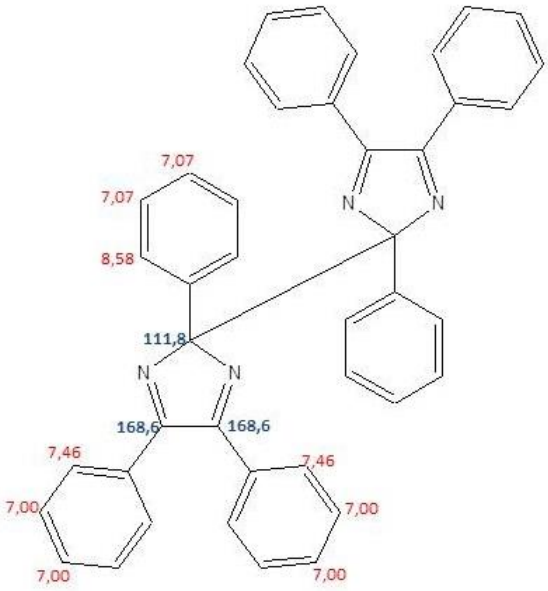


d) ^{1}H-^{13}C NMR HMBC of 1,2'-HABI in toluene-d_8 at rt



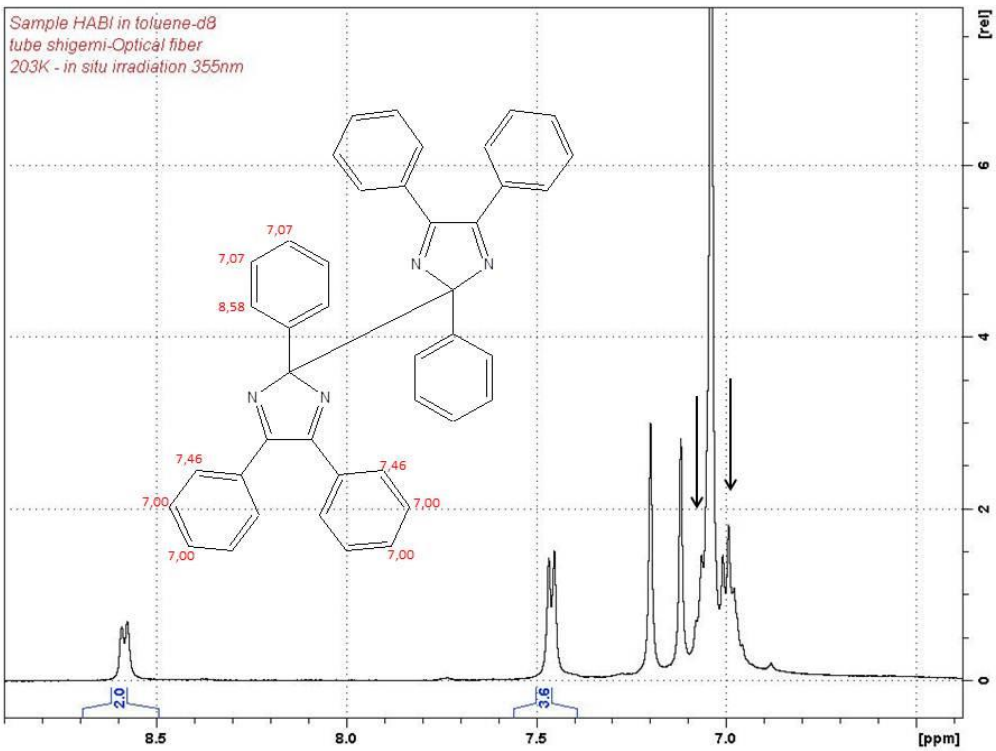
4. NMR characterization of 2,2'-dimer of HABI

a) ^{1}H and ^{13}C chemical shifts of 2,2'-HABI in toluene-d_8 at 203K

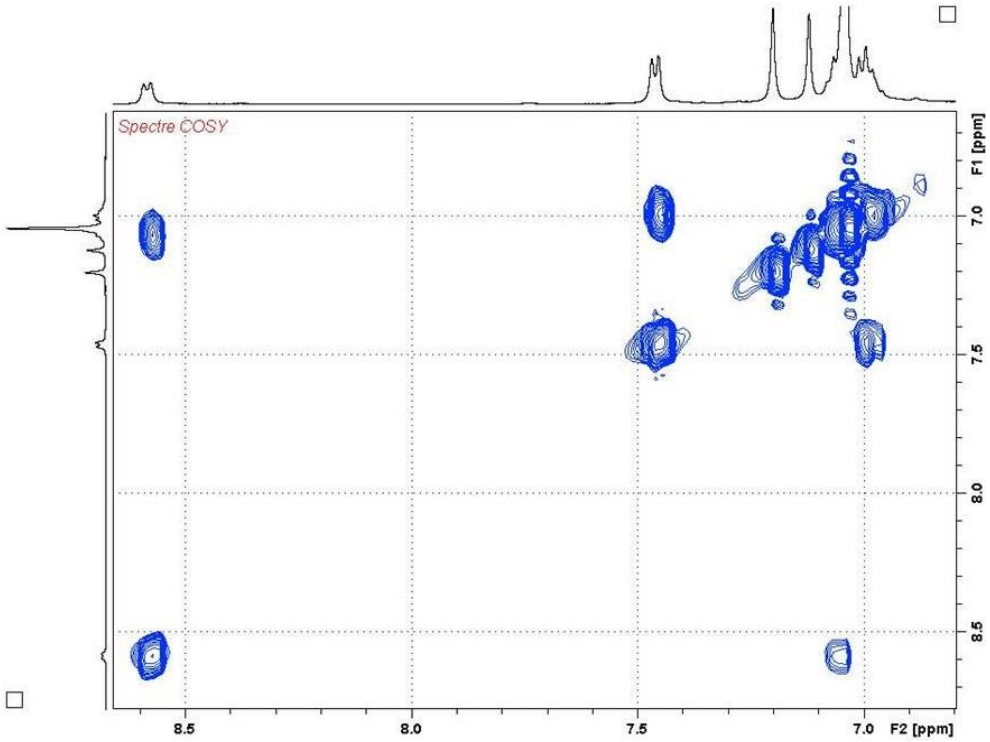


The two imidazolyl are symmetrical so equivalent resonances are observed

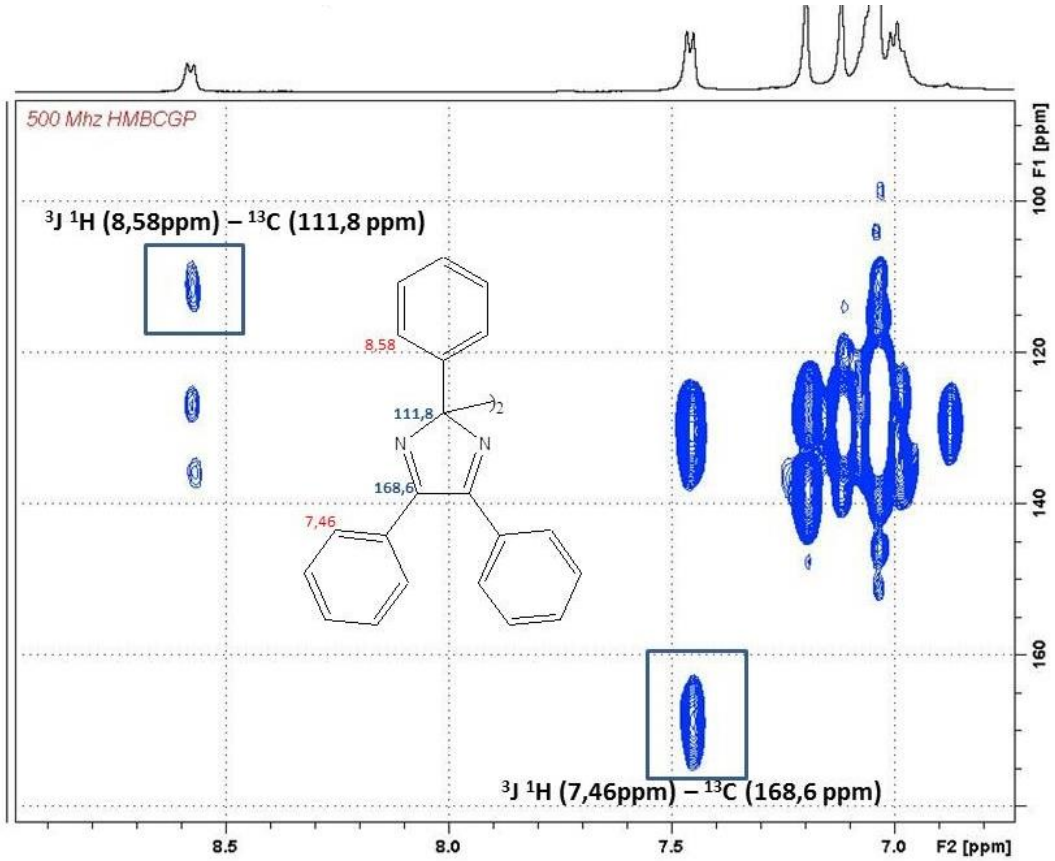
b) ^{1}H NMR spectrum of 2,2'-HABI in toluene-d_8 at 203K



c) ^{1}H-^{1}H NMR COSY of 2,2'-HABI in toluene-d_8 at rt

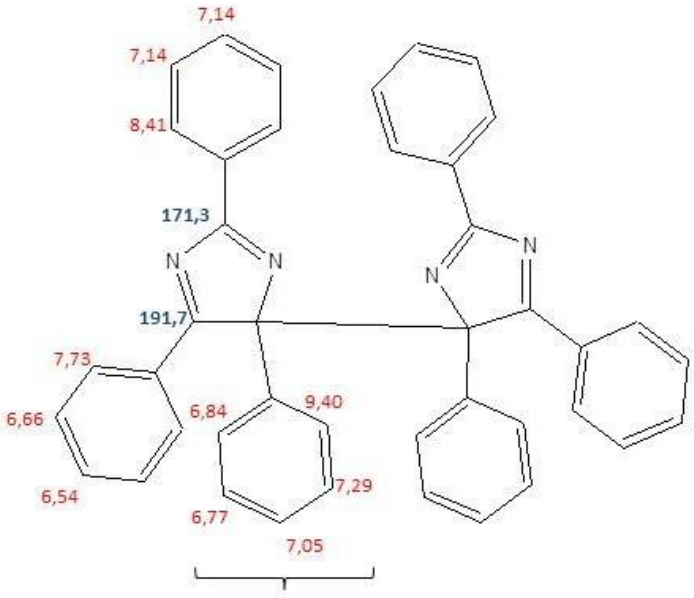


d) ^{1}H-^{13}C NMR HMBC of 2,2'-HABI in toluene-d_8 at 203K



5. NMR characterization of 4,4'-dimer of HABI

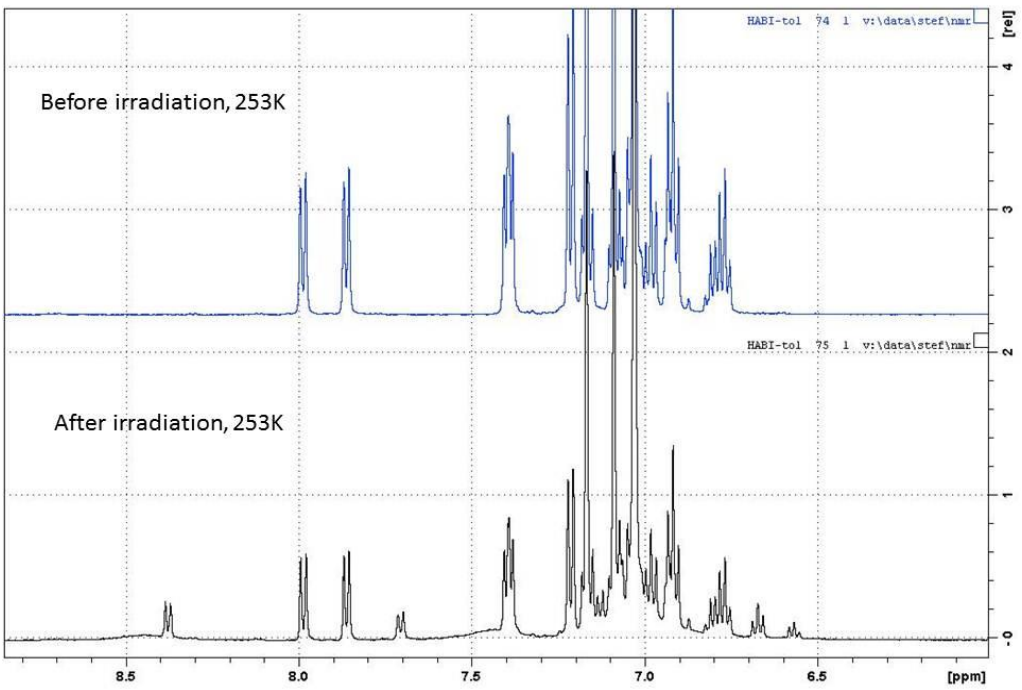
a) ^{1}H and ^{13}C chemical shifts of 4,4'-HABI in toluene-d_8 at 253K



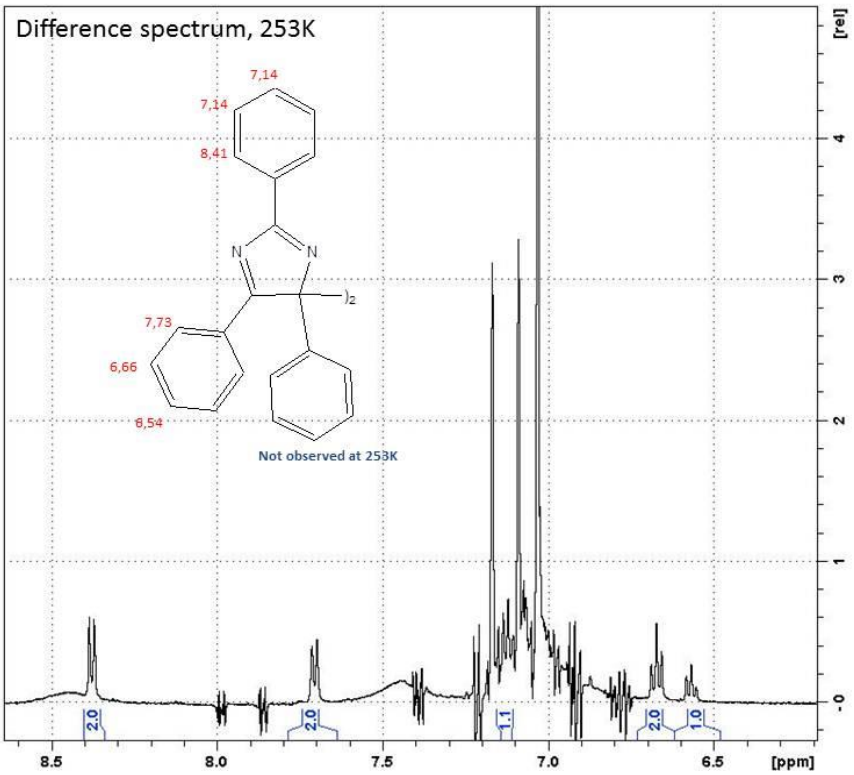
Observed as resolved signals at 193K

The two imidazolyl are symmetrical so equivalent resonances are observed

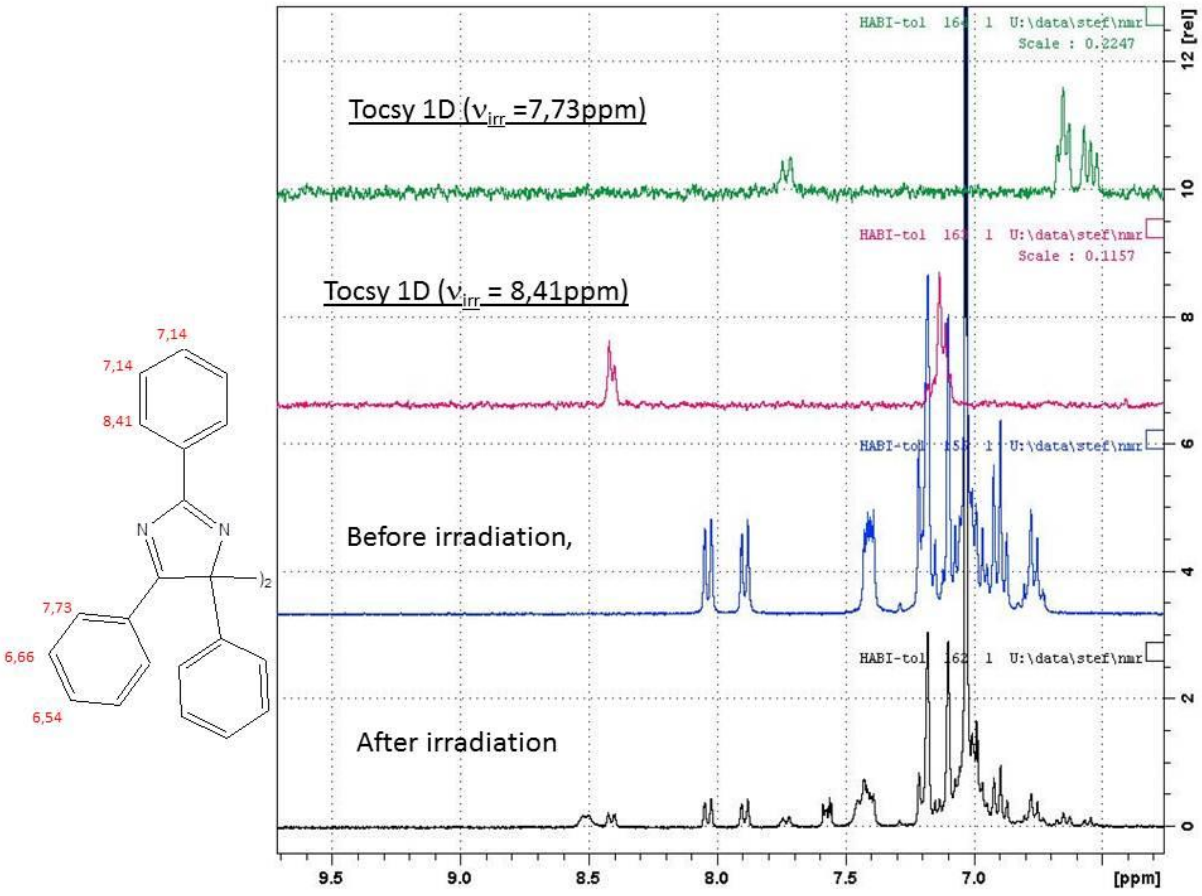
b) ^{1}H NMR spectra of 4,4'-HABI in toluene-d_8 at 253K



c) ^{1}H NMR difference spectrum with integration of 4,4'-HABI in toluene-d_8 at 253K

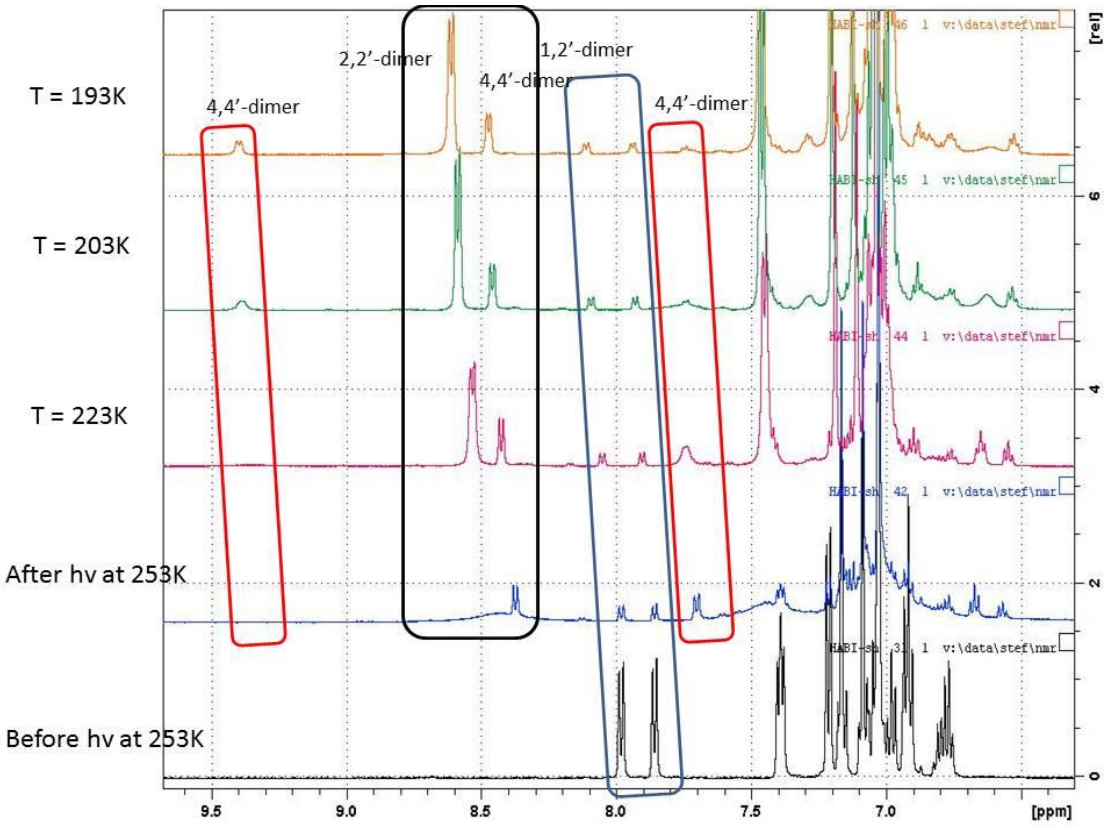


d) ^{1}H NMR TOCSY of 4,4'-HABI in toluene-d_8 at 253K

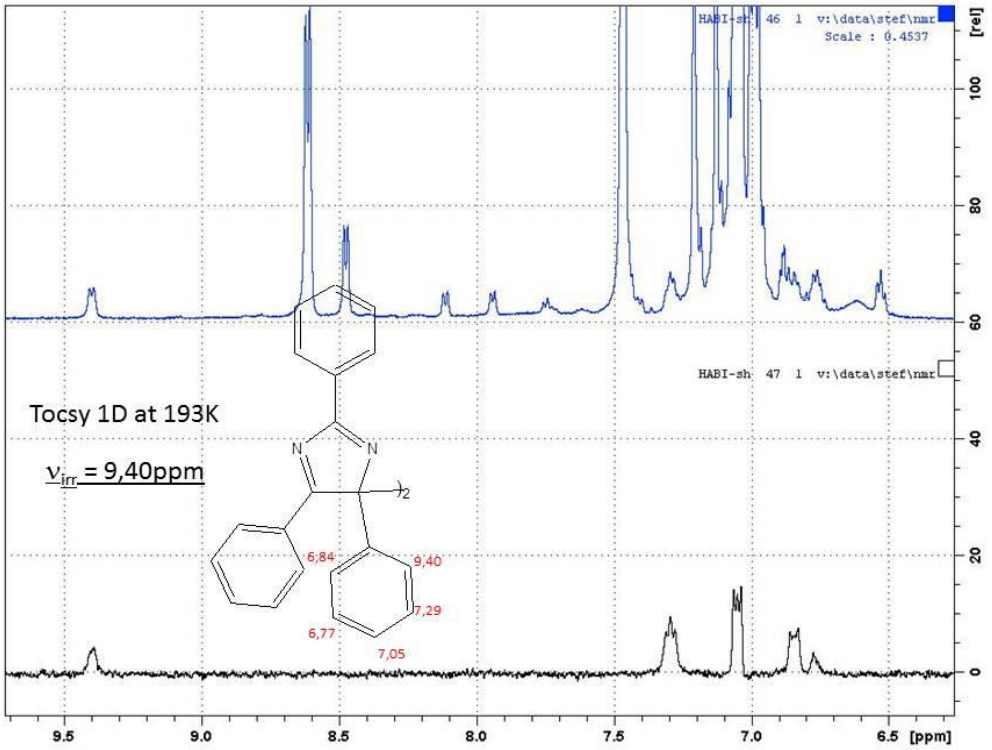


e) ^{1}H NMR spectra at various T of 4,4'-HABI in toluene-d_8

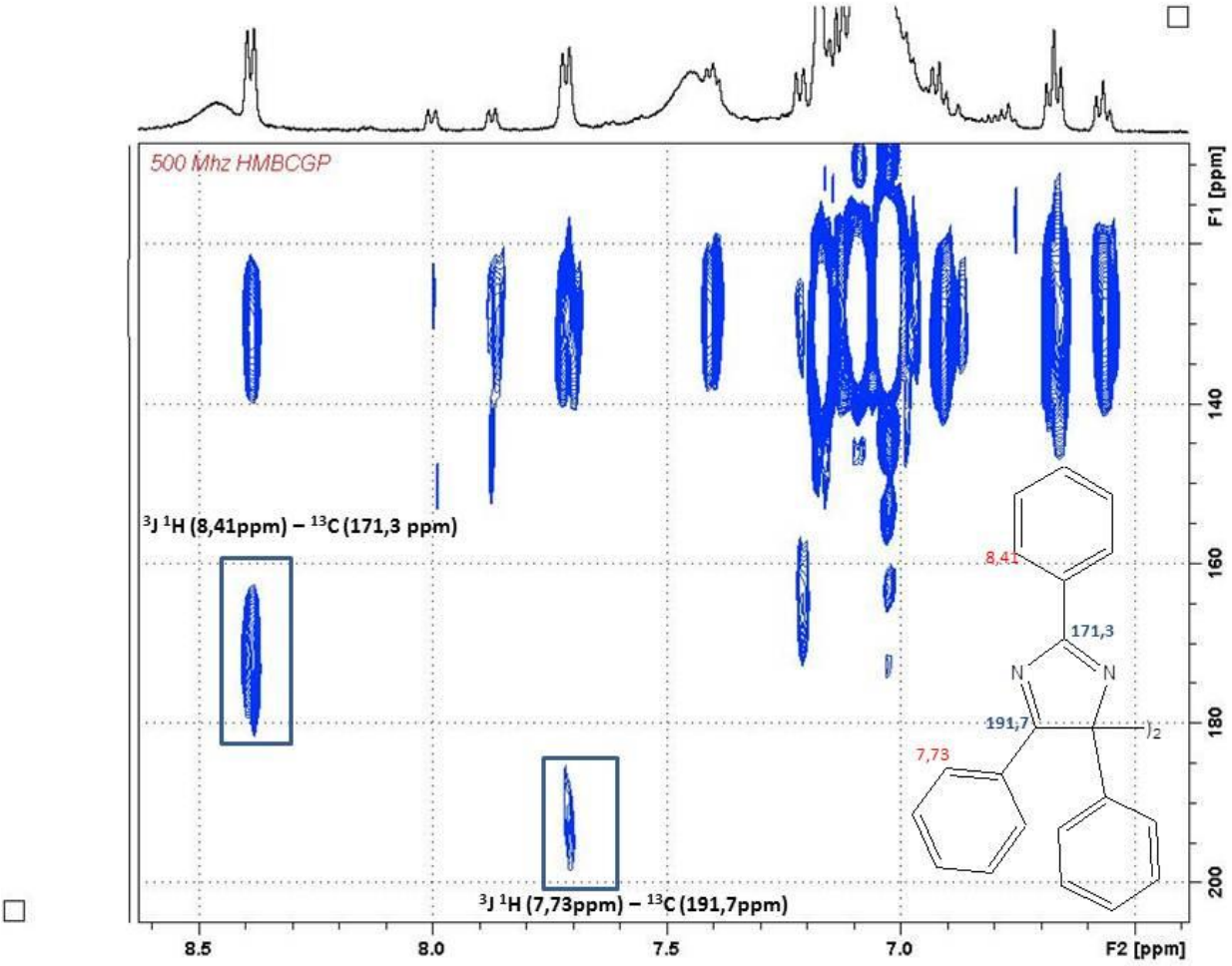
The sample irradiated at 253 K was frozen progressively to evidence the apparition of fine structure for broad signals



f) ^{1}H NMR TOCSY of 4,4'-HABI in toluene-d_8 at 193K

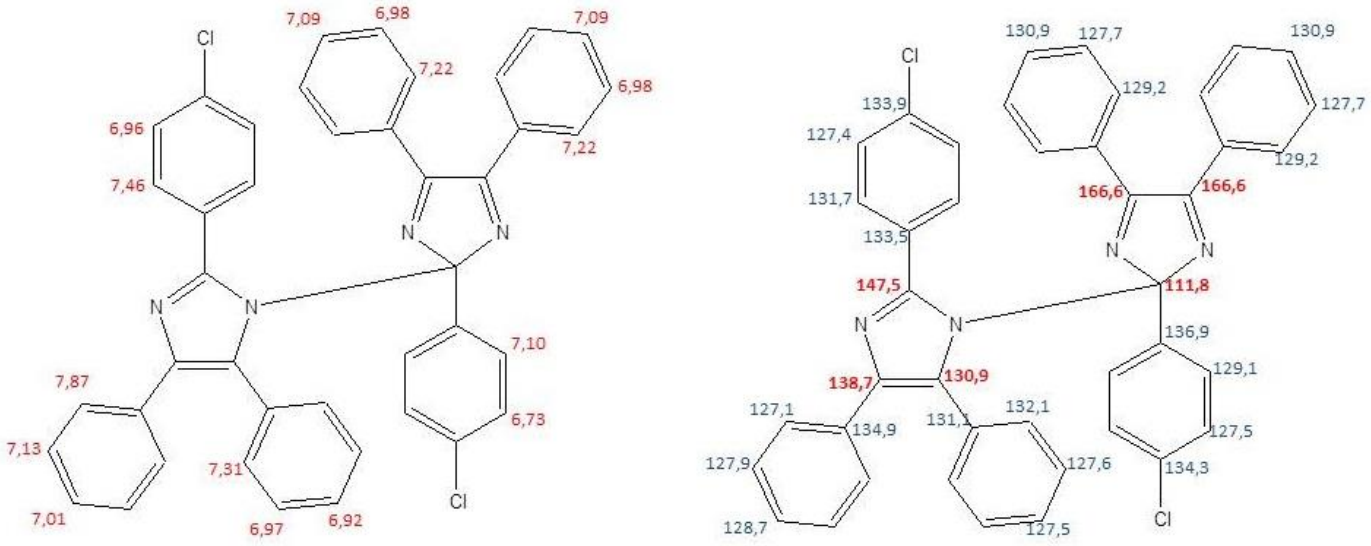


g) ^{1}H-^{13}C NMR HMBC of 4,4'-HABI in toluene-d_8

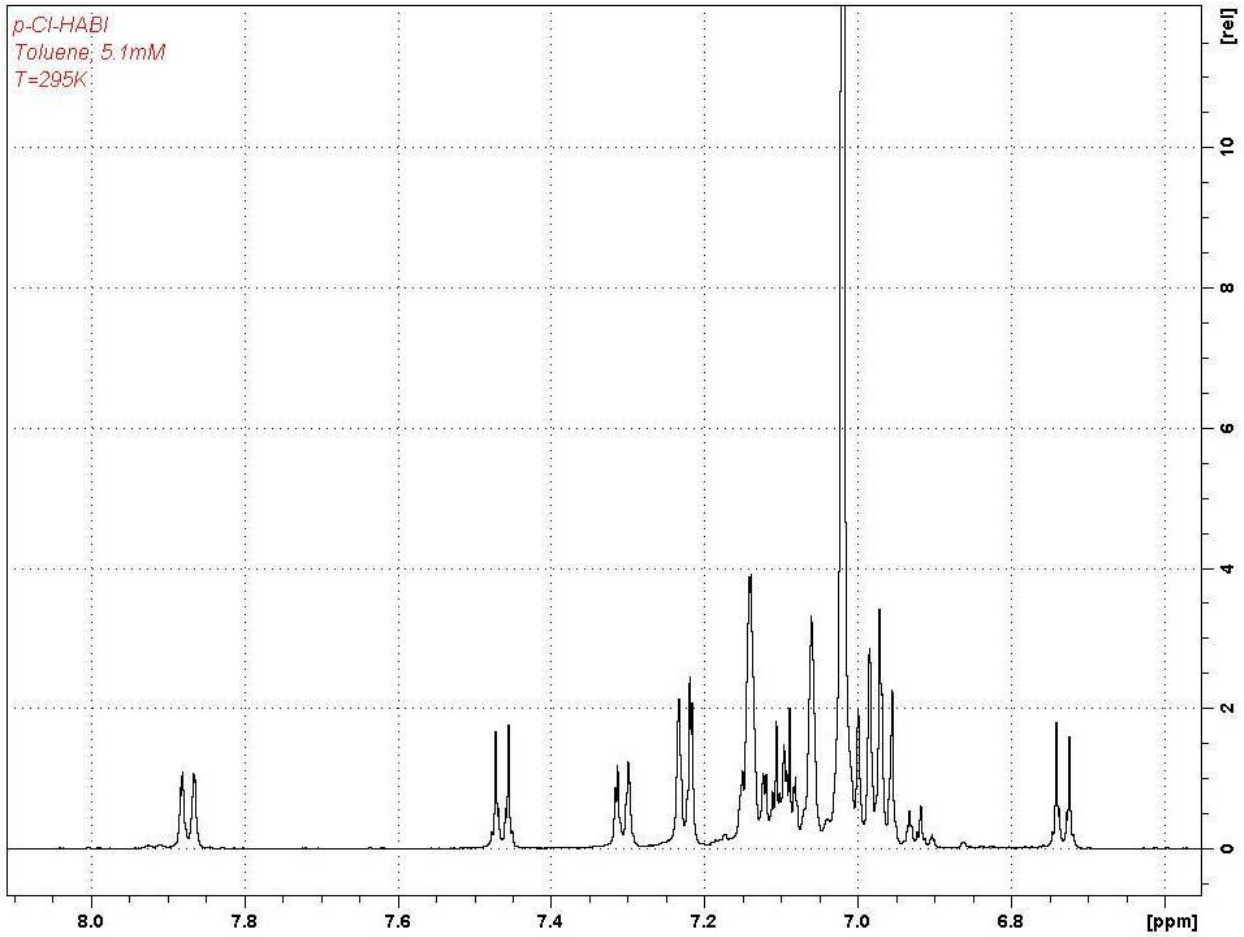


6. NMR characterization of 1,2'-dimer of p-Cl-HABI

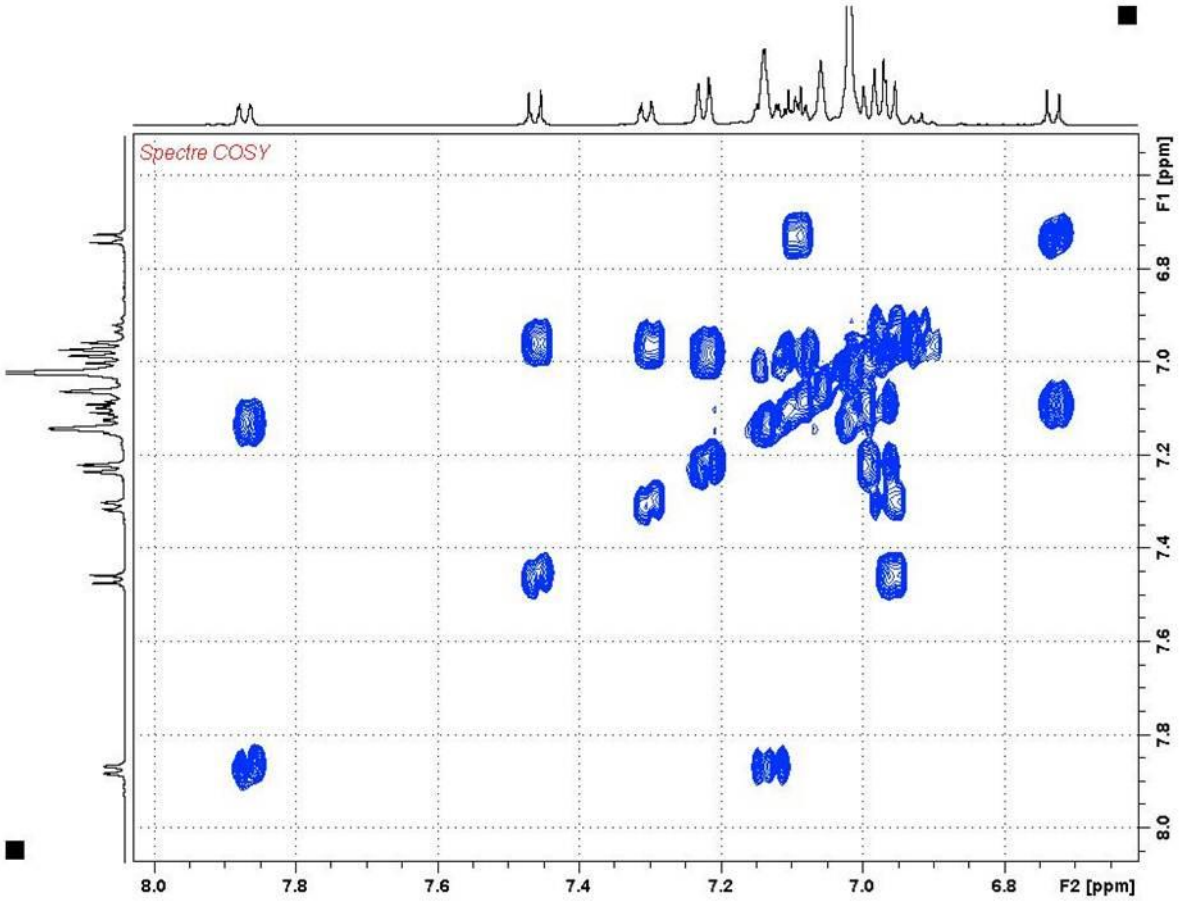
a) ^{1}H and ^{13}C chemical shifts of 1,2'-p-Cl-HABI in toluene-d_8 at rt



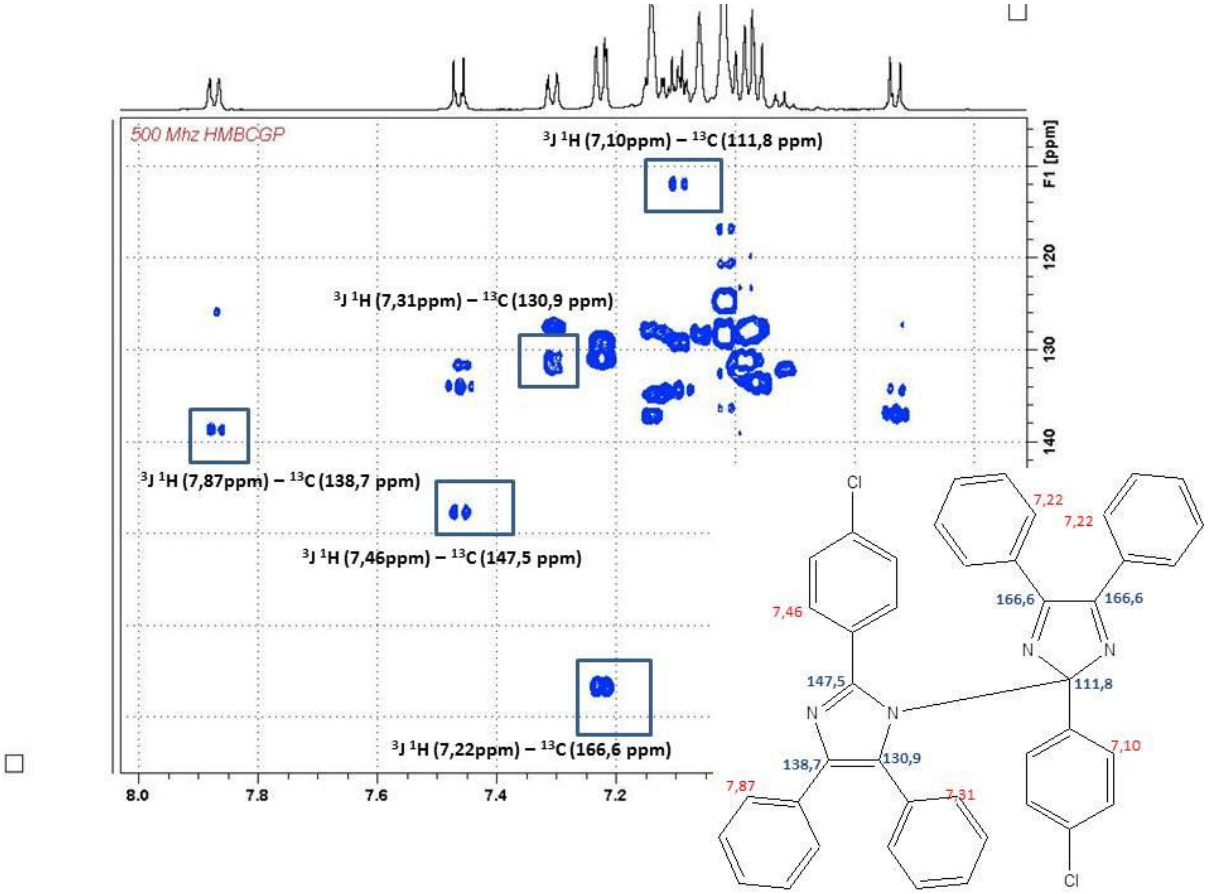
b) ^{1}H NMR spectrum of 1,2'-p-Cl-HABI in toluene-d_8 at rt



c) ^{1}H-^{1}H NMR COSY of 1,2'-p-Cl-HABI in toluene-d_8 at rt

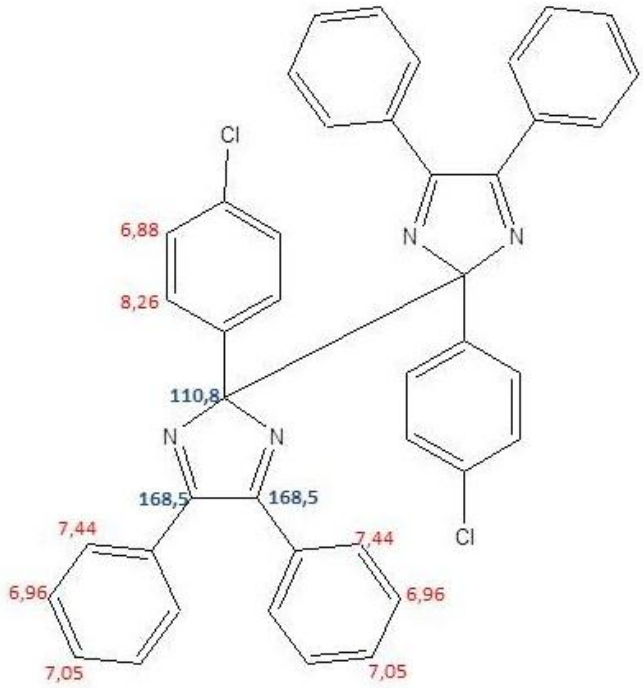


d) ^{1}H-^{13}C NMR HMBC of 1,2'-p-Cl-HABI in toluene-d_8 at rt



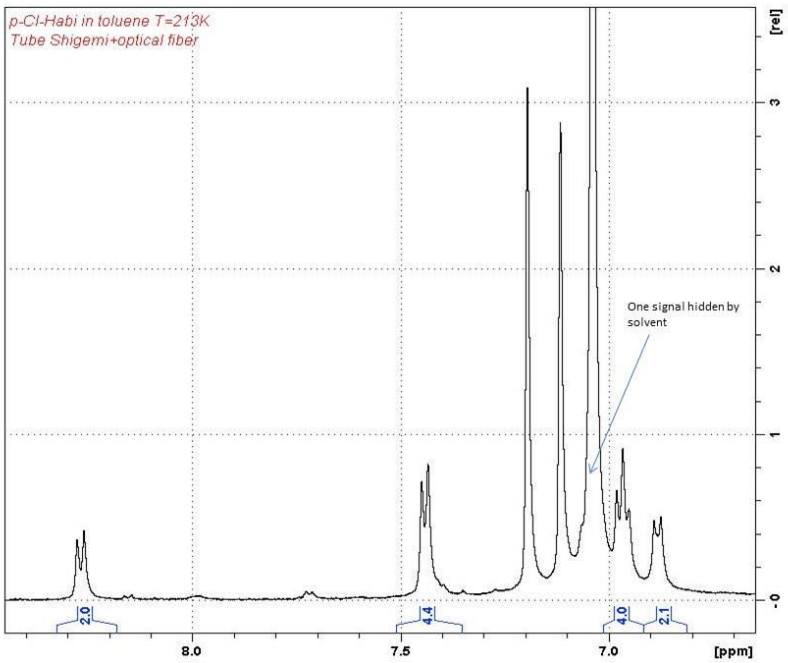
7. NMR characterization of 2,2'-dimer of p-Cl-HABI

a) ^{1}H and ^{13}C chemical shifts of 2,2'-p-Cl-HABI in toluene-d_8 at 213K

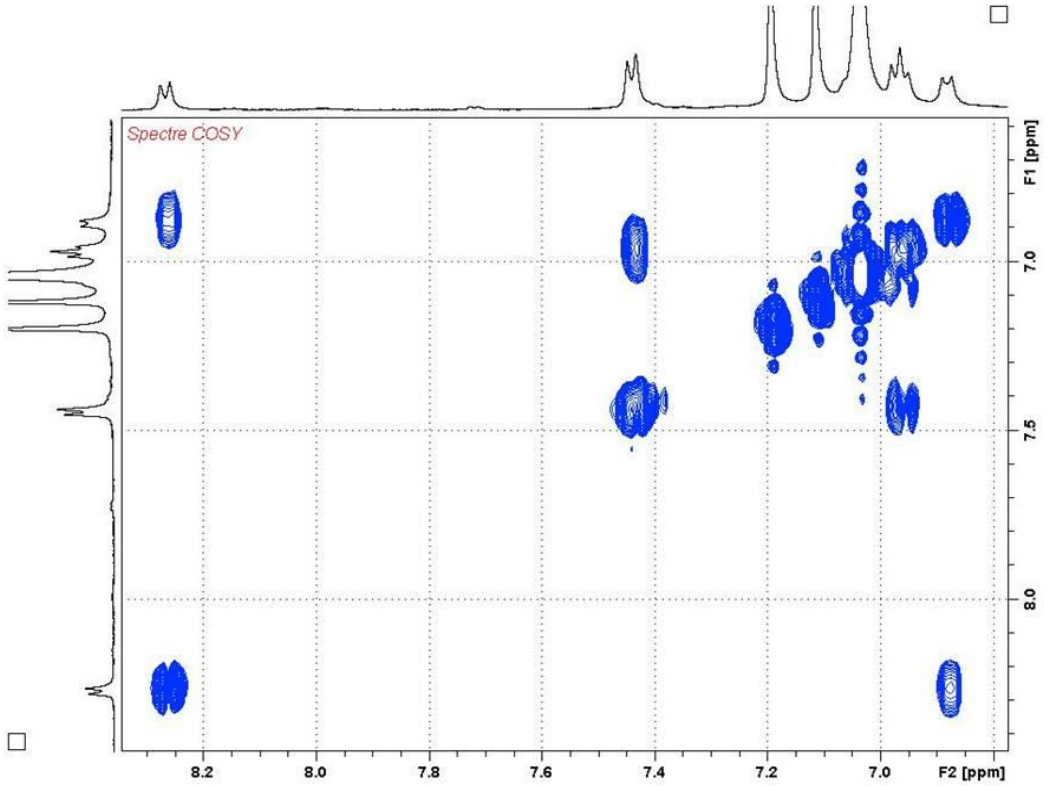


The two imidazolyl are symmetrical so equivalent resonances are observed

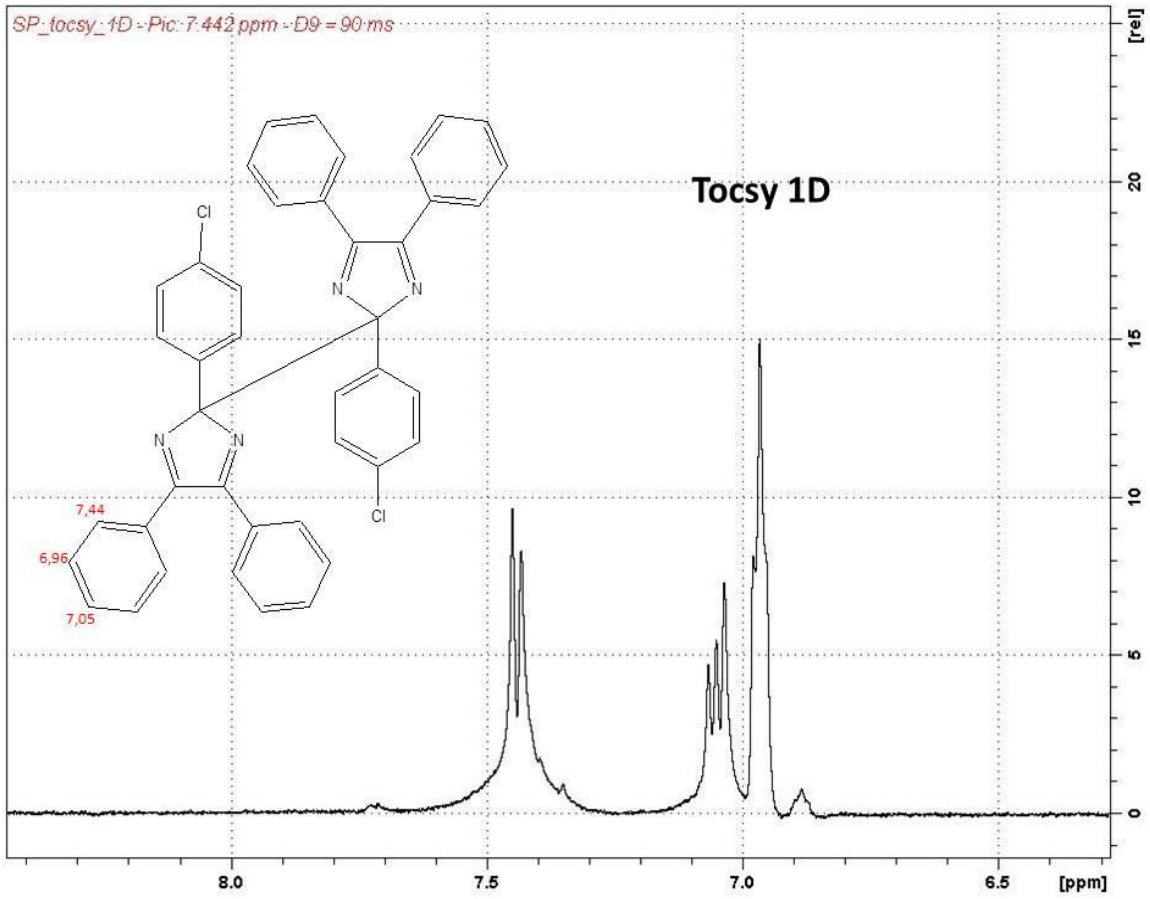
b) ^{1}H NMR spectrum of 2,2'-p-Cl-HABI with integration in toluene-d_8 at 213K



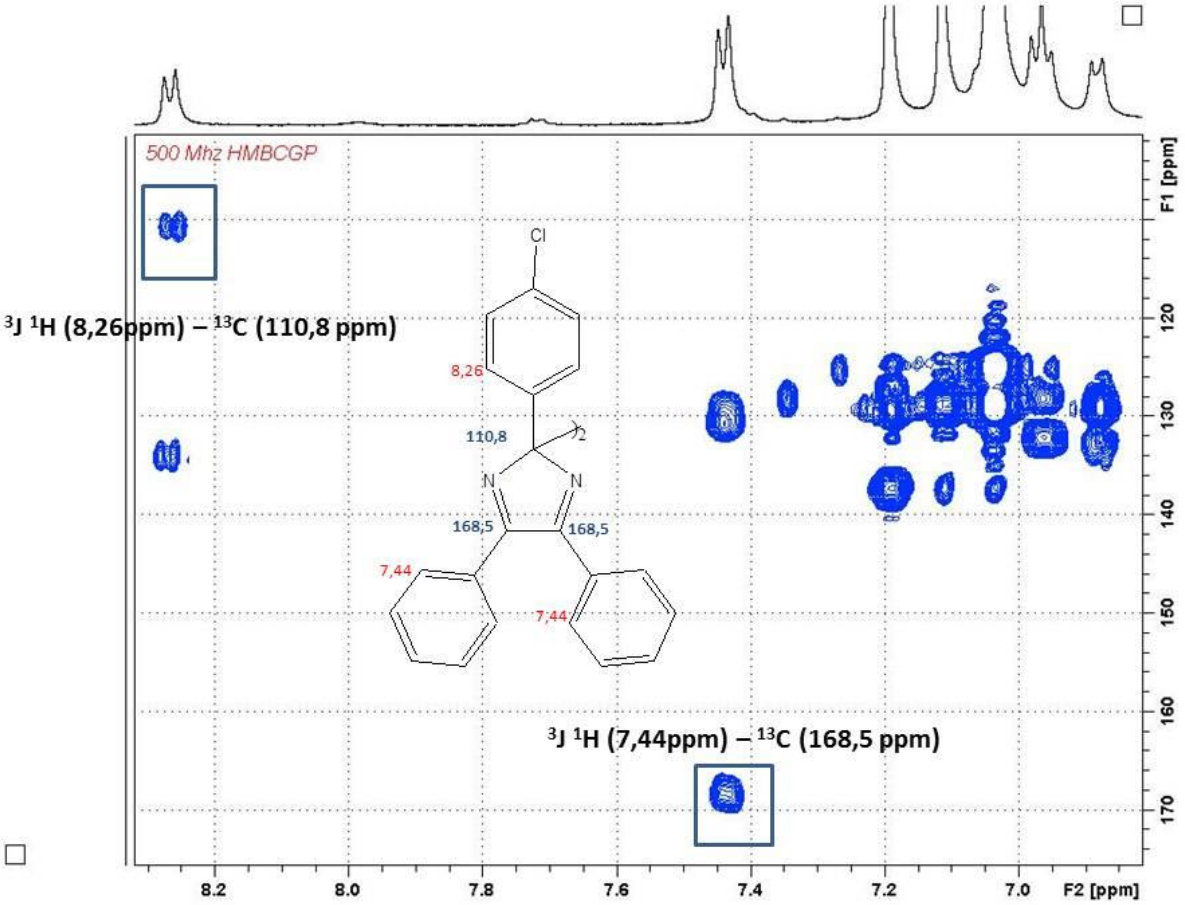
c) ^{1}H-^{1}H NMR COSY of 2,2'-p-Cl-HABI in toluene-d_8 at 213K



d) ^{1}H NMR TOCSY of 2,2'-p-Cl-HABI in toluene-d_8 at 213K

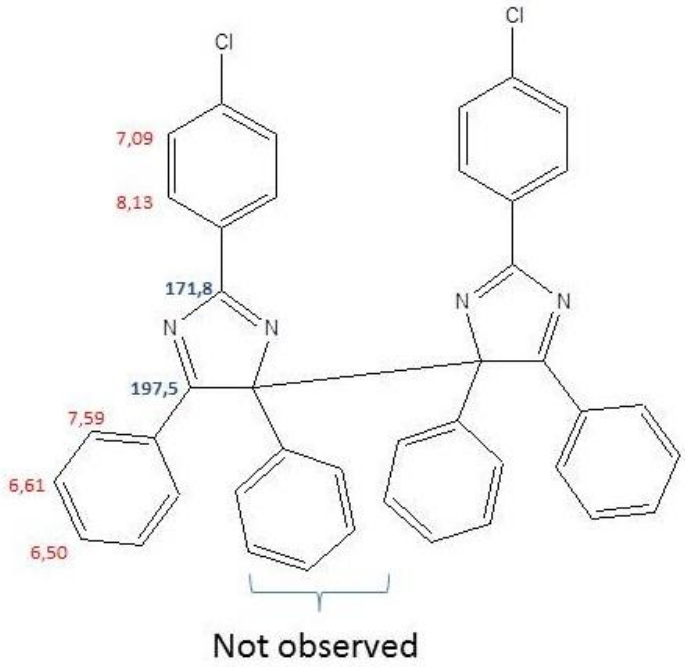


e) ^{1}H-^{13}C NMR HMBC of 2,2'-p-Cl-HABI in toluene-d_8 at 213K

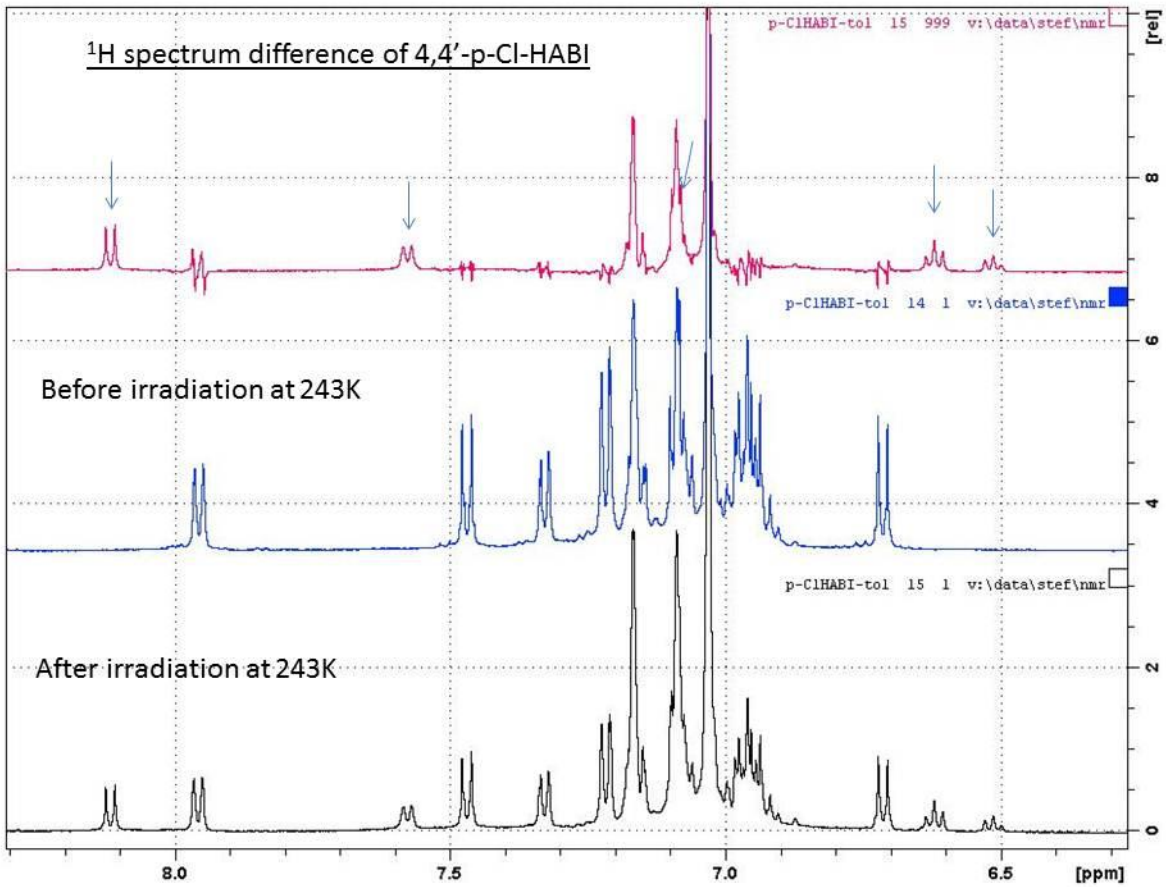


8) NMR characterization of 4,4'-dimer of p-Cl-HABI

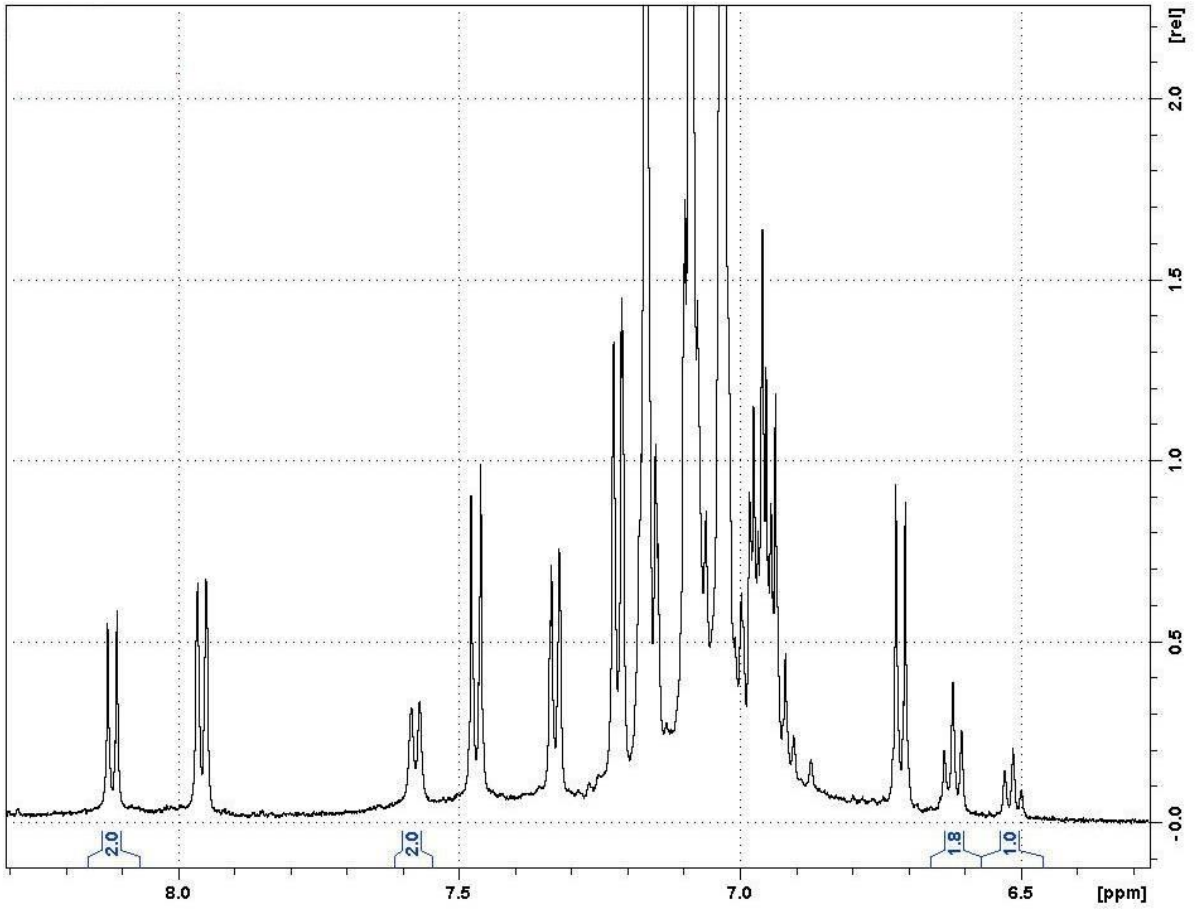
a) ^{1}H and ^{13}C chemical shifts of 4,4'-p-Cl-HABI in toluene-d_8 at 243K



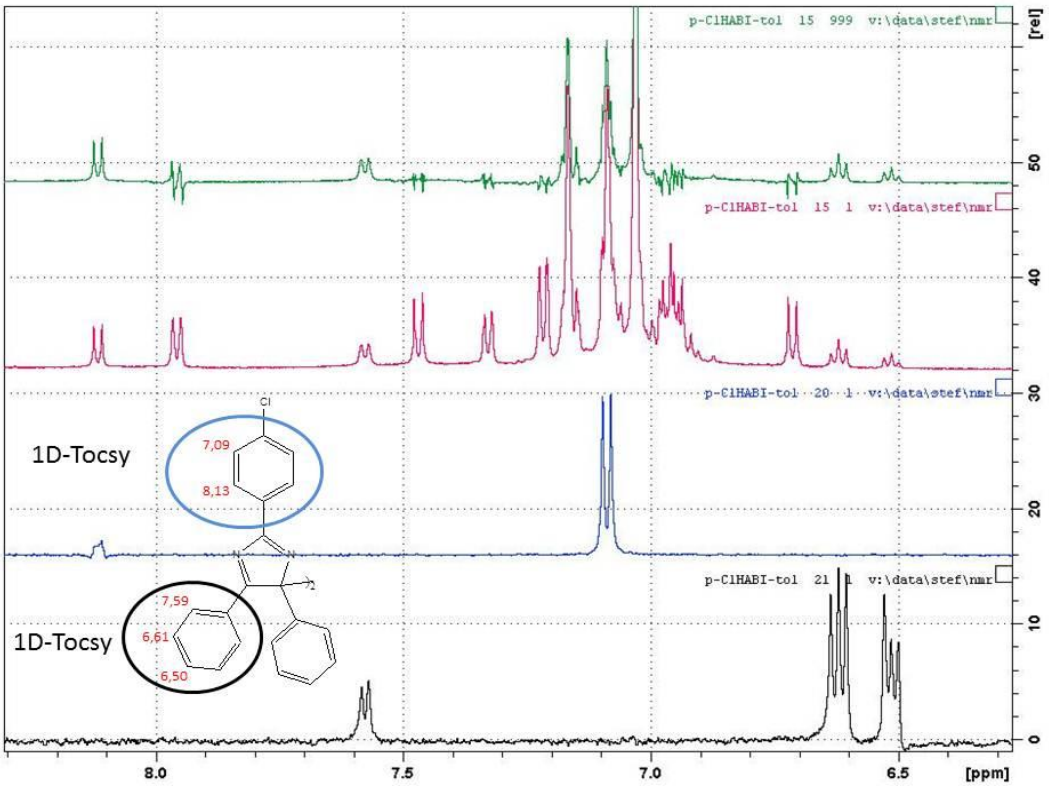
b) ^{1}H NMR spectra of 4,4'-p-Cl-HABI in toluene-d_8 at 243K



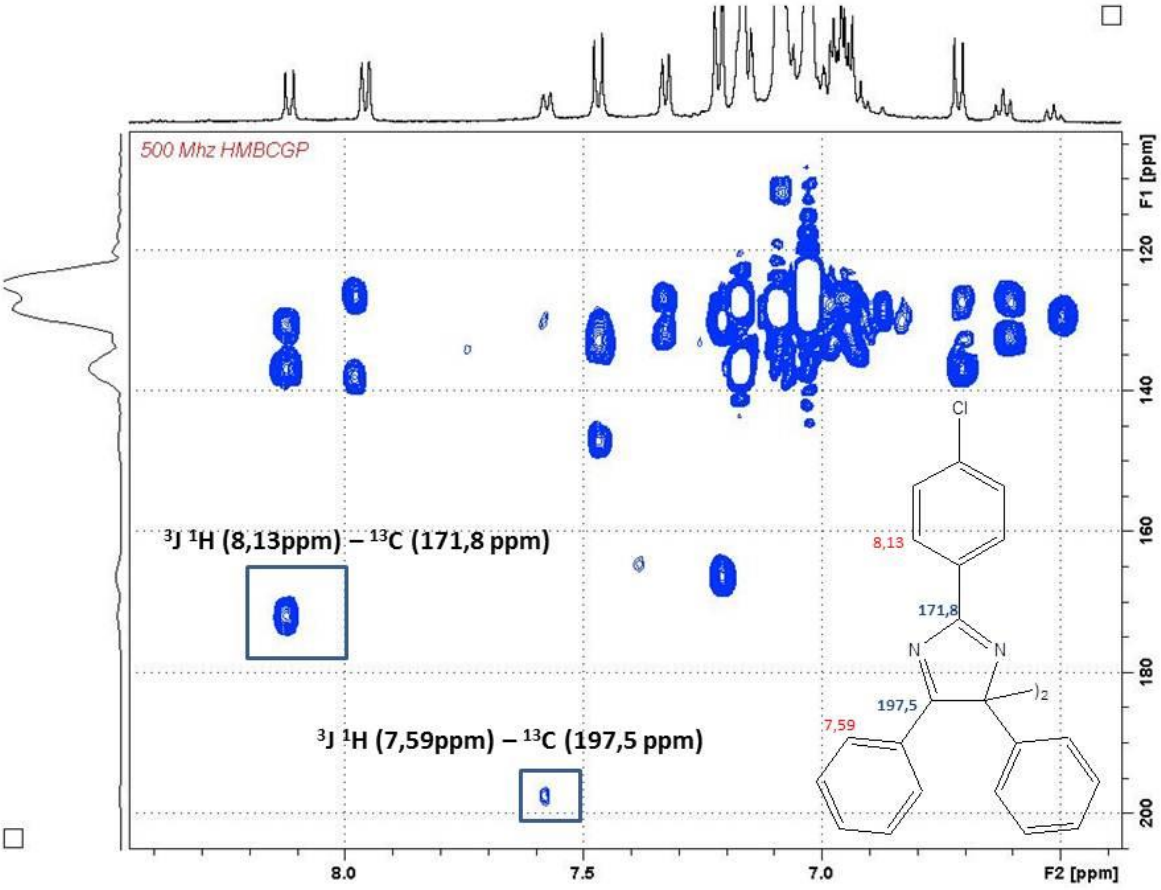
c) ^{1}H NMR spectrum with integration of 4,4'-p-Cl-HABI in toluene-d_8 at 243K



d) ^{1}H NMR TOCSY of 4,4'-p-Cl-HABI in toluene-d_8 at 243K

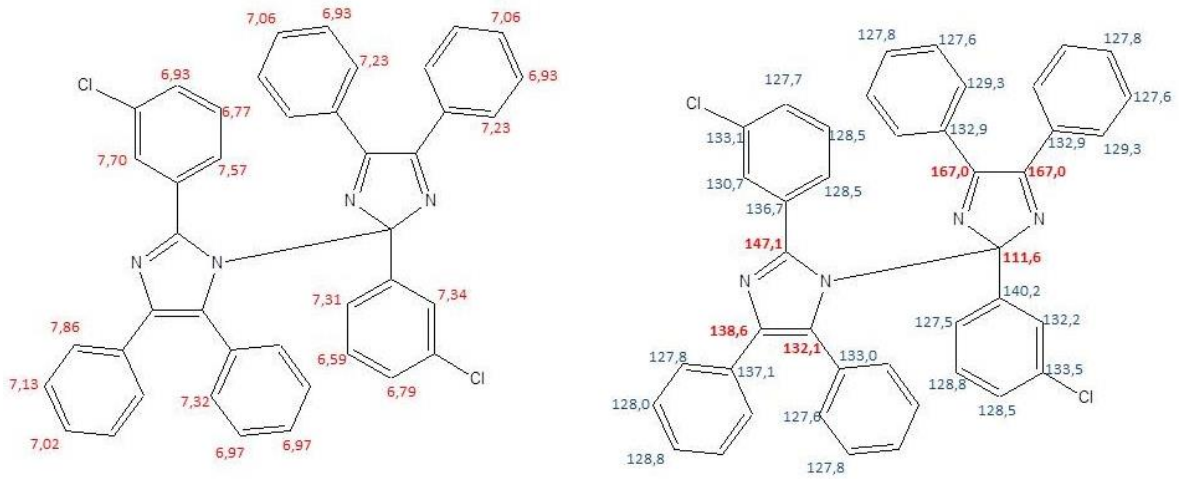


e) ^{1}H-^{13}C NMR HMBC of 4,4'-p-Cl-HABI in toluene-d_8 at 243K

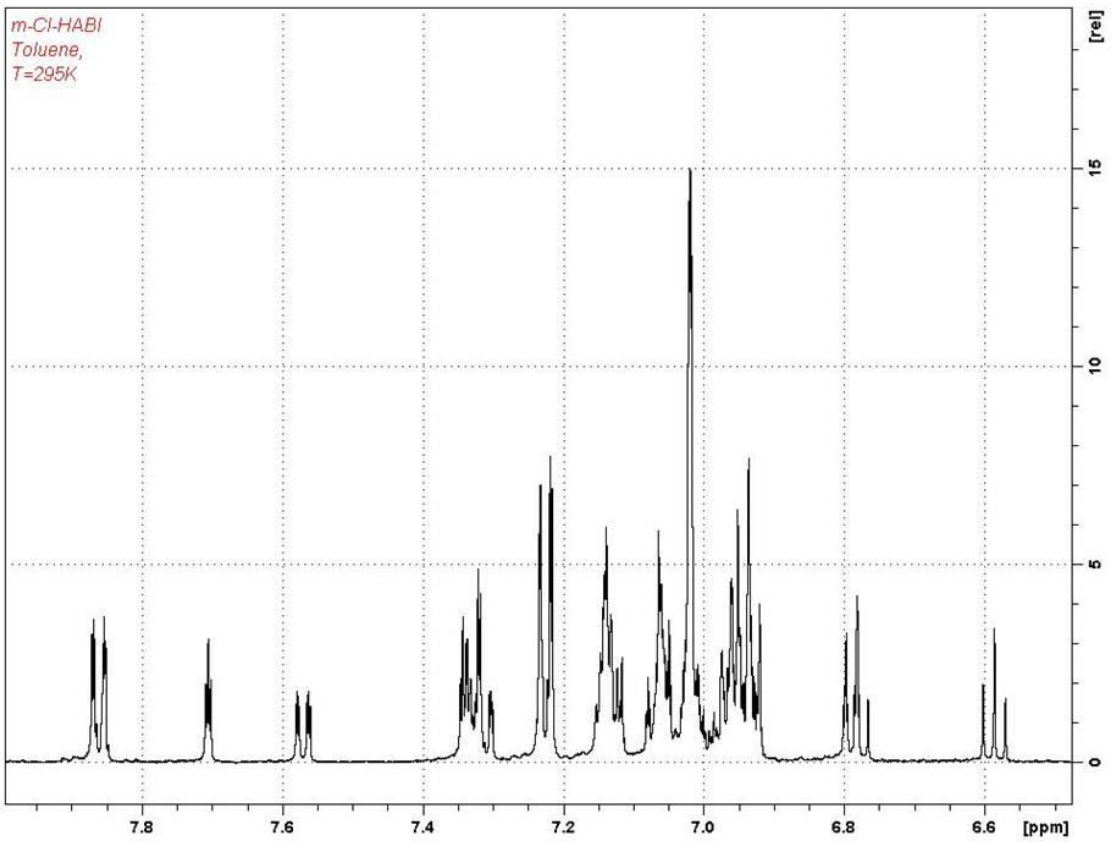


9) NMR characterization of 1,2'-dimer of m-Cl-HABI

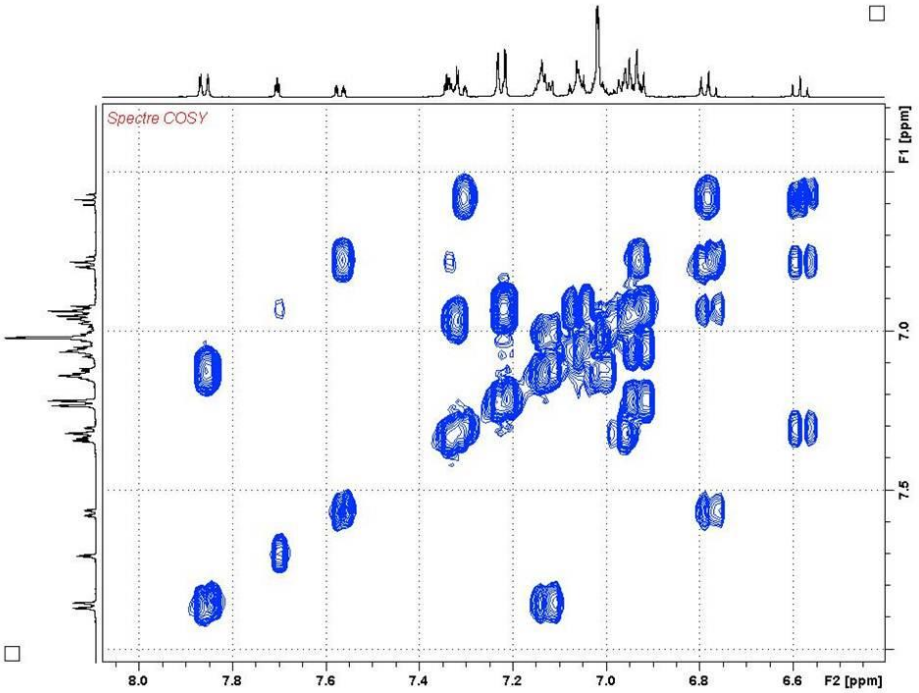
a) ^{1}H and ^{13}C chemical shifts of 1,2'-m-Cl-HABI in toluene-d_8 at rt



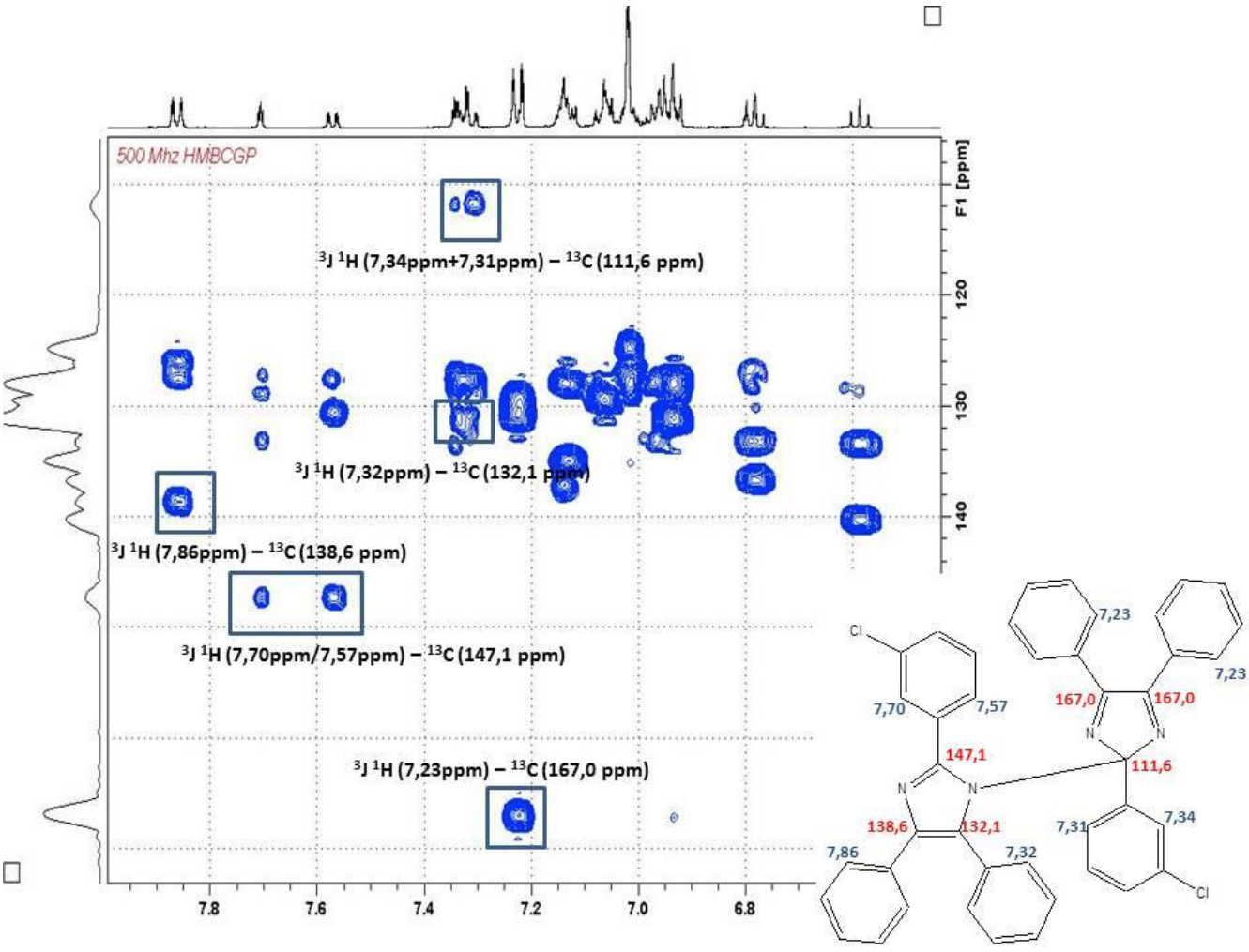
b) ^{1}H NMR spectrum of 1,2'-m-Cl-HABI in toluene-d_8 at rt



c) ^{1}H-^{1}H NMR COSY of 1,2'-m-Cl-HABI in toluene-d_8 at rt

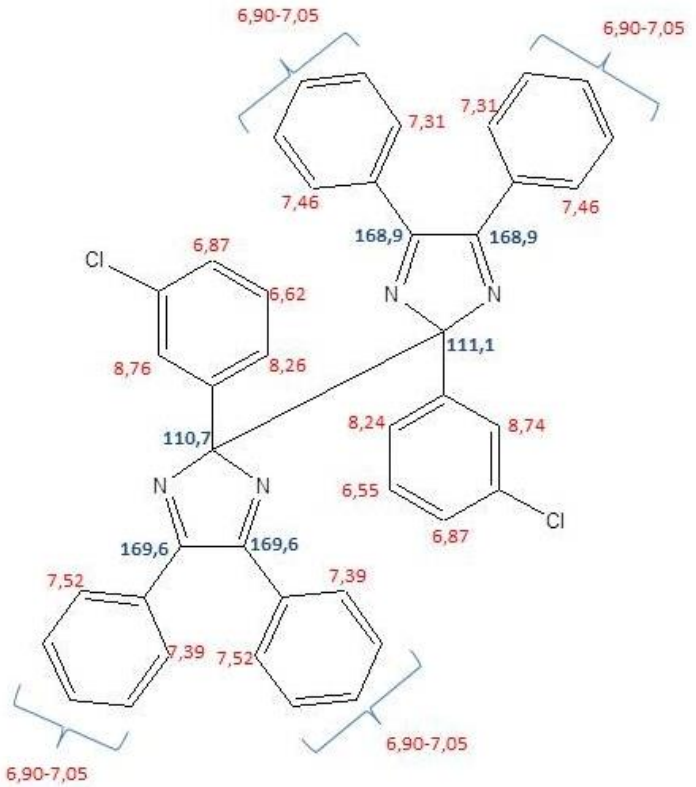


d) ^{1}H-^{13}C NMR HMBC of 1,2'-m-Cl-HABI in toluene-d_8 at rt

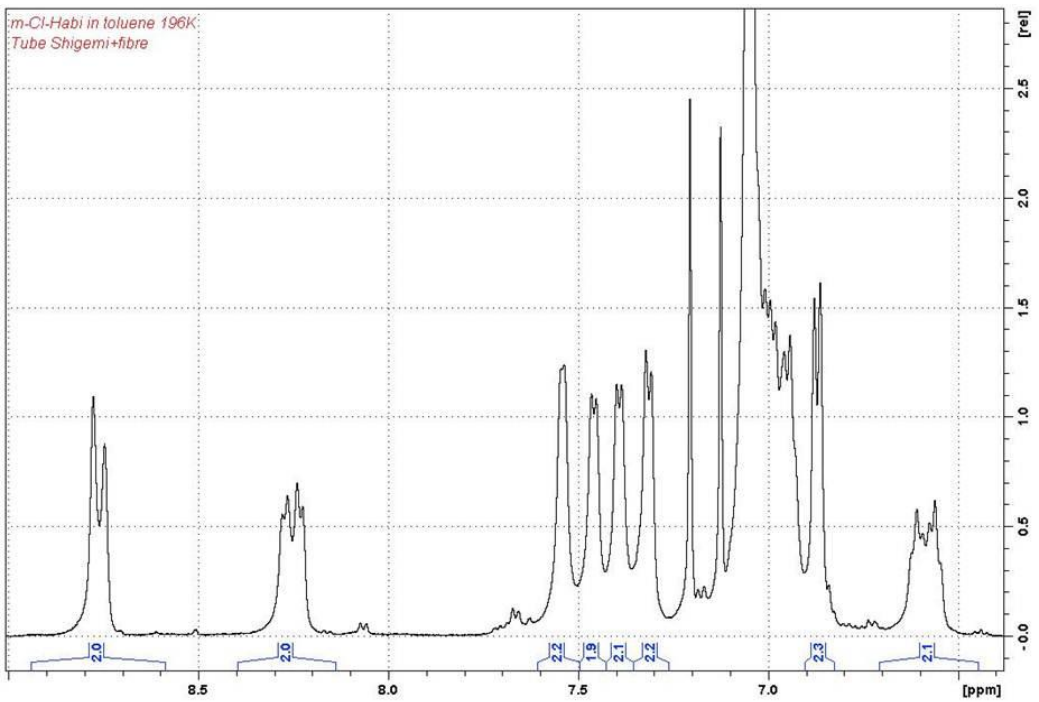


10) NMR characterization of 2,2'-dimer of m-Cl-HABI

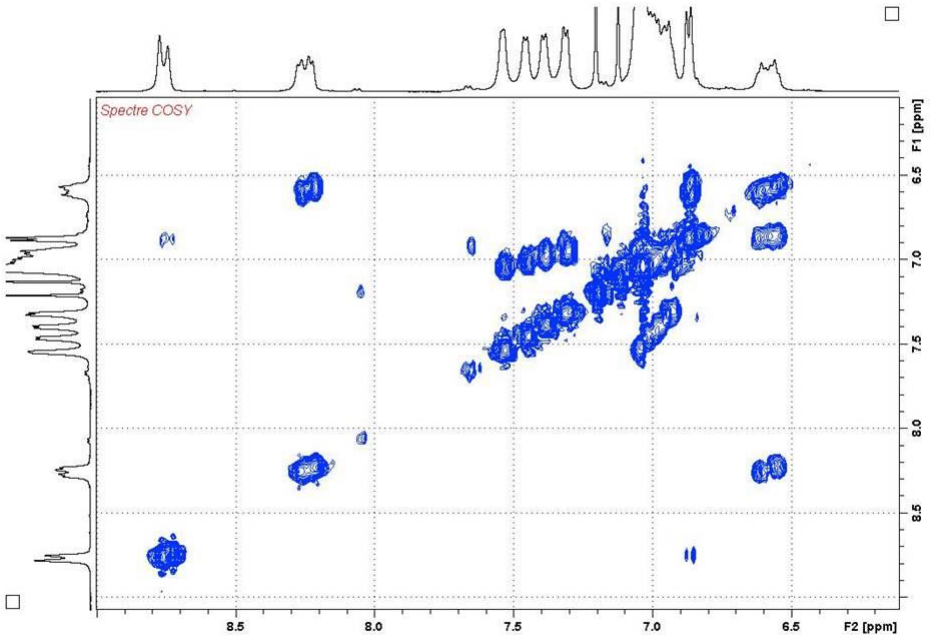
a) ^{1}H and ^{13}C chemical shifts of 2,2'-m-Cl-HABI in toluene-d_8 at 196K



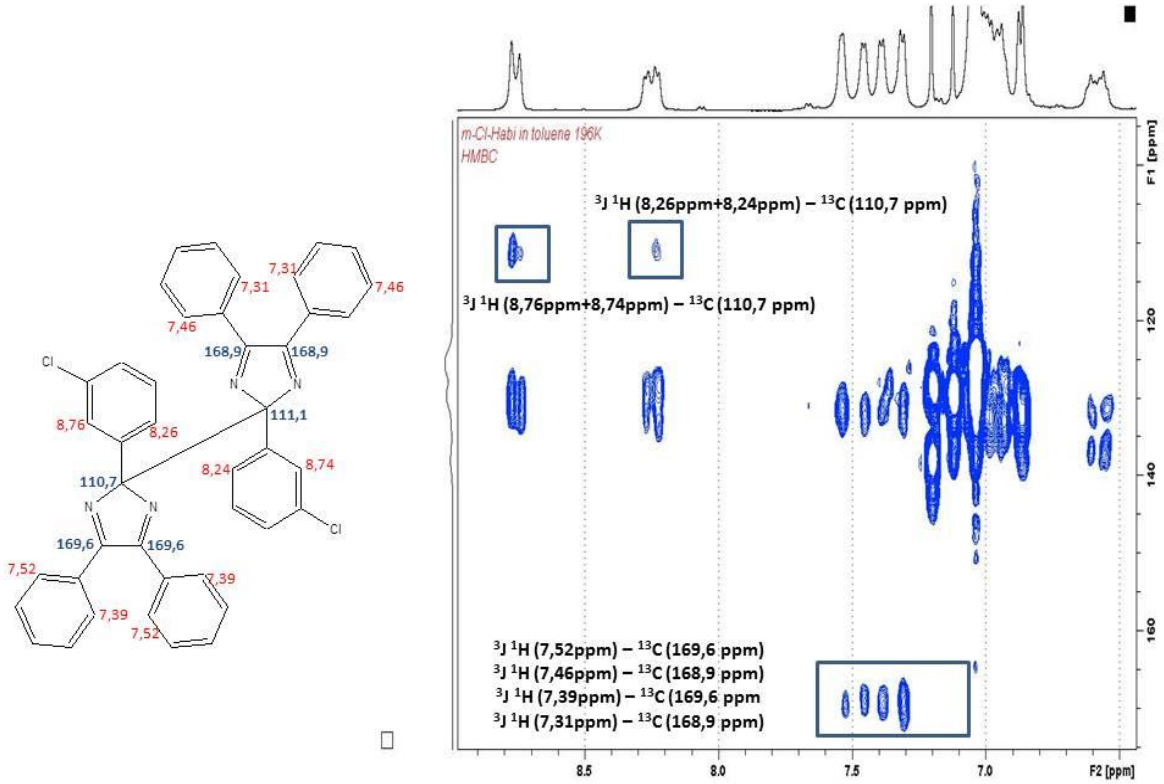
b) ^{1}H NMR spectrum of 2,2'-m-Cl-HABI with integration in toluene-d_8 at 196K



c) ^{1}H-^{1}H NMR COSY of 2,2'-m-Cl-HABI in toluene-d_8 at 196K

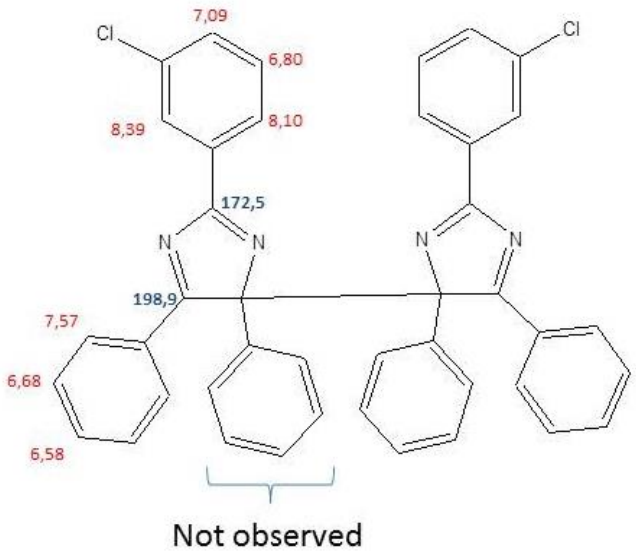


d) ^{1}H-^{13}C NMR HMBC of 2,2'-m-Cl-HABI in toluene-d_8 at 196K

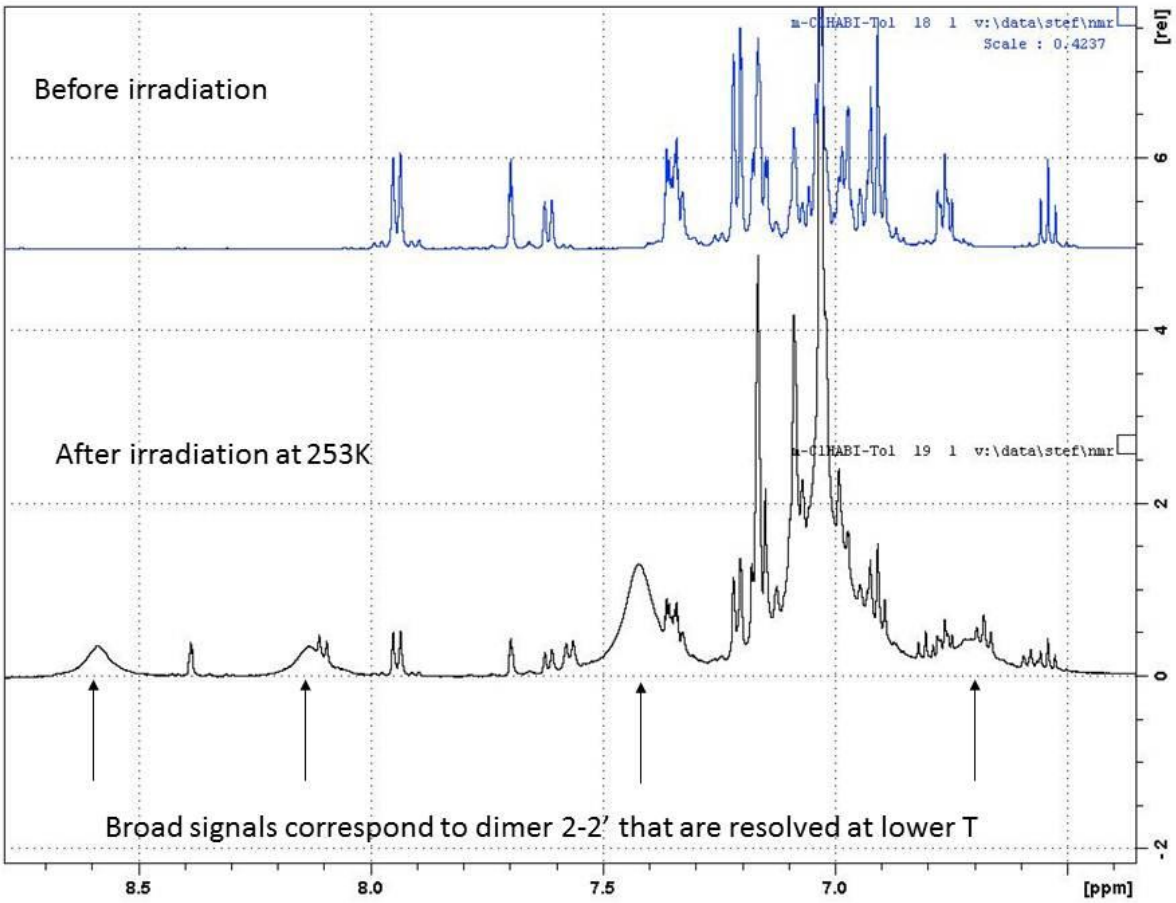


11) NMR characterization of 4,4'-dimer of m-Cl-HABI

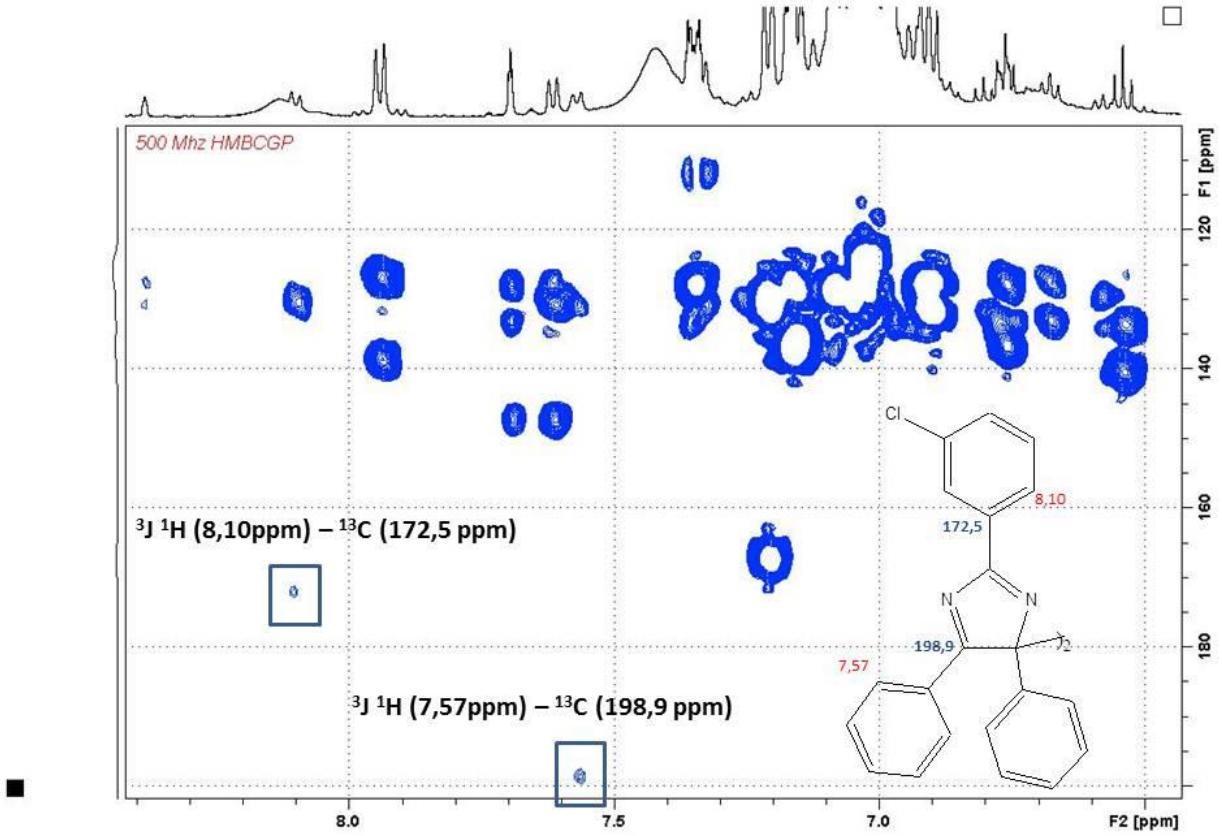
a) ^{1}H and ^{13}C chemical shifts of 4,4'-m-Cl-HABI in toluene-d_8 at 196K



b) ^{1}H NMR spectra of 4,4'-m-Cl-HABI in toluene-d_8 at 196K

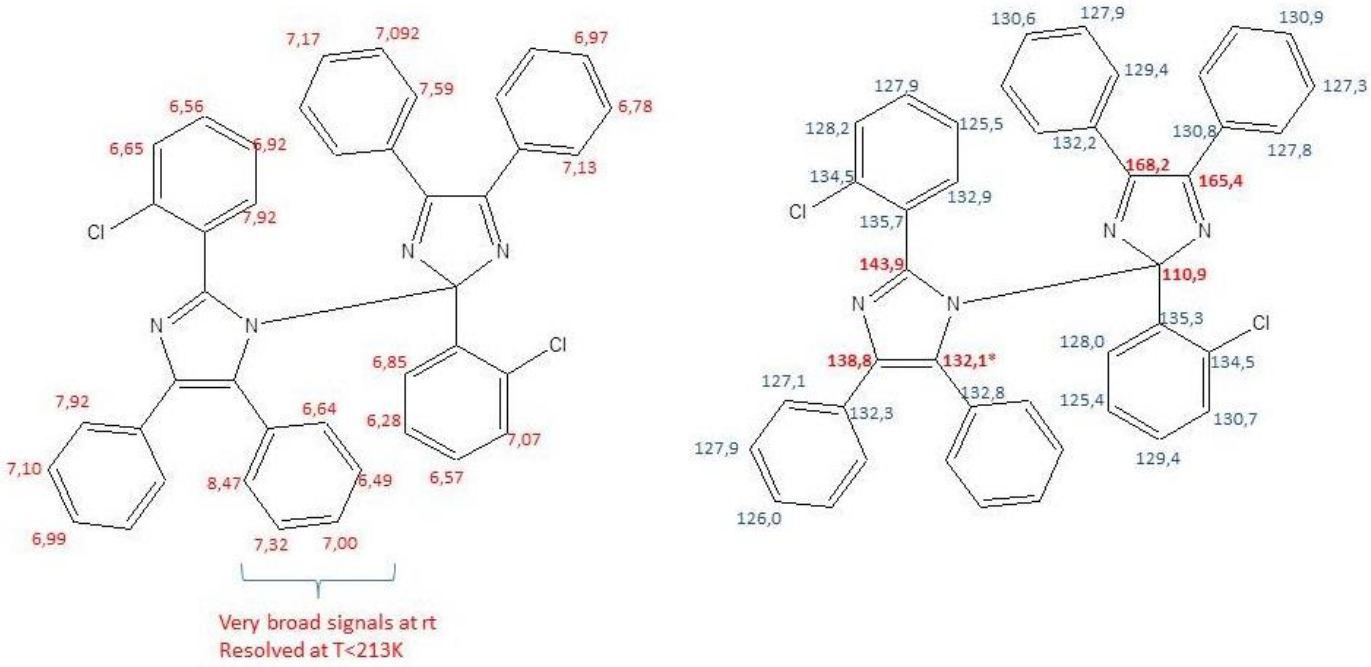


c) ^{1}H-^{13}C NMR HMBC of 4,4'-m-Cl-HABI in toluene-d_8 at 196K

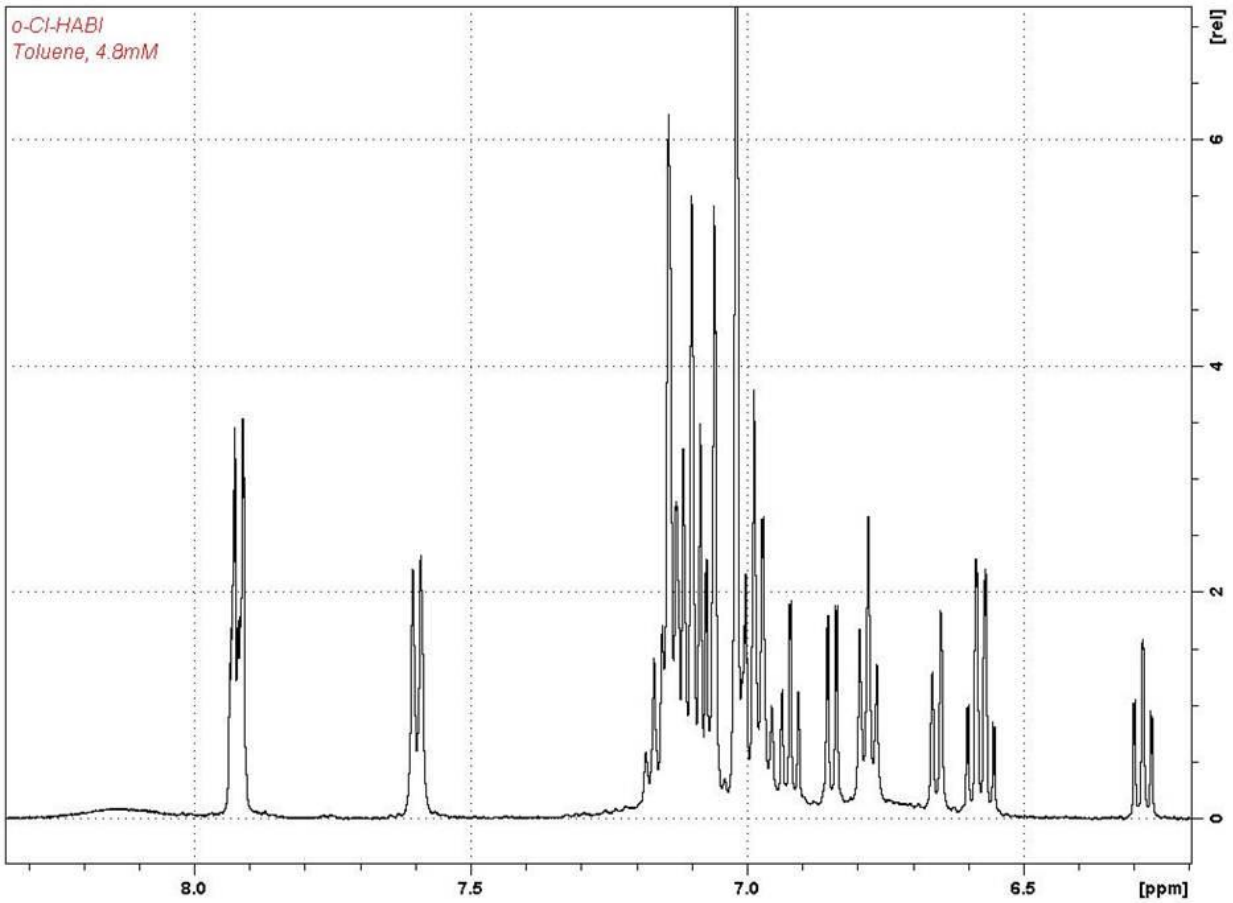


12) NMR characterization of 1,2'-dimer of o-Cl-HABI

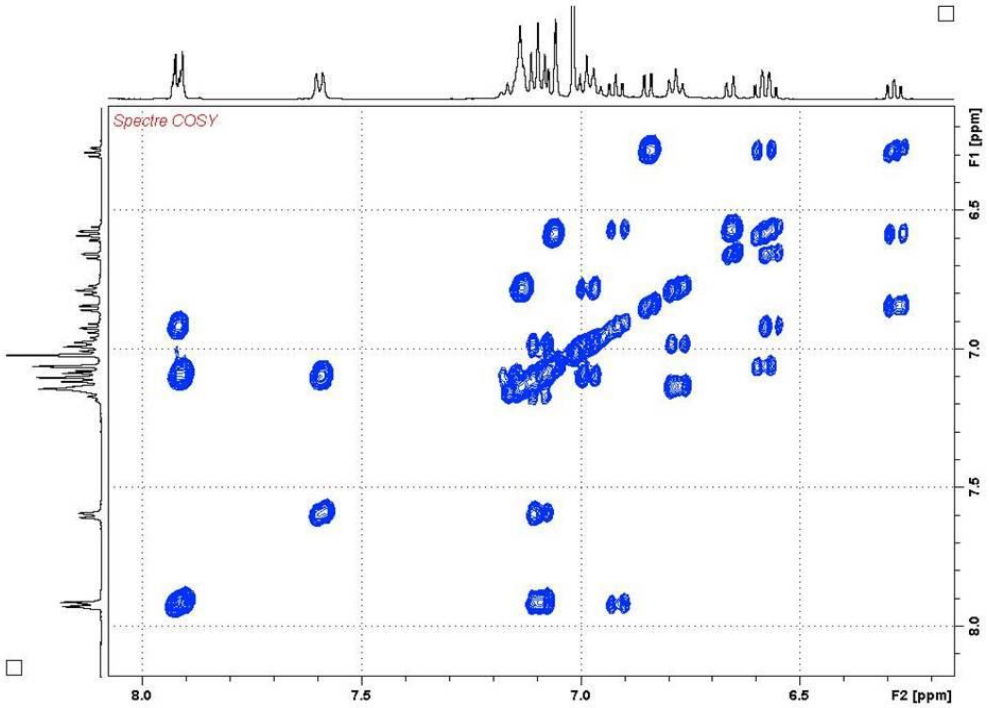
a) ^{1}H and ^{13}C chemical shifts of 1,2'-o-Cl-HABI in toluene-d_8 at rt



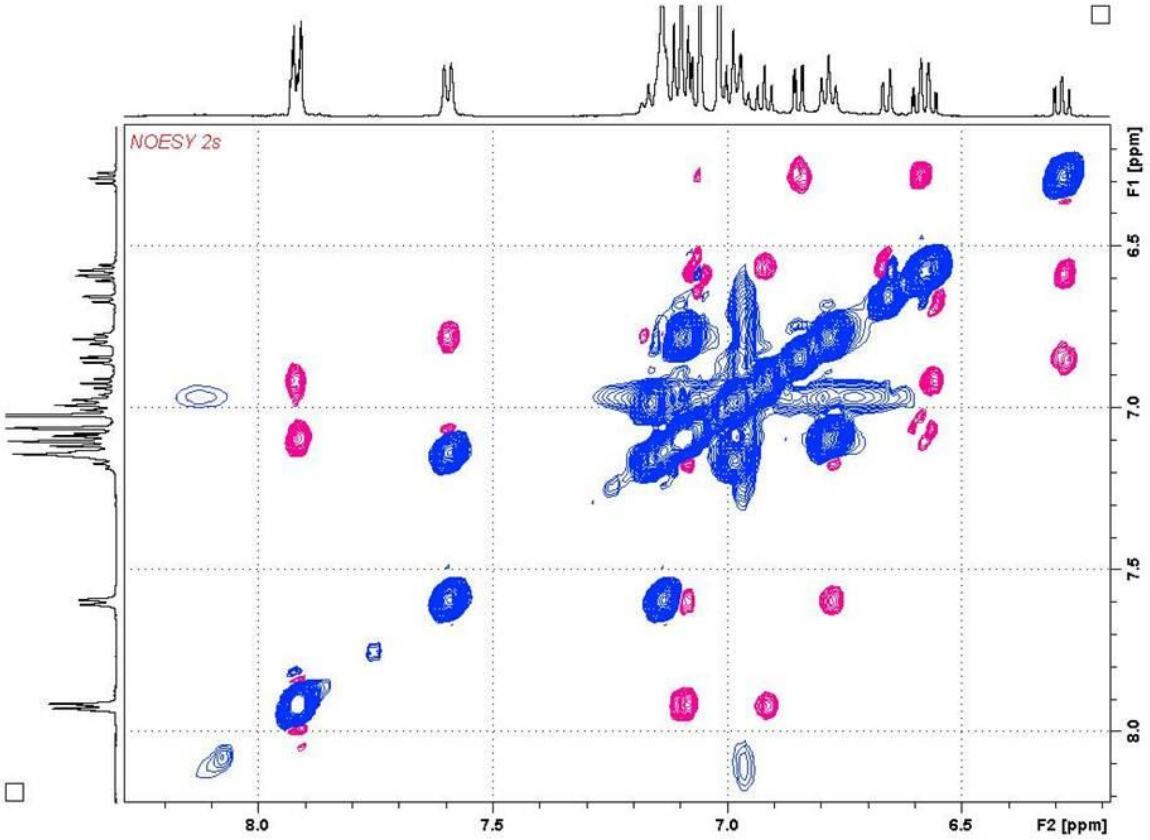
b) ^{1}H NMR spectrum of 1,2'-o-Cl-HABI in toluene-d_8 at rt



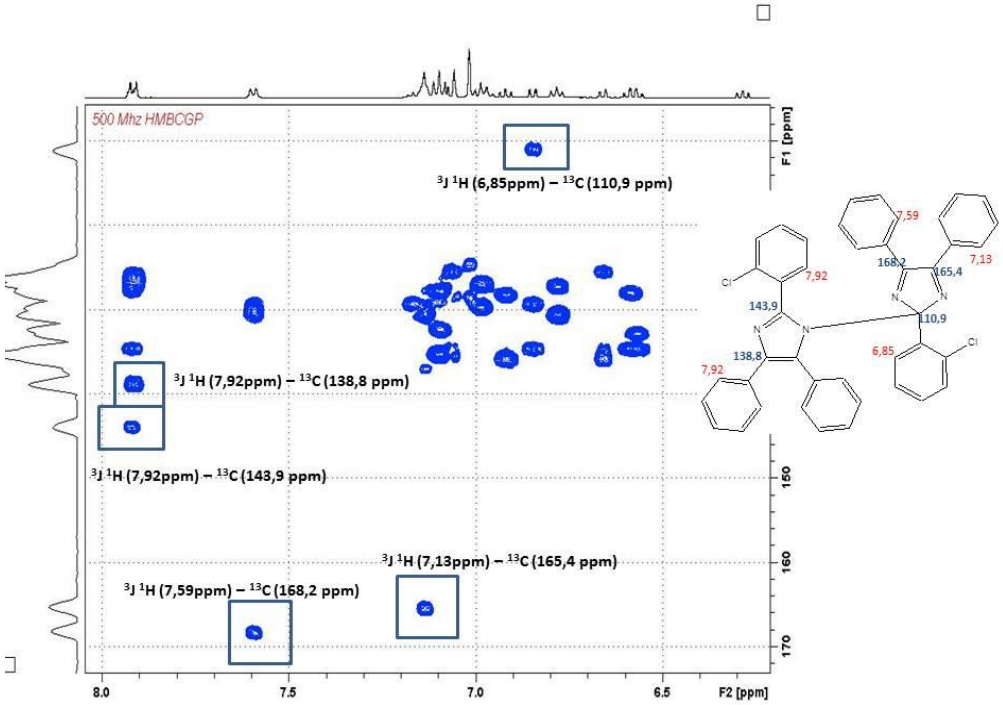
c) ^{1}H-^{1}H NMR COSY of 1,2'-o-Cl-HABI in toluene-d_8 at rt



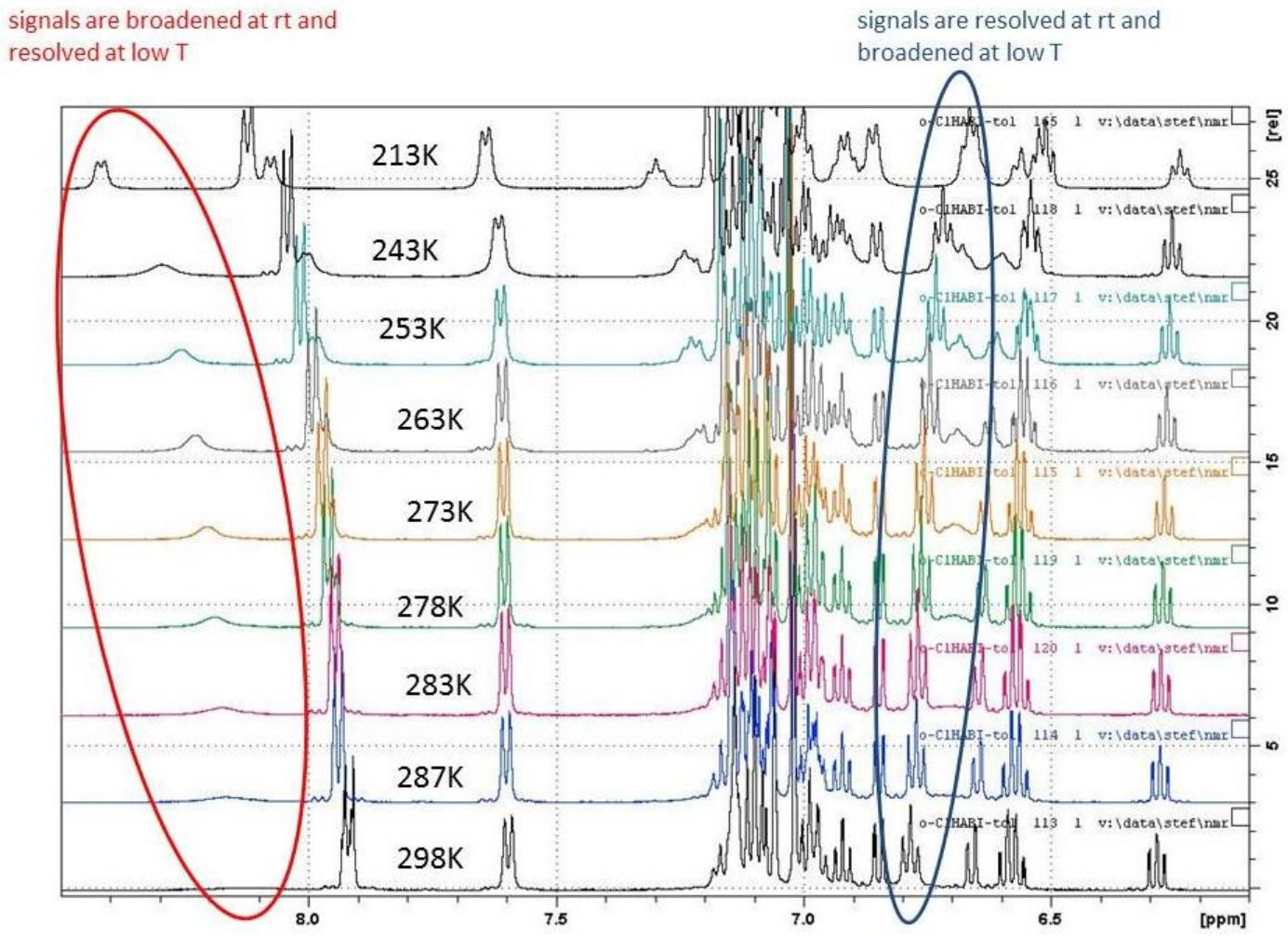
d) ^{1}H NMR NOESY of 1,2'-o-Cl-HABI in toluene-d_8 at rt



e) ^{1}H-^{13}C NMR HMBC of 1,2'-o-Cl-HABI in toluene-d_8 at rt

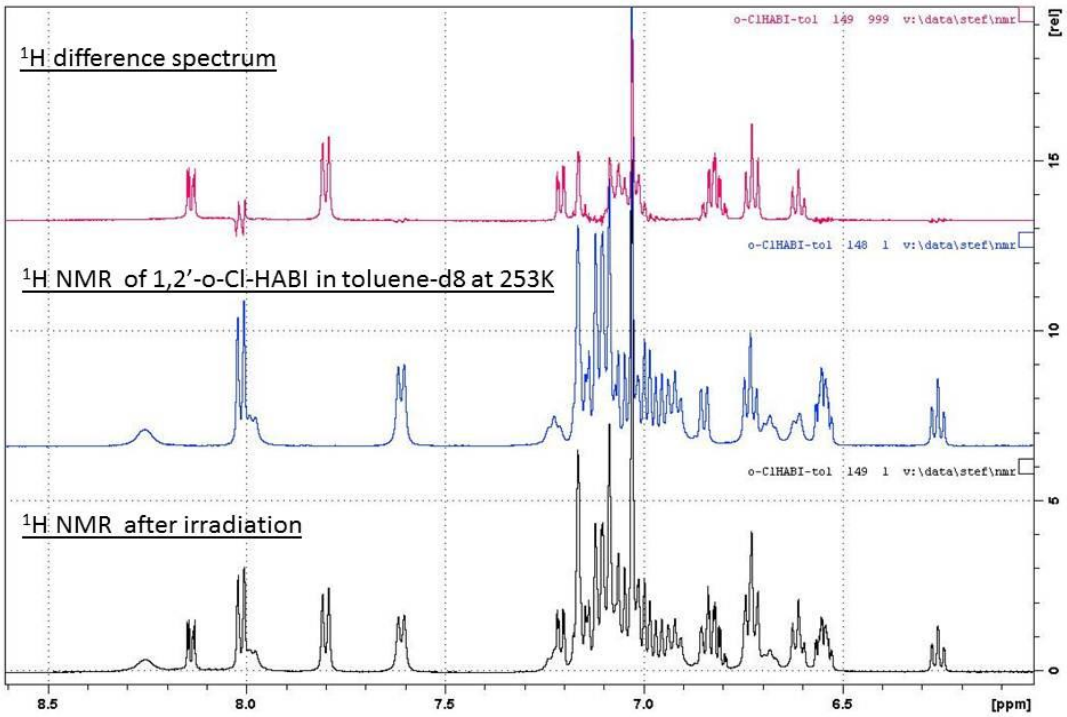


f) ^{1}H NMR spectra at various T of 1,2'o-Cl-HABI in toluene-d_8

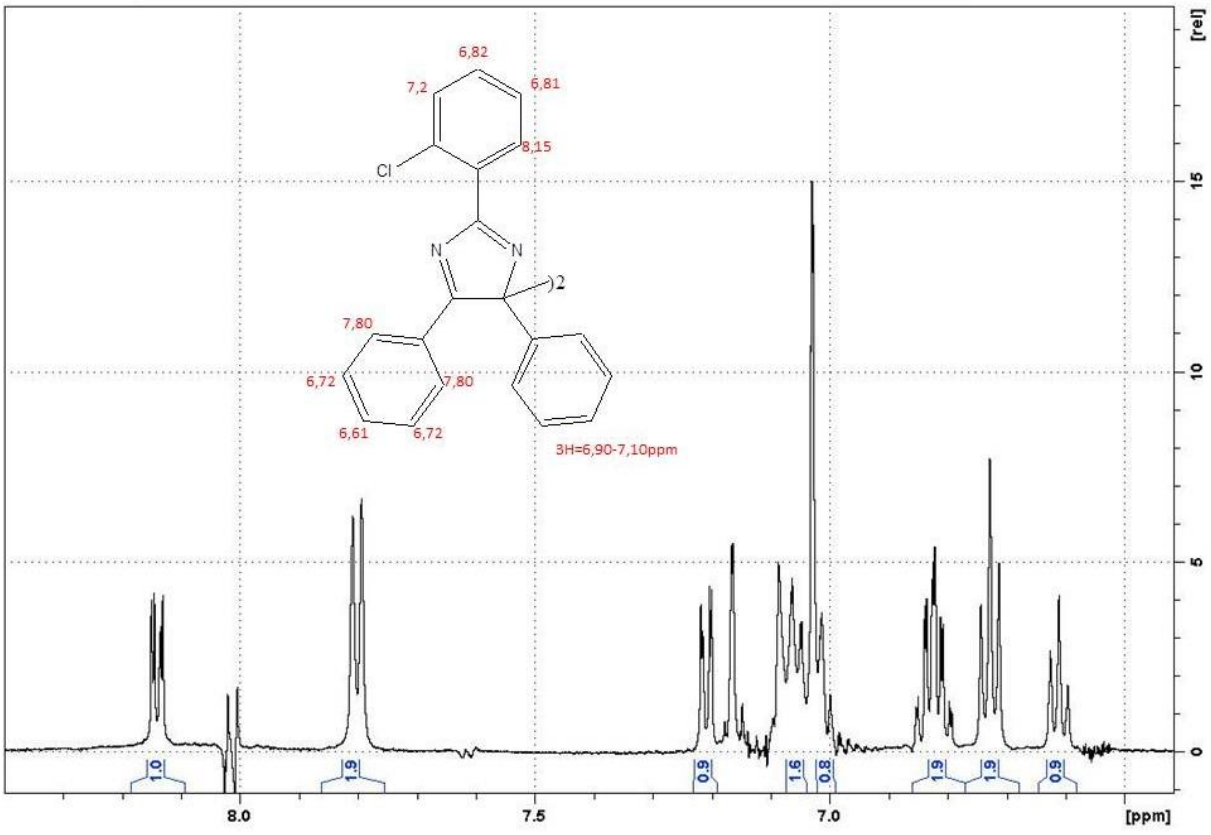


13) NMR characterization of 4,4'-dimer of o-Cl-HABI (isomer 1)

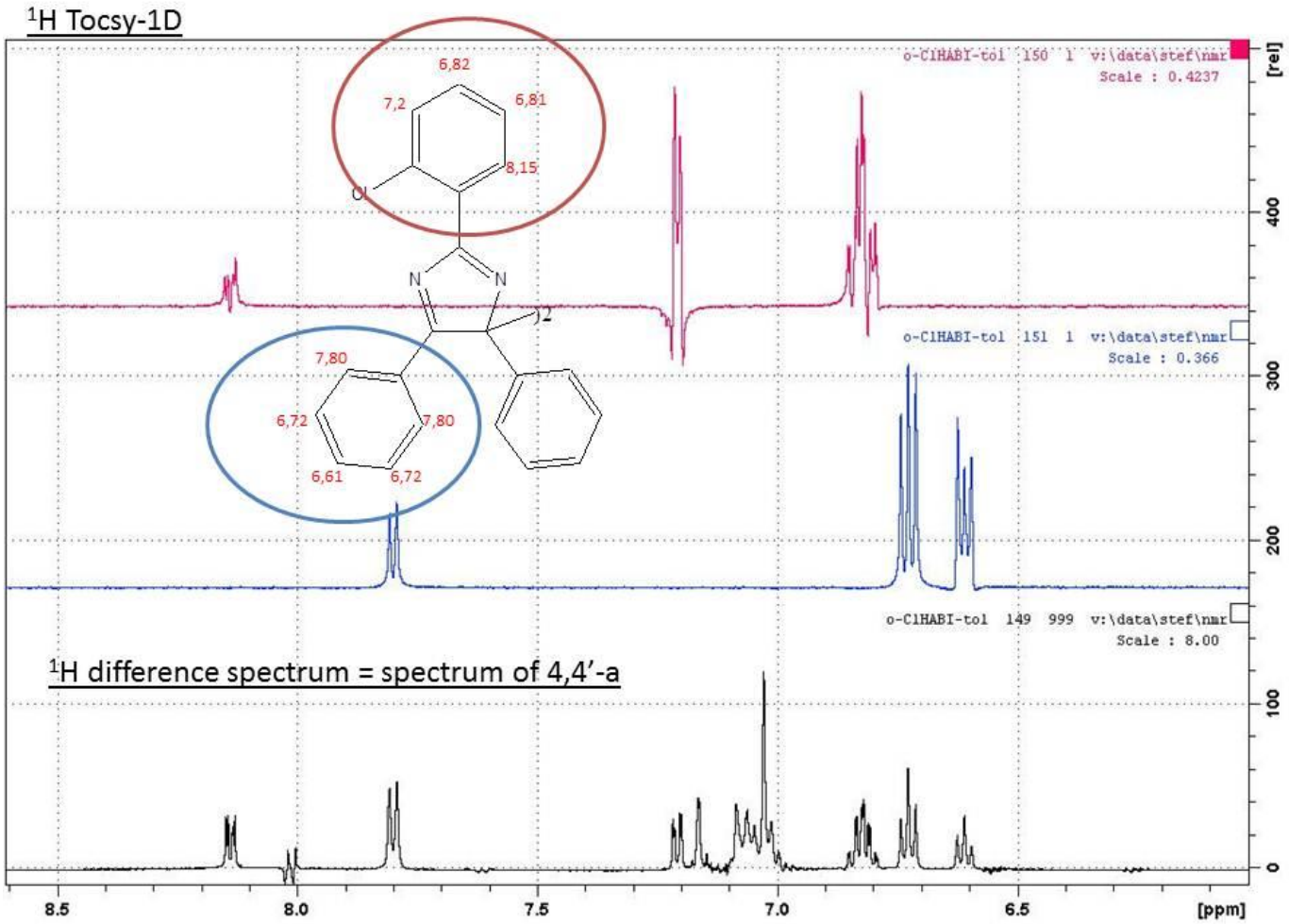
a) ^{1}H NMR spectra of 4,4'-o-Cl-HABI in toluene-d_8 at 253K



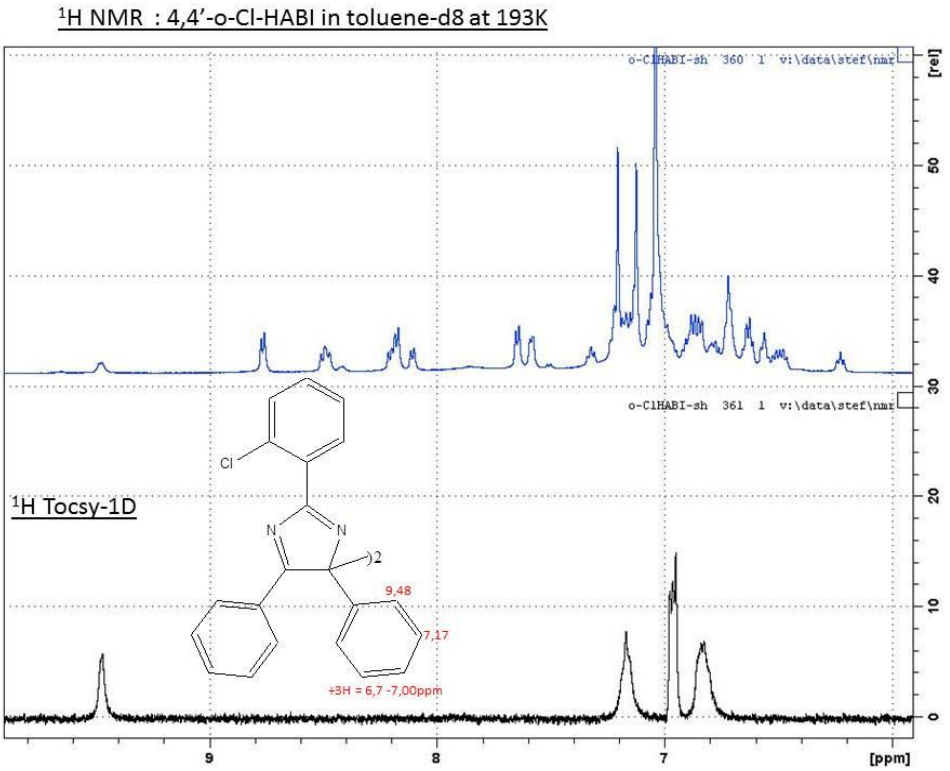
b) ^{1}H NMR difference spectrum of 4,4'-o-Cl-HABI in toluene-d_8 at 253K



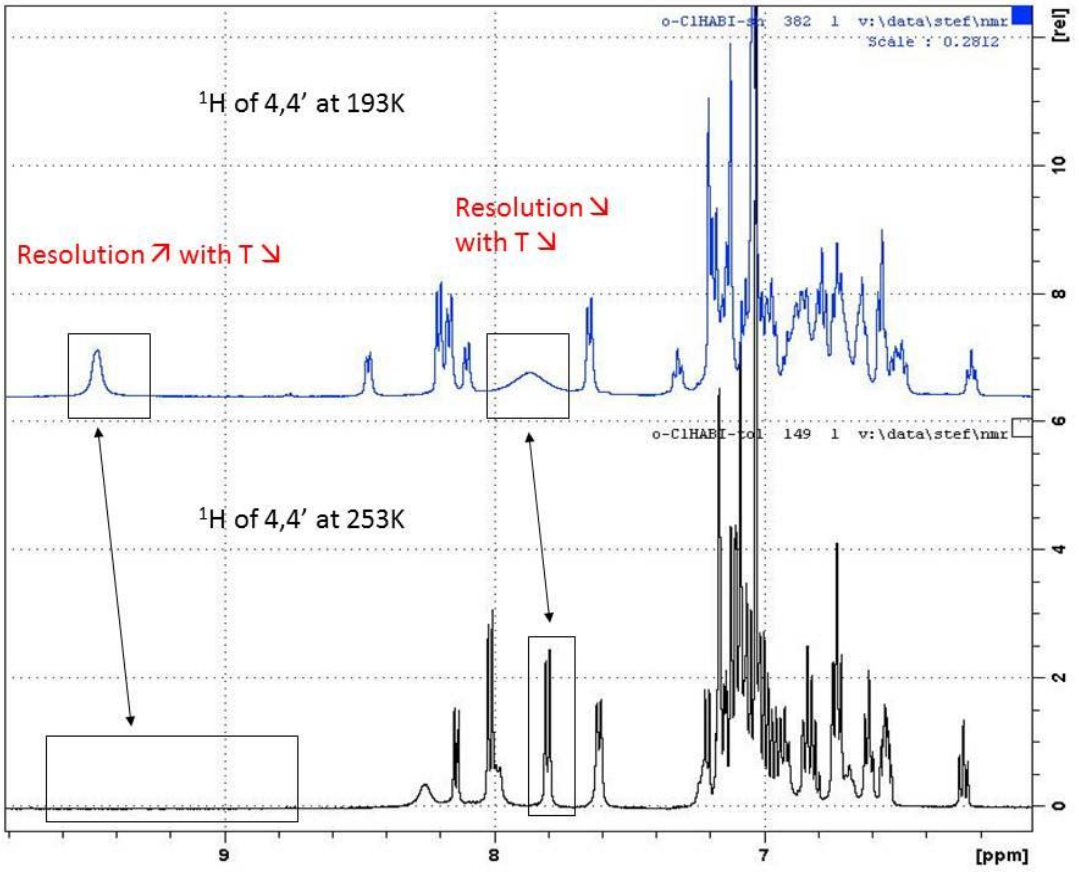
c) ^{1}H NMR TOCSY of 4,4'-o-Cl-HABI in toluene-d_8 at 253K



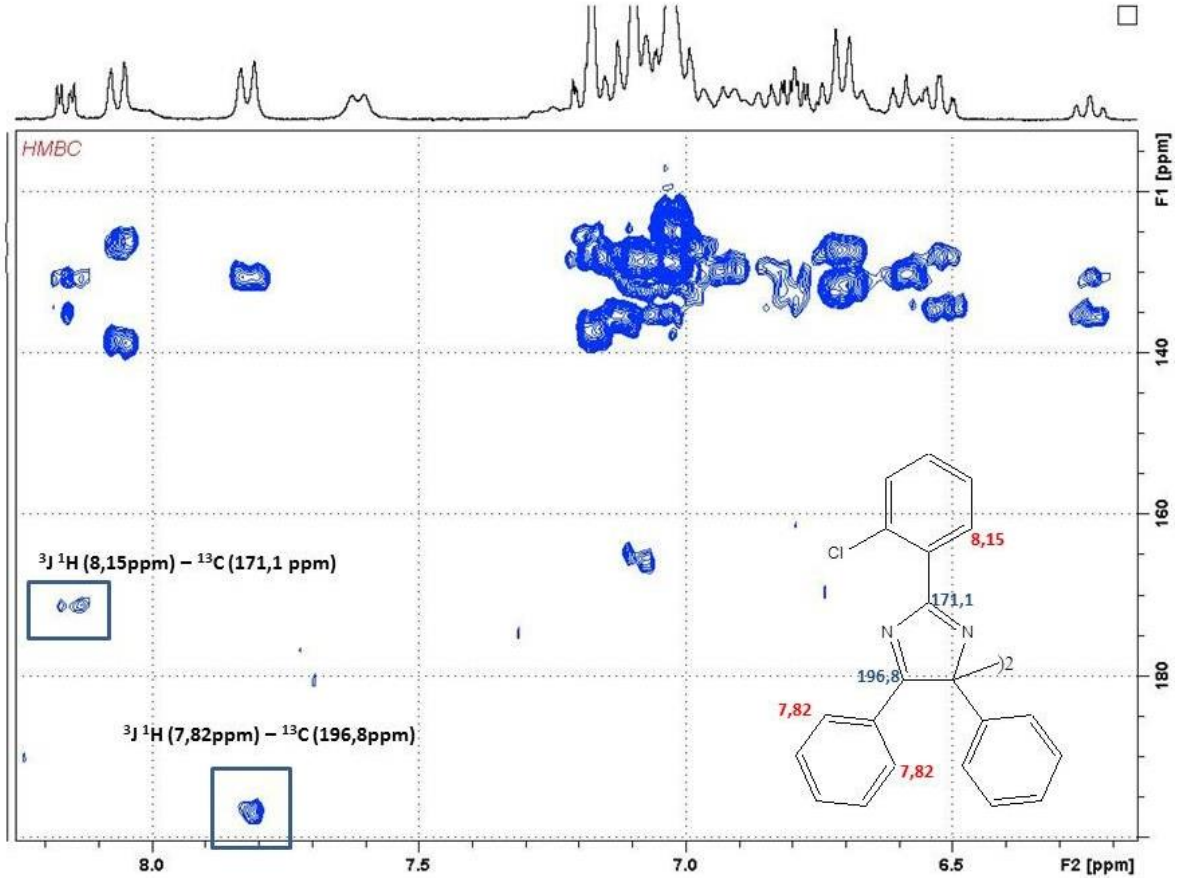
d) ^{1}H NMR spectrum and TOCSY of 4,4'-o-Cl-HABI in toluene-d_8 at 193K



e) ^{1}H NMR spectra Y of 4,4'-o-Cl-HABI in toluene-d_8 at 253 and193K

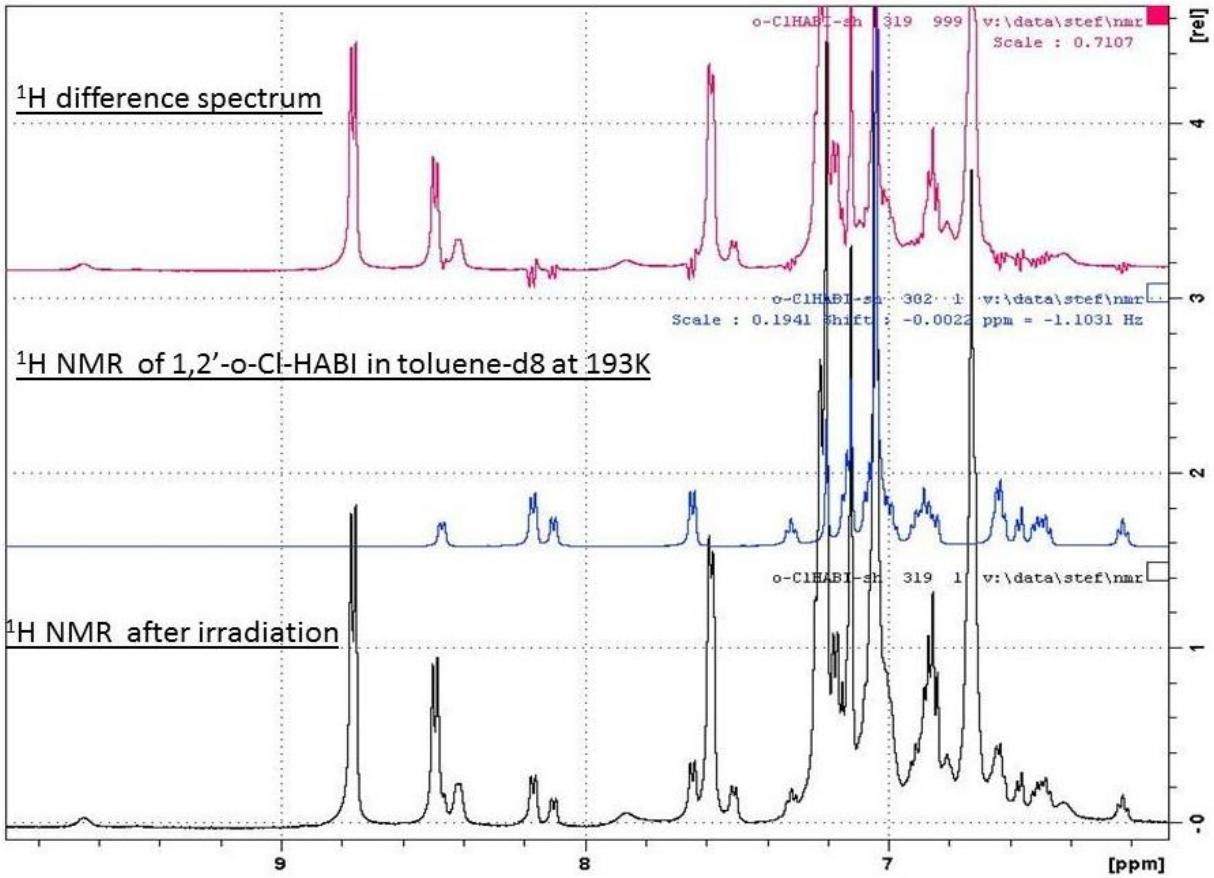


f) ^{1}H-^{13}C NMR HMBC of 4,4'-o-Cl-HABI in toluene-d_8 at 238K

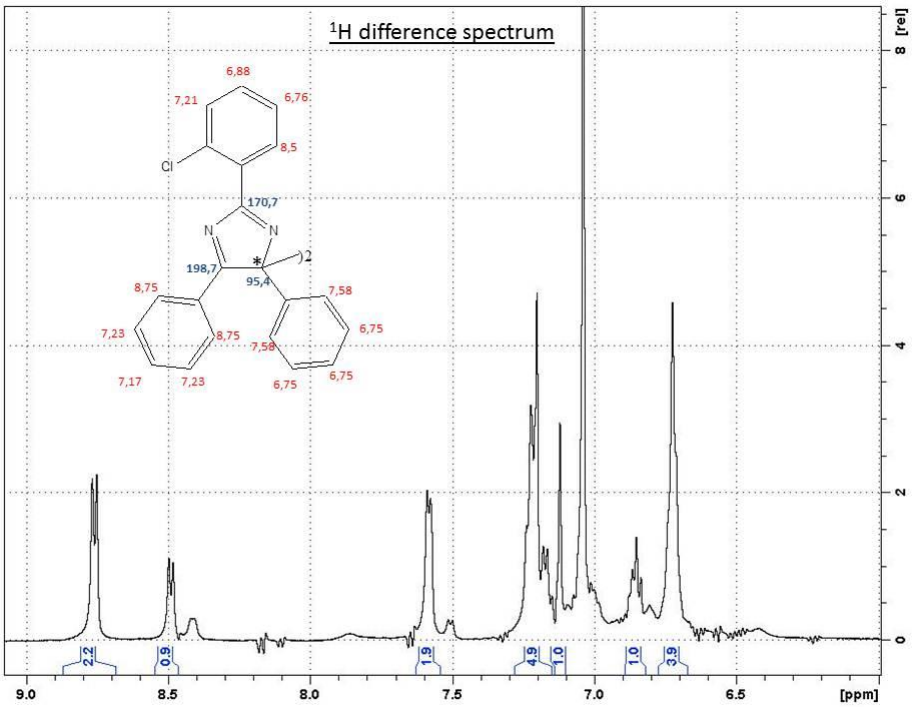


14) NMR characterization of 4,4'-dimer of o-Cl-HABI (isomer 2)

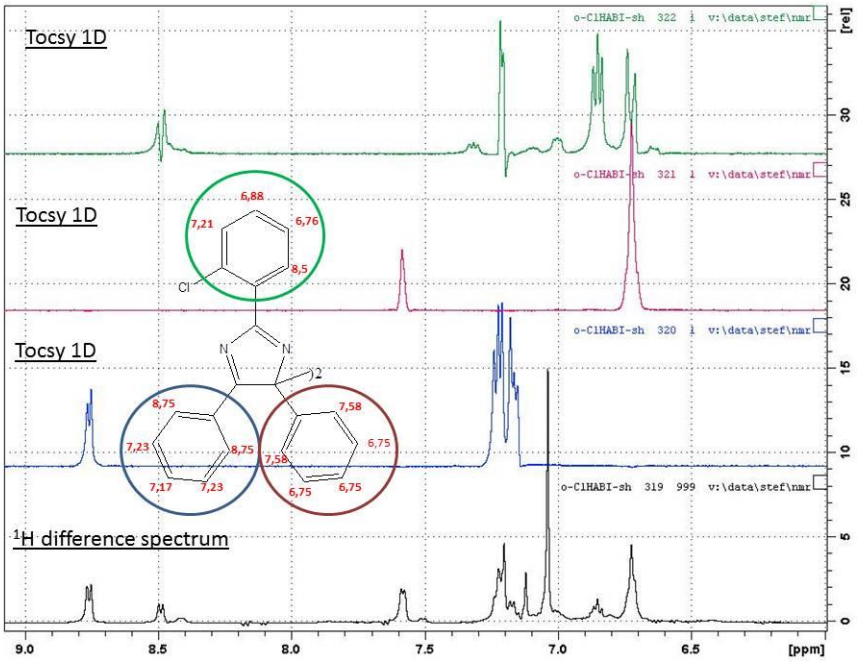
a) ^{1}H NMR spectra of 4,4'-o-Cl-HABI in toluene-d_8 at 193K



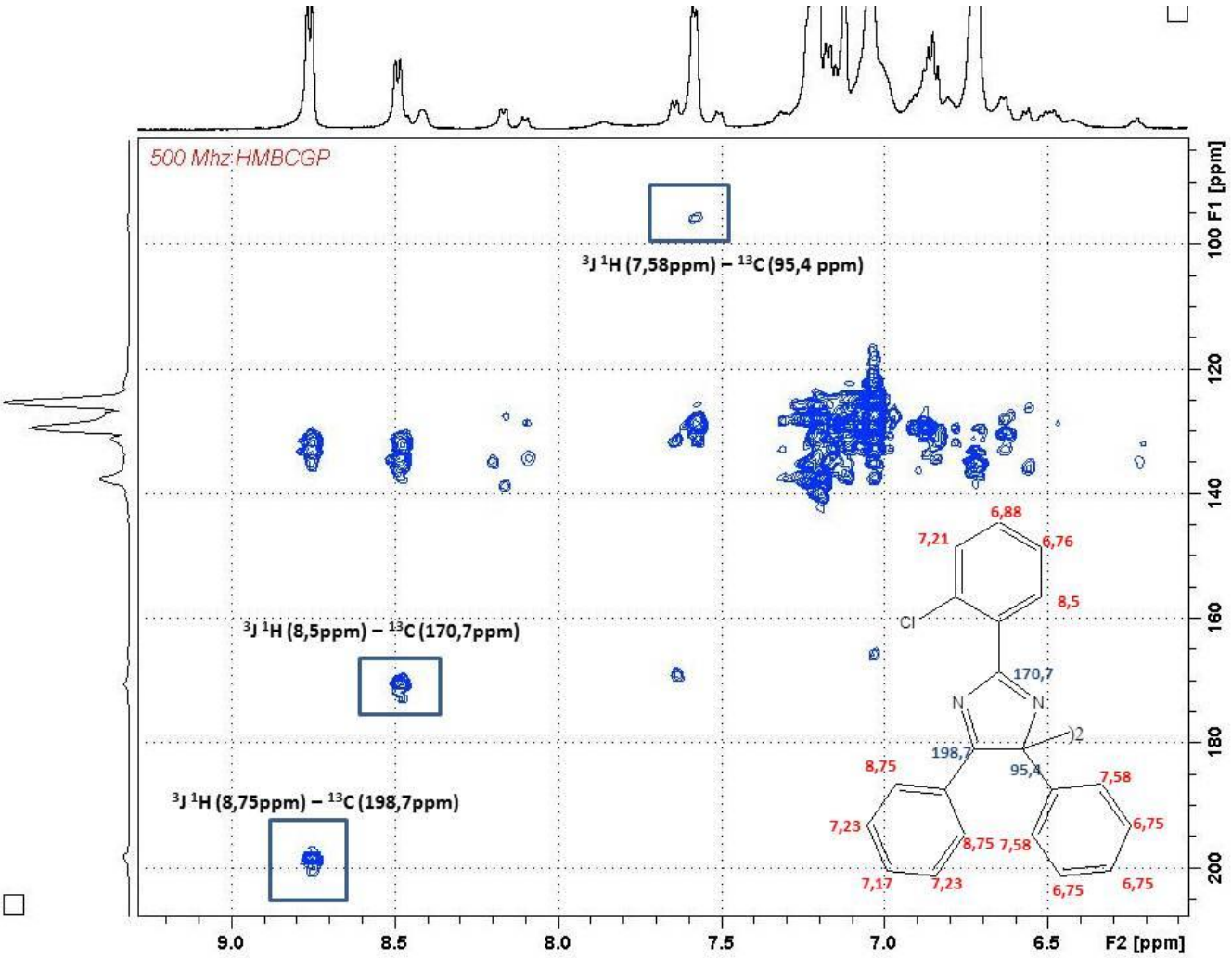
b) ^{1}H NMR difference spectrum with integration of 4,4'-o-Cl-HABI in toluene-d_8 at 193K



c) ^{1}H NMR TOCSY of 4,4'-o-Cl-HABI in toluene-d_8 at 193K



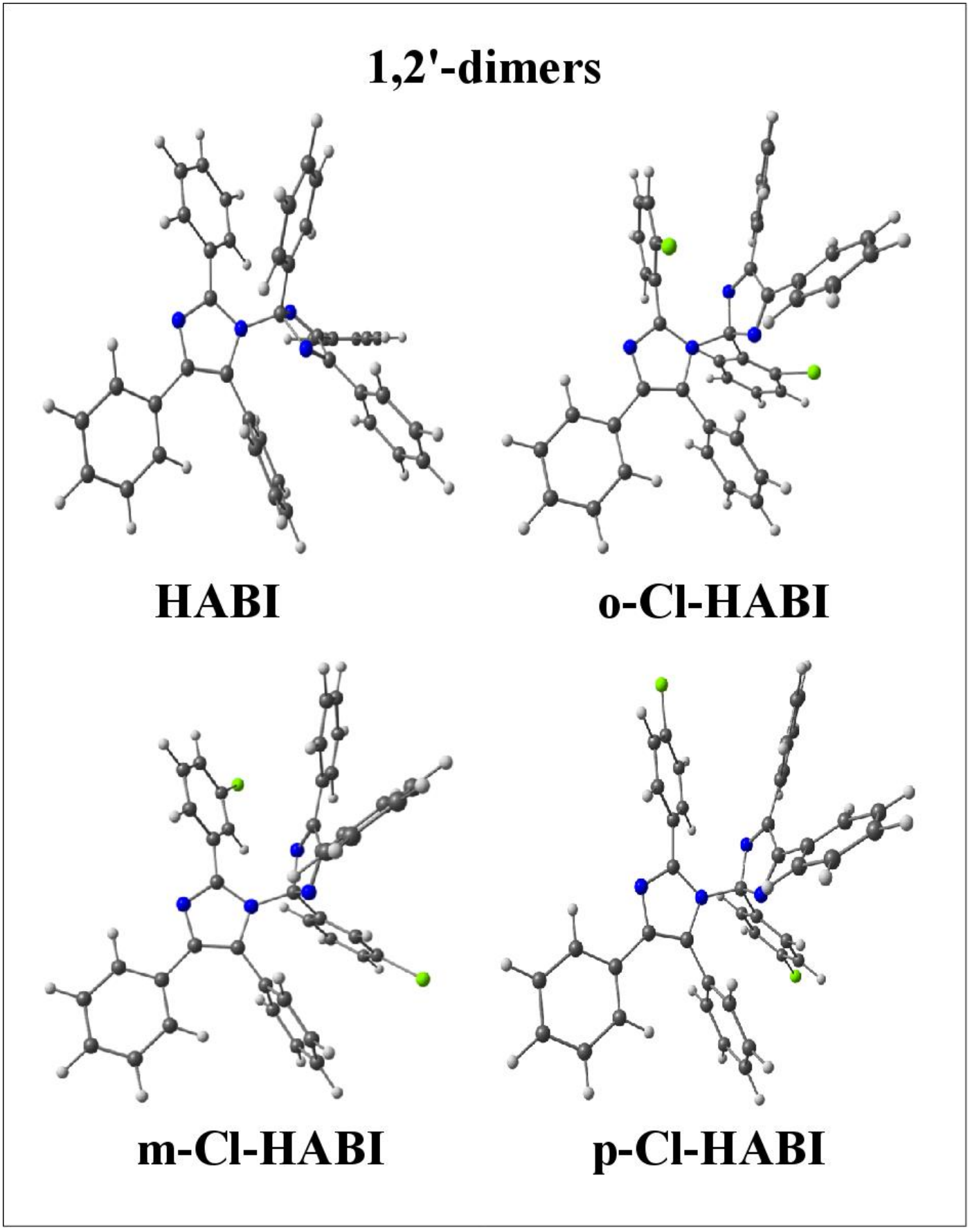
d) ^{1}H-^{13}C NMR HMBC of 4,4'-o-Cl-HABI in toluene-d_8 at 193K



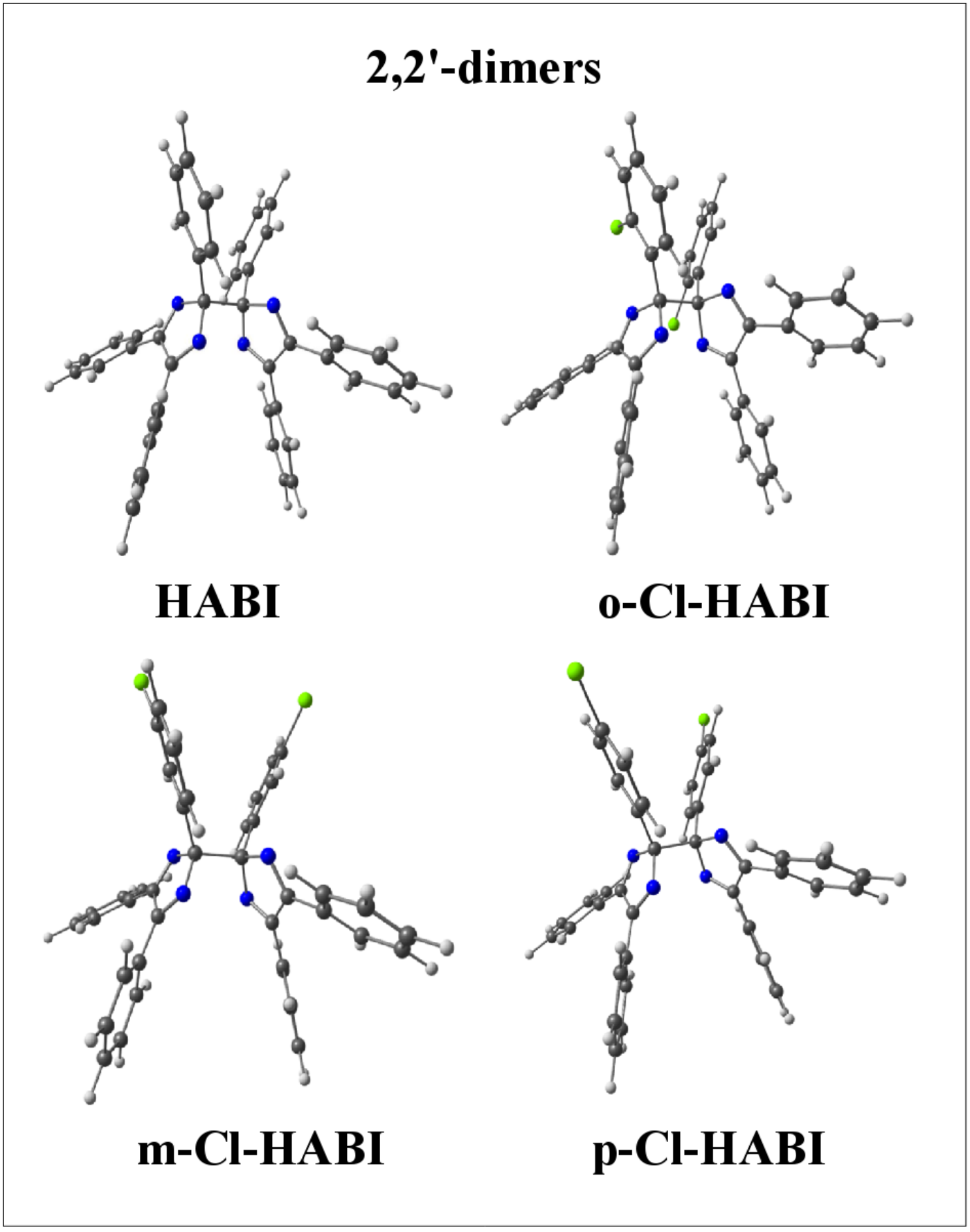
15) ^{13}C NMR calculated data of characteristic carbon atoms in the 1-1', 1-4' and 2-4' HABI dimers.

δ / ppm	C-2	C-4	C-5	C-2'	C-4'	C-5'
			1,1'-Dimer			
HABI	149.5	144	134.8	149.5	144.1	134.9
p-Cl-HABI	148.5	144.4	134.8	148.5	144.4	134.8
m-Cl-HABI	148.1	144.8	135.1	148.3	144.4	135.5
o-Cl-HABI	147	144.3	133.8	147	144.4	133.9
			1,4'-Dimer			
HABI	154.8	147	137.7	182	104.9	203.8
p-Cl-HABI	153.6	147.6	138	181.1	105.1	204.2
m-Cl-HABI	153.6	147.3	138.2	181.3	104.9	204.4
o-Cl-HABI	149.3	147	137.5	179	106.7	202
			2,4'-Dimer			
HABI	114.4	172.3	172.5	180.5	205.9	100.6
p-Cl-HABI	113.8	172.8	172.9	179.6	206.1	100.8
m-Cl-HABI	114.7	171.6	172.1	179.7	206.4	100.8
o-Cl-HABI	117	172.7	171.3	176.1	206.2	104.8

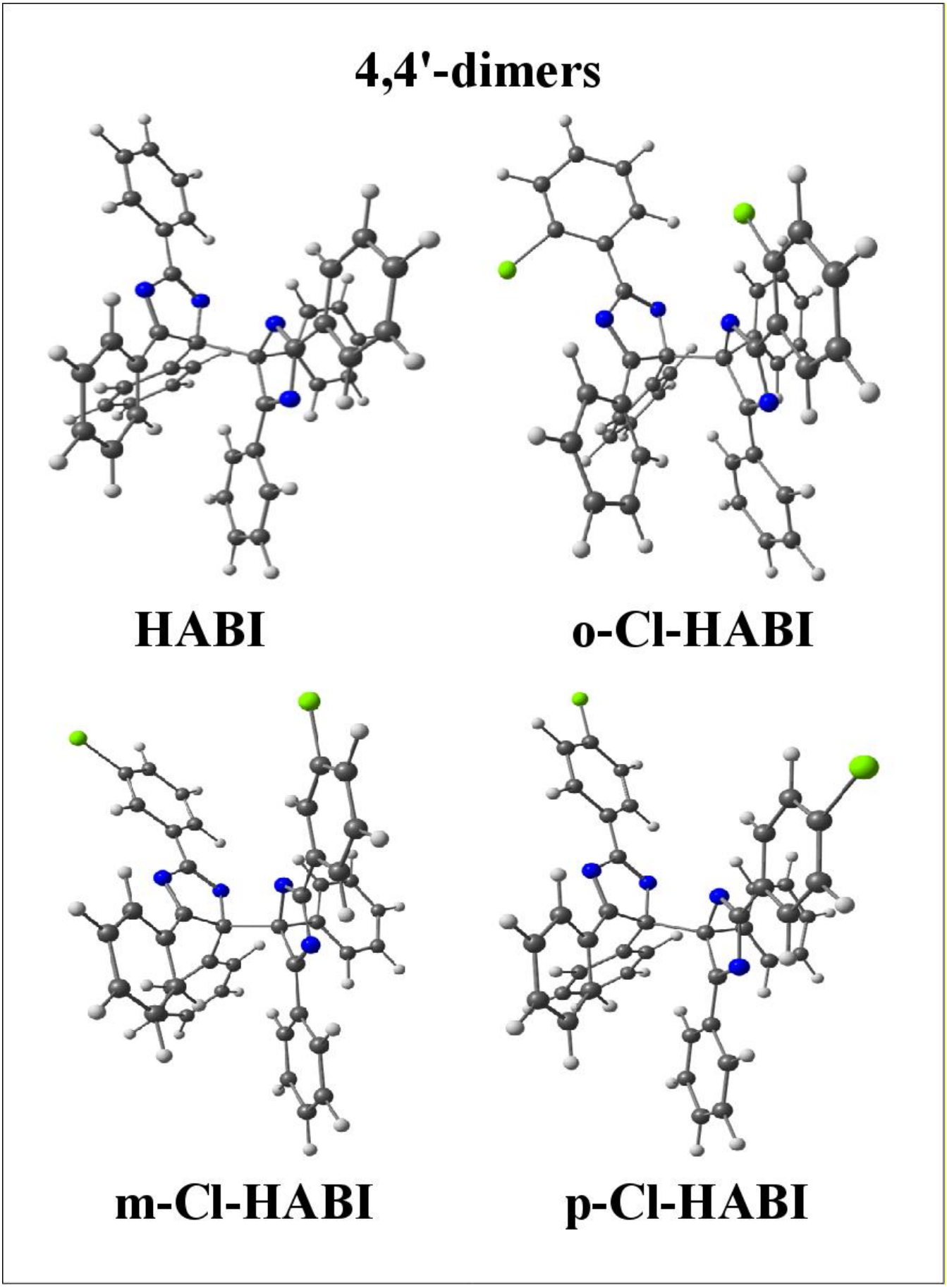
16) DFT-optimized structures of 1-2' dimers



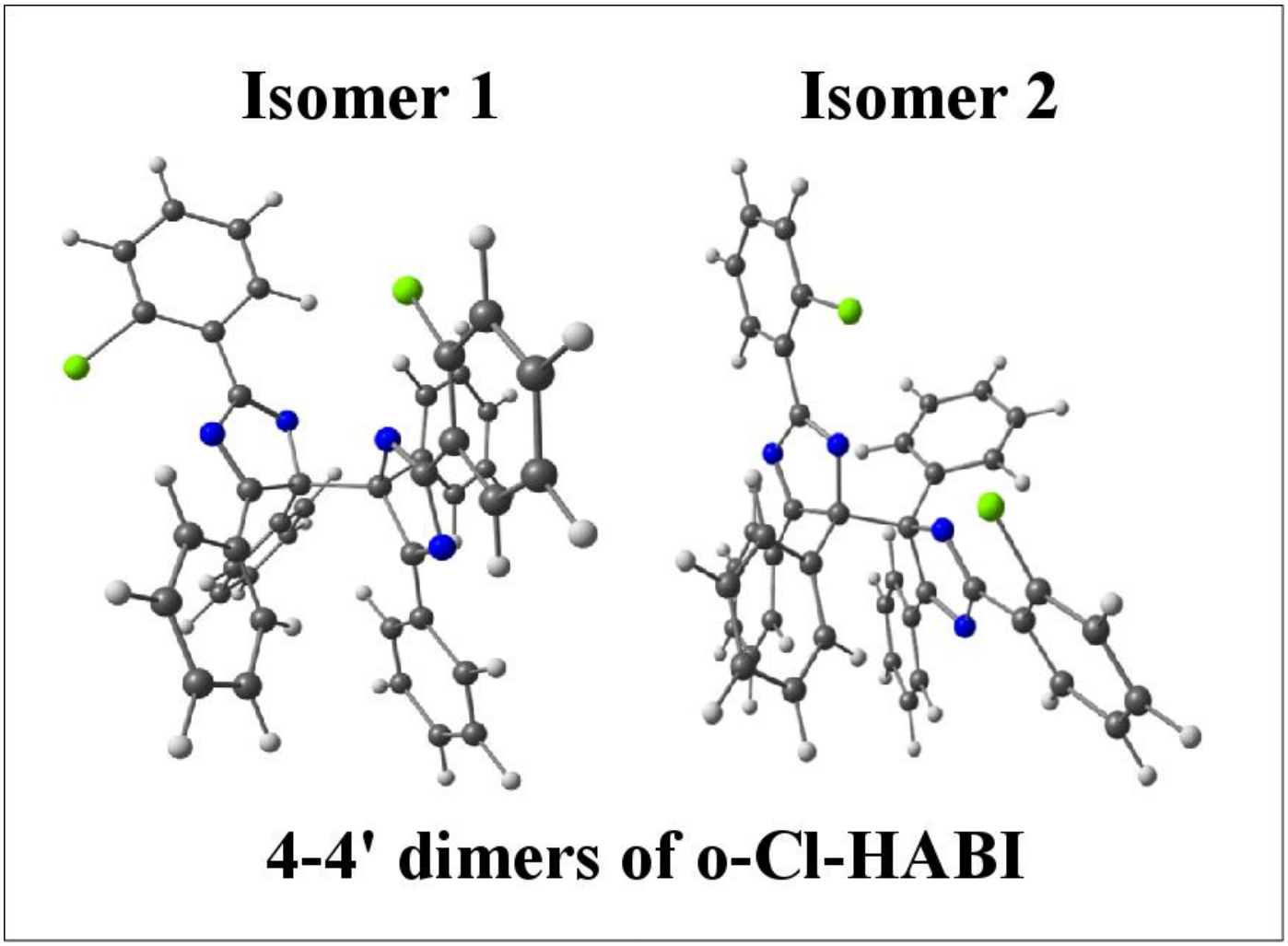
17) DFT-optimized structures of 2-2' dimers



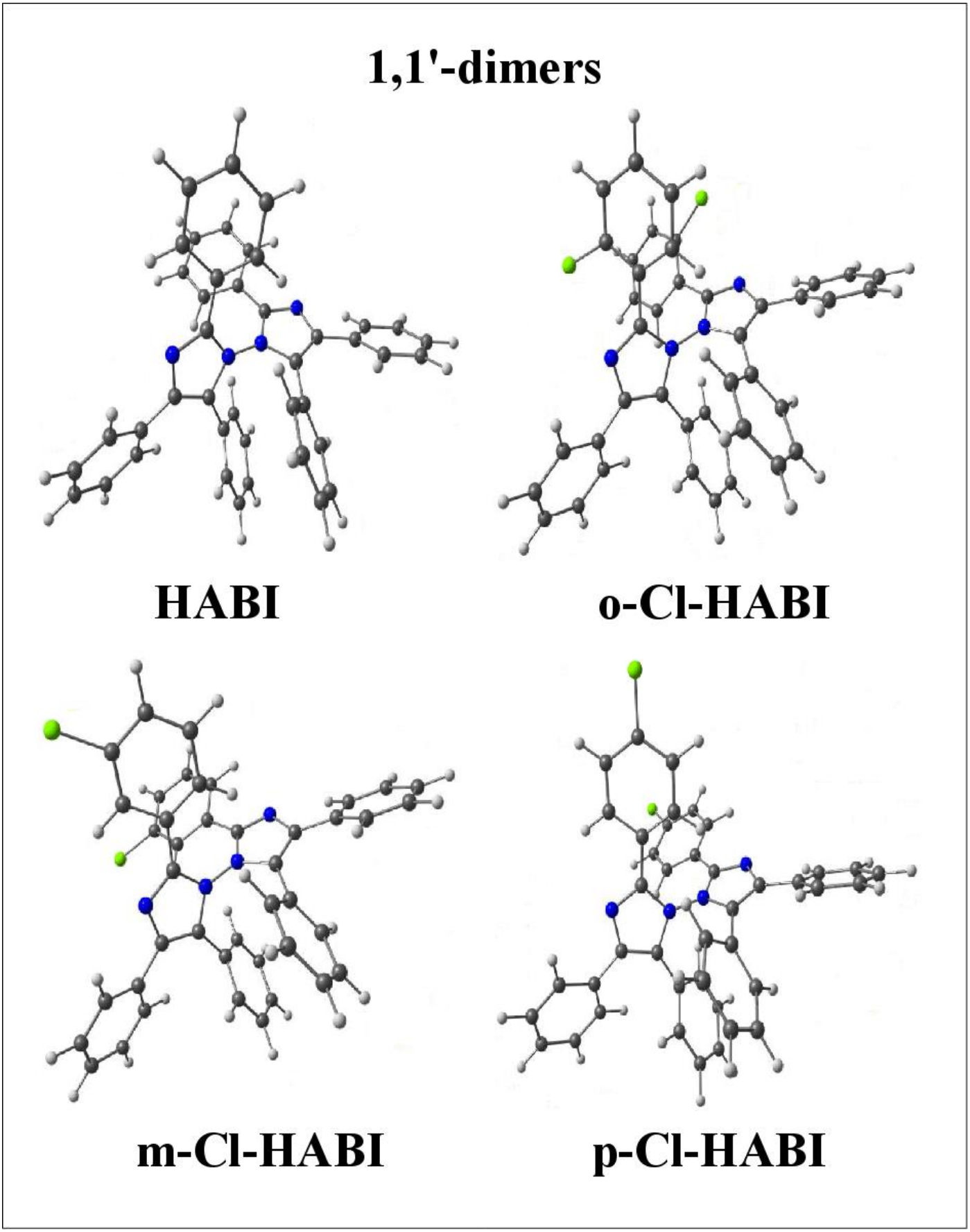
18) DFT-optimized structures of 4-4' dimers



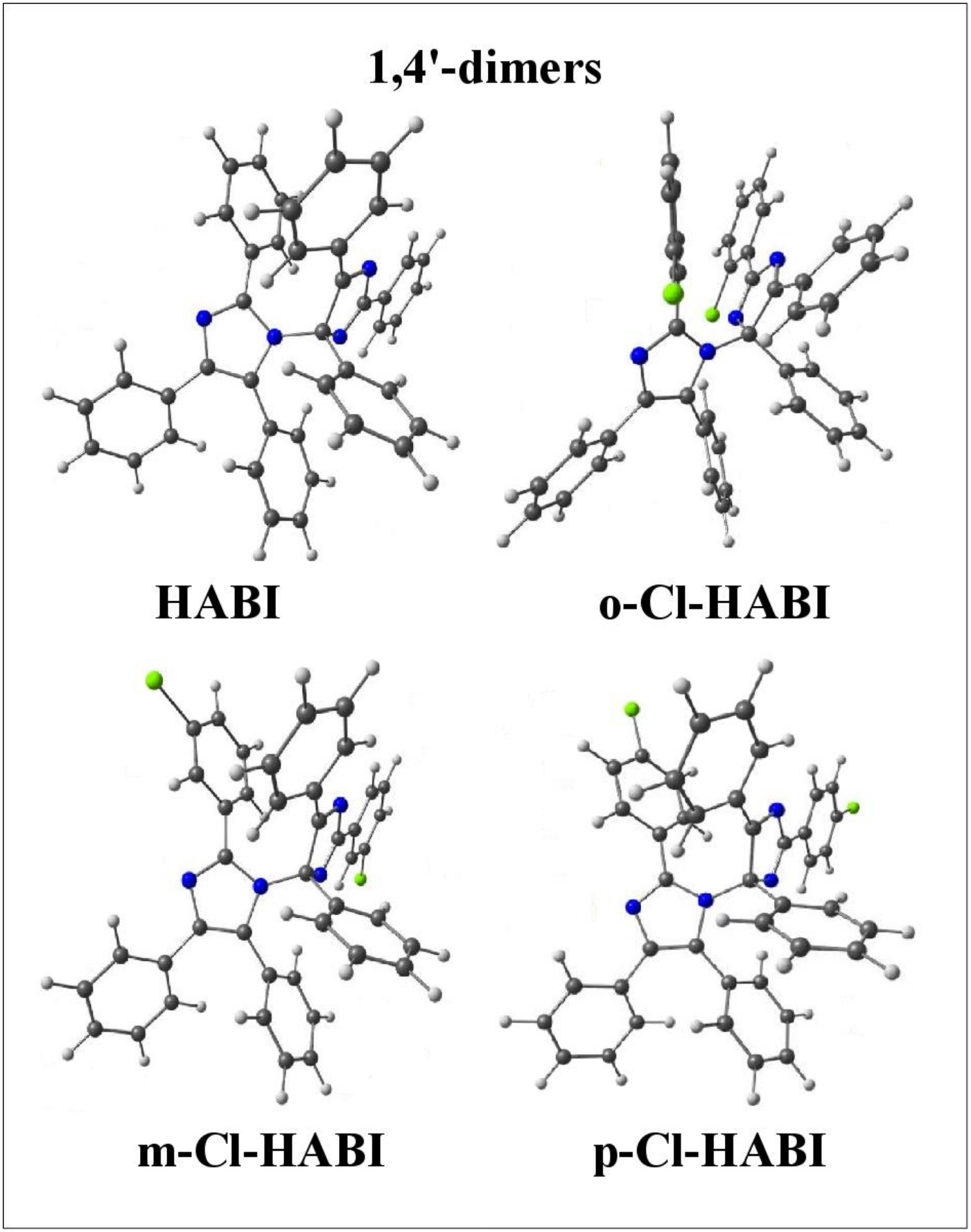
19) DFT-optimized structures of 4-4' dimers of o-Cl-HABI



20) DFT-optimized structures of 1-1' dimers



21) DFT-optimized structures of 1-4' dimers



22) DFT-optimized structures of 2-4' dimers