Electronic Supplementary Material (ESI) for Analyst.

Supplementary Information

Combined Analysis of 1,3-Benzodioxoles by Crystalline Sponge X-ray Crystallography and Laser Desorption Ionization Mass Spectrometry

Yukako Hayashi, Kazuaki Ohara, Rika Taki, Tomomi Saeki and Kentaro Yamaguchi

Faculty of Pharmaceutical Sciences at Kagawa Campus, Tokushima Bunri University, 1314-1 Shido, Sanuki, Kagawa 769-2193, Japan

Table of Contents

· Crystallographic data (Table SI1)

Table SI1 Crystallographic data for the Crystalline sponge, CS **1** encapsulating safrole(**2** ⊂ **1a**), piperonyl acetone (**3** ⊂ **1b**), piperonyl methyl ketone (**4** ⊂ **1b**), and piperonylonitrile (**5** ⊂ **1b**)

CS	**2** ⊂ **1a**	**3** ⊂ **1b**	**4** ⊂ **1b**	**5** ⊂ **1b**
Formula	$C_{53.4}H_{41.4}I_{6.0}N_{12}O_{3.5}Zn_{3.0}$	$C_{64.6}H_{58.3}Cl_{6.0}N_{12.0}O_{6.8}Zn_{3.0}$	$C_{76}H_{64}Cl_6N_{12}O_{12}Zn_3$	$C_{57.1}H_{41.6}Cl_{6.0}N_{14.2}O_{4.5}Zn_{3.0}$
Crystal system	*Monoclinic*	*Monoclinic*	*Monoclinic*	*Monoclinic*
Space group	*C2/c*	*C2/c*	*C2/c*	*C2/c*
***a* (Å)**	35.0630(15)	33.0803(15)	33.1389(13)	33.0732(15)
***b* (Å)**	14.7661(5)	14.4234(6)	14.5129(4)	14.4606(5)
***c* (Å)**	31.2601(12)	32.0307(13)	32.1744(11)	31.2748(12)
***β* (°)**	101.654(4)	102.207(3)	102.912(3)	101.909(3)
***V* (Å^3)**	15851.1(11)	14937.3(11)	15082.7(9)	14635.5(10)
***θ* range (°)**	4.888-65.495	3.355-69.323	2.736-65.342	3.347-65.347
Z	8	8	8	8
Density (g/cm^3)	1.563	1.351	1.538	1.277
Temperature (K)	100	100	100	100
***μ* (mm^{-1})**	19.735	3.551	3.655	3.569
***F* (000)**	7054	6207	7136	5688
index ranges	$-41 \le h \le 41$	$-39 \le h \le 39$	$-38 \le h \le 38$	$-37 \le h \le 38$
h*, *k* ,*l	$-17 \le k \le 17$	$-16 \le k \le 16$	$-16 \le k \le 17$	$-17 \le k \le 16$
	$-36 \le l \le 36$	$-36 \le l \le 37$	$-37 \le l \le 37$	$-36 \le l \le 36$
Crystal size (mm^3)	0.07×0.05×0.03	0.13×0.09×0.03	0.10×0.04×0.02	0.14×0.08×0.03
Total reflections	78506	74079	73402	70935
Unique reflections	13111	13602	12714	12444
R_{int}	0.0709	0.0251	0.0608	0.0327
Completeness	0.959	0.986	0.983	0.992
data	13111	13602	12714	12444
restraints	548	860	410	700
parameters	966	1199	982	1095
GoF (%)	1.022	1.033	1.030	1.013
$R_1/wR_2(I>2\sigma(I))$	0.0574/0.1546	0.0744/0.2442	0.0750/0.2230	0.0601/0.1958
R_1/wR_2	0.1018/0.1803	0.0843/0.2629	0.1041/0.2505	0.0723/0.2119
CCDC	1586123	1586124	1586121	1586122

·X-ray structure analysis of **2** ⊂ **1a**

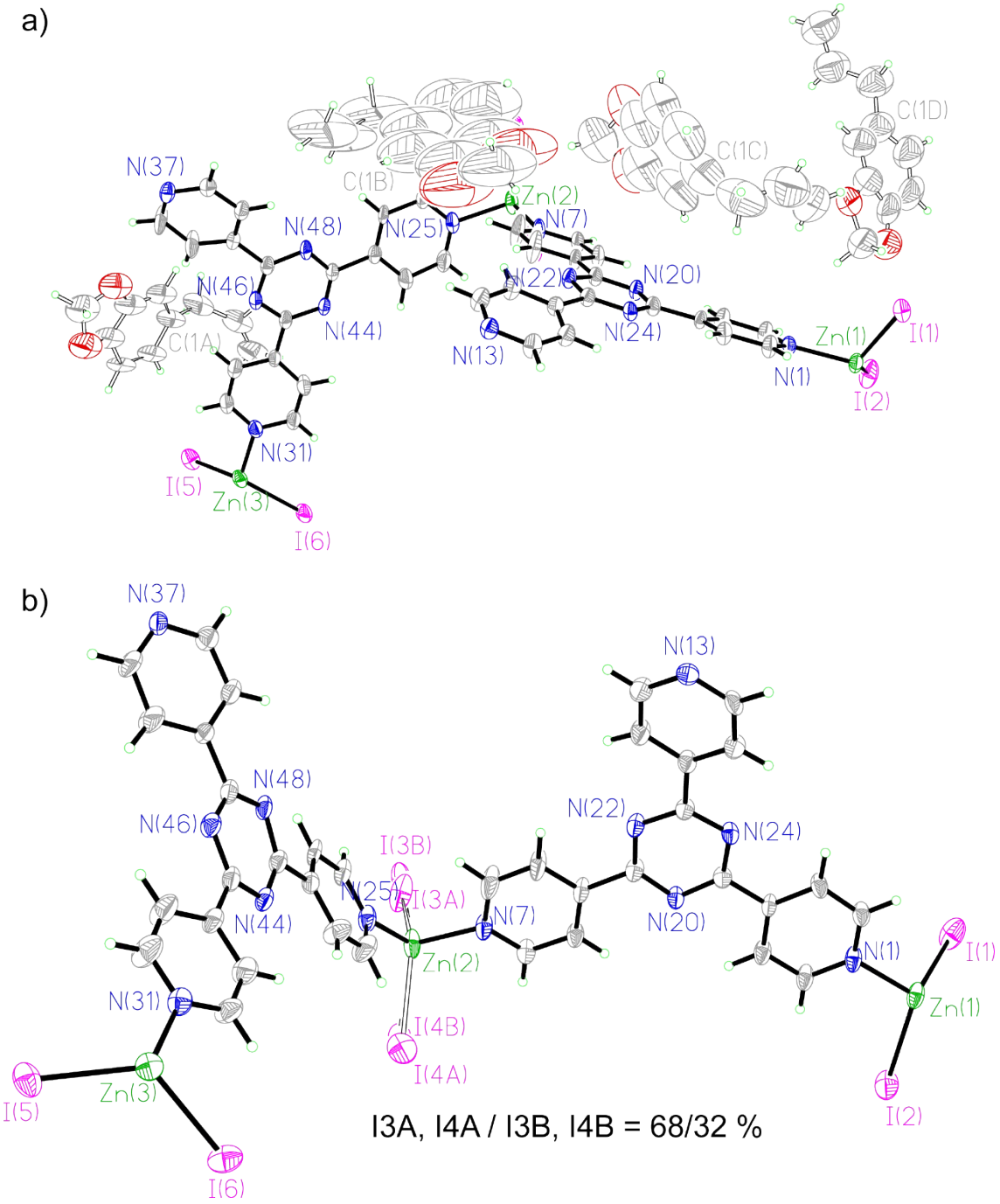
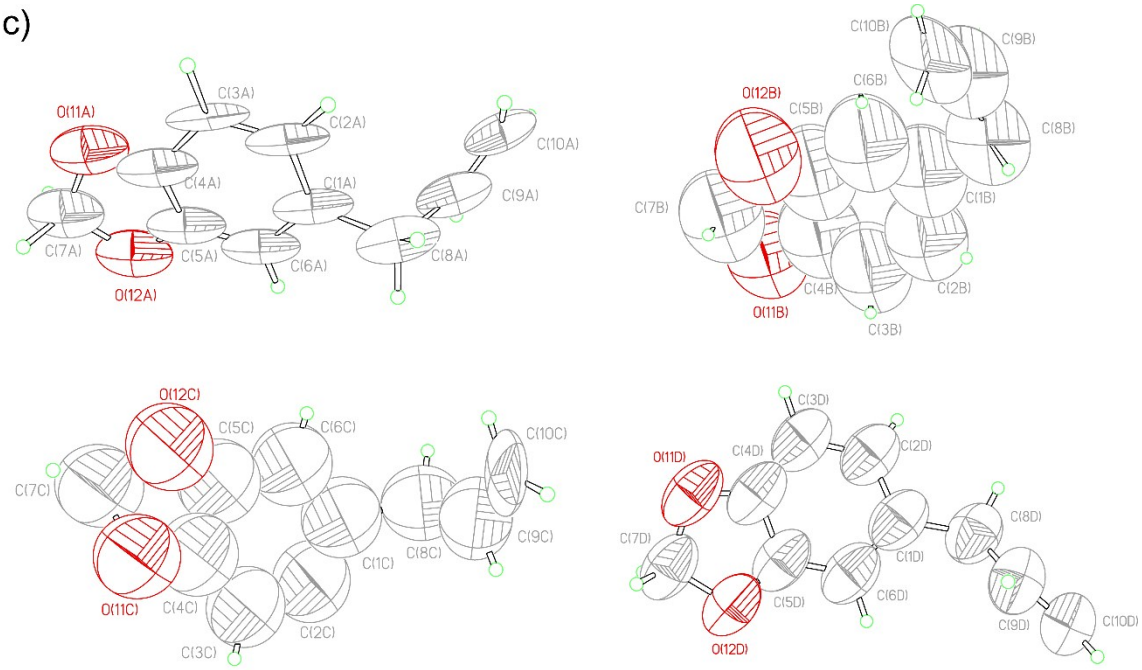


Fig. SI1 ORTEP view (30% probability level) of safrole **2**.
a) full structure; b) the host framework.

c)



C1A to O12A 25 %
C1B to O12B 50 %
C1C to O12C 50 %
C1D to O12D 50 %

Fig. SI2 ORTEP view (30% probability level) of safrole **2**.
c) Molecule of safrole (position A, B, C, D).

·X-ray analysis conditions for guest **2** assigned as A to D.

Some restraints were applied in refinement of a disordered model. By using DFIX restraints, most of the1,2- and 1,3-distances were restrained to target values based on the standard distance of single and double bonds, and SIMU and DELU were applied for the whole disordered molecule in the pore as shown in Fig. SI3.

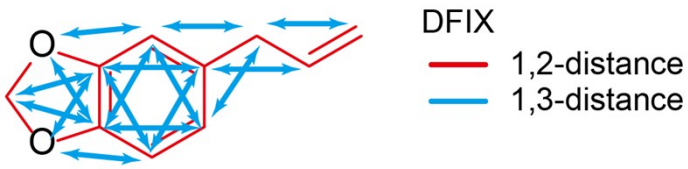


Fig. SI3 Restraints applied in the refinement of **2** ⊂ **1a**.

·X-ray structure analysis of **3** ⊂ **1b**

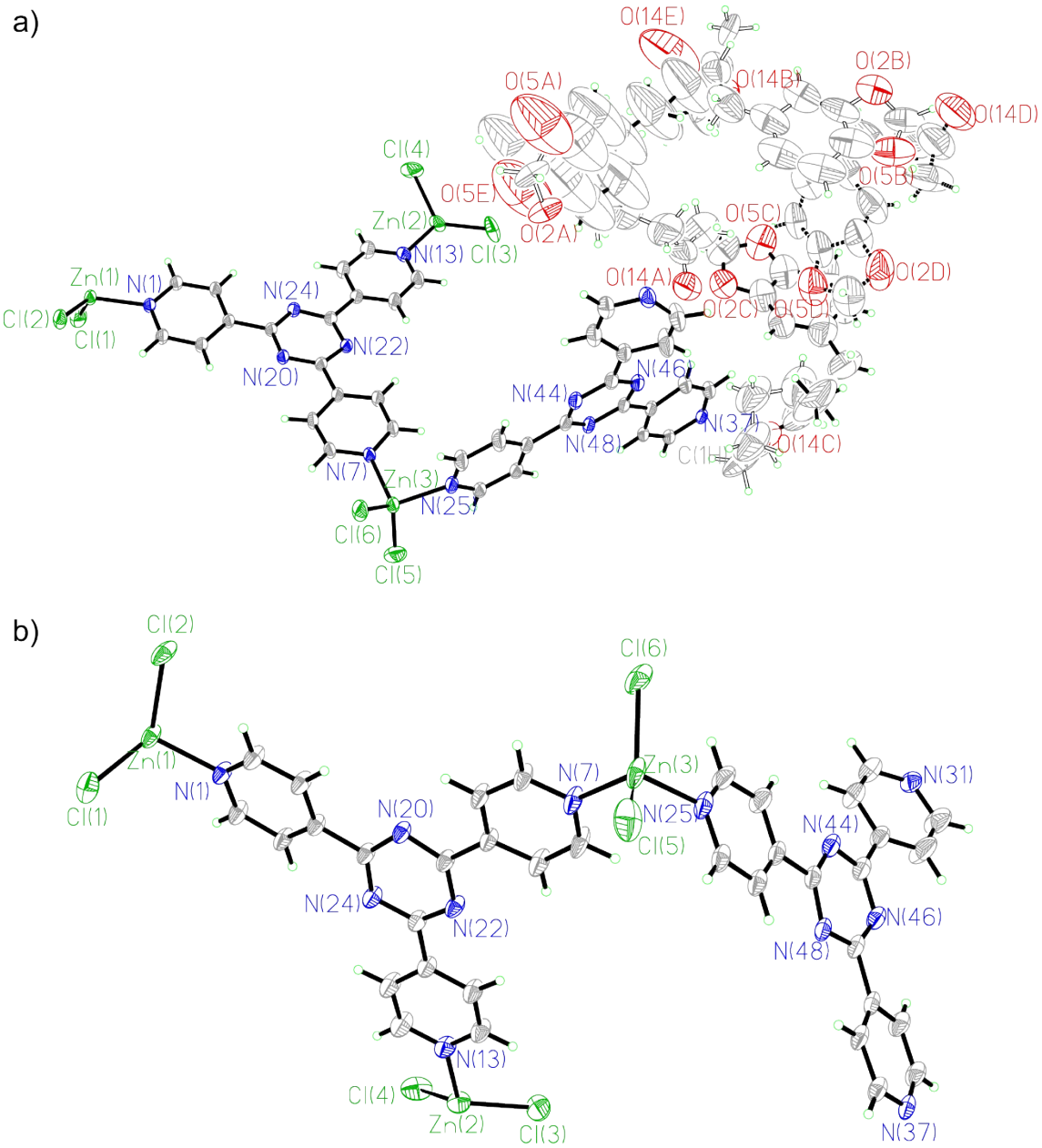


Fig. SI4 ORTEP view (30% probability level) of piperonyl acetone **3**.
a) full structure; b) the host framework.

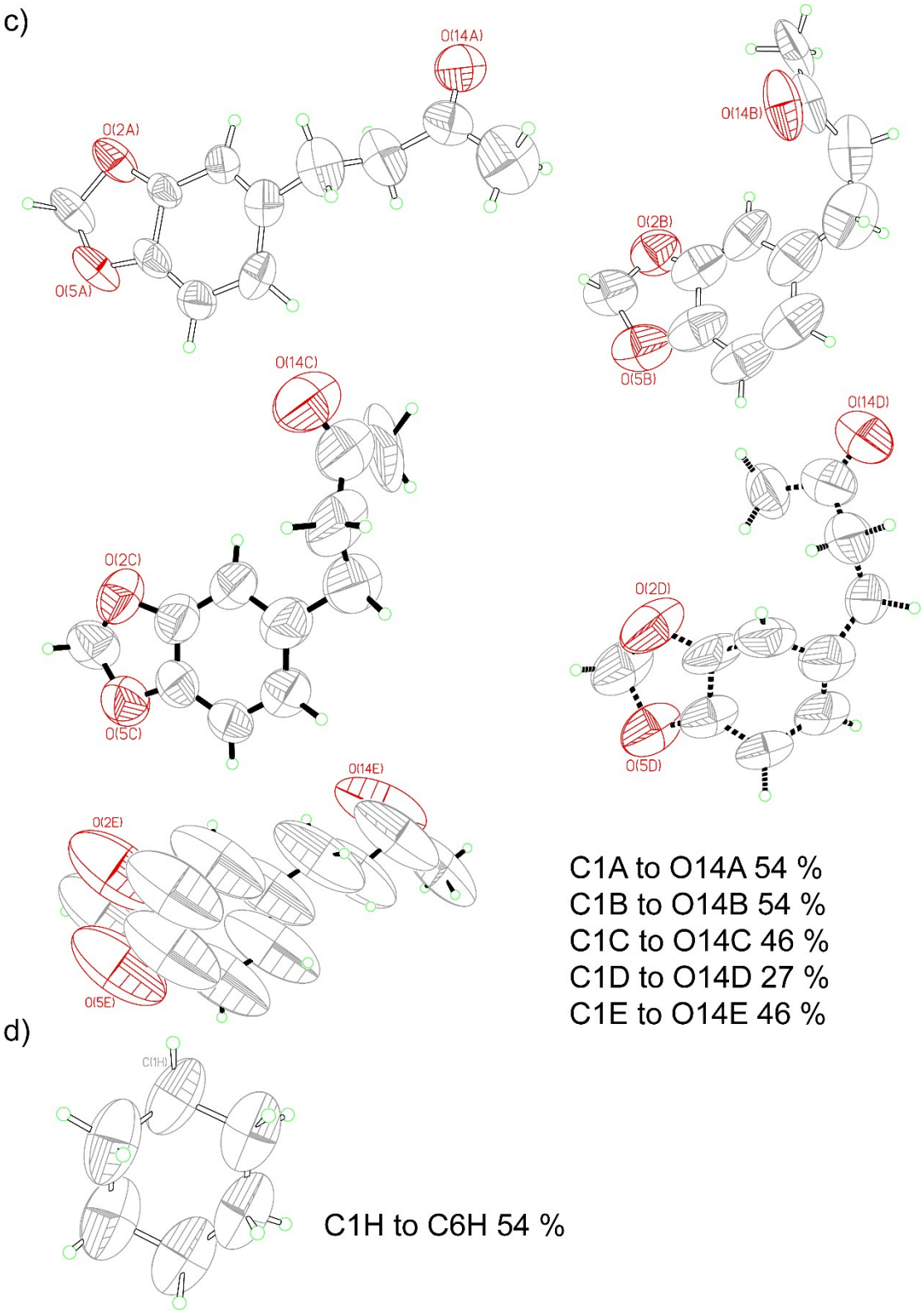


Fig. SI5 ORTEP view (30% probability level) of piperonyl acetone **3**.
c) Molecule of piperonyl acetone (position A, B, C, D, E); d) cyclohexane
X-ray structure analysis of **3** ⊂ **1b**

·X-ray analysis conditions for guest **3** assigned as A to E.

Some restraints were applied in refinement of a disordered model. By using DFIX restraints, most of the1,2- and 1,3-distances were restrained to target values based on the standard distance of single and double bonds, and SIMU and DELU were applied for the whole disordered molecule in the pore as shown in Fig. SI6.

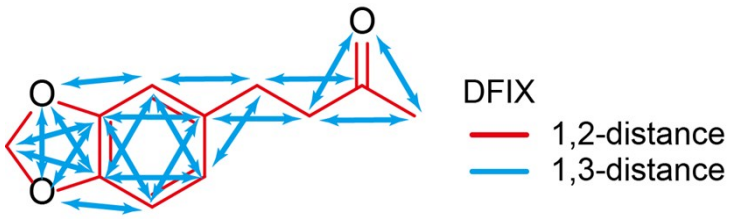


Fig. SI6 Restraints applied in the refinement of **3** ⊂ **1b**.

·X-ray structure analysis of **4** ⊂ **1b**

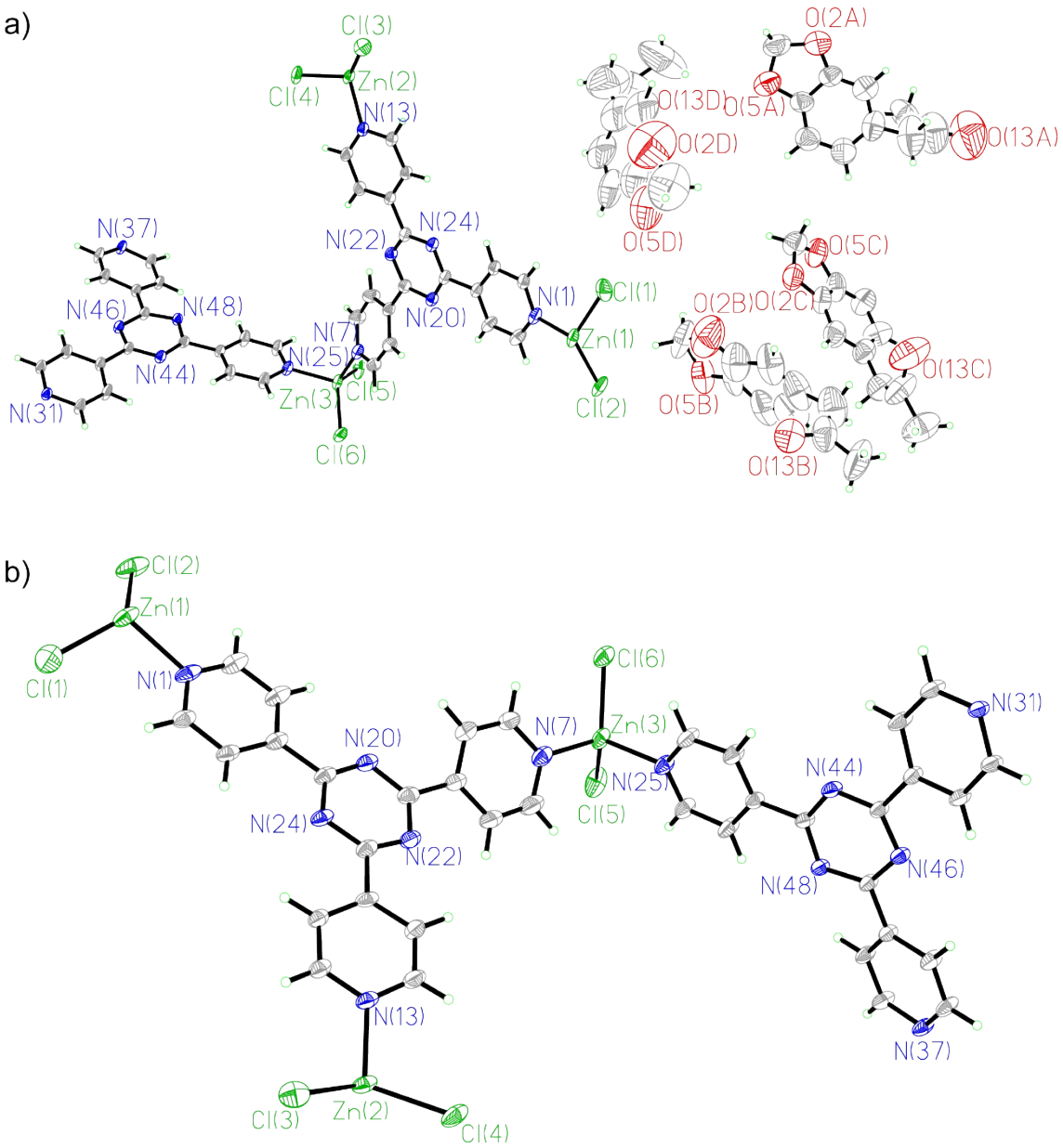
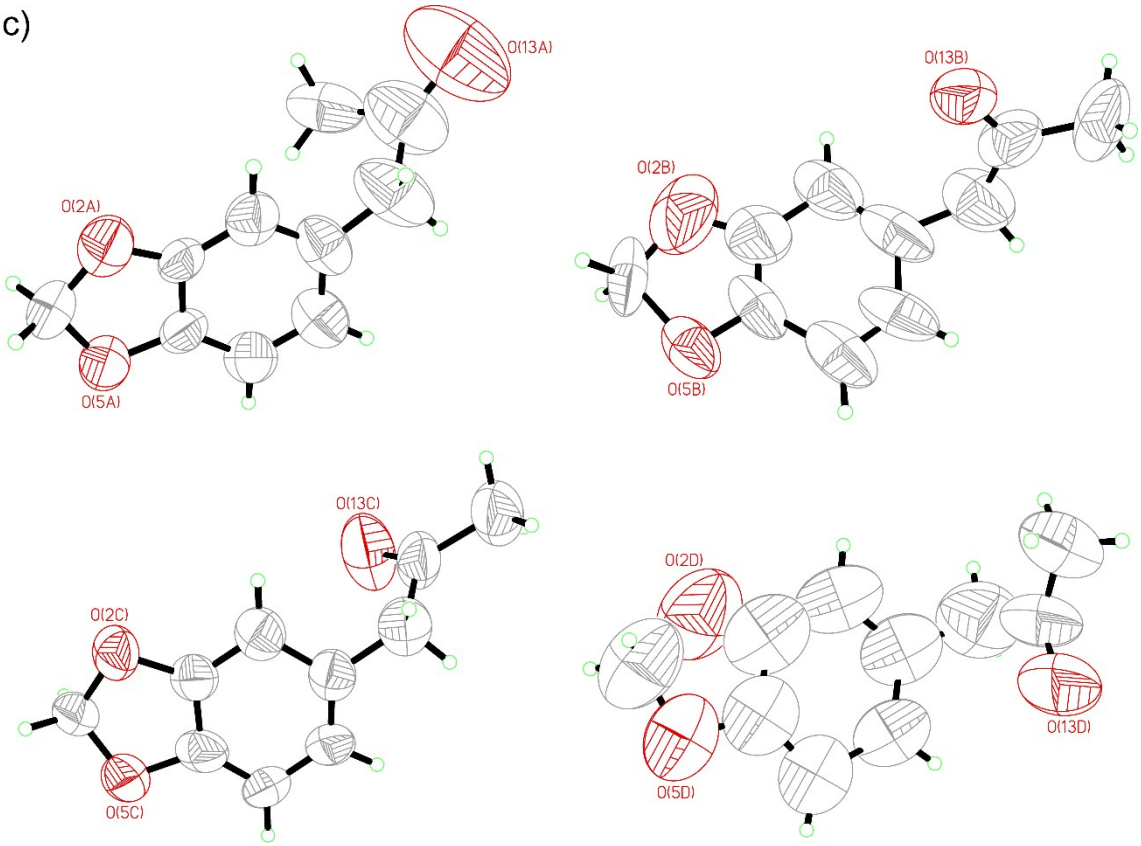


Fig. SI7 ORTEP view (30% probability level) of piperonyl methyl ketone **4**.
a) full structure; b) the host framework.

c)



C1A to O13A 100 %
C1B to O13B 100 %
C1C to O13C 100 %
C1D to O13D 100 %

Fig. SI8 ORTEP view (30% probability level) of piperonyl methyl ketone **4**.
c) Molecule of piperonyl methyl ketone (position A, B, C, D).

·X-ray analysis conditions for guest **4** assigned as A to D.

Some restraints were applied in refinement of a disordered model. By using DFIX restraints, most of the1,2- and 1,3-distances were restrained to target values based on the standard distance of single and double bonds, and SIMU and DELU were applied for the whole disordered molecule in the pore as shown in Fig. SI9.

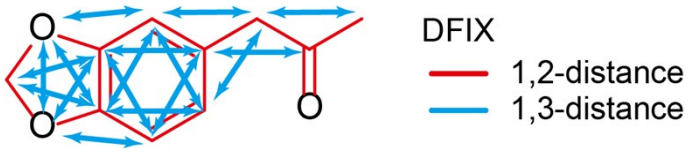
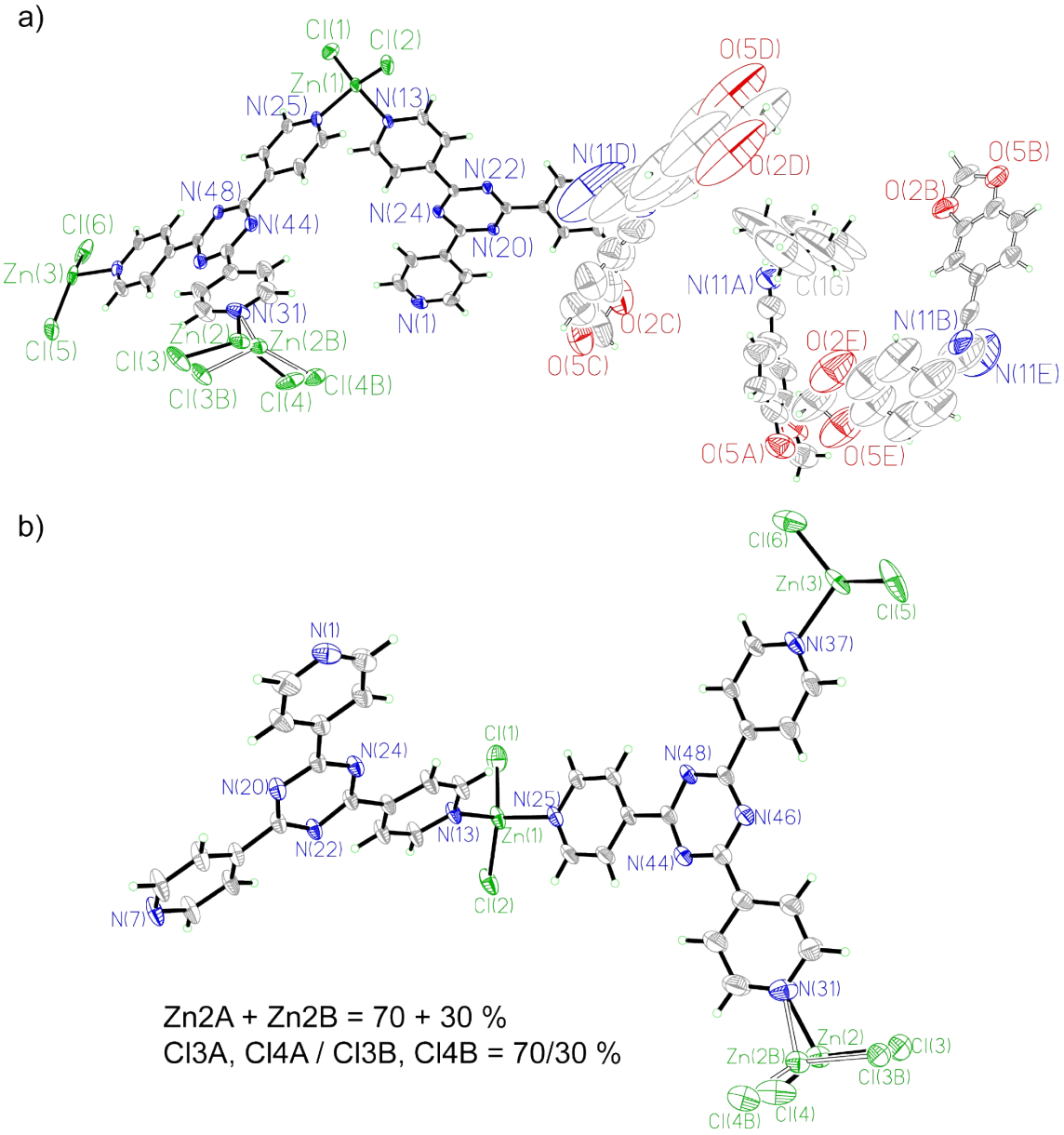


Fig. SI9 Restraints applied in the refinement of **4** ⊂ **1b**.

· X-ray structure analysis of **5** ⊂ **1b**



Zn2A + Zn2B = 70 + 30 %
Cl3A, Cl4A / Cl3B, Cl4B = 70/30 %

Fig. SI10 ORTEP view (30% probability level) of piperonylonitrile **5**.
a) full structure; b) the host framework.

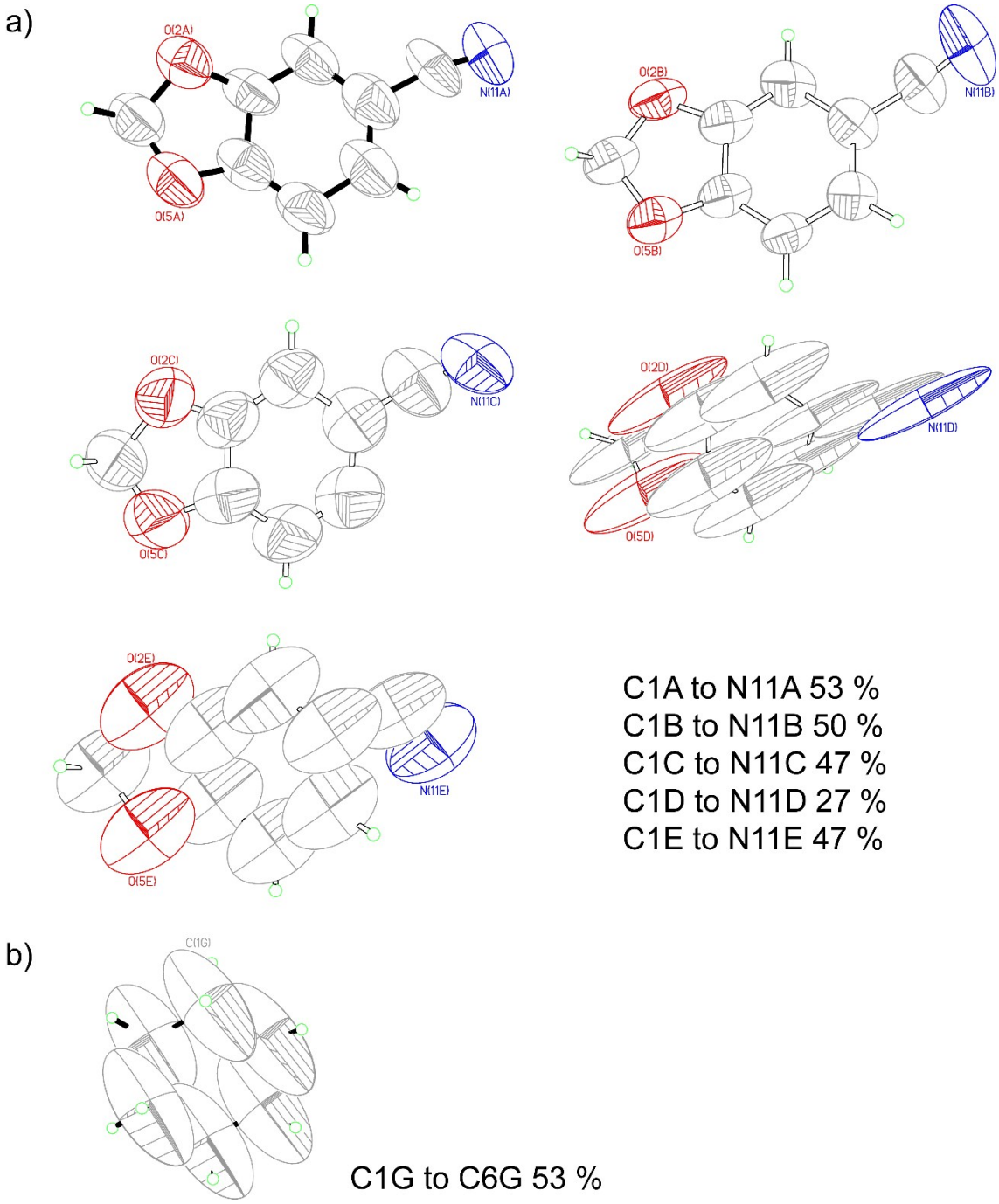


Fig. SI11 ORTEP view (30% probability level) of piperonylonitrile (**5**).
c) Molecule of piperonylonitrile (position A, B, C, D, E); d) cyclohexane

·X-ray analysis conditions for guest **5** assigned as A to E.

Some restraints were applied in refinement of a disordered model. By using DFIX restraints, most of the1,2- and 1,3-distances were restrained to target values based on the standard distance of single and double bonds, and SIMU and DELU were applied for the whole disordered molecule in the pore as shown in Fig. SI12.

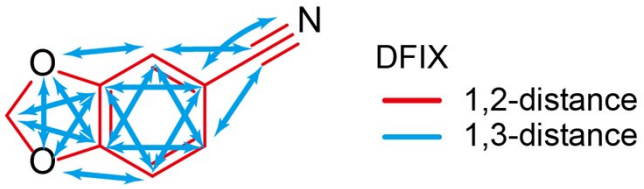


Fig. SI12 Restraints applied in the refinement of **5** ⊂ **1b**.

· NMR data of extracts from **X** ⊂ **1** (**X** = **2** - **5**).

Table SI2 Ratios of guest/TPT after decomposition of the CS

CS	**2** ⊂ **1a**	**3** ⊂ **1b**	**4** ⊂ **1b**	**5** ⊂ **1b**
NMR (guest/TPT ratio)	0.32	1.37	1.66	1.76

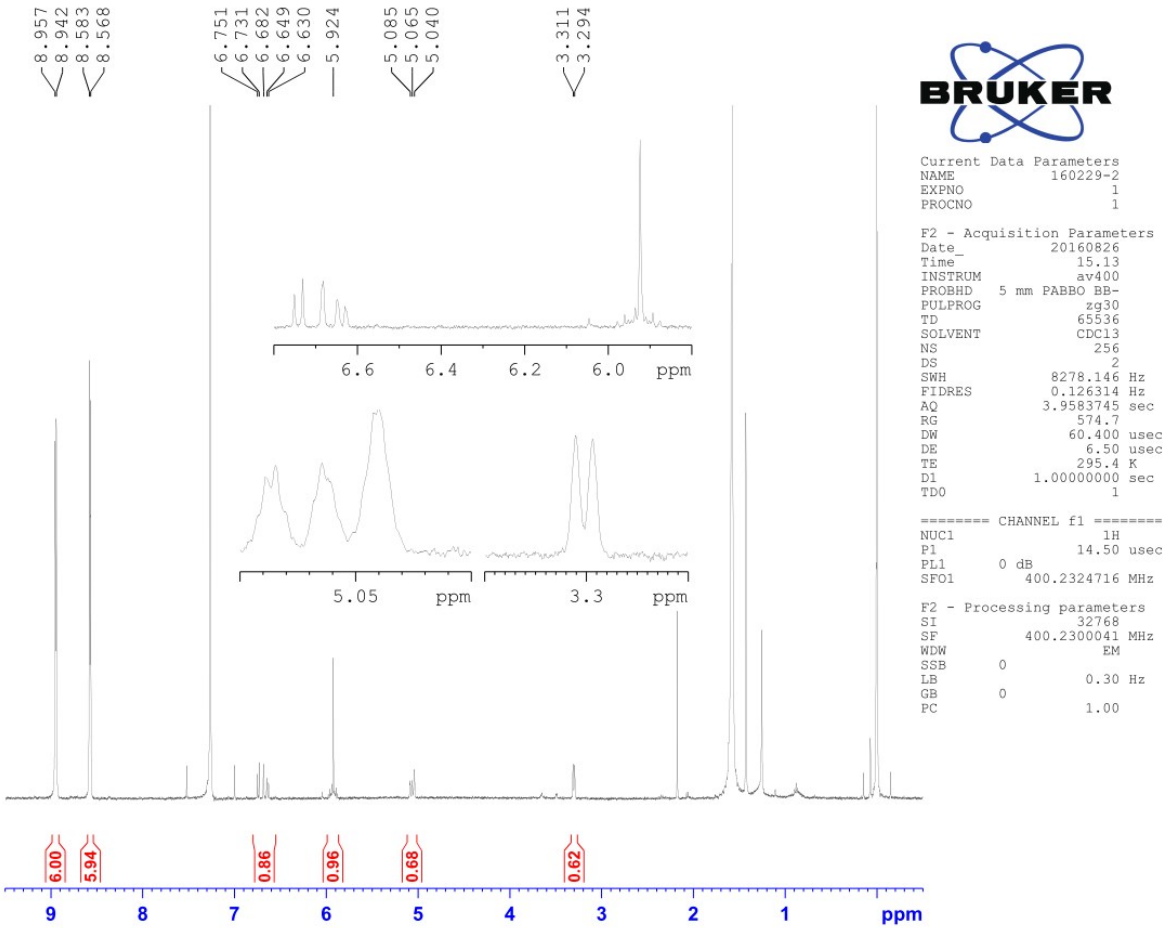


Fig. SI13 ^{1}H NMR spectrum of safrole **2** extracted from crystalline sponge after decomposition with hydrochloric acid. ($CDCl_3$, 300 K, 400 MHz)

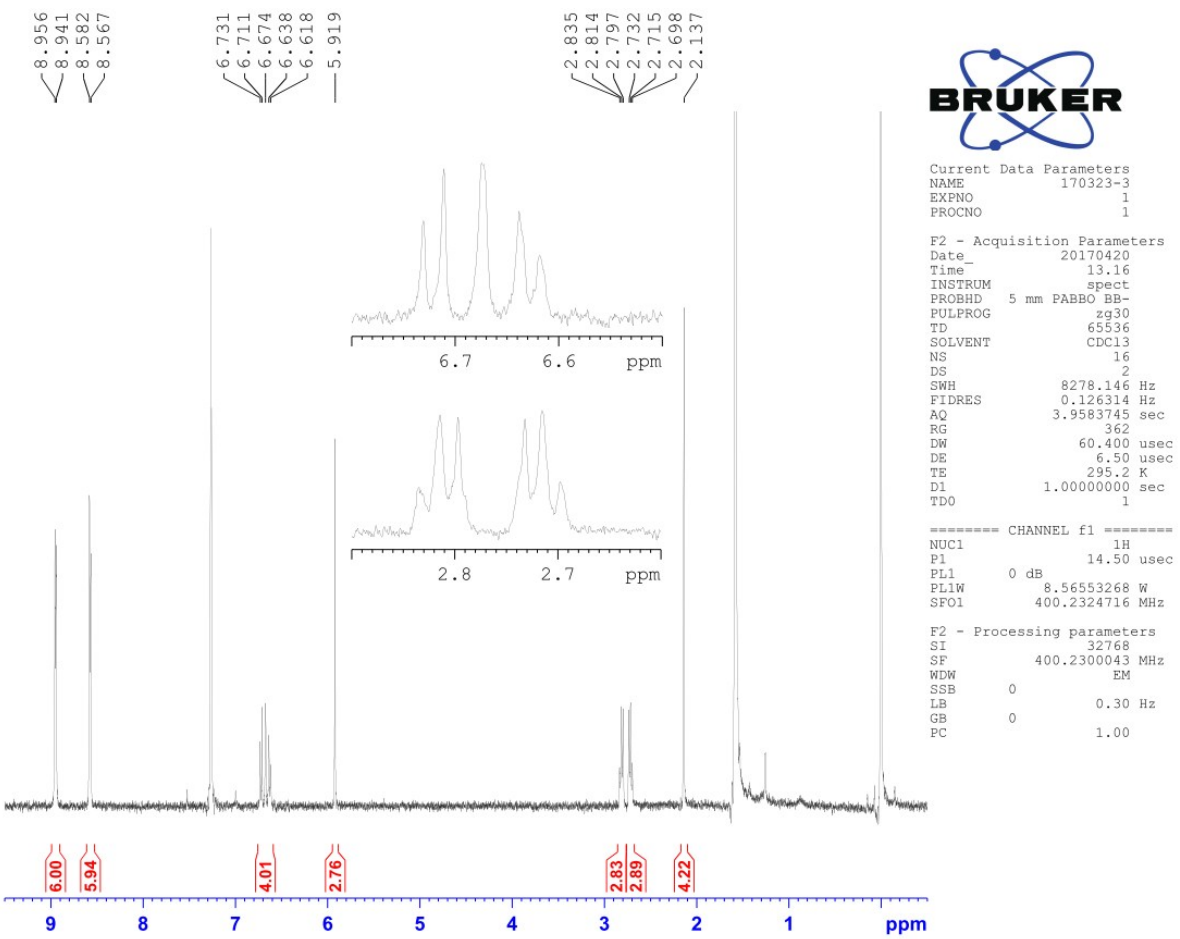


Fig. SI14 ^{1}H NMR spectrum of piperonyl acetone **3** extracted from crystalline sponge after decomposition with hydrochloric acid. ($CDCl_3$, 300 K, 400 MHz)

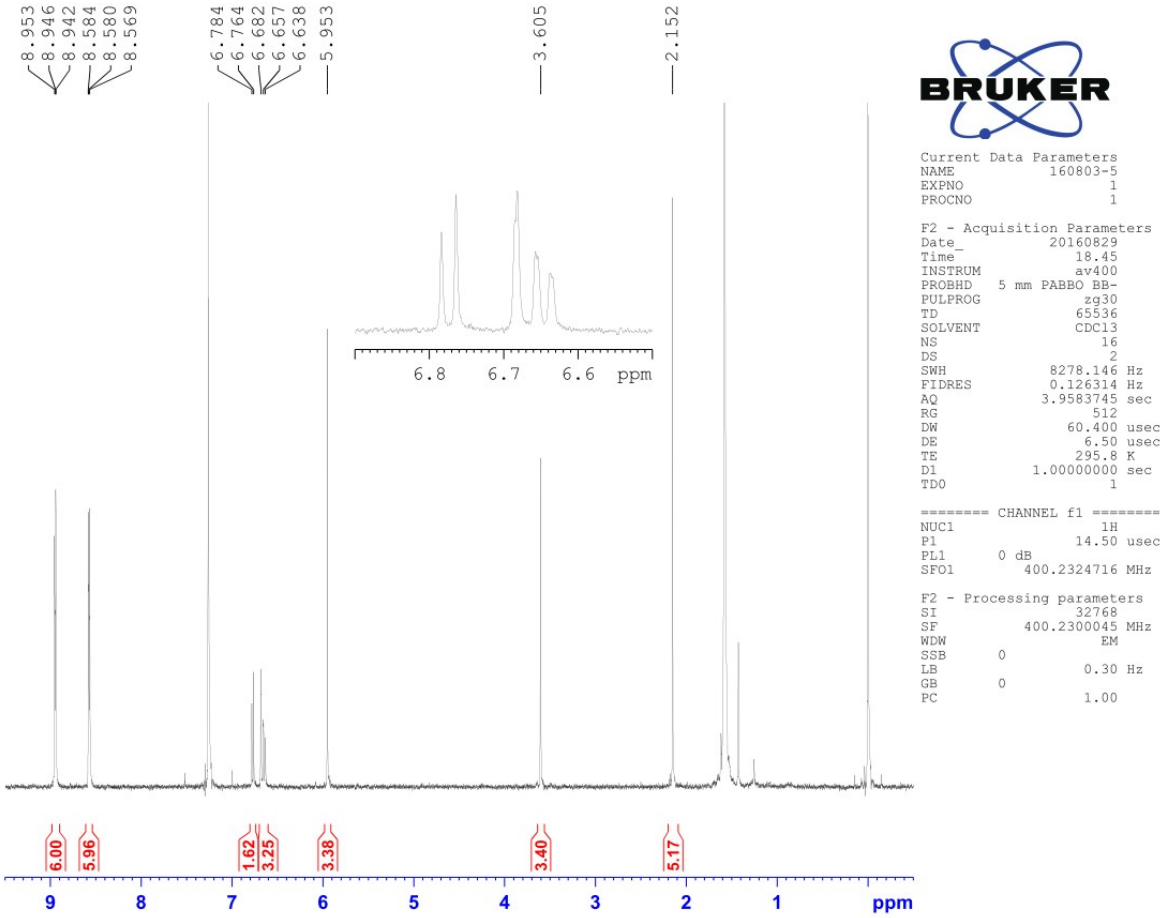


Fig. SI15 ^{1}H NMR spectrum of piperonyl methyl ketone **4** extracted from crystalline sponge after decomposition with hydrochloric acid. ($CDCl_3$, 300 K, 400 MHz)

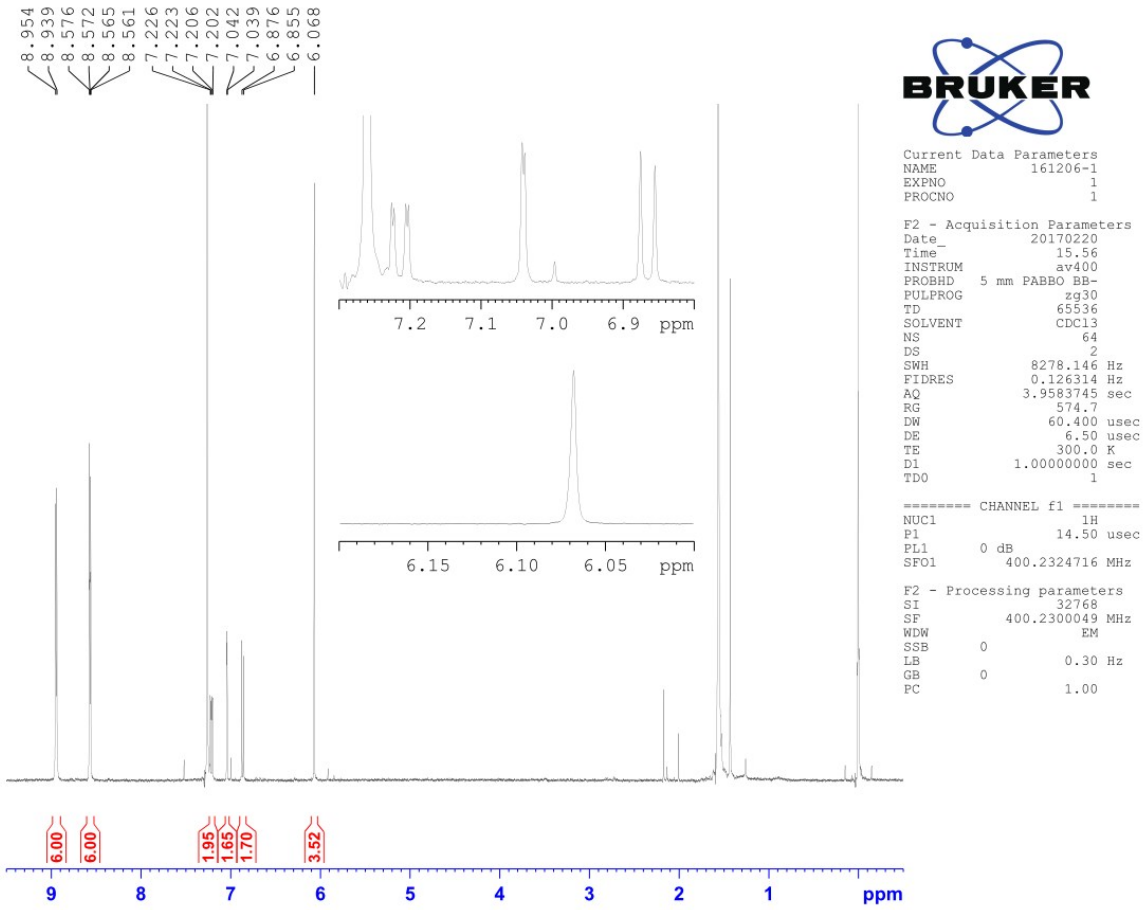


Fig. SI16 ^{1}H NMR spectrum of piperonylonitrile **5** extracted from crystalline sponge after decomposition with hydrochloric acid. ($CDCl_3$, 300 K, 400 MHz)

· Interaction between the CS frameworks and guests for **X** ⊂ **1** (**X** = **2** - **5**)

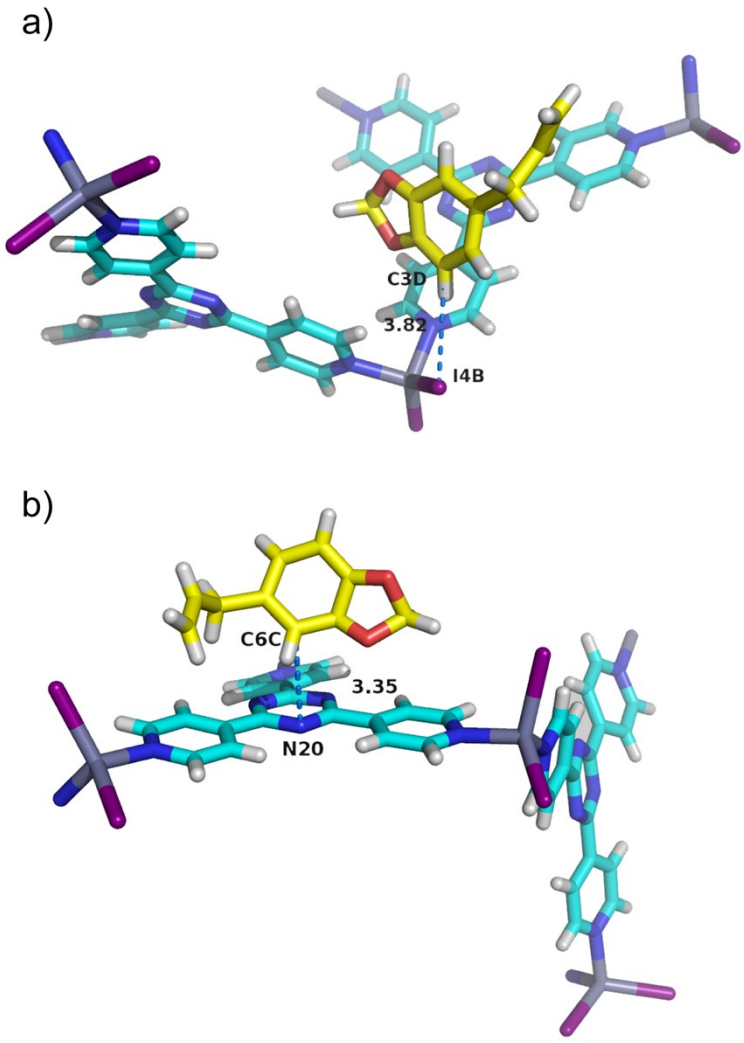


Fig. SI17 Structural analysis drawing of safrole **2**.
a) CH-halogen interaction between molecule D and the iodine atom of ZnI_2, I4B-C3D 3.82(4) Å, b) CH-π interaction between CH of 1,3-benzodioxole group and triazine ring, C6C-N20 3.35(6) Å.

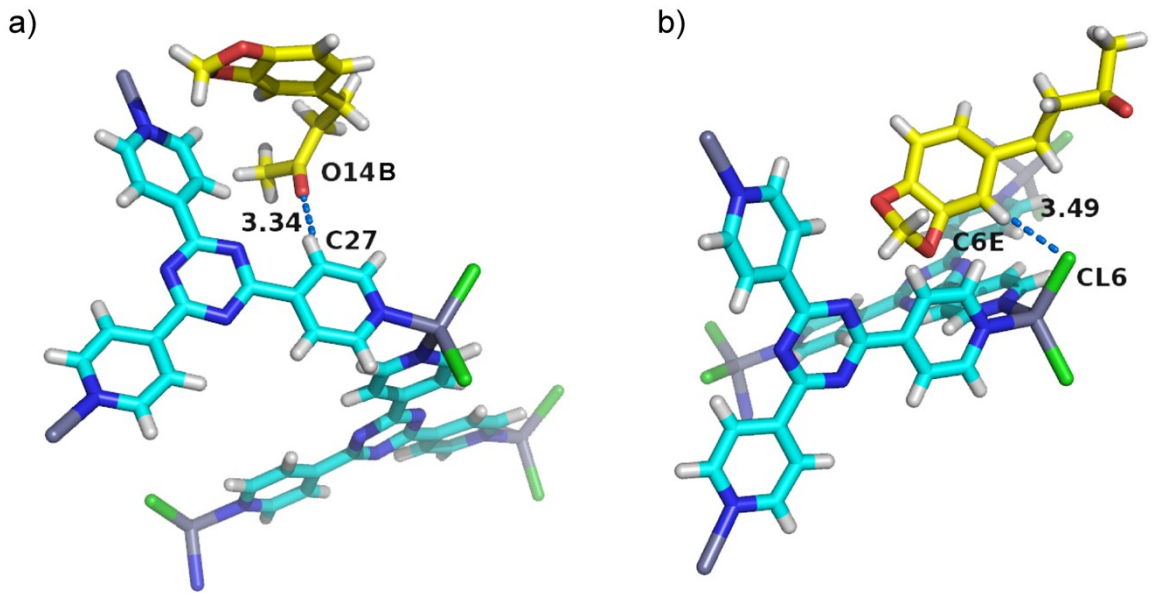


Fig. SI18 Structural analysis drawing of piperonyl acetone **3**.
a) CH-O interaction between molecule of B and the TPT ligand, O14B-C27 3.341(15) Å.
b) CH-halogen interaction between molecule of E and the chlorine atom of $ZnCl_2$, C6E-Cl6 3.49(5) Å.

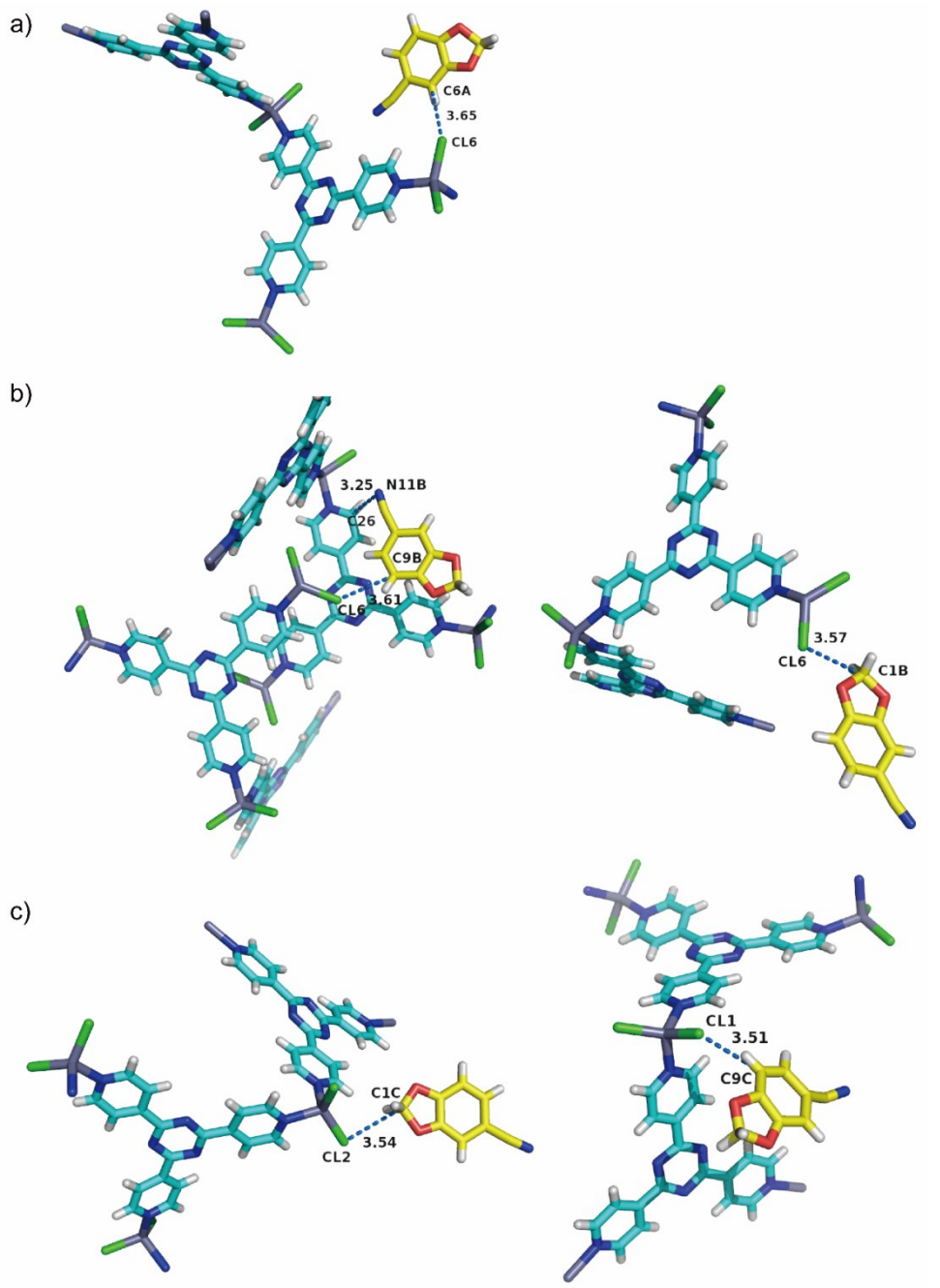


Fig. SI19 Structural analysis drawing of piperonylonitrile **5**.

a) CH-halogen interaction between molecule of A and the chlorine atom of $ZnCl_2$, C6A-Cl6 3.647(19) Å.

b) CH-halogen interaction between molecule of B and the chlorine atom of $ZnCl_2$. C9B-Cl6 3.611(18) Å, and π-π interaction between molecule of B and nitrogen atom of triazine framework, C1B-Cl6 3.57(2) Å.

c) CH-halogen interaction between molecule of C and the chlorine atom of $ZnCl_2$, C1C-Cl2 3.54(3) Å and C9C-Cl1 3.51(3) Å.

・1D average spectrum of the guests for **X** ⊂ **1** (**X** = **4, 5**)

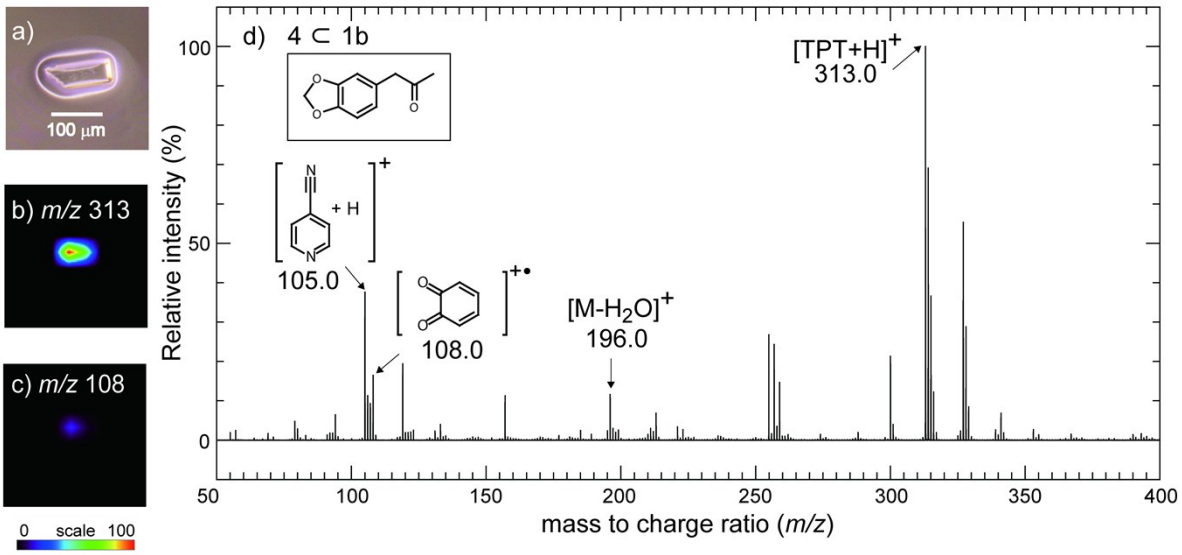


Fig. SI20 Optical image a) and IMS at m/z 313.0 b) and 108.0 c), and 1 D mass spectrum obtained from IMS and some assignments of **4** ⊂ **1b** d)

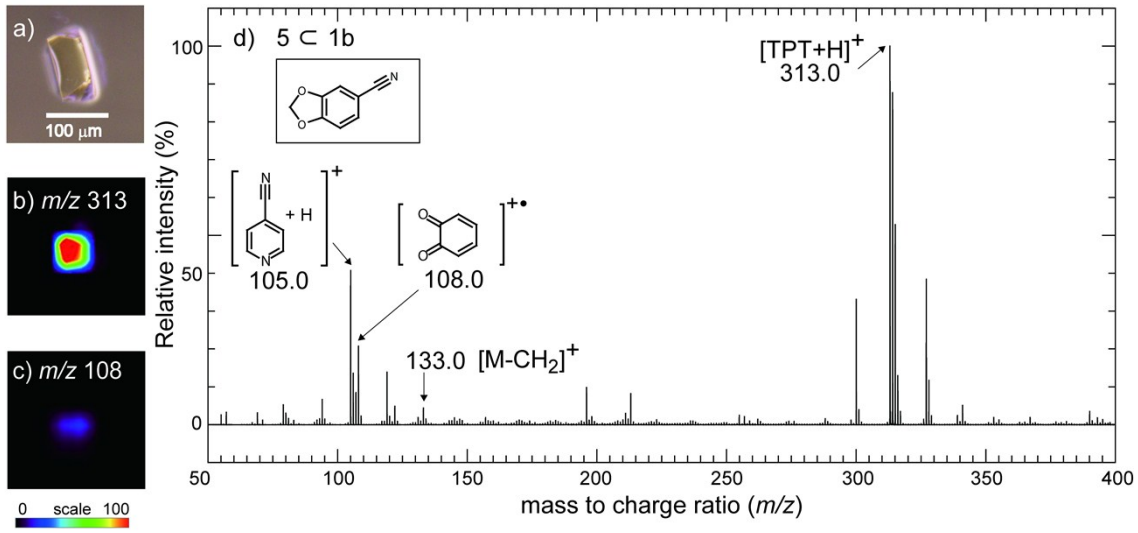


Fig. SI21 Optical image a) and IMS at m/z 313.0 b) and 108.0 c), and 1 D mass spectrum obtained from IMS and some assignments of **5** ⊂ **1b** d).