Supramolecular Architectures in *o*-Carboranyl Alcohols Bearing N-Aromatic Rings: Syntheses, Crystal Structures and Melting Points Correlation

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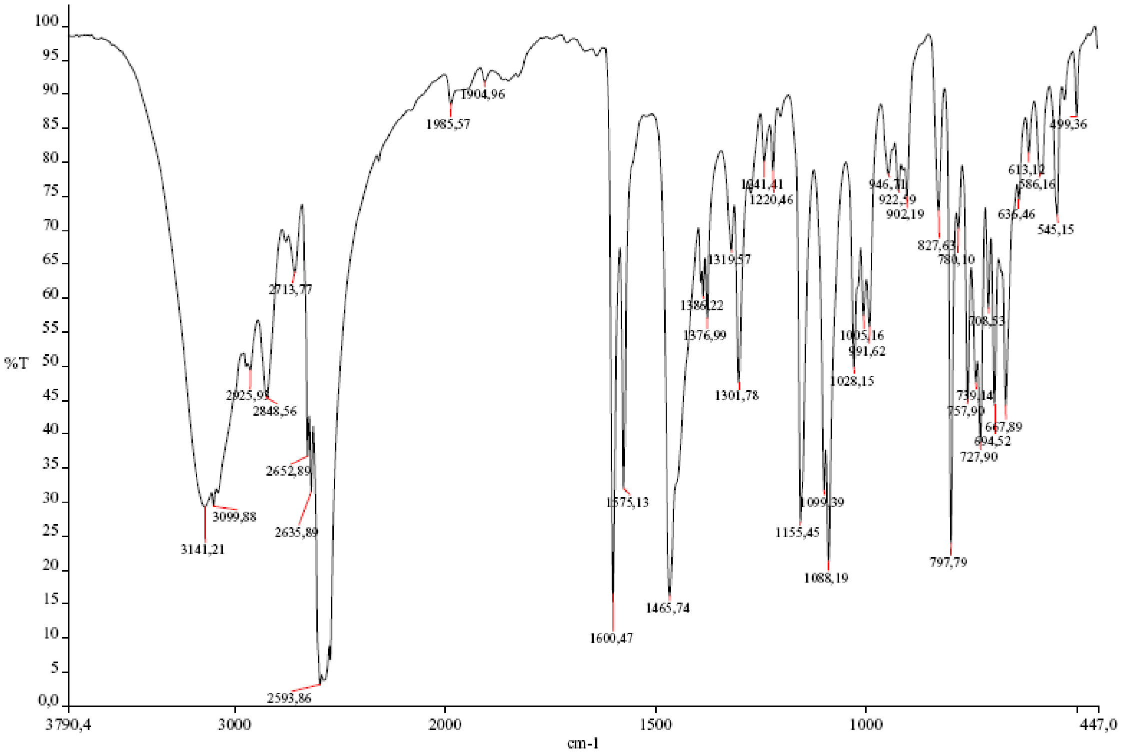
Electronic Supplementary Material for CrystEngComm

IR Spectrum (KBr) for compound (1b)



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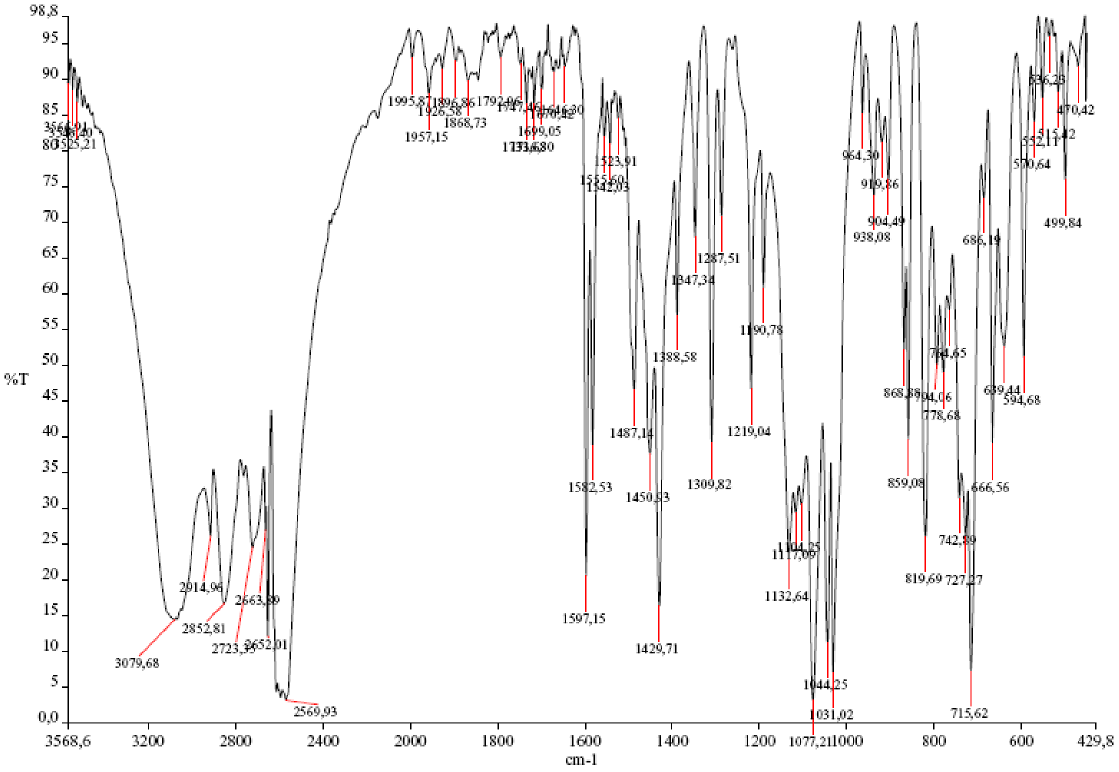

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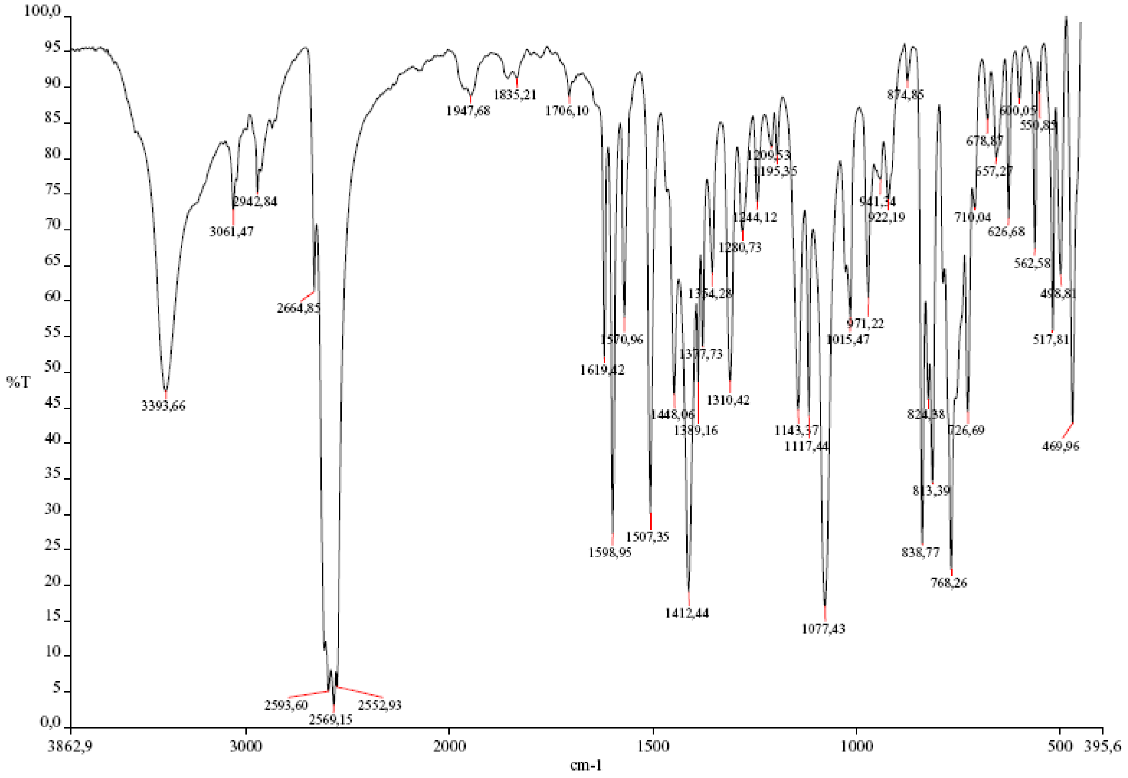

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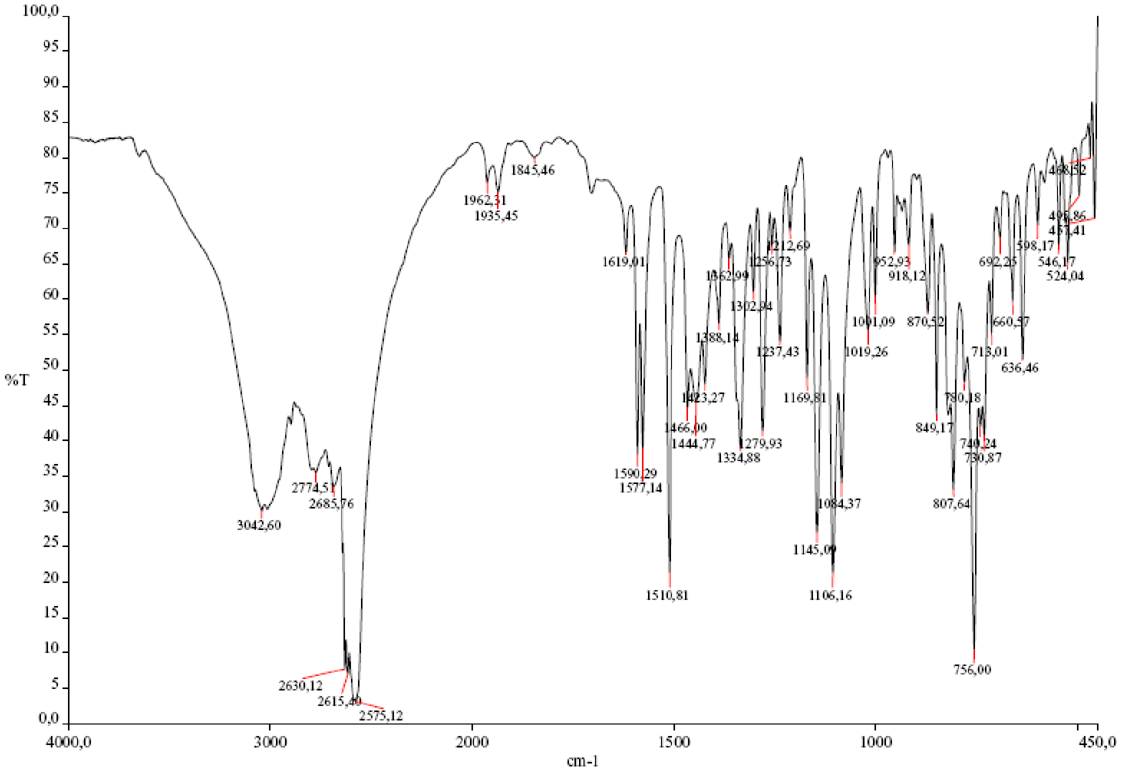

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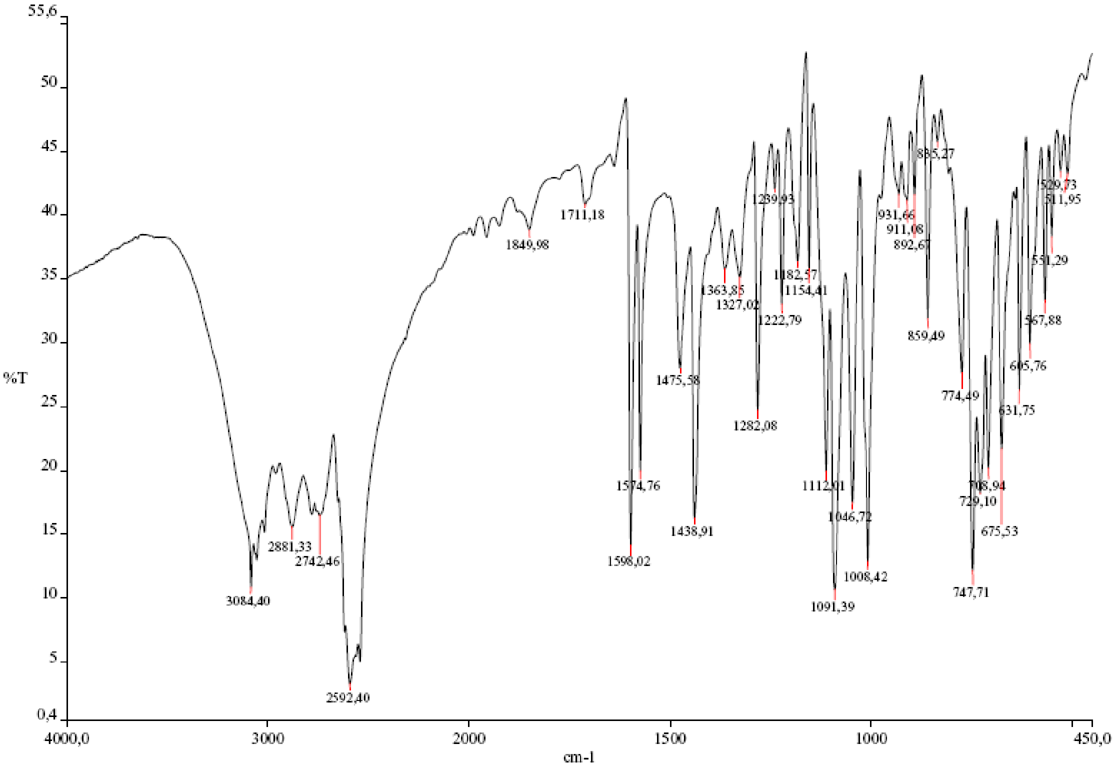

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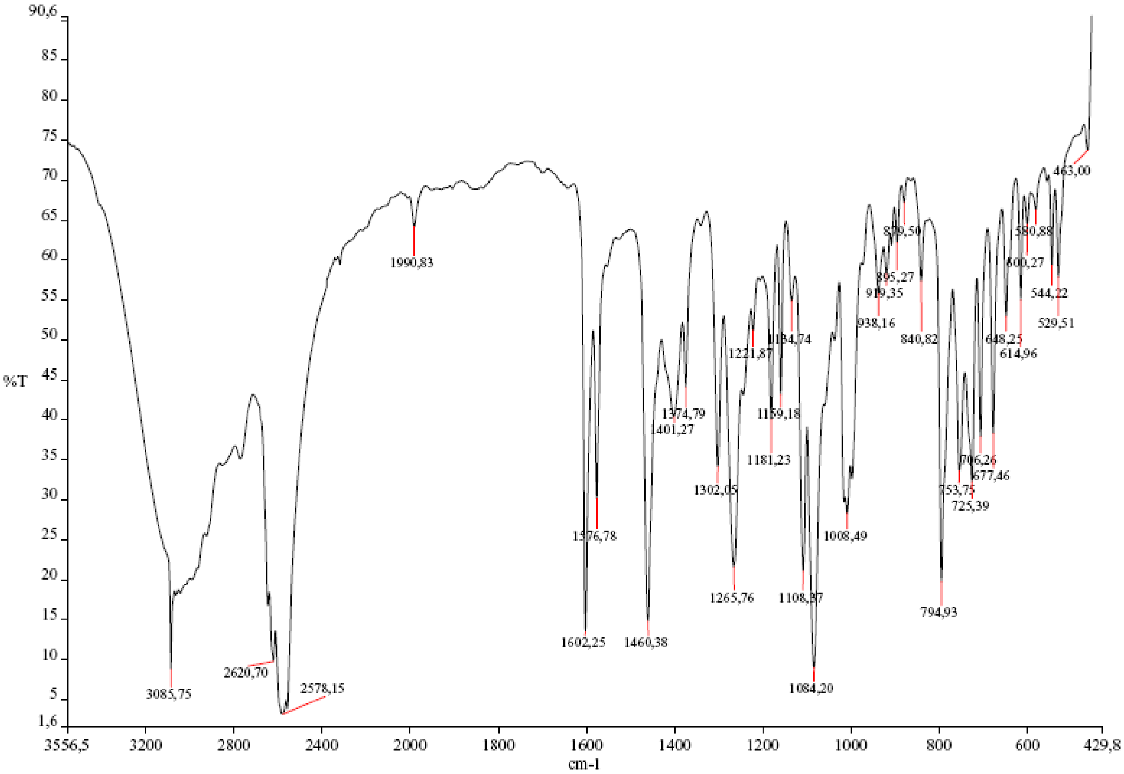

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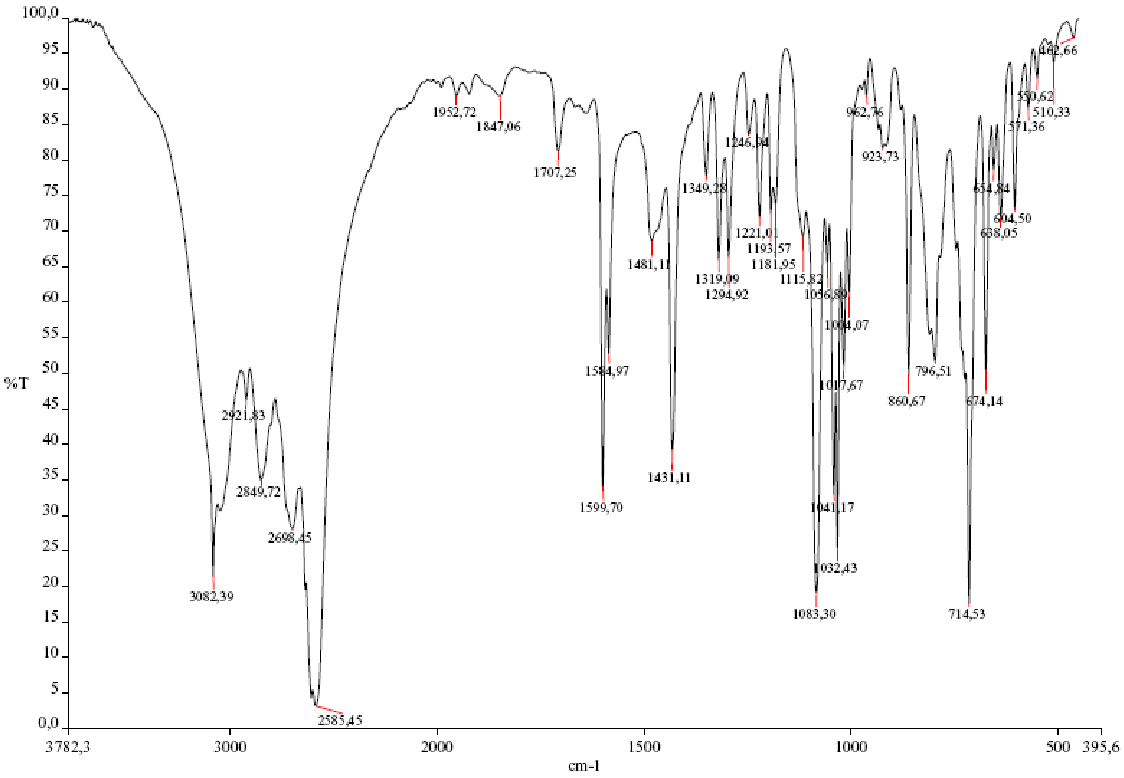

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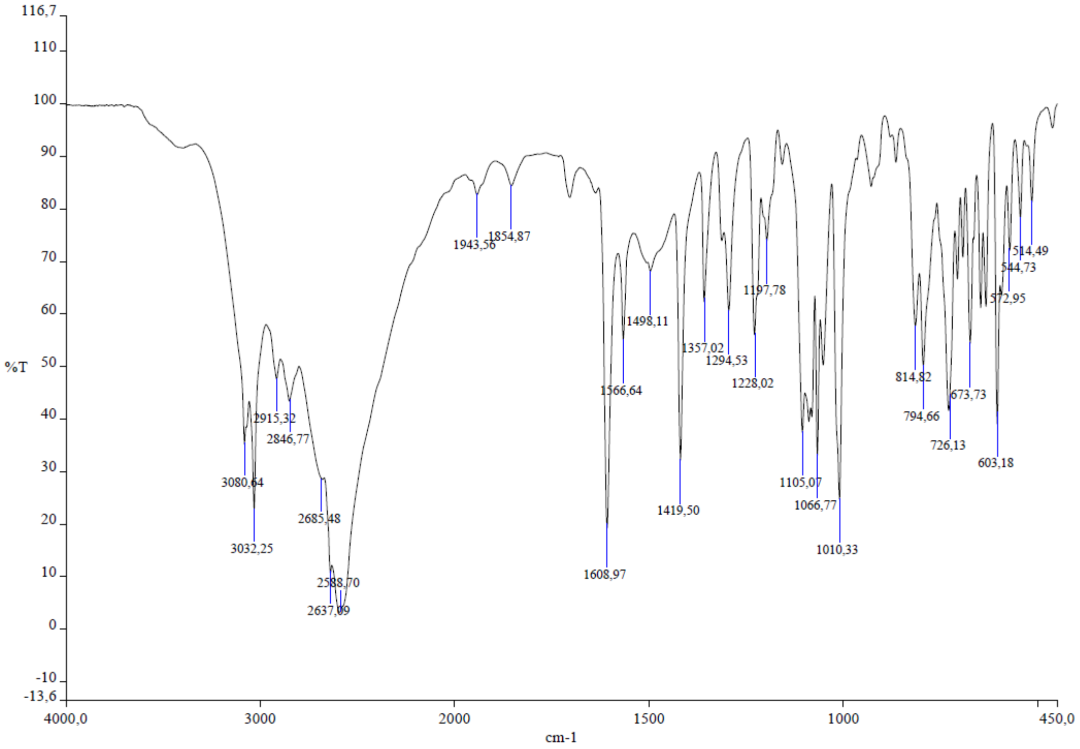

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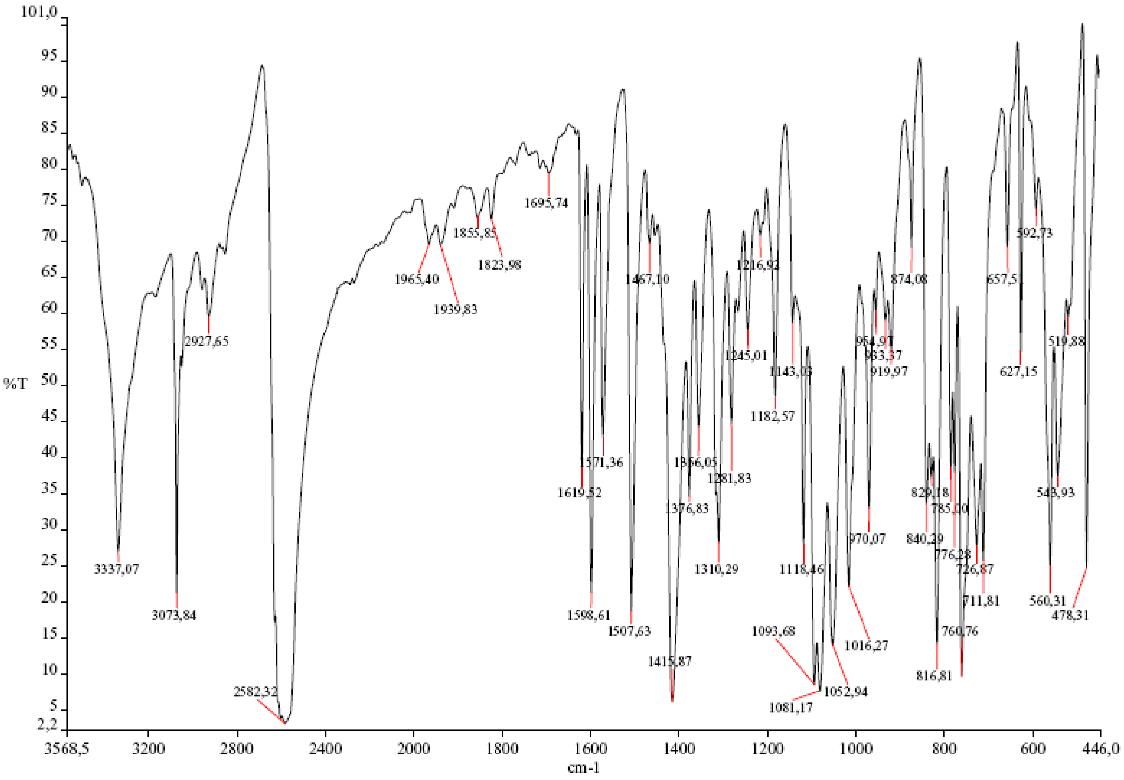

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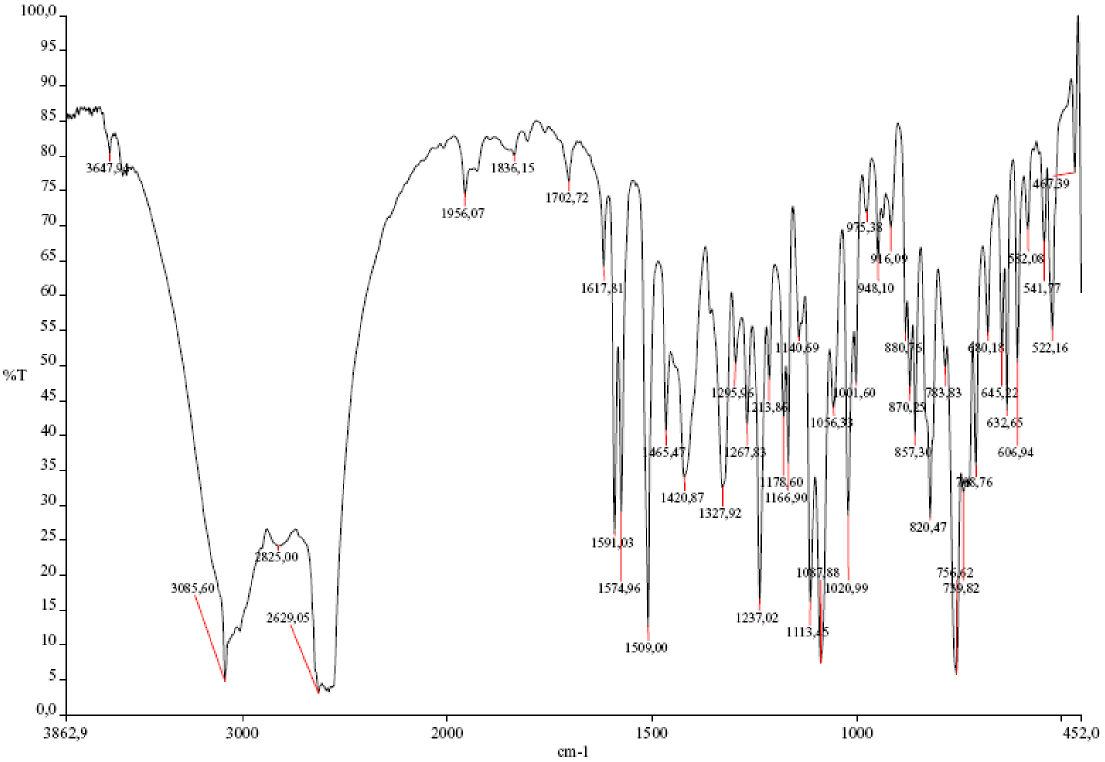

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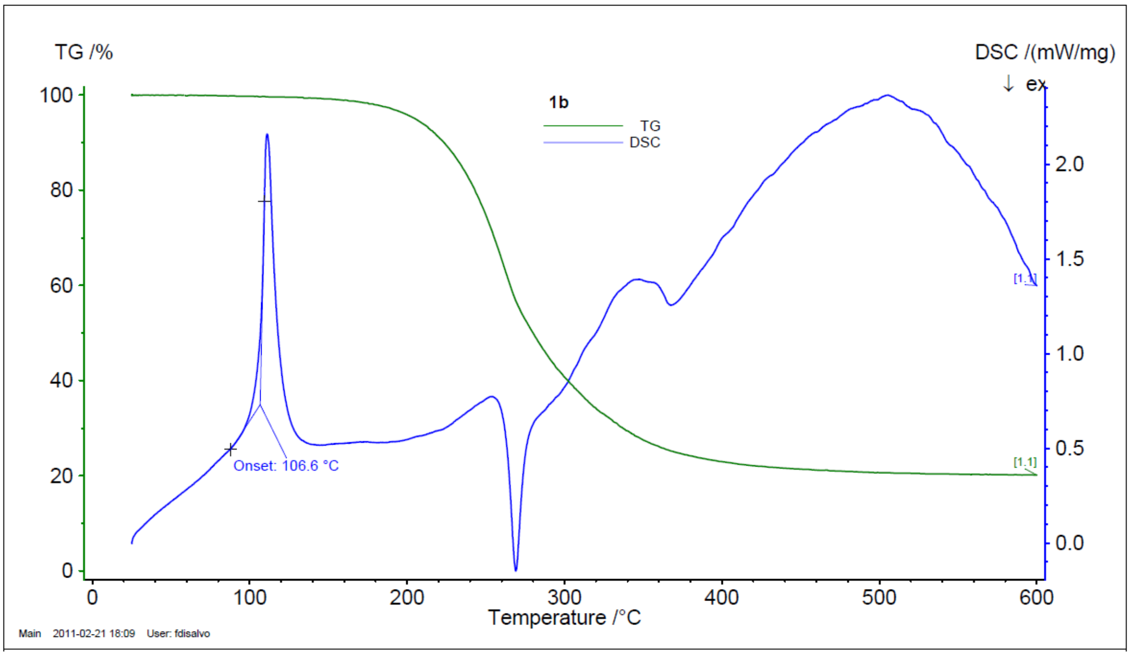

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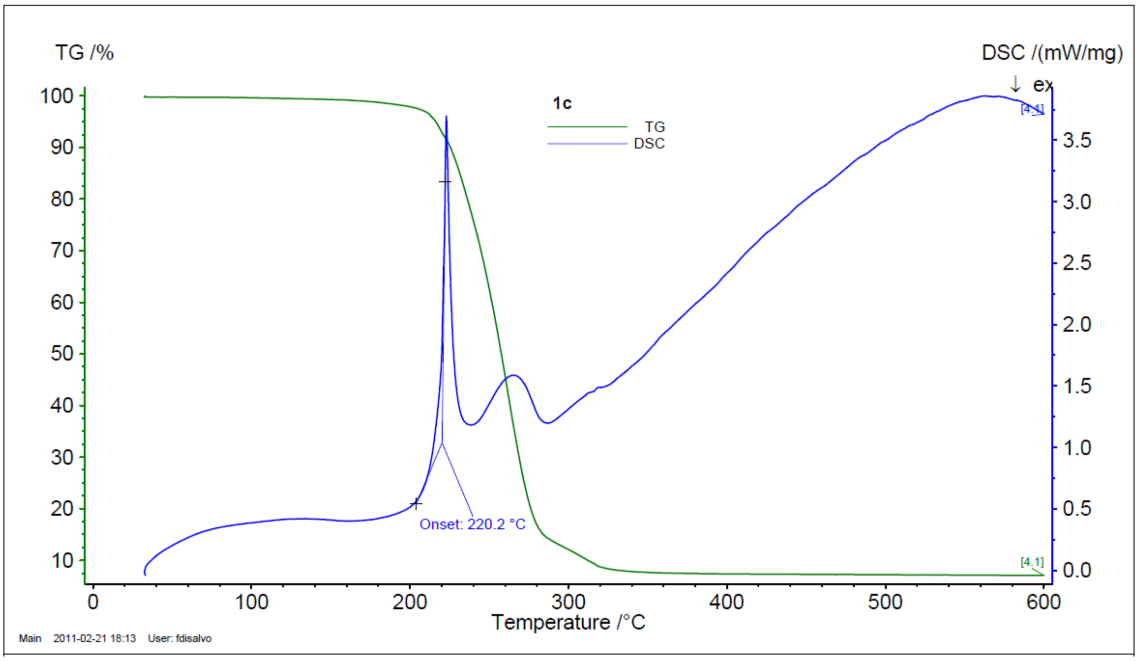

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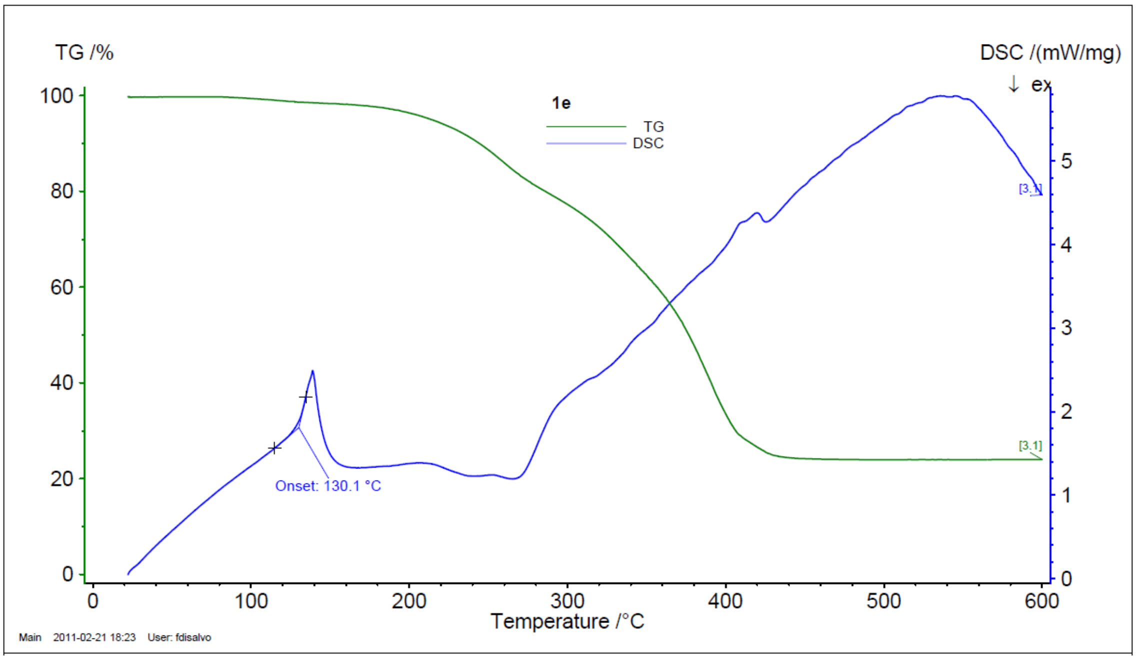

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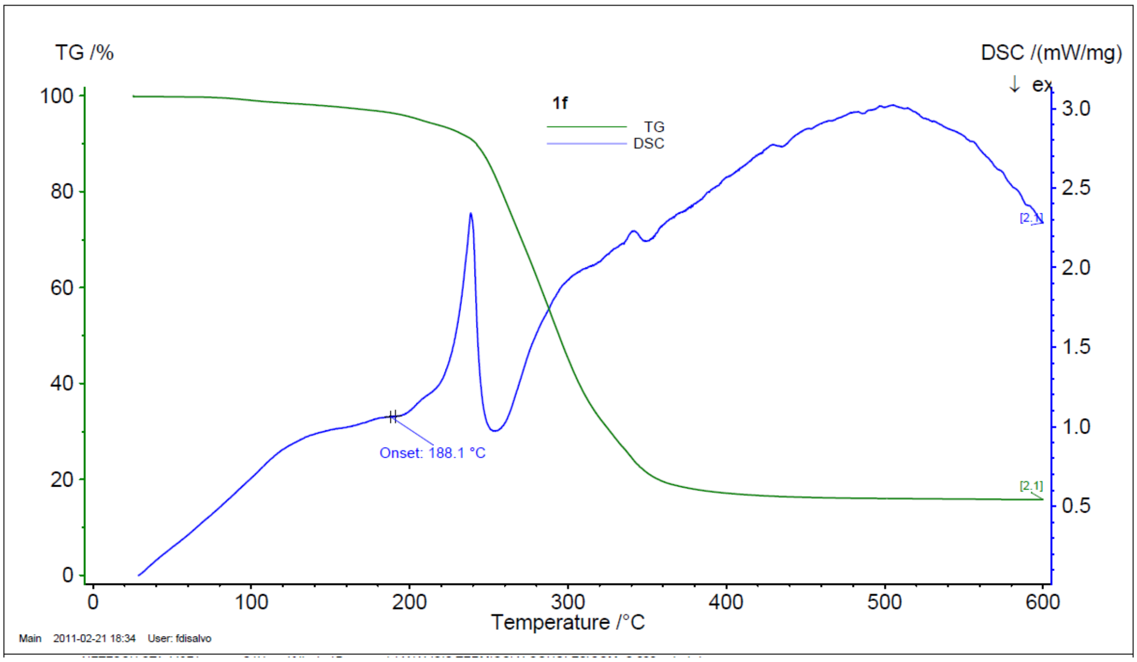

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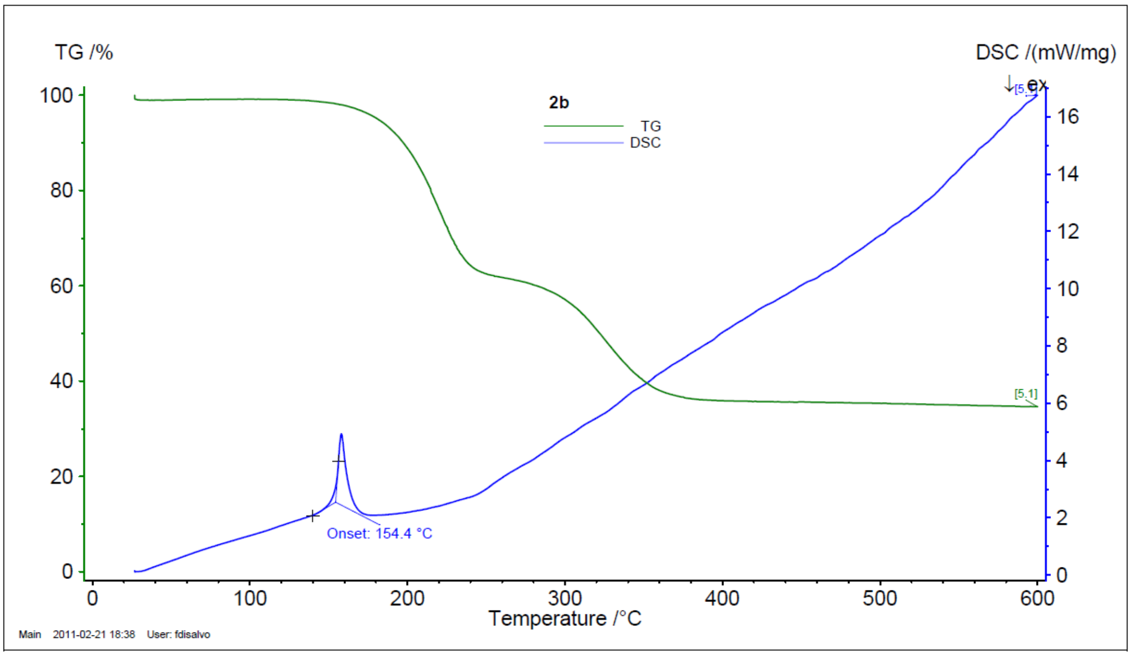

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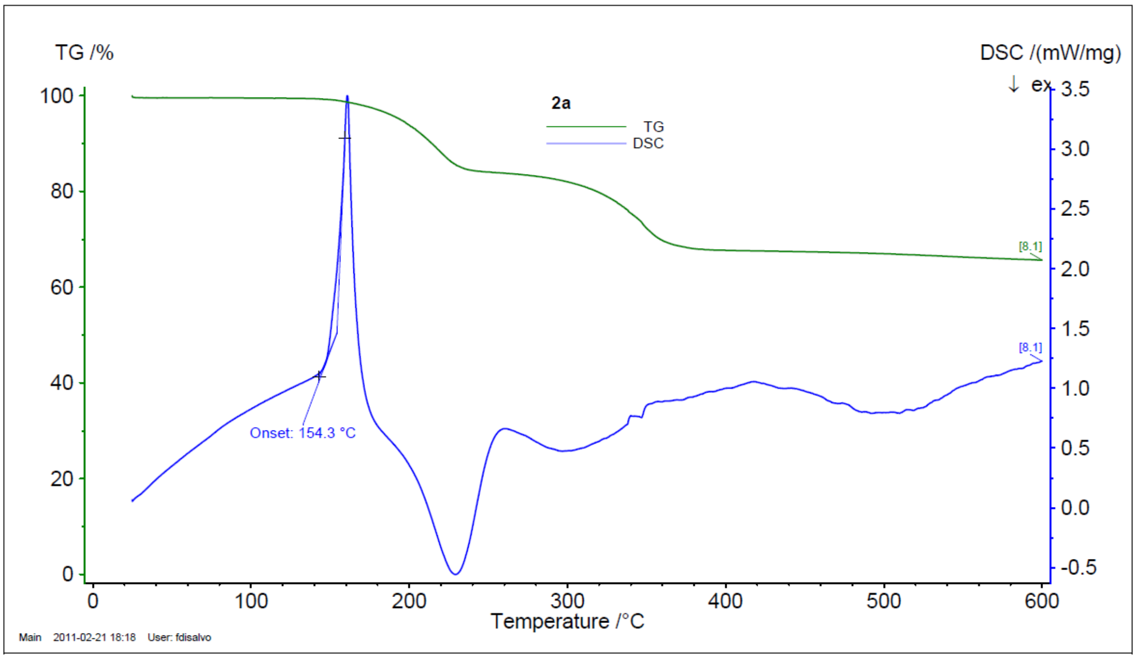

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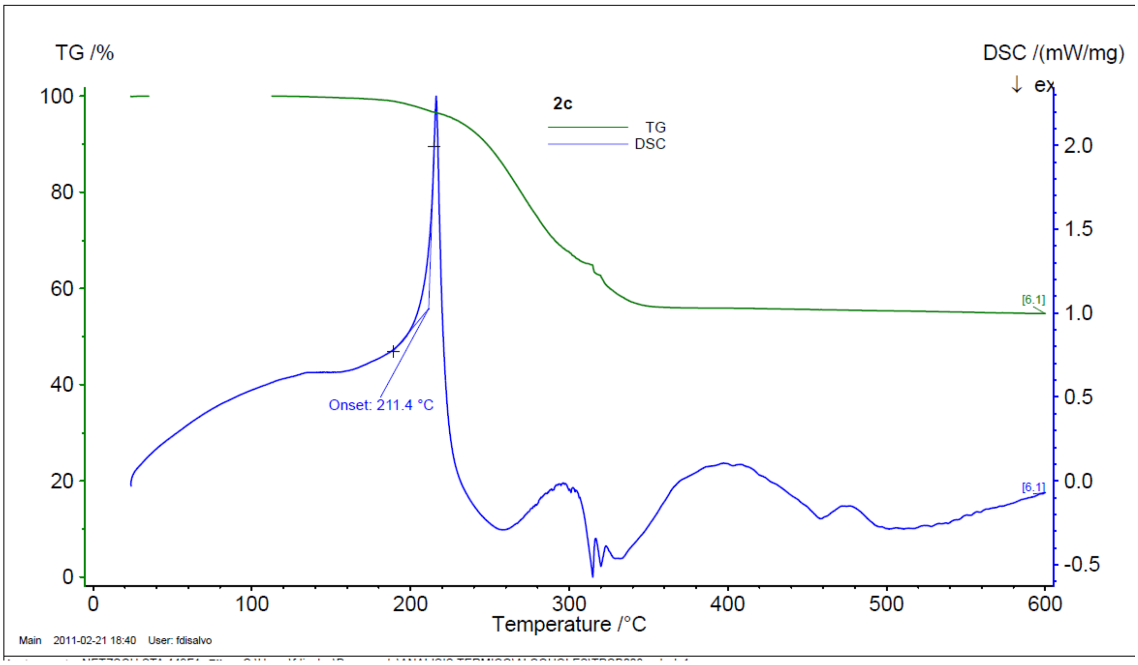

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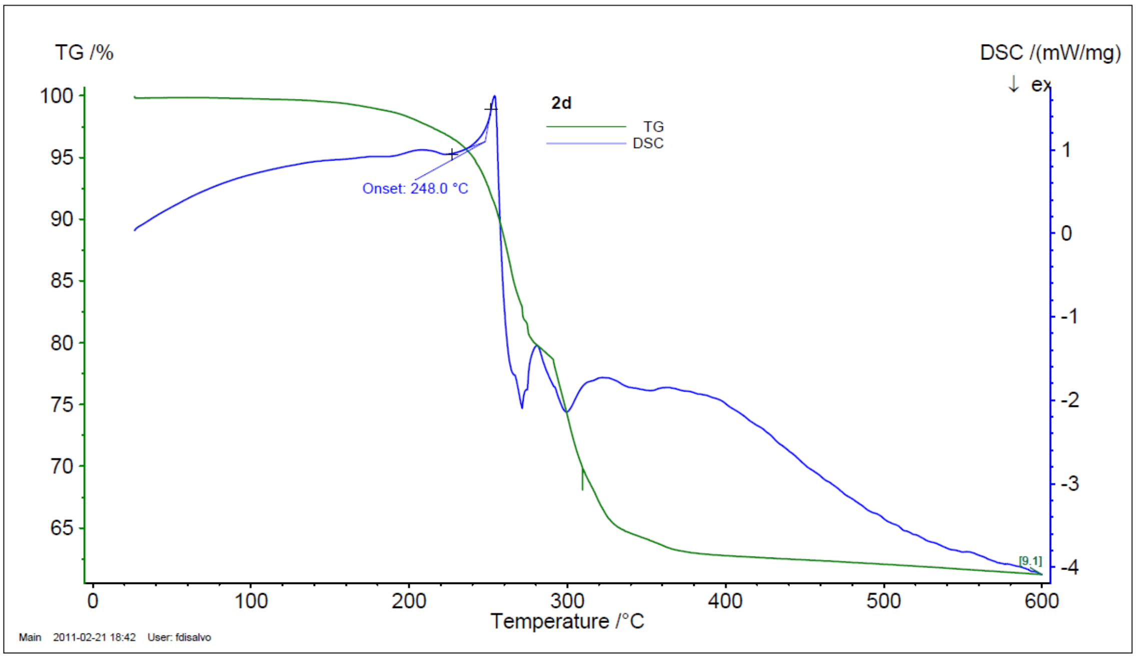

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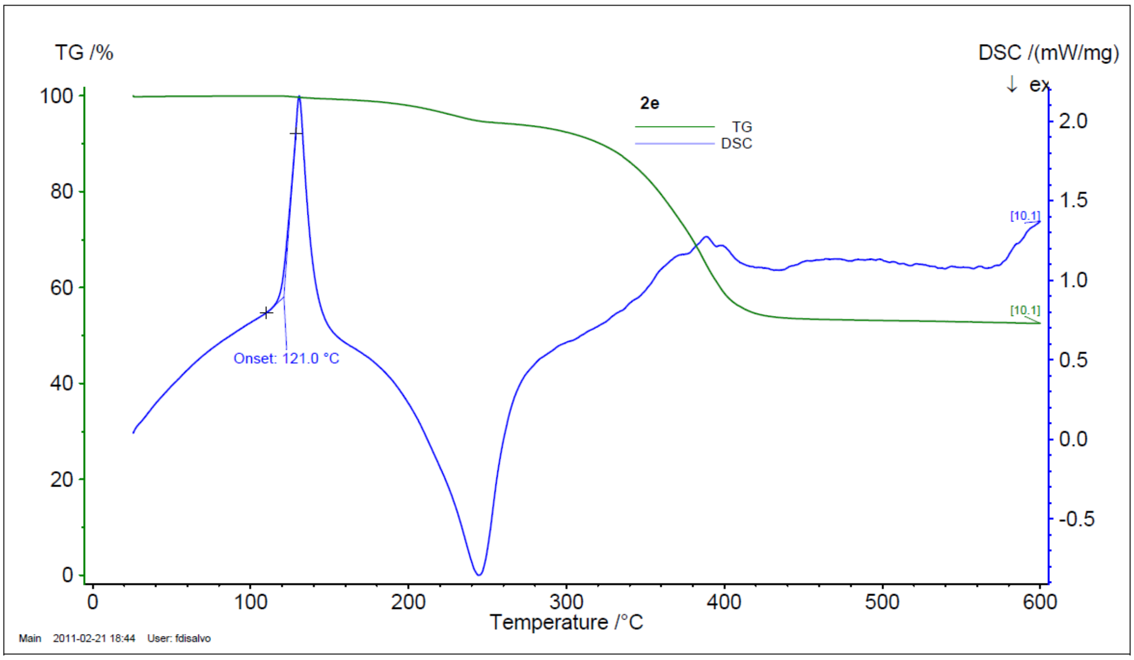

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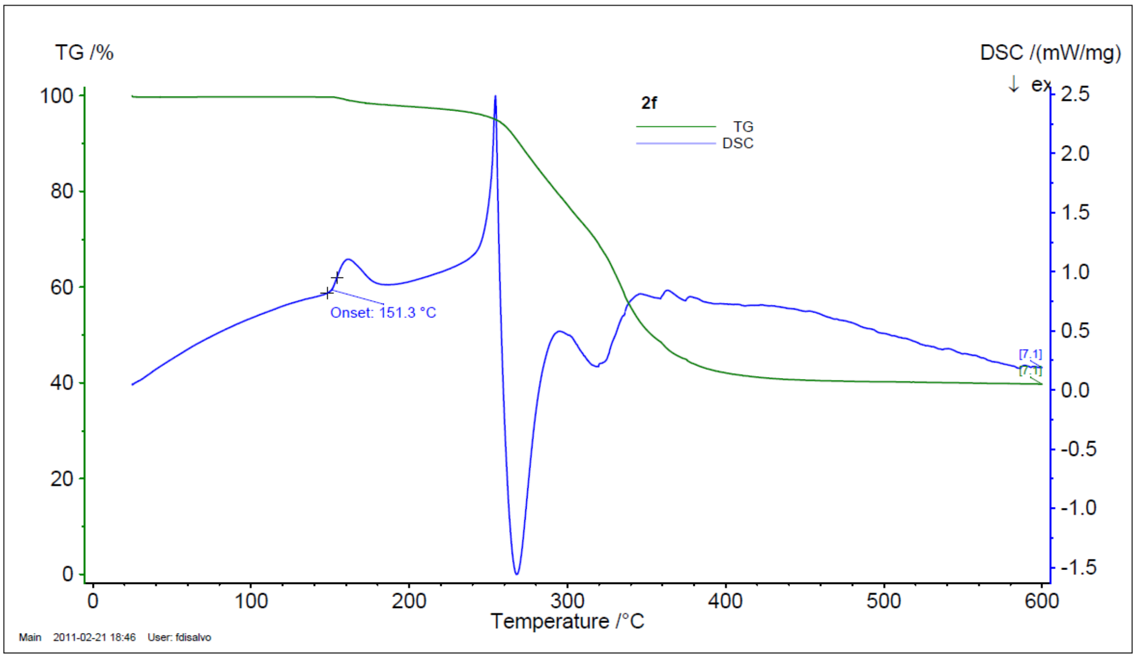

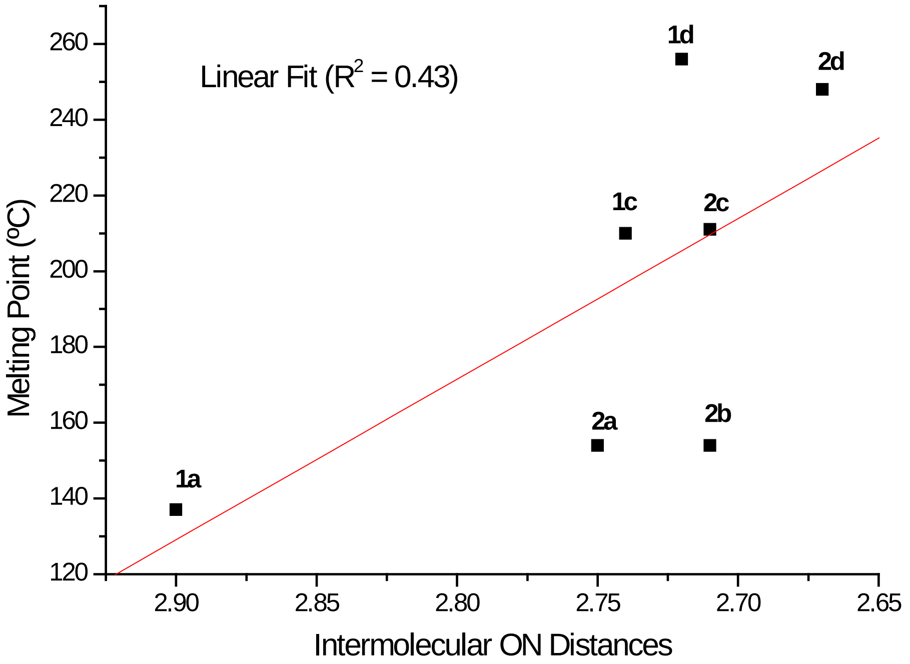

Figure S1. Plot of observed melting points and corresponding O···N intermolecular distances.

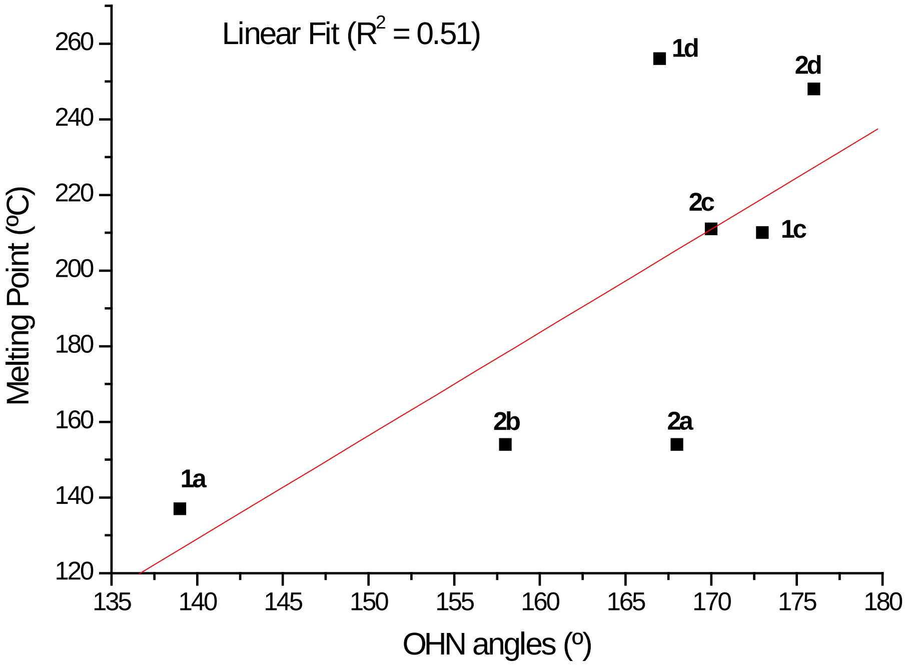

Figure S2. Plot of observed melting points and corresponding OHN intermolecular angles.

DFT CALCULATIONS

Strengths estimations of the OH···N intermolecular hydrogen bonds along the series

The energy for the formation of the dimers of the compounds which show OH···N intermolecular H-bonds were calculated by DFT using B3LYP/6-311+G**. The energy values were obtained according eq.1 using the results of the single point calculations of the structures at their crystallographic positions. The resultant values could be used to estimate the strength of such interaction along the series.

$$E_f^{dim} = E^{dim} - 2\,E^{mon} \qquad \text{eq. 1}$$

Table S1.

SP DRX B3LYP/6-311+G**	
Compound	**E DIM - 2 E monom (Kcal/mol)**
1a	-4.31
1b	--[a]
1c	-7.92
1d	-6.64
1e	--[b]
1f	-7.68
2a	-5.99
2b	-6.97
2c	-5.21
2d	-6.58
2e	--[b]
2f	-6.24

[a] Structure not available. [b] Only intramolecular OHN interactions are present.

Calculated IR spectra

IR spectra of the optimized structures of compounds **1a-f** and **2a-f** were calculated by DFT with the B3LYP/DZVP and B3LYP/6-311+G** level of theory using a scale factor of 0.96 (Table S2).[i] In agreement with experimental results, the most intense bands for the whole series are the BH and OH stretchings around 3681-3503 and 2592-2569 cm^{-1}, respectively. Other relevant signal which is difficult to assign in the experimental spectra is the CO stretching, it is observed in the 1100-1050 cm^{-1} range with medium intensity together with other bands of the pyridine or quinolyne rings. As expected, due to the calculations were performed on the isolated molecules, the values of the OH stretchings for the compounds which give place to intermolecular interactions are much higher than the experimental values. Thus, to model the effect of the OH···N interaction into the OH band of the alcohols, the B3LYP/DZVP IR spectra of the dimers derived from the 2-pyridine (**1a** and **2a**) and 4-pyridine (**1d** and **2d**) were calculated and analyzed together with the 2-quinolyne ones (**1e** and **2e**). The results are summarized in Table S3.

Table S2. Calculated ν(XH) and corrected ν(XH)corr. Stretching Frequencies for monomers of the compounds.

Monomers B3LYP/6-311+G**											
	1a	**2a**	**2b**	**1c**	**2c**	**1d**	**2d**	**1e**	**2e**	**1f**	**2f**
ν(OH)	3649.0	3602.0	3834.7	3814.2	3829.1	3815.0	3831.0	3626.0	3577.1	3816.1	3828.9
ν(OH) corr	3503.0	3503.0	3681.3	3661.6	3675.9	3662.4	3677.8	3481.0	3434.0	3663.5	3675.7
ν(BH)	2675.6	2699.1	2677.5	2694.1	2699.5	2694.0	2683.3	2689.5	2699.0	2693.4	2699.6
ν(BH) corr	2568.6	2591.1	2570.4	2586.3	2591.5	2586.2	2576.0	2581.9	2591.0	2585.7	2591.6
ν(CO)	1097.5	1099.0	1065.0	1037.0	1051.0	1086.0	1054.0	1094.0	1103.0	1083.9	1067.7
ν(CO) corr	1053.6	1055.0	1022.4	995.5	1009.0	1042.6	1011.8	1050.2	1058.9	1040.5	1025.0

Table S3. Calculated ν(OH) and corrected ν(OH)corr. Stretching Frequencies for monomers and the corresponding dimers of selected compounds.

Monomers and Dimers B3LYP/DZVP										
	1a	**1a dim**	**1d**	**1d dim**	**1e**	**2a**	**2a dim**	**2d**	**2d dim**	**2e**
ν(OH)	3602.6	3533.9	3774.3	3357.2	3575.2	3545.2	3408.6	3794.6	3232.3	3527.0
ν(OH) corr	3458.5	3392.5	3623.3	3222.9	3432.2	3403.4	3272.3	3642.8	3103.0	3385.9

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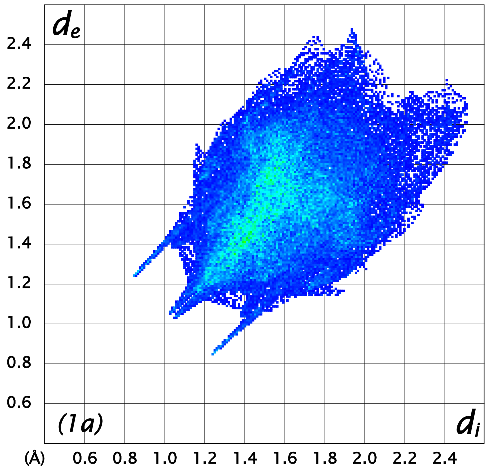
[i] K. Schoonea, J. Smetsa, R. Ramaekersa, L. Houbena, L. Adamowiczb, G. Maes. J. Mol. Str. 649 (2003) 61–68

Hirshfeld Surface Analyses

Legend: Close Contacts X···Y, where: X = atom inside the surface, Y = atom outside the surface. The diagonal lines shown on the Fingerprint Plots represent those combinations of d_i and d_e that sum to the van der Waals radii. Contacts (region of the plot) to the left of this line can be considered to be "close contacts".

Compound (1a)

Full Plot



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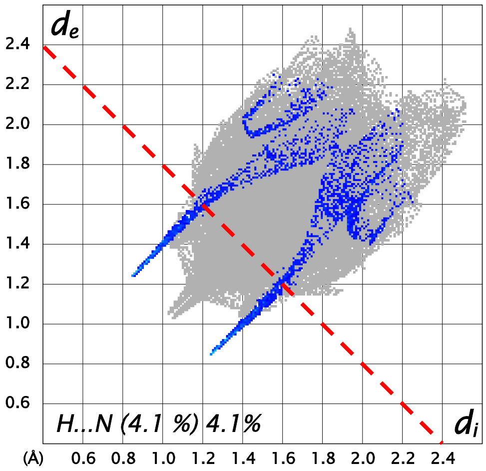
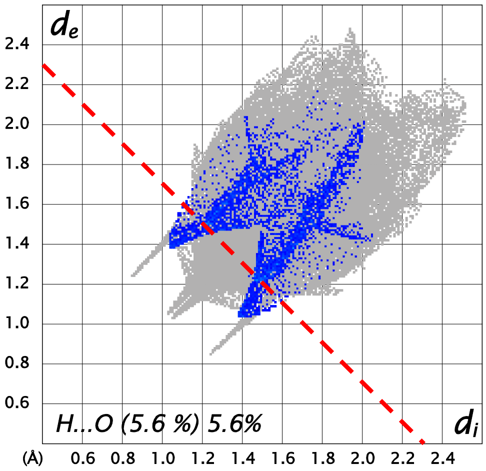
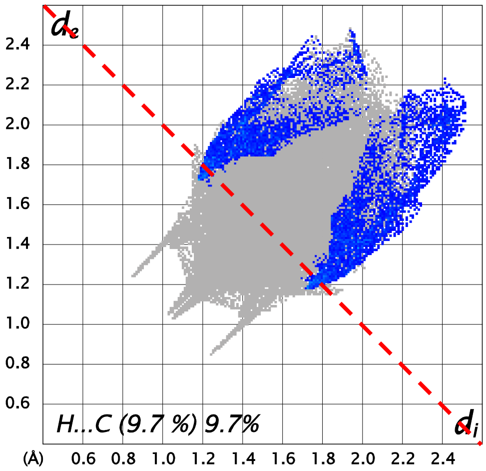
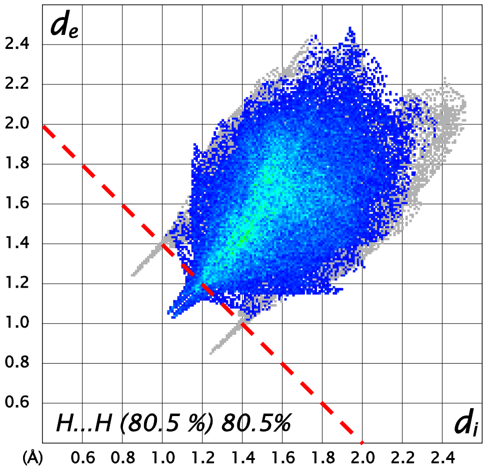


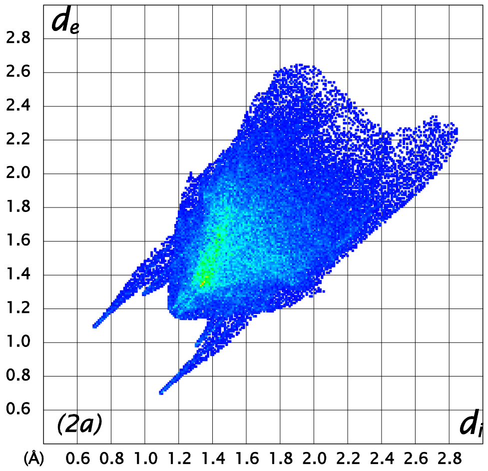






Compound (2a)

Full Plot



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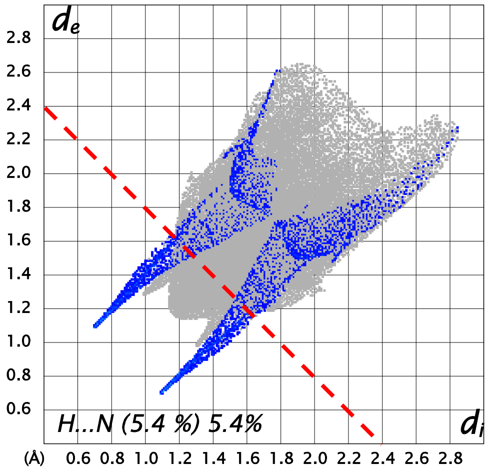
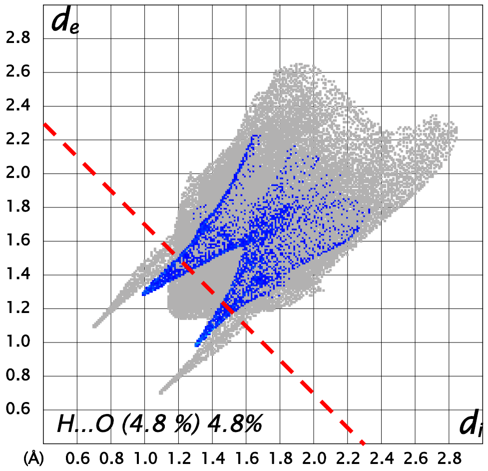
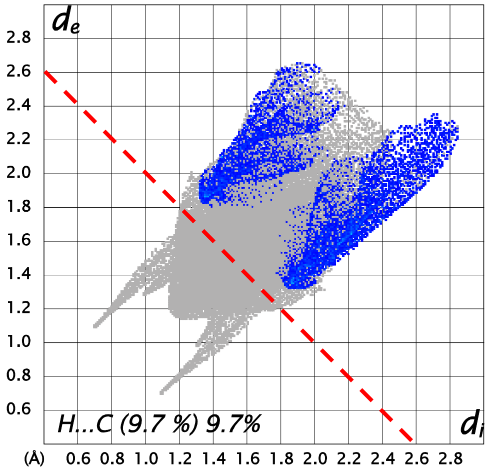
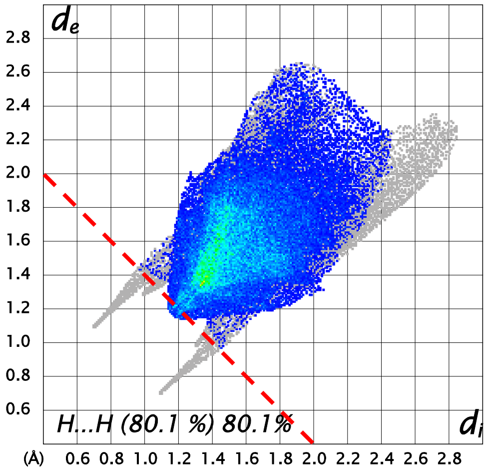


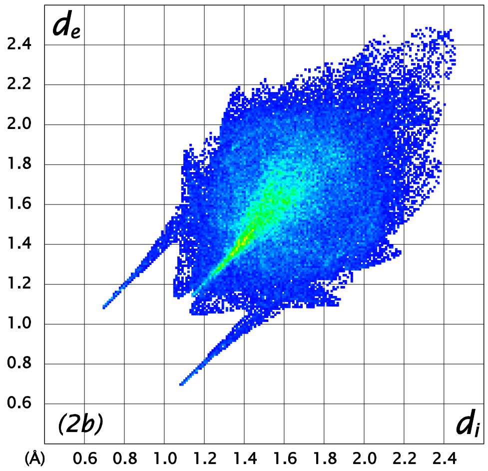






Compound (2b)

Full Plot



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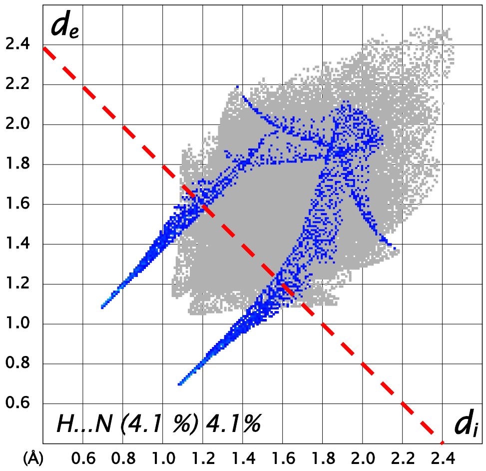

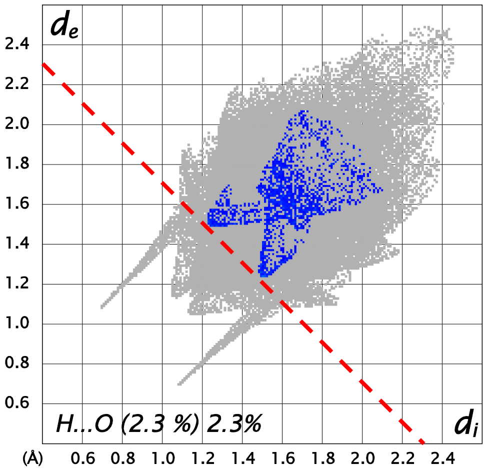

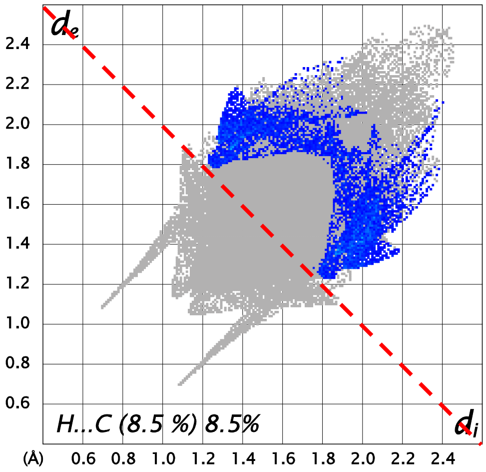

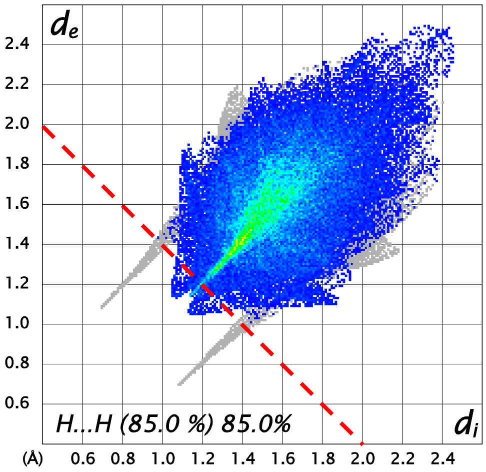

Compound (1c)

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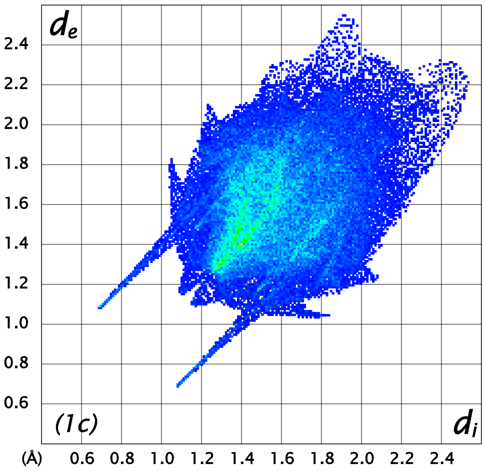

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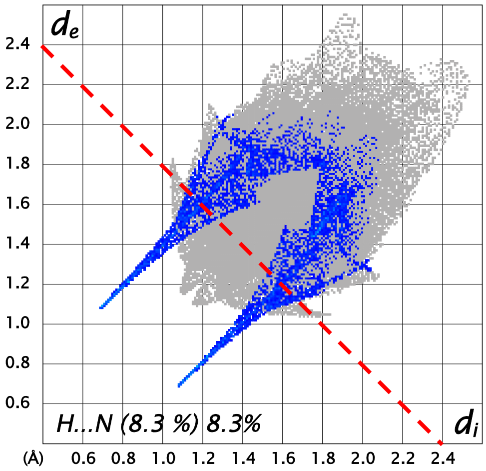

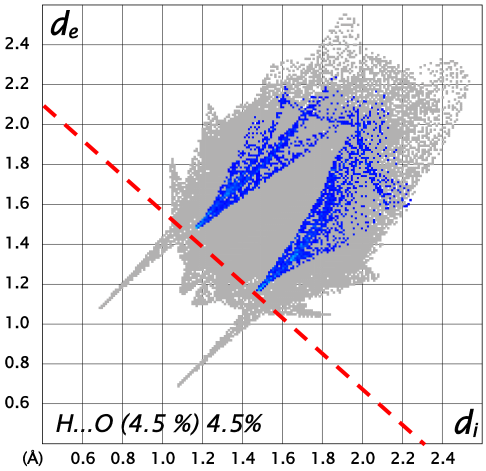

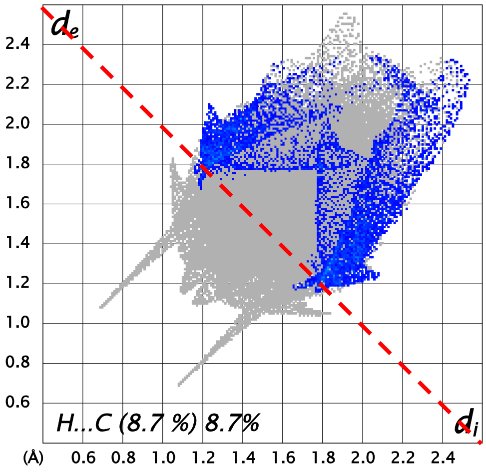

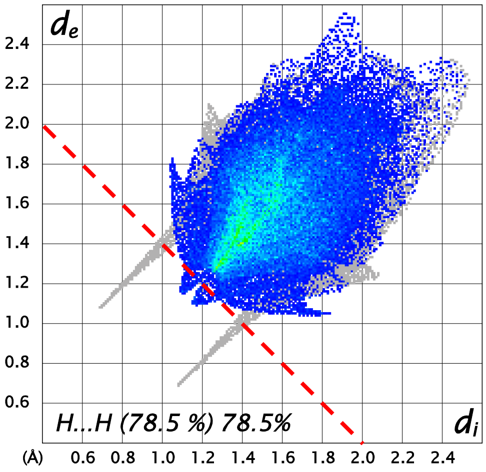

Compound (2c)

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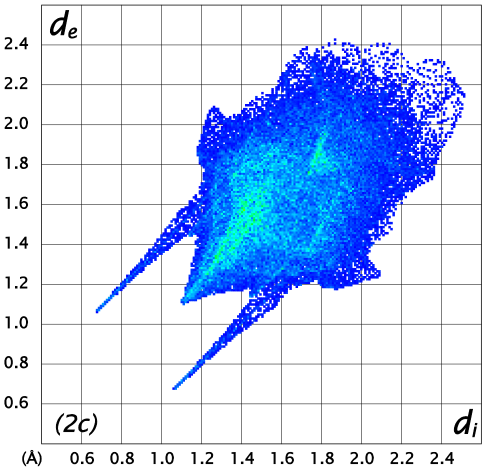

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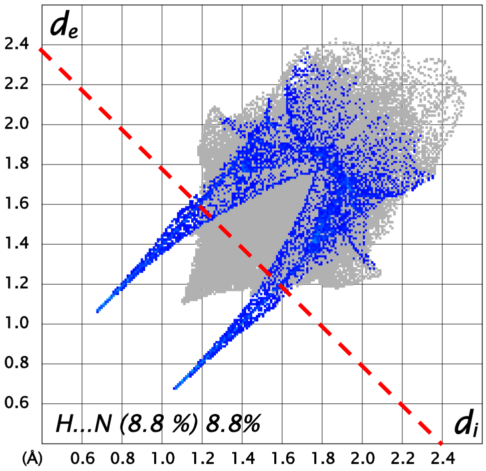

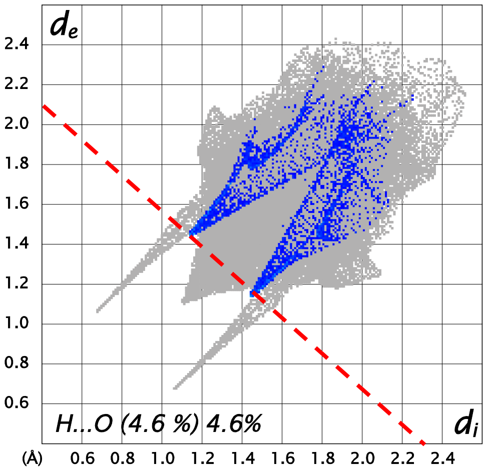

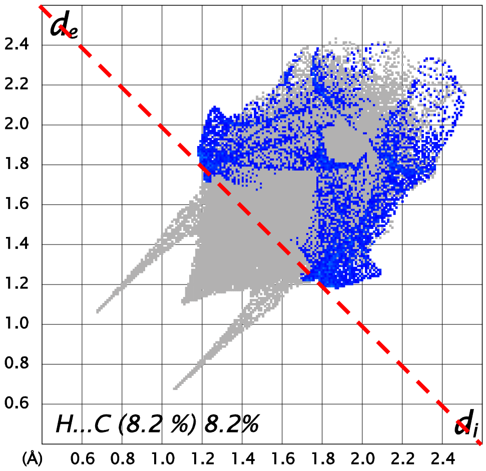

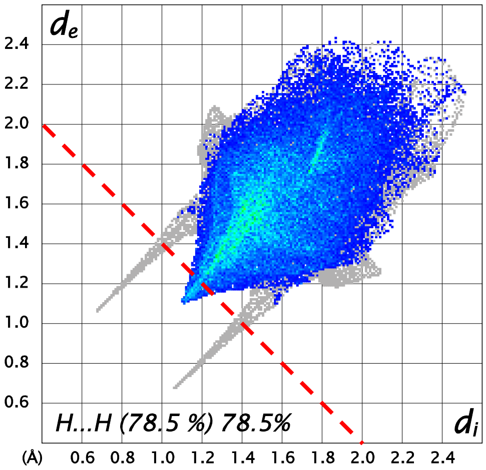

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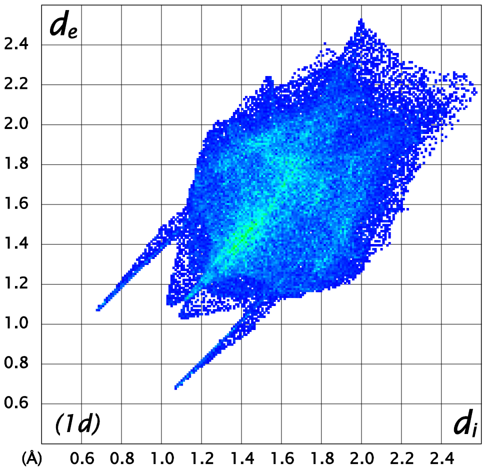

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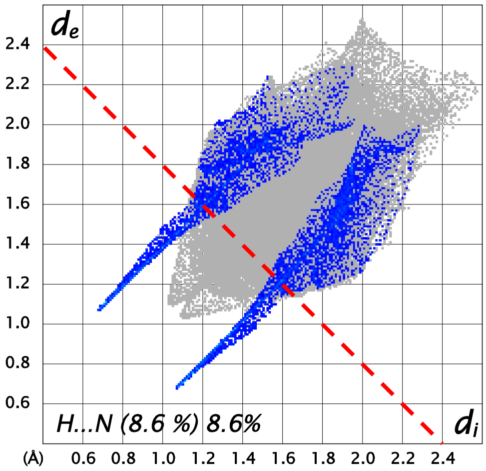

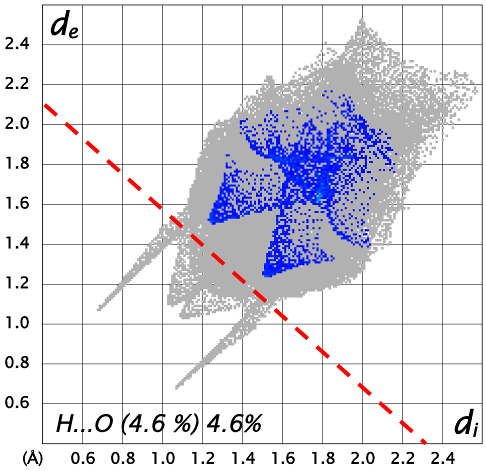

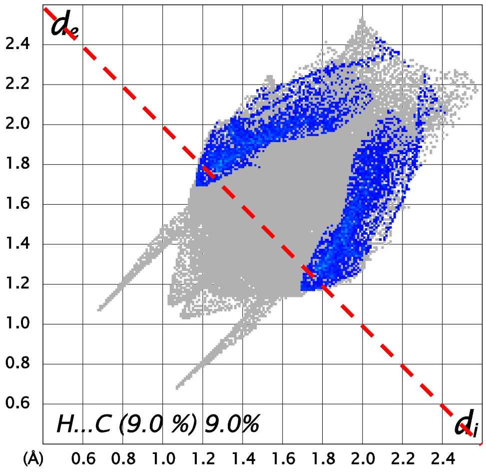

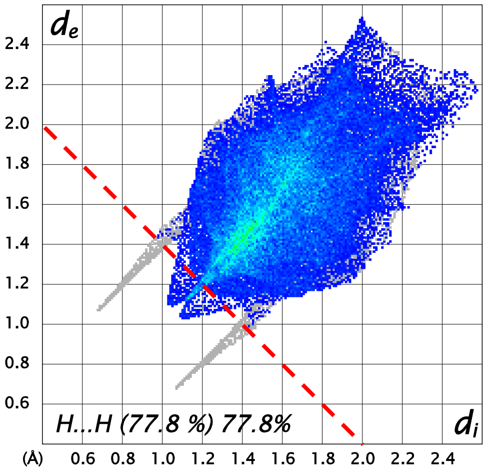

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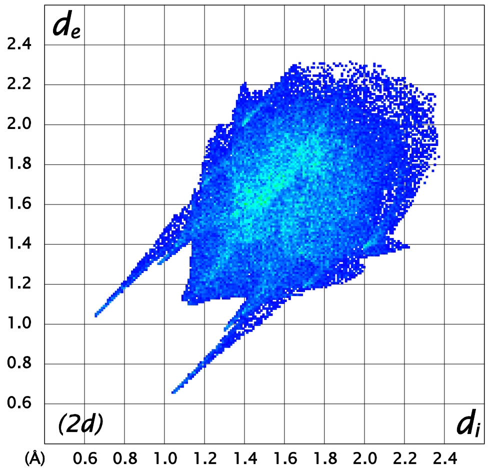
<tr><td colspan="2">
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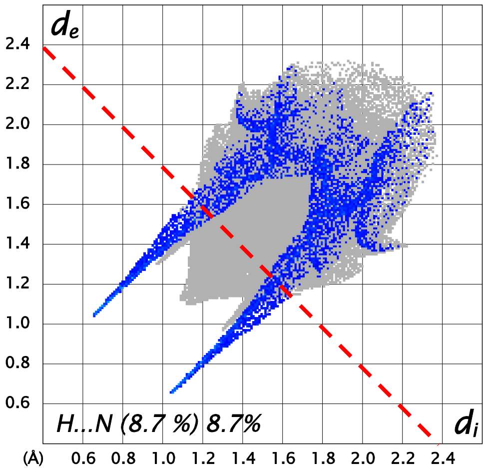
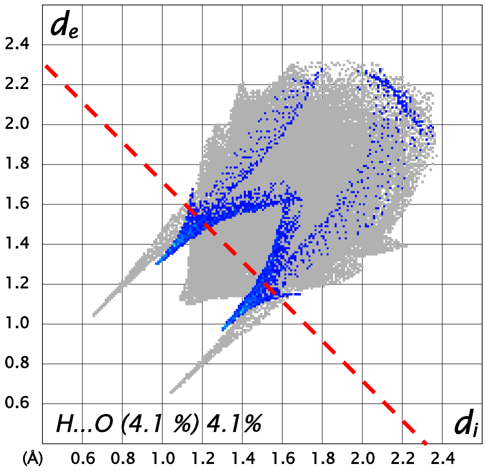
<tr><td>
</td><td>
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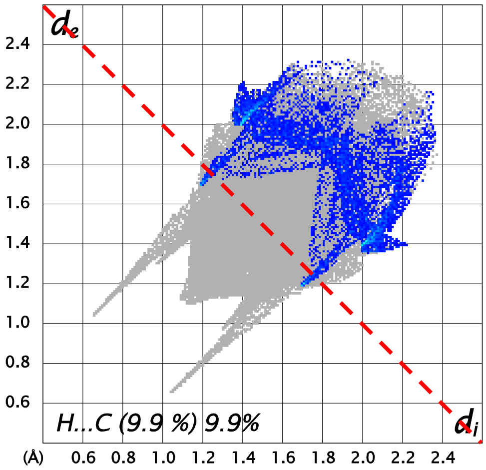
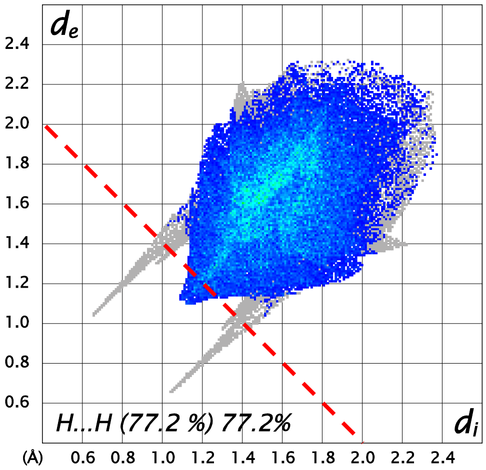
<tr><td>
</td><td>
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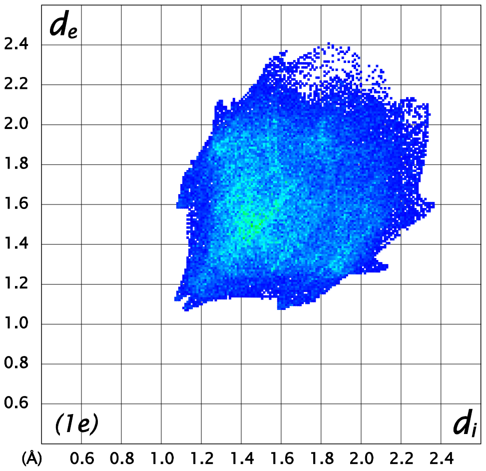
Full Plot



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