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**Supporting information for article:**

**A series of (*E*)-5-(arylideneamino)-1-*tert*-butyl-1*H*-pyrrole-3-carbonitriles and their reduction products to secondary amines: syntheses and X-ray structural studies**

**Mario A. Macías, Juan-Carlos Castillo and Jaime Portilla**

## SUPPORTING INFORMATION

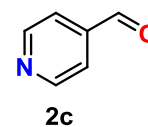
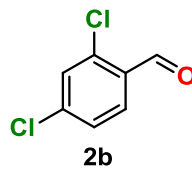
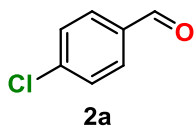
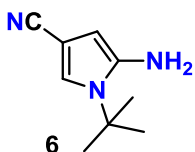
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### 1. Overview of substrates **6/2a–c**, aldimines **7a–c**, and secondary amines **8a–c**

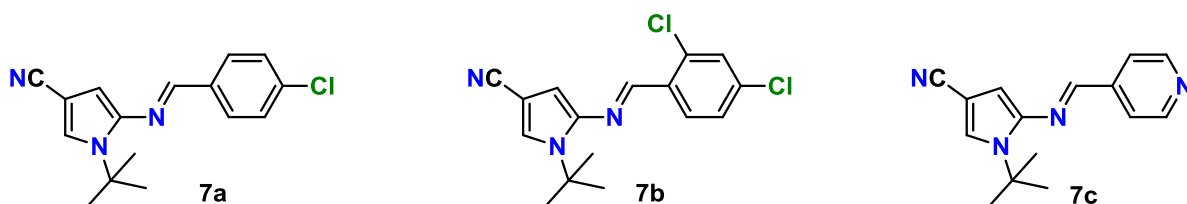
#### Substrates **6/2a–c**

5-Amino-1-(*tert*-butyl)-1*H*-pyrrole-3-carbonitrile **6**, 4-chlorobenzaldehyde **2a**, and 2,4-dichlorobenzaldehyde **2b**, and isonicotinaldehyde **2c**.



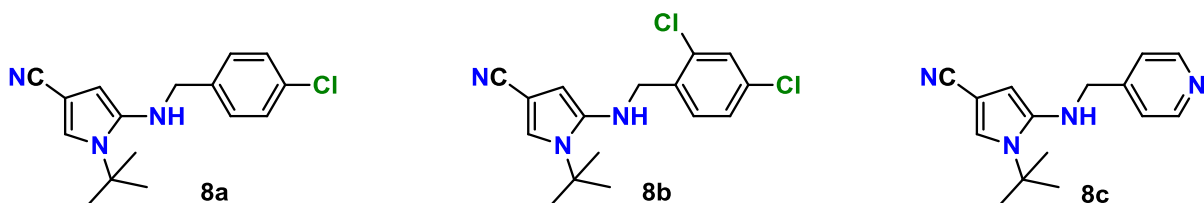
#### Aldimines **7a–c**

(*E*)-1-(*tert*-Butyl)-5-((4-chlorobenzylidene)amino)-1*H*-pyrrole-3-carbonitrile **7a**, (*E*)-1-(*tert*-butyl)-5-((2,4-dichlorobenzylidene)amino)-1*H*-pyrrole-3-carbonitrile **7b**, and (*E*)-1-(*tert*-butyl)-5-((pyridin-4-ylmethylene)amino)-1*H*-pyrrole-3-carbonitrile **7c**.



## Secondary amines 8a–c

1-(*tert*-Butyl)-5-((4-chlorobenzyl)amino)-1*H*-pyrrole-3-carbonitrile **8a**, and 1-(*tert*-butyl)-5-((2,4-dichlorobenzyl)amino)-1*H*-pyrrole-3-carbonitrile **8b**, and 1-(*tert*-butyl)-5-((pyridin-4-ylmethyl)amino)-1*H*-pyrrole-3-carbonitrile **8c**.



## 2. General Information

All reagents and solvents were purchased from commercial sources and used without further purification, unless otherwise noted. All starting materials were weighed and handled in air at room temperature. Reactions under microwave irradiation were performed in oven-dried 10.0 mL sealable Pyrex tubes equipped with a Teflon coated stirring bar (obtained from CEM). All reactions under microwave irradiation ( $\nu = 2.45$  GHz) were performed in a CEM Discover 1-300W system equipped with a built-in pressure measurement sensor. The reactions were monitored by TLC visualized by UV lamp (254 or 365 nm). Flash chromatography was performed on silica gel (230-400 mesh). Melting points were collected using a capillary melting point apparatus and are uncorrected. NMR spectra were recorded at 400 MHz ( $^1\text{H}$ ) and 100 MHz ( $^{13}\text{C}$ ) at 298 K using tetramethylsilane (0 ppm) as the internal reference. NMR spectroscopic data were recorded in  $\text{CDCl}_3$  using as internal standards the residual nondeuteriated signal for  $^1\text{H}$  NMR ( $\delta_{\text{H}}$  7.26 ppm) and the deuteriated solvent signal for  $^{13}\text{C}$  NMR ( $\delta_{\text{C}}$  77.1 ppm) spectroscopy. DEPT spectra were used for the assignment of carbon signals. Chemical shifts ( $\delta$ ) are given in ppm, and coupling constants ( $J$ ) are given in Hz. The following abbreviations are used for multiplicities: s = singlet, d = doublet, t = triplet, and m = multiplet. High-resolution mass spectra (HRMS) were recorded using a Q-TOF spectrometer via electrospray ionization (ESI). Crystallographic data were recorded on a diffractometer using graphite-monochromated Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.71073$

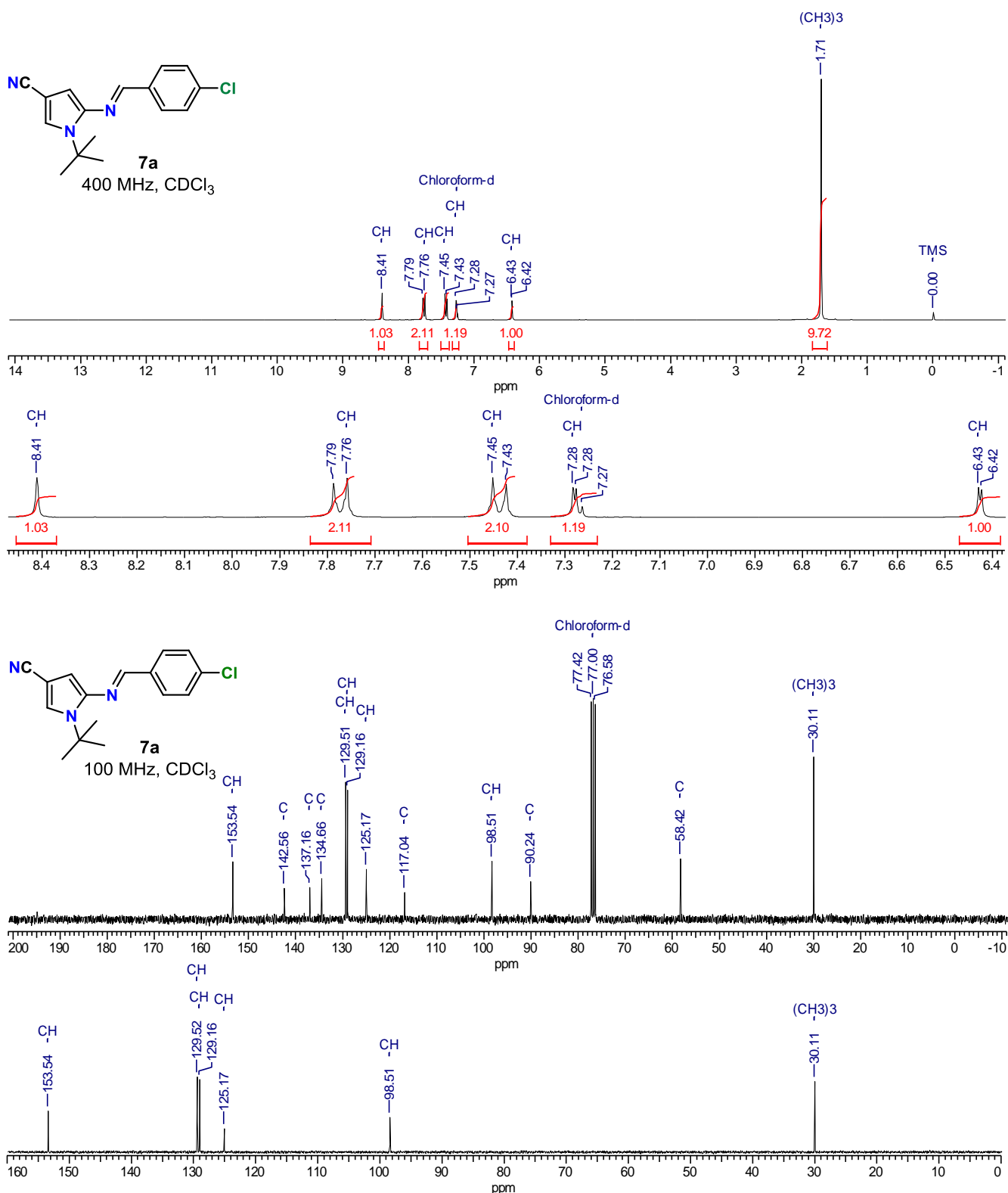
Á). Structures were solved using an iterative algorithm,<sup>1a</sup> subsequently completed by difference Fourier map and refined using the program SHELXL2014,<sup>1b</sup> and the graphic material was prepared using the software Mercury 3.8.<sup>1c</sup> 5-Amino-1-(*tert*-butyl)-1*H*-pyrrole-3-carbonitrile **6** was prepared by protocols reported in the literature.<sup>2</sup>

### 3. References

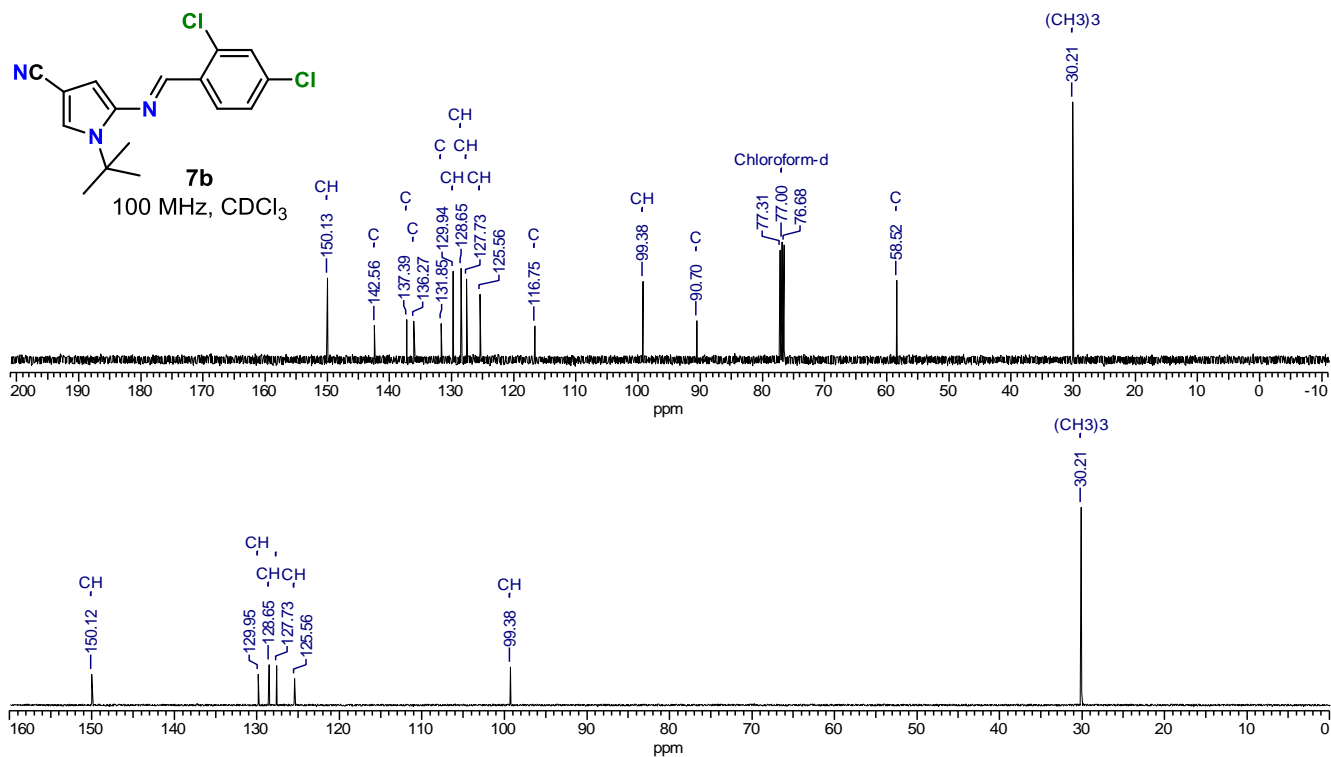
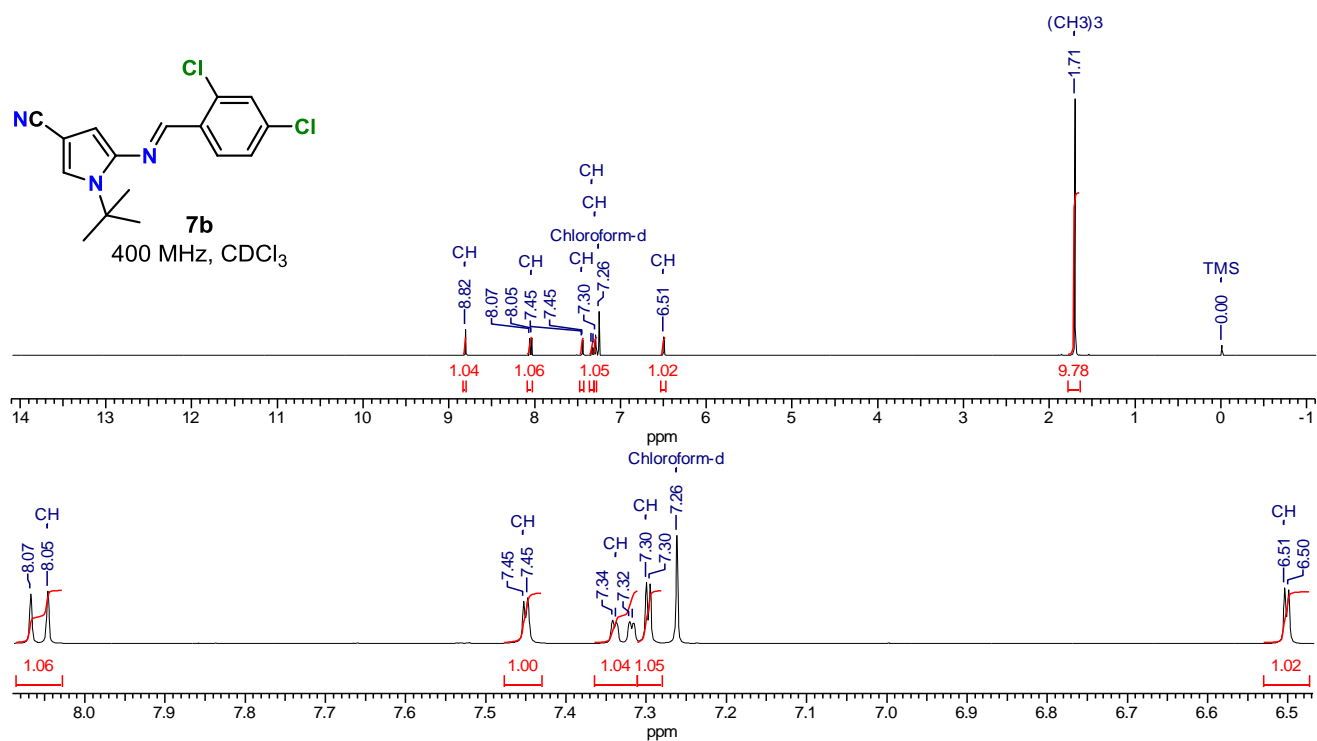
1. (a) Palatinus, L.; Chapuis, G. *J. Appl. Crystallogr.* **2007**, *40*, 786–790; (b) Sheldrick, G. M. *Acta Crystallogr. Sect. C: Cryst. Struct. Chem.* **2015**, *71*, 3–8; (c). Macrae, C.; Bruno, I.; Chisholm, J.; Edgington, P.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P. *J. Appl. Crystallogr.* **2008**, *41*, 466–470.
2. Allegretti, M., Anacardio, R., Cesta, M. C., Curti, R., Mantovanini, M., Nano, G., Topai, A., Zampella, G. *Org. Proc. Res. Dev.* **2003**, *7*, 209–213.

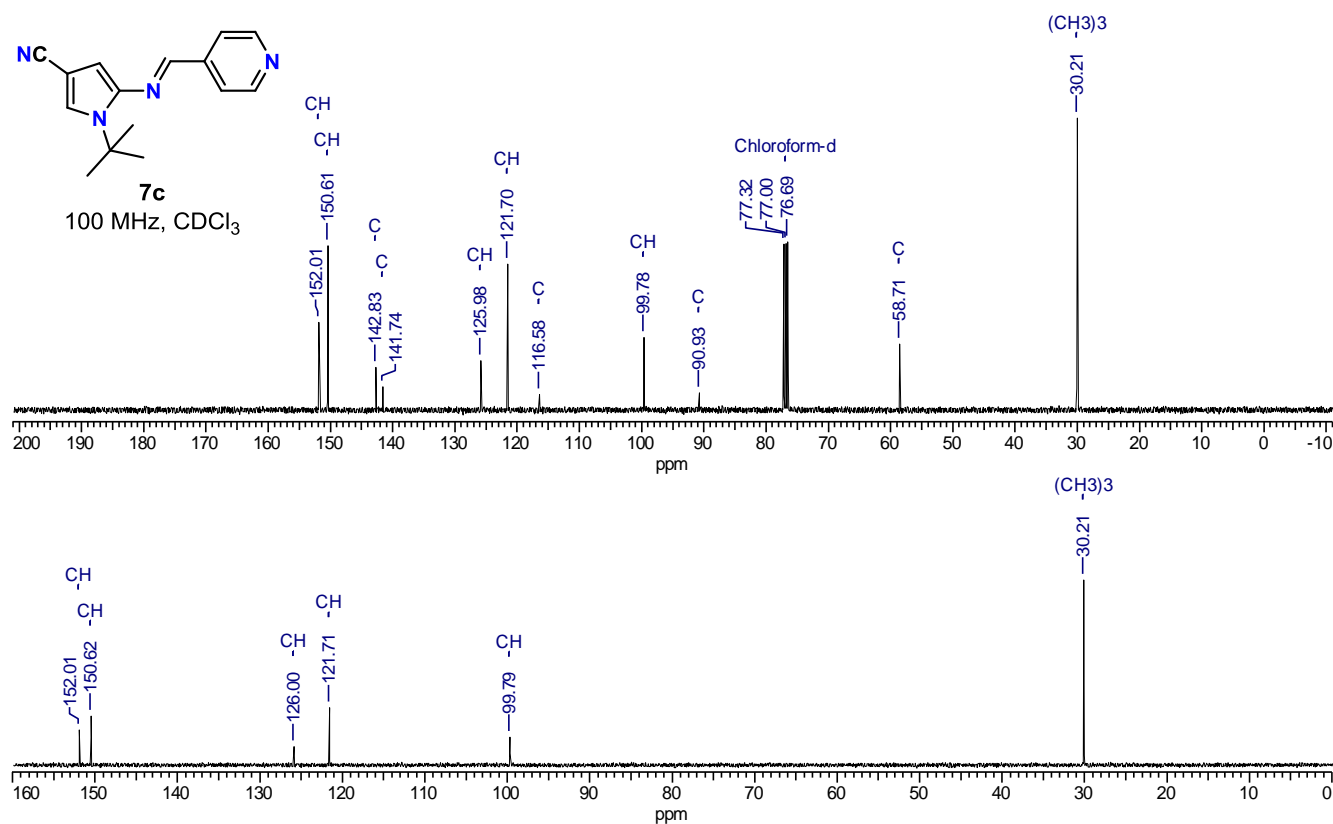
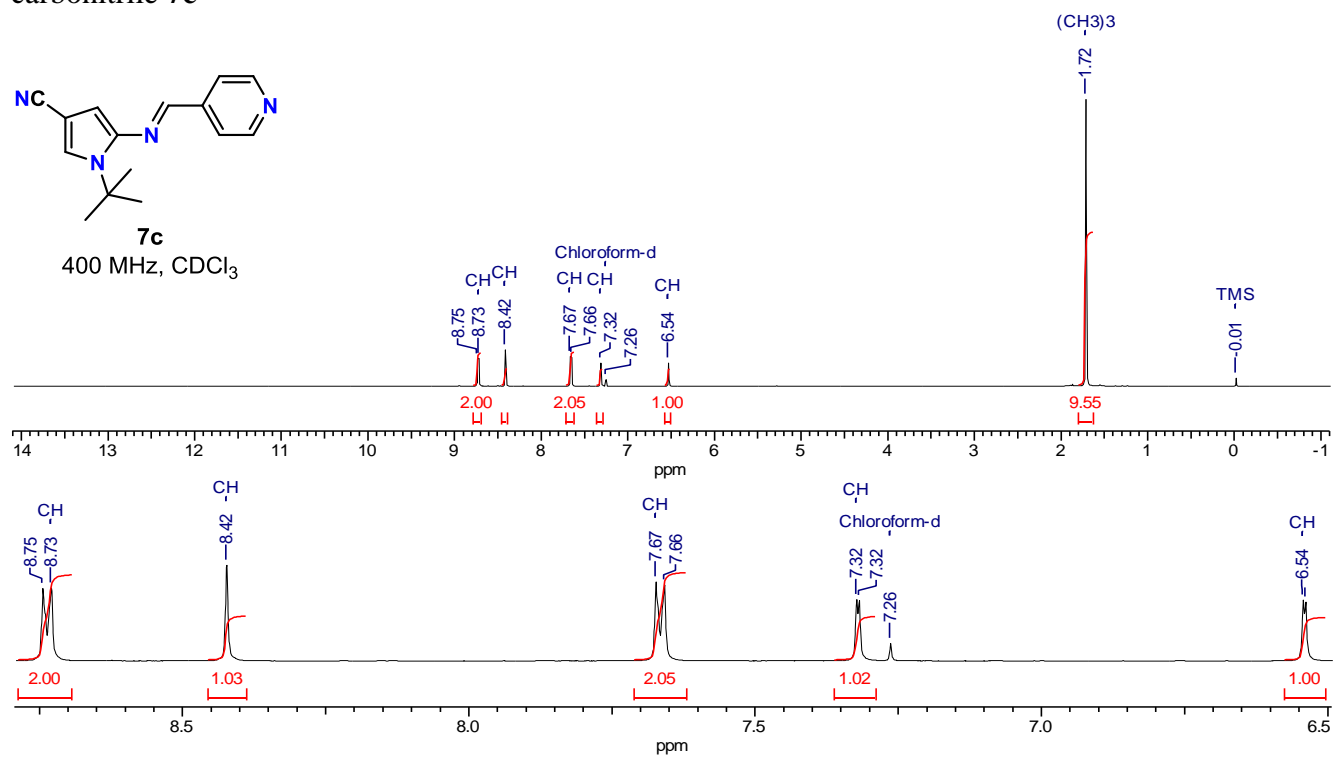
### 4. Copies of NMR spectra

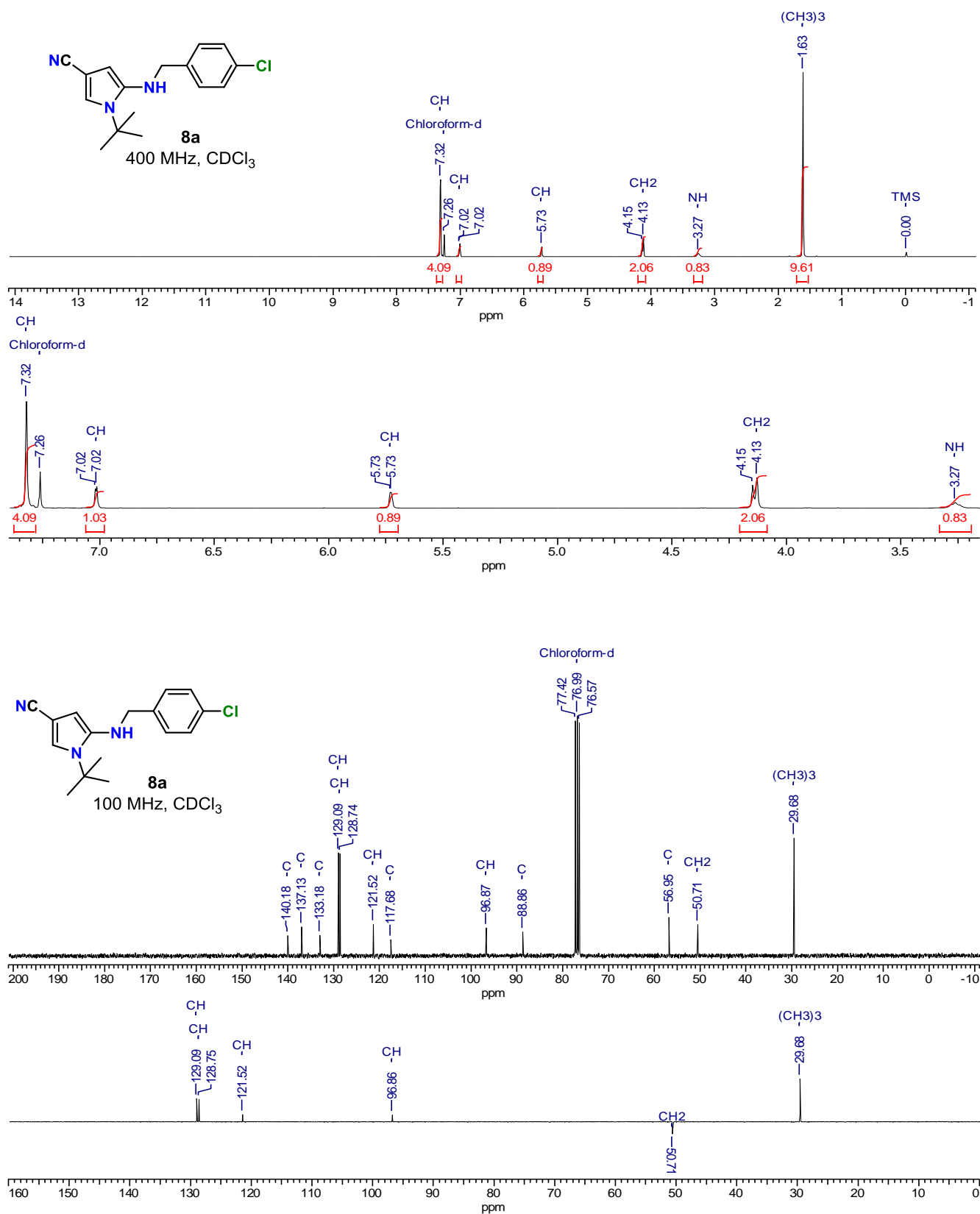
<sup>1</sup>H, <sup>13</sup>C, and DEPT-135 of (*E*)-1-(*tert*-butyl)-5-((4-chlorobenzylidene)amino)-1*H*-pyrrole-3-carbonitrile **7a**



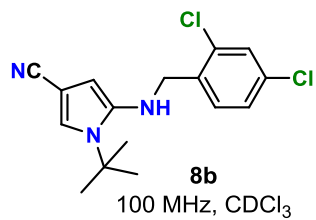
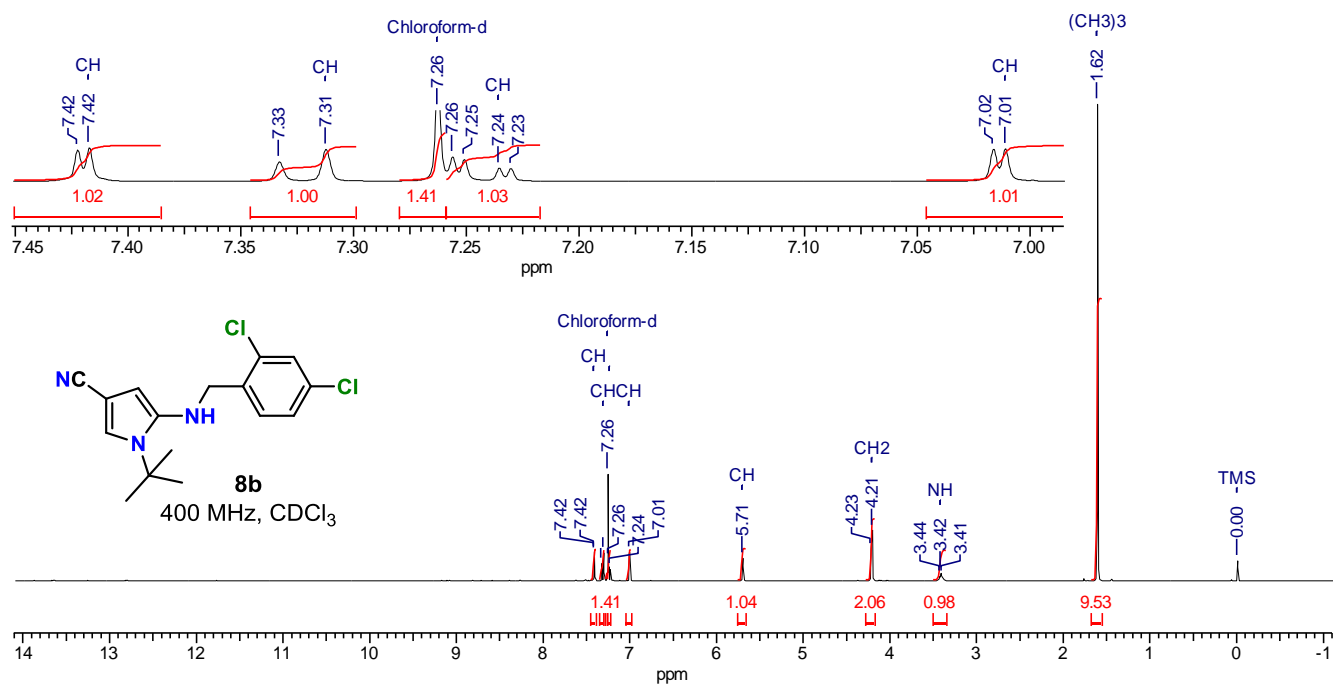
<sup>1</sup>H, <sup>13</sup>C, and DEPT-135 of (*E*)-1-(*tert*-butyl)-5-((2,4-dichlorobenzylidene)amino)-1*H*-pyrrole-3-carbonitrile **7b**

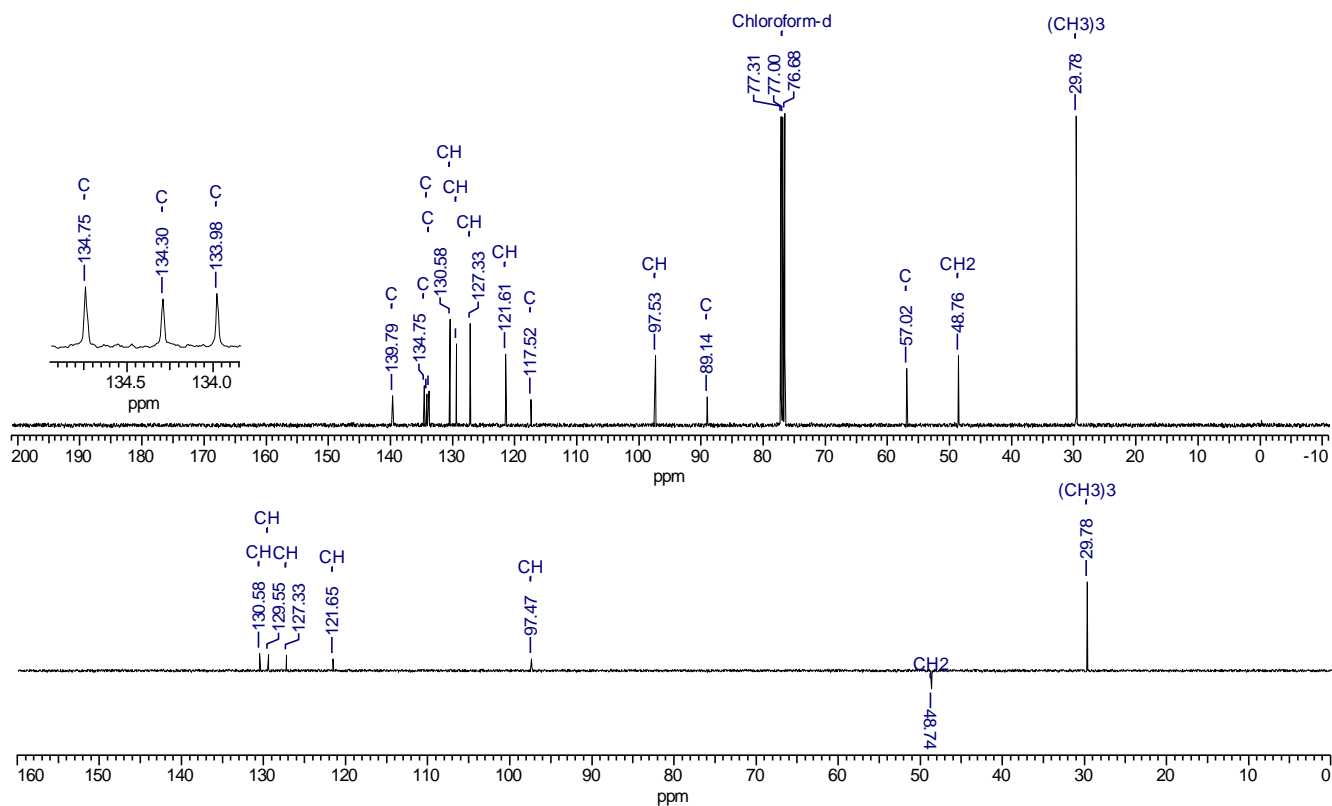


$^1\text{H}$ ,  $^{13}\text{C}$ , and DEPT-135 of (*E*)-1-(*tert*-butyl)-5-((pyridin-4-ylmethylene)amino)-1*H*-pyrrole-3-carbonitrile **7c**

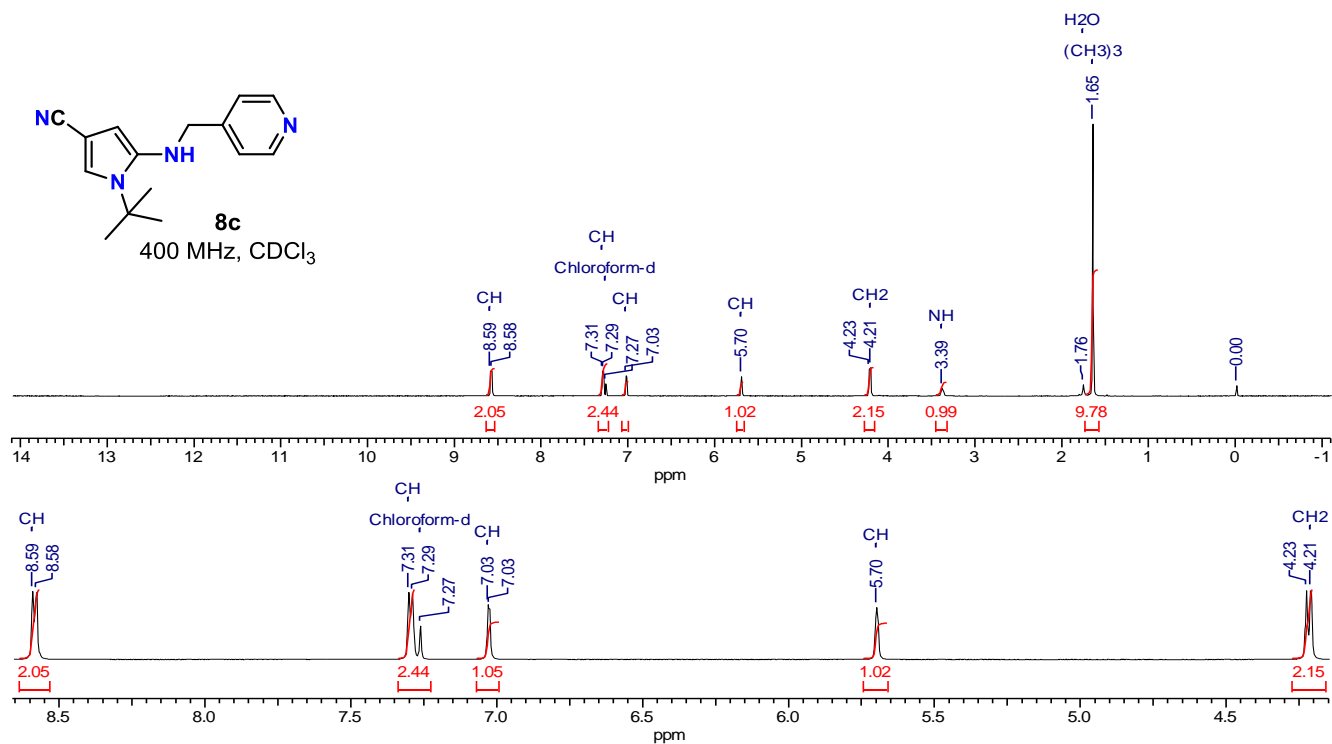
$^1\text{H}$ ,  $^{13}\text{C}$ , and DEPT-135 of 1-(*tert*-butyl)-5-((4-chlorobenzyl)amino)-1*H*-pyrrole-3-carbonitrile **8a**

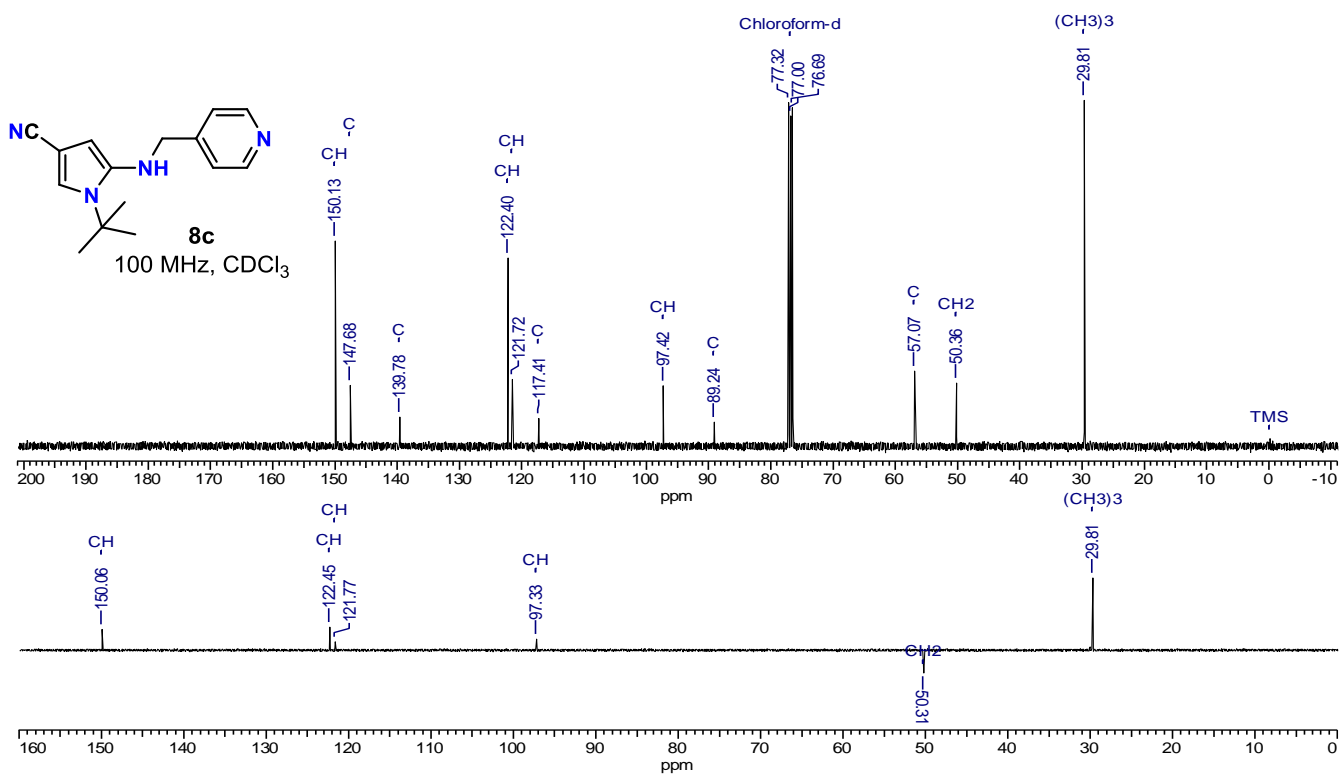


$^1\text{H}$ ,  $^{13}\text{C}$ , and DEPT-135 of 1-(*tert*-butyl)-5-((2,4-dichlorobenzyl)amino)-1*H*-pyrrole-3-carbonitrile **8b**



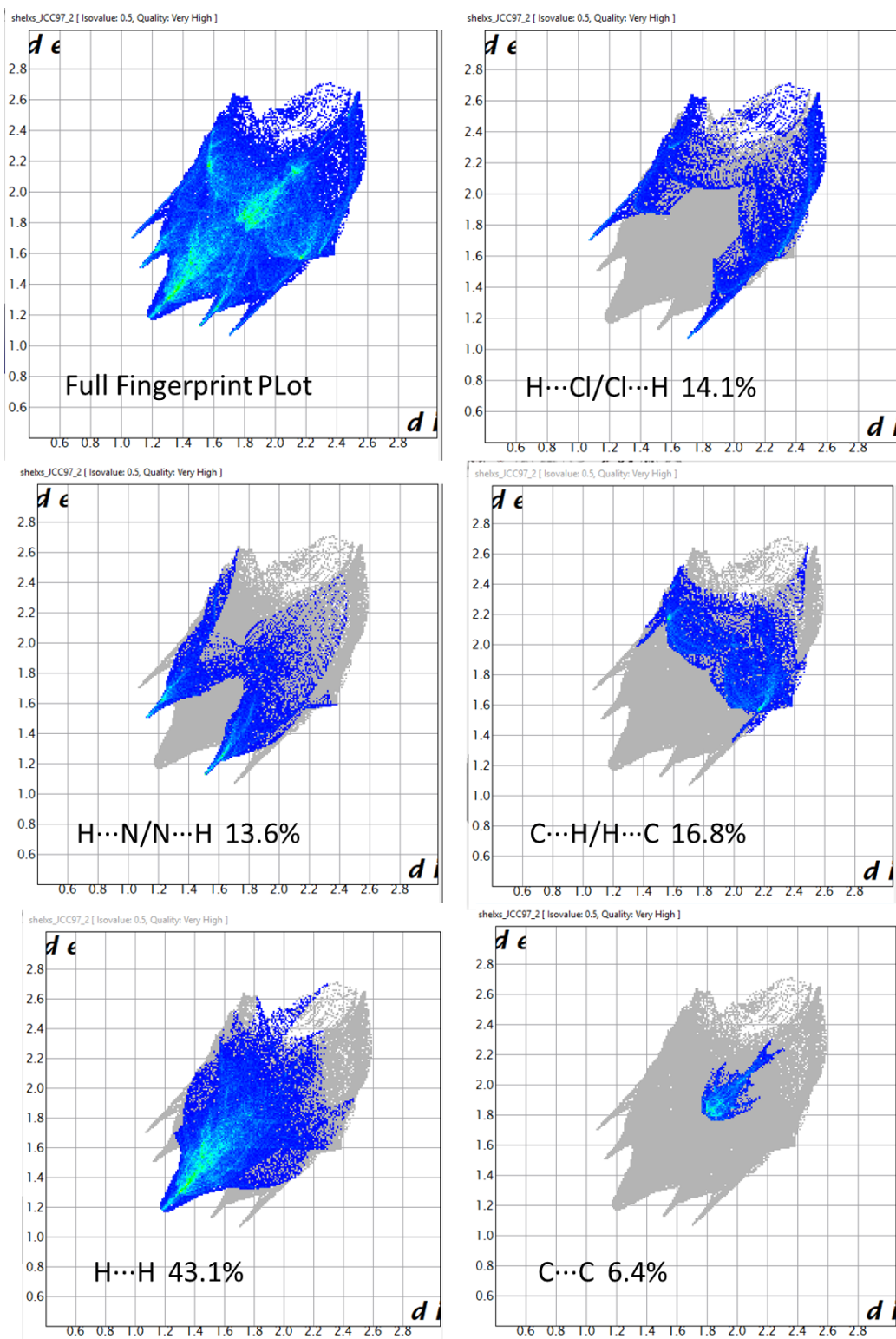
<sup>1</sup>H, <sup>13</sup>C, and DEPT-135 of 1-(*tert*-Butyl)-5-((pyridin-4-ylmethyl)amino)-1*H*-pyrrole-3-carbonitrile **8c**





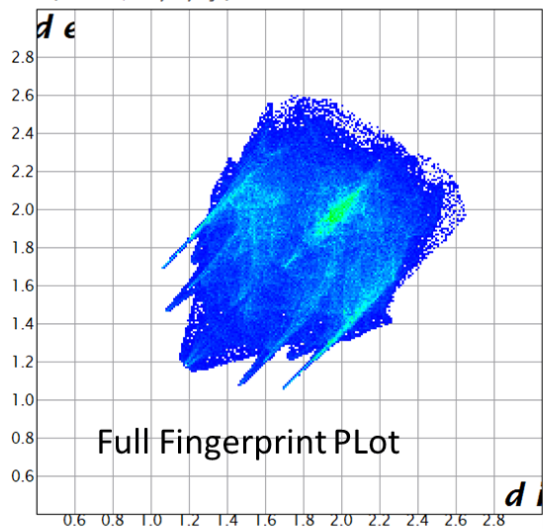
## 5. Two-dimensional fingerprints plots for 7a–c and 8a–b compounds showing contributions from different contacts

Compound 7a

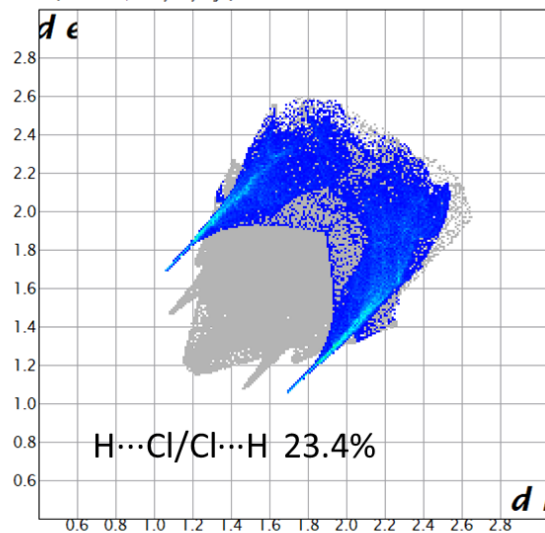


Compound 7b

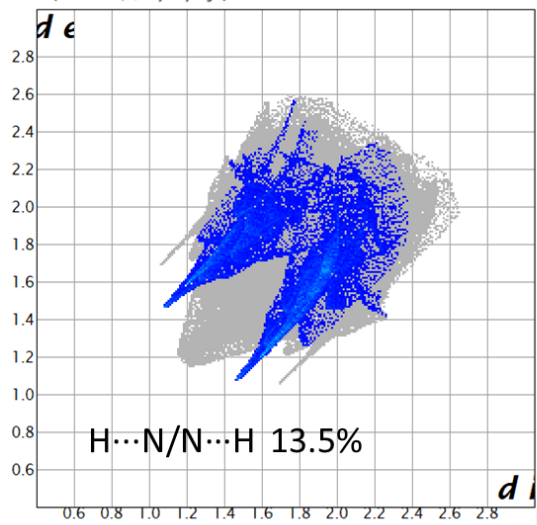
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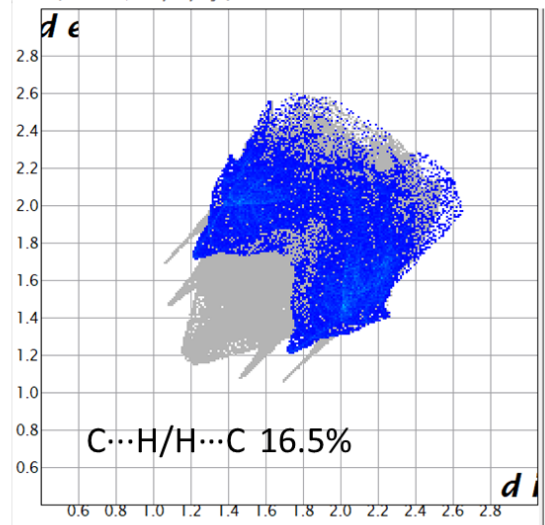
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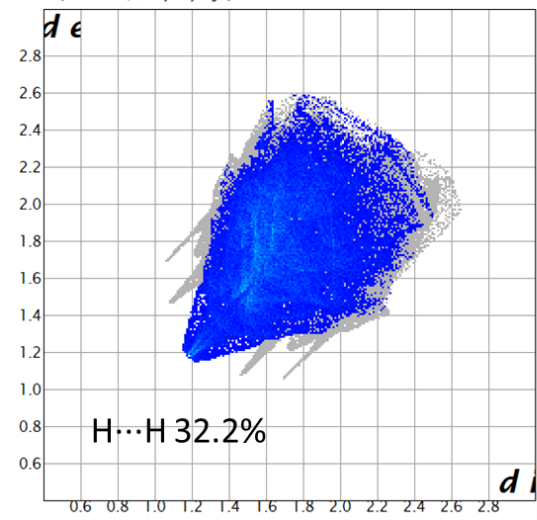
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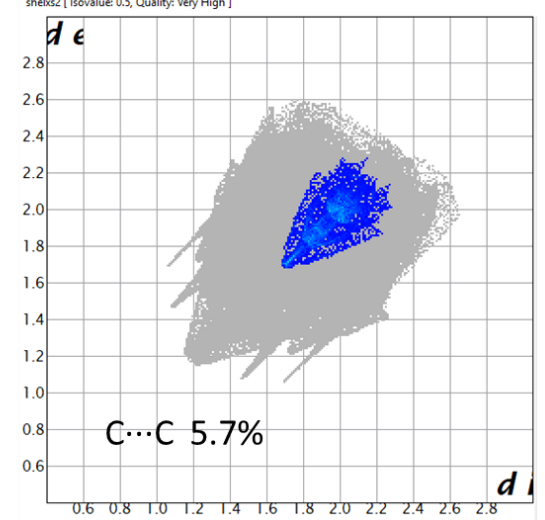
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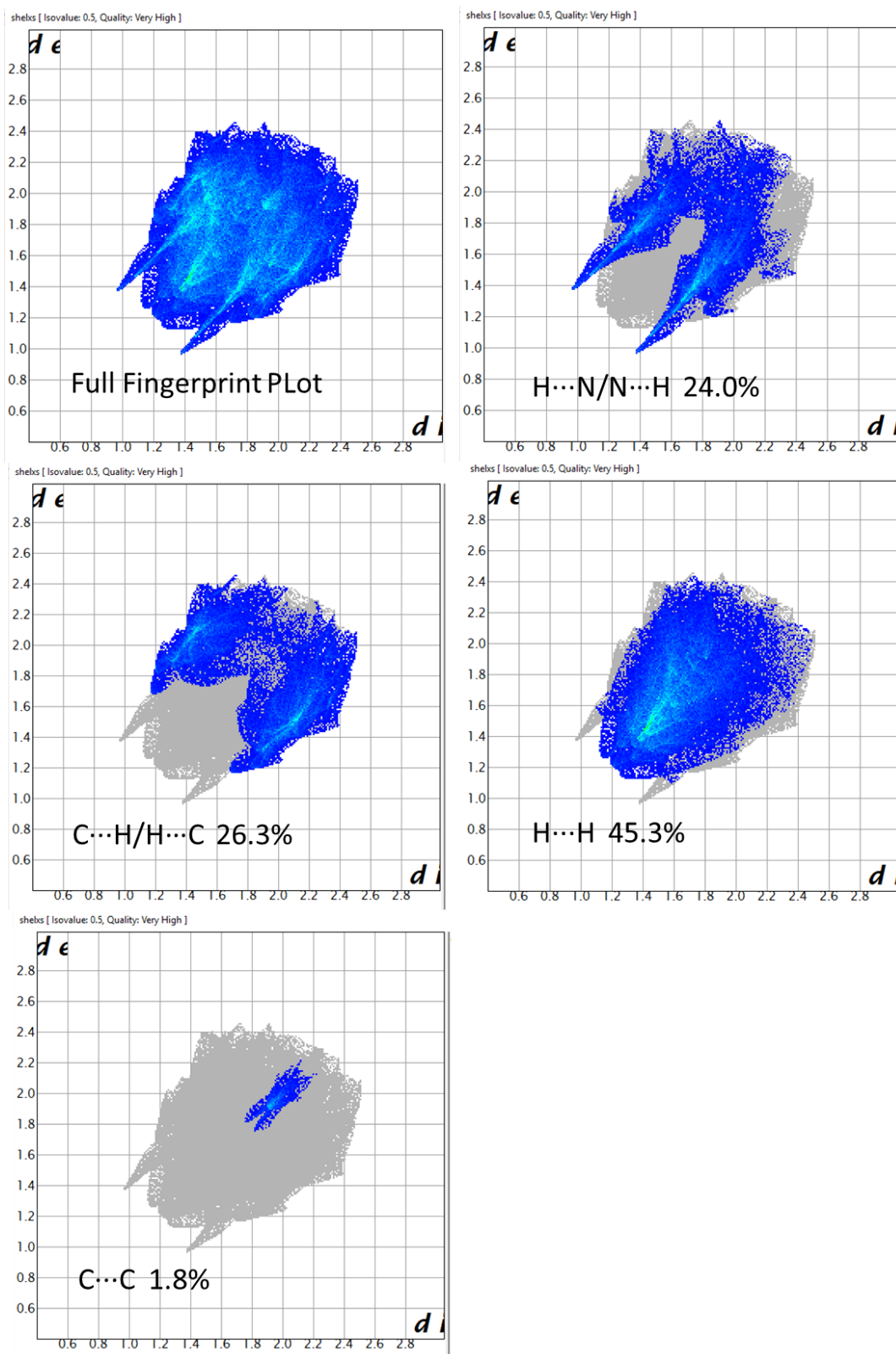
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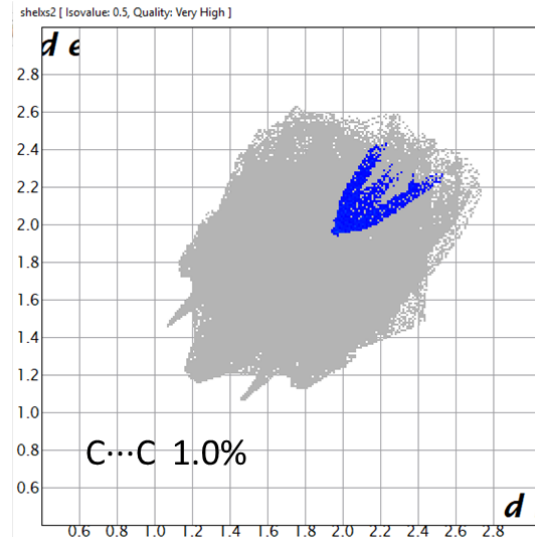
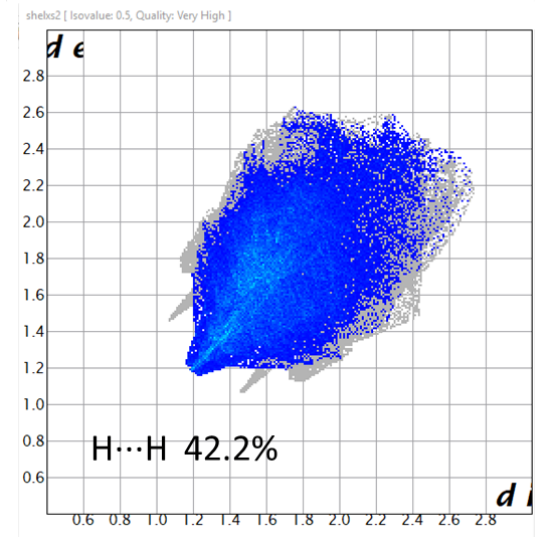
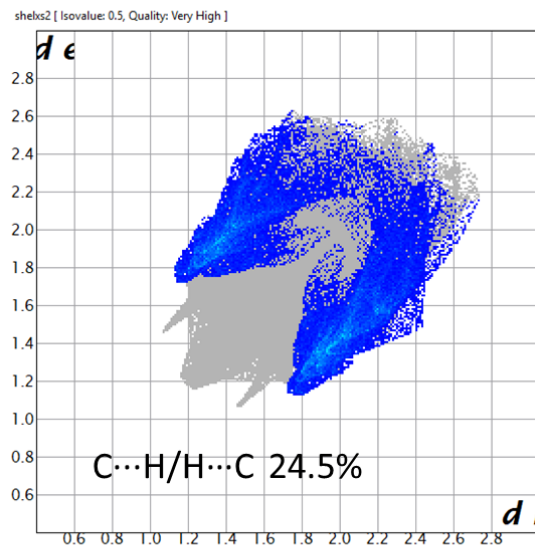
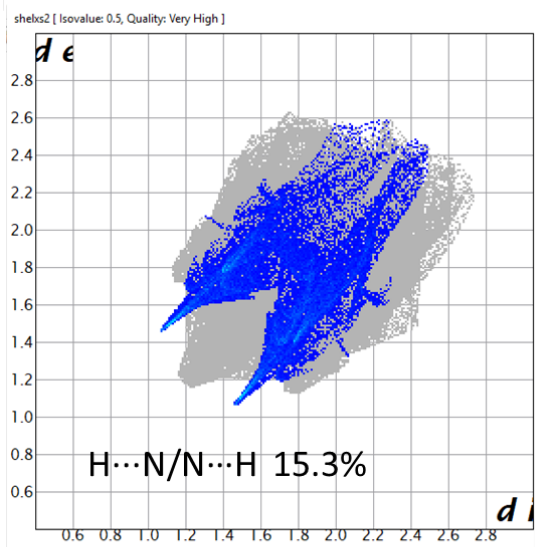
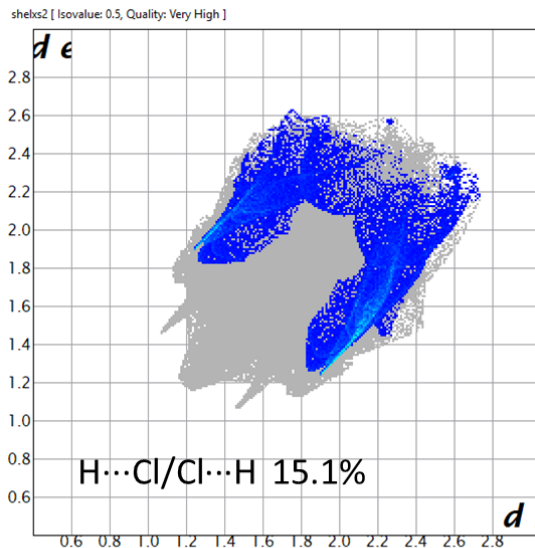
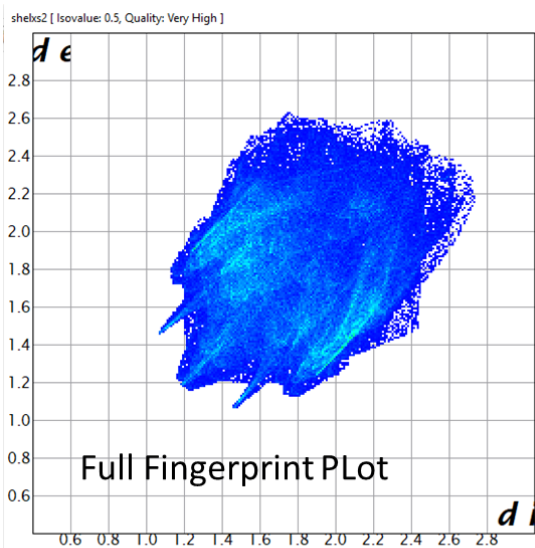
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Compound 7c

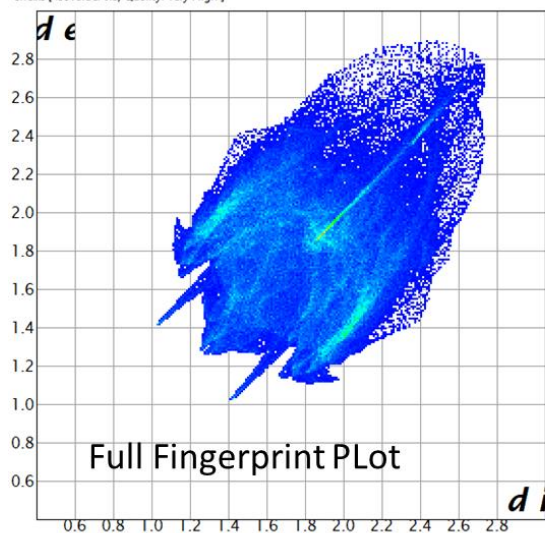


Compound 8a

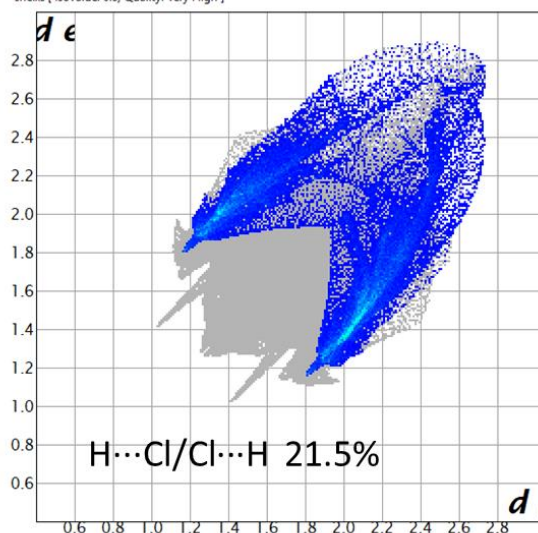


Compound 8b

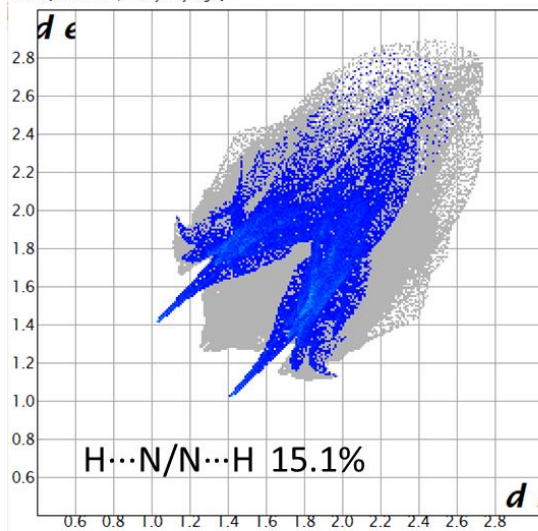
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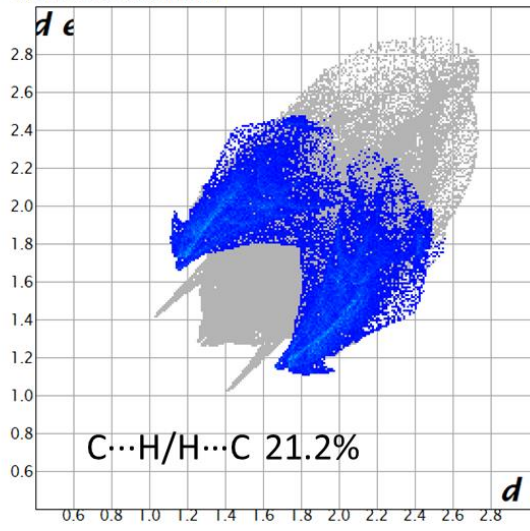
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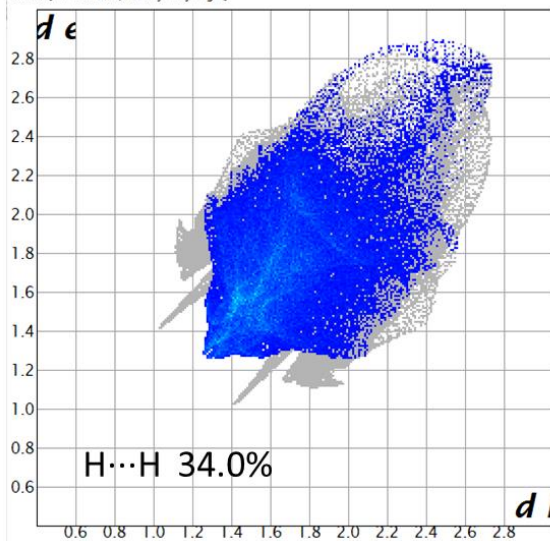
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