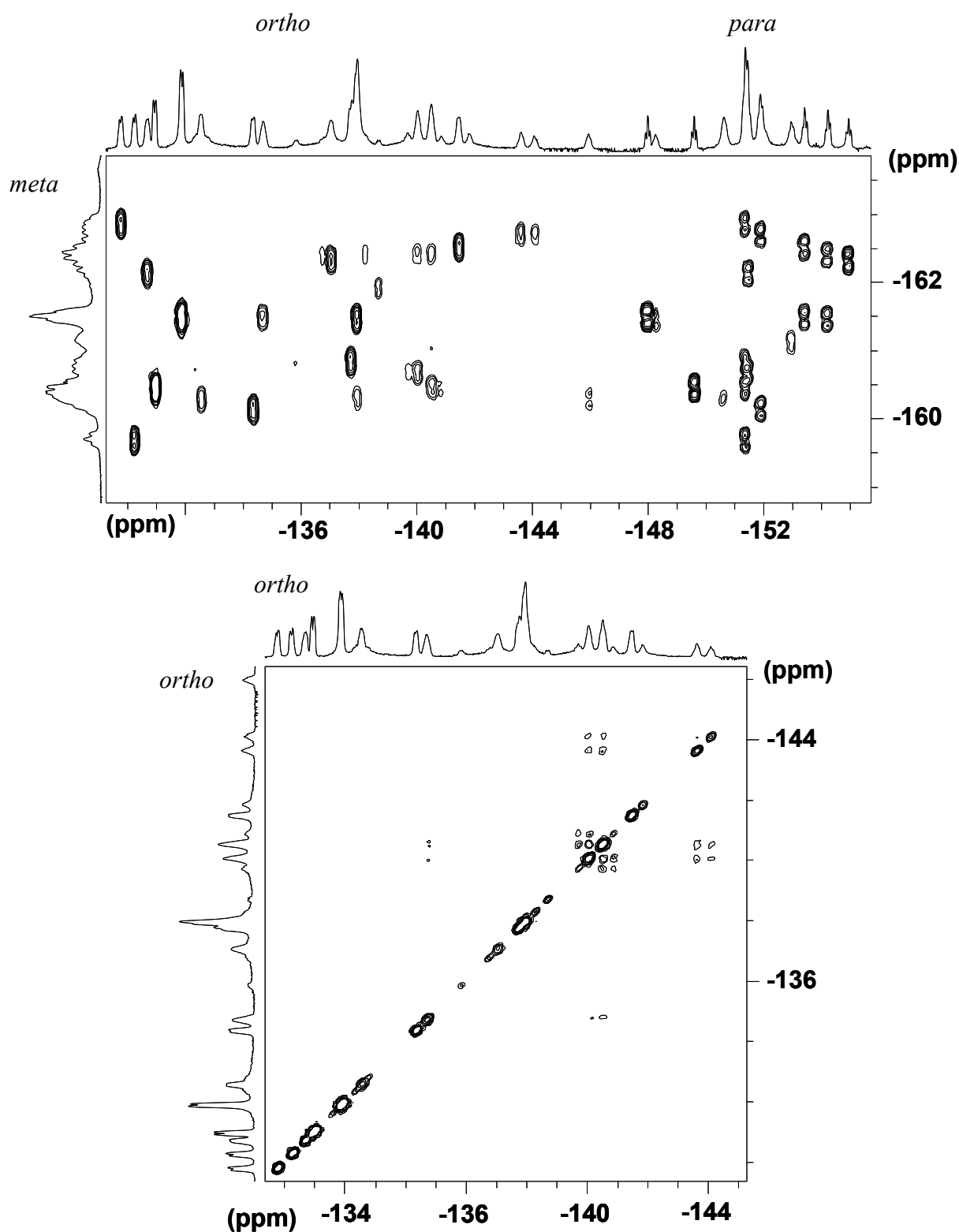


**SUPPORTING INFORMATION**

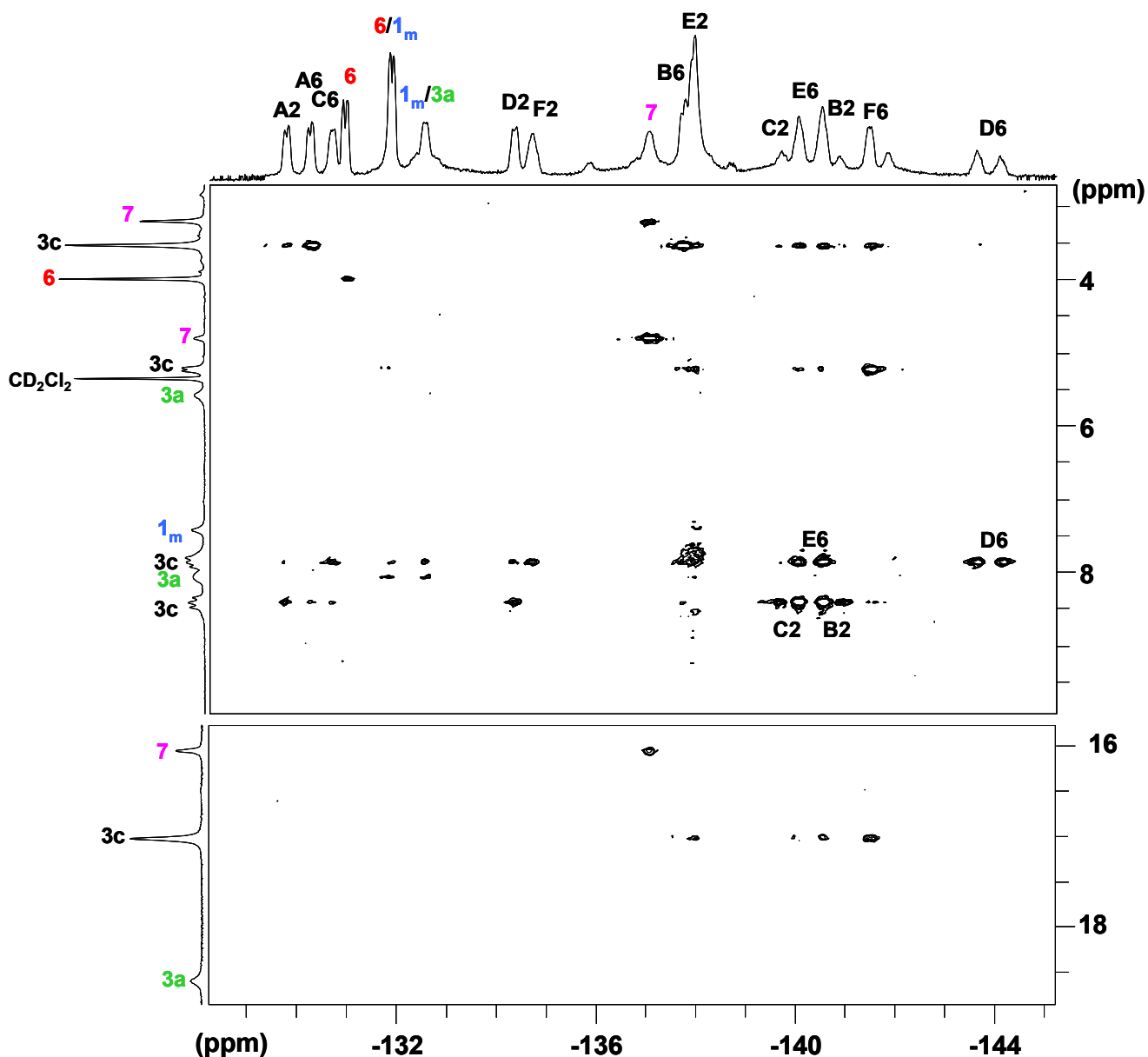
**Title:** Hydrogen Bonding and Lewis Acid–Base Interactions in the System Bis(pentafluorophenyl)borinic Acid / Methanol

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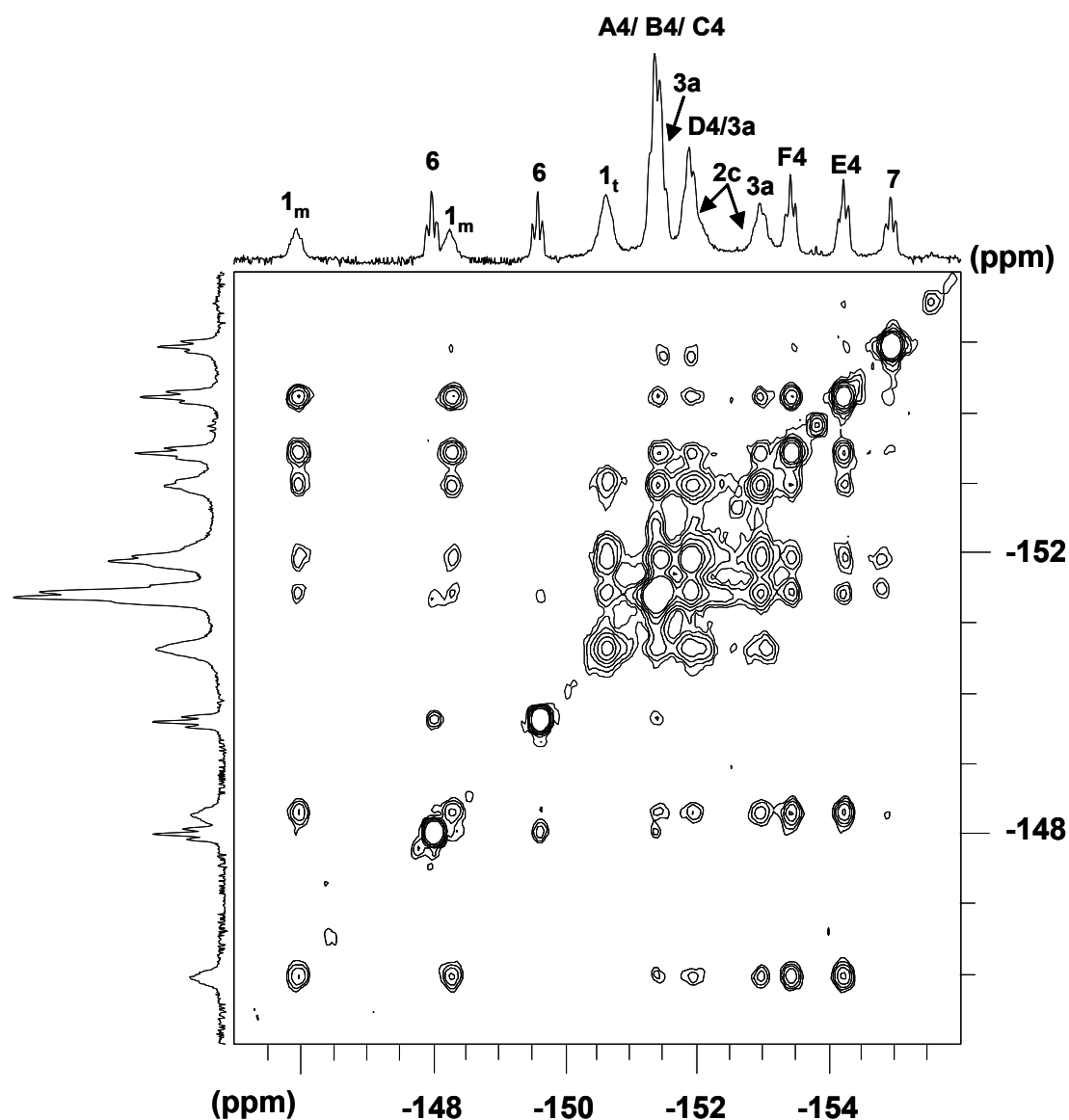


**Figure S1.**  $^{19}\text{F}$  COSY of a solution of **1** treated with 0.3 eq of MeOH ( $\text{CD}_2\text{Cl}_2$ , 183 K) used to identify the resonances belonging to each phenyl ring in the compounds present in the solution. Thirty resonances are observed for **3c**, due to its  $C_1$  symmetry. In the *ortho* region, through space coupling between two couples of fluorine atoms is observable. Six resonances are expected (not always detectable for the low abundance) for **6** and **1<sub>m</sub>** due to the freezing of the hindered rotation around the B-O bond. The assignments relevant for further discussion of the structure are reported in the following figures.



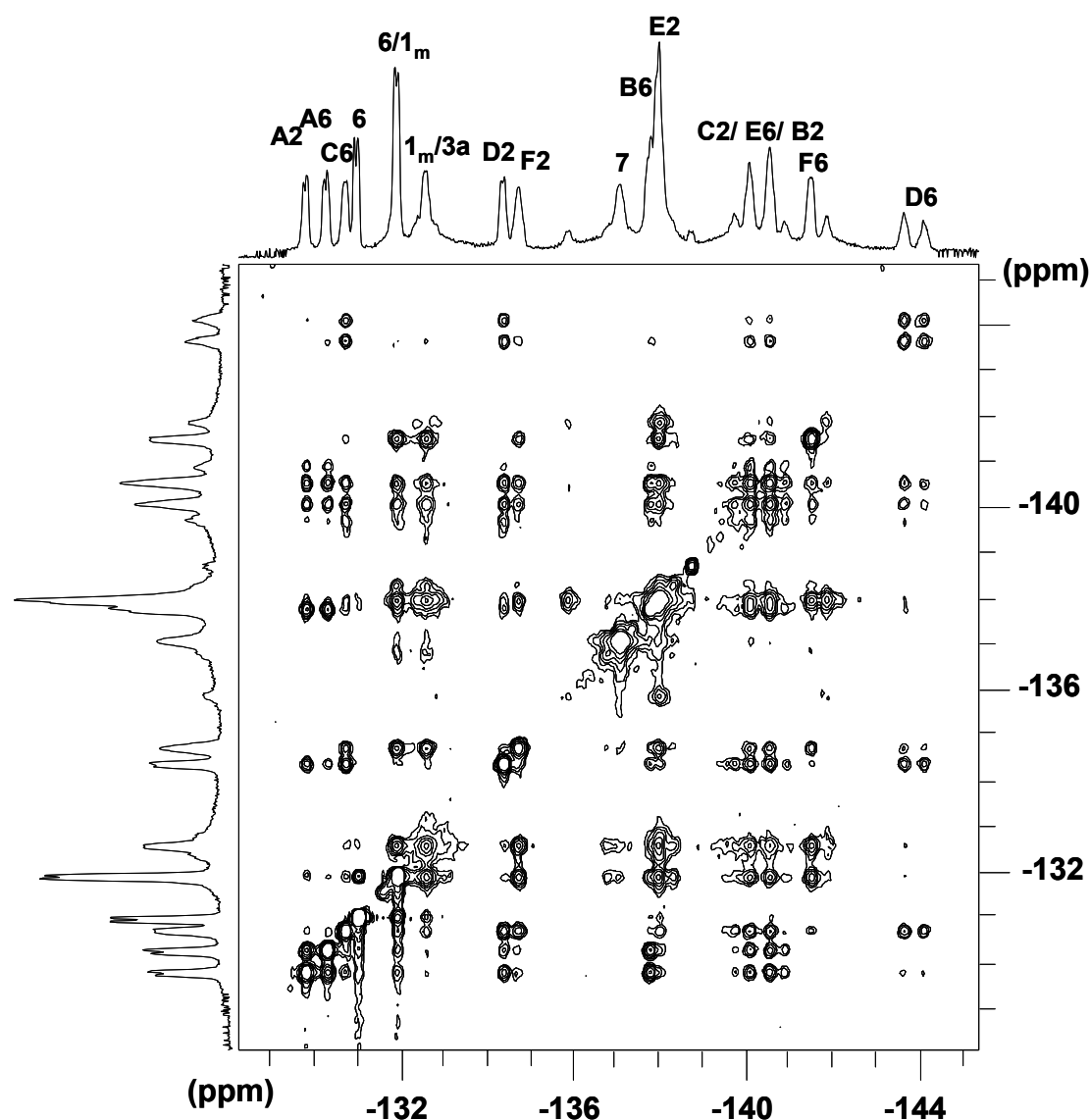
**Figure S2.**  $^{19}\text{F}$ - $^1\text{H}$  HOESY of a solution of **1** treated with 0.3 eq of MeOH ( $\text{CD}_2\text{Cl}_2$ , 183 K,  $\tau_m = 0.3$  s). In the  $^{19}\text{F}$  trace the resonances of **3c** have been labelled according to Scheme 5. The map clearly shows the cross peaks between H<sub>c</sub> and H<sub>d</sub> of **3c** (see Scheme 5) and the couples of fluorines they are dipolarly connected with. Interestingly, the unique  $^{19}\text{F}$  *ortho* resonance of **7** has cross peaks with all its three proton resonances (H<sub>a</sub>, H<sub>b</sub> and CH<sub>3</sub>, see Scheme 1). Noteworthy, the methyl group of **6** presents a cross peak with only one of its *ortho* fluorine resonances, for the freezing of the hindered rotation around the B-O bond.

The resonances of **2c** and **1<sub>t</sub>** (minor components of the solution mixture) have not been indicated for readability reasons, while only some of the  $^{19}\text{F}$  signals of **3a** have been labelled.

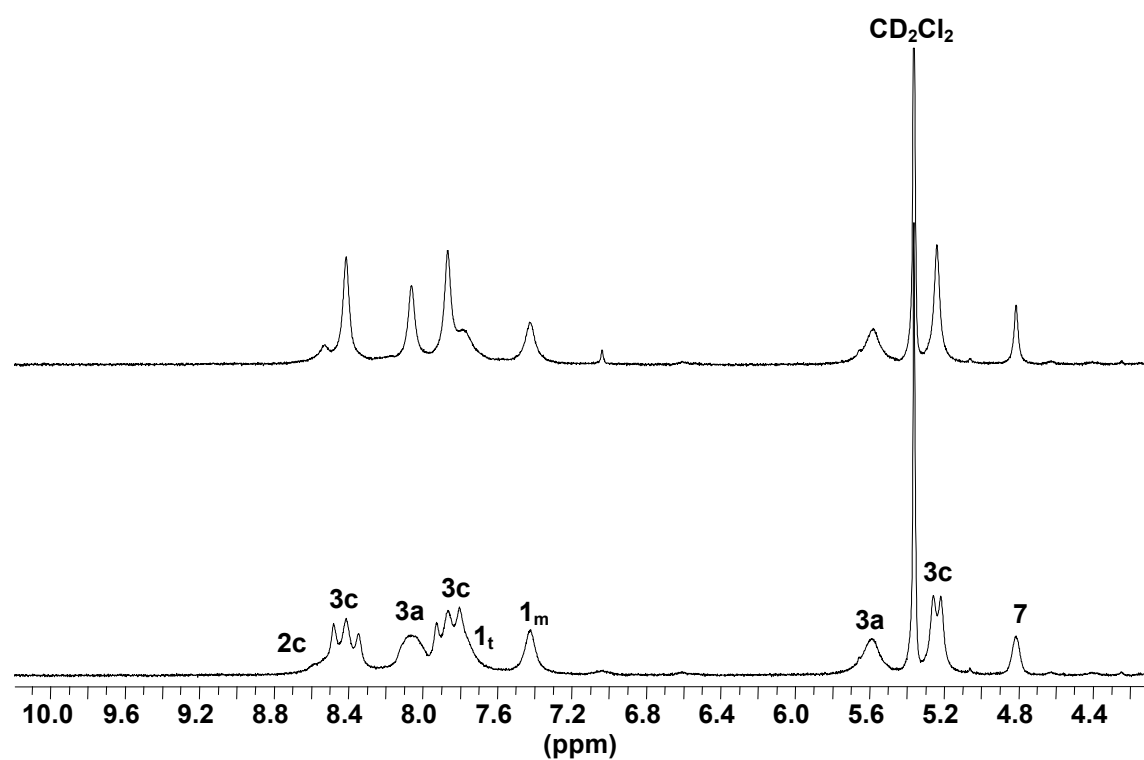


**Figure S3.** *Para* region of a  $^{19}\text{F}$  NOESY/EXSY experiment performed on a solution of **1** treated with 0.3 eq of MeOH ( $\text{CD}_2\text{Cl}_2$ , 183 K,  $\tau_m = 0.3$  s). The resonances of **3c** are labelled according to Scheme 5. To be noticed:

- 1) both **6** and **1<sub>m</sub>** show cross peaks between their *para* signals due to the slow exchange regime of their hindered rotation around the B-O bond;
- 2) **3a** exchanges with **1<sub>m</sub>**;
- 3) **2c** exchanges with **1<sub>t</sub>**;
- 4) **3c** exchange selectively with both **1<sub>m</sub>** and **6**. Rings E and F exchange with **1<sub>m</sub>** whilst rings A and B with methyl borinate. In this latter case only one cross peak is observable in the map due to the accidental overlap of A4 and B4 resonances.



**Figure S4.** *Ortho* region of a  $^{19}\text{F}$  NOESY/EXSY experiment performed on a solution of **1** treated with 0.3 eq of MeOH ( $\text{CD}_2\text{Cl}_2$ , 183 K,  $\tau_m = 0.3$  s). The resonances of **3c** are labelled according to Scheme 5. Resonances of **2c** and **3a** have not been indicated for readability reasons. The map shows NOE cross peaks between the fluorines within the same species together with exchange cross peaks between **1<sub>m</sub>** and **3c**.



**Figure S5.** Selected region of the  $^1\text{H}$  (bottom) and  $\{^{19}\text{F}\}\text{-}^1\text{H}$  (top) NMR spectra of a solution of **1** treated with 0.3 eq of MeOH ( $\text{CD}_2\text{Cl}_2$ , 183 K)