

Scientific report

Metal-organic frameworks based on fluorinated terphenilic ligands for gas storage and separation

Stage 1-2020

Stage 1 summary-The synthesis of the fluorinated aromatic carboxylic acids and of metal-organic frameworks

In accordance with the project plan, in the first stage the synthesis of the three proposed ligands has been accomplished, and coordination polymers preliminary synthesis experiments have been performed using the synthesized ligands and zinc salts. The compounds 2',5'-difluoro-[1,1':4',1''-terphenil]-4,4''-dicarboxylic acid H₂F₂ and 2',3',5',6'-tetrafluoro-[1,1':4',1''-terphenil]-4,4''-dicarboxylic acid H₂F₄, have been synthesized in a single step through a Suzuki-Miyaura coupling reaction. For the preparation of the third ligand 2',5'-bis(trifluoromethyl)-[1,1':4',1''-terphenil]-4,4''-dicarboxylic acid H₂CF₃, 2 steps were needed- one for bromination of the substrate 1,4-bis(trifluoromethyl)benzene followed by the same Suzuki-Miyaura coupling reaction. The encountered difficulties regarding the precursors and final compounds solubility have been overcome through the judicious identification of the adequate solvent mixtures. The structure and purity of the ligands have been confirmed through ¹H, ¹³C and ¹⁹F NMR. Moreover, the H₂F₂ and H₂CF₃ ligands have been isolated as crystals and their structure was further confirmed by single crystal X ray diffraction. Preliminary synthesis test have been performed in order to prepare metal-organic frameworks using the synthesized ligands and zinc nitrate. During these experiments different reaction temperatures and solvent mixtures were tested. In this stage, a part of the results were disseminated by means of an oral presentation at SESIUNEA DE COMUNICARI STIINTIFICE A TINERILOR CERCETATORI, POARTA DESCHISA SPRE VIITOR, 19 Noiembrie 2020, Iasi, Romania.

The scientific description of stage 1

(i) *The synthesis of the 2',5'-difluoro-[1,1':4',1''-terphenil]-4,4''-dicarboxylic acid H₂F₂.*

Validated reaction protocol: 0.5 g (1.839 mmol) 1,4-dibromo-2,5-difluorobenzene and 0.8 g (4.5 mmol) 4-carboxyphenylboronic acid were dissolved in 75 mL tetrahydrofuran (THF), followed by the addition of 15 mL of deionized water and 3 g potassium carbonate. The mixture was degassed under vacuum followed by argon sparging for 10 minutes, after which 0.15 g of catalyst Tetrakis(triphenylphosphine)palladium(0) were added. The argon sparging was continued for an additional 5 minutes. The reaction mixture was refluxed for 72 h. The reaction flask was then allowed to cool to room temperature and the pH value of the reaction mixture

was brought to 1-2 units using 36% hydrochloric acid under vigorous stirring. The resulting precipitate was collected by filtration and washed with water until the pH value reached a neutral value, followed by washing with acetone and ethanol. After drying the crude product was dispersed in 65% nitric acid with an ultrasound bath. The white precipitate was collected through filtration, washed with water until the pH value reached a neutral value and dried at 80 °C. Recrystallization of the product from DMF afforded the desired product 2',5'-difluoro-[1,1':4',1''-terphenil]-4,4''-dicarboxylic acid as colorless crystals (0.43 g, η =66 %).

(ii) *The synthesis of 2',3',5',6'-tetrafluoro-[1,1':4',1''-terphenil]-4,4''-dicarboxylic acid H2F4.*

Validated reaction protocol: 0.5 g (1.62 mmol) 1,4-dibromo-2,3,5,6-tetrafluorobenzene and 0.7 g (4.21 mmol) 4-carboxyphenylboronic acid were dissolved in 50 mL dioxane followed by the addition of 20 mL deionized water, 20 mL ethanol and 2.42 g potassium carbonate. The mixture was degassed under vacuum followed by argon sparging for 10 minutes, after which 0.15 g of catalyst Tetrakis(triphenylphosphine)palladium(0) were added. The argon sparging was continued for an additional 5 minutes. The reaction mixture was refluxed for 72 h. The reaction flask was then allowed to cool to room temperature and the pH value of the reaction mixture was brought to 1-2 units using 36% hydrochloric acid under vigorous stirring. The resulting precipitate was collected by filtration and washed with water until the pH value reached a neutral value, followed by washing with acetone and ethanol. After drying the crude product was dispersed in 65% nitric acid with an ultrasound bath. The white precipitate was collected through filtration, washed with water until the pH value reached a neutral value and dried at 80 °C. Recrystallization of the product from DMF afforded the desired product 2',3',5',6'-tetrafluoro-[1,1':4',1''-terphenil]-4,4''-dicarboxylic acid as a white powder (0.48 g, η =76 %).

(iii) *The synthesis of bis(trifluoromethyl)-[1,1':4',1''-terphenil]-4,4''-dicarboxylic acid H2CF3.* The ligand synthesis was preceded by the bromination of the substrate 1,4-bis(trifluoromethyl)benzene using an adapted protocol.ⁱ

Validated bromination reaction protocol: The substrate 1,4-bis(trifluoromethyl)benzene (2 g, 9.34 mmol, 1.448 mL) was dispersed at 60 °C in a mixture of trifluoroacetic acid (30 mL) and 98% sulfuric acid (8 mL). The bromination agent N-Bromosuccinimide (5 g, 28.09 mmol) was added slowly as a solid in the course of 3 h under intense stirring. The reaction mixture was stirred at 60 °C for 48 h. After cooling to room temperature, the resulting dispersion was poured over 500 mL of deionized water. The resulting precipitate was collected through filtration and washed with water up until a neutral pH. After drying at room temperature, 3.47 g of off-white powder was obtained. The structure

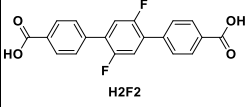
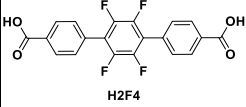
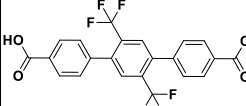
and purity of the compound was verified through NMR spectroscopy and is similar to that reported in the literature.

Validated reaction protocol for the synthesis of bis(trifluoromethyl)-[1,1': 4',1''-terphenil]-4,4''-dicarboxylic acid: 0.75 g (2 mmol) 1,4-dibromo-2,5-bis(trifluoromethyl)benzene and 0.9 g (6 mmol) 4-carboxyphenylboronic acid were dissolved in 45 mL DMSO, followed by the addition of 5 mL deionized water and 3.2 g potassium carbonate. The mixture was degassed under vacuum followed by argon sparging for 10 minutes, after which 0.2 g of catalyst Tetrakis(triphenylphosphine)palladium(0) were added. The argon sparging was continued for an additional 5 minutes. The reaction mixture was heated at 80 °C for 72 h. The reaction flask was then allowed to cool to room temperature and the pH value of the reaction mixture was brought to 1-2 units using 36% hydrochloric acid under vigorous stirring. The resulting precipitate was collected by filtration and washed with water until the pH value reached a neutral value, followed by washing with acetone and ethanol. After drying the crude product was dispersed in 65% nitric acid with an ultrasound bath. The white precipitate was collected through filtration, washed with water until the pH value reached a neutral value and dried at 80 °C. Recrystallization of the product from DMF afforded the desired product bis(trifluoromethyl)-[1,1': 4',1''-terphenil]-4,4''-dicarboxylic acid as a colorless crystals (0.62 g, η =68 %).

(iv) coordination polymers preliminary synthesis steps with the three aromatic fluorinated ligands

A series of metal-organic frameworks preliminary synthesis steps have been accomplished using the three synthesized ligands **H2F2**, **H2F4** and **H2CF3** and zinc nitrate (Table 1). No acid modulator was used in these experiments.

Table 1 Description of the MOF preliminary synthesis experiments with the three ligands.

Sample	Ligand	Reaction mixture	T (°C)	Results/observations
1F2	 H2F2	0.017 g H2F2, 0.06 g Zn(NO ₃) ₂ · 6H ₂ O, 5 mL DMF	80	White opaque agglomerate
2F2		0.017 g H2F2, 0.06 g Zn(NO ₃) ₂ · 6H ₂ O, 3 mL DMF, 3 mL MeOH	100	White opaque agglomerate
2F3		0.017 g H2F2, 0.06 g Zn(NO ₃) ₂ · 6H ₂ O, 3 mL DMF, 3 mL EtOH	100	White opaque agglomerate
1F4	 H2F4	0.02 g H2F4, 0.06 g Zn(NO ₃) ₂ · 6H ₂ O, 5 mL DMF	80	White opaque agglomerate
2F4		0.02 g H2F4, 0.06 g Zn(NO ₃) ₂ · 6H ₂ O, 3 mL DMF, 3 mL MeOH	100	Decanted fine powder
3F4		0.02 g H2F4, 0.06 g Zn(NO ₃) ₂ · 6H ₂ O, 3 mL DMF, 3 mL EtOH	100	Decanted fine powder
1CF3	 H2CF3	0.022 g H2CF3, 0.06 g Zn(NO ₃) ₂ · 6H ₂ O, 5 mL DMF	80	Decanted fine powder
2CF3		0.022 g H2CF3, 0.06 g Zn(NO ₃) ₂ · 6H ₂ O, 3 mL DMF, 3 mL MeOH	100	White agglomerate on the vial

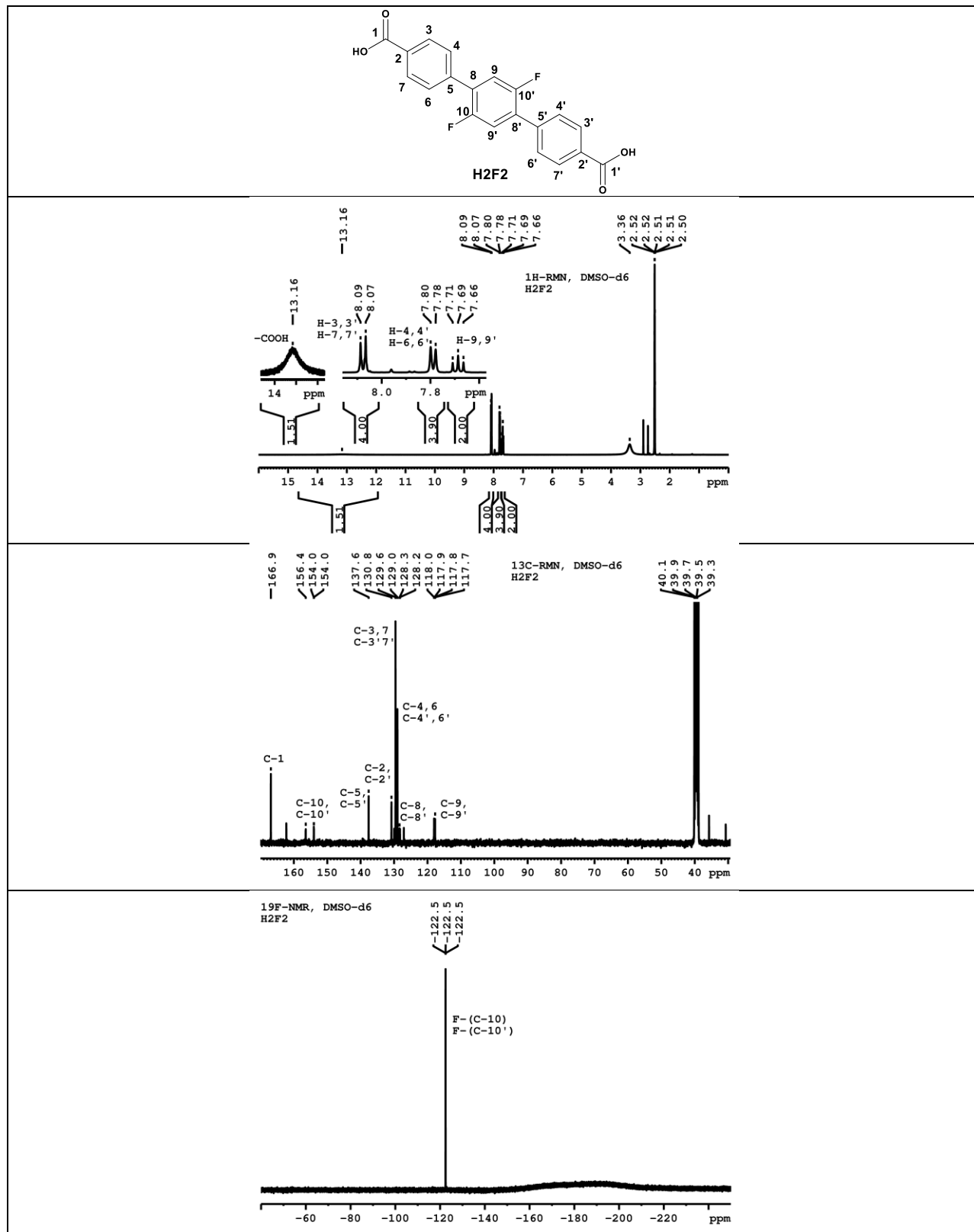
				sidewalls
3CF3		0.022 g H ₂ CF ₃ , 0.06 g Zn(NO ₃) ₂ · 6H ₂ O, 3 mL DMF, 3 mL EtOH	100	White agglomerate on the vial sidewalls

The dissolution of the ligands was possible only after heating to the corresponding reaction temperature with the exception of H₂CF₃ which readily dissolves at room temperature. No crystal was isolated from these experiments, which could lead to the network structure identification.

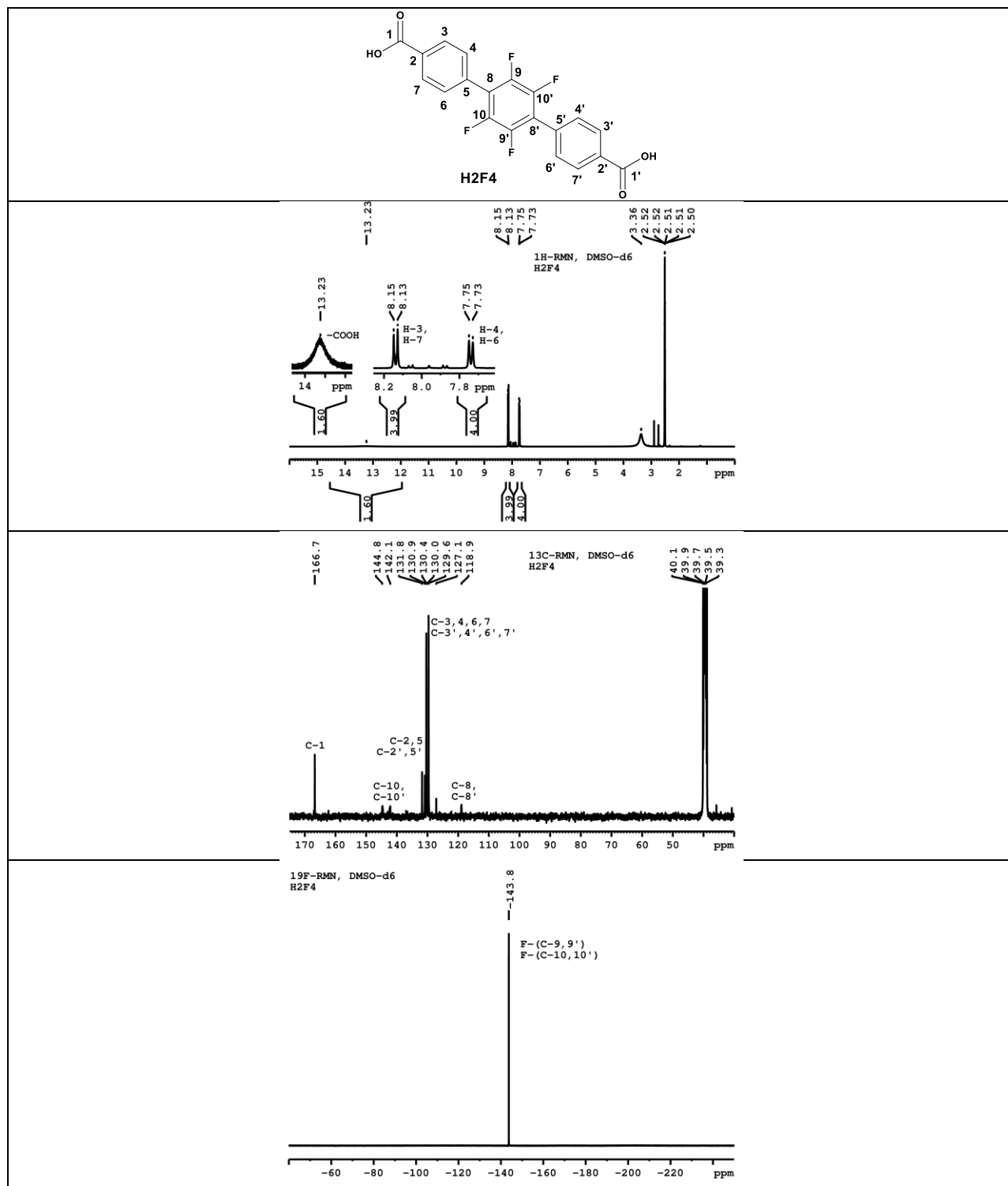
Project Director

Dr. Ioan-Andrei Dascalu

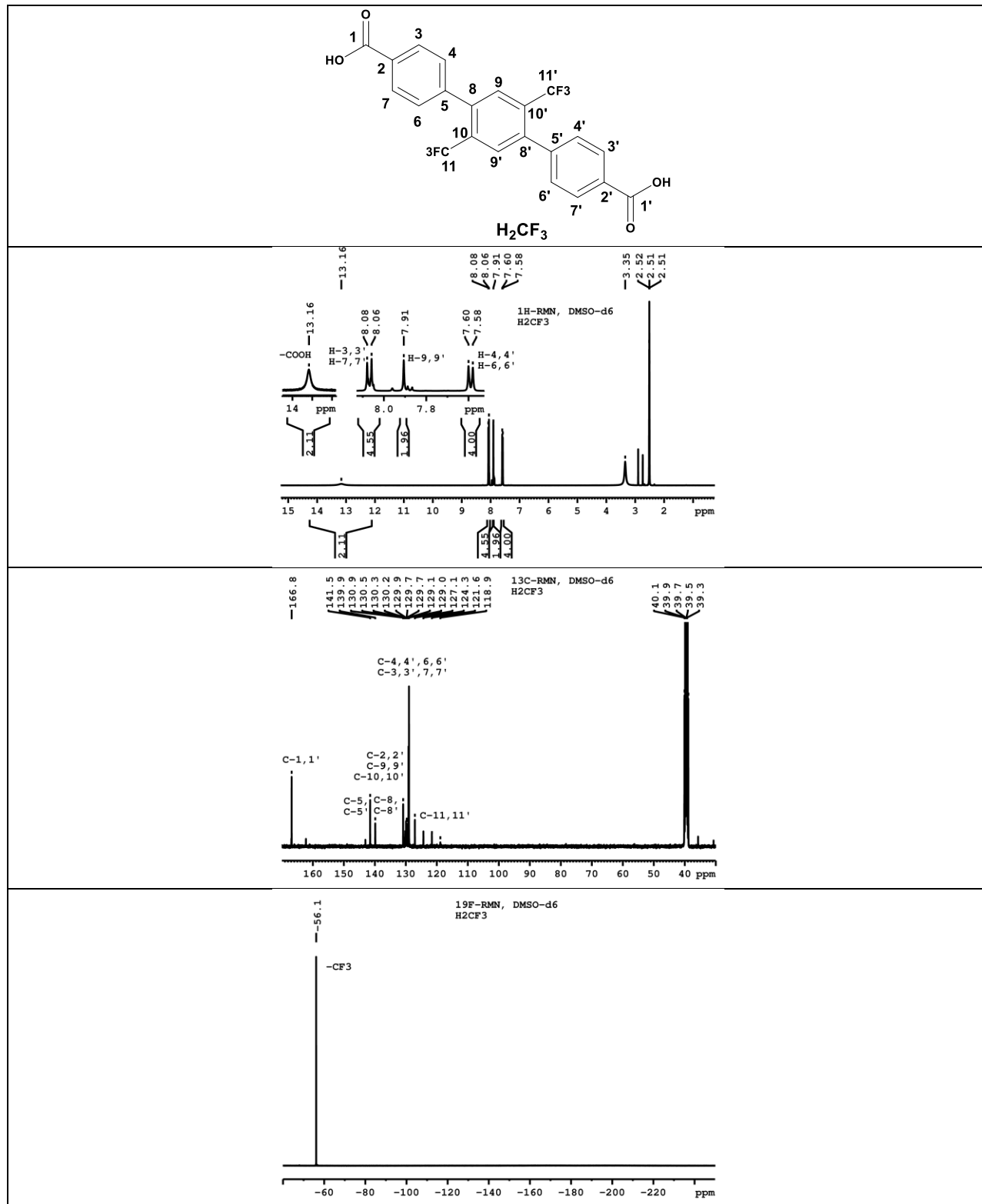
Annex 1. Annotated structure and ^1H , ^{13}C and ^{19}F NMR spectra of 2',5'-difluoro-[1,1':4',1''-terphenil]-4,4''-dicarboxylic acid **H2F2**.



Annex 2. Annotated structure and ^1H , ^{13}C and ^{19}F NMR spectra of 2',3',5',6'-tetrafluoro-[1,1':4',1'']-terphenyl]-4,4''-dicarboxylic acid **H2F4**.



Annex 3. Annotated structure and ^1H , ^{13}C and ^{19}F NMR of bis(trifluoromethyl)-[1,1':4,1''-terphenil]-4,4''-dicarboxylic H_2CF_3



ⁱ Y. Kim, T. M. Swager, *Chem. Commun.*, 2005, 3, 372–374.