

ADVANCED FUNCTIONAL MATERIALS

Supporting Information

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Spirobifluorene Dimers: Understanding How The
Molecular Assemblies Drive The Electronic Properties

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Synthesis

All manipulations of oxygen and moisture-sensitive materials were conducted with a standard Schlenk technique. All glassware was kept in an oven at 80°C. Argon atmosphere was generated by three repetitive cycles of vacuum/Argon using a schlenck ramp. Commercially available reagents and solvents were used without further purification other than those detailed below. THF and toluene were obtained through a PURE SOLV™ solvent purification system. Light petroleum refers to the fraction with bp 40-60°C. Analytical thin layer chromatography was carried out using aluminum backed plates coated with Merck Kieselgel 60 GF254 and visualized under UV light (at 254 and 360 nm). Flash chromatography was carried out using Teledyne Isco CombiFlash® Rf 400 (UV detection 200-360nm), over standard silica cartridges (Redisep® Isco or Puriflash® columns Interchim). In order to be purified through a recycling size exclusion chromatography apparatus, the compounds were solubilized in HPLC grade chloroform (stabilized with ethanol). Prior to injection, the solution was filtered through a 0.45 µm PTFE filter. Purification was performed on a LC-9160 II NEXT system from the Japan Analytical Industry Co., Ltd. (JAI) equipped with coupled UV-vis 4Ch NEXT through a set of two JAIGEL-2H columns at an elution rate of 10 mL.min⁻¹ (CHCl₃). ¹H and ¹³C NMR spectra were recorded using Bruker 300 MHz instruments (¹H frequency, corresponding ¹³C frequency: 75 MHz); chemical shifts were recorded in ppm and J values in Hz. The residual signals for the NMR solvents used are 5.32 ppm (proton) and 54.00 ppm (carbon) for CD₂Cl₂, 7.26 ppm (proton) and 77.16 ppm (carbon) for CDCl₃ and 77.16 ppm (carbon), 2.090 ppm (proton) for toluene-d₈. In the ¹³C NMR spectra, signals corresponding to C, CH, CH₂ or CH₃ groups, assigned from DEPT experiment, are noted. The following abbreviations have been used for the NMR assignment: s for singlet, d for doublet, t for triplet, q for quadruplet and m for multiplet. High resolution mass spectra were recorded at the Centre Régional de Mesures Physiques de l'Ouest (CRMPO-Rennes) on a Thermo Ficher Q-Exactive instrument or a Bruker MaXis 4G or a Bruker Ultraflex III.

X-ray

Crystals were picked up with a cryoloop and then frozen at 150 K under a stream of dry N₂. Data were collected on a D8 VENTURE Bruker AXS diffractometer with Mo-Kα radiation (λ = 0.71073 Å).

Structures were solved by direct methods (SIR92)¹ and refined (SHELXL-2014/7)² by full-matrix least-squares methods as implemented in the WinGX software package.³ An empirical absorption (multi-scan) correction was applied. Hydrogen atoms were introduced at calculated positions (riding model) included in structure factor calculation but not refined. Refinement parameters are summarized in **Error! Reference source not found.**-4 (see below).

CCDC deposition numbers

1,1''-(SBF)₂ : 1893598

1,2''-(SBF)₂ : 1893599

1,3''-(SBF)₂ : 1893604

1,4''-(SBF)₂ : 1893605

2,2''-(SBF)₂ : 1487806

2,3''-(SBF)₂ : 2084186

3,3''-(SBF)₂ : 2084188

2,4''-(SBF)₂ : 2084187

3,4''-(SBF)₂ : 2084189

4,4''-(SBF)₂ : 752166

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication data: **2,3''-(SBF)₂** (2084186), **3,3''-(SBF)₂** (2084188), **2,4''-(SBF)₂** (2084187) and **3,4''-(SBF)₂** (2084189). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk].

Figures were generated with Mercury software 3.9.

Table S1. Crystal data and structure refinement for **2,4-(SBF)₂**.

Empirical formula	C51 H31 Cl3	
Formula weight	750.11	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 13.3666(13) Å	α = 90°.
	b = 9.1498(10) Å	β = 101.062(3)°.
	c = 30.724(3) Å	γ = 90°.
Volume	3687.8(6) Å ³	
Z	4	
Density (calculated)	1.351 Mg/m ³	
Absorption coefficient	0.286 mm ⁻¹	
F(000)	1552	
Crystal size	0.21 x 0.04 x 0.02 mm ³	
Theta range for data collection	2.245 to 27.538°.	
Index ranges	-17 ≤ h ≤ 17, -10 ≤ k ≤ 11, -39 ≤ l ≤ 34	
Reflections collected	36411	
Independent reflections	8451 [R(int) = 0.0859]	
Completeness to theta = 25.242°	99.7 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8451 / 0 / 487	
Goodness-of-fit on F ²	1.049	
Final R indices [I > 2σ(I)]	R1 = 0.0623, wR2 = 0.1563	
R indices (all data)	R1 = 0.0814, wR2 = 0.1699	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.676 and -0.710 e.Å ⁻³	

Table S2. Crystal data and structure refinement for **2,3-(SBF)₂**.

Empirical formula	C100 H60	
Formula weight	1261.48	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 20.1325(7) Å	$\alpha = 90^\circ$.
	b = 9.0691(3) Å	$\beta = 113.6800(10)^\circ$.
	c = 20.0508(7) Å	$\gamma = 90^\circ$.
Volume	3352.7(2) Å ³	
Z	2	
Density (calculated)	1.250 Mg/m ³	
Absorption coefficient	0.071 mm ⁻¹	
F(000)	1320	
Crystal size	0.17 x 0.12 x 0.02 mm ³	
Theta range for data collection	2.209 to 27.505°.	
Index ranges	-26<=h<=26, -11<=k<=11, -26<=l<=21	
Reflections collected	28219	
Independent reflections	7670 [R(int) = 0.0517]	
Completeness to theta = 25.242°	99.9 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	7670 / 0 / 452	
Goodness-of-fit on F ²	1.065	
Final R indices [I>2sigma(I)]	R1 = 0.0496, wR2 = 0.1247	
R indices (all data)	R1 = 0.0649, wR2 = 0.1367	
Extinction coefficient	0.0119(11)	
Largest diff. peak and hole	0.357 and -0.244 e.Å ⁻³	

Table S3. Crystal data and structure refinement for **3,4-(SBF)₂**.

Empirical formula	C ₅₄ H ₃₈ O	
Formula weight	702.84	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 13.5878(18) Å	α = 90°.
	b = 8.5673(12) Å	β = 105.808(4)°.
	c = 16.620(2) Å	γ = 90°.
Volume	1861.6(4) Å ³	
Z	2	
Density (calculated)	1.254 Mg/m ³	
Absorption coefficient	0.073 mm ⁻¹	
F(000)	740	
Crystal size	0.09 x 0.03 x 0.01 mm ³	
Theta range for data collection	2.265 to 26.514°.	
Index ranges	-16 ≤ h ≤ 16, -10 ≤ k ≤ 10, -20 ≤ l ≤ 20	
Reflections collected	7098	
Independent reflections	7098 [R(int) = 0.1]	
Completeness to theta = 25.242°	92.9 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	7098 / 1 / 498	
Goodness-of-fit on F ²	1.102	
Final R indices [I > 2σ(I)]	R1 = 0.0796, wR2 = 0.1719	
R indices (all data)	R1 = 0.1181, wR2 = 0.1852	
Absolute structure parameter	0(8)	
Extinction coefficient	0.105(9)	
Largest diff. peak and hole	0.570 and -0.460 e.Å ⁻³	

Table S4. Crystal data and structure refinement for **3,3-(SBF)₂**.

Empirical formula	C50 H30	
Formula weight	630.74	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 19.130(6) Å	$\alpha = 90^\circ$.
	b = 18.466(6) Å	$\beta = 90^\circ$.
	c = 19.129(6) Å	$\gamma = 90^\circ$.
Volume	6757(4) Å ³	
Z	8	
Density (calculated)	1.240 Mg/m ³	
Absorption coefficient	0.070 mm ⁻¹	
F(000)	2640	
Crystal size	0.28 x 0.15 x 0.12 mm ³	
Theta range for data collection	2.398 to 25.640°.	
Index ranges	-20 ≤ h ≤ 23, -21 ≤ k ≤ 23, -23 ≤ l ≤ 23	
Reflections collected	25579	
Independent reflections	6841 [R(int) = 0.0925]	
Completeness to theta = 25.242°	99.1 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6841 / 0 / 451	
Goodness-of-fit on F ²	1.031	
Final R indices [I > 2σ(I)]	R1 = 0.0545, wR2 = 0.1197	
R indices (all data)	R1 = 0.1155, wR2 = 0.1582	
Extinction coefficient	n/a.	
Largest diff. peak and hole	0.212 and -0.229 e.Å ⁻³	

Spectroscopic studies

Cyclohexane (spectroscopic grade, Acros), 2-MeTHF (spectroscopic grade, sigma aldrich), 1 N solution of sulfuric acid in water (Standard solution, Alfa Aesar), and quinine sulfate dihydrate (99+%, ACROS organics) were used without further purification.

UV-visible spectra were recorded using an UV-Visible spectrophotometer SHIMADZU UV-1605. Molar extinction coefficients (ϵ) were calculated from the gradients extracted from the plots of absorbance vs concentration with five solutions of different concentrations for each sample and at least two mother solutions were prepared.

$$A = \epsilon \times l \times C$$

Above, l refers to the path length and C to the sample concentration.

Emission spectra were recorded with a HORIBA Scientific Fluoromax-4 equipped with a Xenon lamp or a JASCO 8300 Fluorescence spectrometer equipped with a high-speed chopper offering phosphorescence spectra measured using a 5 ms delay.

Quantum yields in solution (ϕ_{sol}) were calculated relative to quinine sulfate ($\phi_{ref} = 0.546$ in H_2SO_4 1 N). ϕ_{sol} was determined according to the following equation,

$$\phi_{sol} = \phi_{ref} \times \frac{Grad_s}{Grad_r} \times \left(\frac{\eta_s}{\eta_r}\right)^2$$

where subscripts s and r refer respectively to the sample and reference, $Grad$ is the gradient from the plot of integrated fluorescence intensity vs absorbance, η is the refracting index of the solvent ($\eta_s = 1.426$ for cyclohexane). Five solutions of different concentration ($A < 0.1$) of the sample and five solutions of the reference (quinine sulfate) were prepared. The integrated area of the fluorescence peak was plotted against the absorbance at the excitation wavelength for both the sample and reference. The gradients of these plots were then injected in the equation to calculate the reported quantum yield value for the sample.

Fluorescent decay measurements were carried out on the HORIBA Scientific Fluoromax-4 equipped with its TCSPC pulsed source interface.

Low temperature (77 K) measurements were performed in 2-MeTHF which freezes as a transparent glassy matrix. Measurements were carried in a single block quartz tube containing the solution, which was placed in an oxford Optistat Cryostat cooled with liquid nitrogen.

Electrochemical studies

Electrochemical experiments were performed under argon atmosphere using a Pt disk electrode (diameter 1 mm). The counter electrode was a vitreous carbon rod. The reference electrode was either a silver wire in a 0.1 M $AgNO_3$ solution in CH_3CN for the studies in oxidation or a Silver wire coated by a thin film of AgI (silver(I)iodide) in a 0.1 M Bu_4NI solution in DMF for the studies in reduction. Ferrocene was added to the electrolyte solution at the end of a series of experiments. The ferrocene/ferrocenium (Fc/Fc^+) couple served as internal standard. The three electrodes cell was connected either to a PAR Model 273 potentiostat/galvanostat (PAR, EG&G, USA) monitored with the ECHEM Software or to a potentiostat/galvanostat (Autolab/PGSTAT101) monitored with the Nova 2.1 Software. Activated Al_2O_3 was added in the electrolytic solution to remove excess moisture. For a further comparison of the electrochemical and optical properties, all potentials are referred to

the SCE electrode that was calibrated at - 0.405 V vs. Fc/Fc⁺ system. we estimated the electron affinity (EA) or lowest unoccupied molecular orbital (LUMO) and the ionization potential (IP) or highest occupied molecular orbital (HOMO) from the redox data. The LUMO level was calculated from: LUMO (eV) = -[E_{onset}^{red} (vs SCE) + 4.4]. Similarly the HOMO level was calculated from: HOMO (eV) = - [E_{onset}^{ox} (vs SCE) + 4.4], based on a SCE energy level of 4.4 eV relative to the vacuum. The electrochemical gap was calculated from: $\Delta E^{el} = |\text{HOMO-LUMO}|$ (in eV).

Theoretical modelling

Full geometry optimization of the ground state (S0) and frequency calculations were performed with Density Functional Theory (DFT)⁴⁻⁵ using the hybrid Becke-3 0 parameter exchange functional and the Lee-Yang-Parr non-local correlation functional⁶ (B3LYP) implemented in the Gaussian 16 program suite,⁷ using the 6-31G(d) basis set and the default convergence criterion implemented in the program. Geometry optimization of the first excited singlet and triplet states (S1 and T1) was performed using Time-Dependent Density Functional Theory (TD-DFT) calculations using the B3LYP functional and the 6-31+G(d) basis set. HOMO and LUMO representation and levels were obtained through TD-DFT calculations performed using the extended 6-311+G(d,p) basis set on the previously optimized geometry of S0. Spin density (SD) representation was obtained through TD-DFT calculations performed using the extended 6-311+G(d,p) basis set and a triplet spin on the previously optimized geometry of T1.

This work was granted access to the HPC resources of CINES under the allocation 2021-A0100805032 awarded by GENCI. Figures were generated with GaussView 6.0 and GaussSum 3.0.

The dimers were synthesized following the scheme presented below following literature procedure.⁸⁻¹¹

1,1''-(SBF)₂ : ¹¹

1,2''-(SBF)₂ : ¹¹

1,3''-(SBF)₂ : ¹¹

1,4''-(SBF)₂ : ¹¹

2,2''-(SBF)₂ : ⁸

2,3''-(SBF)₂ : This work (see below)

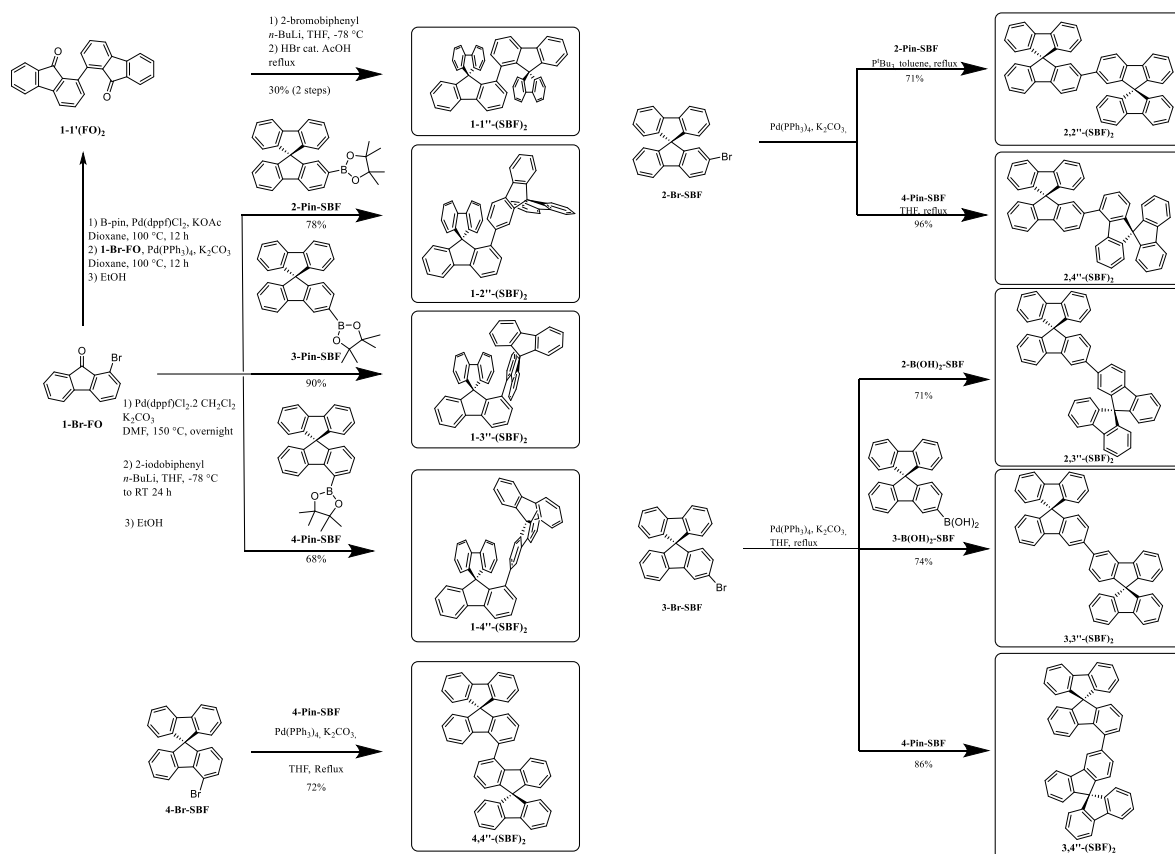
3,3''-(SBF)₂ : ¹⁰

2,4''-(SBF)₂ : This work (see below)

3,4''-(SBF)₂ : ¹⁰

4,4''-(SBF)₂ : ⁹

2,3''-(SBF)₂ and **2,4''-(SBF)₂** were synthesized as presented below.



Scheme S1. Synthesis of the ten SBF dimers

2,3''-(SBF)₂. 3-bromo-9,9'-spirobi[fluorene] (500 mg, 1.26 mmol, 1.0 eq), 9,9'-spirobi[fluorene]-2-ylboronic acid (546 mg, 1.51 mmol, 1.2 eq), K₂CO₃ (870 mg, 6.30 mmol, 5.0 eq) and [1,1'-bis(diphenylphosphino)ferrocene]palladium(II) dichloride (107 mg, 0.146 mmol, 0.12 eq) were dissolved in dry DMF (28 mL) under an argon atmosphere and refluxed overnight. After cooling to RT, a saturated solution of NH₄Cl was added and the crude was extracted with CH₂Cl₂. The organic layer was washed with H₂O, dried over MgSO₄, filtered and solvent was removed under reduced pressure. The residue was further purified with flash chromatography on silica gel [column conditions: silica cartridge (40 g); solid deposit on Celite®; λdetection: (254 nm, 280 nm); CH₂Cl₂/light petroleum from 5% to 30% over 40 min at 40 mL/min], giving the *title compound* as a white solid (563 mg, 0.893 mmol); yield 71%; m.p.: 265 °C, ¹H NMR (300 MHz, CD₂Cl₂) δ 7.98 (d, *J* = 7.9 Hz, 1H), 7.94 – 7.80 (m, 7H), 7.73 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.47 – 7.29 (m, 6H), 7.22 – 7.06 (m, 7H), 7.01 (d, *J* = 1.7 Hz, 1H), 6.76 (d, *J* = 7.6 Hz, 2H), 6.73 – 6.59 (m, 5H) ppm; ¹³C NMR (75 MHz, CD₂Cl₂) δ 150.0, 149.6, 149.5, 149.1, 149.0, 148.2, 142.8, 142.3, 142.2, 141.9, 141.8, 141.6, 141.4, 141.2, 128.3, 128.3, 128.2, 128.2, 127.4, 127.3, 124.3, 124.3, 124.2, 123.1, 120.9, 120.7, 120.6, 120.5, 119.1, 66.5, 66.1 ppm; IR (ATR, platinum) 2969.4, 2949.0, 2927.6, 2913.9, 2881.8, 2867.9, 2840.7, 1473.7, 1446.5, 1414.7, 1152.2, 1104.4, 1031.1, 948.9, 885.0, 817.2, 777.8, 748.2, 728.6, 663.6, 648.4, 633.6, 621.1, 594.0, 510.3, 417.2 cm⁻¹; HMRS (MALDI, DCTB): Found [M⁺] 630.236, C₅₀H₃₀ required 630.2342

2,4''-(SBF)₂. 4-bromo-9,9'-spirobi[fluorene] (500 mg, 1.26 mmol, 1.0 eq), 9,9'-spirobi[fluorene]-2-ylboronic acid (546 mg, 1.51 mmol, 1.2 eq), K₂CO₃ (870 mg, 6.30 mmol, 5.0 eq) and [1,1'-bis(diphenylphosphino)ferrocene]palladium(II) dichloride (107 mg, 0.146 mmol, 0.12 eq) were

dissolved in dry DMF (28 mL) under an argon atmosphere and refluxed overnight. After cooling to RT, a saturated solution of NH_4Cl was added and the crude was extracted with CH_2Cl_2 . The organic layer was washed with H_2O , dried over MgSO_4 , filtered and solvent was removed under reduced pressure. The residue was further purified with flash chromatography on silica gel [column conditions: silica cartridge (40 g); solid deposit on Celite[®]; λ detection: (254 nm, 280 nm); CH_2Cl_2 /light petroleum from 5% to 30 % over 60 min at 40 mL/min], giving the *title compound* as a white solid (762 mg, 1.20 mmol); yield 96%; mp= 209°C, ^1H NMR (300 MHz, CD_2Cl_2) δ 8.10 (dd, J = 7.8, 0.7 Hz, 1H), 8.05 – 7.95 (m, 1H), 7.93 – 7.81 (m, 4H), 7.63 (dd, J = 7.8, 1.6 Hz, 1H), 7.51 – 7.33 (m, 5H), 7.23 – 6.81 (m, 7H), 6.78 – 6.72 (m, 1H), 6.71 – 6.64 (m, 2H), 6.63 – 6.48 (m, 2H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 149.43, 149.21, 148.95, 148.62, 141.95, 141.78, 141.52, 141.43, 141.38, 140.32, 138.39, 137.74, 129.78, 128.98, 127.97, 127.92, 127.83, 127.77, 127.71, 127.31, 127.26, 127.04, 125.16, 123.83, 123.48, 122.89, 122.72, 120.54, 120.27, 120.05, 66.09, 65.54. HMRS (MALDI, DCTB): Found [M^+] 630.234, $\text{C}_{50}\text{H}_{30}$ required 630.2342

Electrochemistry

2,3''-(SBF)₂

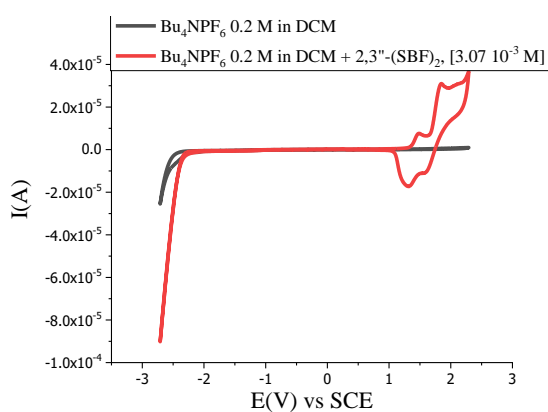


Figure S1. CVs recorded in Bu_4NPF_6 0.2M in DCM, Working Platinum electrode (diameter 1mm), sweep-rate 100 mV/s. In Black, CVs of the electrolytic medium before addition of $2,3''\text{-(SBF)}_2$, in Red: CVs in presence of $2,3''\text{-(SBF)}_2$ [3.07×10^{-3} M].

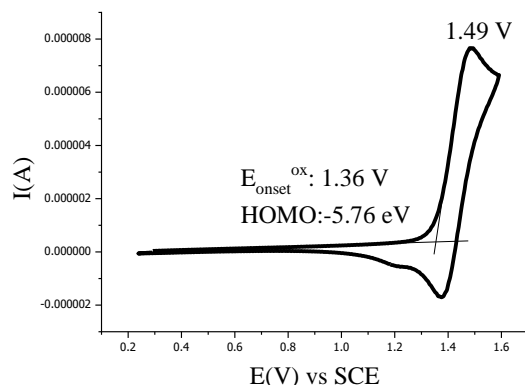


Figure S2. CVs recorded in Bu_4NPF_6 0.2M in DCM, working Platinum electrode (diameter 1mm), sweep-rate 100 mV/s in presence of $2,3''\text{-(SBF)}_2$ [$3.07 \cdot 10^{-3}\text{M}$], one cycle between 0.23 and 1.59 V.

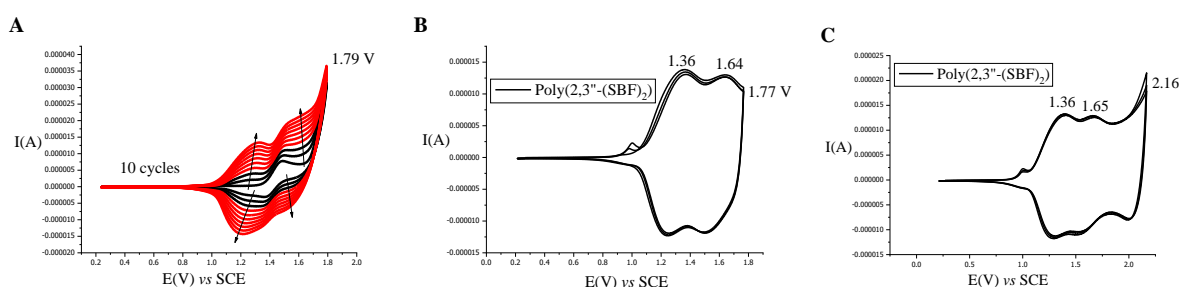


Figure S3. CVs recorded in Bu_4NPF_6 0.2M in DCM, Working Platinum electrode (diameter 1mm), sweep-rate 100 mV/s. **A.** in presence of $2,3''\text{-(SBF)}_2$ [$3.07 \cdot 10^{-3}\text{M}$], ten cycles between 0.23 and 1.79 V. **B** and **C.** Study of the modified platinum electrode ($\text{Poly}(2,3''\text{-(SBF)}_2)$ deposit formed in **A**), in Bu_4NPF_6 0.2M in DCM between 0.23 and 1.77 V (**B**) or 0.23 and 2.16 V (**C**).

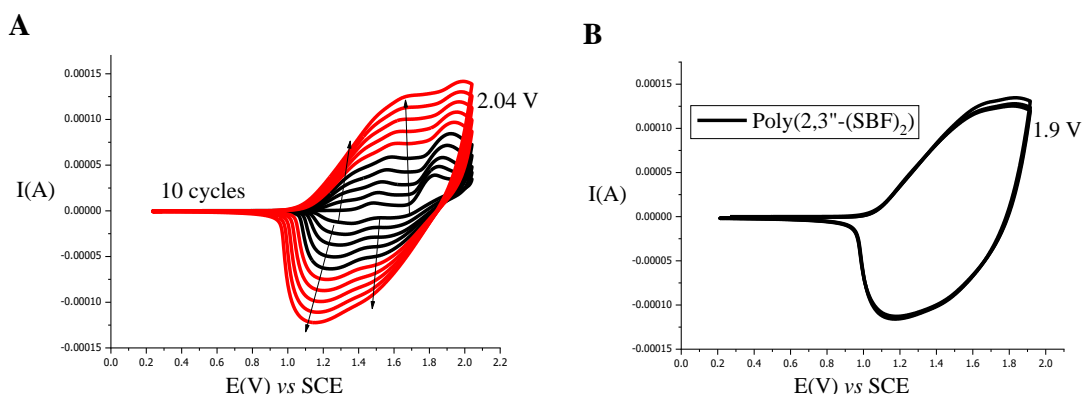


Figure S4. CVs recorded in Bu_4NPF_6 0.2M in DCM, Working Platinum electrode (diameter 1mm), sweep-rate 100 mV/s. **A.** in presence of $2,3''\text{-(SBF)}_2$ [$3.07 \cdot 10^{-3}\text{M}$], ten cycles between 0.23 and 2.04 V. **B.** Study of the modified platinum electrode ($\text{Poly}(2,3''\text{-(SBF)}_2)$ deposit formed in **A**), in Bu_4NPF_6 0.2M in DCM between 0.2 and 1.9 V.

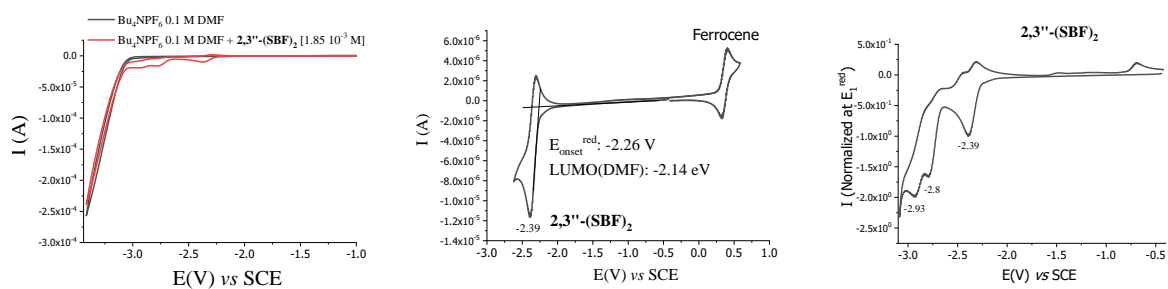


Figure S5. **Left.** CVs recorded in Bu_4NPF_6 0.1M in DMF, Working Platinum electrode (diameter 1mm), sweep-rate 100 mV/s, sweeps between -1.0 and -3.5 V. In Black, CVs of the electrolytic medium before addition of $2,3''\text{-(SBF)}_2$, in Red: CVs in presence of $2,3''\text{-(SBF)}_2$ [$1.85 \cdot 10^{-3}$ M]. **Middle.** CVs recorded in Bu_4NPF_6 0.1M in DMF, Working Platinum electrode (diameter 1mm), sweep-rate 100 mV/s, cycle between 0.6 and -2.6 V in presence of $2,3''\text{-(SBF)}_2$ [$1.78 \cdot 10^{-3}$ M] and of ferrocene. **Right.** CVs recorded in Bu_4NPF_6 0.1M in DMF, Working Platinum electrode (diameter 1mm), sweep-rate 100 mV/s, cycle between -0.4 and -3.1 V in presence of $2,3''\text{-(SBF)}_2$ [$1.85 \cdot 10^{-3}$ M].

2,4''-(SBF)₂

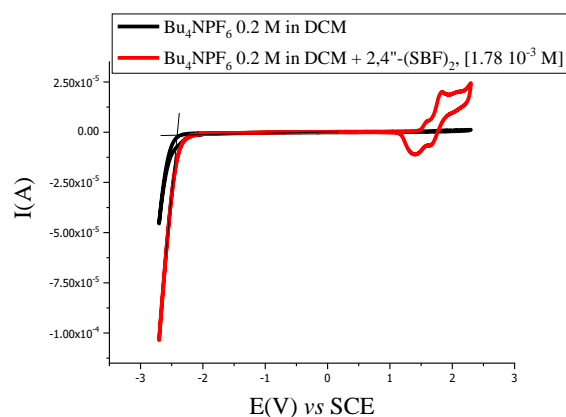


Figure S6. CVs recorded in Bu₄NPF₆ 0.2M in DCM, Working Platinum electrode (diameter 1mm), sweep-rate 100 mV/s. In Black, CVs of the electrolytic medium before addition of **2,4''-(SBF)₂**, in Red: CVs in presence of **2,4''-(SBF)₂** [1.78 10⁻³M].

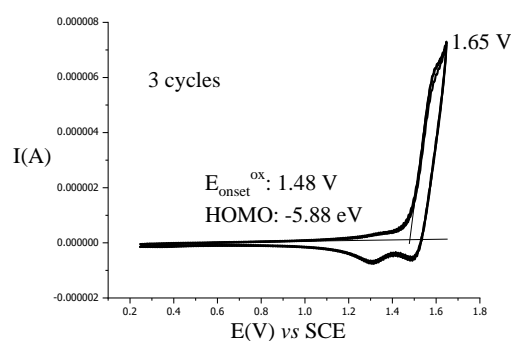


Figure S7. CVs recorded in Bu₄NPF₆ 0.2M in DCM, Working Platinum electrode (diameter 1mm), sweep-rate 100 mV/s in presence of **2,4''-(SBF)₂** [1.78 10⁻³M], three cycles between 0.2 and 1.65 V.

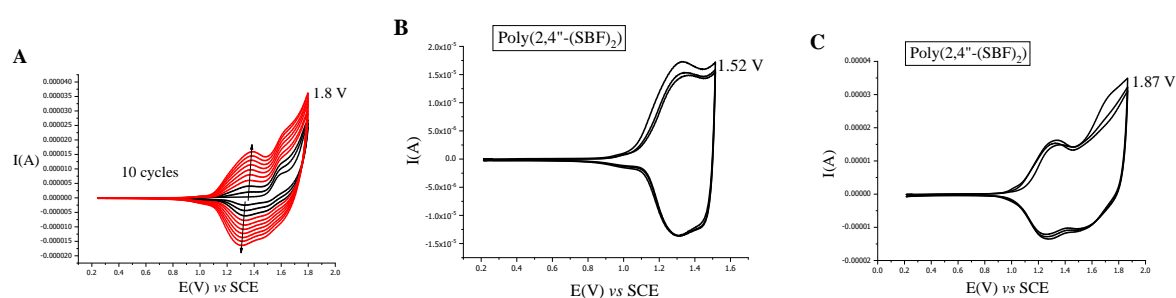


Figure S8. CVs recorded in Bu₄NPF₆ 0.2M in DCM, Working Platinum electrode (diameter 1mm), sweep-rate 100 mV/s. **A.** in presence of **2,4''-(SBF)₂** [1.78 10⁻³M], ten cycles between 0.2 and 1.80 V. **B** and **C.** Study of the modified platinum electrode (**Poly(2,4''-(SBF)₂** deposit formed in **A**), in Bu₄NPF₆ 0.2M in DCM between 0.2 and 1.52 V (**B**) or 0.2V and 1.87 V (**C**).

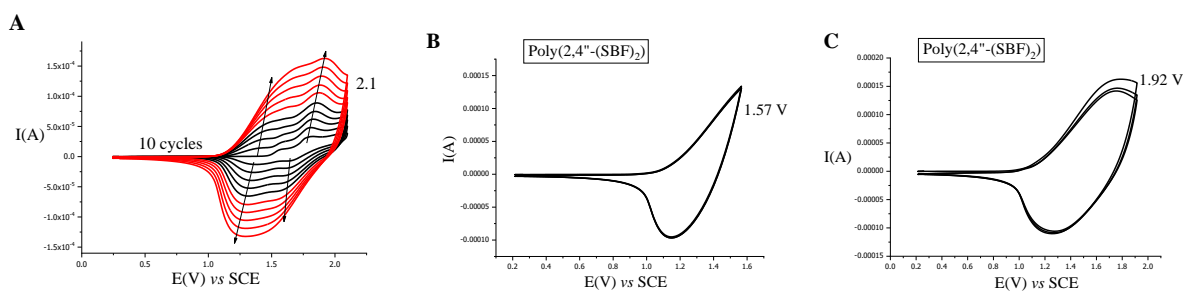


Figure S9. CVs recorded in Bu_4NPF_6 0.2M in DCM, Working Platinum electrode (diameter 1mm), sweep-rate 100 mV/s. **A.** in presence of $2,4''\text{-(SBF)}_2$ [$1.78 \cdot 10^{-3}\text{M}$], ten cycles between 0.2 and 2.1 V. **B** and **C.** Study of the modified platinum electrode ($\text{Poly}(2,4''\text{-(SBF)}_2)$ deposit formed in **A**), in Bu_4NPF_6 0.2M in DCM between 0.2 and 1.57 V (**B**) or 0.2V and 1.92 V (**C**).

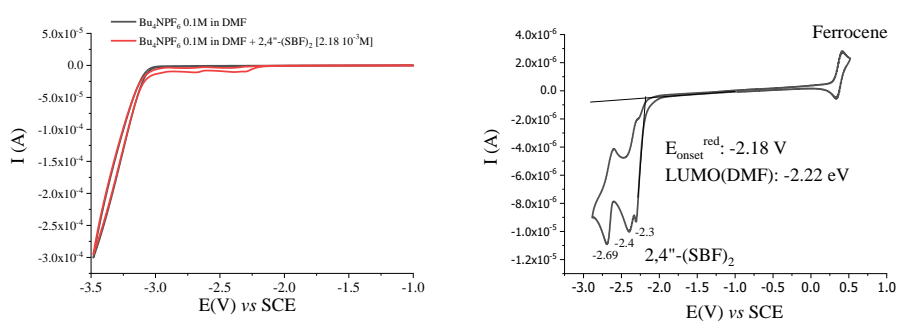
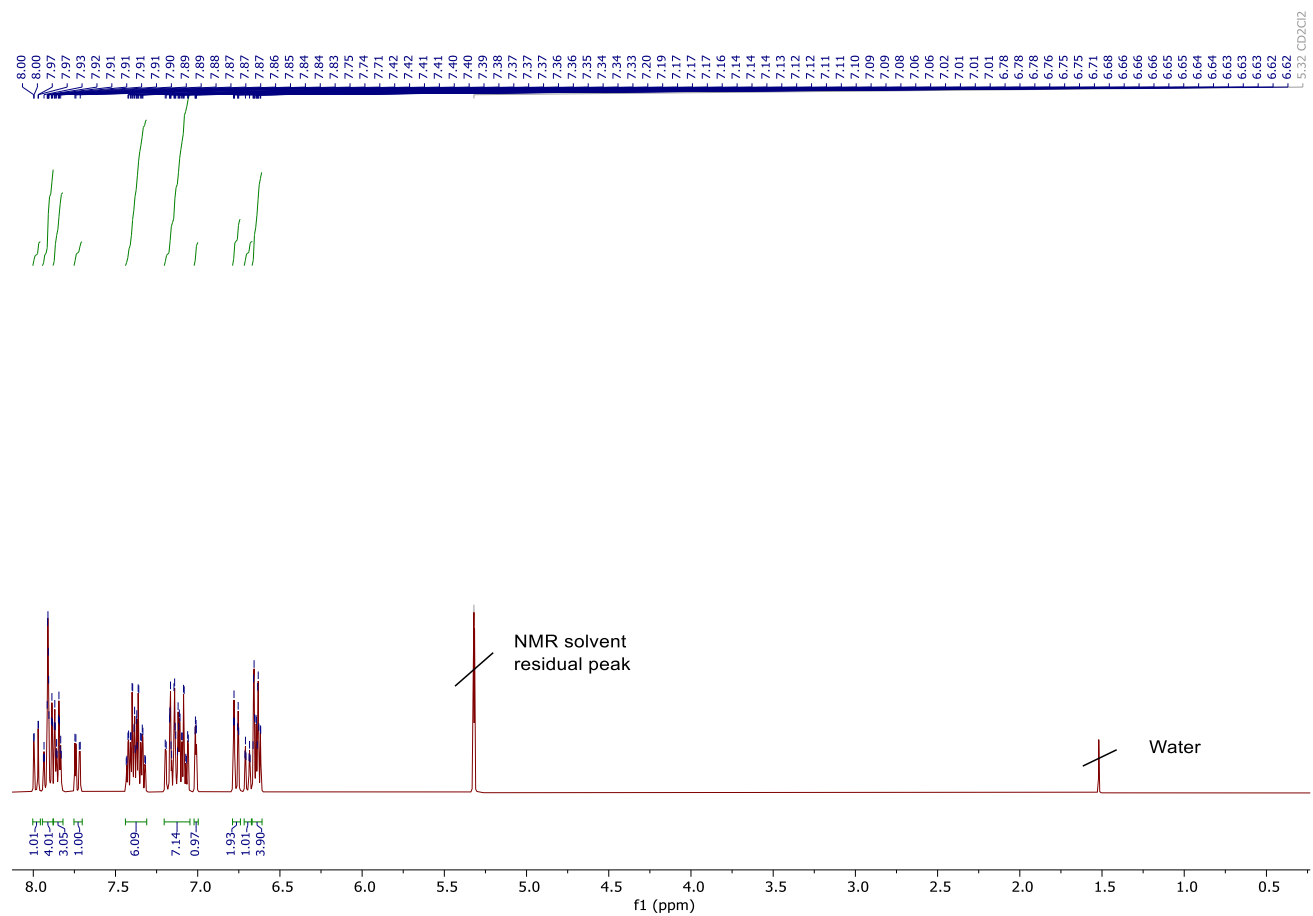


Figure S10. **Left.** CVs recorded in Bu_4NPF_6 0.1M in DMF, Working Platinum electrode (diameter 1mm), sweep-rate 100 mV/s, cycles between -1.0 and -3.5 V. In Black, CVs of the electrolytic medium before addition of $2,4''\text{-(SBF)}_2$, in Red: CVs in presence of $2,4''\text{-(SBF)}_2$ [$2.18 \cdot 10^{-3}\text{M}$]. **Right.** CVs recorded in Bu_4NPF_6 0.1M in DMF, Working Platinum electrode (diameter 1mm), sweep-rate 100 mV/s, cycle between 0.59 and -2.9 V in presence of $2,4''\text{-(SBF)}_2$ [$2.18 \cdot 10^{-3}\text{M}$] and of ferrocene.

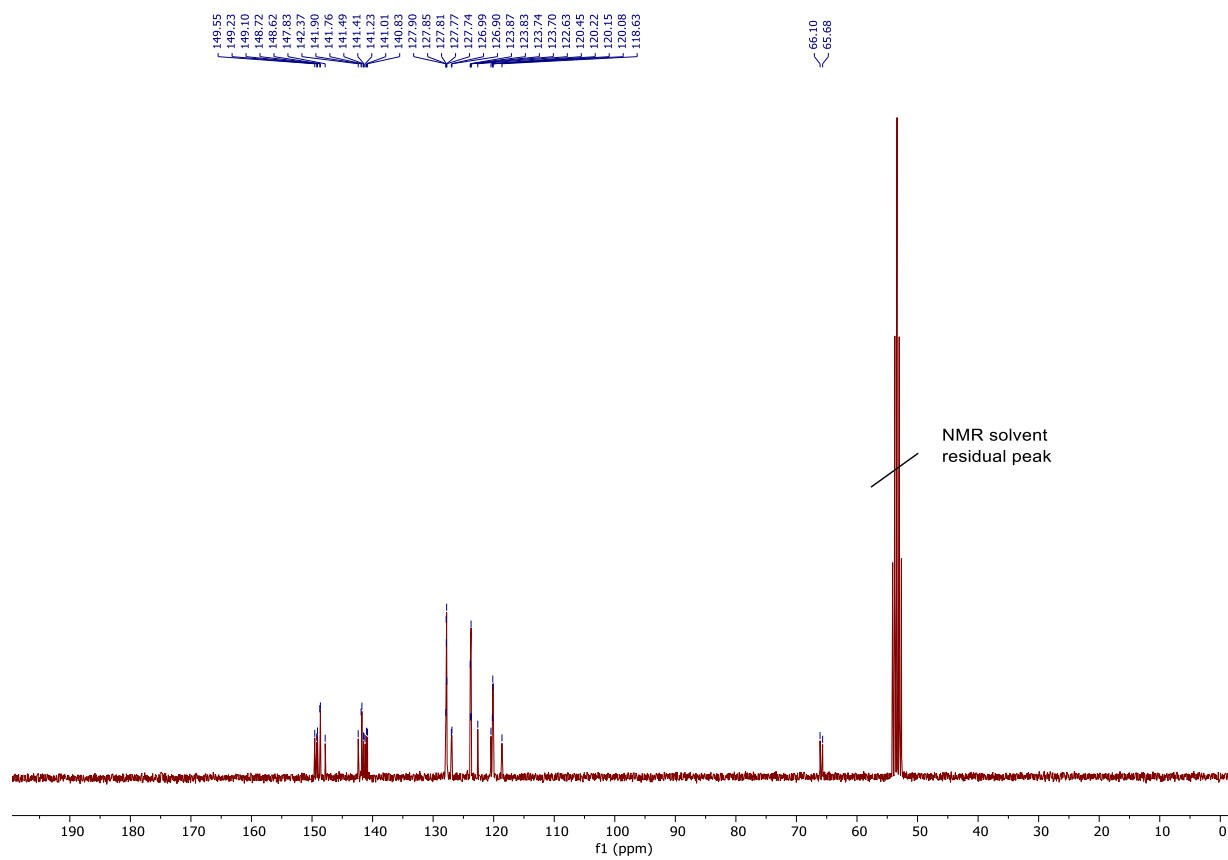
COPY OF NMR SPECTRA

2,4''-(SBF)₂

¹H-NMR (CD₂Cl₂)

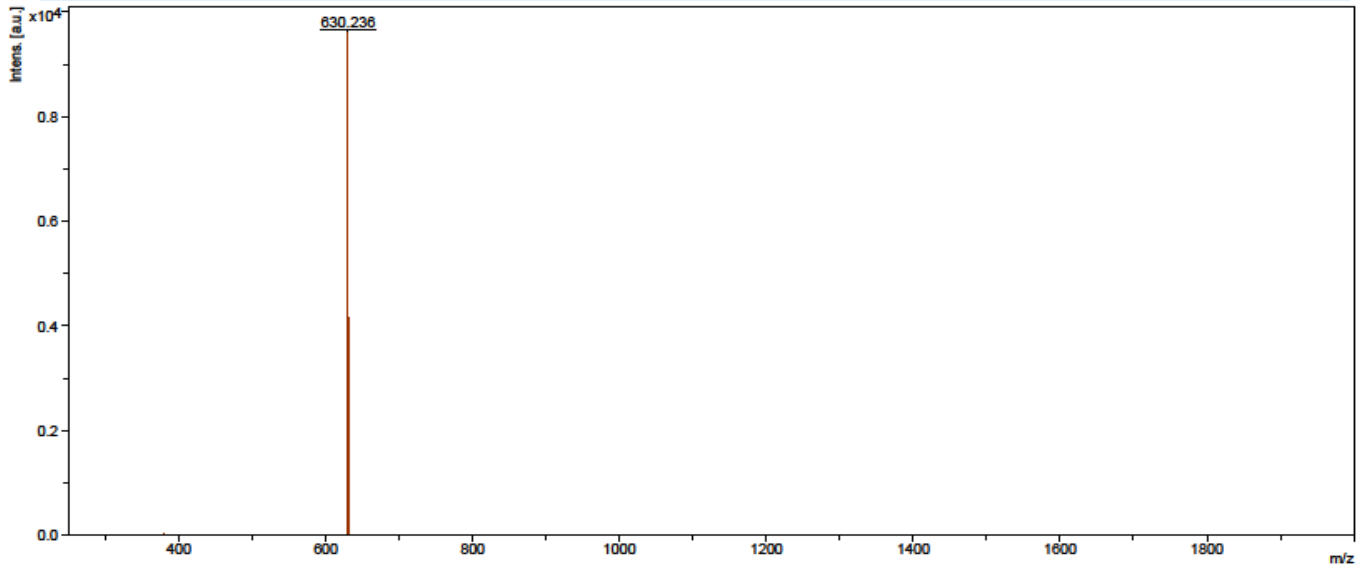


$^{13}\text{C-NMR}$ (CD_2Cl_2)



Centre régional de mesures physiques de l'Ouest (CRMPO) - RAPPORT D'ANALYSE

F. LUCAS 2,3-diSBF

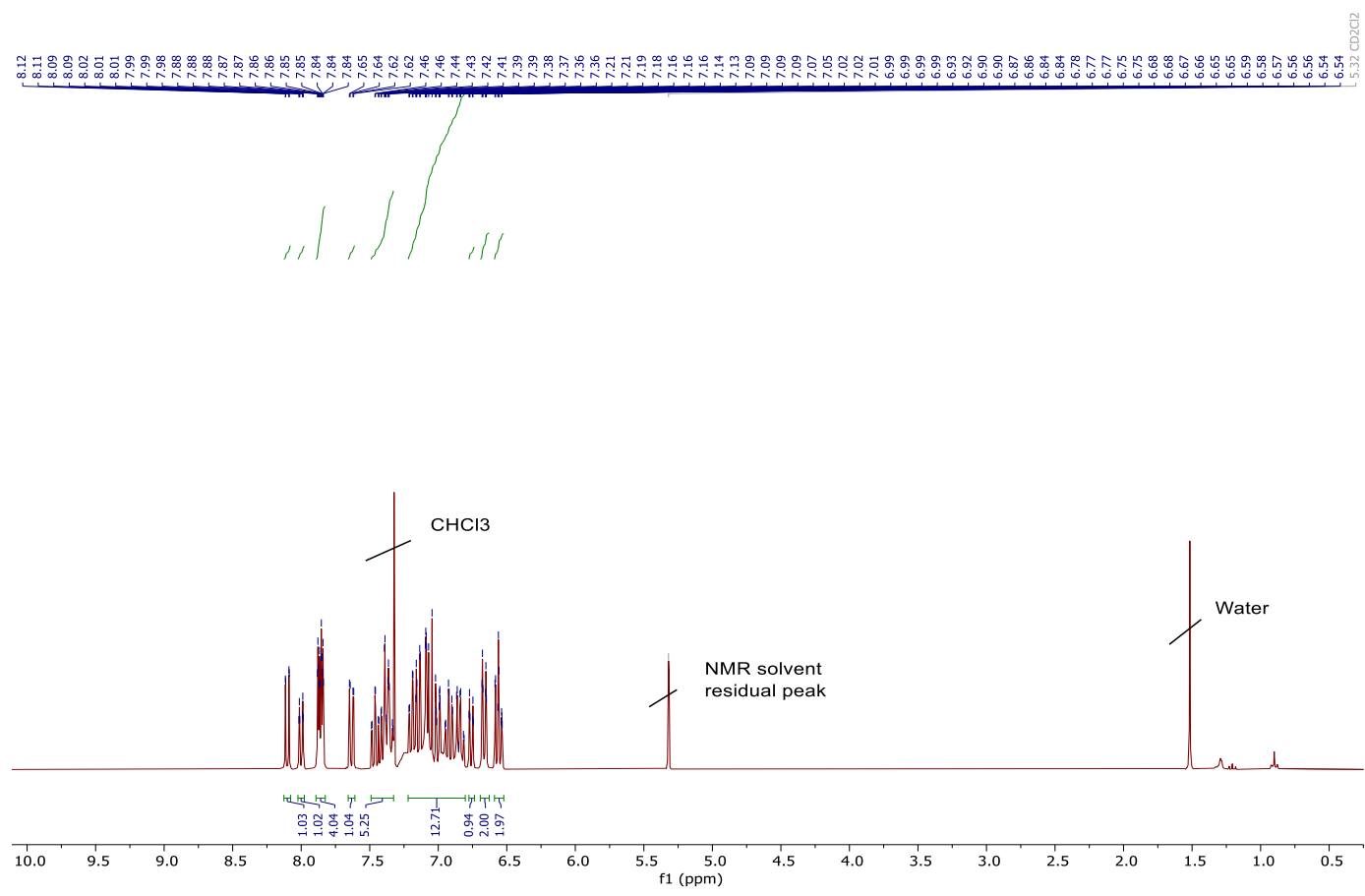


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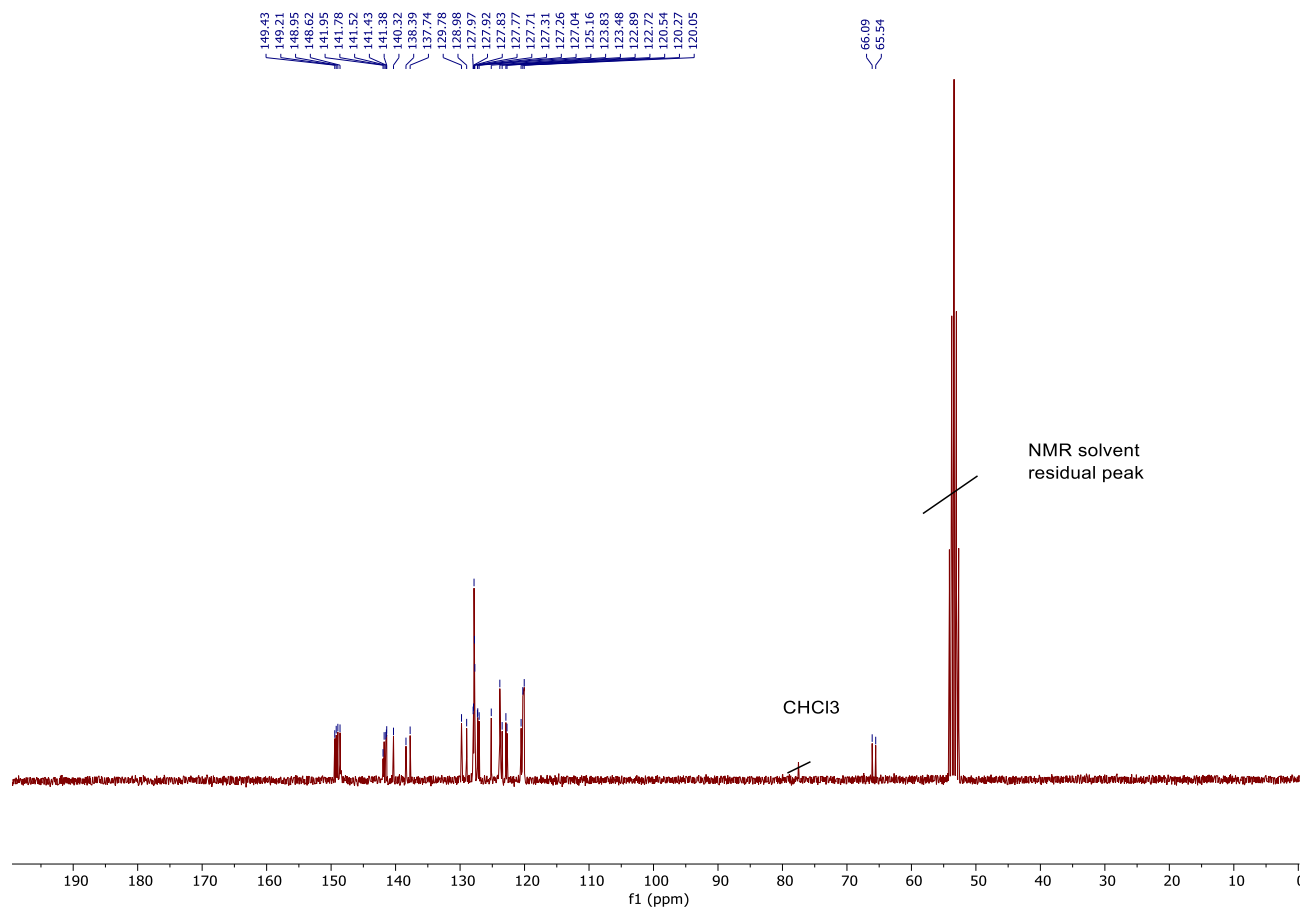
Bruker Daltonics

2,4''-(SBF)₂

¹H-NMR (CD₂Cl₂)

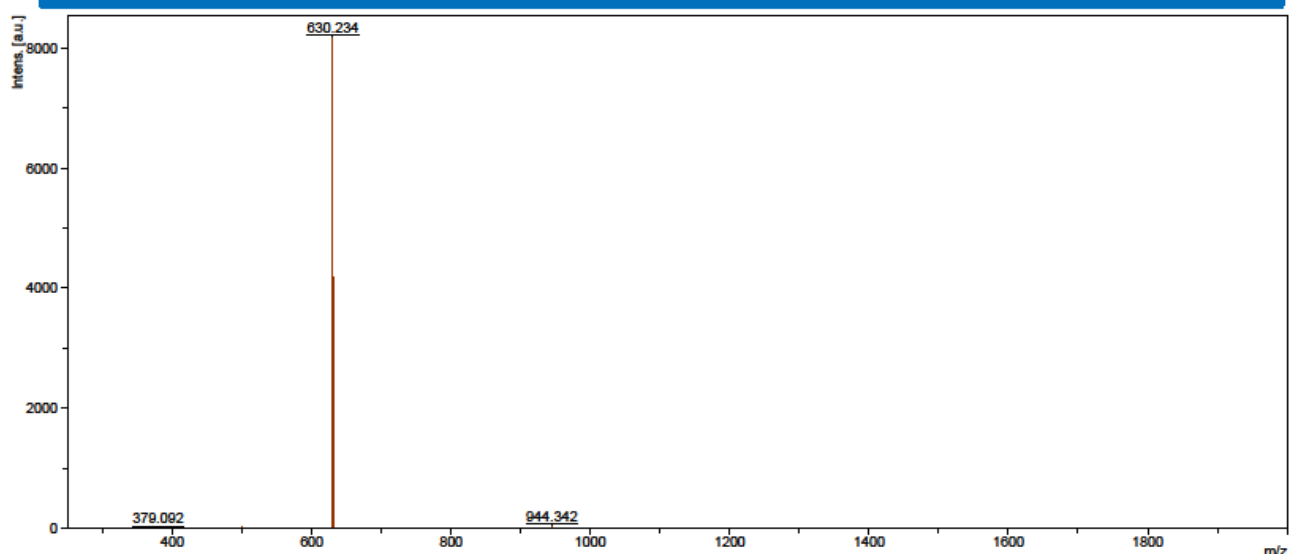


¹³C-NMR (CD₂Cl₂)



Centre régional de mesures physiques de l'Ouest (CRMPO) - RAPPORT D'ANALYSE

F. LUCAS 2,4-diSBF



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