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Supporting Information for

Nanoheterogeneous Catalysis in Electrochemically Induced Olefin Perfluoroalkylation

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Experimental

General Considerations

Reactions were carried out under ambient atmosphere. Yields refer to purified and spectroscopically pure compounds. NMR experiments were carried out with Bruker spectrometers AVANCE-400 and AVANCE-500. Chemical shifts are reported on the δ (ppm) scale relative to the residual solvent signals for ^1H and ^{13}C and to external C_6F_6 (−164.9 ppm) for ^{19}F NMR spectra. A Bruker D8 Quest diffractometer was used for X-ray crystal structure determinations. The amount of Ni(II) in supernatant solutions was performed using atomic absorbance spectrometer AAS 1N (Carl Zeiss Jena) with the use of oxidative air-acetylene flame (air 520 $l \cdot h^{-1}$; acetylene – 100 $l \cdot h^{-1}$). Detection wavelength was 324.8 nm. Calibration plots were built in 0.05-1.0 $\mu g \cdot ml^{-1}$ and 1.0-10.0 $\mu g \cdot ml^{-1}$ range of $NiCl_2$ in the presence of 0.1 M HNO_3 as a background. The solutions containing more than 10 $\mu g \cdot ml^{-1}$ of Ni(II) were diluted by the background solution. Preparative electrolyses were carried out using a B5-49 dc source at a current strength of 100 mA h^{-1} in 30-mL three-electrode cell. The potential of the working electrode was detected by a V7-27 dc voltmeter. Ag/$AgNO_3$, 10^{-2} M in CH_3CN was a reference electrode. The working surface of the platinum cylindrical cathode used as a working electrode was 20.0 cm^2. A ceramic plate with the pore size 900 nm was used as a membrane. A platinum grid served as an anode, and the anolyte was a saturated solution of the background used in the catholyte in the corresponding solvent. Purified anhydrous solvents were stored under a dry argon atmosphere. The supporting salt $[Et_4N]BF_4$ was prepared by mixing an aqueous solution of $[Et_4N]OH$ and HBF_4 until the neutral pH value of the indicator. The precipitate formed ($[Et_4N]BF_4$) was filtered off, doubly recrystallized from ethanol, and dried in a vacuum desiccator at 100 °C for 48 h. 6-H-Perfluoroiodohexane (purchased from P&M Invest), alpha-methylstyrene (Acros Organics) and alpha,4-dimethylstyrene (Alfa Aesar) were used without further purification. $[(bpy)NiBr_2]$ complex was prepared according the reported procedure [1].

Synthesis of the silica nanoparticles decorated by AEPTS.

Synthesis of the silica nanoparticles and their decoration by AEPTS groups were performed according to reverse microemulsion procedure, which is documented in our previous work [2]. The quantitative analysis of amino-groups at the surface of silica nanoparticles modified by AEPTS was carried out due to the fluorescent procedure with the use of fluorescamine [3]. Alanine solutions in the concentration range 0,408-5,37μM were used to make the calibration curve. Excitation of samples was performed at 390 nm, and emission detected at 490 nm with 2 nm slit width for both excitation and emission.

Immobilization of the $[(bpy)NiBr_2]$ complex.

An aqueous dispersion (2 ml) of AEPTS-SNs (11 $g \cdot L^{-1}$) was mixed with 0.5 ml of an aqueous solution of $[(bpy)NiBr_2]$ (0.1 M) and 1.5 ml of water. The mixture was ultrasonificated within 20 minutes, with further intensive stirring for 30 minutes. Afterwards the AEPTS-SNs were separated from the aqueous phase by the centrifugation within 30 minutes. The concentration of $[(bpy)NiBr_2]$ in the aqueous phase after the separation was determined by atomic absorption spectroscopy. The quantity of $[(bpy)NiBr_2]$ bound with the AEPTS-SNs was calculated from the difference between the Ni(II) concentration before (0.0106 M) and after (0.0097 M) the mixing with aqueous colloids of the nanoparticles (5.5 $g \cdot L^{-1}$) and the phase separation. These values are averaged from three independent measurements. Taking into account the molar concentrations of the Ni(II) complexes ($0.86 \cdot 10^{-3}$ M) and AEPTS-SNs ($2.3 \cdot 10^{-7}$ M) the average number of the Ni(II) complexes per each AEPTS-SN is 3700, which confirms with the above mentioned number of AEPTS-groups on the silica surface. The concentration of the nanoparticles was calculated on the basis of their density (1.96 $g \cdot L^{-1}$) and radius (17 nm). The detailed description of the calculation is represented in our previous work [4].

Scanning electron microscopy analysis

The immobilized catalyst was investigated by electron microscopy analysis before and after perfluoroalkylation reaction (the reaction described in Table 1, entry 1 of the article). The solutions were applied to the surface of titanium foil previously cleared by sonification in acetone. Then the sample was exsiccated at low heat (not above 40 °C). The morphology of sample surfaces were characterized in plan-view by SEM using high-resolution microscope Merlin Carl Zeiss combined with ASB (Angle Selective Backscattering) and SE InLens (Secondary Electrons Energy selective Backscattering) detectors, which was also equipped for energy-dispersive X-ray spectroscopy (EDX) analysis with AZTEC X-MAX energy-dispersion spectrometer from Oxford Instruments. Before the reaction, the weight ratios Ni : Si was 0.03-0.04, that consists with the result obtained by the fluorescent analysis (0.02). After the reaction, the weight ratios Ni : Si was 0.03-0.08, and the weight ratios Ni : Br was 0.37-0.40.

Preparative electrolysis

3.44 mmol of the olefinic substrate, 3.44 mmol of 6-H-perfluoroiodohexane and 0.34 mmol of $[(bpy)NiBr_2]$ complex were mixed in 20 ml of DMF-water mixture in an electrochemical cell with separation of anode and cathode compartments. Electrolysis were carried out at ambient temperature under argon atmosphere and vigorous stirring. The cathode potential was equal to -1.5 V vs. Ag/$AgNO_3$ reference electrode (the first reduction wave for $[(bpy)NiBr_2]$ complex).The amount of electricity passed through the electrolyte were $2F$ per one mole of 6-H-perfluoroiodohexane. After completing the electrolysis, the immobilized catalyst was separated by centrifugation, and the solution was washed with distilled water (100 ml) and extracted with benzene (three times with 30 ml). The organic layer was dried over magnesium sulfate and filtered. The residual solution was concentrated under reduced pressure, and the products were purified by silica gel column chromatography (ethyl acetate-hexane).

Test of Immobilized Catalyst Leaching

4 ml of aqueous solution of [(bpy)$NiBr_2$] complex immobilized on AEPTS-SNs (1 mol %) were added to 16 ml of DMF solution of 3.44 mmol of α-methylstyrene and 3.44 mmol of 6-H-perfluorohexyl iodide. The mixture was kept stirring for 4 hours. Then, the heterogeneous catalyst was separated and the residue solution was tested in electroreduction reaction performed as described above. No transformation of the olefinic substrate was observed and no dimeric or monomeric products were obtained in the reaction mixture after completing the electrolysis.

Characterization of New Compounds:

2,3-Dimethyl-2,3-bis(4’-methylphenyl)-1,4-bis(6-H-perfluorohexyl)butane (1a). Colorless crystals. Both diastereomers: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.56 (dd, *J*=18.3; 3.1 Hz, 6H); 2.35 (s, 6H); 2.07-2.21, 2.27-2.41, 2.51-2.64, 3.05-3.18 (m, 4H); 5.99 (tt, *J*=51.9; 5.2 Hz, 2H); 6.88-7.10 (m, 8H). ^{19}F NMR (470.6 MHz, $CDCl_3$): δ = -101.54-(-102.20) (m, 2 CF_2); -109.53-(-110.64) (m, 2 CF_2); -120.15 (2 CF_2); -120.30 (2 CF_2); -122.02-(-122.34) (m, 8 CF_2); -128.15 (4 CF_2); -135.61 (2 CF_2); -135.70 (2 CF_2). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.80 (2C); 21.04 (d, *J*=4.4 Hz); 21.50 (d, *J*=4.0 Hz); 34.42 (t, *J*=18.9 Hz); 34.48 (t, *J*=19.1 Hz); 46.19; 46.41; 107.59 (tt,*J*=254.9; 31.4 Hz); no signals for other carbons in CF_2 groups were detected due to strong spin-spin couplings; 127.93; 128.04 (2C); 128.19; 136.48; 136.53; 137.63; 137.93.

1-(6H-Perfluorohexyl)-2-(4’-methylphenyl)propane (1b). Colorless oil. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.38 (dd, *J*=6.9; 0.8 Hz, 3H); 2.33 (s, 3H);2.21-2.47 (m, 2H); 3.20-3.27 (m, 1H); 6.03 (tt, *J*=51.9; 5.2 Hz, 1H); 7.10-7.15 (m, 4H). ^{19}F NMR (470.6 MHz, $CDCl_3$): δ = -111.58 (ABq, $\Delta\nu_{AB}$=654.6 Hz, J_{AB}=270.0 Hz); -120.28; -122.07; -122.22; -128.09; -135.56. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 20.96; 22.85; 32.58; 38.42 (t, *J*=21.3 Hz); 107.59 (tt,*J*=255.1; 30.8 Hz); no signals for other carbons in CF_2 groups were detected due to strong spin-spin couplings; 126.44 (2C); 129.38 (2C); 136.24; 142.74.

1-(6H-Perfluorohexyl)-2-phenylpropane (2b). Colorless oil. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.42 (d, *J*=7.1, 3H); 2.26-2.52 (m, 2H); 3.25-3.32 (m, 1H); 6.03 (tt, *J*=52.0; 5.2 Hz, 1H),; 7.23-7.36 (m, 5H). ^{19}F NMR (470.6 MHz, $CDCl_3$): δ = -111.59 (ABq, $\Delta\nu_{AB}$=628.2 Hz, J_{AB}=270.0 Hz); -120.32; -122.12; -122.24; -128.17; -135.65. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 22.74; 33.03; 38.38 (t, *J*=21.1 Hz); 107.63 (tt, *J*=254.8; 31.3 Hz); 118.46 (tt,*J*=255.9; 30.7 Hz); no signals for other carbons in CF_2 groups were detected due to strong spin-spin couplings; 126.60 (2C); 126.71; 128.74 (2C); 145.73.

References

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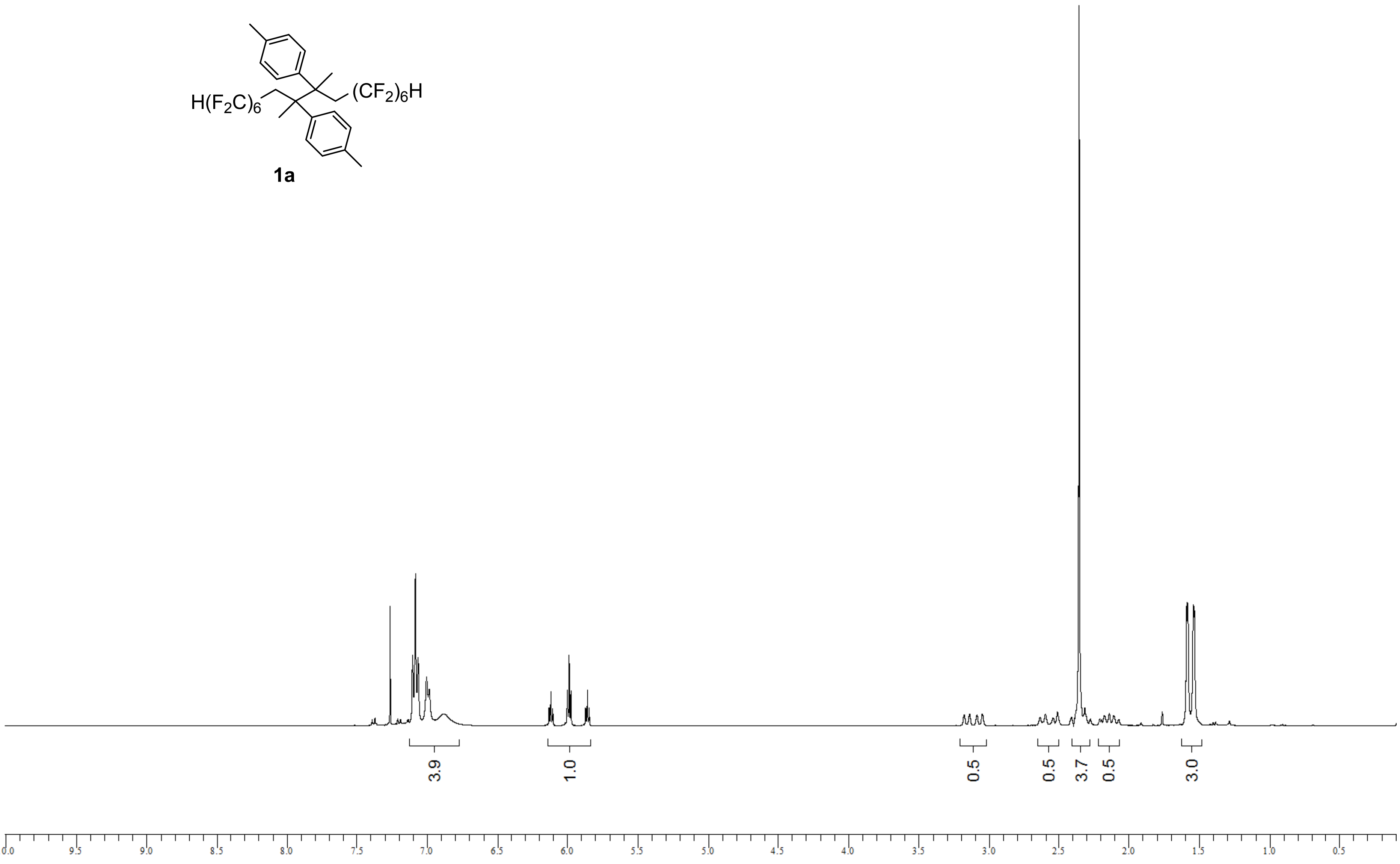
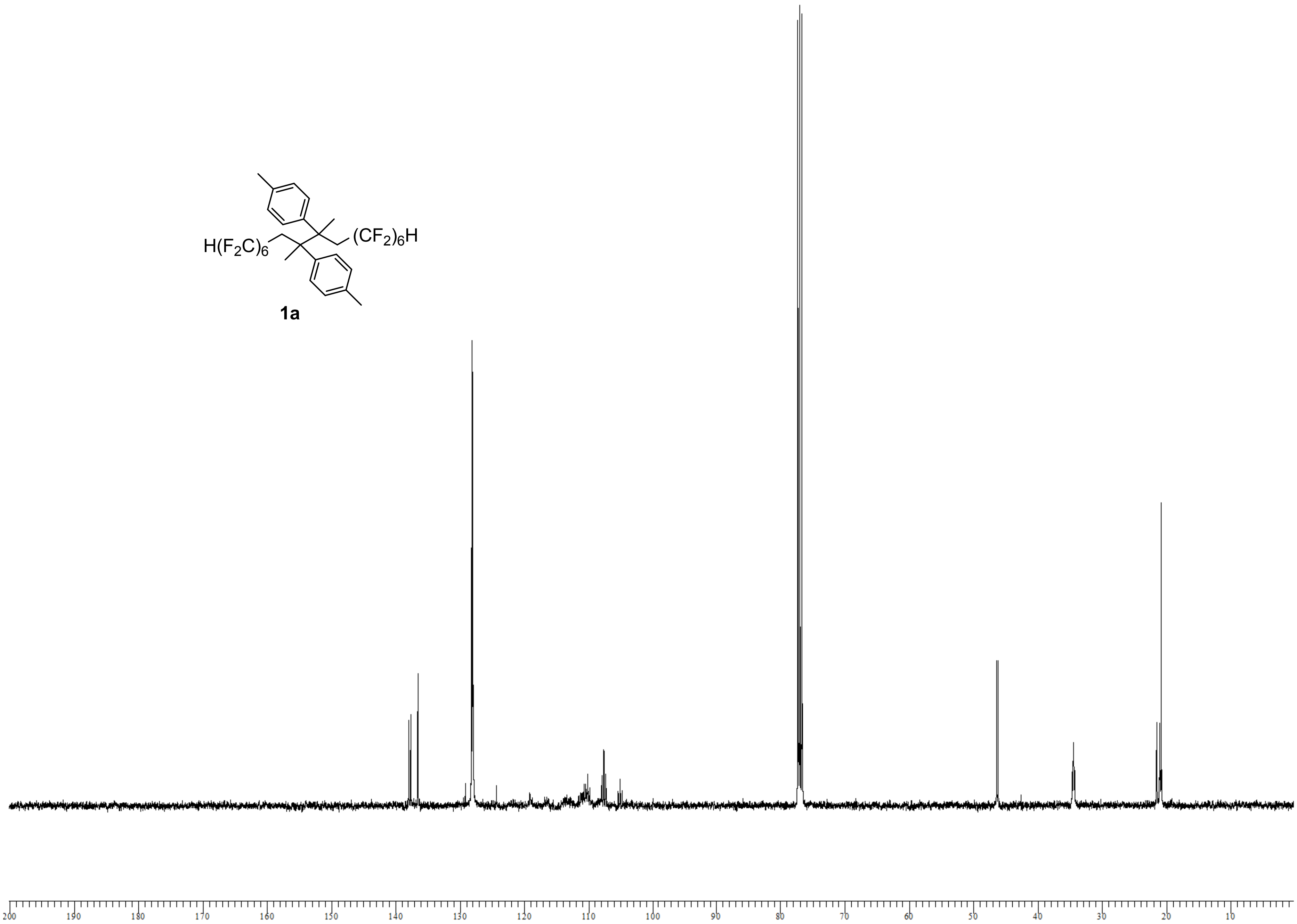
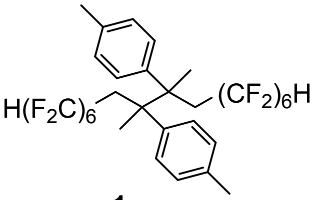
Compound **1a**: both diastereomers ^{1}H NMR (400.1 MHz, $CDCl_3$)



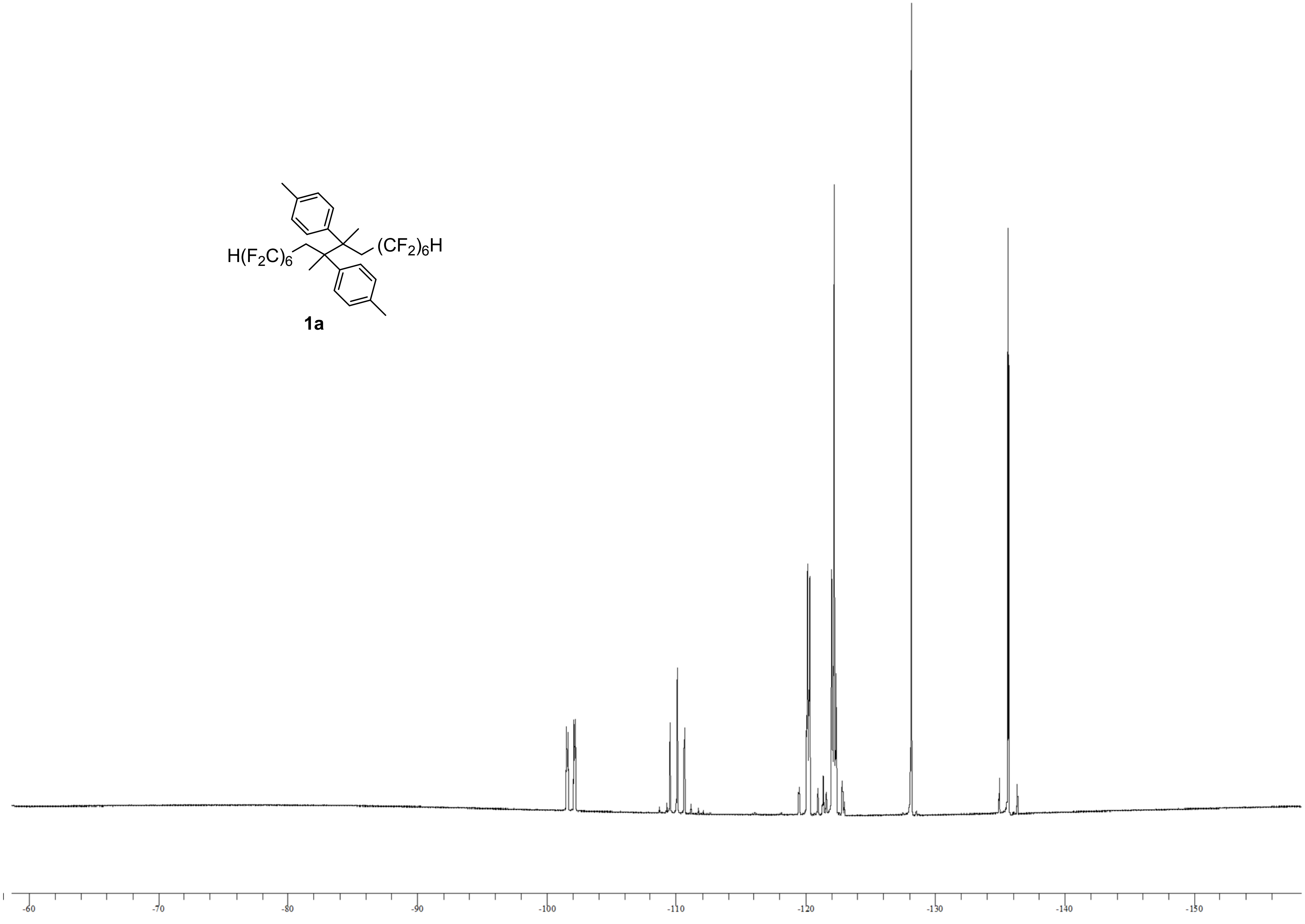
Compound **1a**: both diastereomers ^{13}C NMR (100.6 MHz, $CDCl_3$)



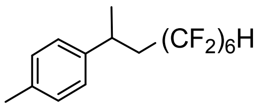
Compound **1a**: both diastereomers ^{19}F NMR (470.6 MHz, CDCl$_3$)



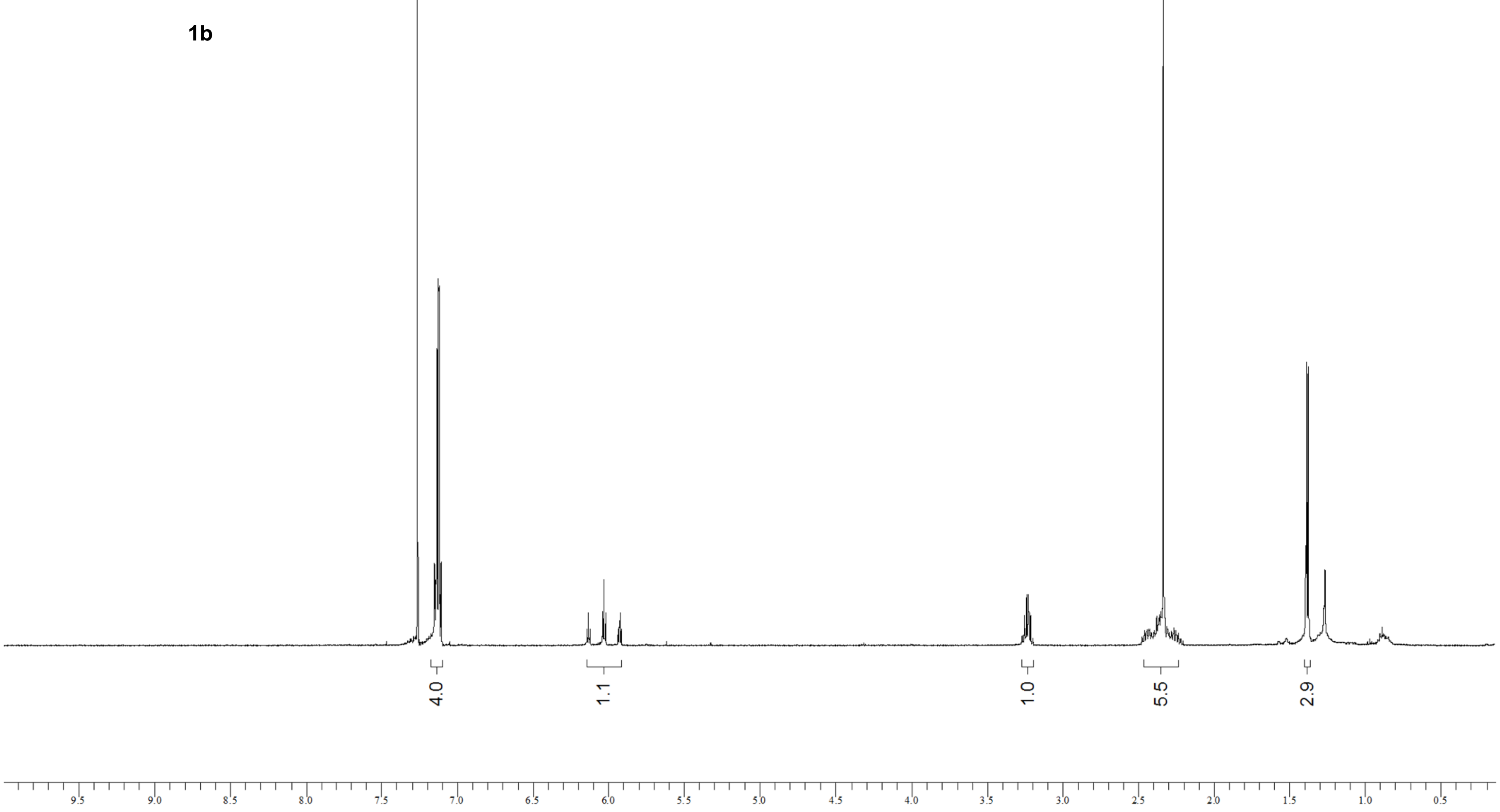
1a



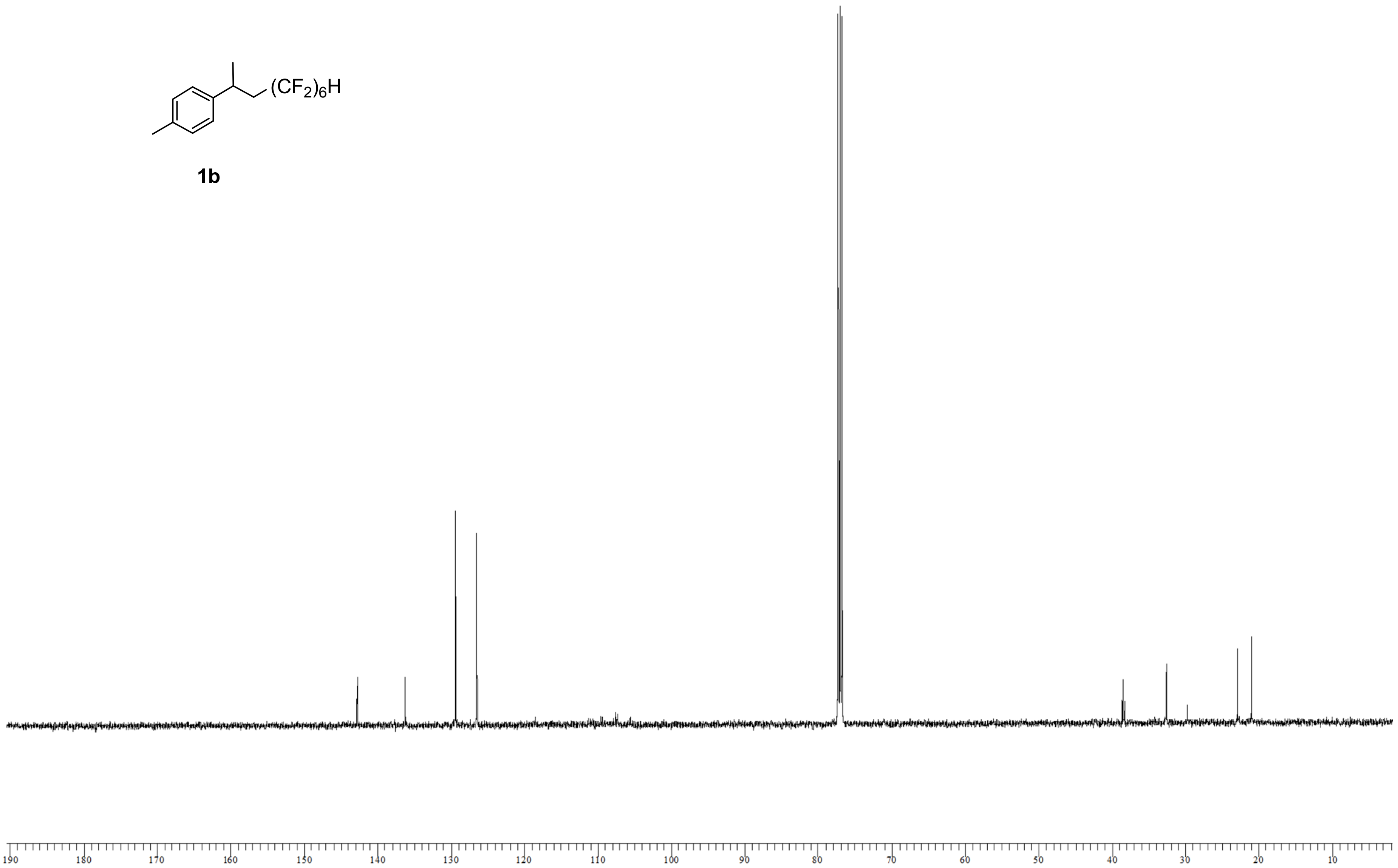
Compound **1b**: ^{1}H NMR (500.1 MHz, CDCl$_3$)



1b

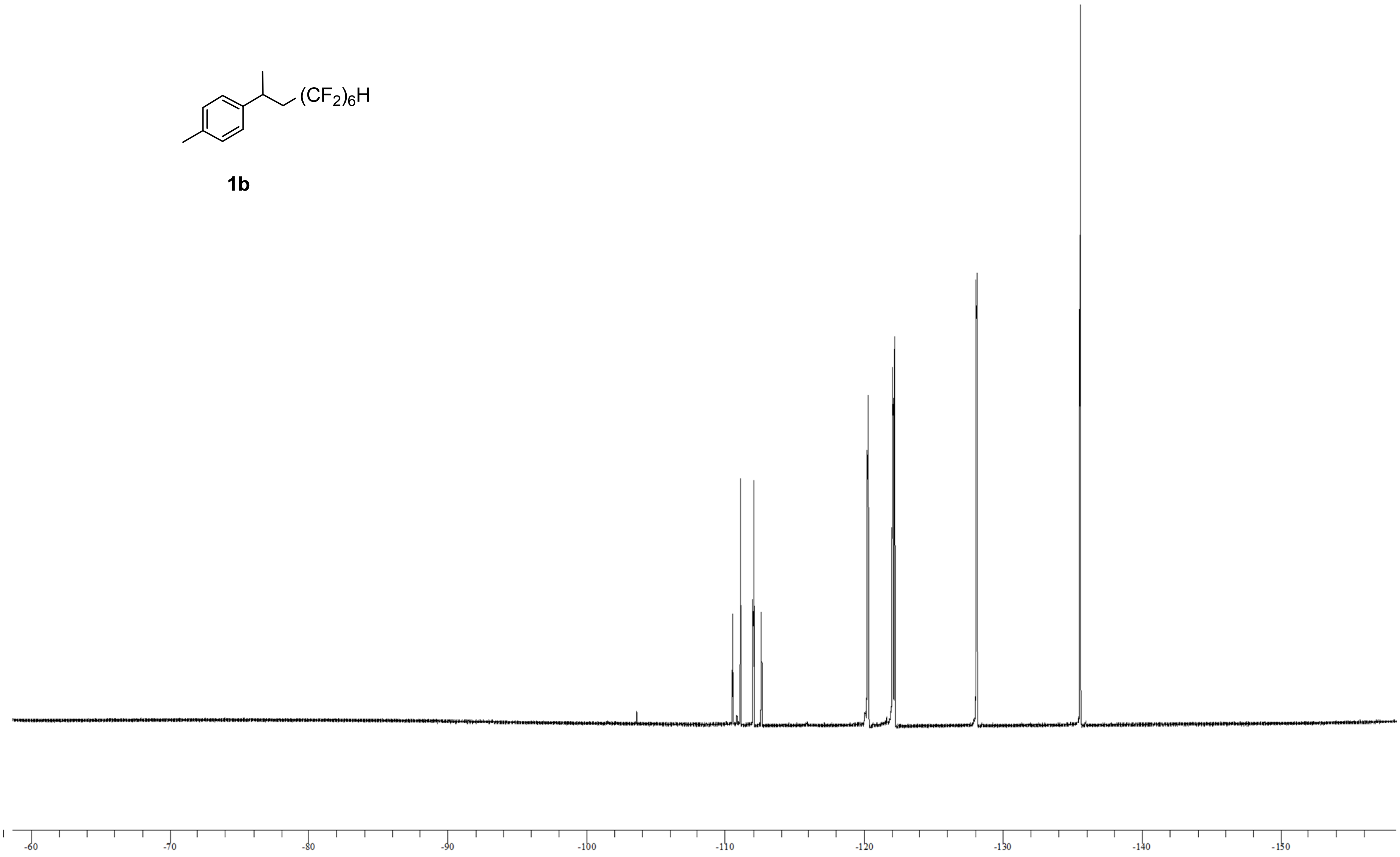


Compound **1b**: ^{13}C NMR (125.8 MHz, CDCl$_3$)

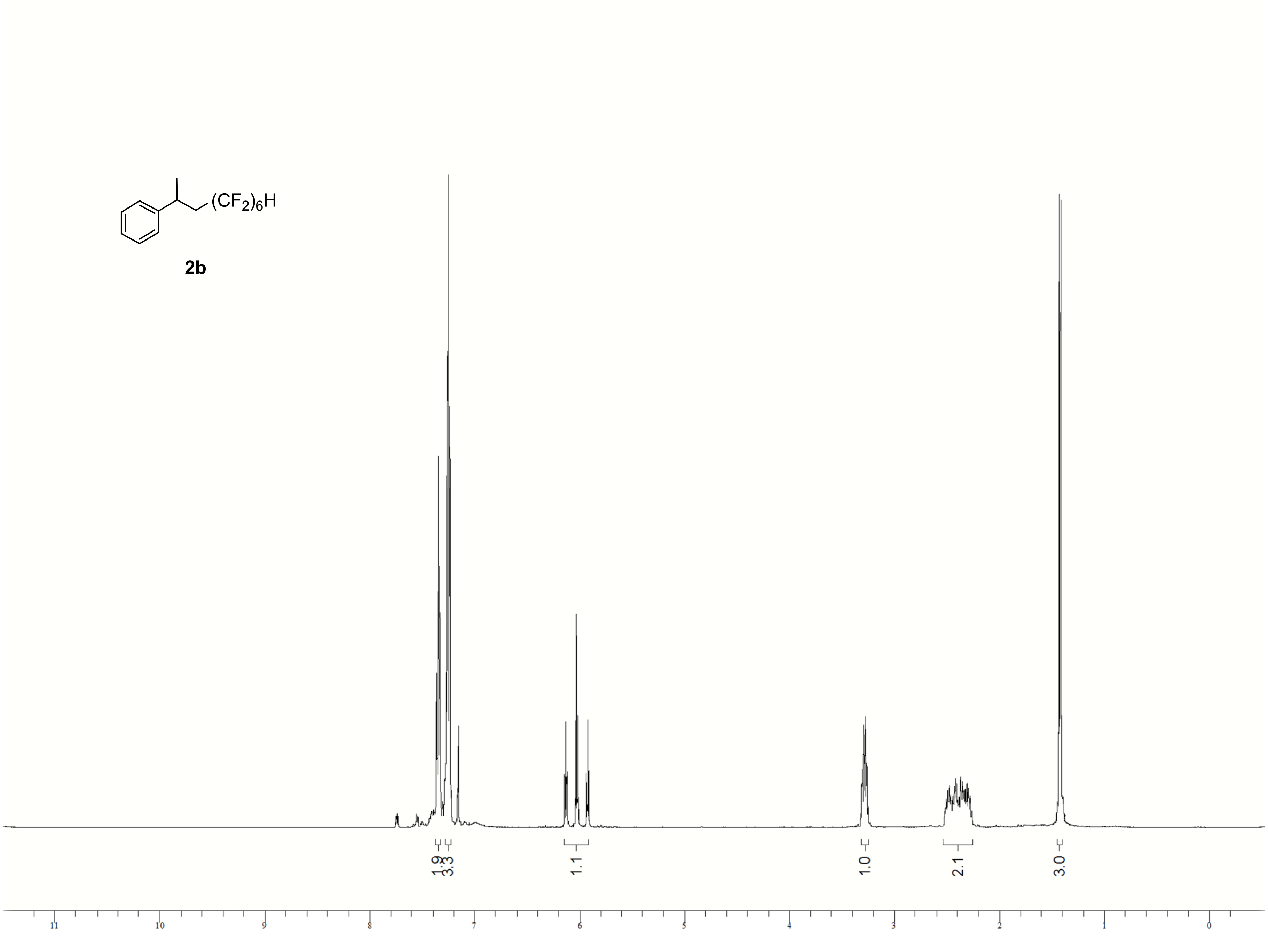


1b

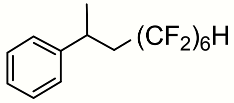
Compound **1b**: ^{19}F NMR (470.6 MHz, CDCl$_3$)



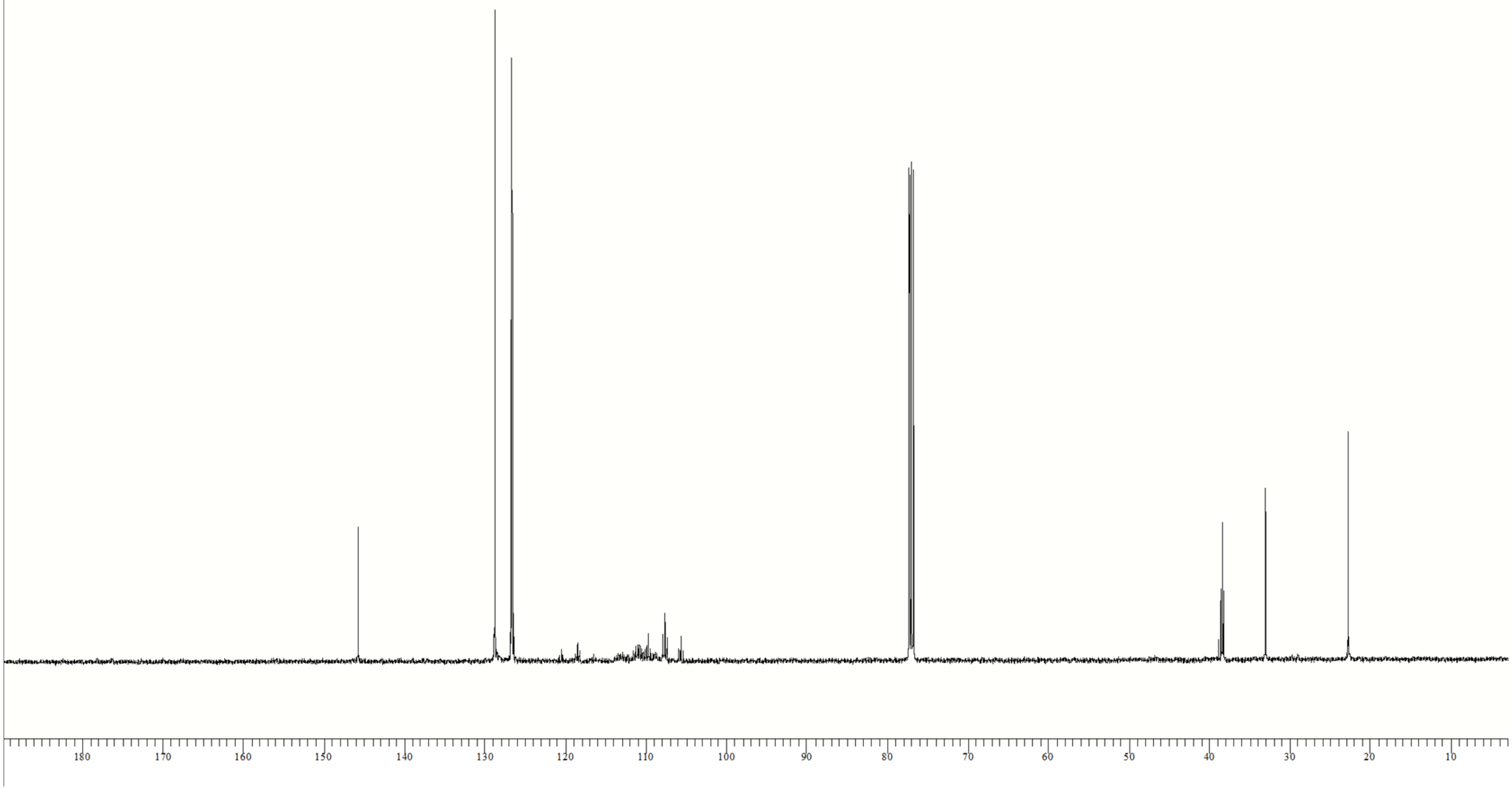
Compound **2b**: ^{1}H NMR (500.1 MHz, $CDCl_3$)



Compound **2b**: ^{13}C NMR (125.8 MHz, CDCl$_3$)



2b



Compound **2b**: ^{19}F NMR (470.6 MHz, CDCl$_3$)

2b