

## Supplementary Information

### Synthesis of 2-aminoBODIPYs by palladium catalysed amination

Rua B. Alnoman, Patrycja Stachelek, Julian G. Knight,\* Anthony Harriman, and Paul G. Waddell

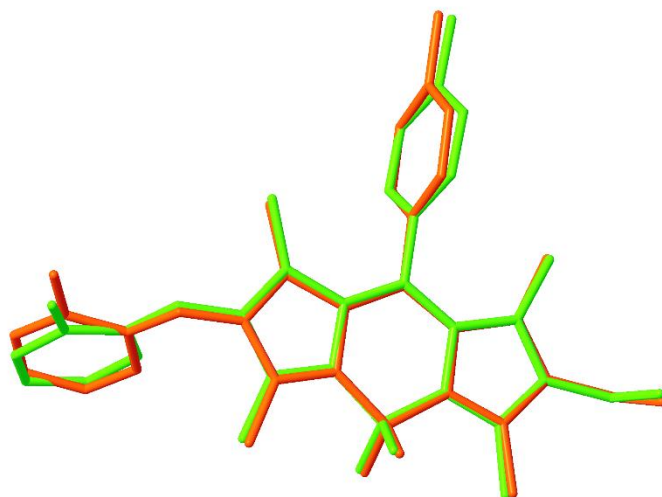
#### Materials

**(3,5-Dimethyl-1H-pyrrol-2-yl)(p-tolyl)methanone 4.** Zinc oxide (0.30 g, 3.72 mmol) was taken in a flame-dried Schlenk tube. 2,4-Dimethyl pyrrole (1.00 g, 14.9 mmol) and *p*-toluoyl chloride (2.30 g, 14.9 mmol) were then added and the mixture was stirred at room temperature for 5 minutes. The solid crude was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (60 mL) and washed with an aqueous solution of sodium bicarbonate (100 mL × 2). The aqueous layer was back extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 30 mL). The combined organic layers were dried (MgSO<sub>4</sub>) and the solvent was removed under pressure. The resulting orange crude product was purified by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>) to give the title compound **4** as a sand coloured solid (1.75 g, 55%). The spectroscopic data obtained for this compound were consistent with those reported in the literature.<sup>S1</sup>

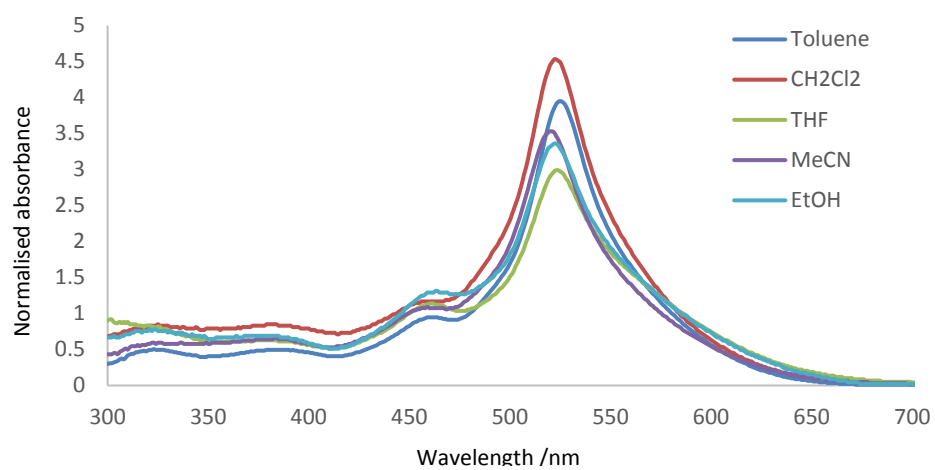
<sup>S1</sup> A. R. Katritzky, K. Suzuki, S. K. Singh and H.-Y. He, *J. Org. Chem.*, 2003, **68**, 5720.

#### Fluorescence titration

Separate solutions of triphosgene (20 µg mL<sup>-1</sup>) and the BODIPY 6-ethyl-4,4-difluoro-1,3,5,7-tetramethyl-8-(4-methylphenyl)-2-(2-aminophenyl)amino-4-bora-3a,4a-diaza-s-indacene **9** (25 µg mL<sup>-1</sup>) dissolved in MeCN containing Et<sub>3</sub>N (3% v/v) were prepared by dilution. Aliquots of the triphosgene solution were added to a series of mixtures of 2 mL of the BODIPY solution and an additional volume of 3% (v/v) Et<sub>3</sub>N in MeCN calculated such that the final total volume was 5 mL in each case and the final concentrations of the BODIPY = 21 µM and of triphosgene = 0, 0.40, 0.67, 1.21, 1.62, 2.02, 2.43, 2.70, 3.37 µM. The fluorescence emission spectrum (λ<sup>ex</sup> = 490 nm) was recorded directly after mixing. It was confirmed that the emission spectrum was unchanged after 60 min.

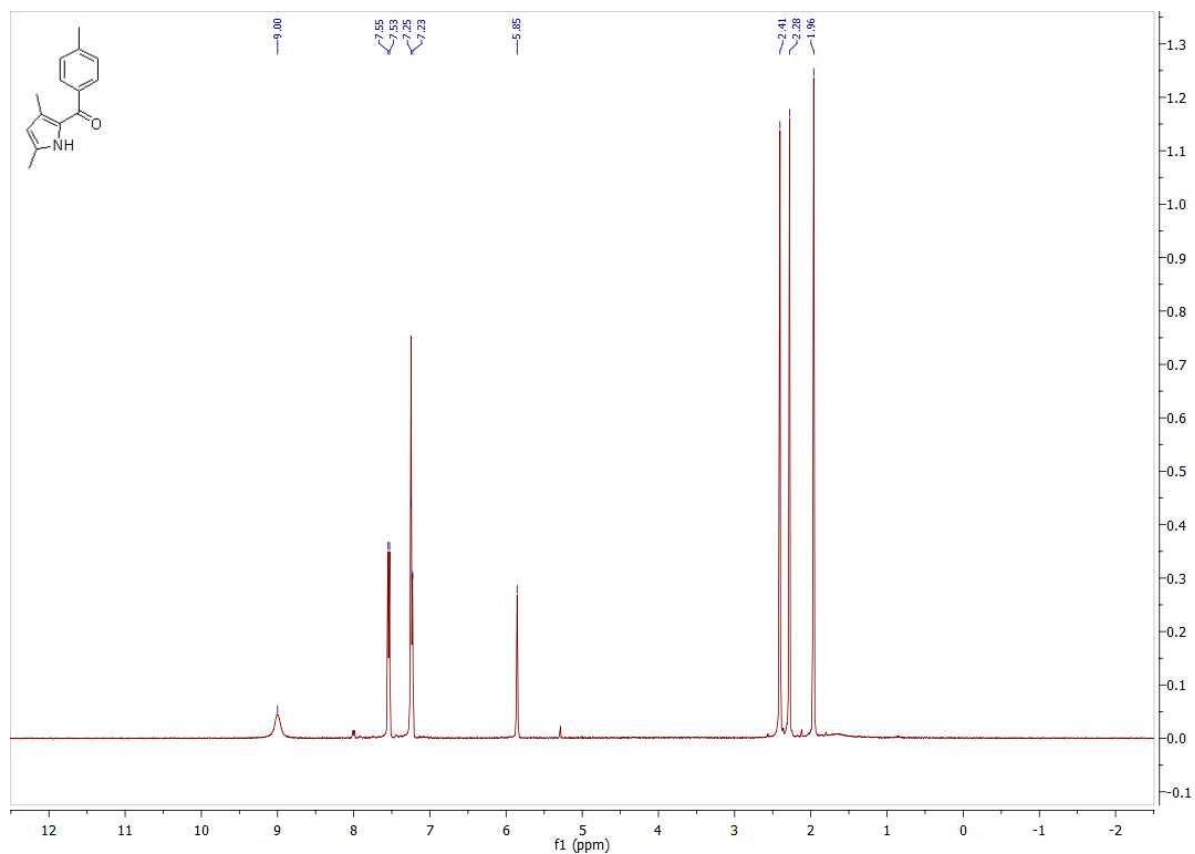


**Figure S1.** Overlay of the two independent molecules in the asymmetric unit of the X-ray structure of compound **6d**.

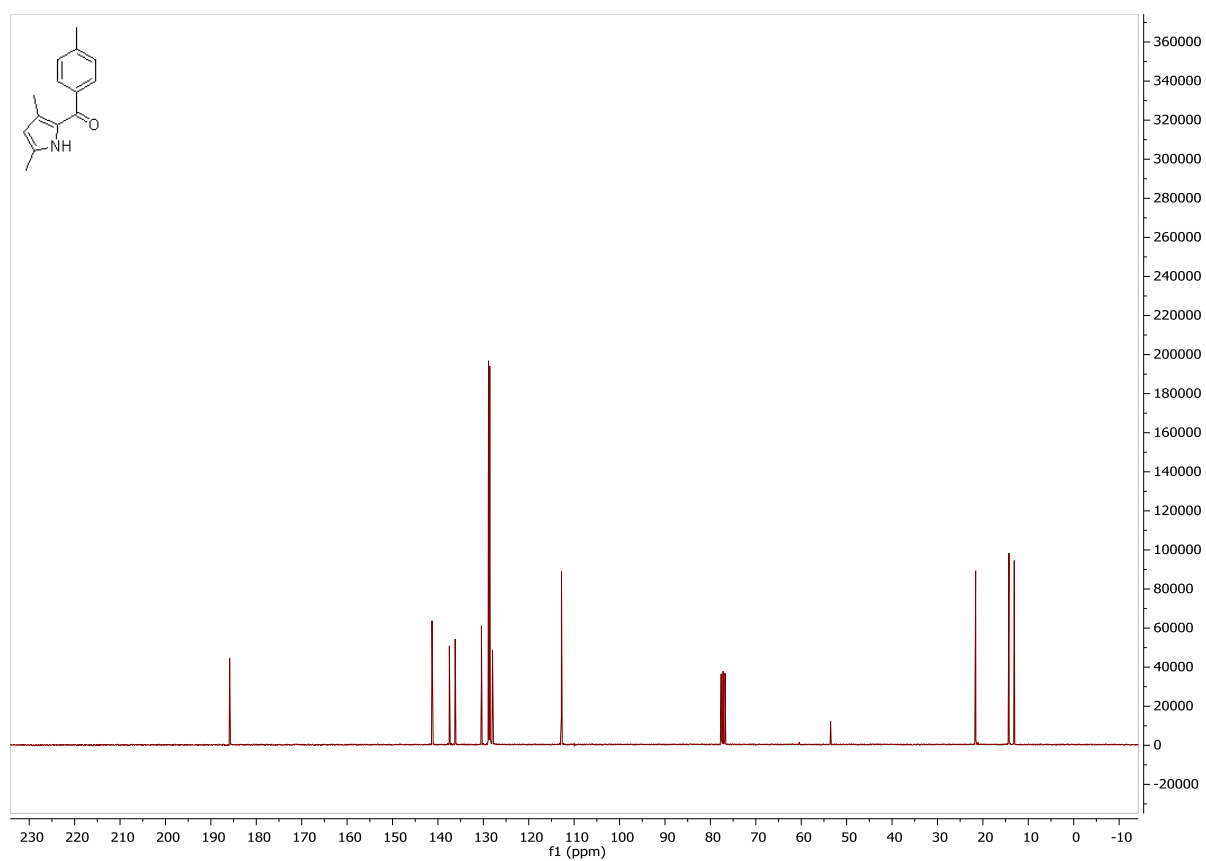


**Figure S2.** Absorption spectra in terms of the molar absorption coefficient ( $\epsilon$ ) for **6a** in the solvents indicated.

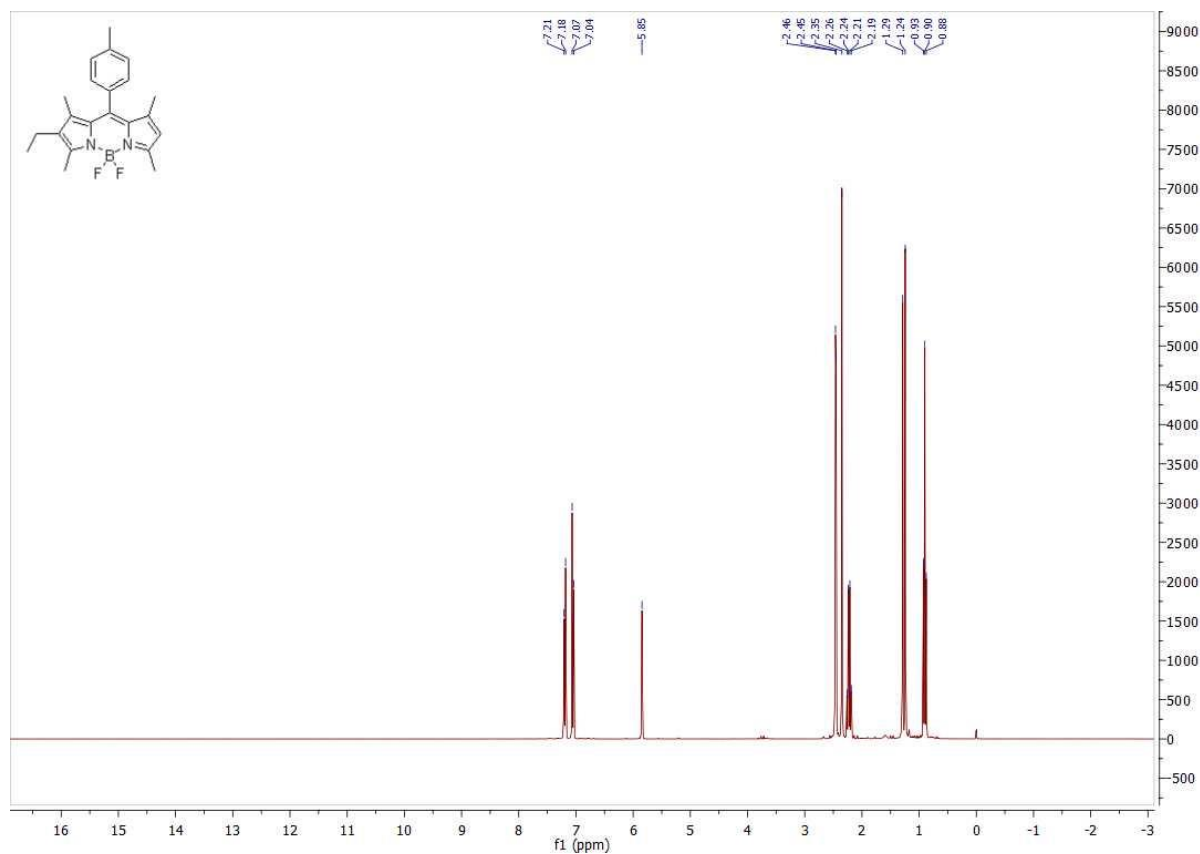
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



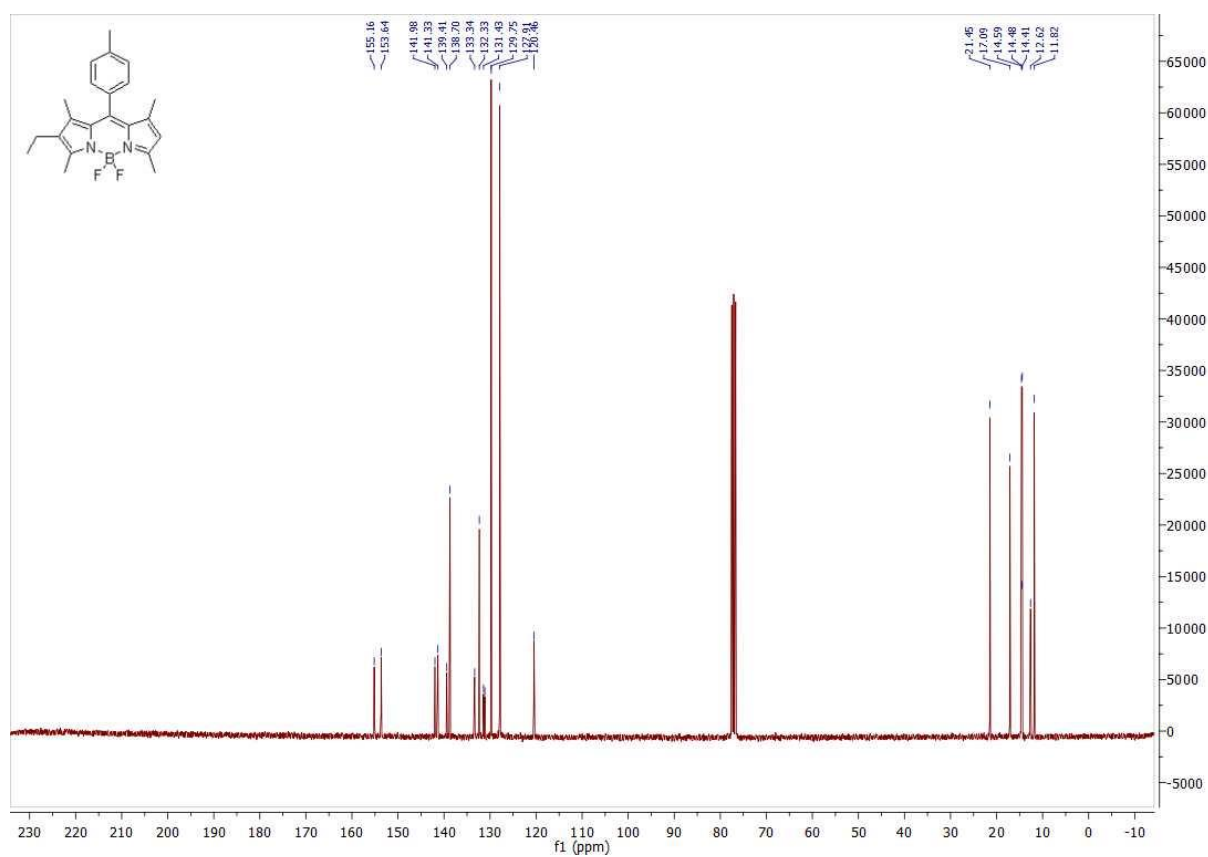
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )



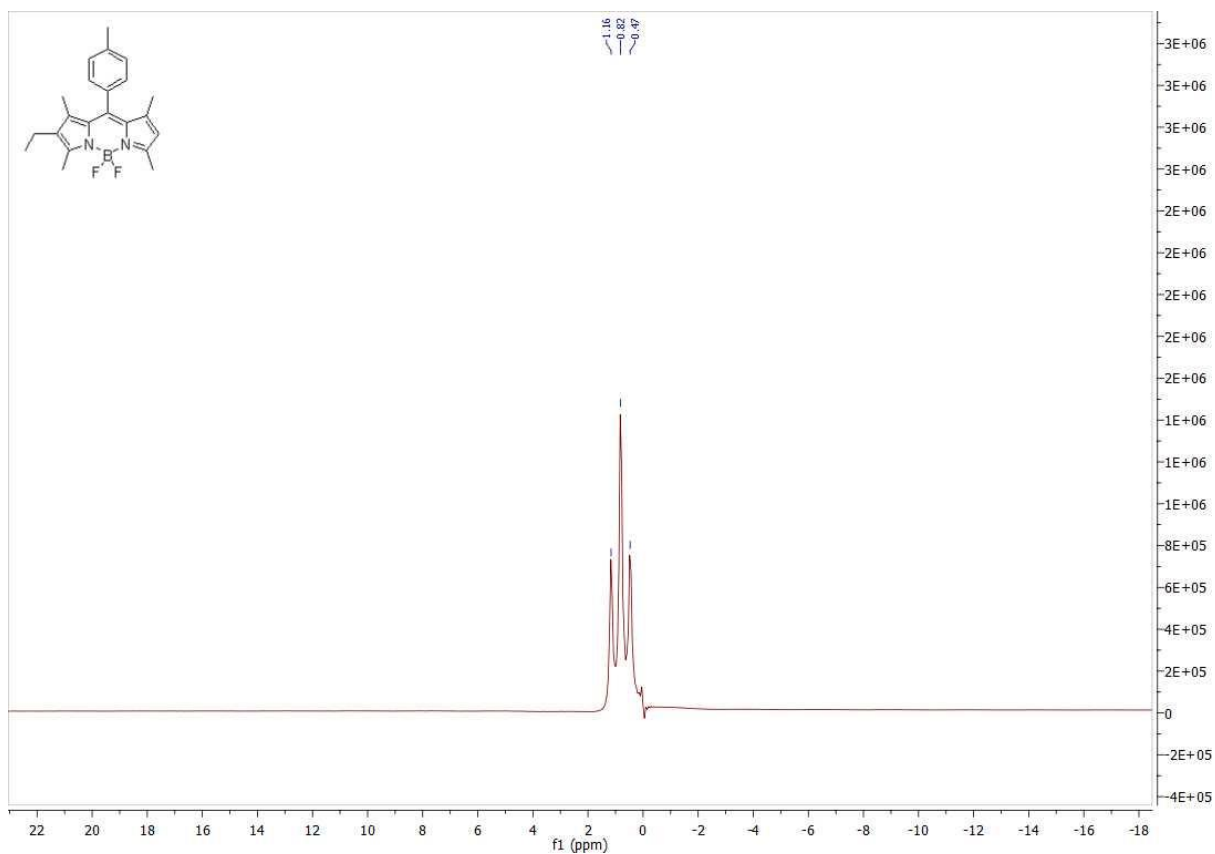
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )



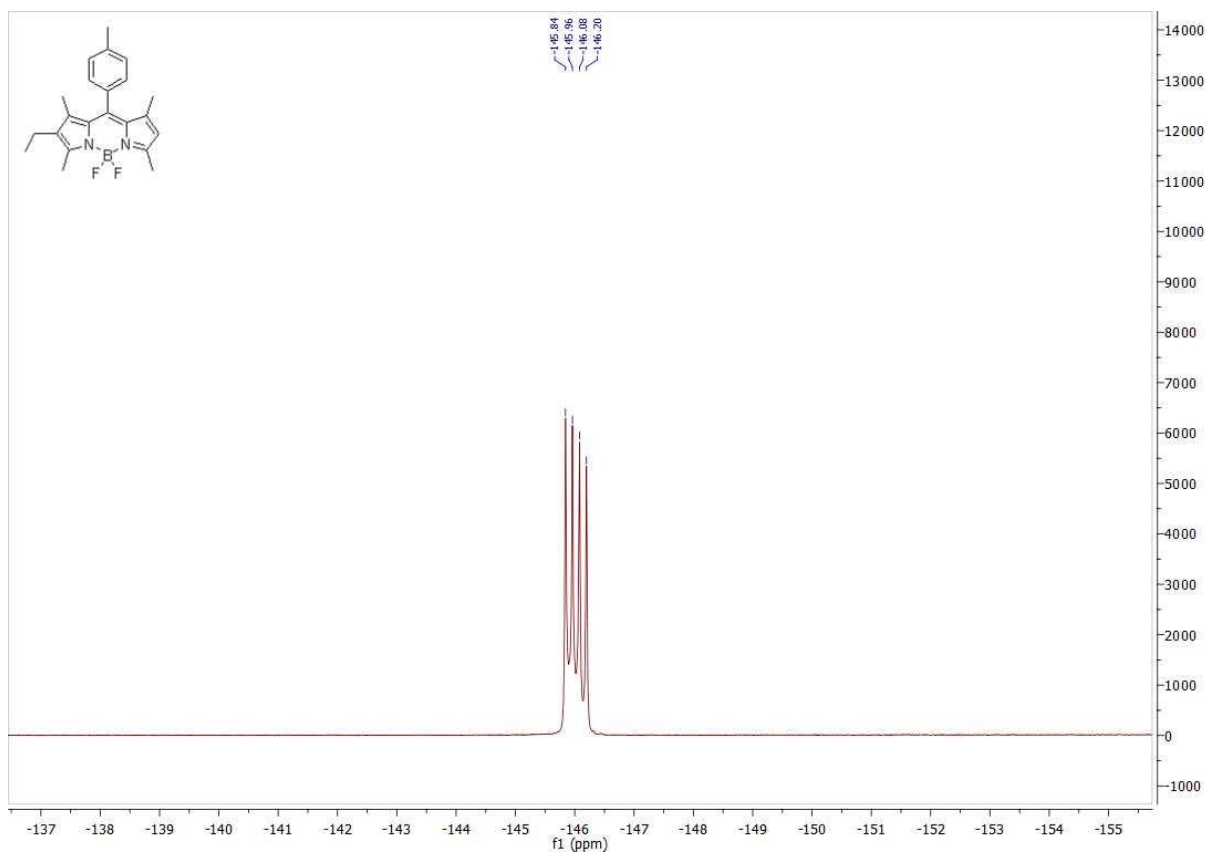
$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )



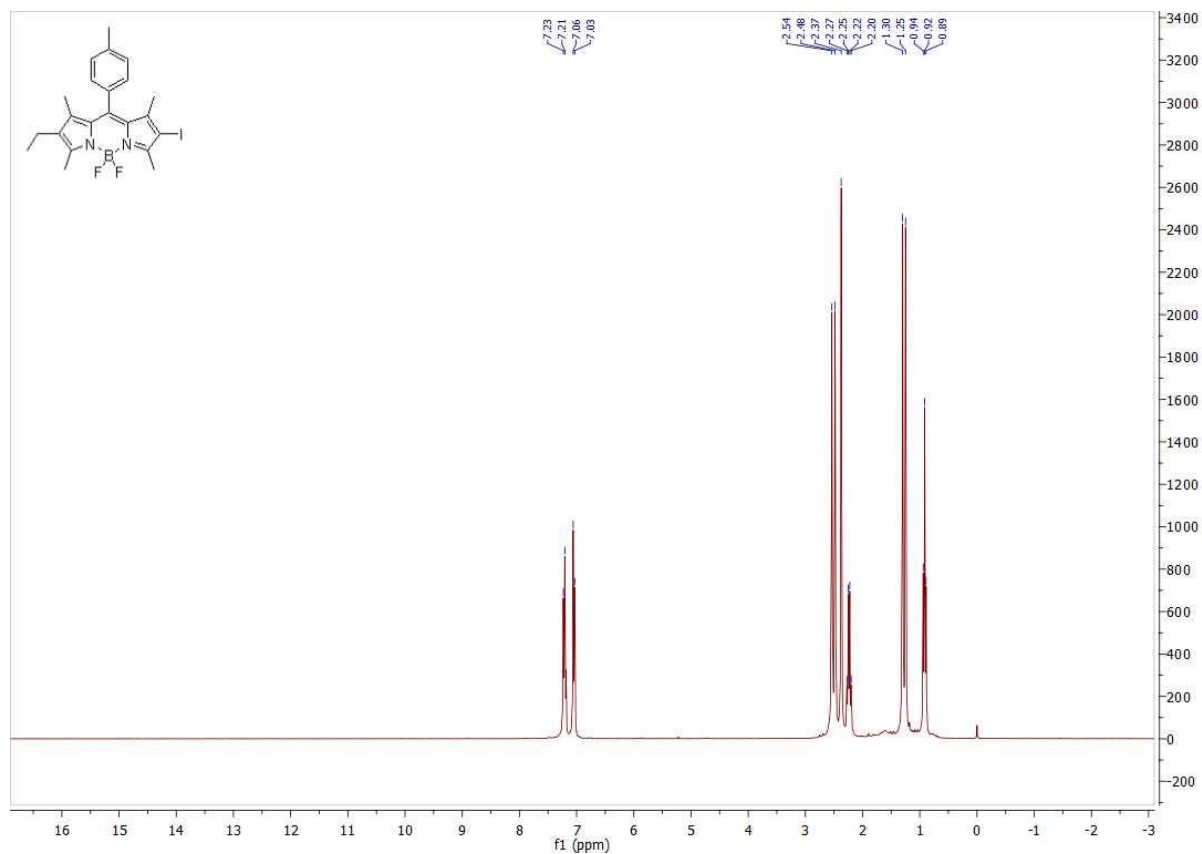
$^{11}\text{B}$  NMR (96 MHz,  $\text{CDCl}_3$ )



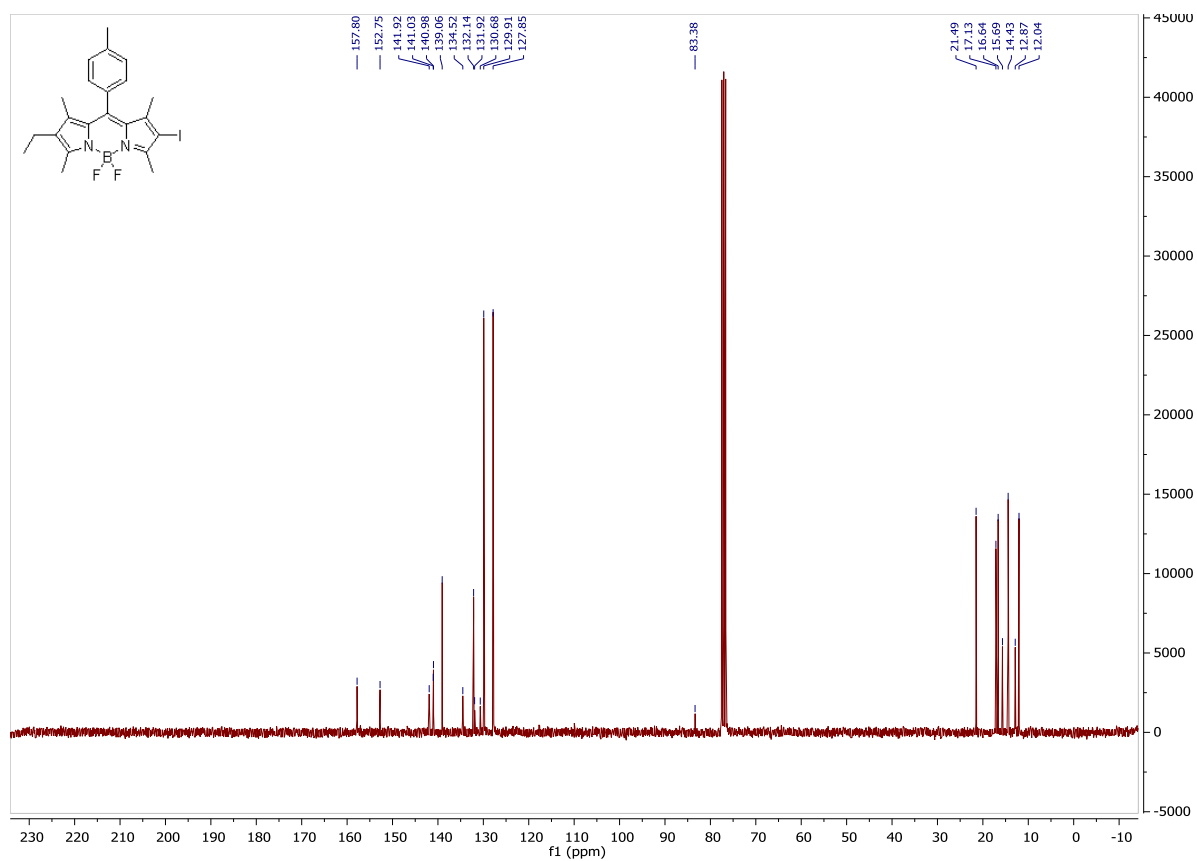
$^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )



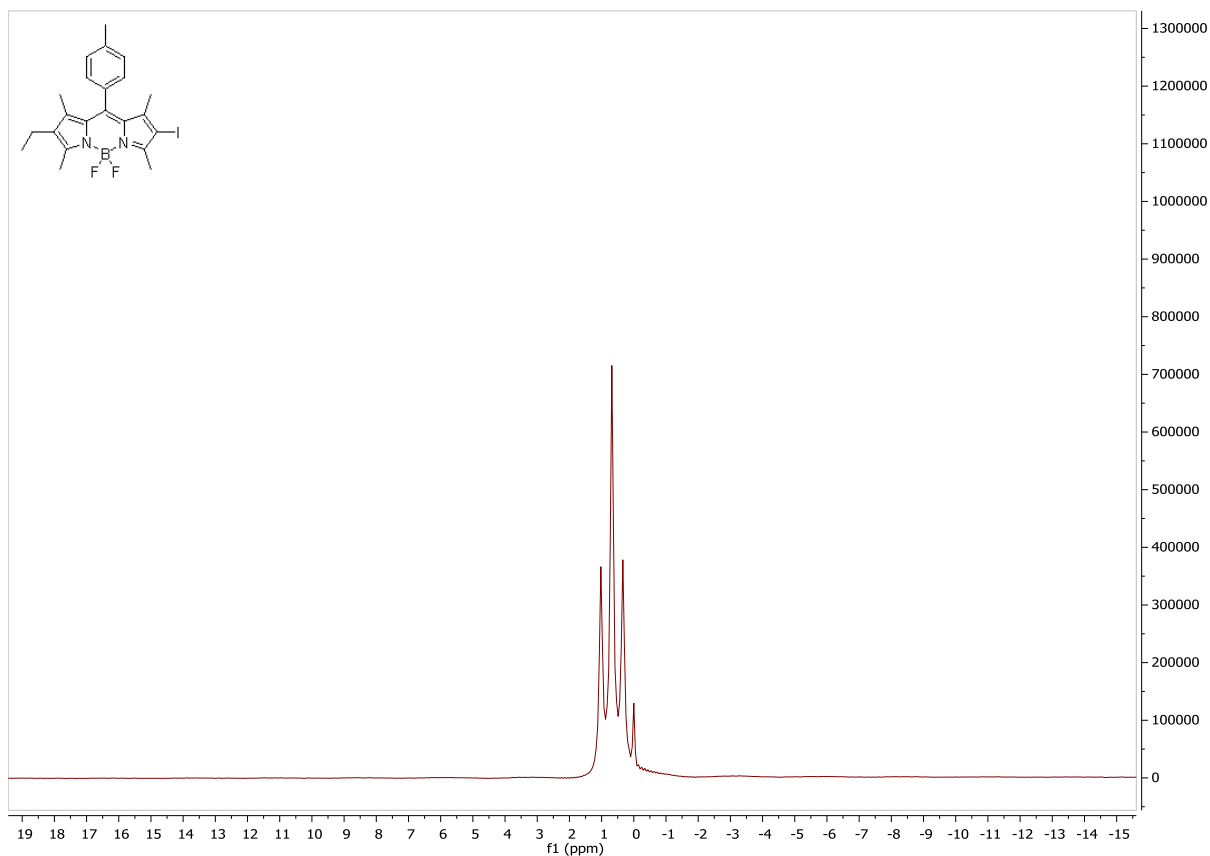
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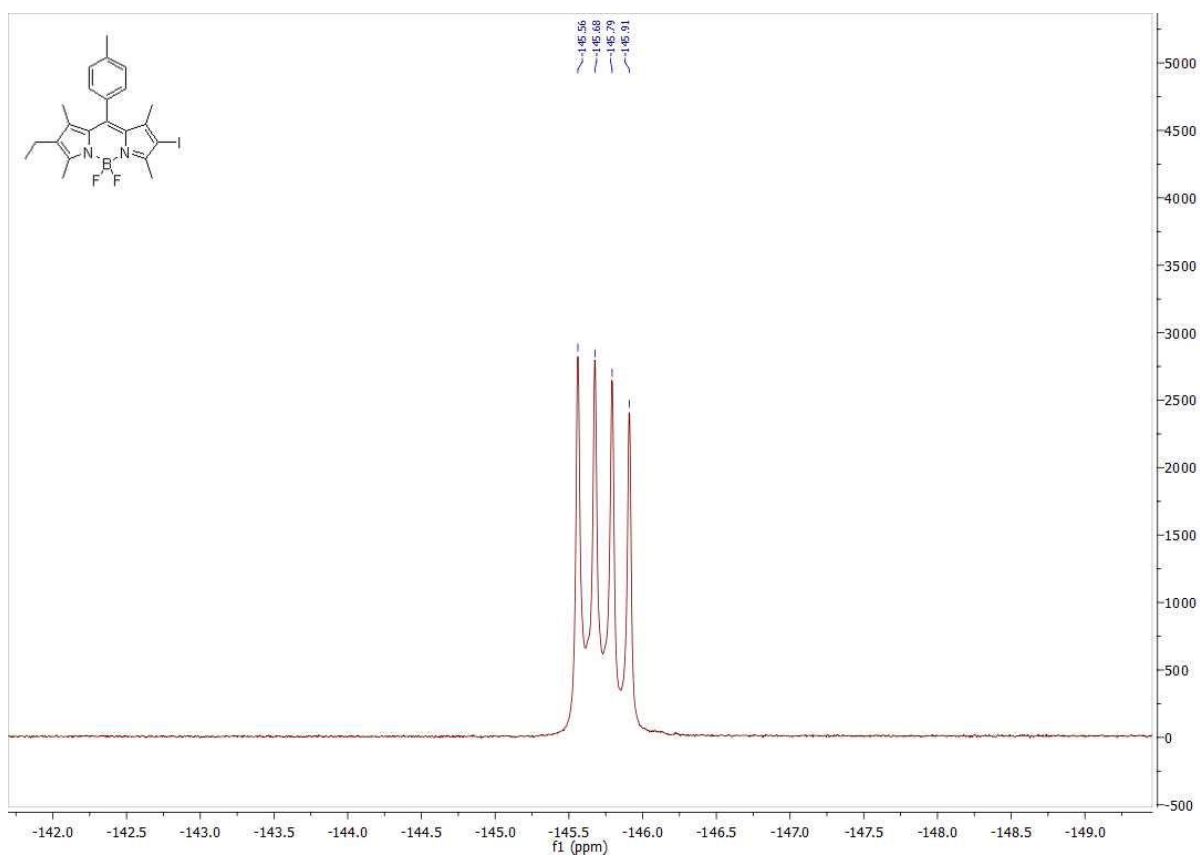
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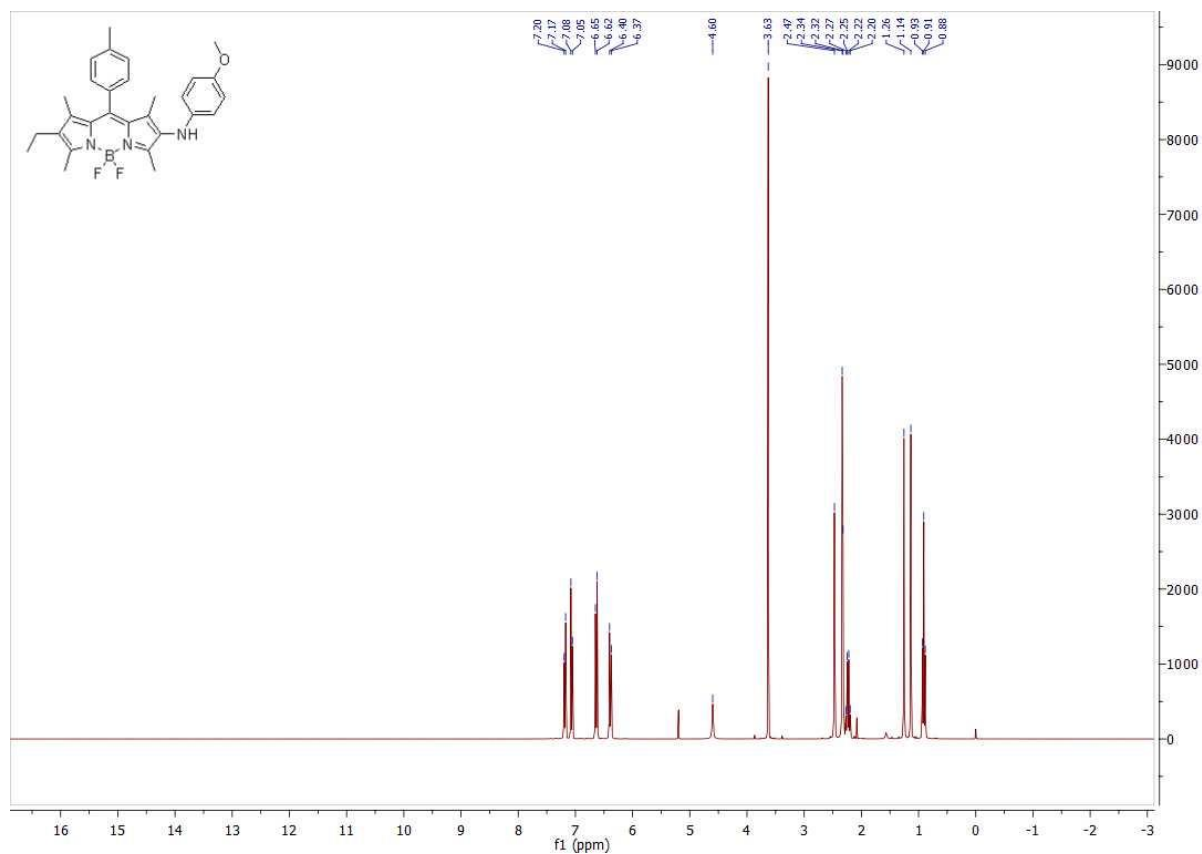
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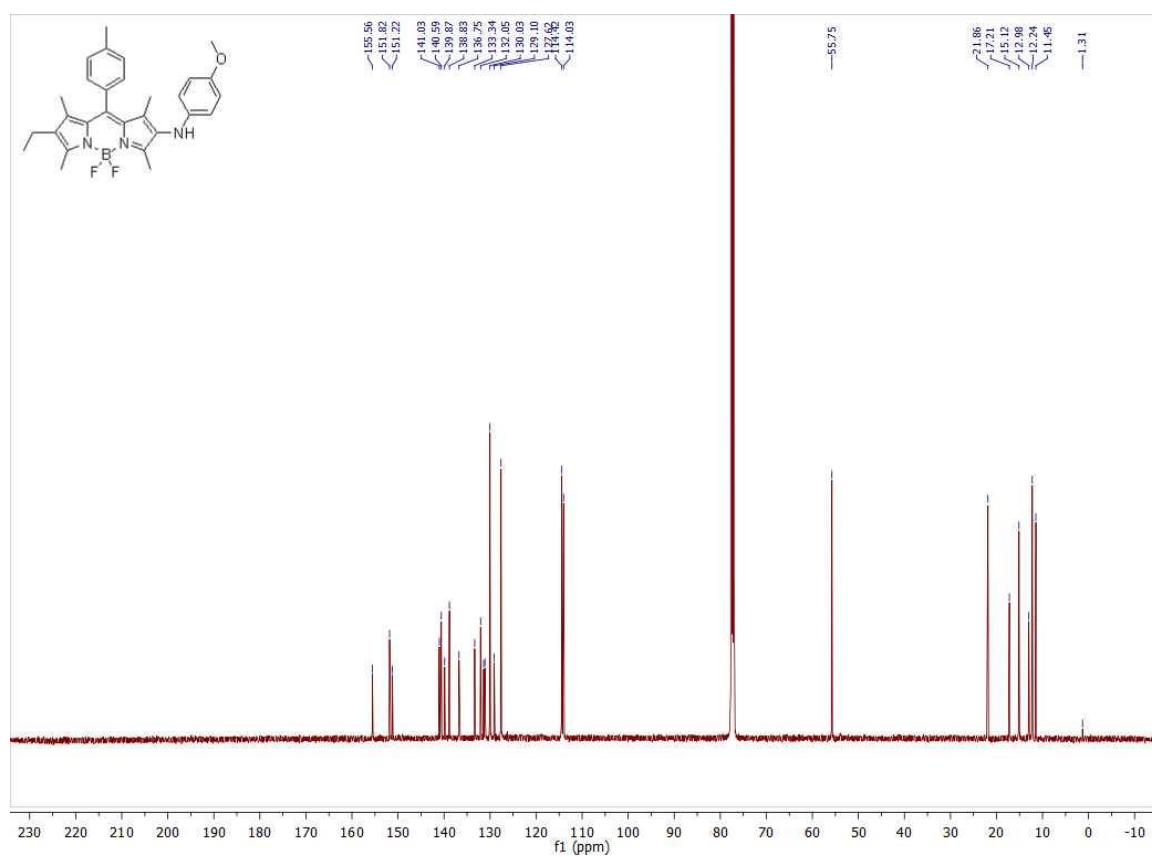
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$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )

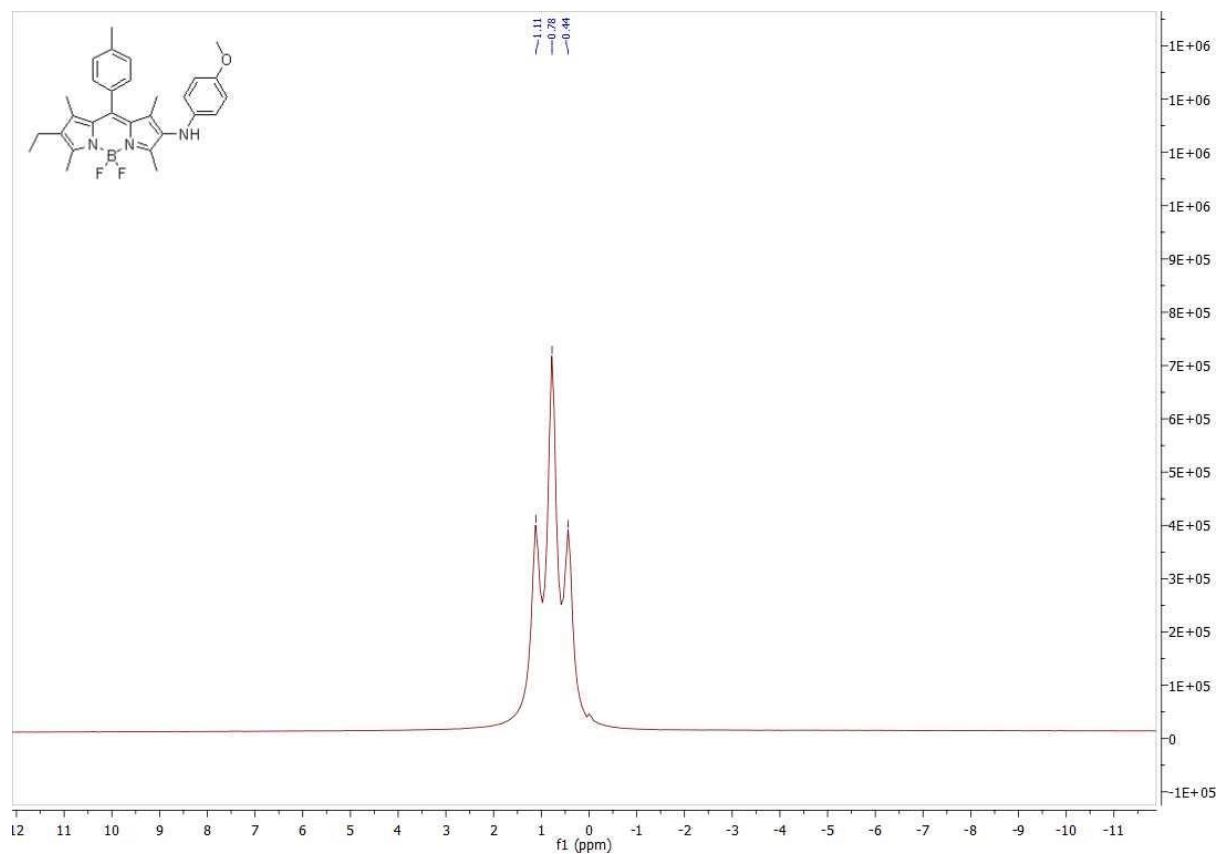


$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

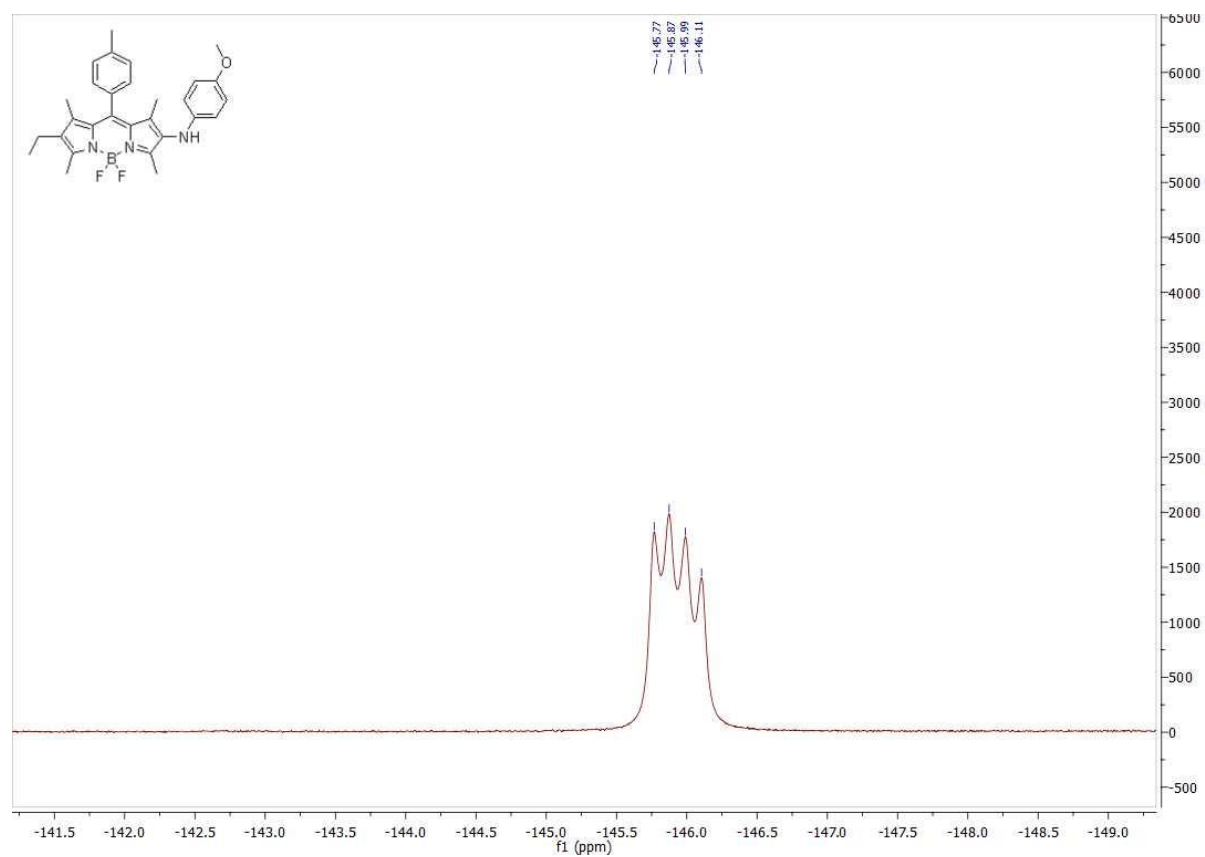




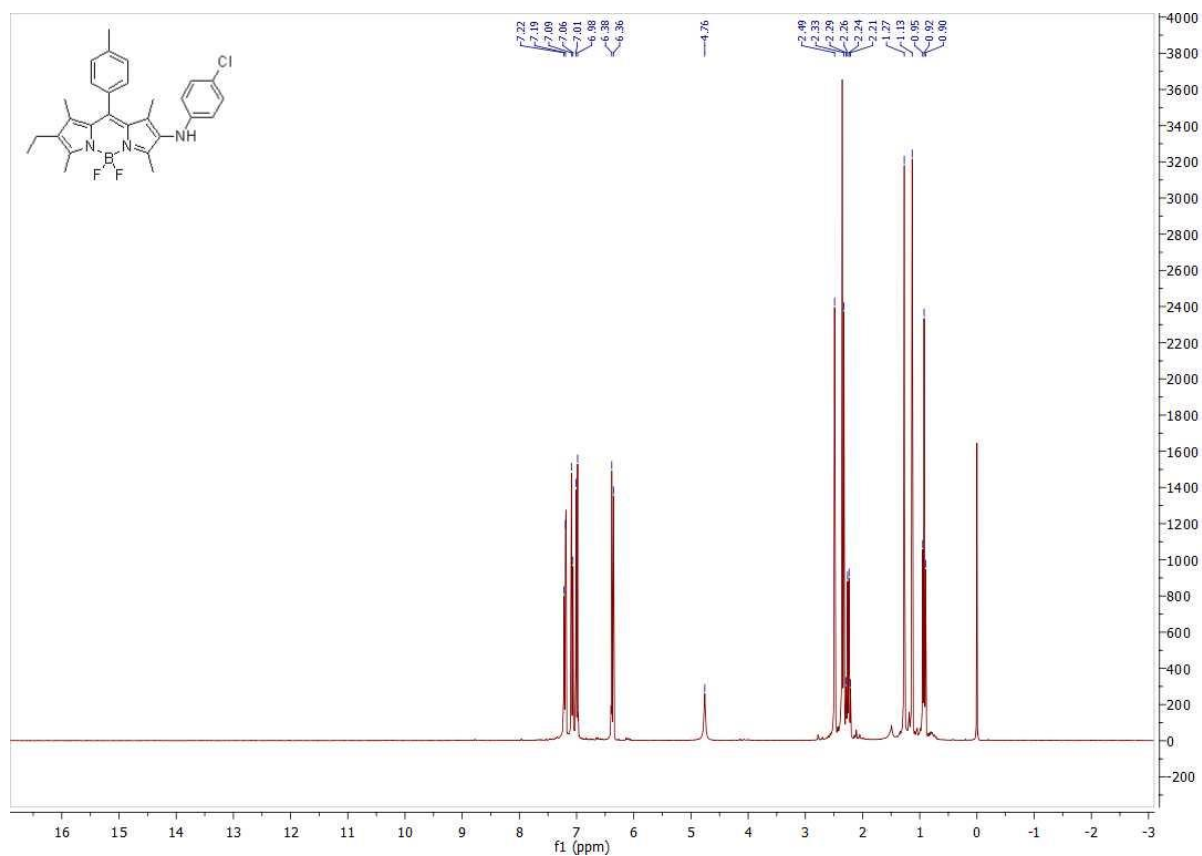
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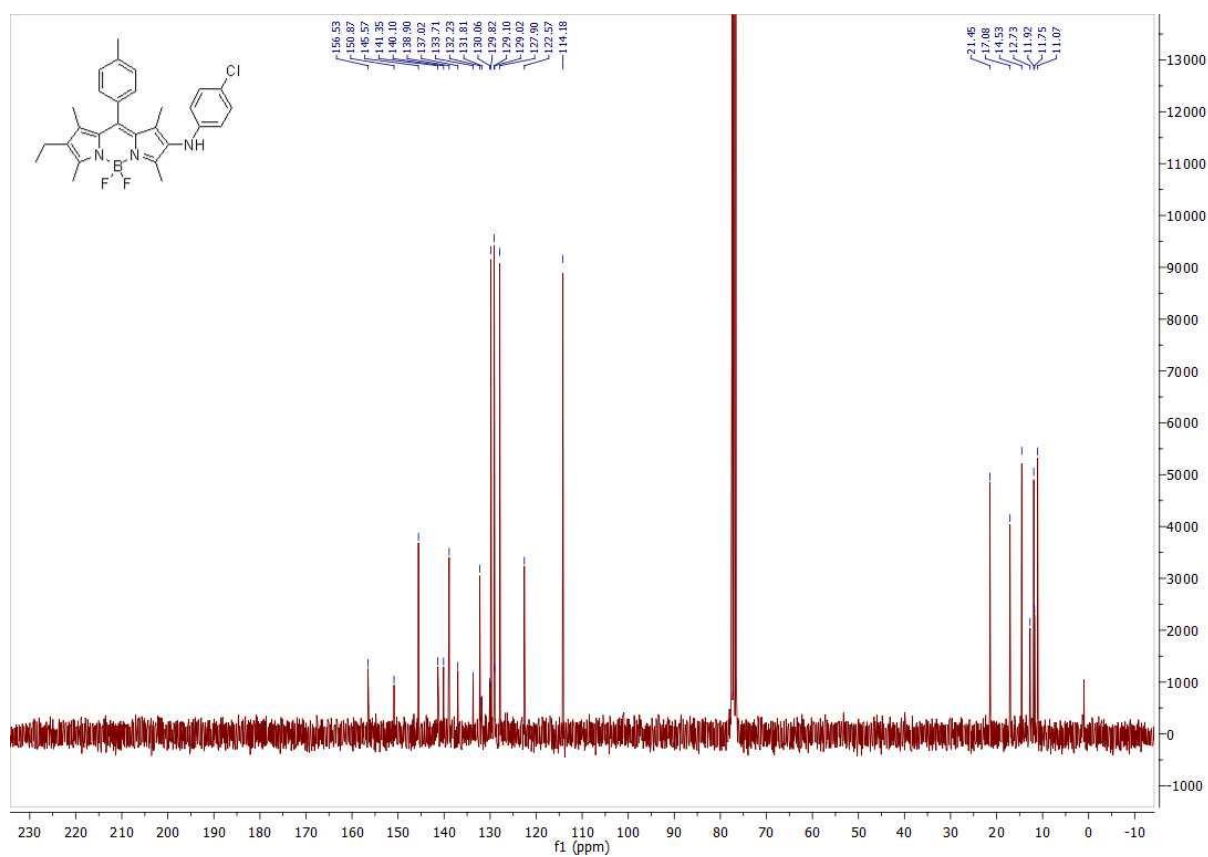
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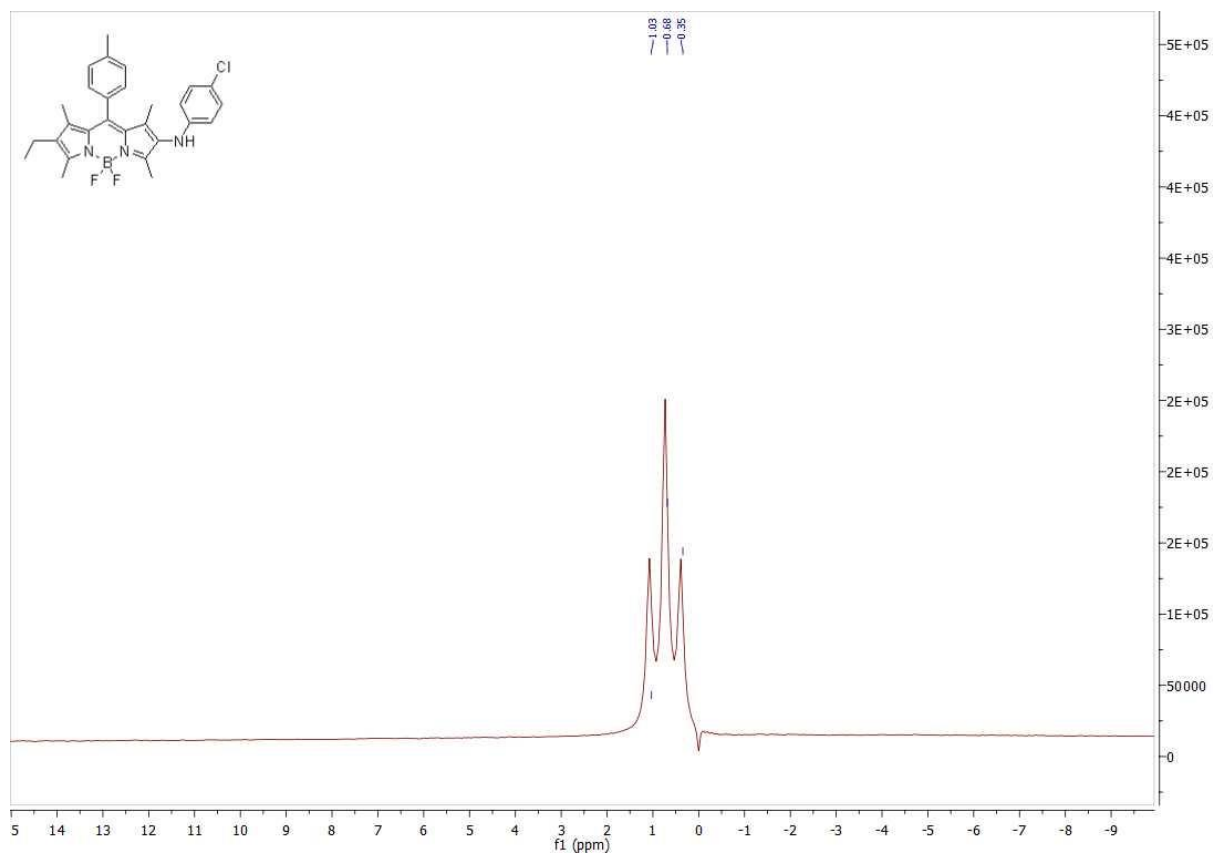
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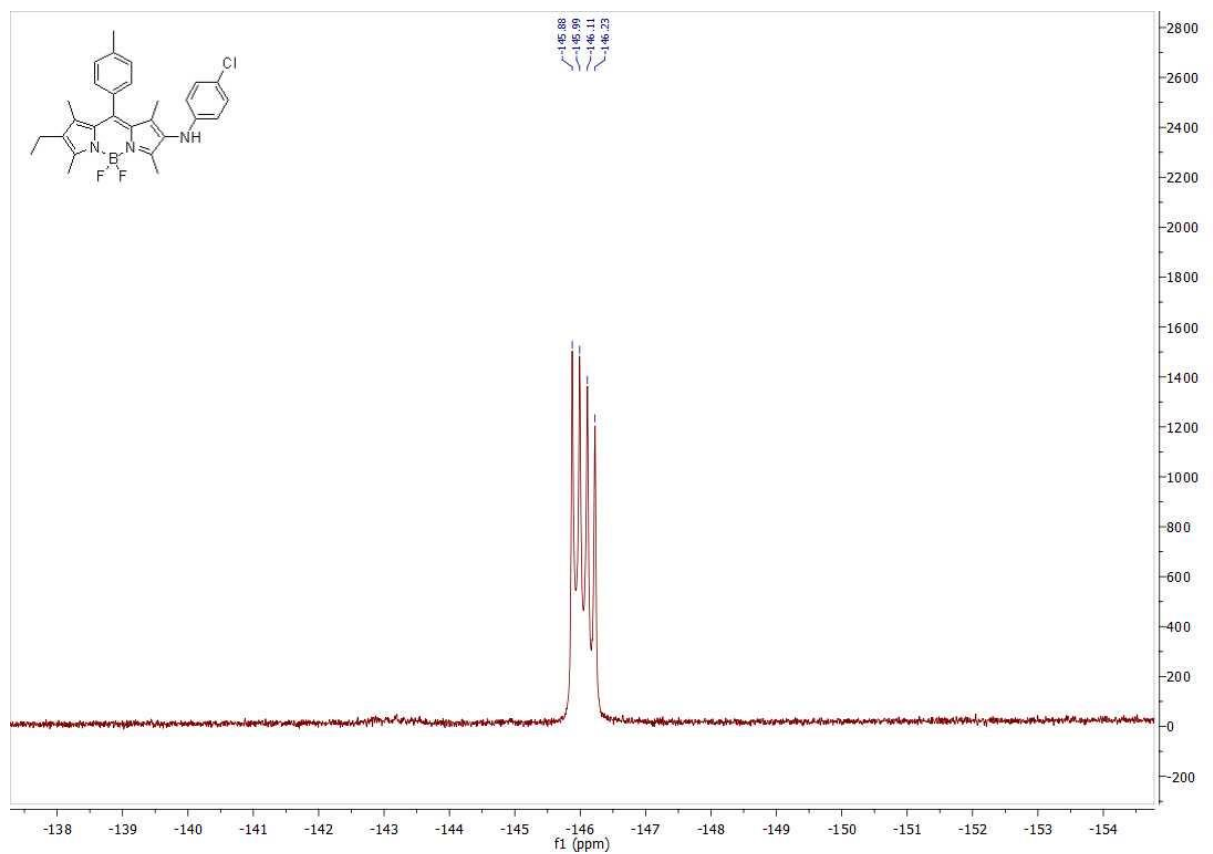
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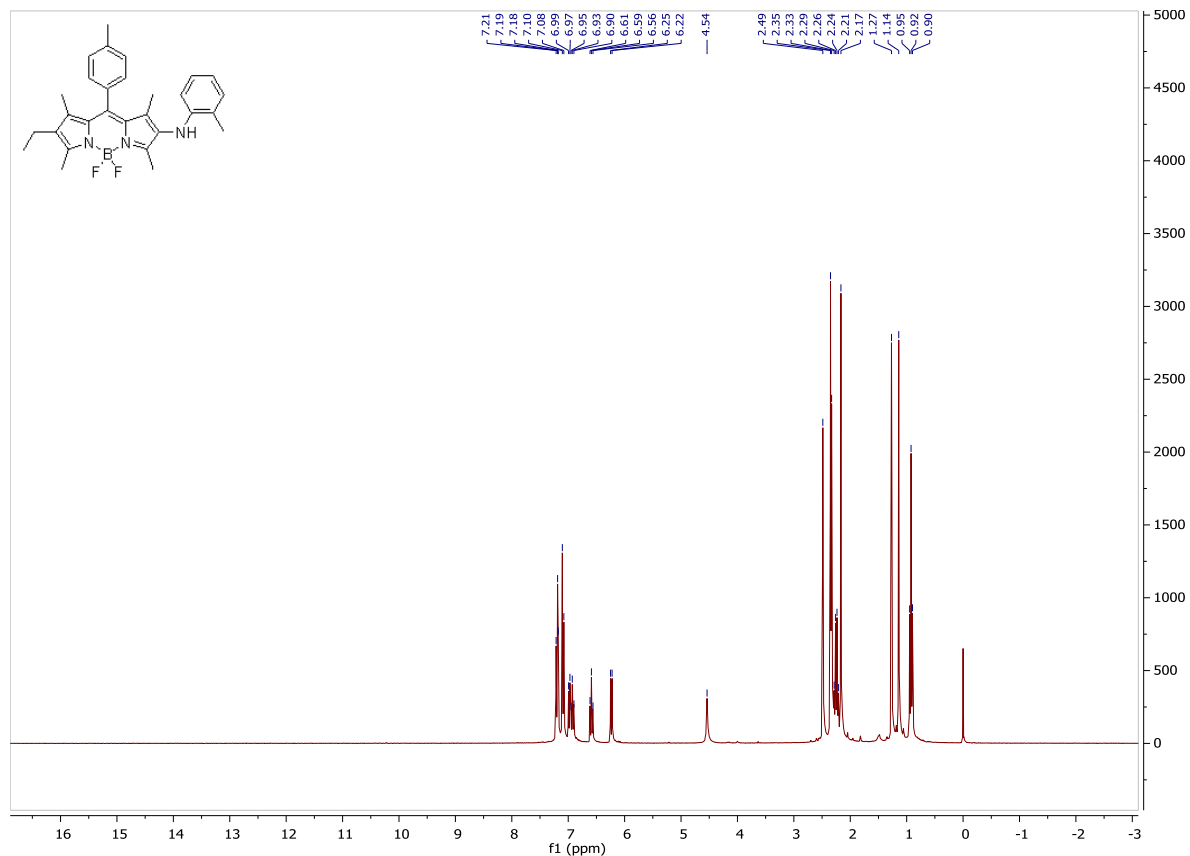
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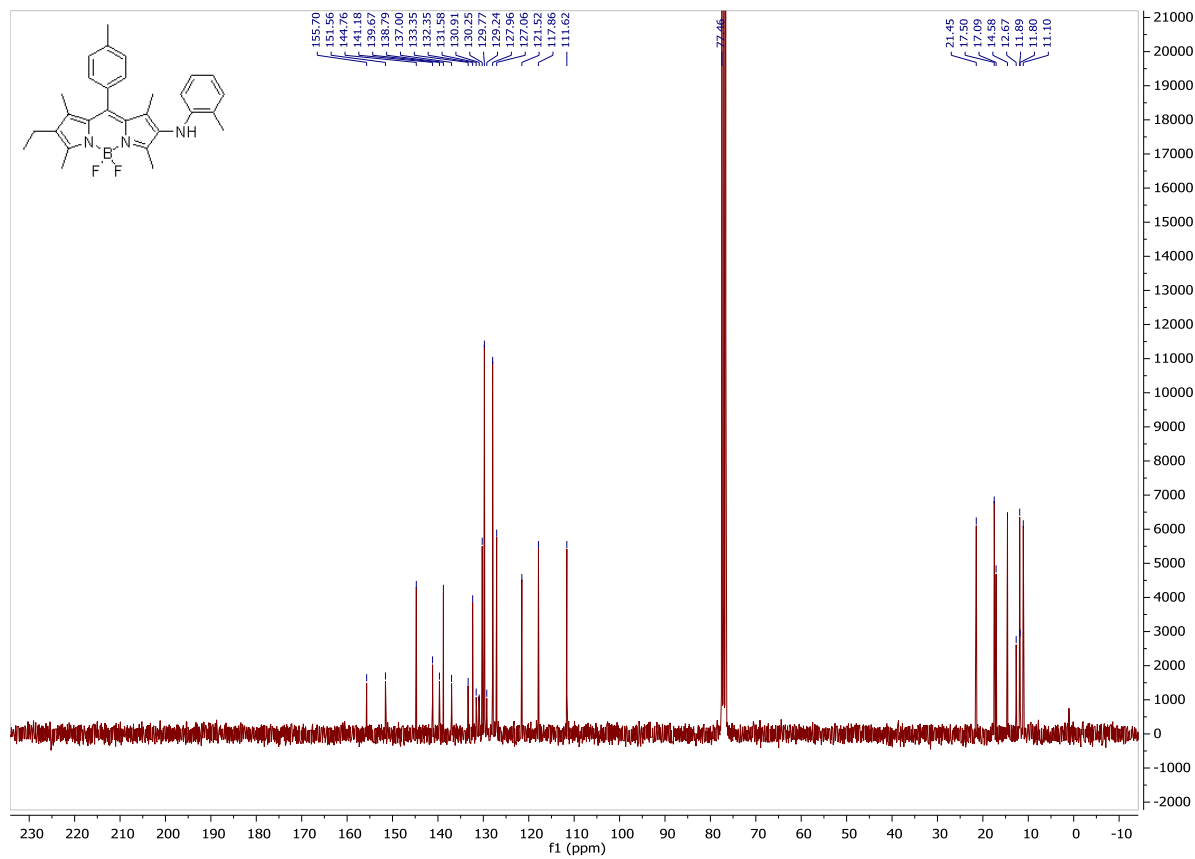
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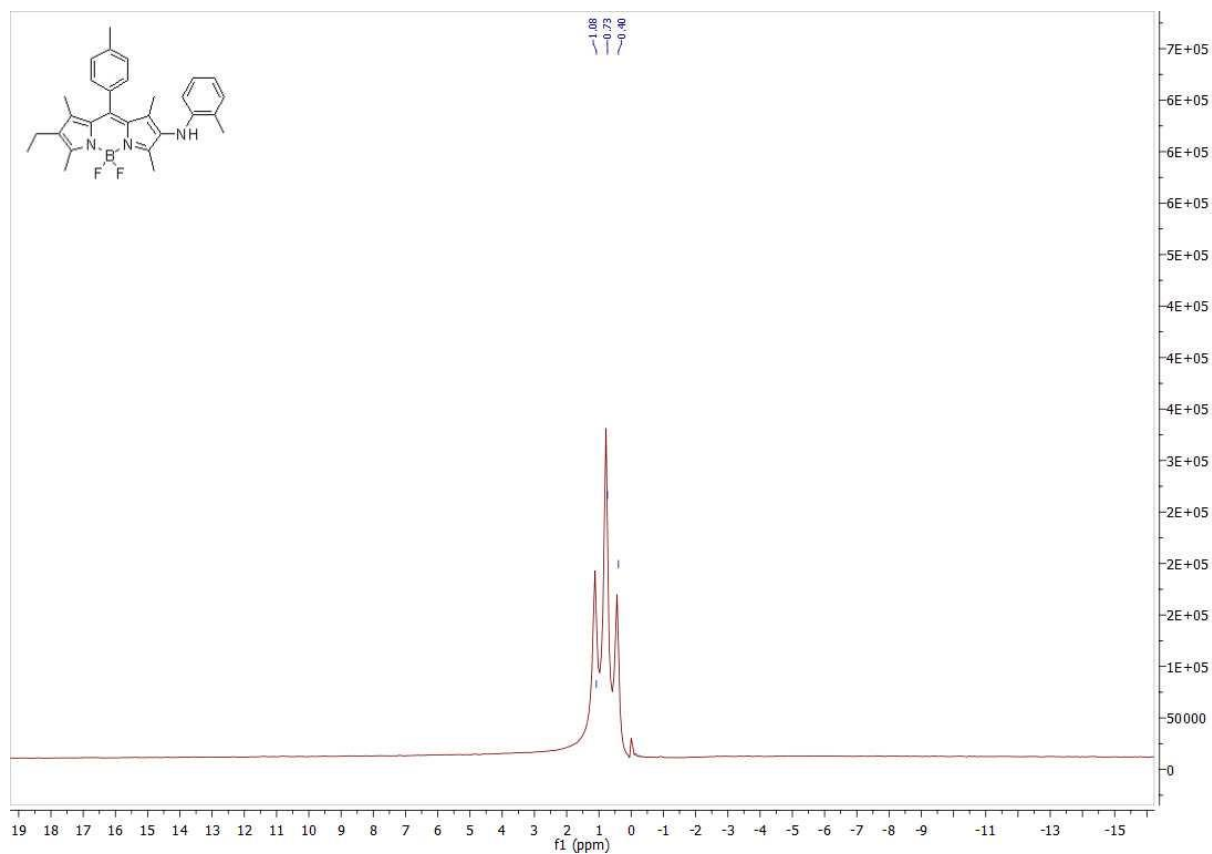
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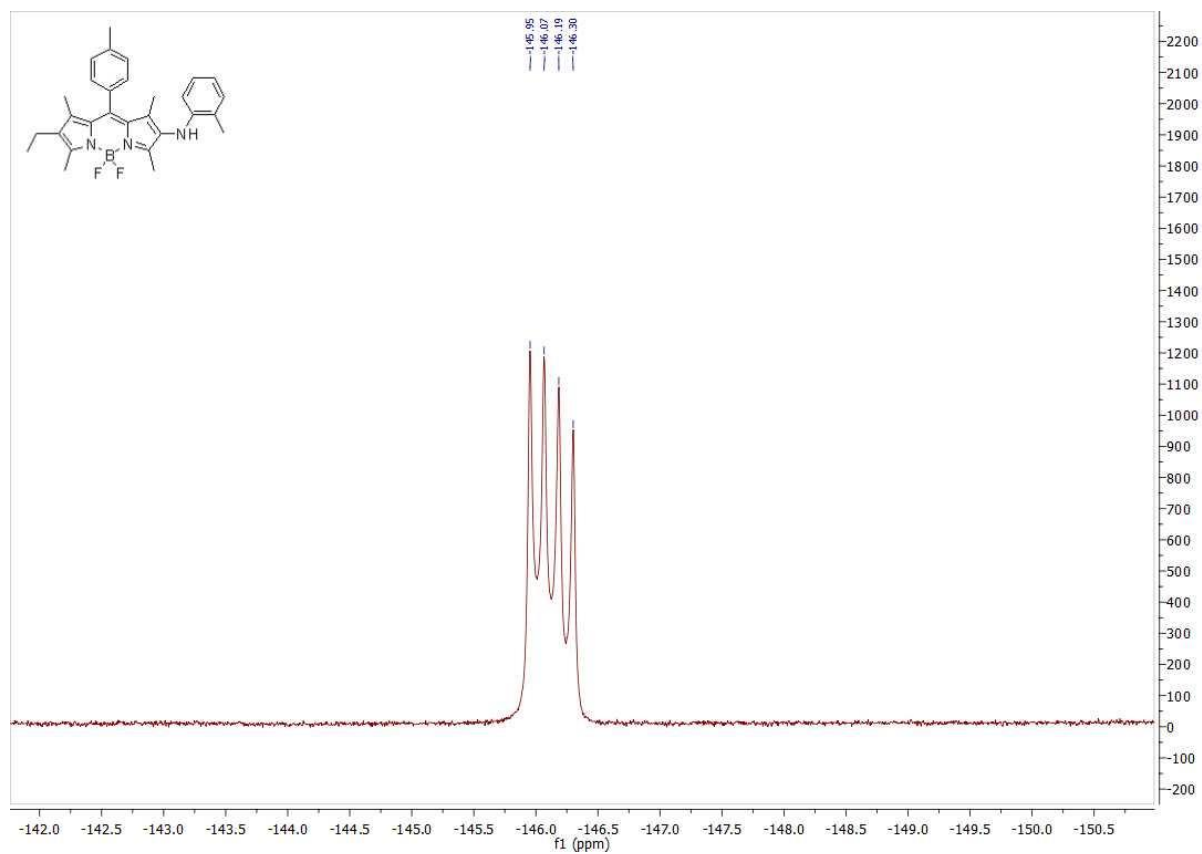
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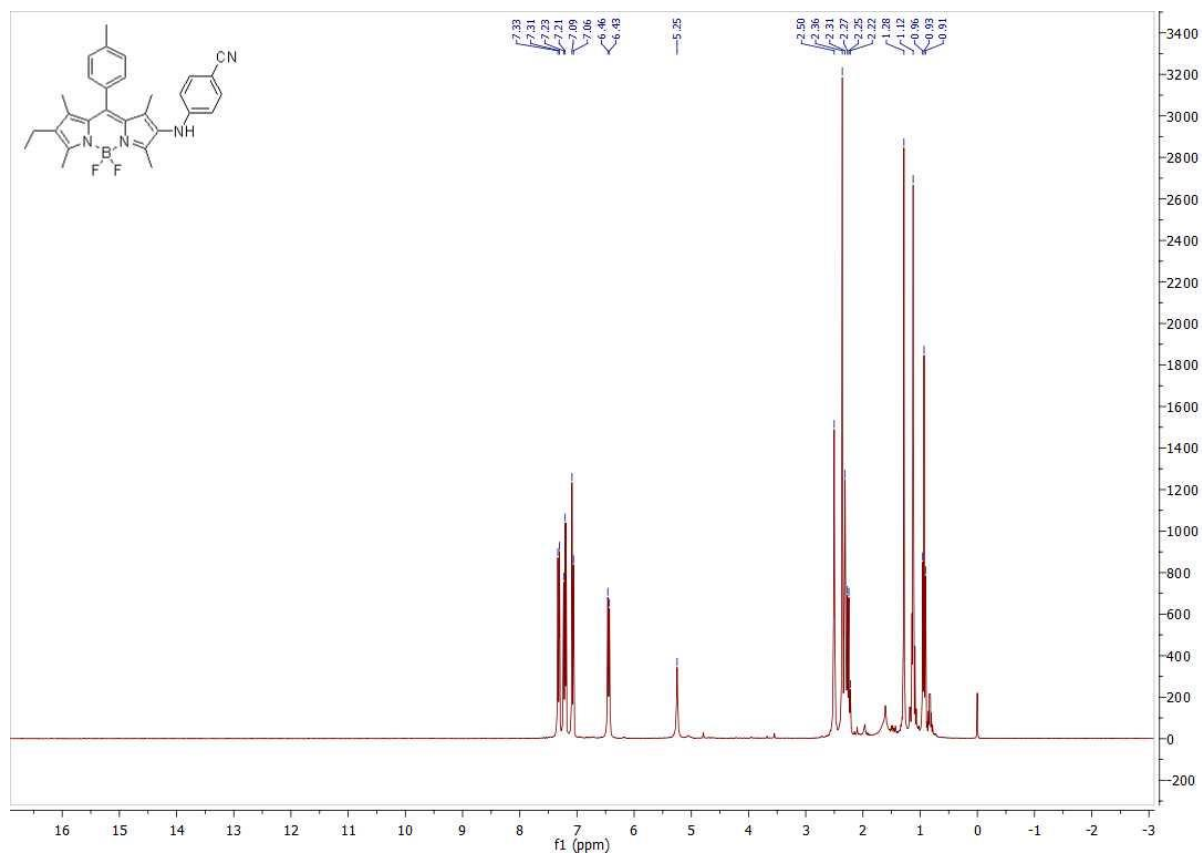
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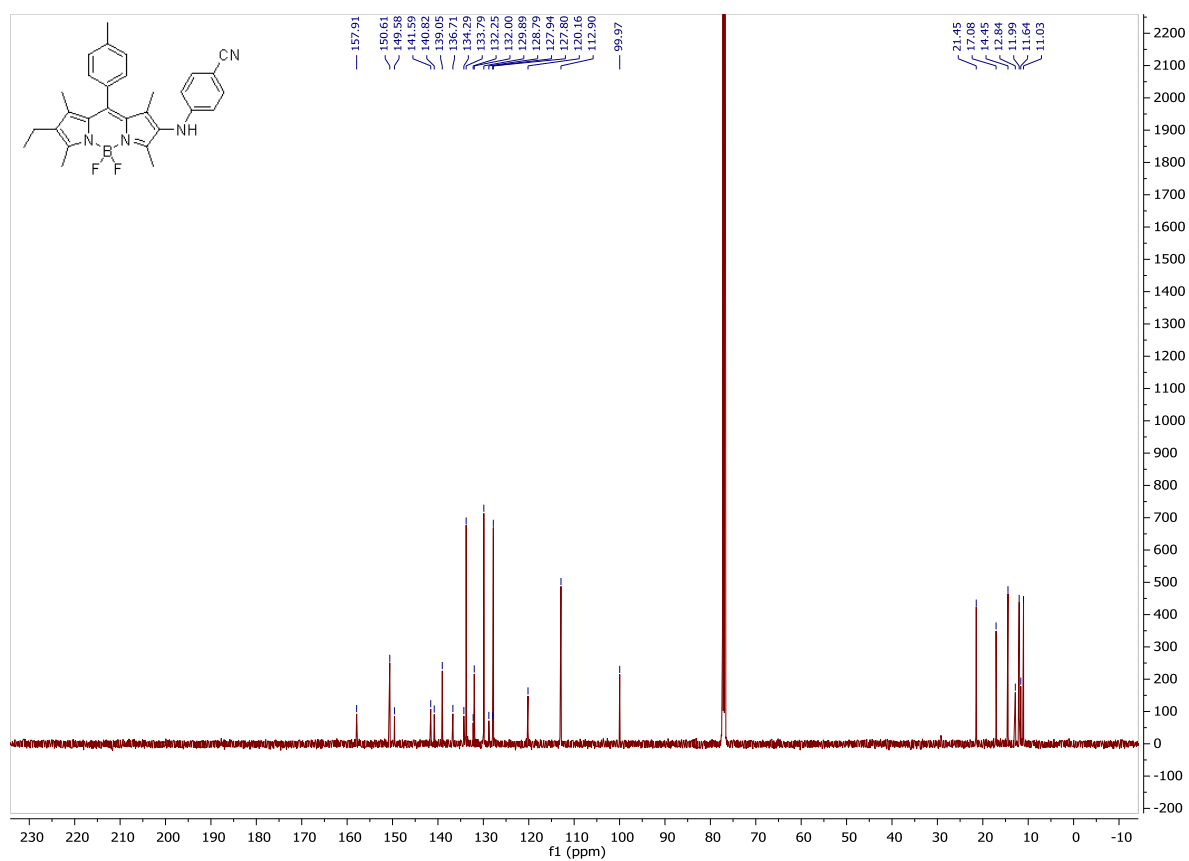
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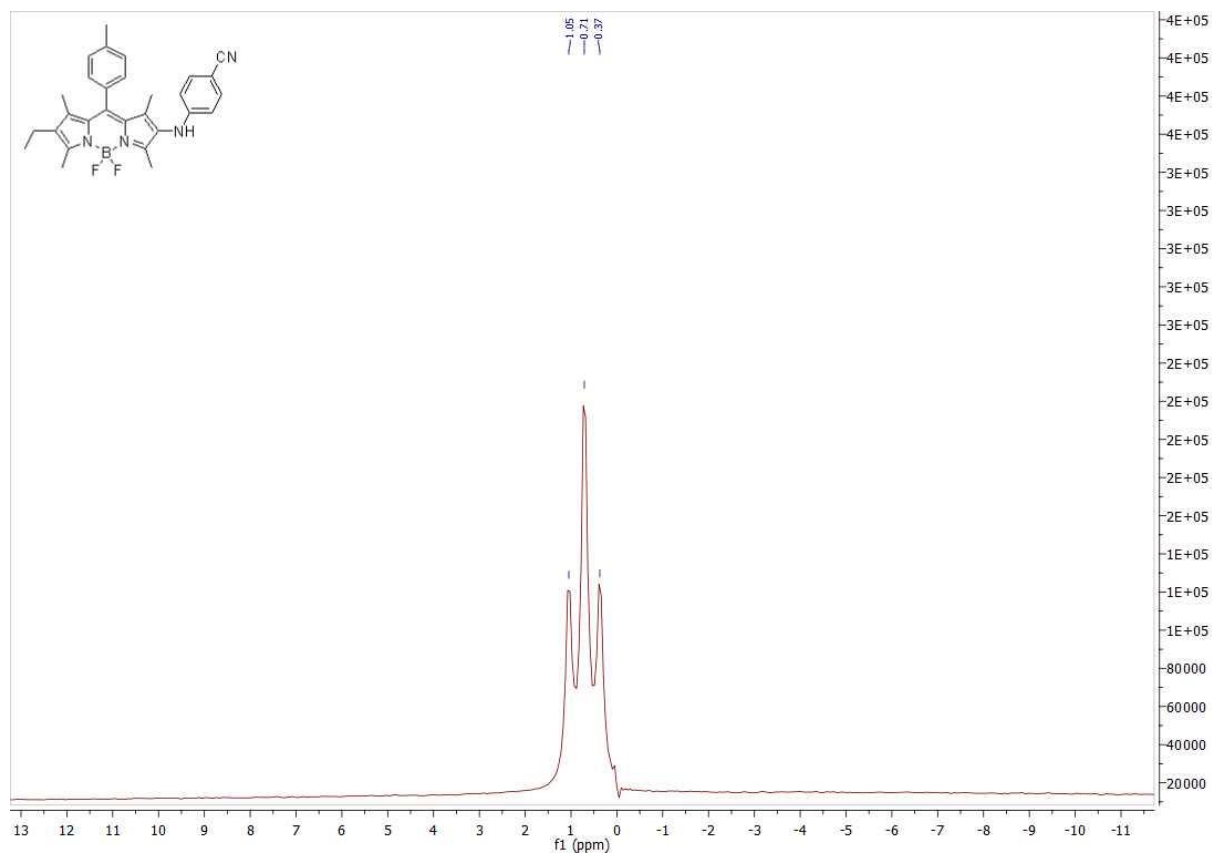
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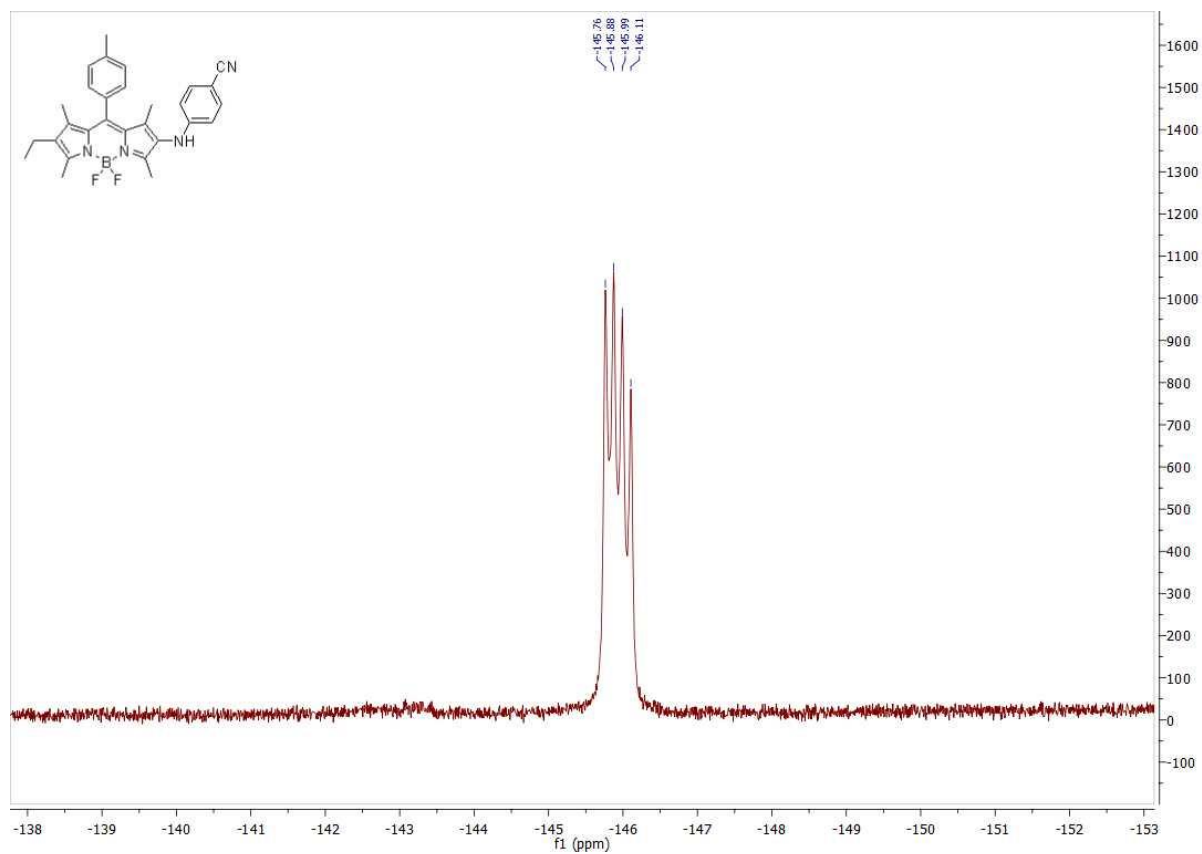
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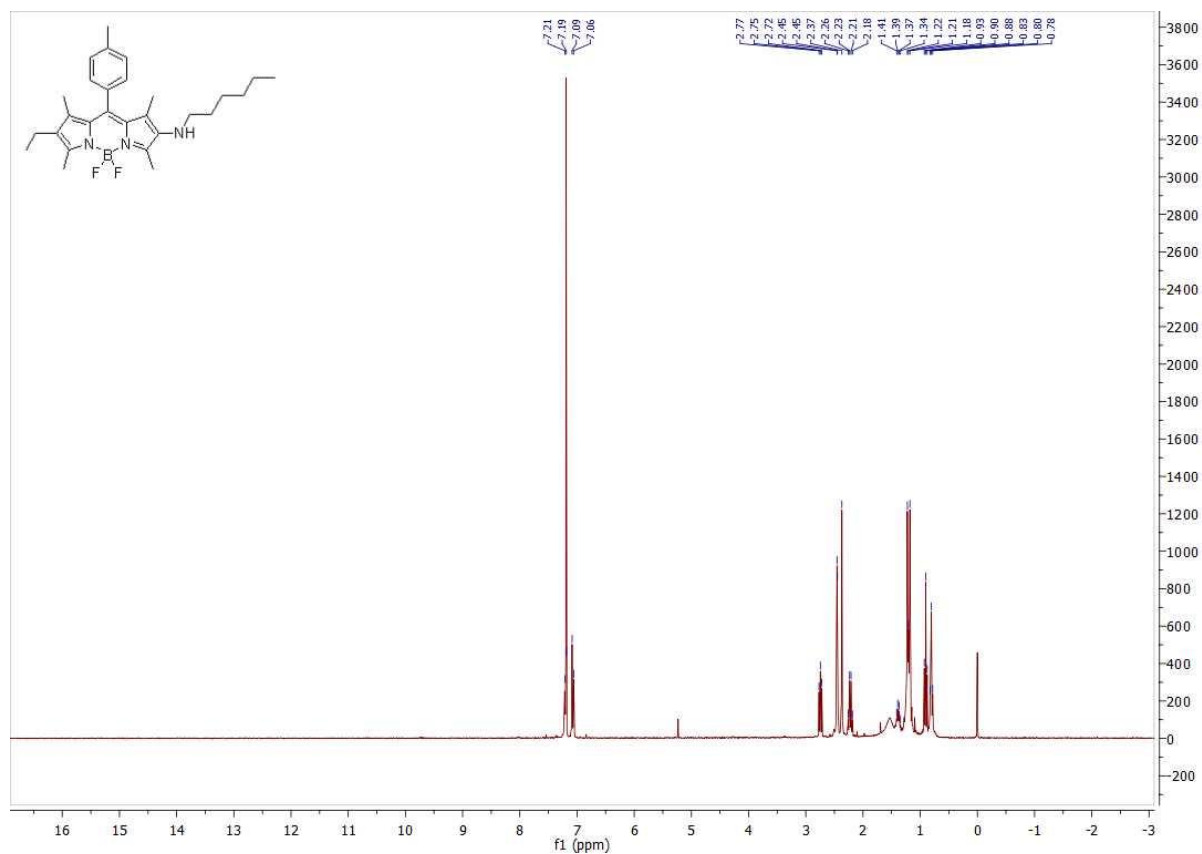
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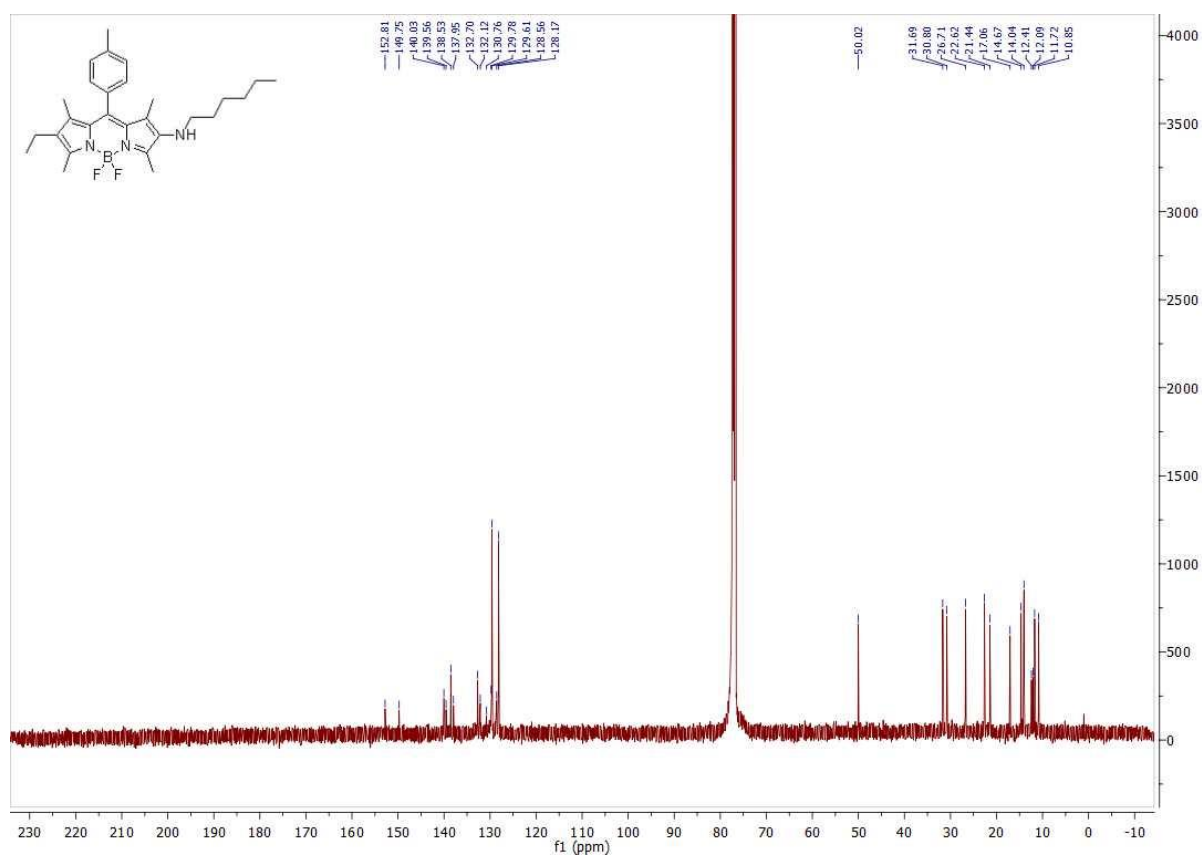
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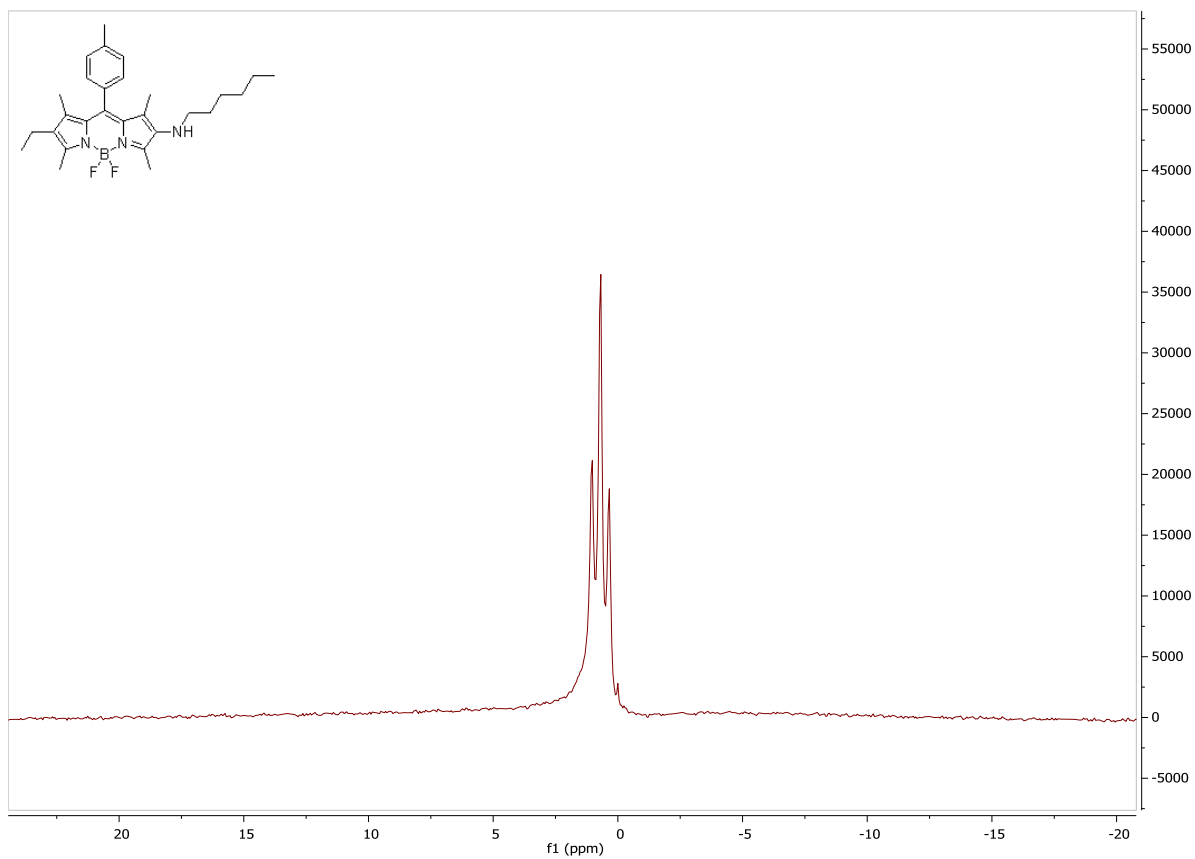


$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )

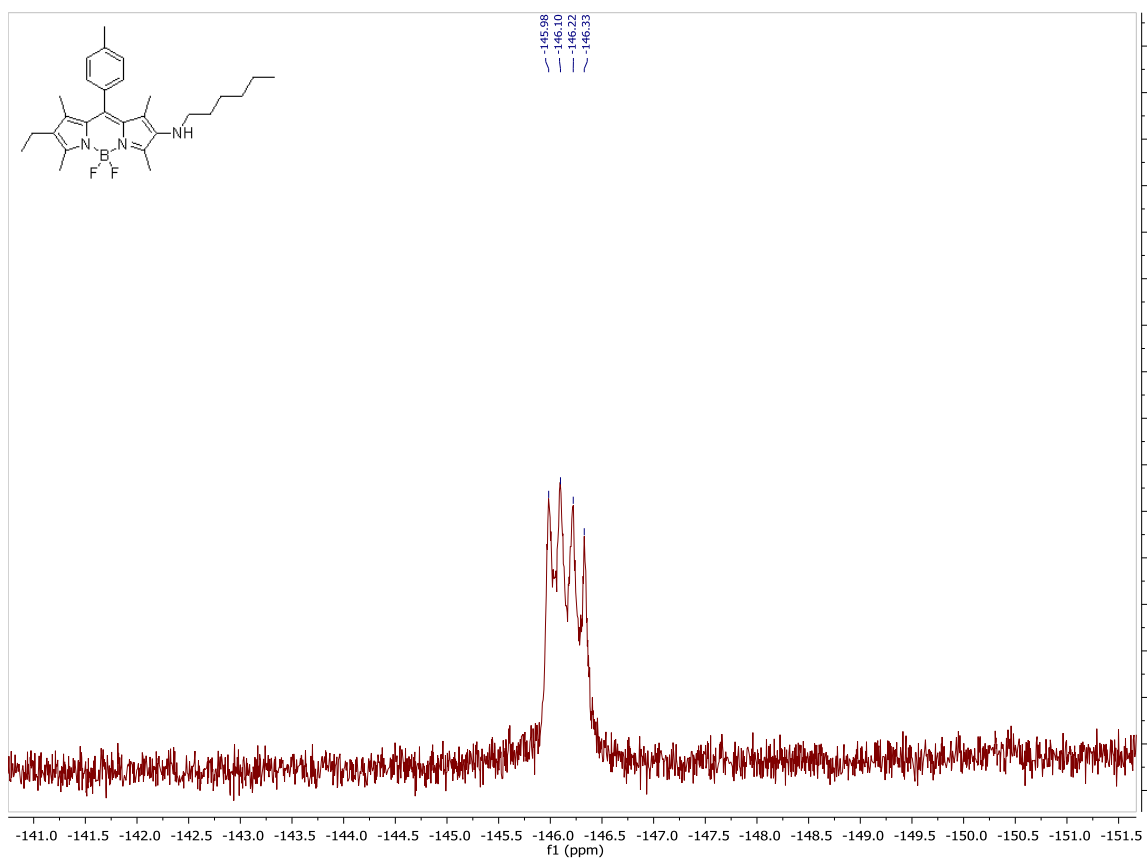




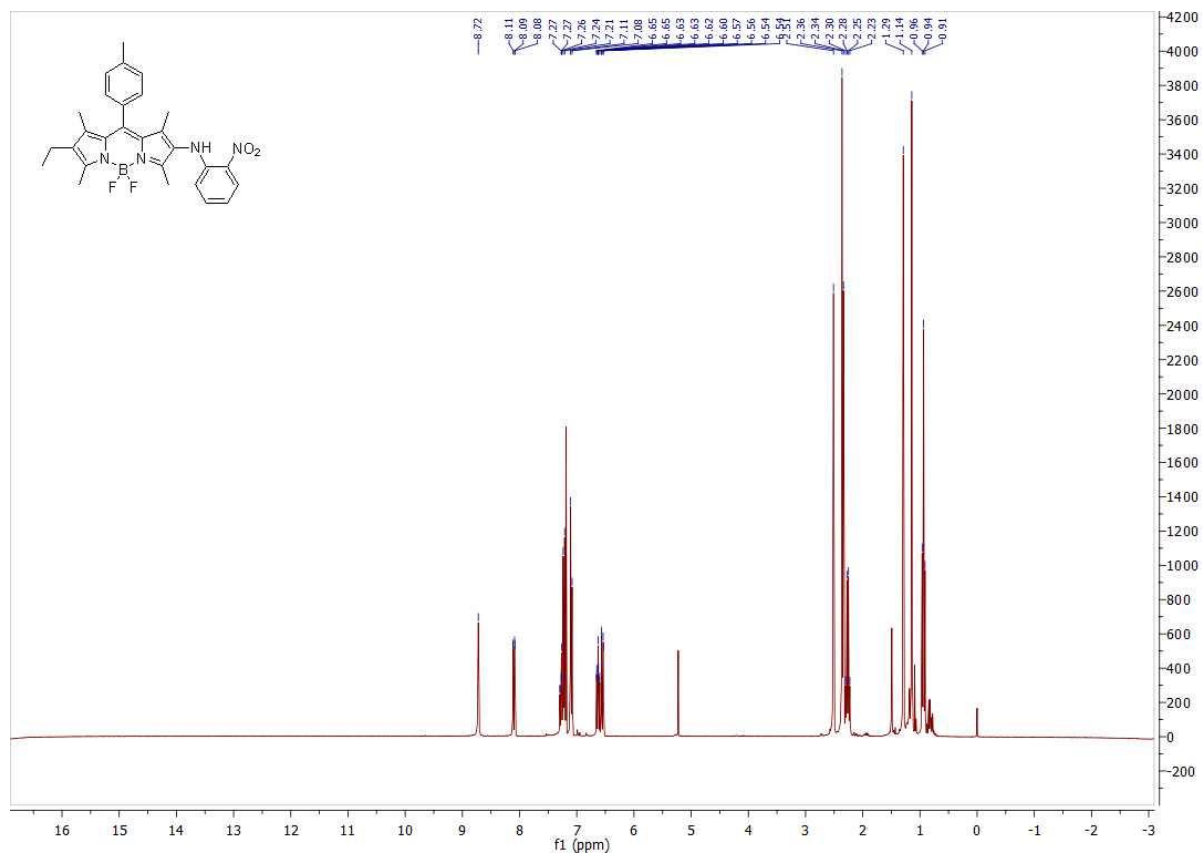
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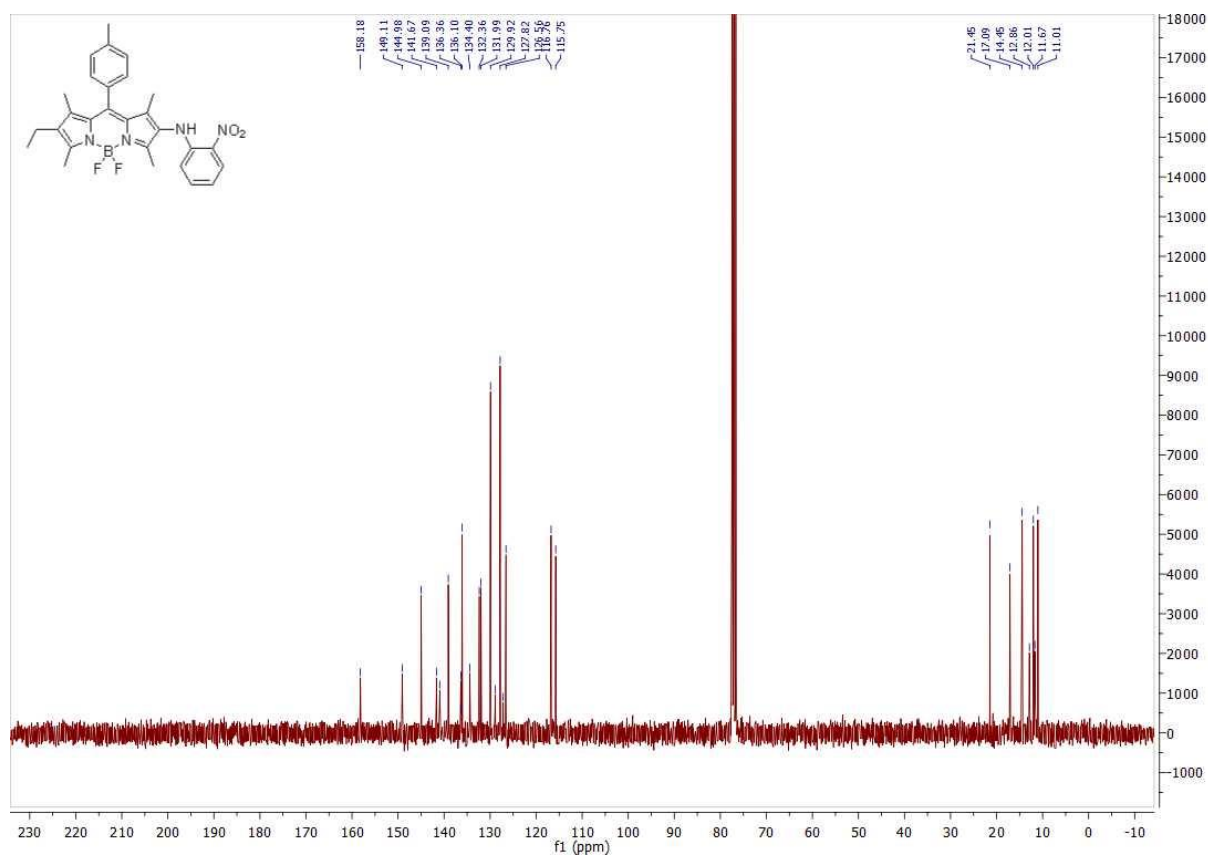
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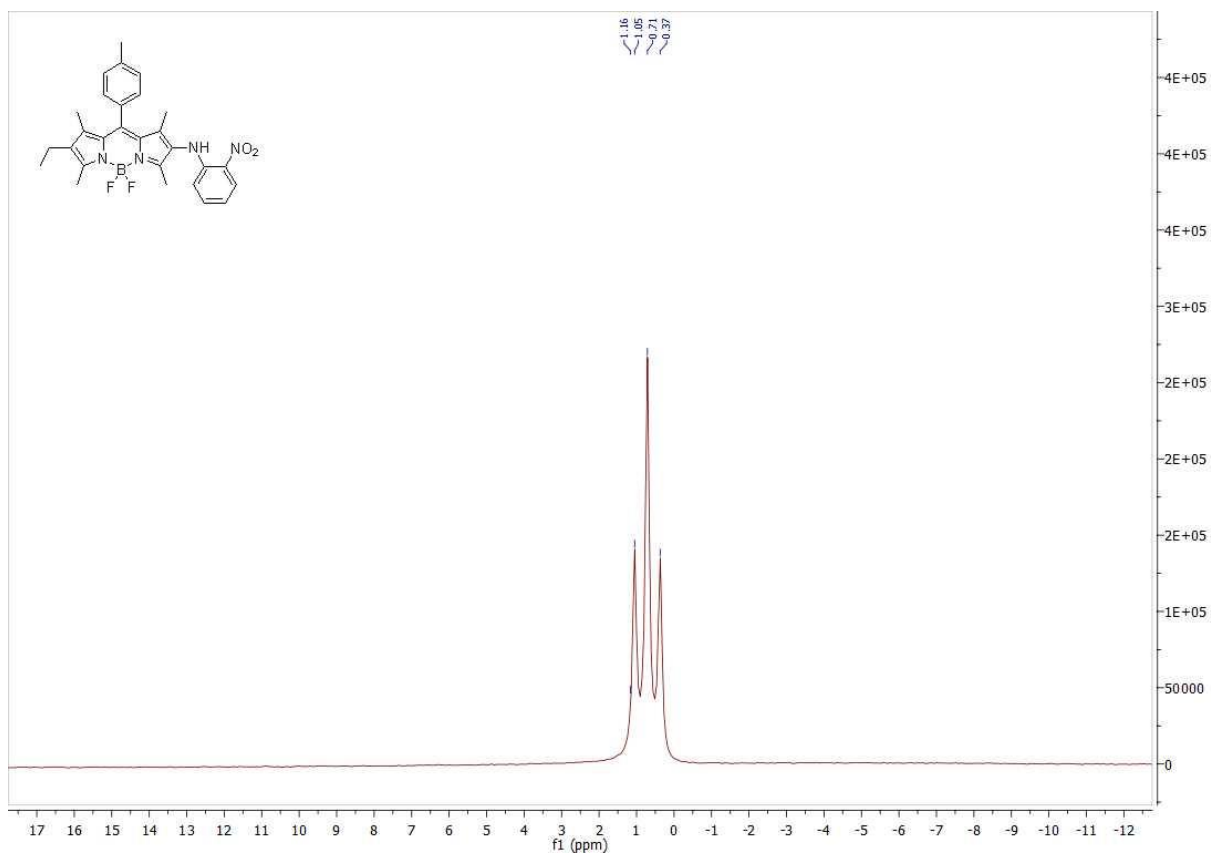
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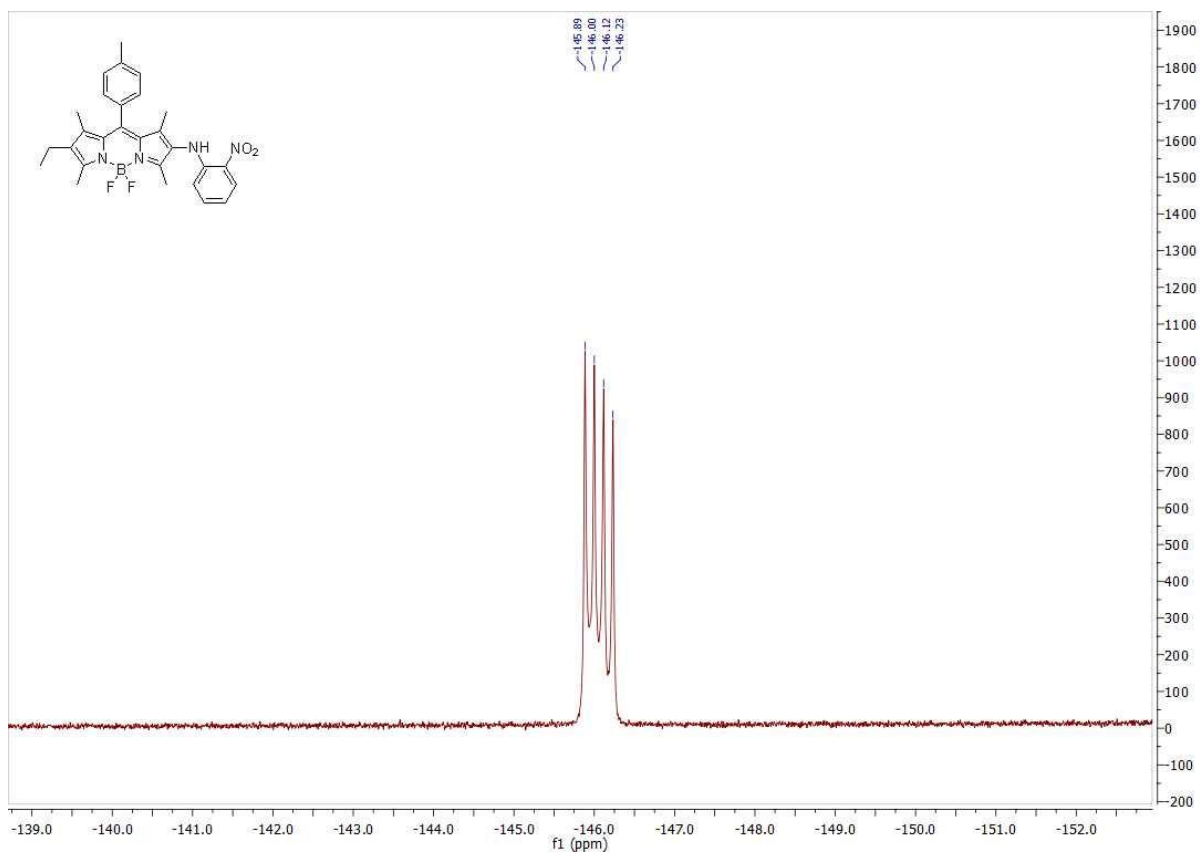
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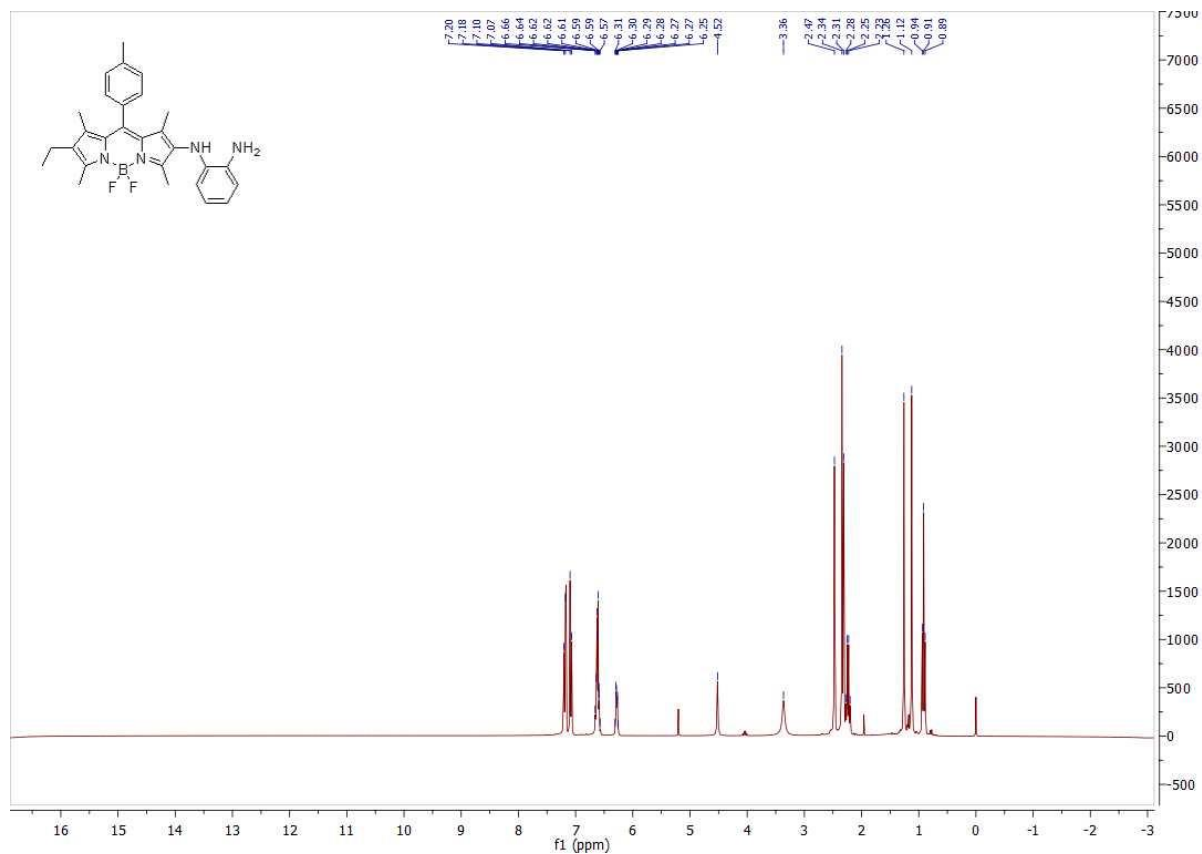
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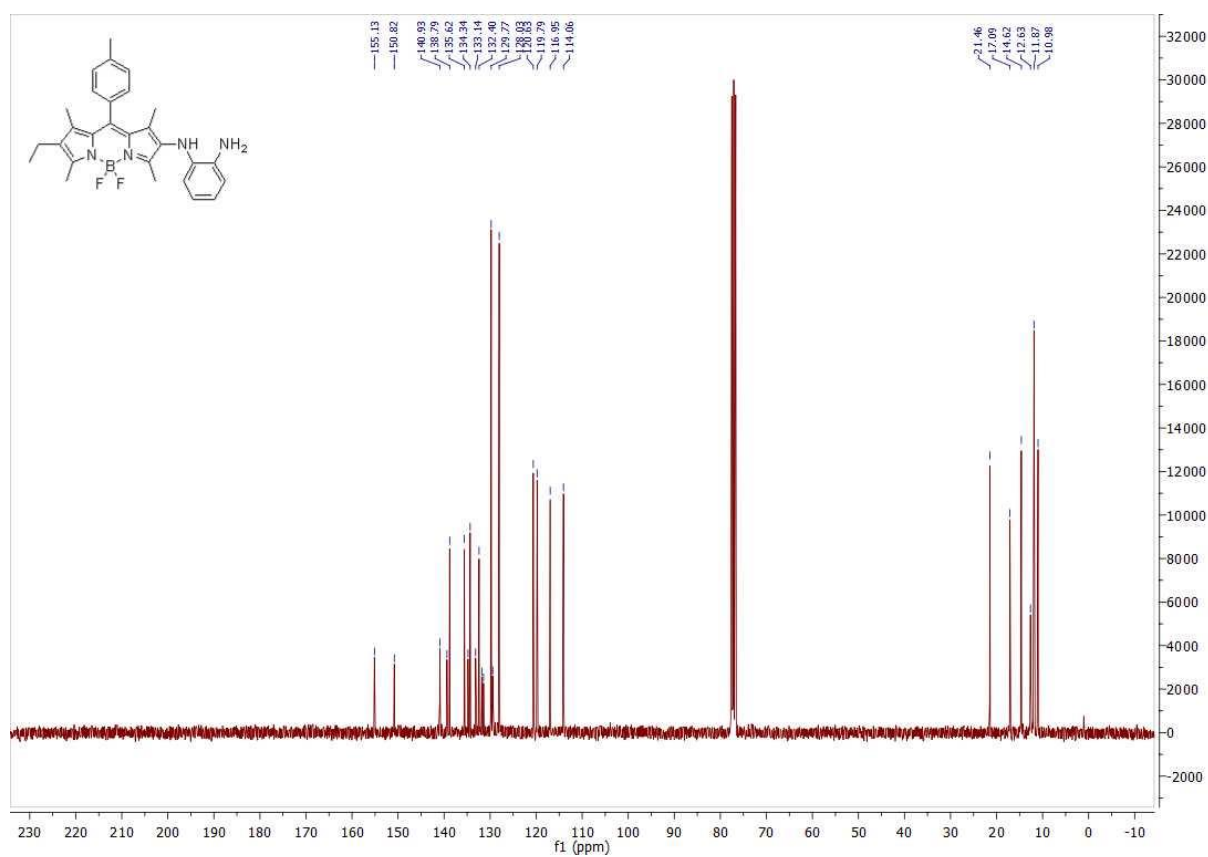
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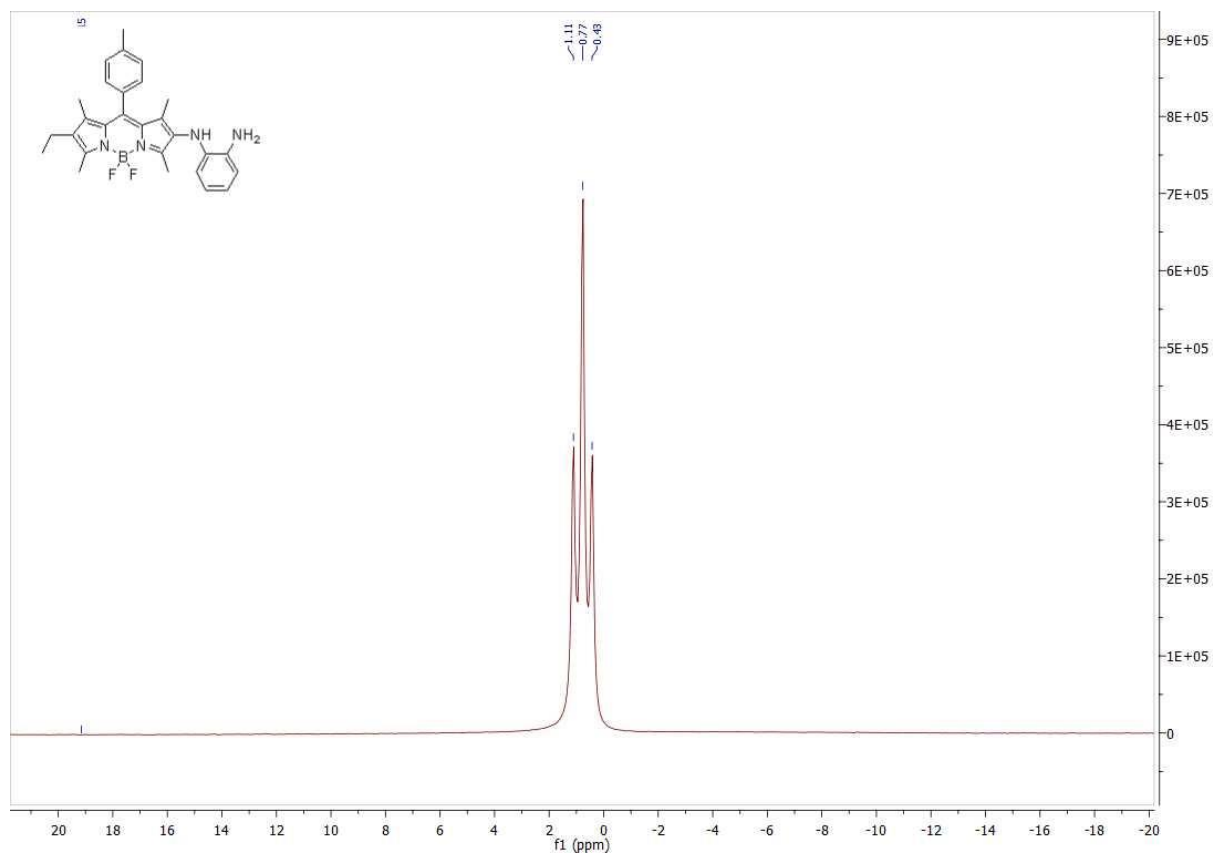
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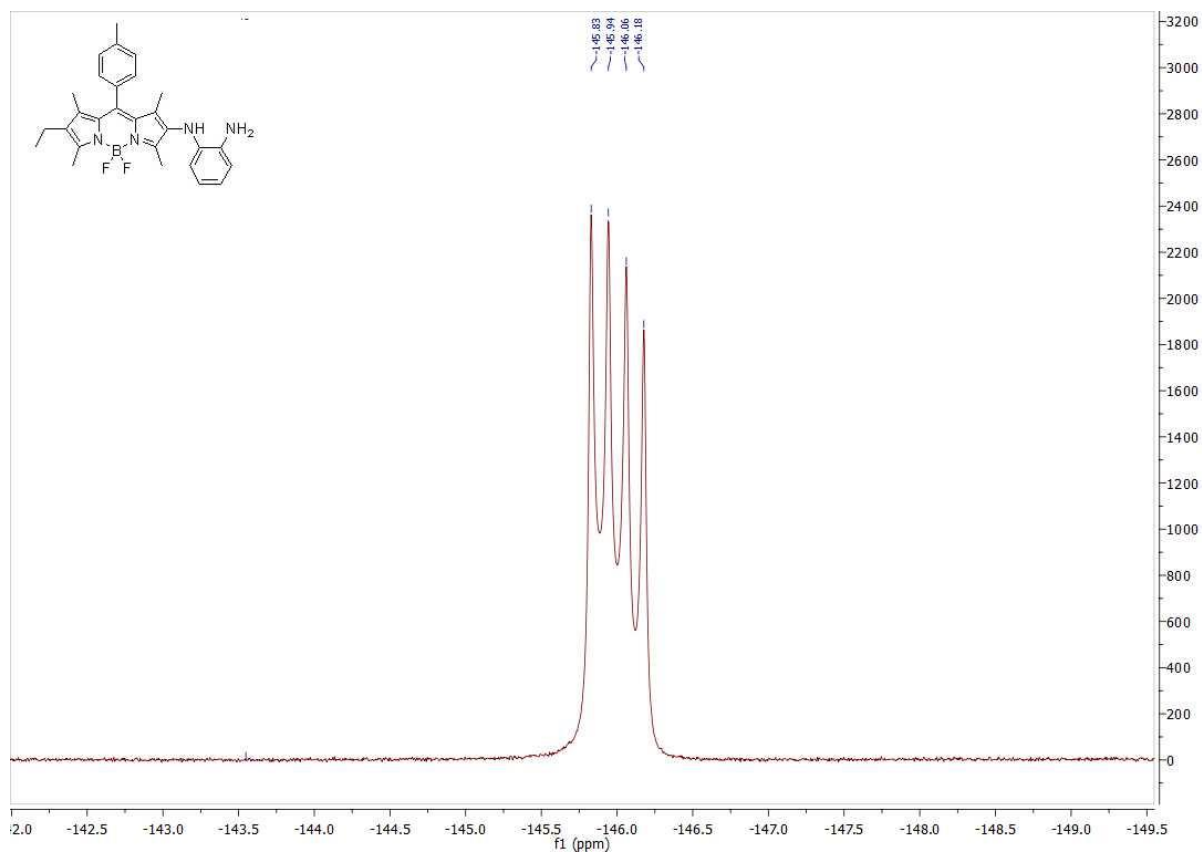
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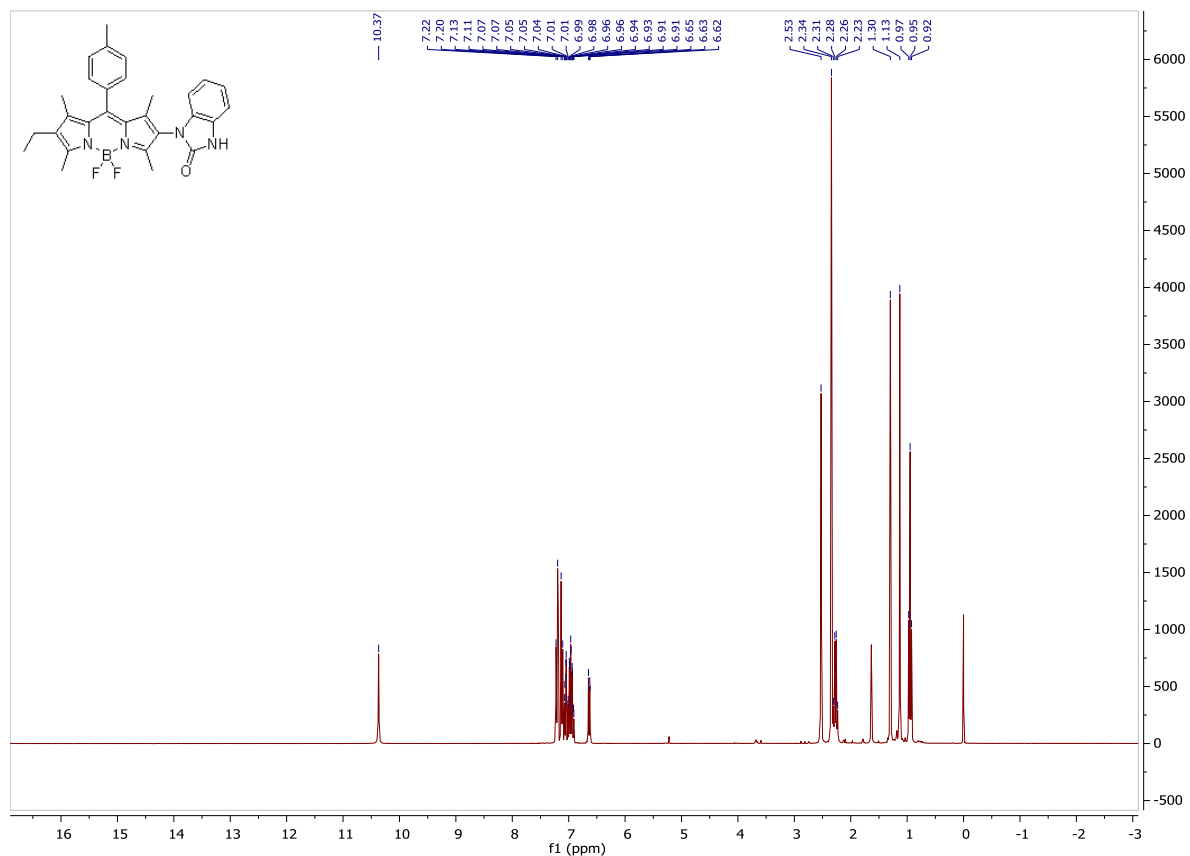
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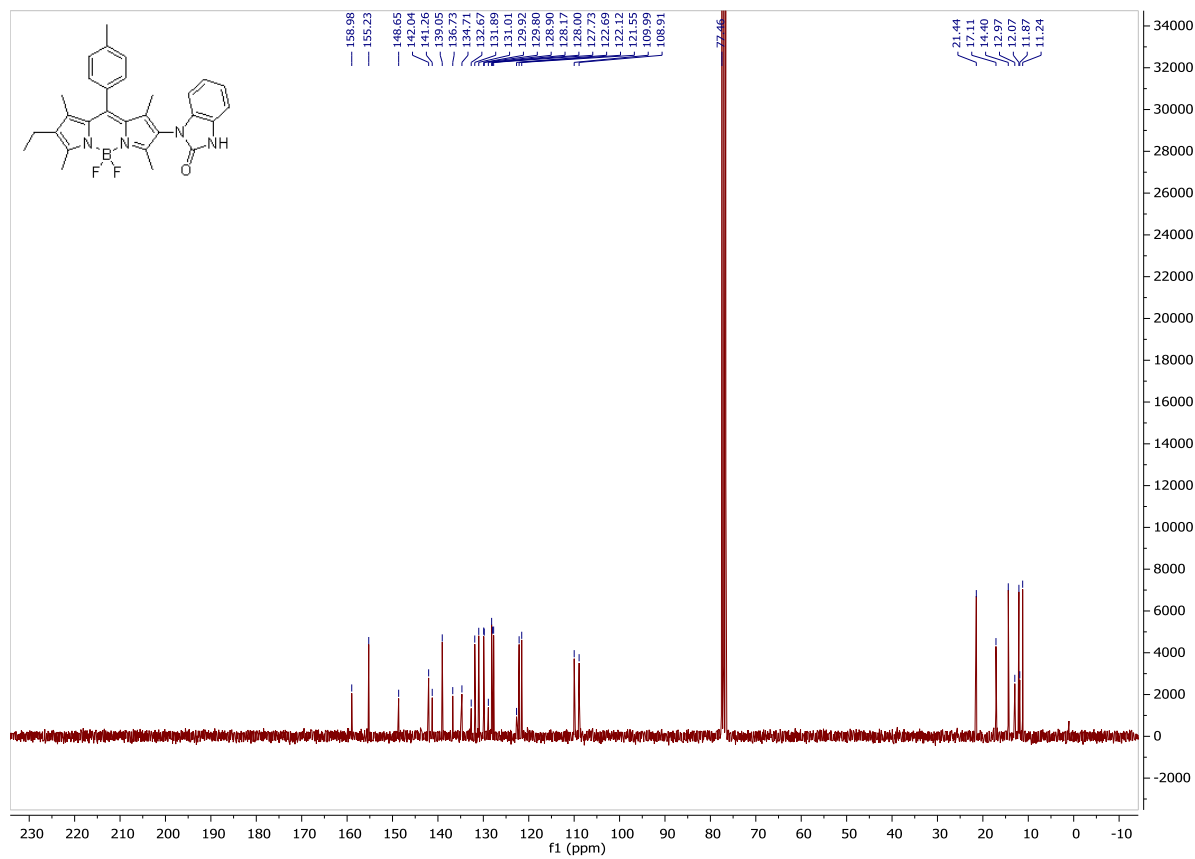
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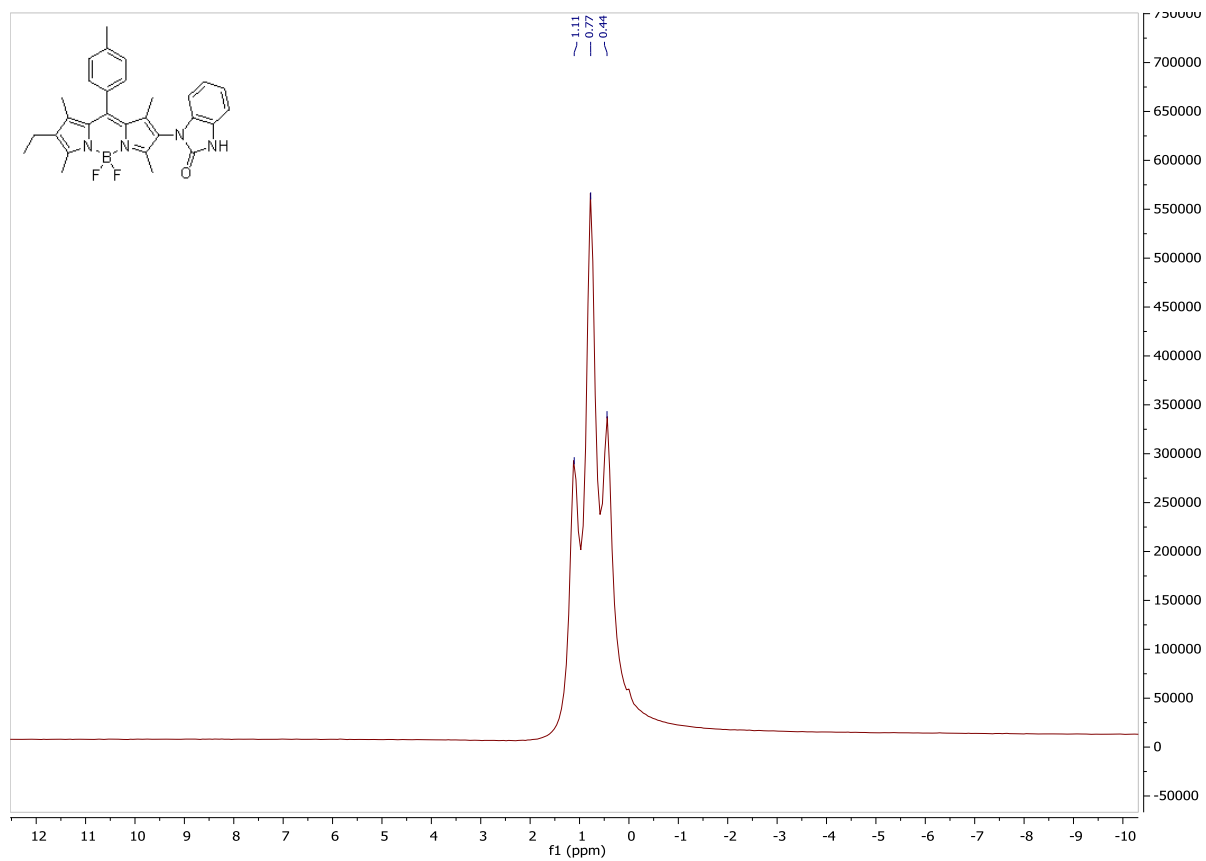
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$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )



$^{11}\text{B}$  NMR (96 MHz,  $\text{CDCl}_3$ )



$^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )

