

BiCl₃ catalyzed synthesis of 2-amino-1,4-naphthoquinones and 1,4-naphthoquinon-2-sulfides and one-pot sequential amine-arylation of 1,4-naphthoquinone

Supporting Information

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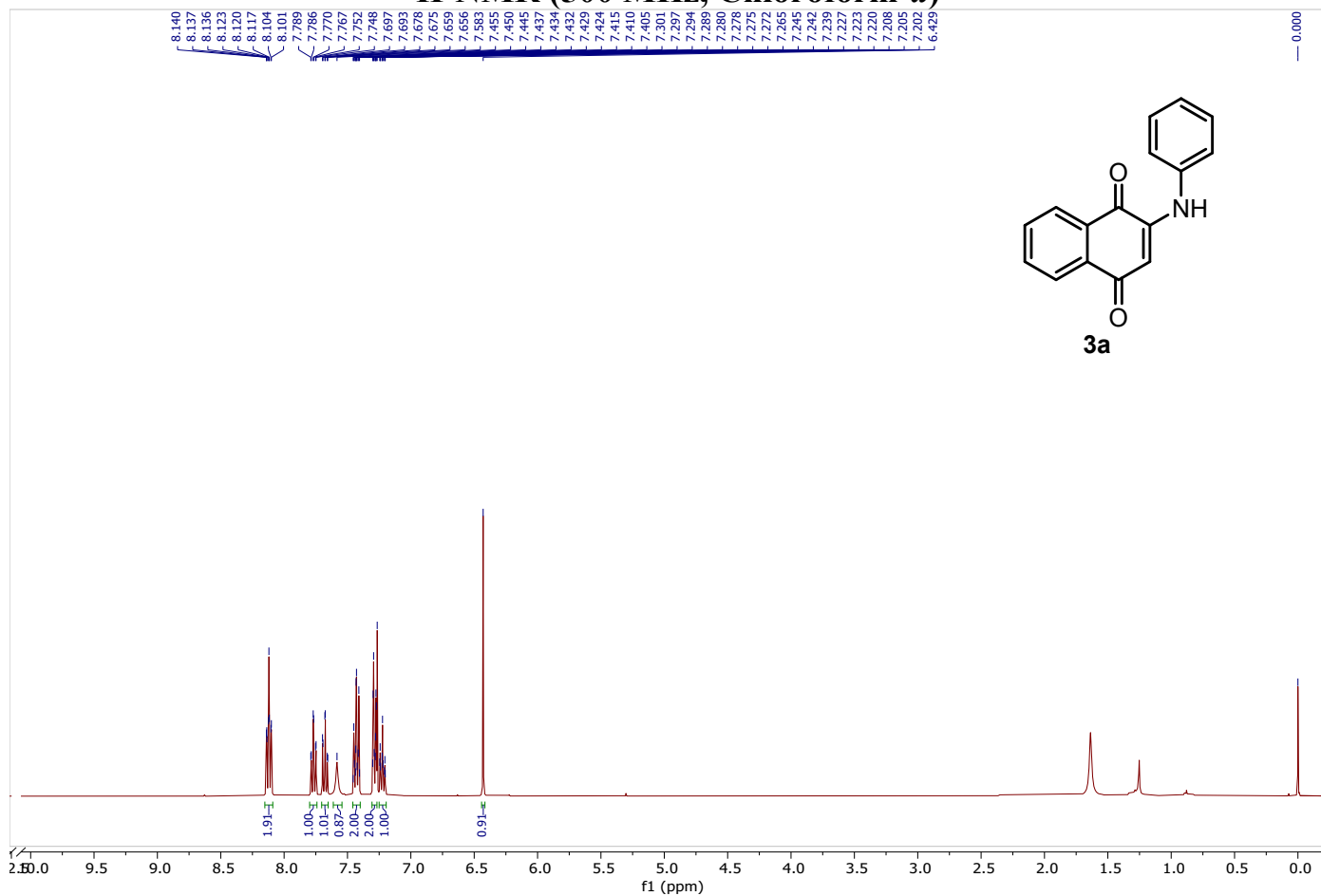
General procedure for gram-scale synthesis of 2-amino-1,4-naphthoquinones (3):

To a stirred suspension of 1,4-naphthoquinone (**1**, 7.0 mmol) in methanol (15 mL) at room temperature (30 °C), amine (**2**, 7.0 mmol) was slowly added dropwise. BiCl₃ (4 mol%) was added and the reaction mixture was stirred for approximately 12 hrs in a round bottom flask at room temperature (30 °C) under open-air atmosphere. After completion of the reaction (as monitored by TLC), the reaction mixture was filtered through a Whatman filter paper grade-1. The residue was washed with ice-cold methanol (3×15 mL) and dried. The residue obtained without any further purification is the required 2-amino-1,4-naphthoquinone **3**.

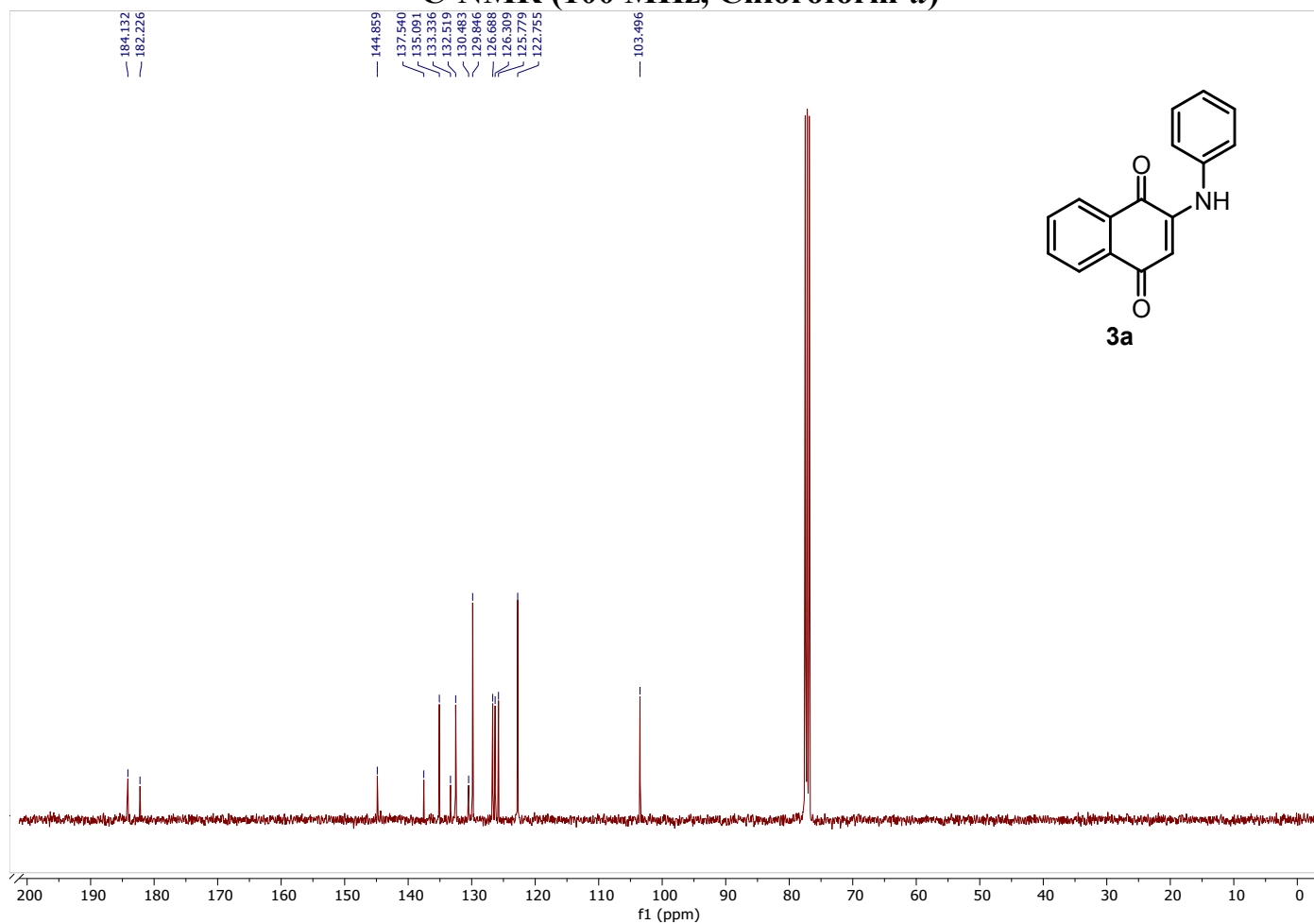
General procedure for gram-scale synthesis of 2-amino-3-aryl-1,4-naphthoquinones (7):

To a stirred suspension of 1,4-naphthoquinone (**1**, 7.0 mmol) in acetonitrile (15 mL), amine (**2**, 8.4 mmol) was slowly added dropwise. BiCl₃ (4 mol%) was added and the reaction mixture was stirred for approximately for 12 hrs in a 50 mL round bottom flask at 50 °C under open-air atmosphere. After completion of the 1st step of the reaction (as monitored by TLC), aryl hydrazine (**6**, 10.5 mmol), K₂S₂O₈ (21 mmol) and CH₃CN (5 mL) were added to the reaction mixture and continued with stirring at 50 °C for another 10 hrs under open air condition. After completion of 2nd step of the reaction (as monitored by TLC) water (20 mL) was added to the reaction mixture and extracted with ethyl acetate (3x20 mL). The organic layer was washed with brine (1x15 mL) and dried over anhydrous sodium sulfate. The organic layer was concentrated under rotary evaporator and column chromatographed on silica gel (230-400 mesh) using 1: 9 ethyl acetate–hexane as the eluent to get the pure 2-amino-3-aryl-1,4-naphthoquinone **7**.

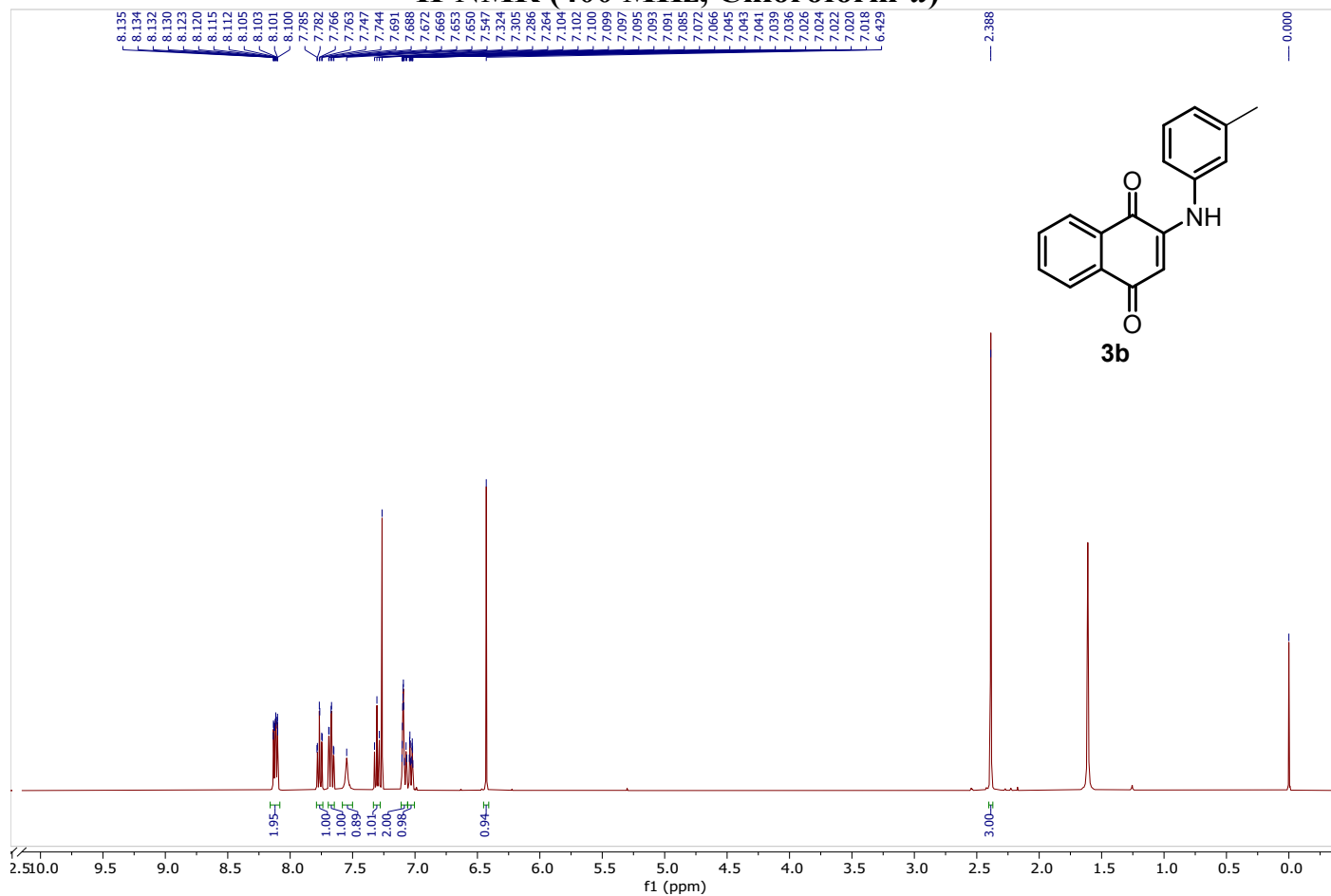
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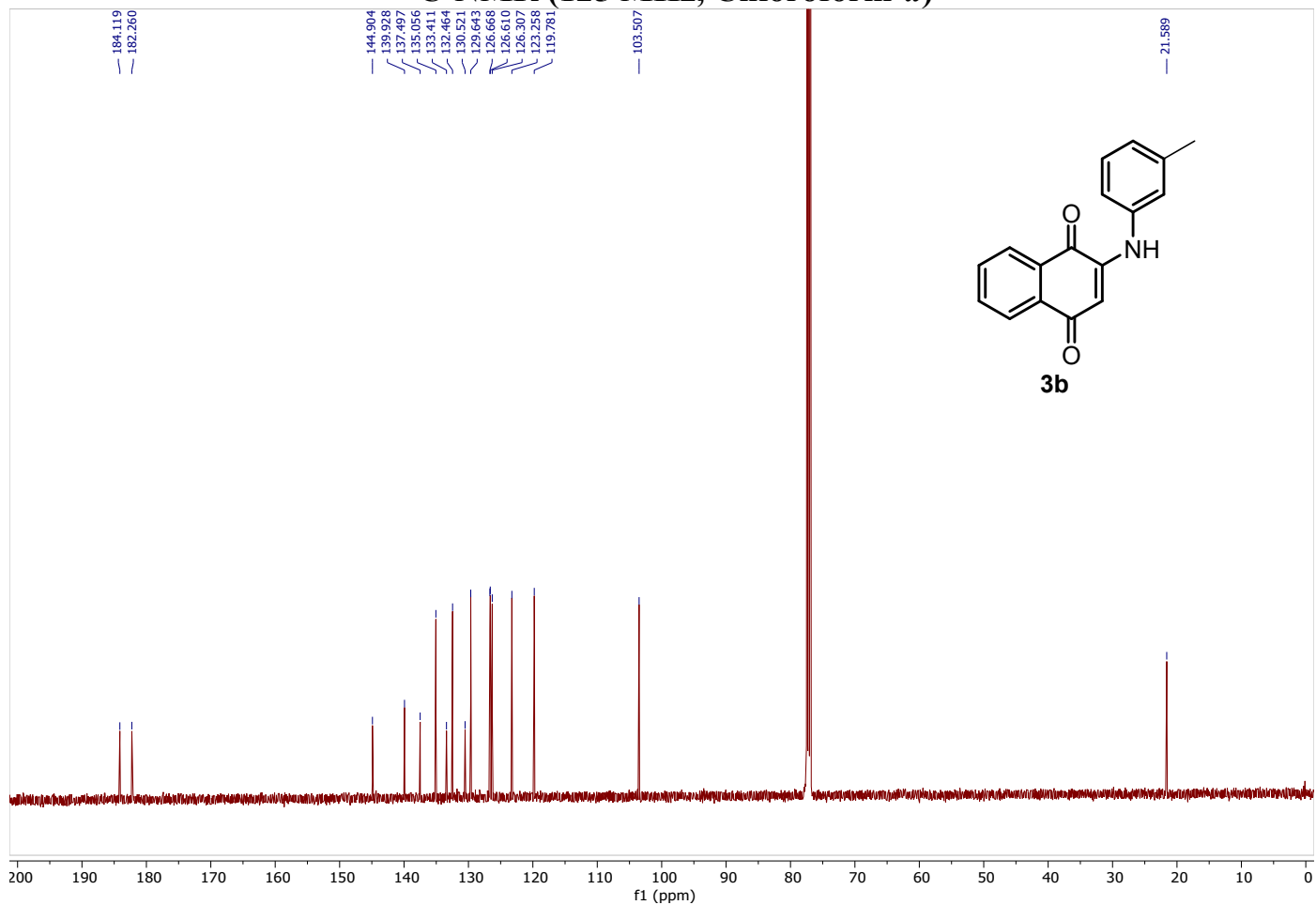
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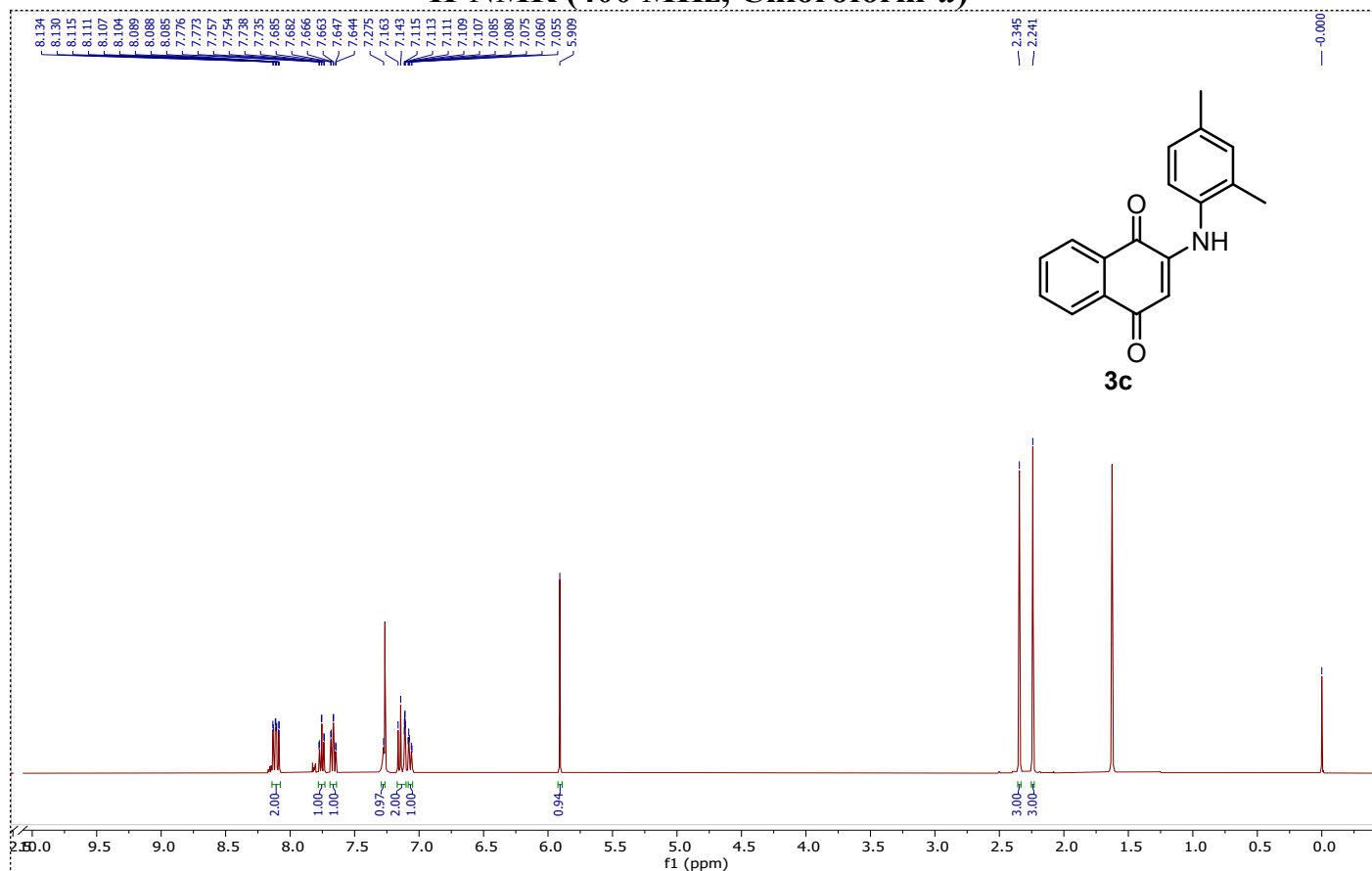
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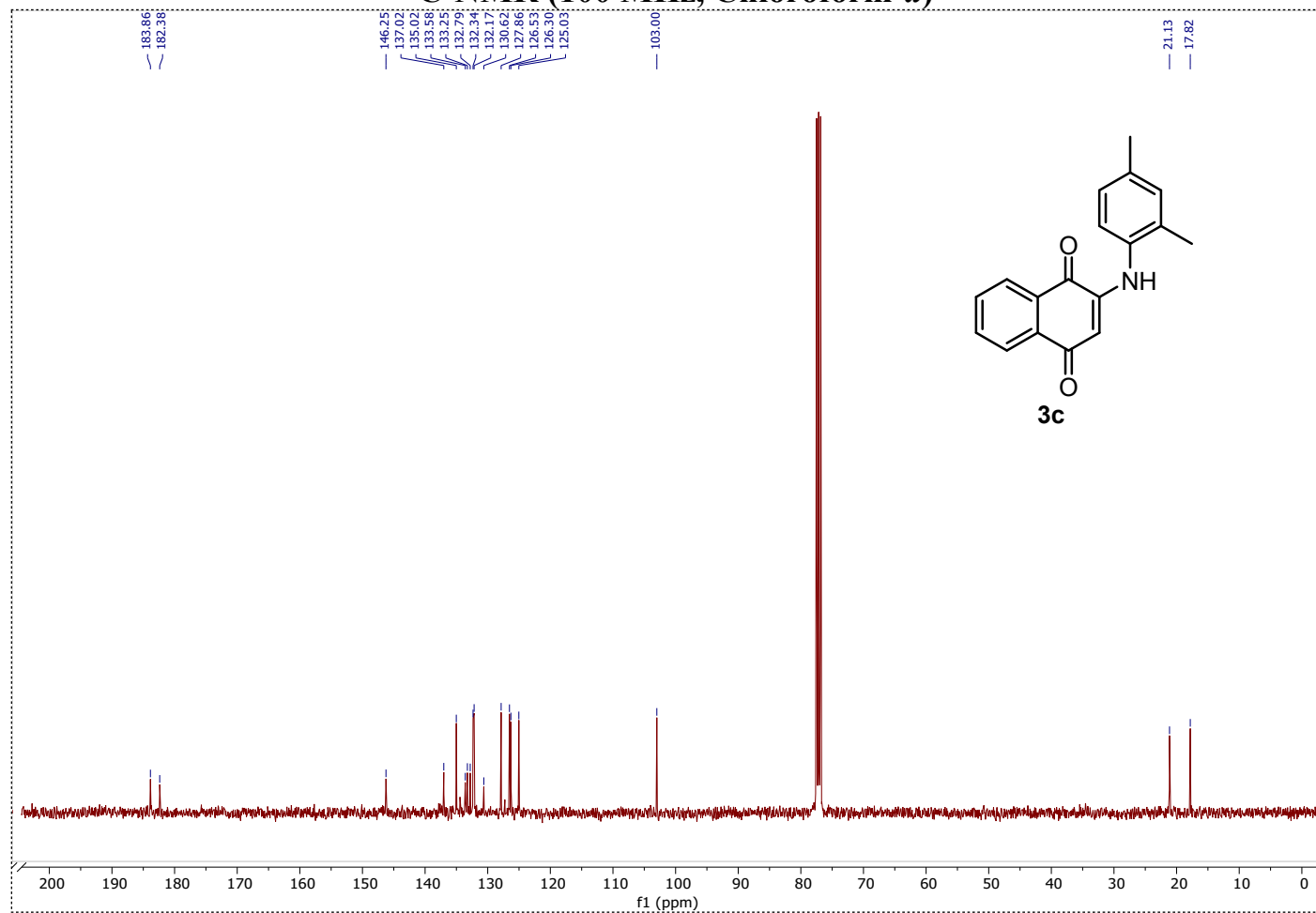
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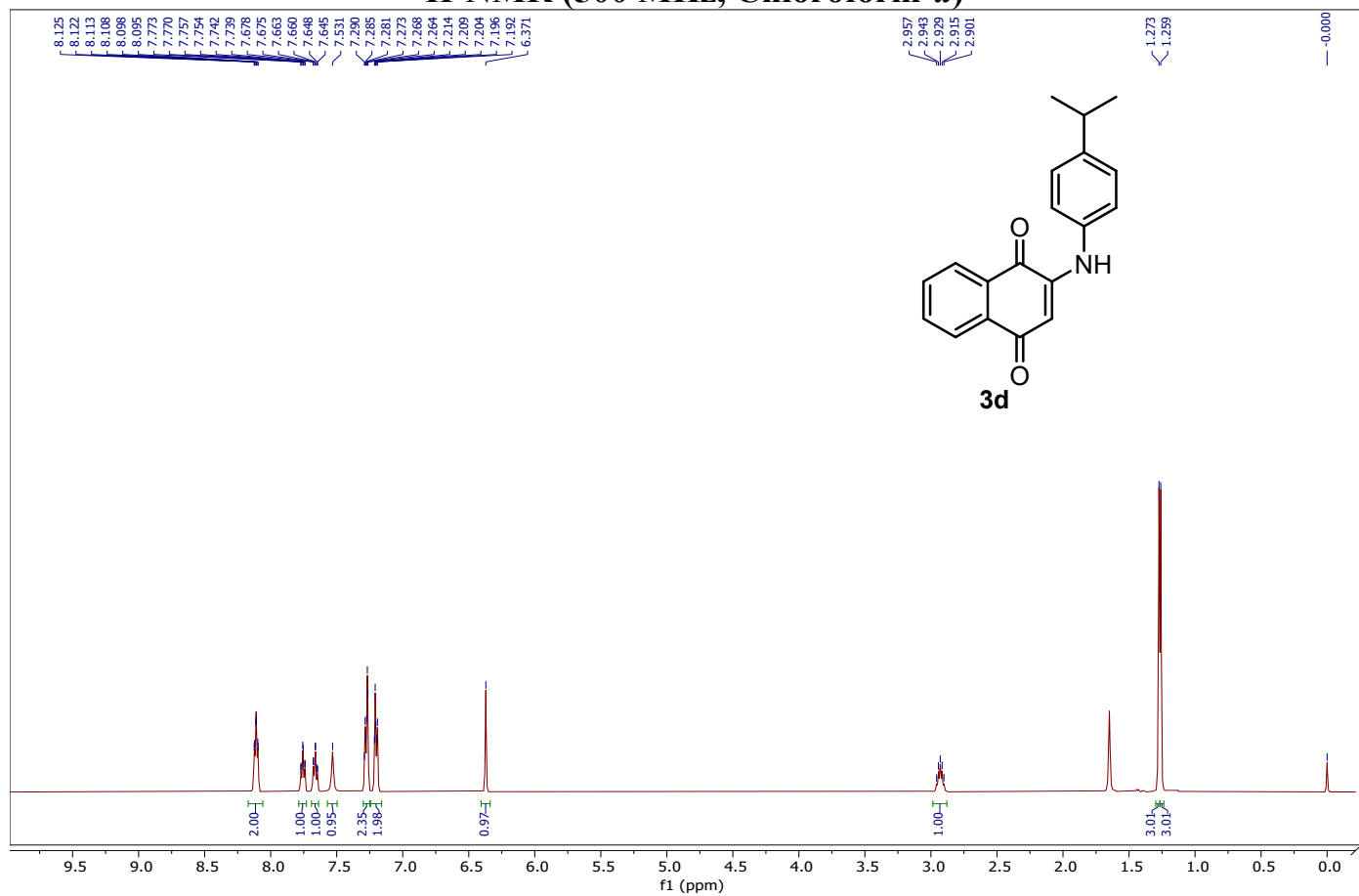
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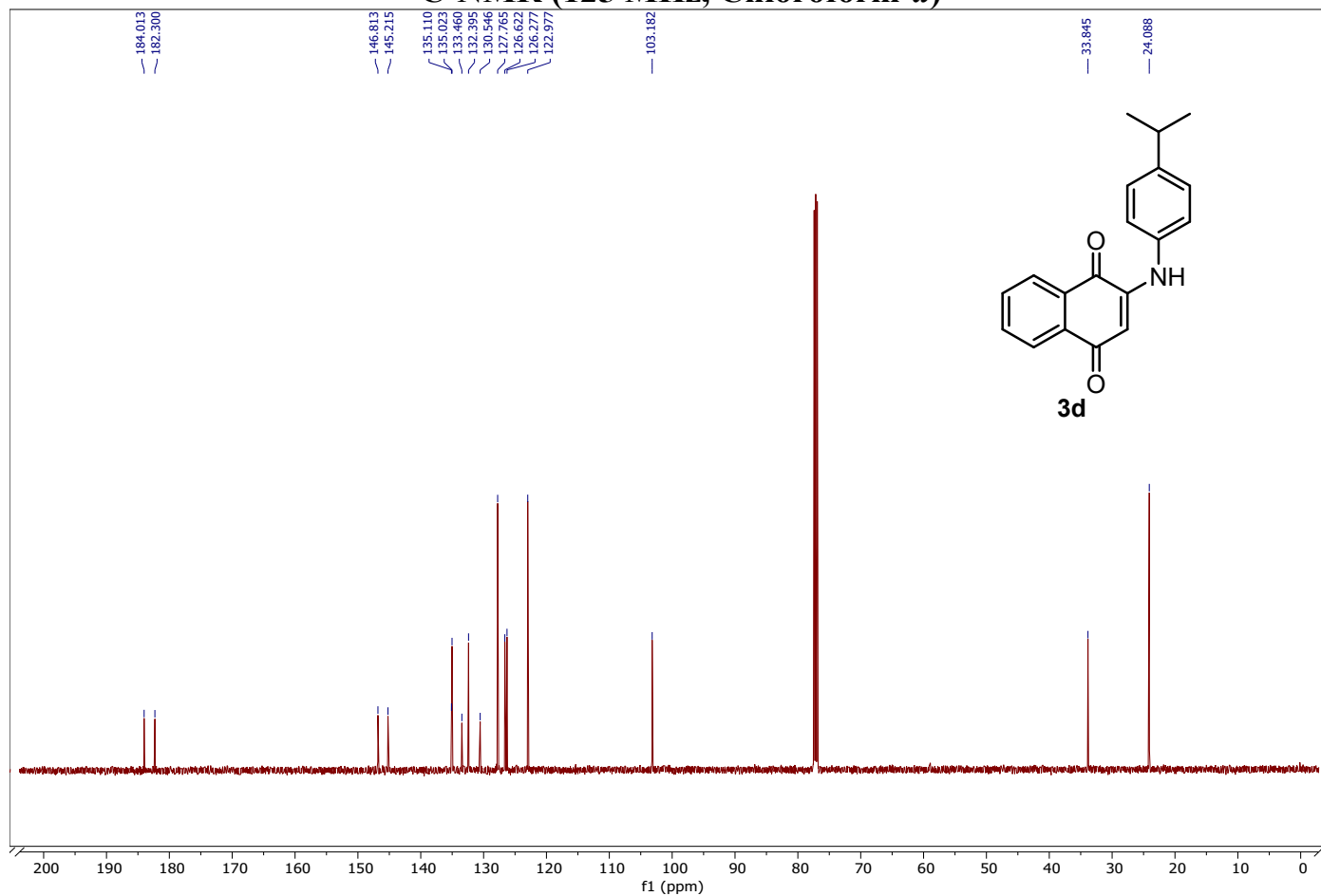
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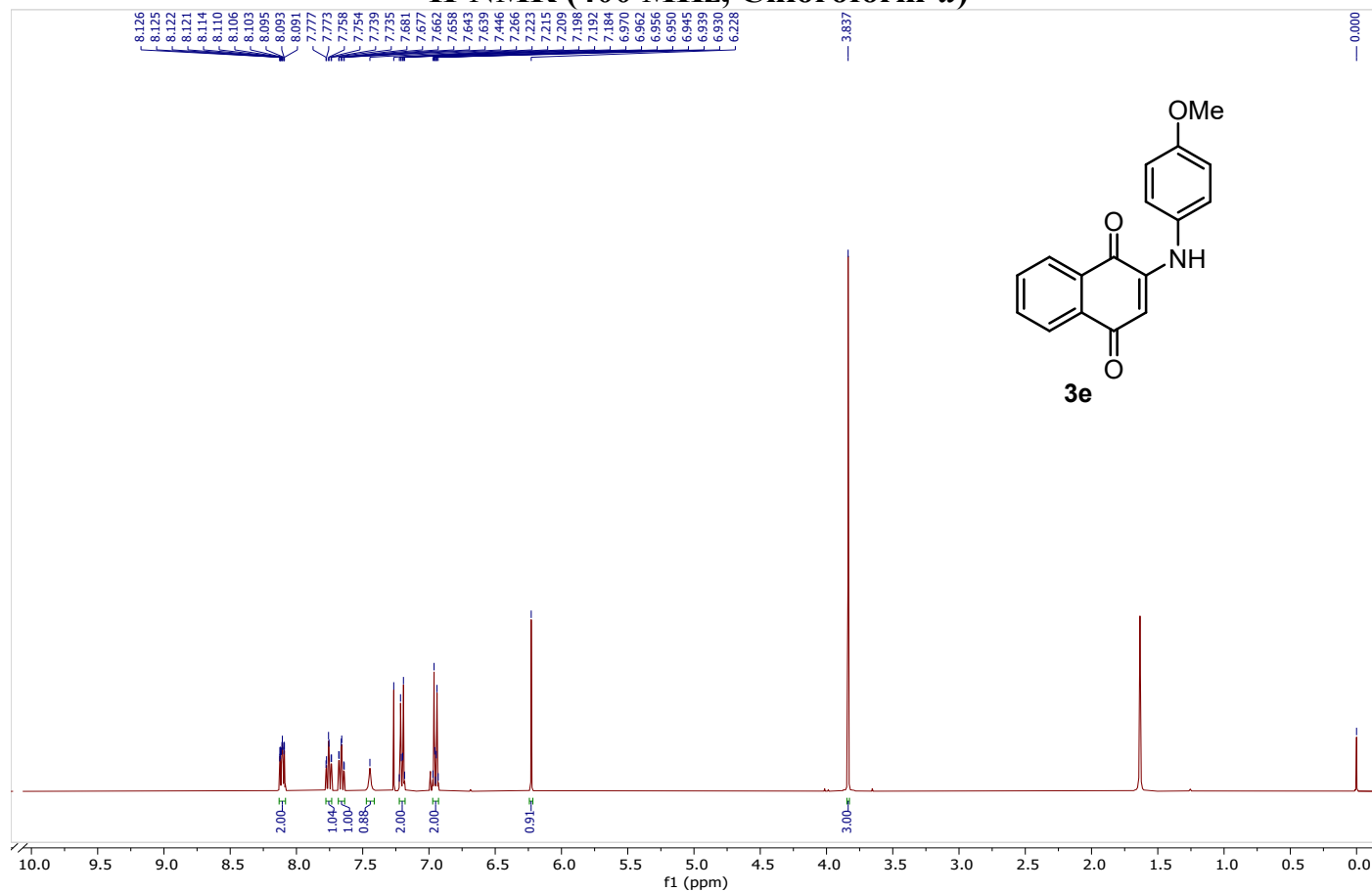
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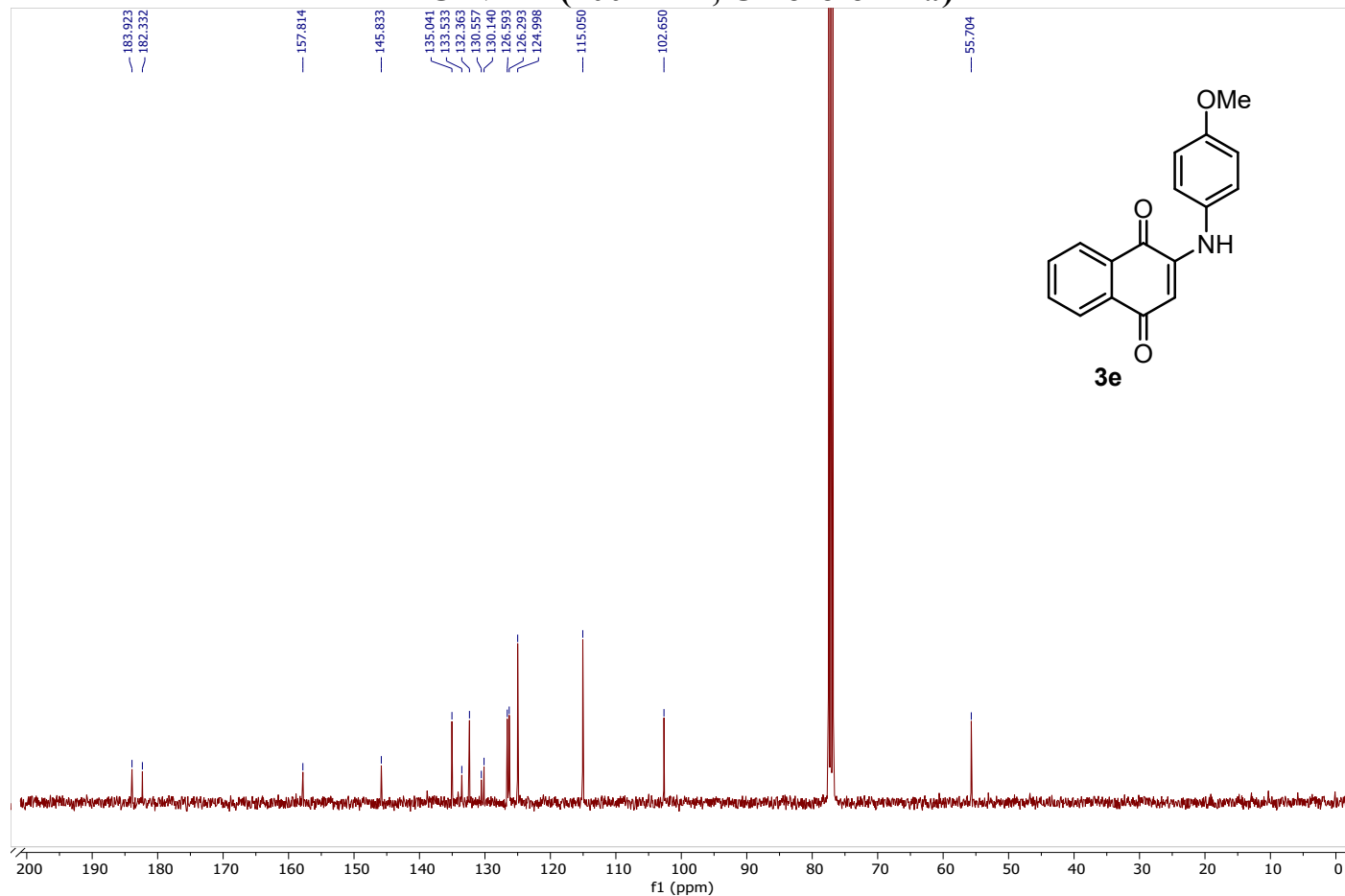
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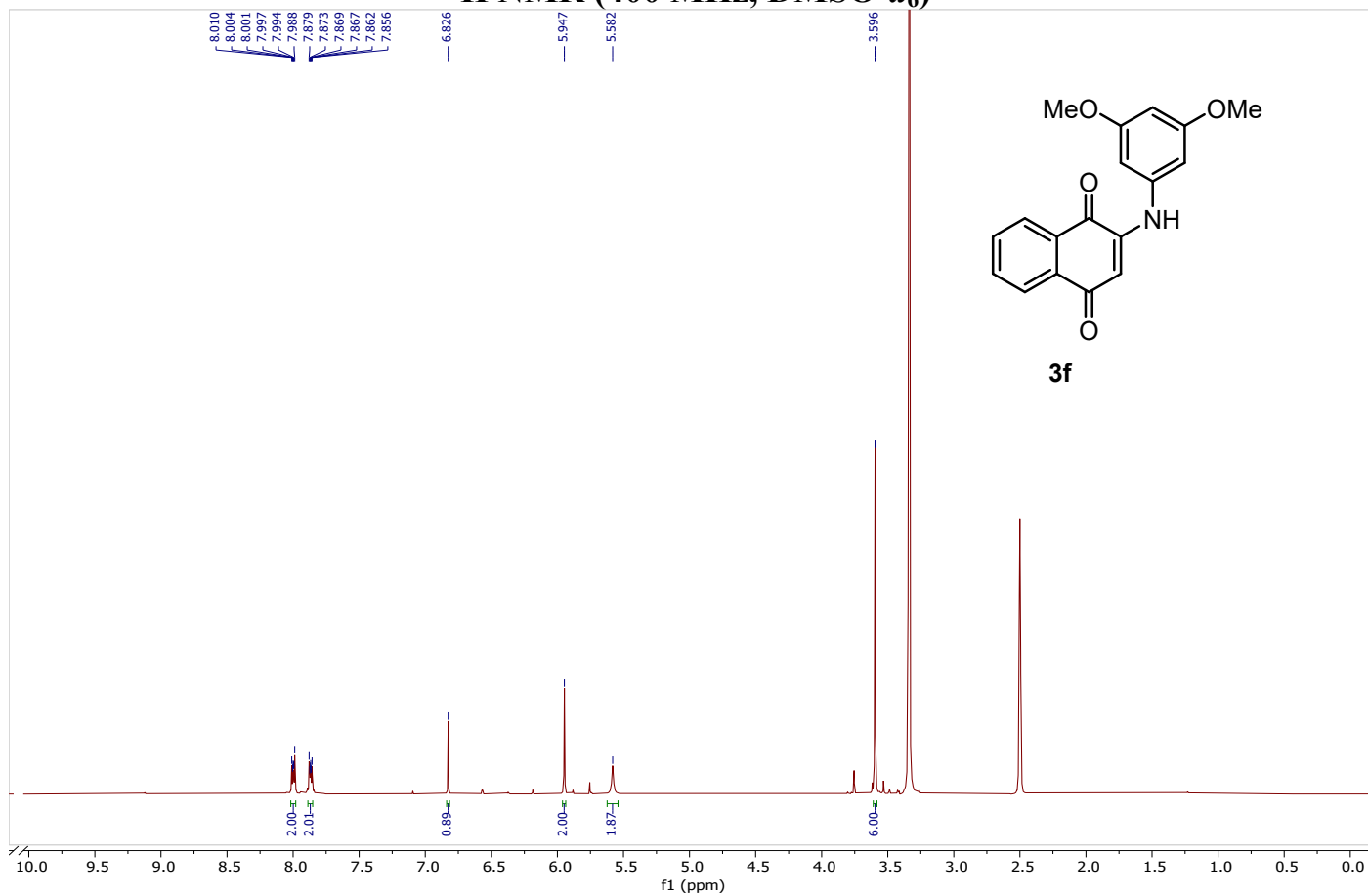
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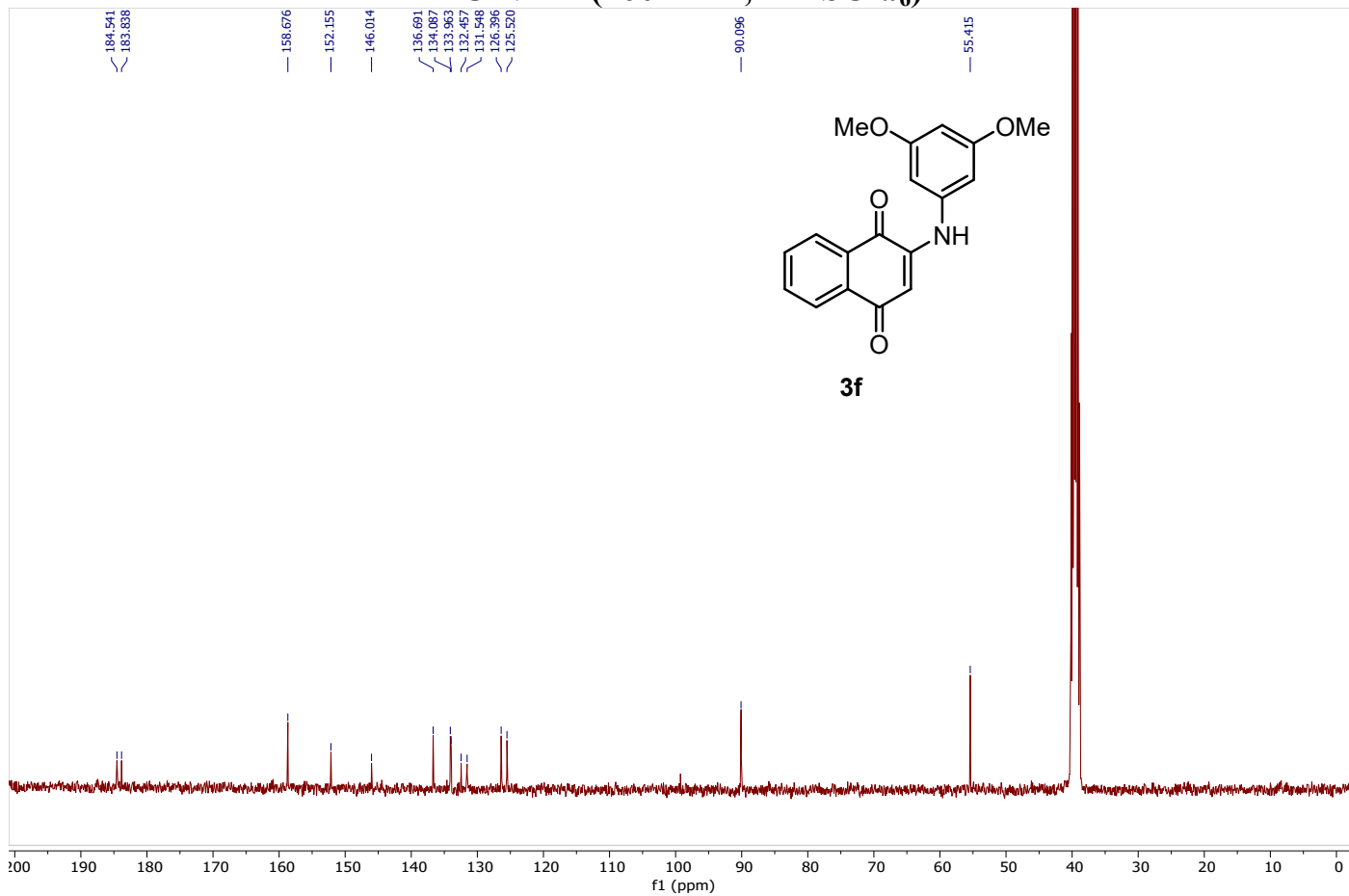
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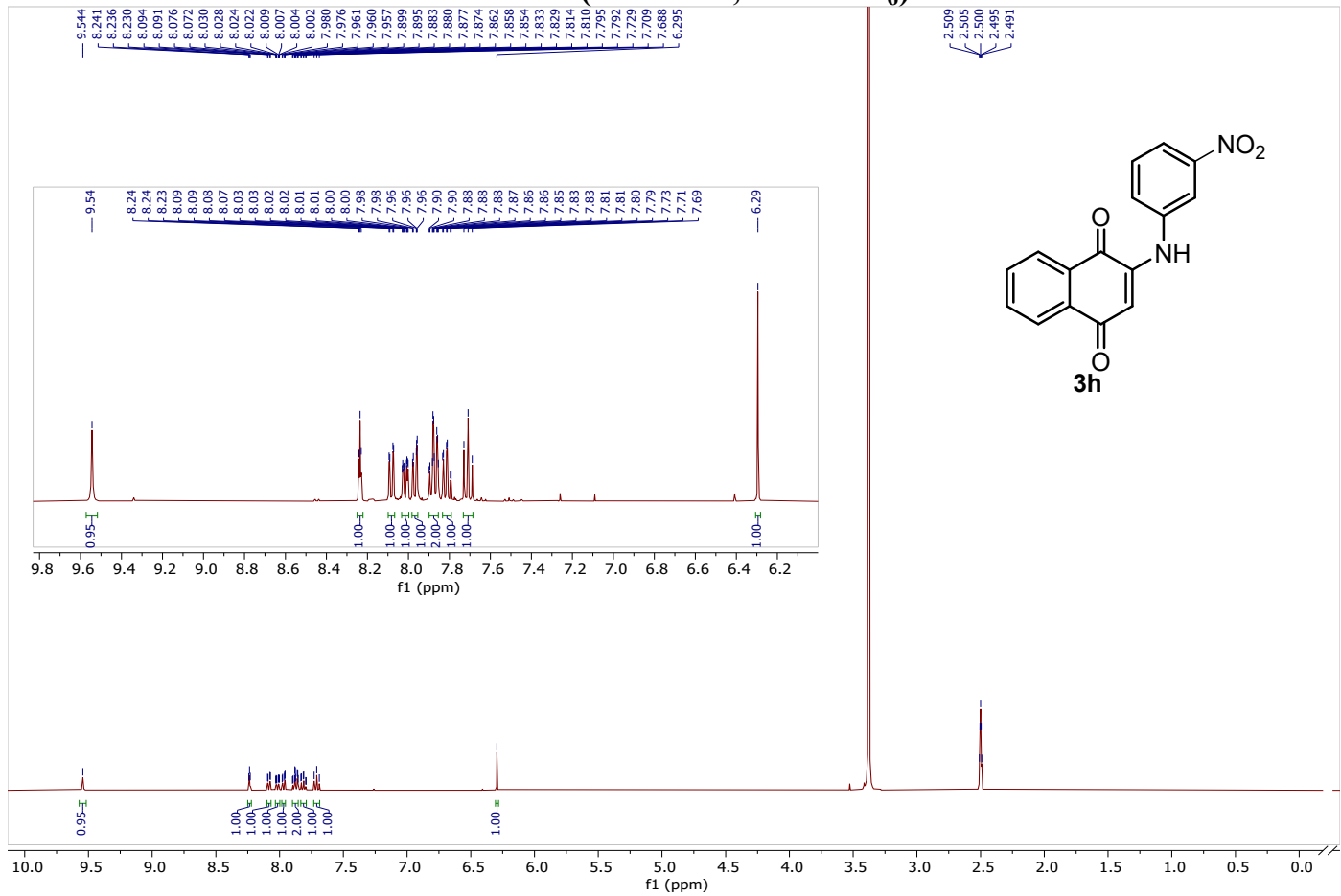
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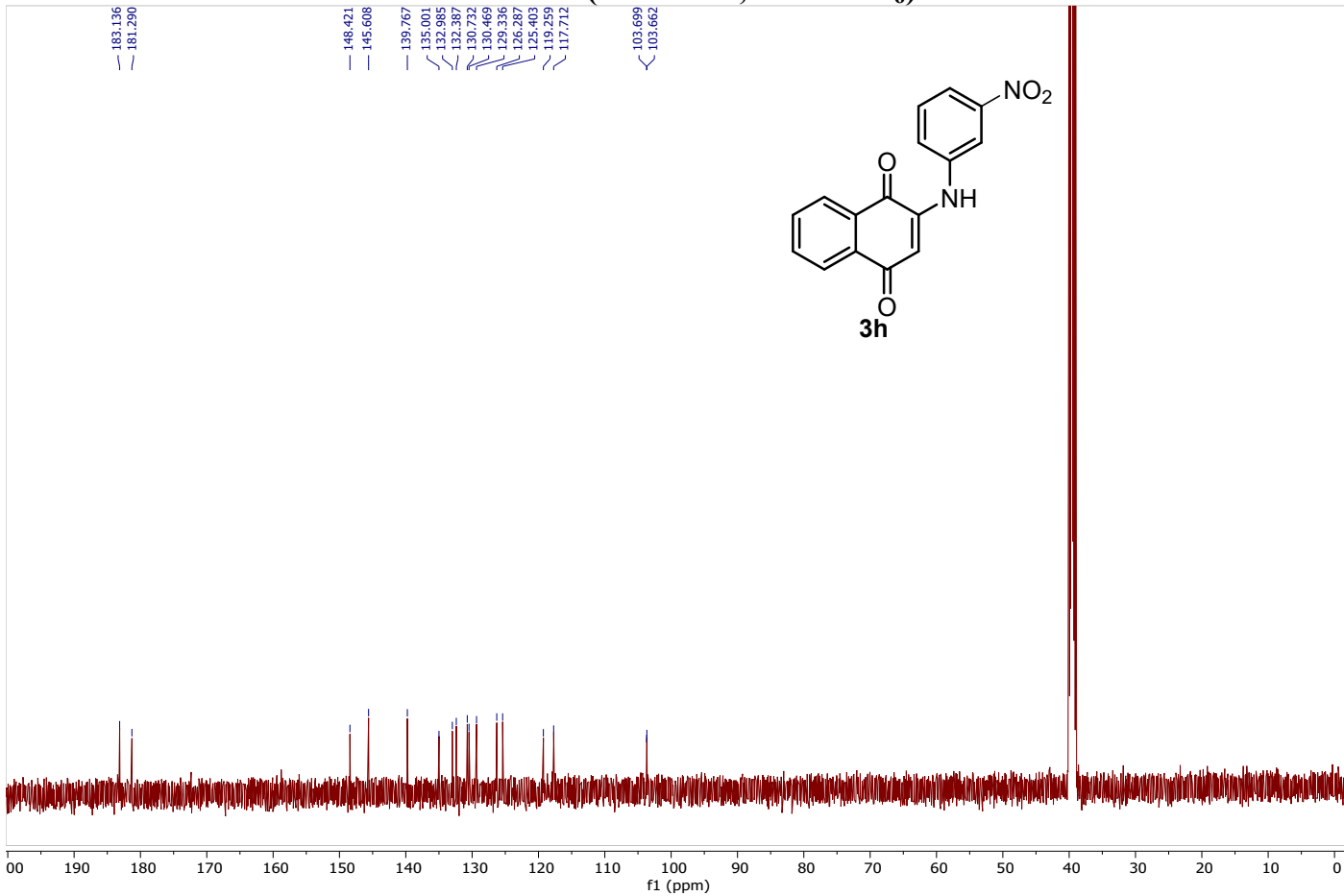
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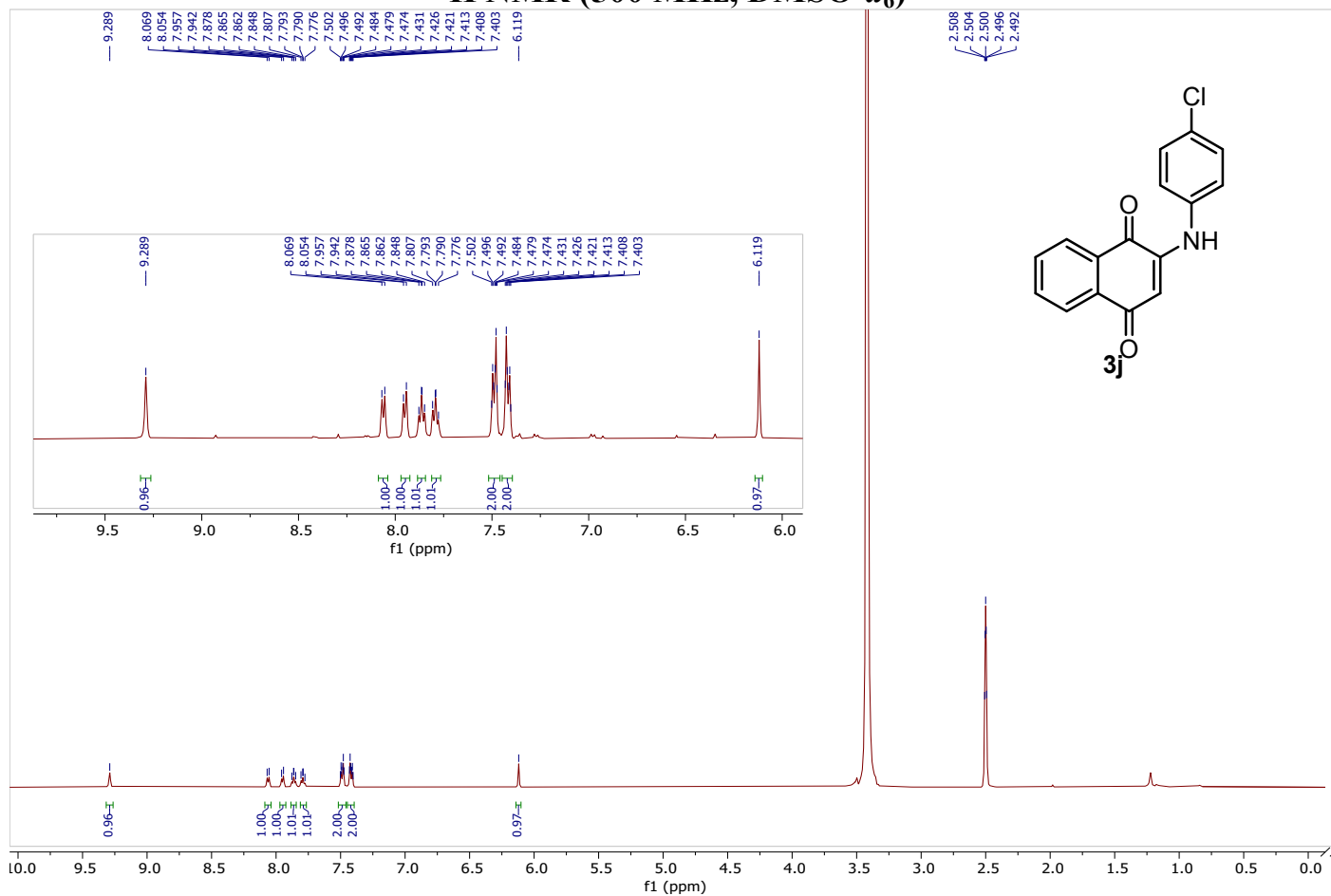
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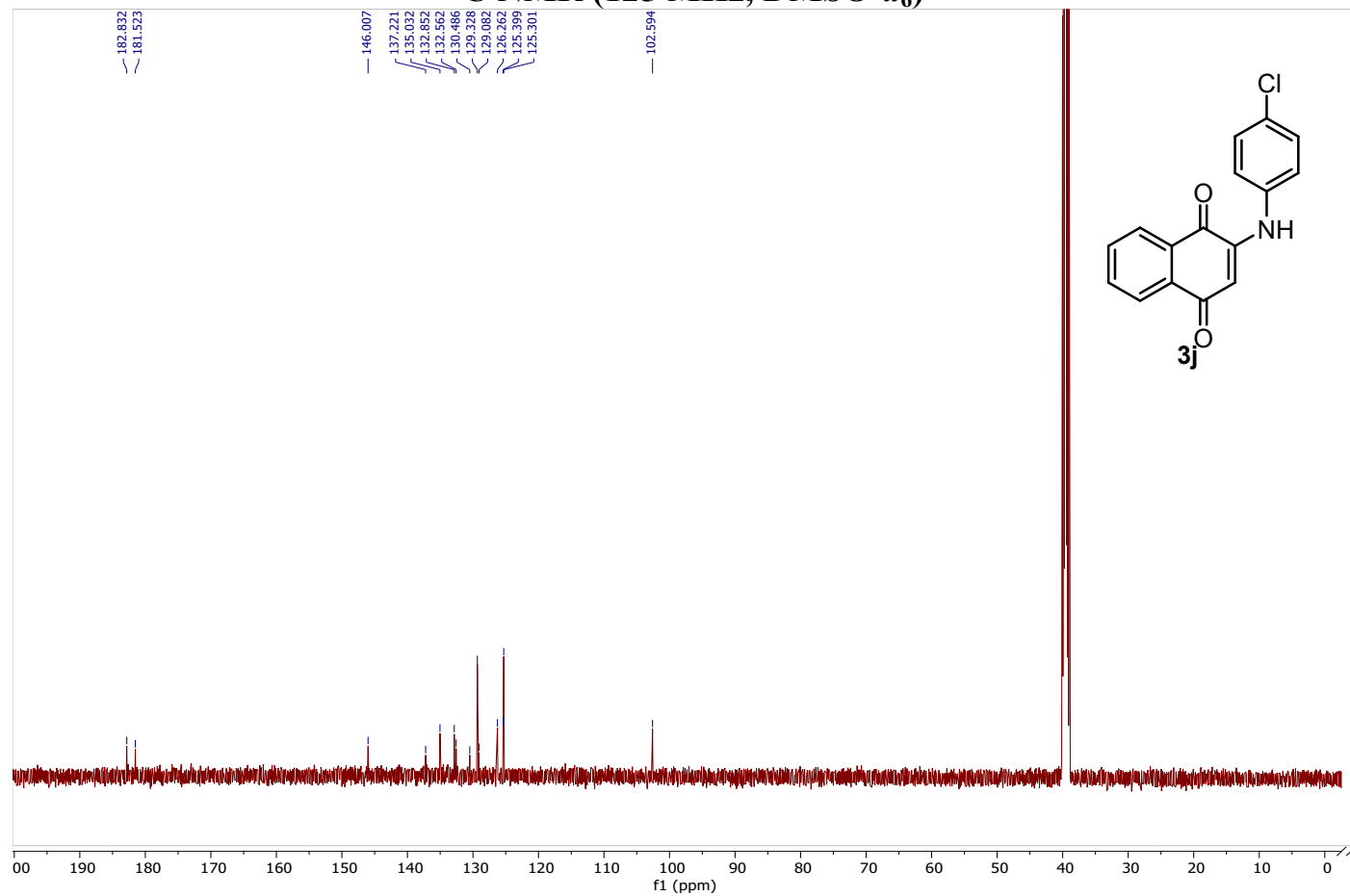
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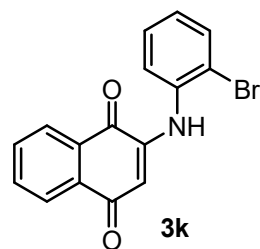
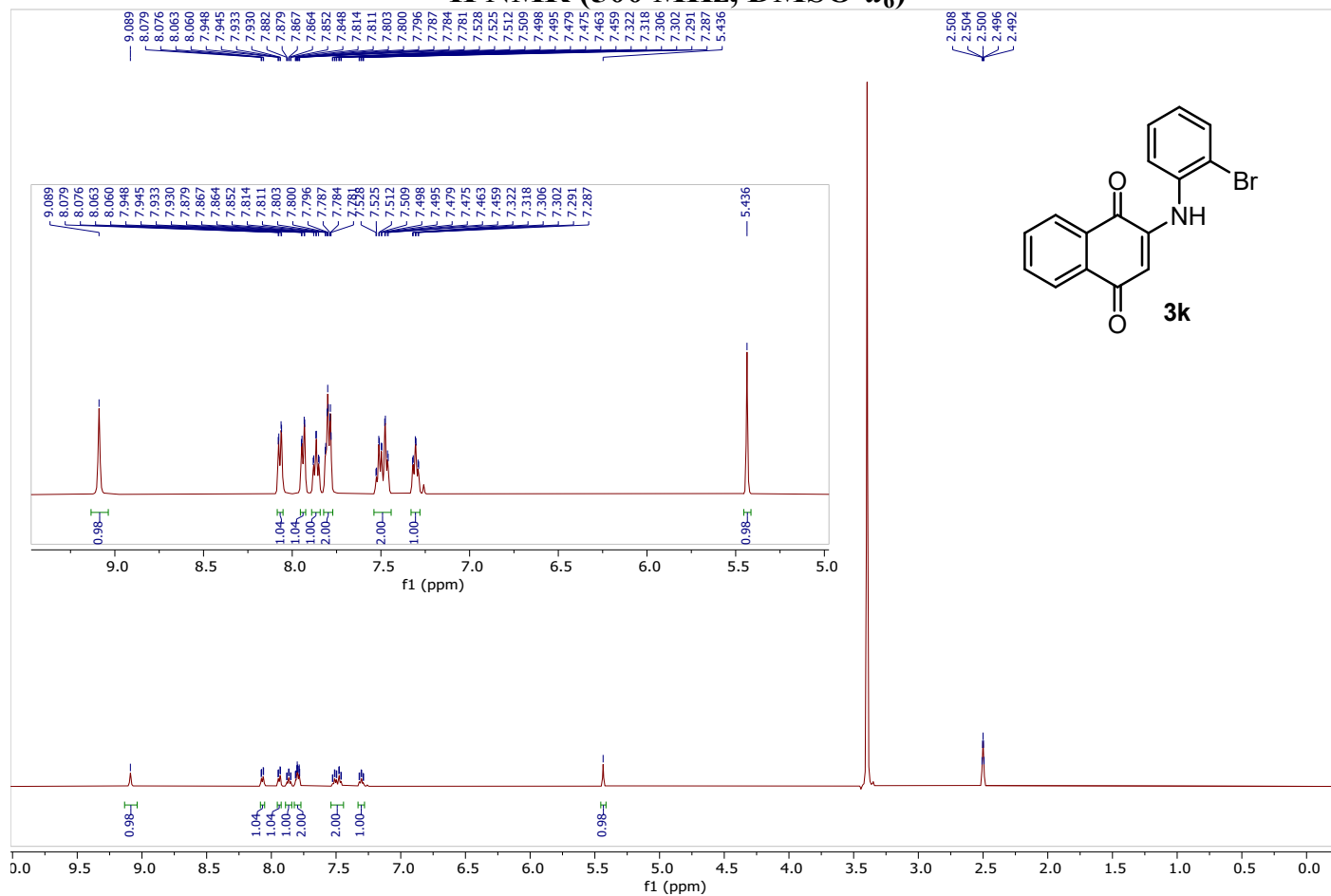
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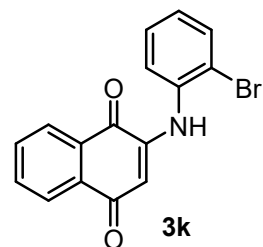
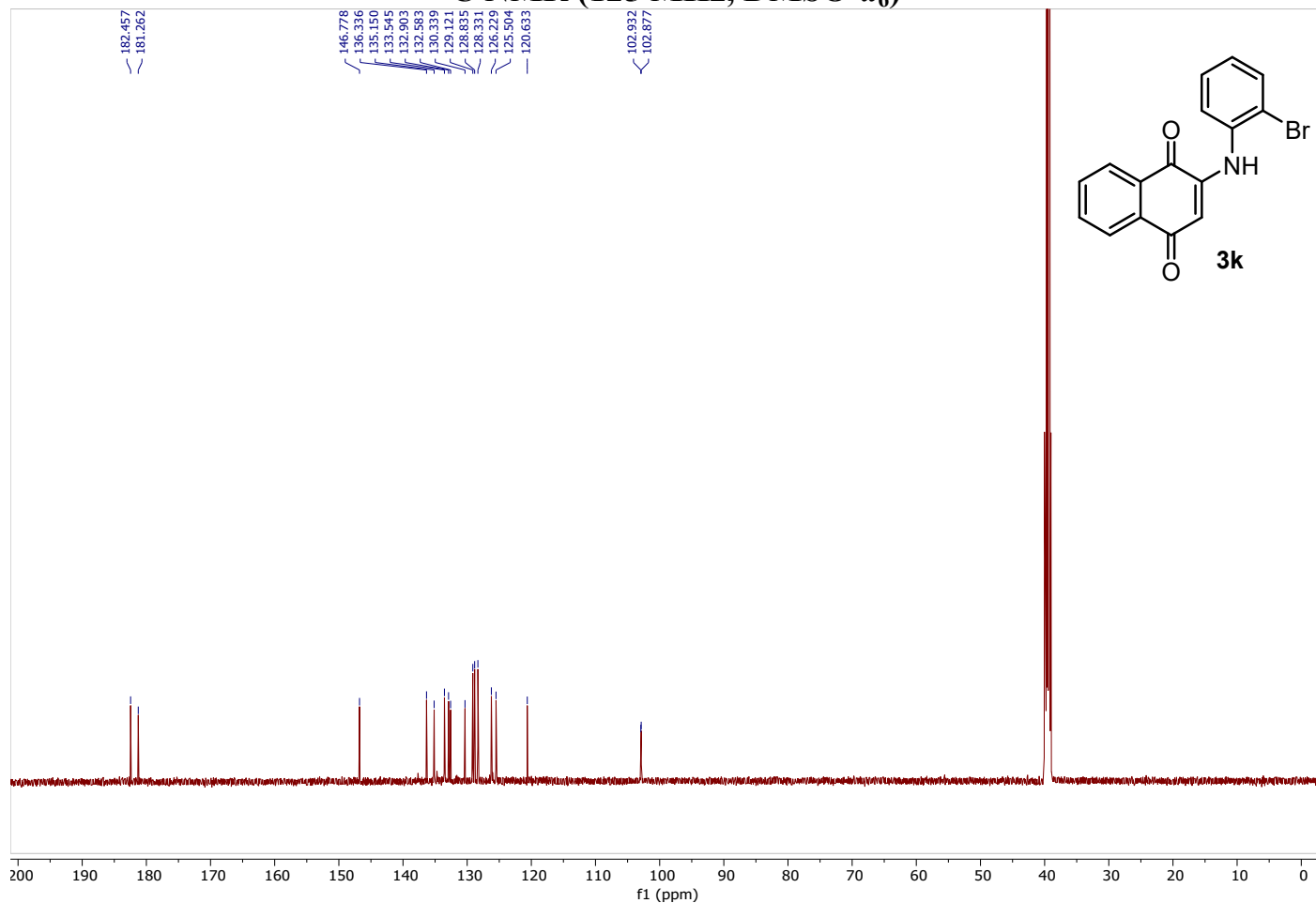
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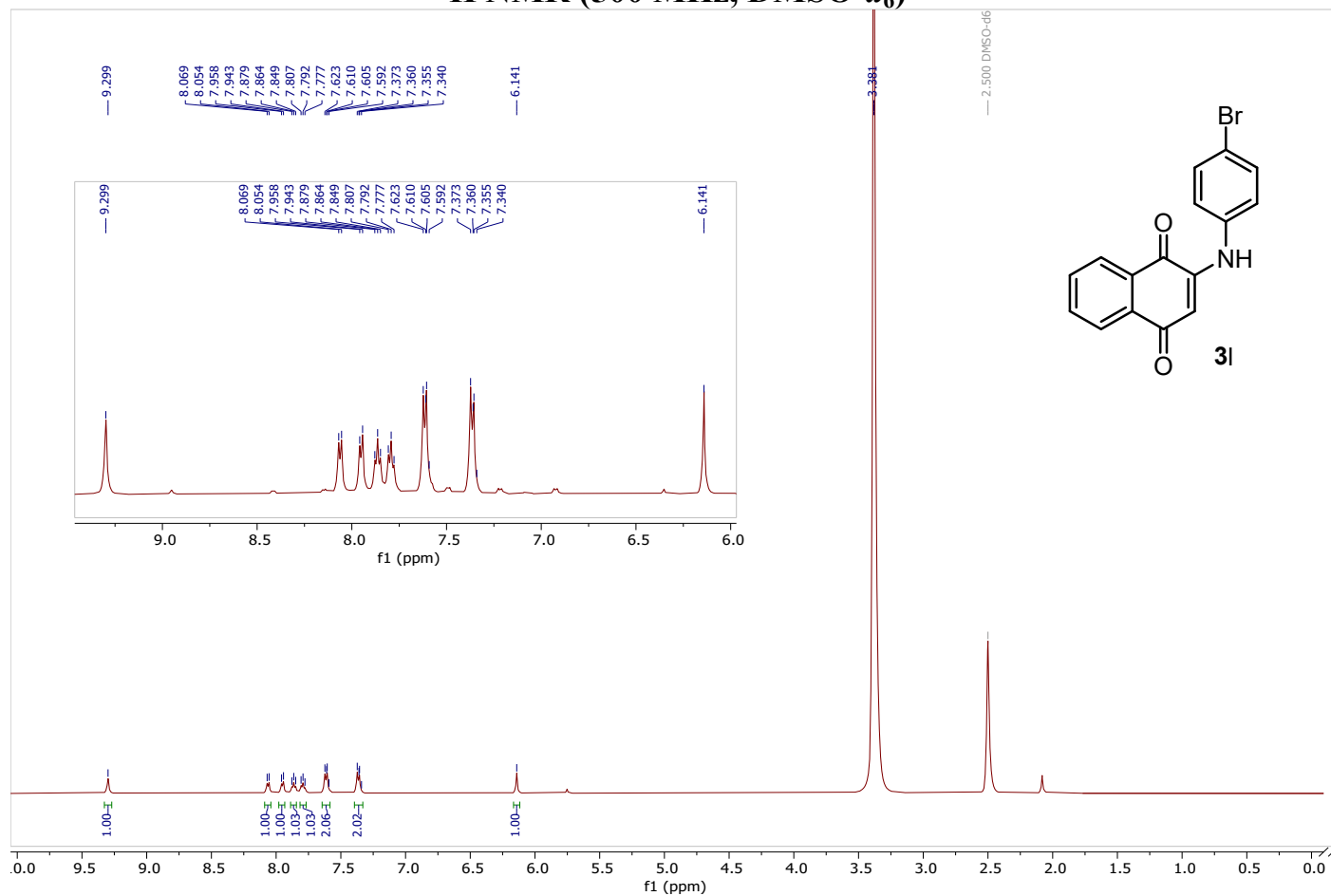
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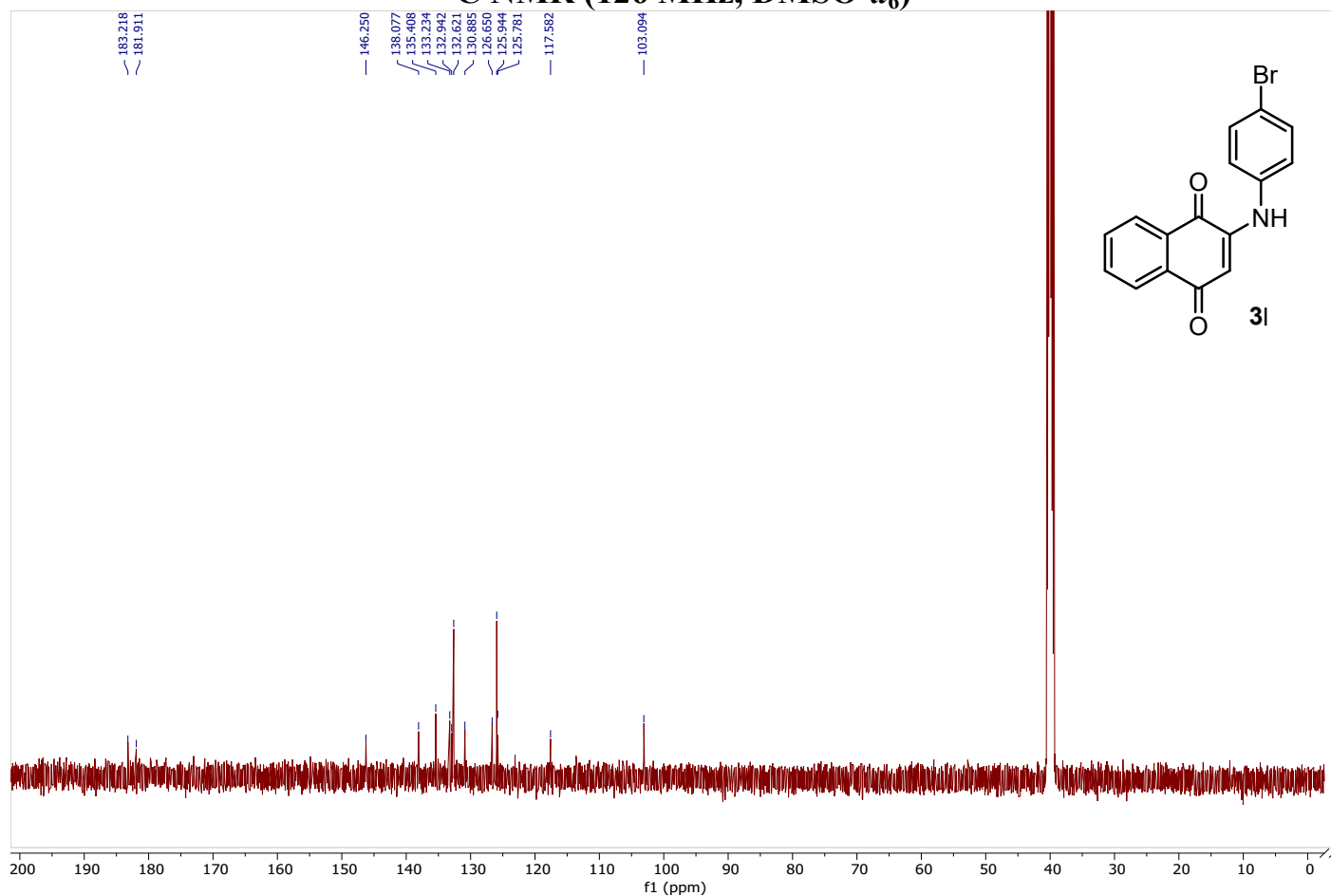
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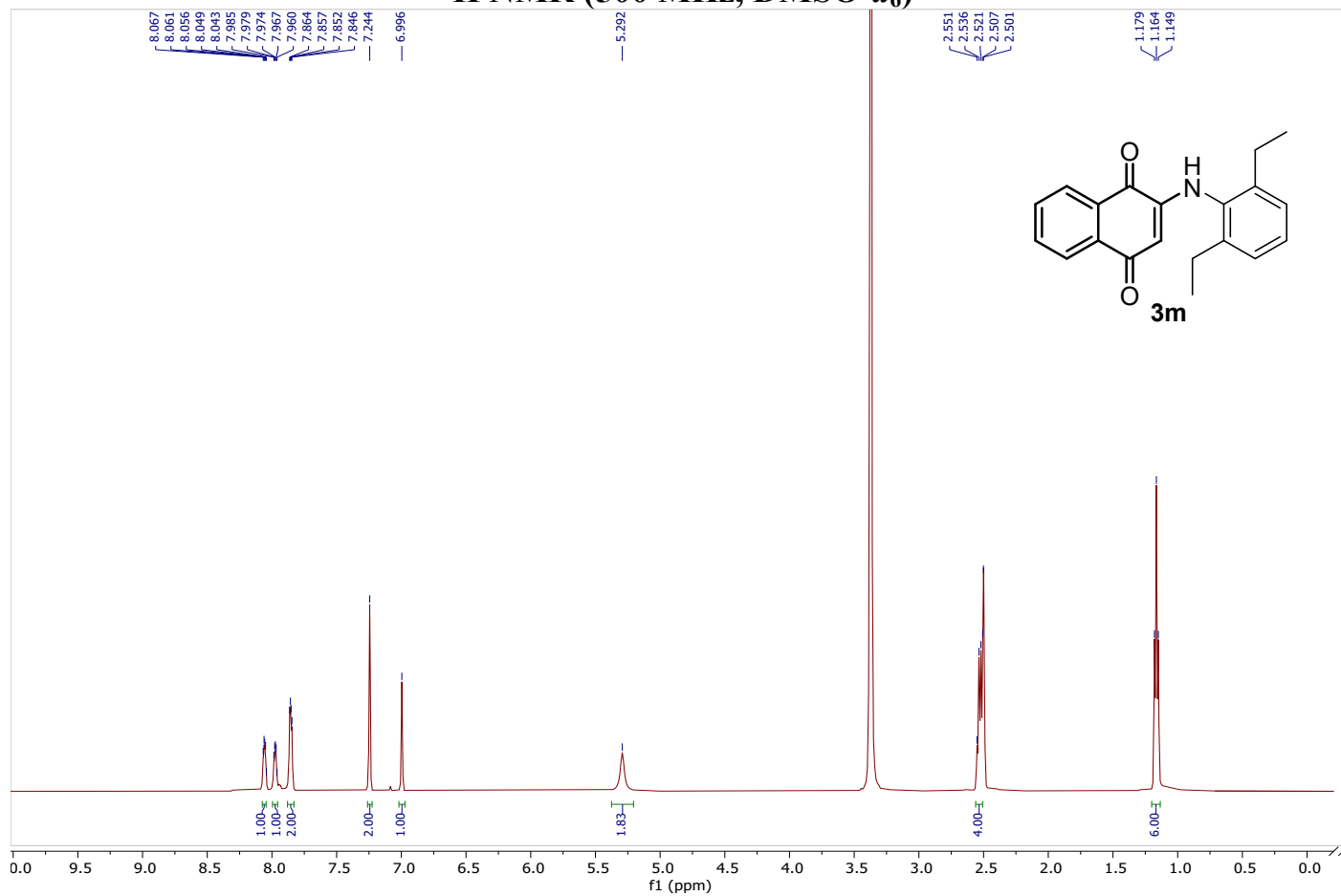
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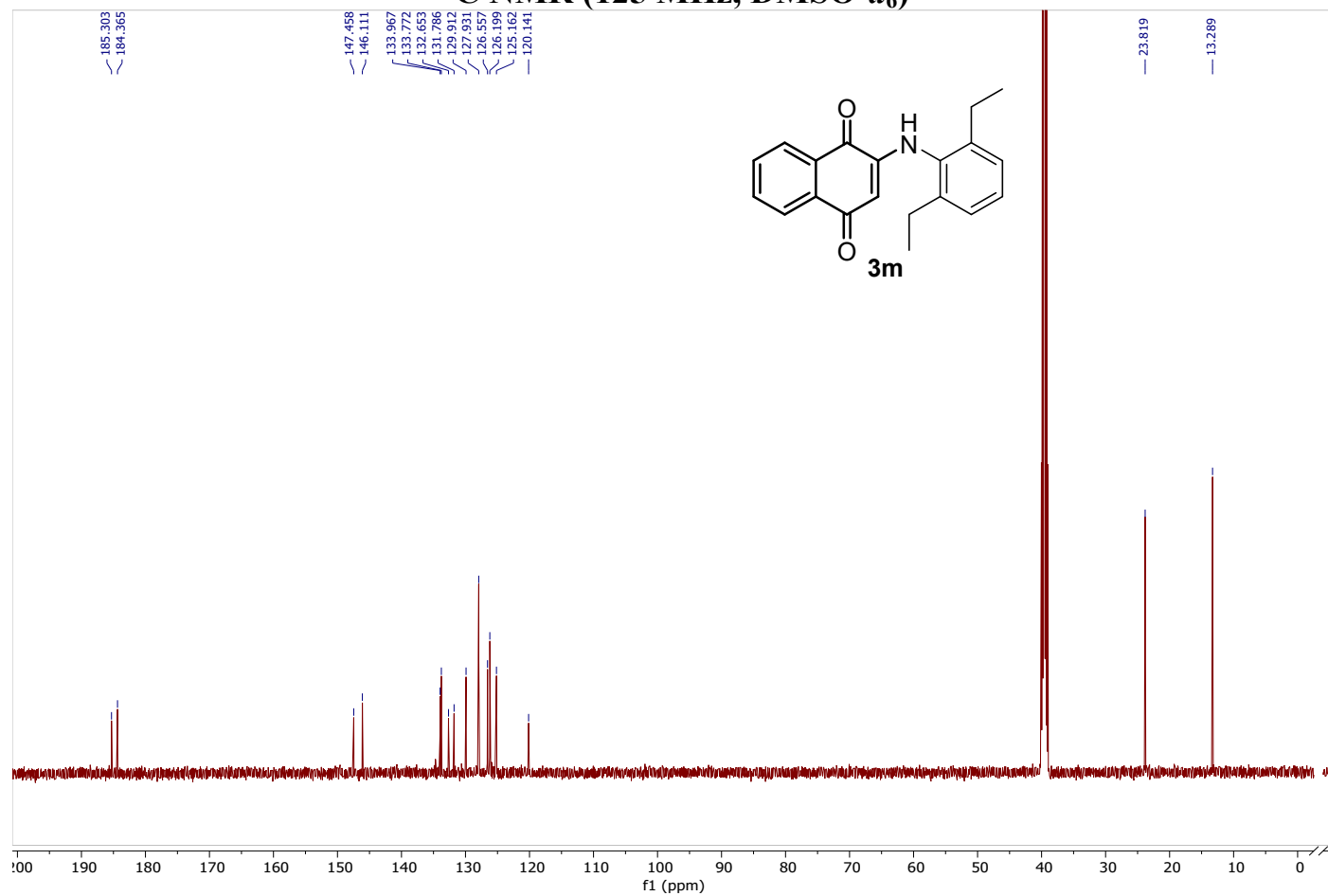
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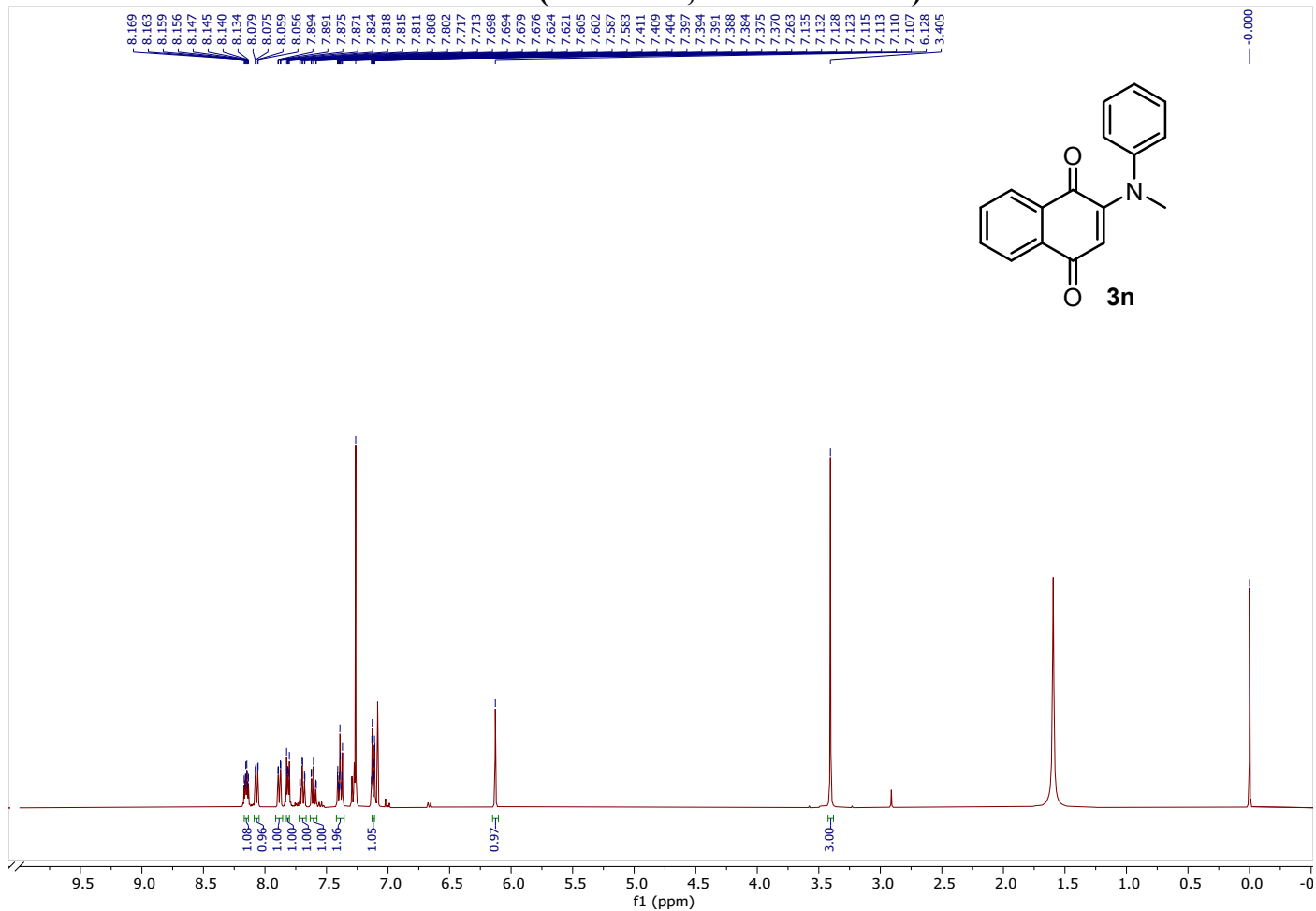
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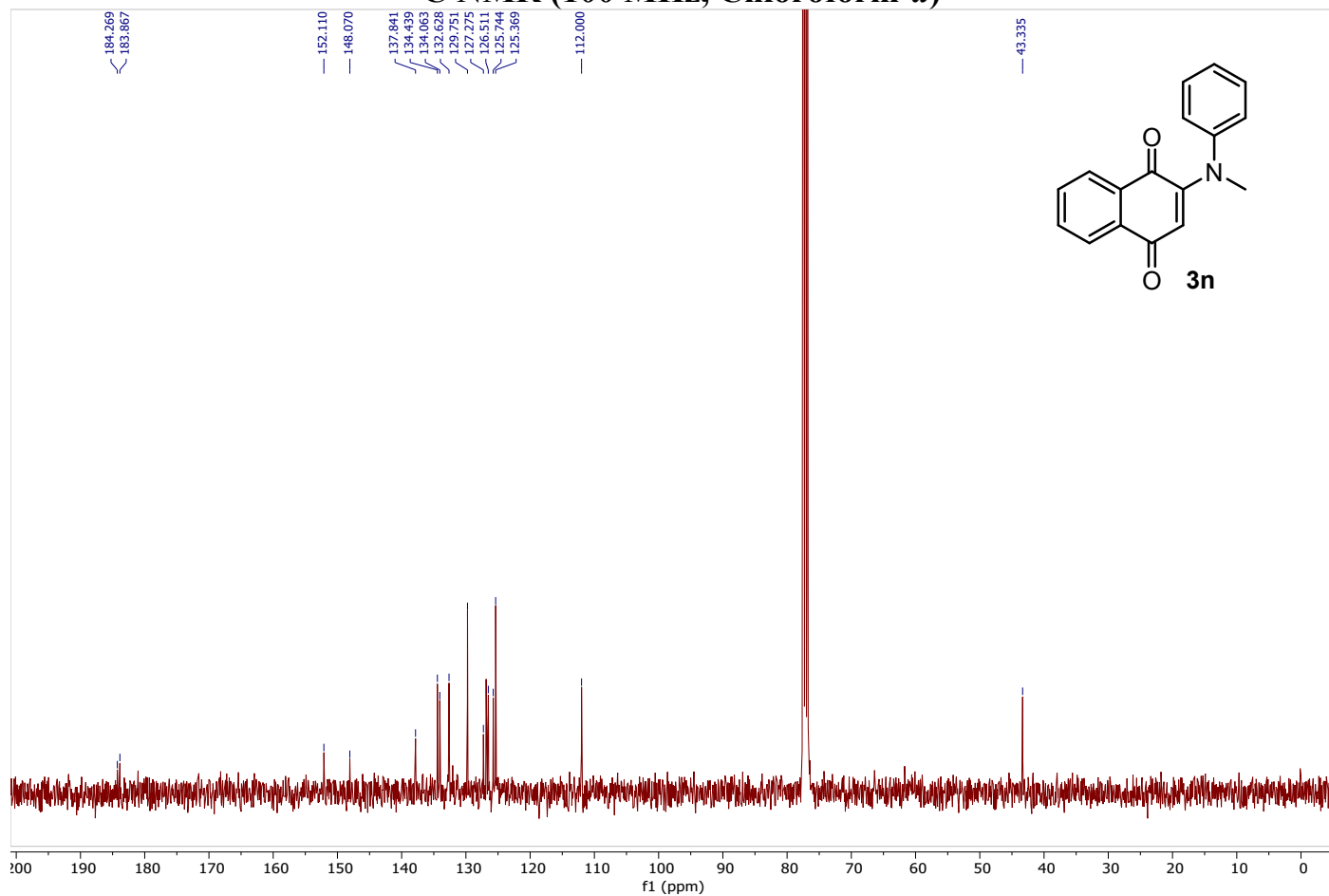
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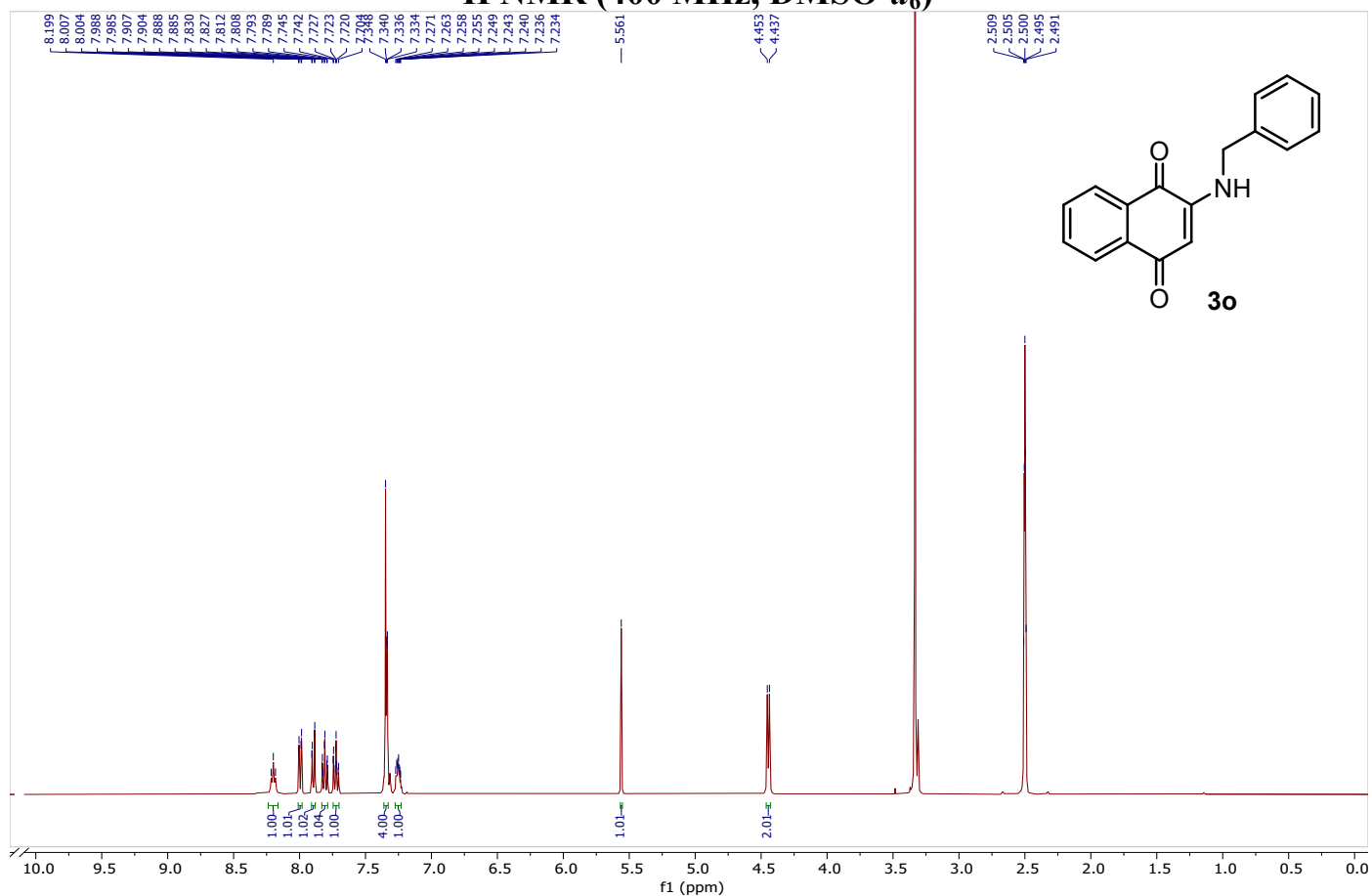
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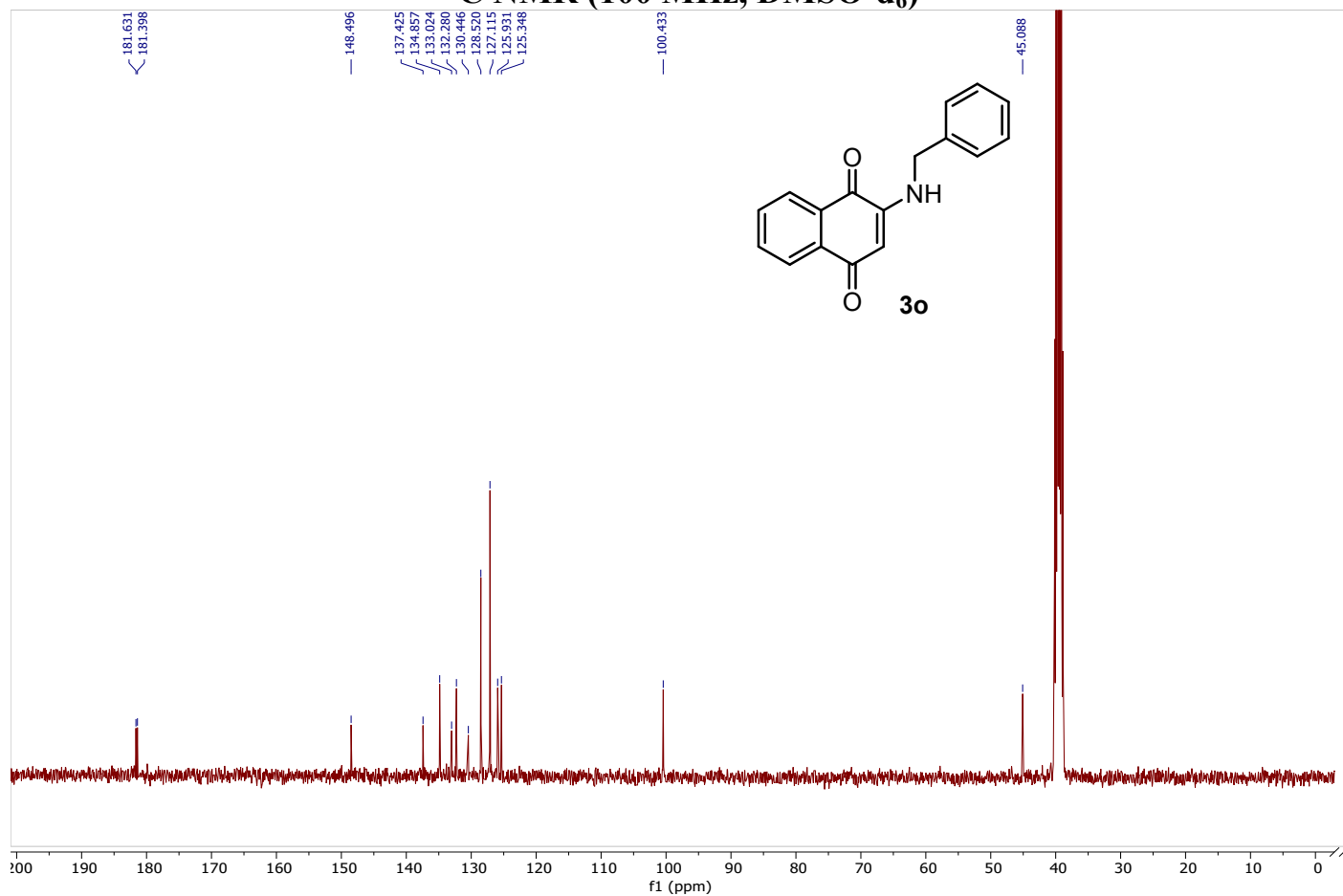
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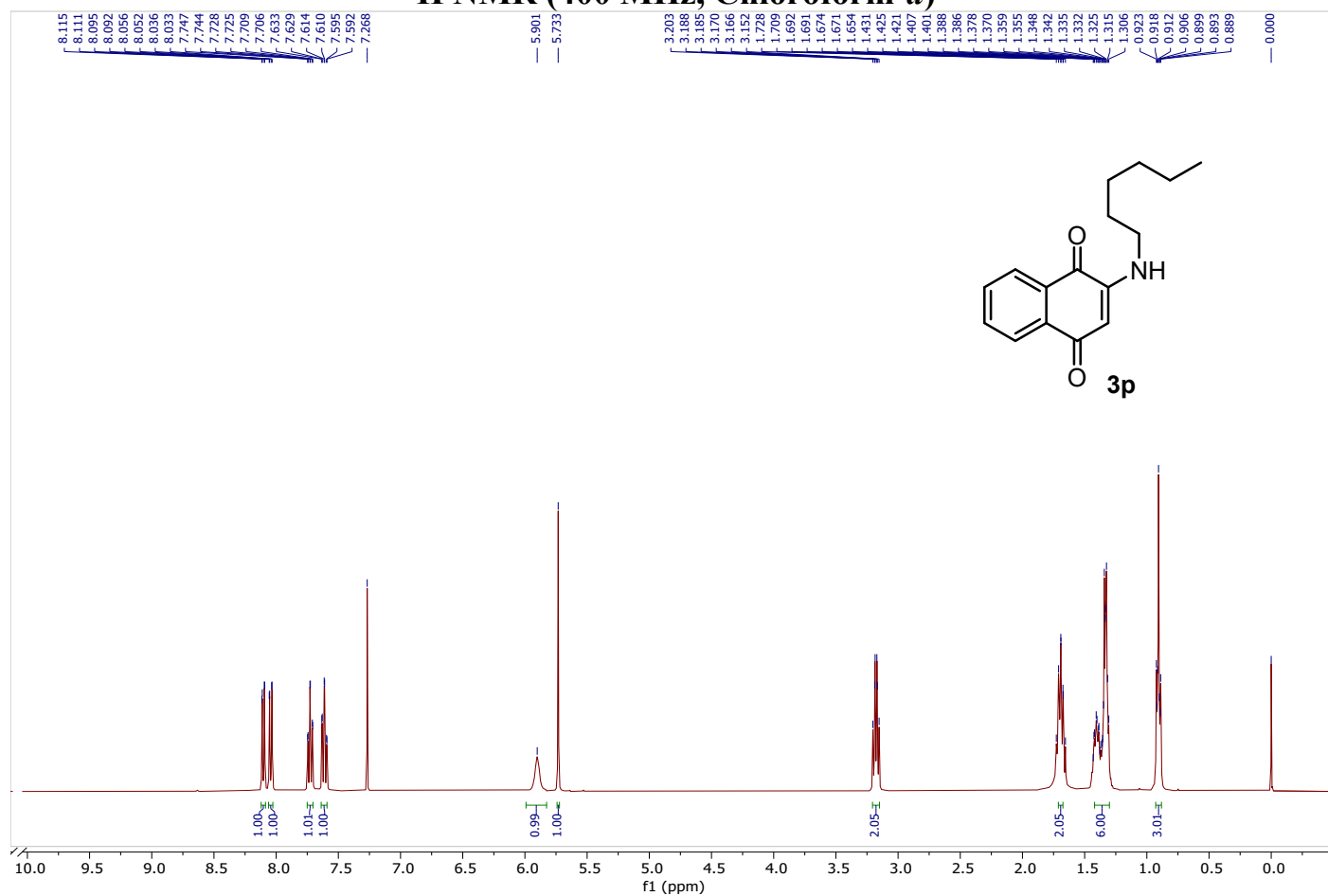
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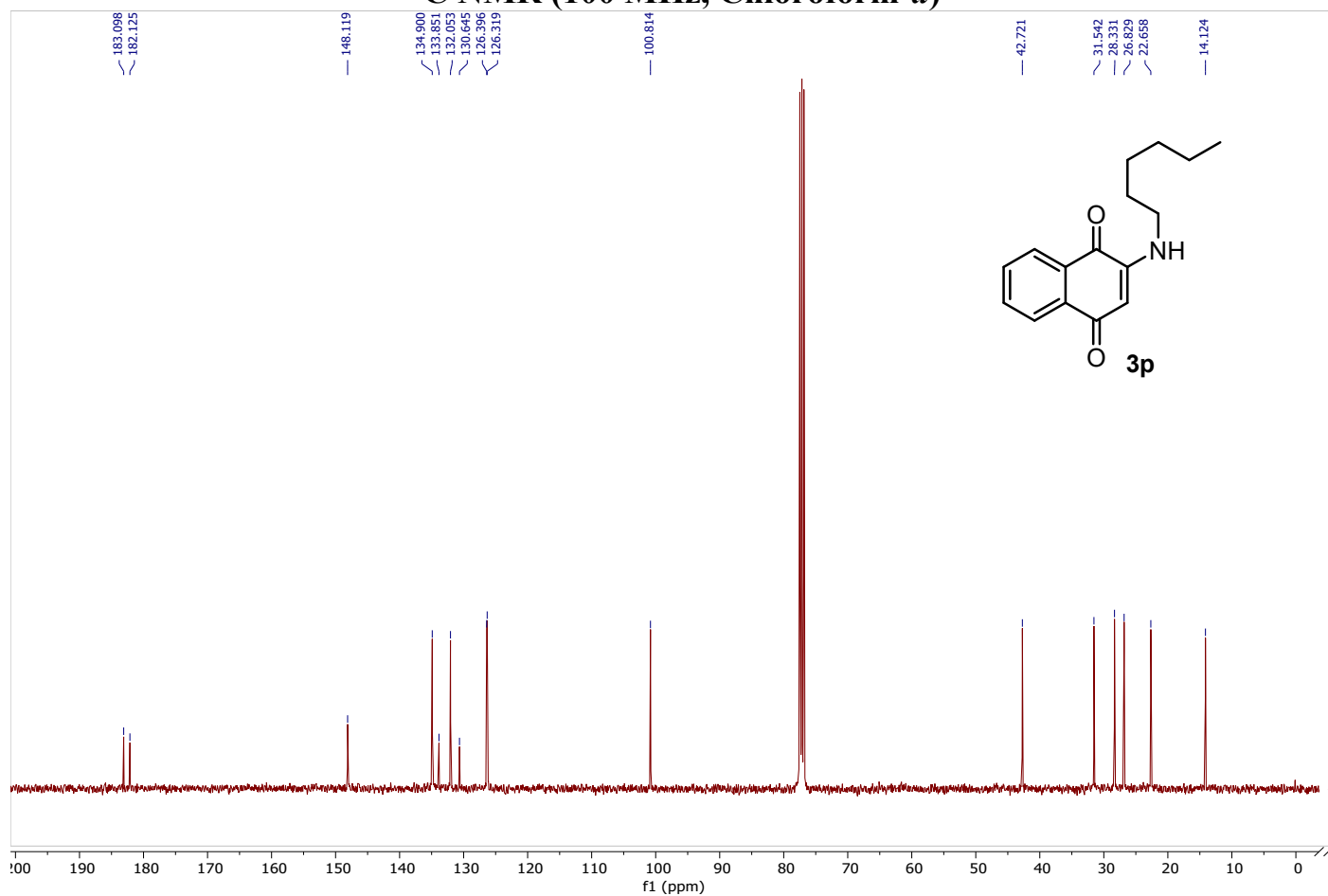
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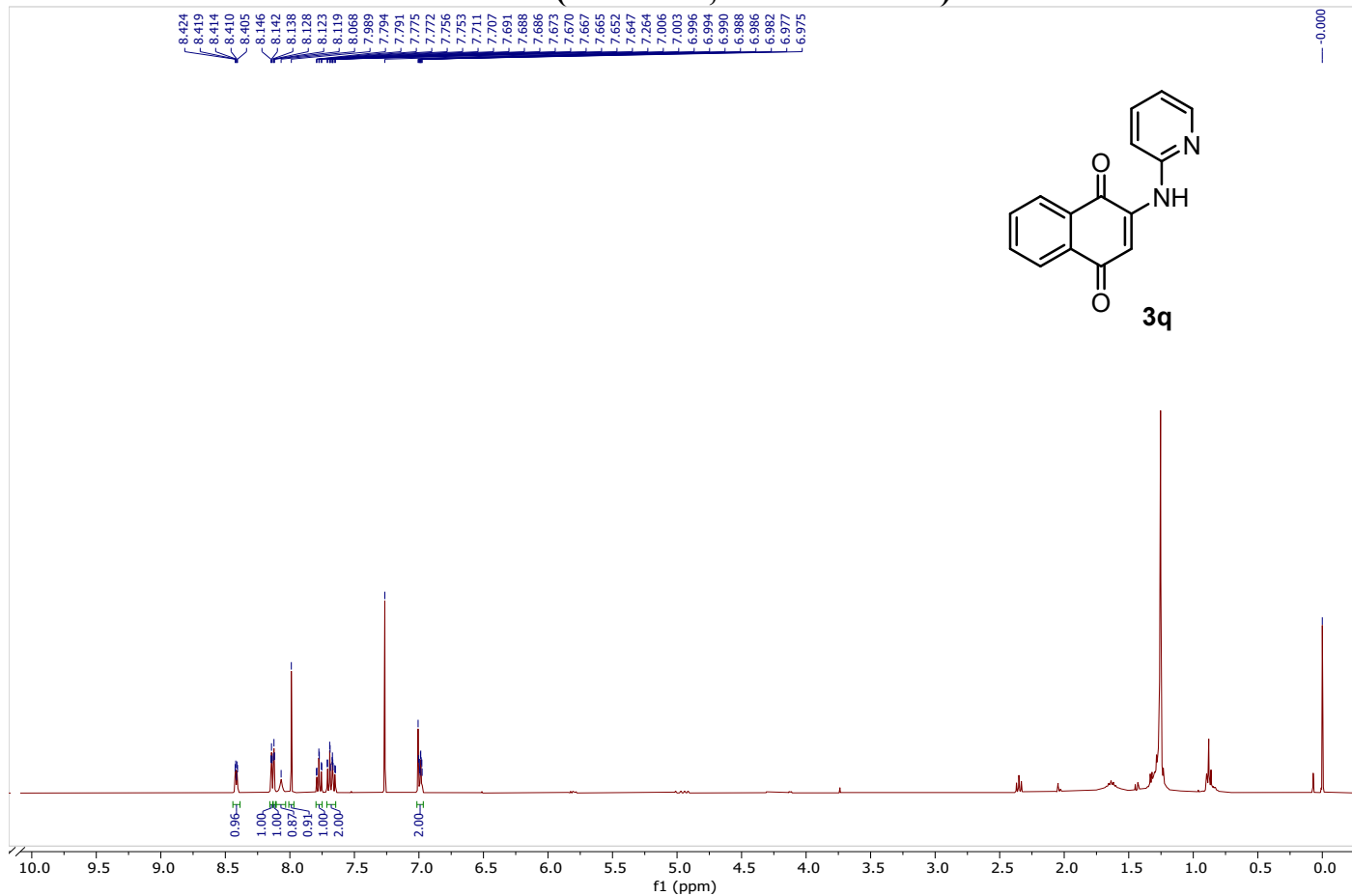
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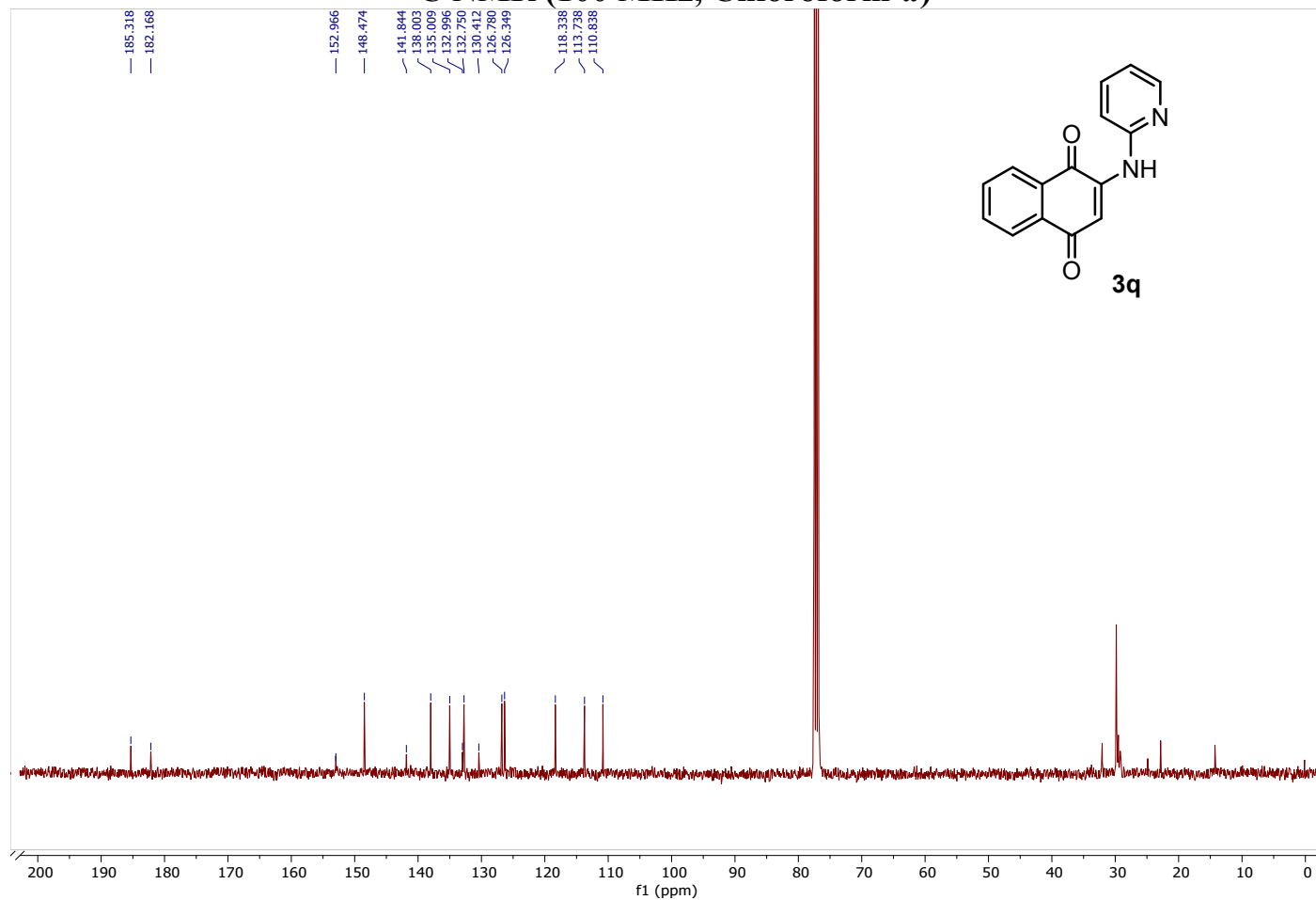
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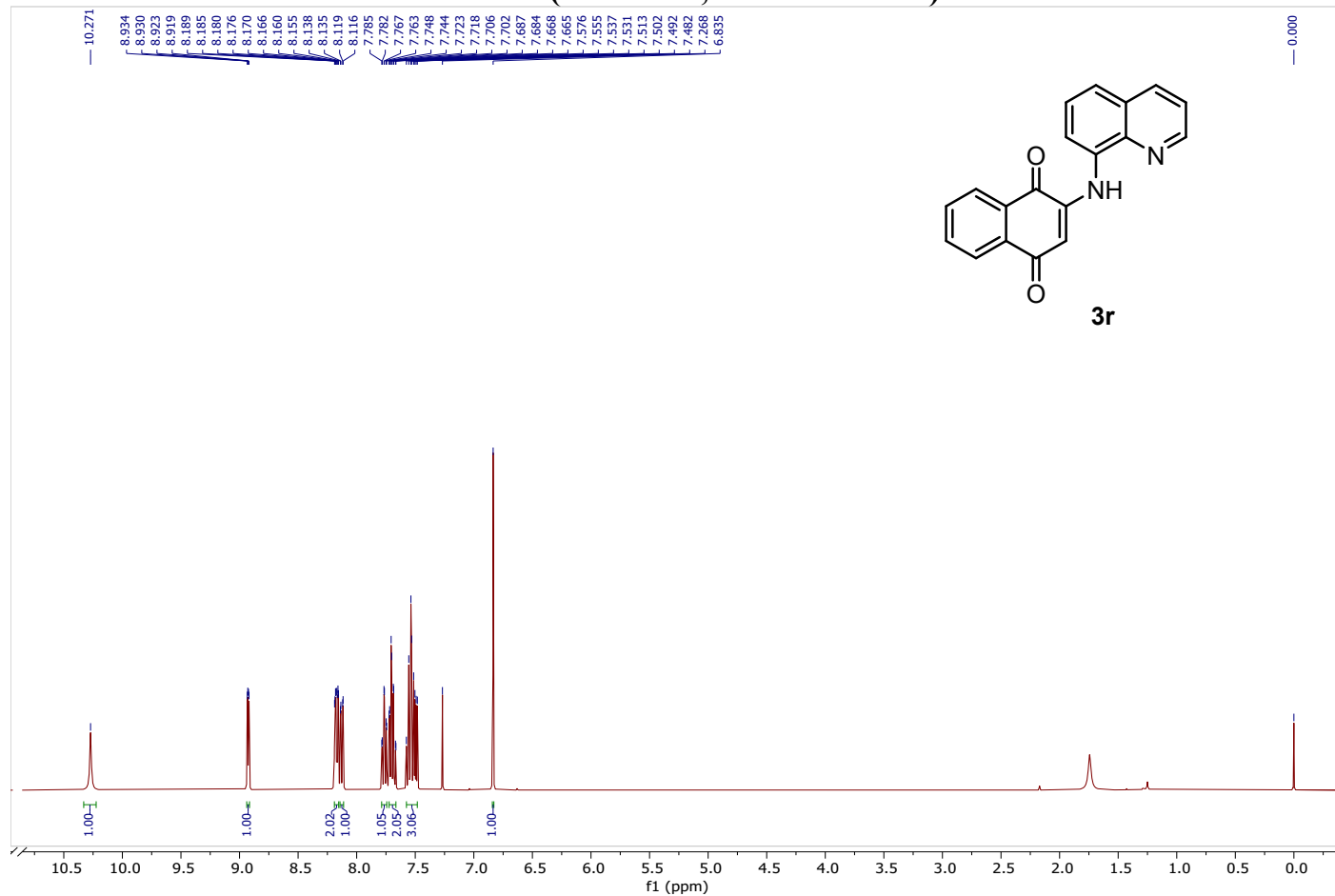
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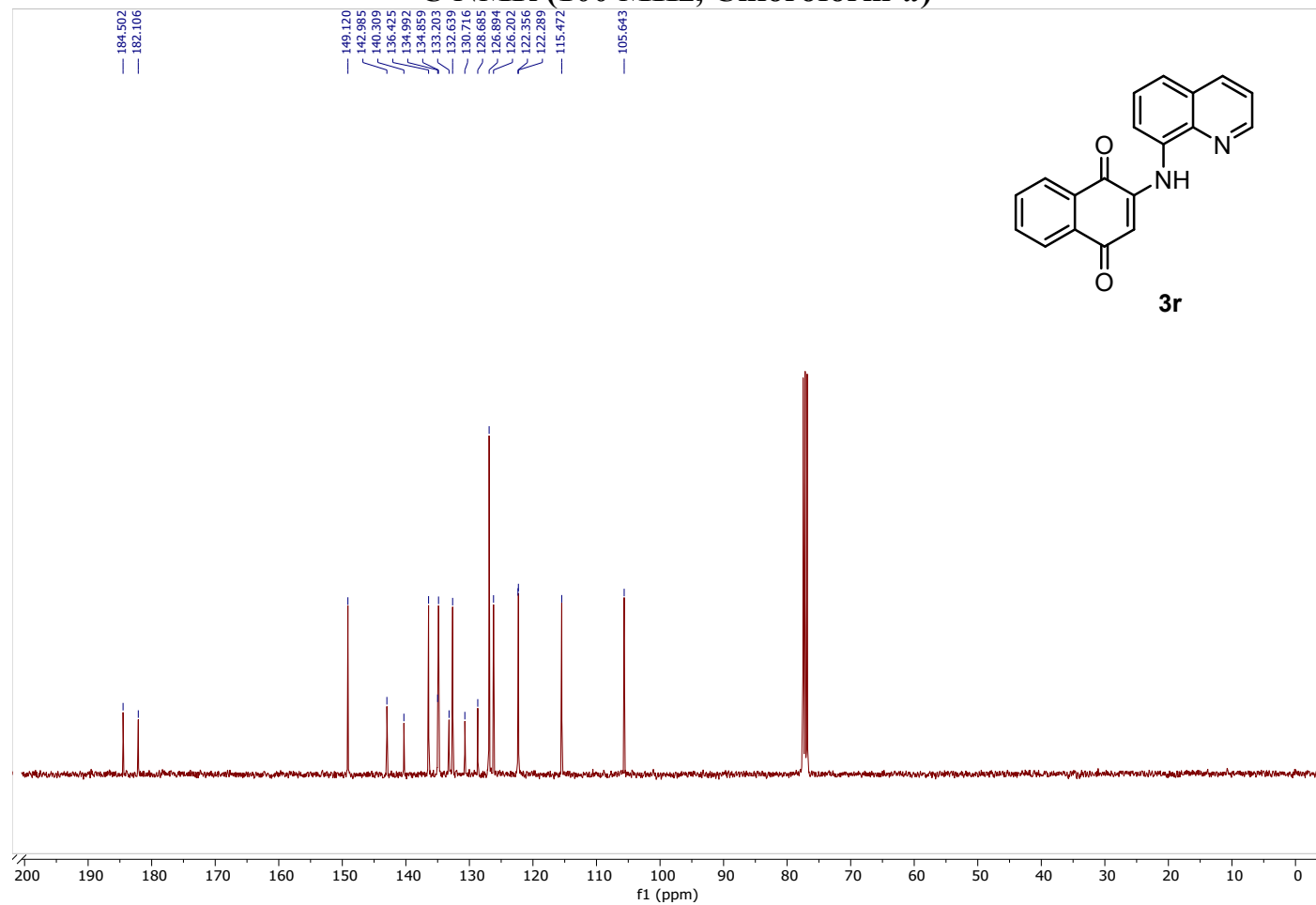
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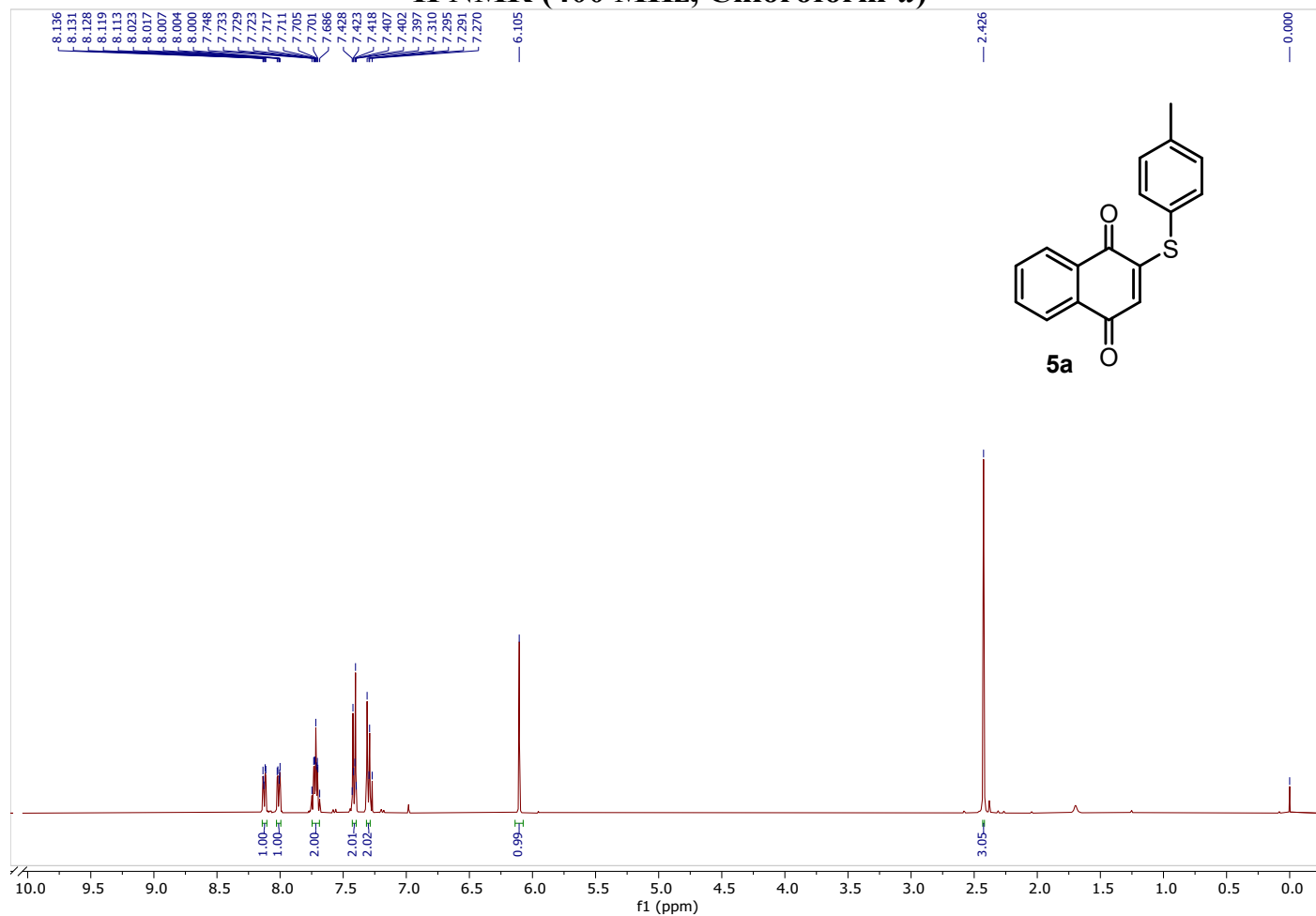
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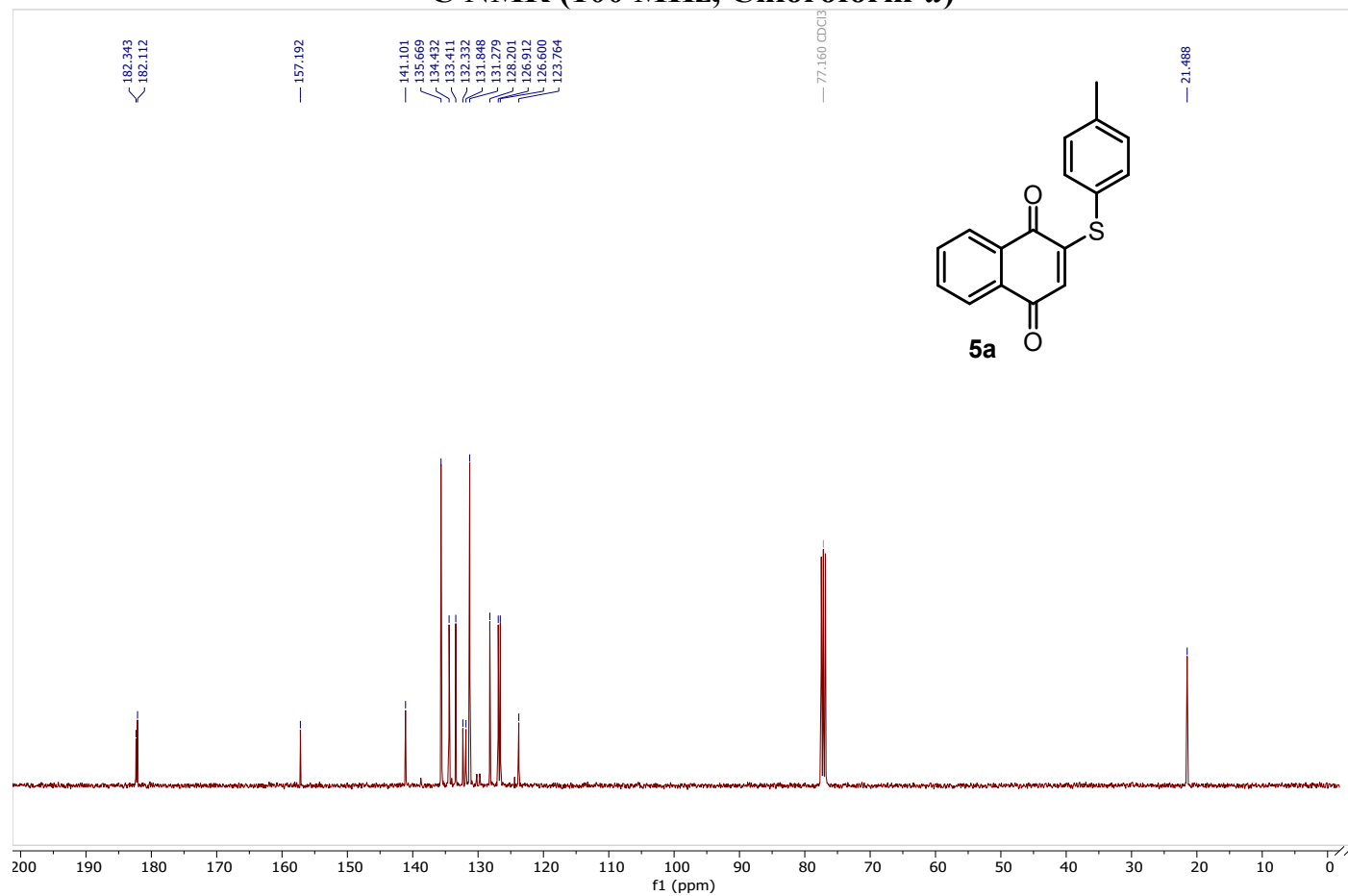
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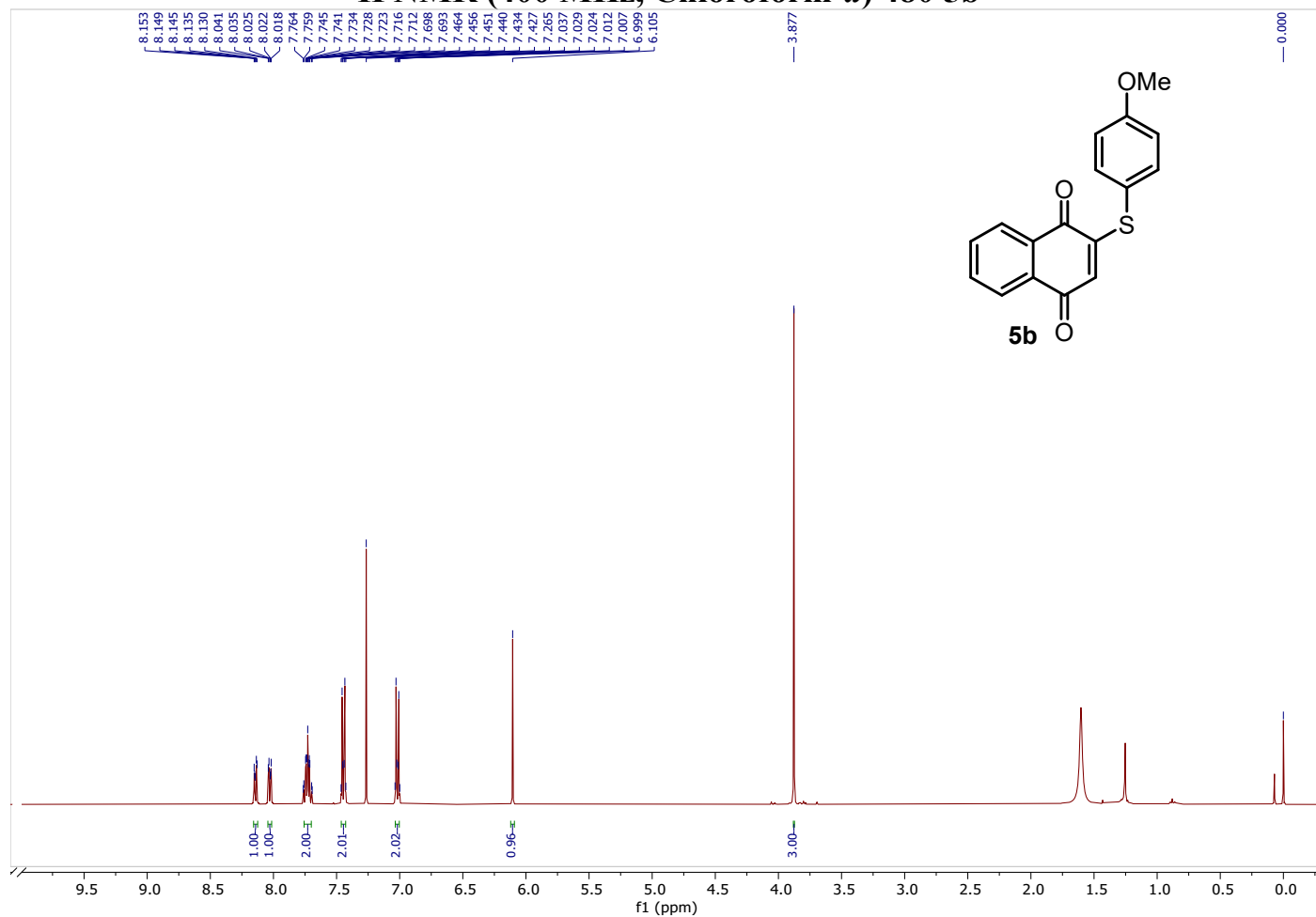
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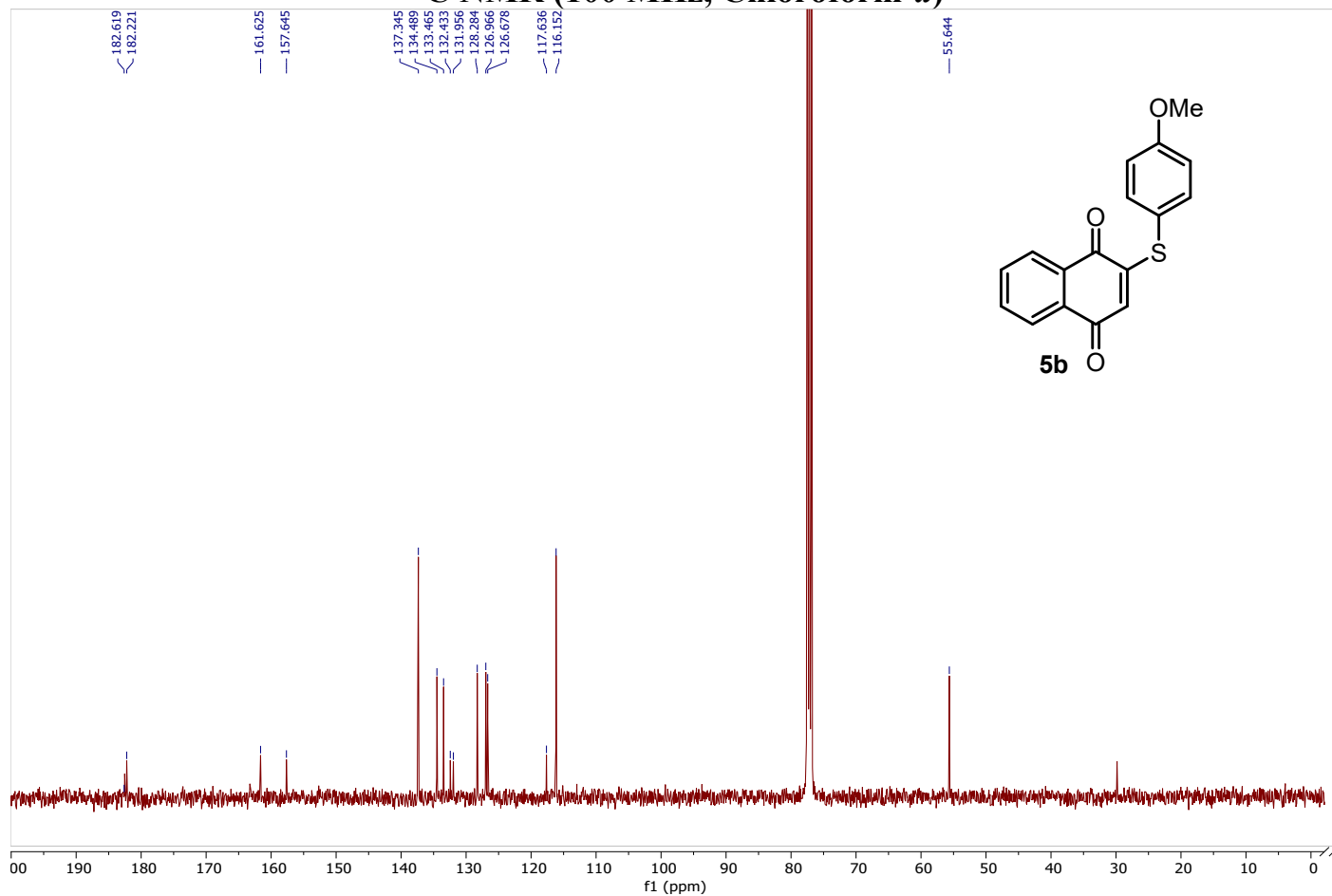
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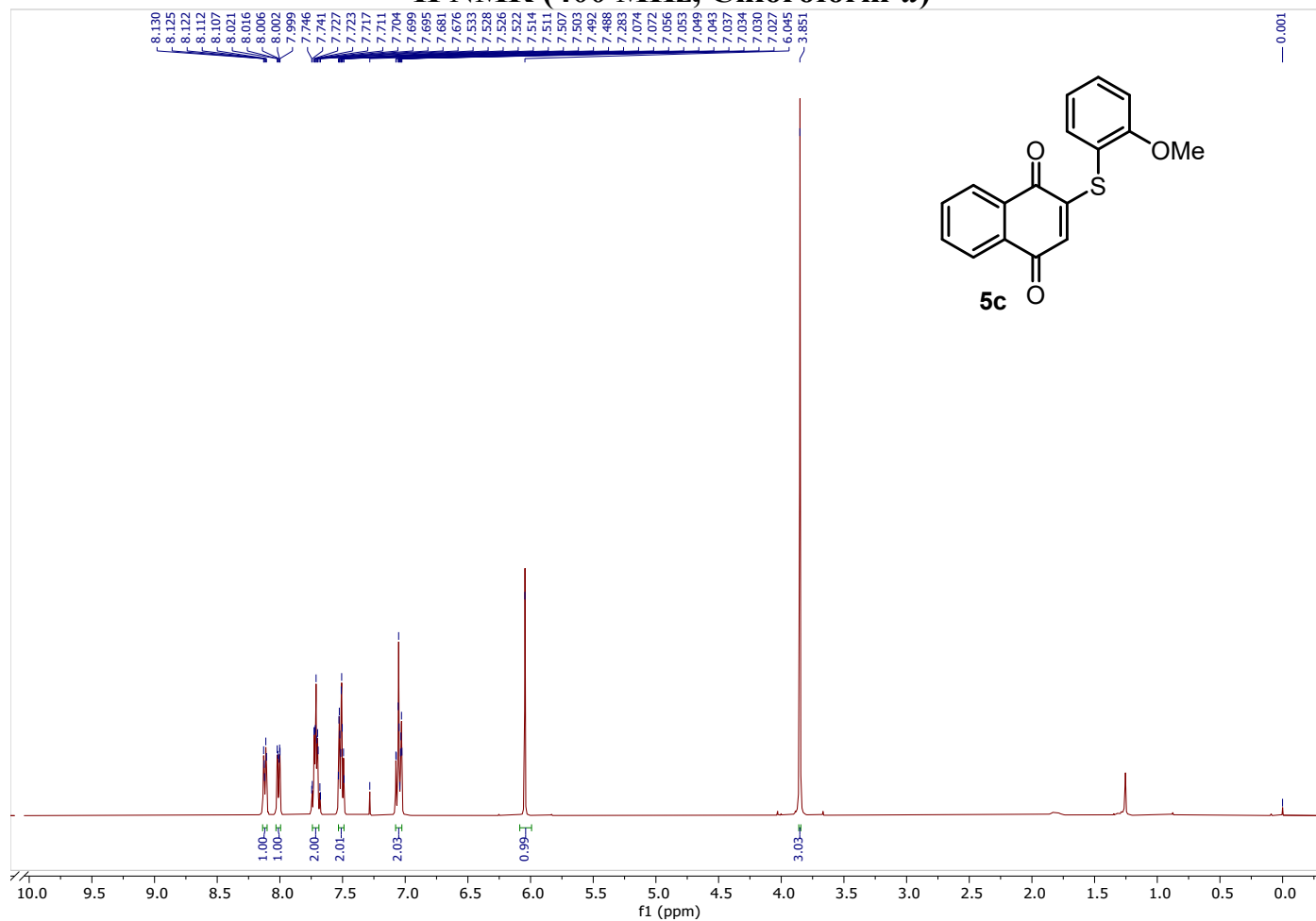
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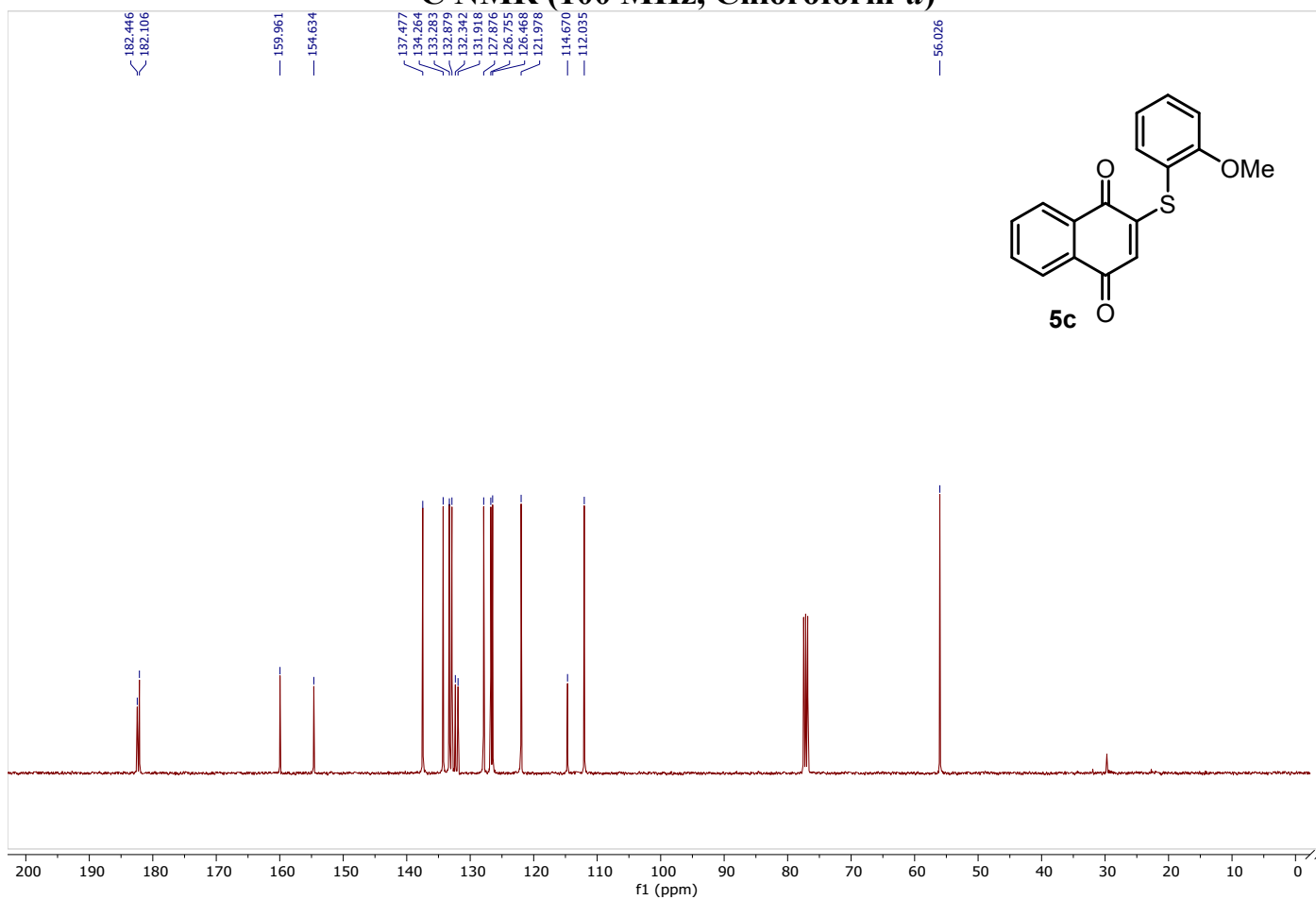
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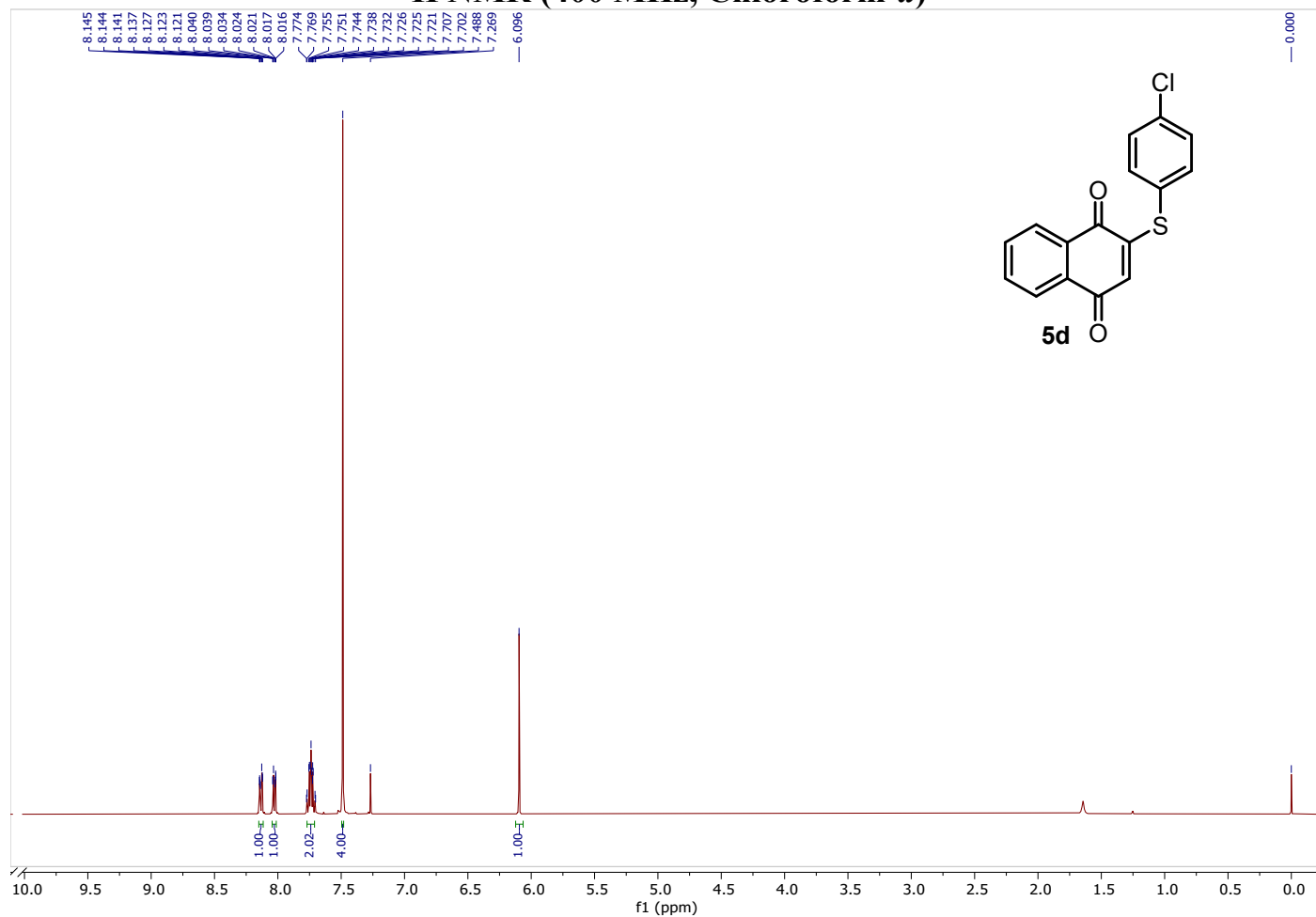
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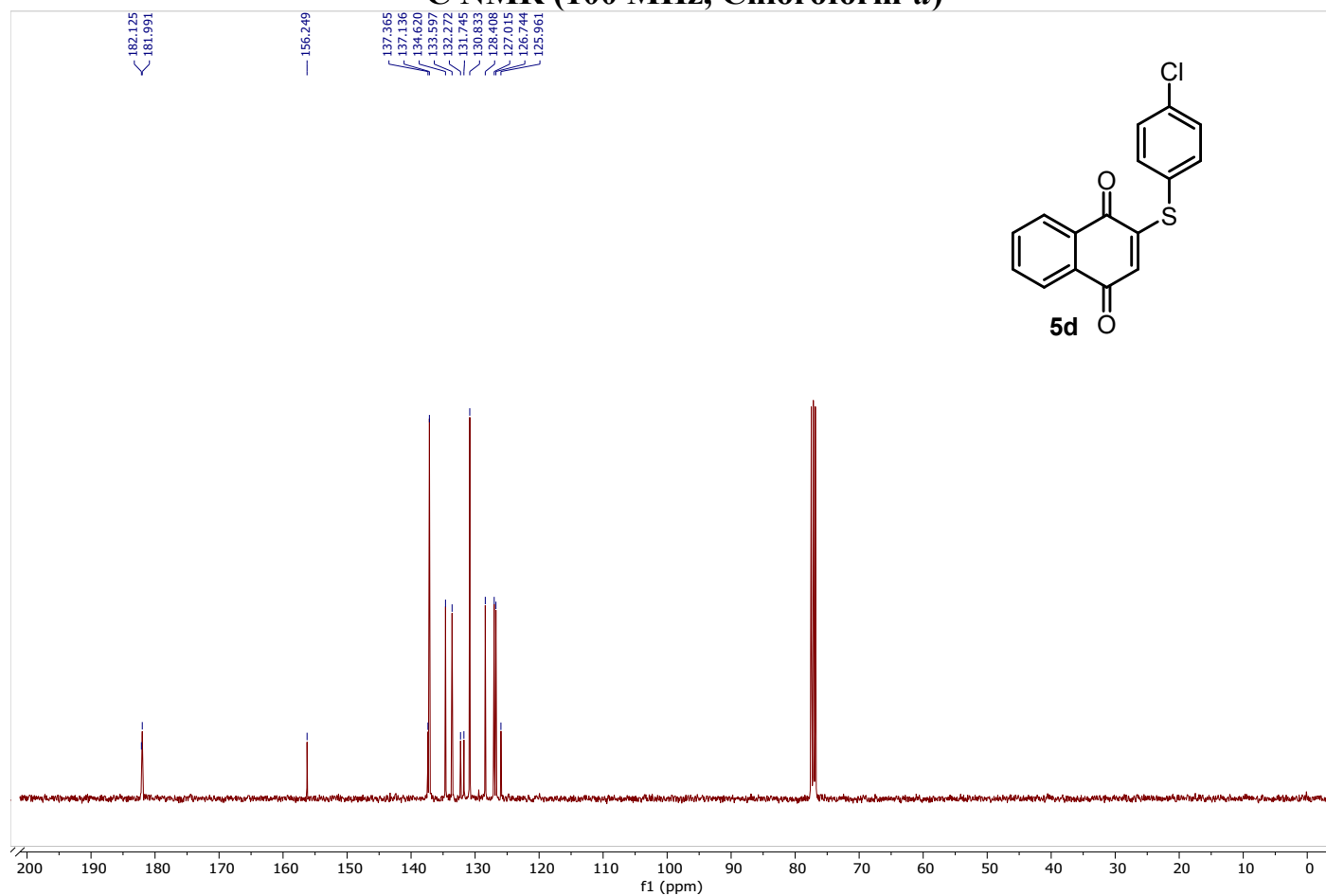
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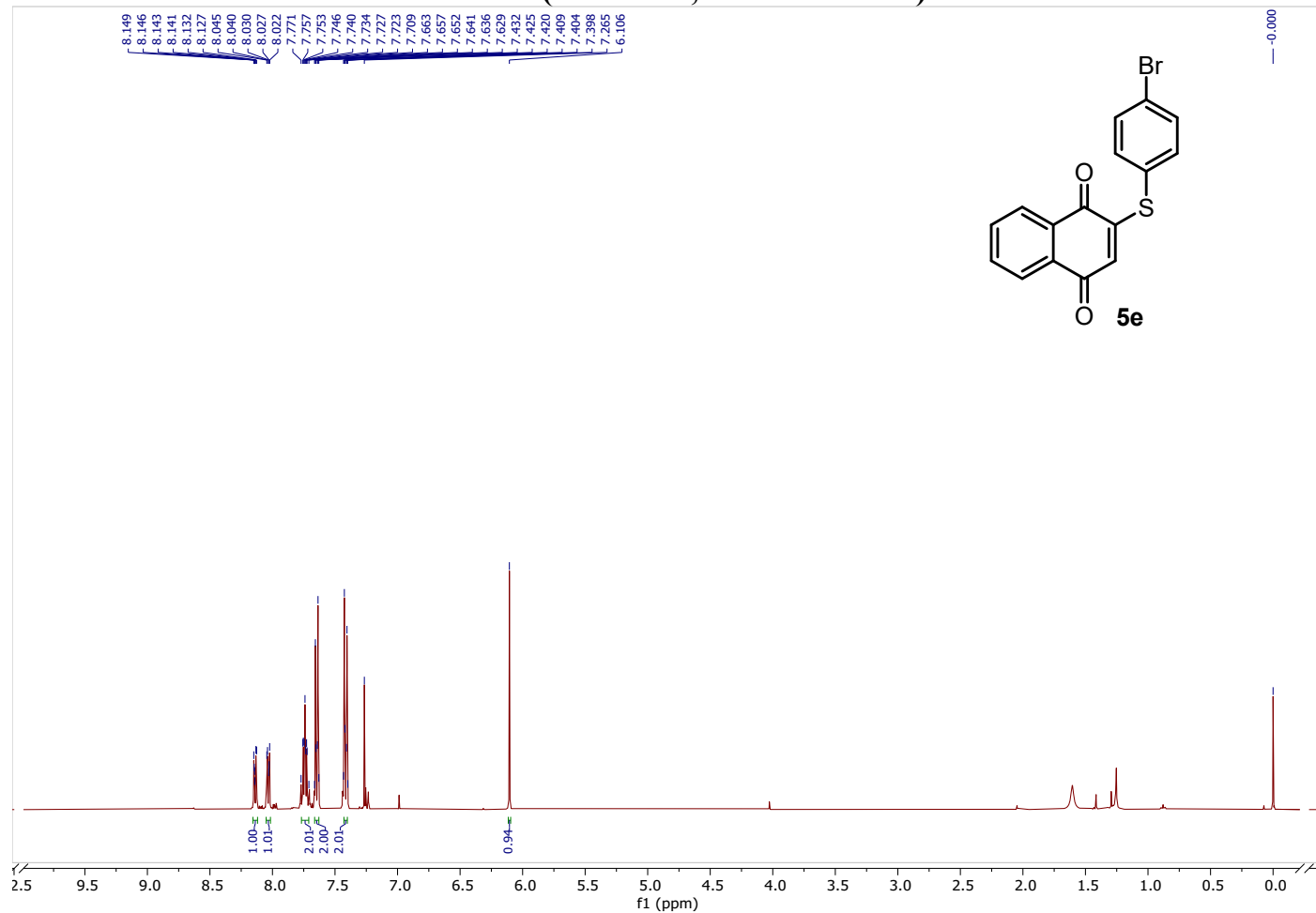
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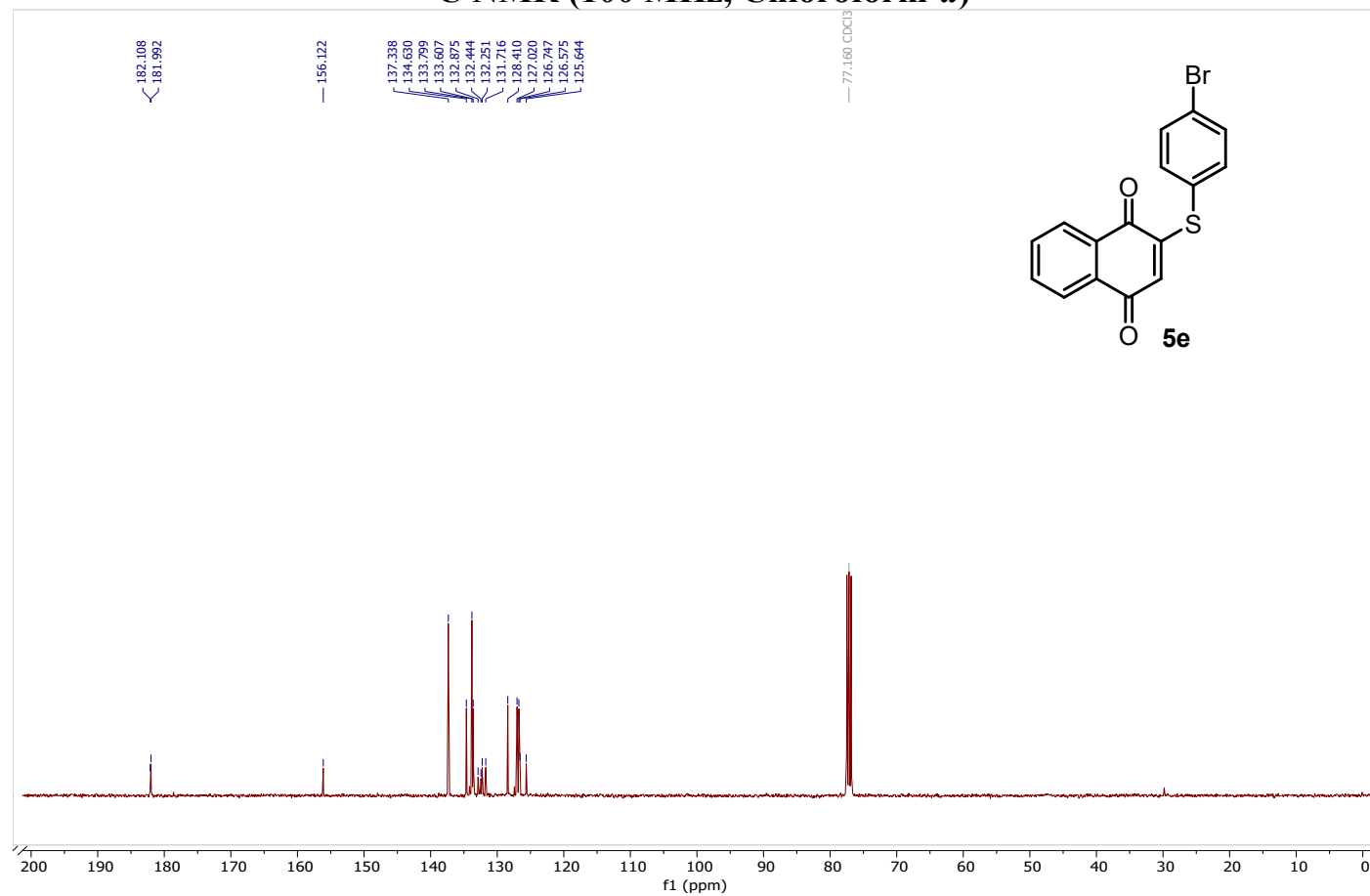
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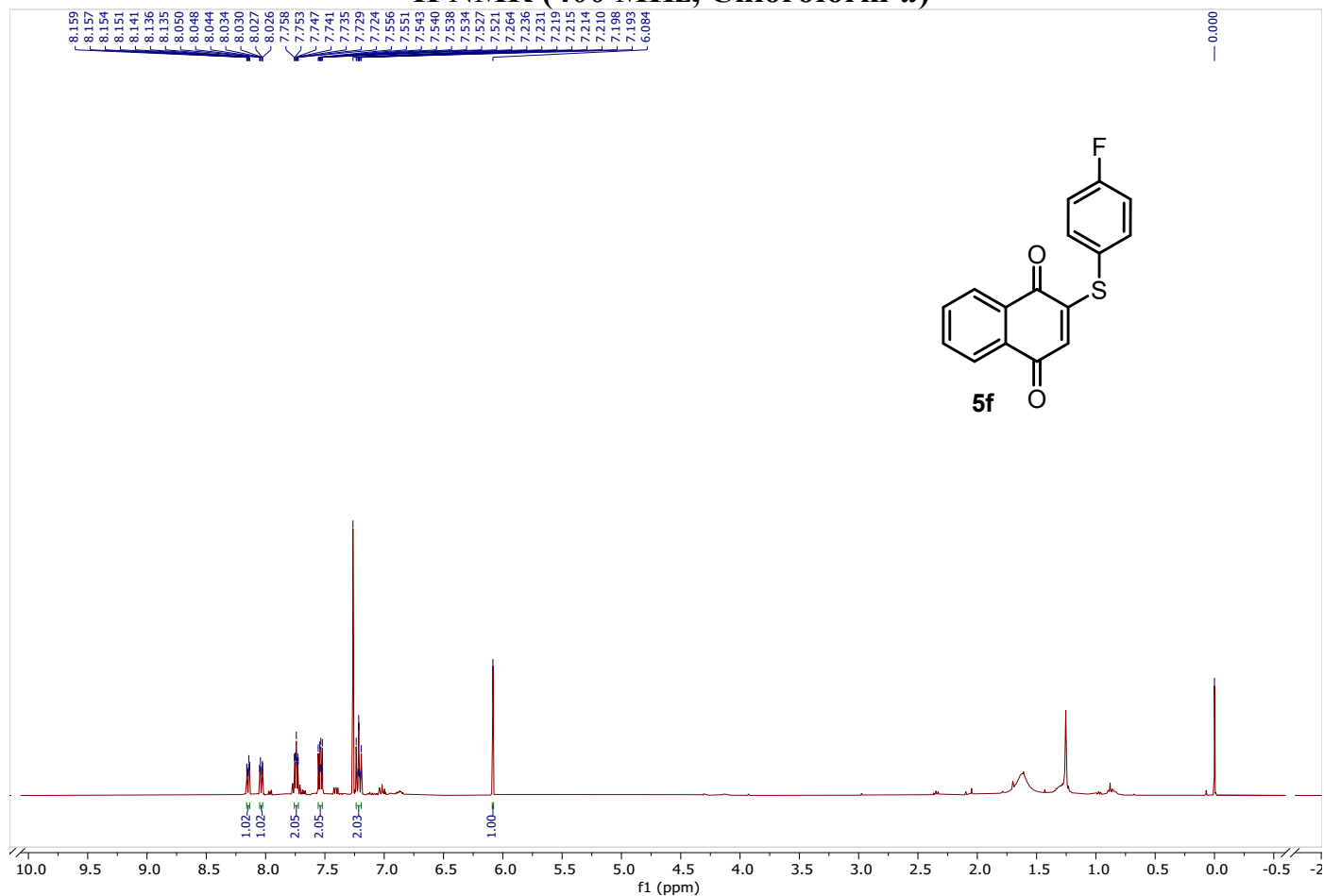
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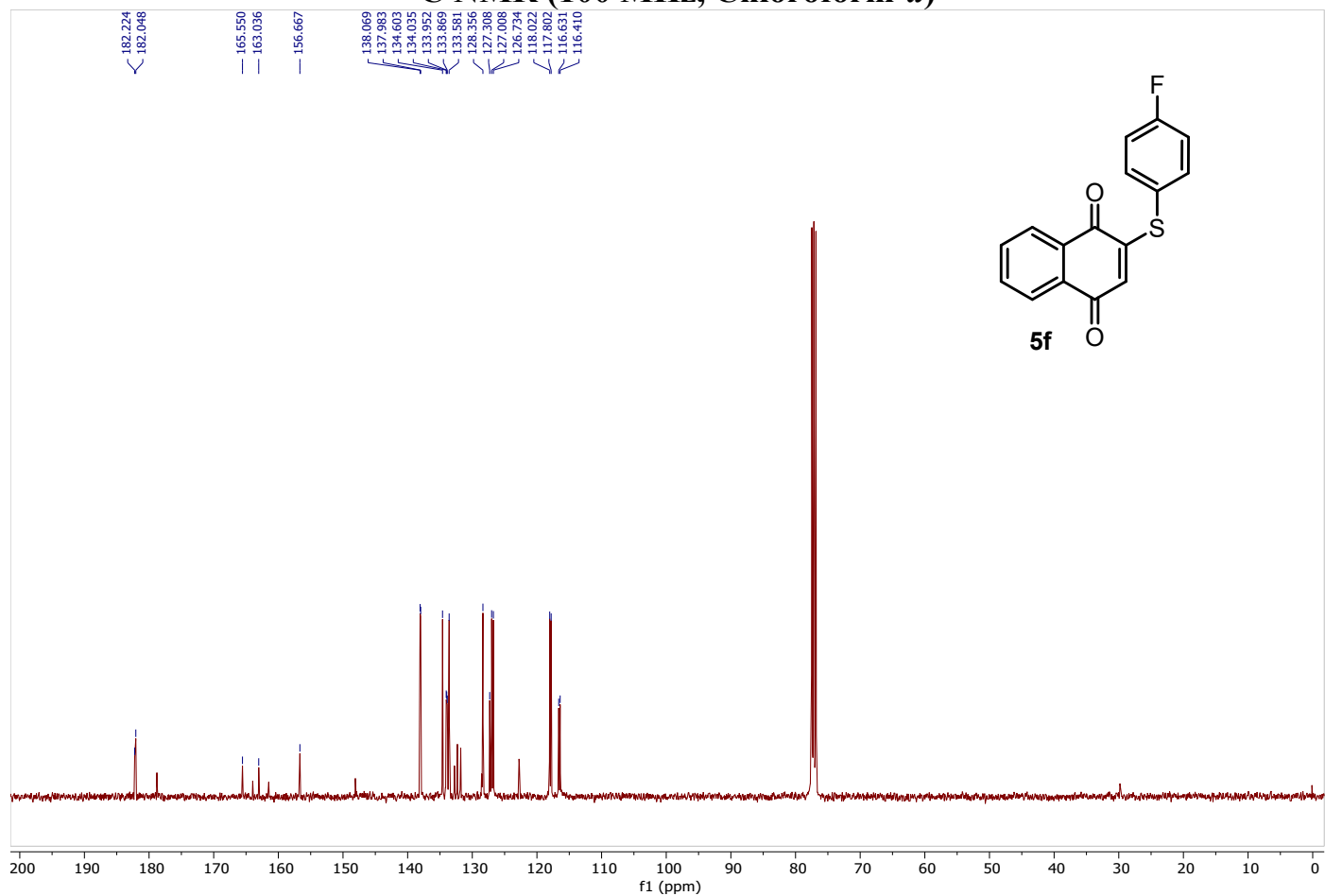
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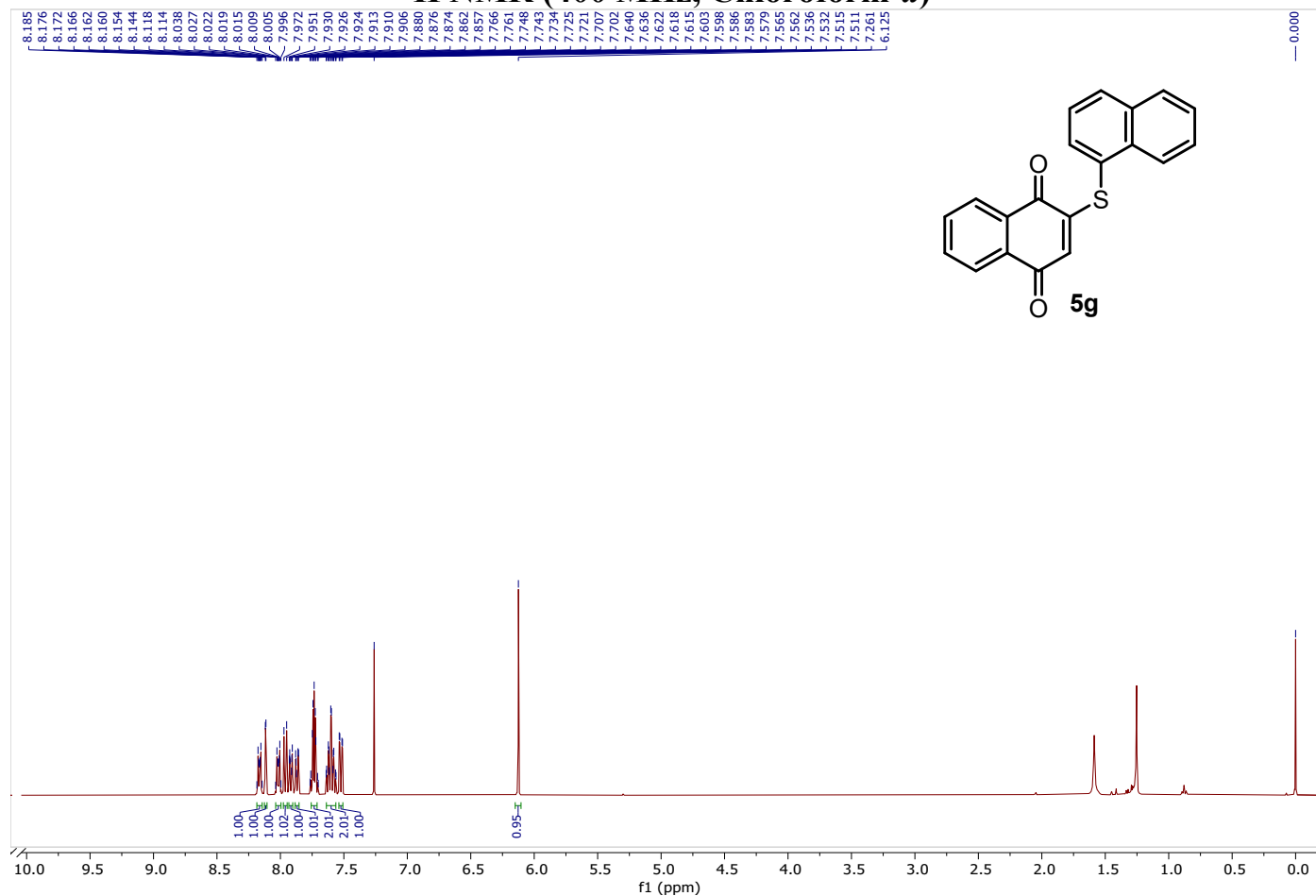
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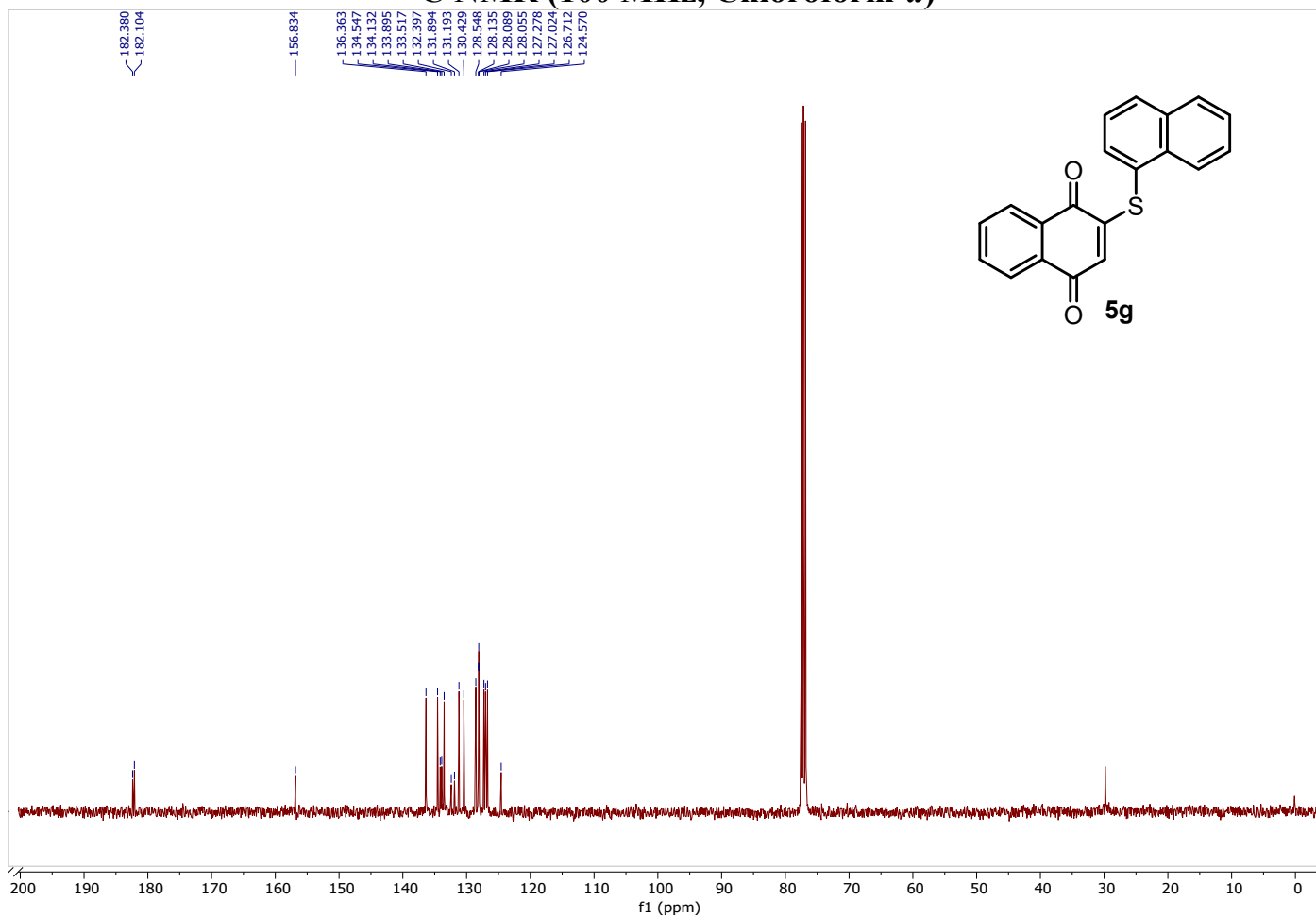
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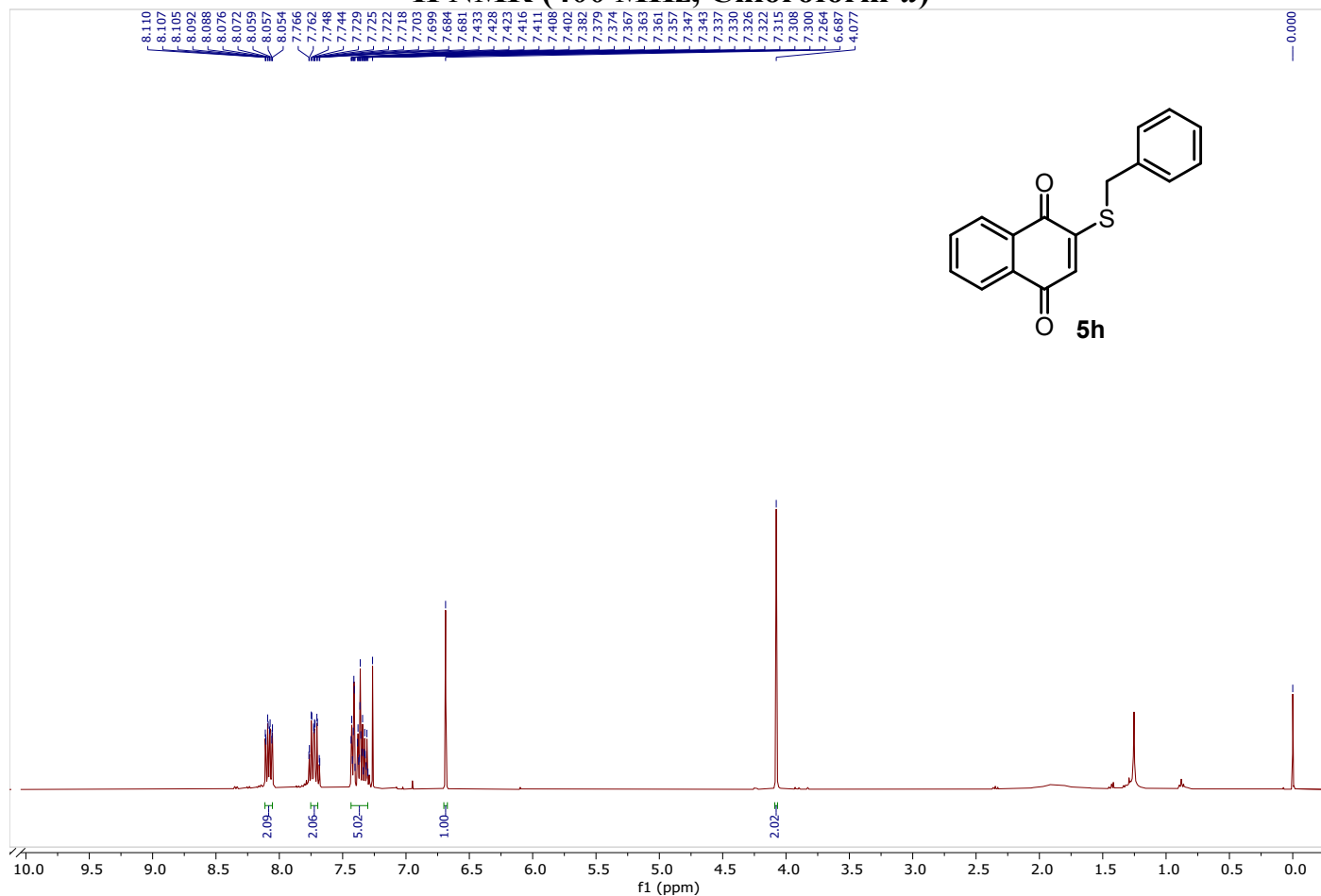
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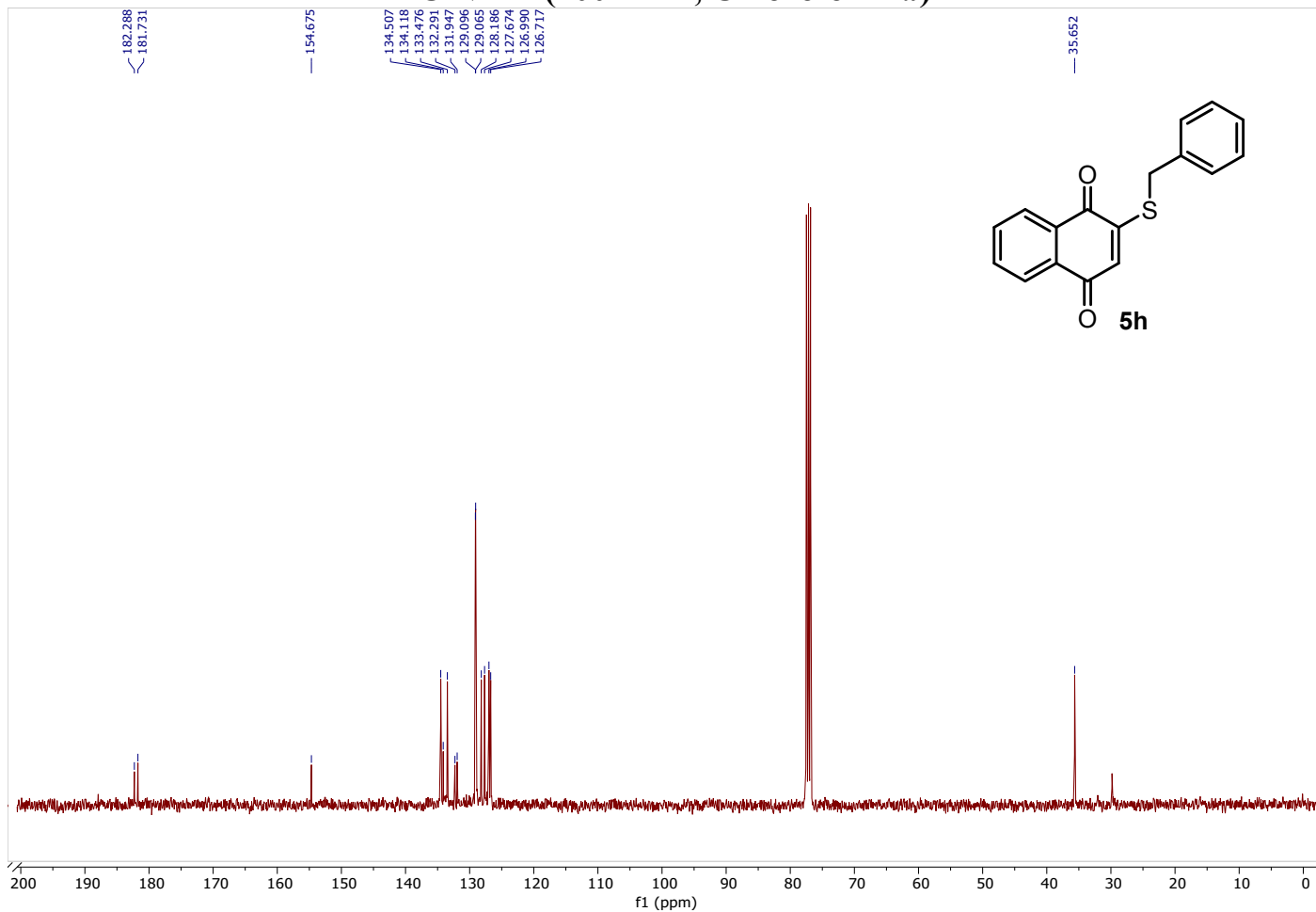
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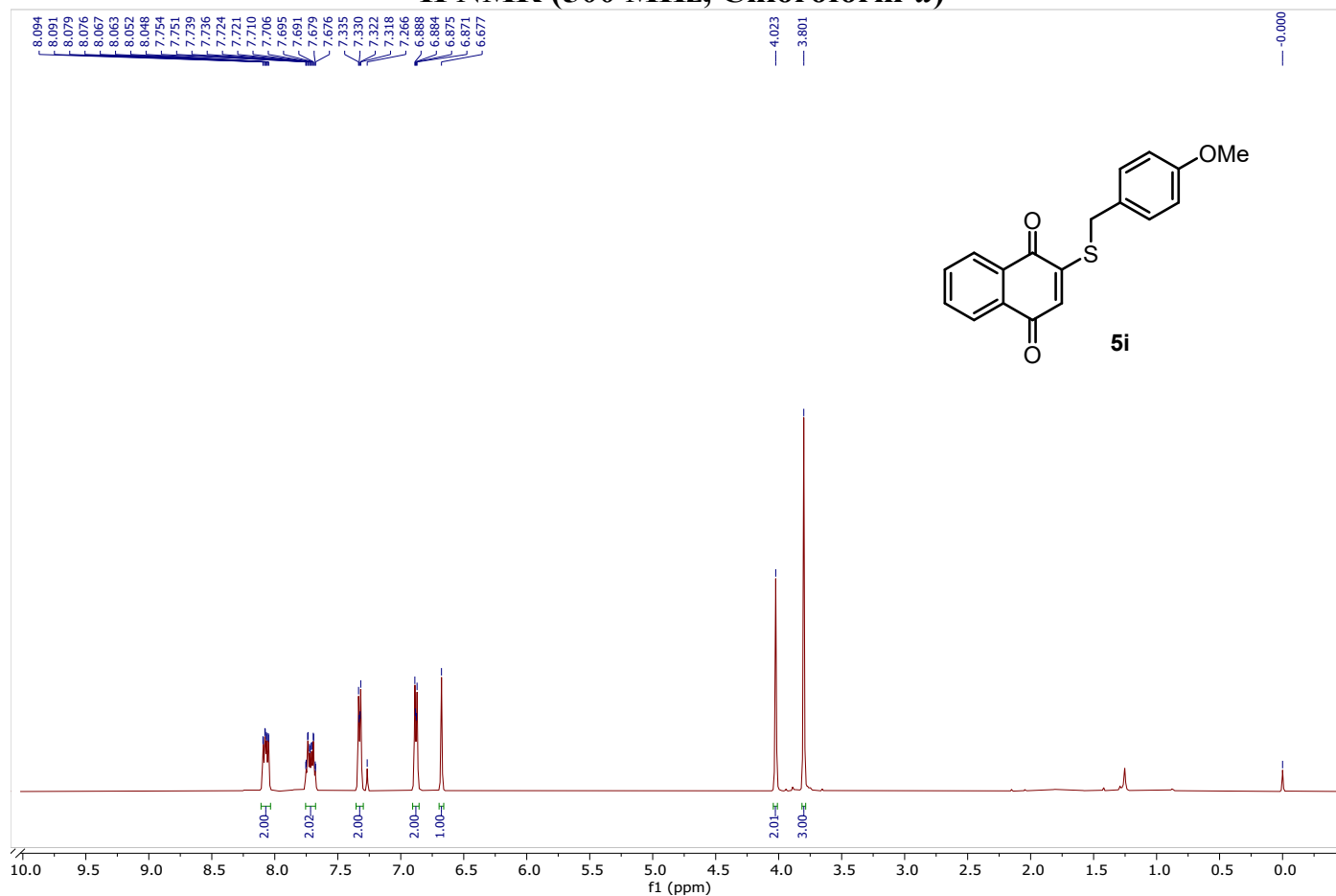
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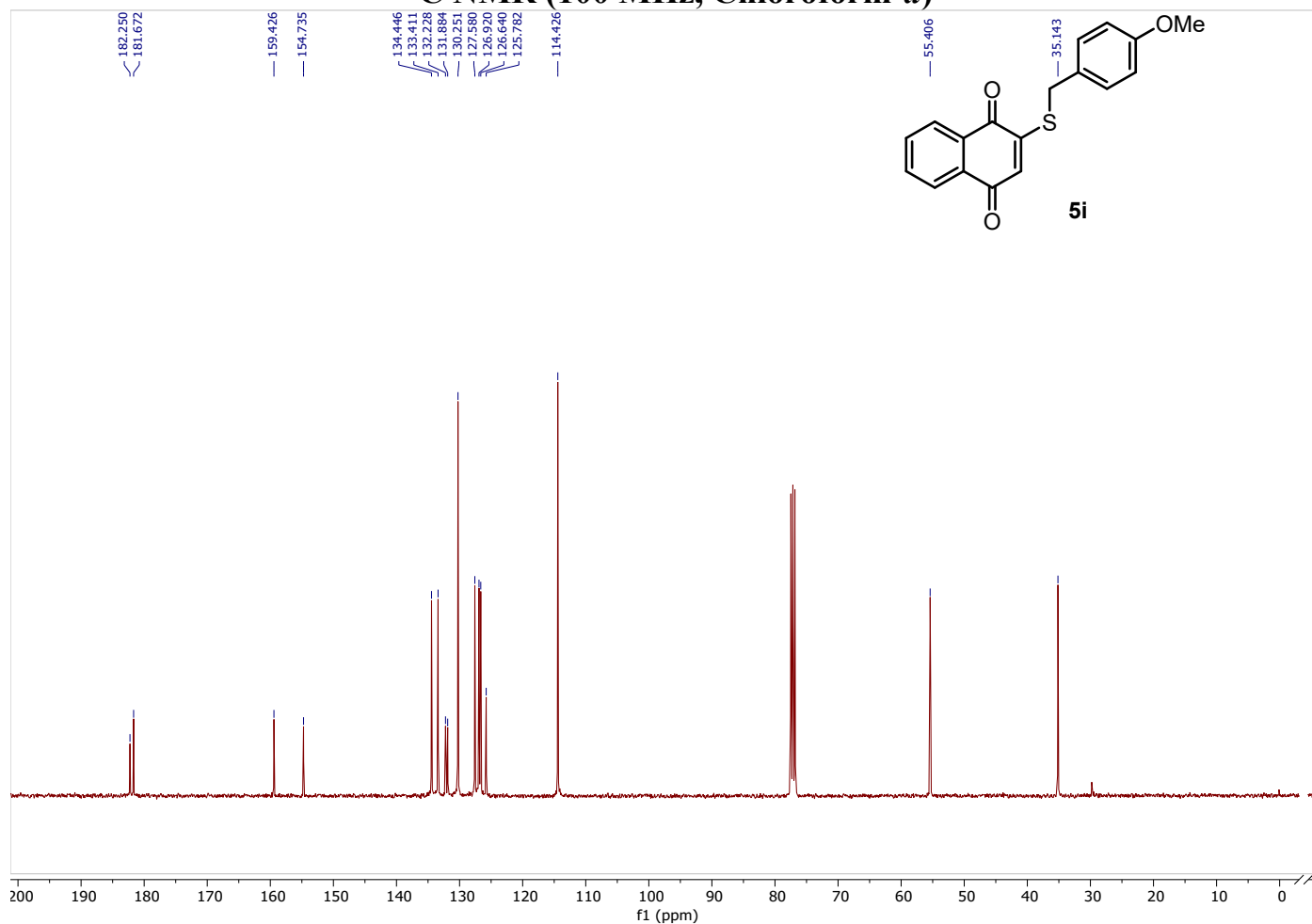
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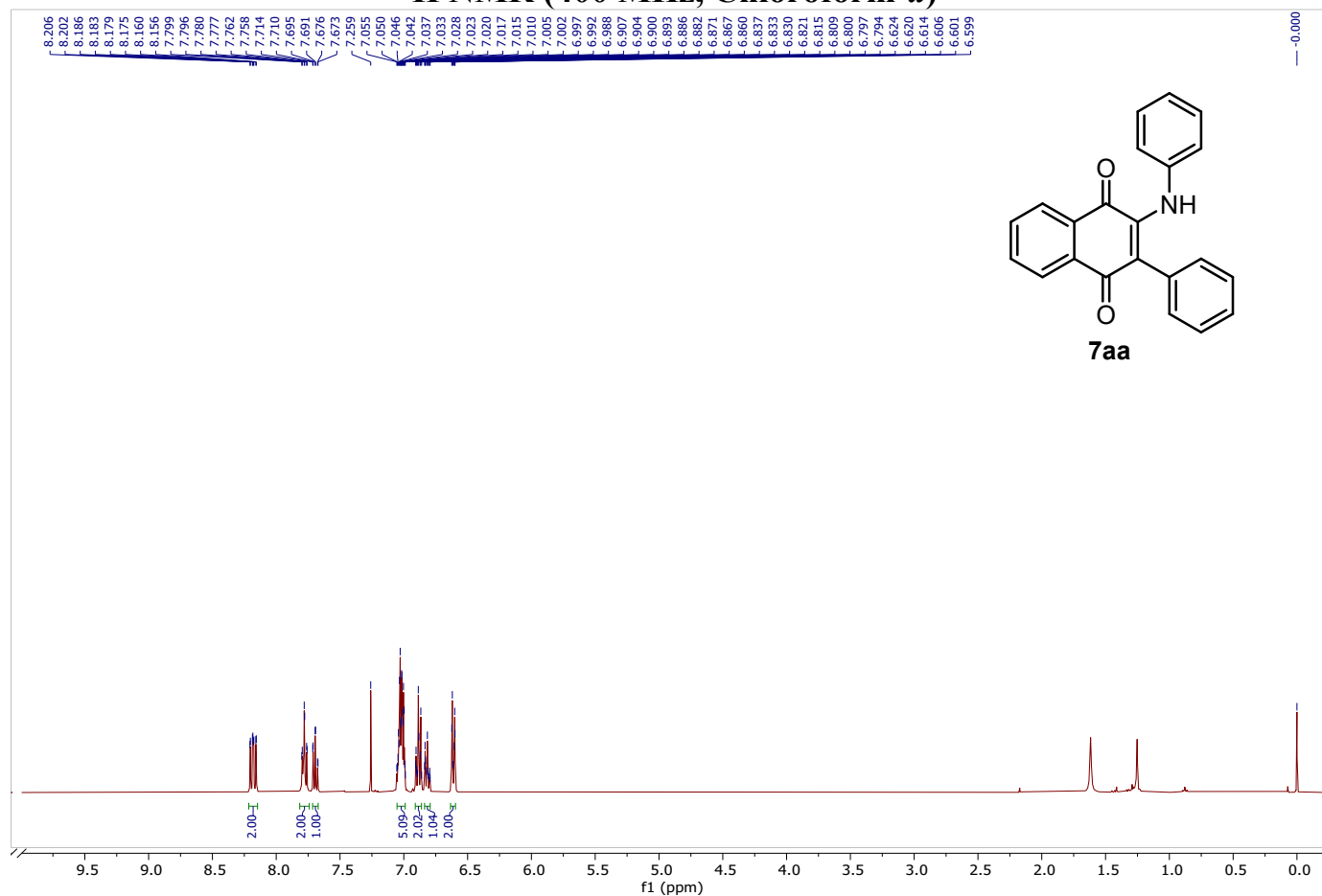
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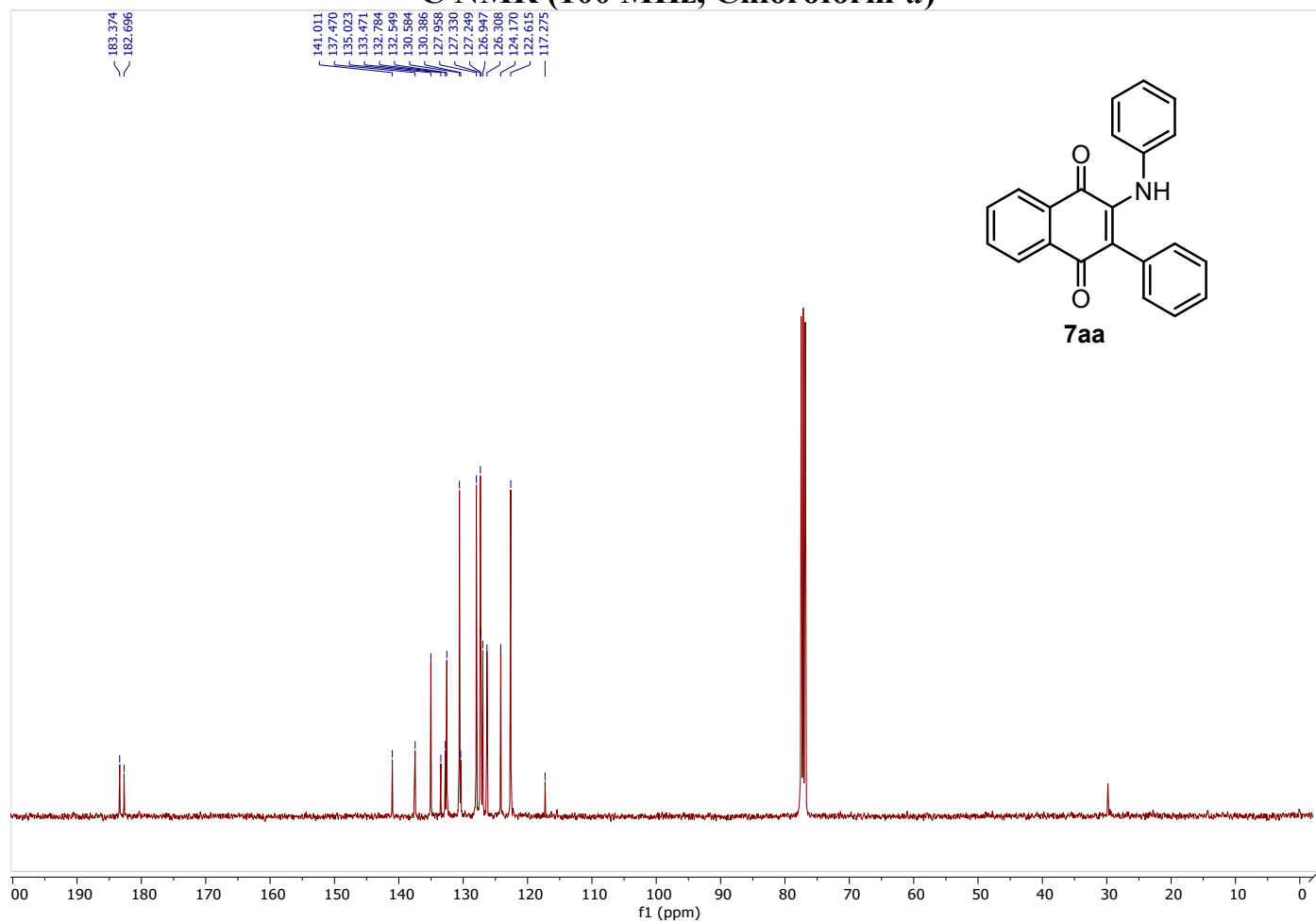
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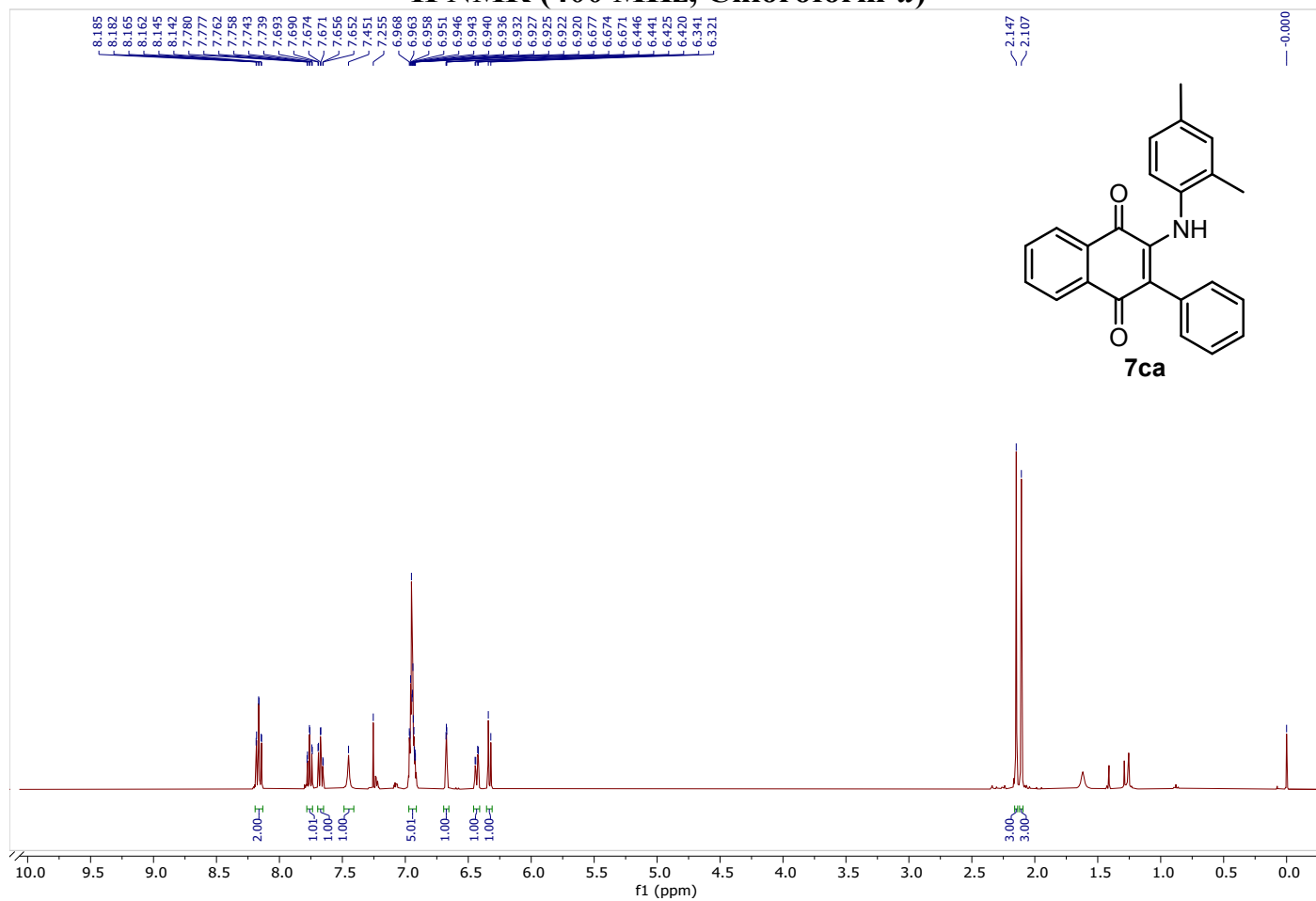
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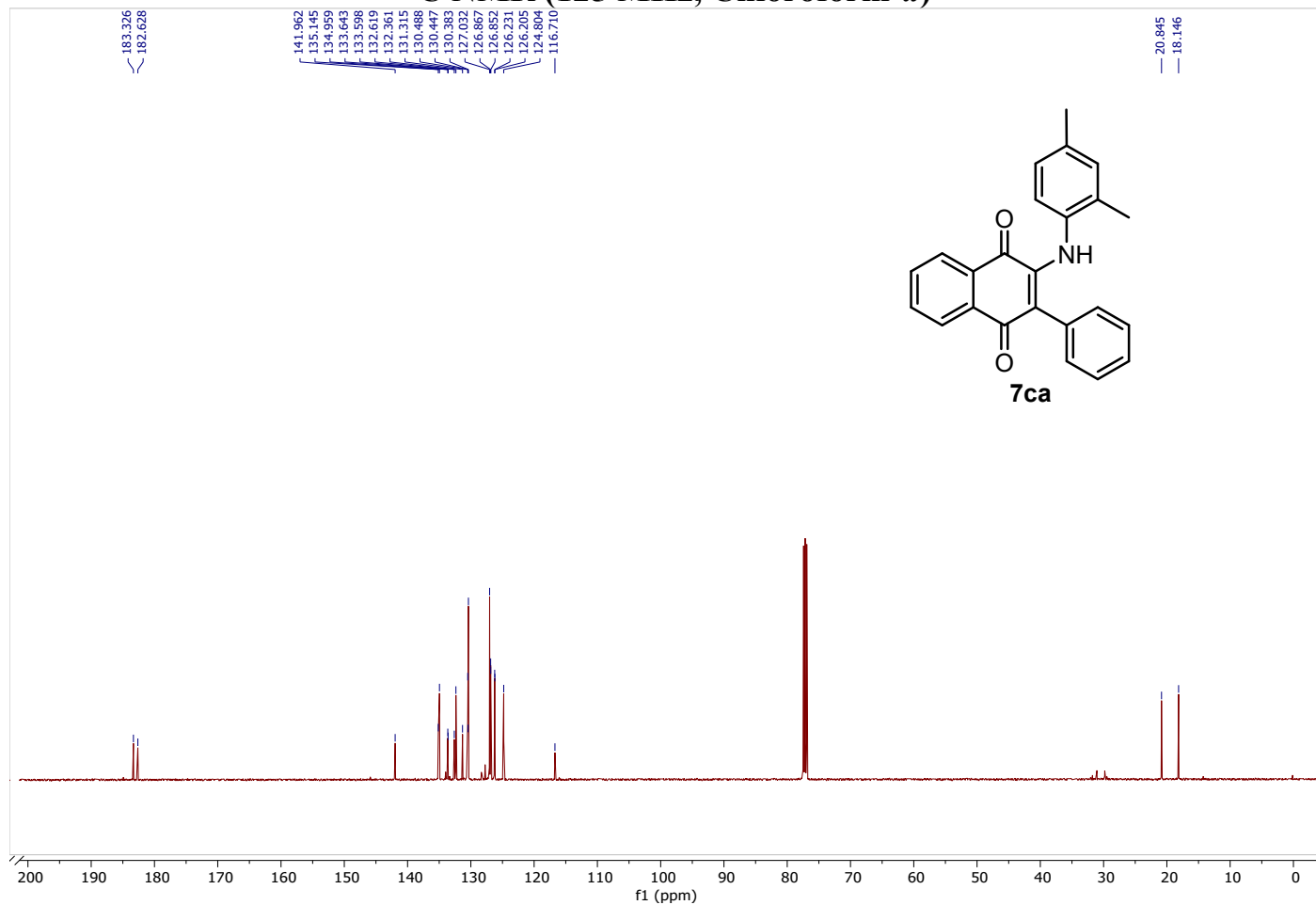
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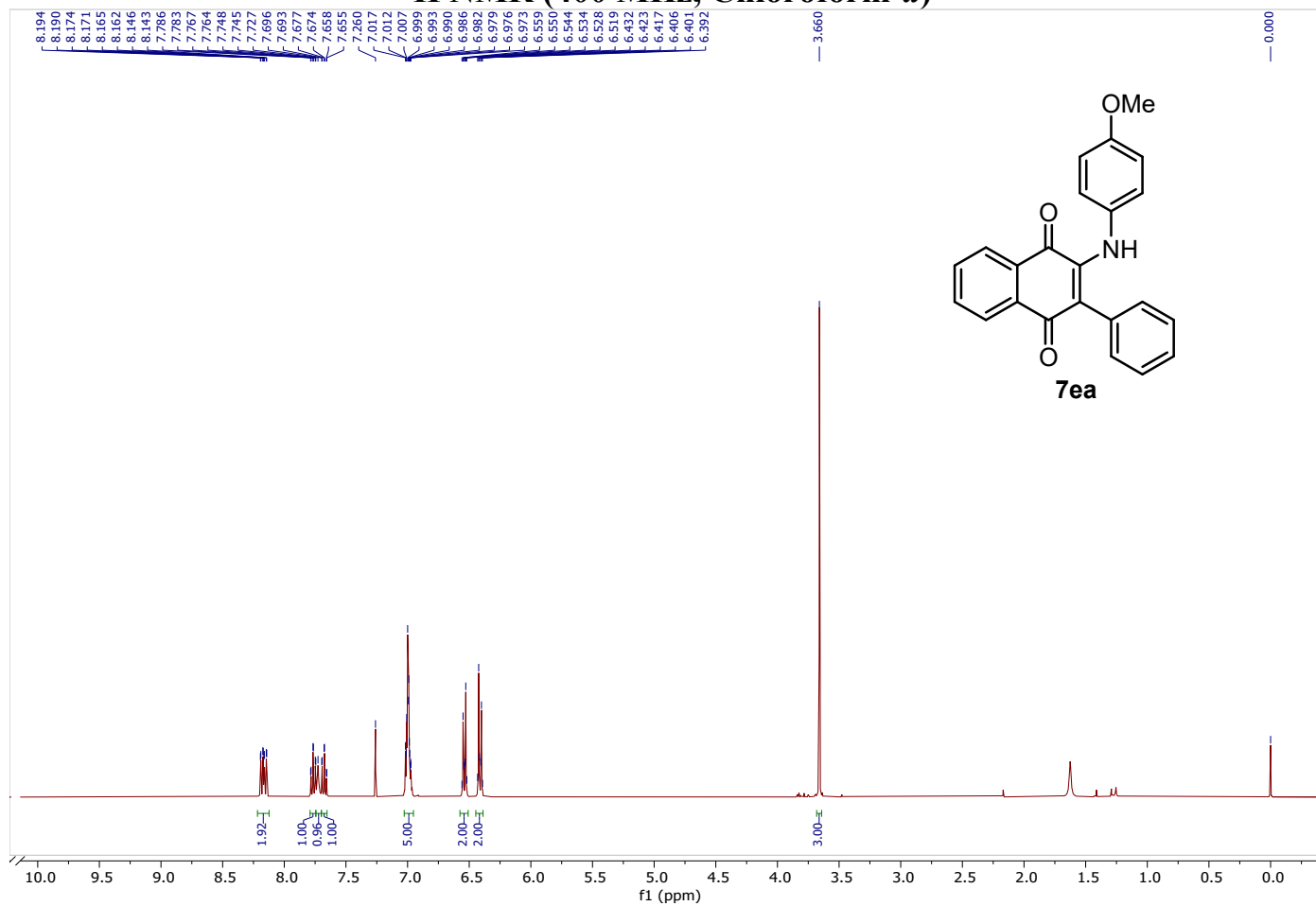
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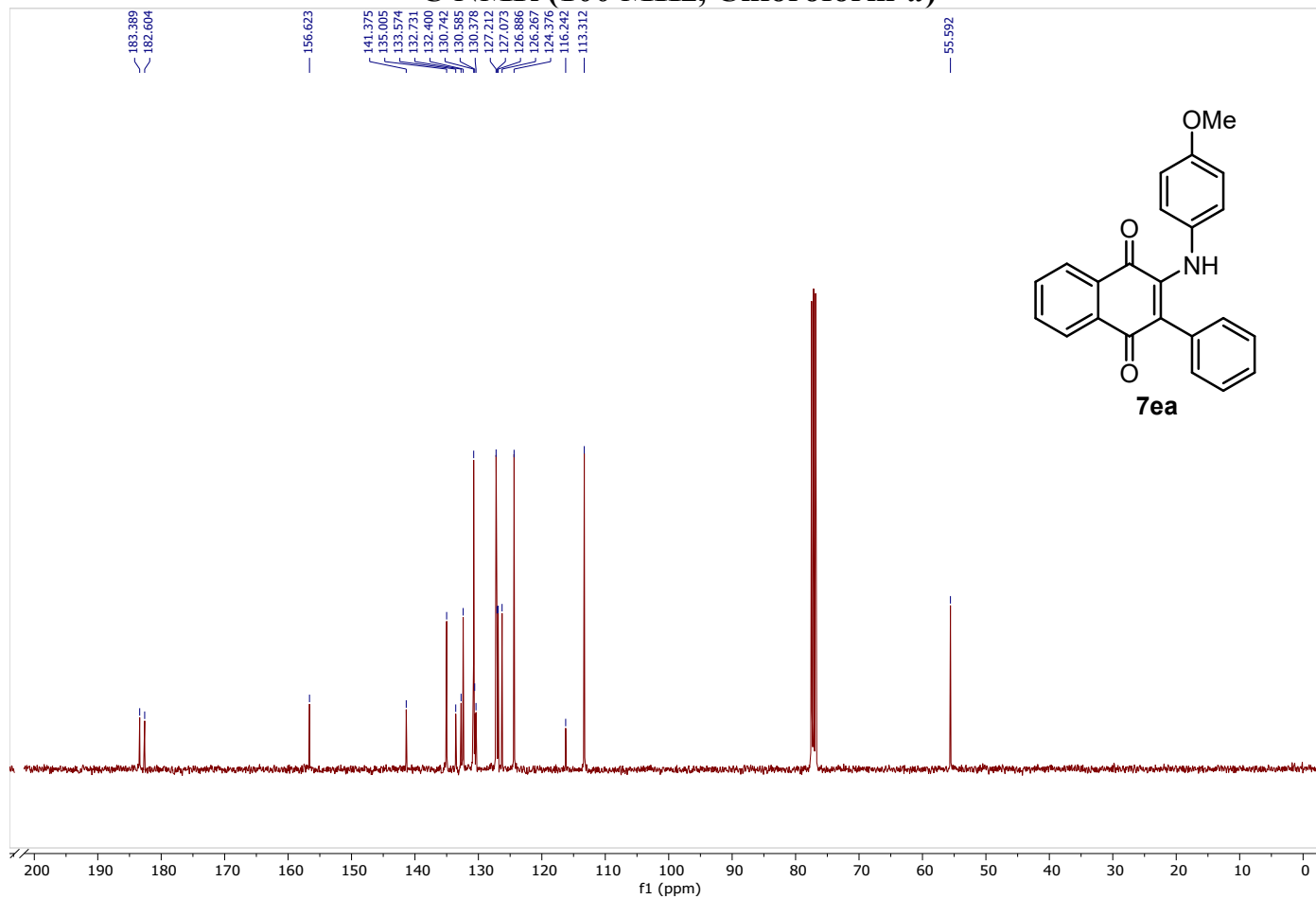
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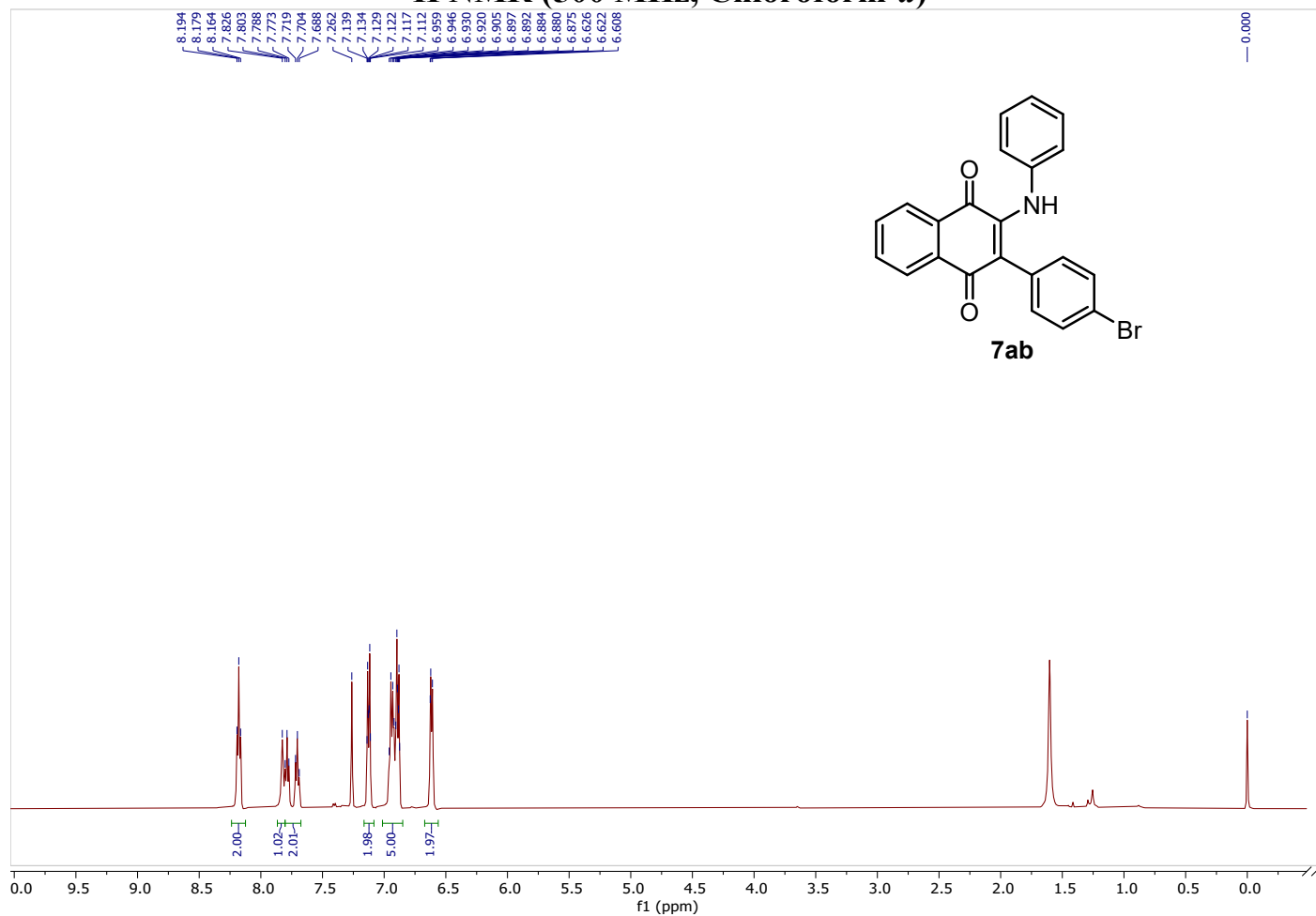
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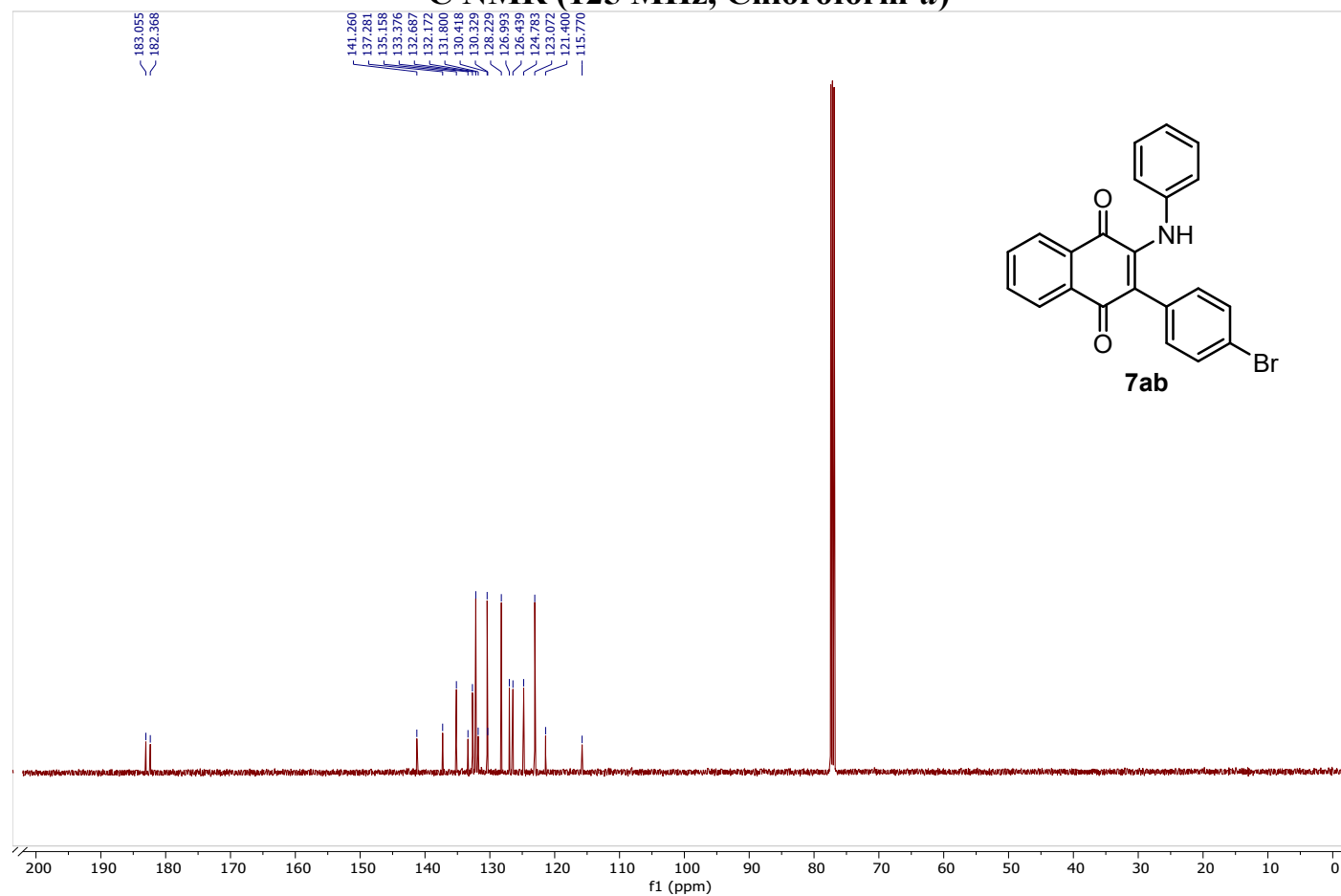
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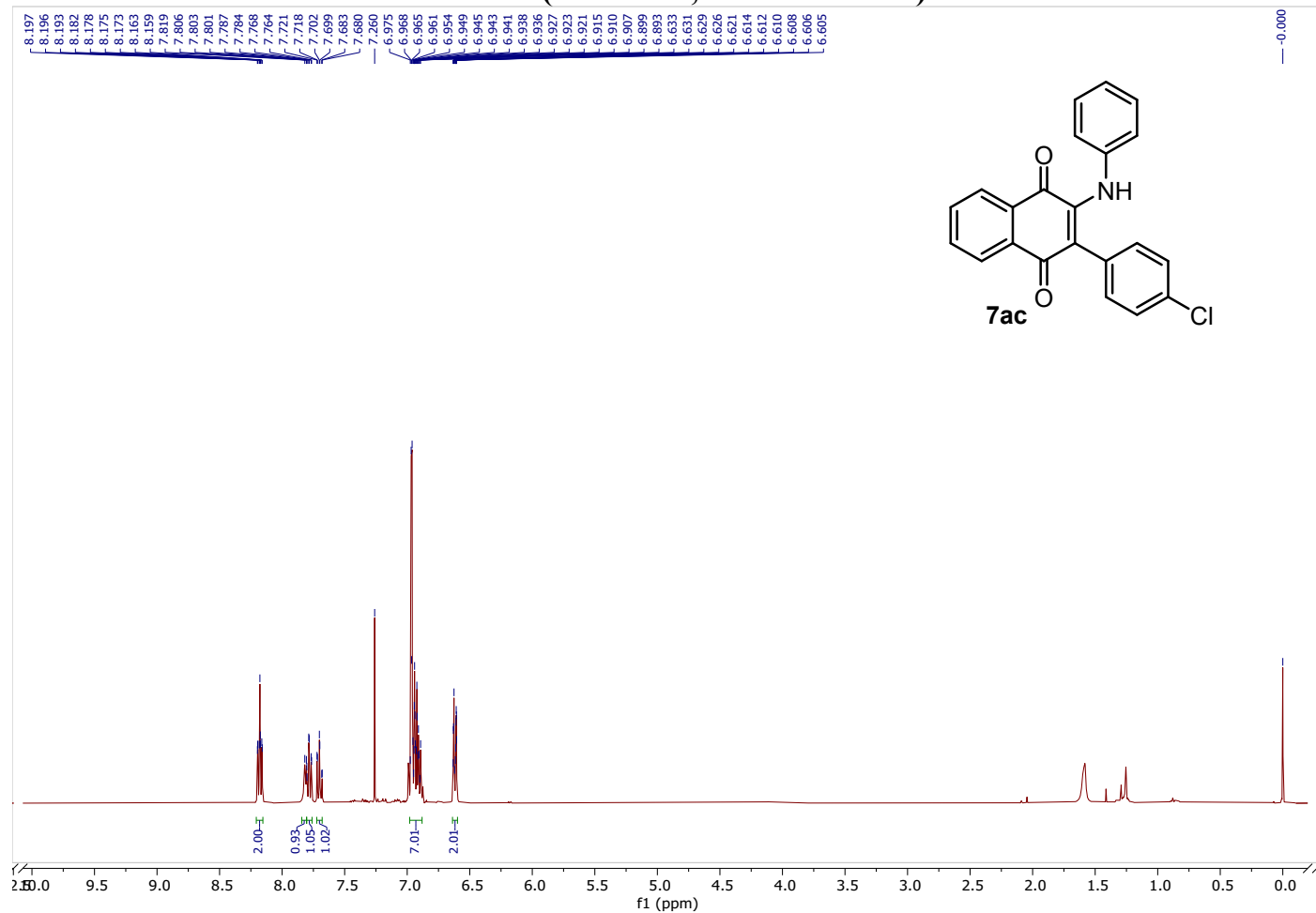
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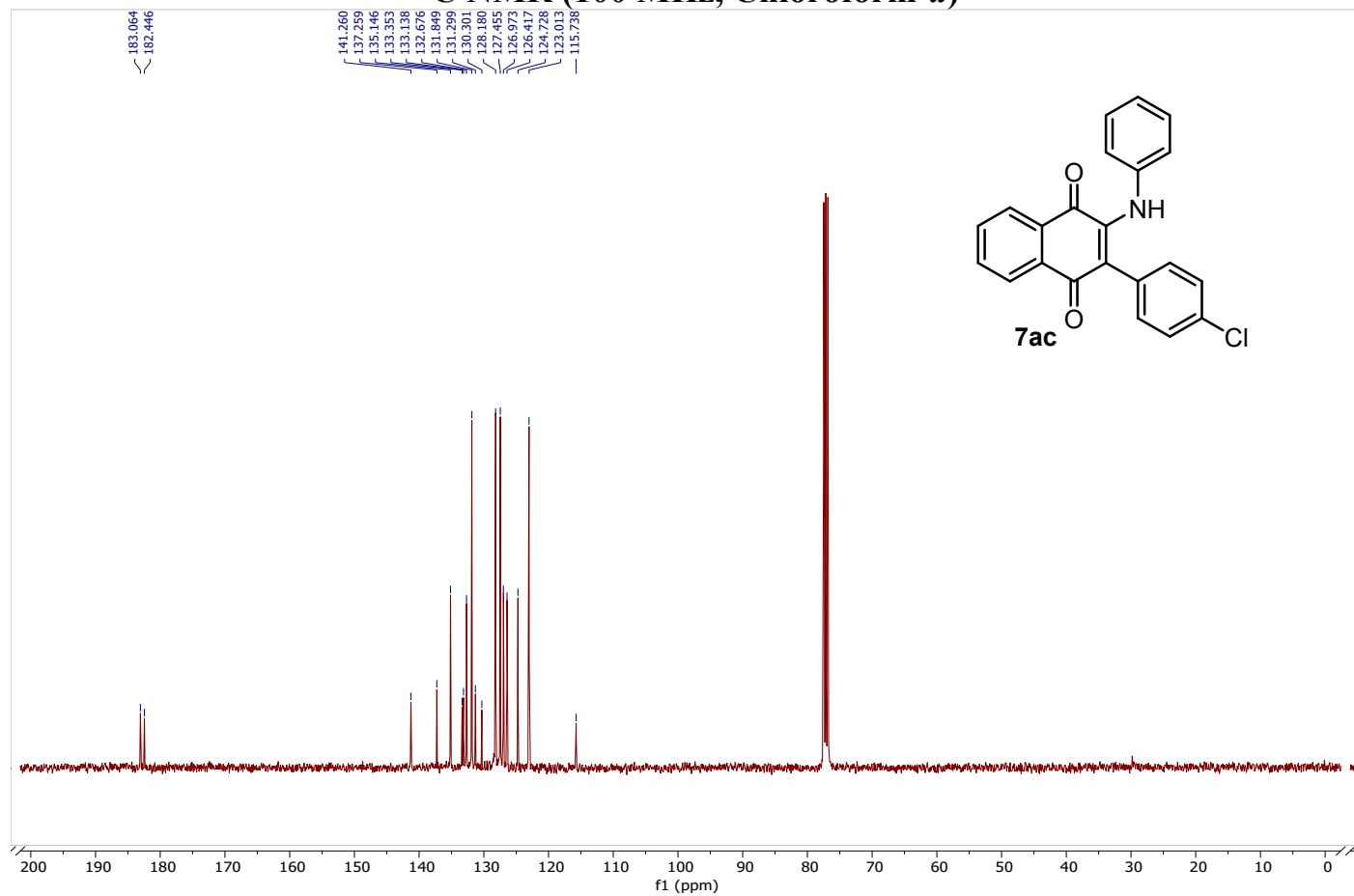
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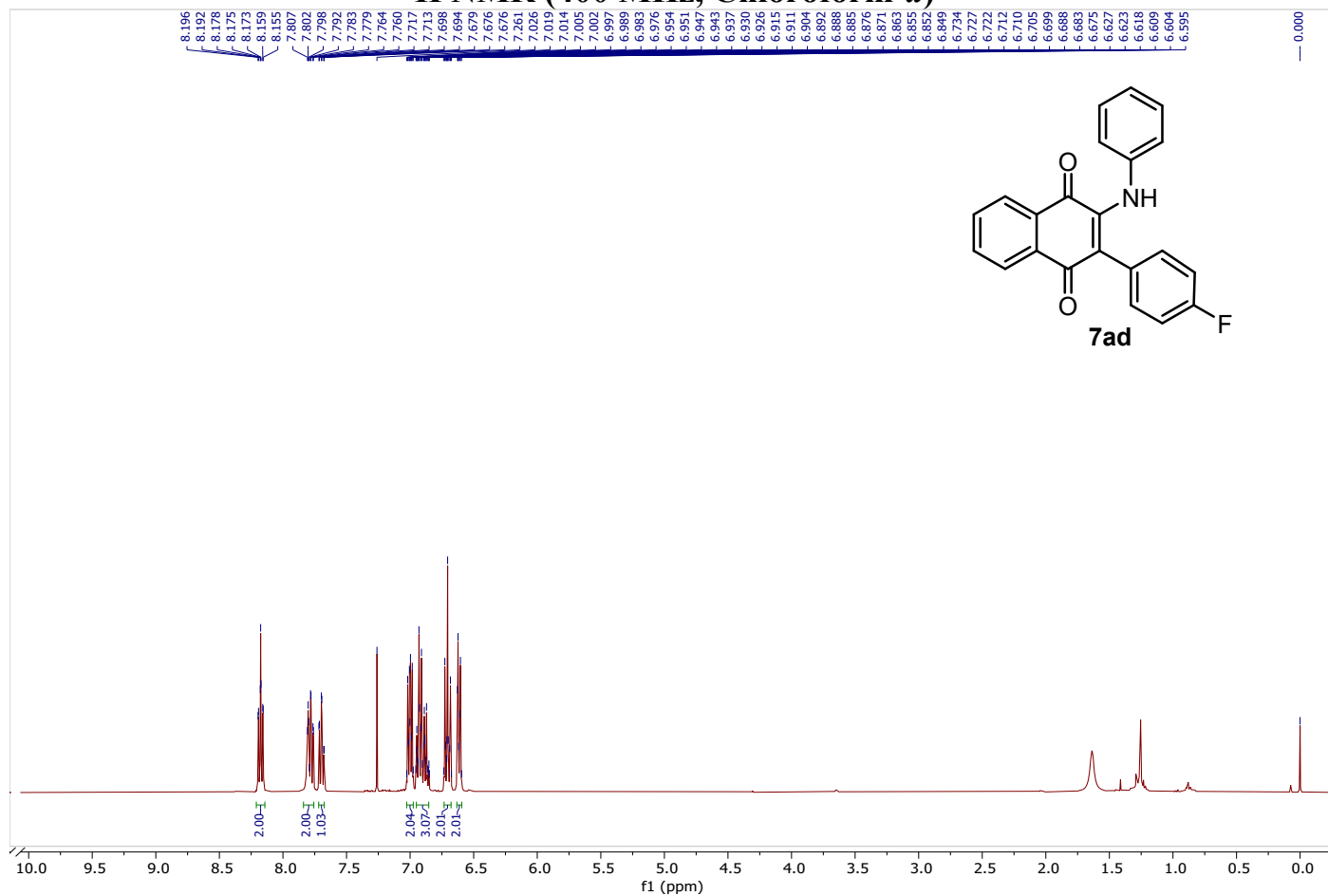
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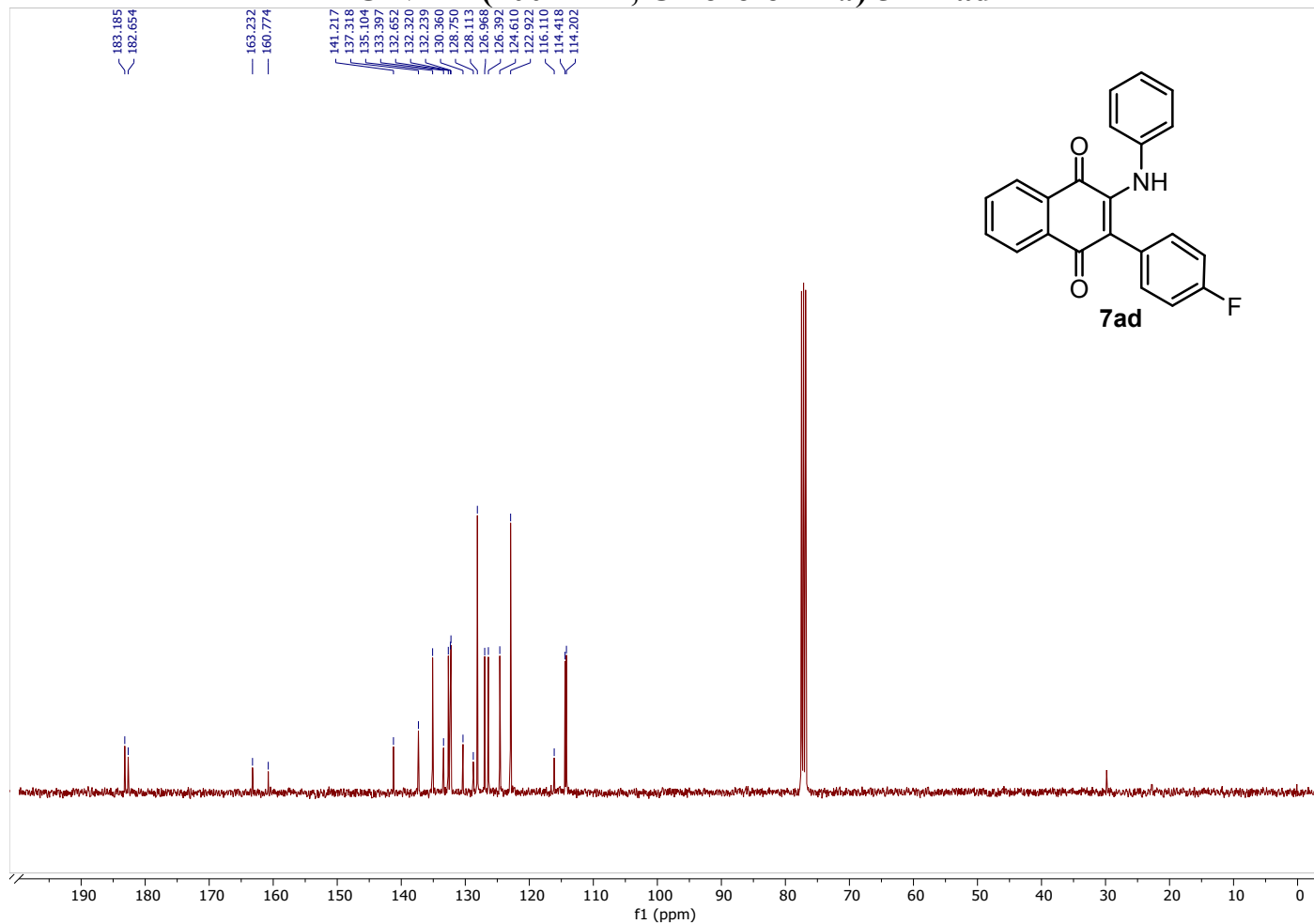
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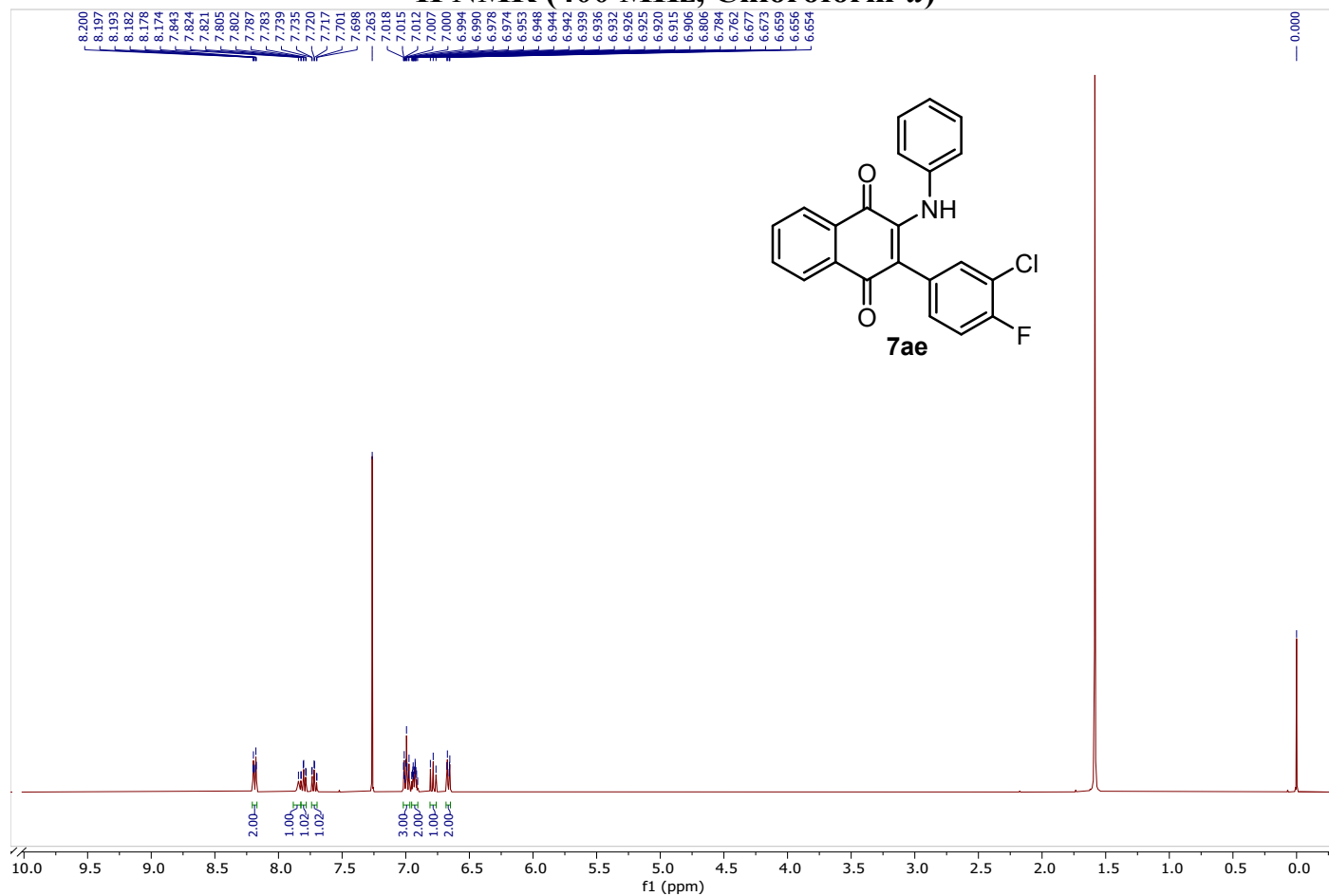
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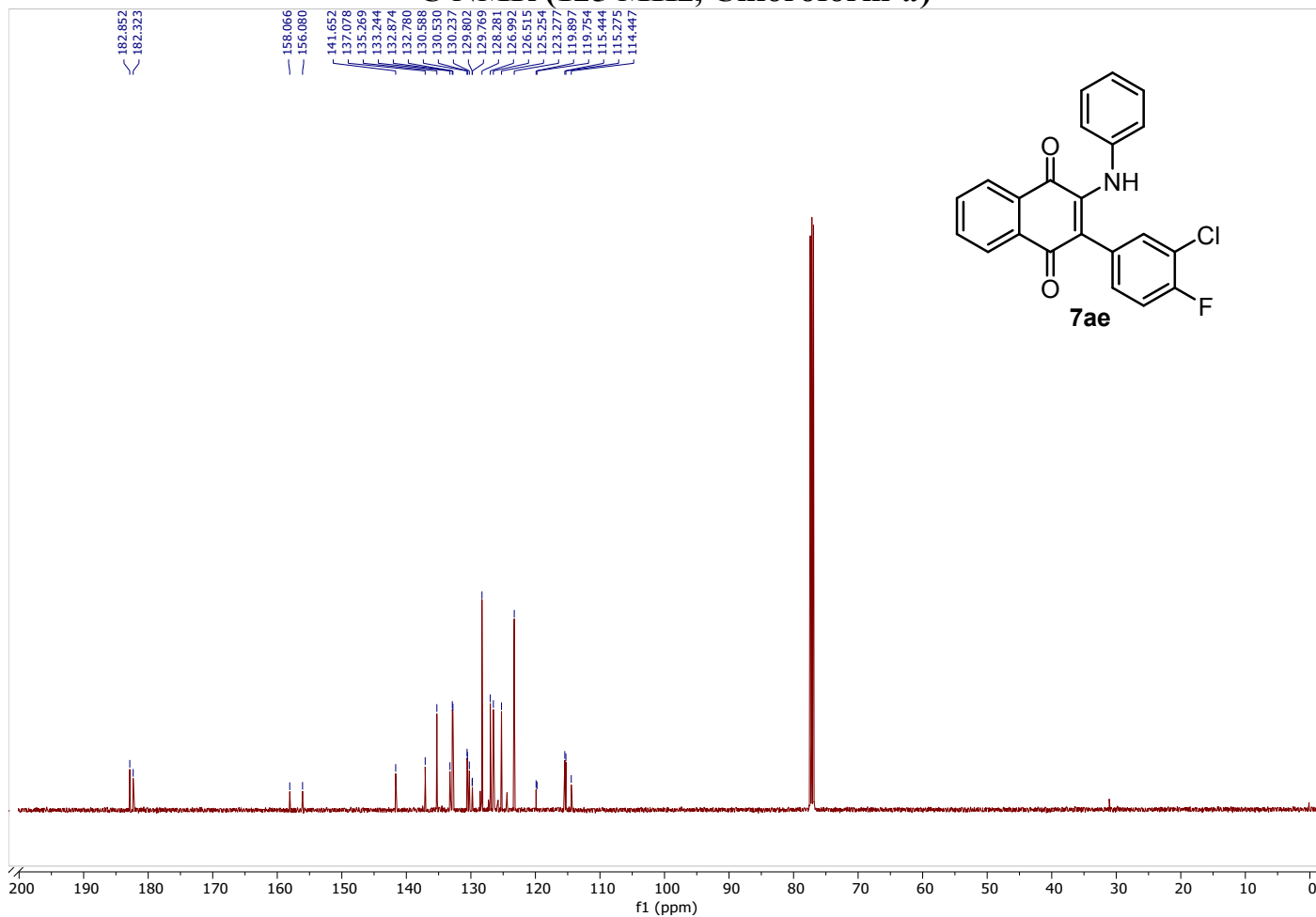
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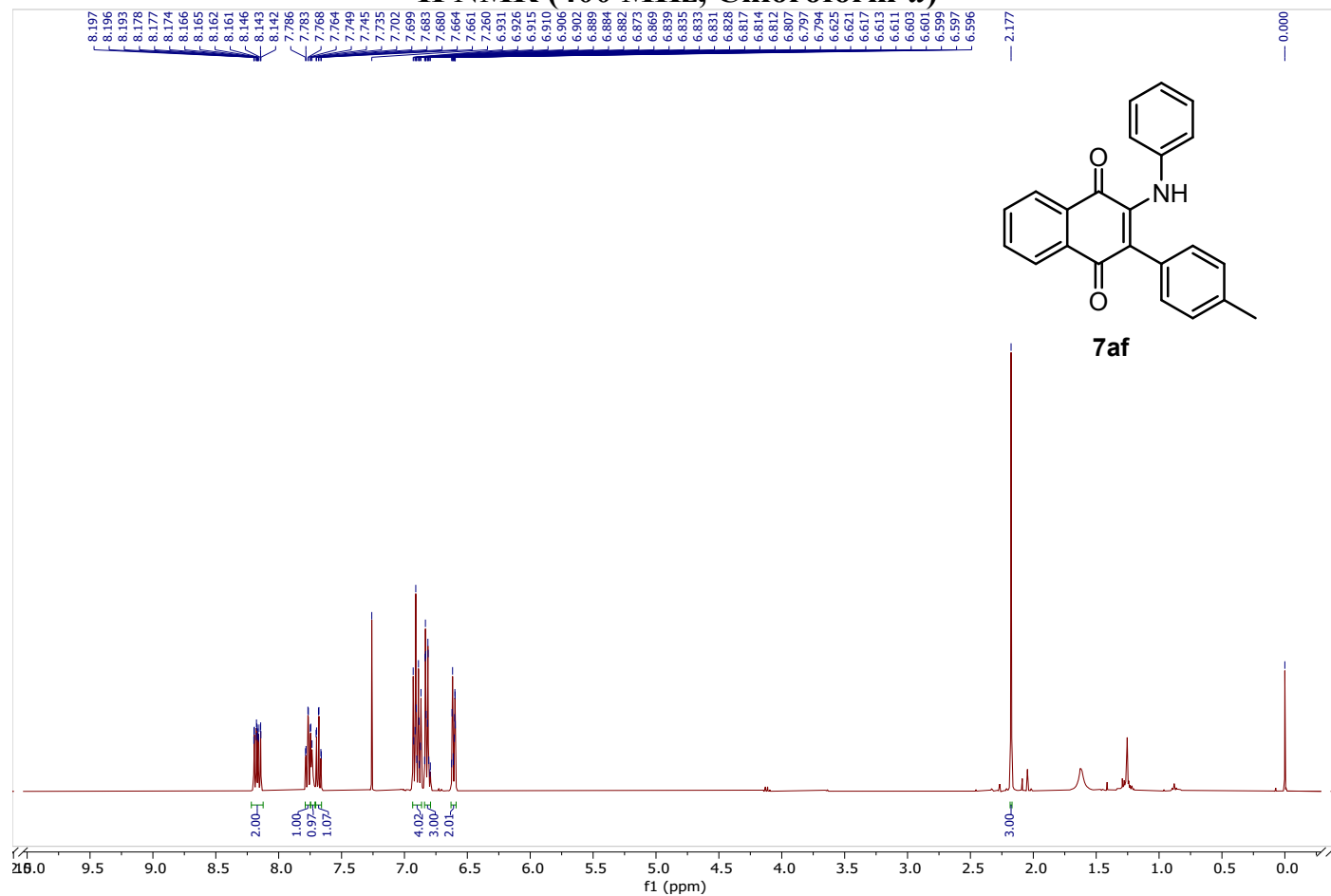
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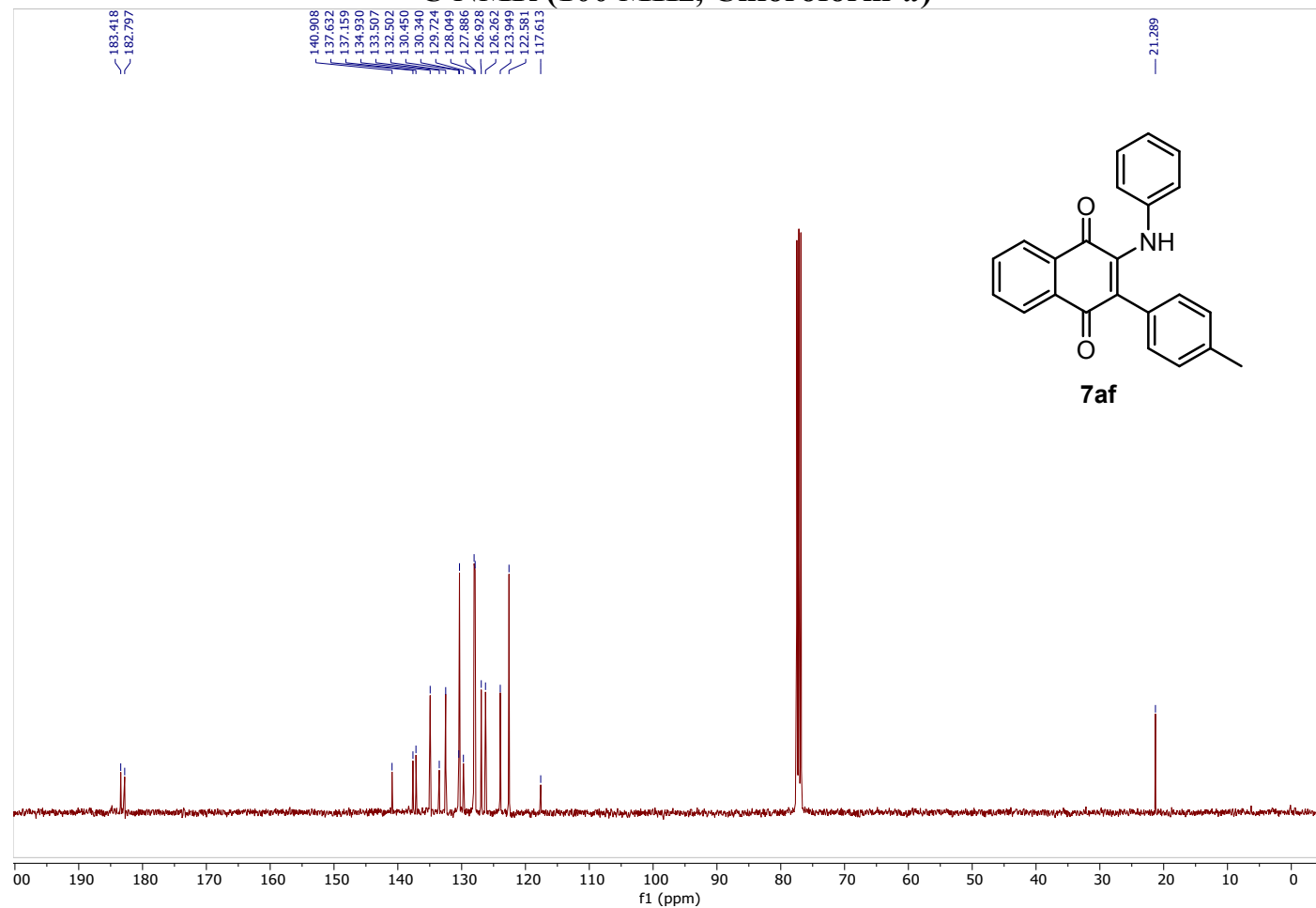
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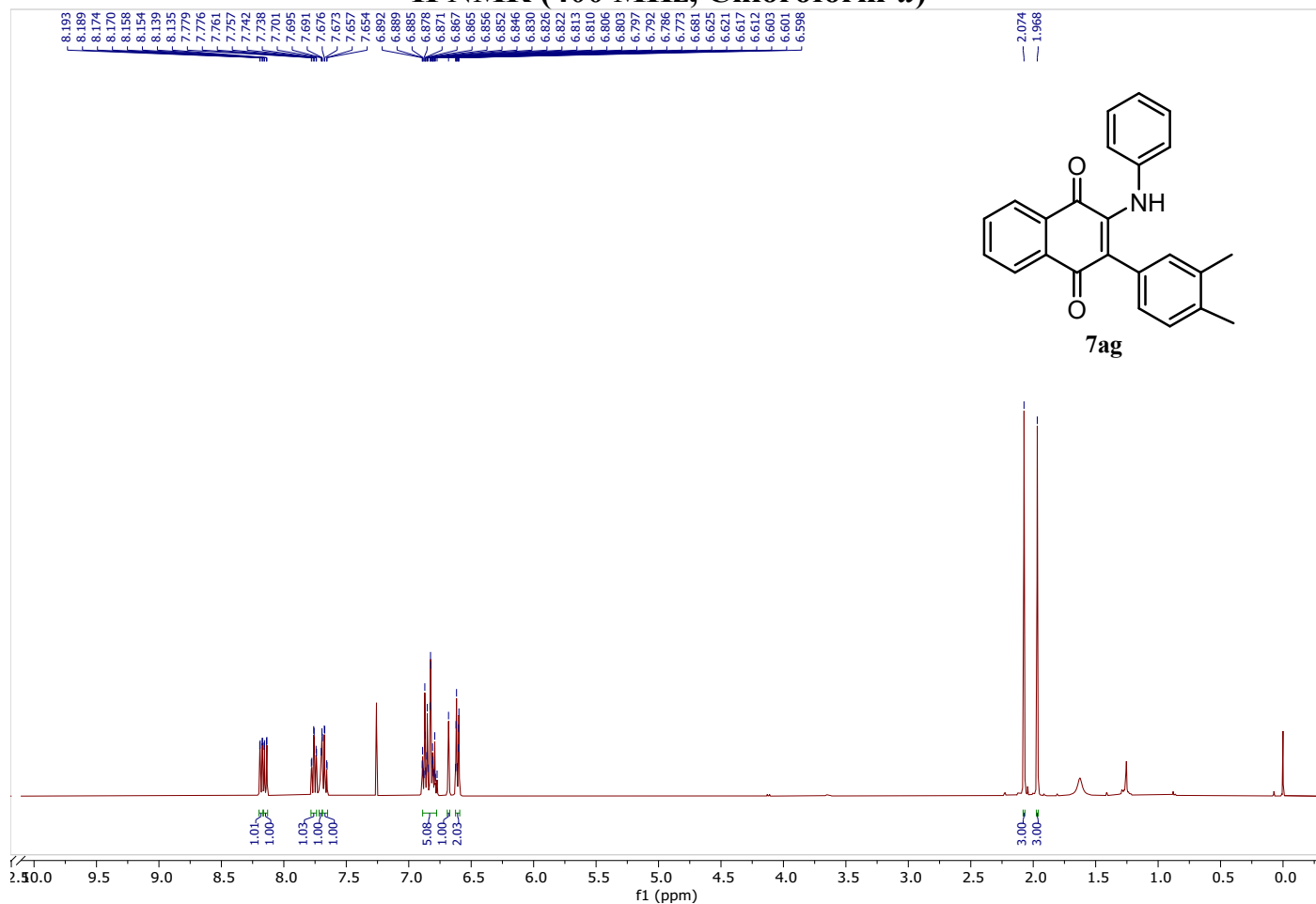
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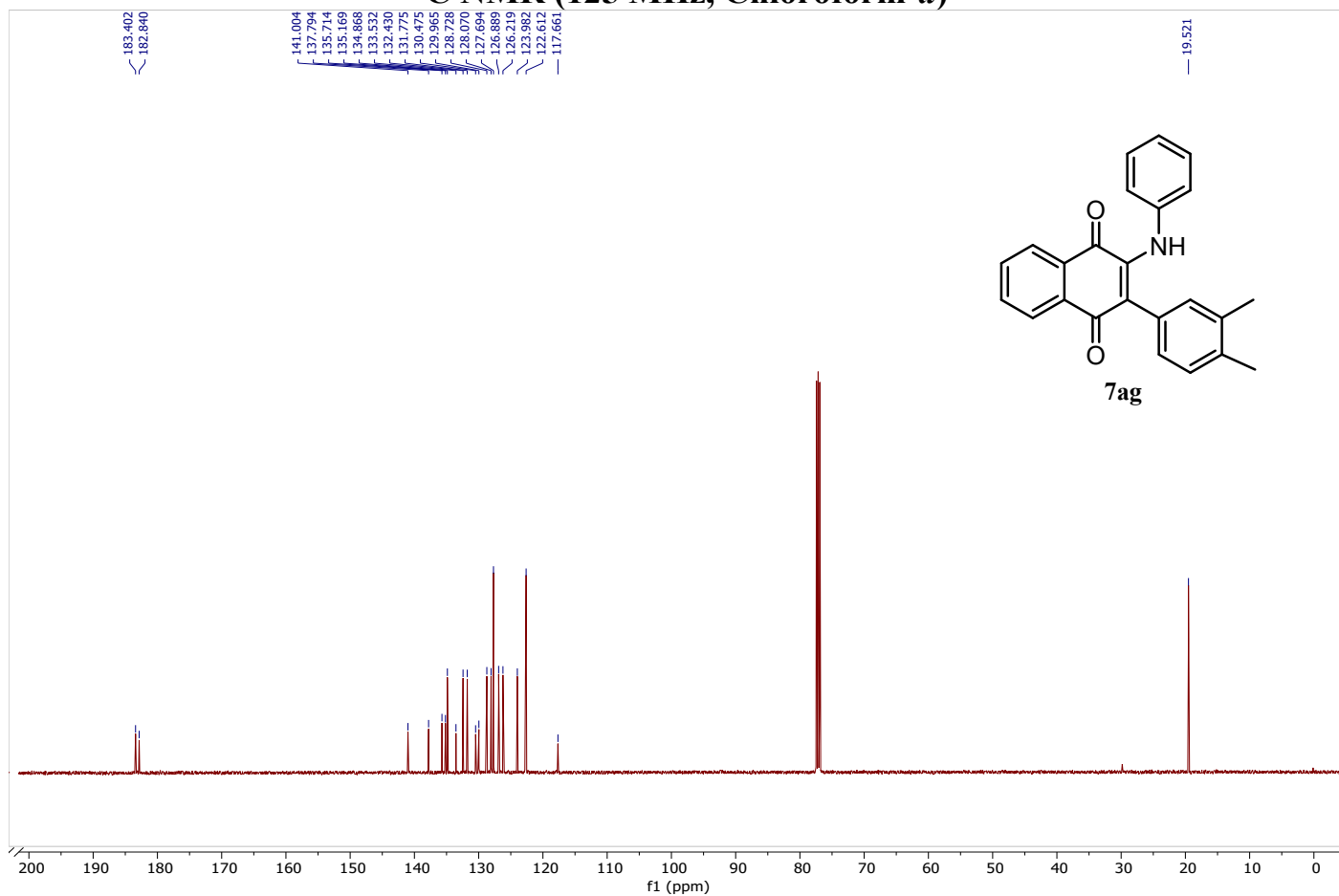
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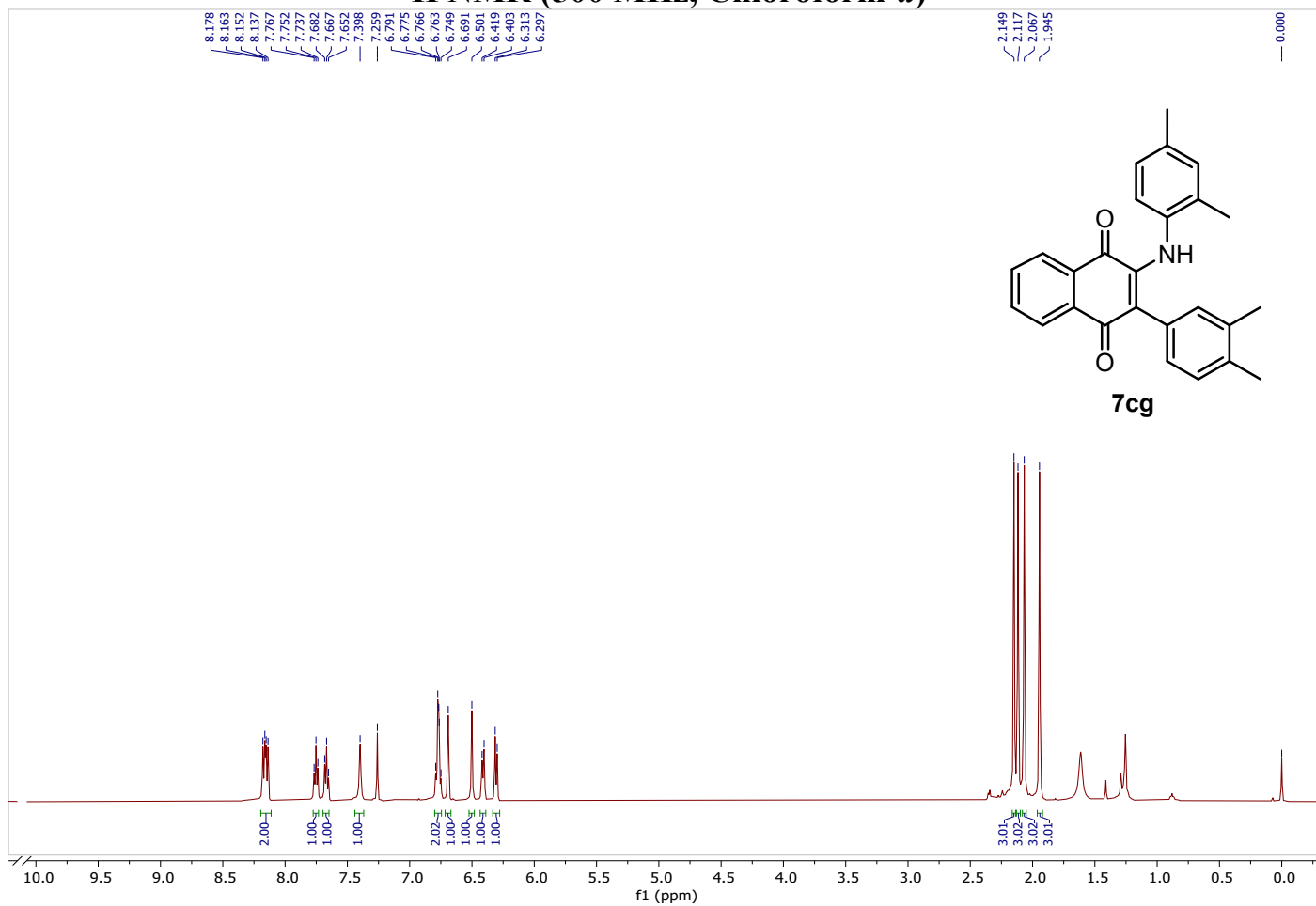
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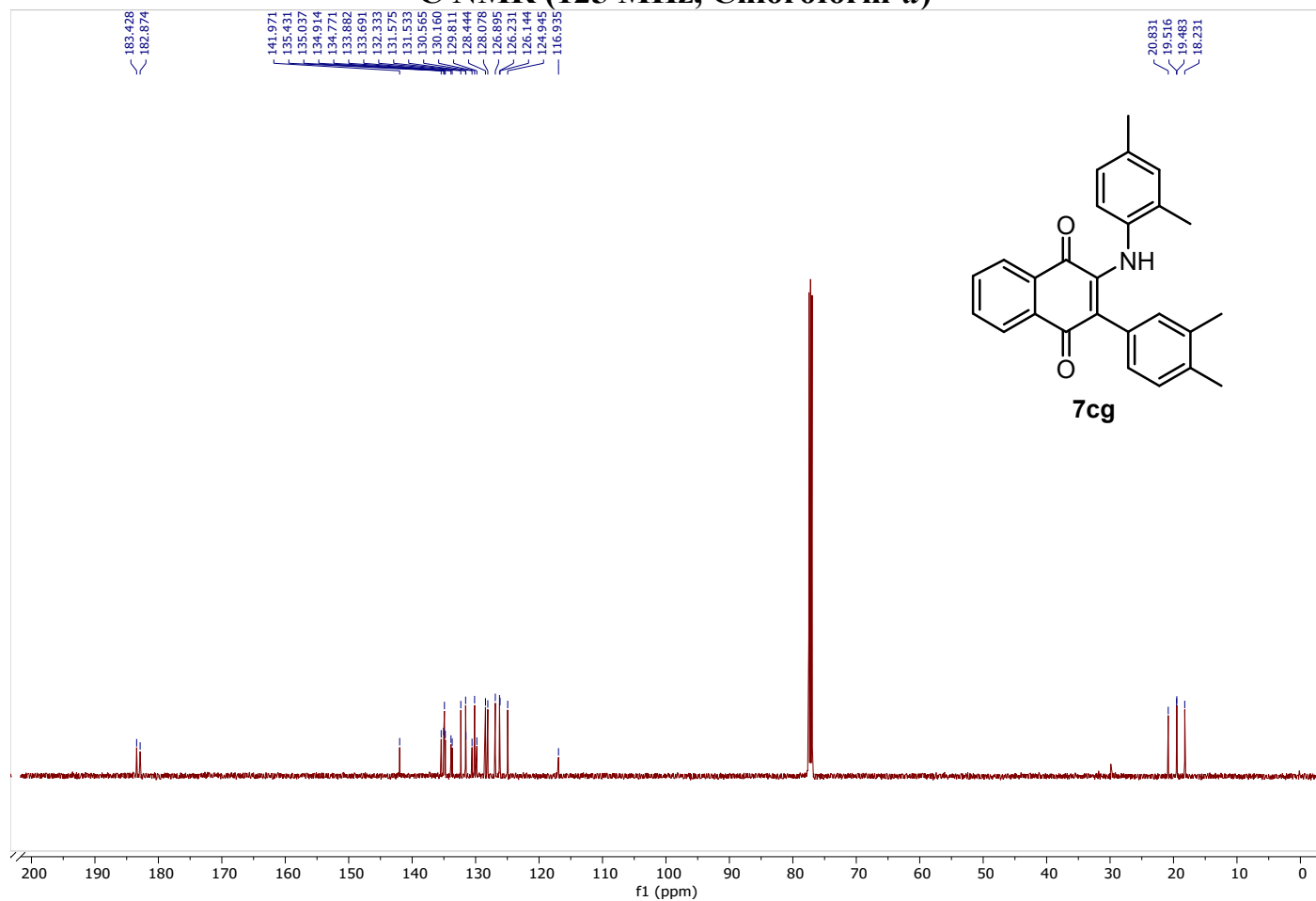
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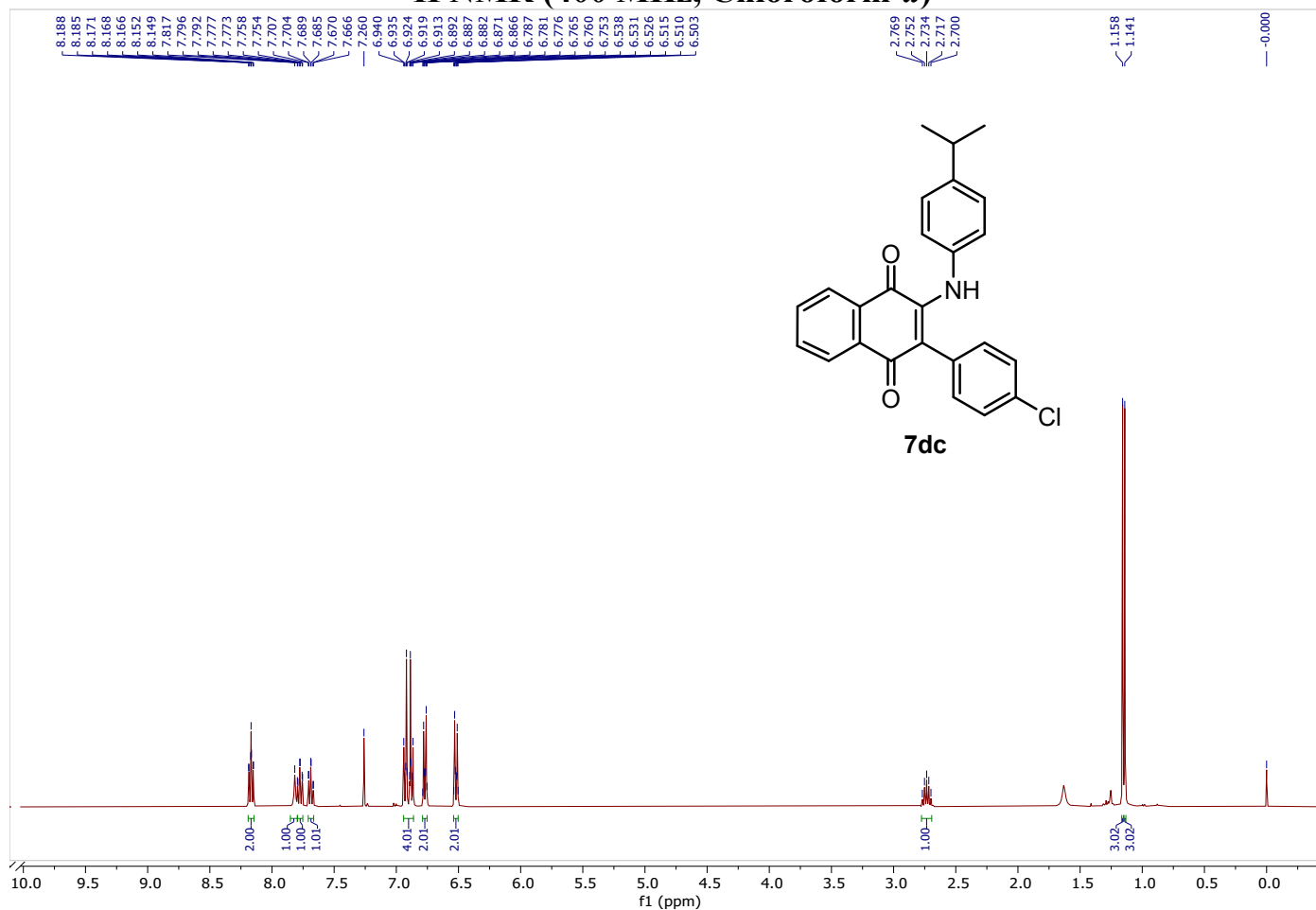
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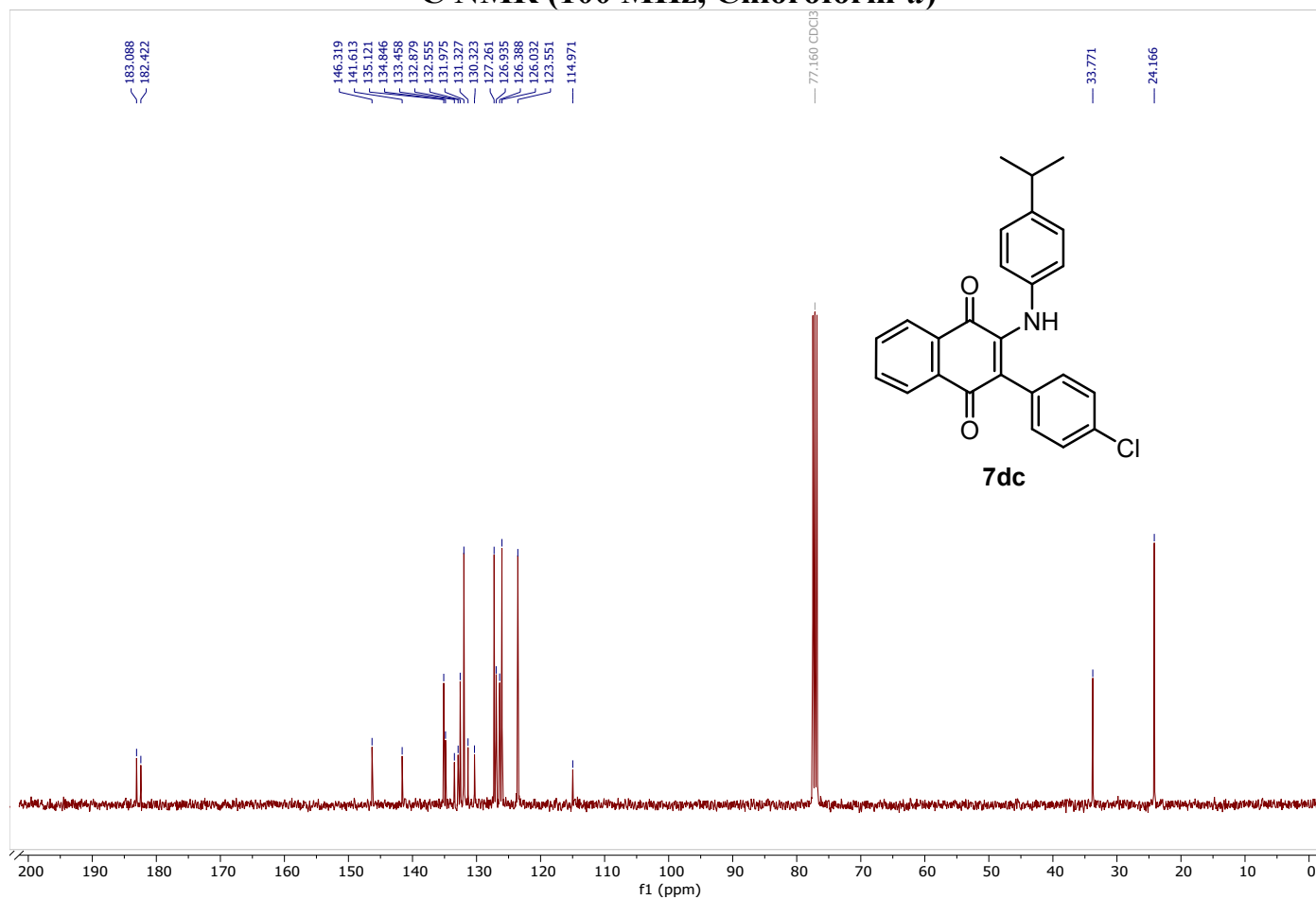
¹³C NMR (125 MHz, Chloroform-*d*)



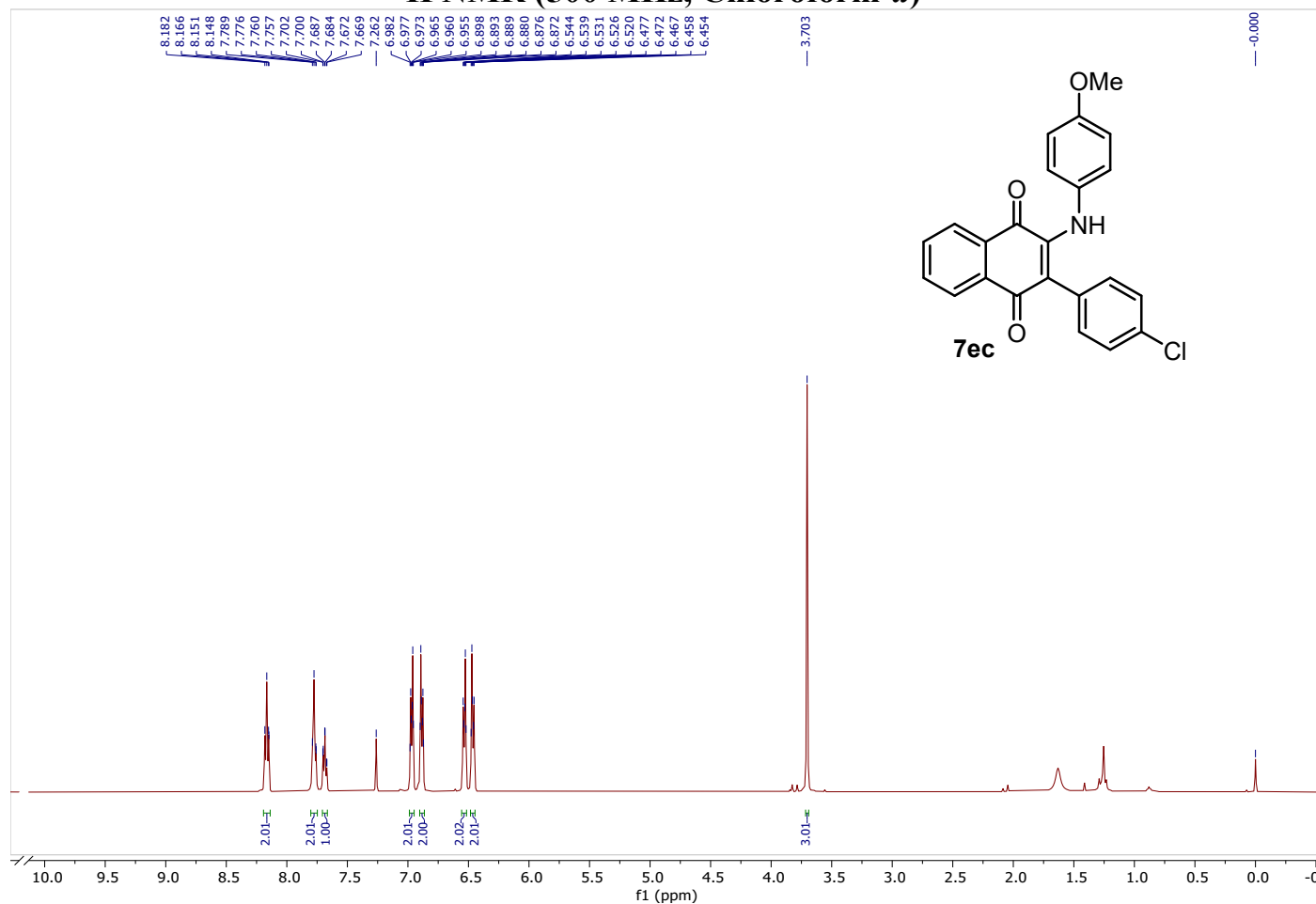
¹H NMR (400 MHz, Chloroform-*d*)



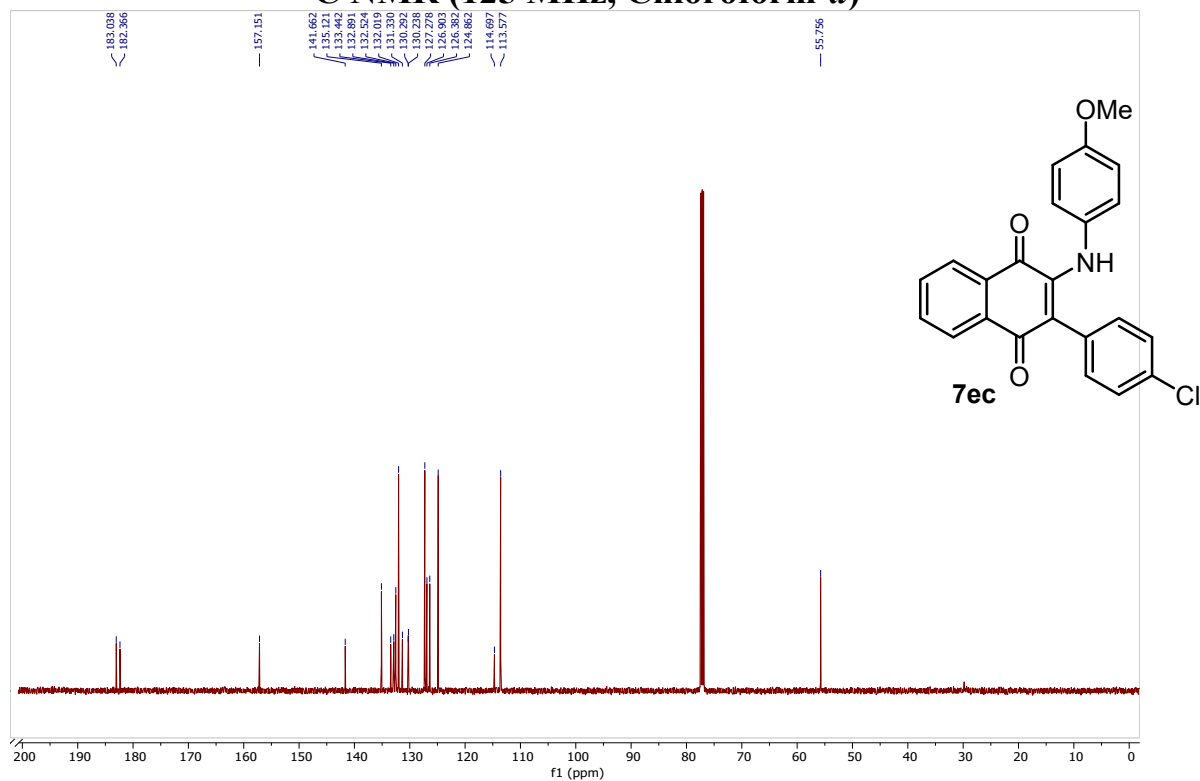
¹³C NMR (100 MHz, Chloroform-*d*)



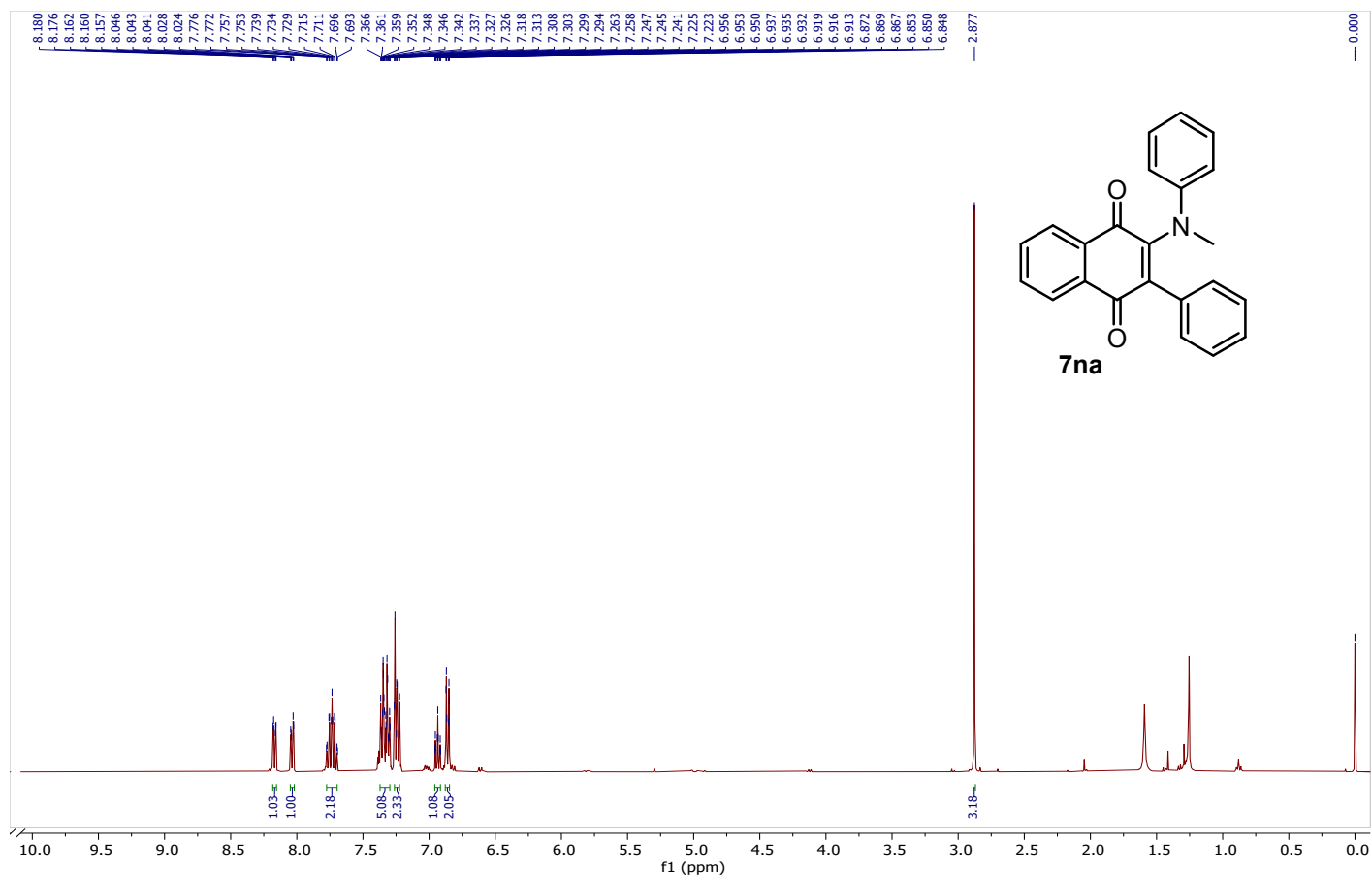
¹H NMR (500 MHz, Chloroform-*d*)



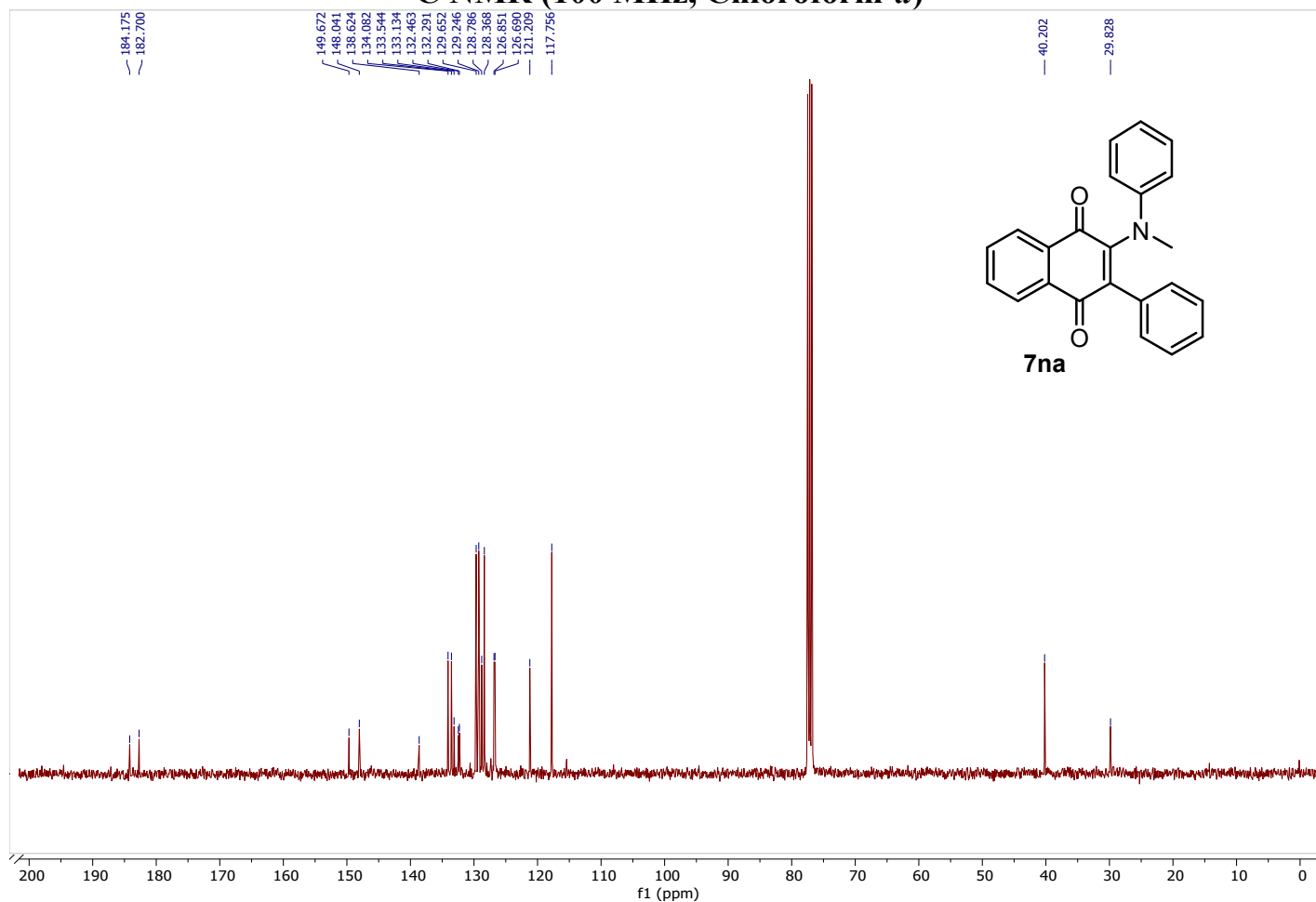
¹³C NMR (125 MHz, Chloroform-*d*)



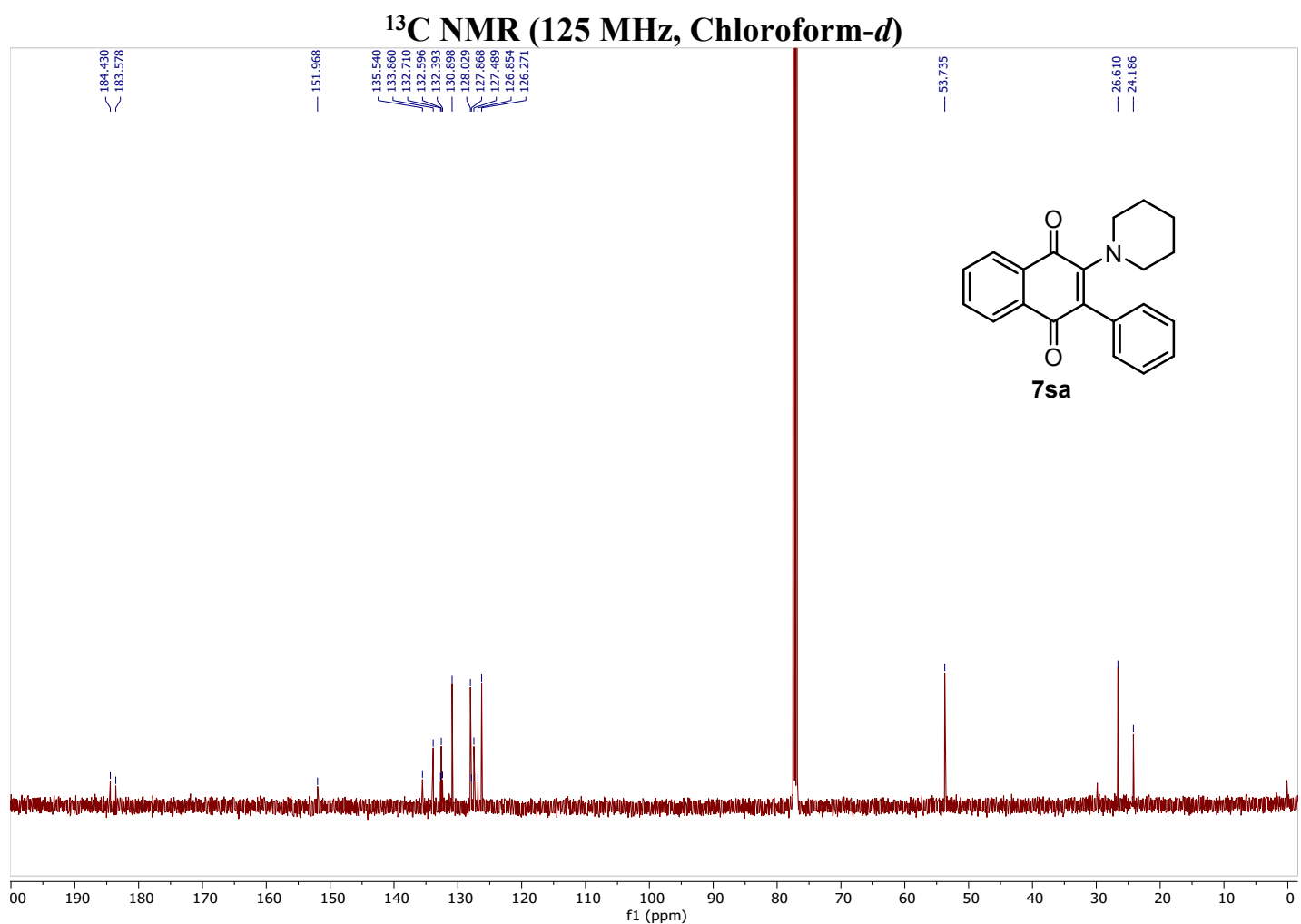
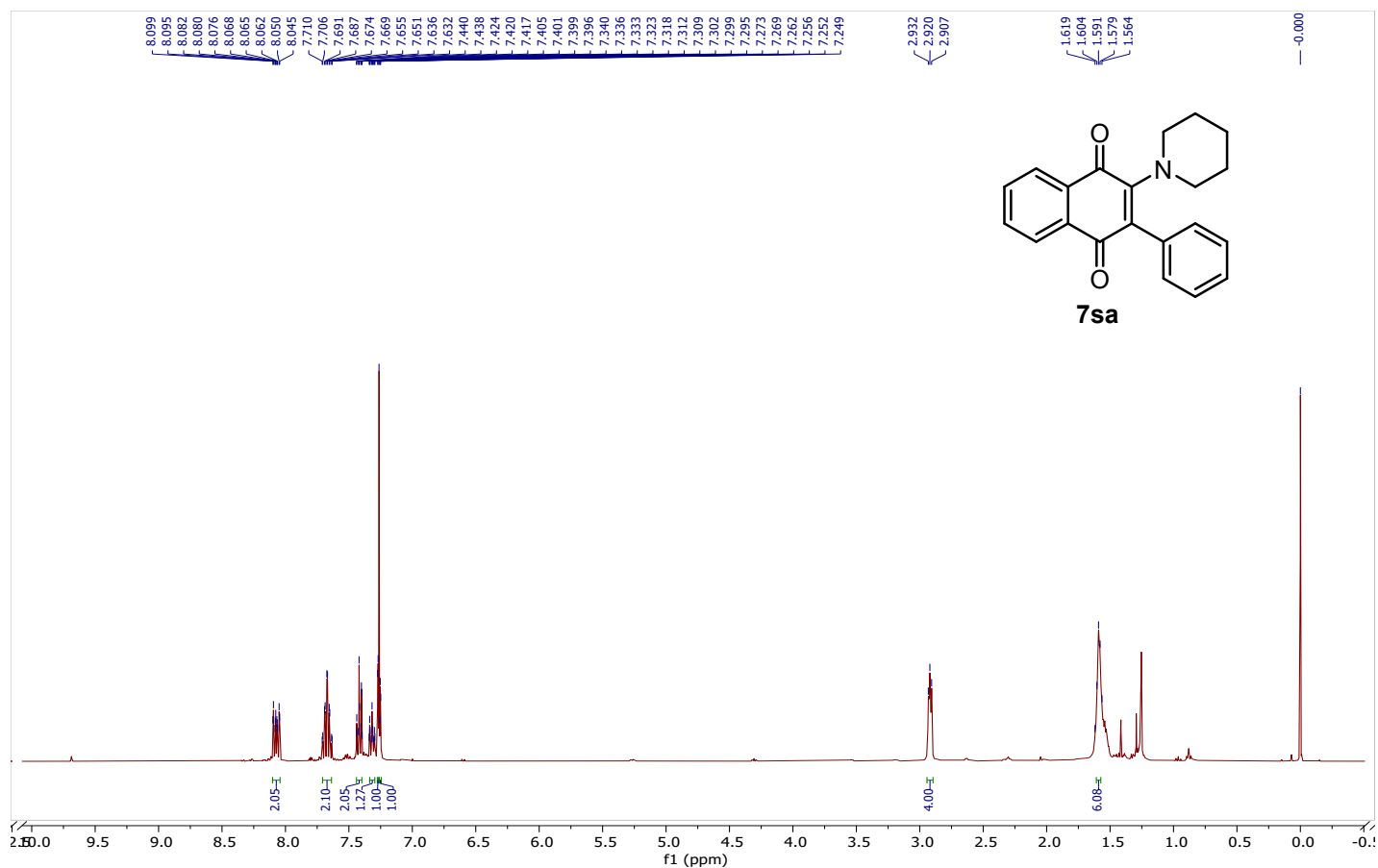
¹H NMR (400 MHz, Chloroform-*d*)



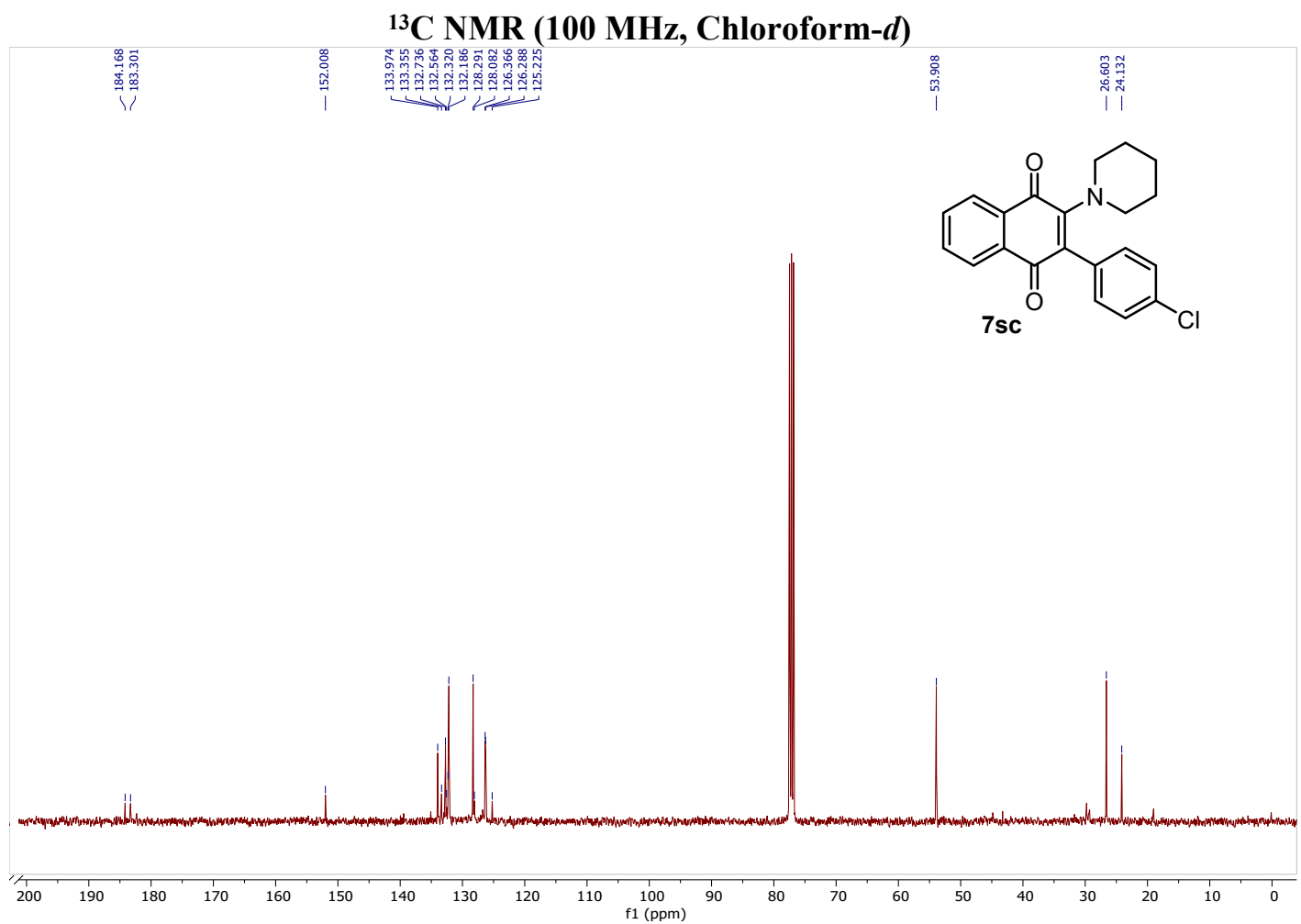
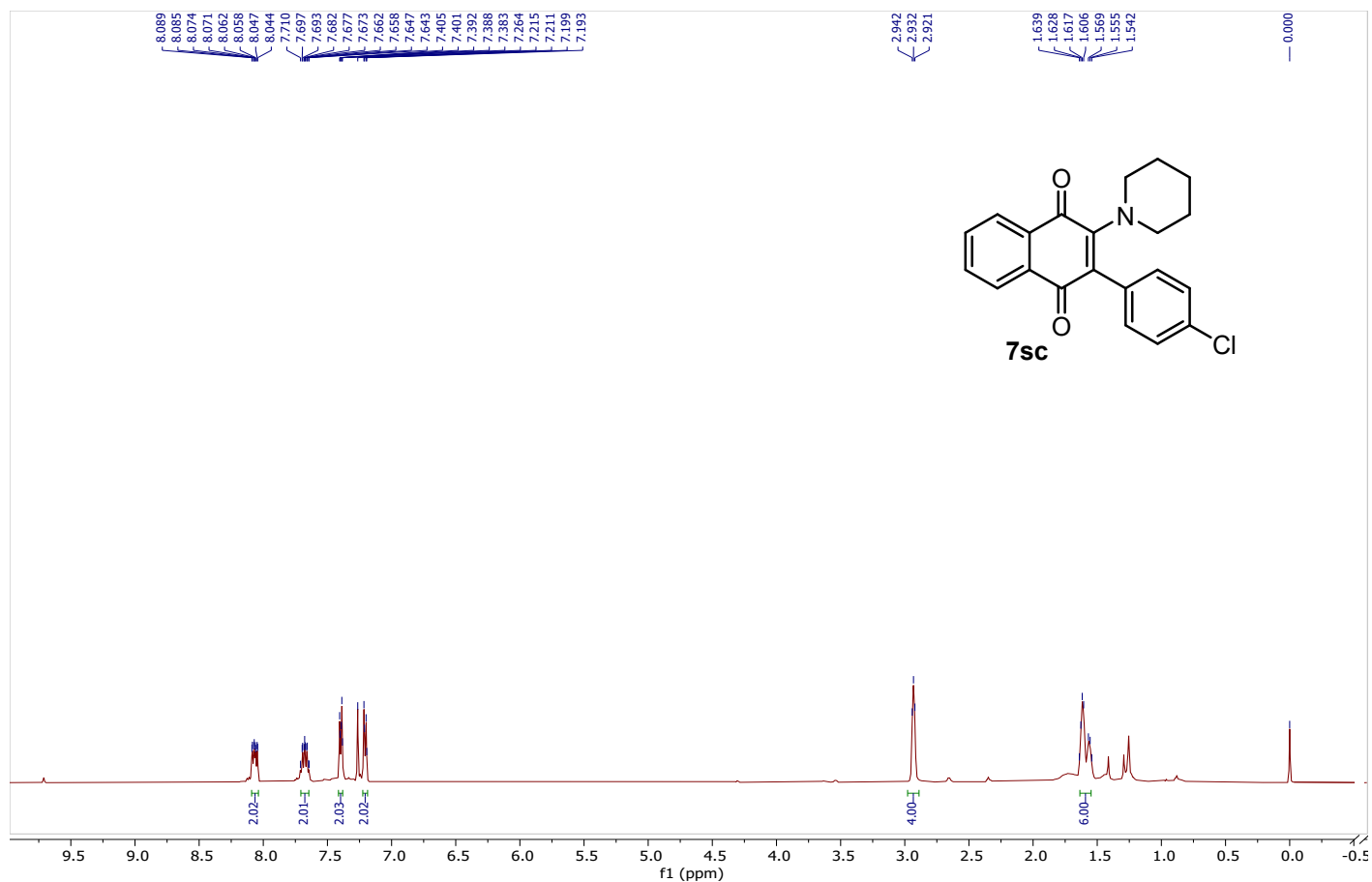
¹³C NMR (100 MHz, Chloroform-*d*)



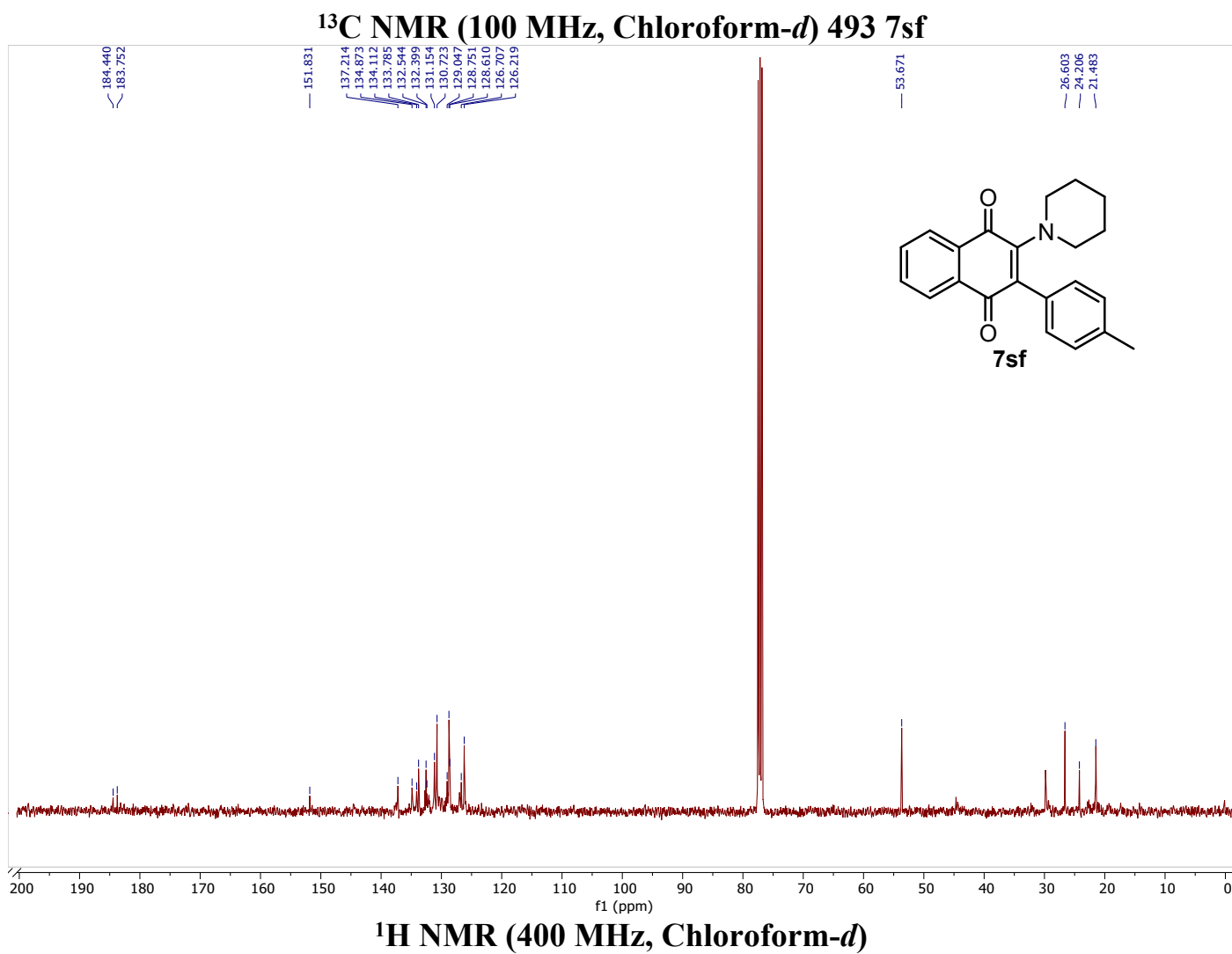
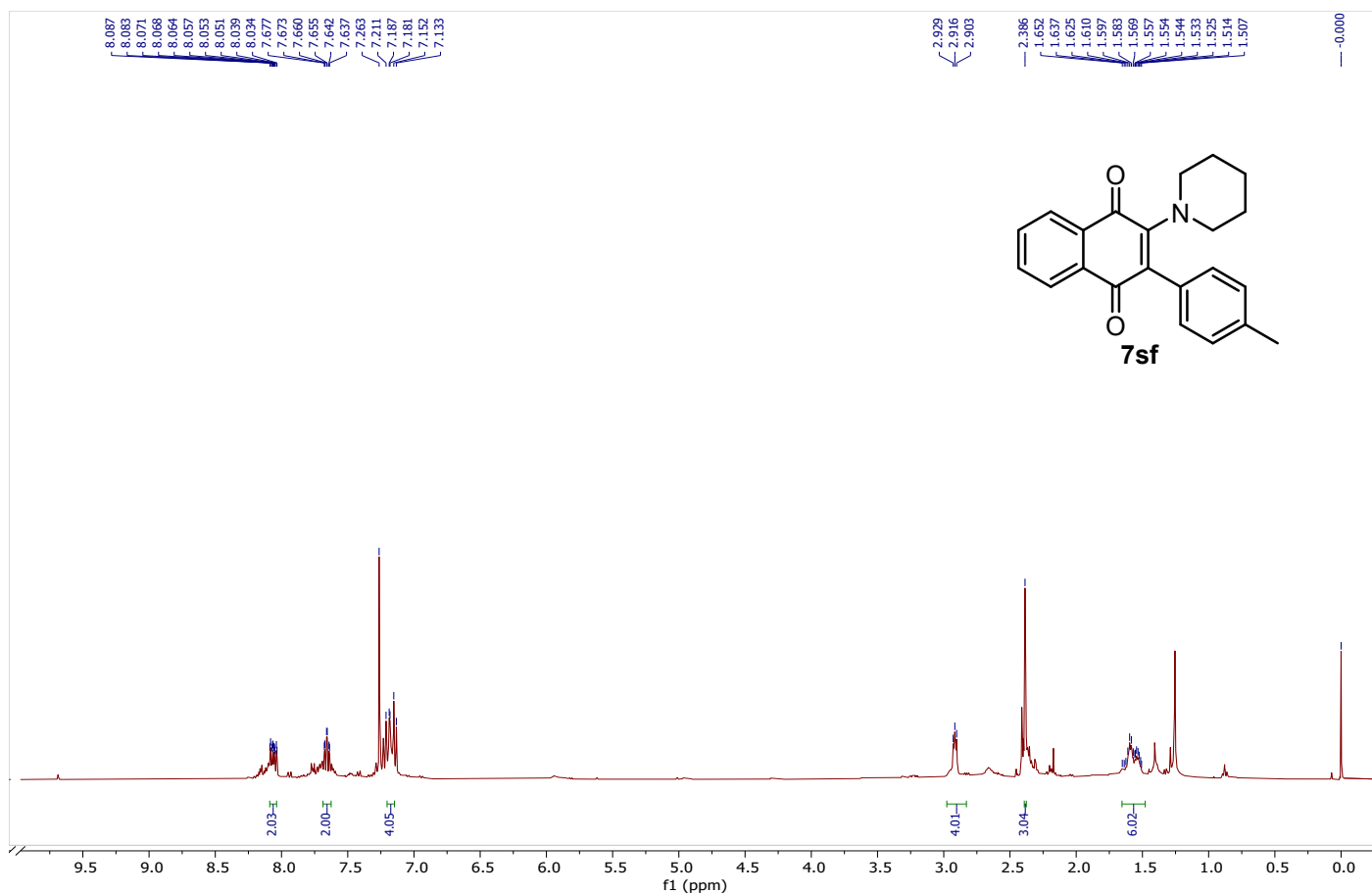
¹H NMR (400 MHz, Chloroform-*d*)

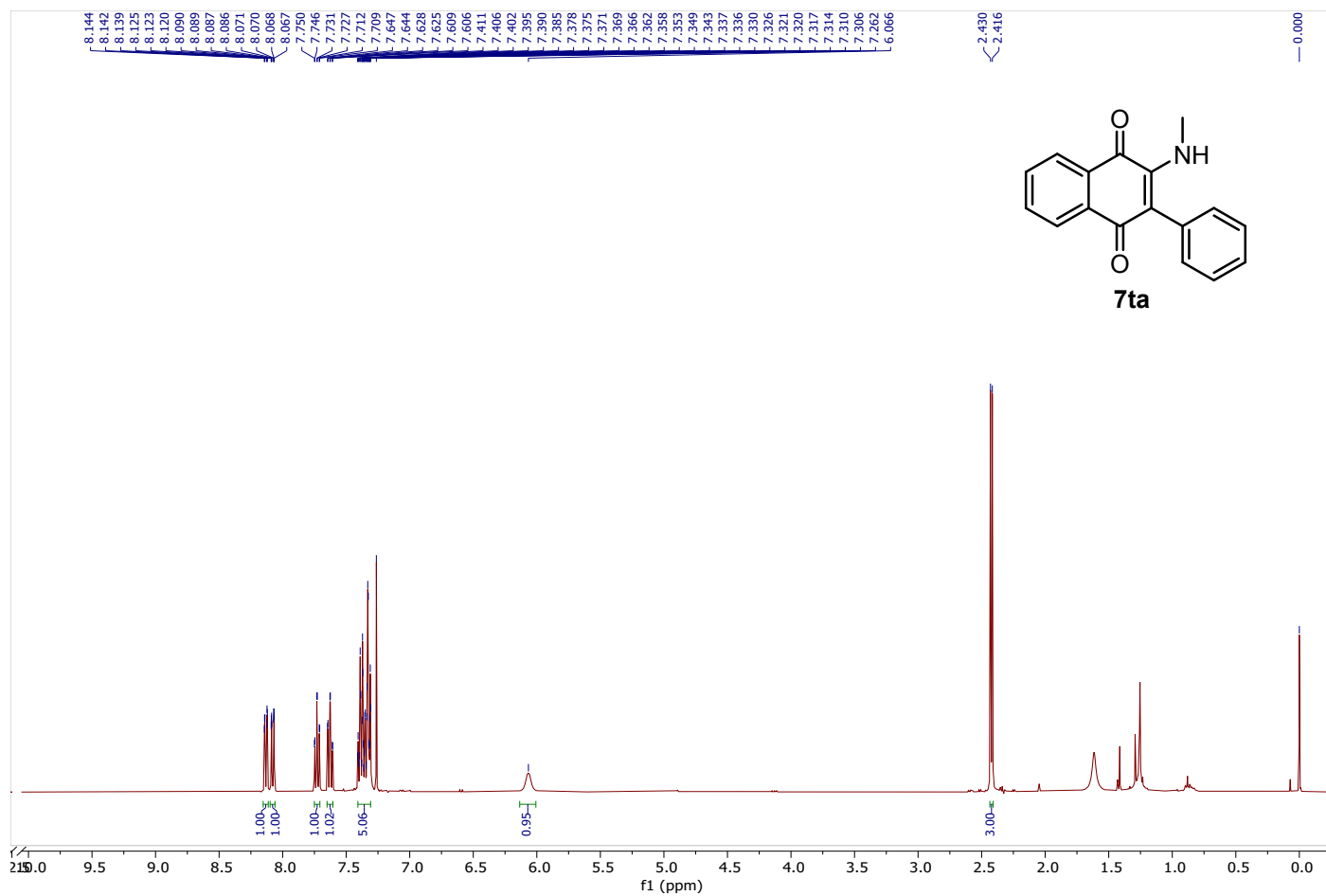


¹H NMR (500 MHz, Chloroform-*d*)

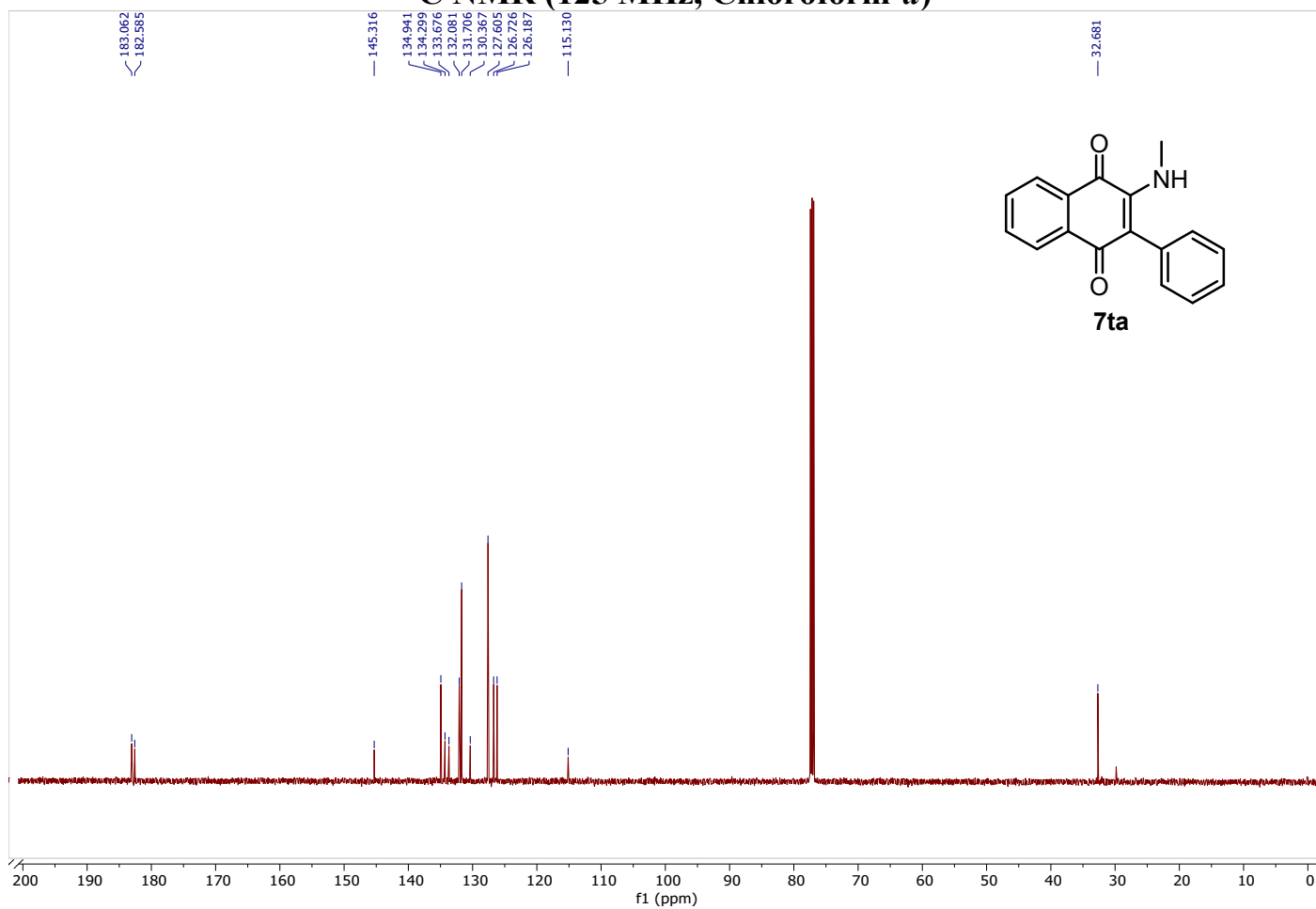


¹H NMR (400 MHz, Chloroform-*d*)





¹³C NMR (125 MHz, Chloroform-*d*)



HRMS data of the control experiment for the adduct 8

