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SUPPORTING INFORMATION

For

An Efficient and Metal Free Synthesis of Benzylpyridines Using HI through Deoxygenation Reaction

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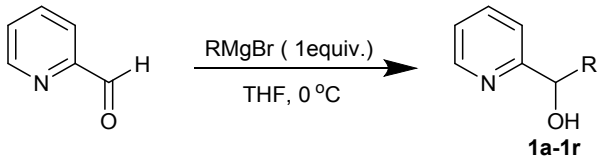
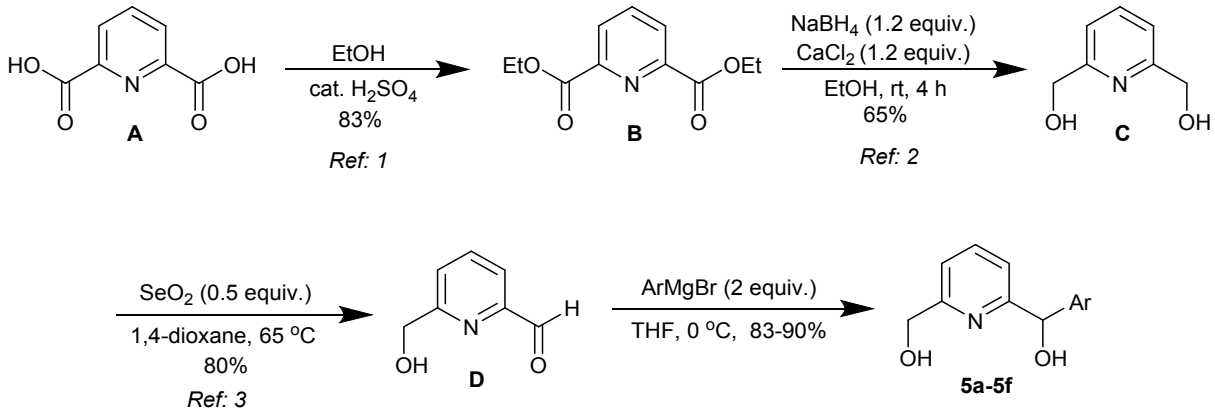
Synthesis of secondary alcohols (1a-1r):

Magnesium turnings were placed in a oven dried two neck 50 mL round bottom flask and the flask was further dried by hot air gun with applying vacuum. Then the setup was allowed to room temperature, refilled with nitrogen. Under nitrogen flow, a catalytic amount of iodine was added, followed by freshly distilled THF. The reaction mixture was cooled to 0 ^{o}C followed by corresponding aryl halide was added by drop wise. After the disappearance of the iodine color, the reaction was allowed to stir at room temperature for 2 hours. Once all the magnesium turnings were dissolved, the reaction mixture was cooled to 0 ^{o}C then pyridine-2-aldehyde (dissolved in THF) was added dropwise to the Grignard reagent. The reaction was monitored by TLC and the reaction mixture was quenched by *aqueous* NH_4Cl and extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and the solvent was evaporated under vacuum. The residue was purified by column chromatography with ethyl acetate/hexanes solvents to provide pure products (**1a-1r**).



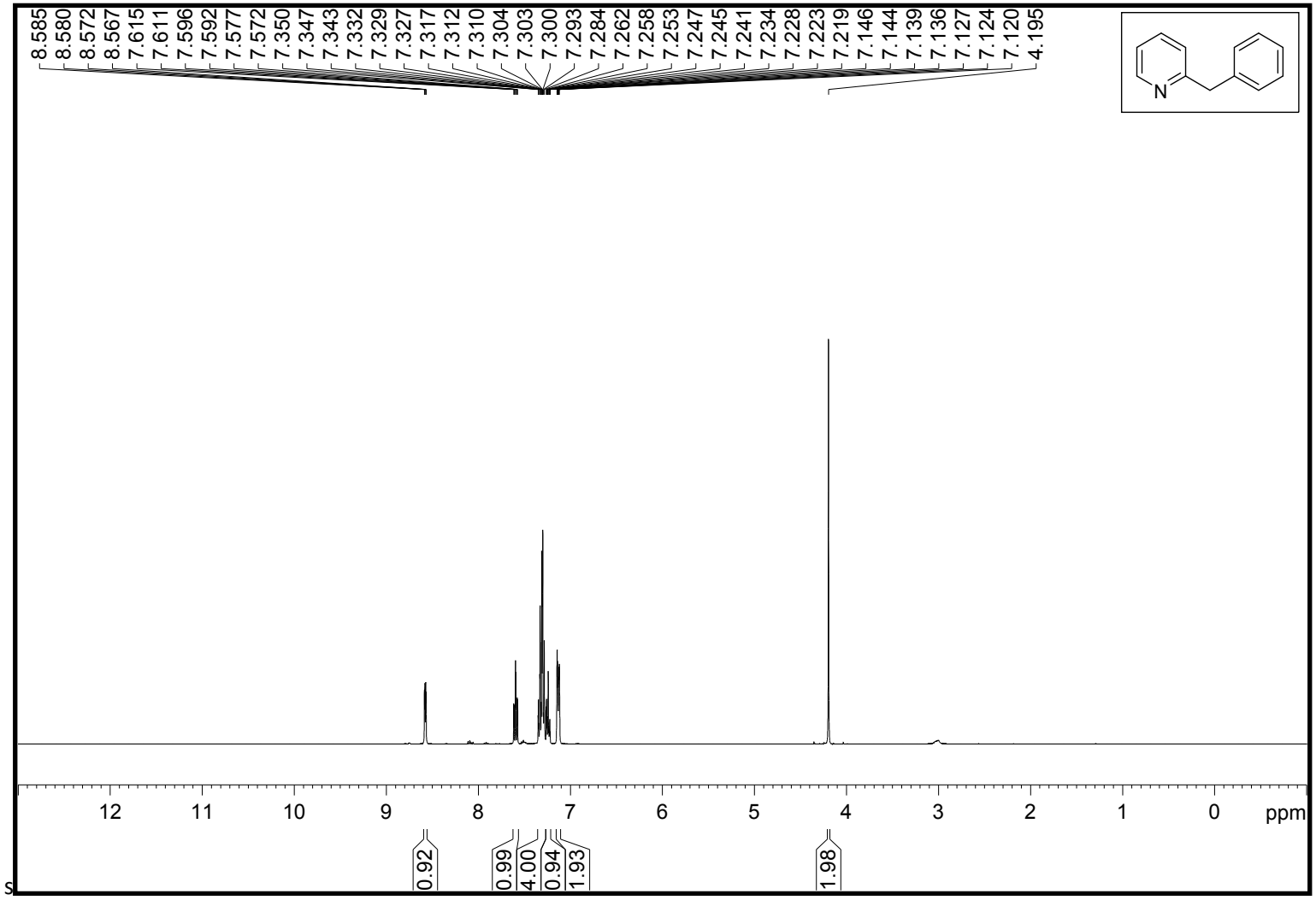
Synthesis of primary and secondary alcohols (5a-5e):

Commercially available 2,6-pyridine-di-carboxylic **A** was esterified with catalytic amount of acid in ethanol as solvent to provide ester **B** in 83% yield.[1] This diester **B** was reduced to 2,6-pyridine-di-methanol **C** using sodium borohydride and calcium chloride in ethanol using literature procedure.[2] The mono aldehyde **D** was prepared using selenium dioxide, by oxidation of compound **C** in 1,4-dioxane.[3] The resulting monoaldehyde was converted to di-alcohol (**5a-5e**) having primary and secondary alcohol group using corresponding aryl magnesium bromide (2 equivalents).

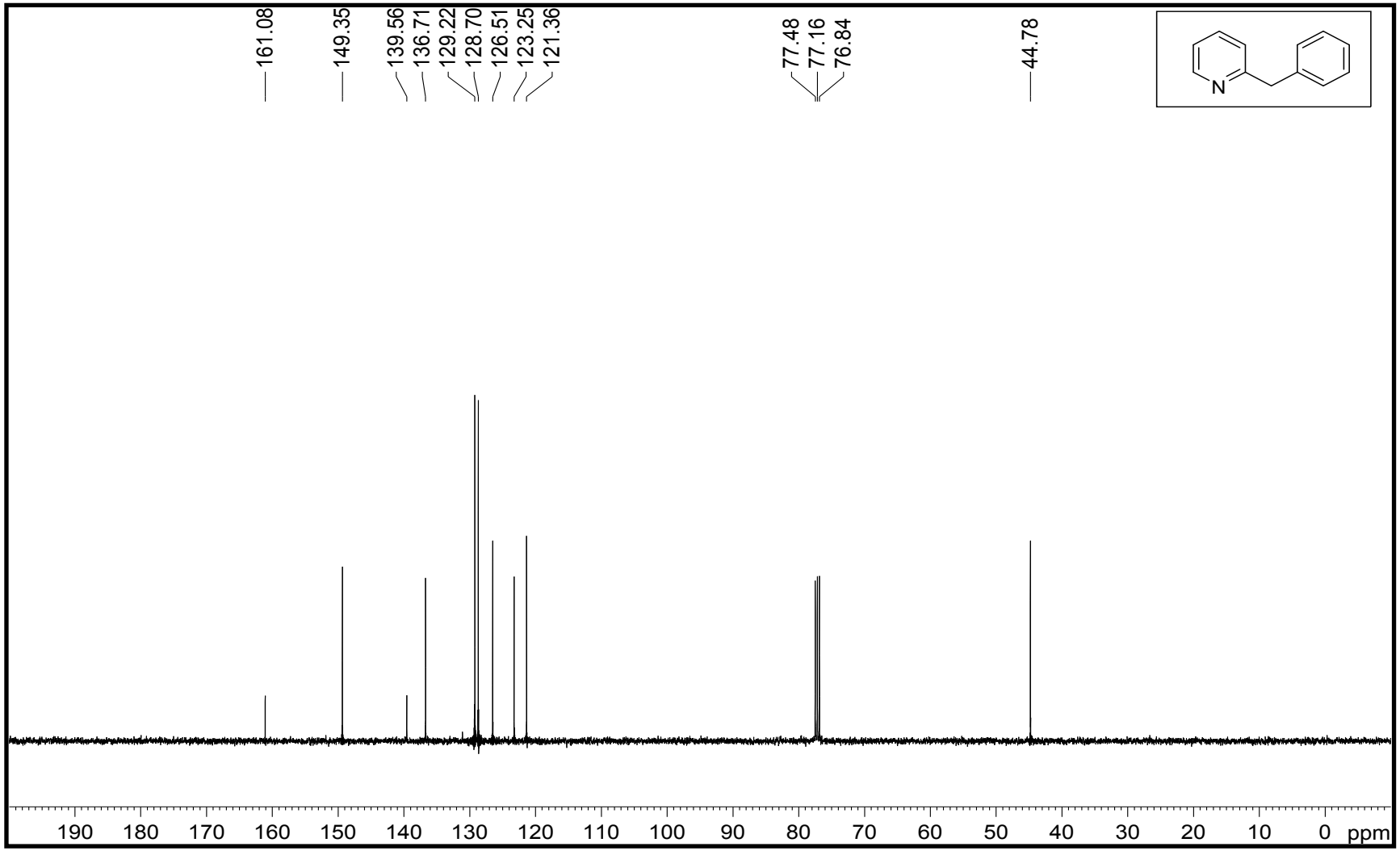


Reference:

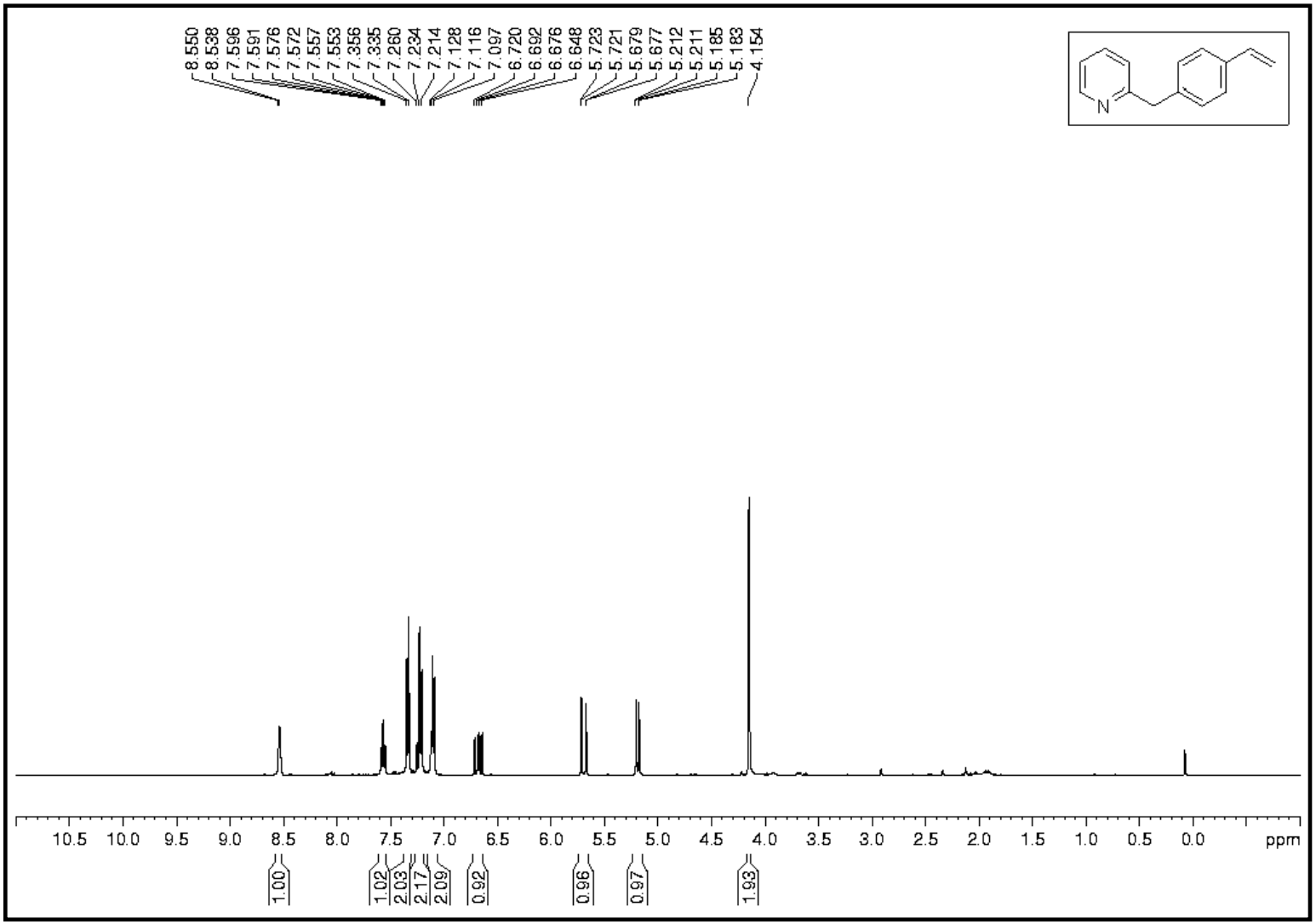
1. X. Li, C. Zhan, Y. Wang and J. Yao, *Chem. Commun.*, 2008, 2444-2446.
2. X. Wu, Y. He and C. Wu, *Wuhan Univ. J. Nat. Sci.*, 1996, **1**, 105-106.
3. N. M. Shavaleev, R. Scopelliti, F. Gumy and J.-C. G. Bunzli, *Inorg. Chem.*, 2009, **48**, 6178-6191.



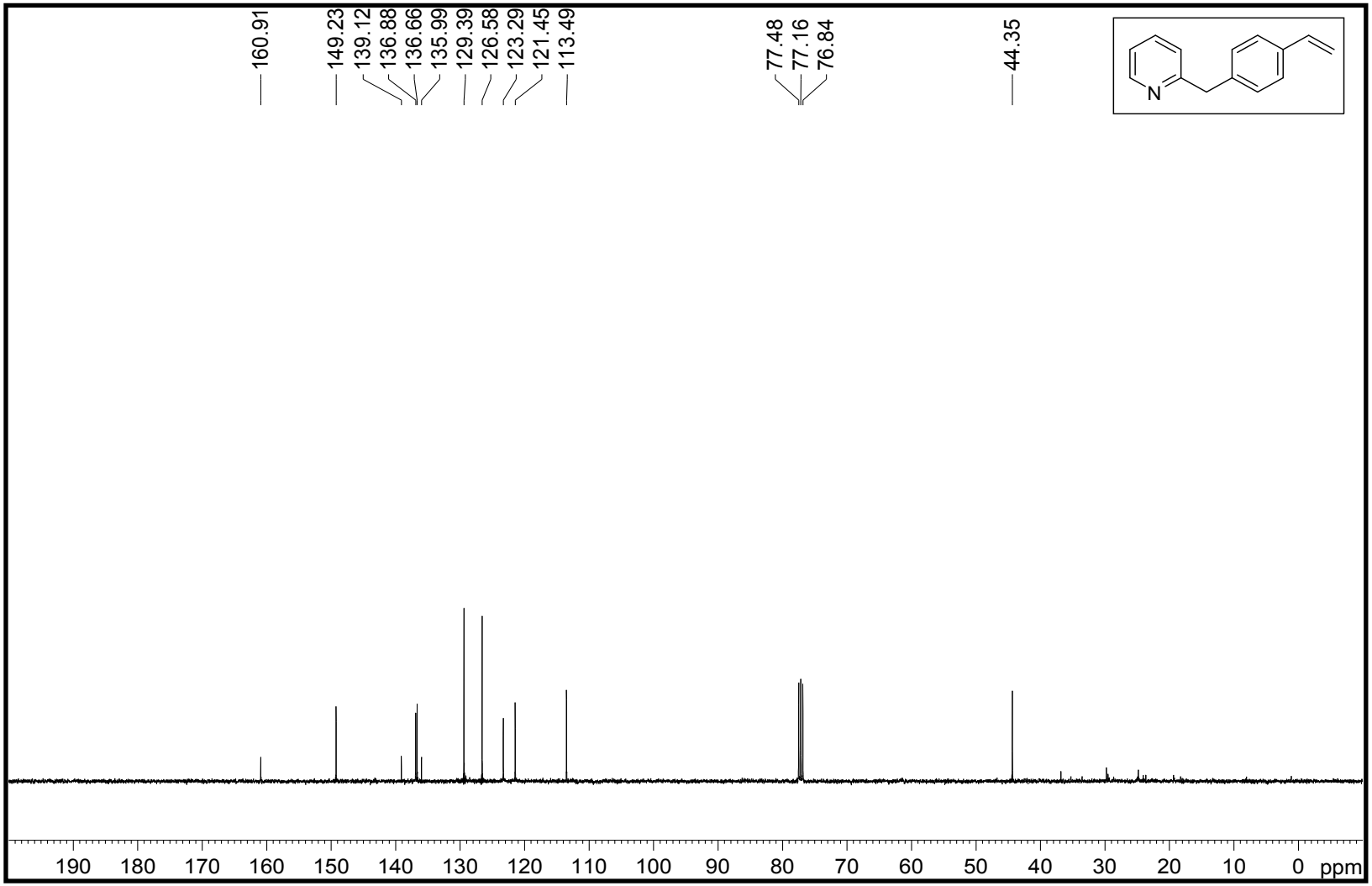
400 MHz ^{1}HNMR spectrum of **2a** in $CDCl_3$



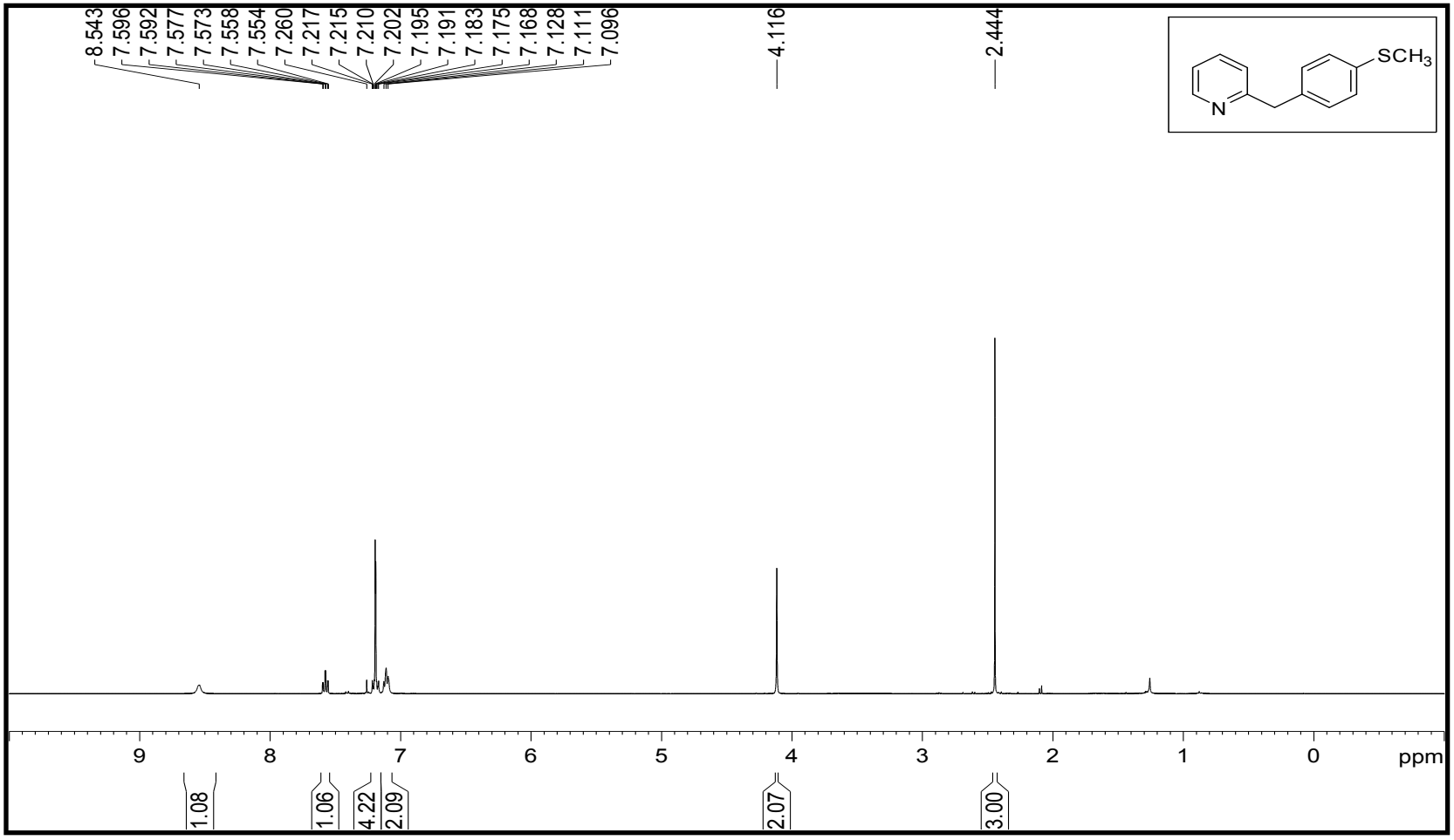
100 MHz ^{13}C NMR spectrum of **2a** in $CDCl_3$



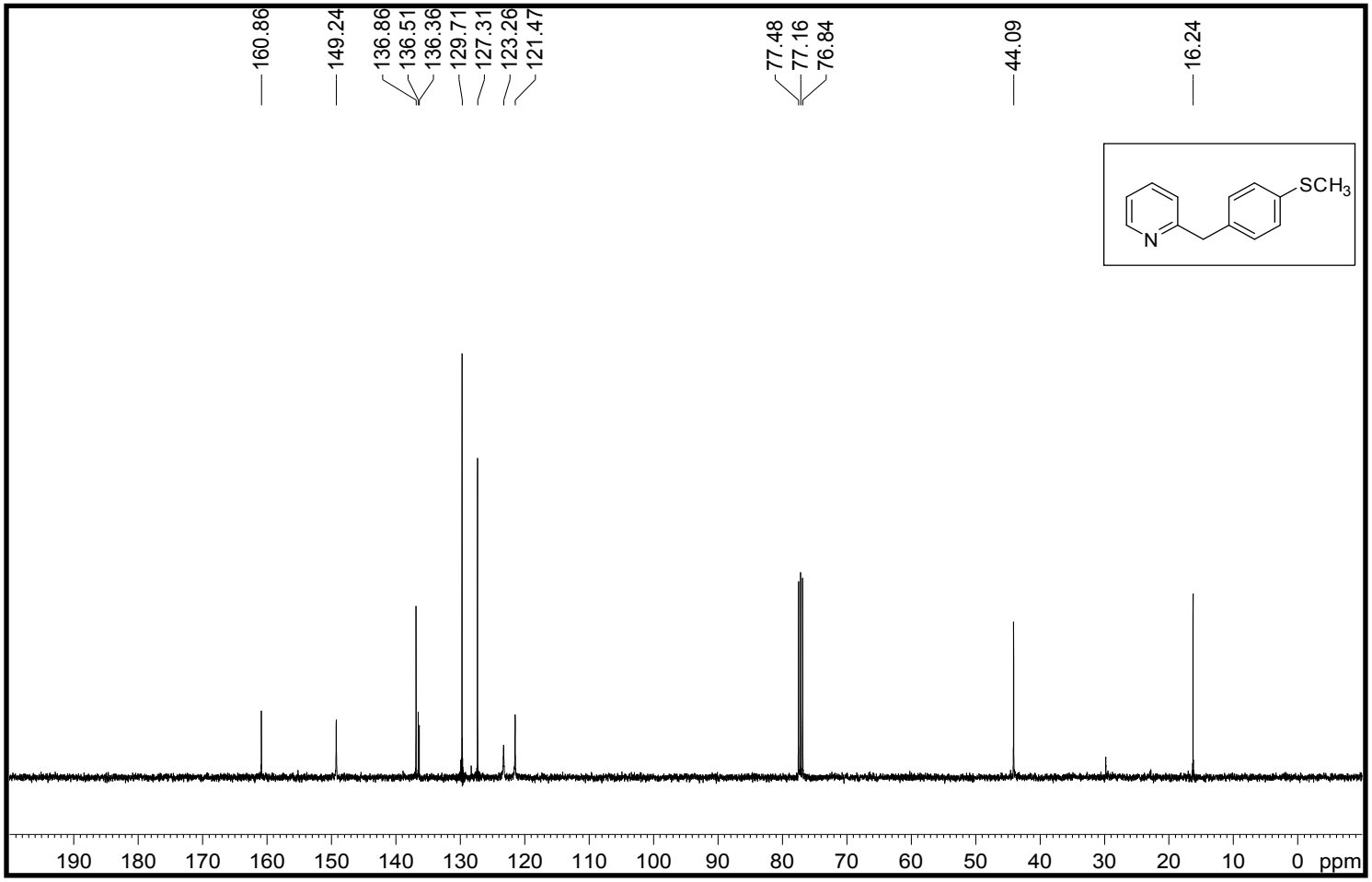
400 MHz ^{1}H NMR spectrum of **2b** in $CDCl_3$



100 MHz ^{13}C NMR spectrum of **2b** in $CDCl_3$



400 MHz ^{1}HNMR spectrum of **2c** in $CDCl_3$



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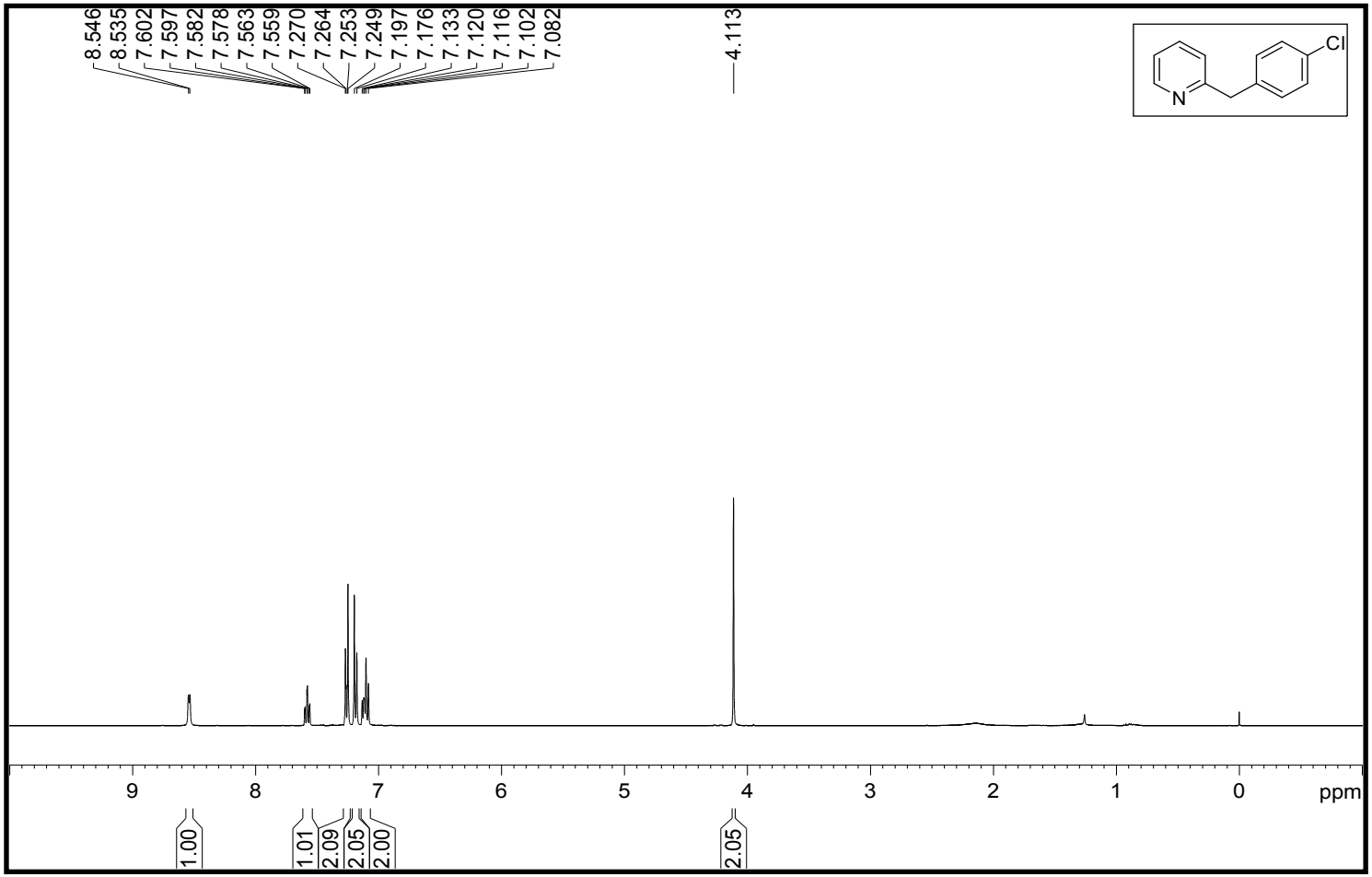

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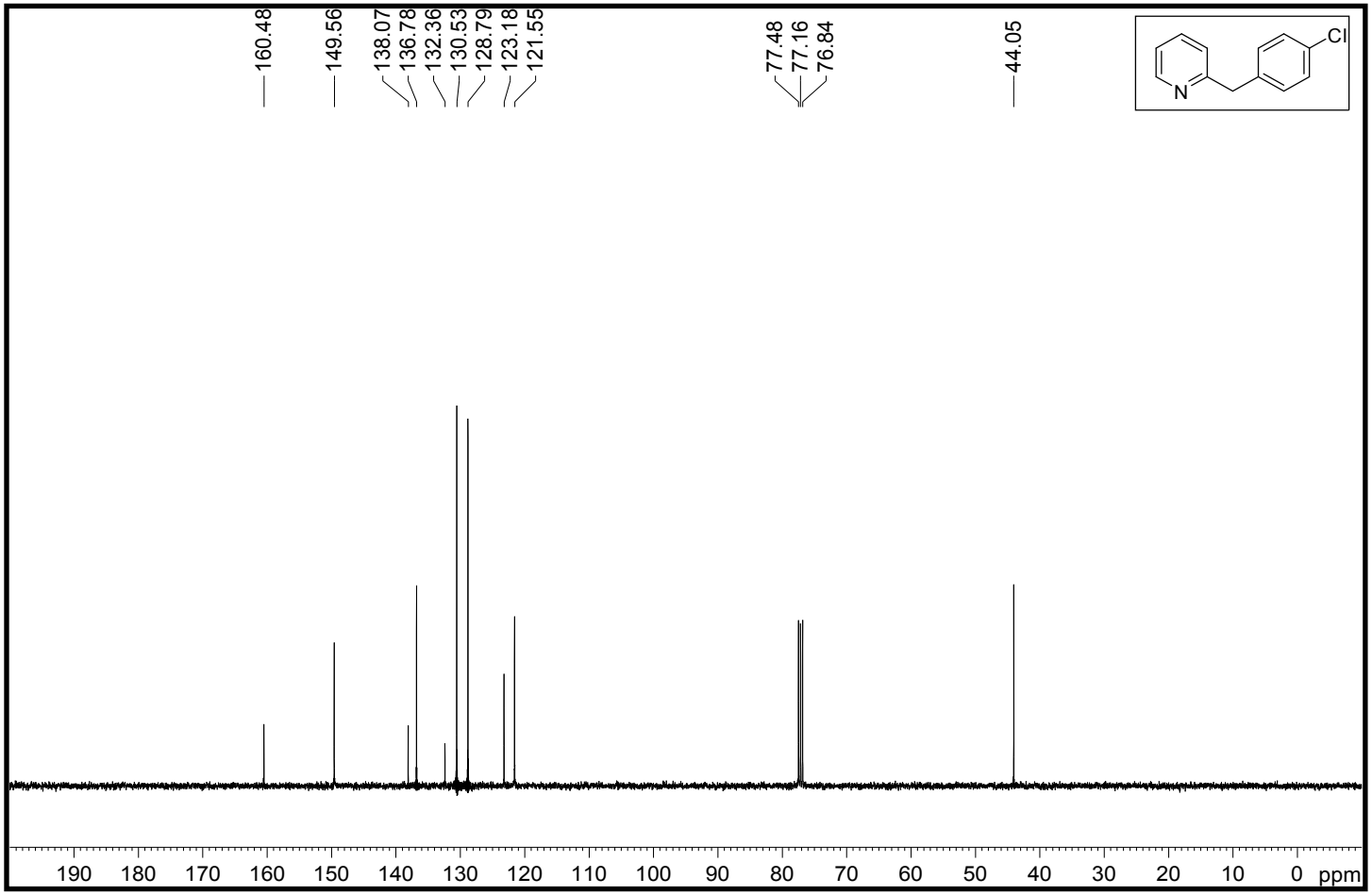

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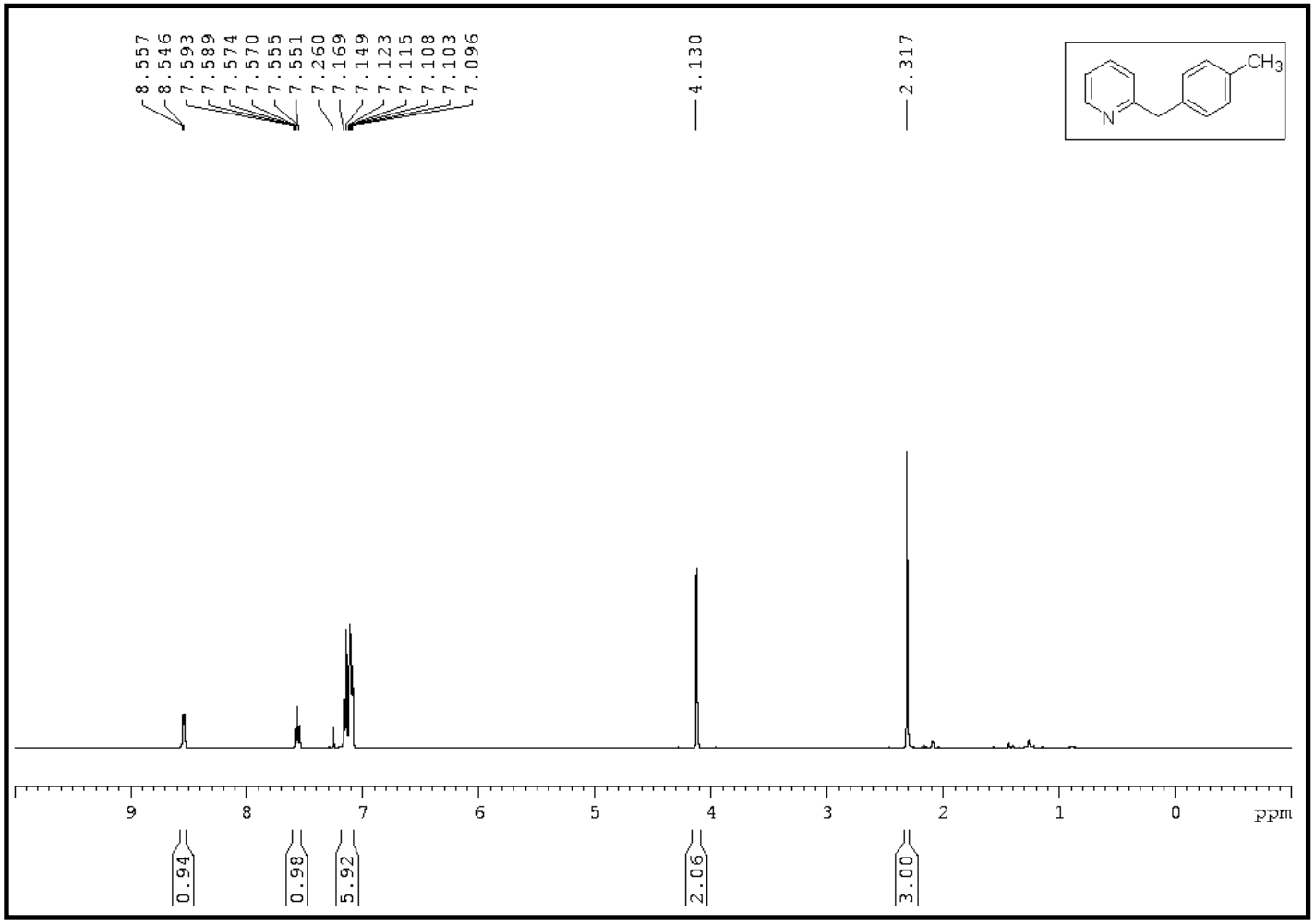

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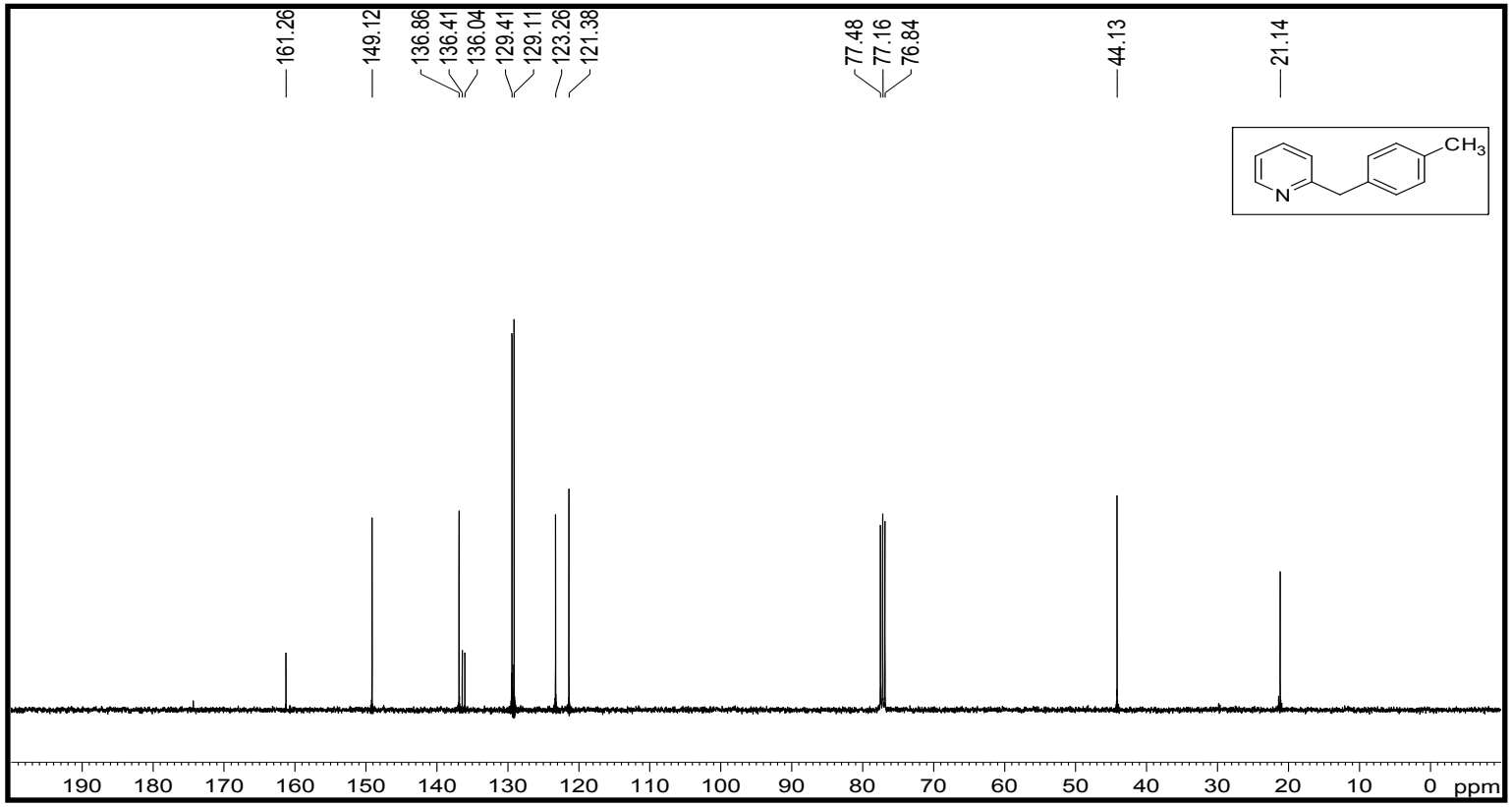

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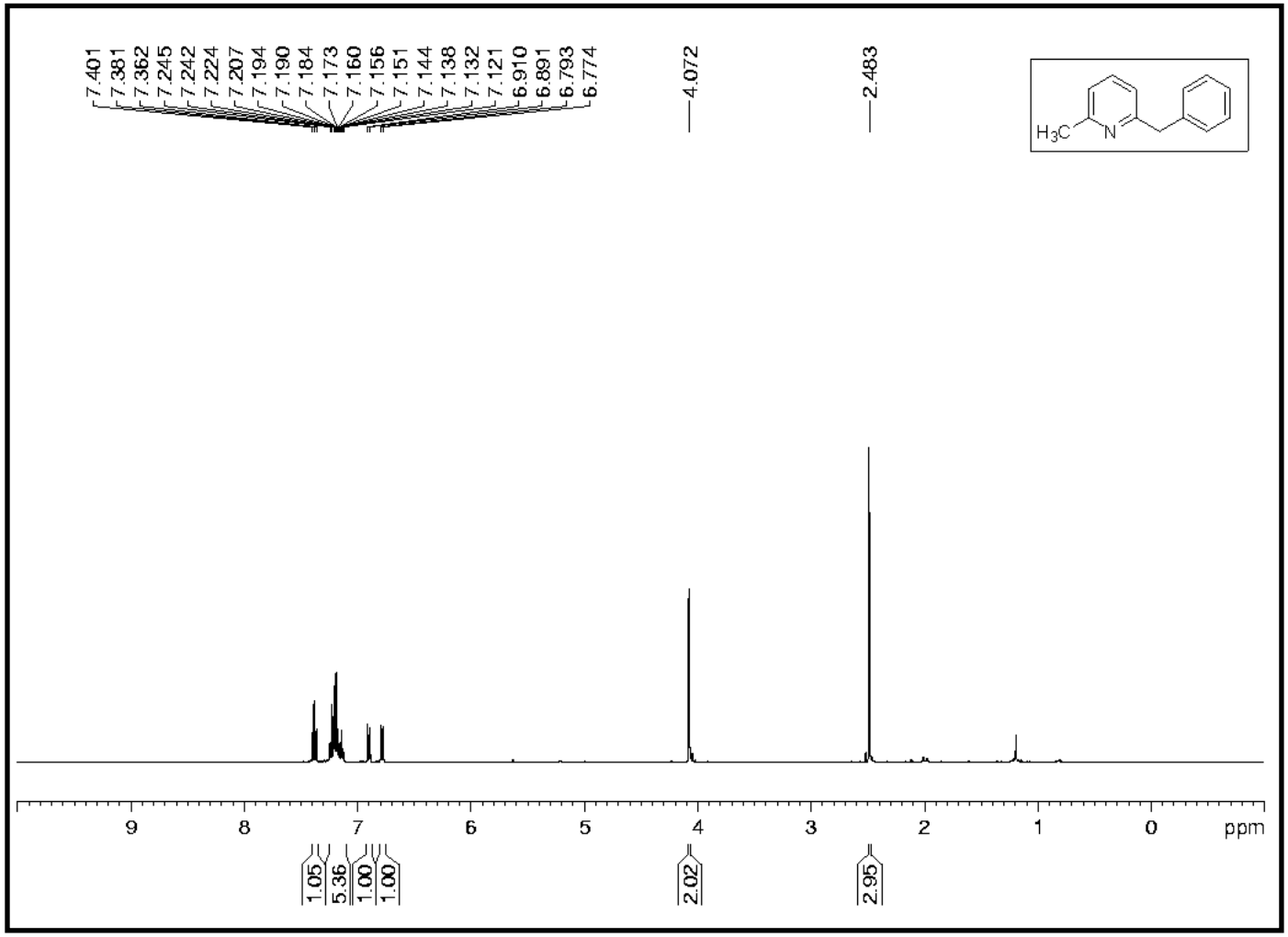

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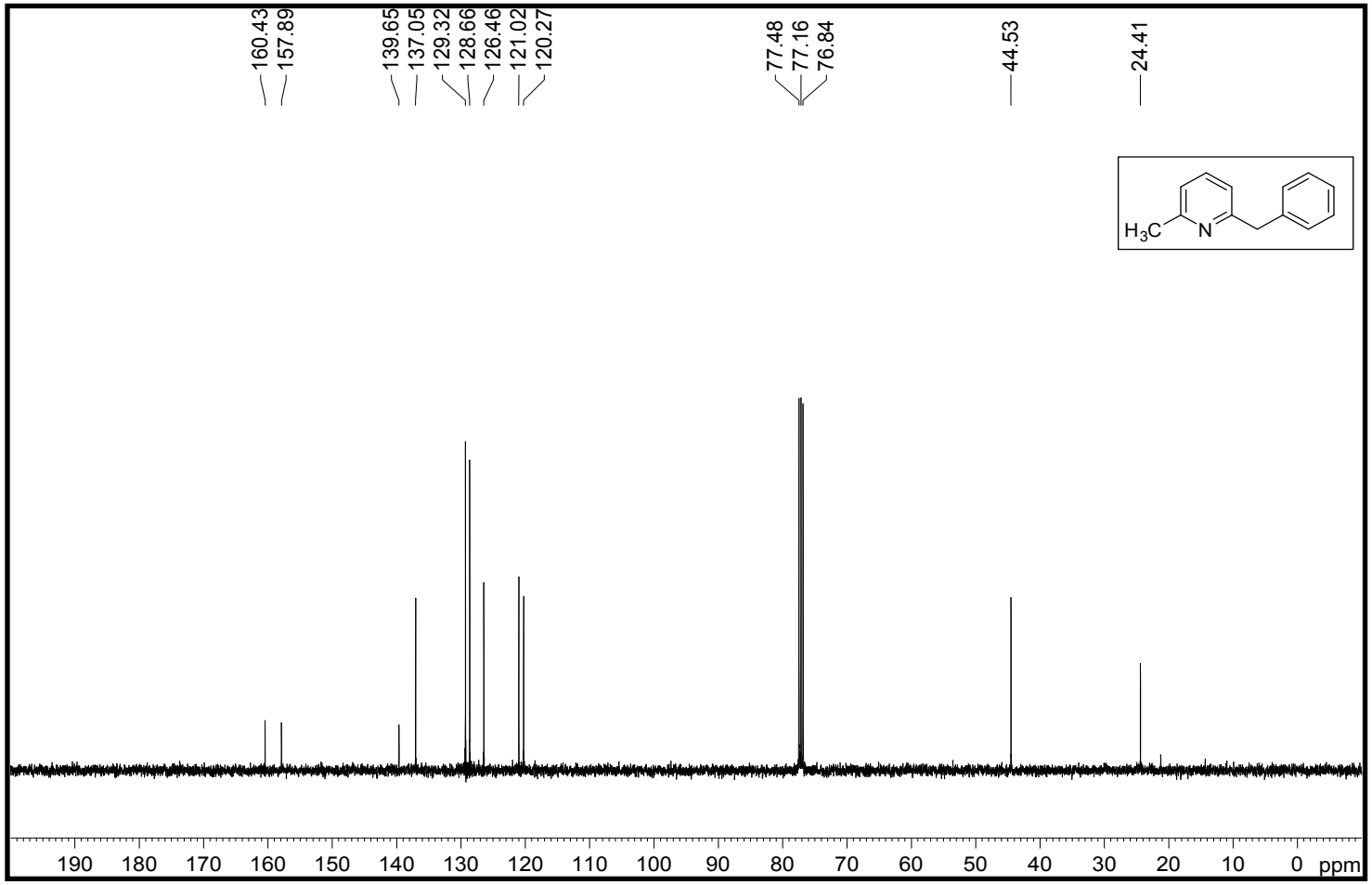
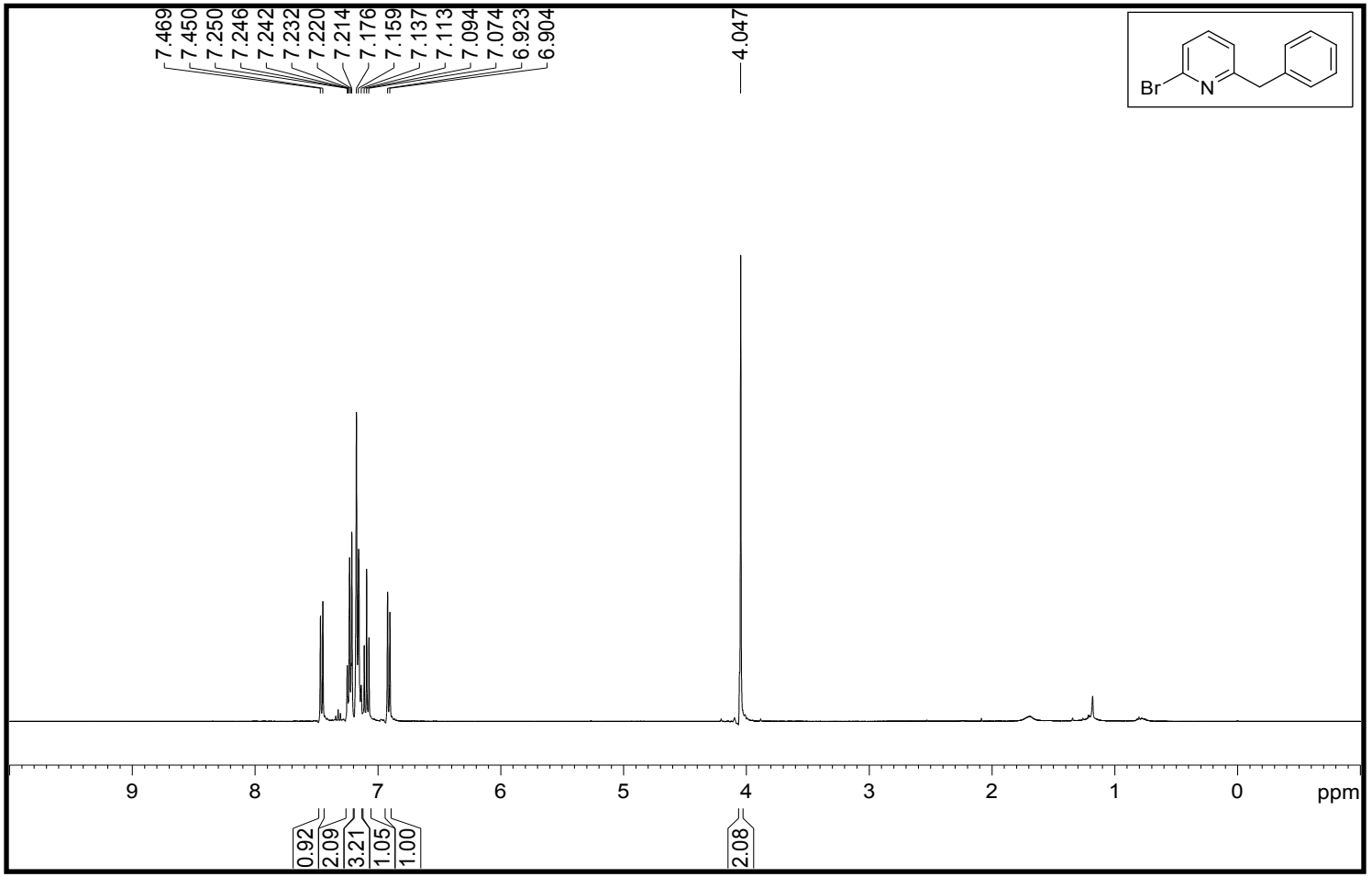


100 MHz ^{13}C NMR spectrum of **2f** in $CDCl_3$



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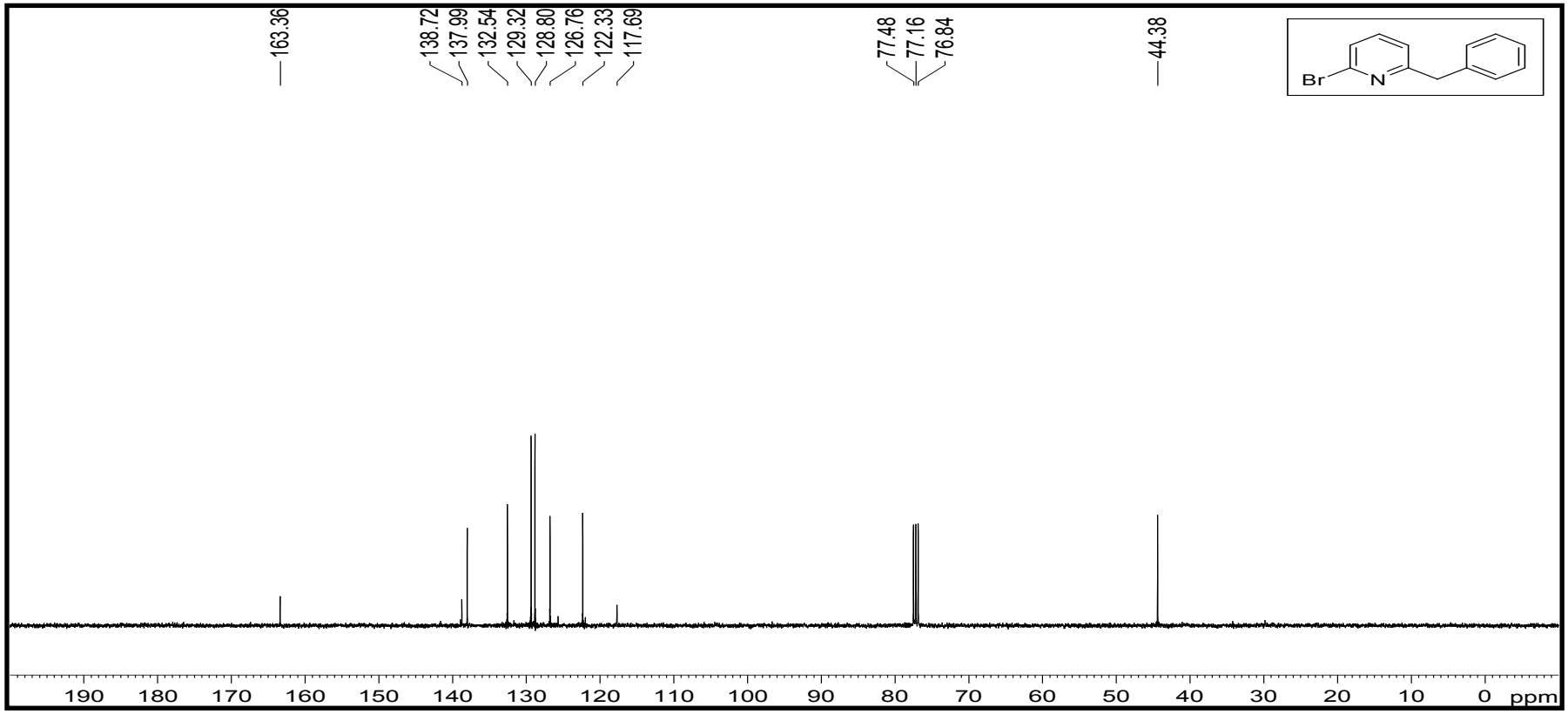

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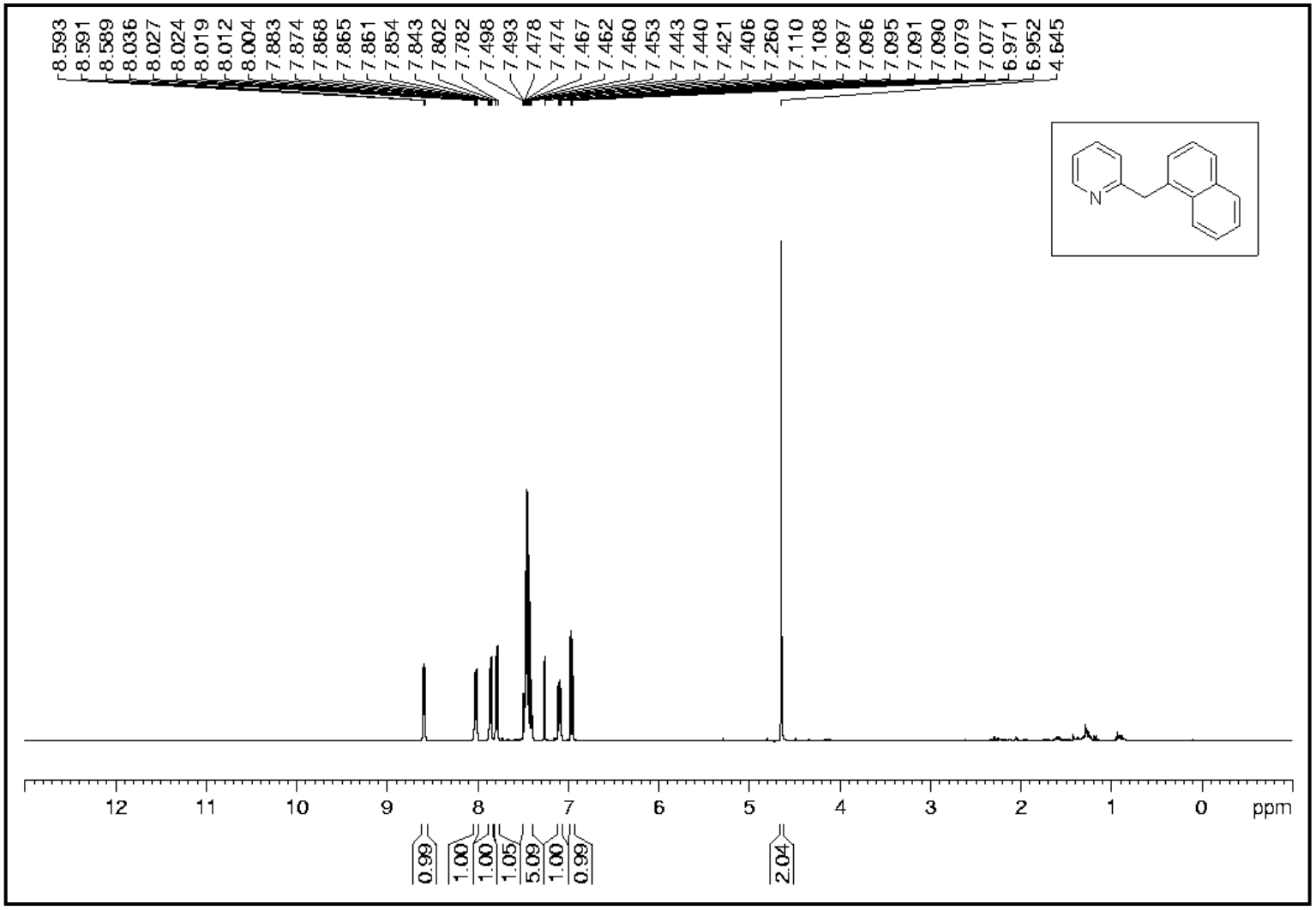

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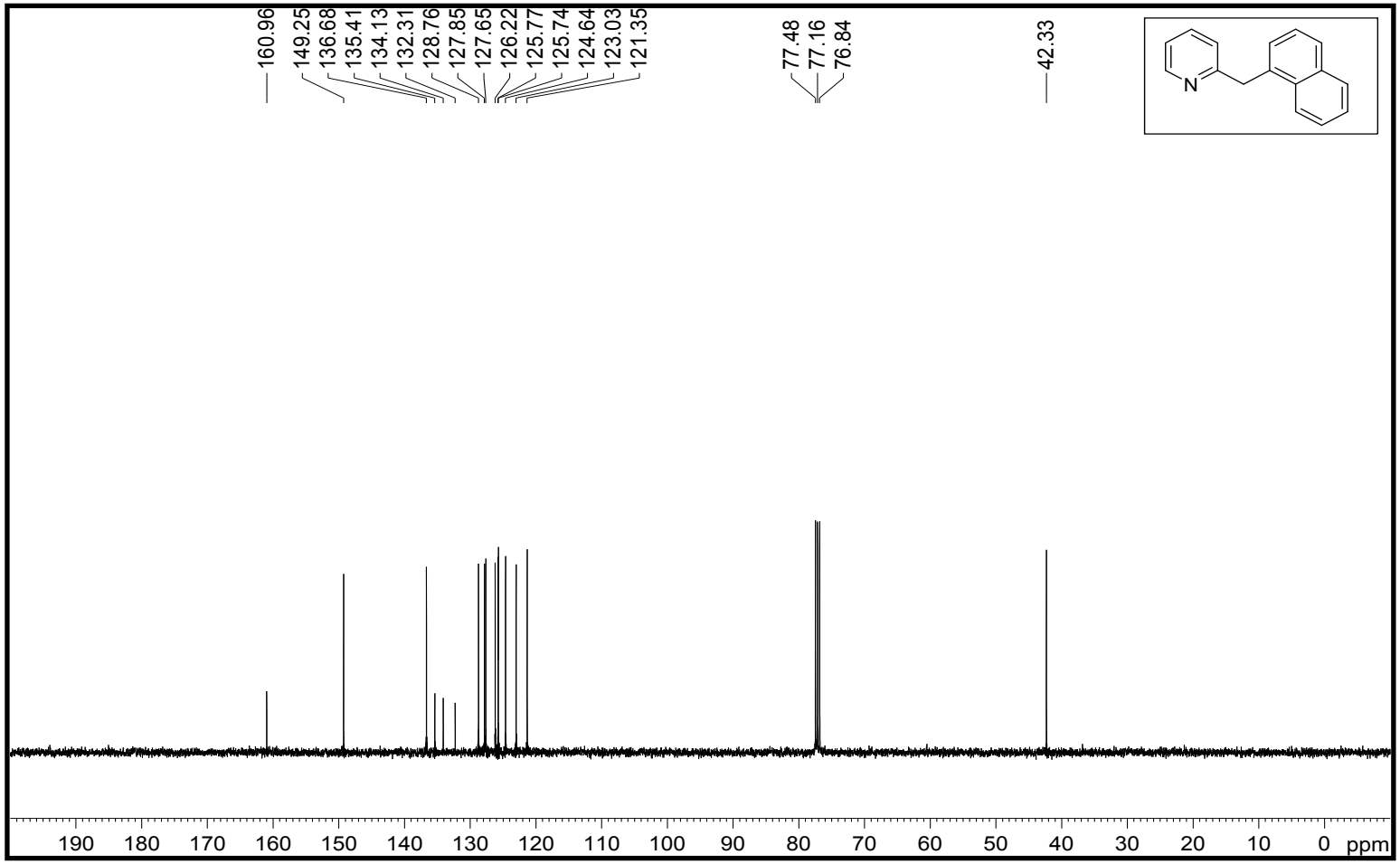
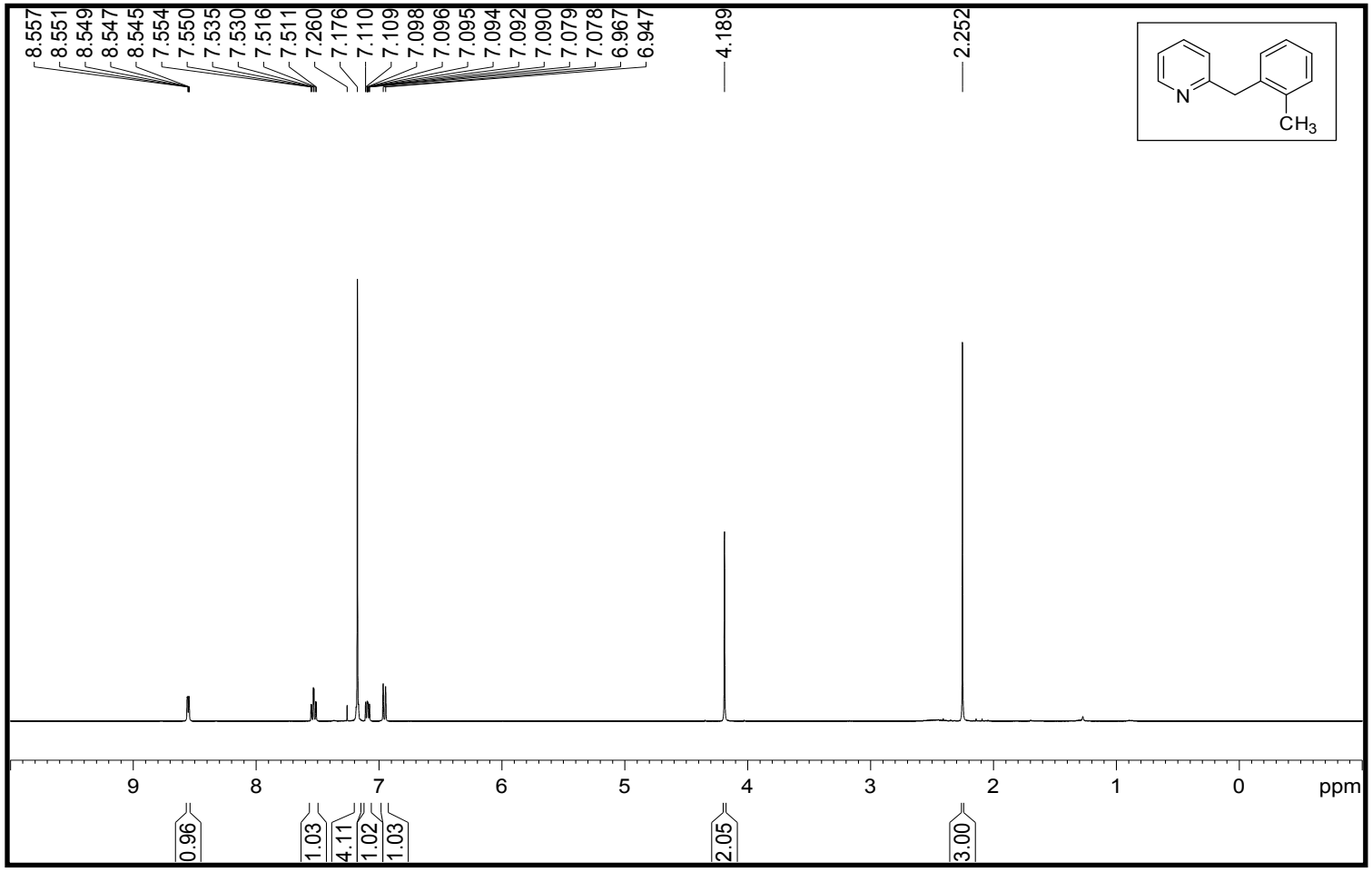


100 MHz ^{13}C NMR spectrum of **2h** in $CDCl_3$



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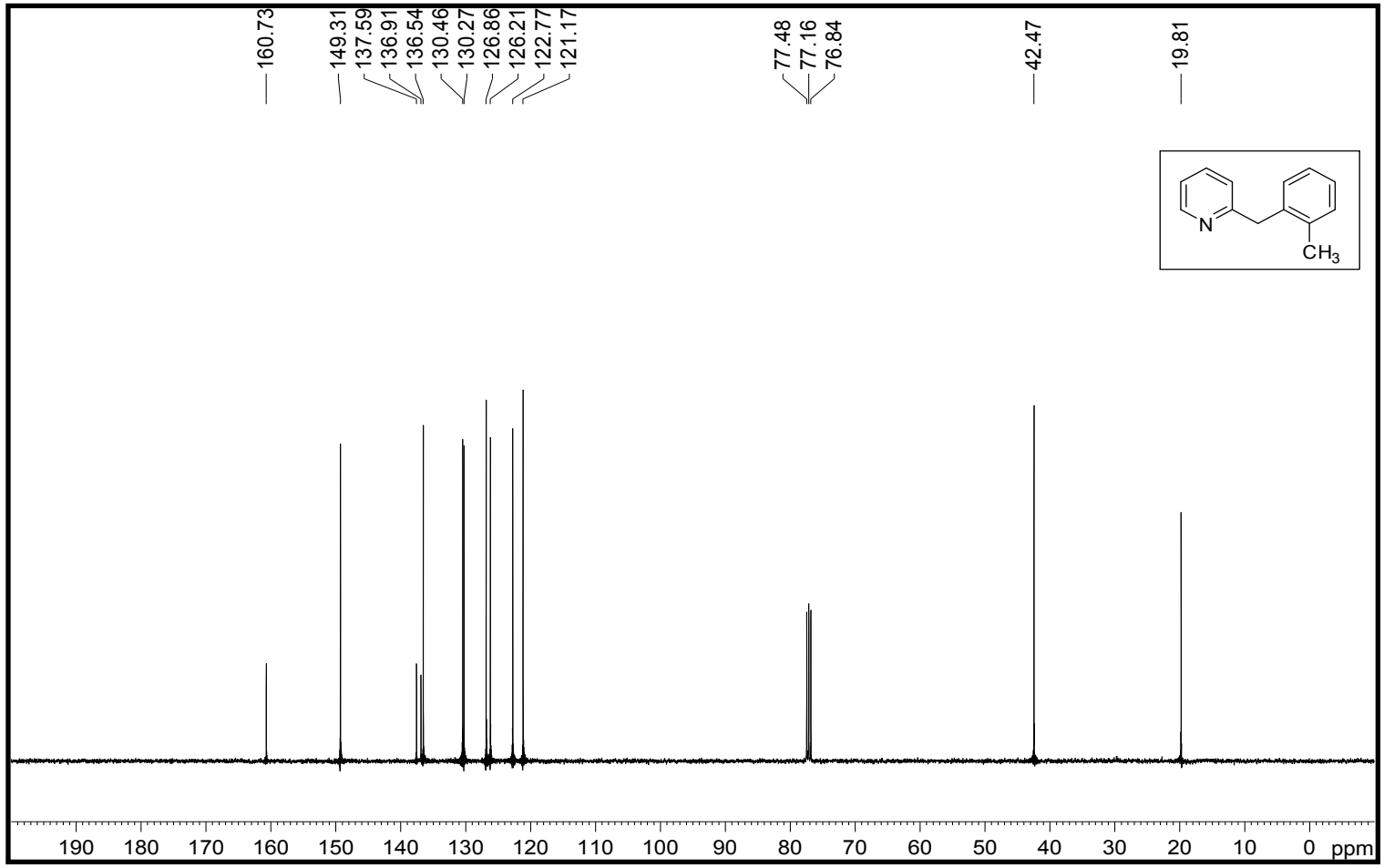

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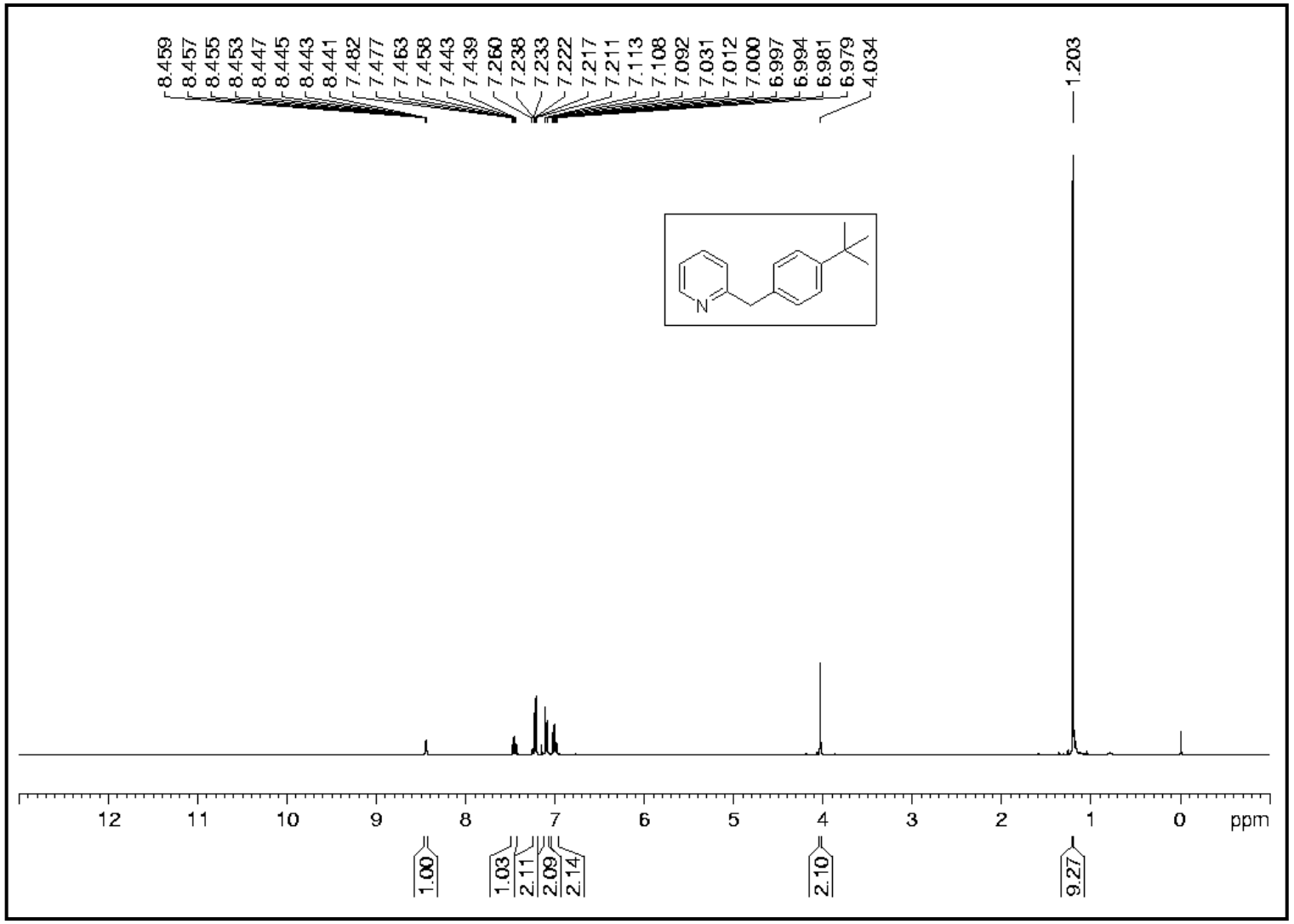

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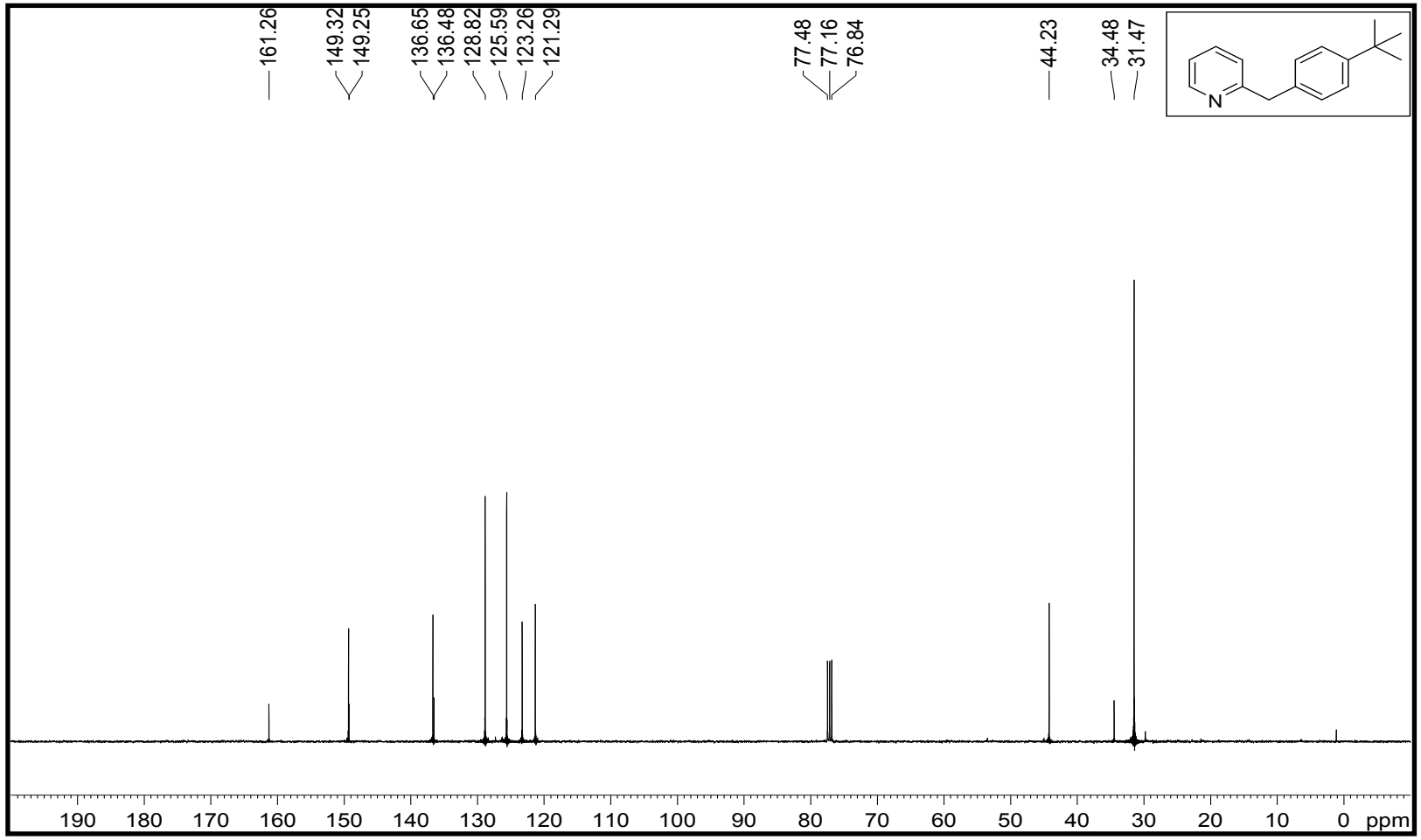

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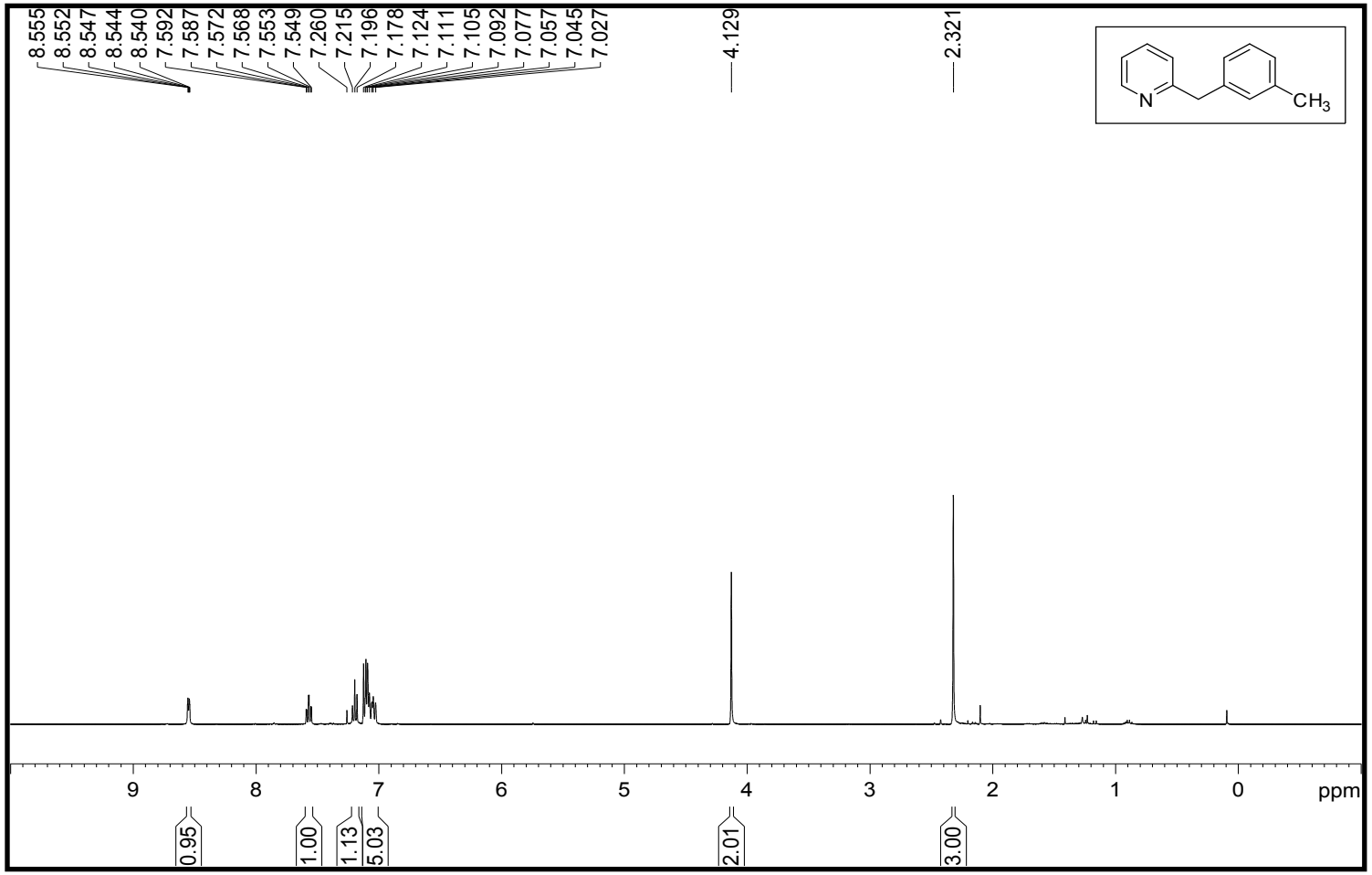

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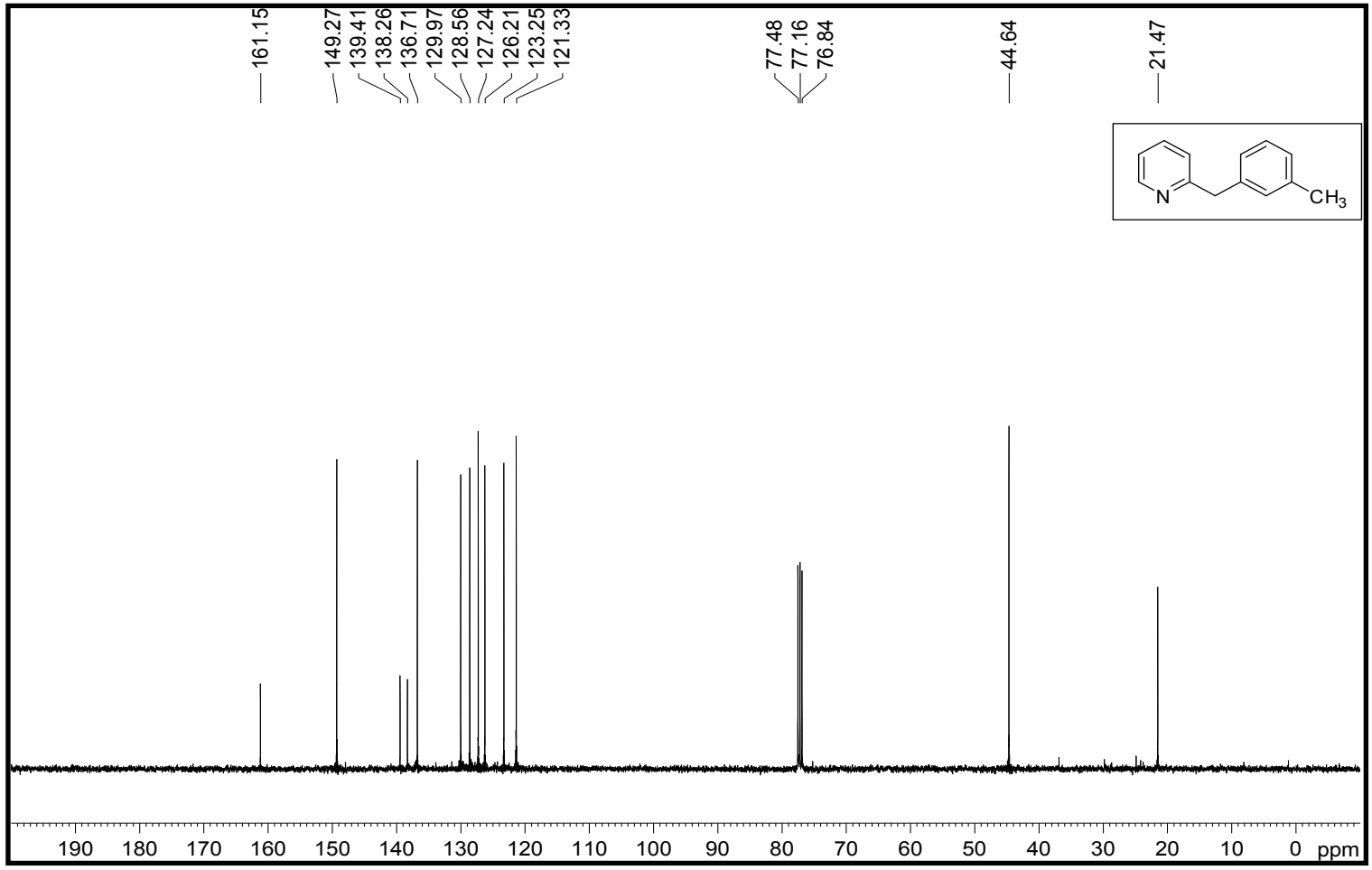

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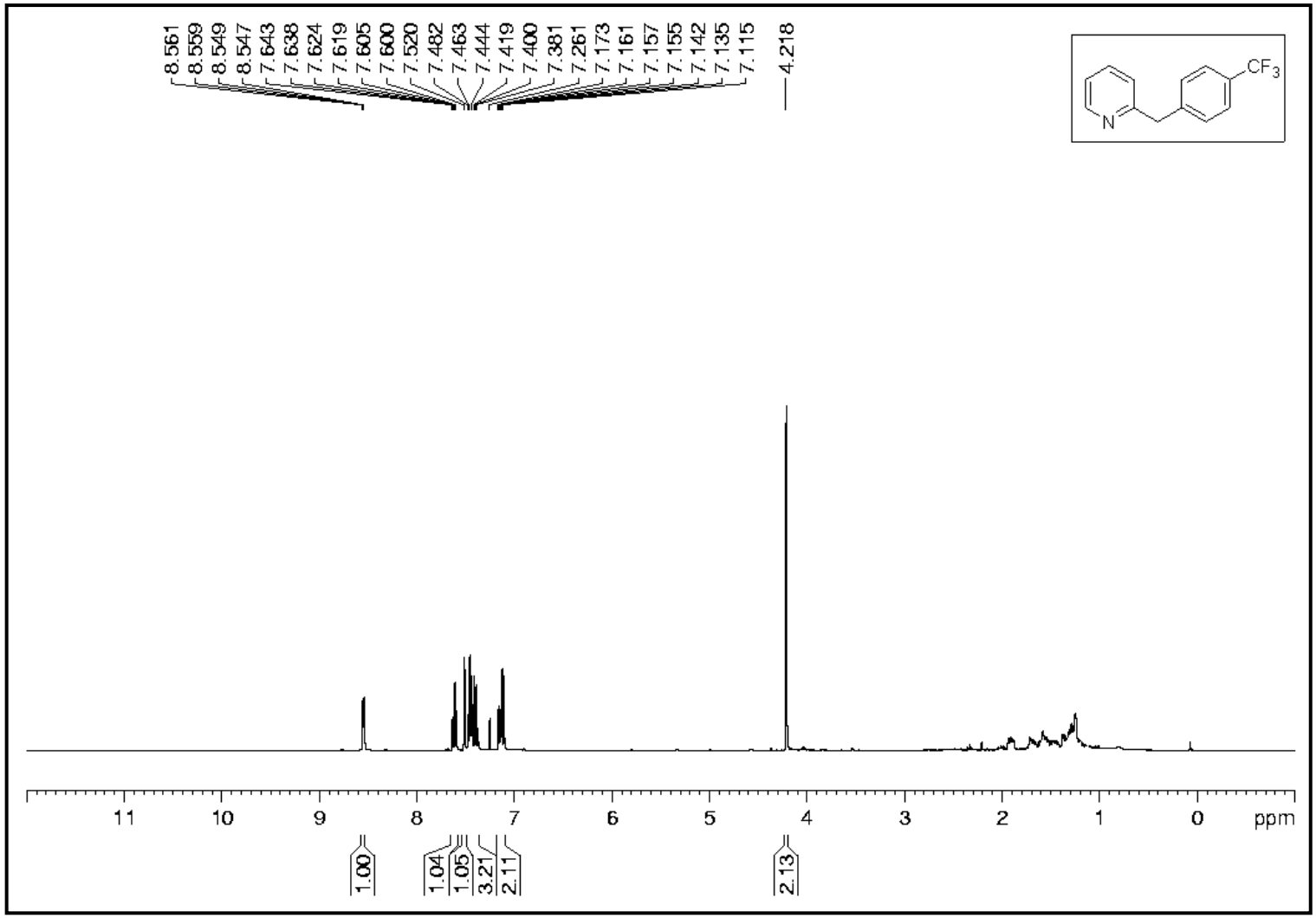

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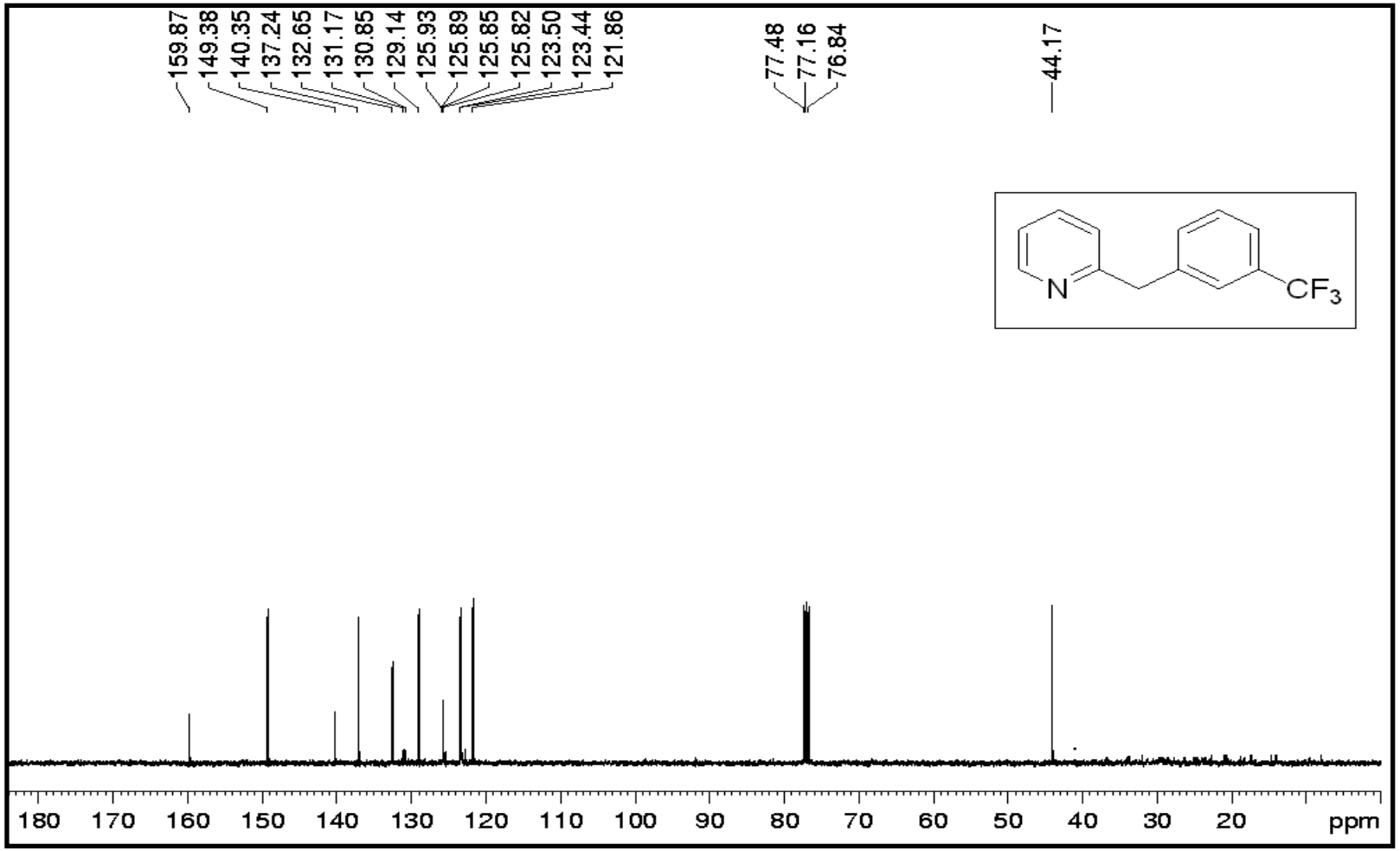

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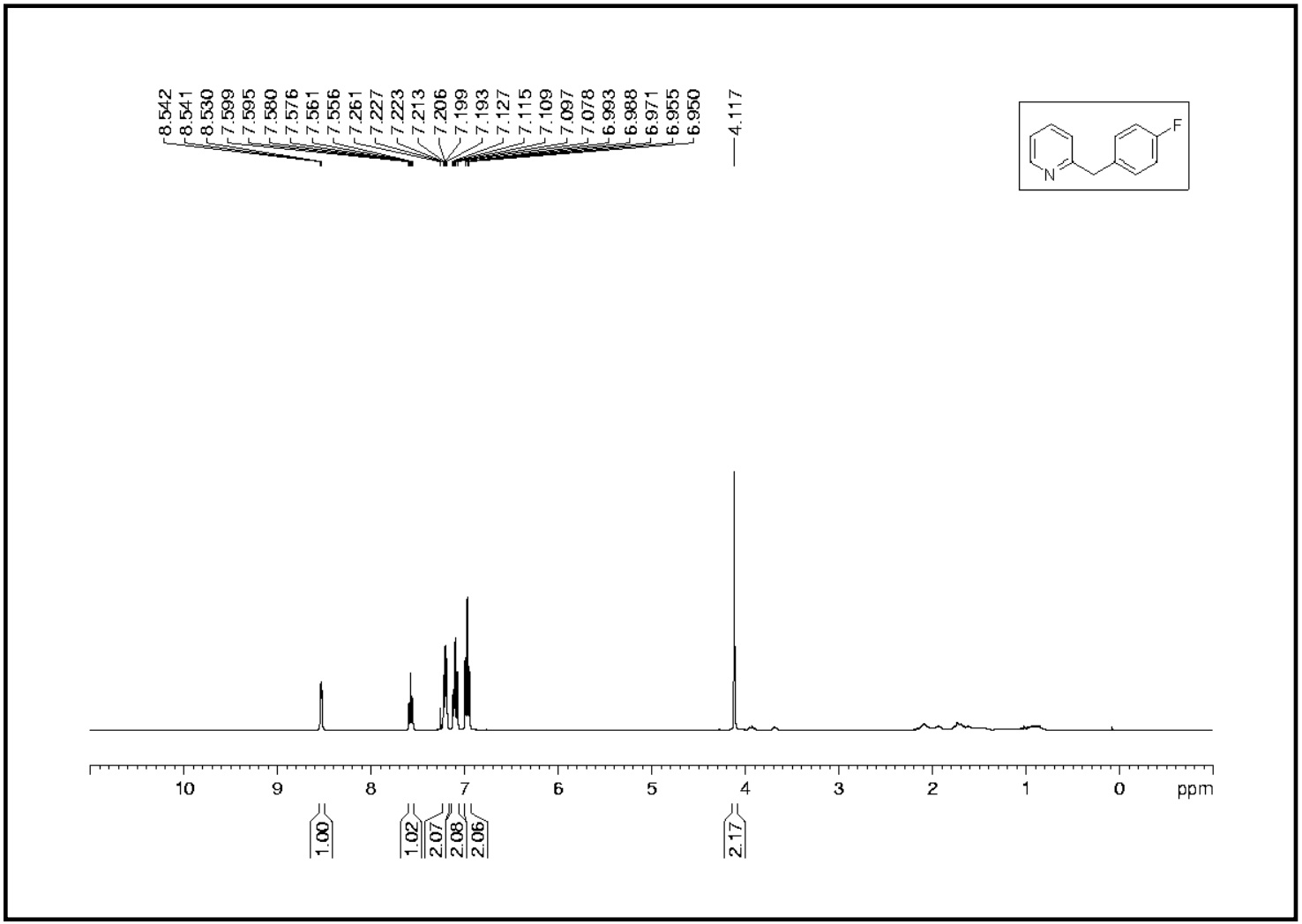

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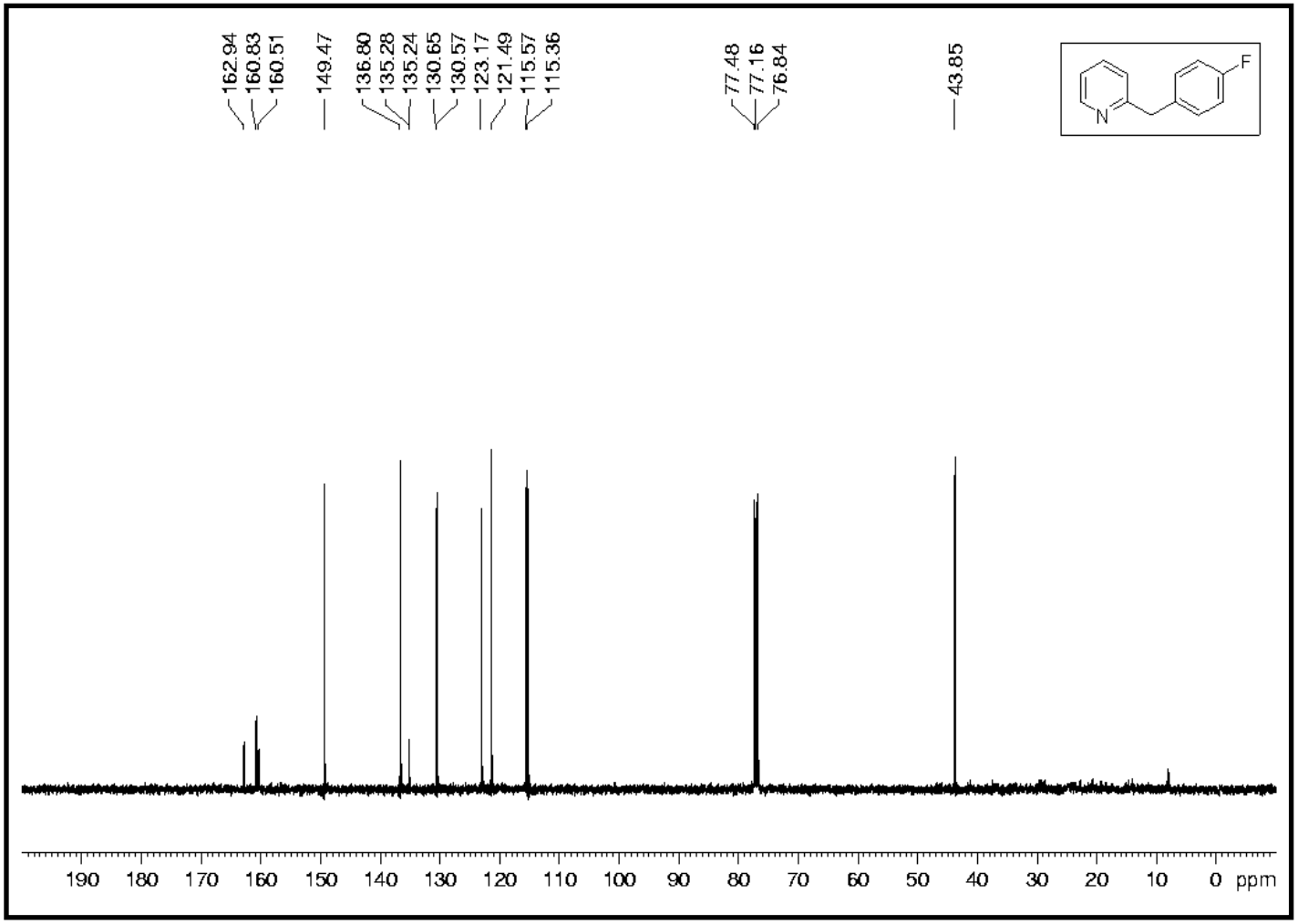
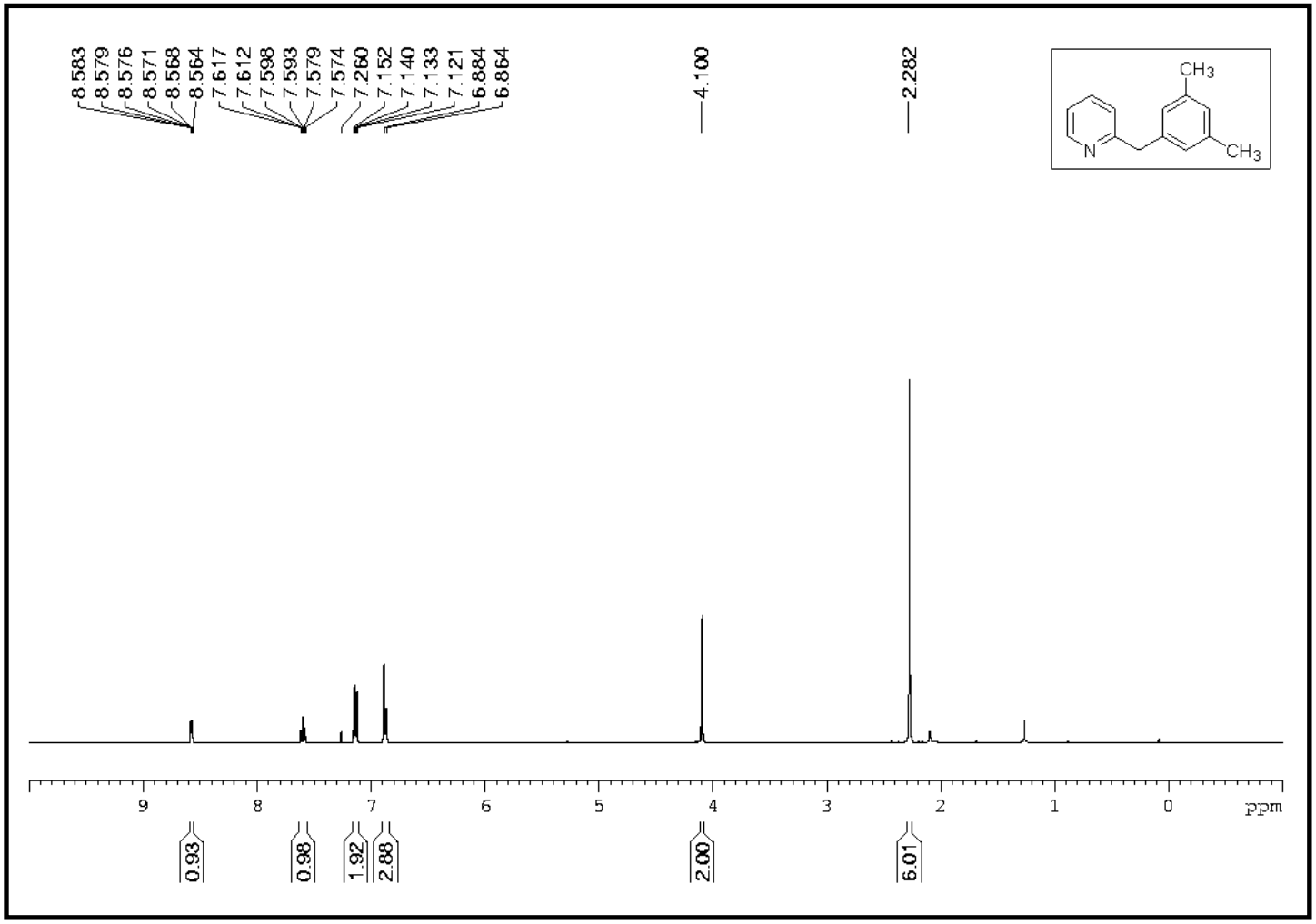


100 MHz ^{13}C NMR spectrum of **2m** in $CDCl_3$



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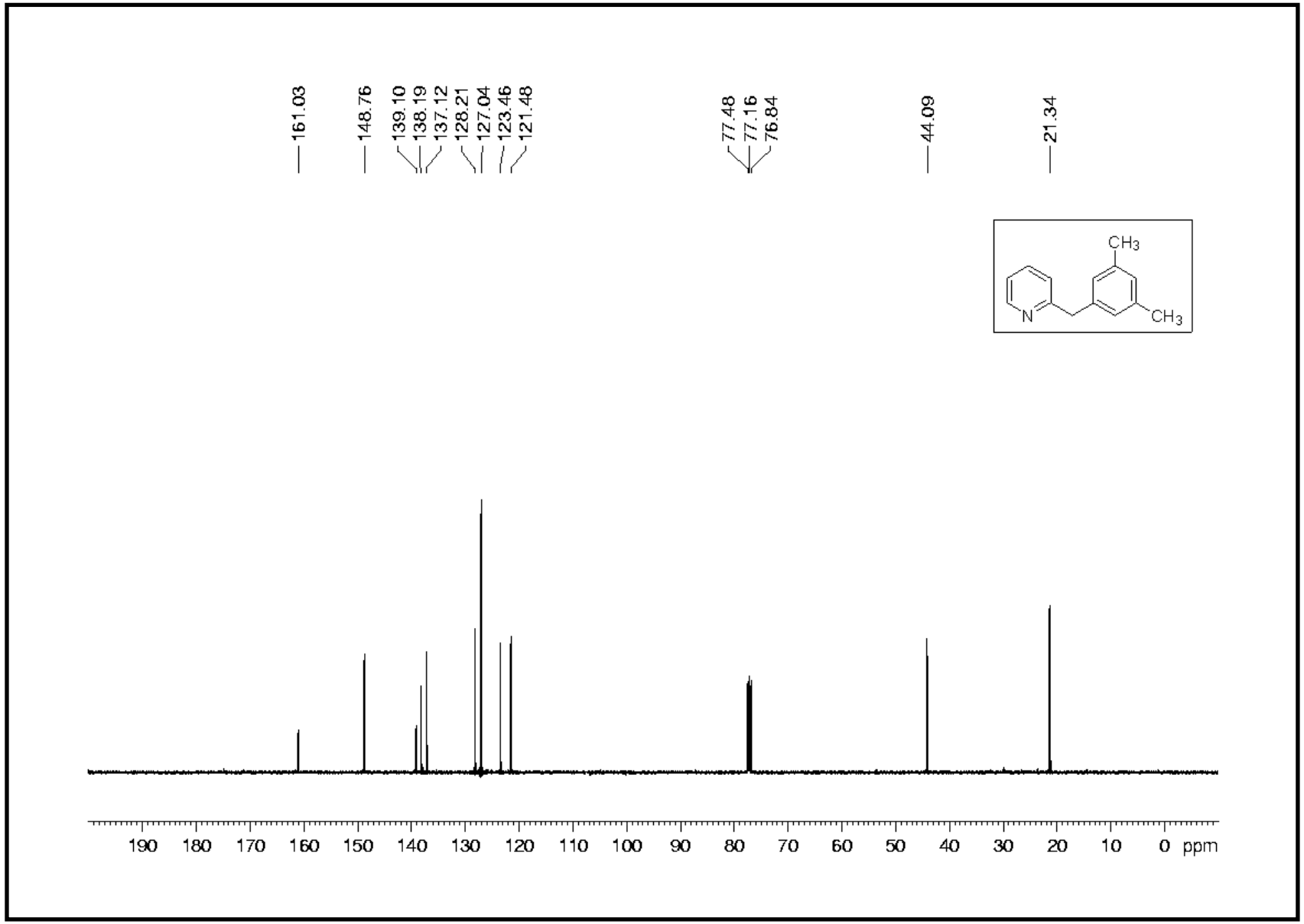

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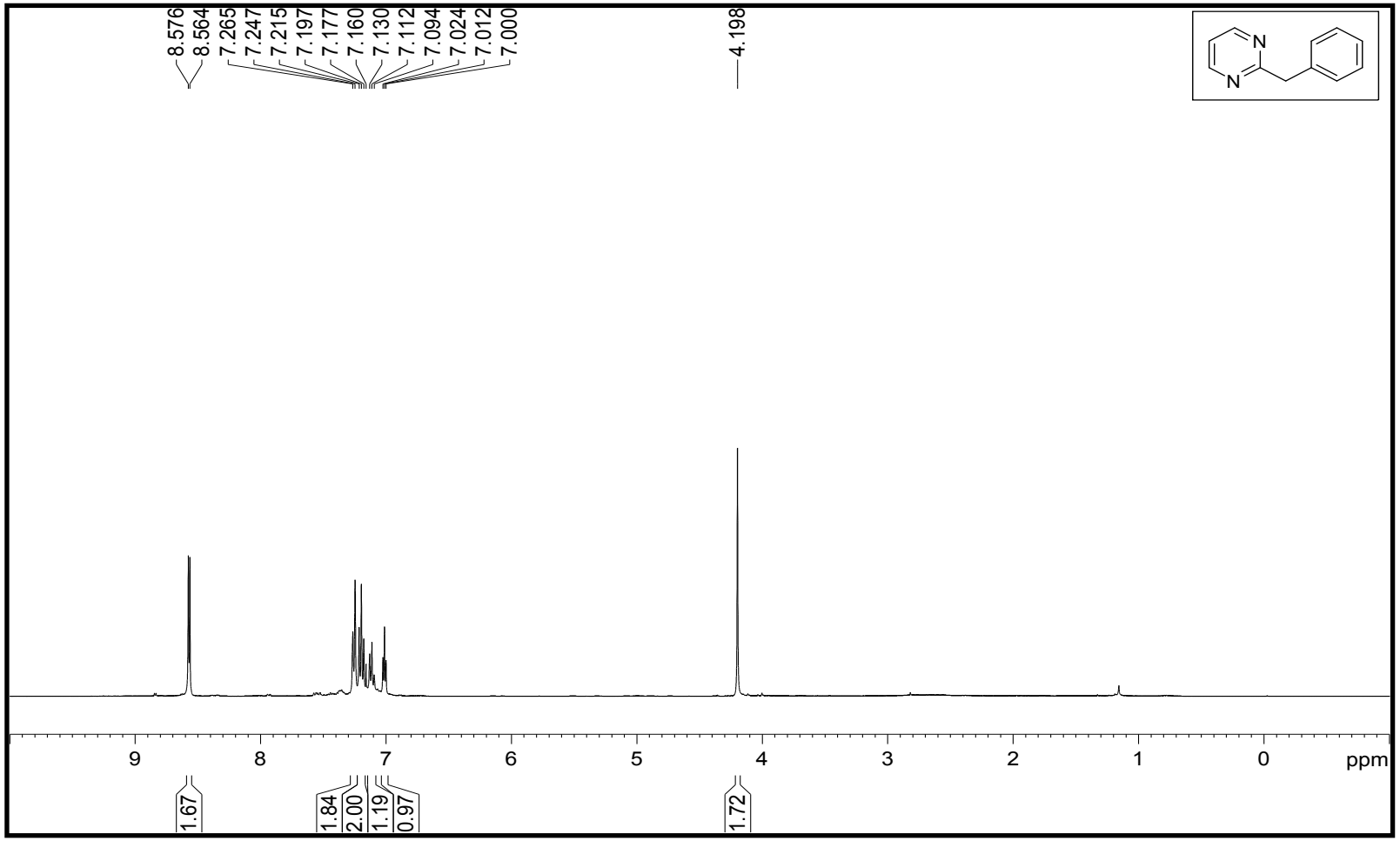

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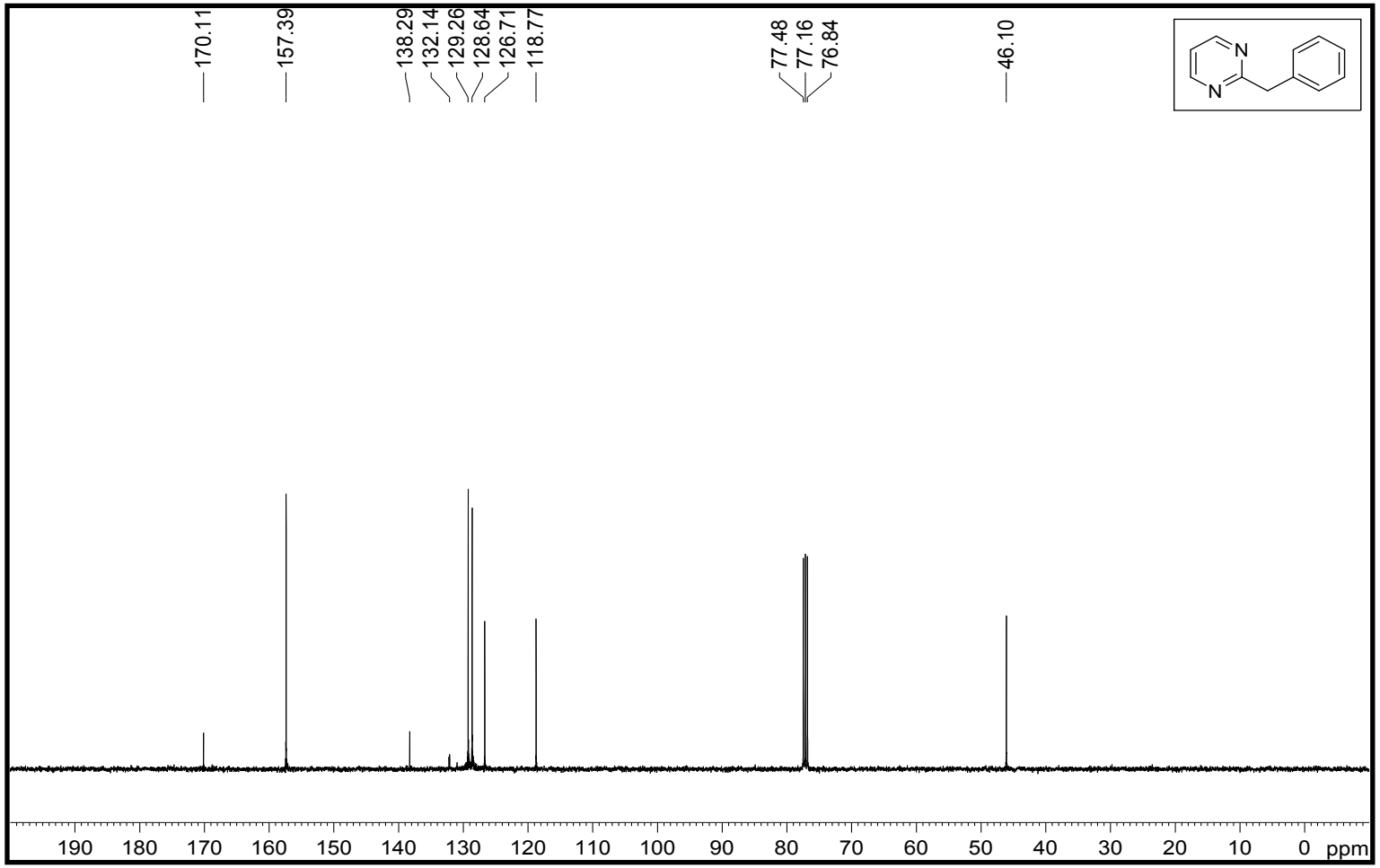

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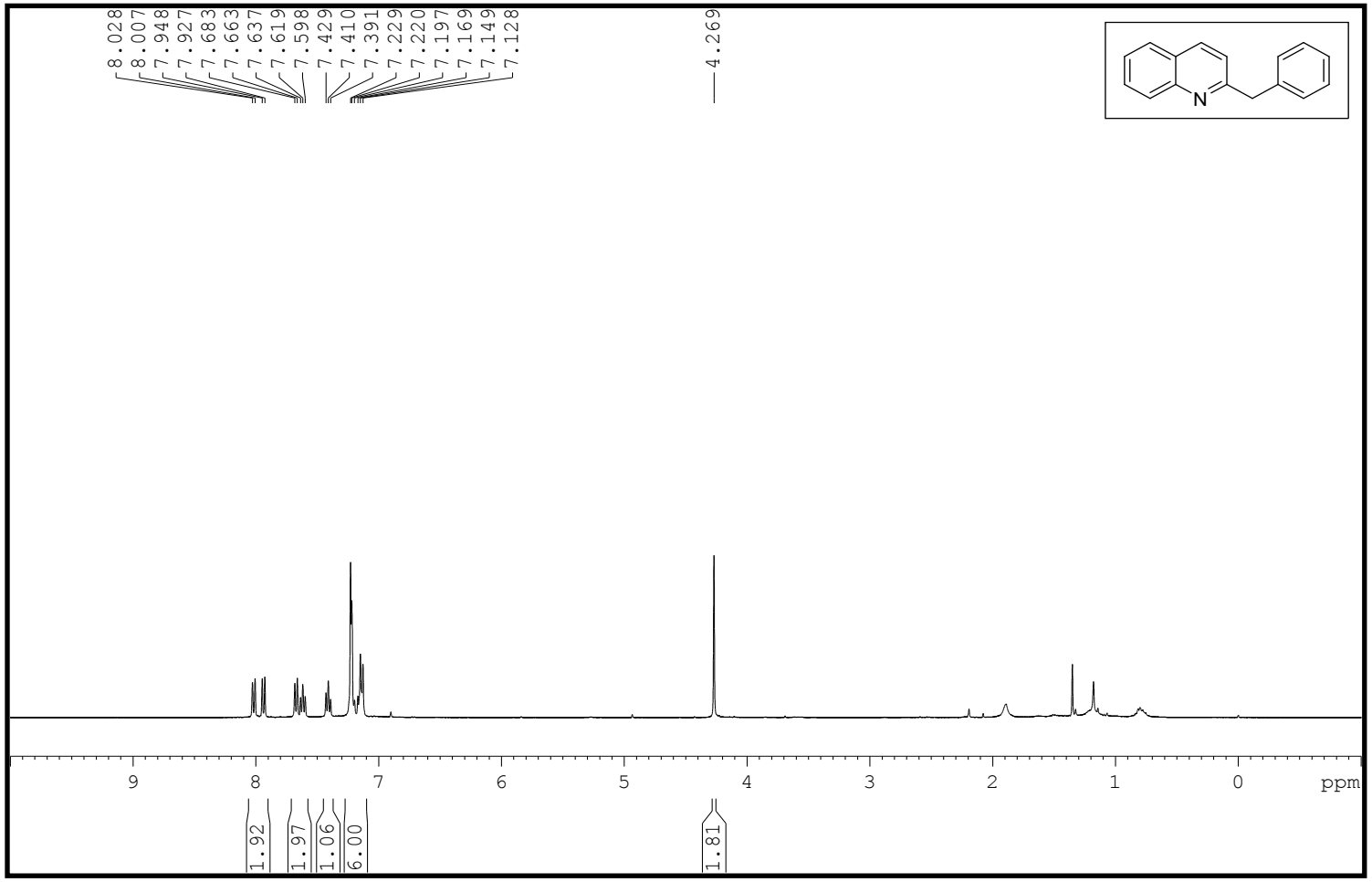

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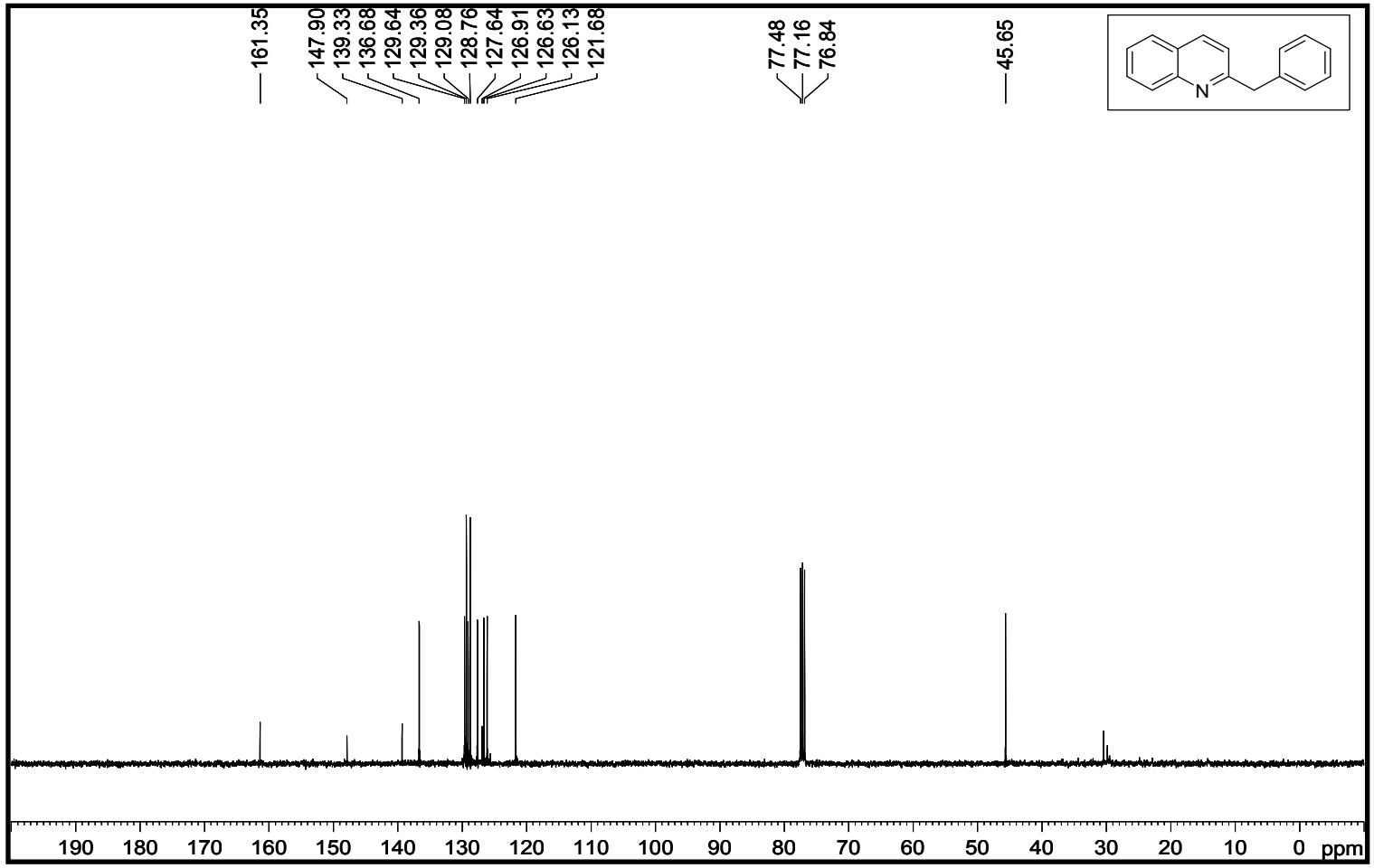
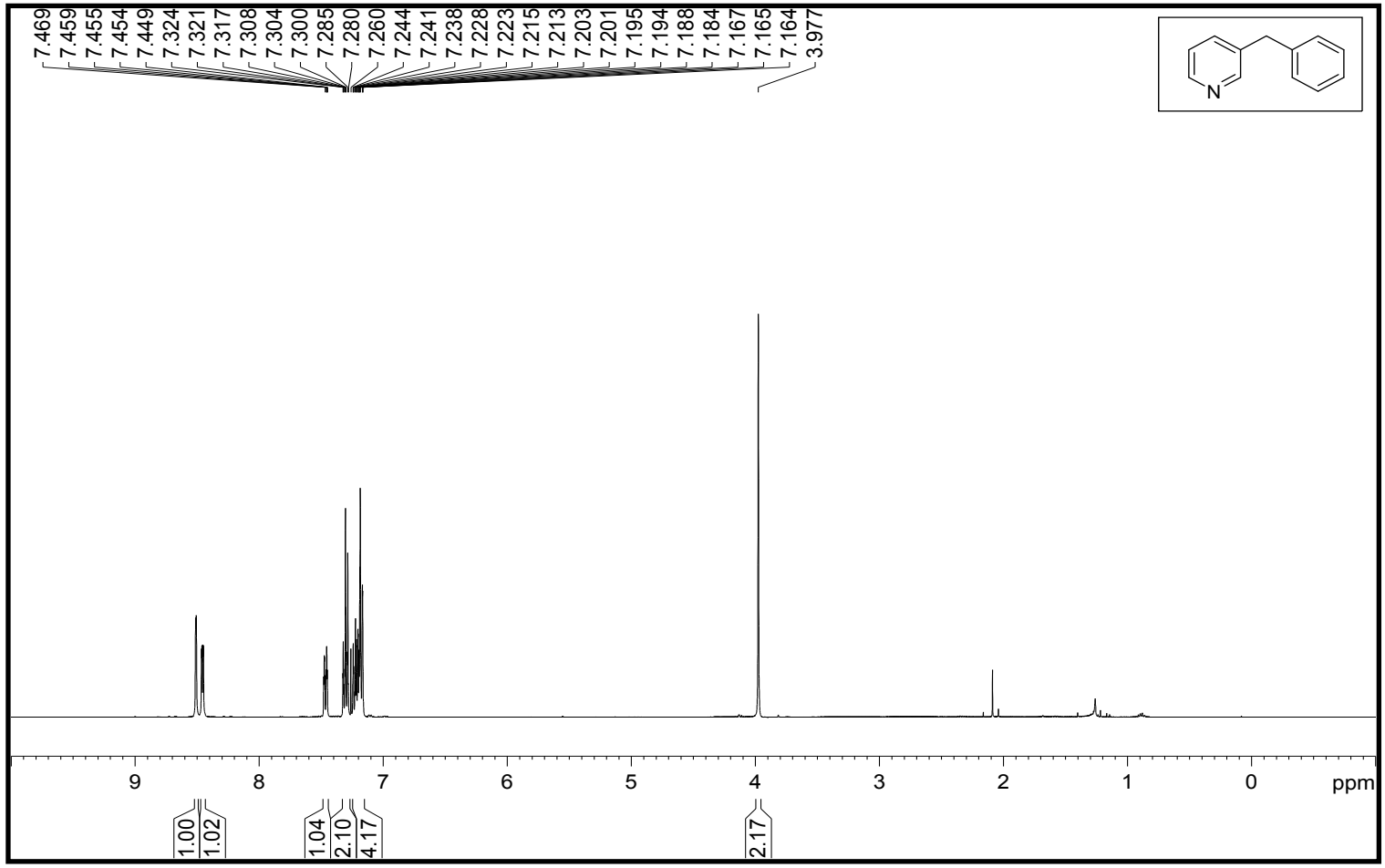


100 MHz ^{13}C NMR spectrum of **2p** in $CDCl_3$



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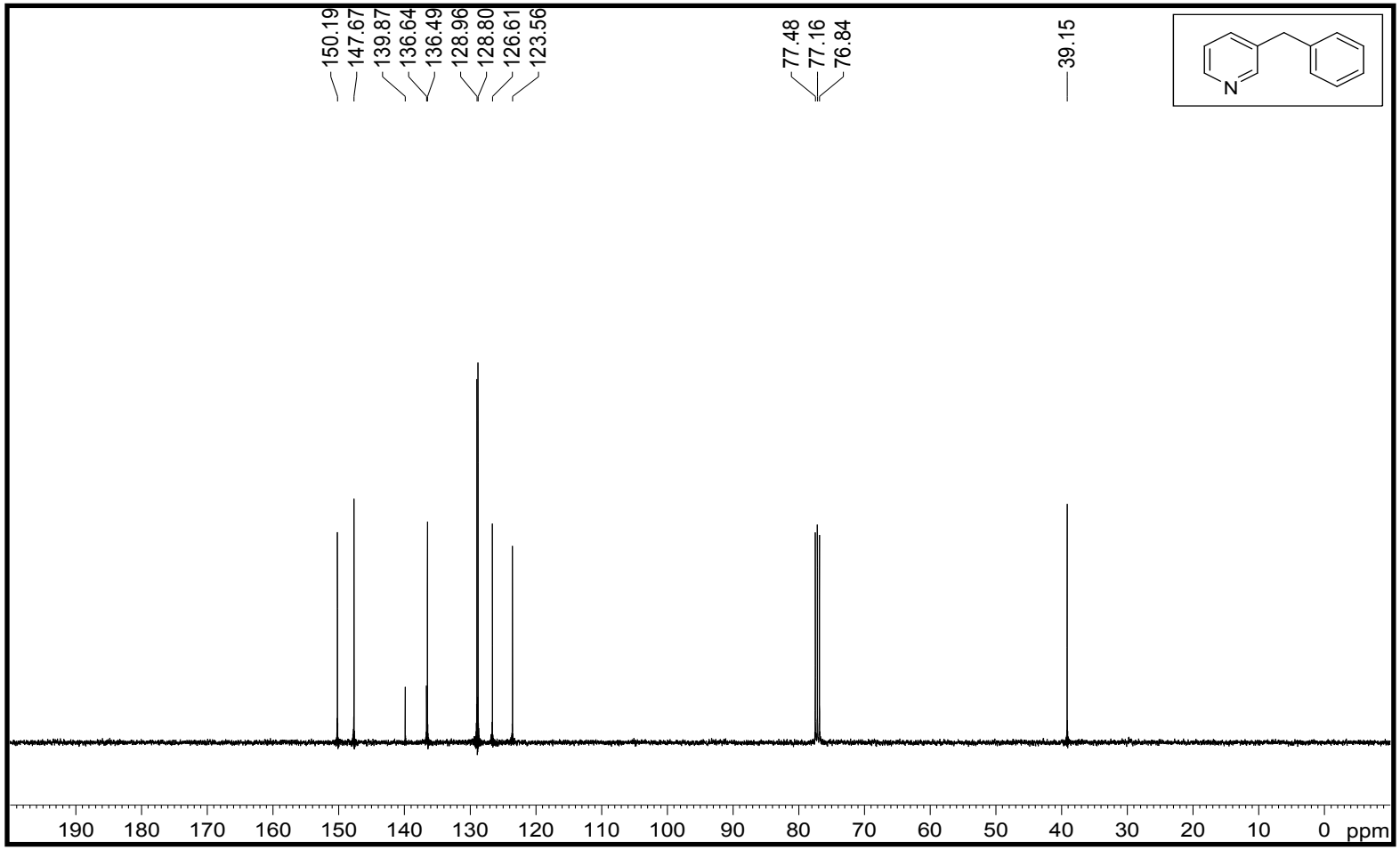
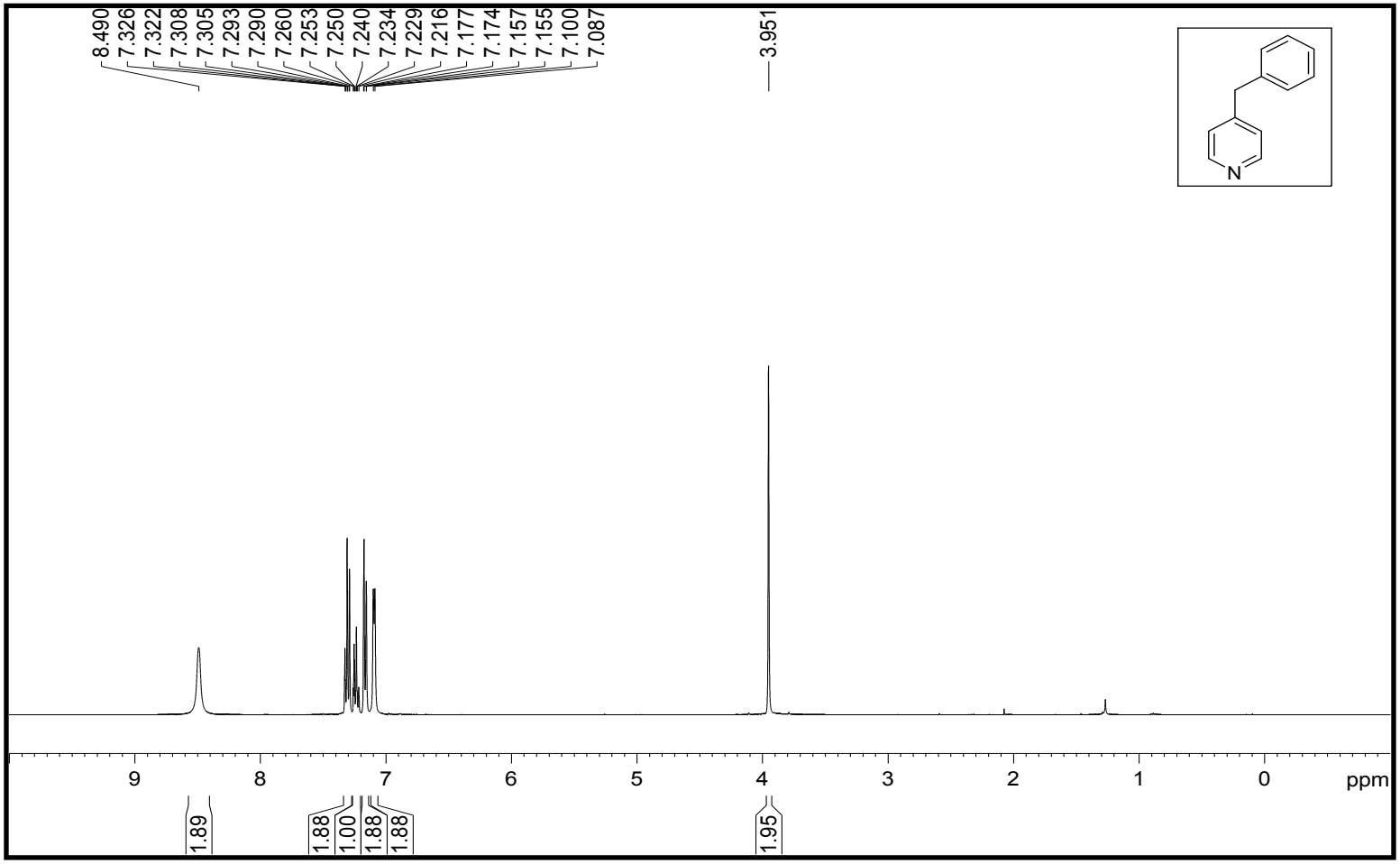


100 MHz ^{13}C NMR spectrum of **2q** in $CDCl_3$



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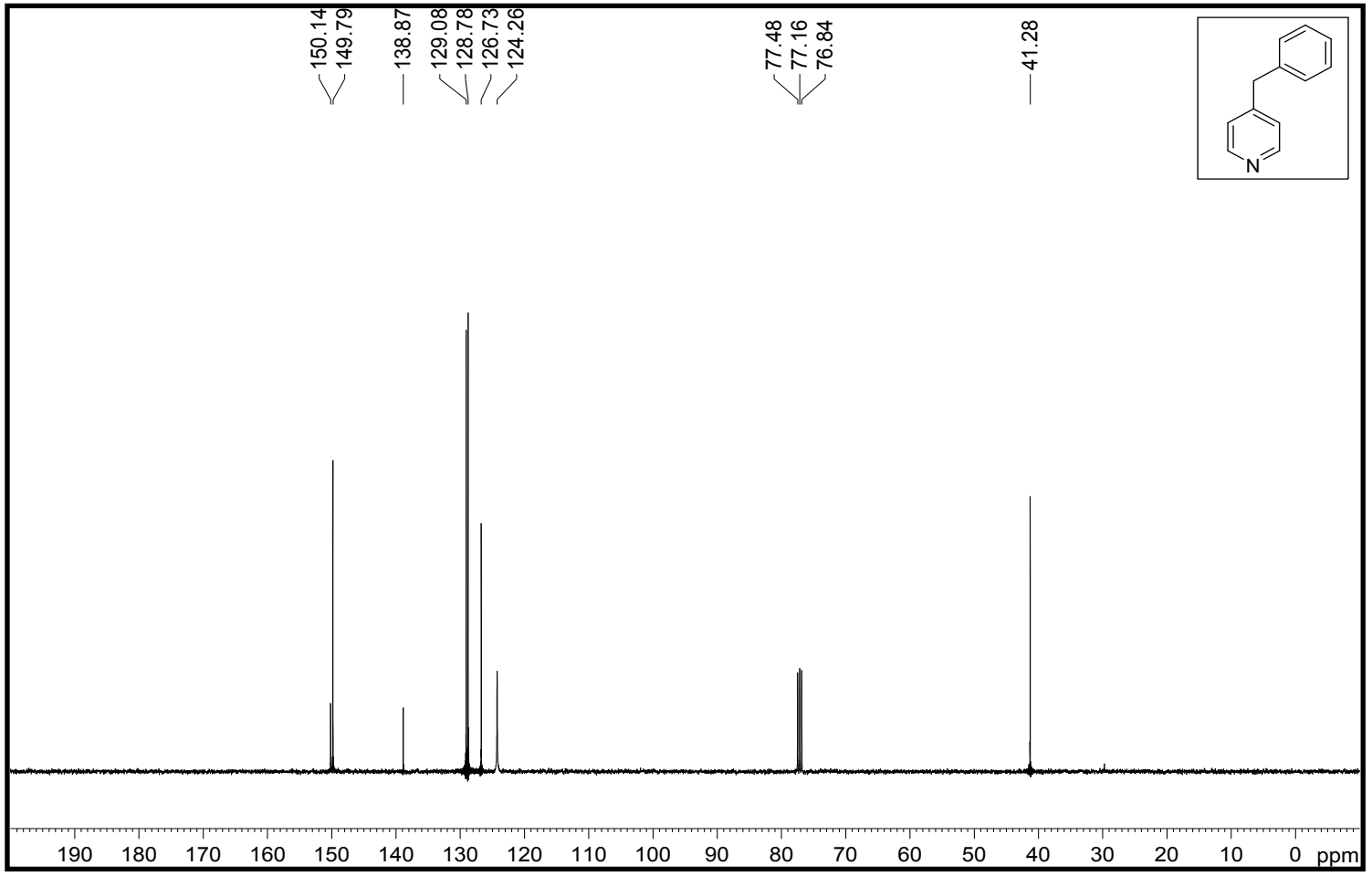

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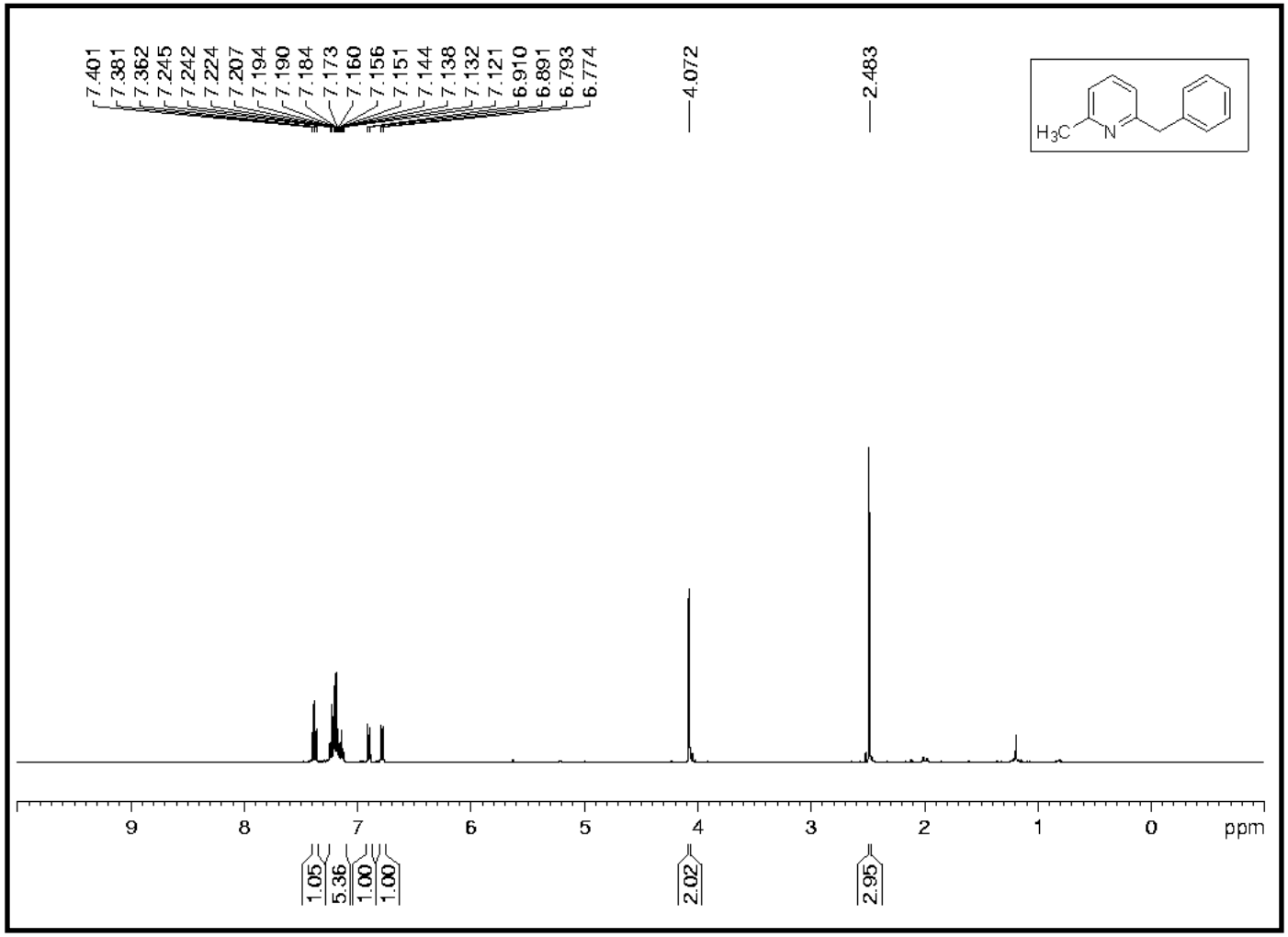
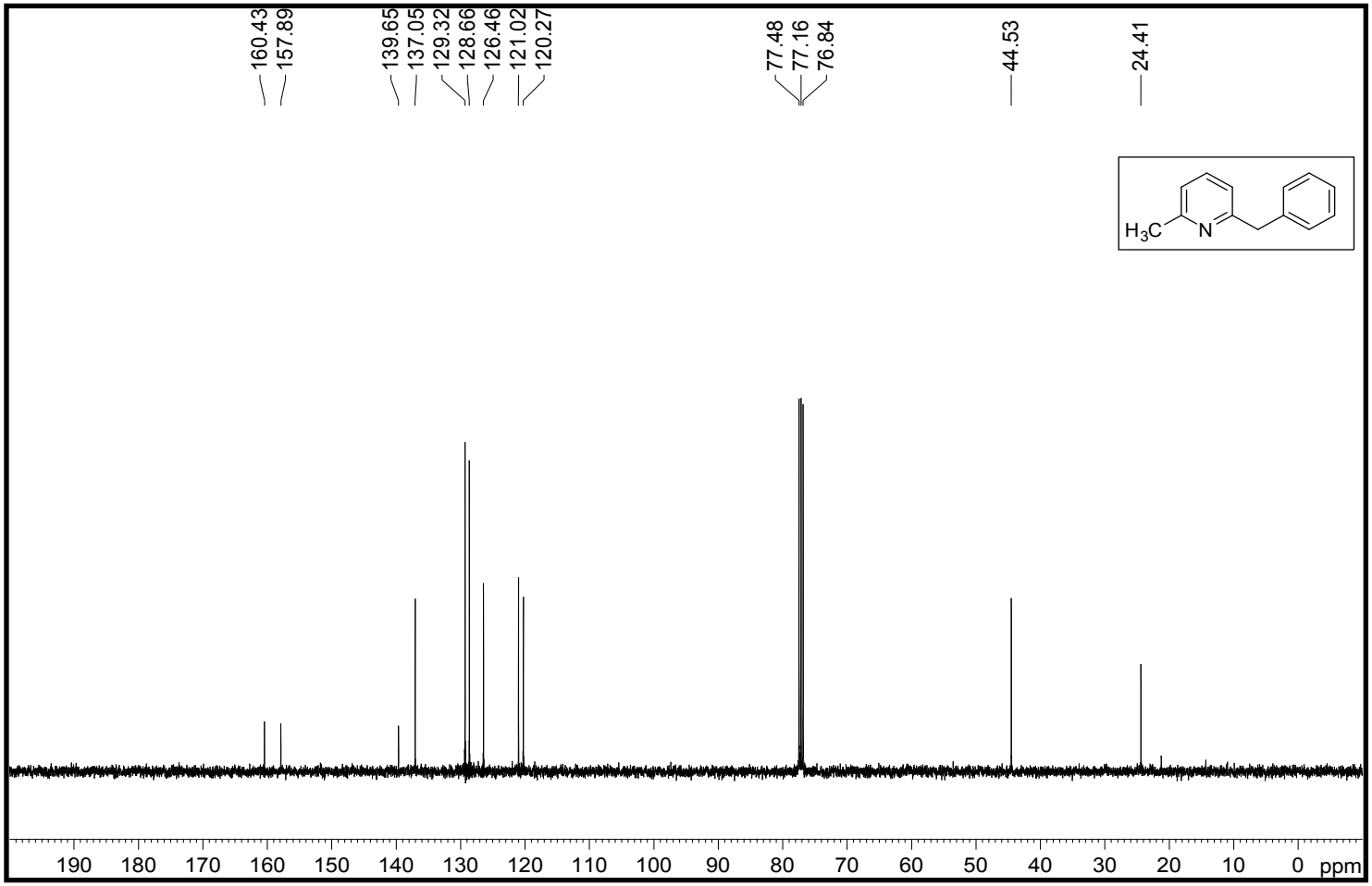
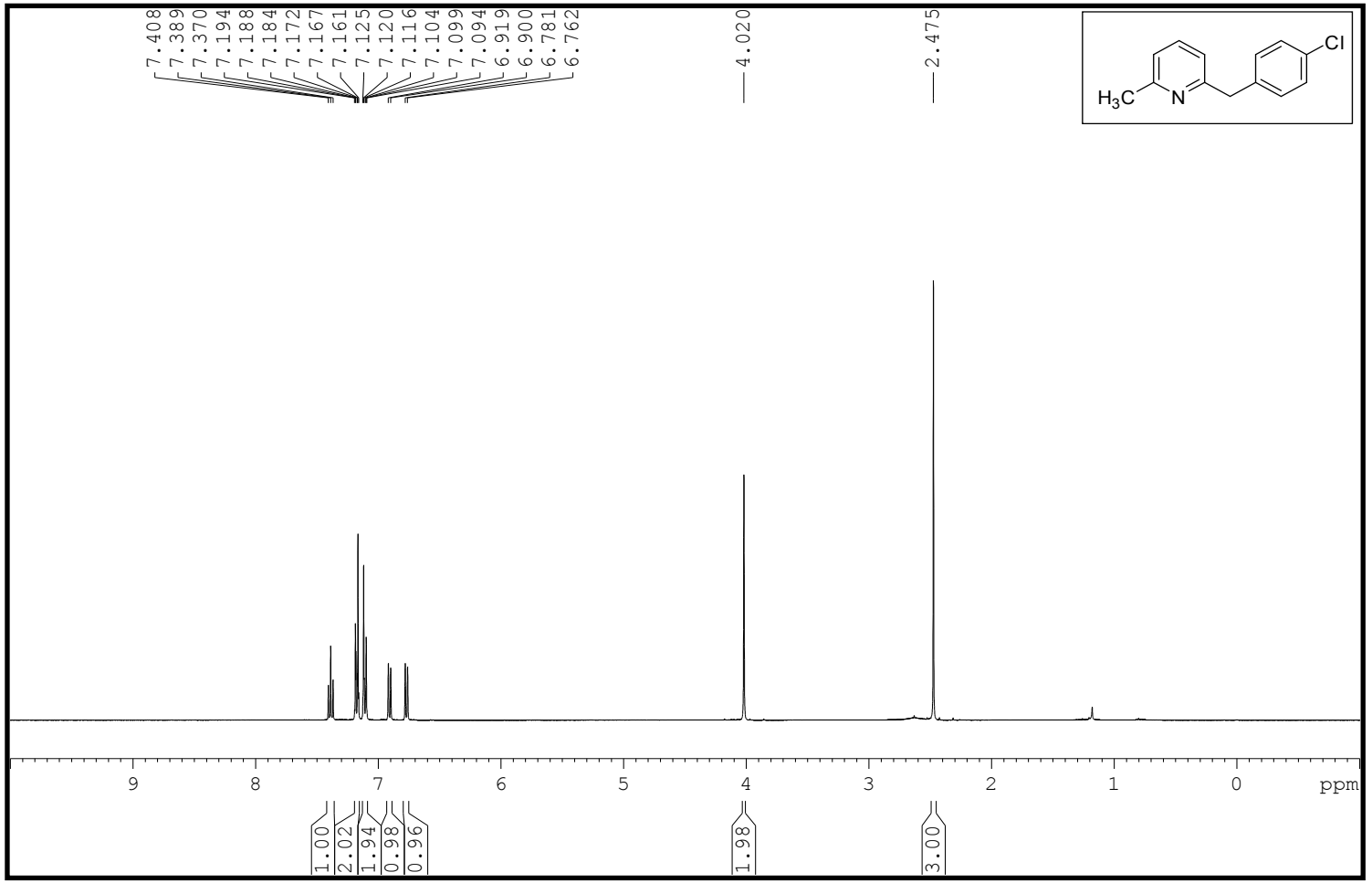


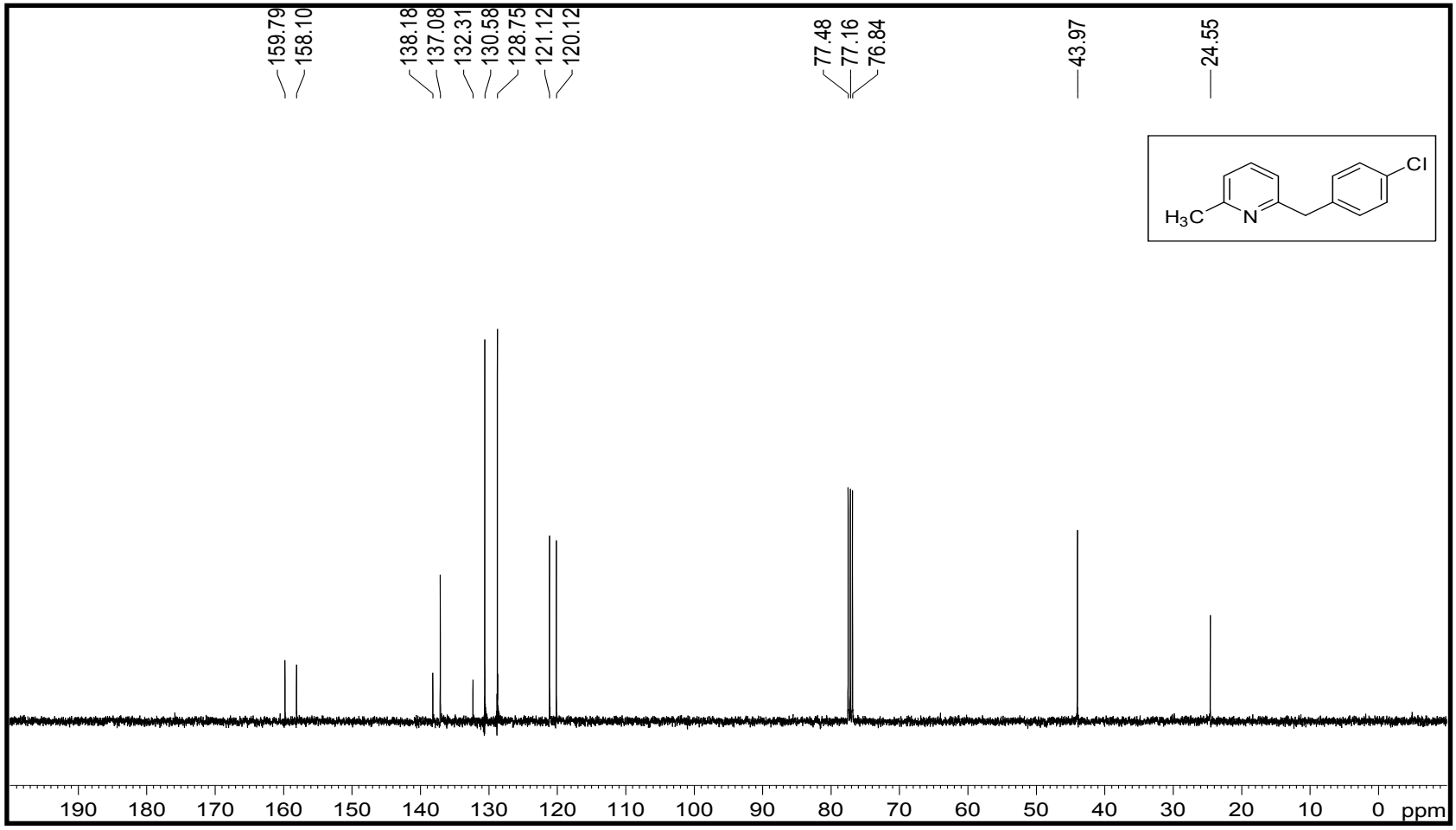
400 MHz ^{1}H NMR spectrum of **6a** in $CDCl_3$



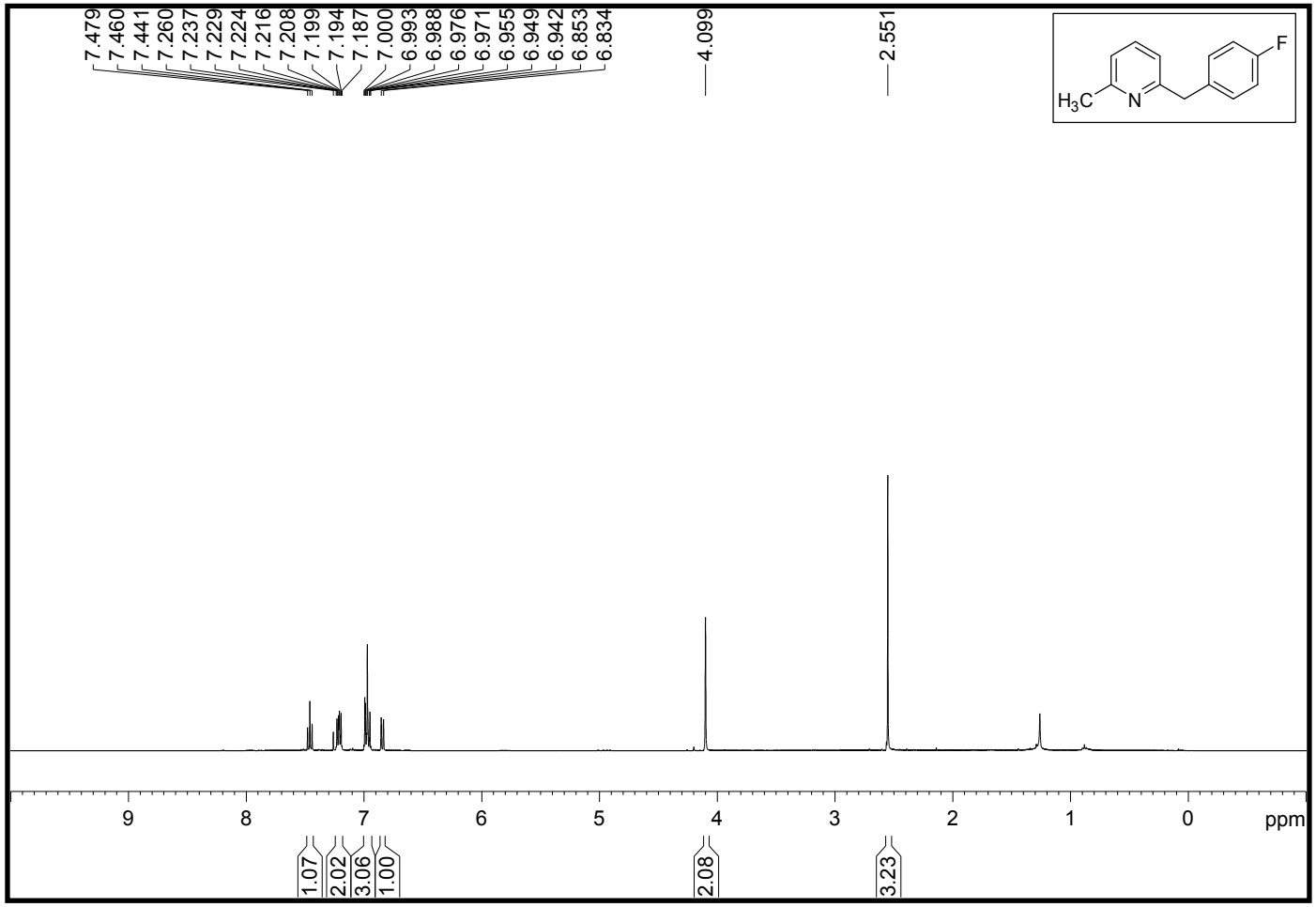
100 MHz ^{13}C NMR spectrum of **6a** in $CDCl_3$



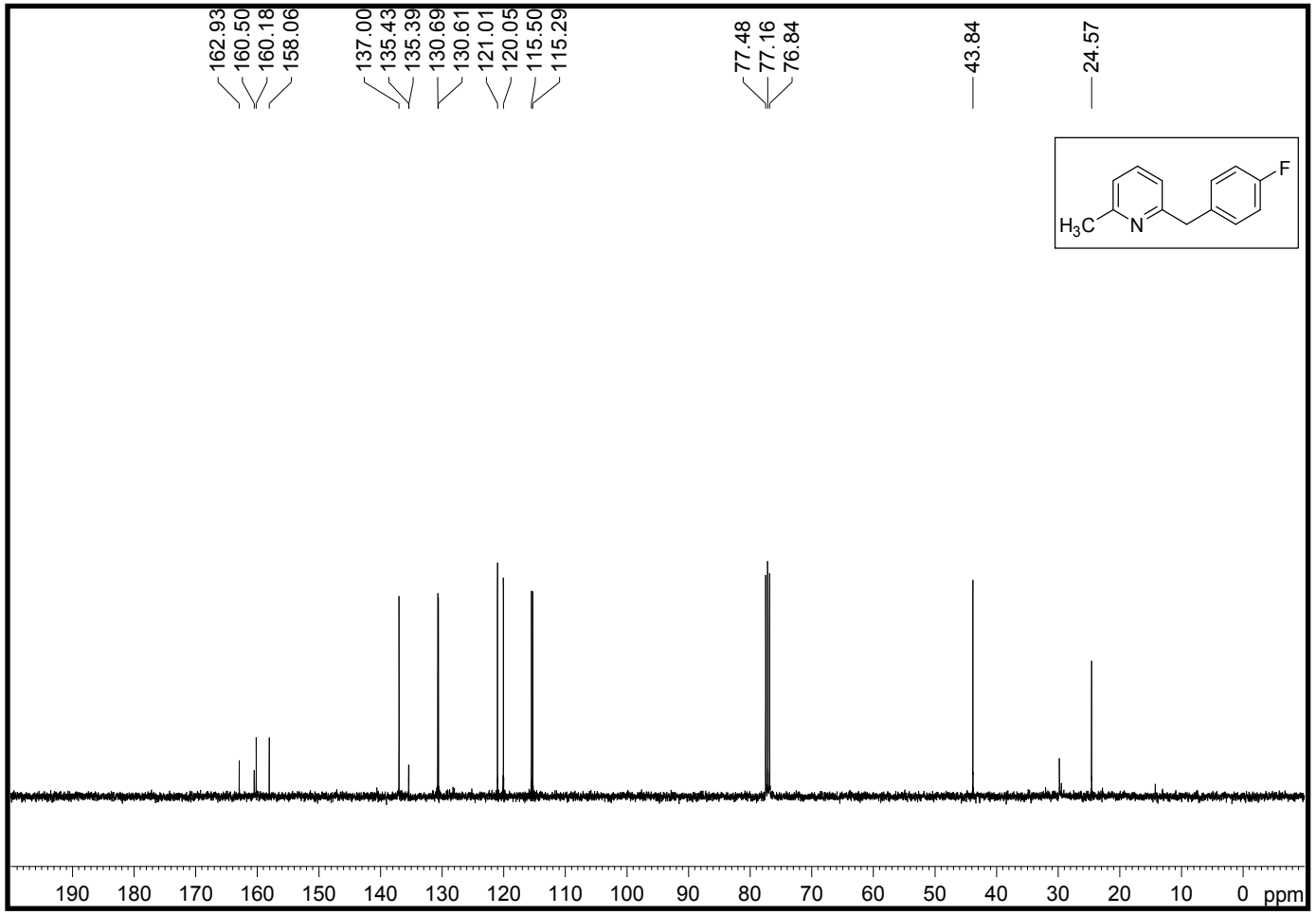
400 MHz ^{1}H NMR spectrum of **6b** in $CDCl_3$



100 MHz ^{13}C NMR spectrum of **6b** in $CDCl_3$



400 MHz ^{1}H NMR spectrum of **6c** in $CDCl_3$



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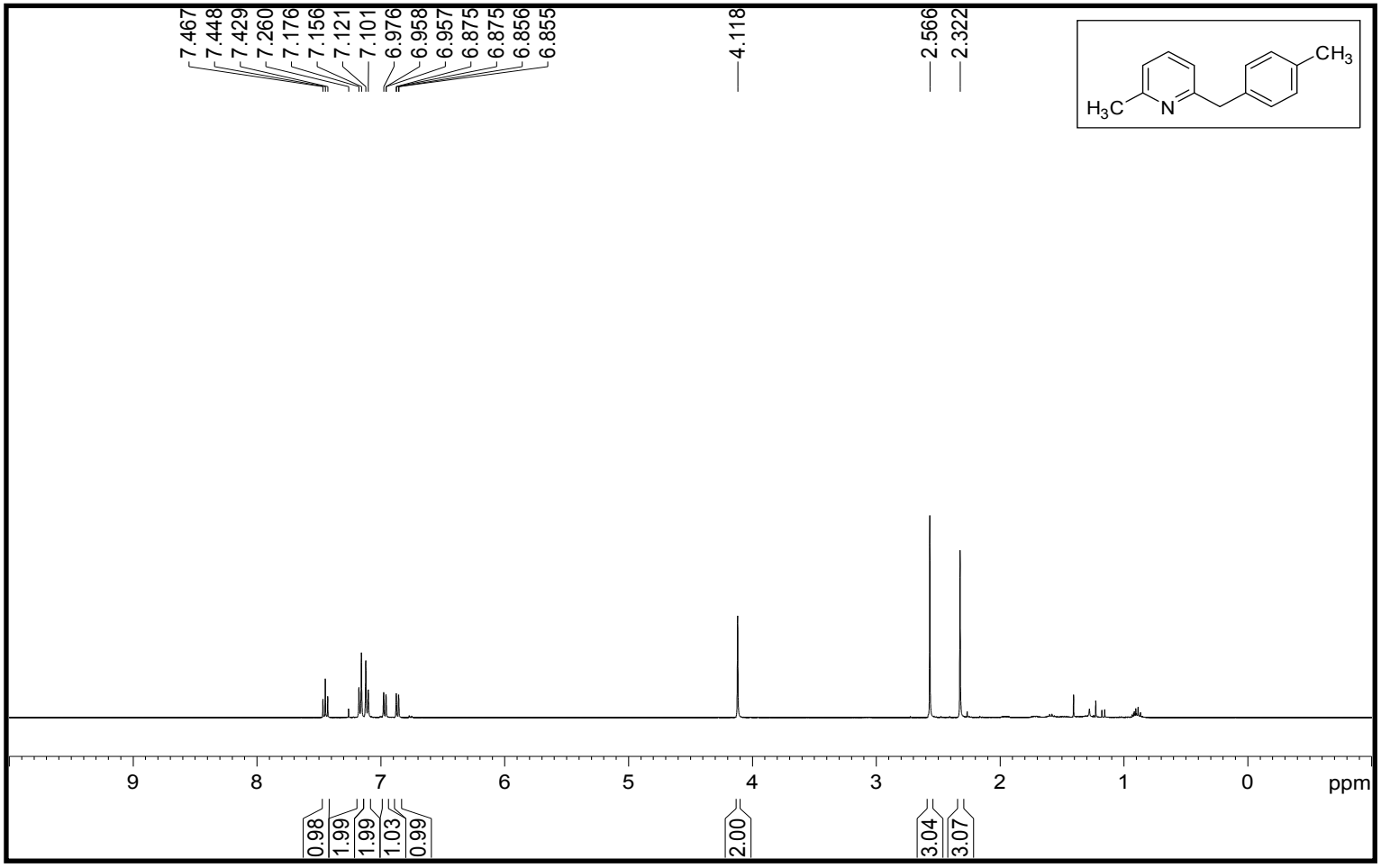

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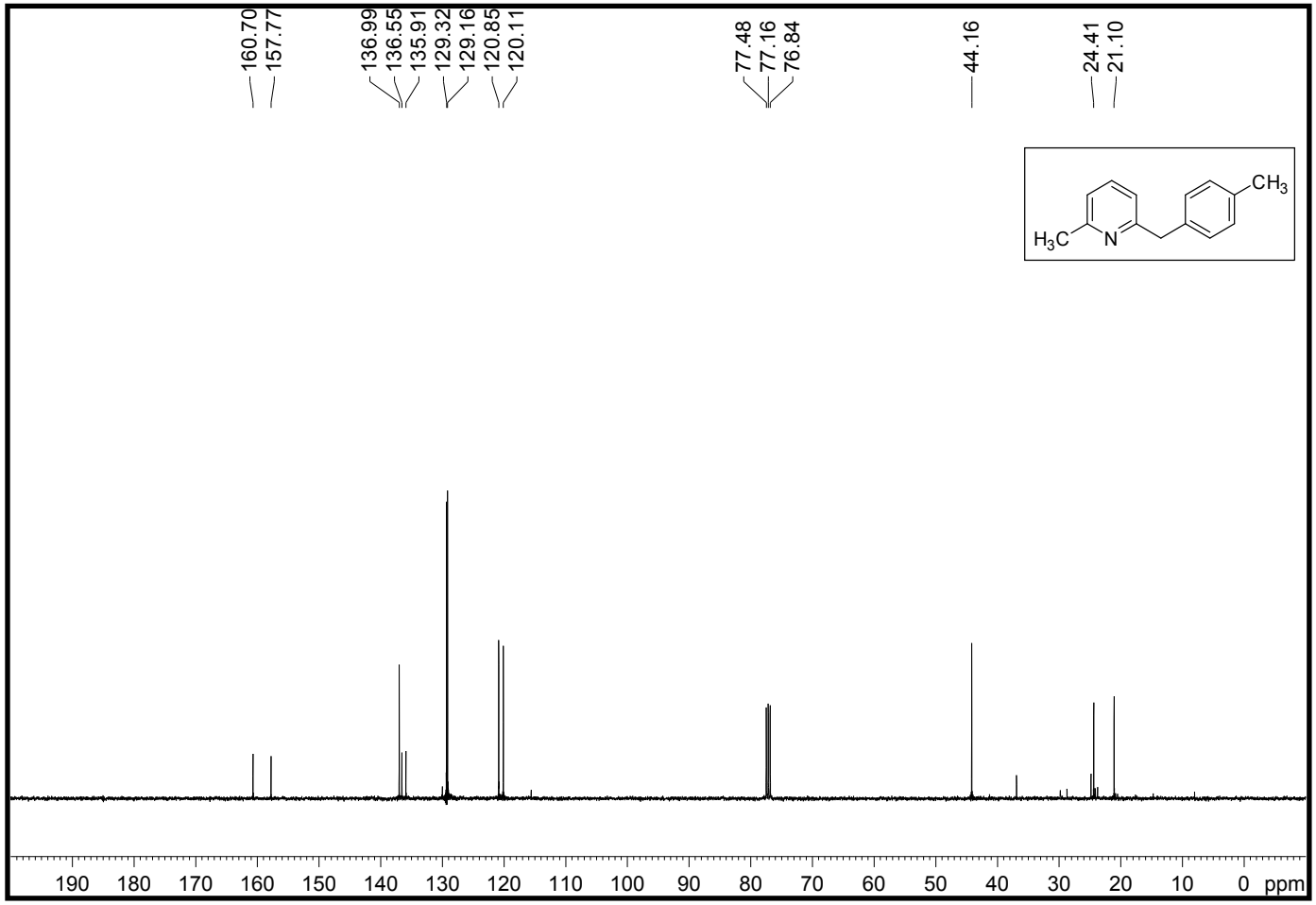

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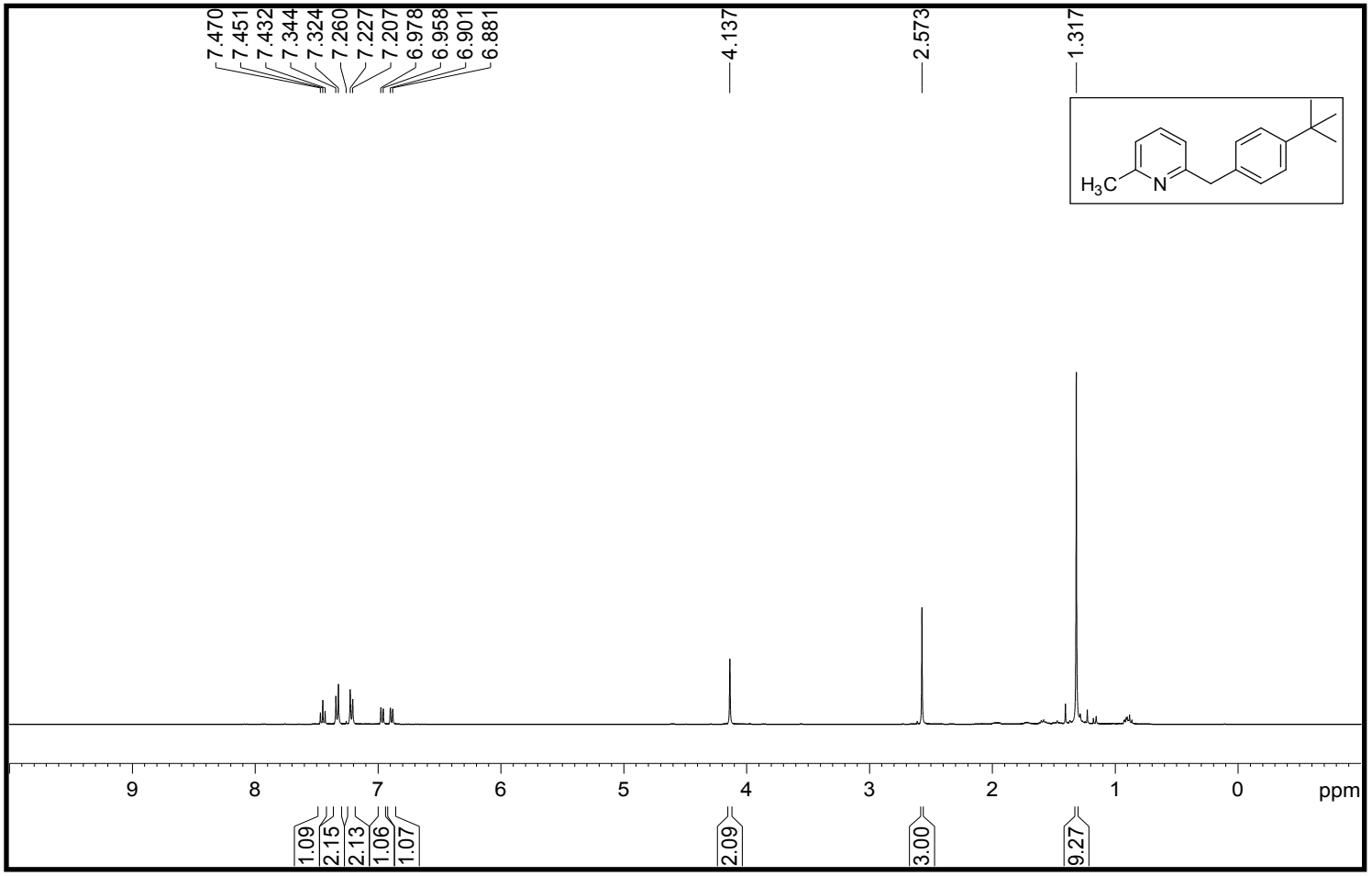

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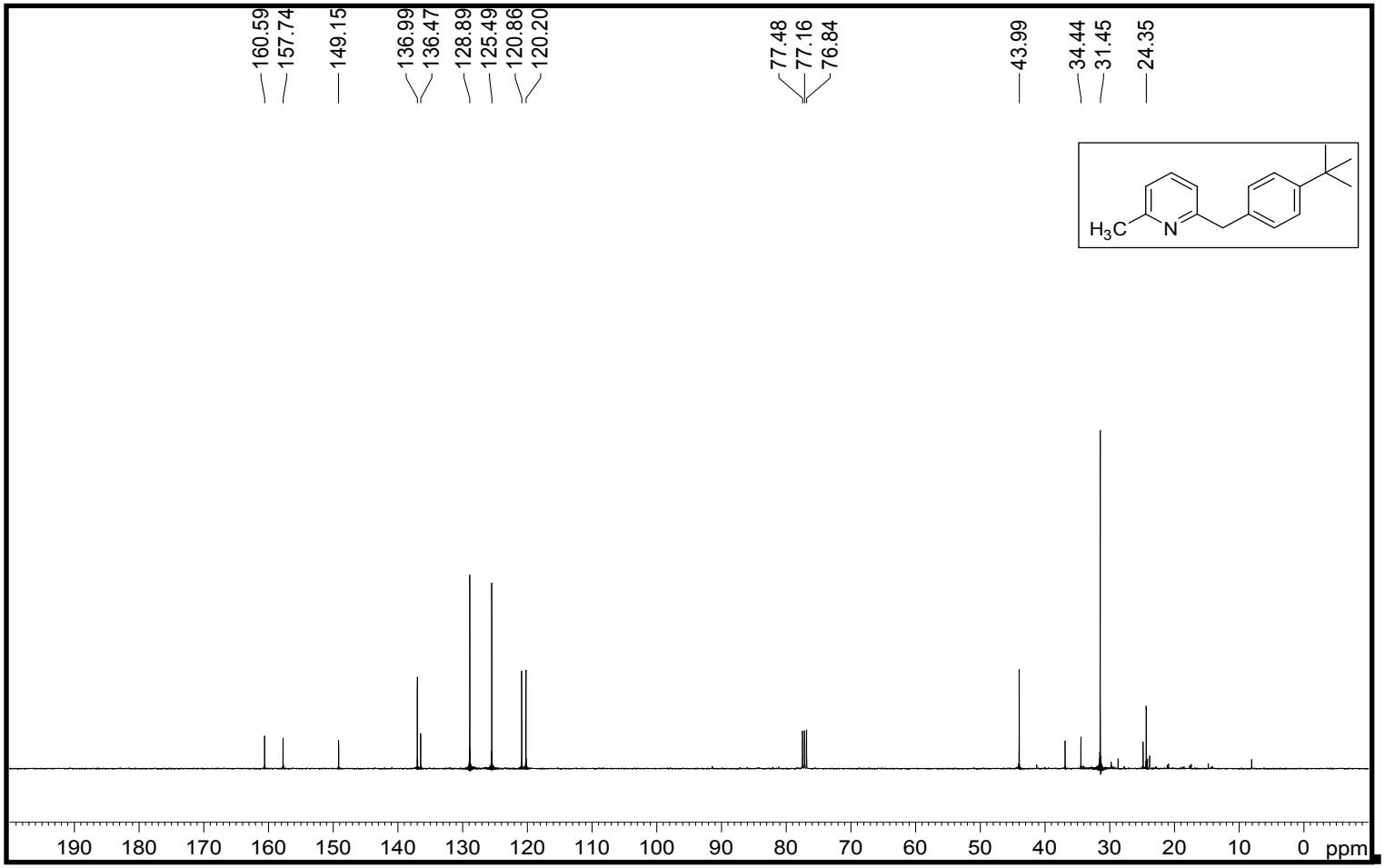

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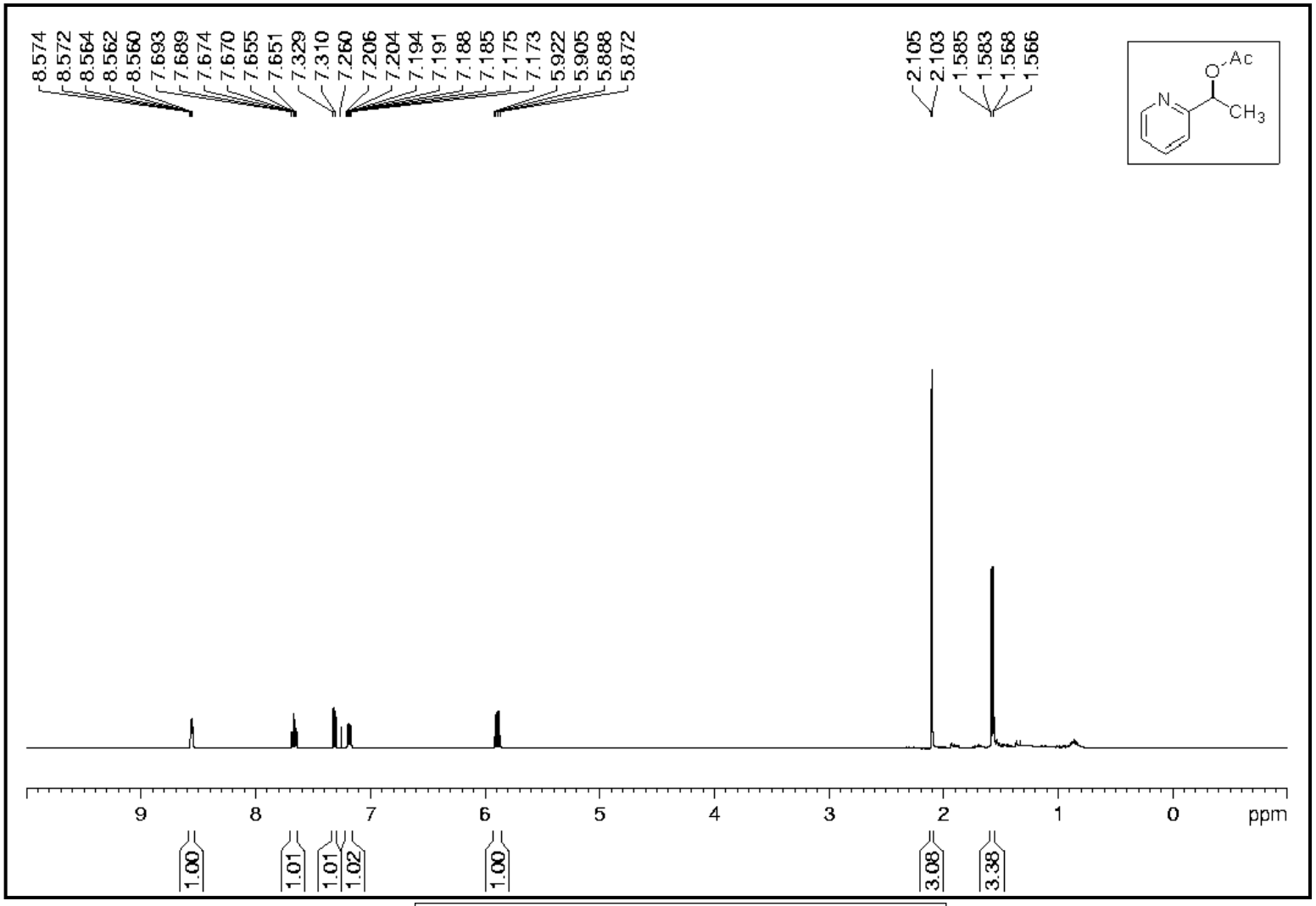

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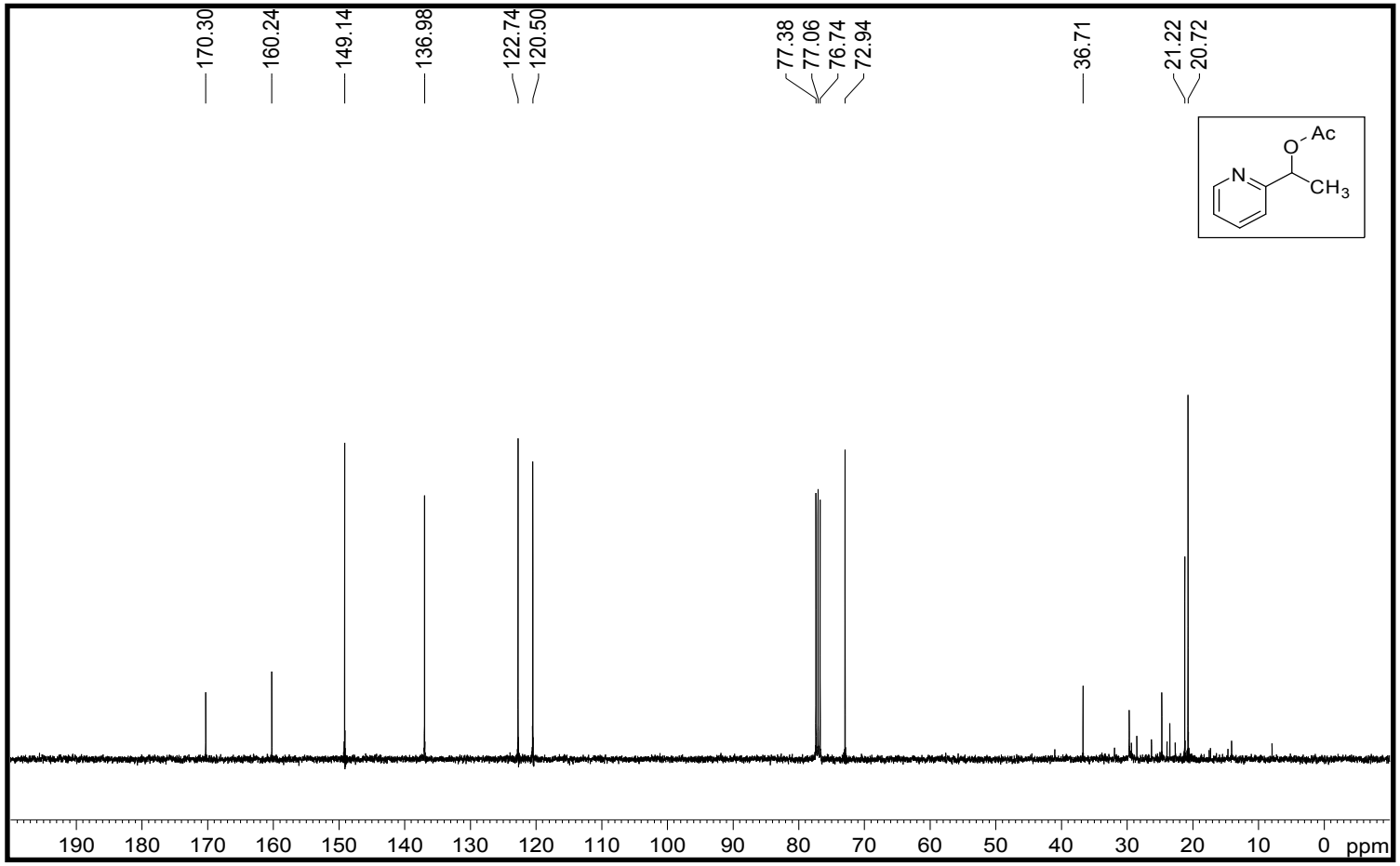
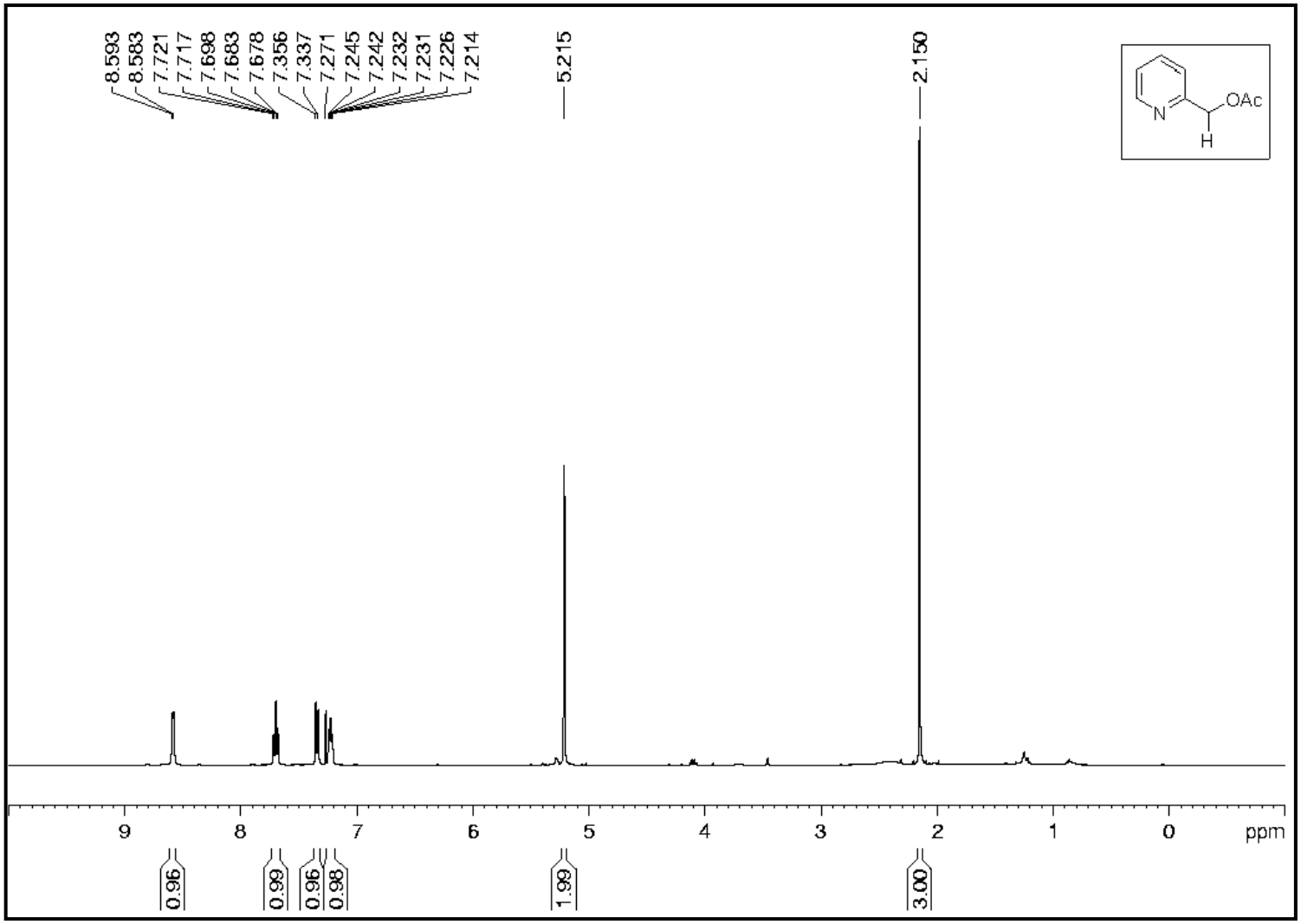
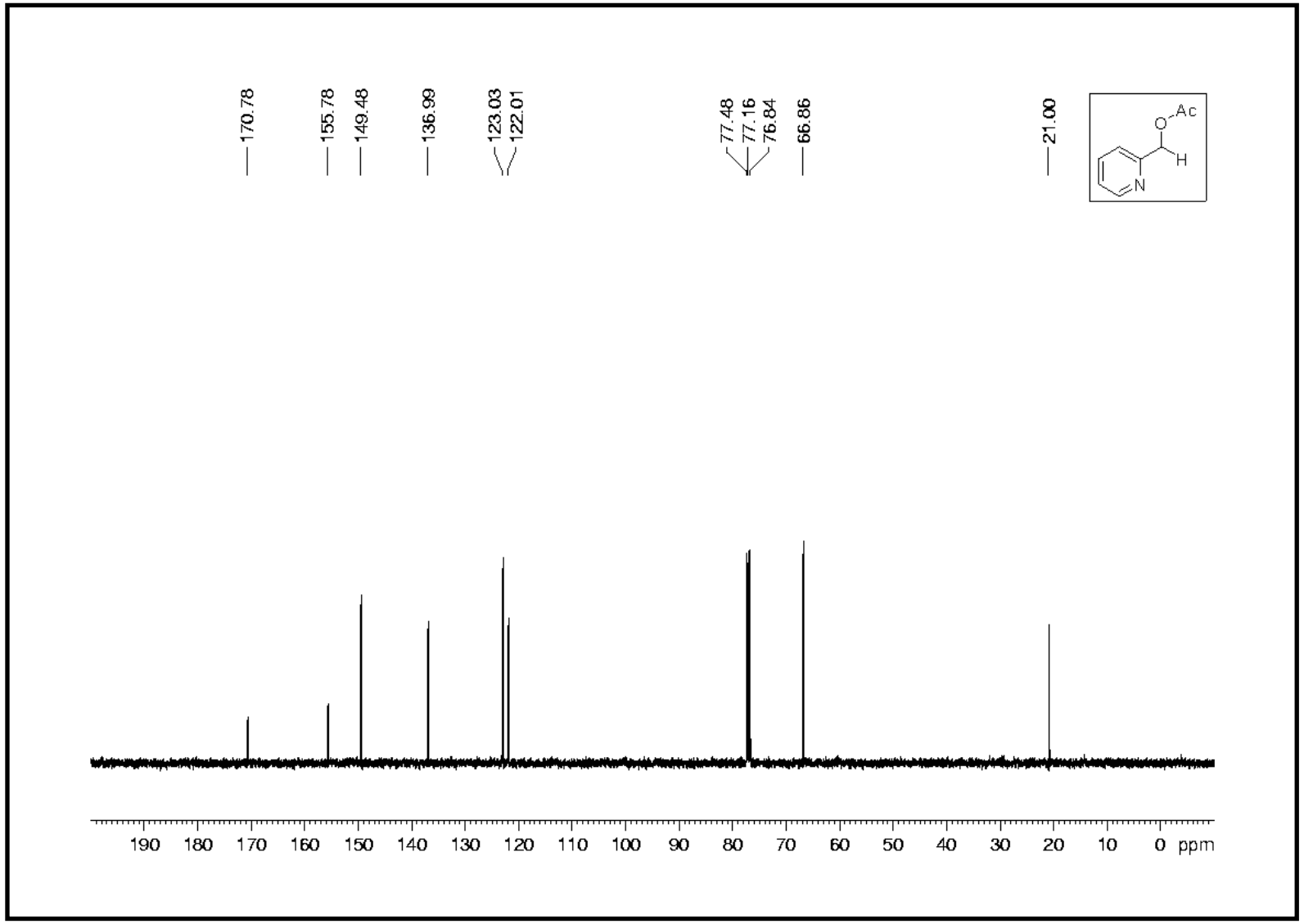


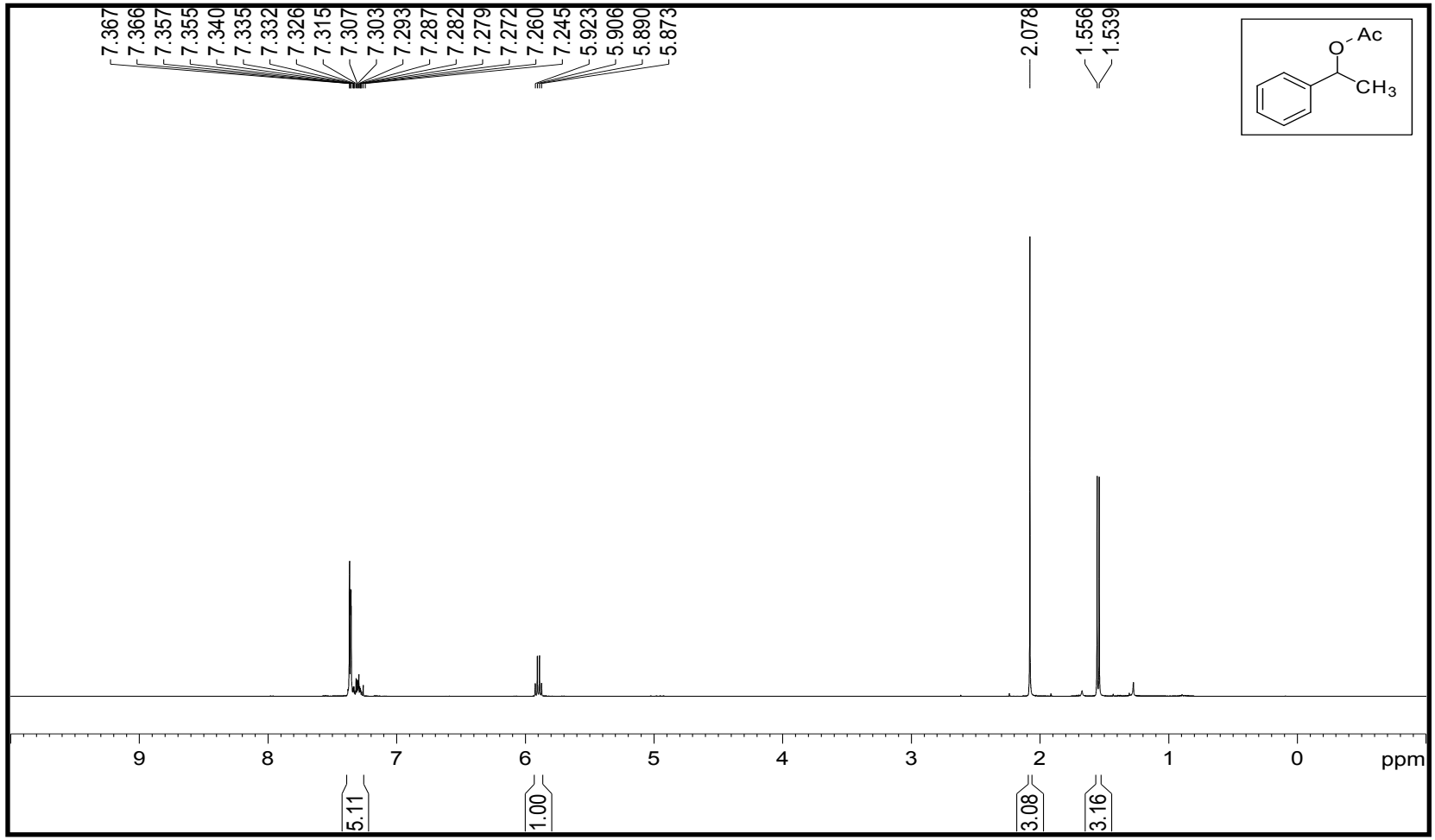
100 MHz ^{13}C NMR spectrum of **8a** in $CDCl_3$



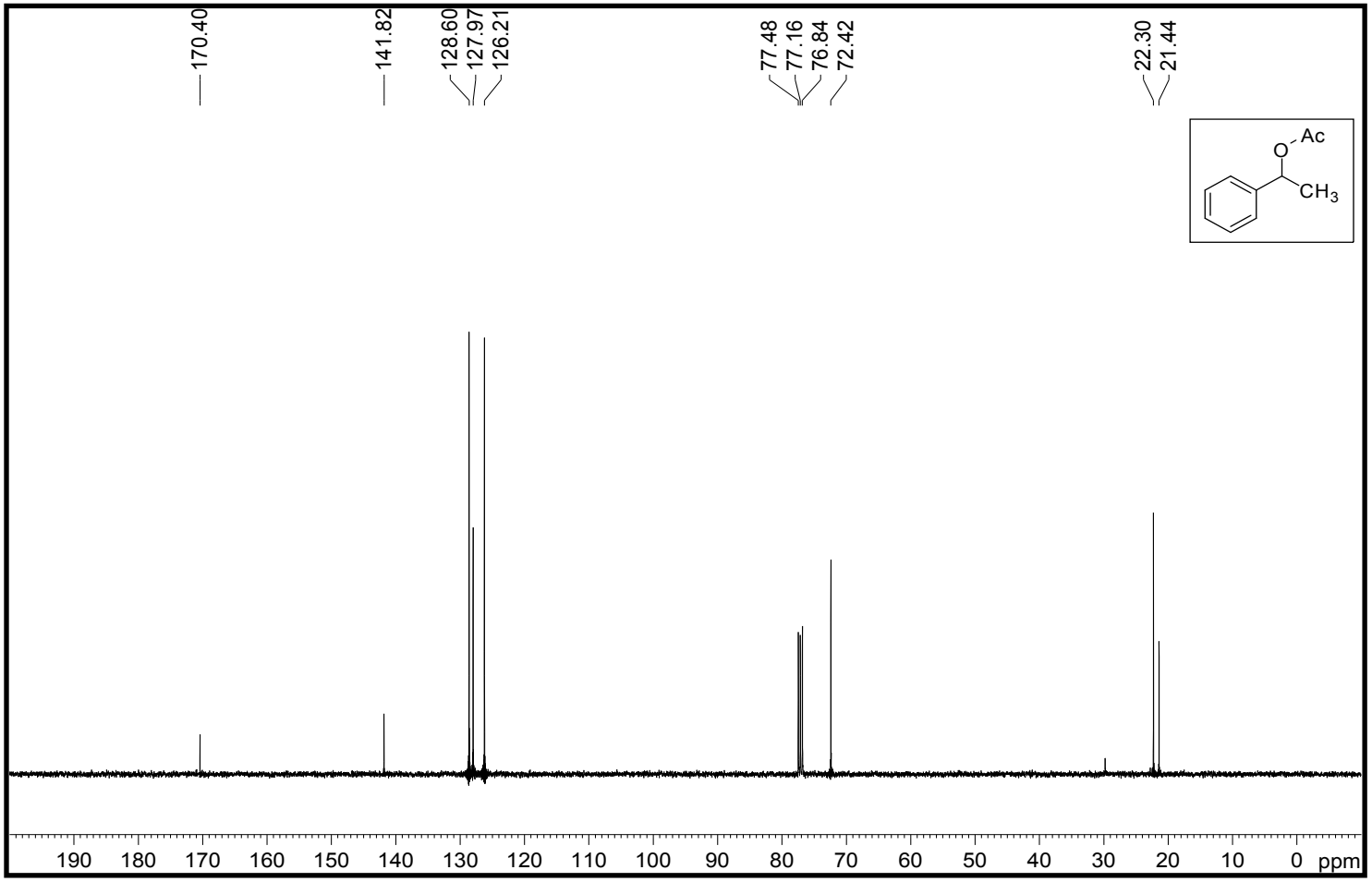
400 MHz ^{1}H NMR spectrum of **8b** in $CDCl_3$



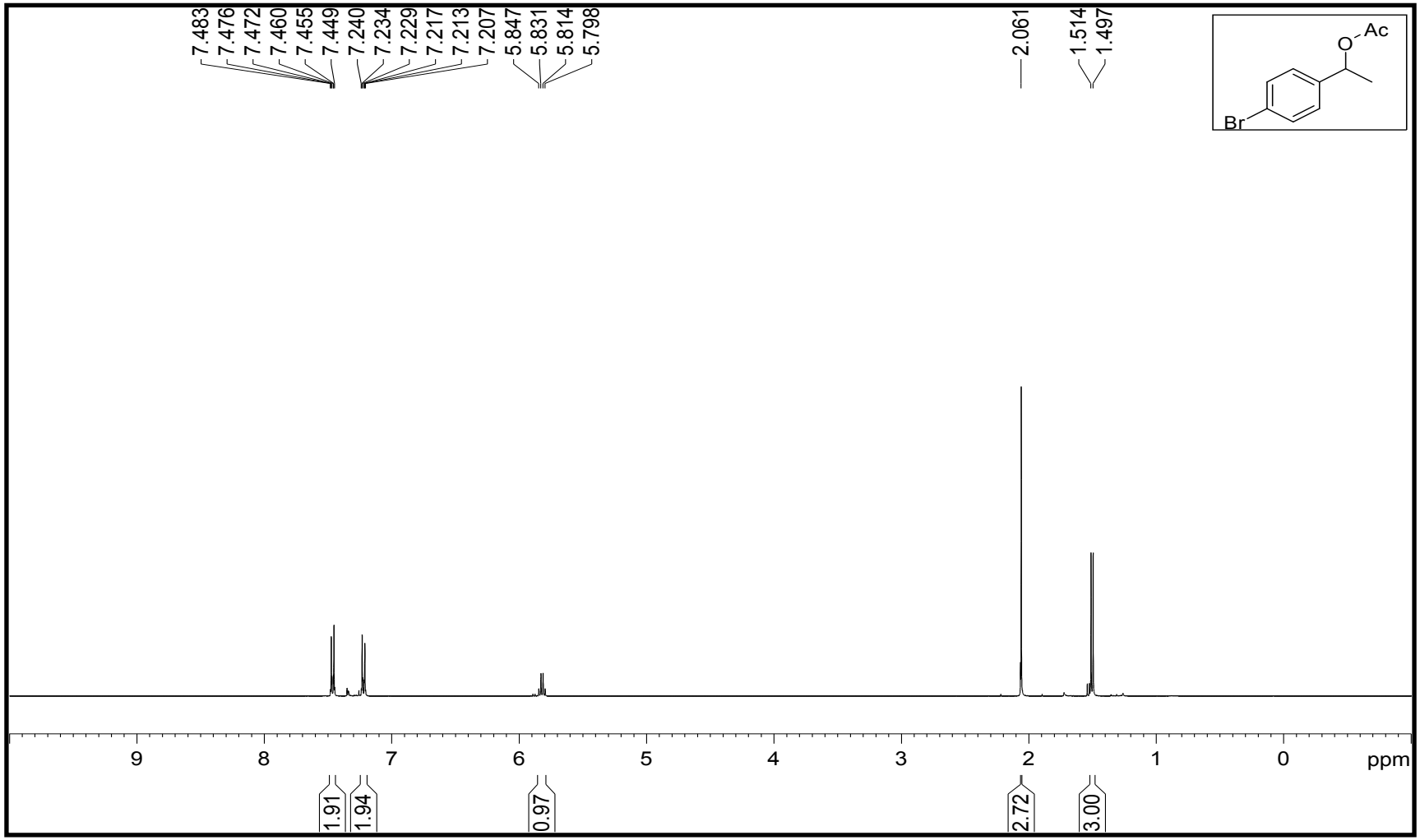
100 MHz ^{13}C NMR spectrum of **8b** in $CDCl_3$



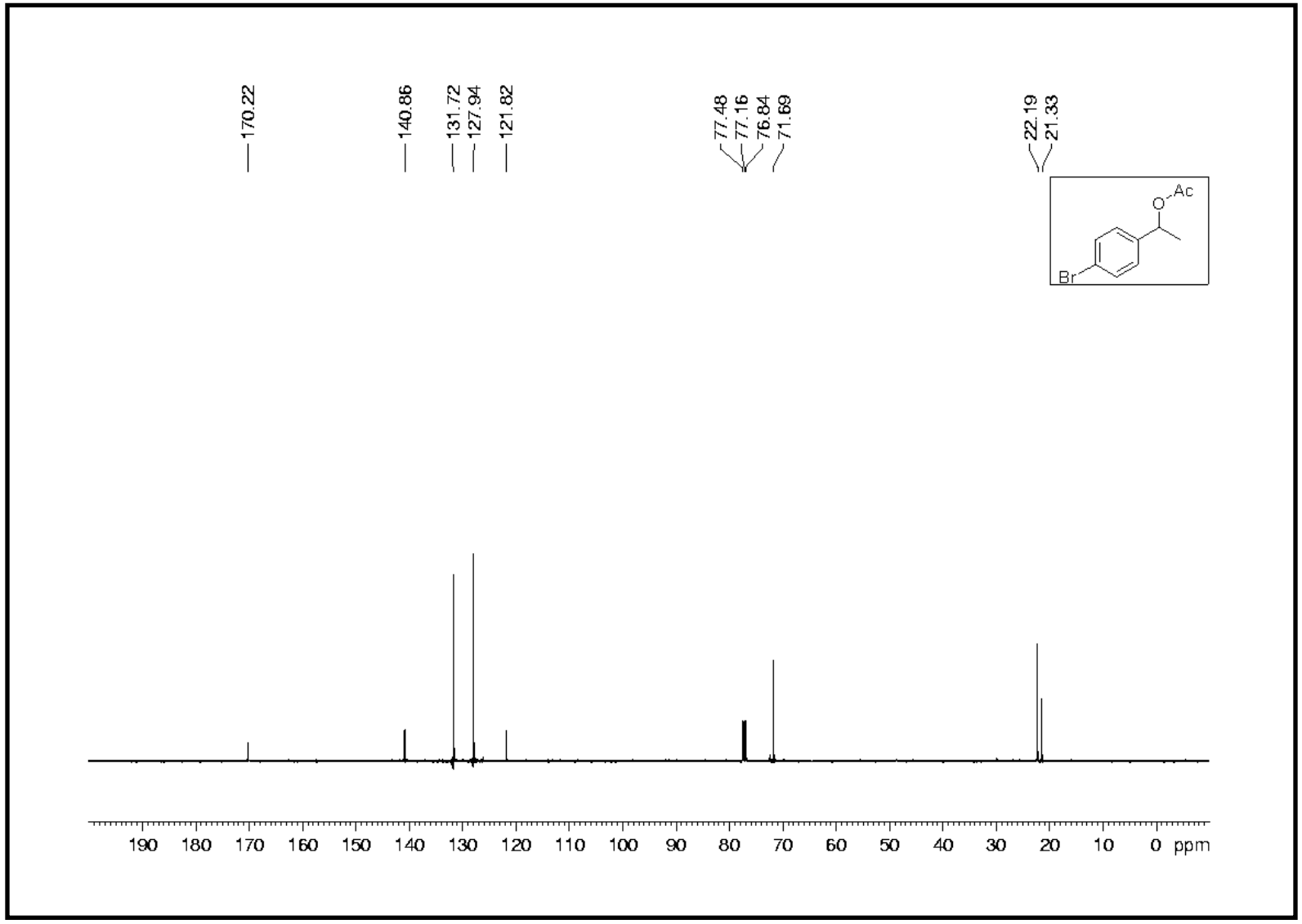
400 MHz ^{1}H NMR spectrum of **8c** in $CDCl_3$



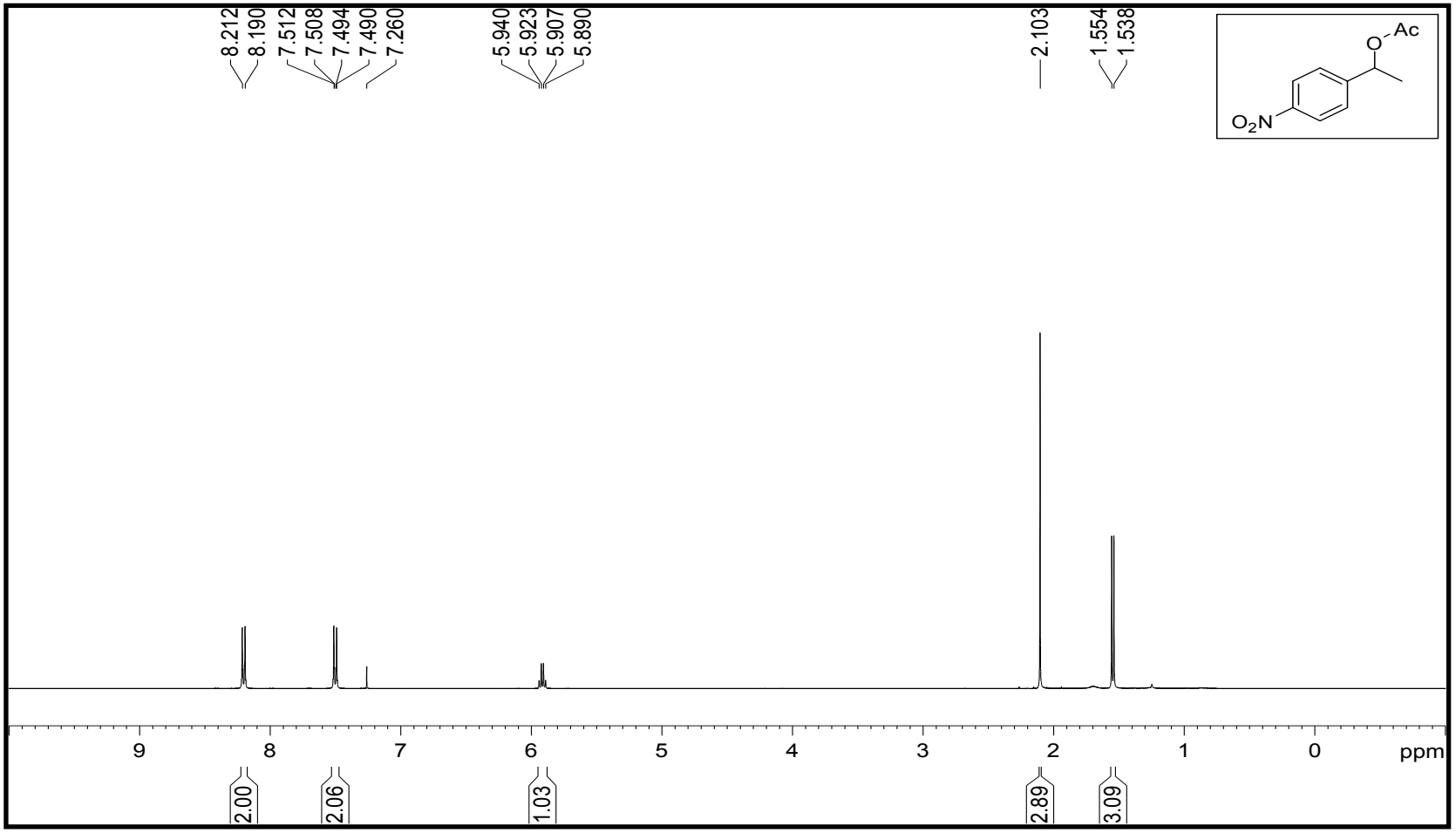
100 MHz ^{13}C NMR spectrum of **8c** in $CDCl_3$



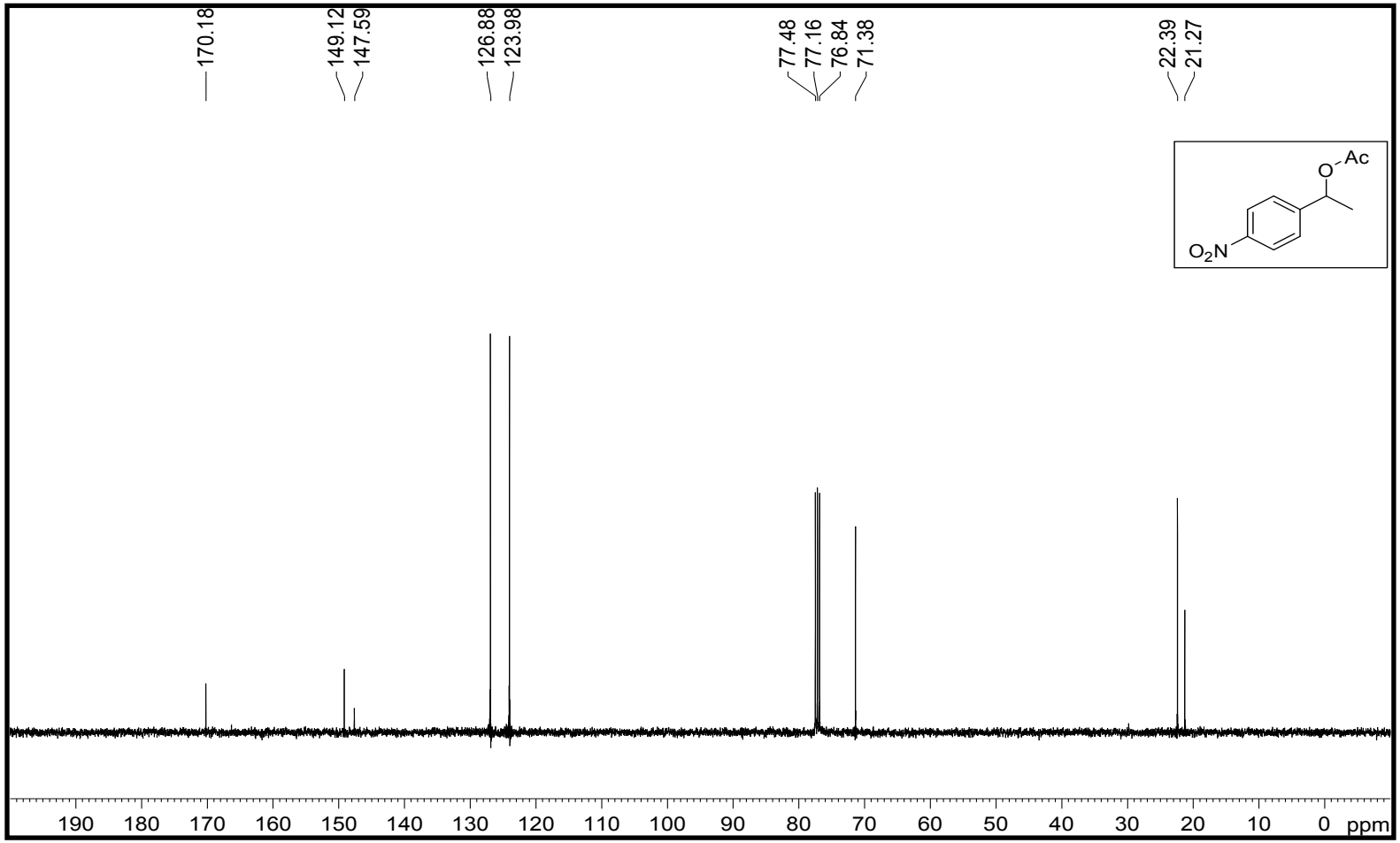
400 MHz ^{1}H NMR spectrum of **8d** in $CDCl_3$



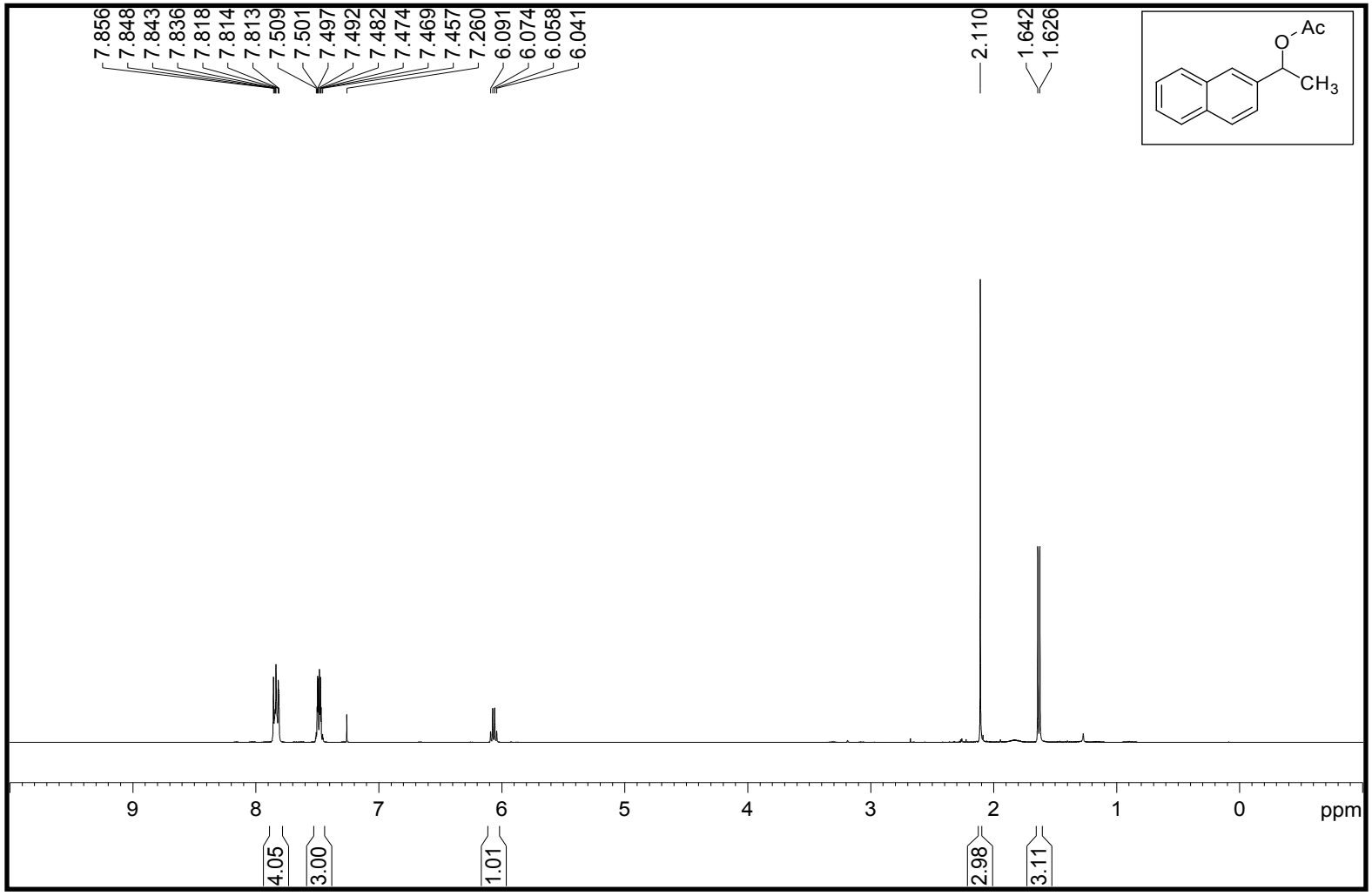
100 MHz ^{13}C NMR spectrum of **8d** in $CDCl_3$



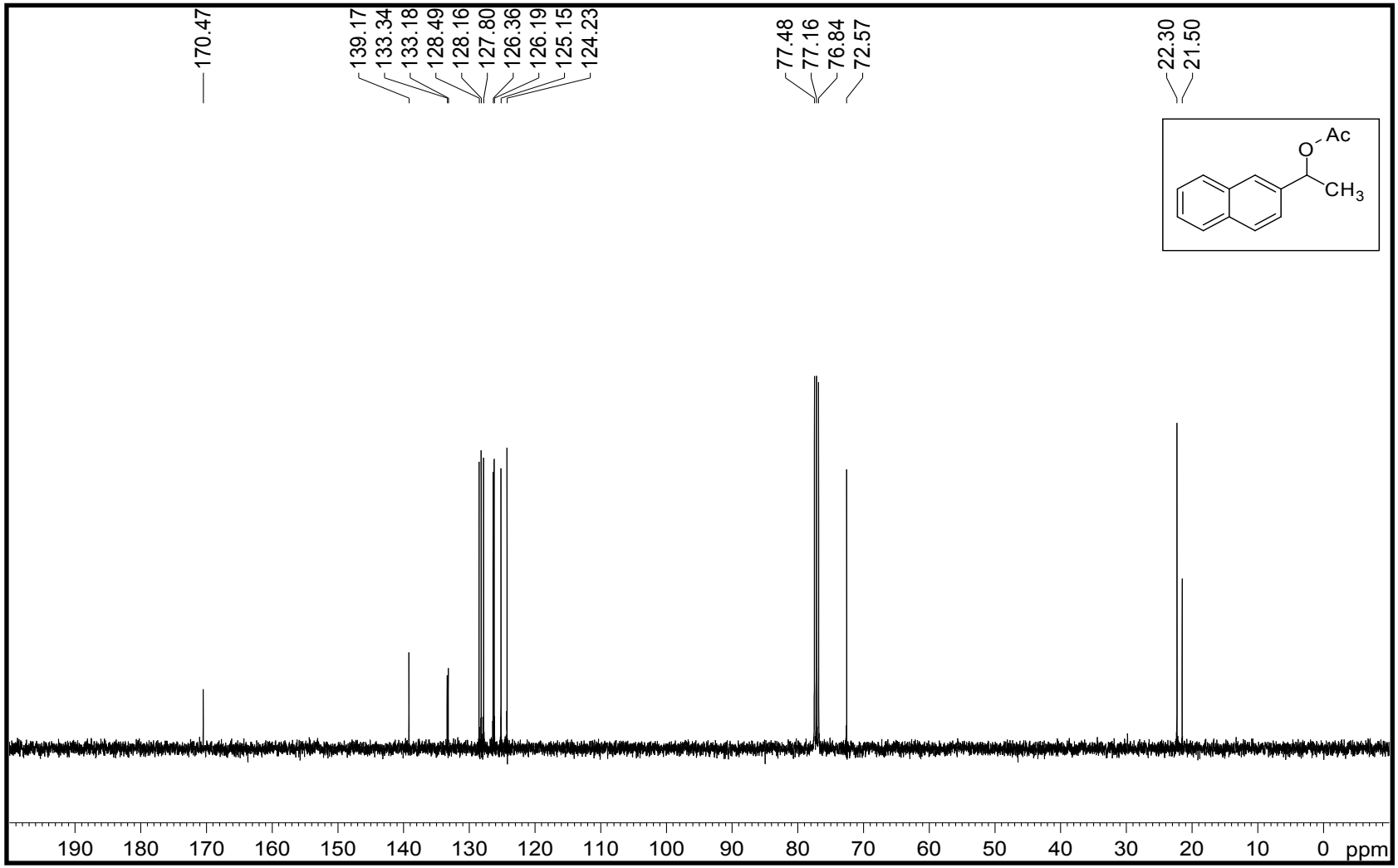
400 MHz ^{1}H NMR spectrum of **8e** in $CDCl_3$



100 MHz ^{13}C NMR spectrum of **8e** in $CDCl_3$



400 MHz ^{1}H NMR spectrum of **8f** in $CDCl_3$



100 MHz ^{13}C NMR spectrum of **8f** in $CDCl_3$