Supporting Information

For

Highly efficient palladium(II) hydrazone based catalysts for the Suzuki coupling reaction in aqueous medium

Subramanian Muthumari and Rengan Ramesh *

School of Chemistry, Bharathidasan University, Tiruchirappalli 620 024, Tamil Nadu, India

*To whom correspondence should be made: Tel: +91-431-2407053, Fax: +91-431-2407045, E-mail: ramesh_bdu@yahoo.com

Supporting Information

1. Experimental Section

Materials

$[PdCl_2(PPh_3)_2]$, benzhydrazide, Thiophene-2-aldehyde and substrates for the Suzuki- Miyaura coupling reaction were purchased from Sigma Aldrich and used without further purification. All other reagents used were purchased from commercial sources and used as received. The solvents were distilled following the standard procedures.[1] The benzhydrazone ligand was prepared as reported in the literature.[2]

Physical Measurements and Instrumentation

Melting point was recorded in the Boetius micro heating table and is uncorrected. The microanalysis of carbon, hydrogen, nitrogen and sulfur was recorded by Elementar Vario EL III analyzer. Infrared spectrum of the complex was recorded in KBr pellets with a Perkin-Elmer 597 spectrophotometer in the range 4000-400 cm^{-1}. The electronic spectrum of the complex in DMF solution was recorded with a Cary 300 Bio UV–Vis Varian spectrophotometer in the range 800-260 nm using cuvettes of 1 cm path length. The ^1H and ^{13}C and spectra were recorded with Bruker 400 MHz spectrometer at frequencies of 400, 100 and 160 MHz respectively. Chemical shifts are given in ppm referenced to the deuterated solvents.

2.NMR spectrum of complexes

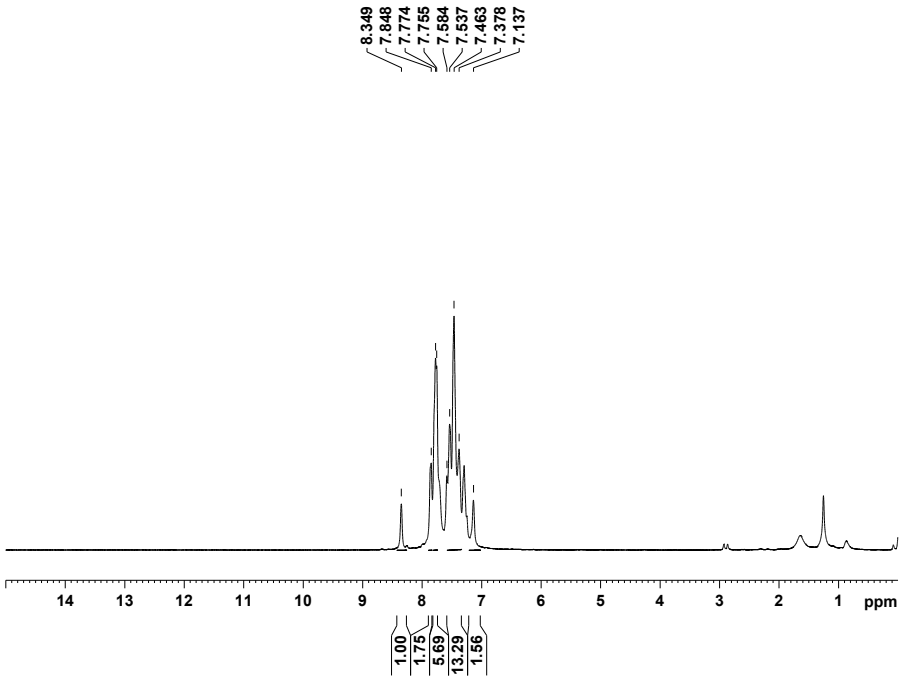
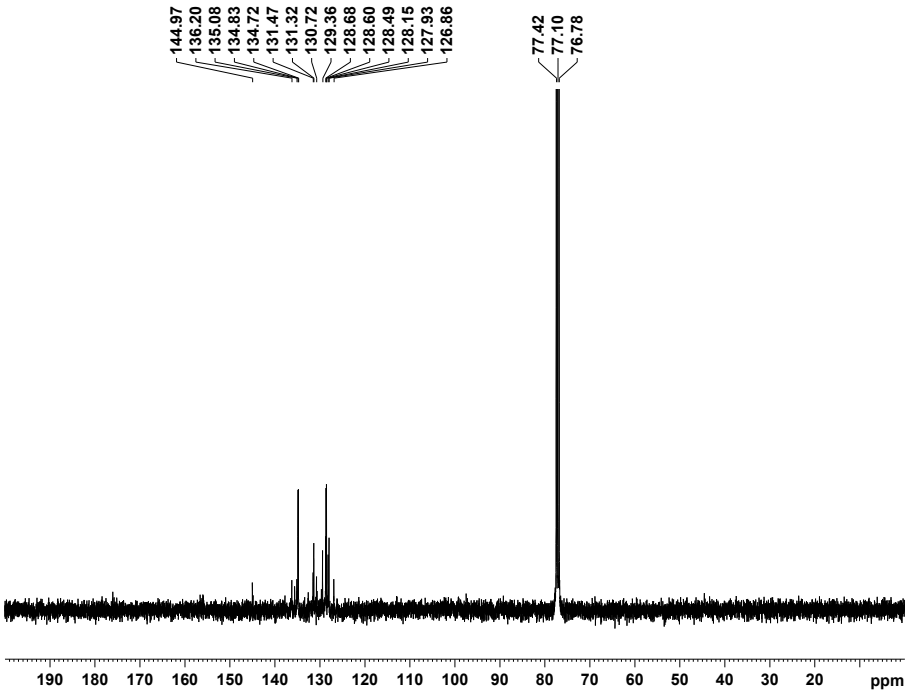


Figure S1. ^1H NMR spectrum of complex **1**



^{13}C NMR spectrum of complex **1**

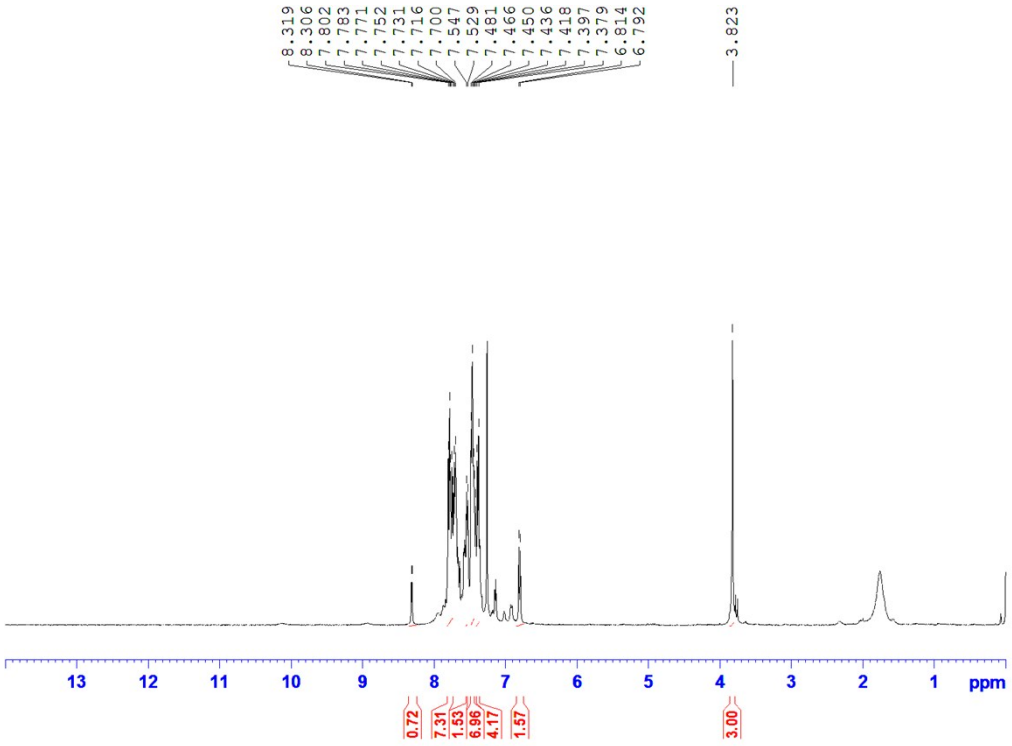
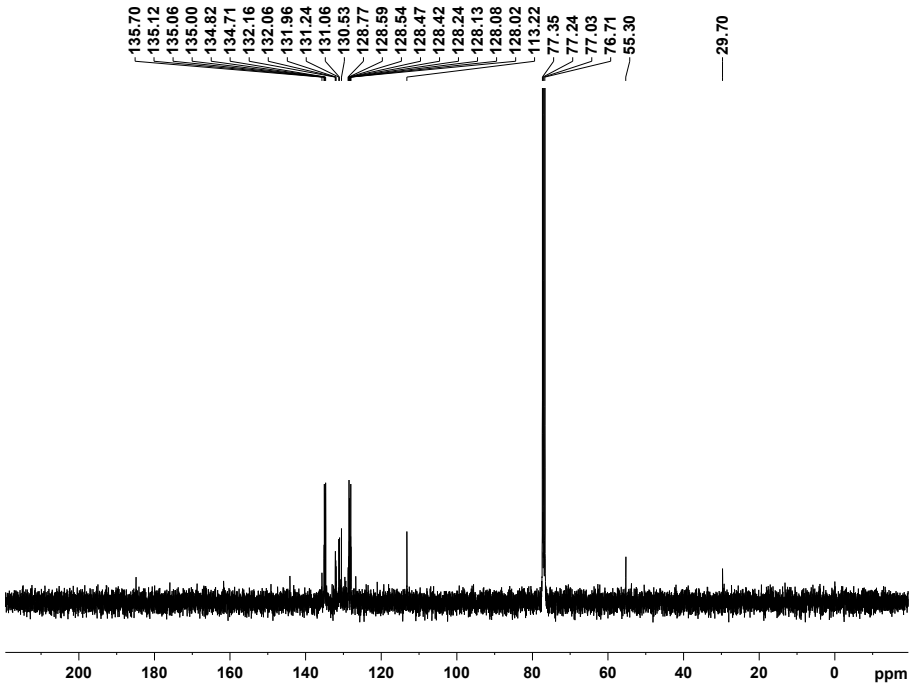


Figure S2. ^{1}H NMR spectrum of complex **2**



^{13}C NMR spectrum of complex **2**

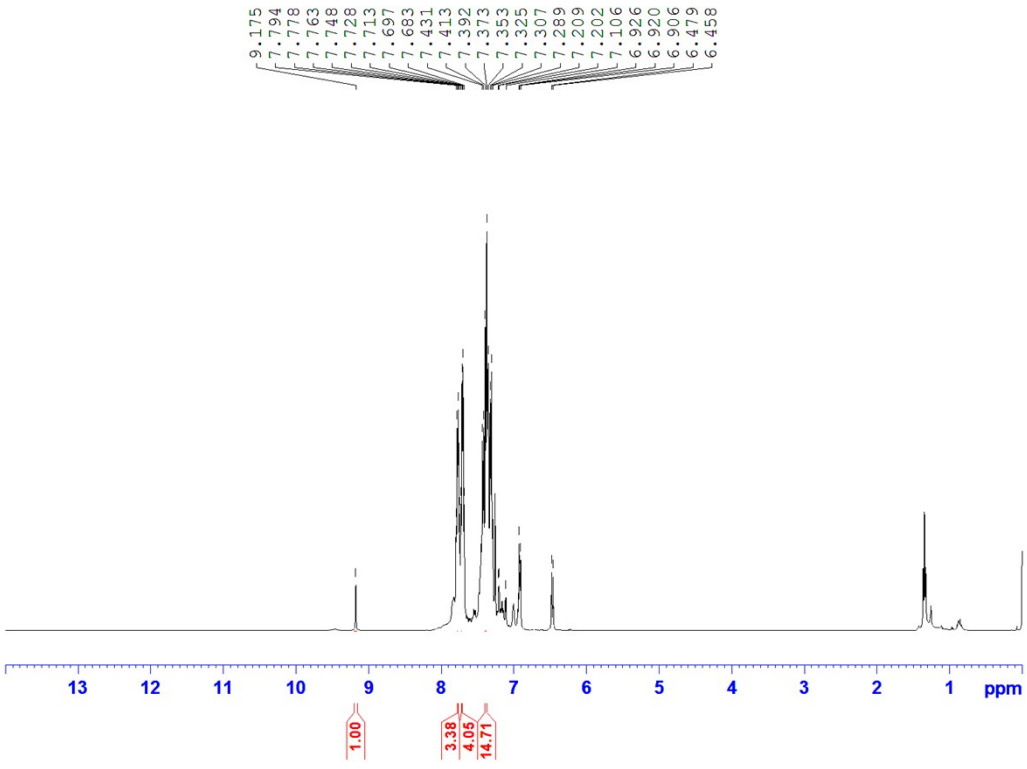
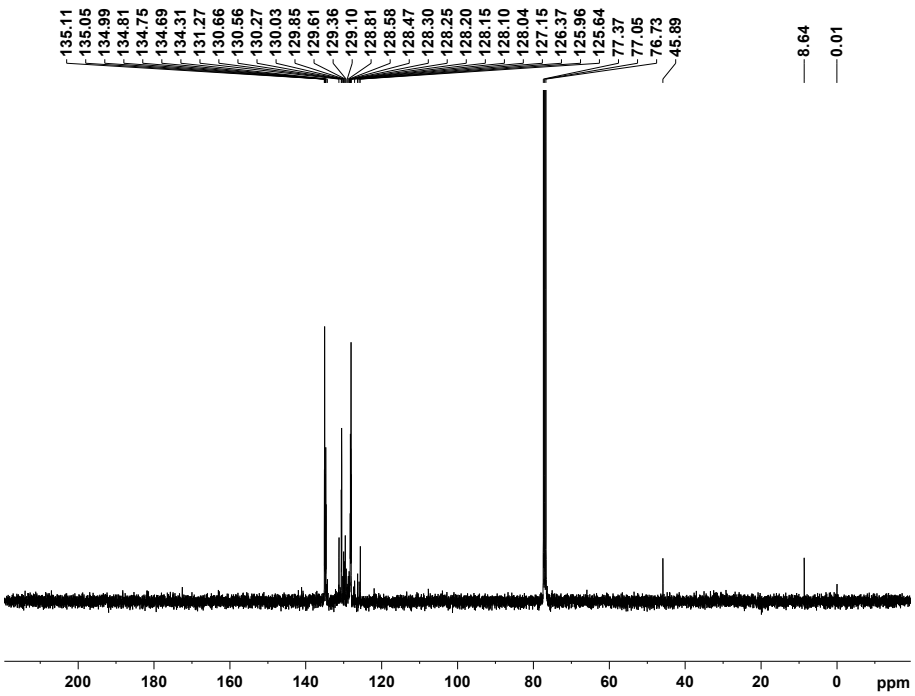


Figure S3. ^{1}H NMR spectrum of complex **3**



^{13}C NMR spectrum of complex **3**

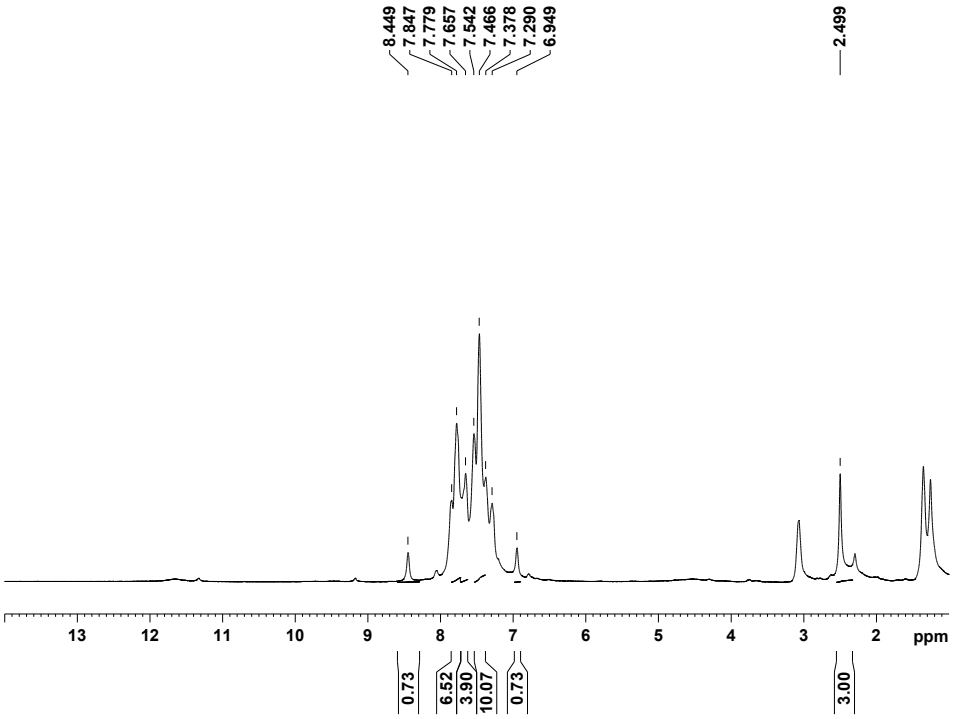
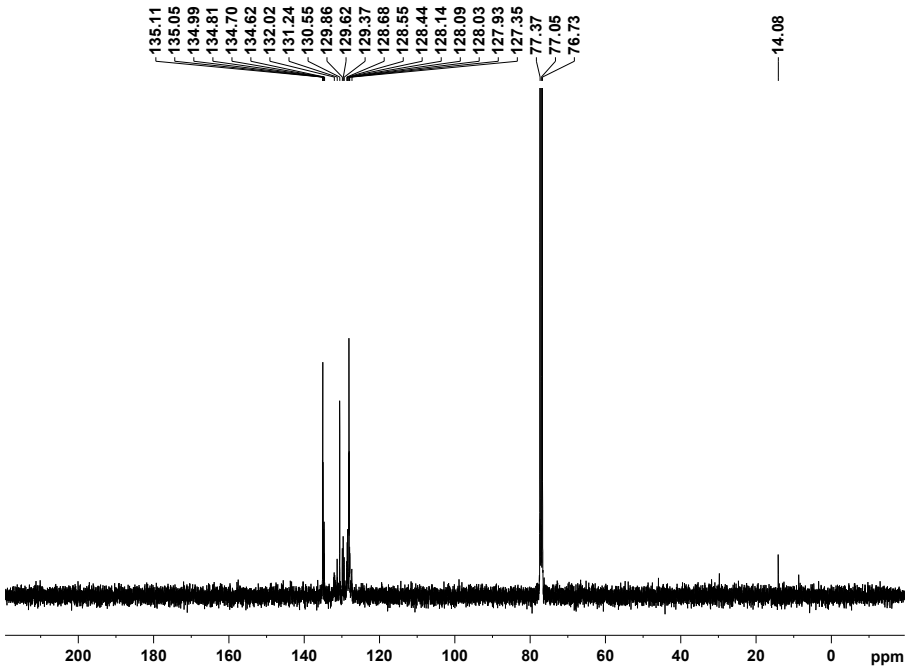


Figure S4. ^{1}H NMR spectrum of complex **4**



^{13}C NMR spectrum of complex **4**

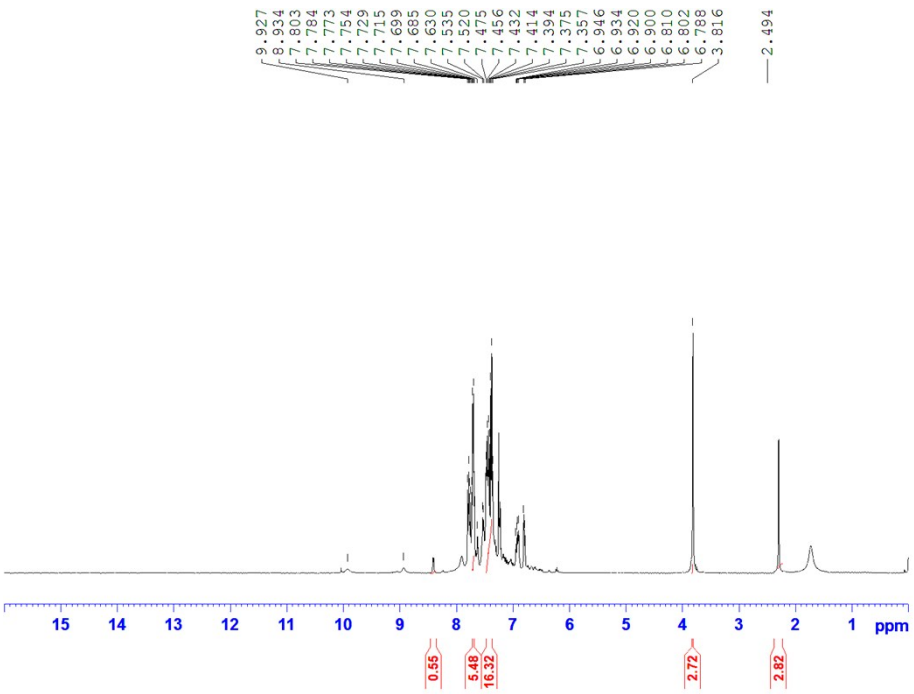
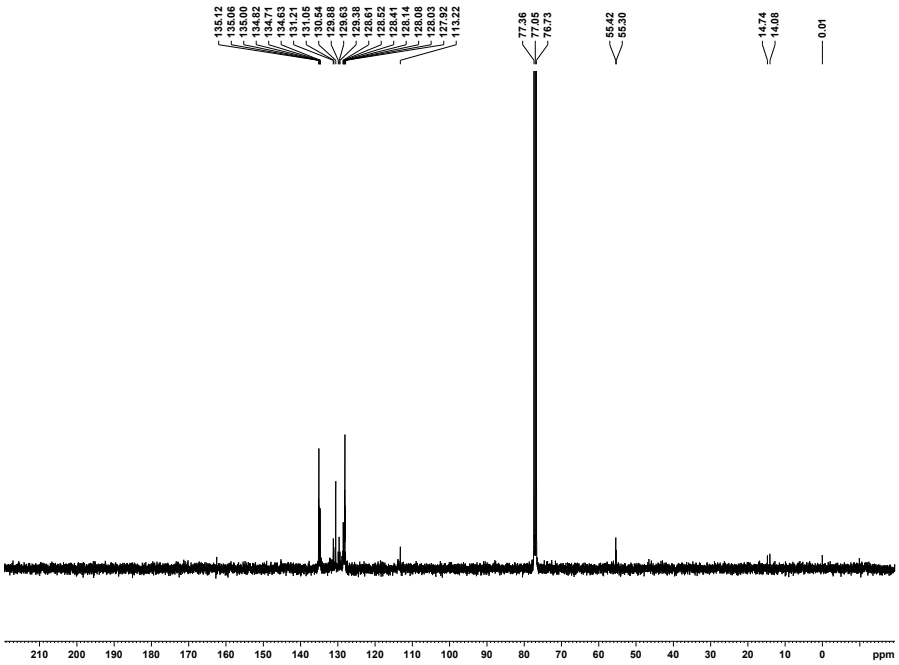


Figure S5. ^{1}H NMR spectrum of complex **5**



^{13}C NMR spectrum of complex **5**

3. X-ray crystallography

Single crystals of the complex was obtained by the slow evaporation of DMF/Ethanol solution of the complex at room temperature. The data collection was carried out with Oxford Xcalibur single crystal X-ray diffractometer using monochromated Mo K_α radiation (kI = 0.71073 Å) at 293 K. The structure was solved by SIR92[3] and refined by full-matrix least squares on F^2 using SHELXL 97.[4] All non-hydrogen atoms were refined anisotropically and the hydrogen atoms in the structure were located from the difference Fourier map and constrained to the ideal positions in the refinement procedure. The unit cell parameters were determined by the method of difference vectors using reflections scanned from three different zones of the reciprocal lattice. The intensity data were measured using ω and φ scan with a frame width of 0.5°. Frame integration and data reduction were performed using the CRYSALIS PRO software.[5]

4. NMR data for the Suzuki-Miyaura coupling products

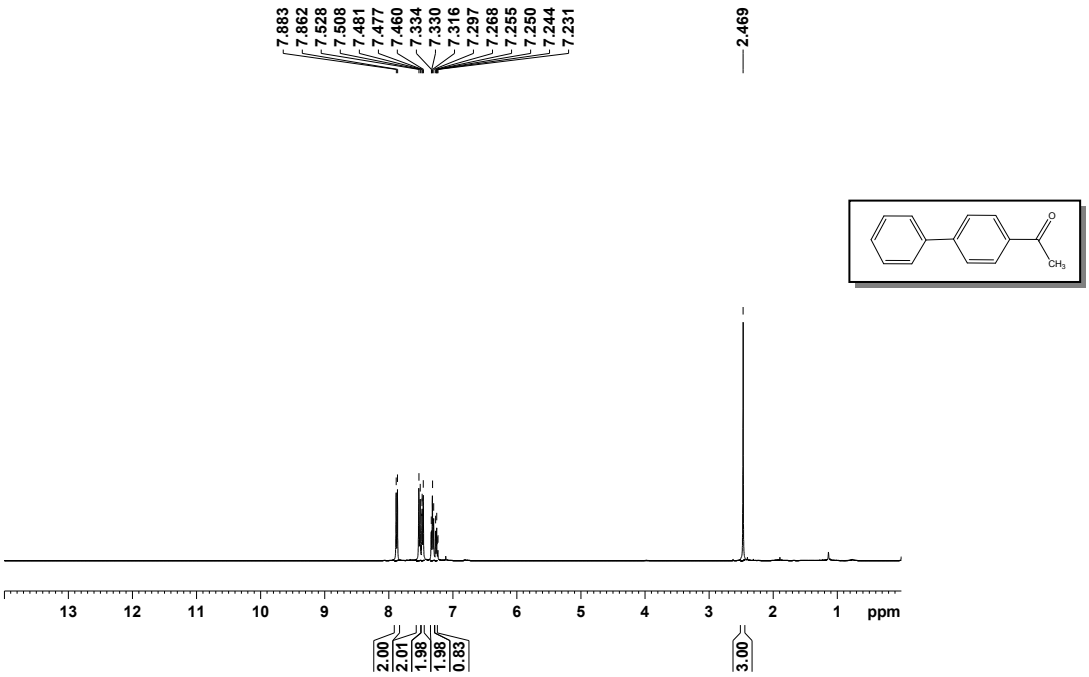
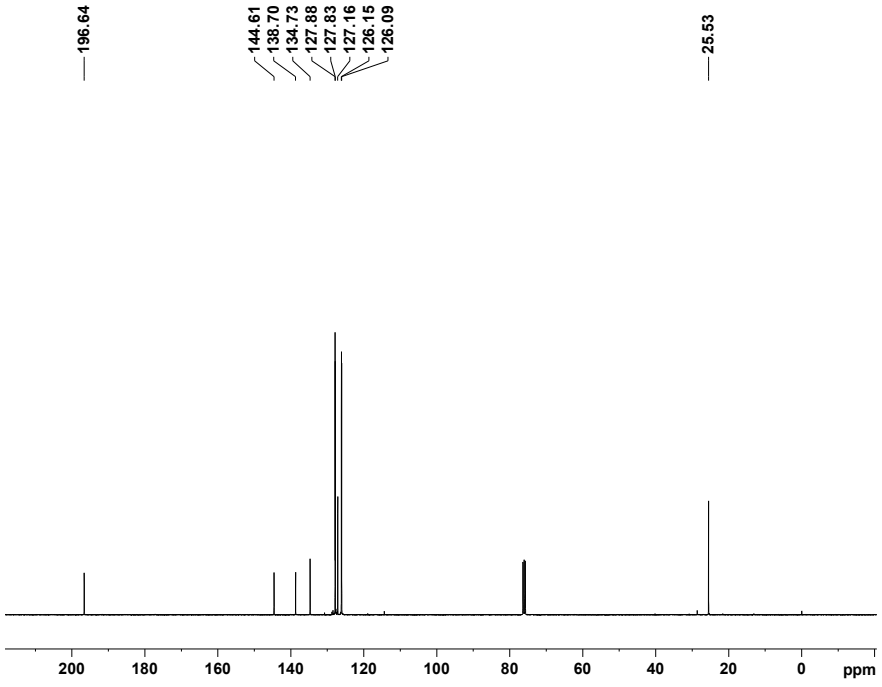


Fig. (Table 5, entry 1)



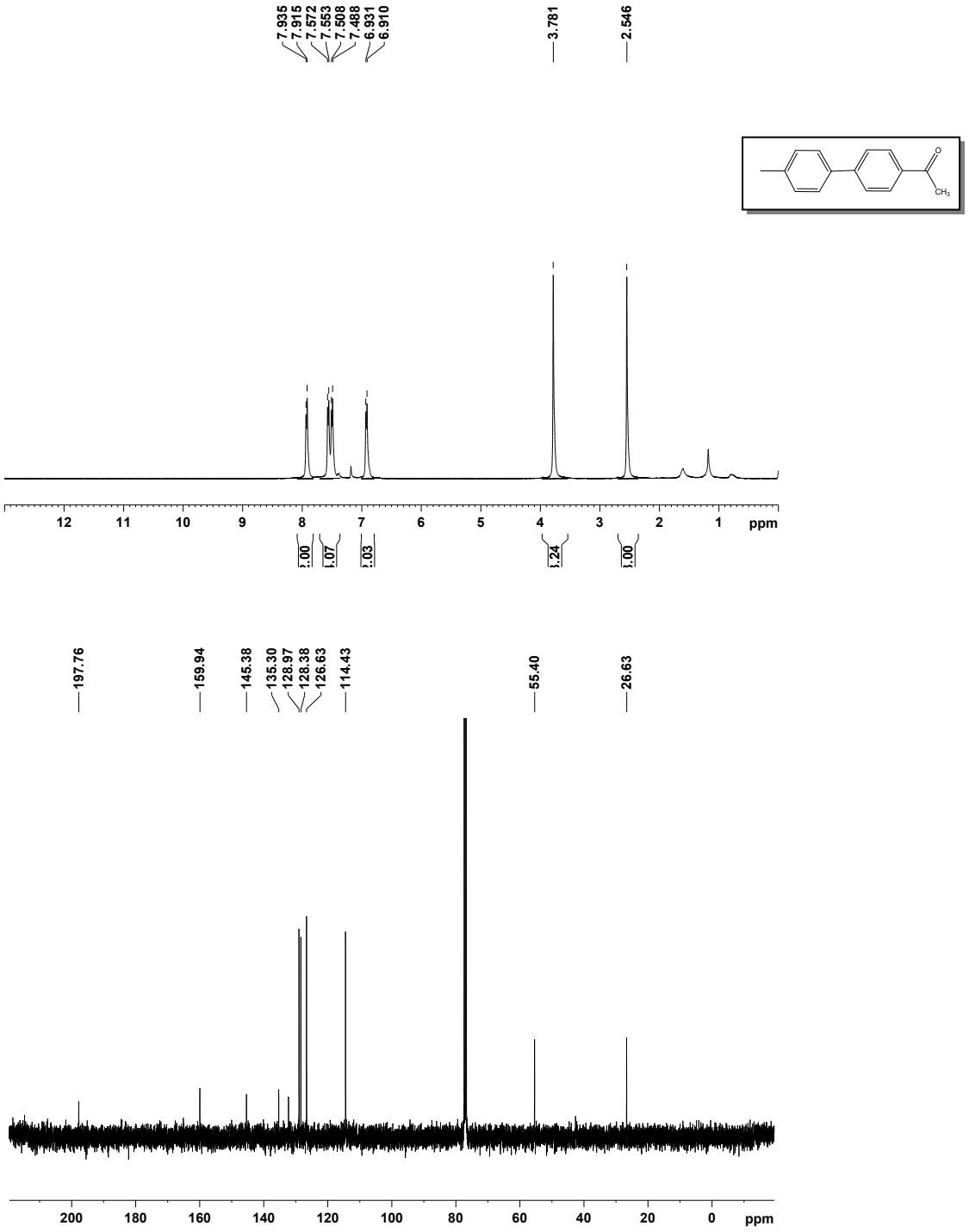


Fig. (Table 5, entry 2)

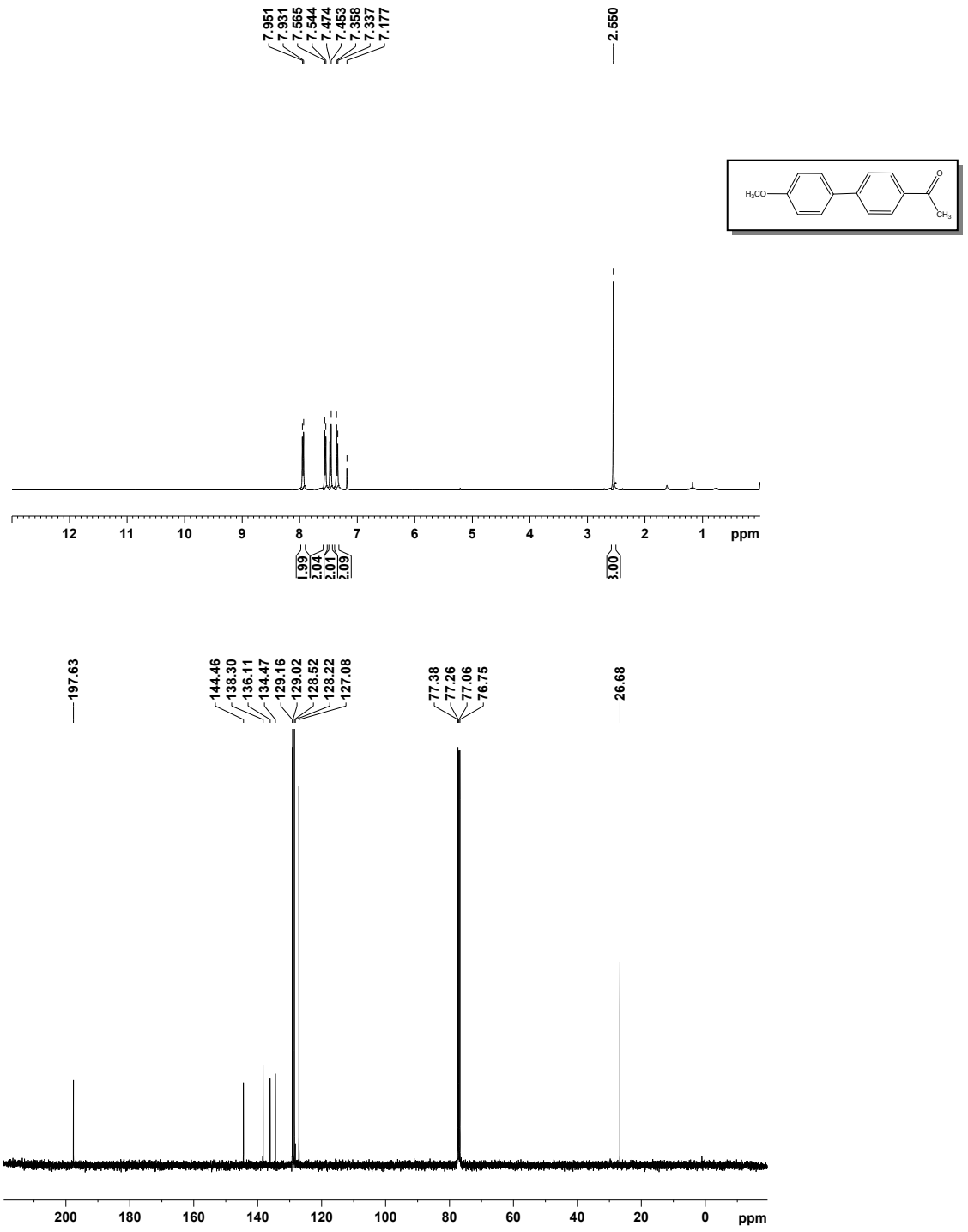


Fig. (Table 5, entry 3)

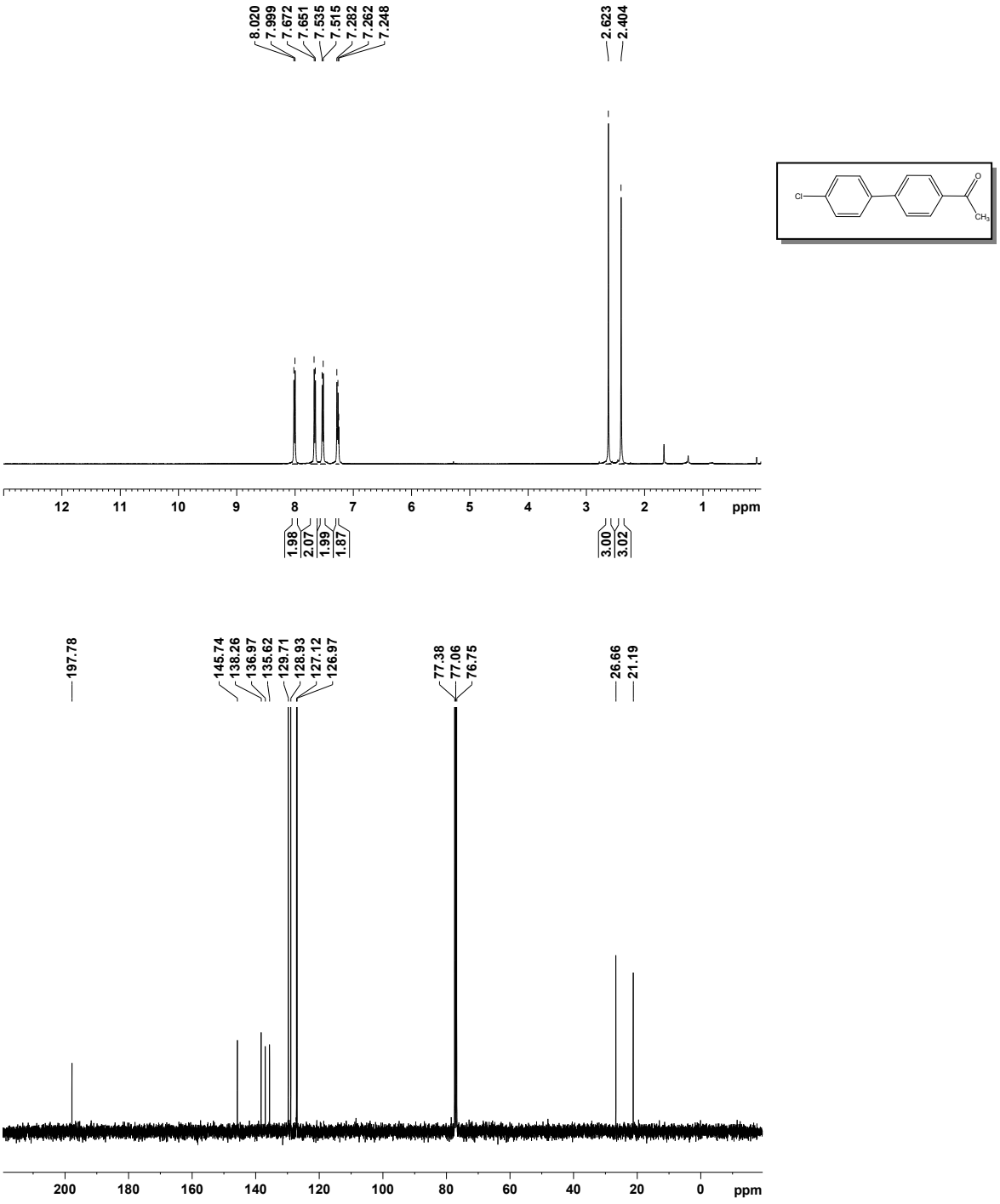


Fig. (Table 5, entry 4)

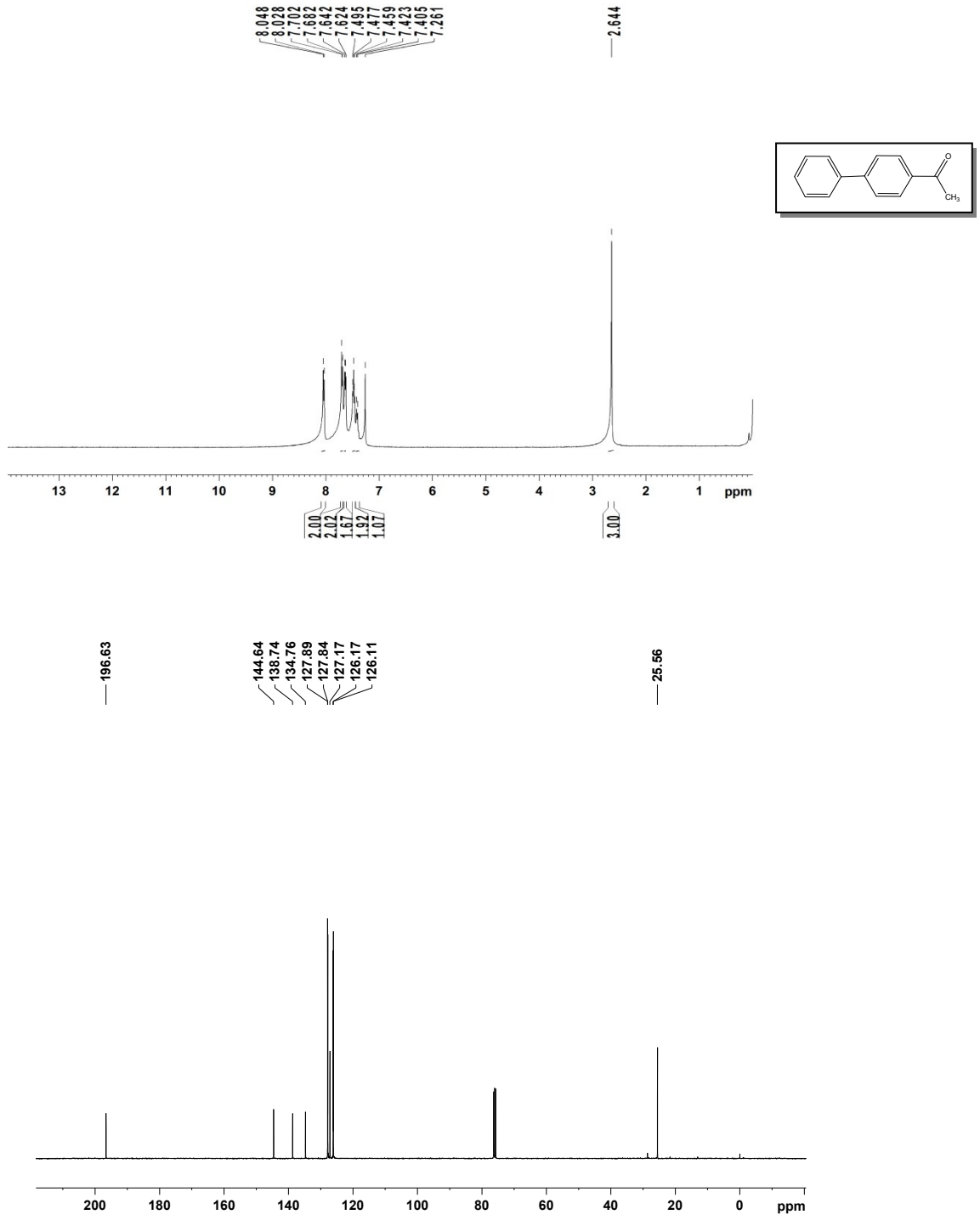
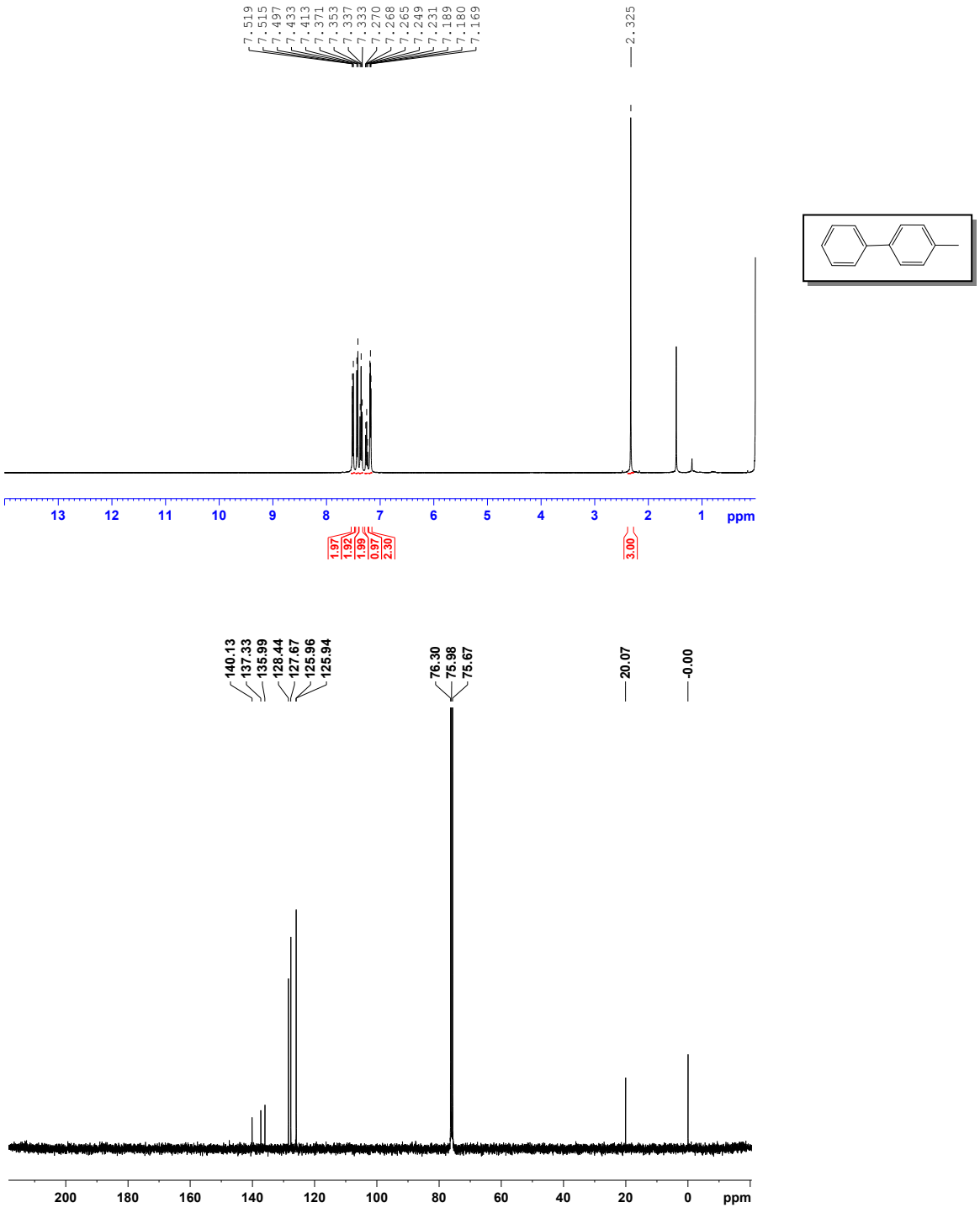


Fig. (Table 5, entry 5)



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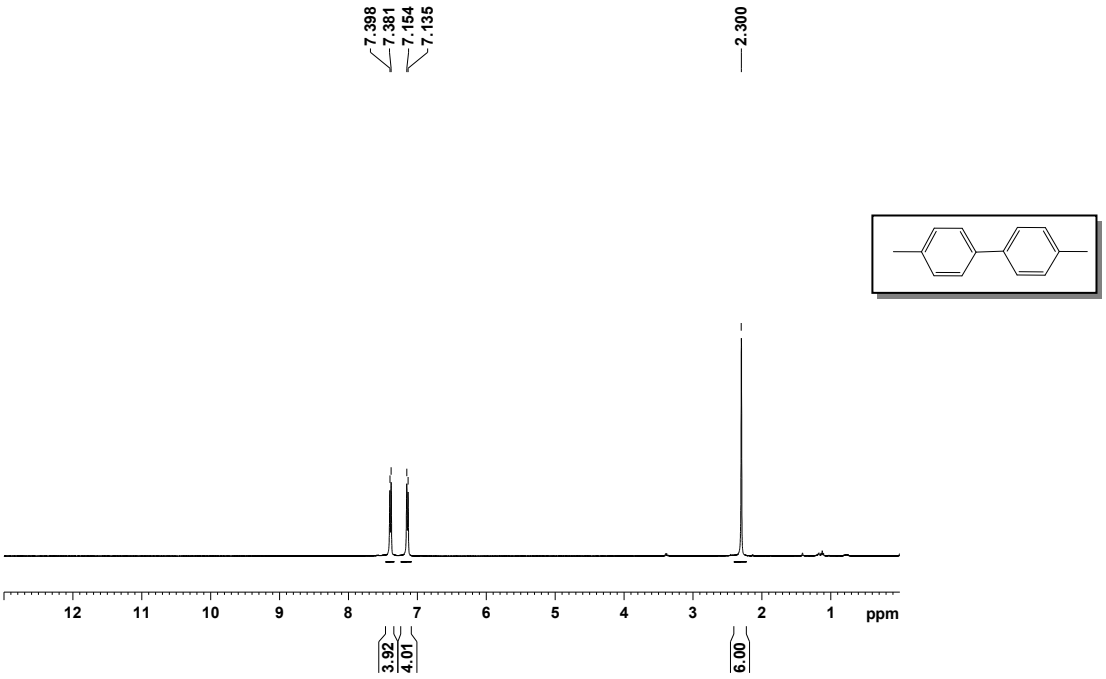

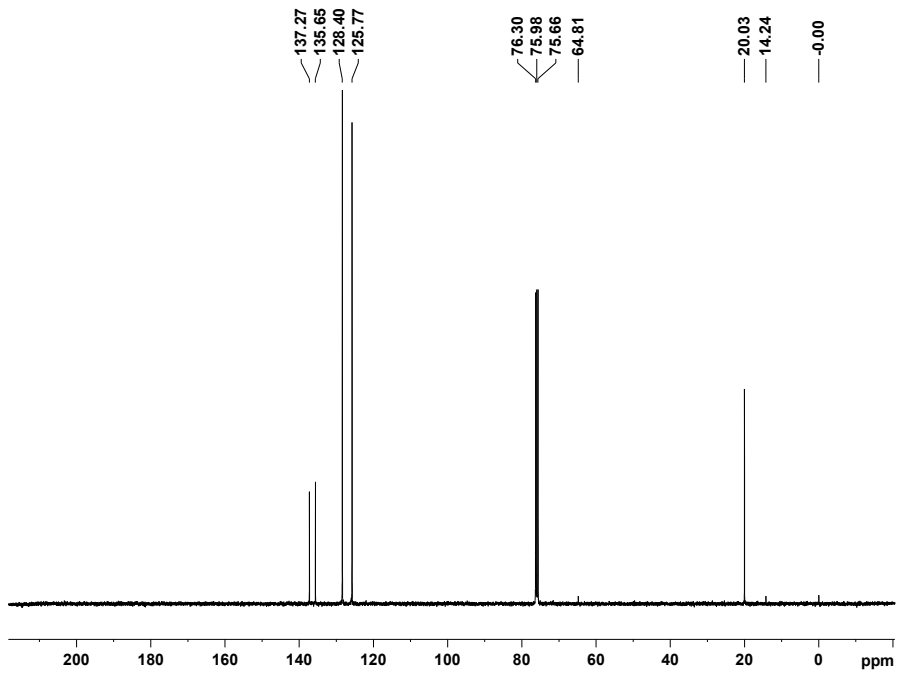

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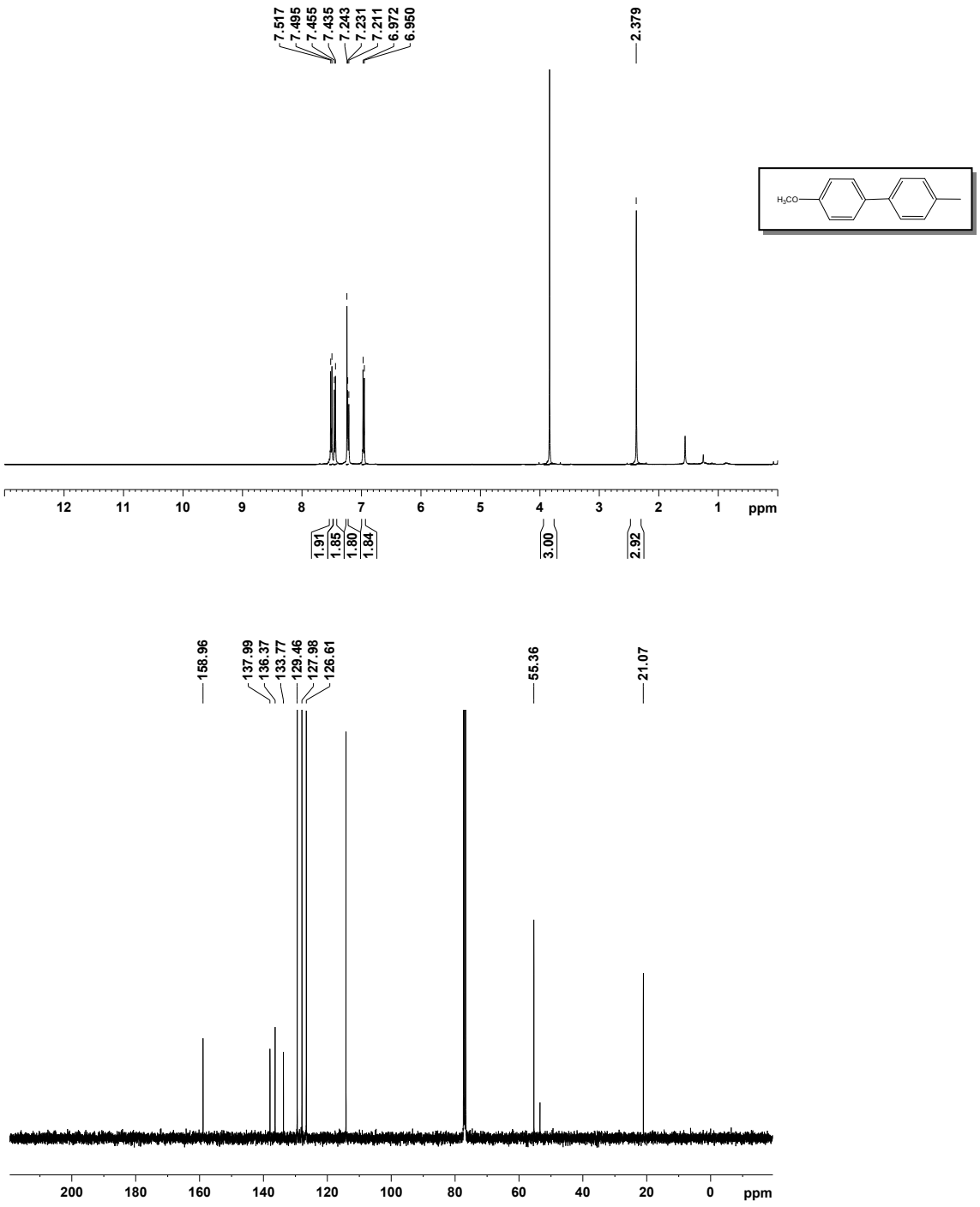

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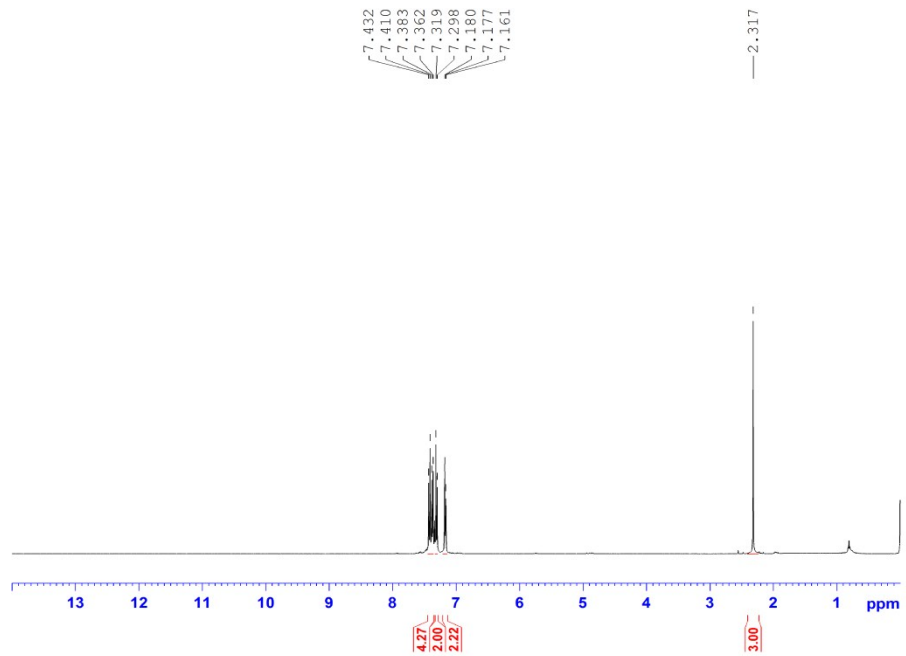

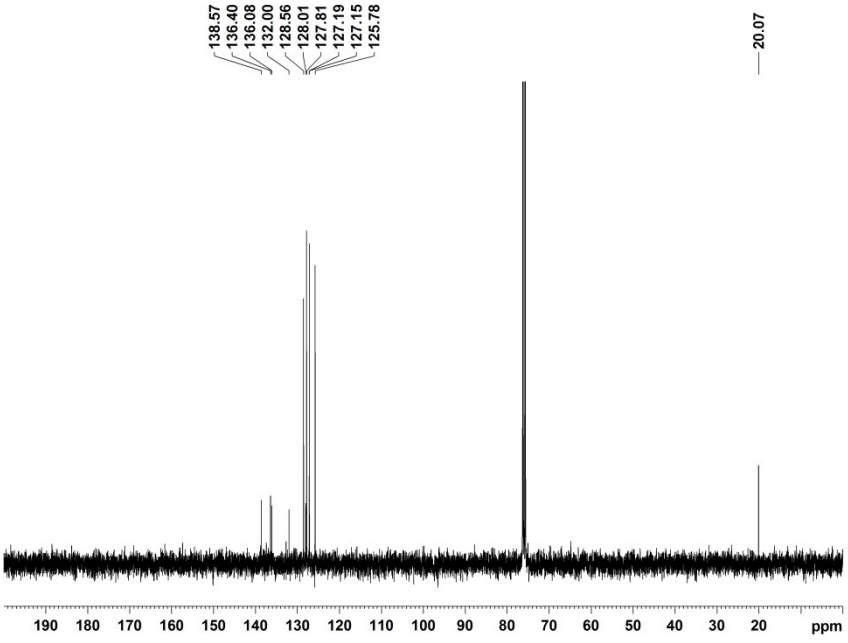

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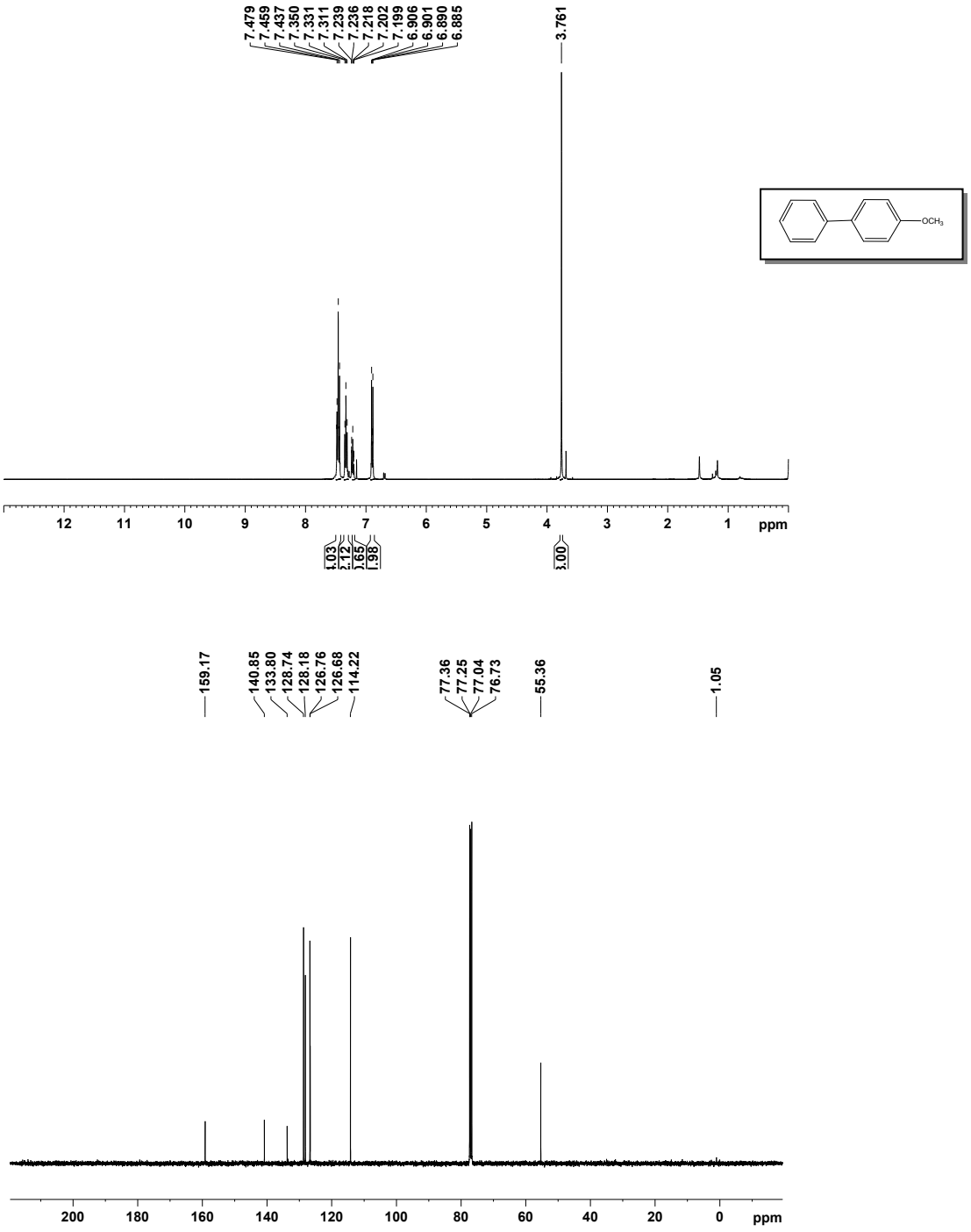

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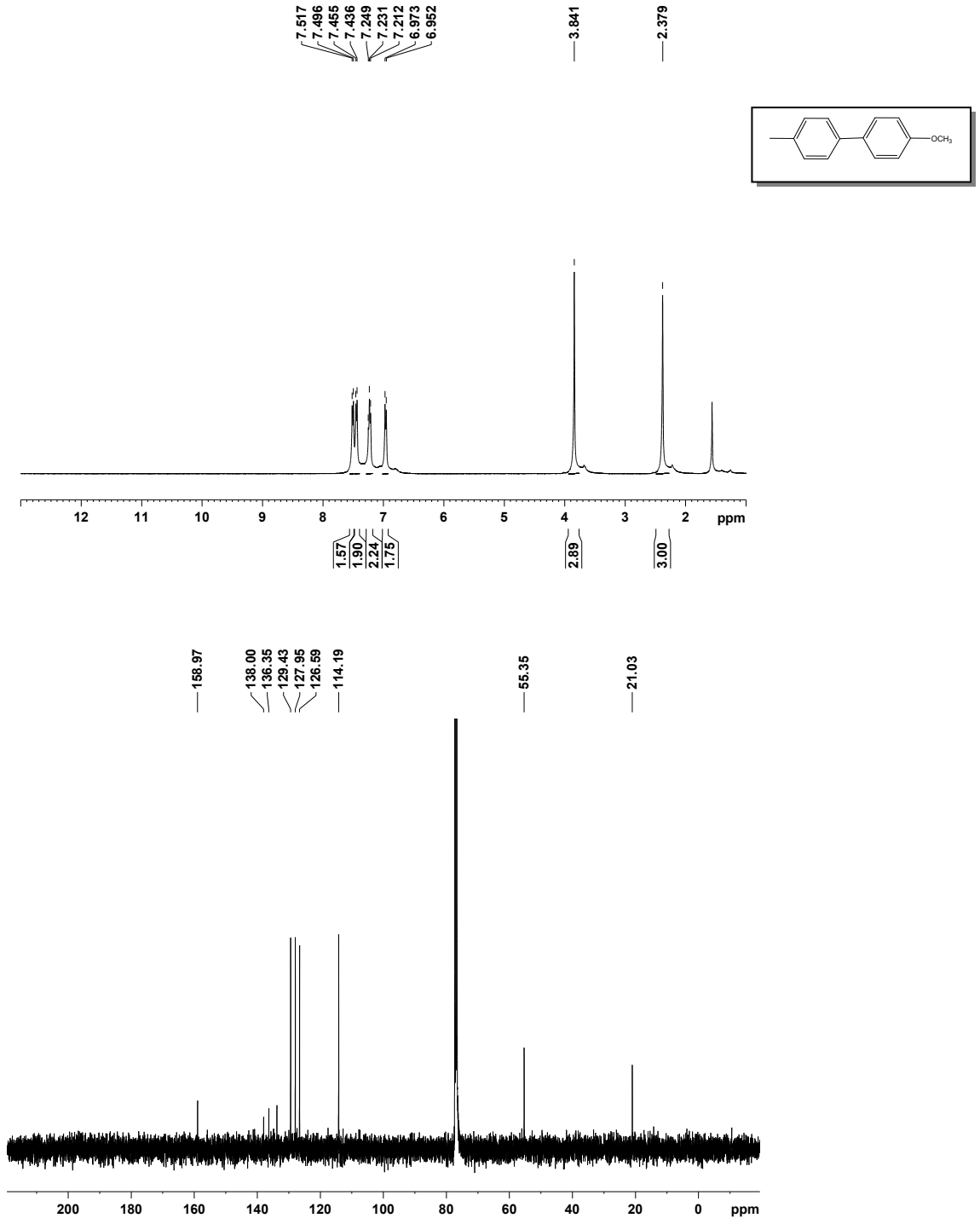

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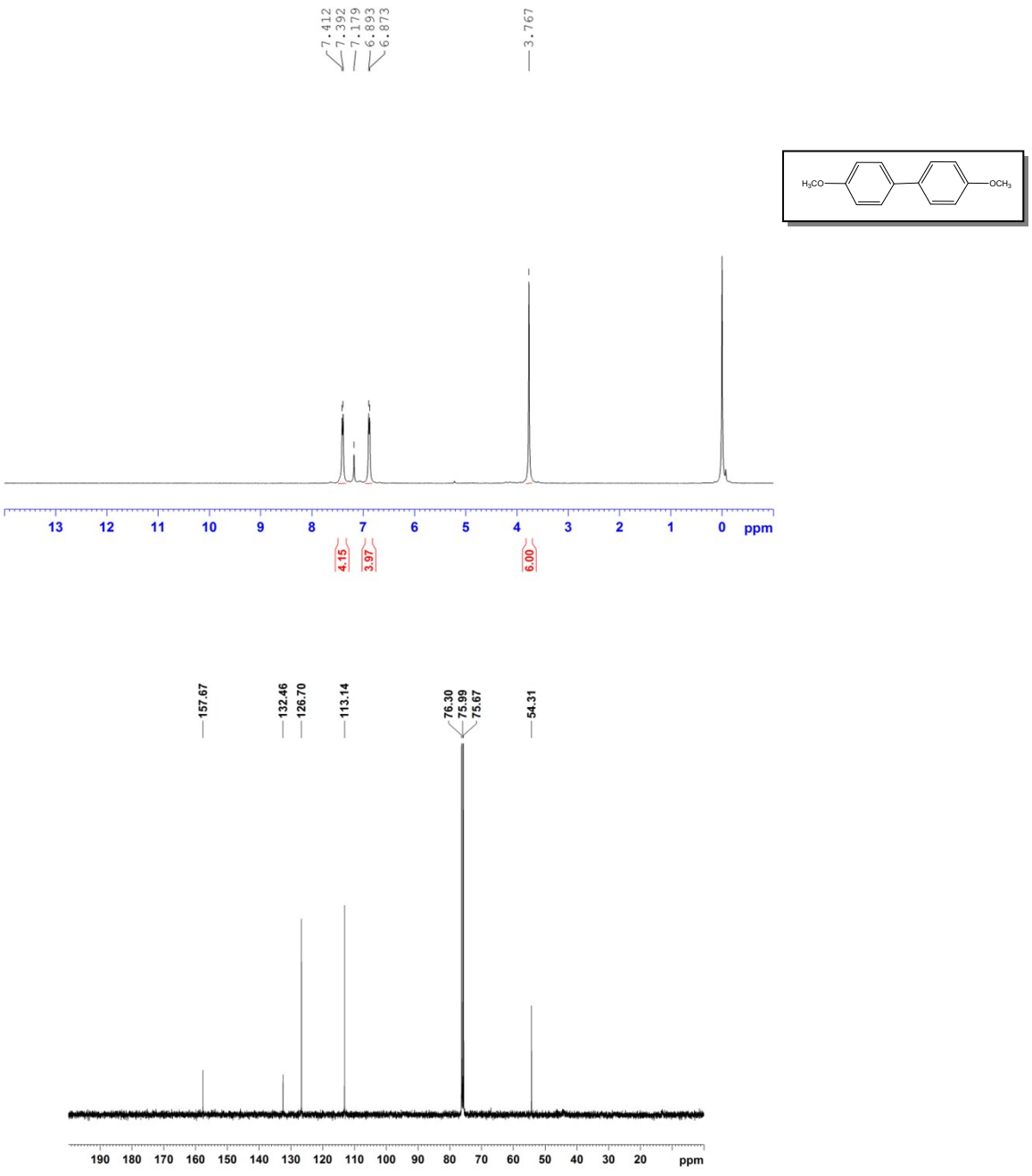

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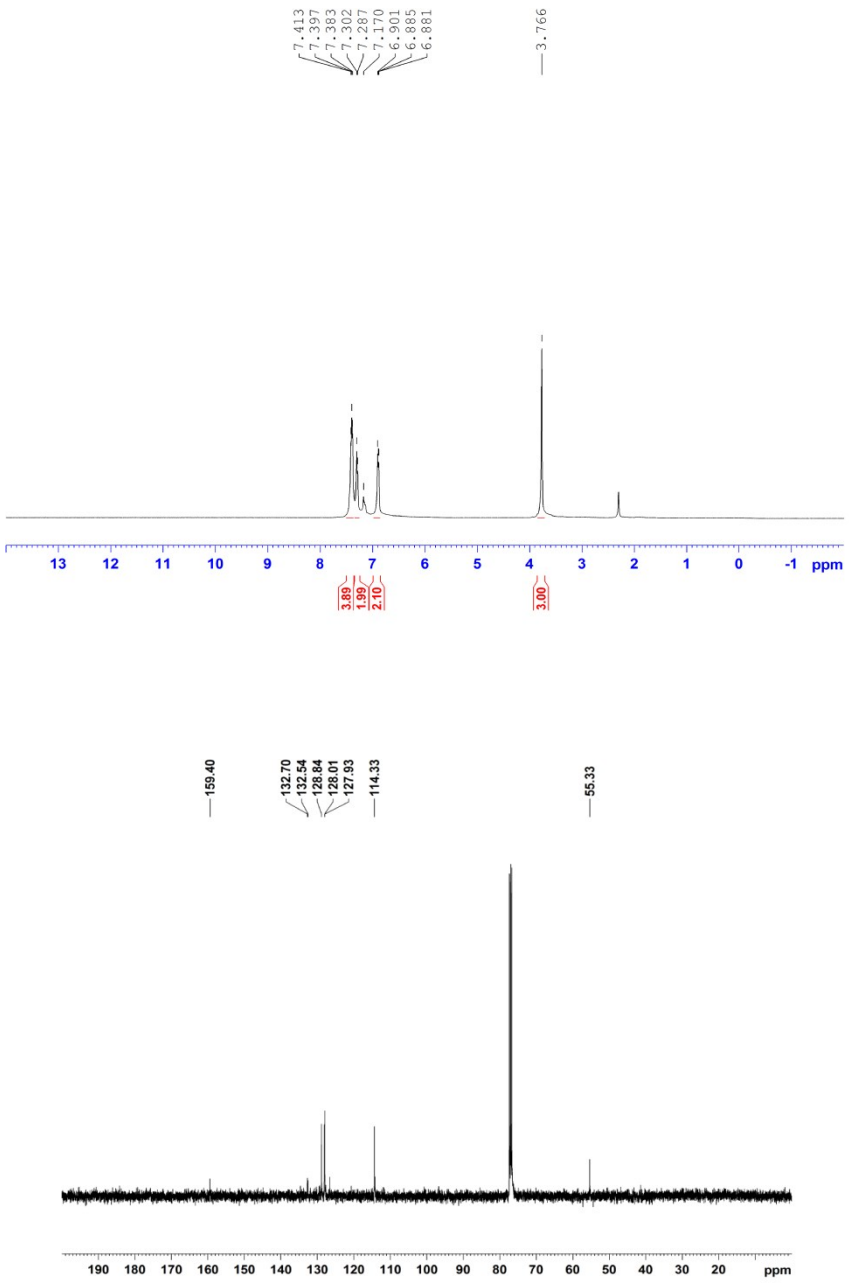

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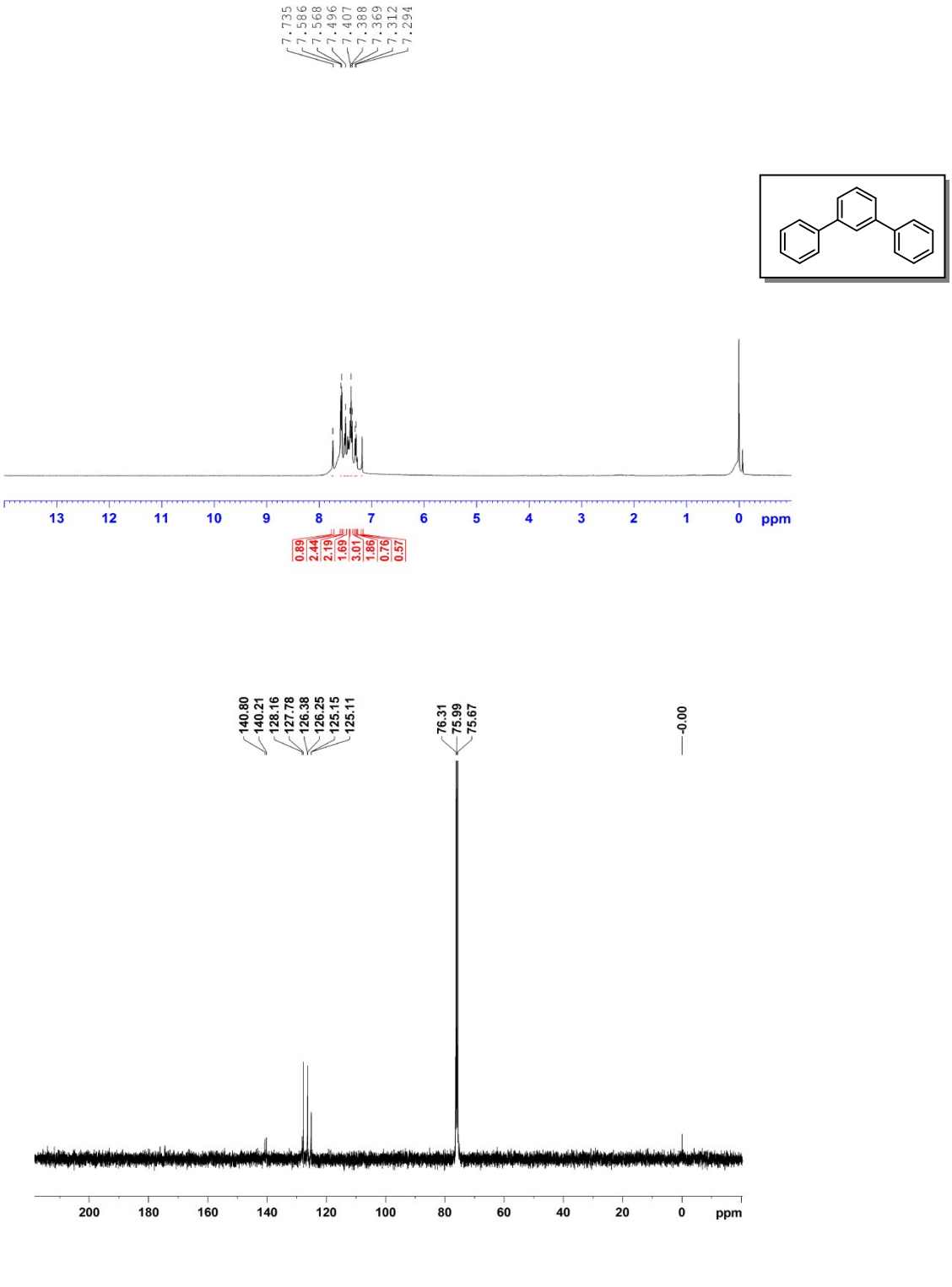

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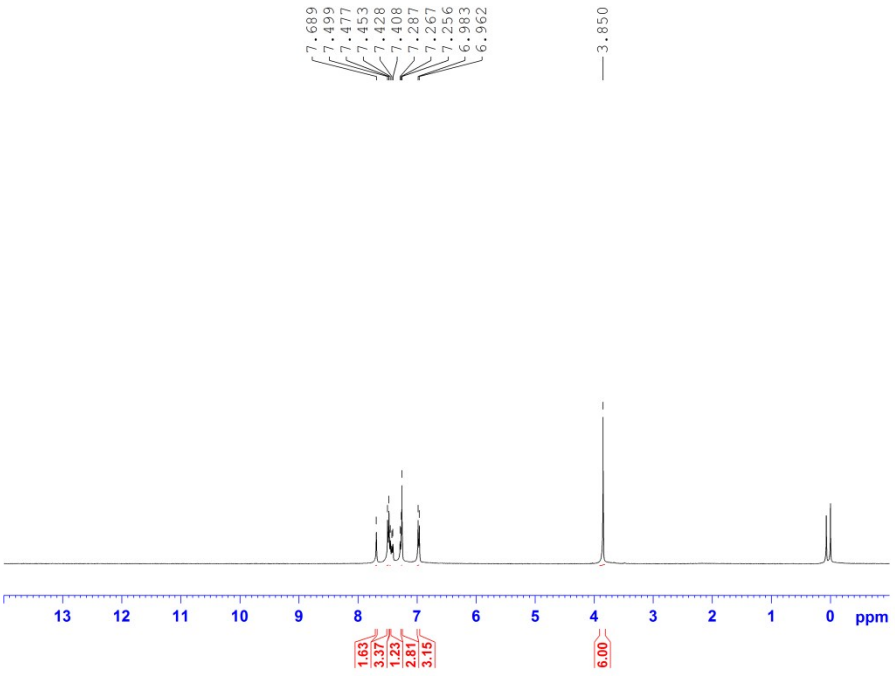

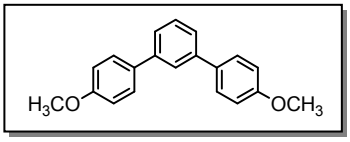

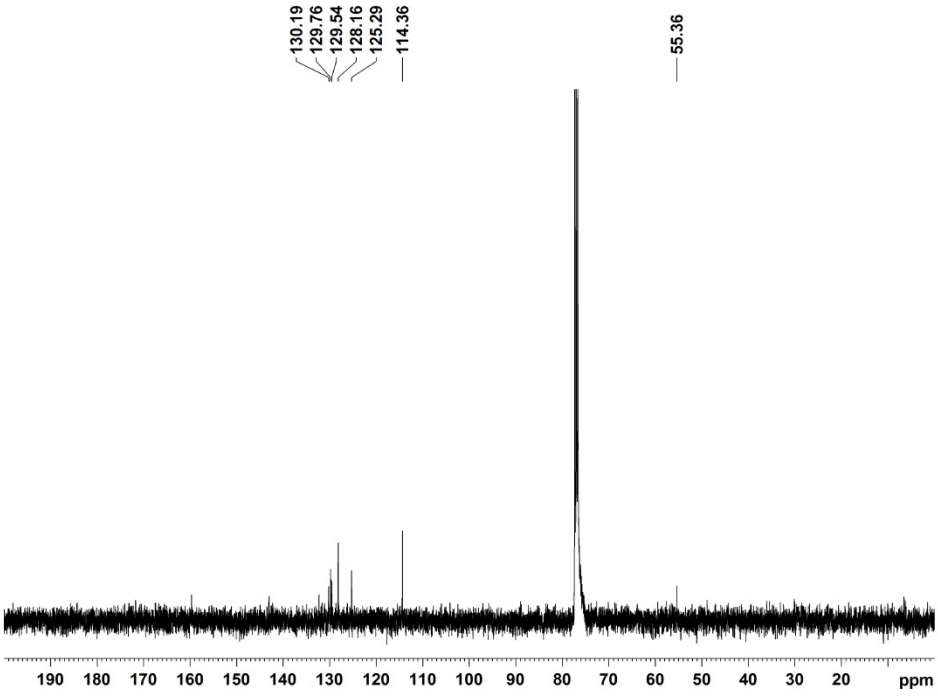

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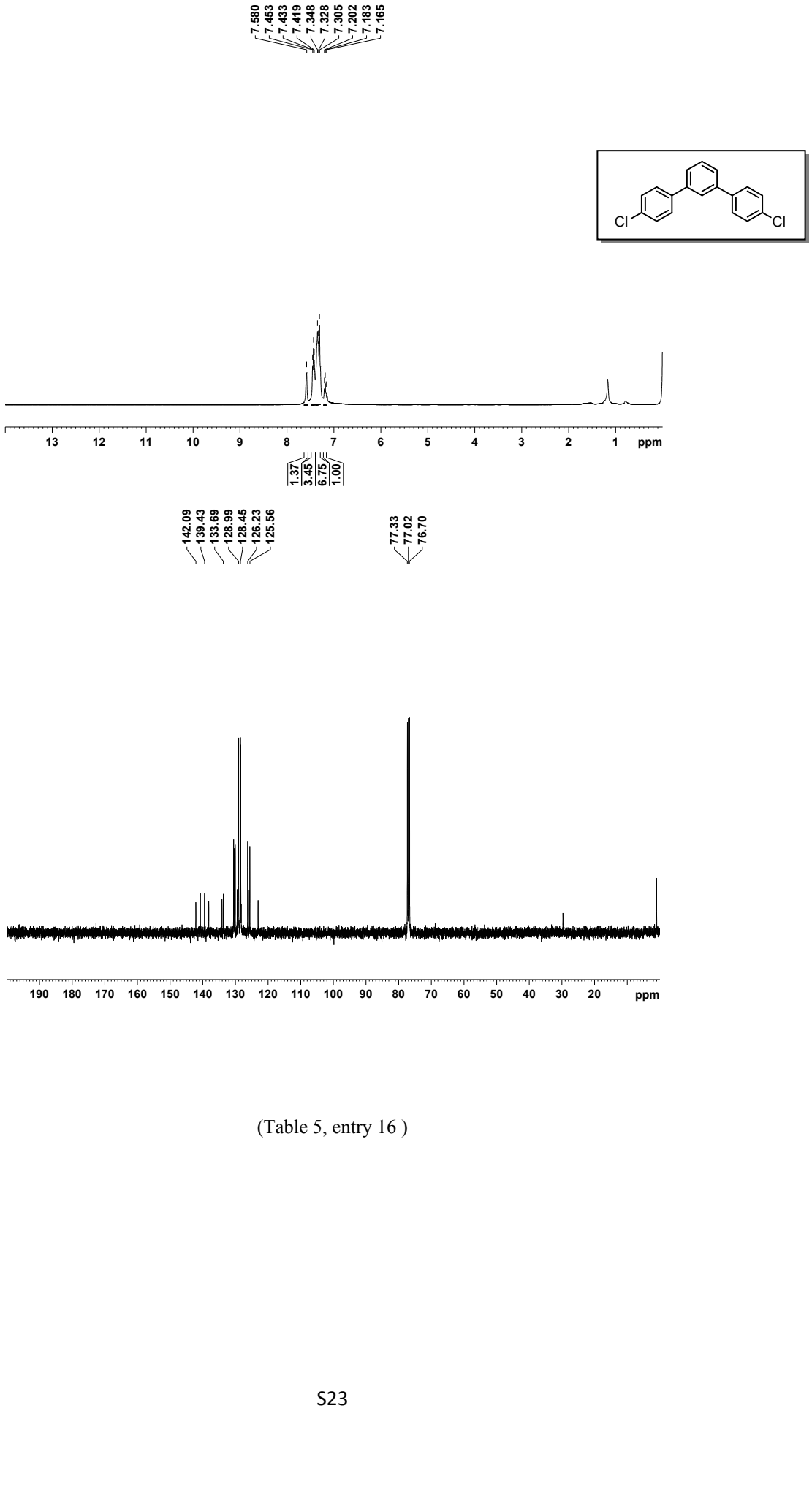

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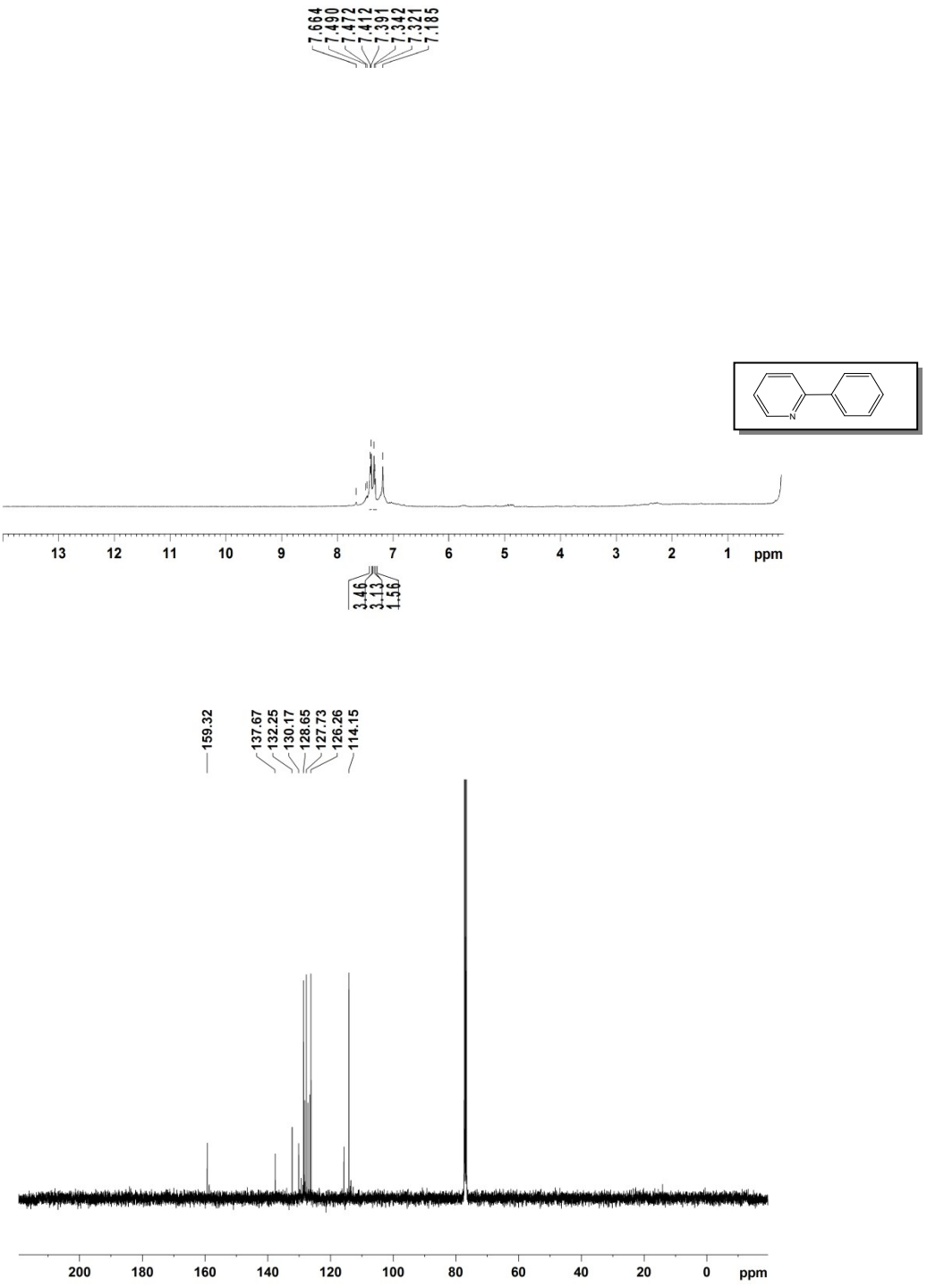

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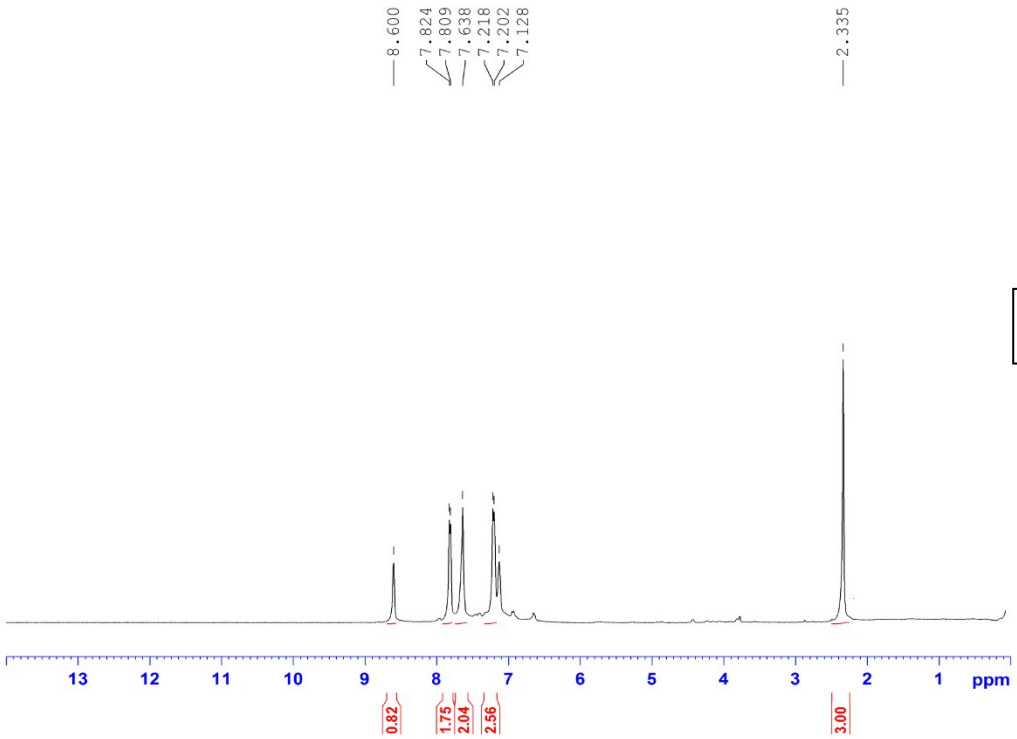

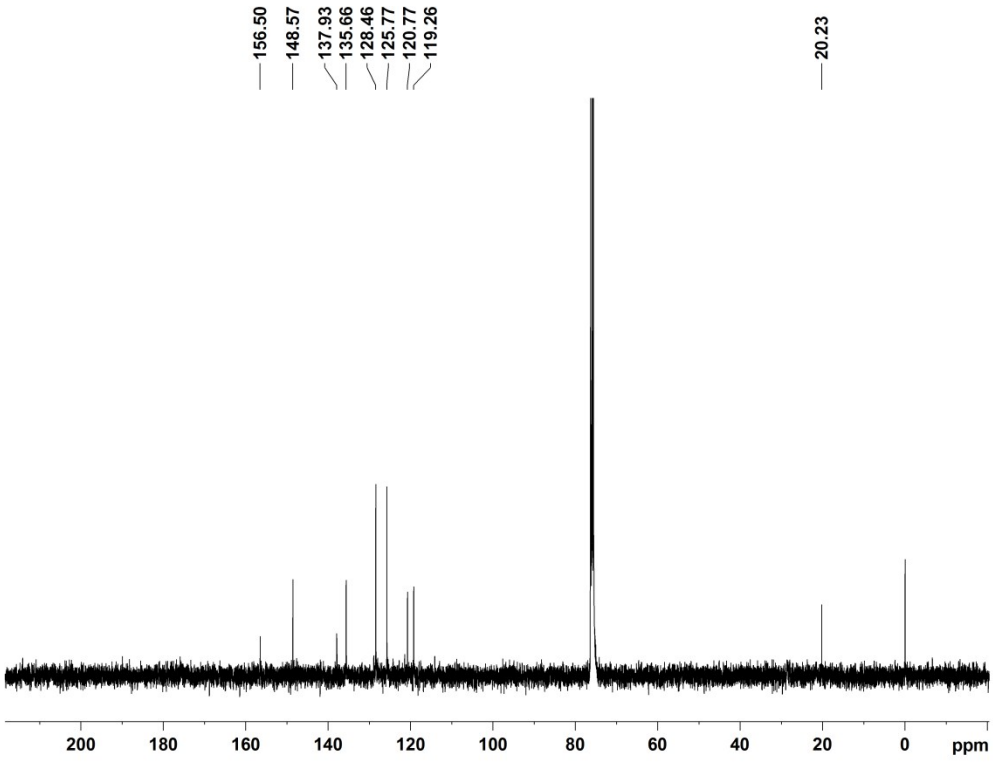

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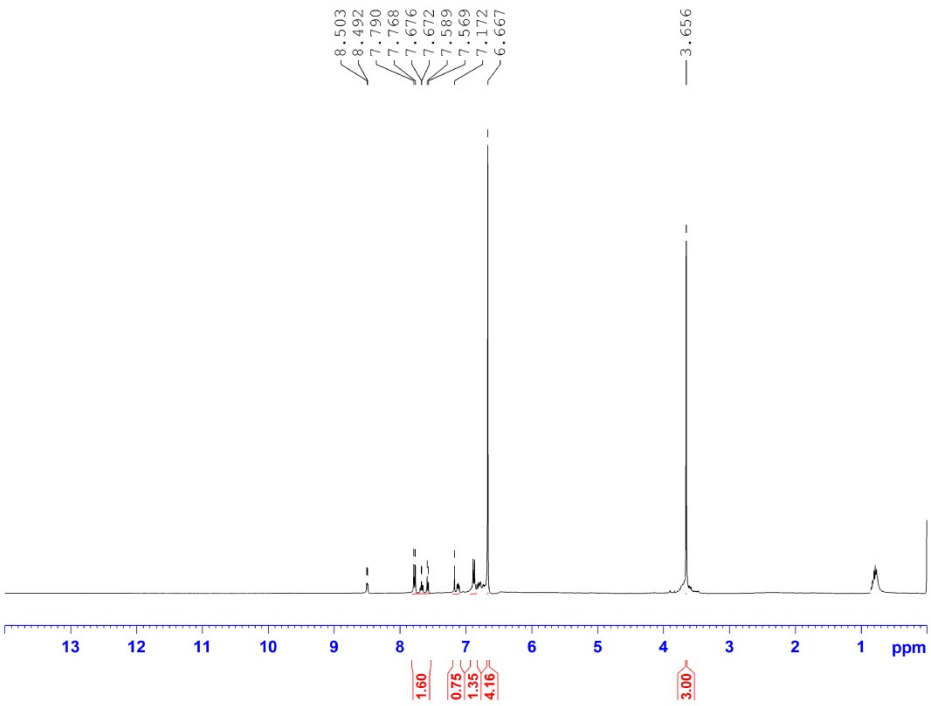

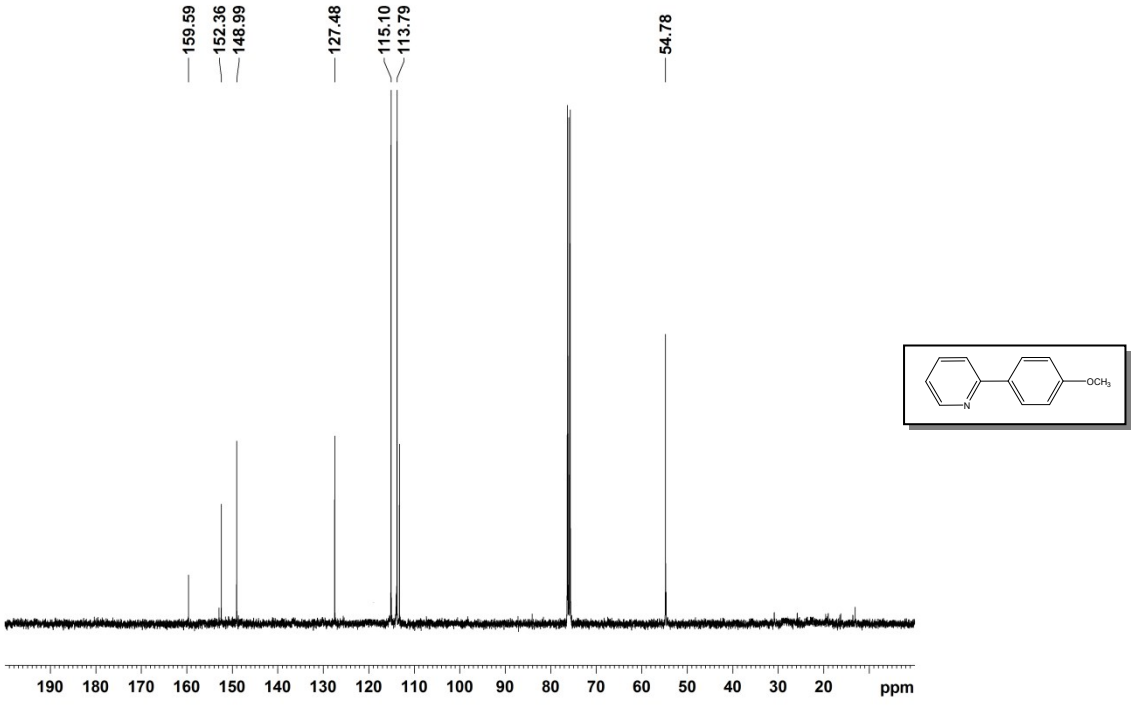

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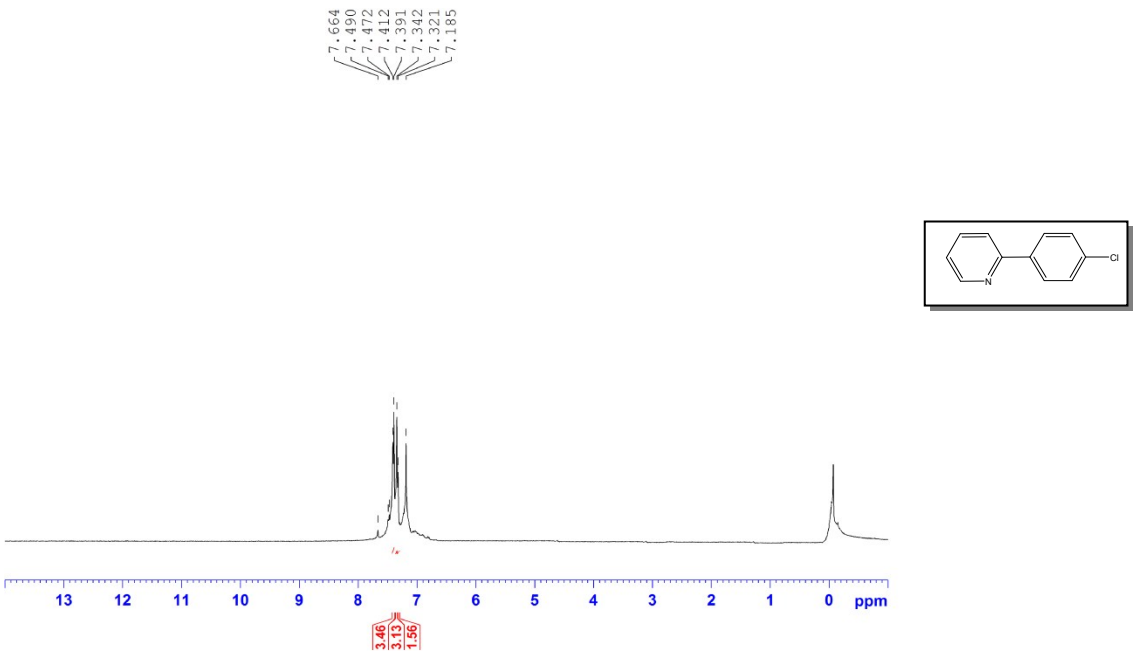

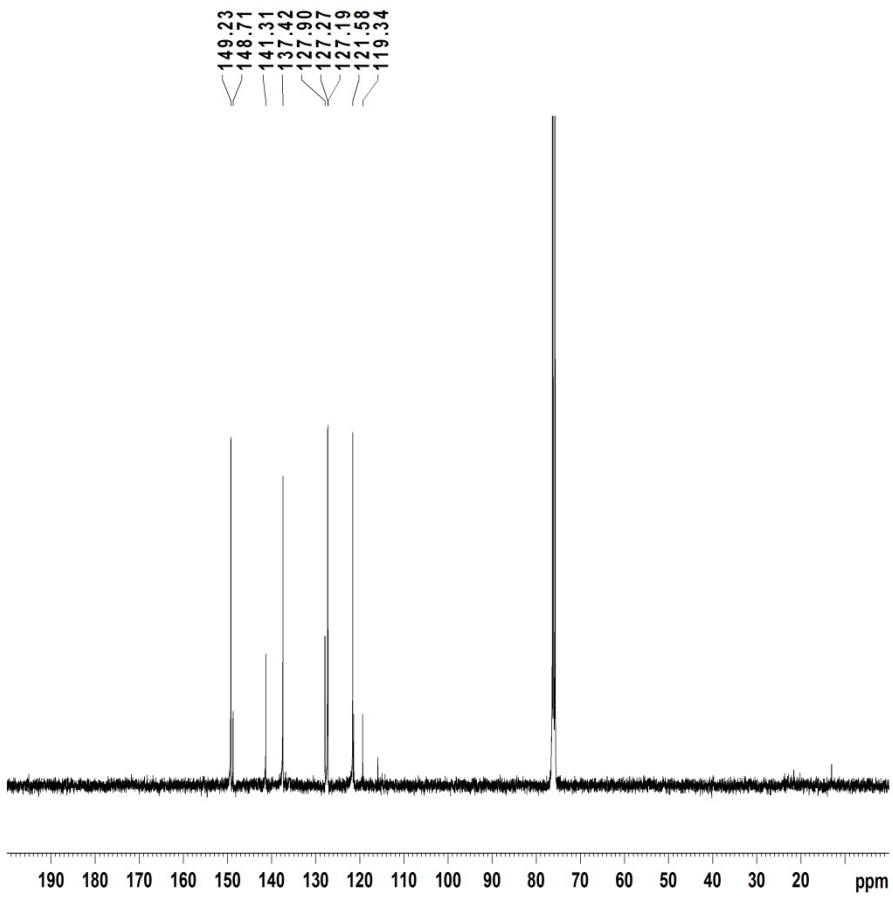

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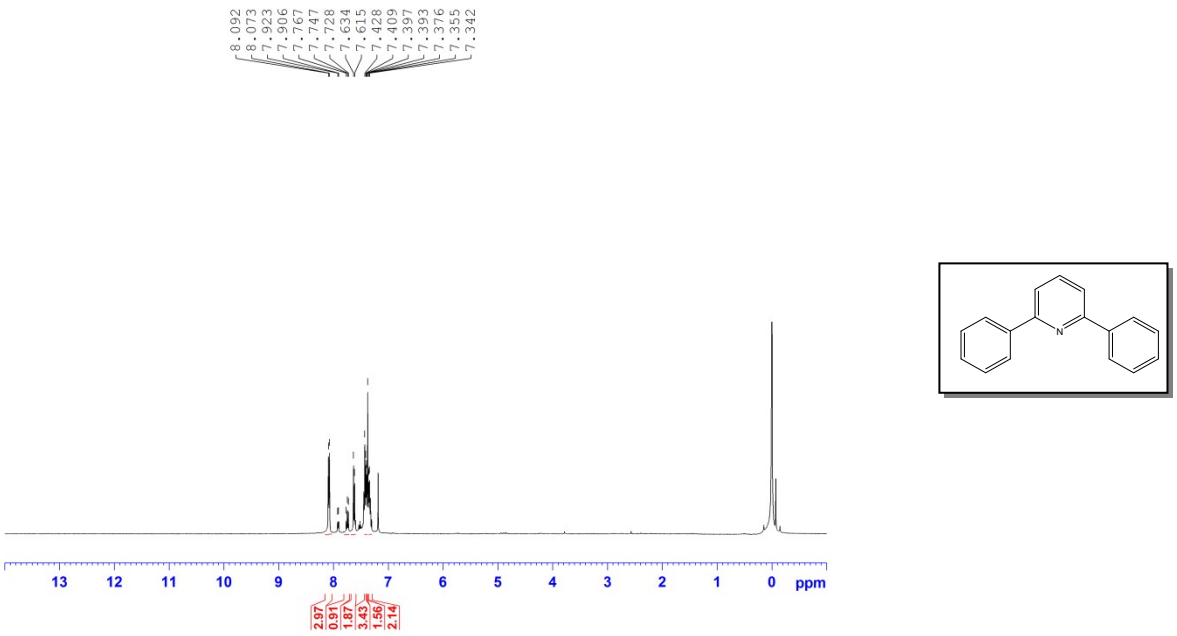

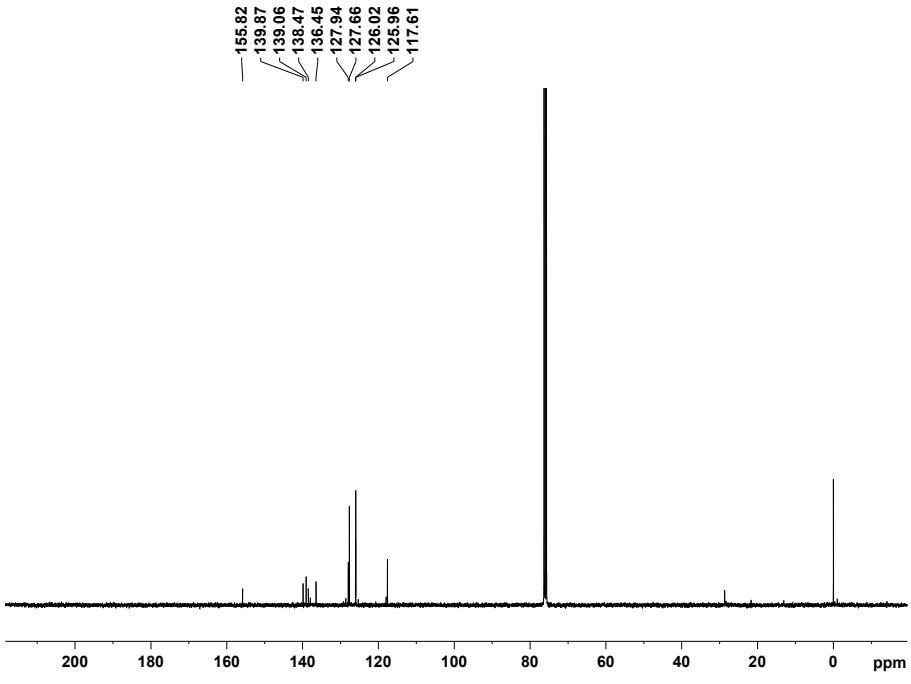

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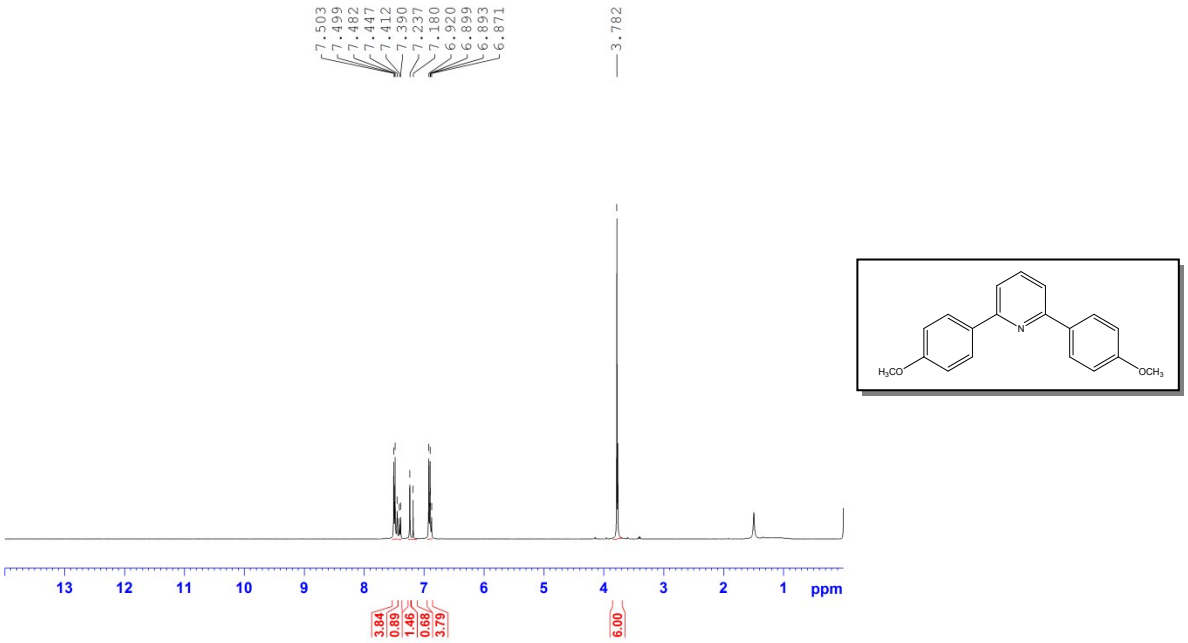

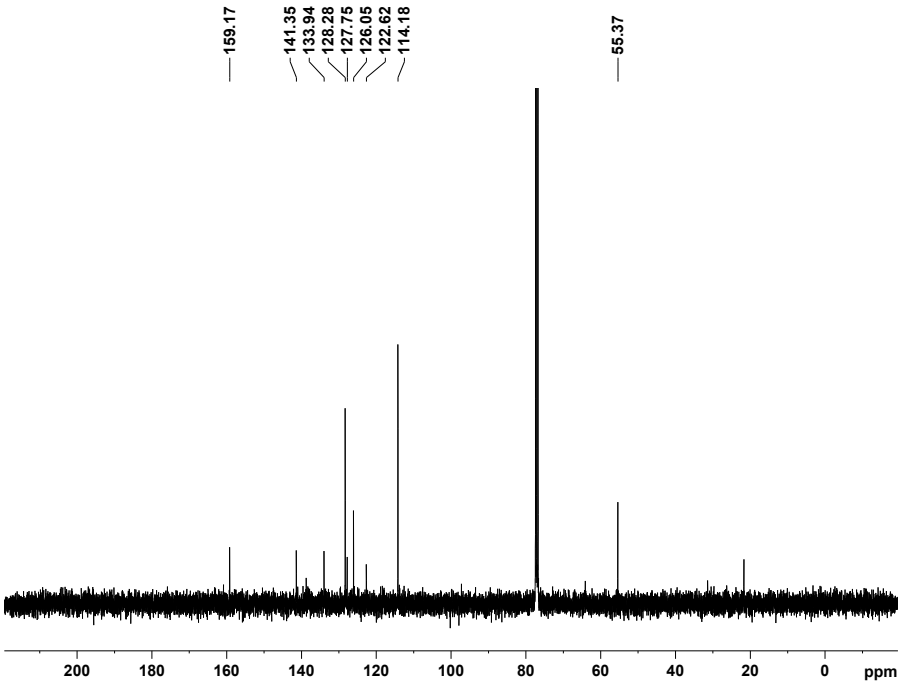

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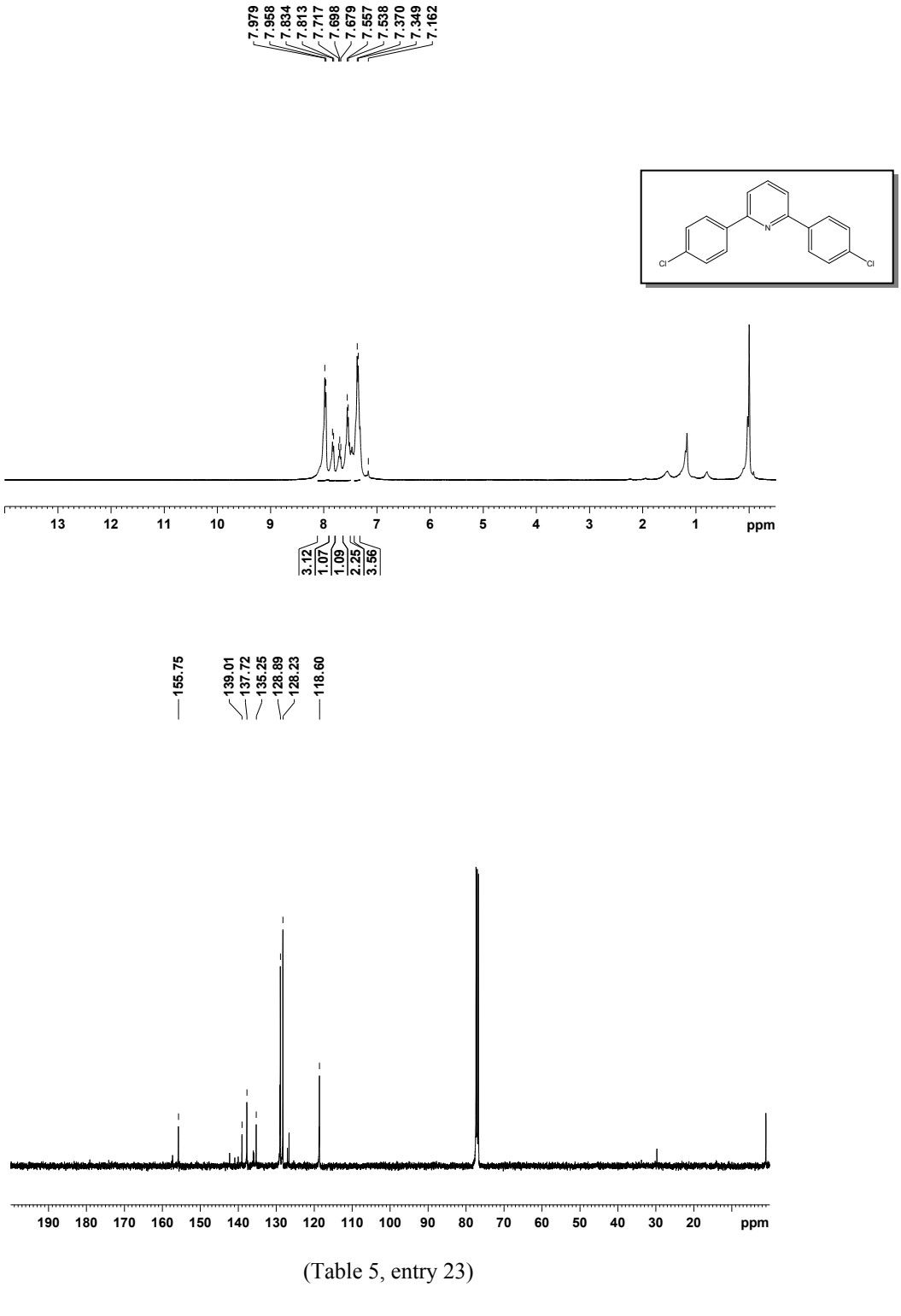

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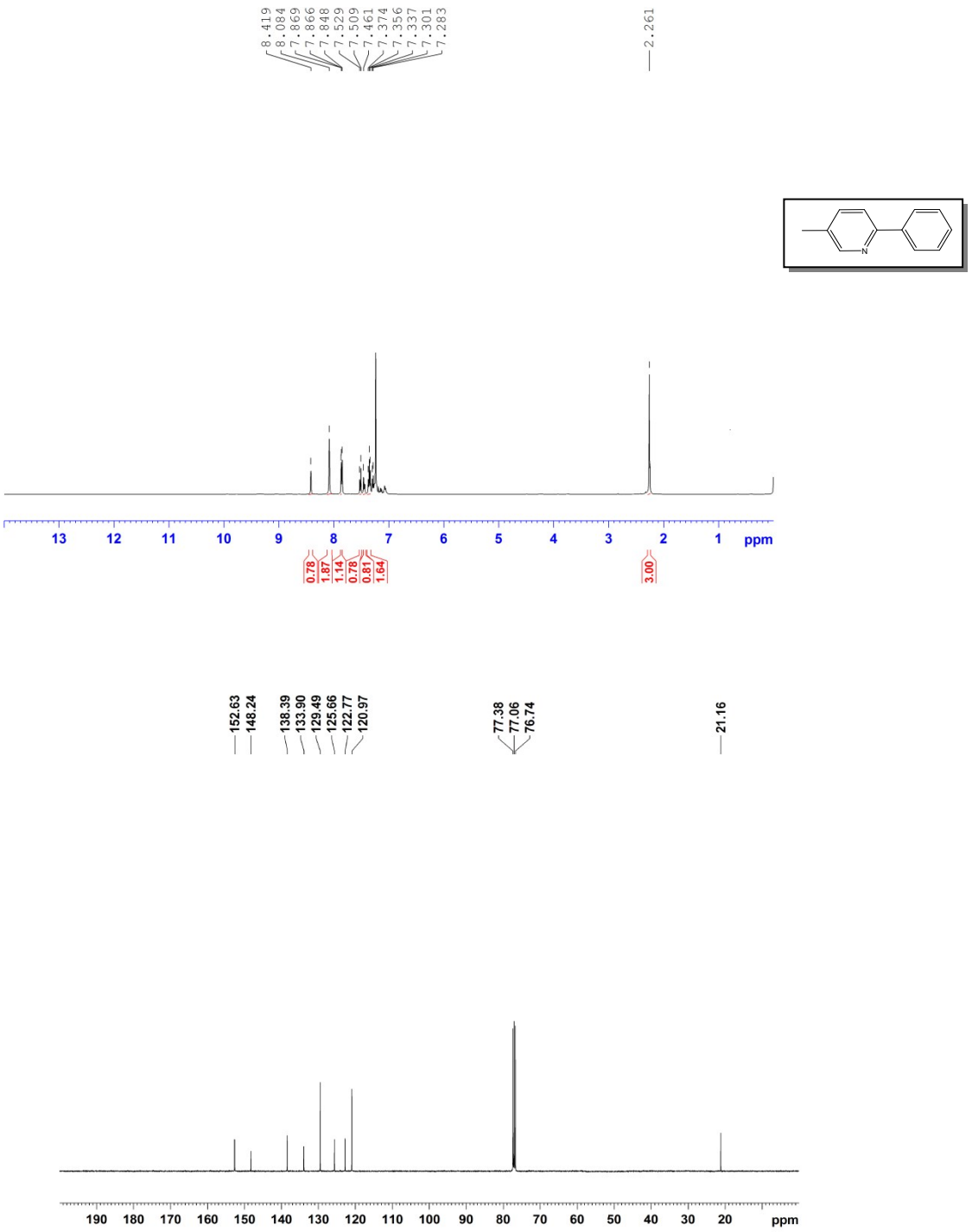

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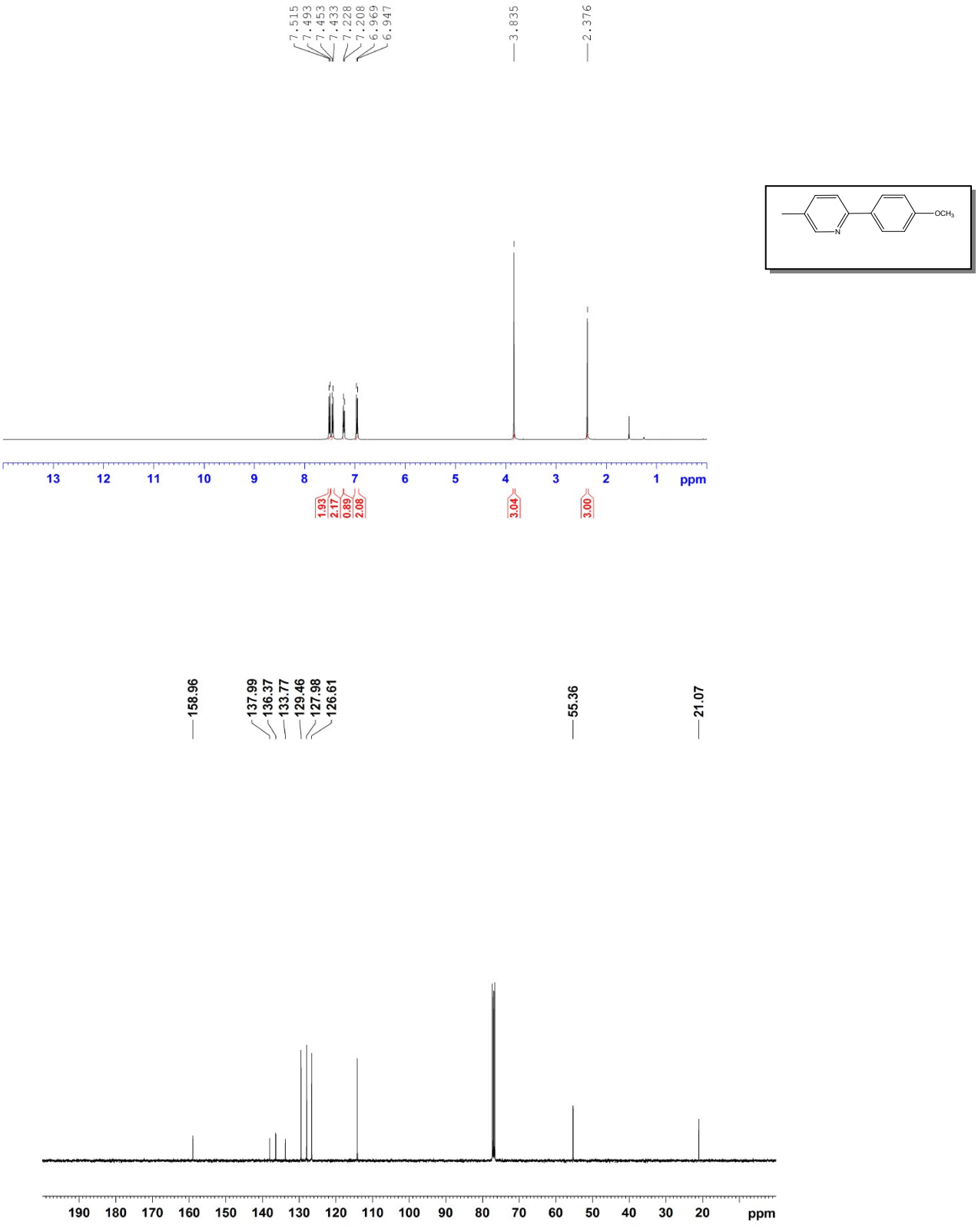

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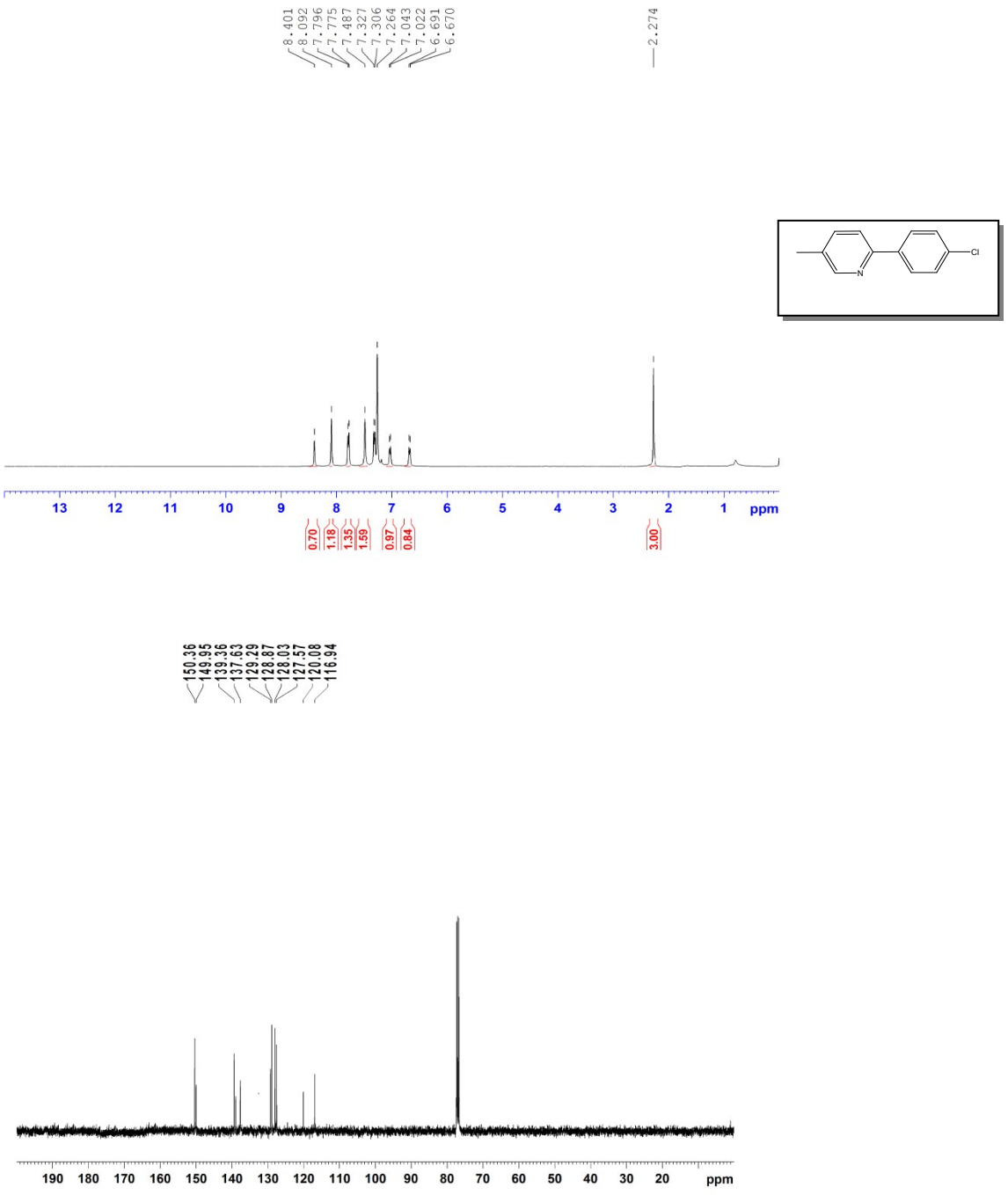

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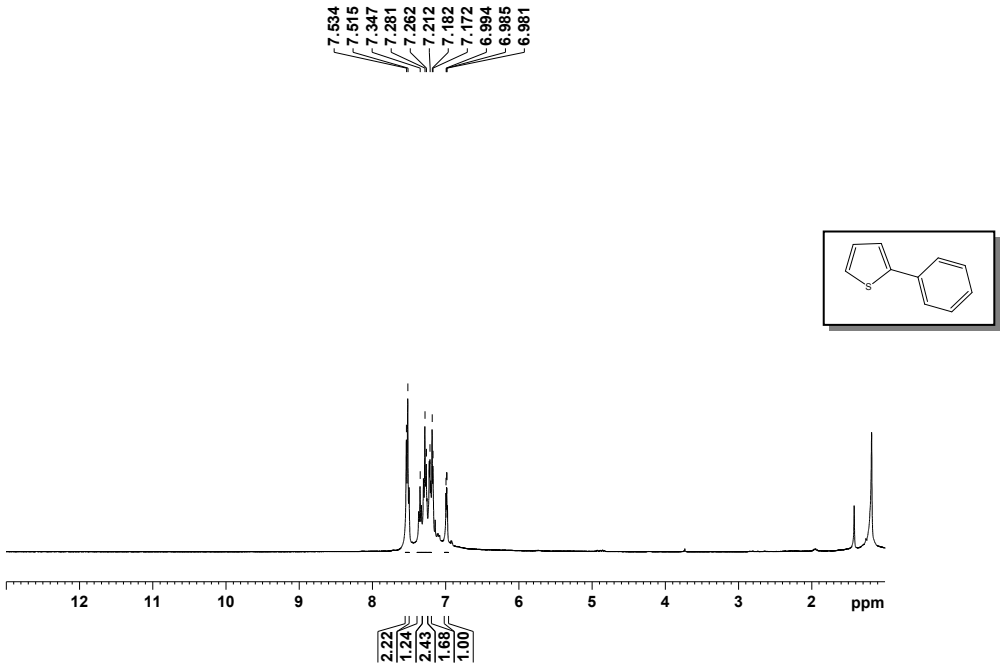

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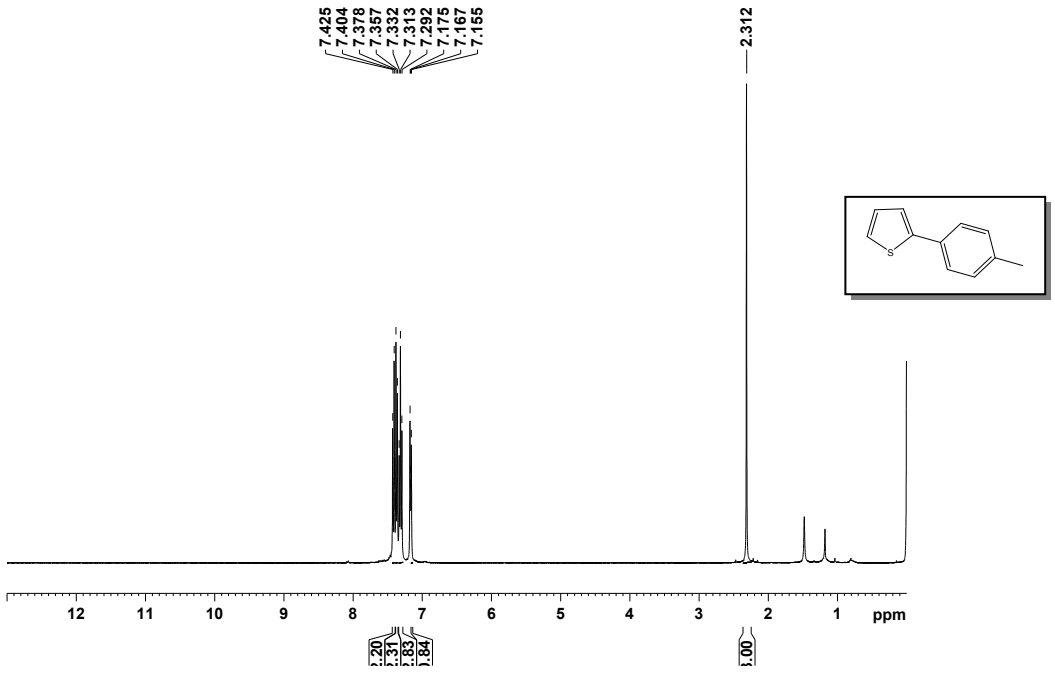

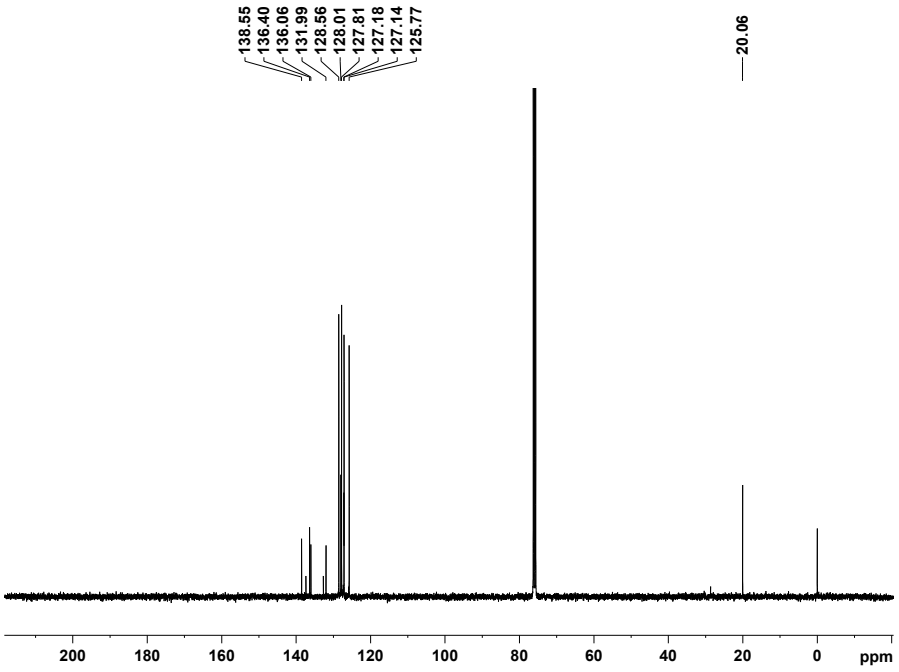

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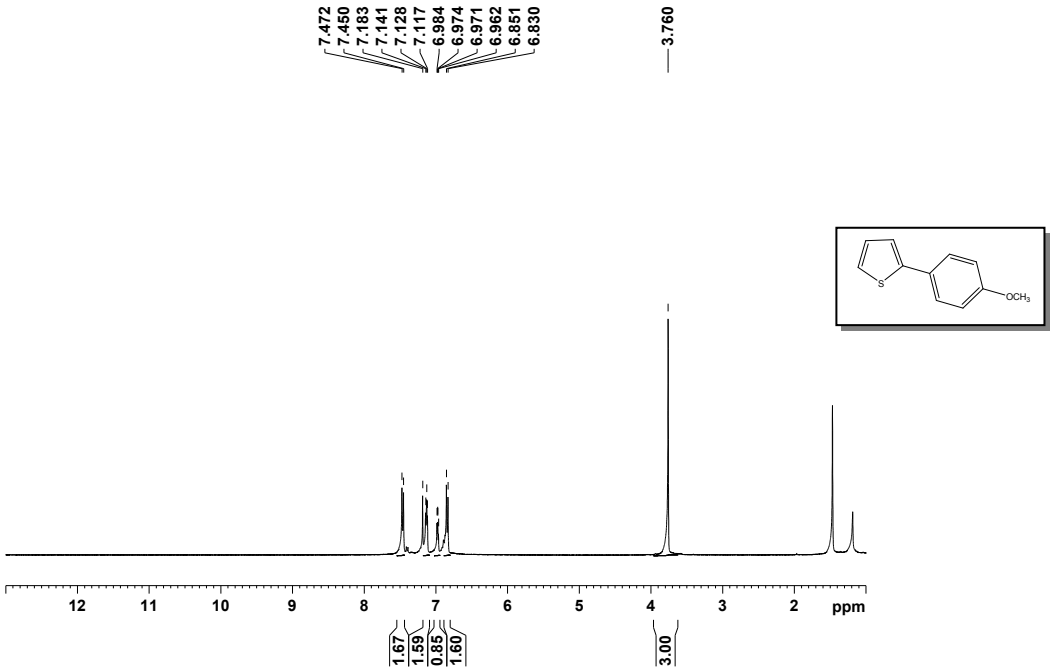

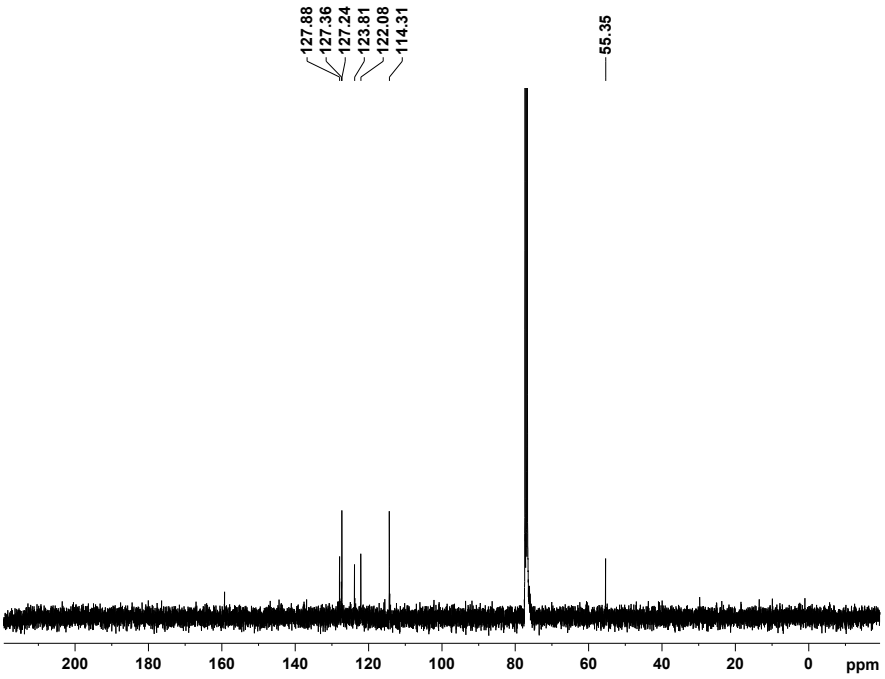

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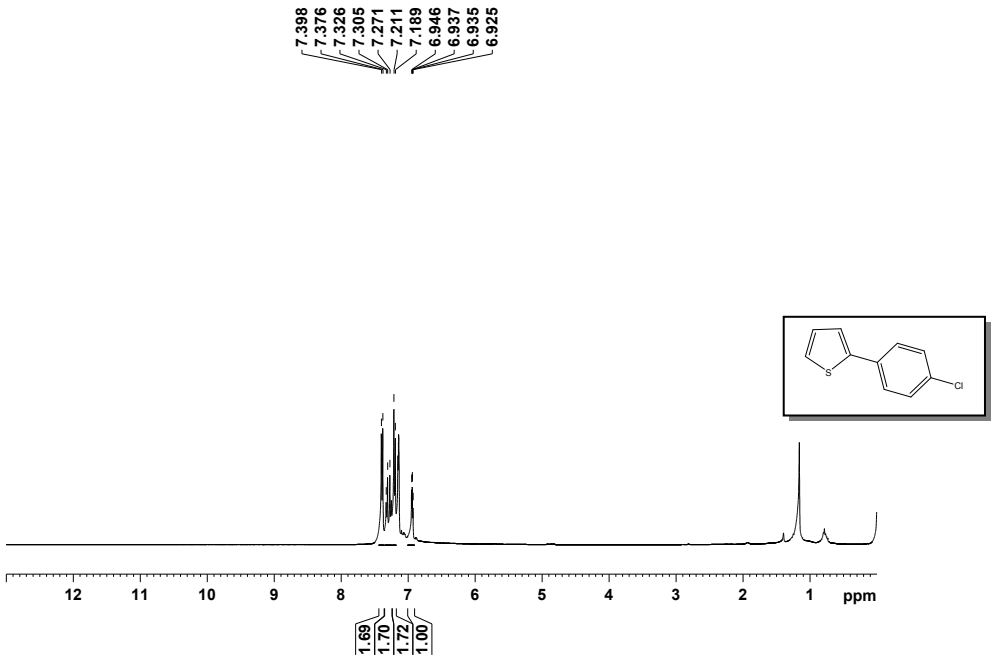

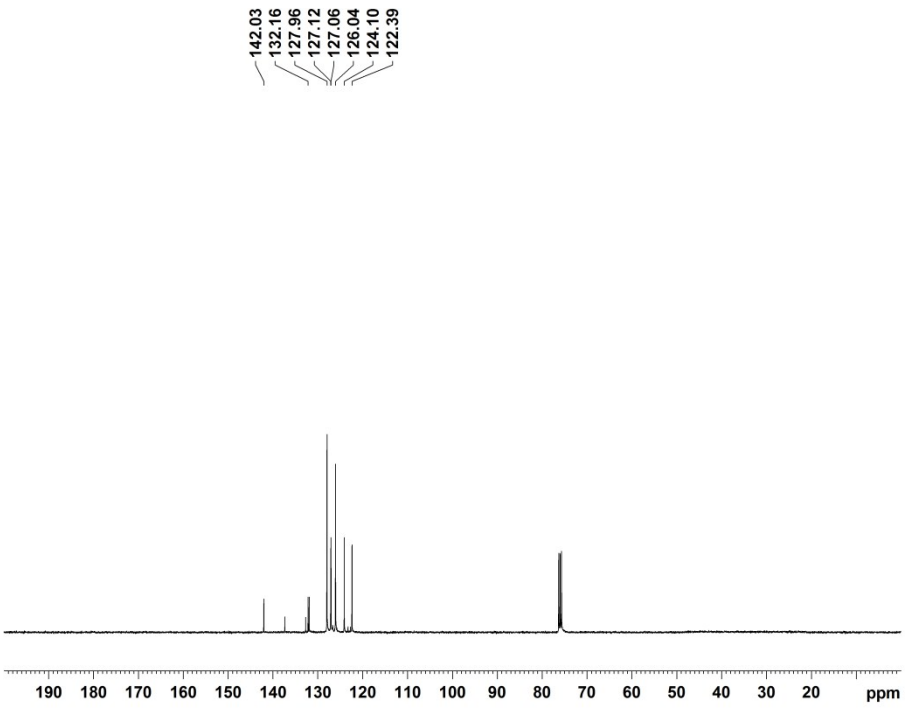

(Table 5, entry 30)

5. Recycling of the catalyst

The cross-coupling reaction was carried out as described above using 4-bromoacetophenone (1 mmol), t-butyl acrylate (2 mmol), K_2CO_3 (2mmol) and complex **1** (0.001 mmol) in DMF (2 mL) for 10 h at 100 °C. At the end of each cycle, the product mixture was cooled to room temperature the aqueous layer was extracted with diethyl ether (3x3 mL), and the flask was charged again with 4-bromoacetophenone (1 mmol) and phenylboronic acid and K_2CO_3. Every time after cooling and extraction with diethyl ether, the reagents and base were added and the reaction was repeated. The combined organic layer was dried over sodium sulfate and evacuated in vacuo and the residue was analyzed by 1H NMR. The recovered catalyst was dried under vacuum and then used for next reaction cycles under identical conditions with new portions of reagents.

6. References

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