Electronic Supplementary Material (ESI) for Organic and Biomolecular Chemistry

Supporting Information

Nano $CuFe_2O_4$ as a Magnetically Separable and Reusable Catalyst for the Synthesis of Diaryl / Aryl Alkyl Sulfides via Cross-Coupling Process under Ligand Free Conditions

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General Information:

Aryl halides (99%), diphenyl disulphide (99.5%), benzenethiol (99%), nano-$CuFe_2O_4$ (99.9%) and other aryl halides were purchased from Sigma Aldrich and Fluka used without purification. All experiments were carried out under nitrogen atmosphere. Column chromatography was carried out with 60-120 sized mesh silicagel using hexane as eluent. Analytical TLC was performed with Merck silica gel 60 F_{254} plates, and the products were visualized by UV detection. ^1H NMR and ^{13}C NMR (Avance 300, Innova 400 MHz and Brucker Gemini 200 MHz) spectra were recorded in $CDCl_3$ using TMS as internal standard. Chemical shifts (δ) are reported in ppm, and spin-spin coupling constants (J) are in Hz. Melting points were determined on a Fischer-Johns melting point apparatus. IR and MS were recorded on a Thermo Nicolet Nexus 670 FT-IR spectrometer and Finnegan MAT 1020 mass spectrometer operating at 70 eV.

Representative Experimental Procedure for the Synthesis of Diphenyl Sulfides by using $CuFe_2O_4$ as a Catalyst: To a stirred solution of aryl halide (1.0 mmol) and thiol (1.0 mmol) in dry DMSO (2.0 mL) were added $CuFe_2O_4$ nano powder (5 mol%, 12 mg) and Cs_2CO_3 (1.0 equiv) and the reaction mixture was heated at 100 ^0C under nitrogen atmosphere. After the completion of the reaction for 24 h, as monitored by TLC. The reaction mixture was extracted with ethyl acetate (3x10 ml). The combined organic layers were dried with anhydrous Na_2SO_4. The solvent was evaporated under vacuum to give the crude product, which was purified by column chromatography with hexane as eluent to get the expected products in good yields. The purity of the product was confirmed by ^1H, ^{13} C and Mass spectroscopy.

Recyclability of the catalyst: After completion of the reaction, catalyst was magnetically separated from reaction mixture after completion of the reaction, washed with ethyl acetate and acetone, air dried and used directly for further catalytic reactions. No significant loss of catalyst ($CuFe_2O_4$) activity was observed up to four cycles.

Characterisation of the $CuFe_2O_4$ nano Catalyst:

From SEM, XRD spectral studies, it is revealed that the $CuFe_2O_4$ nanoparticles remained in the same state, even after four cycles.

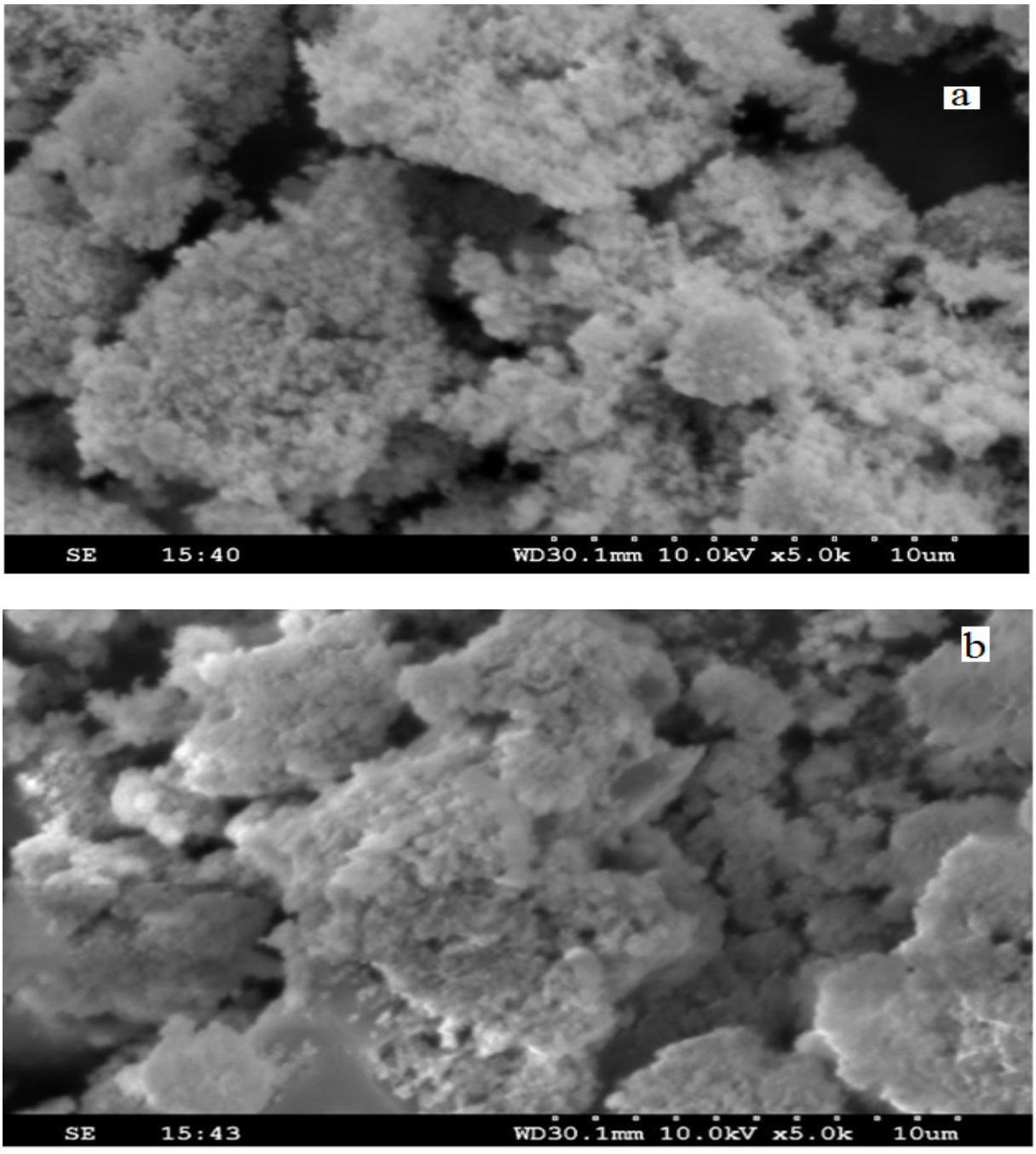


Fig. 1 **SE**M-analysis of (a) native $CuFe_2O_4$ catalyst and (b) reused catalyst after fourth cycle.

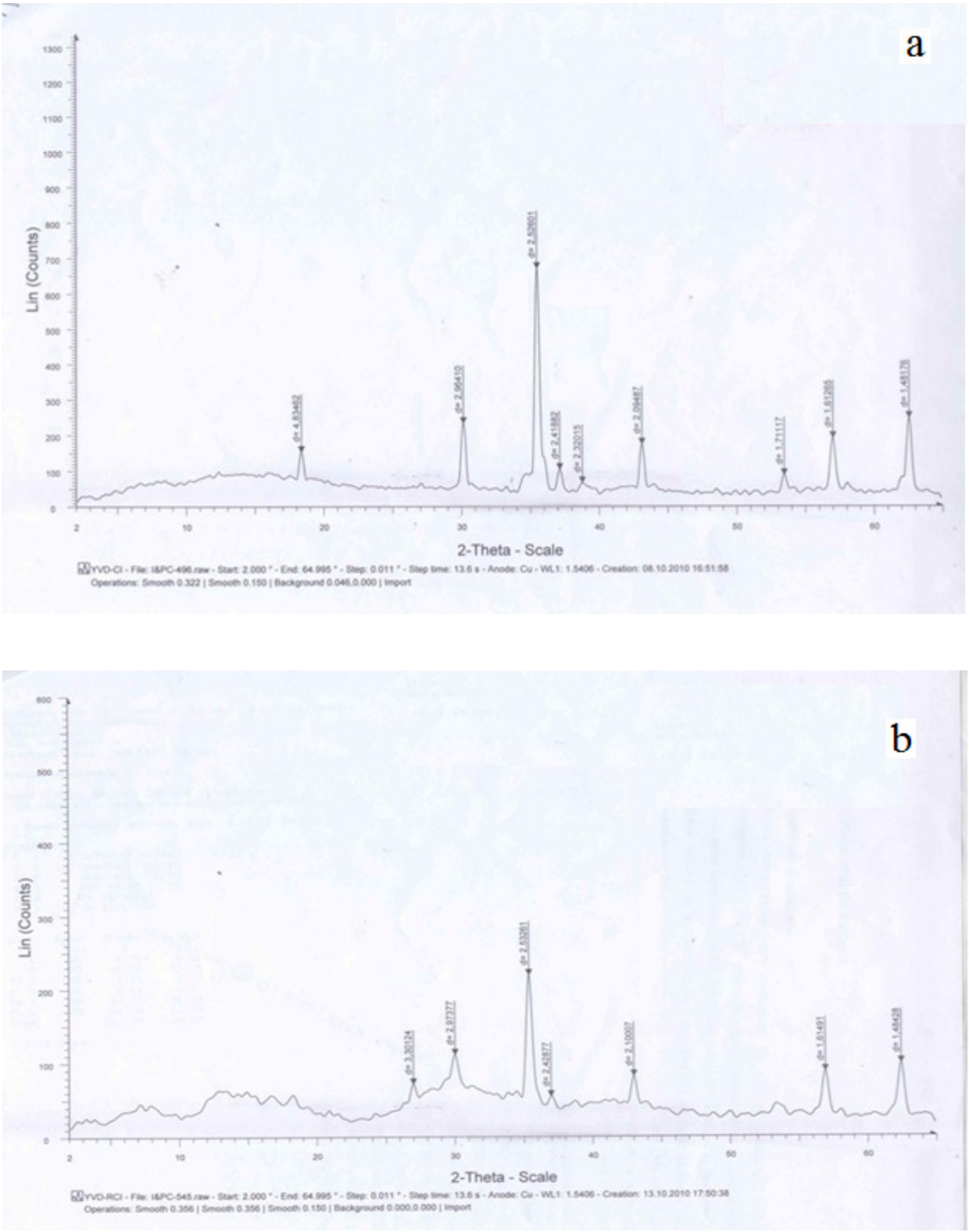
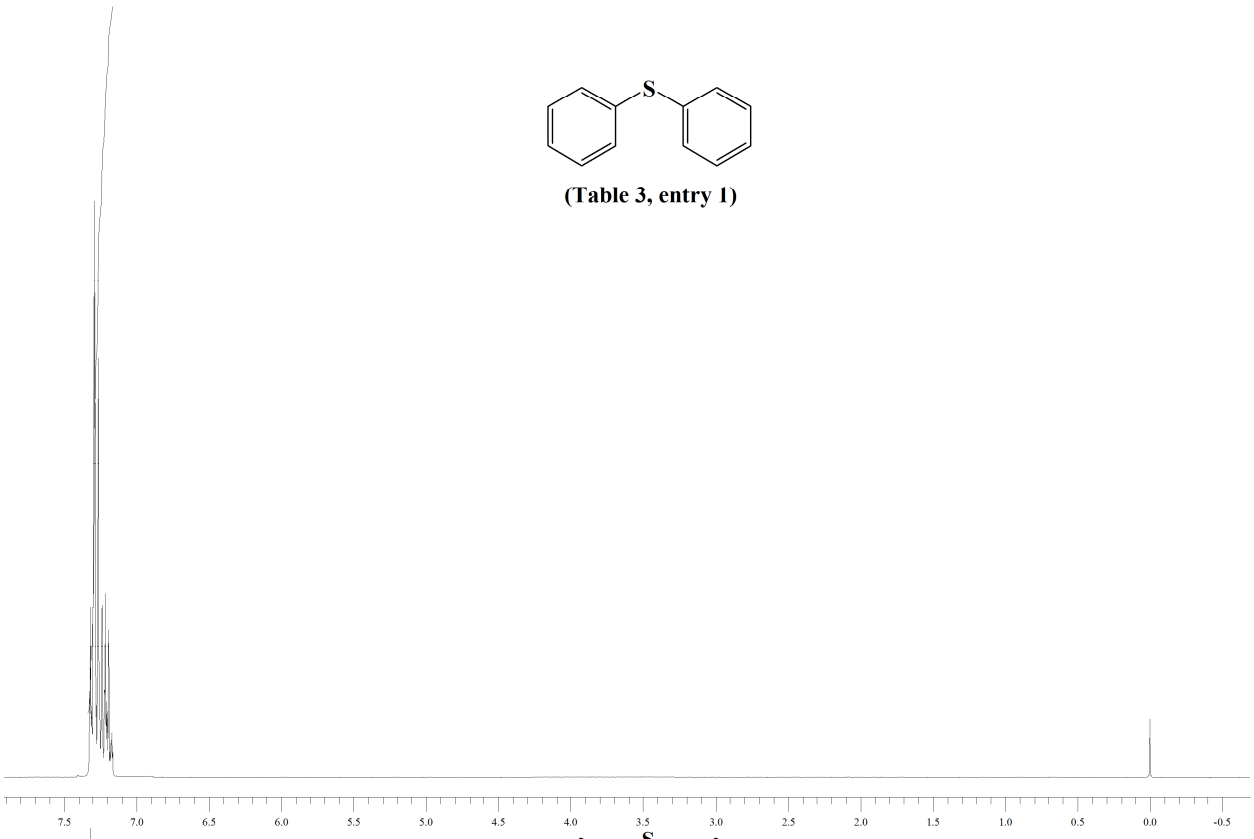


Fig. 2 XRD-analysis of (a) native $CuFe_2O_4$ catalyst and (b) reused catalyst after fourth cycle.

Copies of ^{1}H NMR and ^{13}C NMR of Compounds

(Table 3, entry 1)



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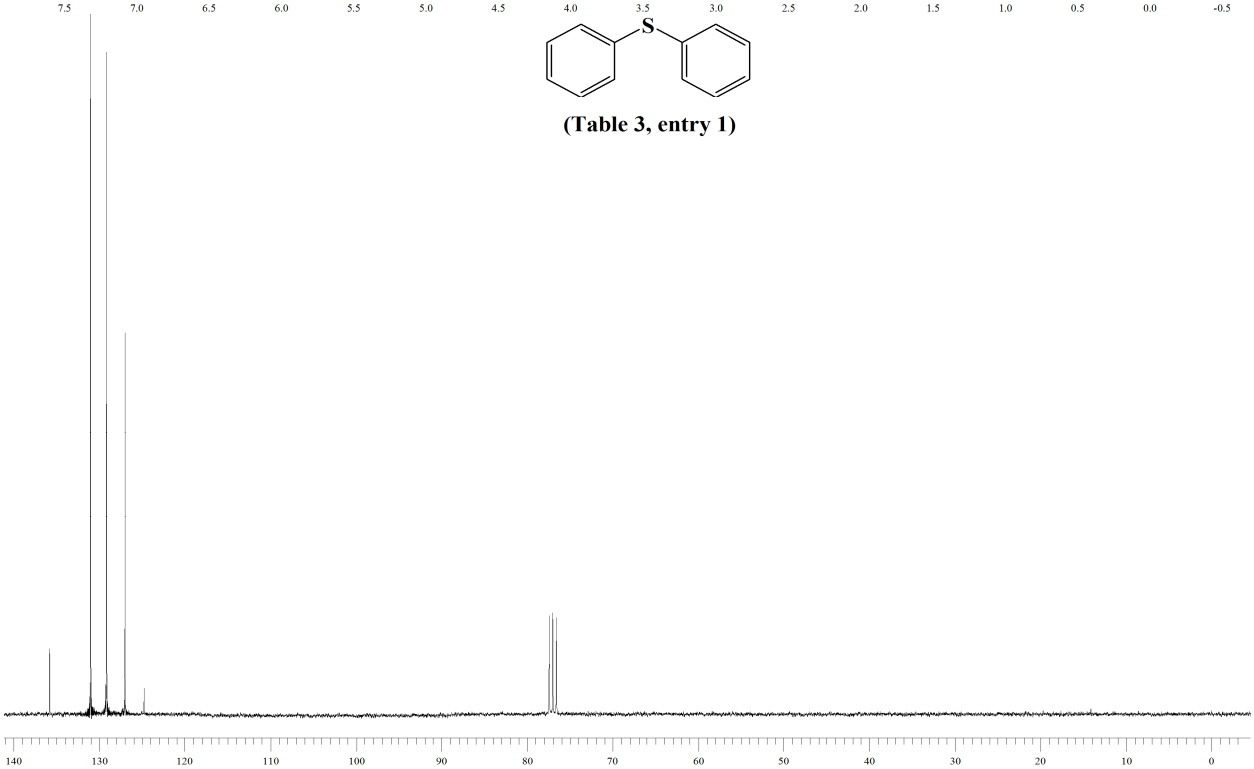

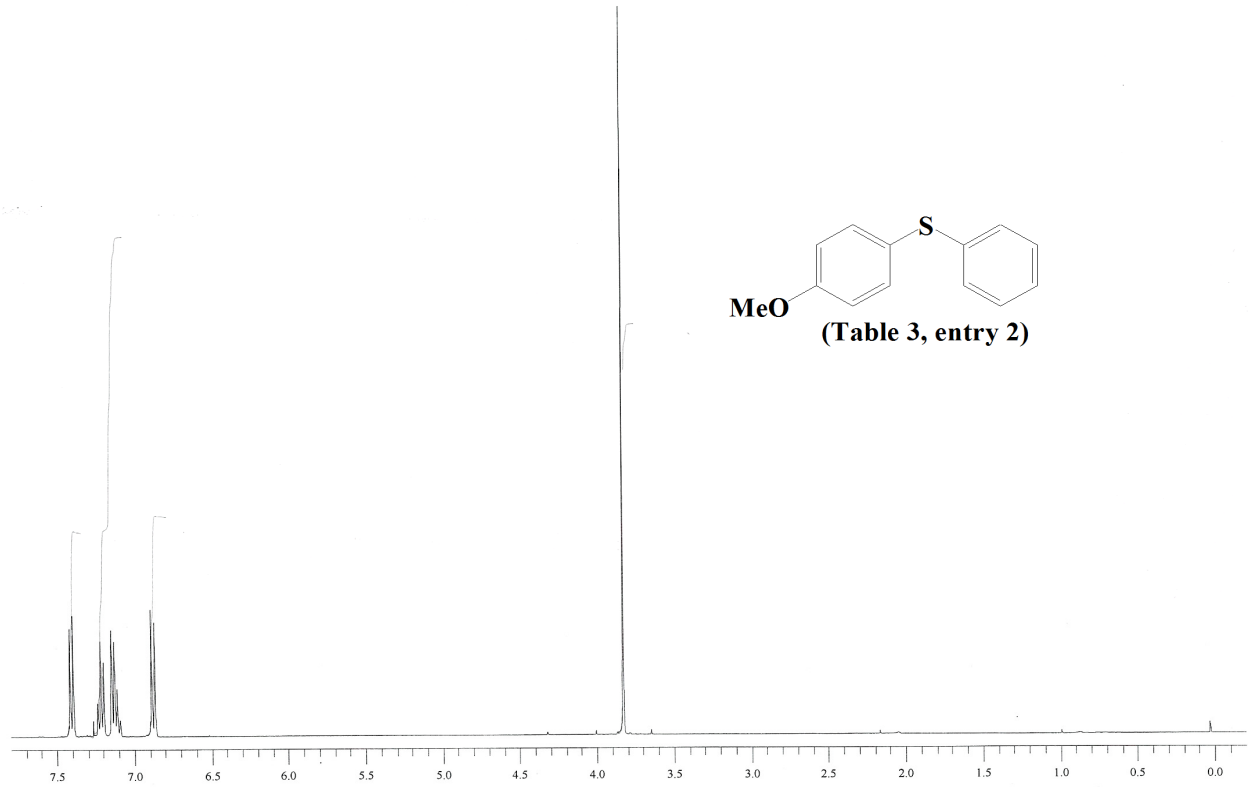

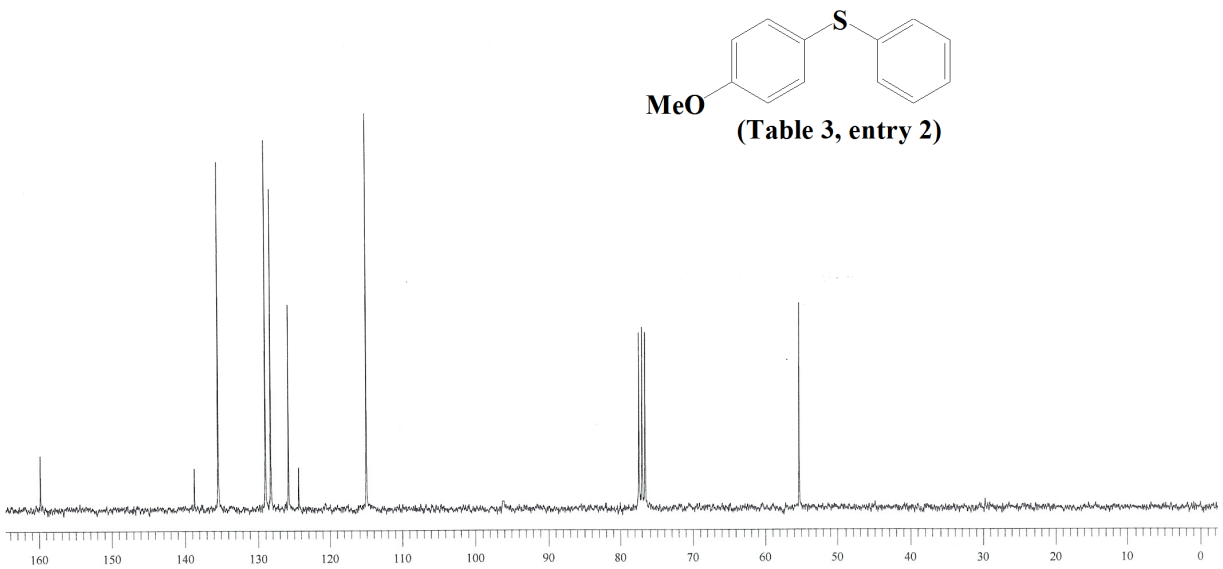

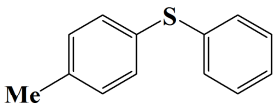

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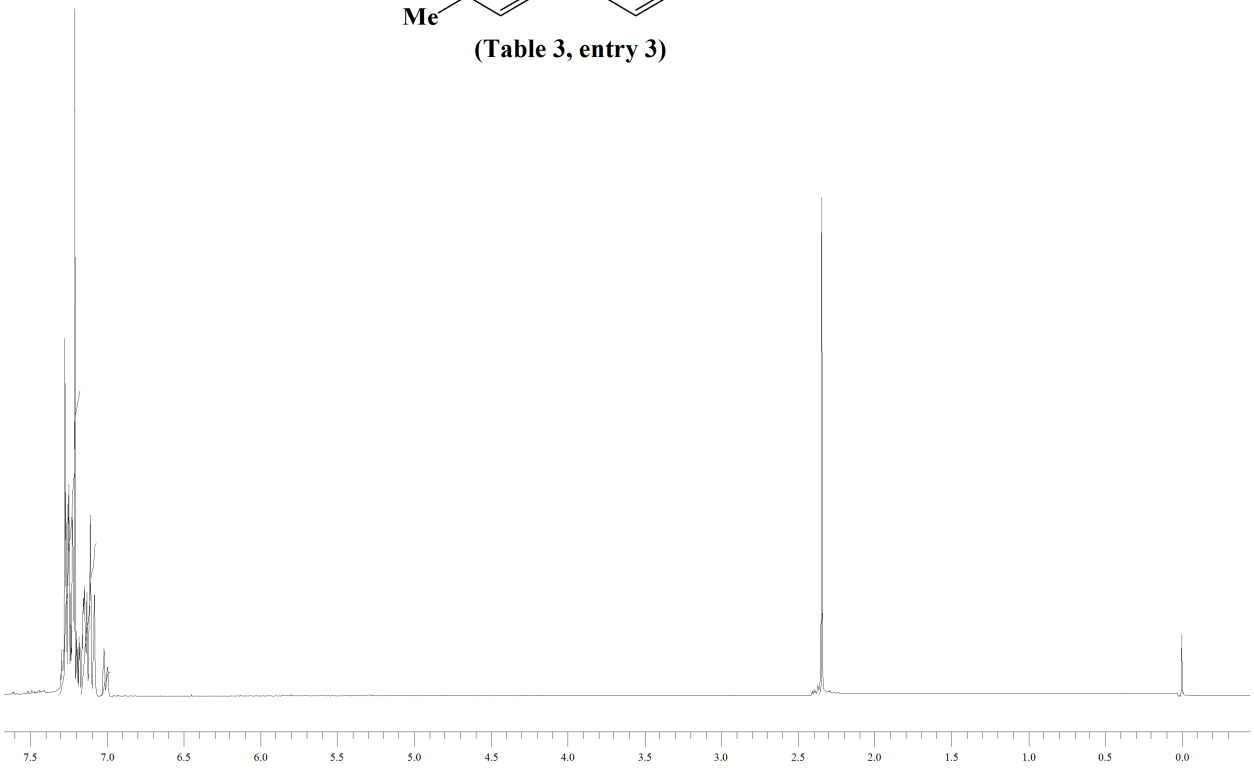

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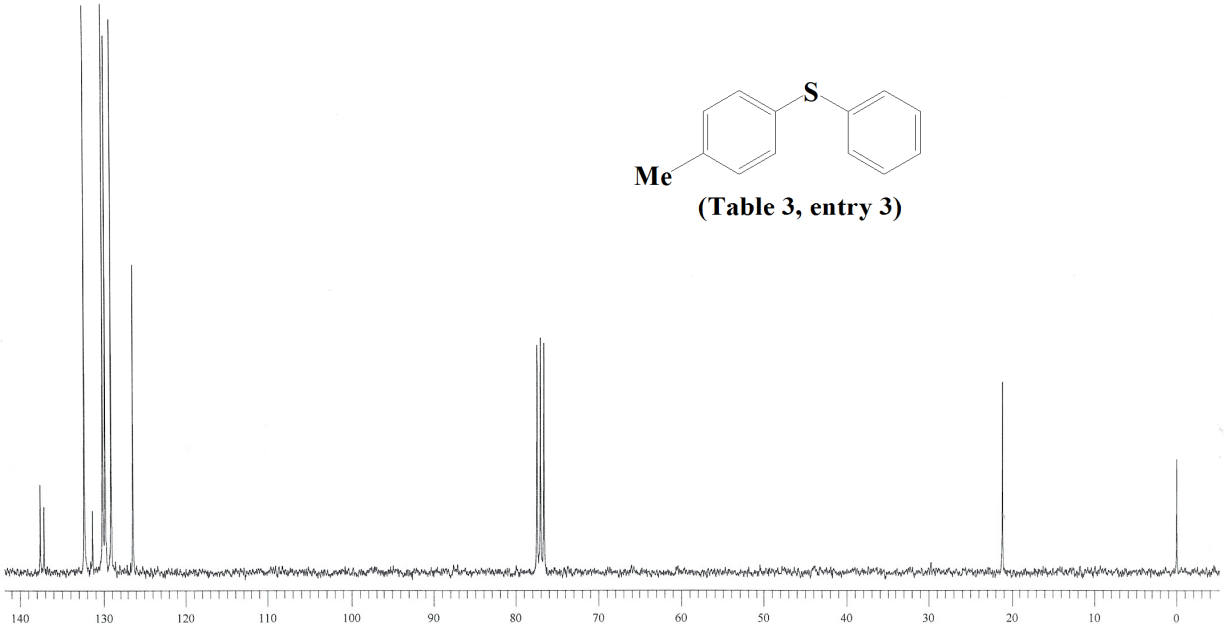

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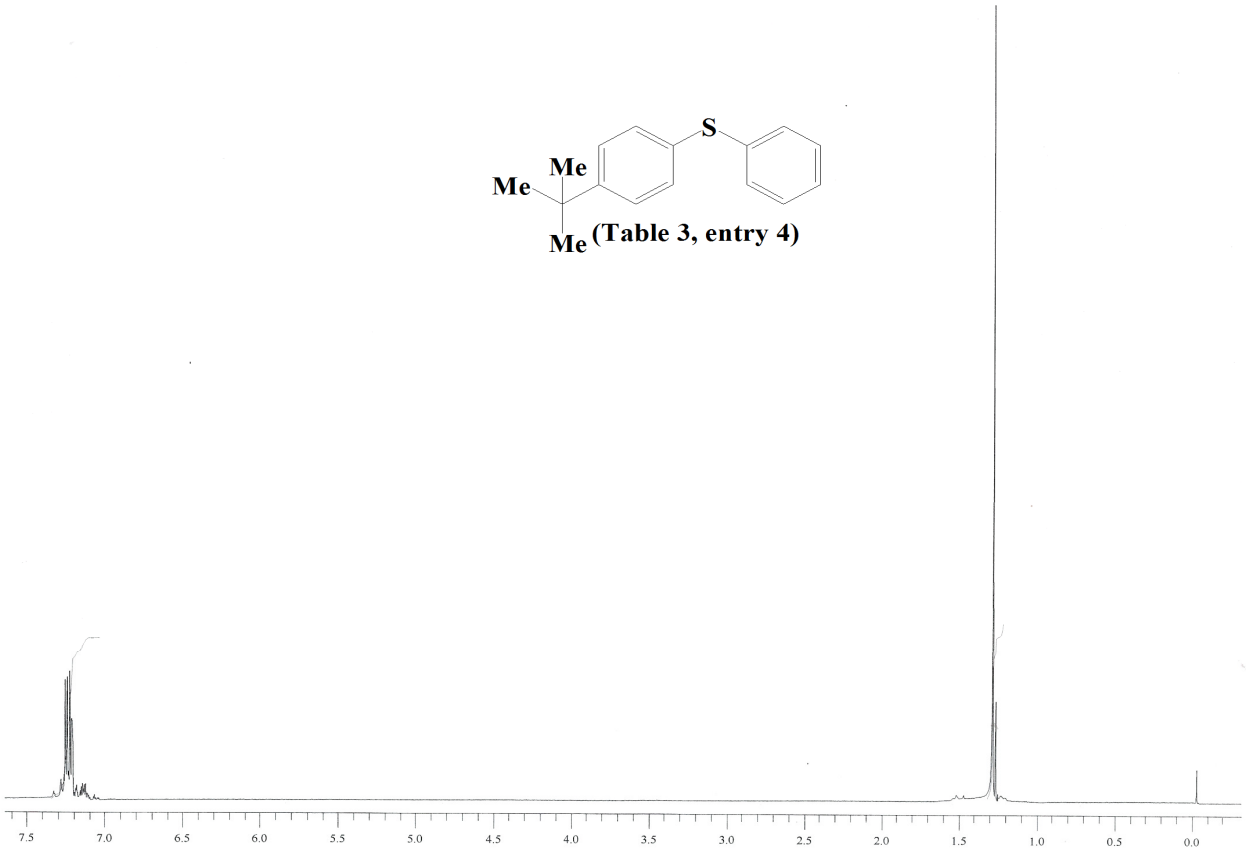

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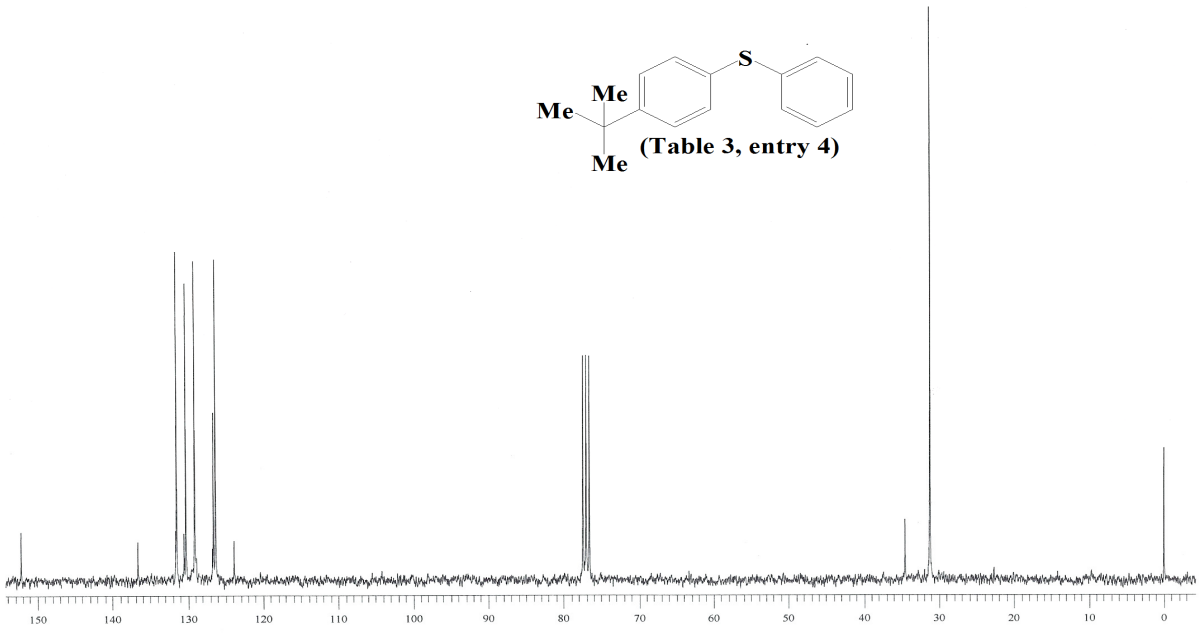

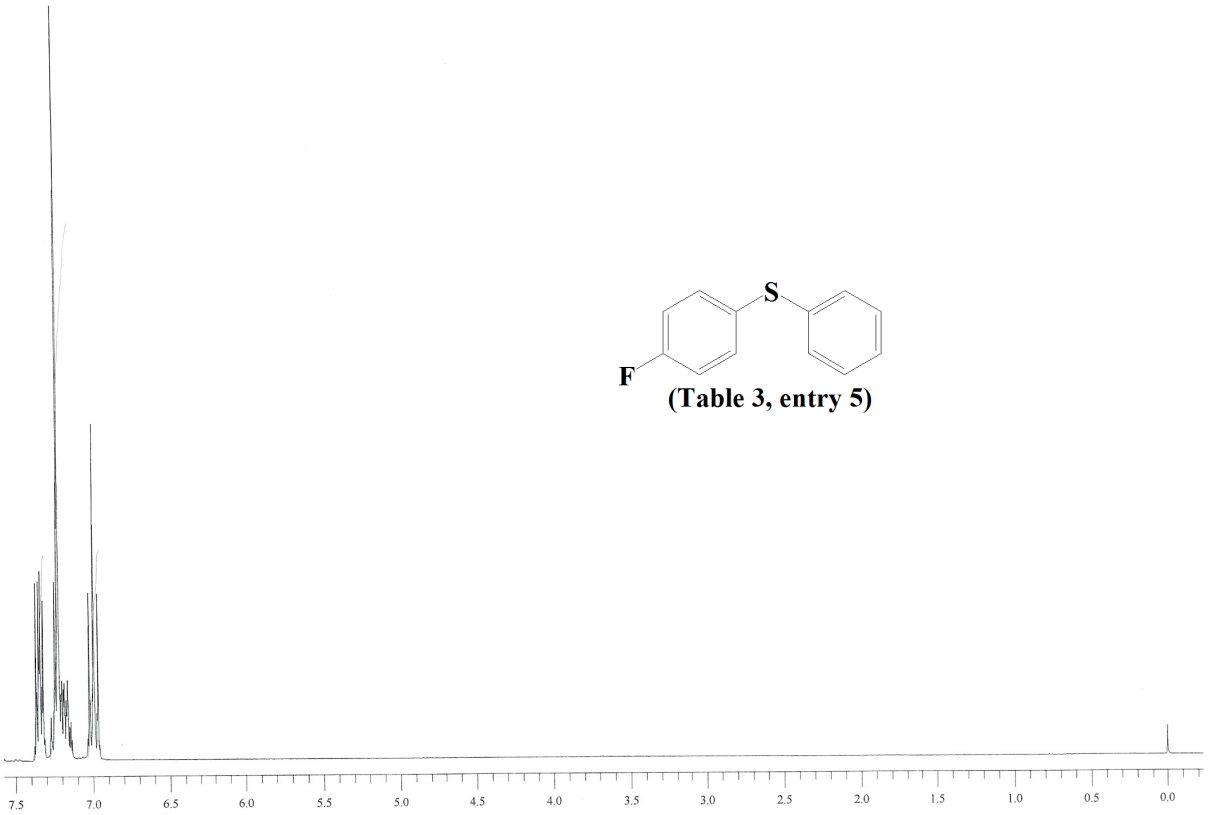

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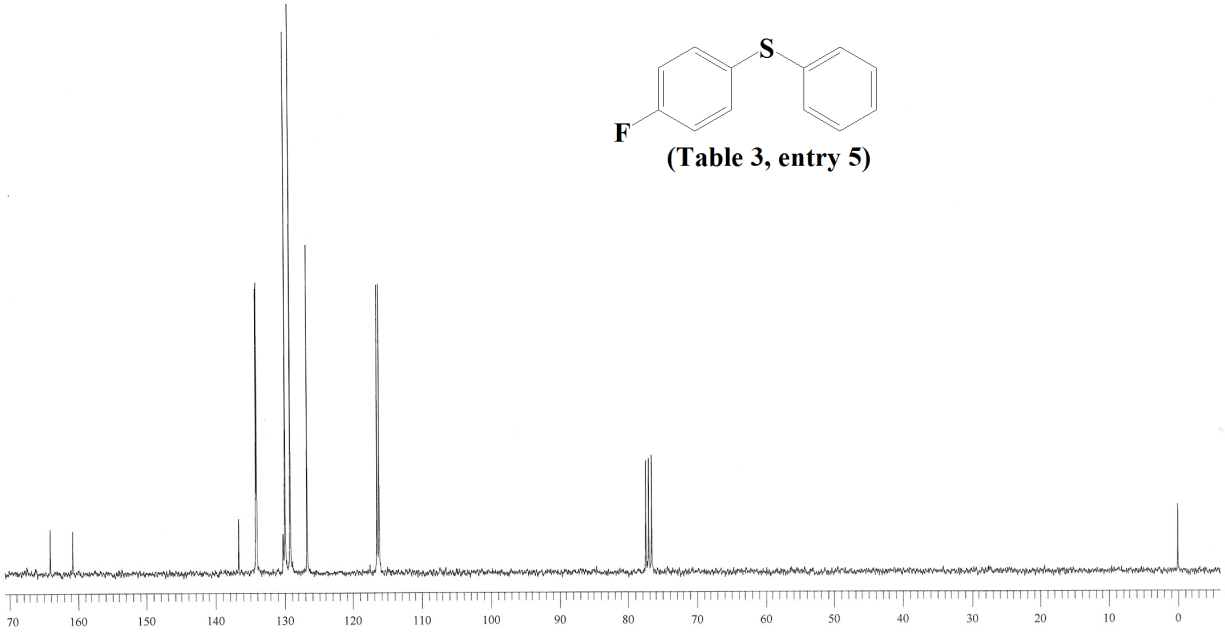

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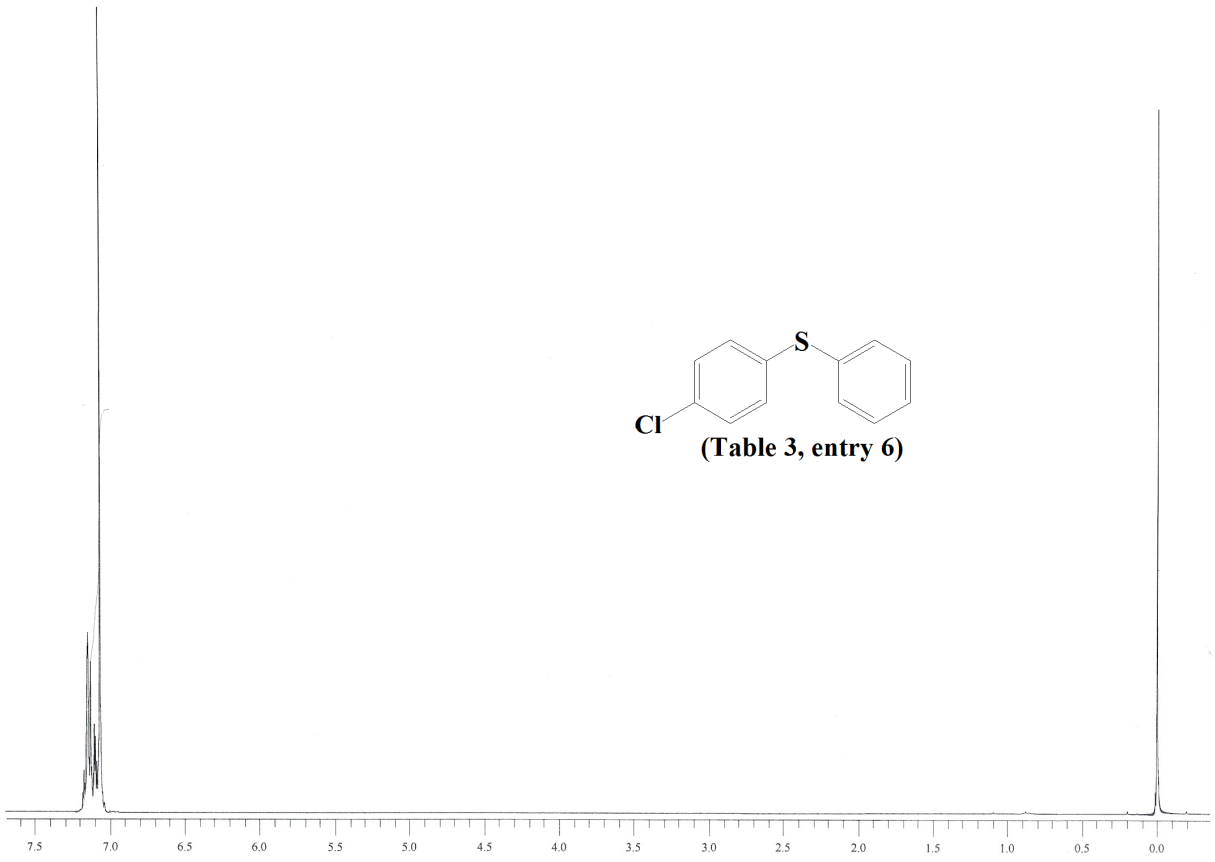

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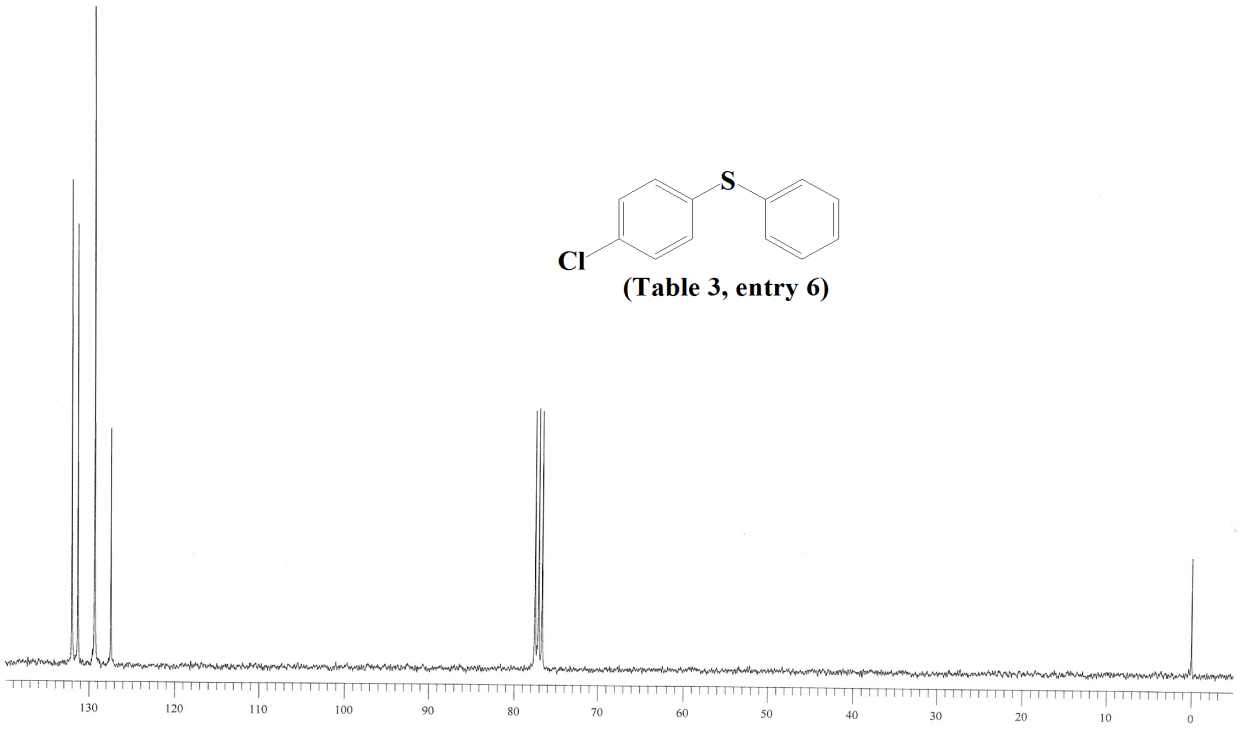

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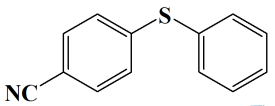

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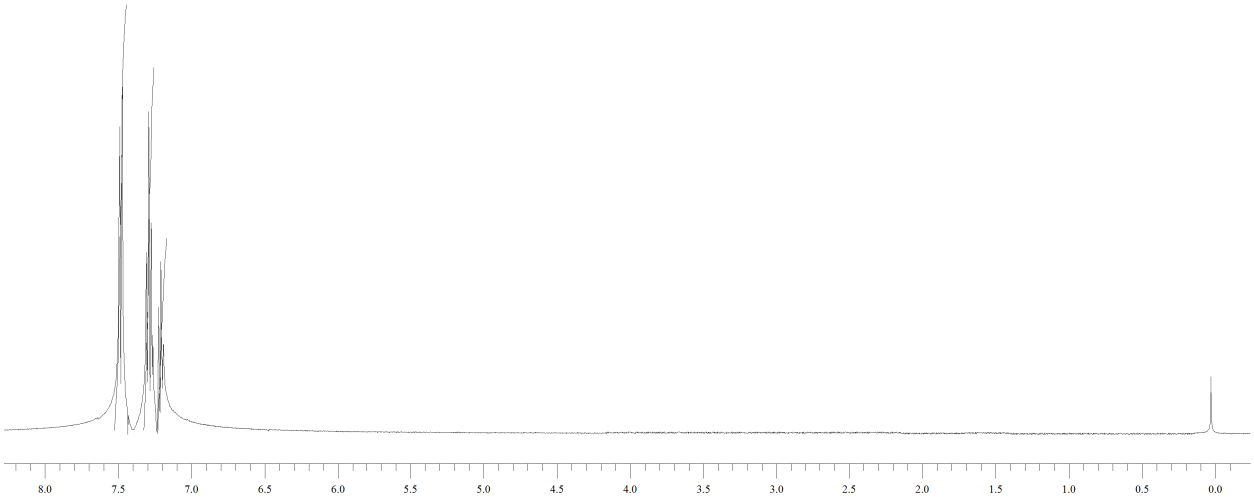

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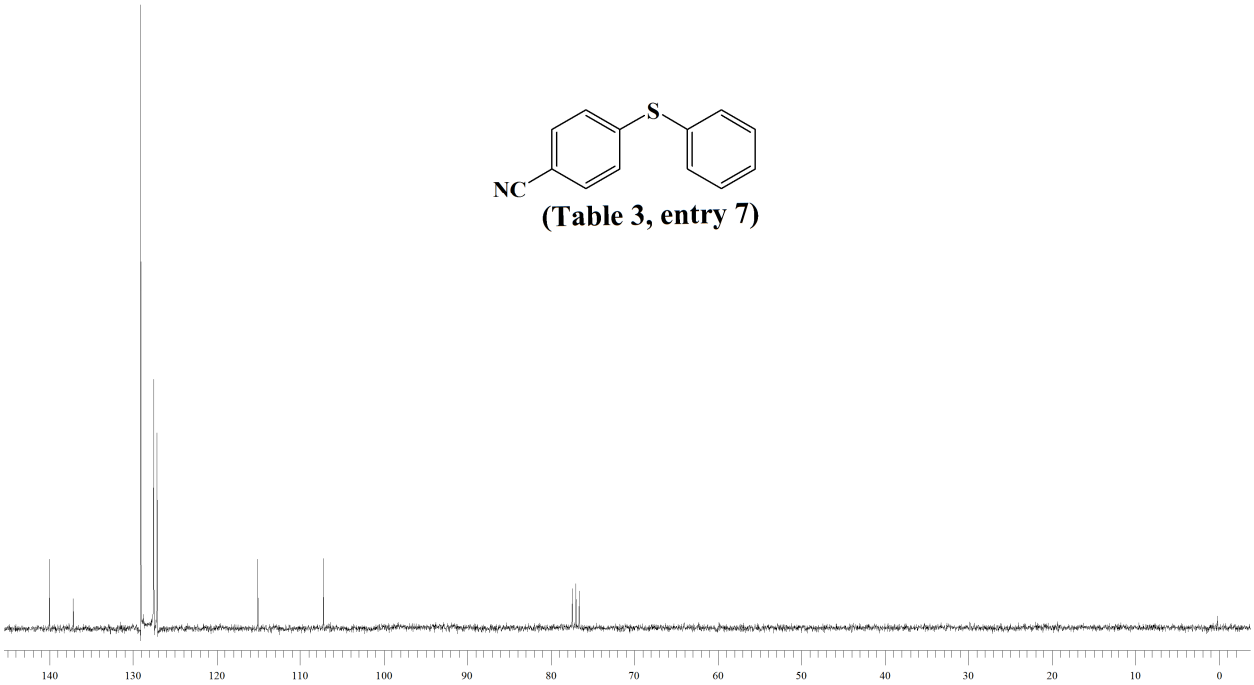

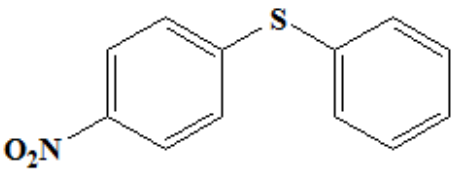

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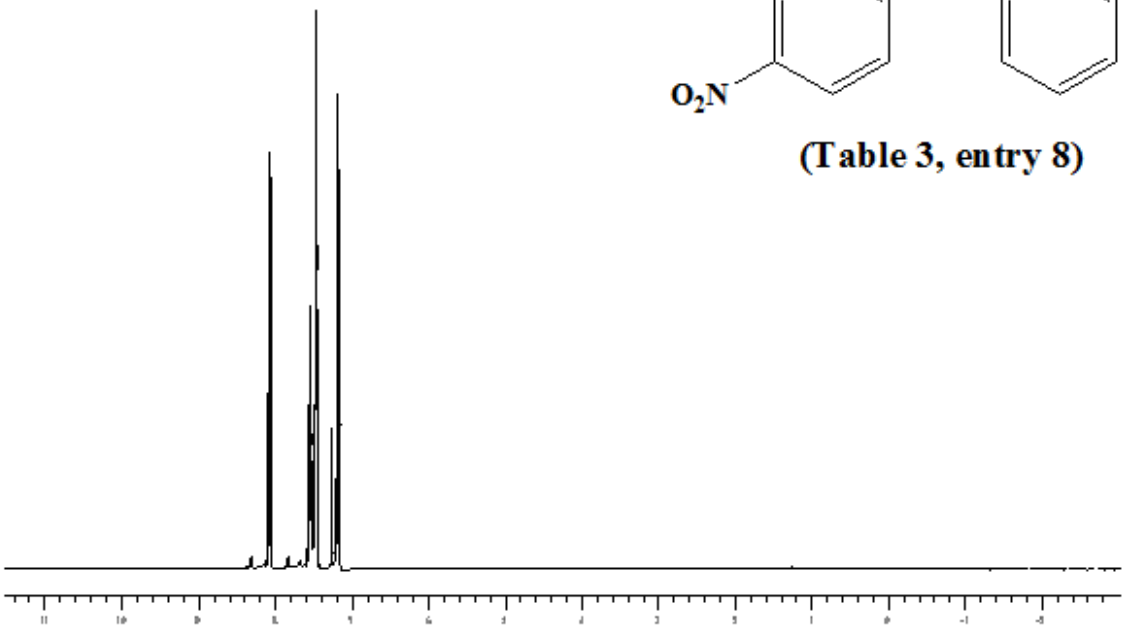

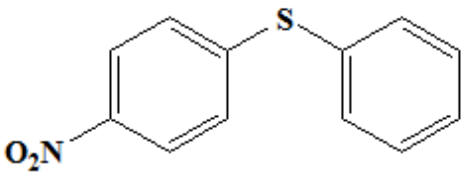

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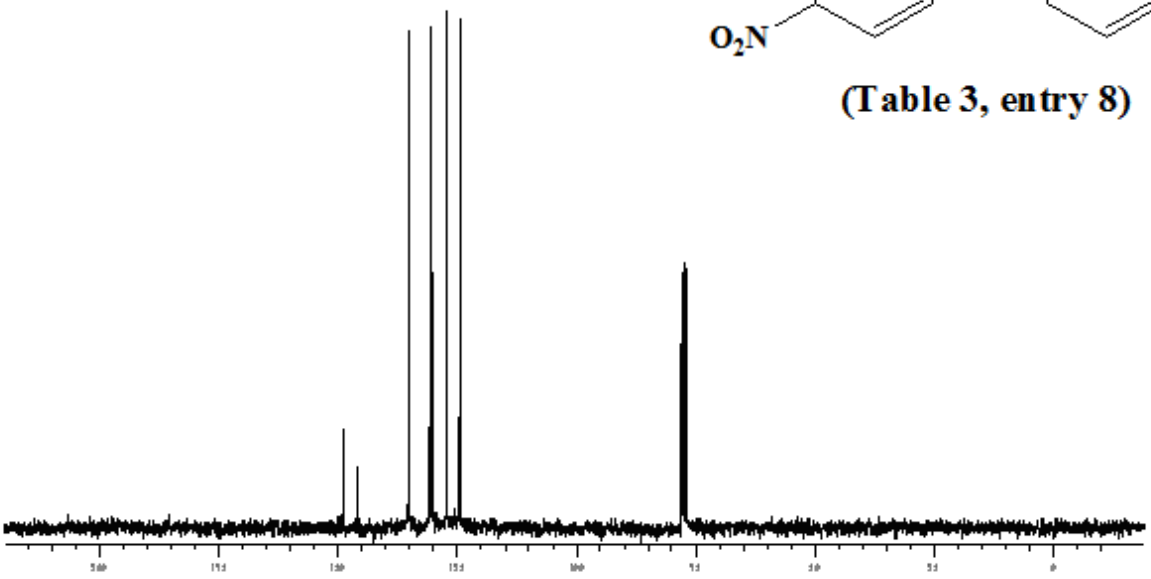

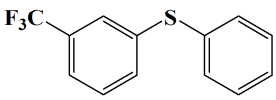

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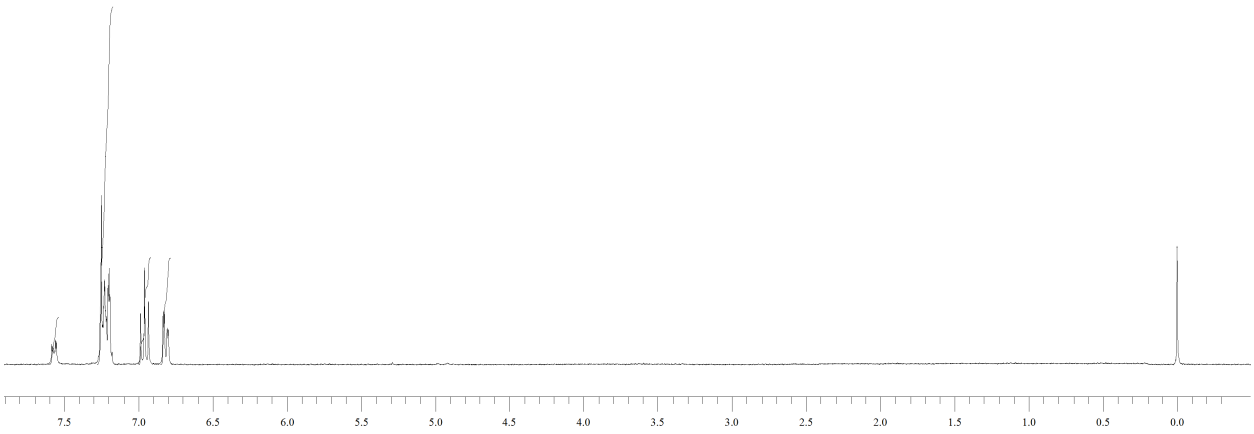

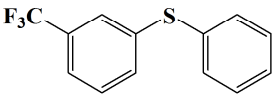

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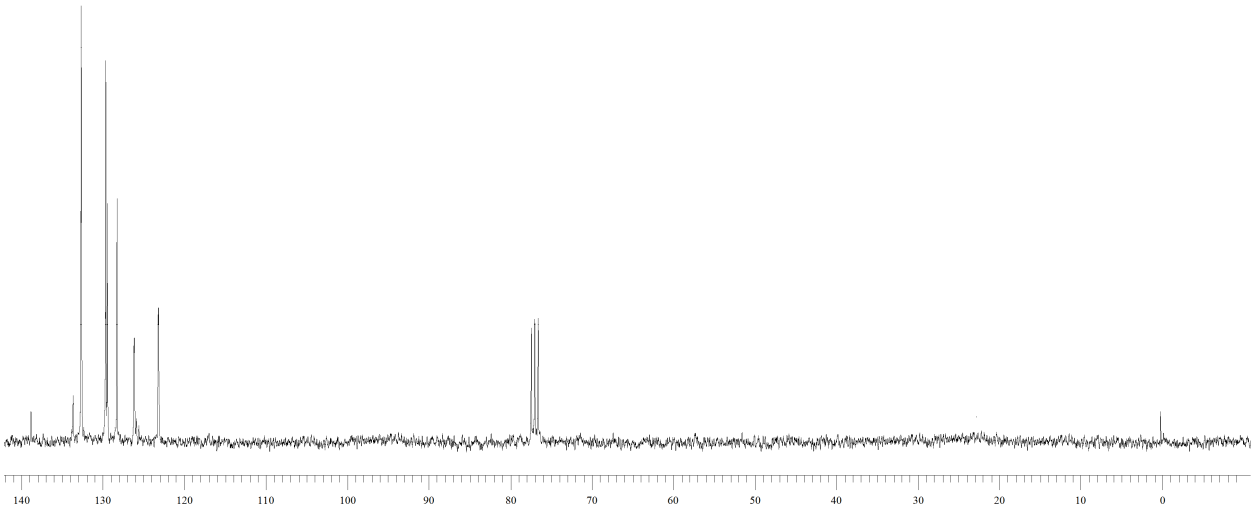

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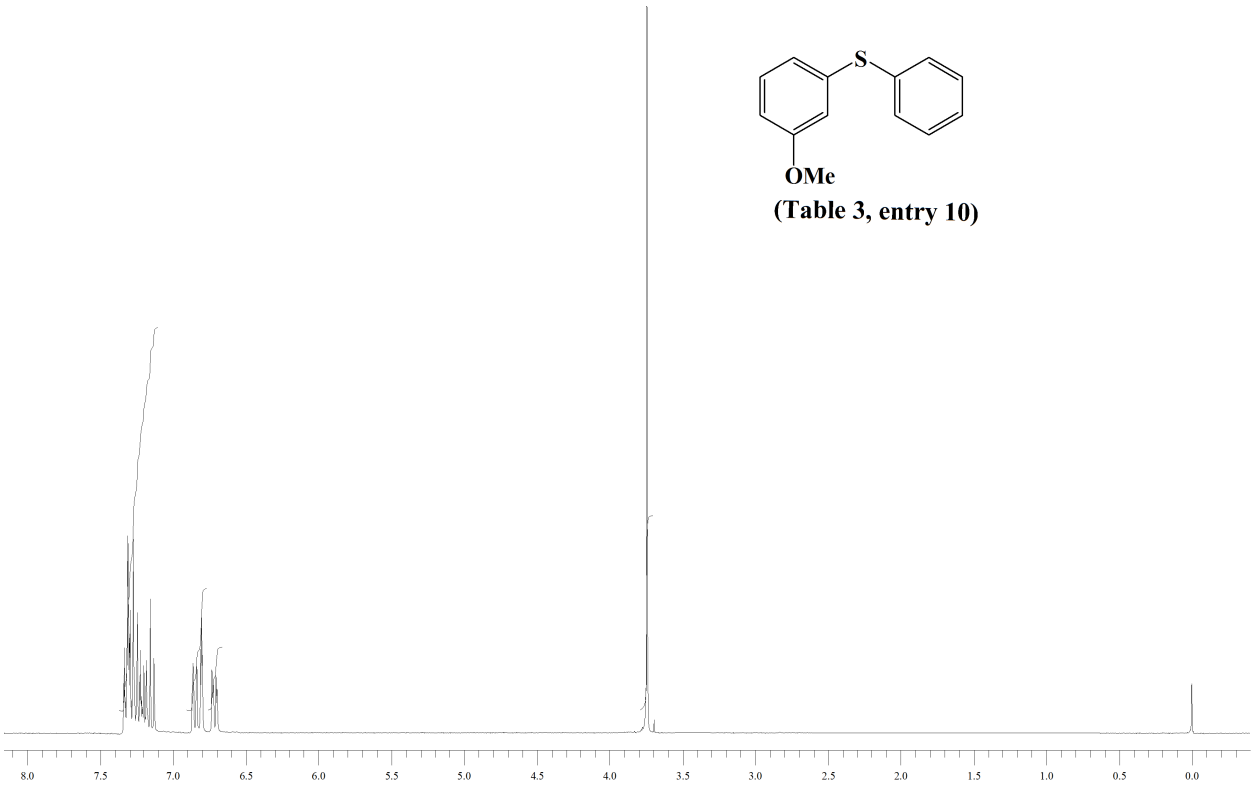

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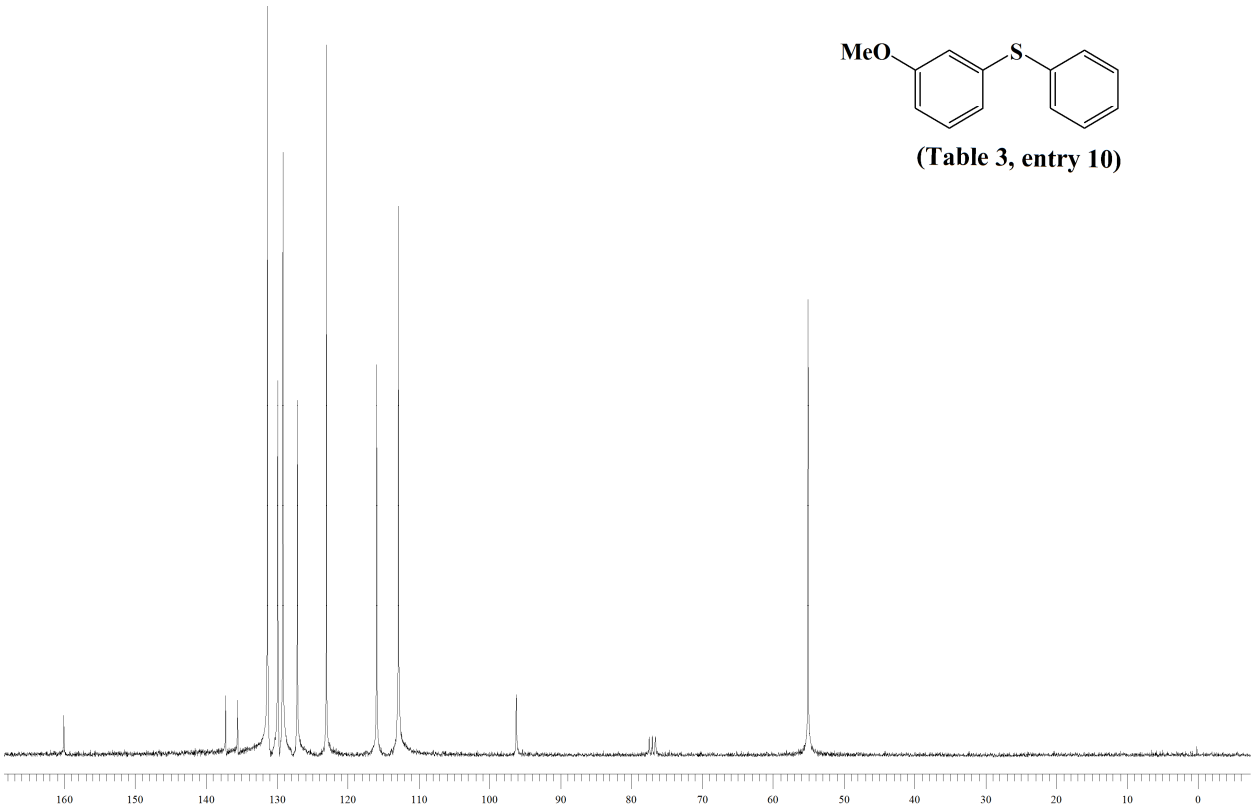

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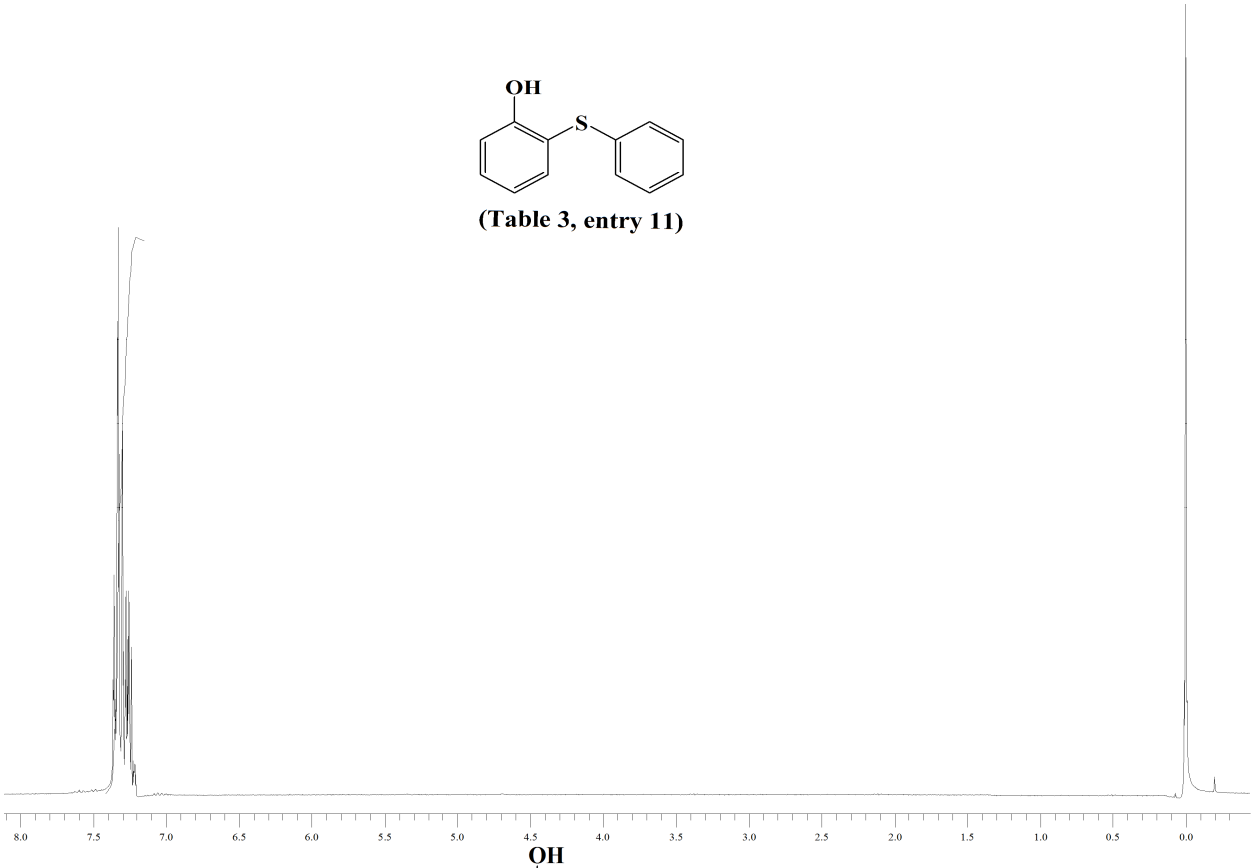

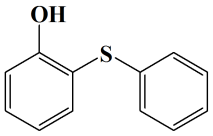

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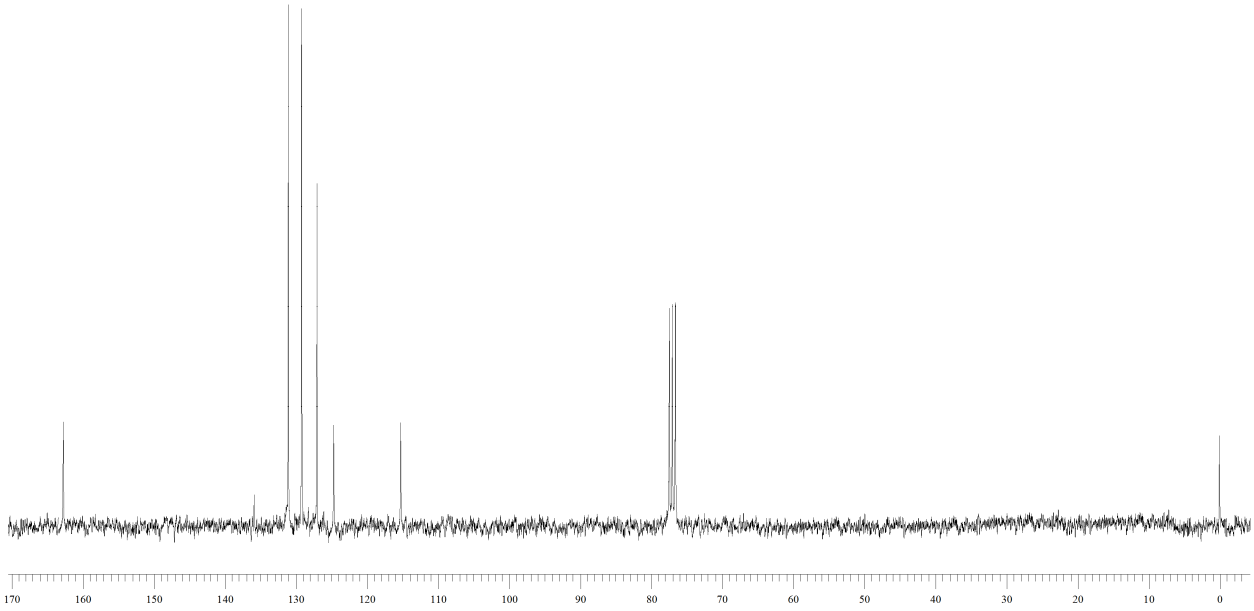

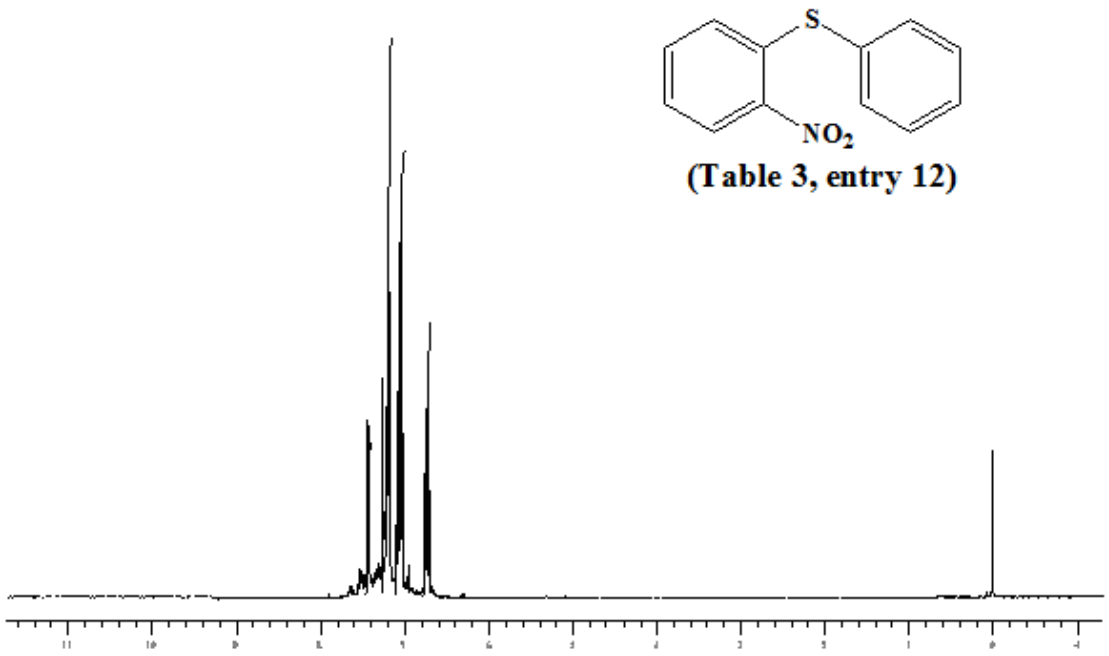

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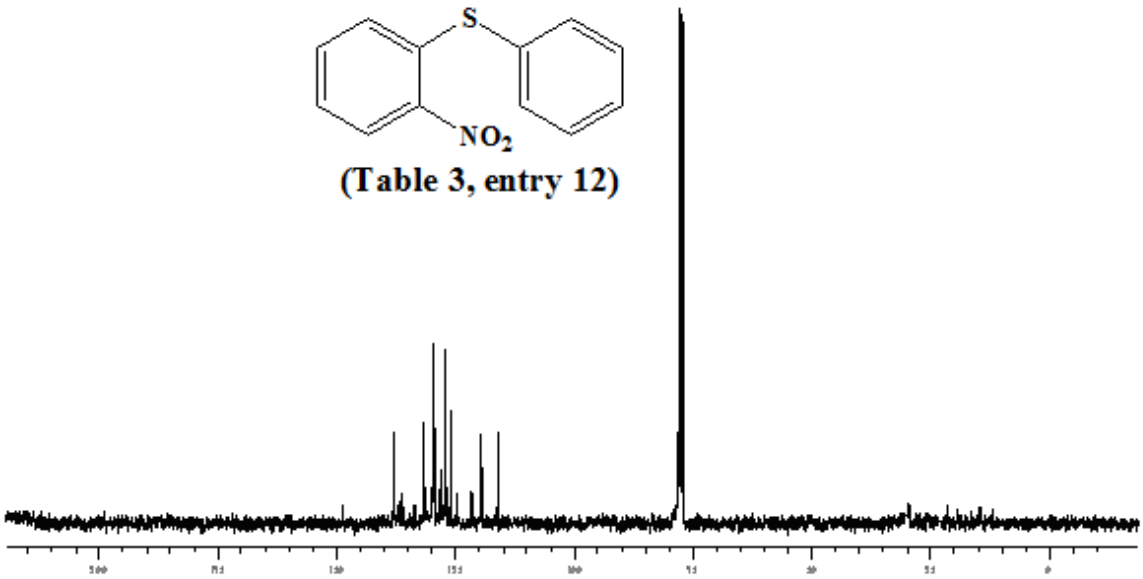

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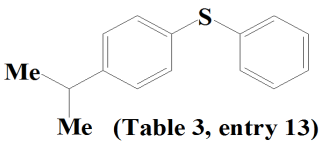

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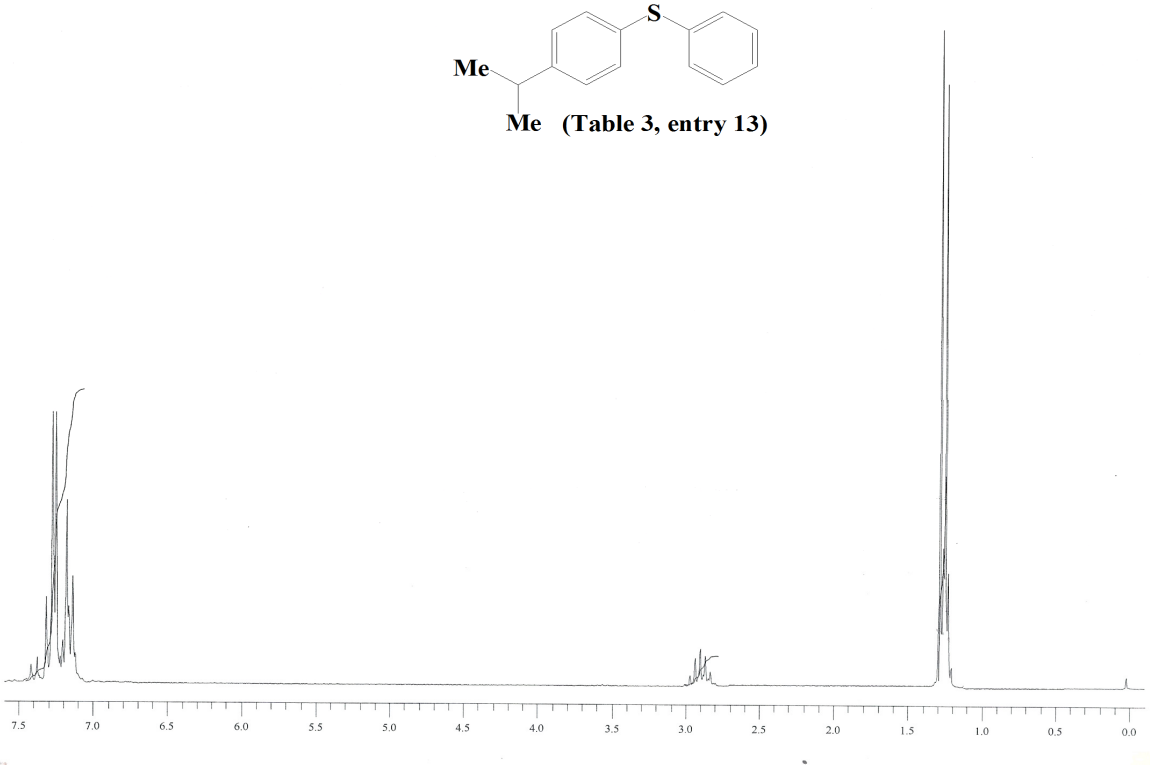

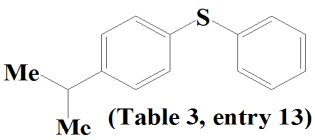

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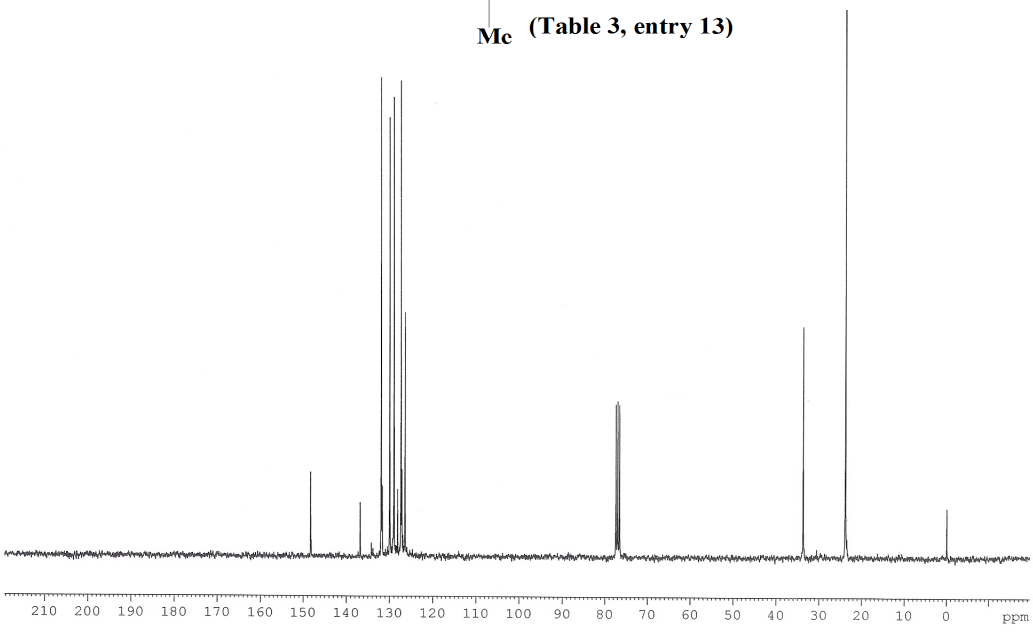

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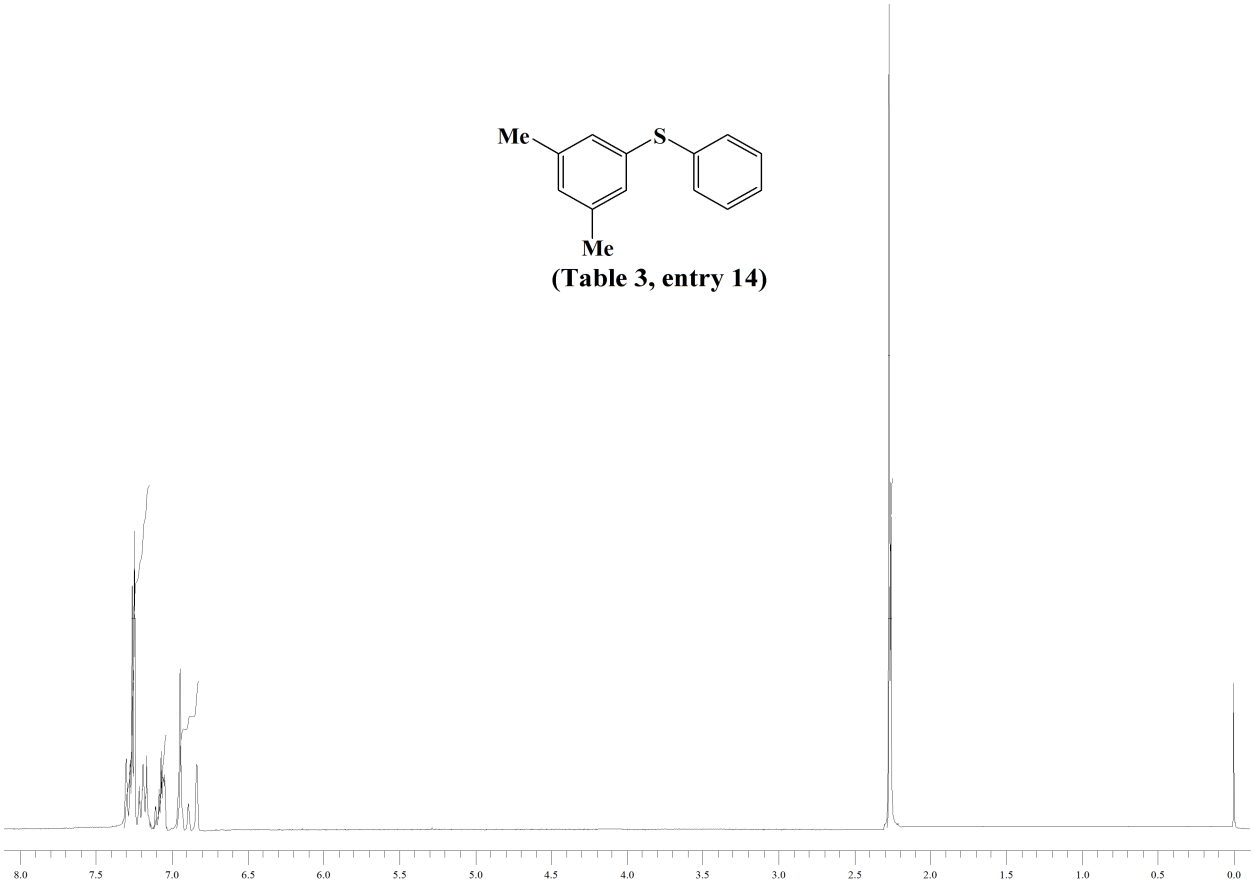

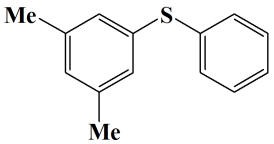

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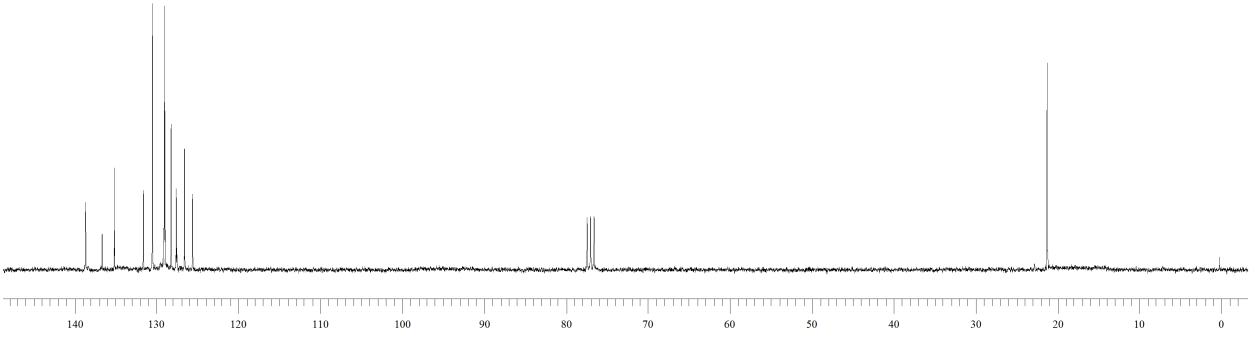

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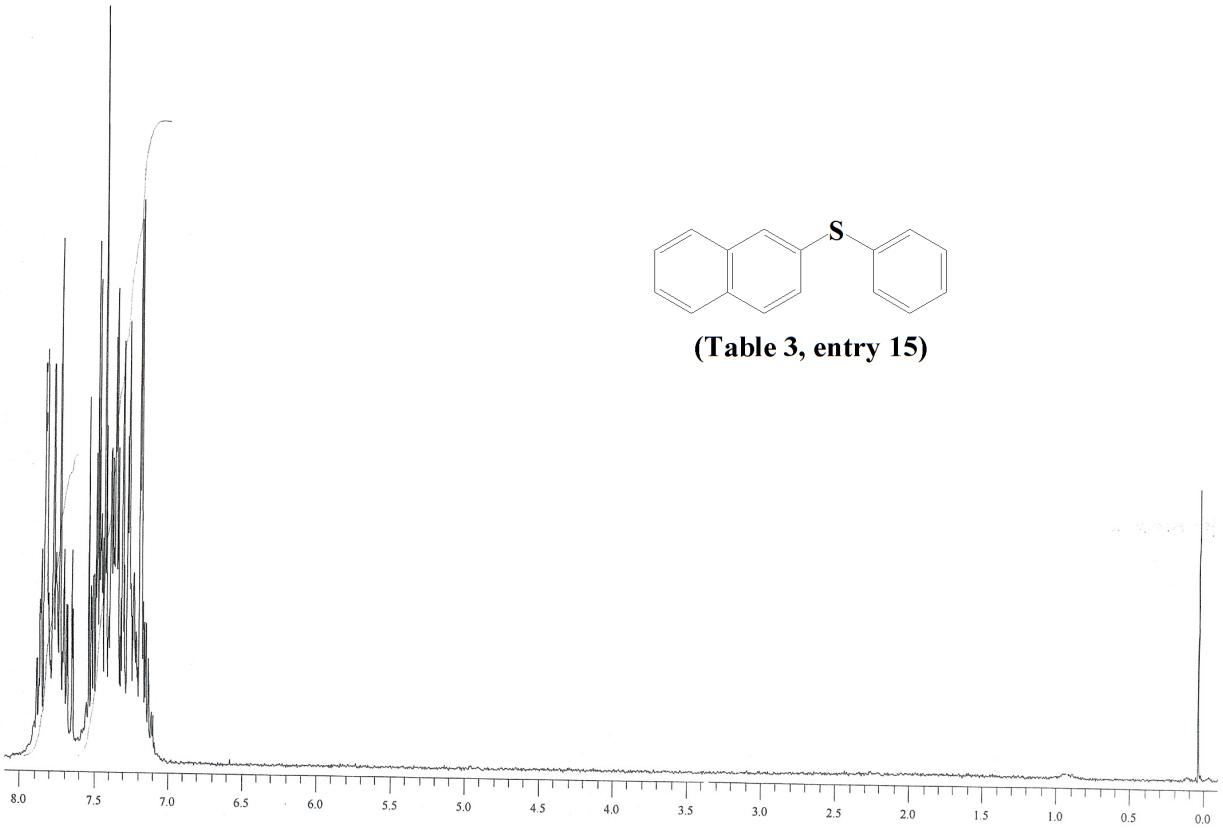

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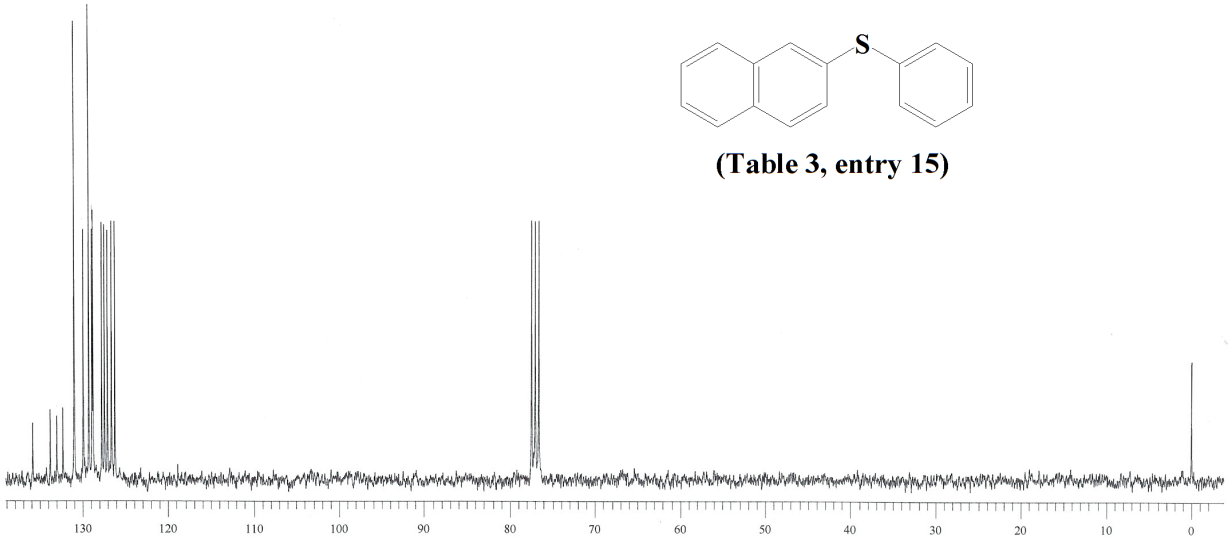

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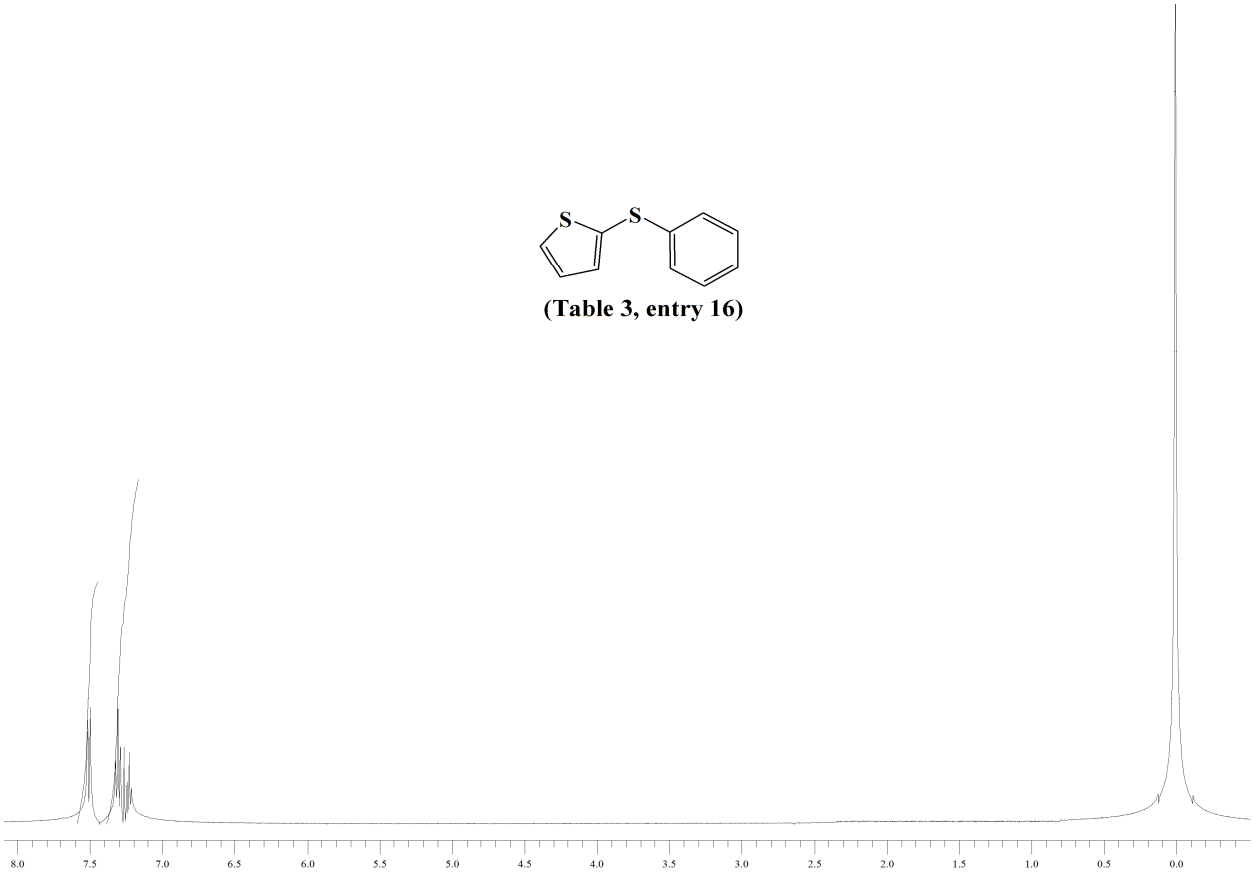

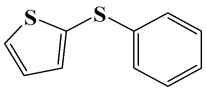

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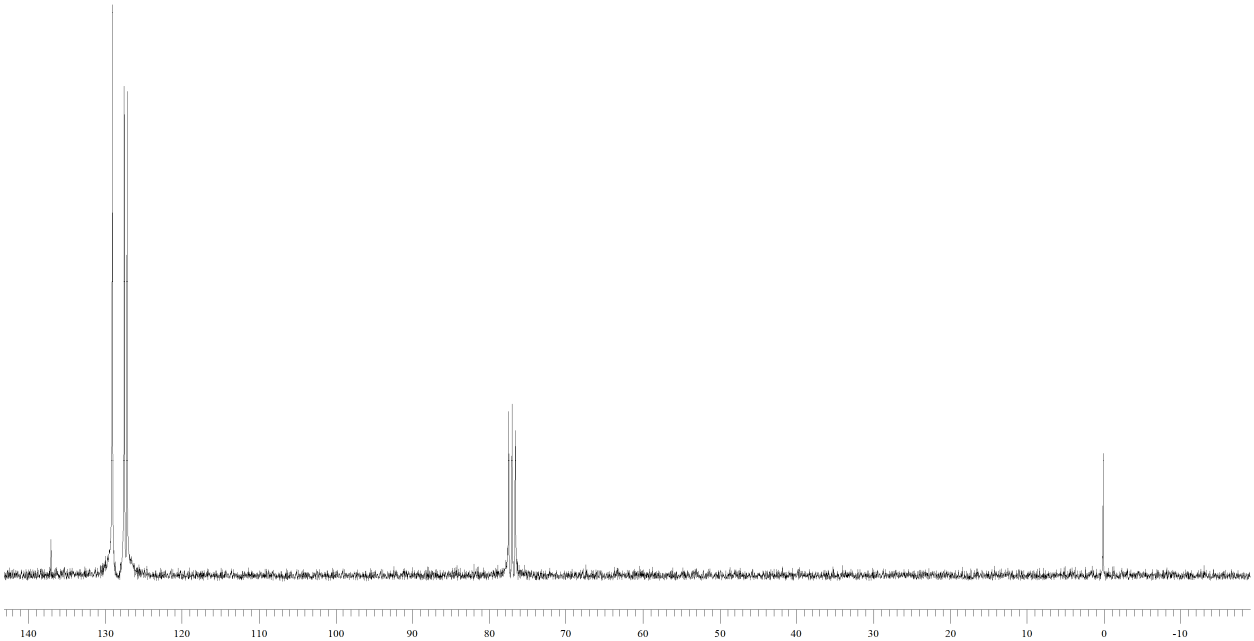

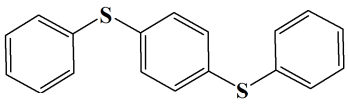

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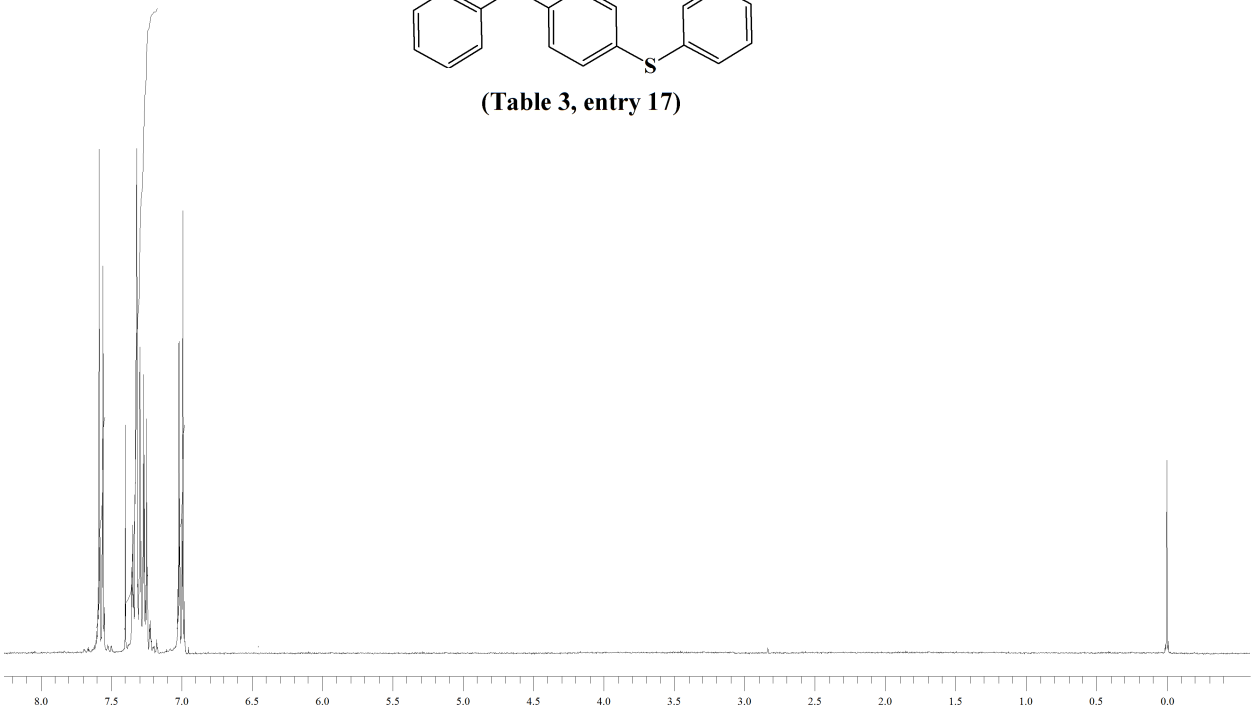

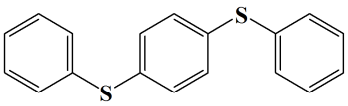

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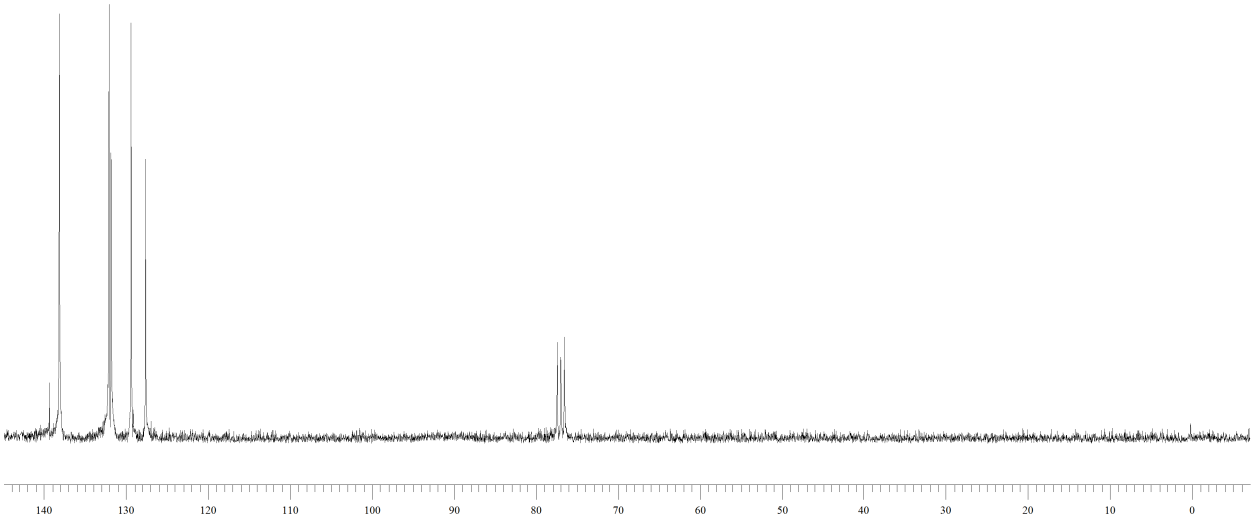

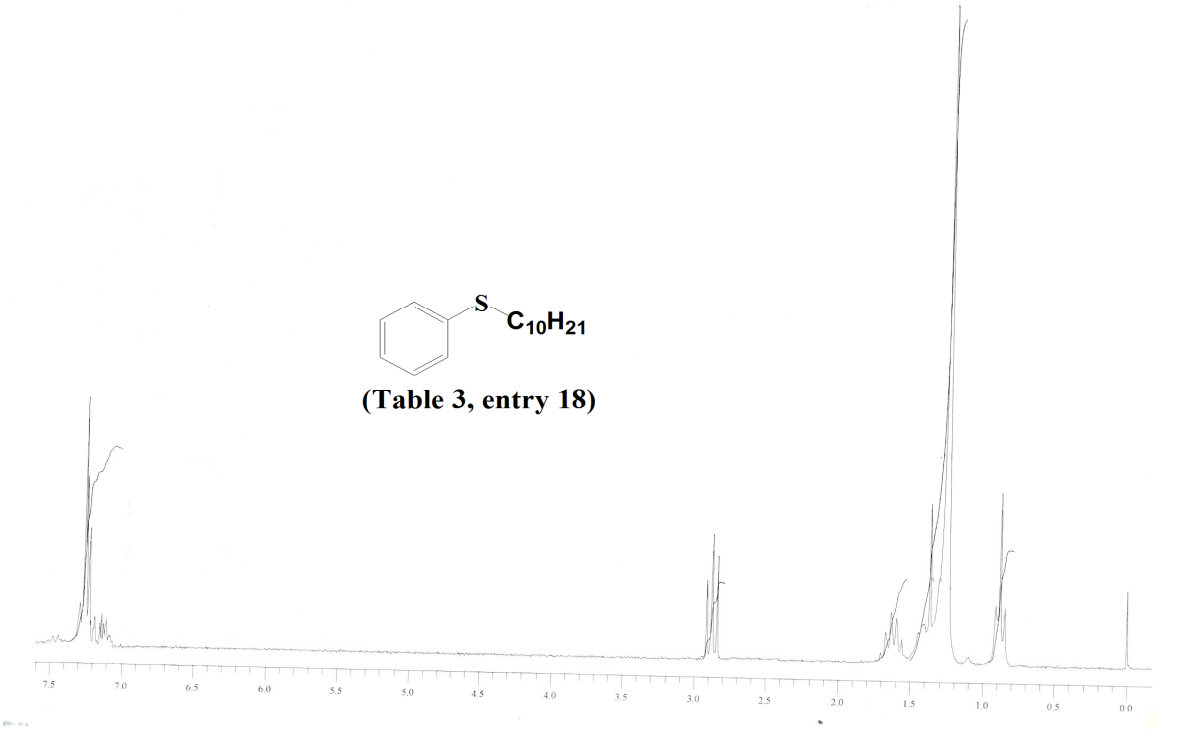

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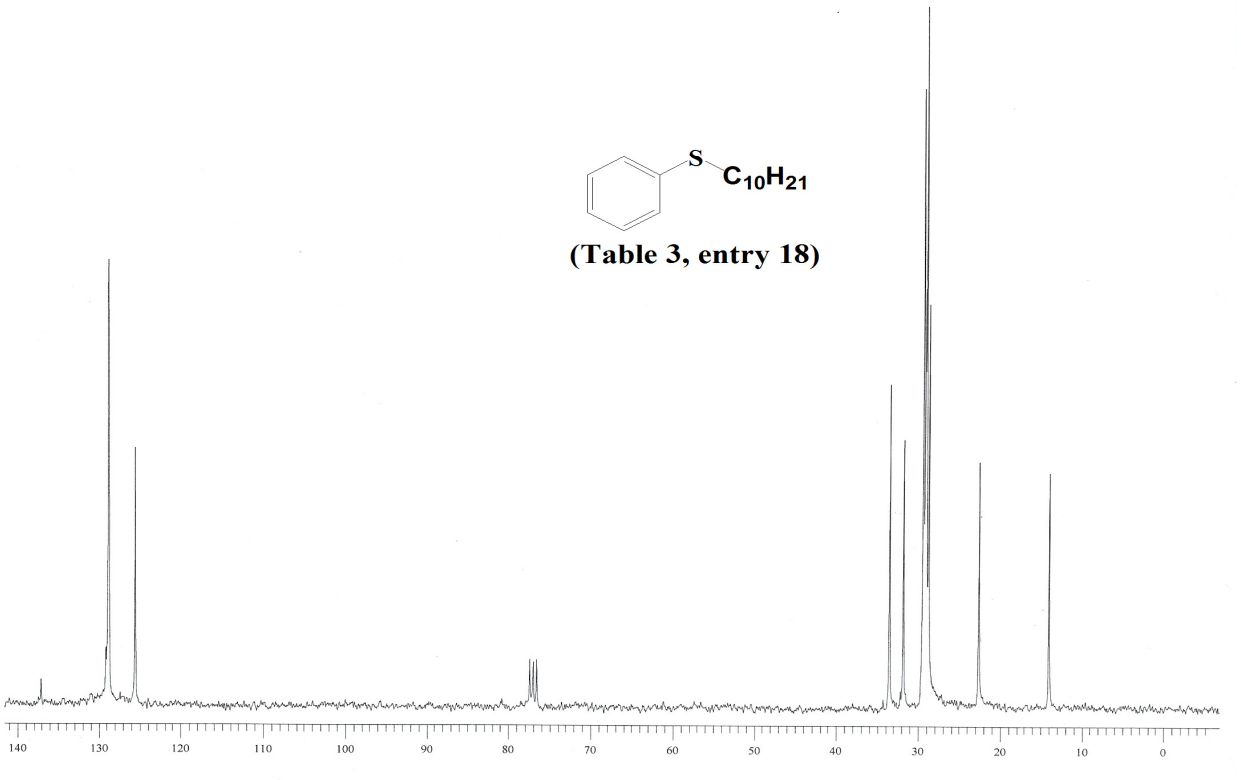

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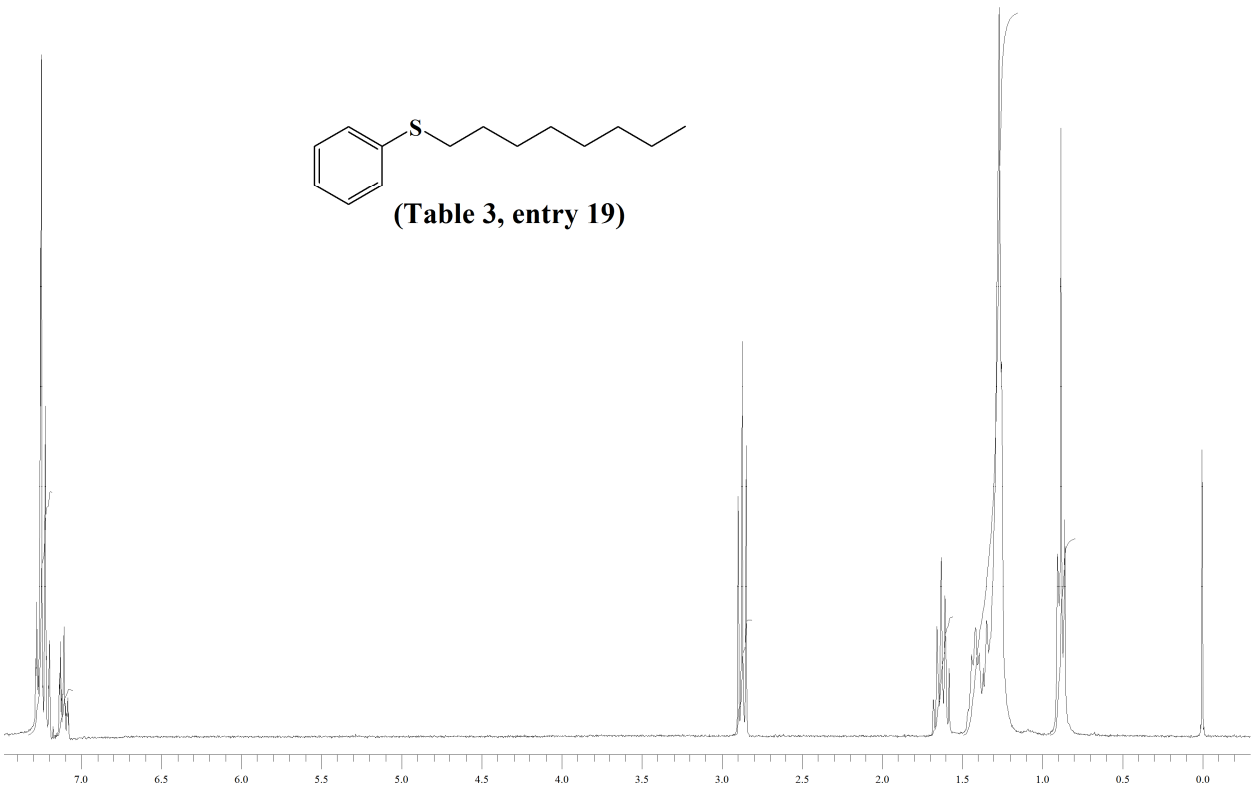

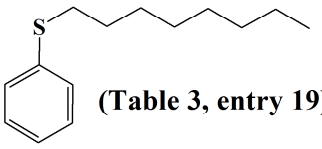

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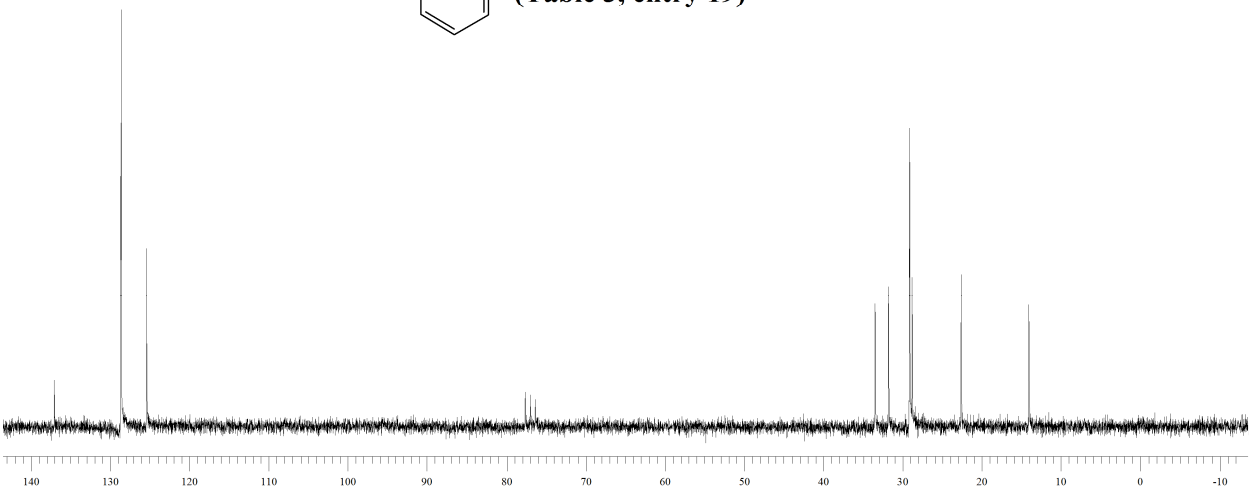

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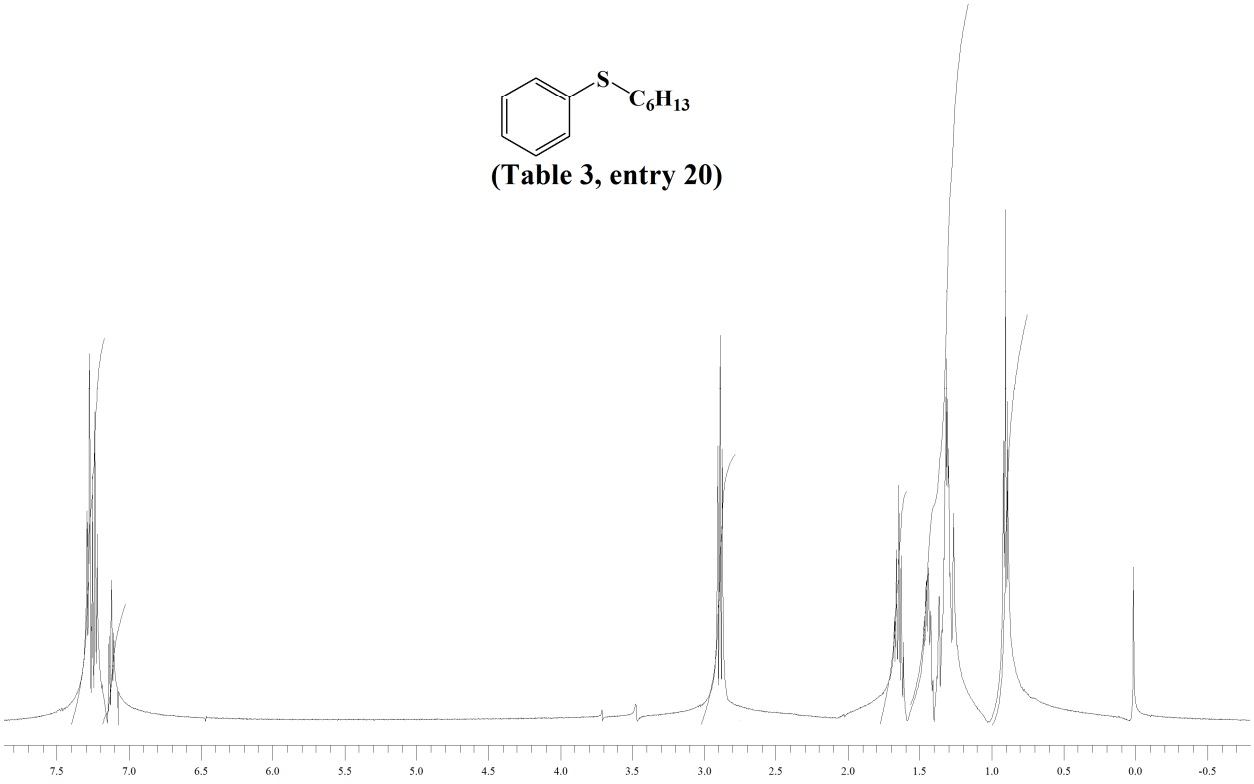

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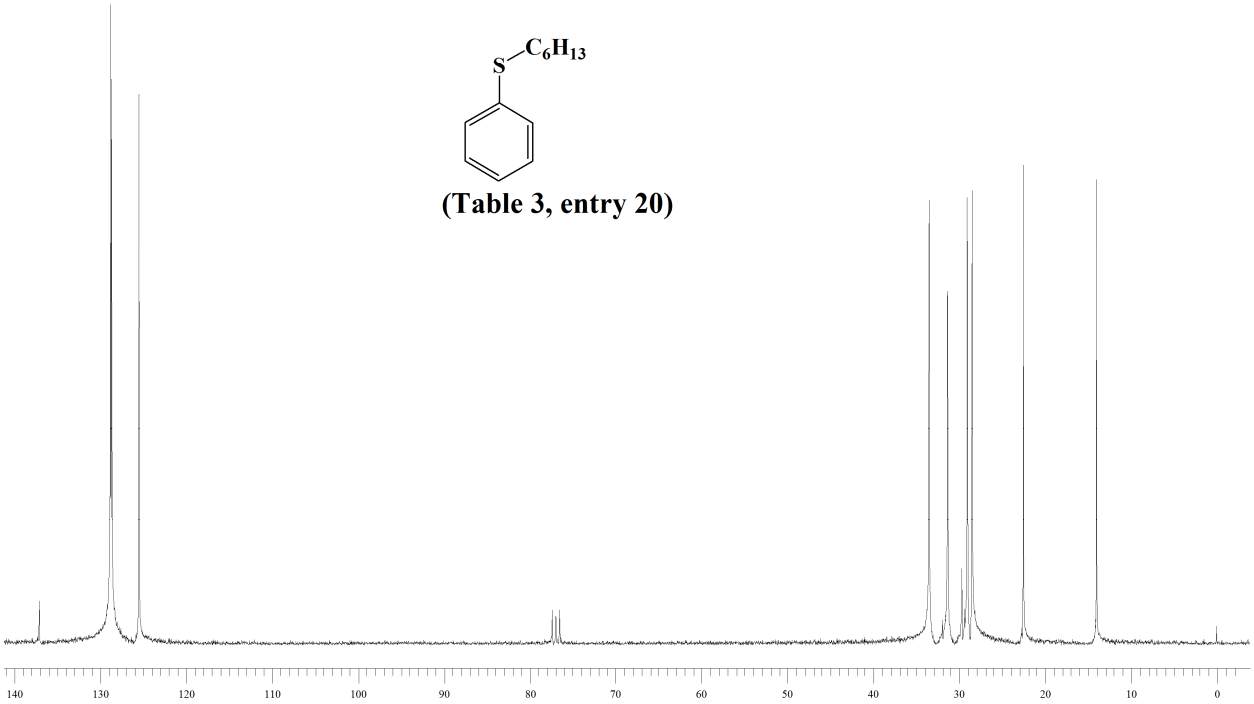

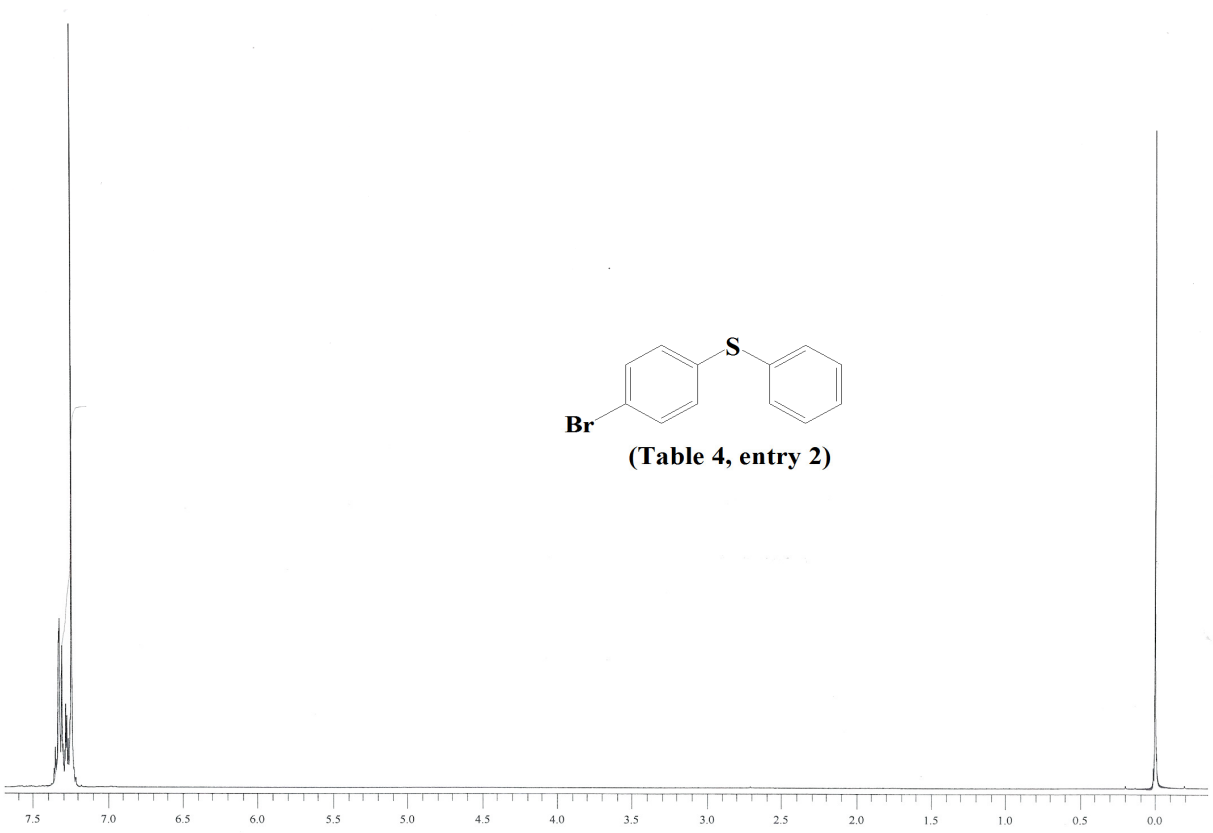

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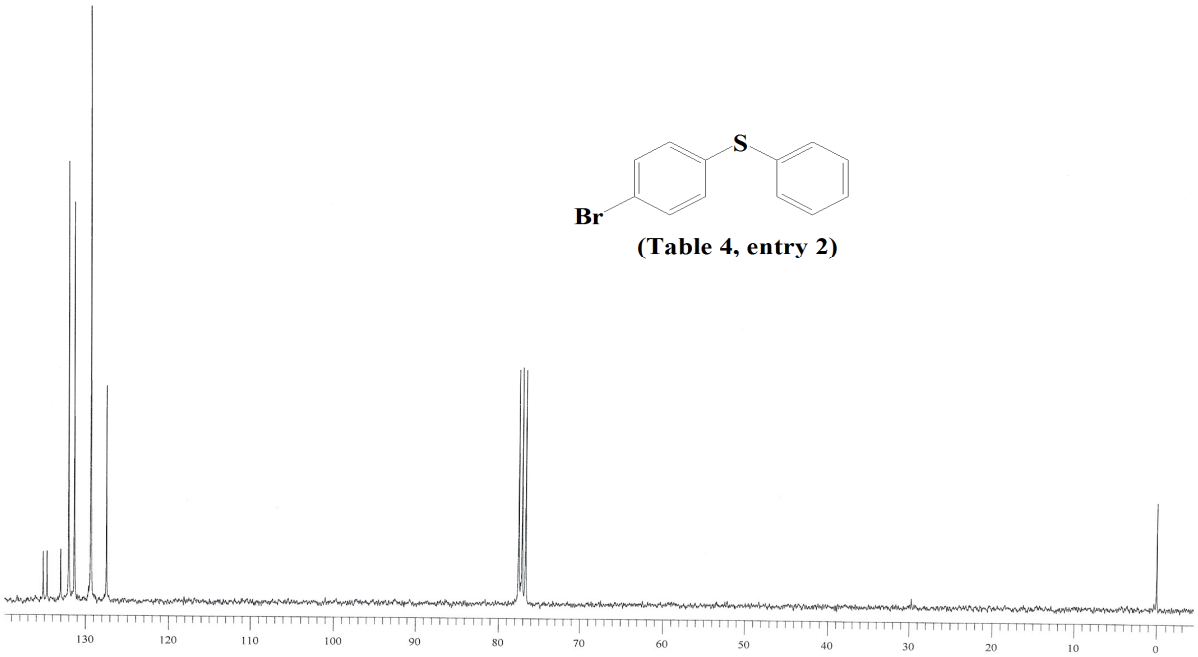

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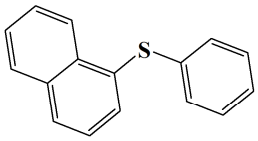

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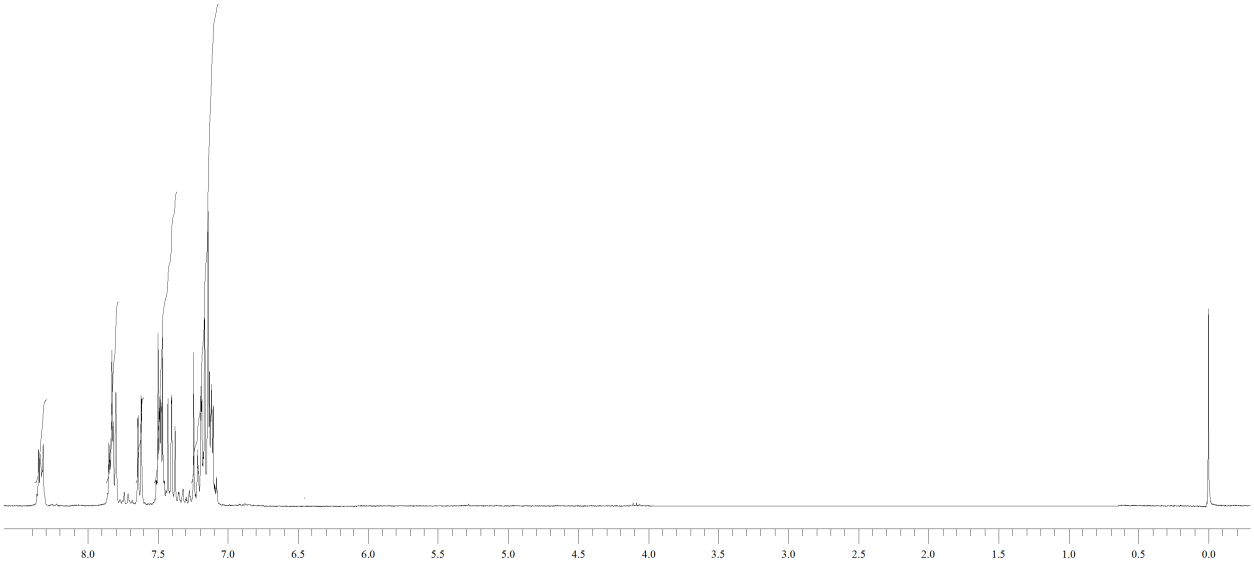

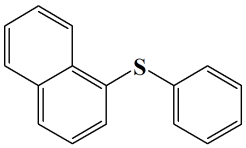

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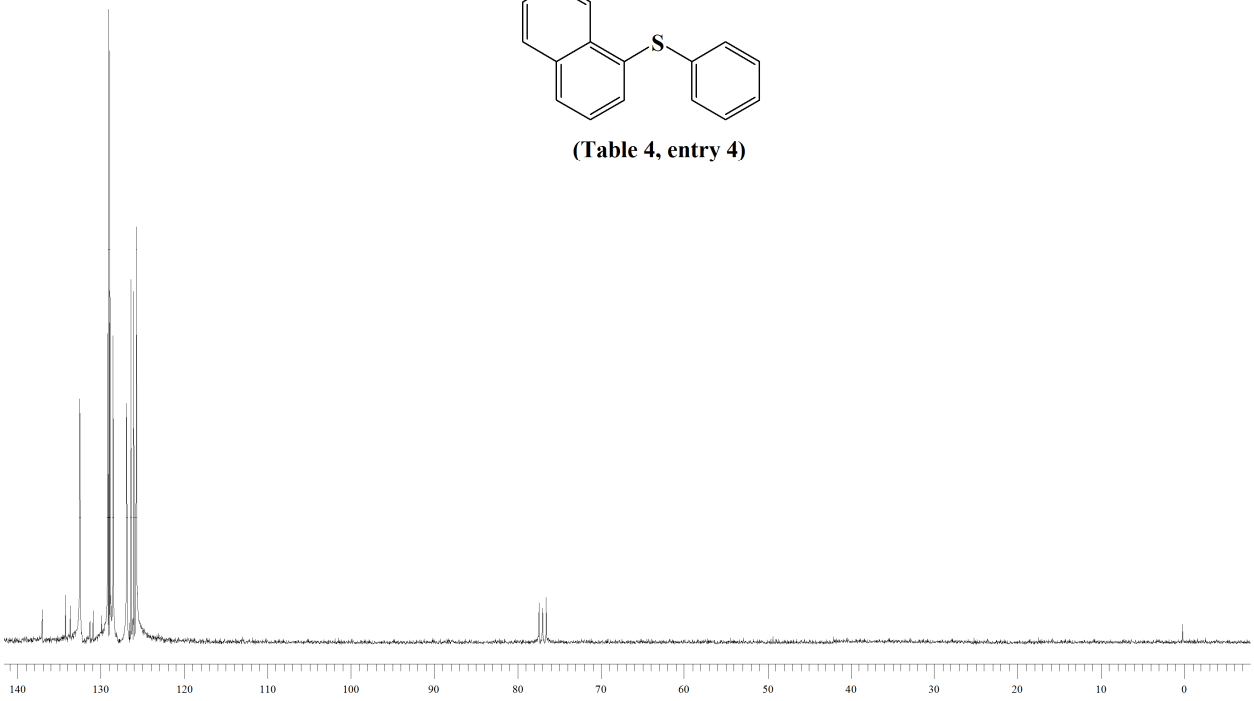

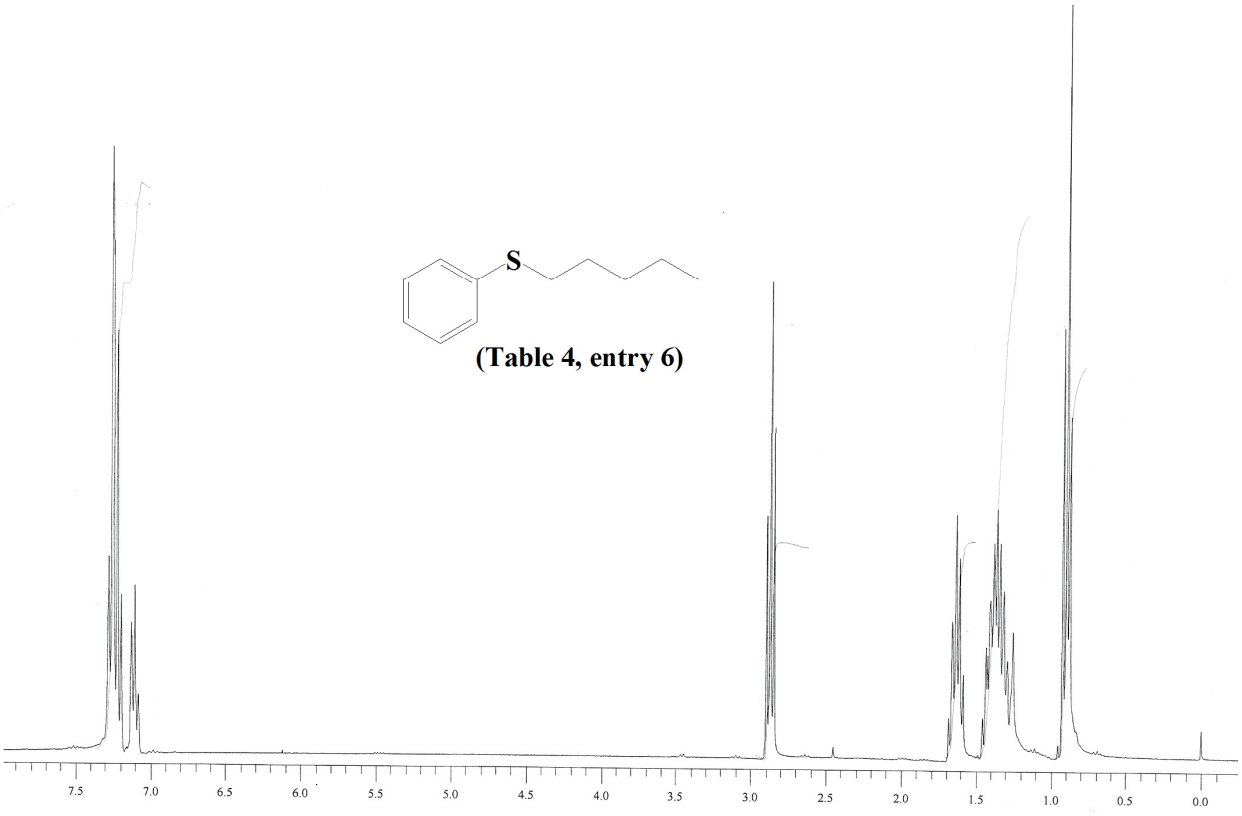

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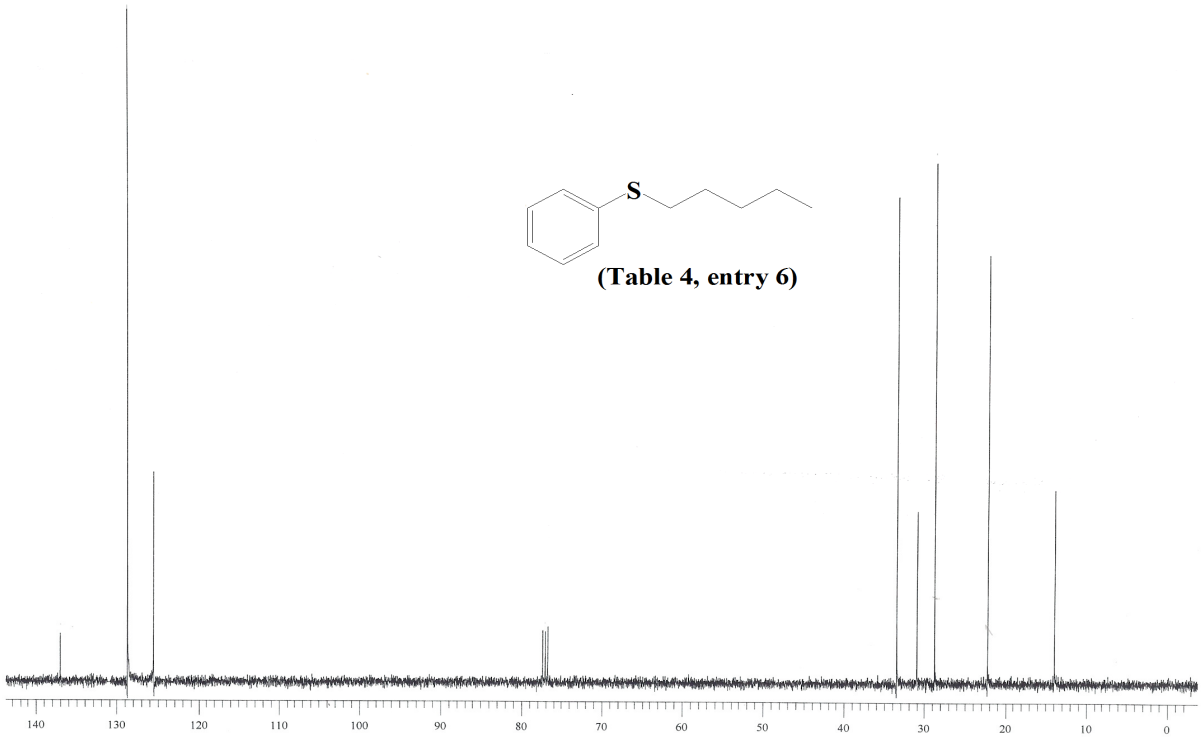

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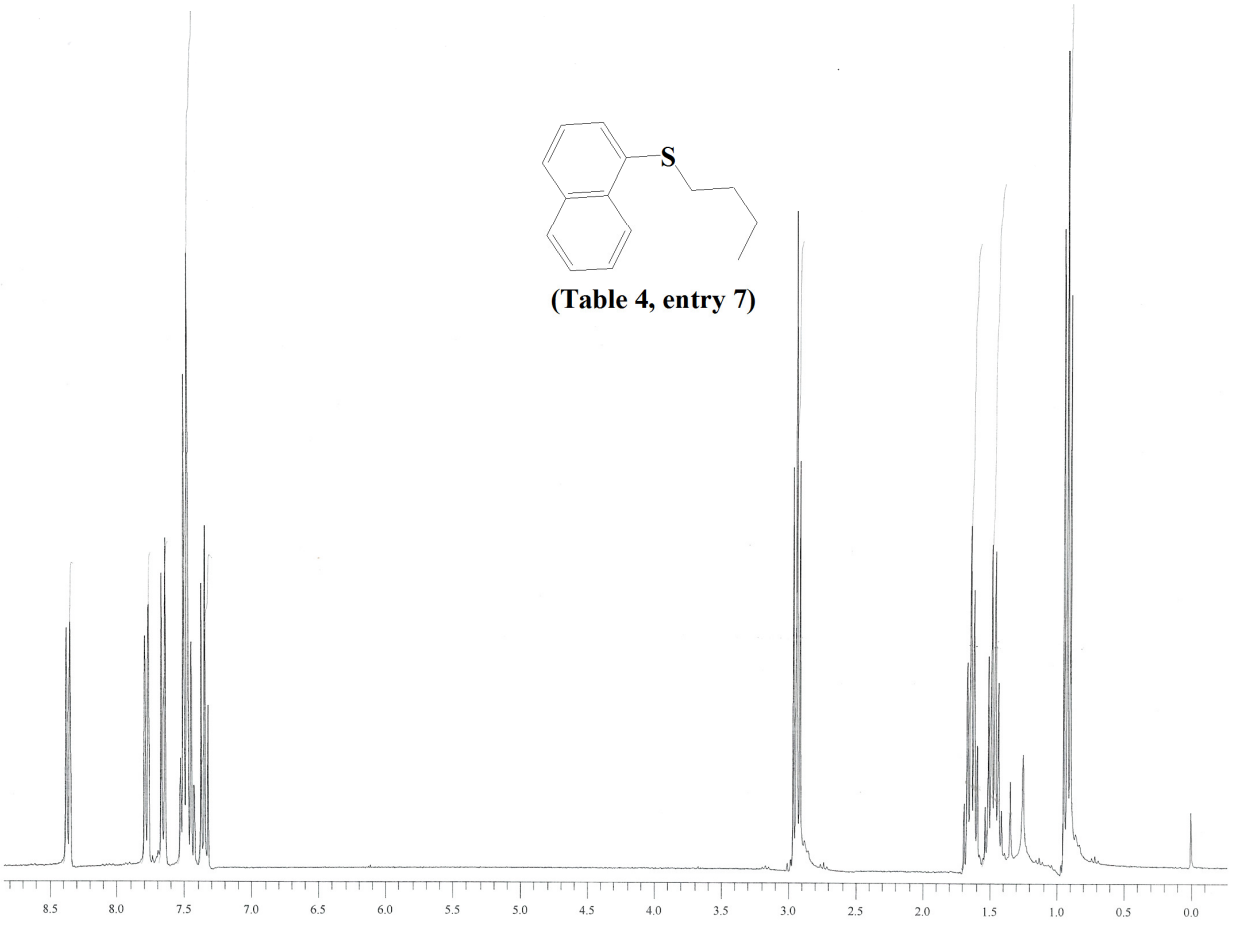

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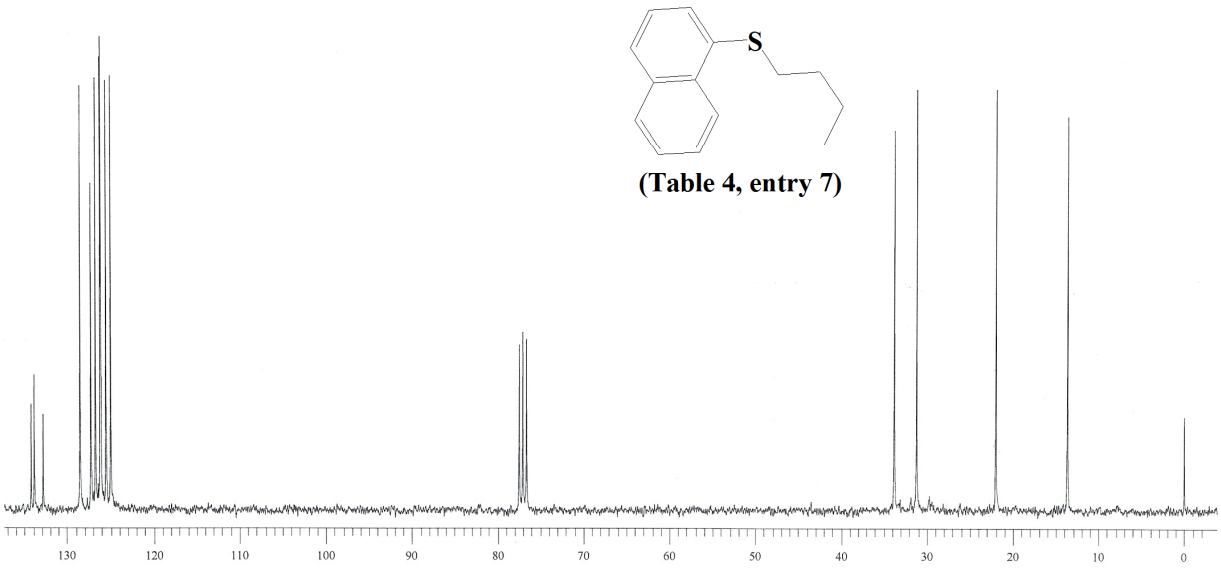

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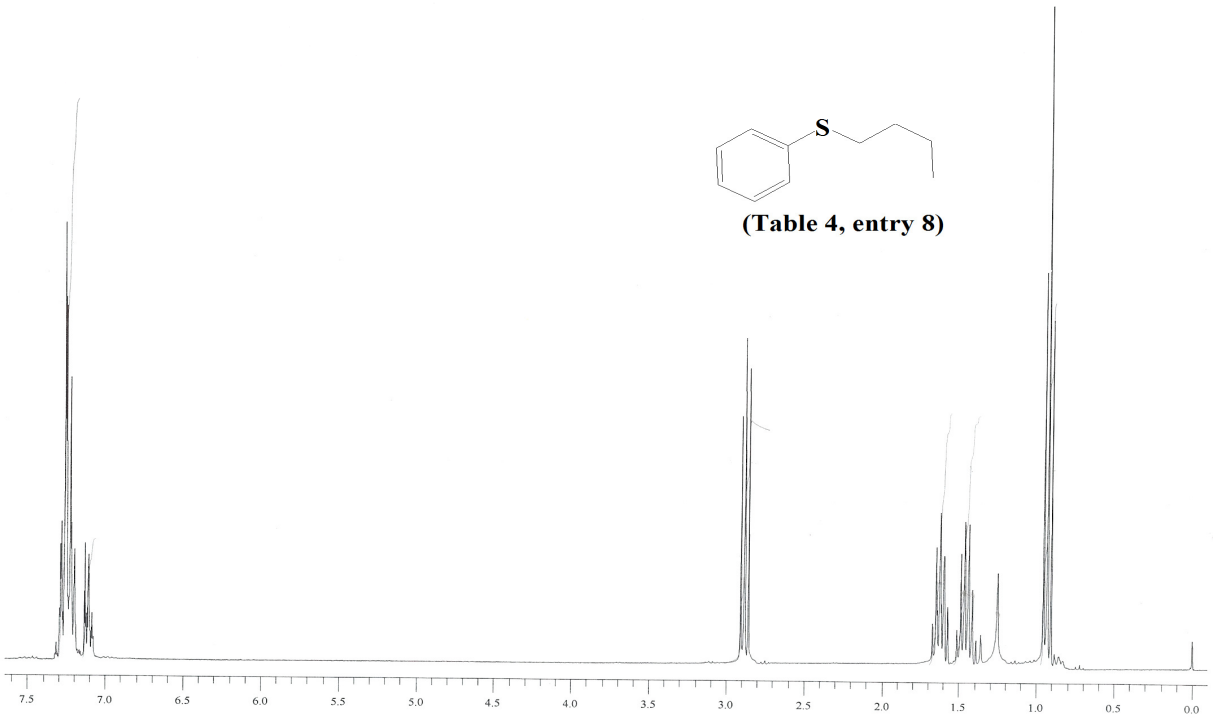

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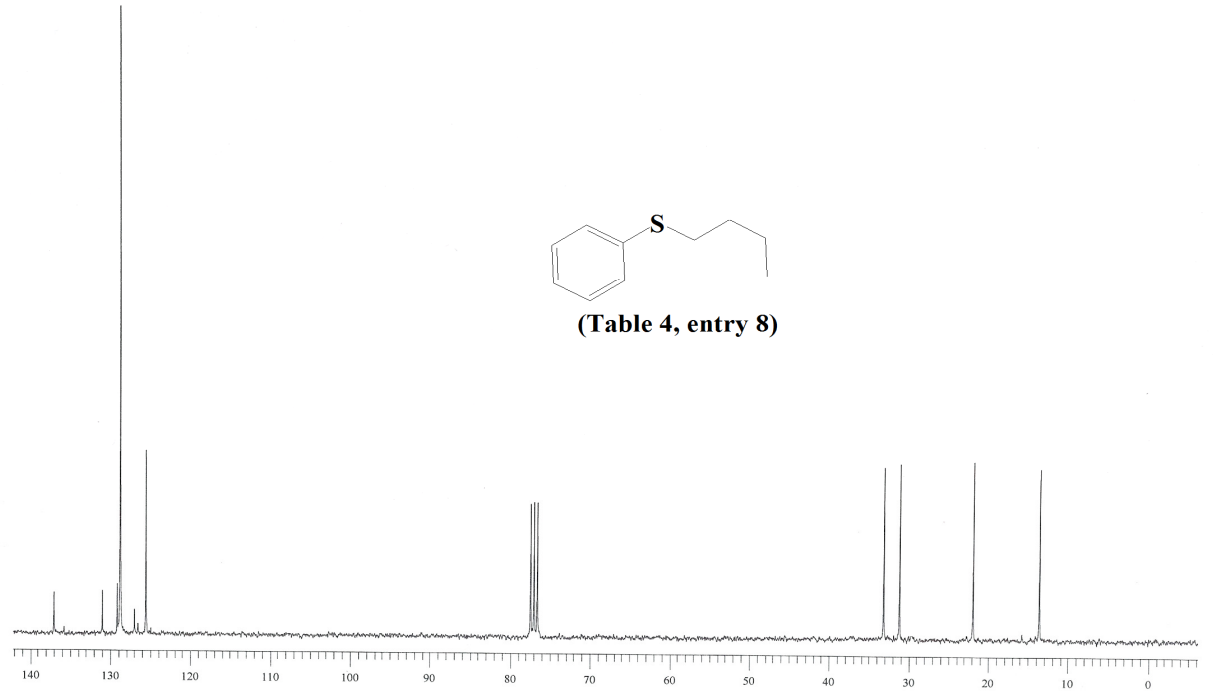

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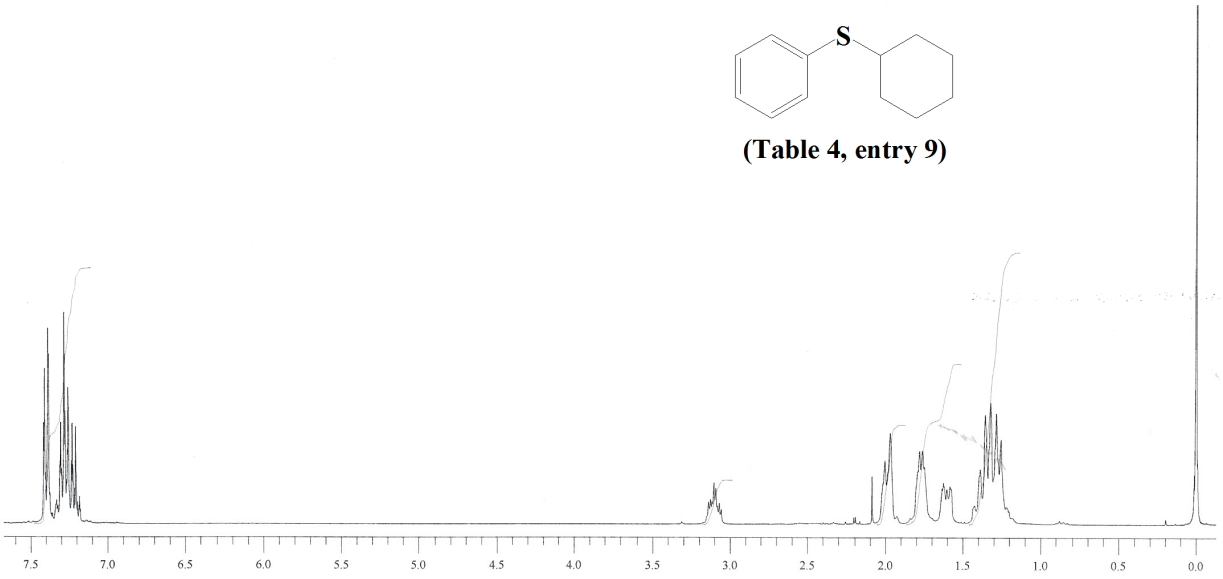
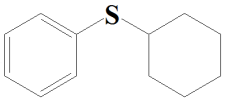
(Table 4, entry 9)





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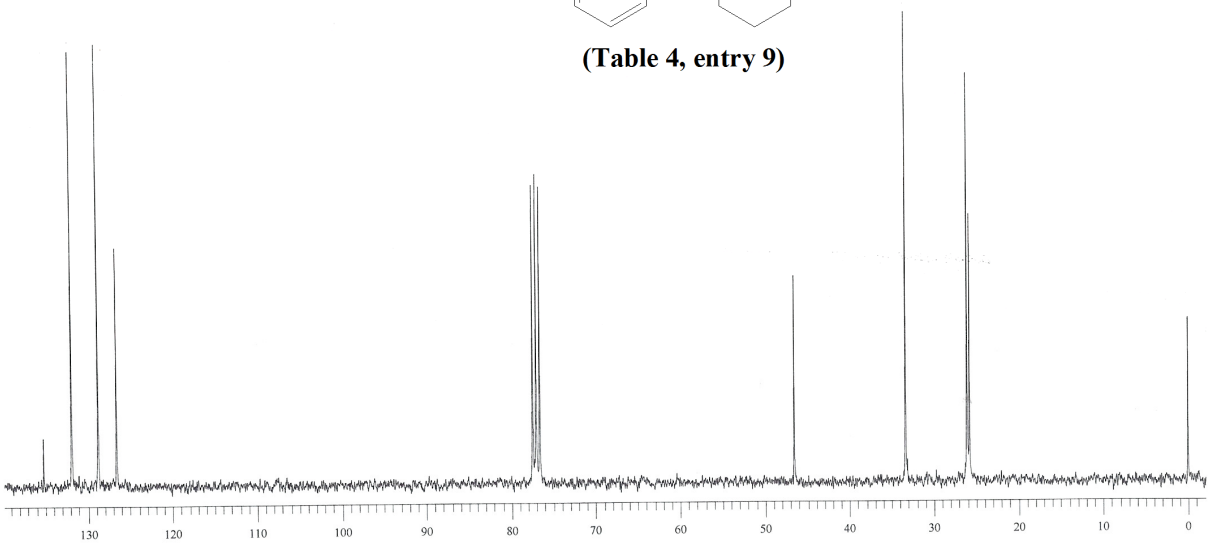

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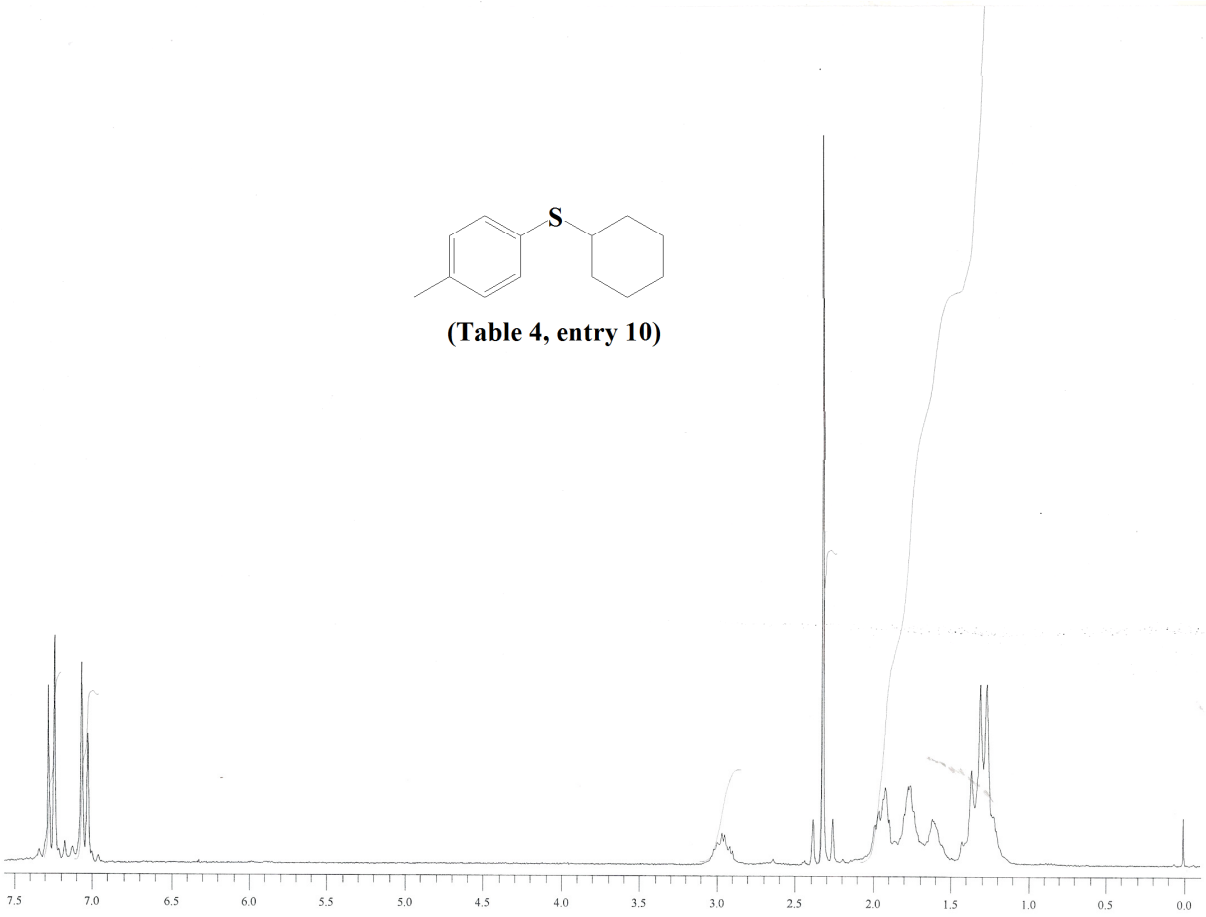

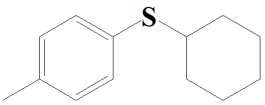

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