Supplementary Material

Metal-free coupling/isomerization reaction of isocyanide and cyclic 1,3-dione: a selective Csp^3-H functionalization strategy for C-C bond formation

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1 General Information

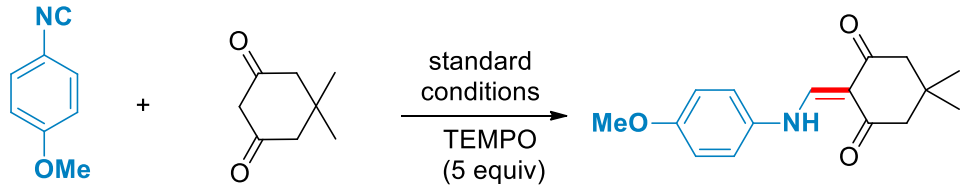
The NMR spectra were recorded on Bruker AC-500 spectrometer (500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR) with $CDCl_3$ as the solvent and TMS as internal reference. ^{1}H NMR spectral data were reported as follows: chemical shift (δ, ppm), multiplicity, integration, and coupling constant (Hz). ^{13}C NMR spectral data were reported in terms of the chemical shift. The following abbreviations were used to indicate multiplicities: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet. Low-resolution mass spectra were obtained on a Shimadzu LCMS-2010EV spectrometer in ESI mode and reported as m/z. High-resolution mass spectra (HRMS) were recorded on a Bruker Daltonics, Inc. APEXIII 7.0 TESLA FTMS instrument. Melting points were obtained on a X-4 digital melting point apparatus without correction. Purification of products was accomplished by column chromatography packed with silica gel. Unless otherwise stated, all reagents were commercially purchased and used without further purification.

2 General Procedure

Under air atmosphere, a sealable reaction tube with a Teflon-coated screw cap equipped with a magnetic stir bar was charged with isocyanide **1** (0.5 mmol), 1,3-dione **2** (1.0 mmol) and DTBP (3.0 equiv.) in DCE (5.0 mL) at room temperature. The rubber septum was then replaced by a Teflon-coated screw cap, and the reaction vessel placed in an oil bath at 80 °C for 12 h. After the reaction was completed, it was cooled to room temperature and monitored by TLC. The solvent was then removed under reduced pressure and the residue was purified by column chromatography on silica gel to afford product **3**-**4**.

3 Preliminary Mechanistic Study and Control Experiment

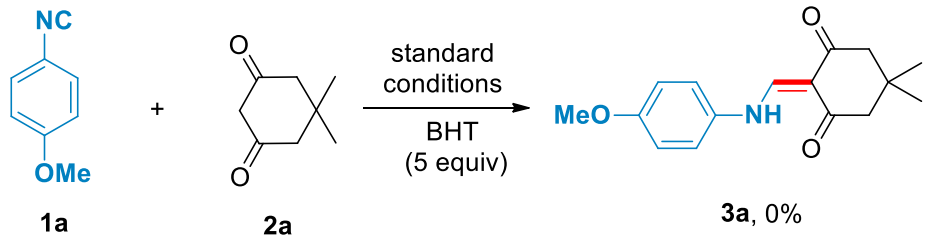
a) Reaction with radical scavenger TEMPO



1a **2a** **3a**, 0%

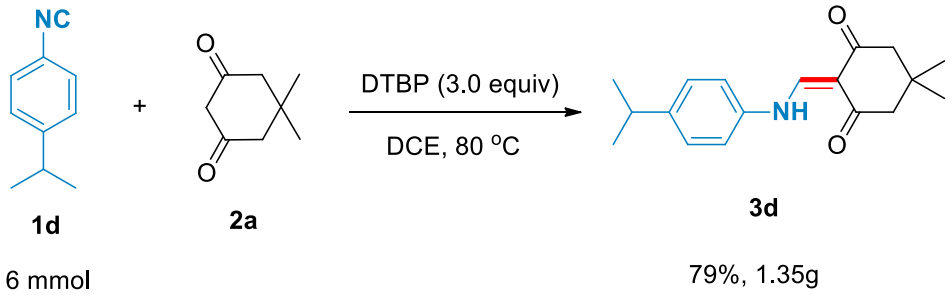
Under air atmosphere, a sealable reaction tube with a Teflon-coated screw cap equipped with a magnetic stir bar was charged with isocyanide **1a** (0.5 mmol), 5,5-dimethylcyclohexane-1,3-dione **2a** (1.0 mmol) and DTBP (3.0 equiv.) in DCE (5.0 mL) at room temperature. To this mixture TEMPO (5 equiv.) was added. The rubber septum was then replaced by a Teflon-coated screw cap, and the reaction vessel placed in an oil bath at 80 °C for 12 h. After the reaction was completed, it was cooled to room temperature and monitored by TLC.

b) Reaction with radical scavenger BHT



Under air atmosphere, a sealable reaction tube with a Teflon-coated screw cap equipped with a magnetic stir bar was charged with isocyanide **1a** (0.5 mmol), 5,5-dimethylcyclohexane-1,3-dione **2a** (1.0 mmol) and DTBP (3.0 equiv.) in DCE (5.0 mL) at room temperature. To this mixture BHT (5 equiv.) was added. The rubber septum was then replaced by a Teflon-coated screw cap, and the reaction vessel placed in an oil bath at 80 °C for 12 h. After the reaction was completed, it was cooled to room temperature and monitored by TLC.

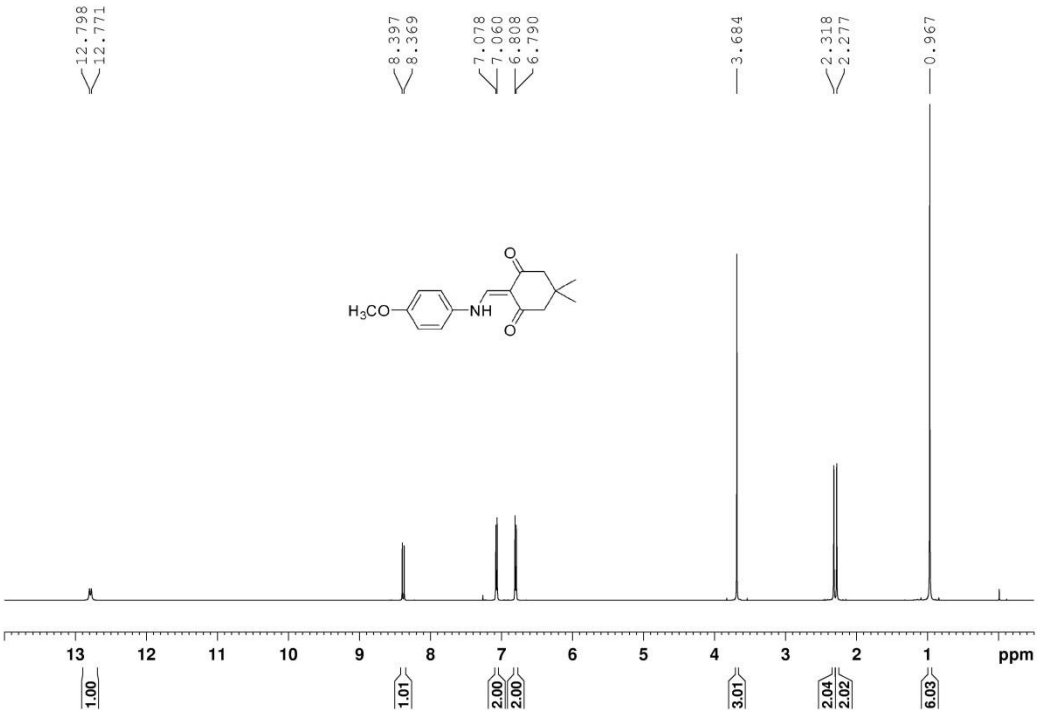
c) Gram-scale coupling reaction

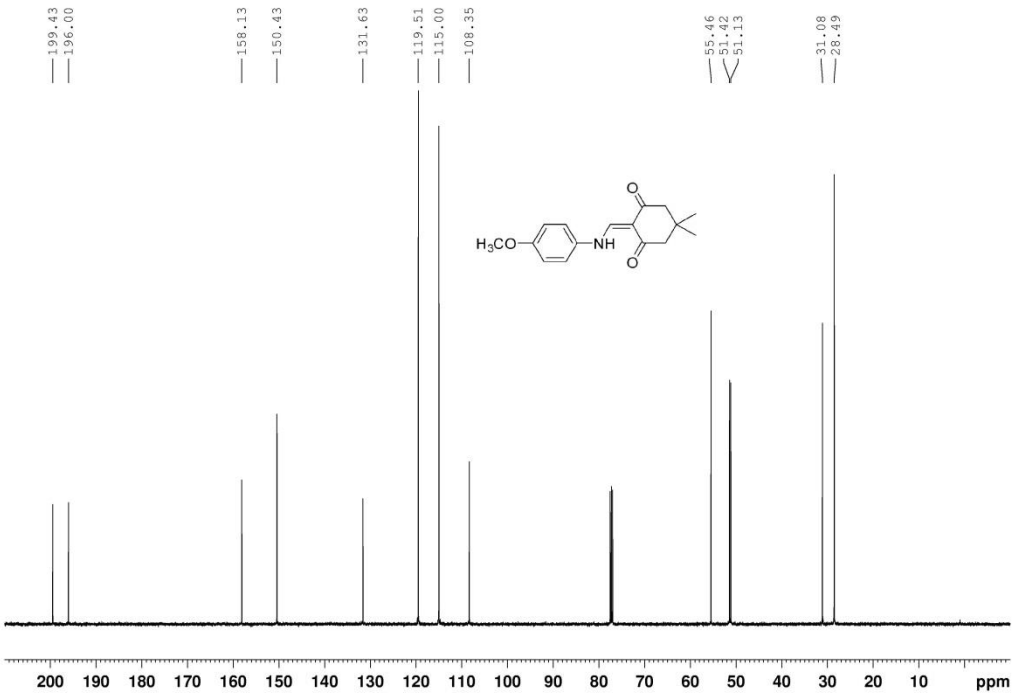


Under air atmosphere, a sealable reaction tube with a Teflon-coated screw cap equipped with a magnetic stir bar was charged with isocyanide **1d** (0.5 mmol), 5,5-dimethylcyclohexane-1,3-dione **2a** (1.0 mmol) and DTBP (3.0 equiv.) in DCE (5.0 mL) at room temperature. The rubber septum was then replaced by a Teflon-coated screw cap, and the reaction vessel placed in an oil bath at 80 °C for 12 h. After the reaction was completed, it was cooled to room temperature and monitored by TLC. The solvent was then removed under reduced pressure and the residue was purified by column chromatography on silica gel to afford product.

4 ^{1}H NMR and ^{13}C NMR Spectra of All Compounds

Compound **3a**





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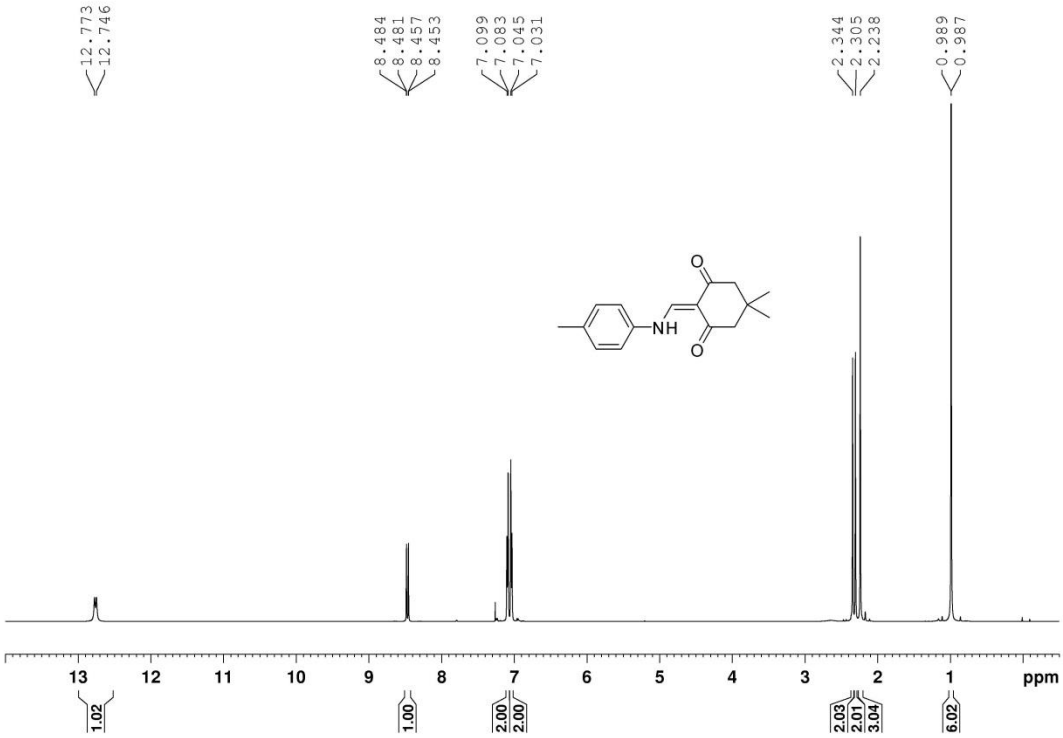

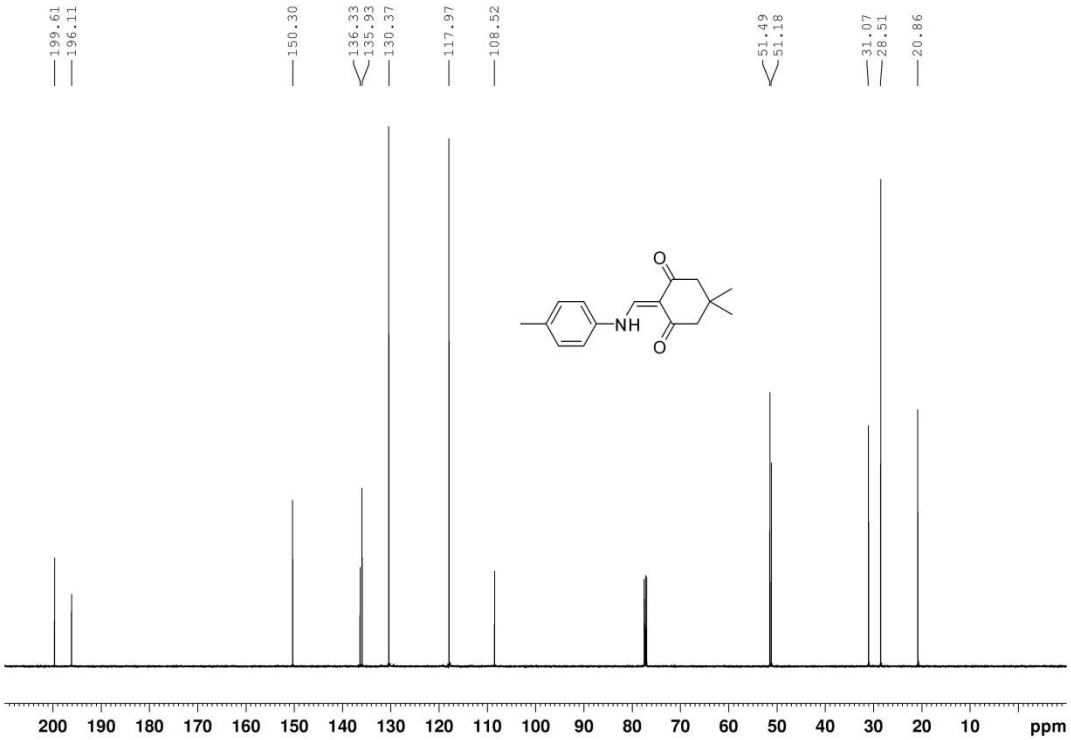

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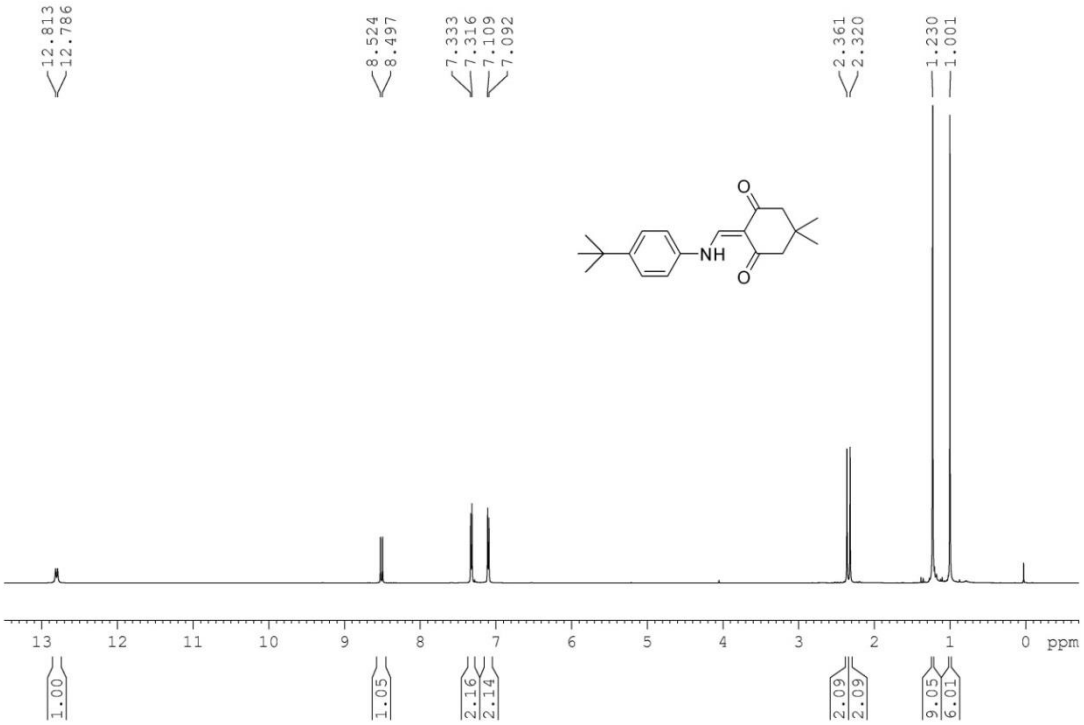

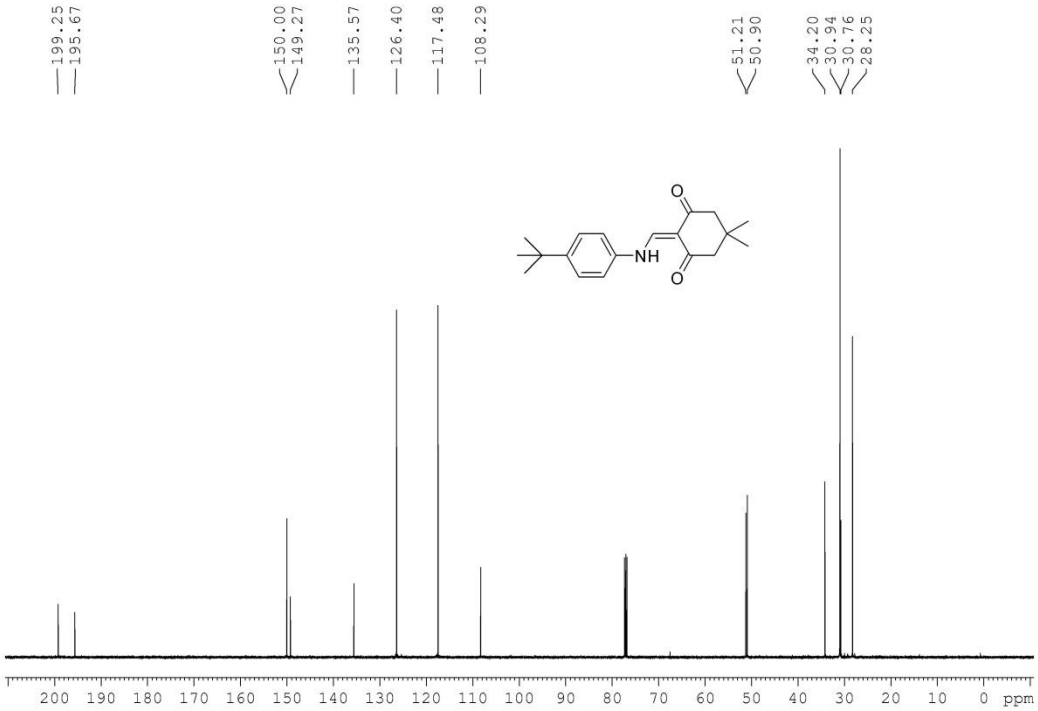

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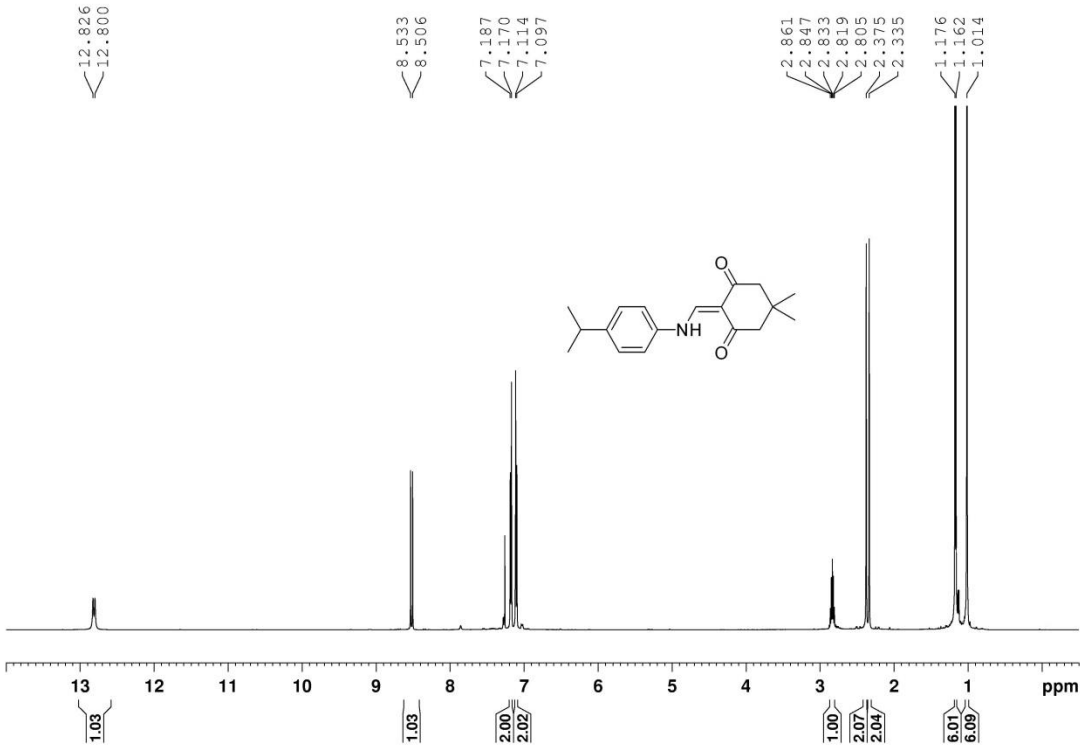

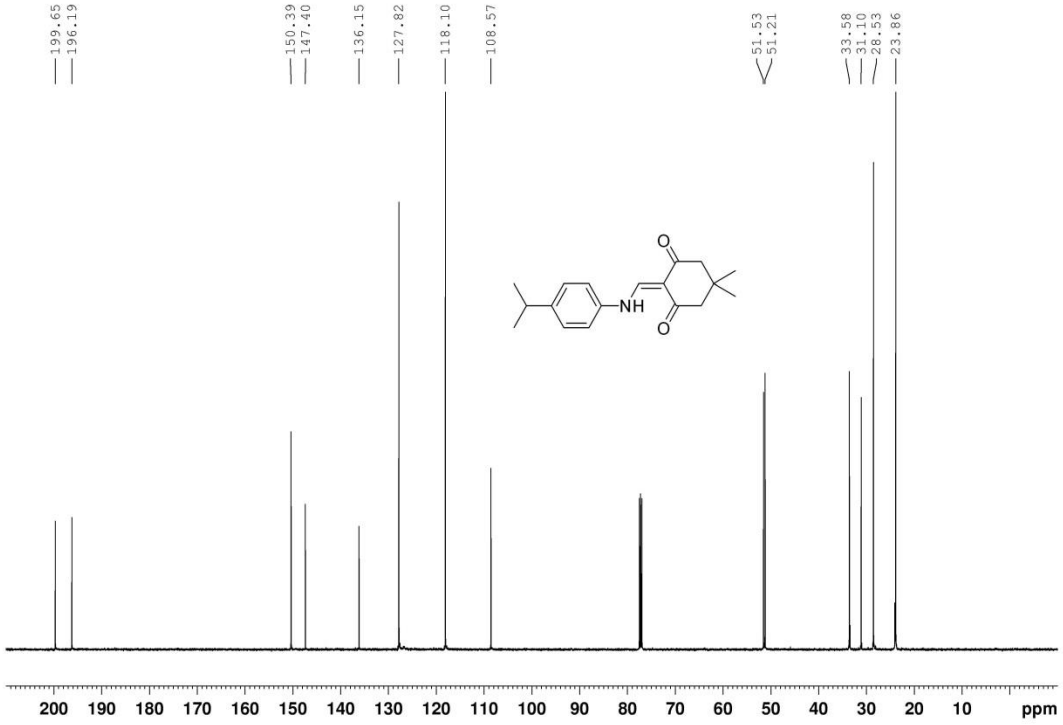

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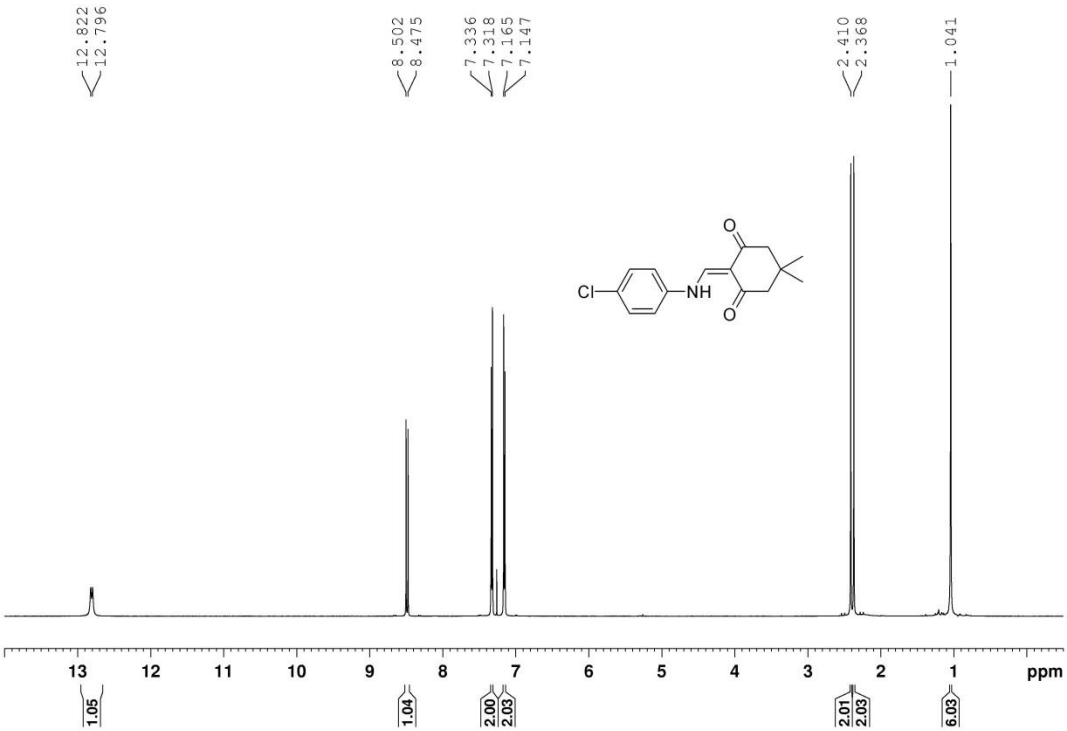

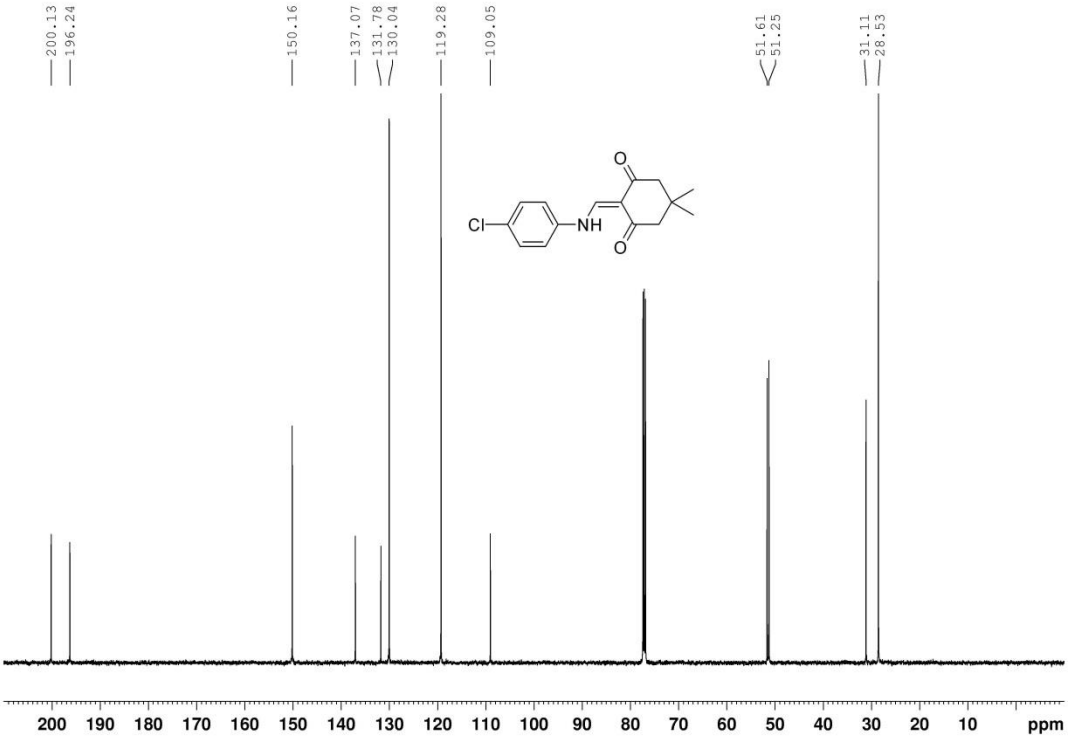

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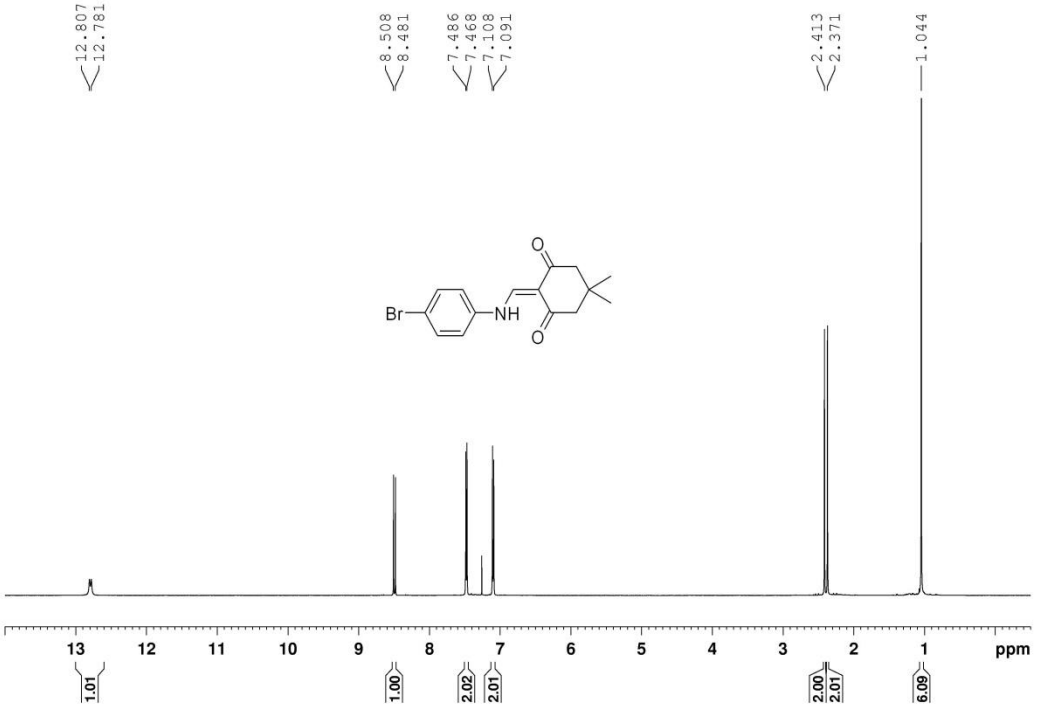

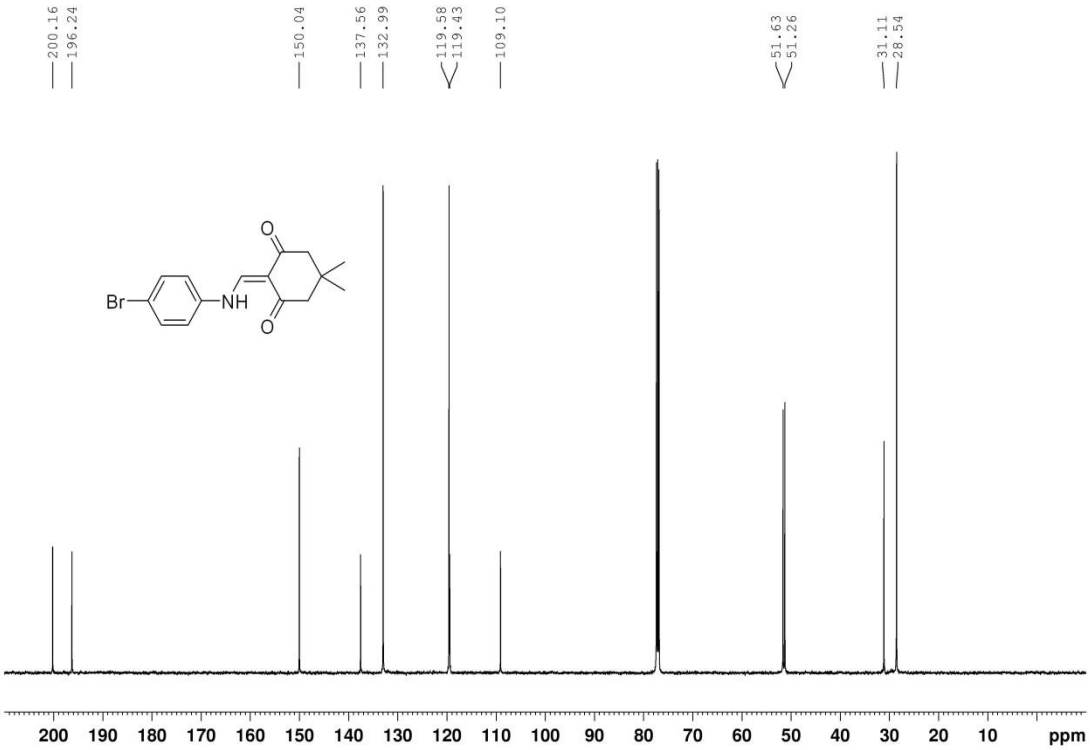

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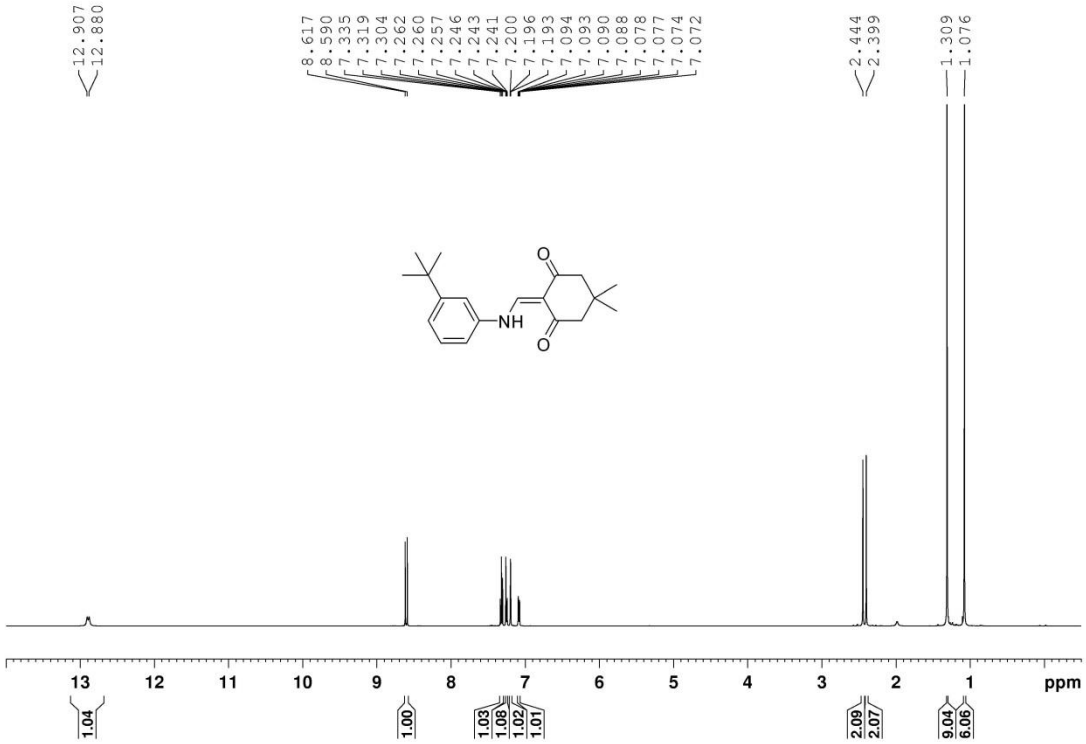

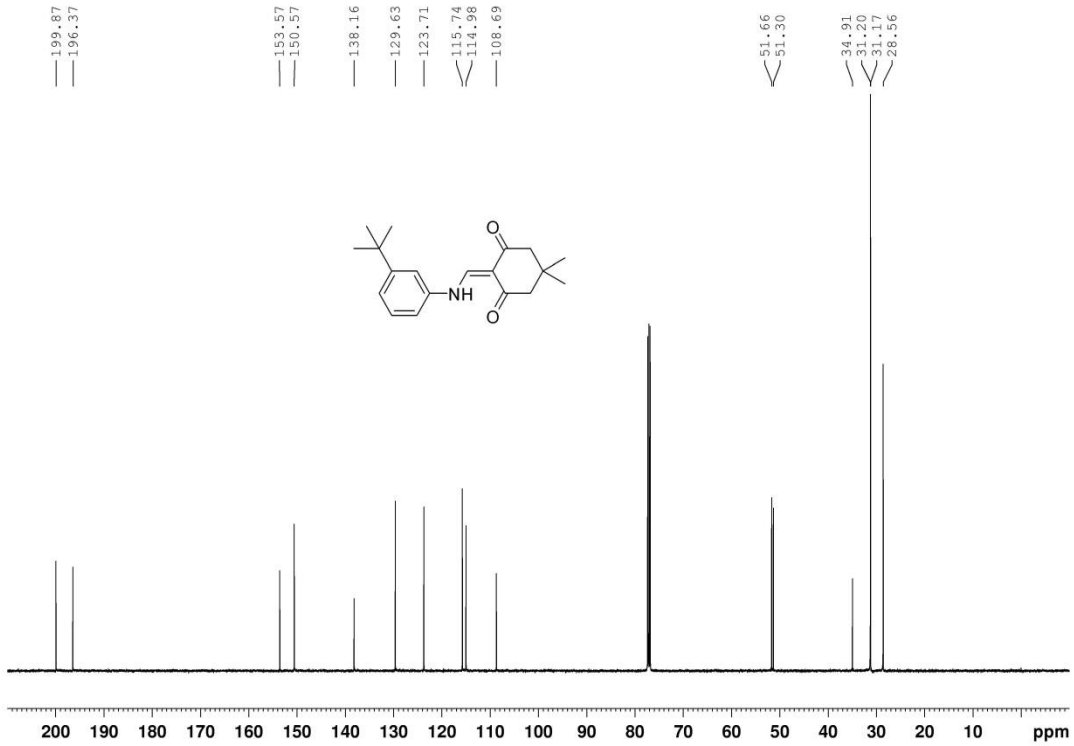

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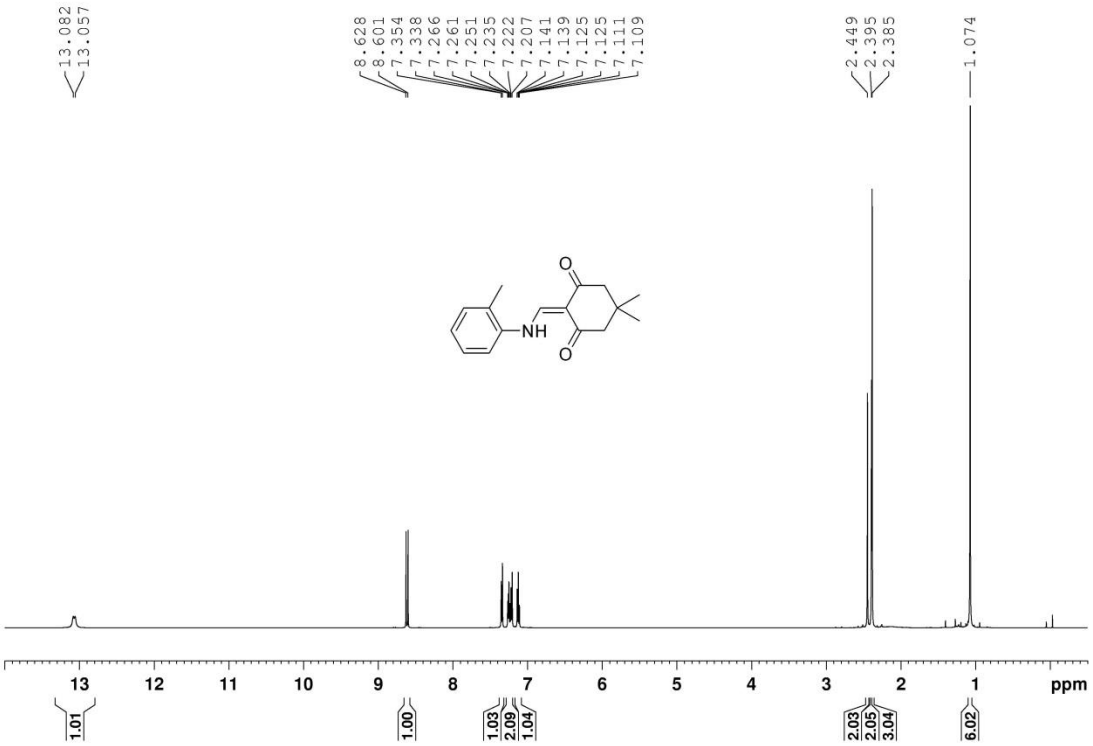

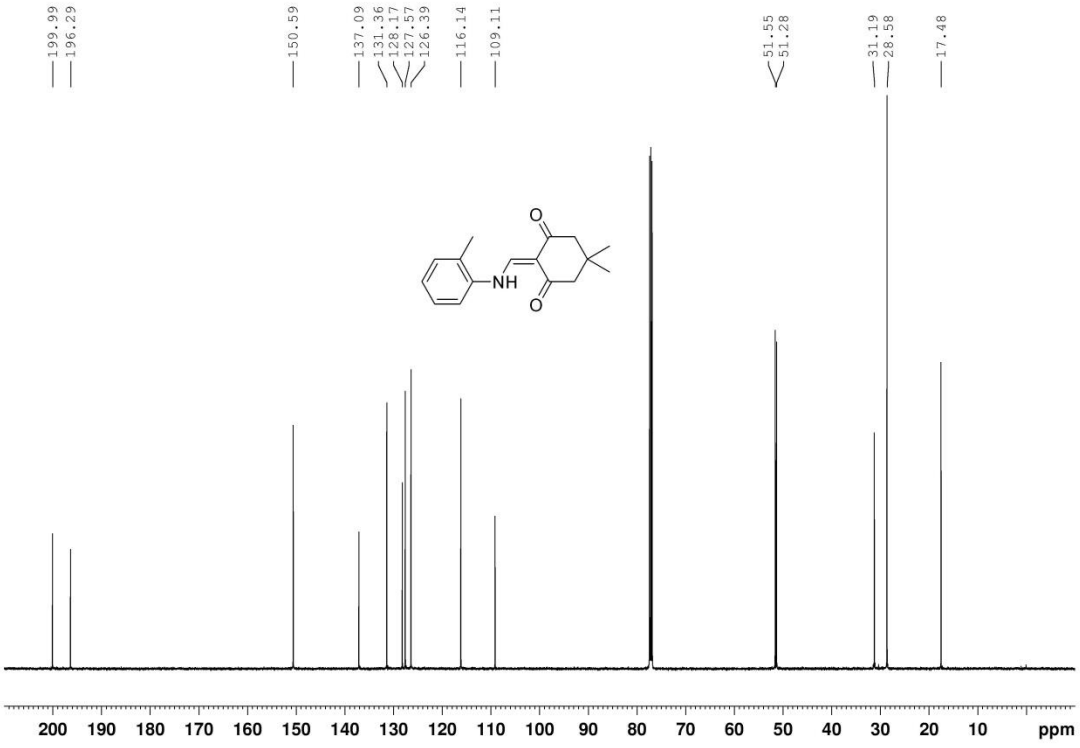

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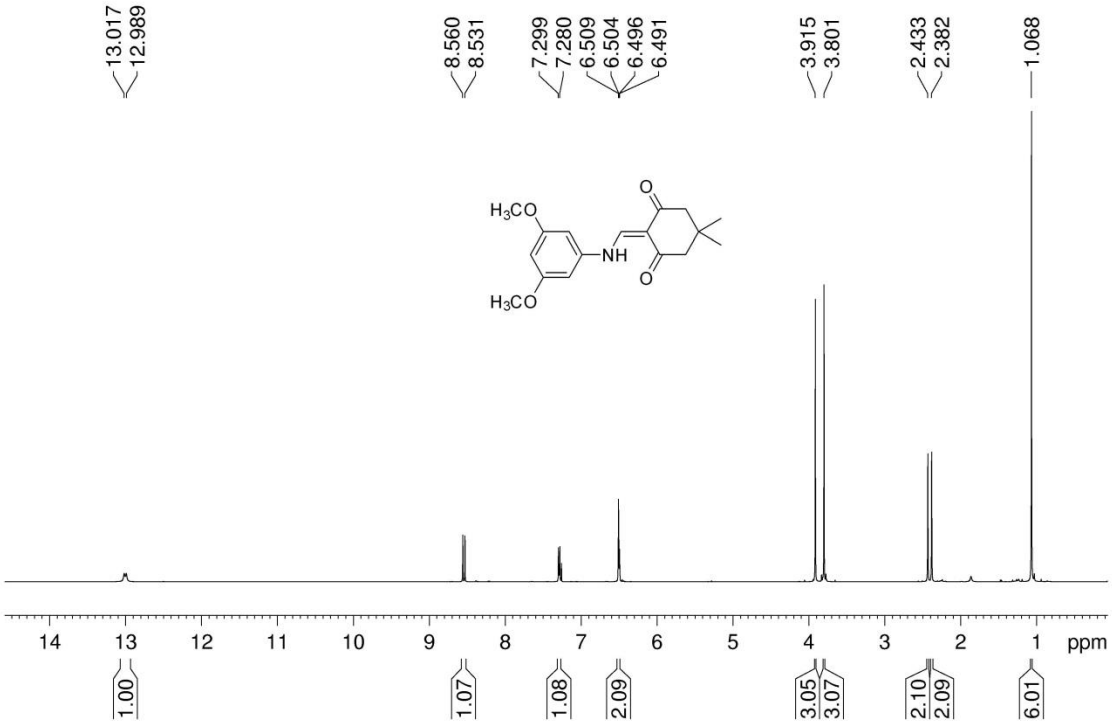

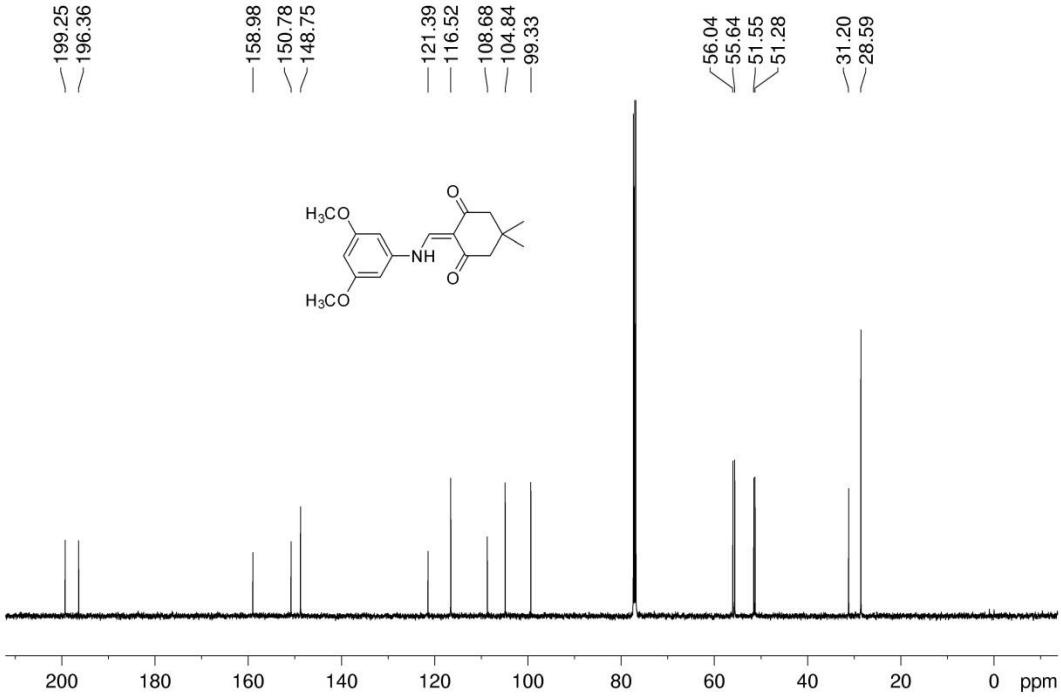

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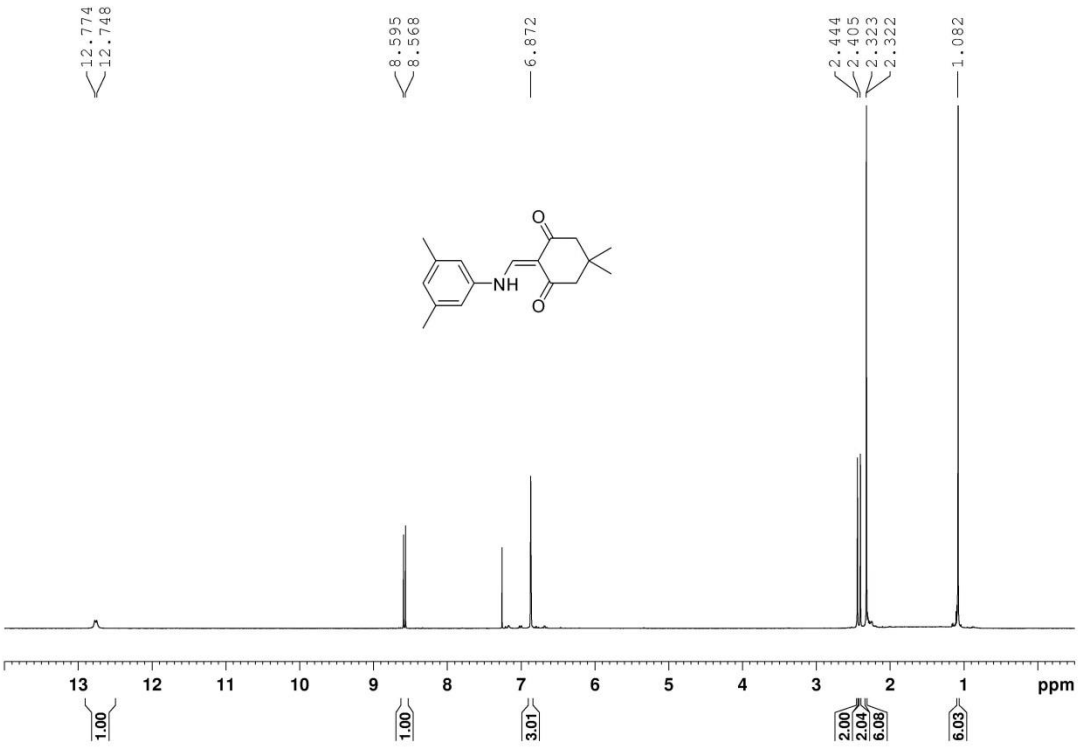

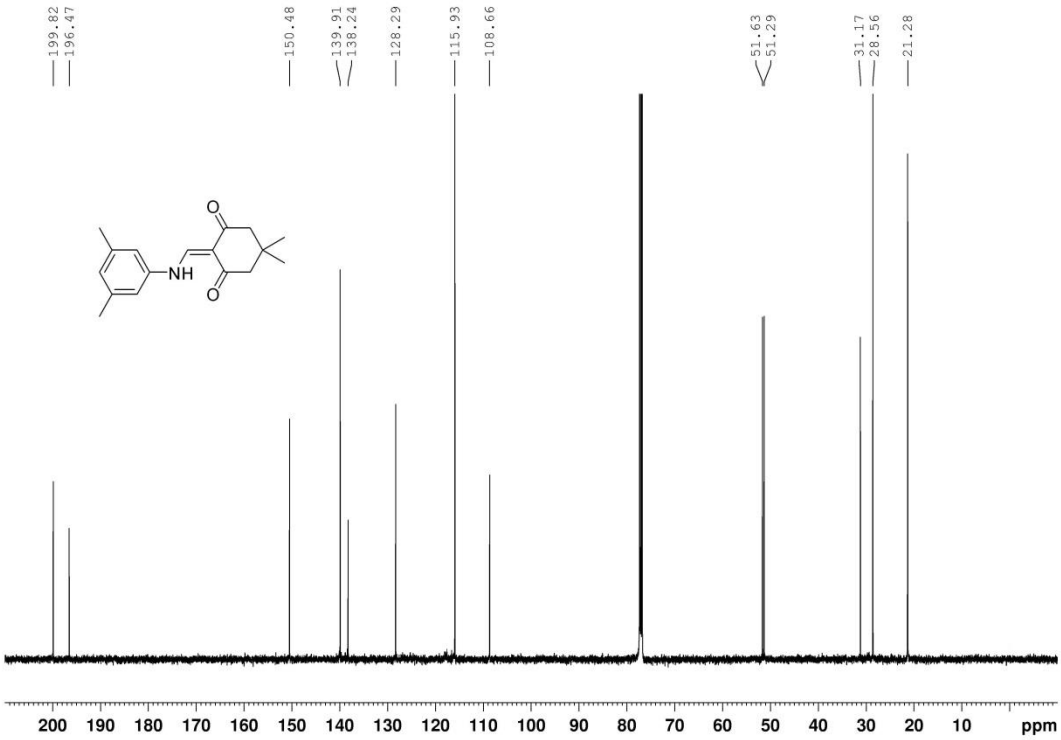

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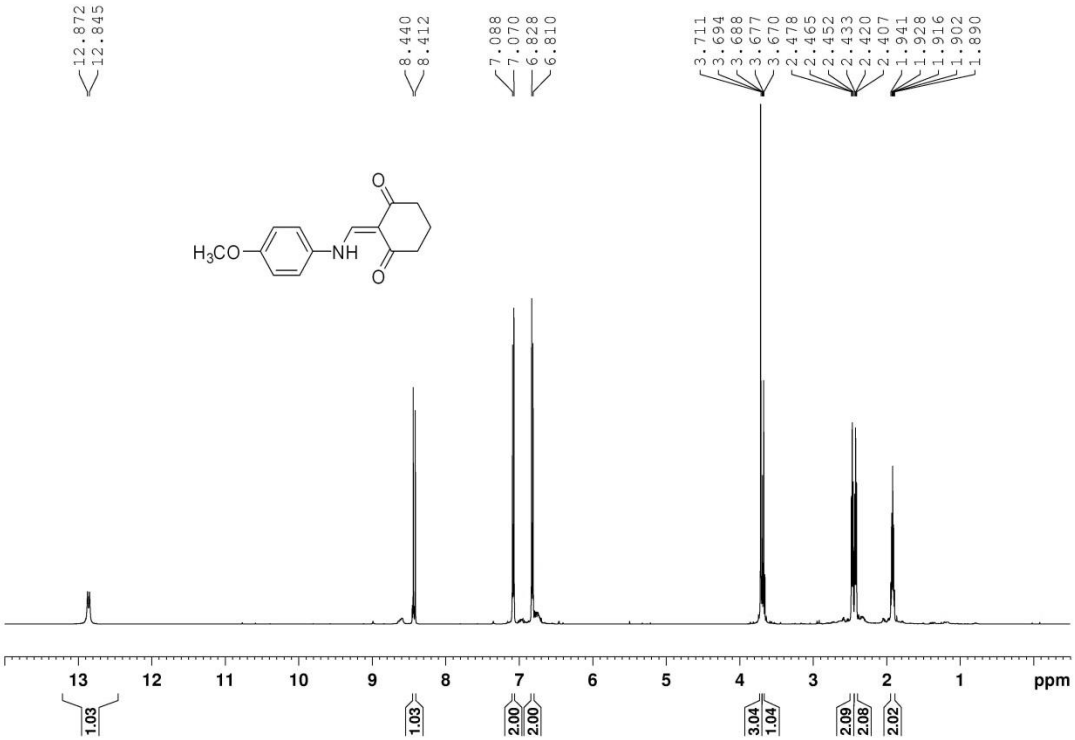

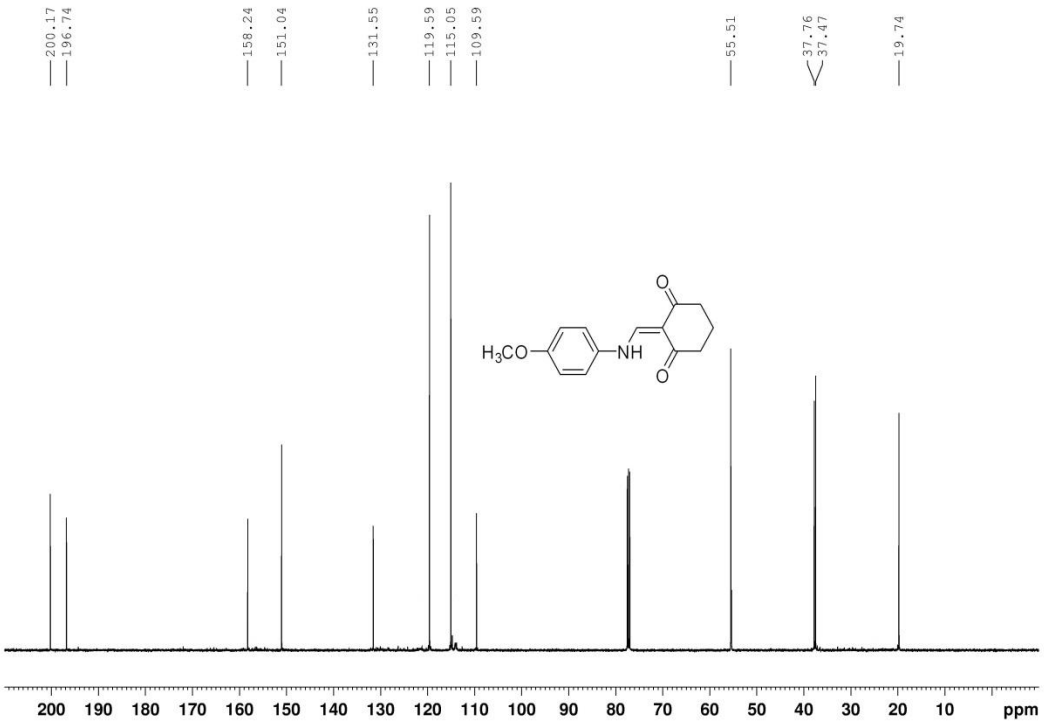

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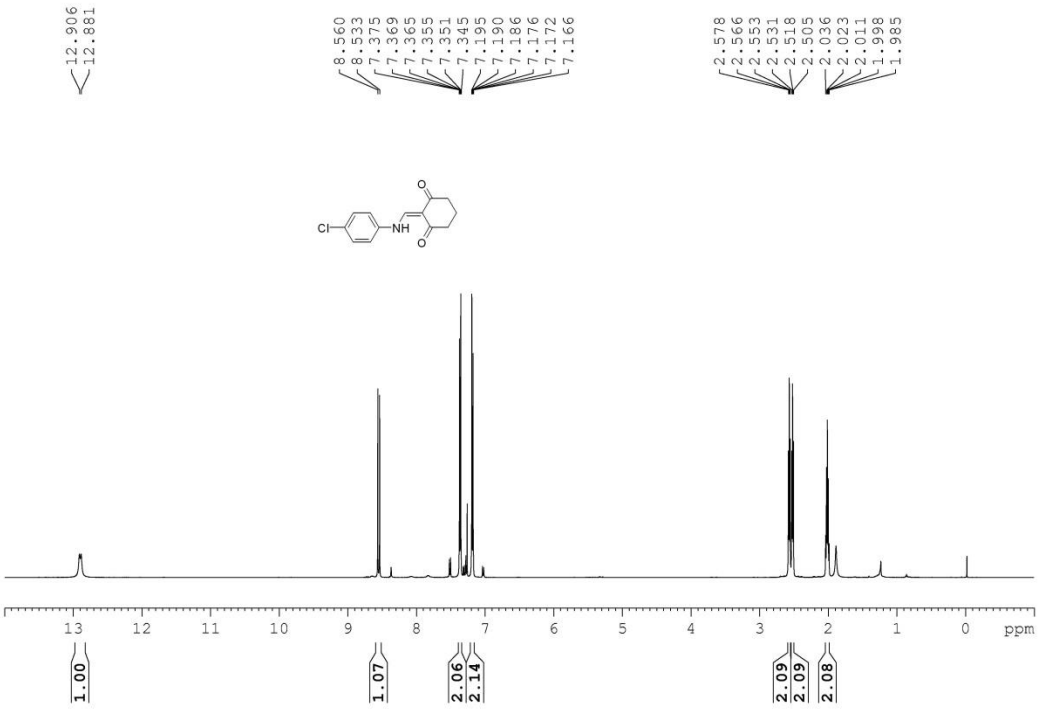

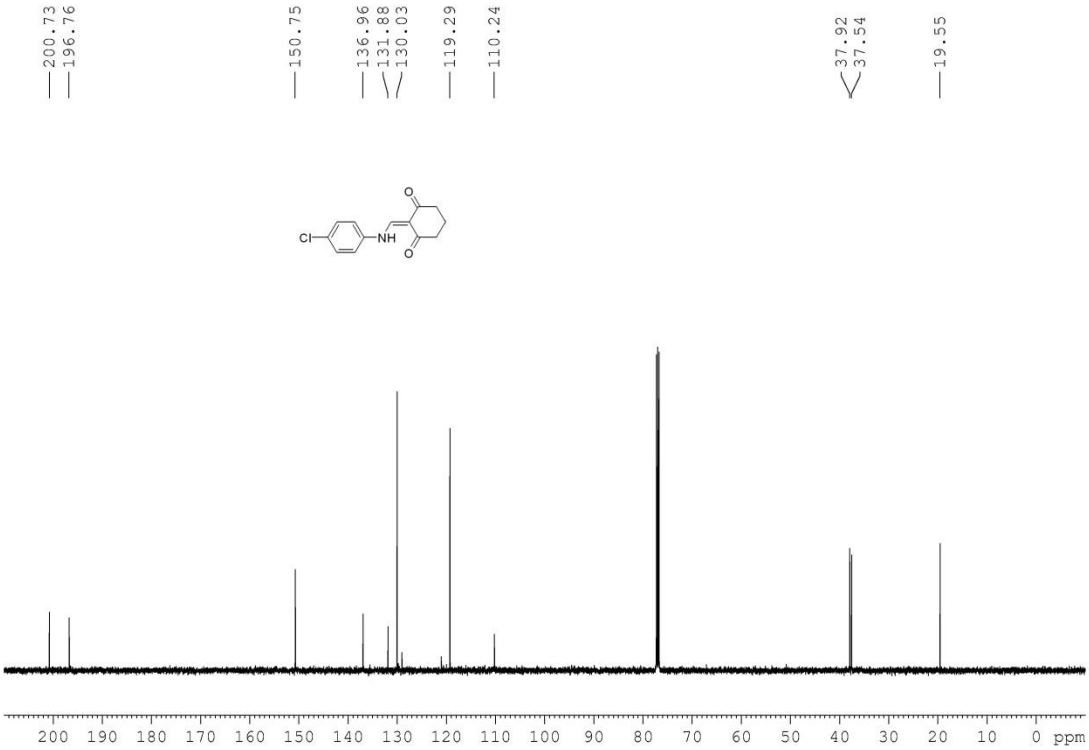

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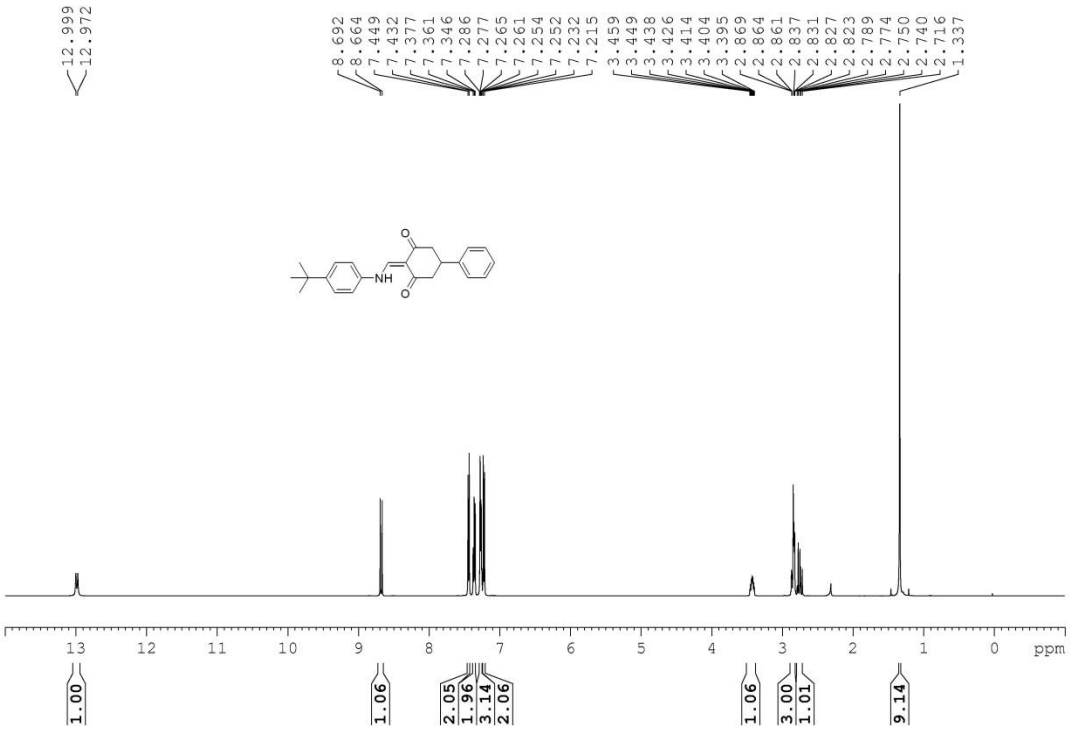

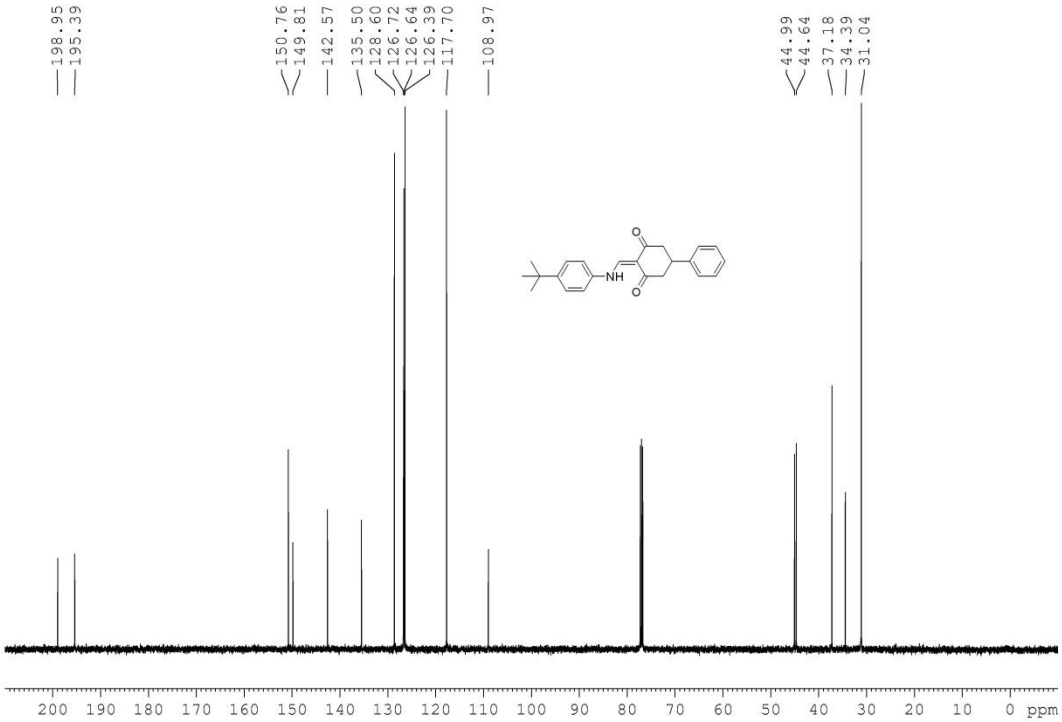

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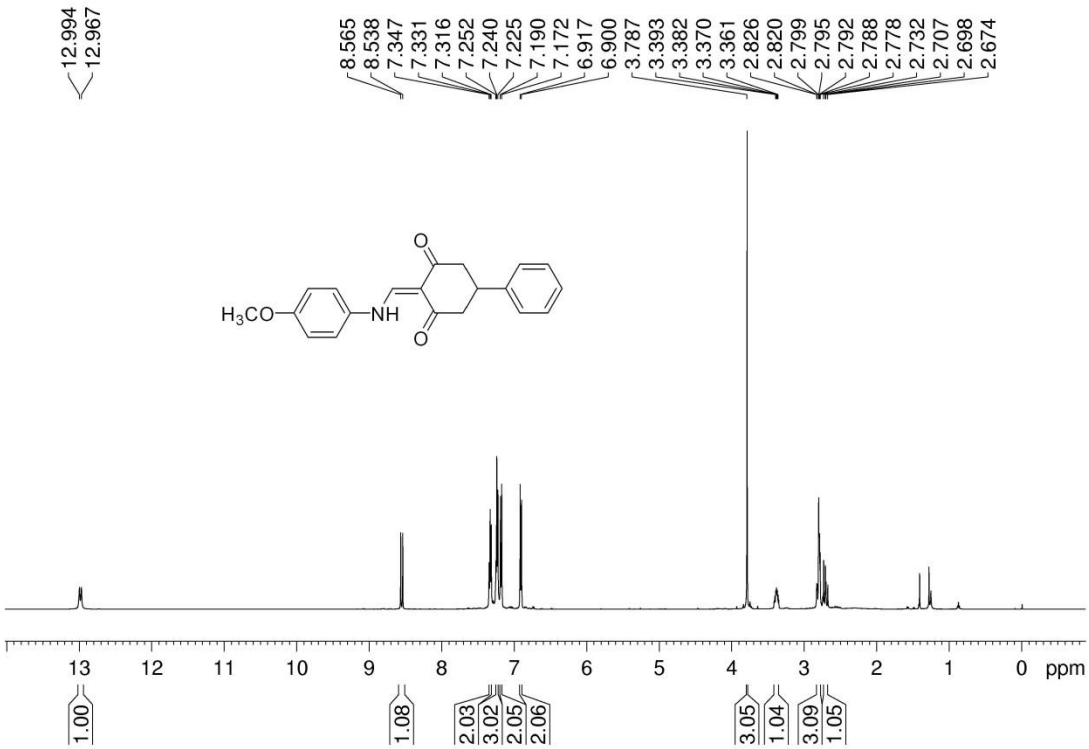

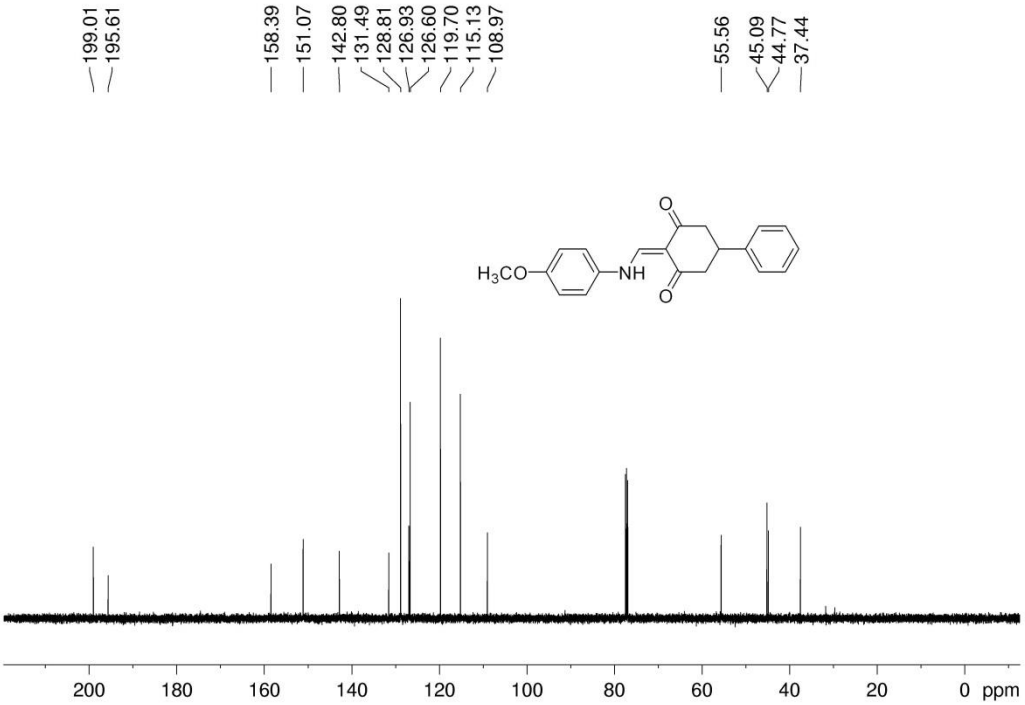

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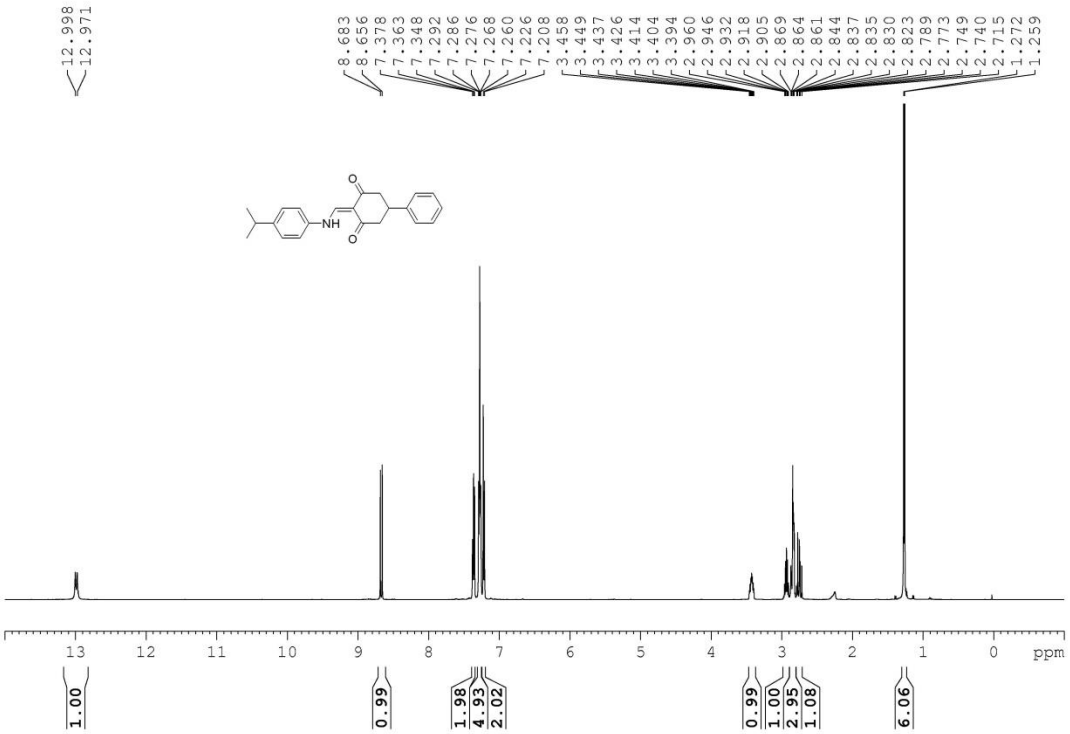

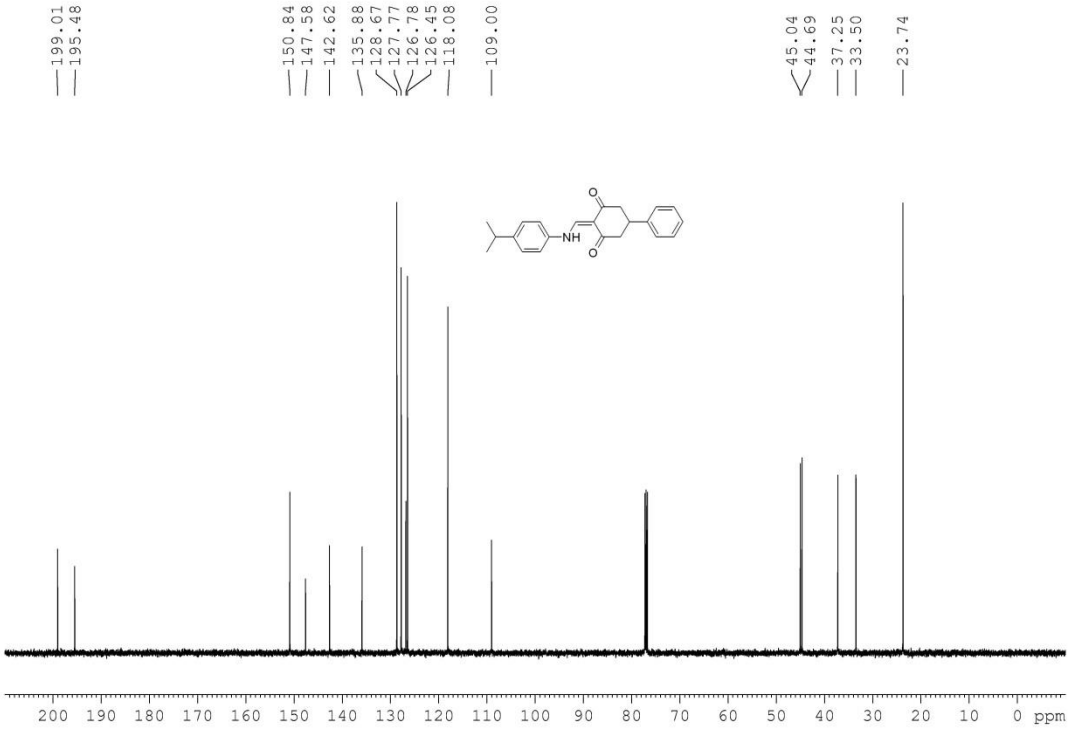

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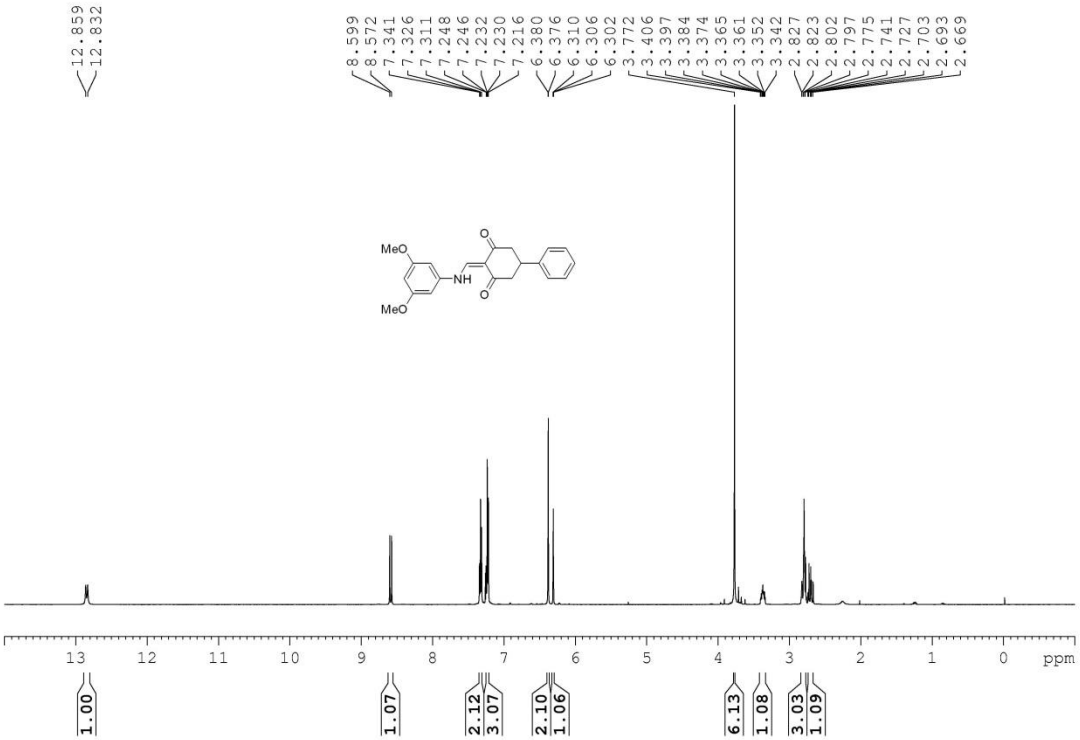

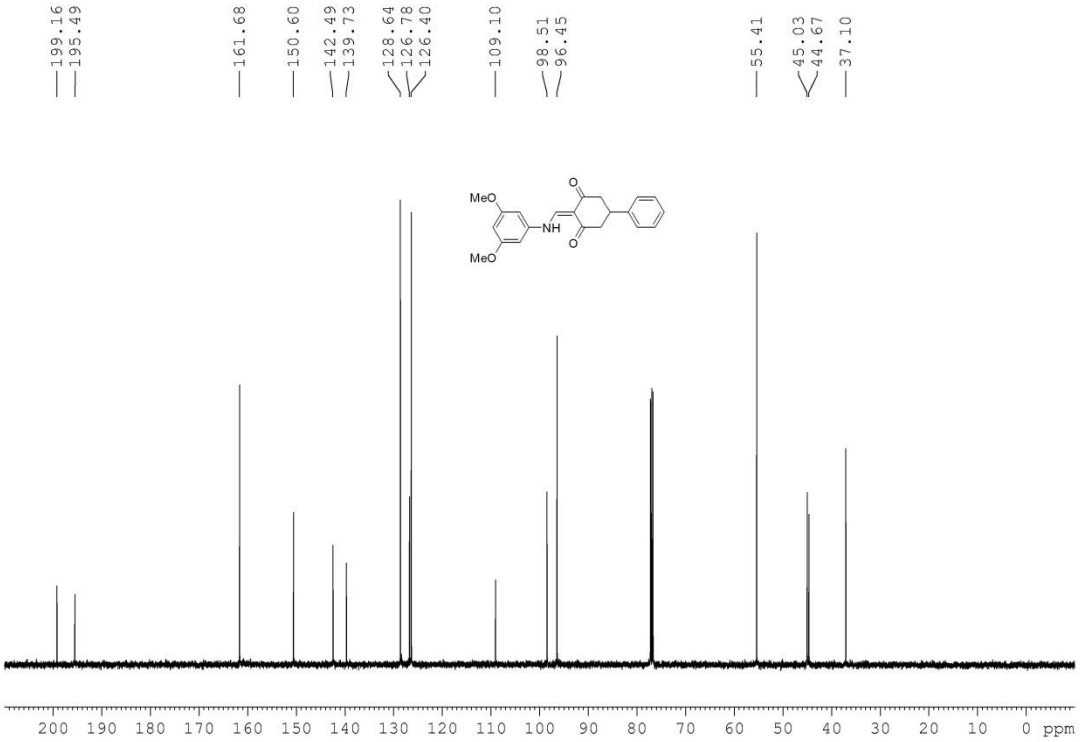

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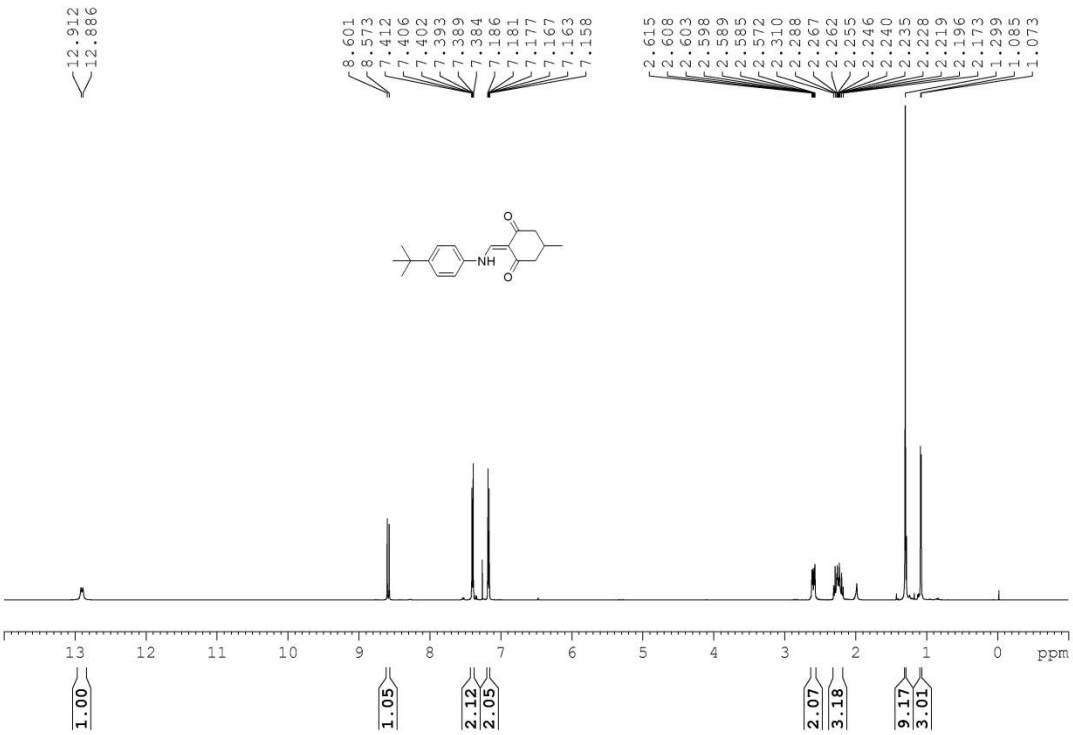

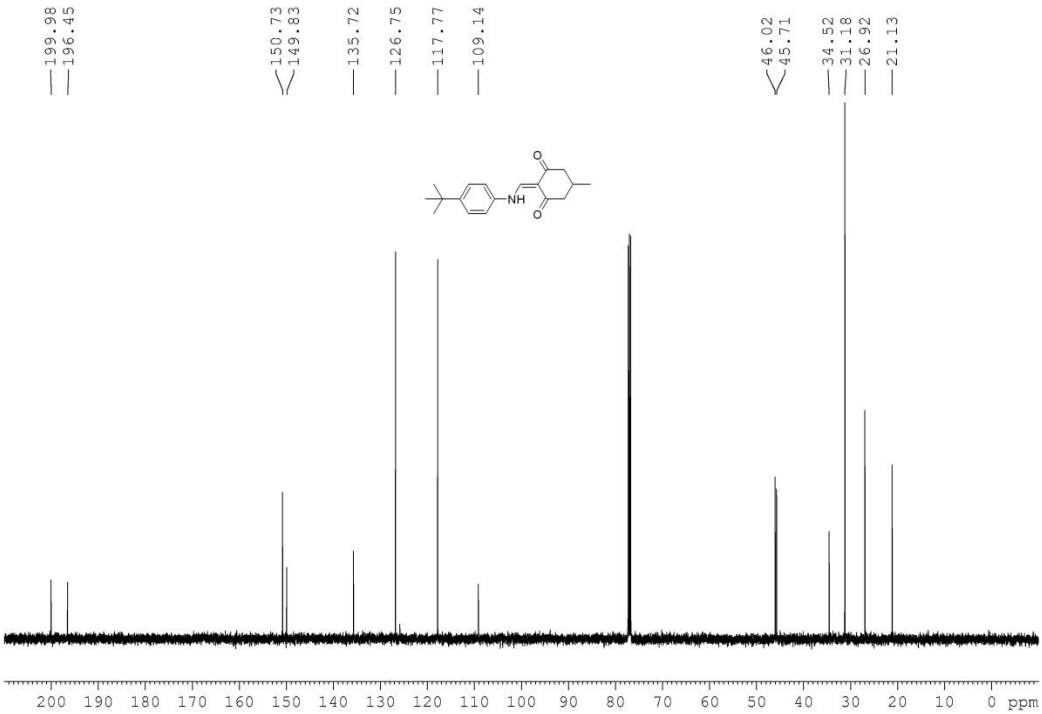

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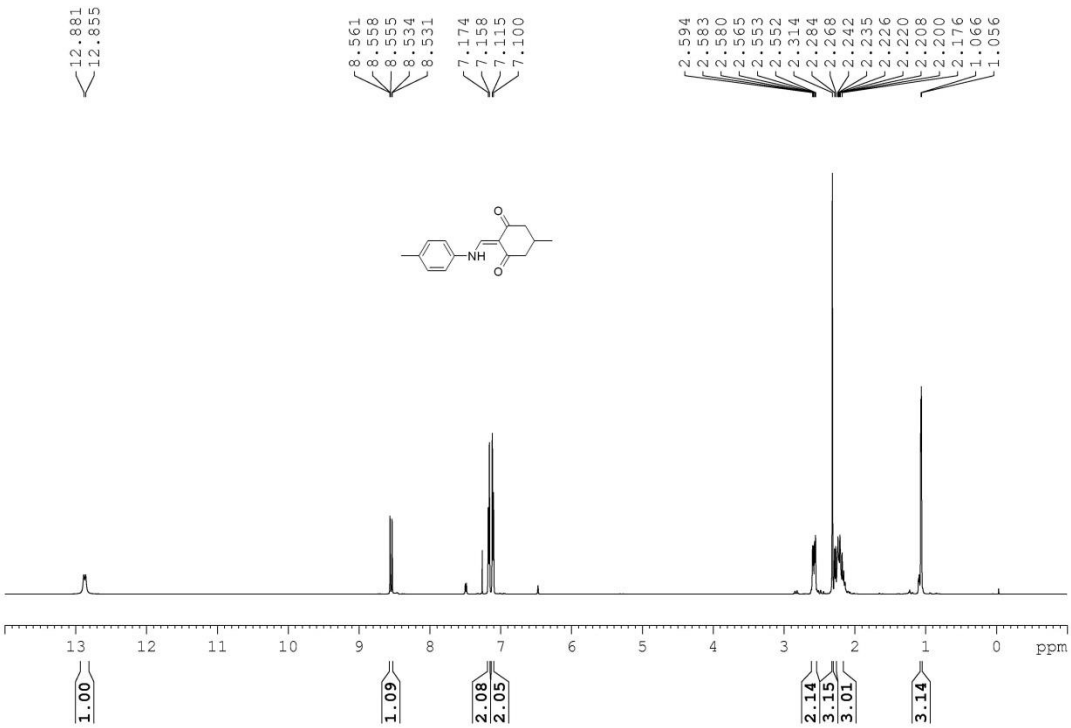

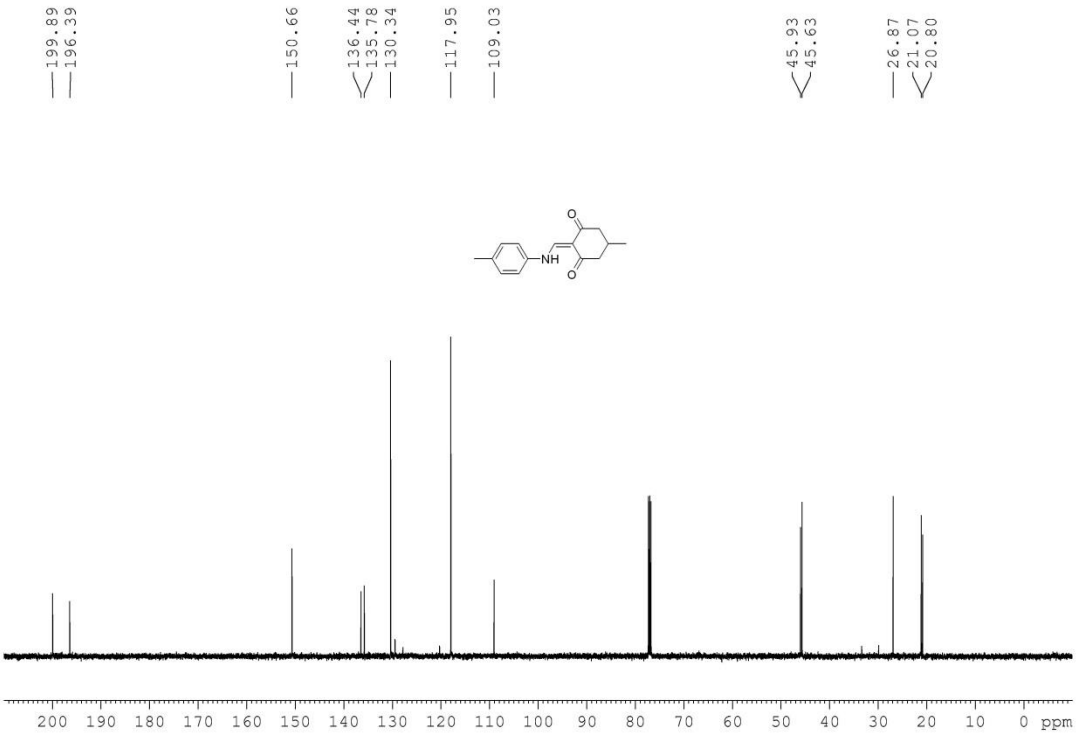

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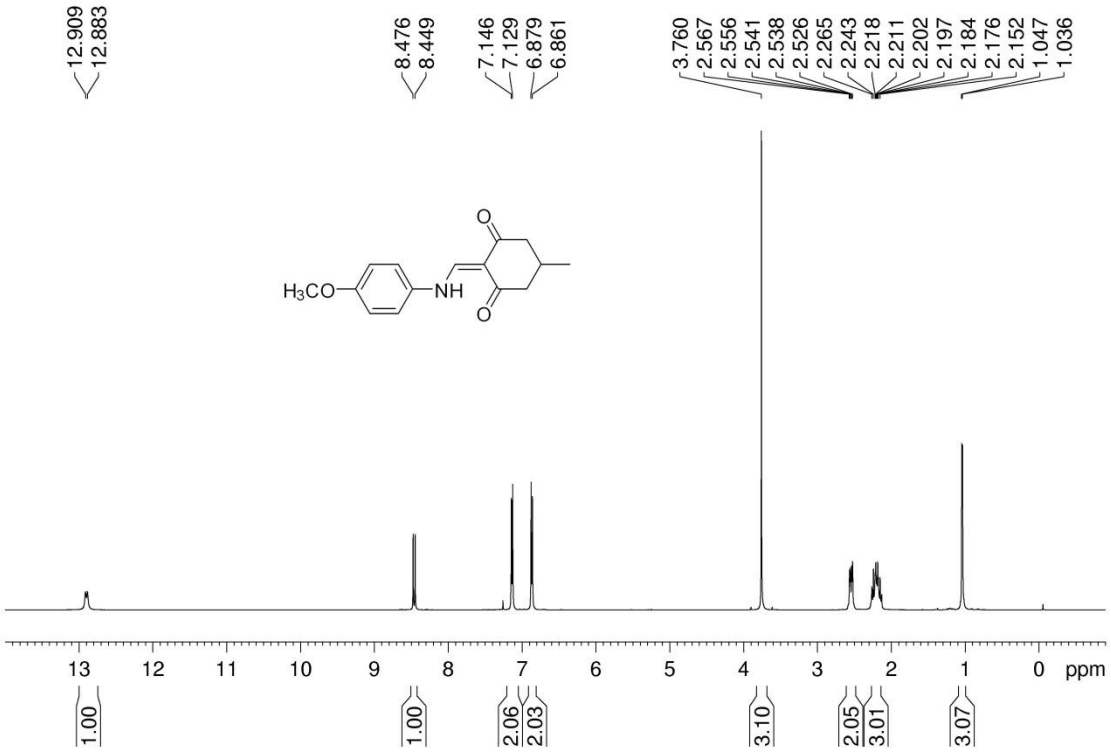

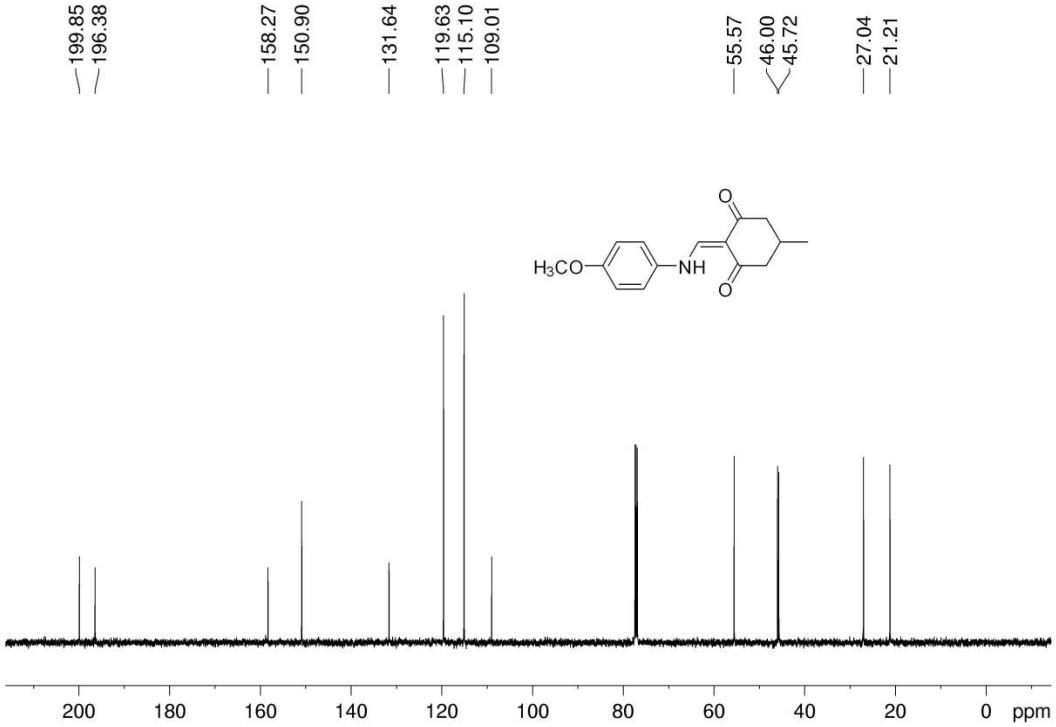

Compound **4j**