Supporting Information

Transition-Metal-Free Oxidative Decarboxylative Cross Coupling of α, β-Unsaturated Carboxylic Acids with Cyclic Ethers under Air Conditions: Mild Synthesis of α-Oxyalkyl Ketones

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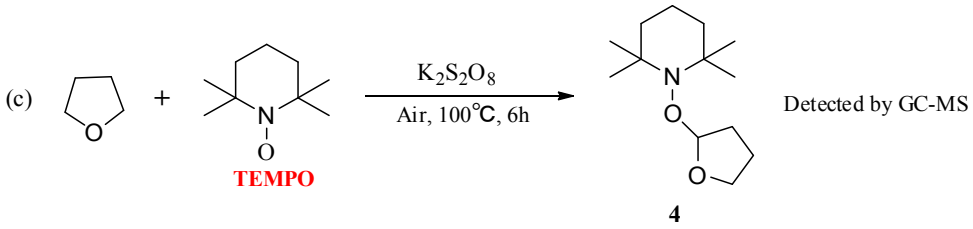
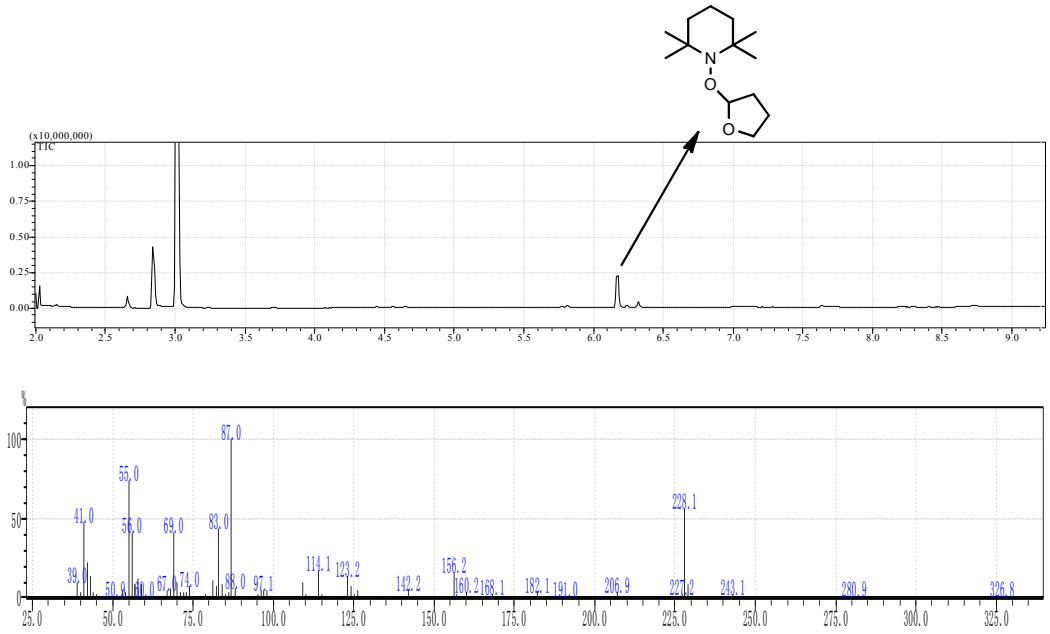
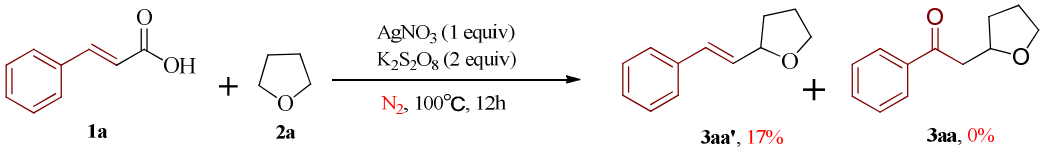
Scheme S1. Radical Trapping Experiment:





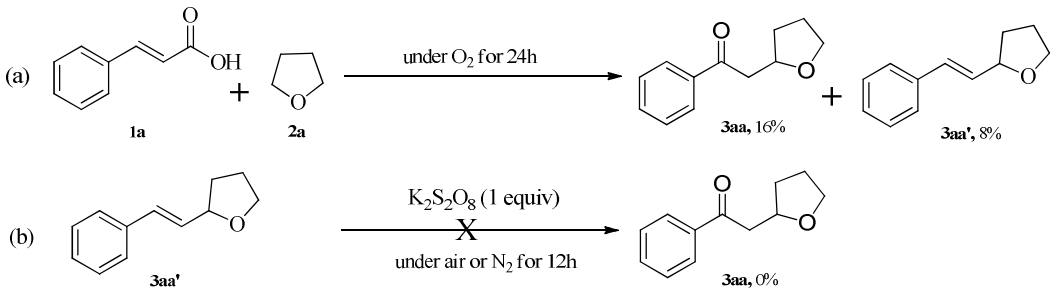
General Procedure: To a 20 mL Schlenk tube was added 2,2,6,6-tetramethyl-1-piperidinyloxy TEMPO (62.8 mg, 0.4 mmol), $K_2S_2O_8$ (90.8 mg, 0.4 mmol), tetrahydrofuran (1.5 ml). The reaction mixture was stirred at 100 ^oC for 6 h in sealed conditions. Upon completion of the reaction, the resulting mixture was dilute by EtOAc and washed with equal amounts of saturated $NaHCO_3$ solution, then the organic phase was separated and washed with water, and the water phase was extracted by EtOAc for three times. All organic phase thus obtained were dried over anhydrous Na_2SO_4 and filtered. The resulting mixture was analyzed by GC-MS.

Scheme S2.1. Additional Experiments for Mechanism:



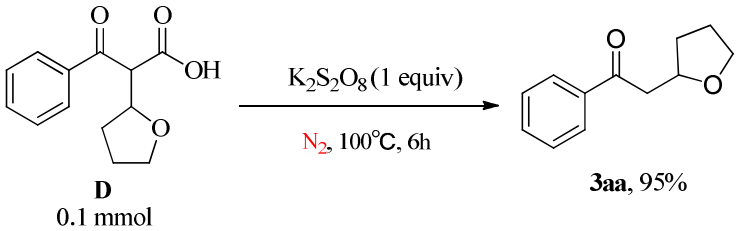
In the appearing of 1 equiv of $AgNO_3$, the model reaction was able to produce alkenylation product 3aa' in isolated 17% yields under N_2 atomsphere, what's more, there is no ketone products were found in the reaction solution.

Scheme S2.2. Additional Experiments about the Alkylation Product 3aa':



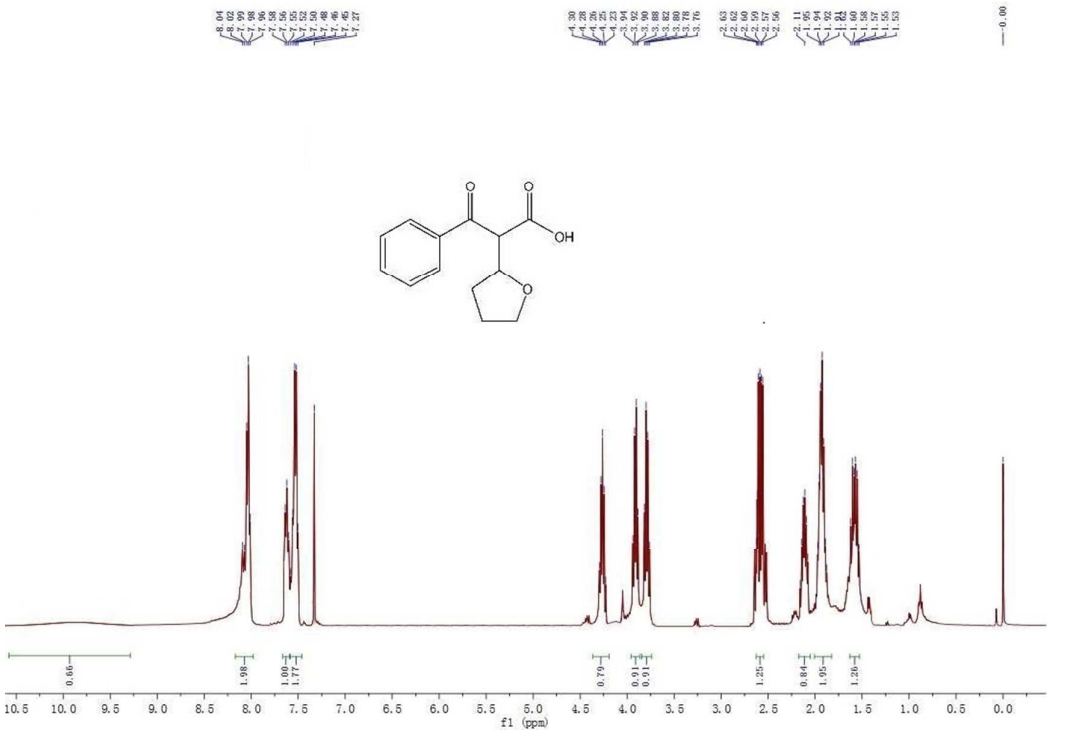
After the model reaction was conducted only with the existence of O_2 for 24h two kinds of products were obtained in about 16% and 8% yields, which implied the reaction was undergone an alkylation intermediate **3aa'** to form the ketone product, then **3aa'** was employed as the substrates, but there had no ketone products formed.

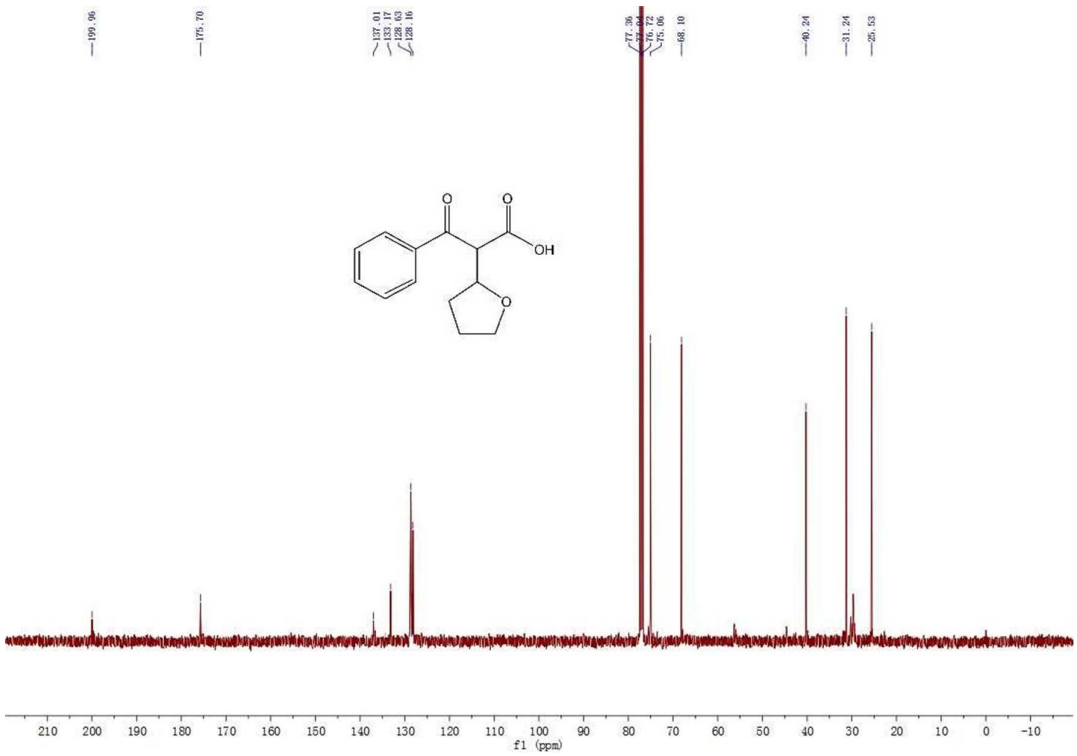
Scheme S3. Control Experiments for Mechanism:



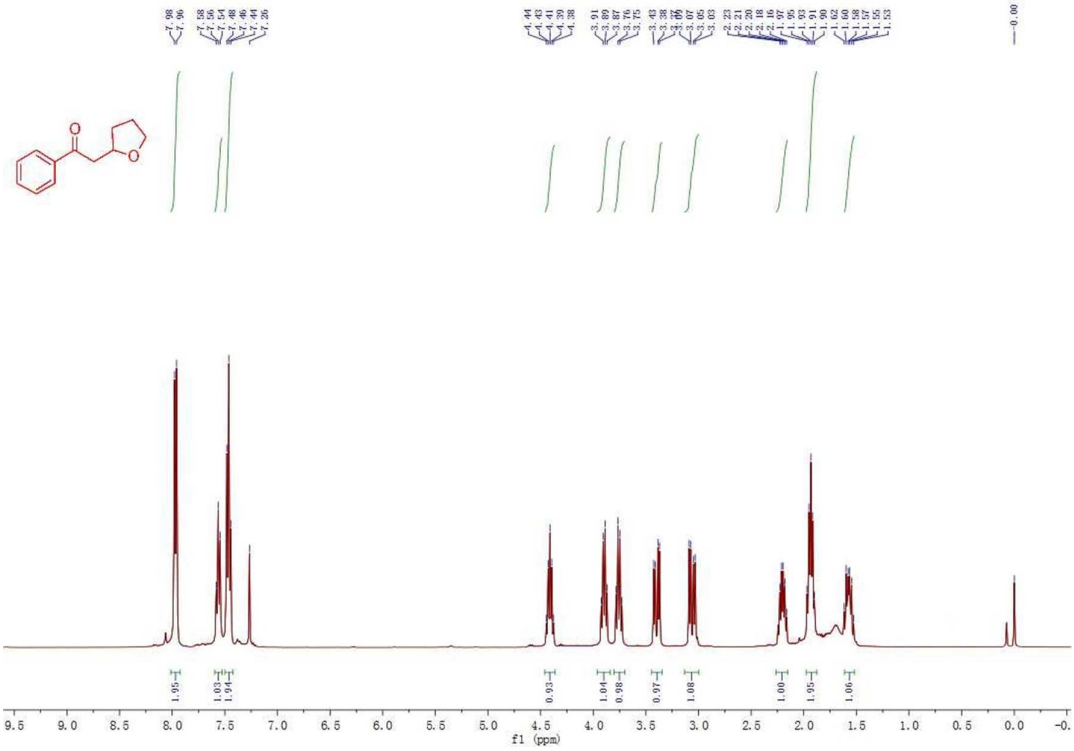
In the presence of 1 equiv of $K_2S_2O_8$, Intermediate acid **D** (0.1 mmol, 23.4 mg) was able to transform into the desired product **3aa** in 95% yields under nitrogen and thermal conditions. The synthesis of intermediate acid **D** was according to ref 17 and 14b.

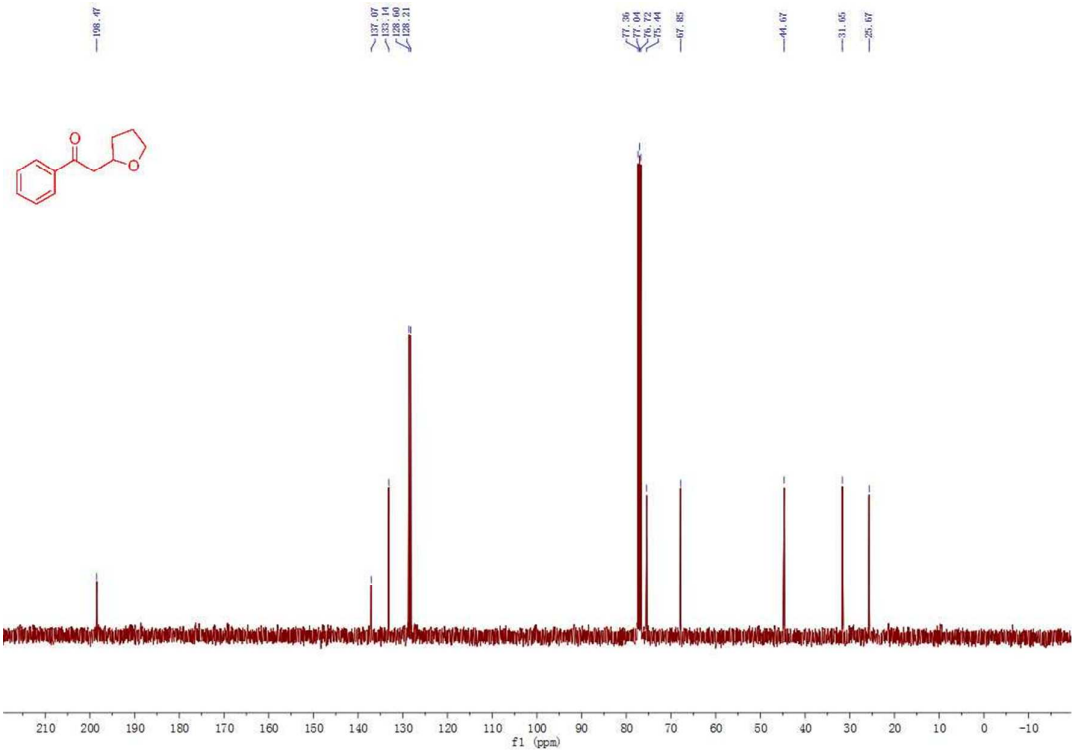
NMR Spectra for compound D:



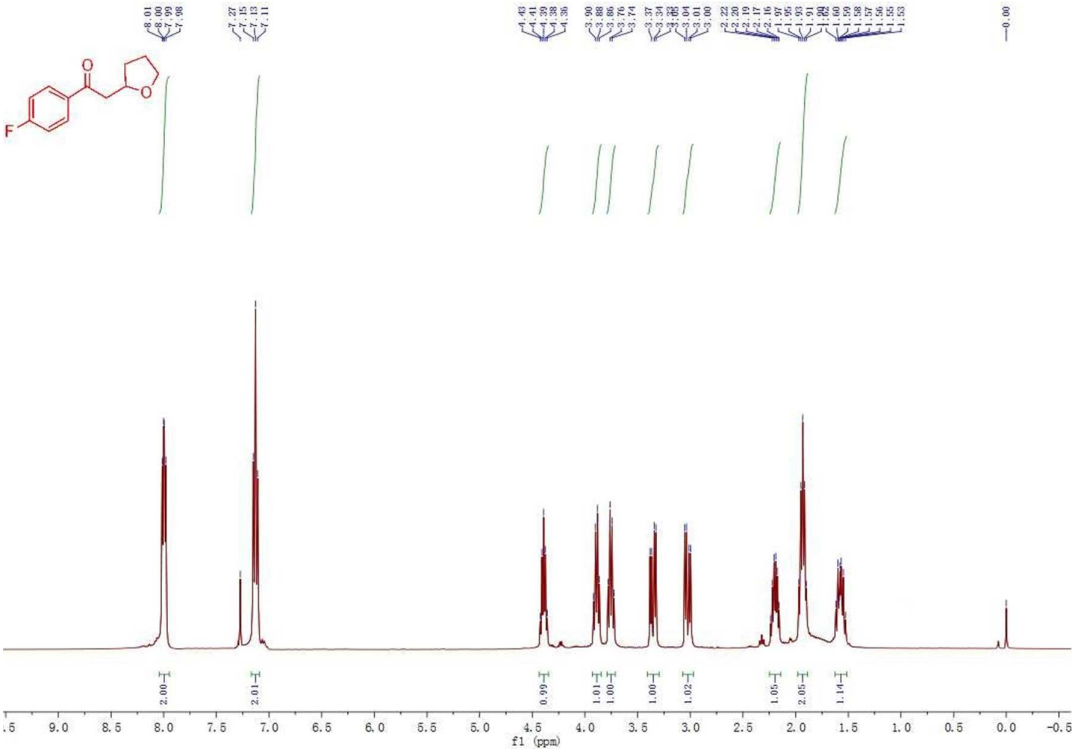


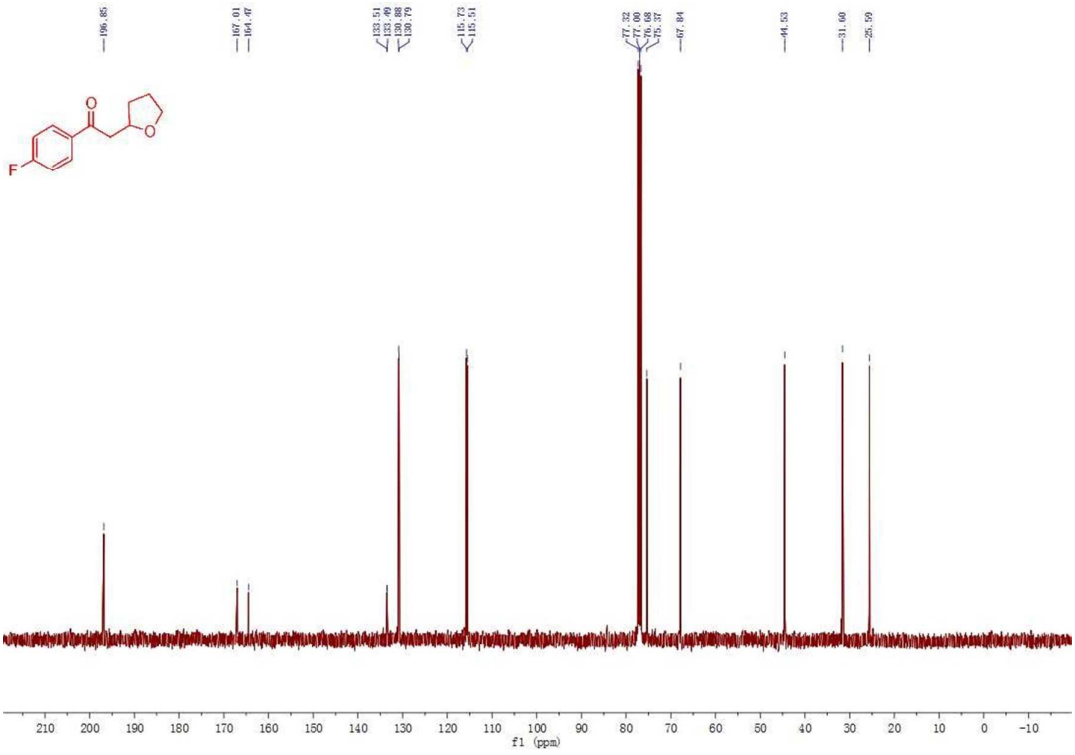
NMR Spectra for 3aa



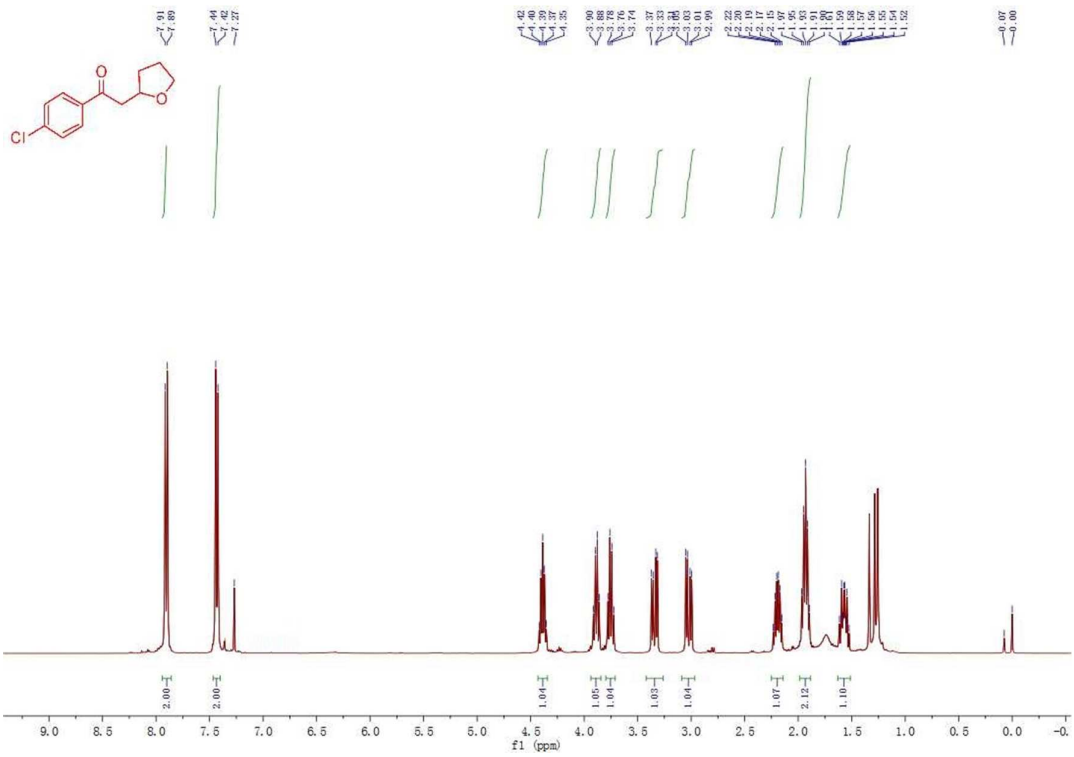


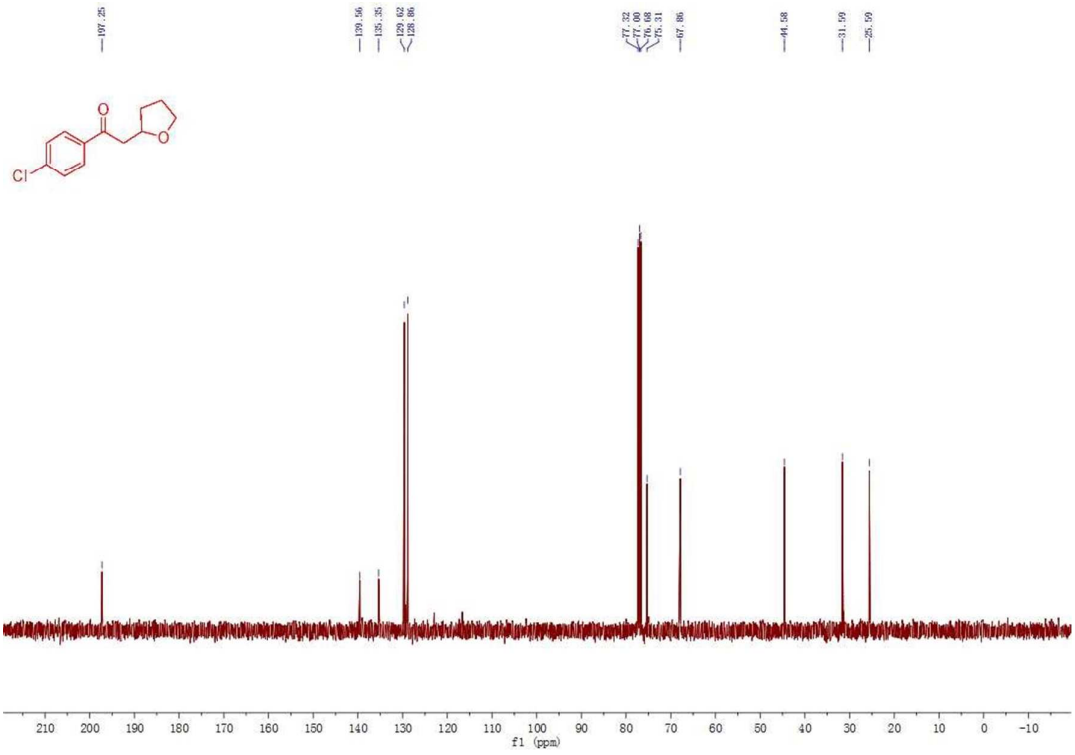
NMR Spectra for 3ba



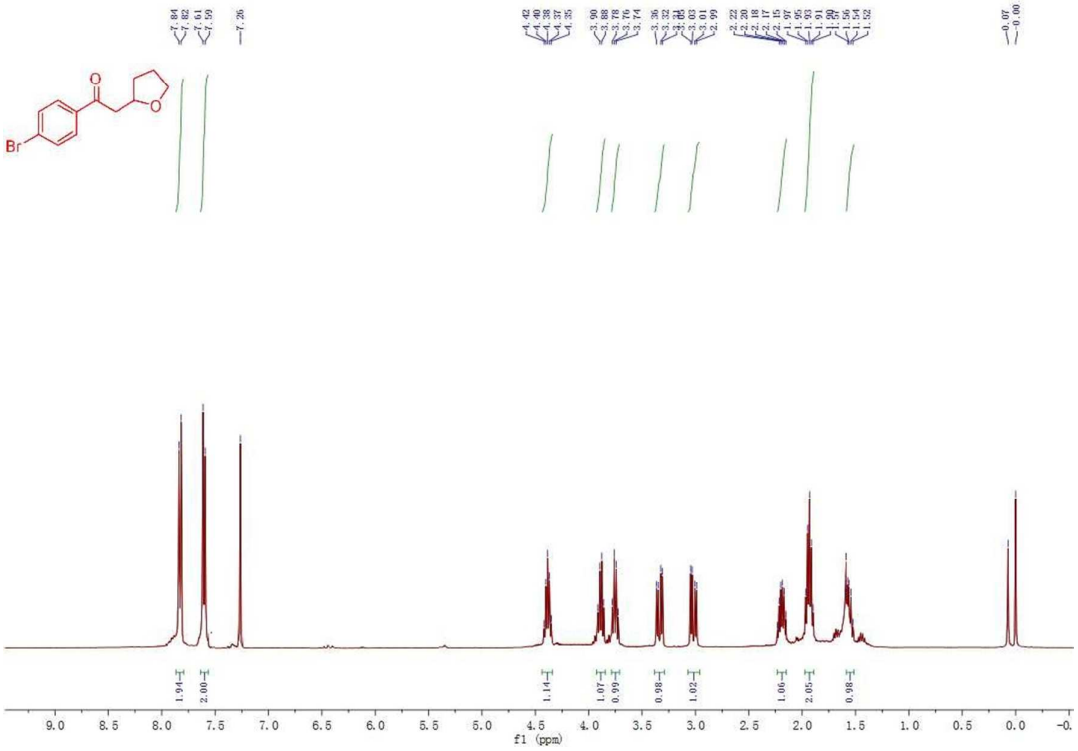


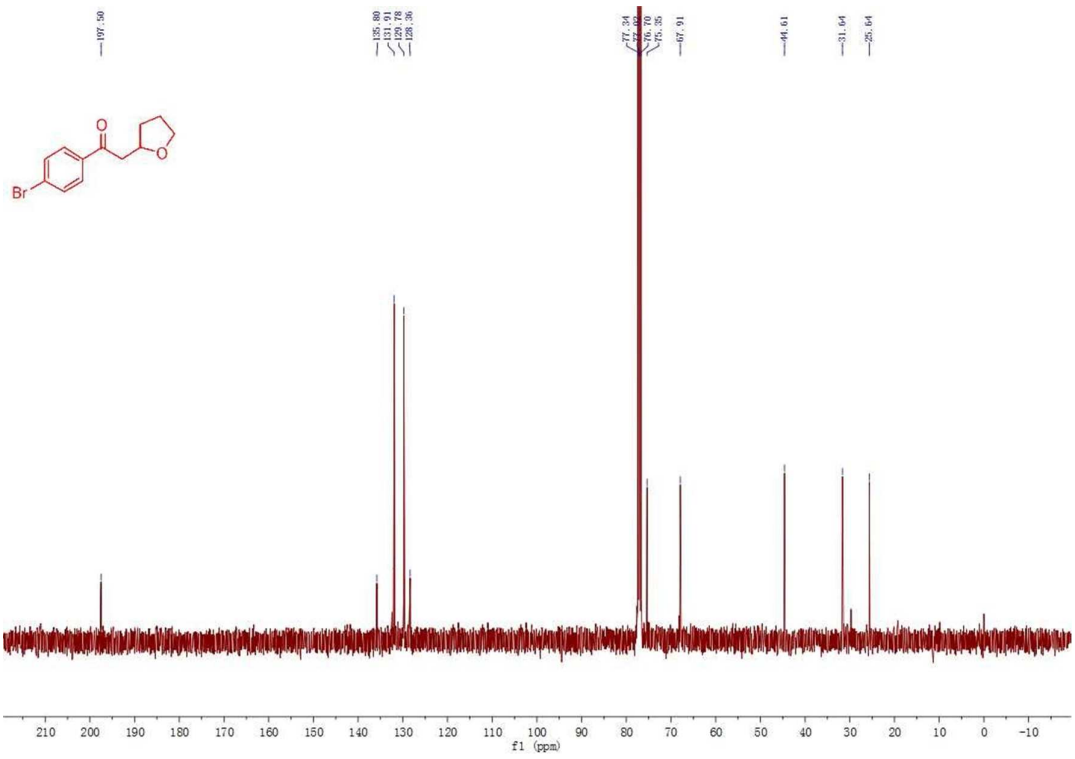
NMR Spectra for 3ca



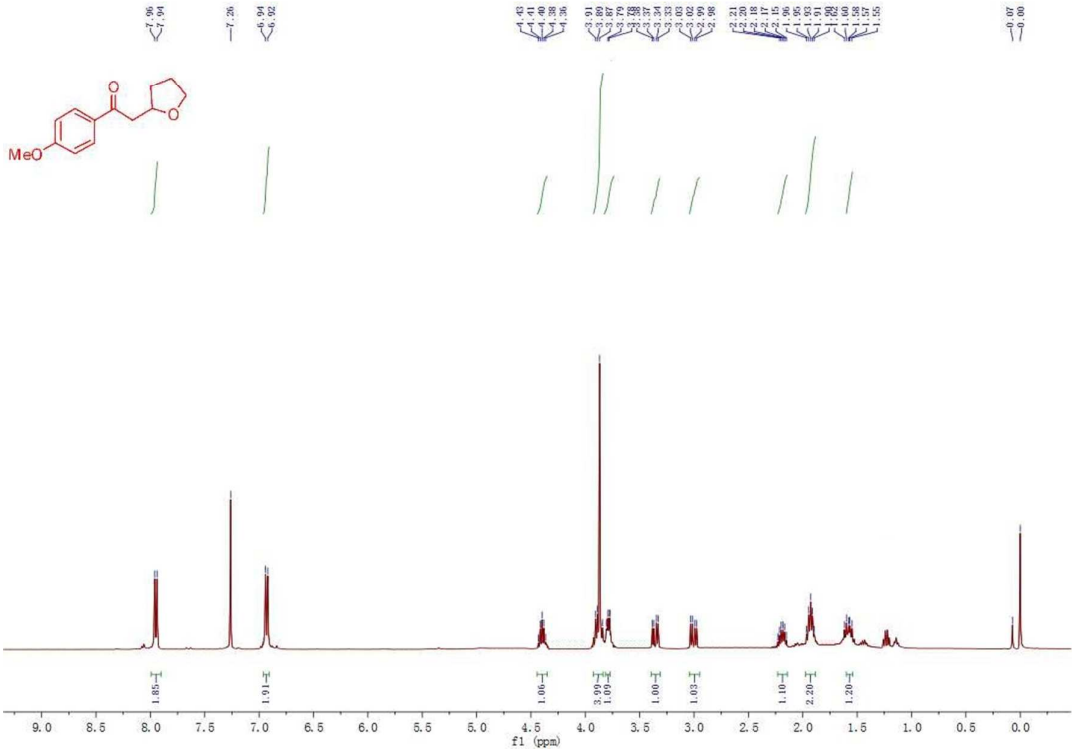


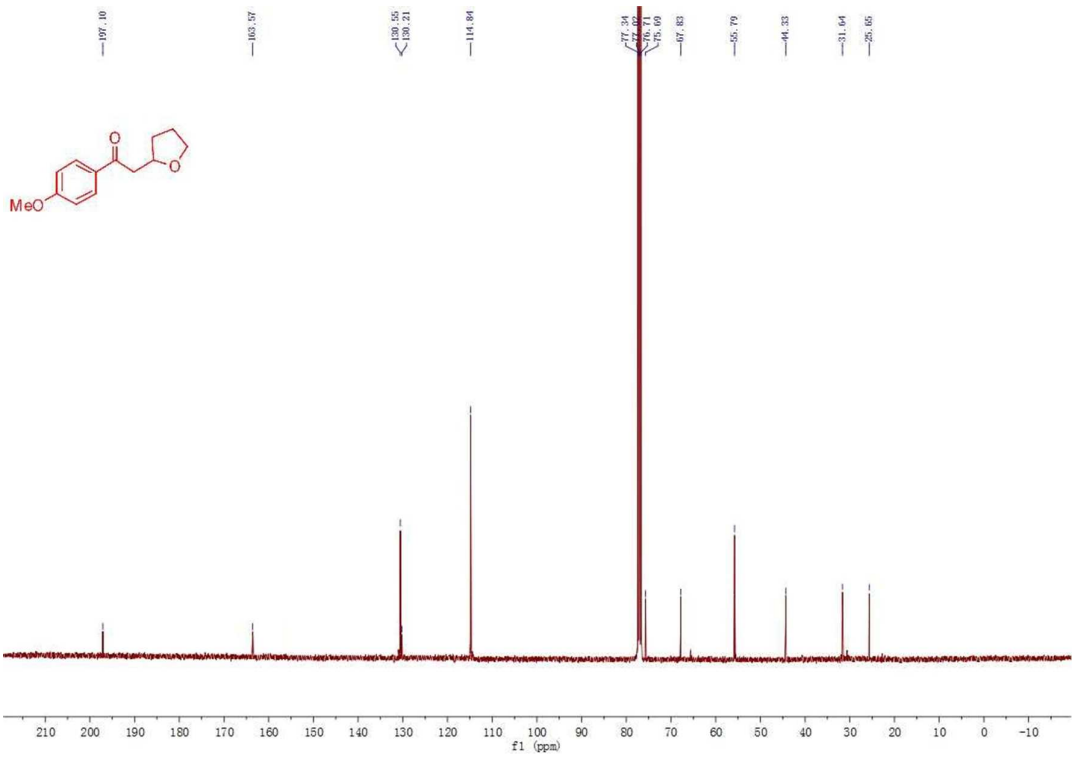
NMR Spectra for 3da



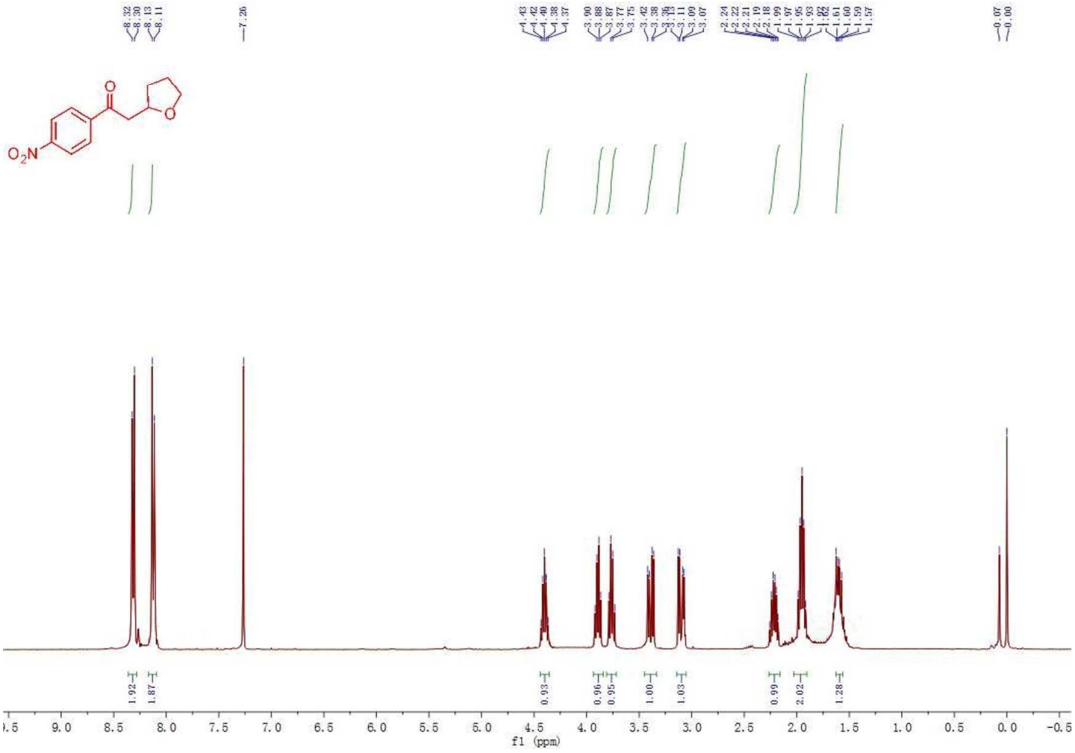


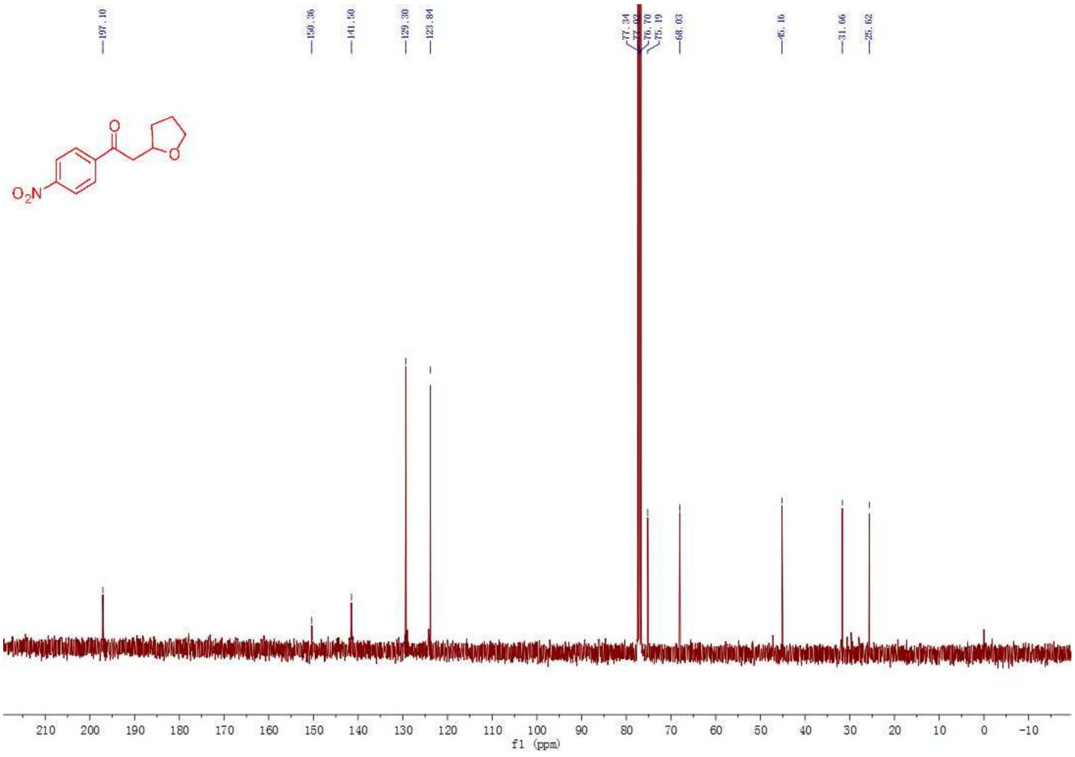
NMR Spectra for 3ea



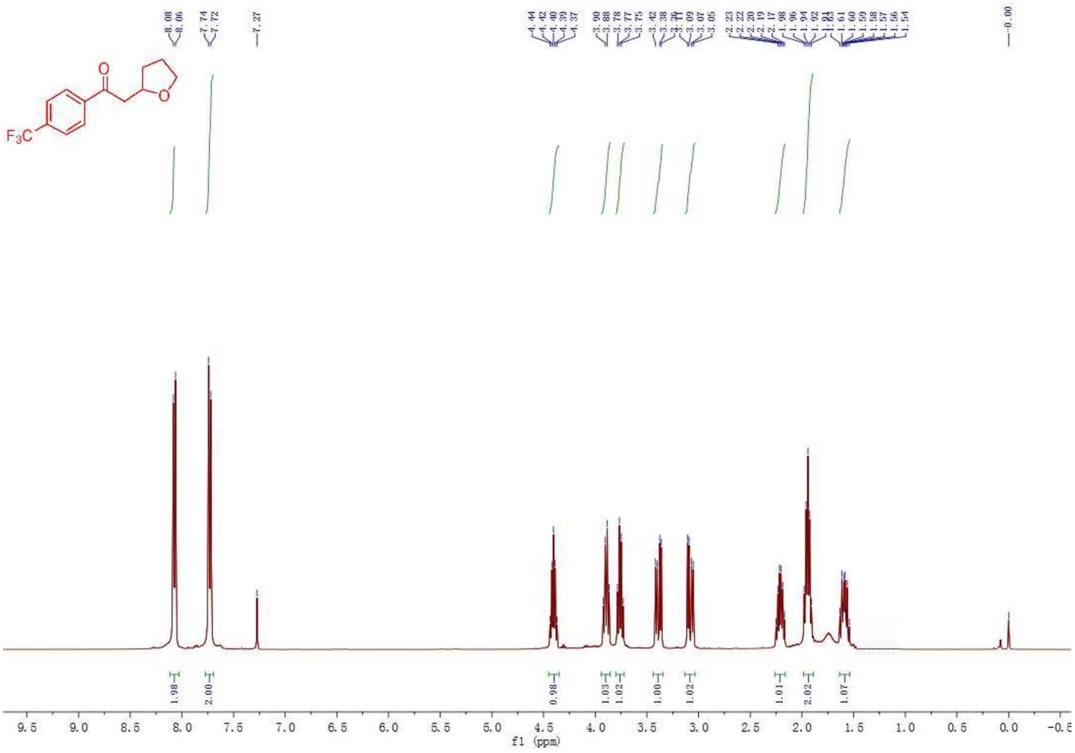


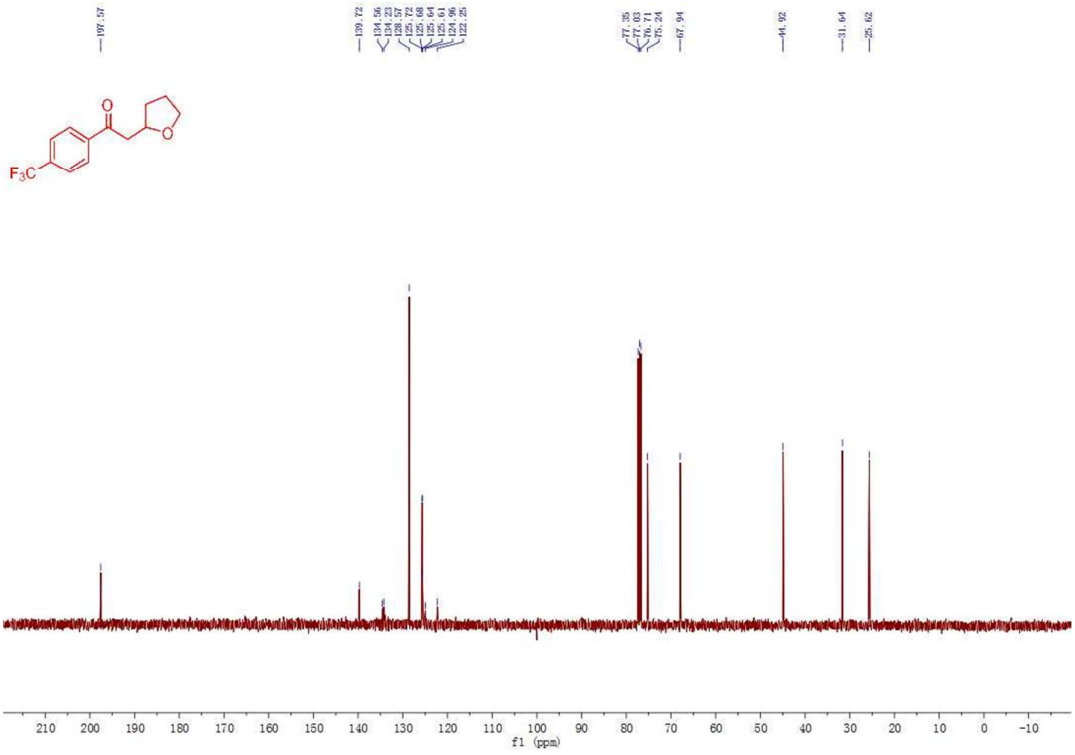
NMR Spectra for 3fa



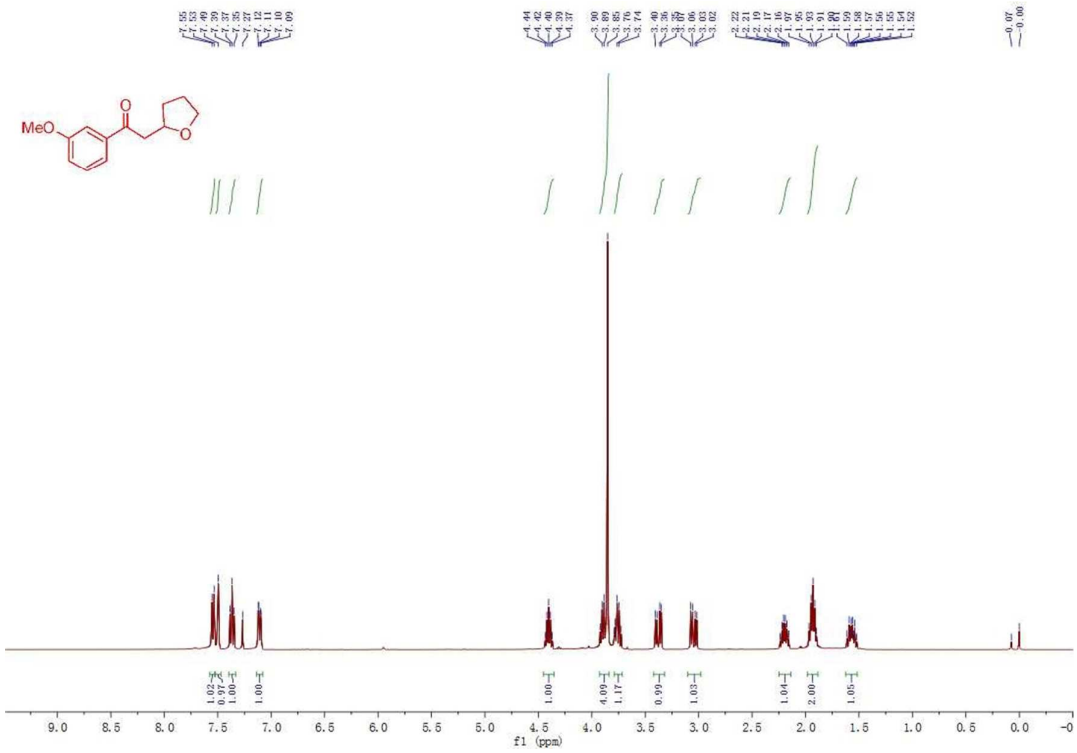


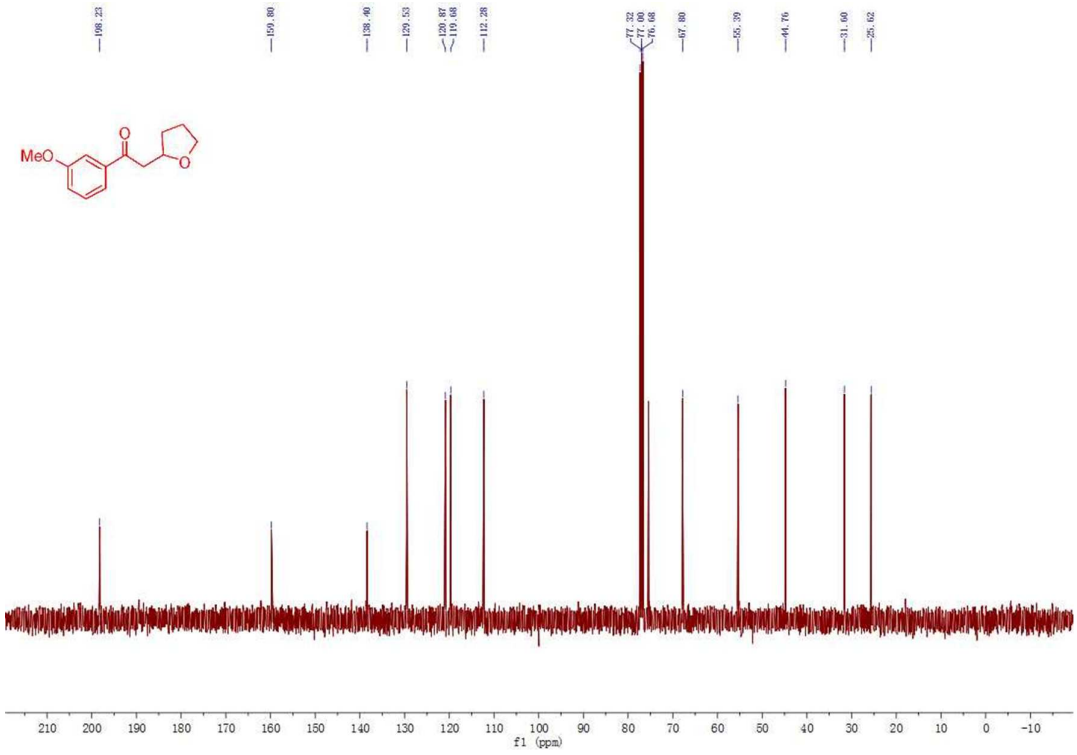
NMR Spectra for 3ga



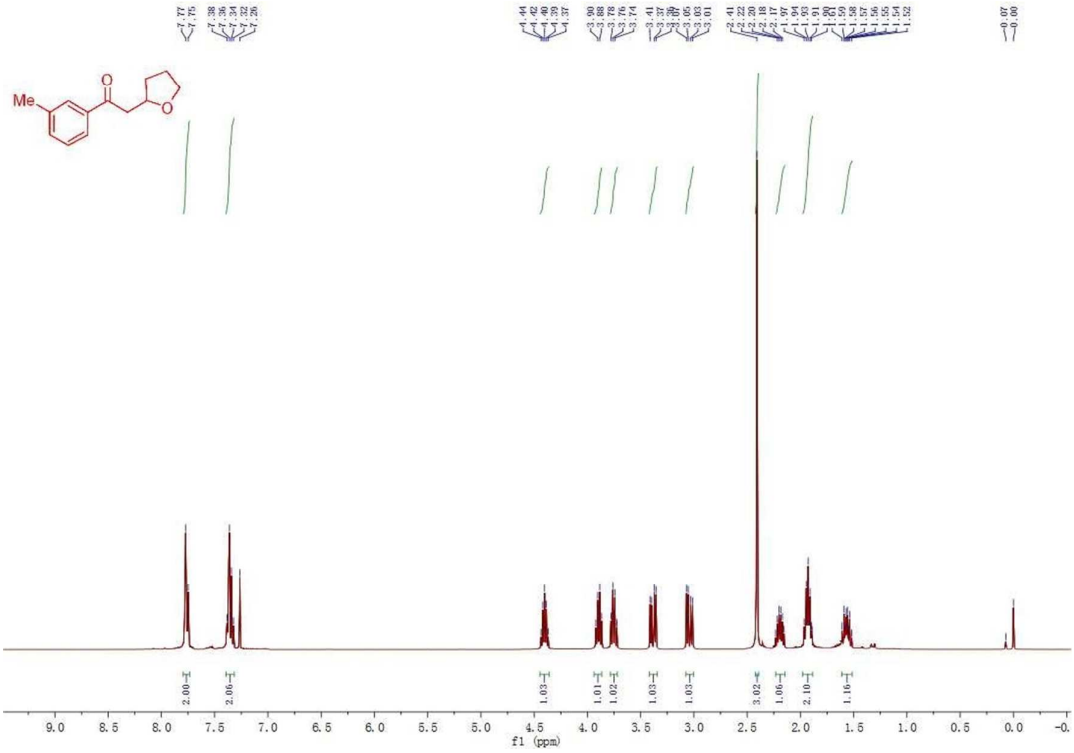


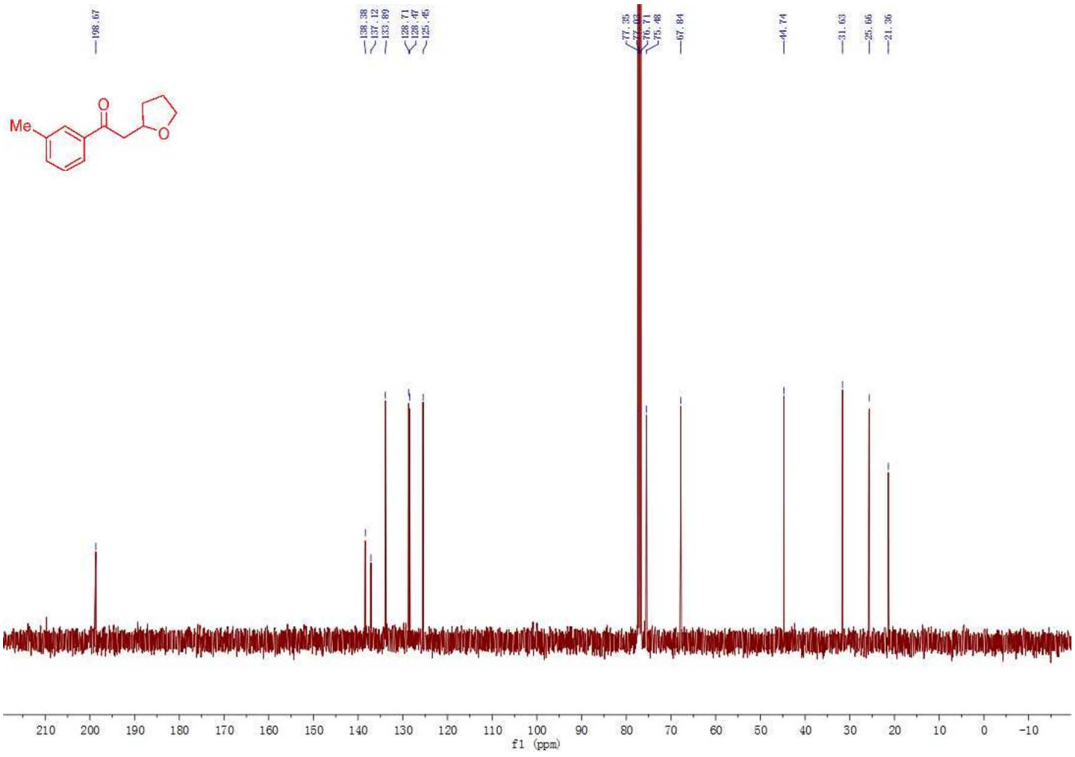
NMR Spectra for 3ha





NMR Spectra for 3ia





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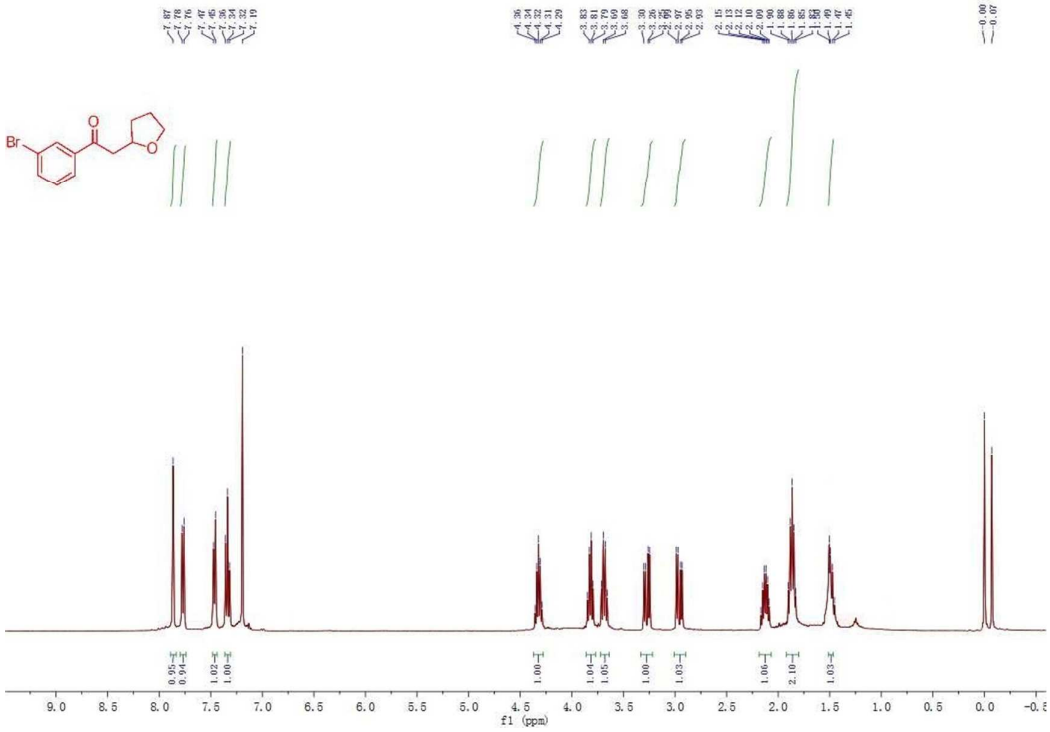
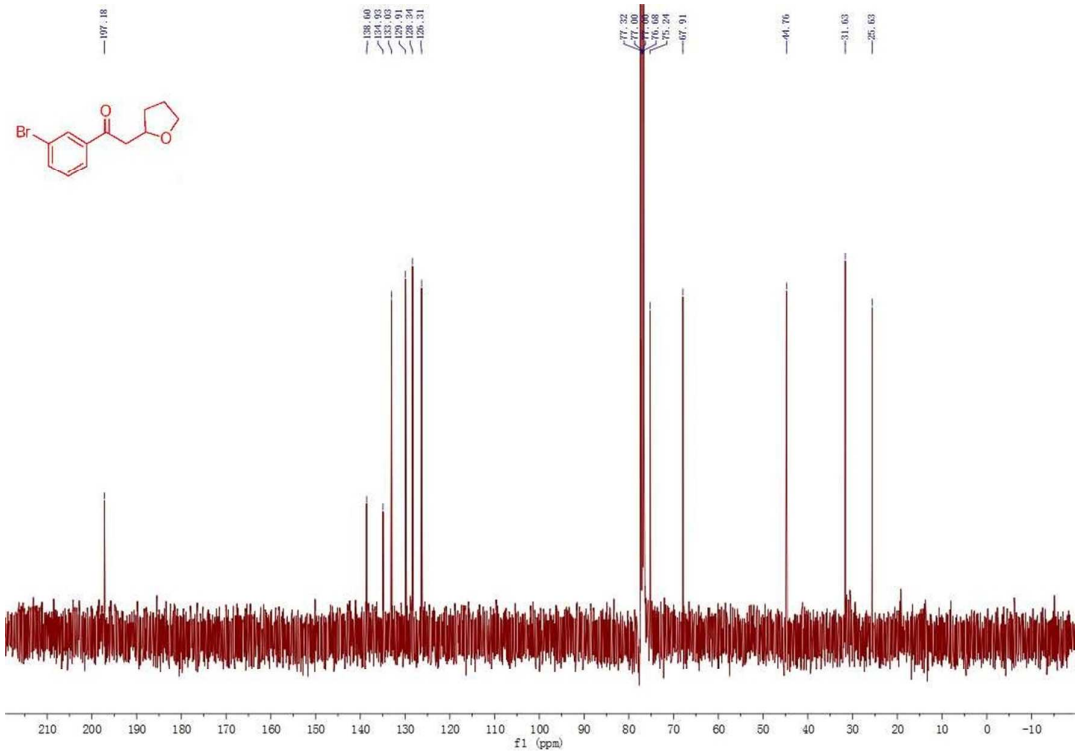
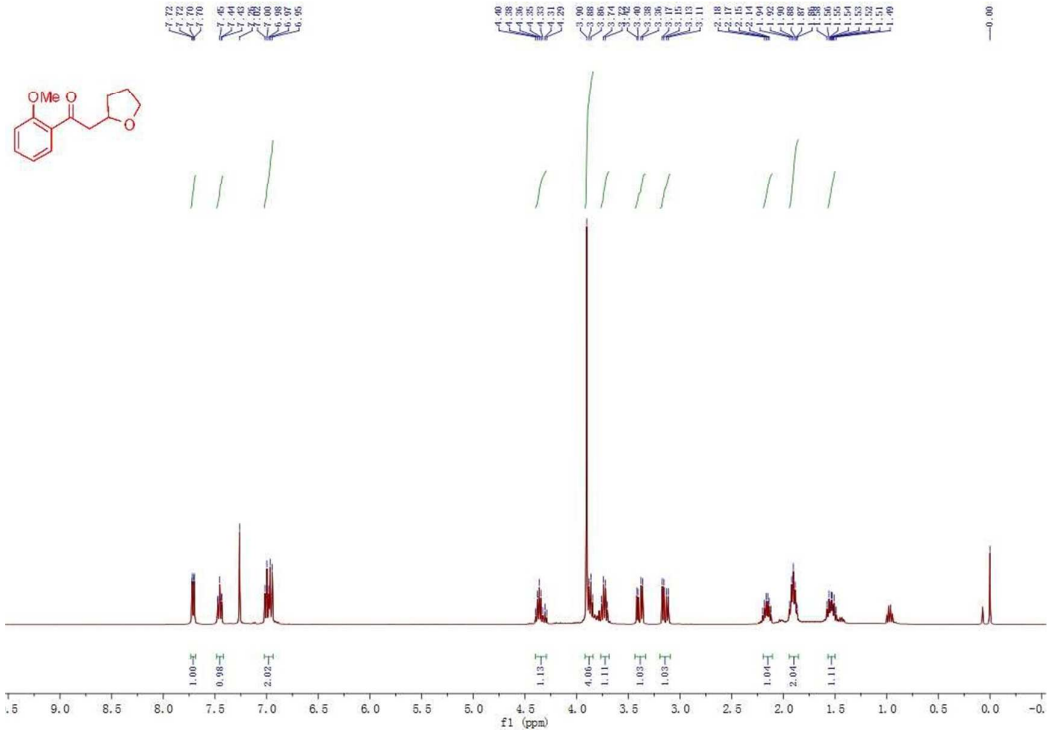
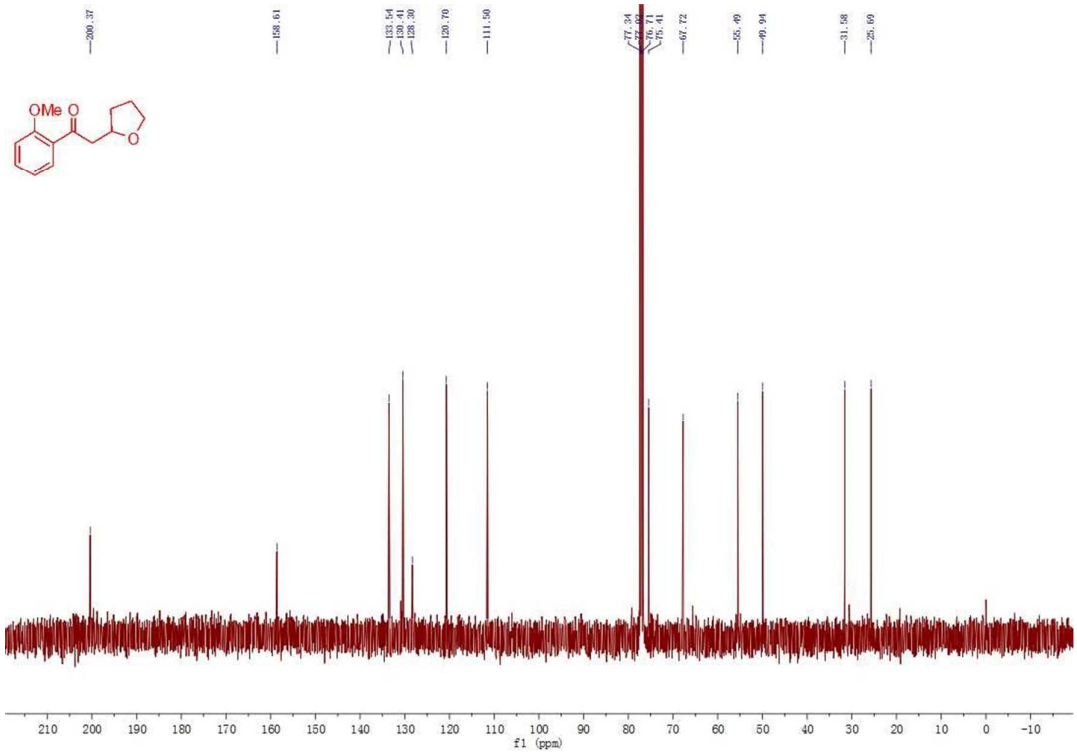




NMR Spectra for 3ka





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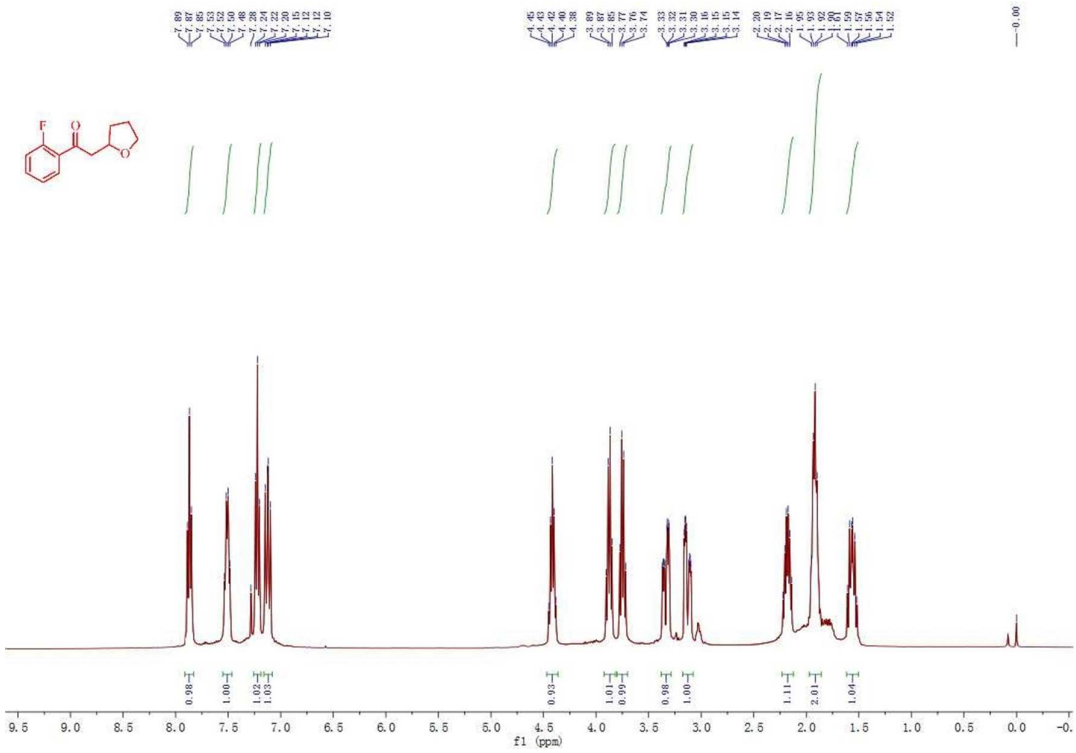

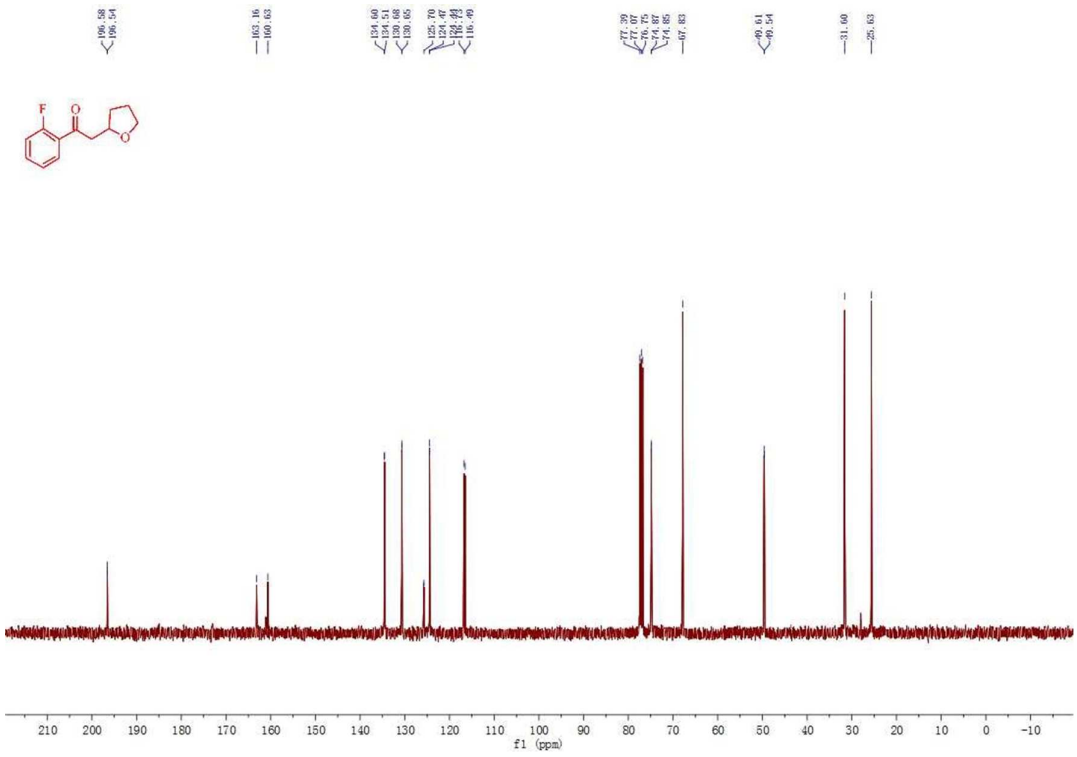

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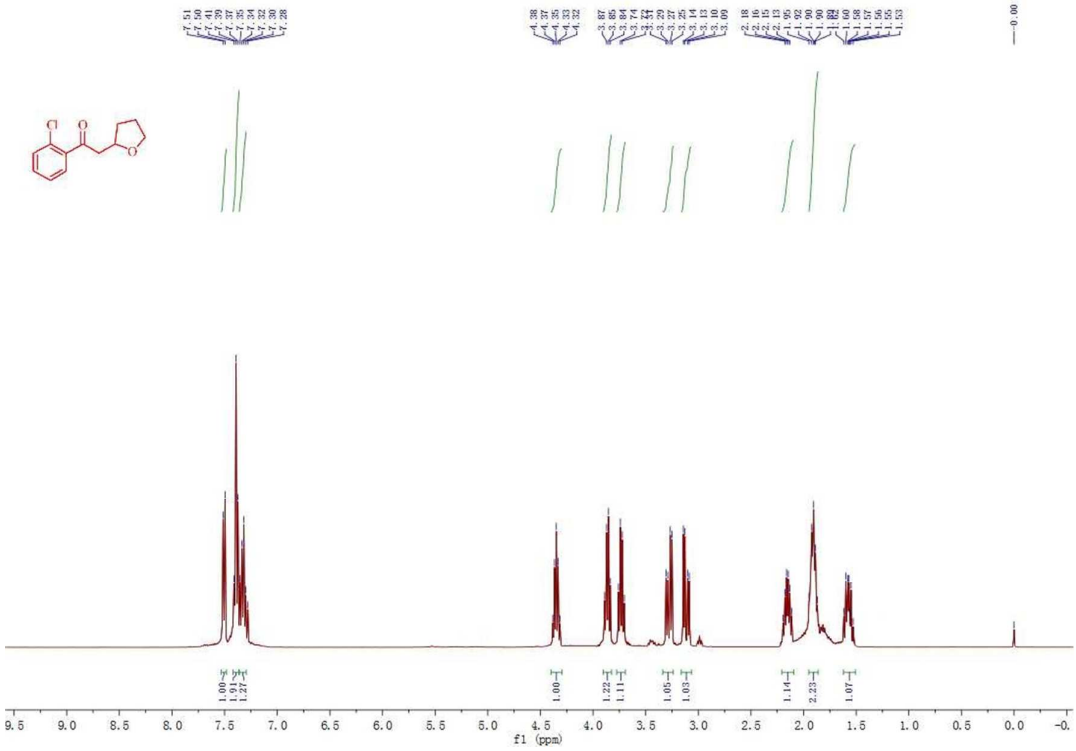

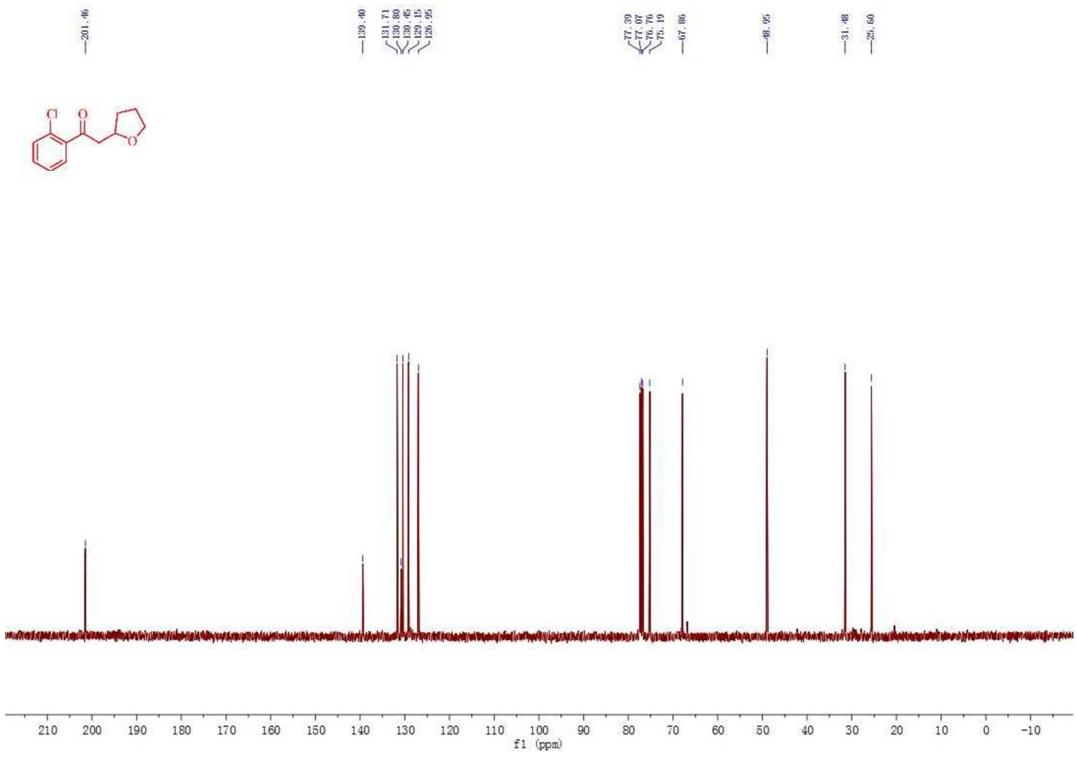

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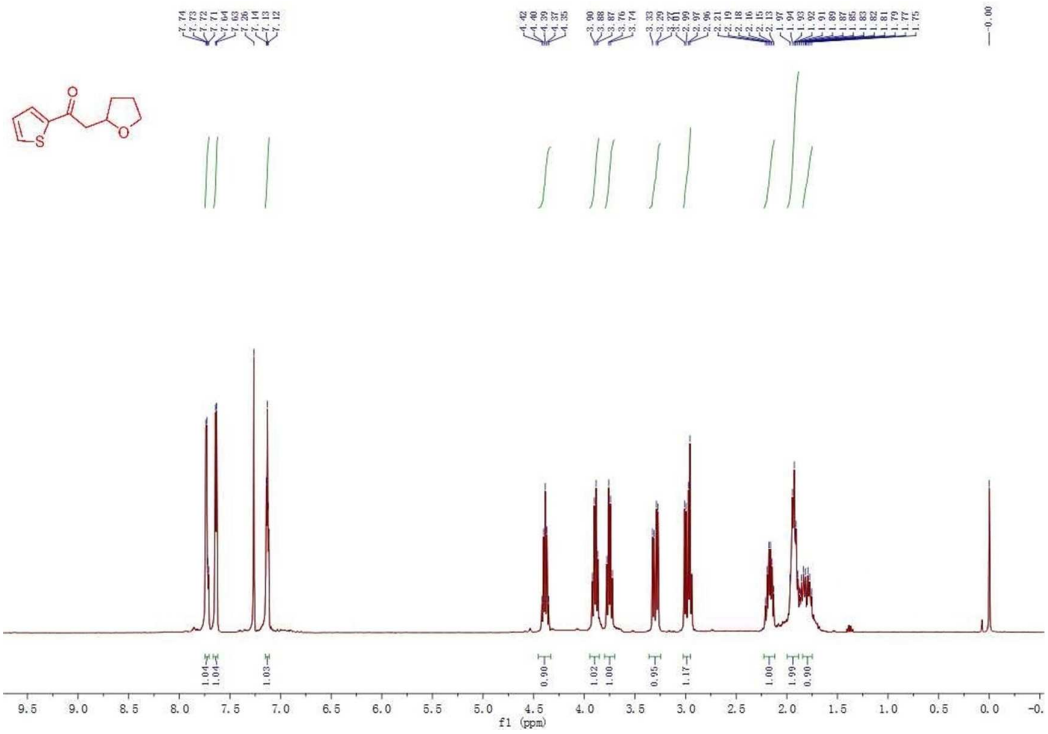

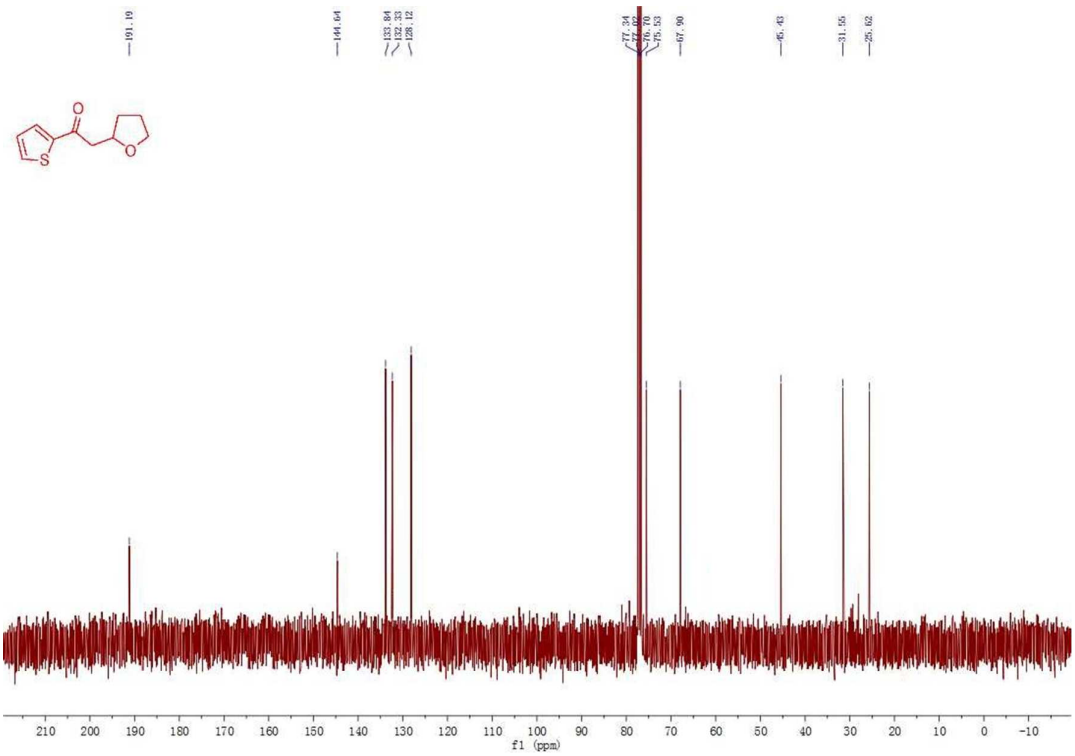

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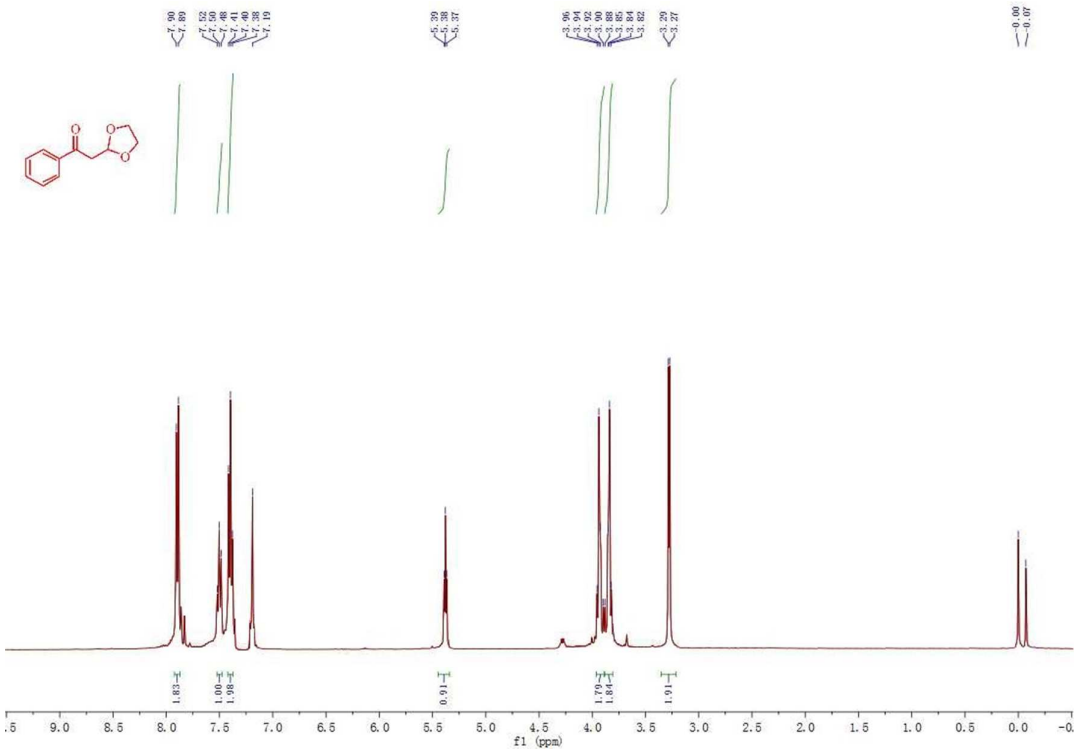
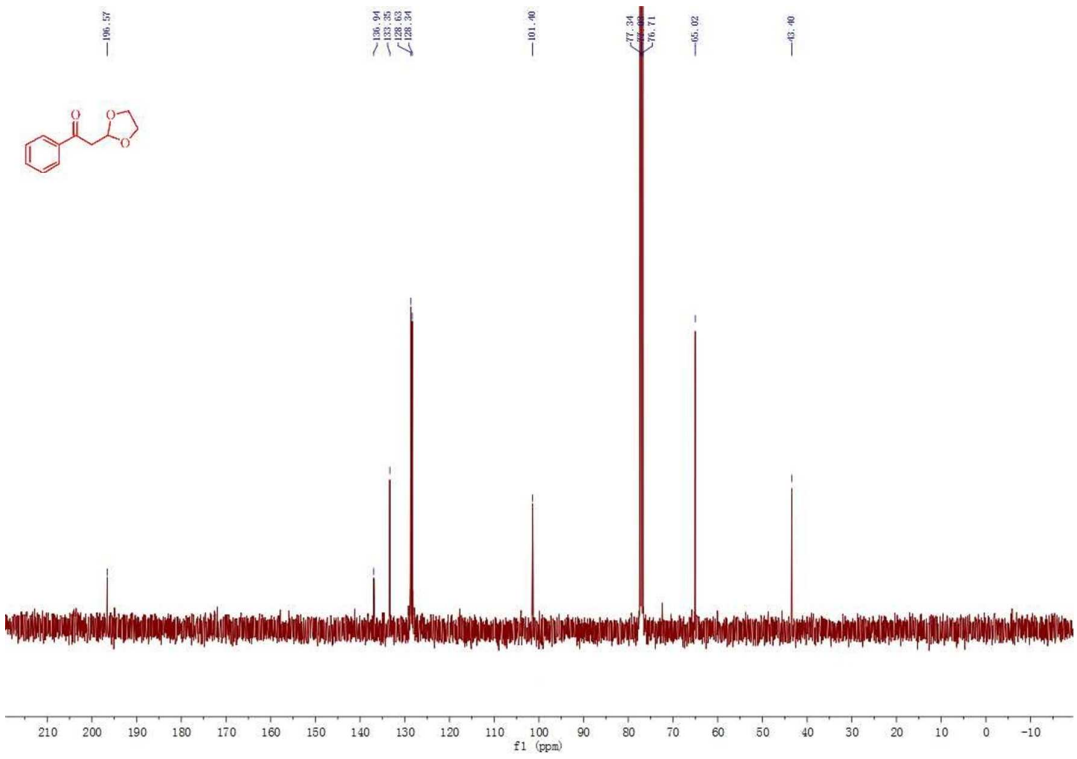
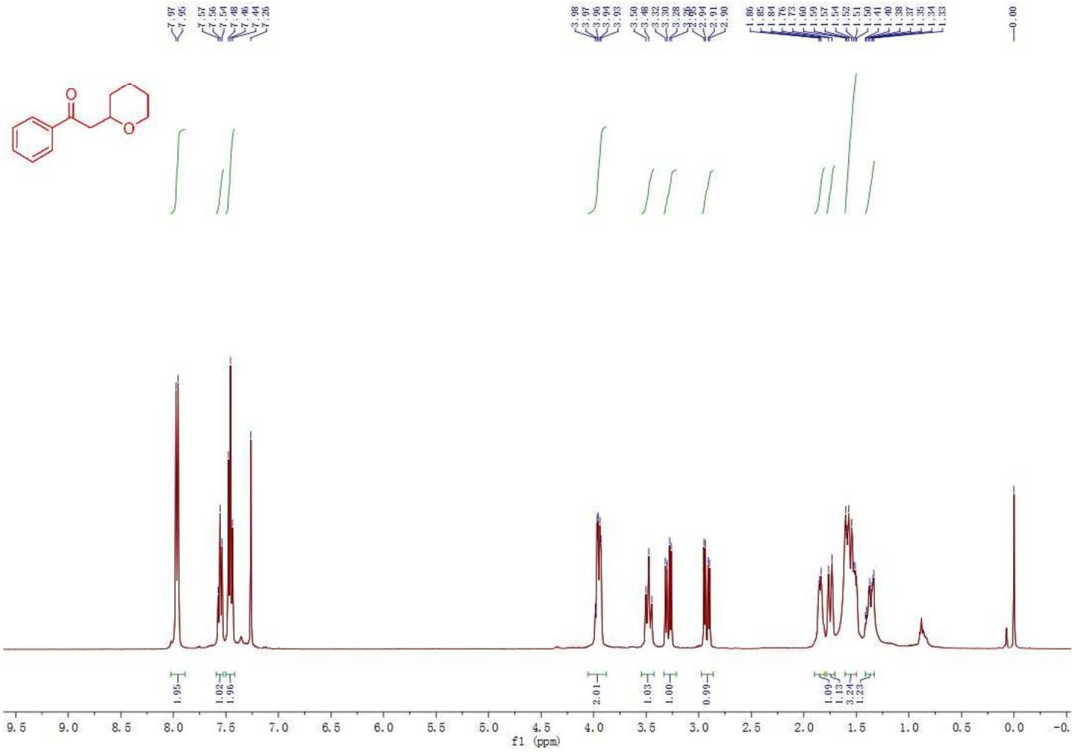
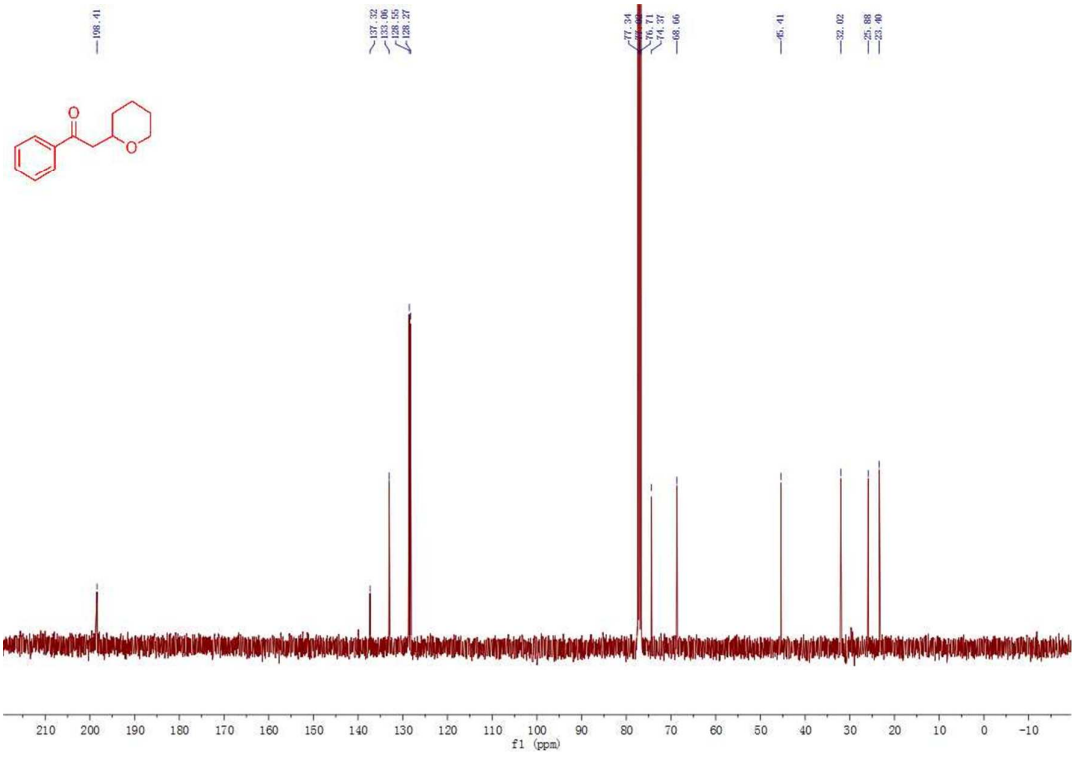




NMR Spectra for 3af





NMR Spectra for 3ag