

## Supporting Information

# Iridium-Catalyzed and pH-Dependent Reductions of Nitroalkenes to Ketones

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## 1. Methods for calculating the product distribution

All the  $\alpha$ -methyl- $\beta$ -(4-substituted-phenyl)nitroethylenes, the nitroalkanes, oximes, and ketones products are known compounds. Thus, we used the  $^1\text{H}$  NMR spectra to analyze the crude reaction mixtures in the optimization of the conditions. We take the  $^1\text{H}$  NMR of the crude reaction mixture in Table 1, entry 3 (Figure S1) as an example. The data were summarized in Table S1.

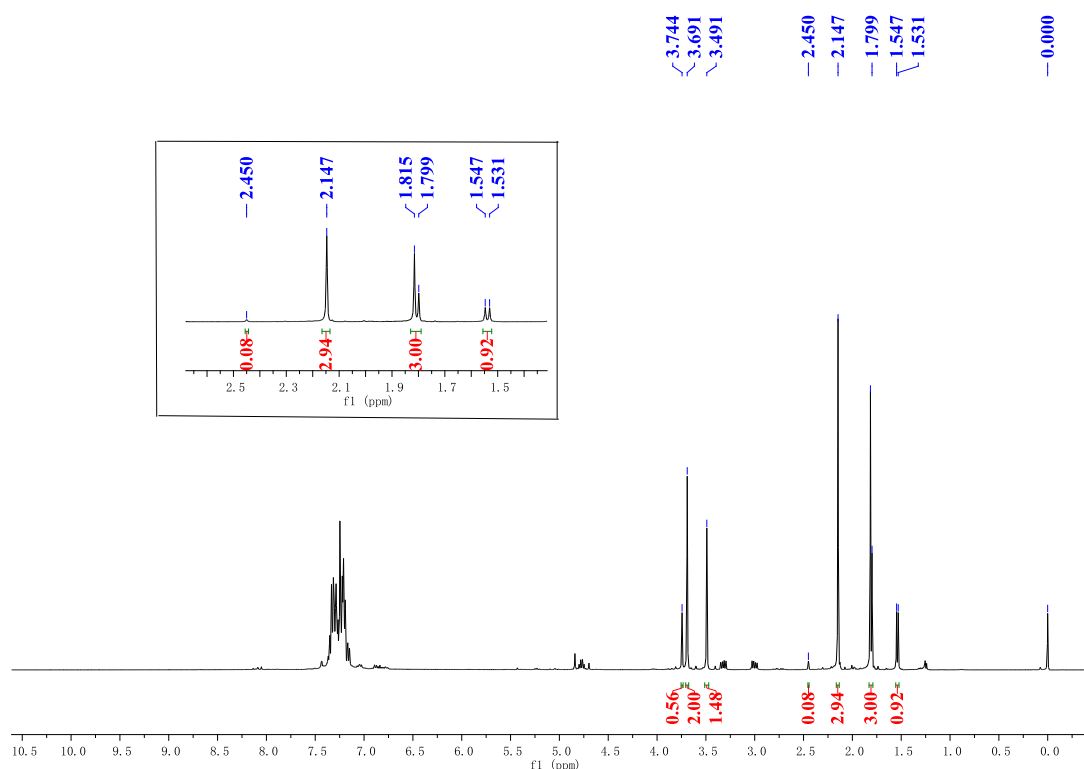


Figure S1. The  $^1\text{H}$  NMR of the crude reaction mixture in Table 1, entry 3

This mixture contains nitroalkene (**1a**), nitroalkane (**2a**), *Z*- and *E*-oxime (**3a**), and ketone (**4a**). All these four kinds of compounds contain electronically different methyl groups, which were well discriminated by the  $^1\text{H}$  NMR.

Table S1. Methods for calculating the product distribution and yield.

Compound	<b>1a</b>	<b>2a</b>	<b>3a</b>	<b>4a</b>
$\delta$ (Me)	2.45 (s)	1.54 (d, $J = 6.6$ Hz, 1H).	1.82 (s), 1.80 (s)	2.15 (s)
Integral	0.08	0.92	3.00	2.94
Molar ratio (%)	1	13	43	43

Therefore, the conversion of **1a** was 99%; the yield of **2a** is 13%; the yield of **3a** is 43%; the yield of **4a** is 43%.

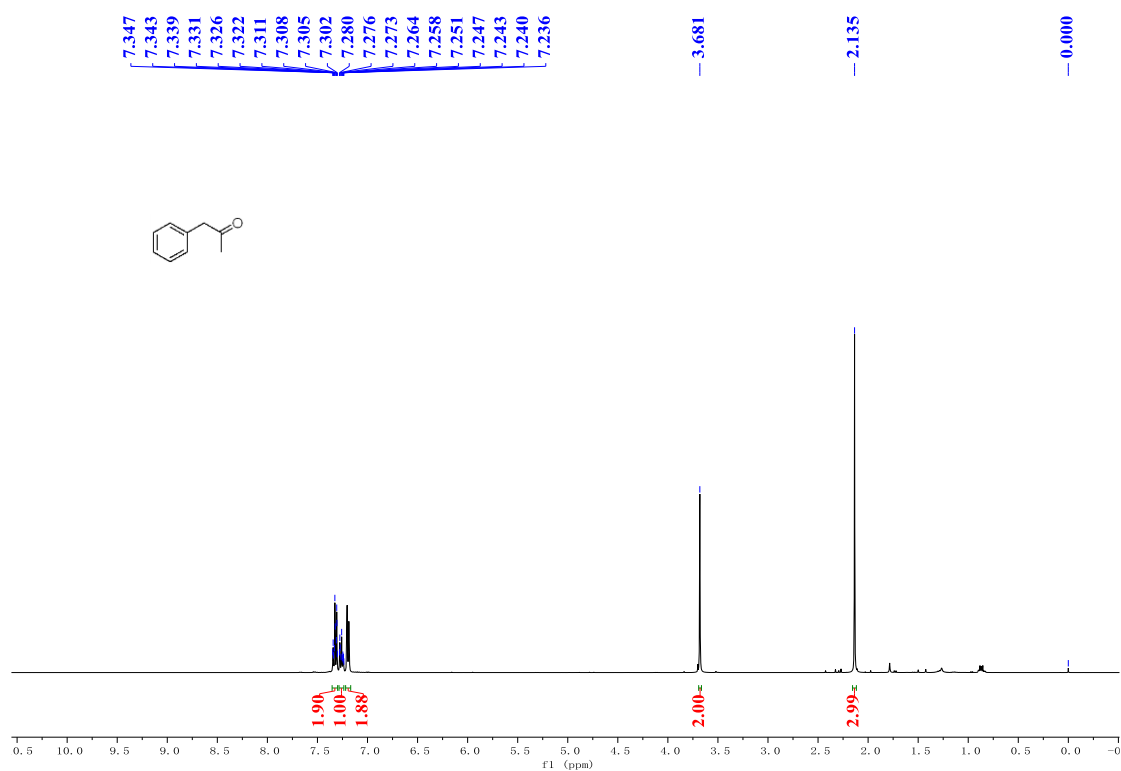
## 2. Gram-scale synthesis

A 250-mL round bottom flask was charged with (2-nitroprop-1-en-1-yl)benzene (**1a**) (1.50 g, 9.2 mmol), EtOH (36.8 mL), **C3** catalyst (2.1 mg, 0.00368 mmol), deionized water (36.8 mL), HCO<sub>2</sub>H (2.84 mL), and H<sub>2</sub>SO<sub>4</sub> (3.68 mol/L, 0.92 mL). The mixture was stirred at 80 °C for 3 h. Then HCl (36.8 mL) was added and the mixture was stirred for another 1 h. After cooling to room temperature, diluting with water (74 mL), extracting with ethyl acetate (100 mL x 3), the organic phase was washed with saturated sodium bicarbonate and dried over anhydrous sodium sulfate. The organic phase was evaporated under reduced pressure and the residue was purified by flash column chromatography to afford 1-phenylpropan-2-one (**4a**) as a yellowish oil (0.86 g, 70%).

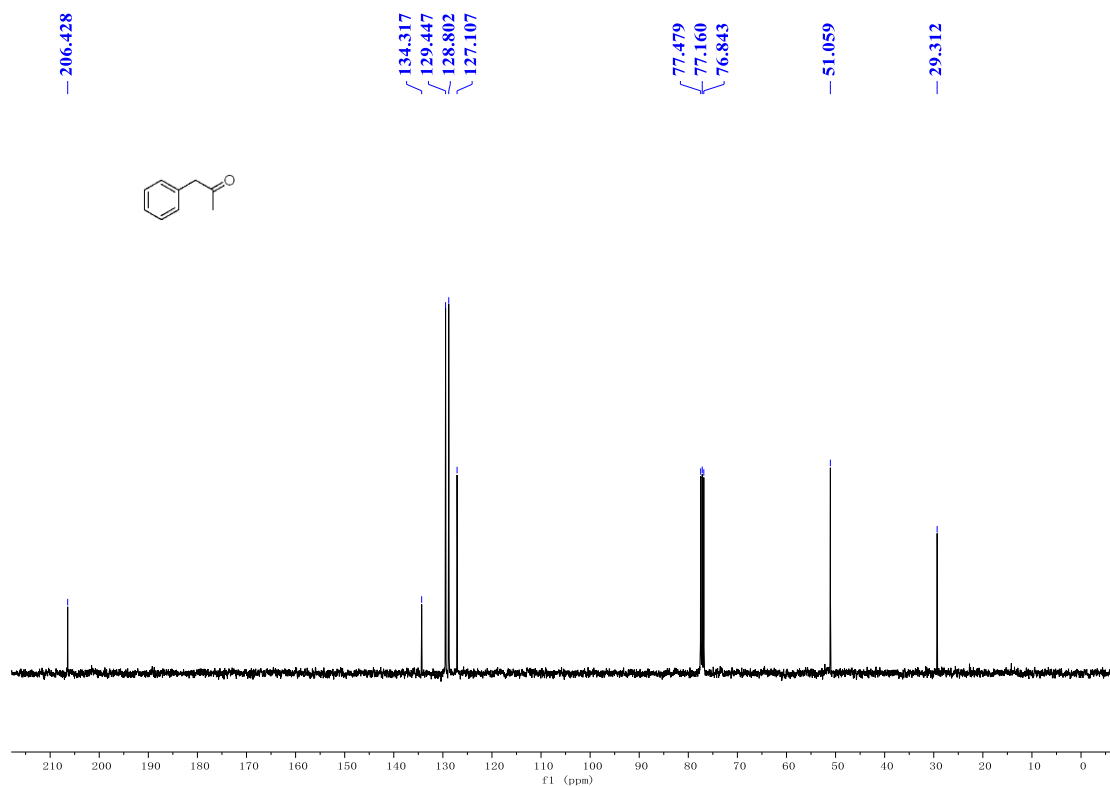
## 3. Copies of NMR Spectra

### 3.1 <sup>1</sup>H and <sup>13</sup>C Spectra of products

$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of 1-phenylpropan-2-one (**4a**)

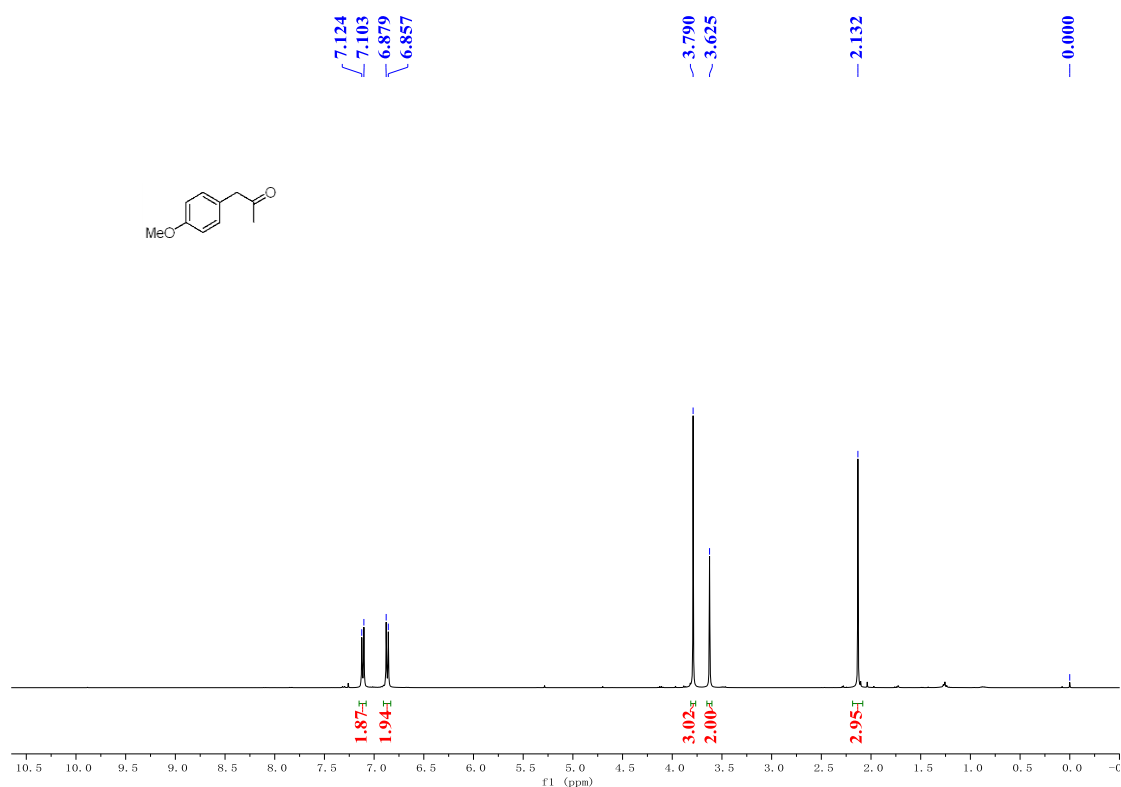


$^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of 1-Phenylpropan-2-one (**4a**)

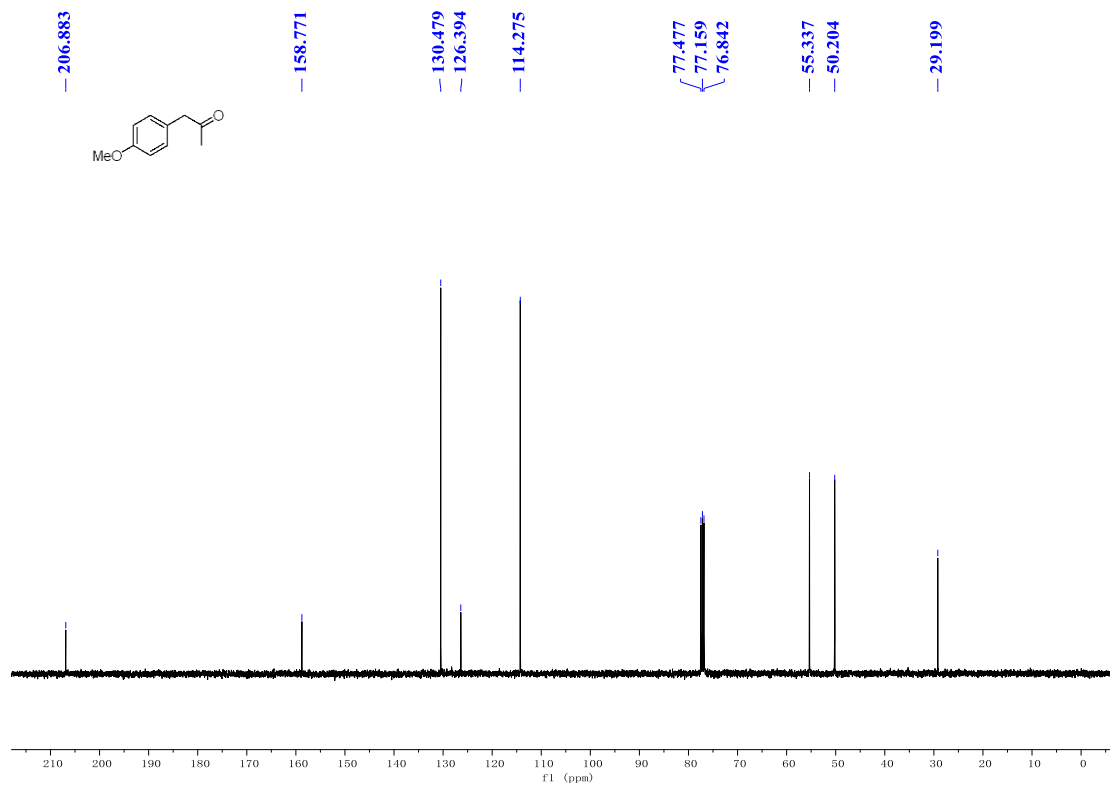




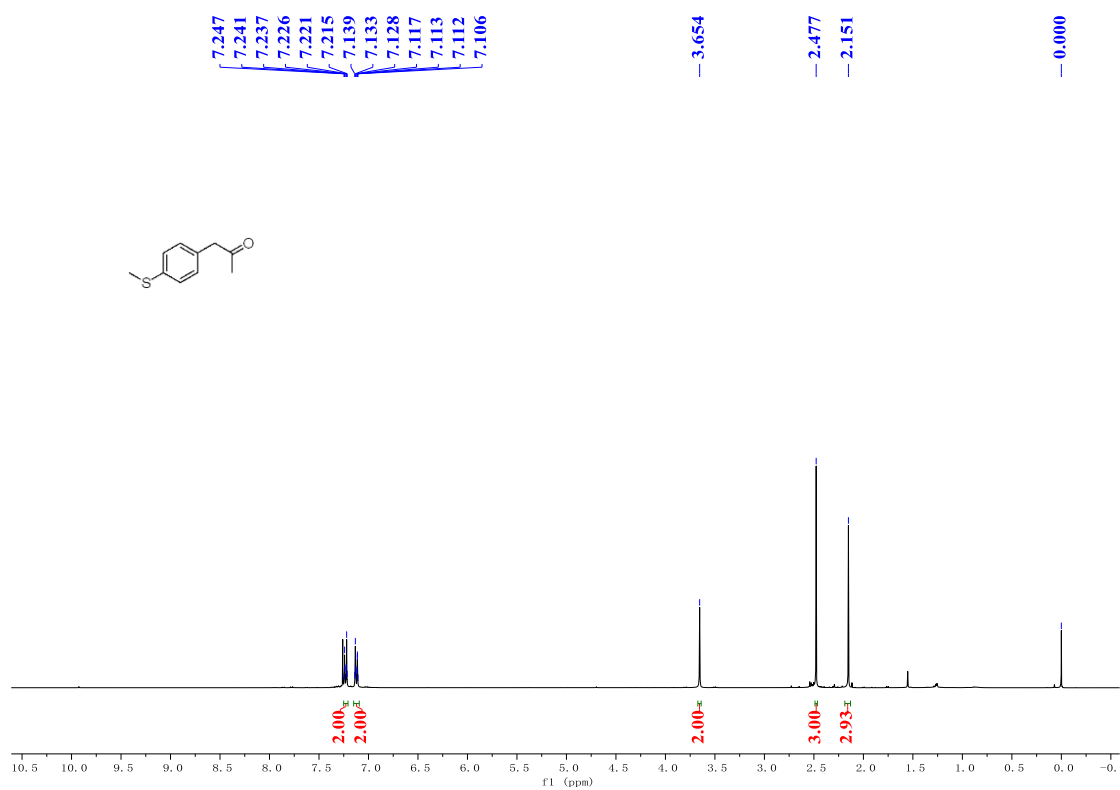
$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of 1-(4-methoxyphenyl)propan-2-one (**4b**)



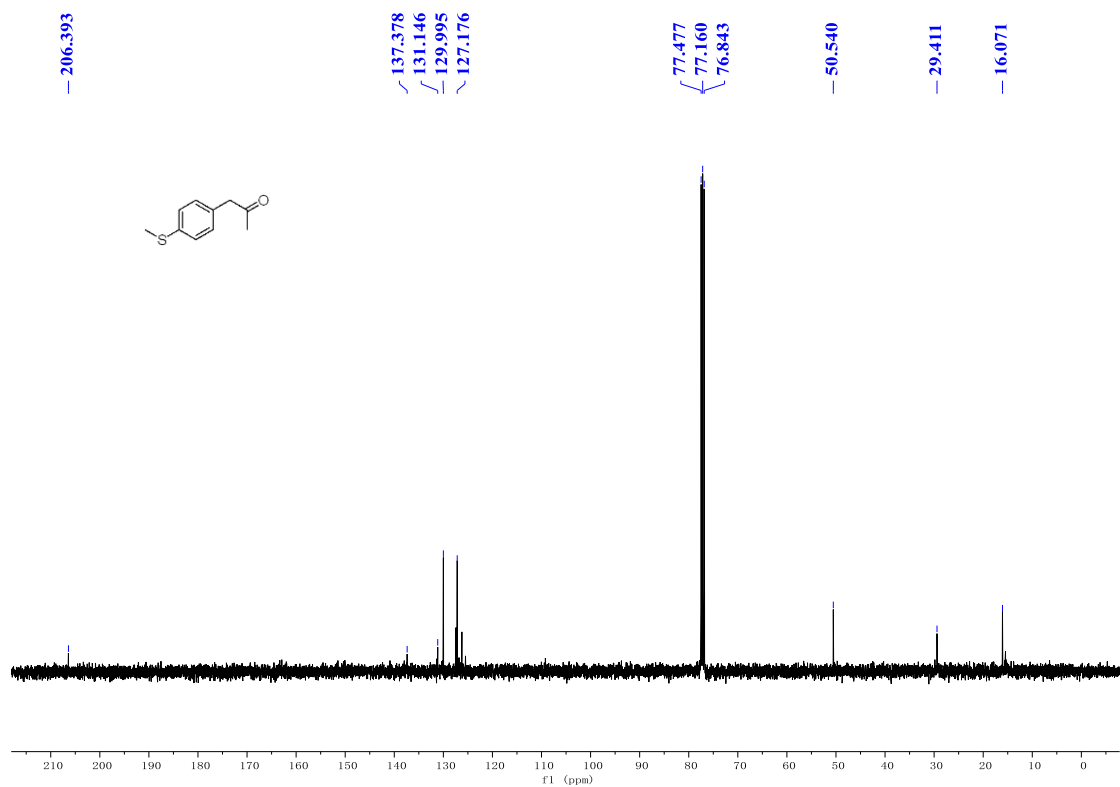
$^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of 1-(4-methoxyphenyl)propan-2-one (**4b**)



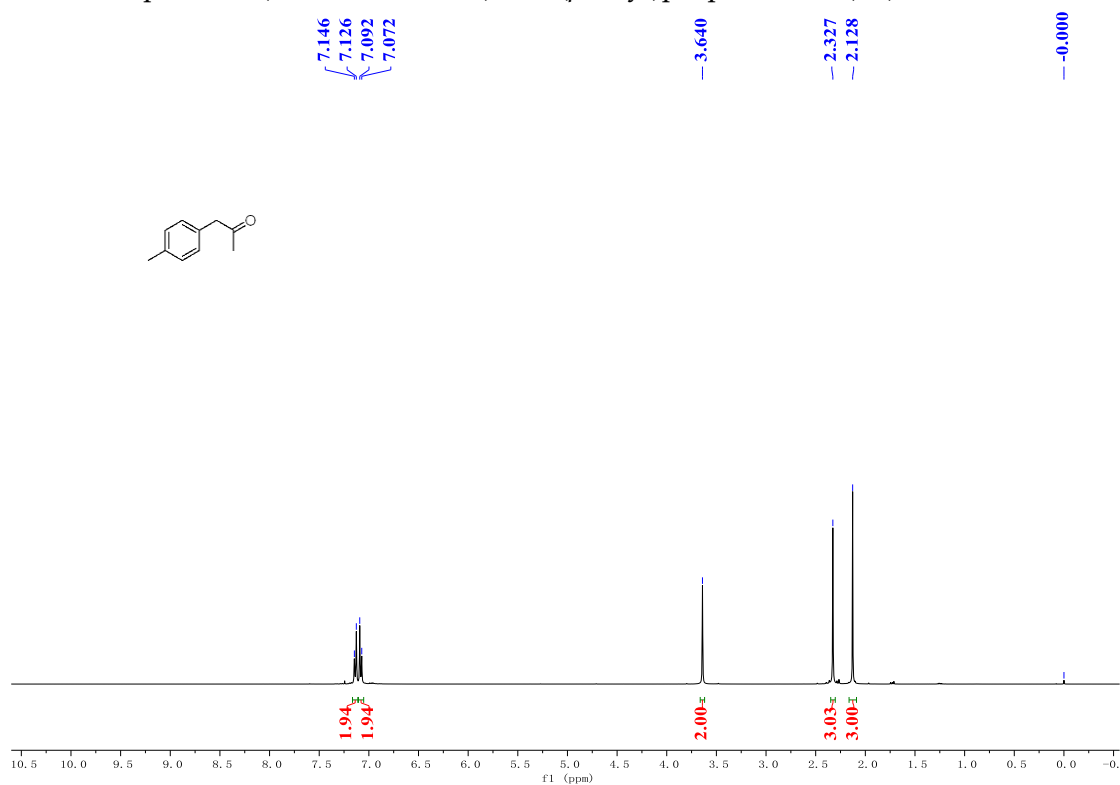
$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of 1-(4-(methylthio)phenyl)propan-2-one (**4c**)



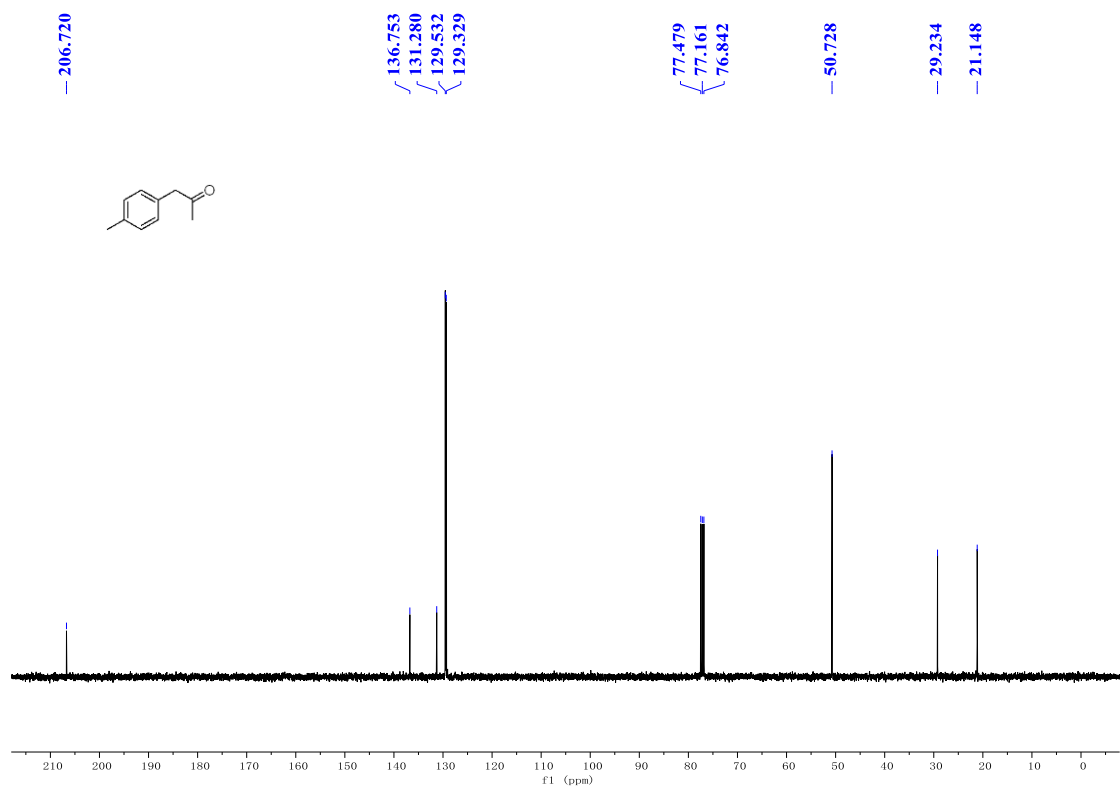
$^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of 1-(4-(methylthio)phenyl)propan-2-one (**4c**)



$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of 1-(*p*-tolyl)propan-2-one (**4d**)

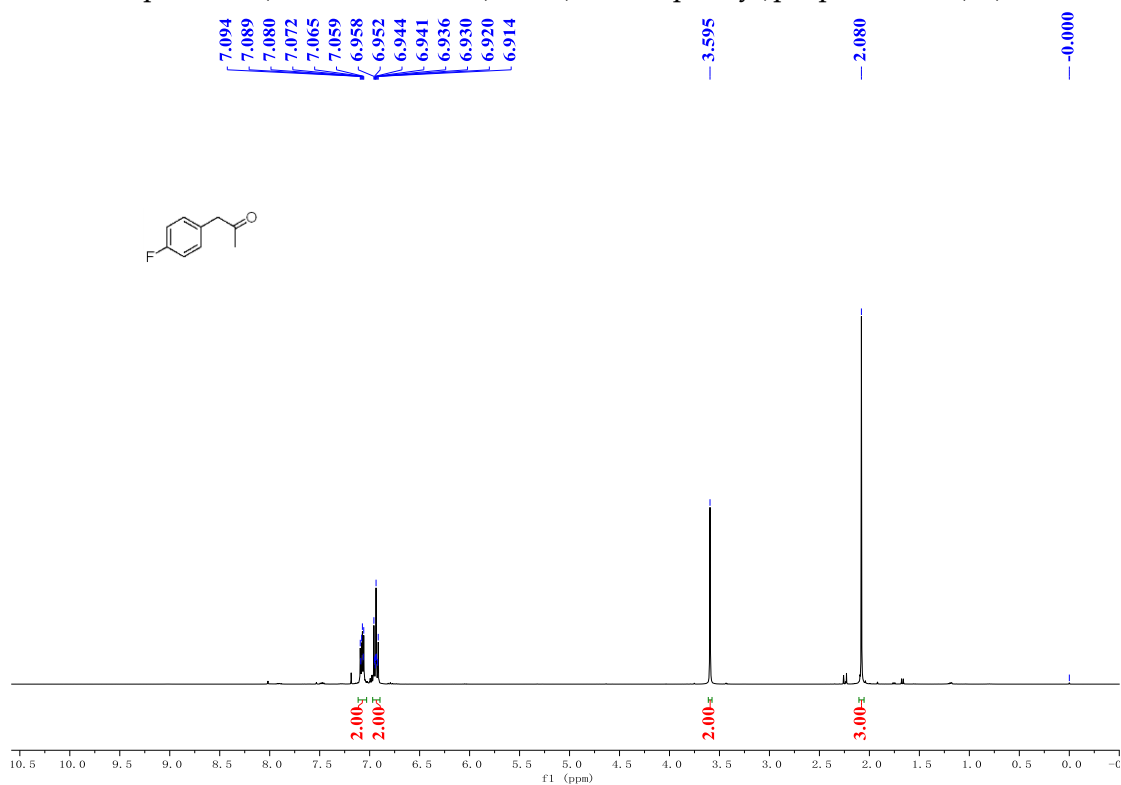


$^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of 1-(*p*-tolyl)propan-2-one (**4d**)

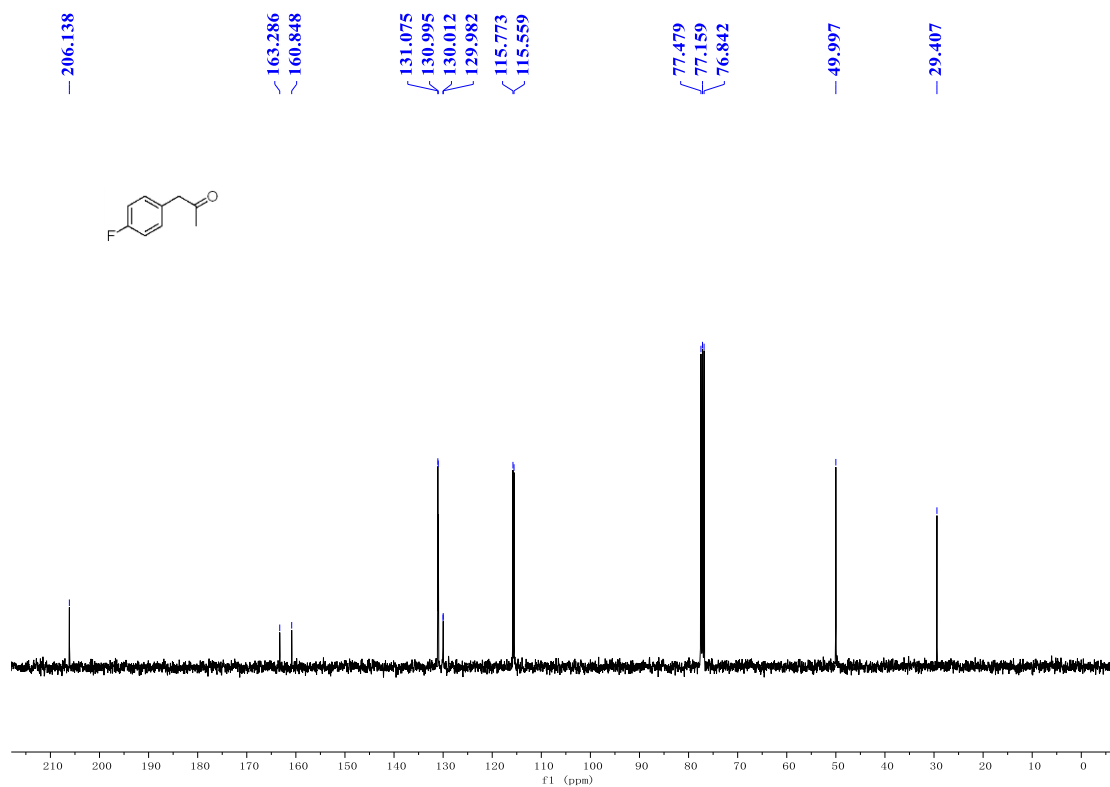




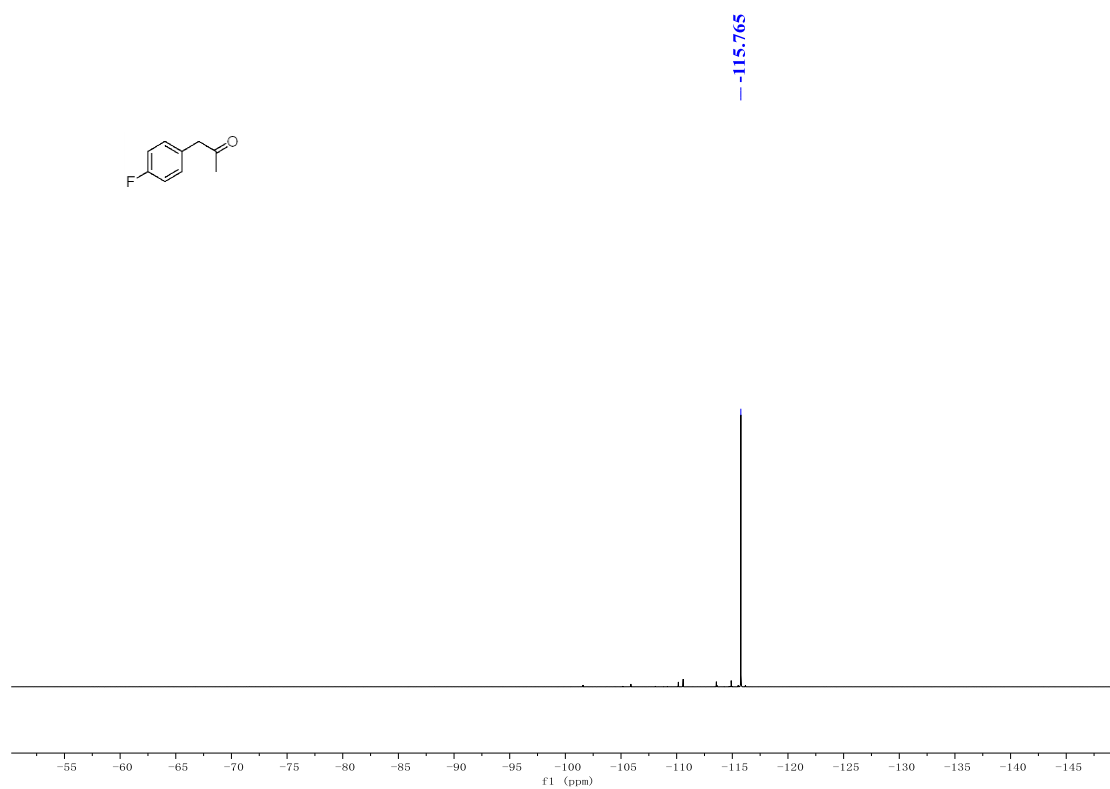
$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of 1-(4-fluorophenyl)propan-2-one (**4e**)



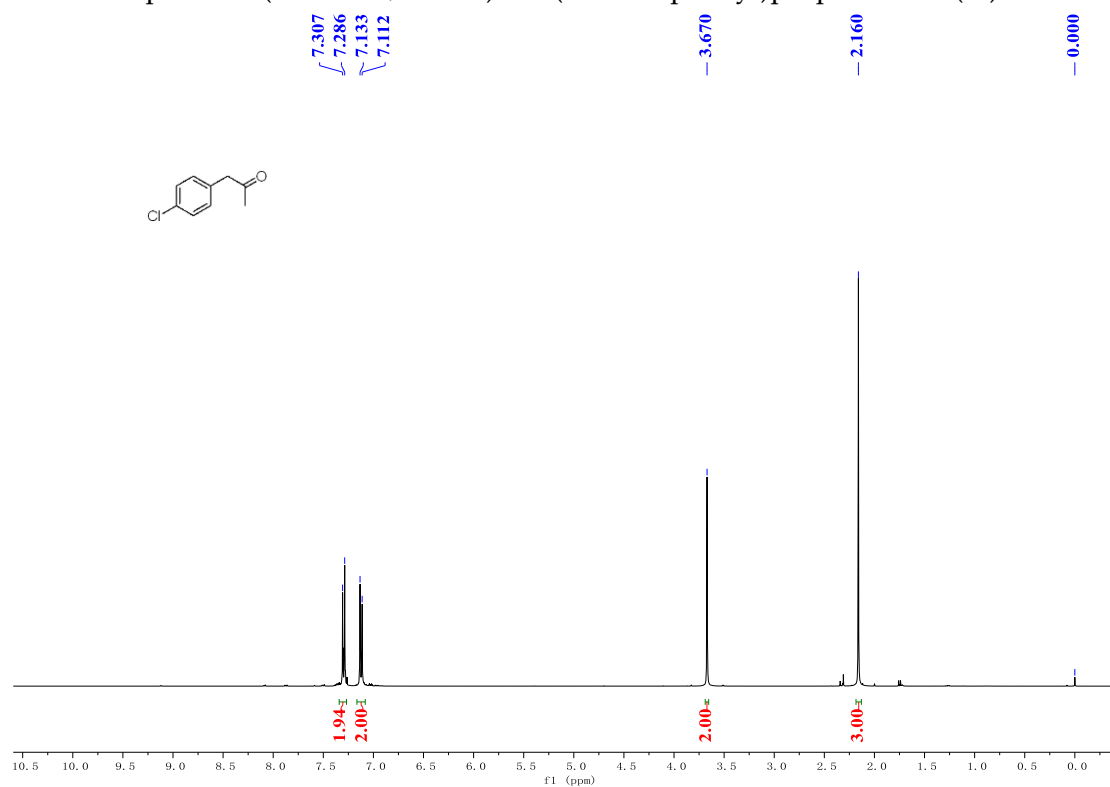
$^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of 1-(4-fluorophenyl)propan-2-one (**4e**)



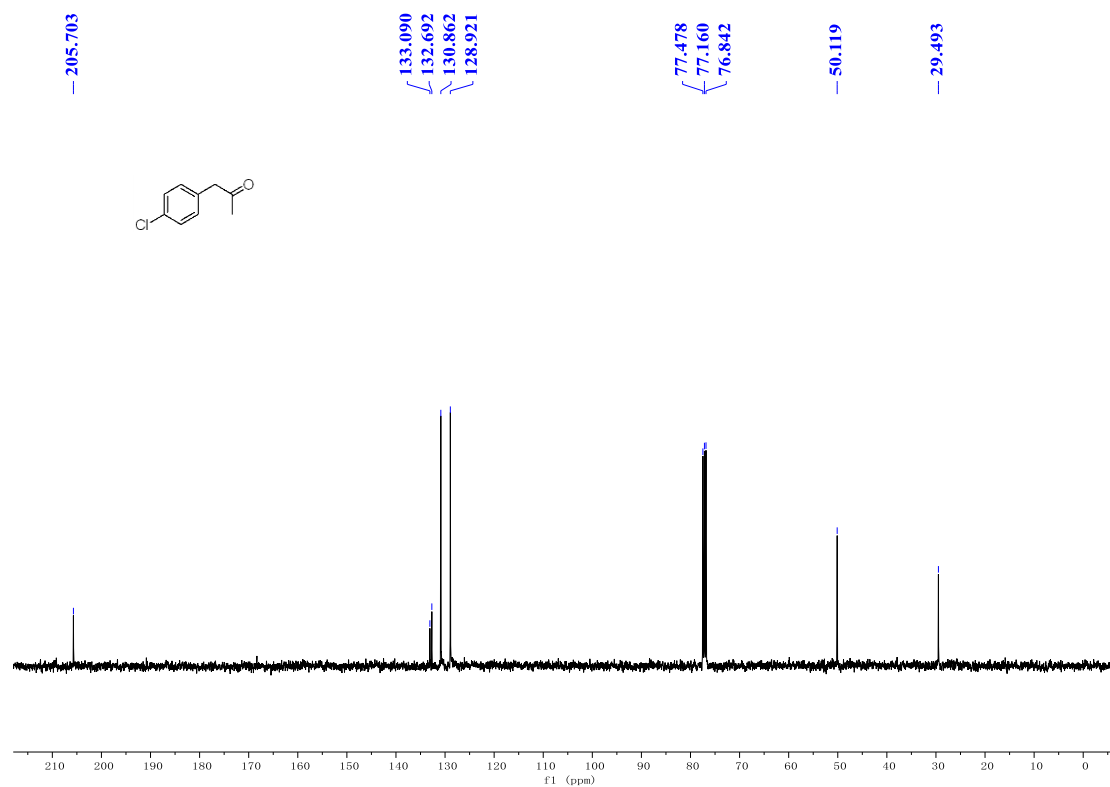
$^{19}\text{F}$  NMR spectrum (377 MHz,  $\text{CDCl}_3$ ) of 1-(4-fluorophenyl)propan-2-one (**4e**)



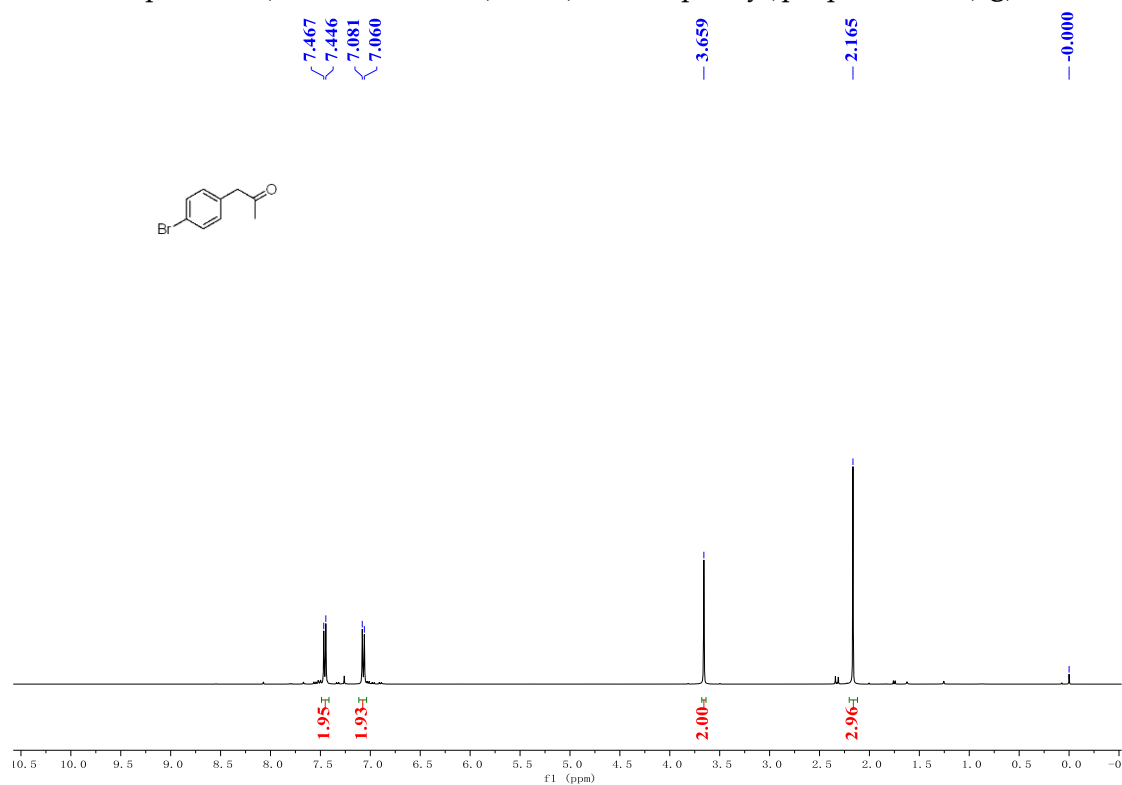
$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of 1-(4-chlorophenyl)propan-2-one (**4f**)



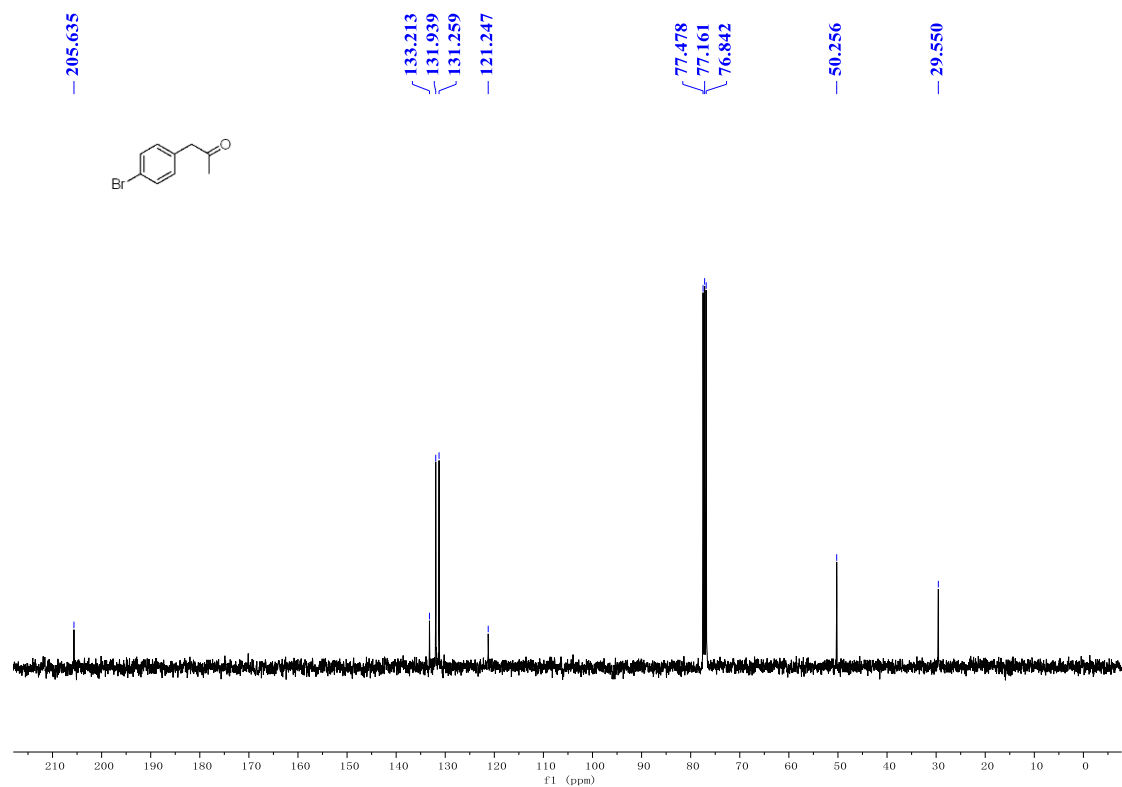
$^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of 1-(4-chlorophenyl)propan-2-one (**4f**)



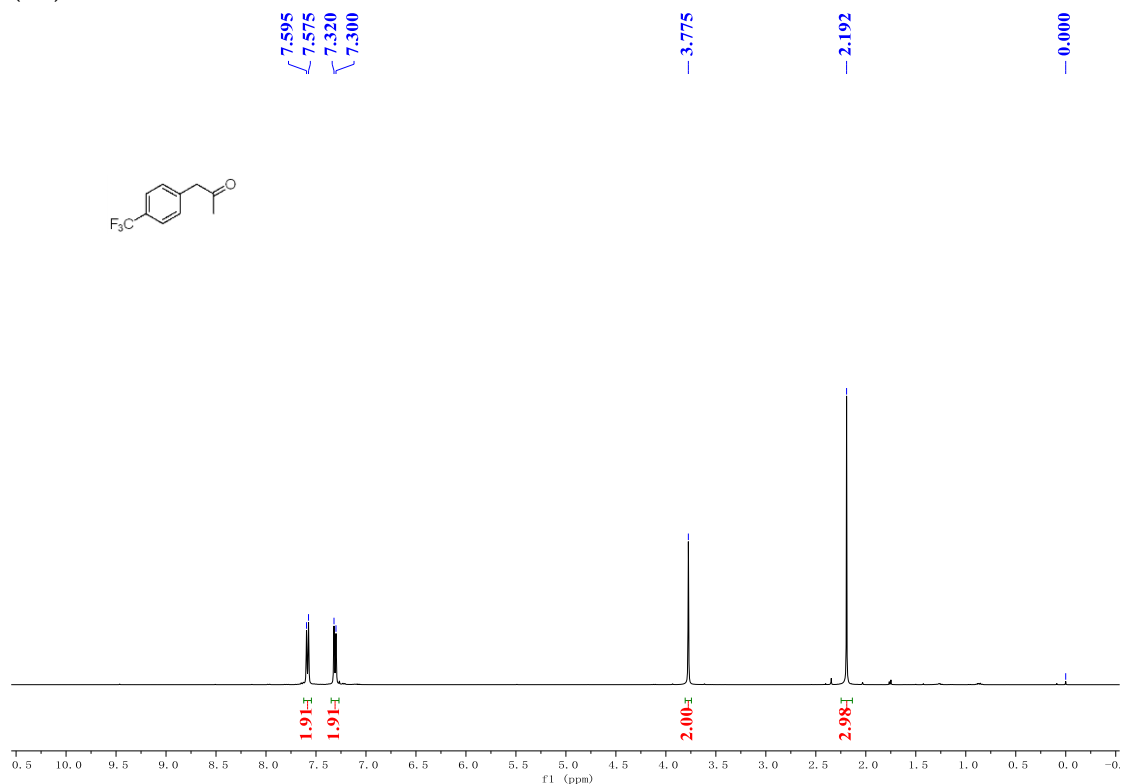
$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of 1-(4-bromophenyl)propan-2-one (**4g**)



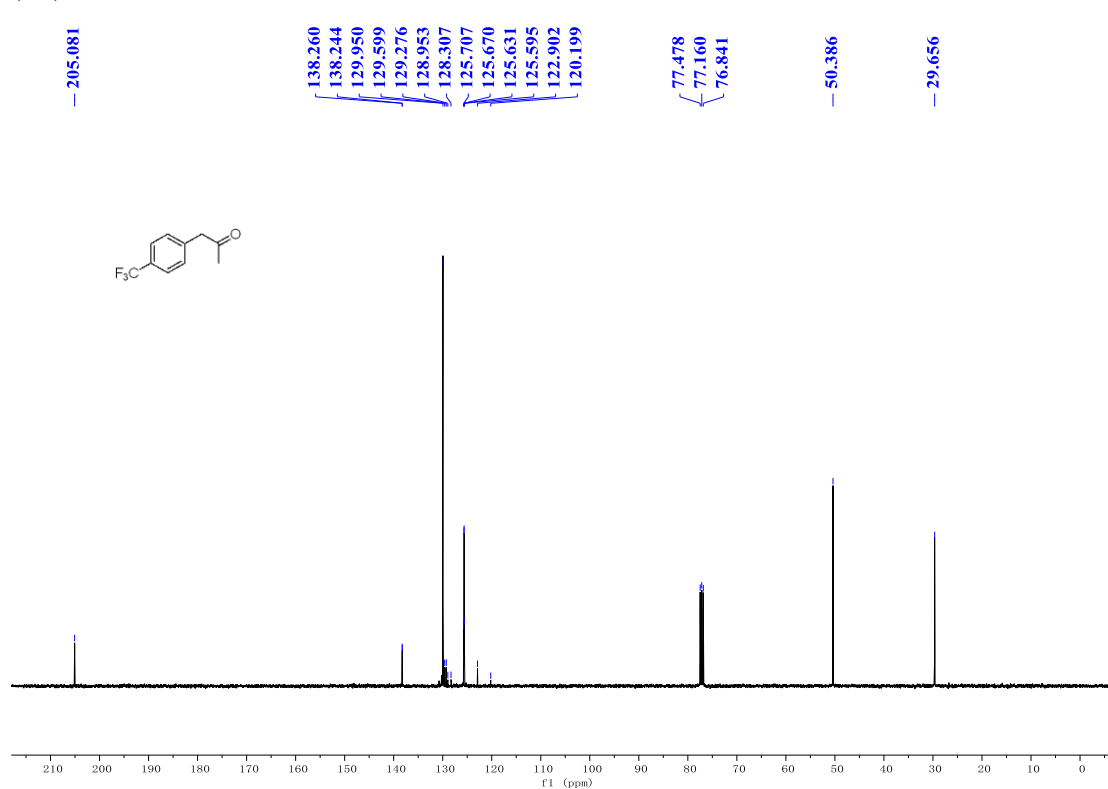
$^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of 1-(4-bromophenyl)propan-2-one (**4g**)



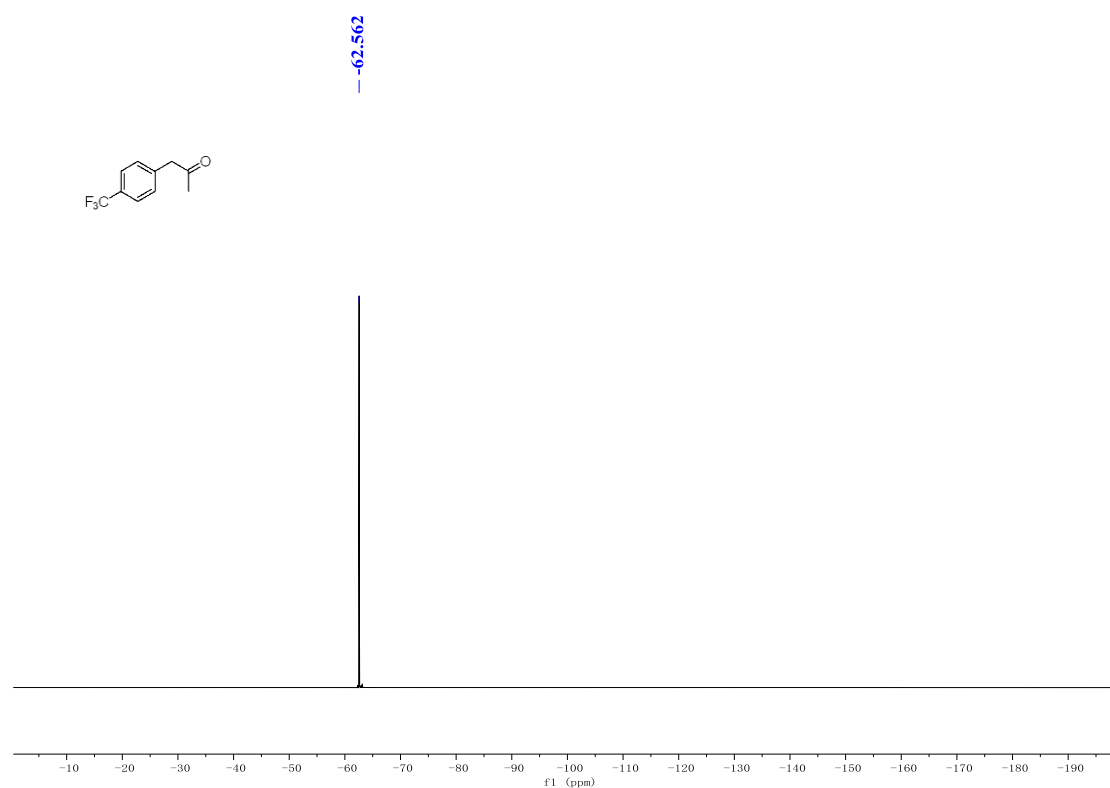
$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of 1-(4-(trifluoromethyl)phenyl)propan-2-one (4h)



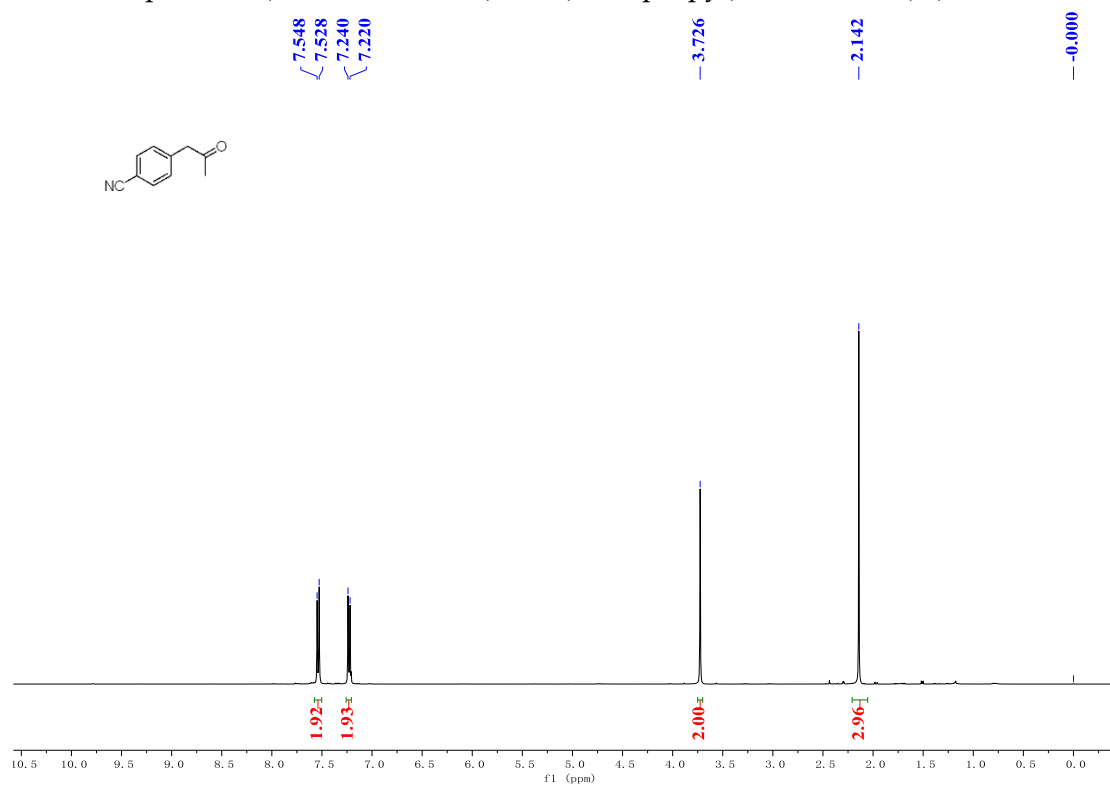
$^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of 1-(4-(trifluoromethyl)phenyl)propan-2-one (4h)



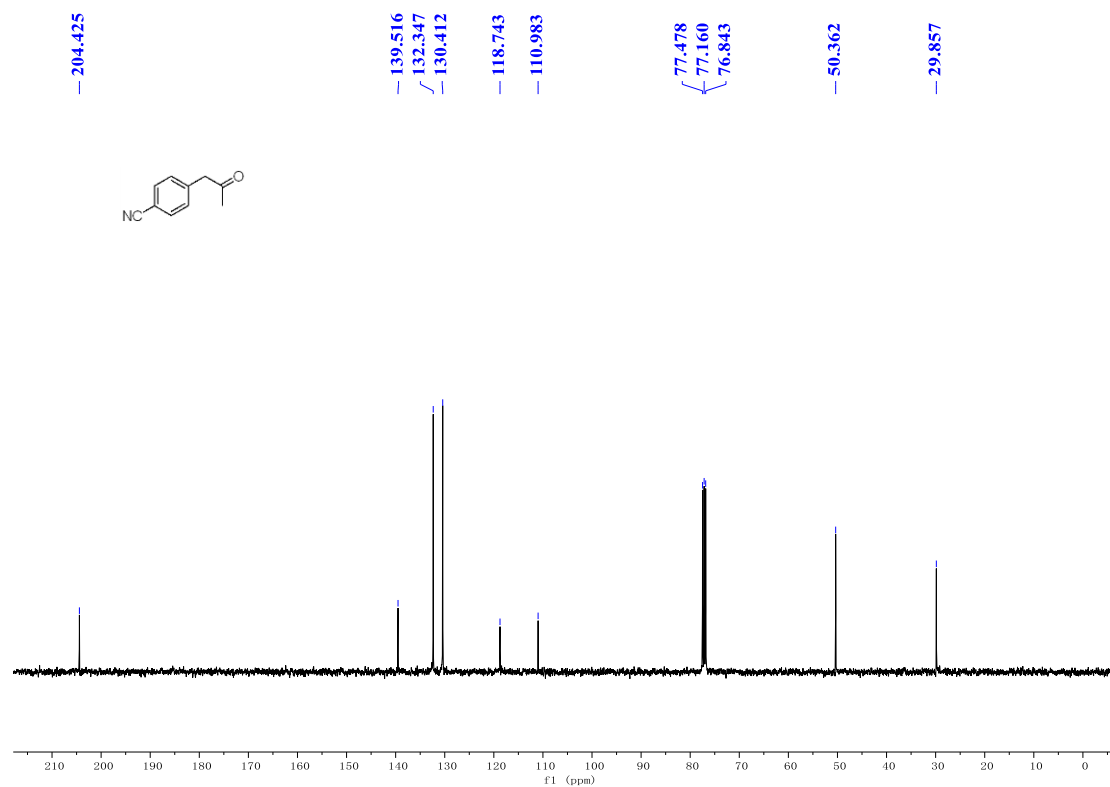
$^{19}\text{F}$  NMR spectrum (377 MHz,  $\text{CDCl}_3$ ) of 1-(4-(trifluoromethyl)phenyl)propan-2-one  
(4h)



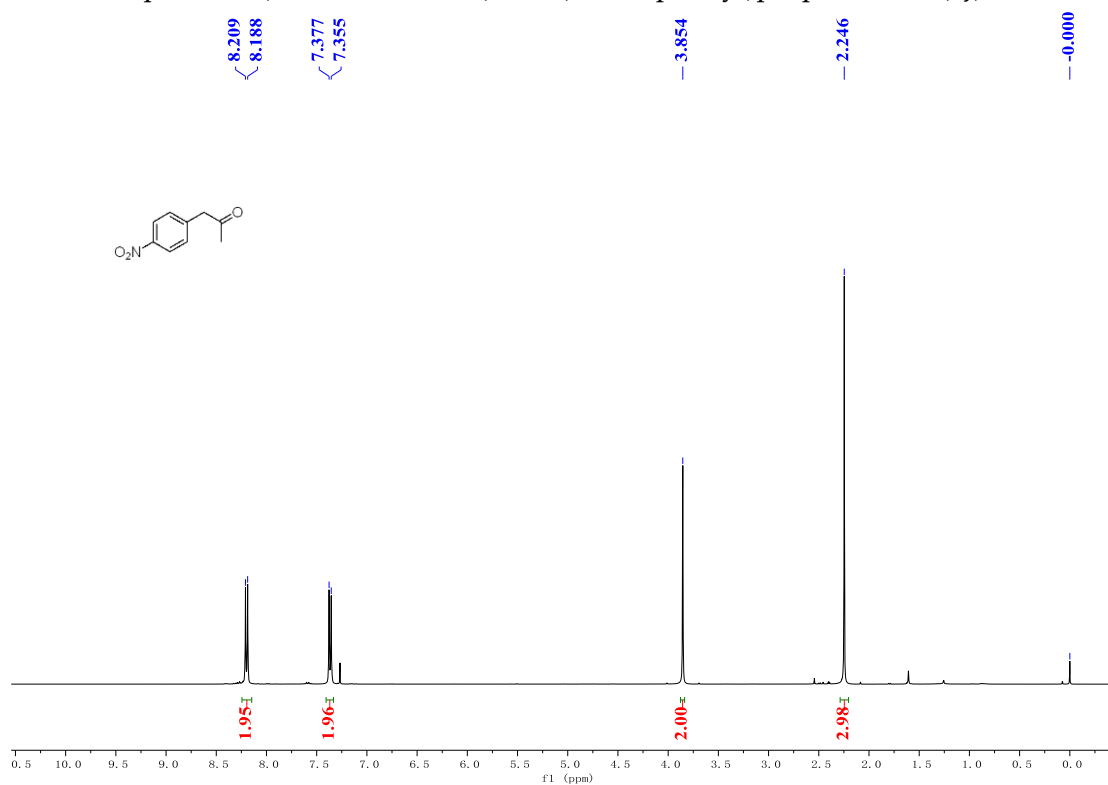
$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of 4-(2-oxopropyl)benzonitrile (**4i**)



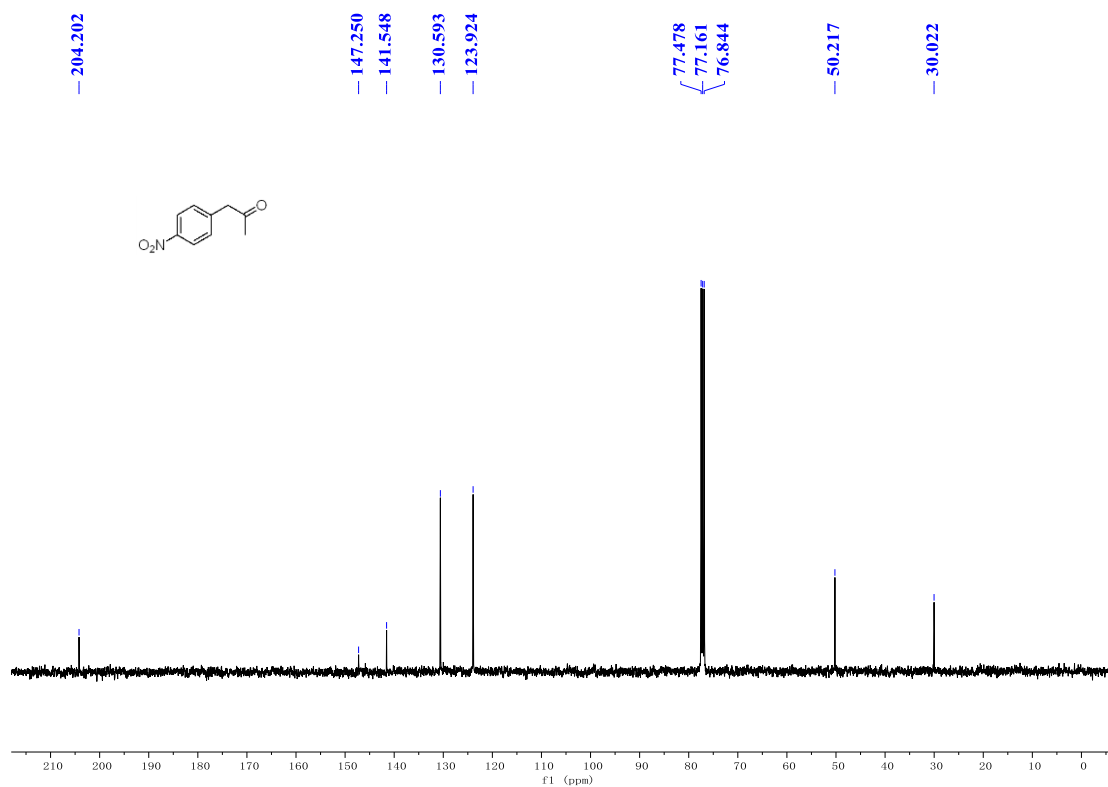
$^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of compound 4-(2-oxopropyl)benzonitrile (**4i**)



$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of 1-(4-nitrophenyl)propan-2-one (**4j**)

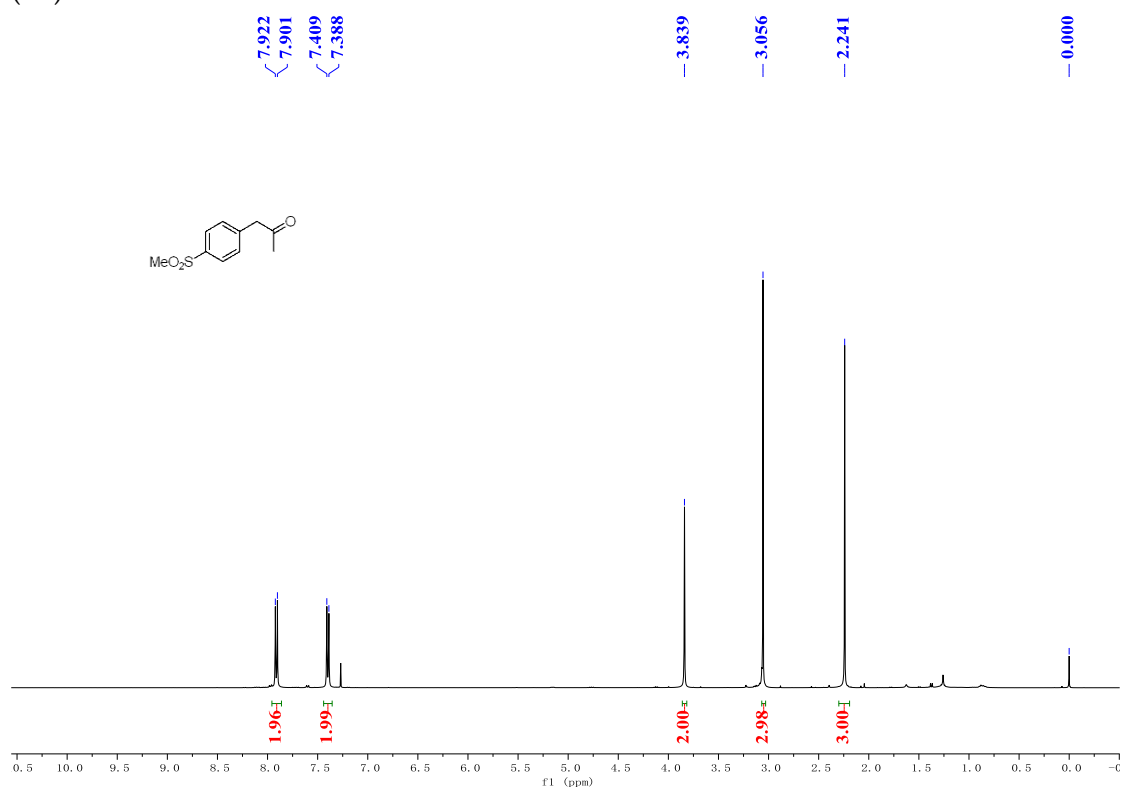


$^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of 1-(4-nitrophenyl)propan-2-one (**4j**)

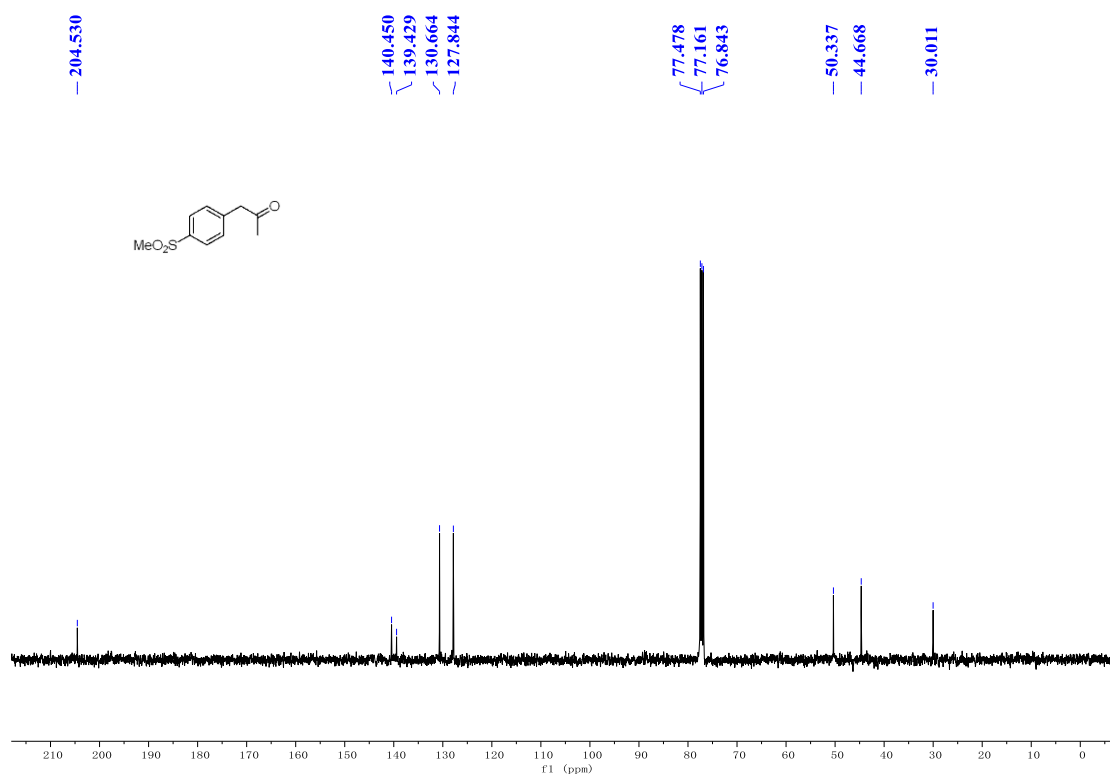




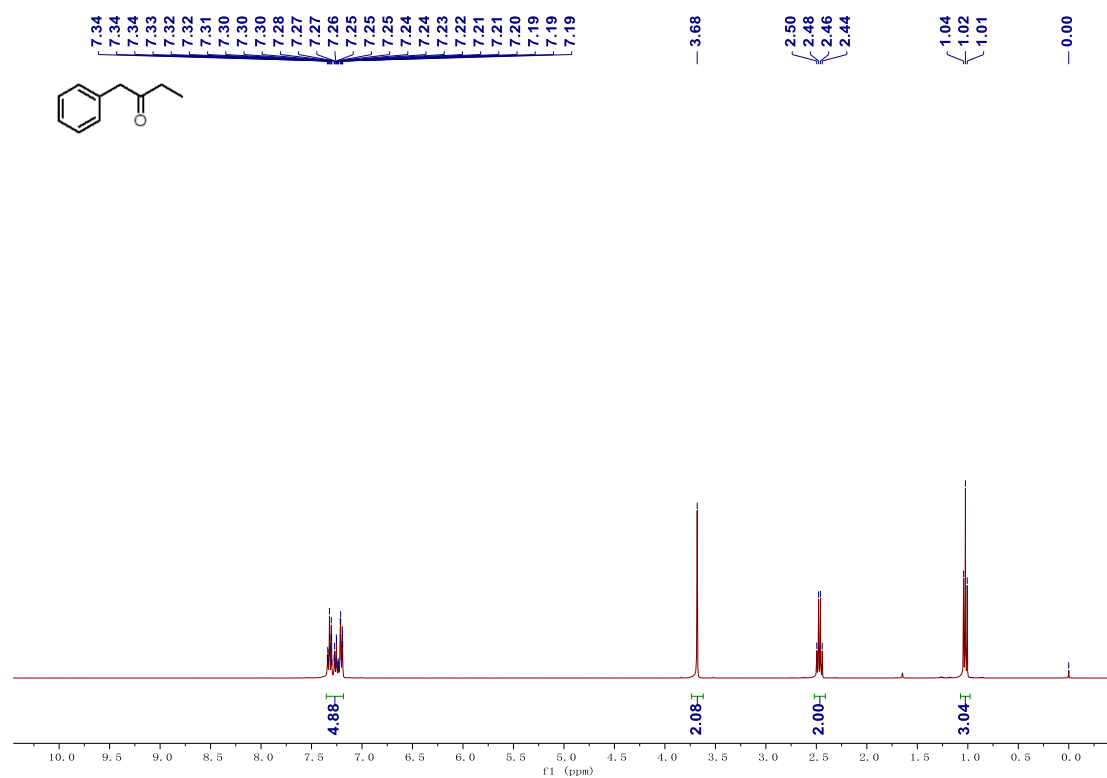
$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of 1-(4-(methylsulfonyl)phenyl)propan-2-one (**4k**)



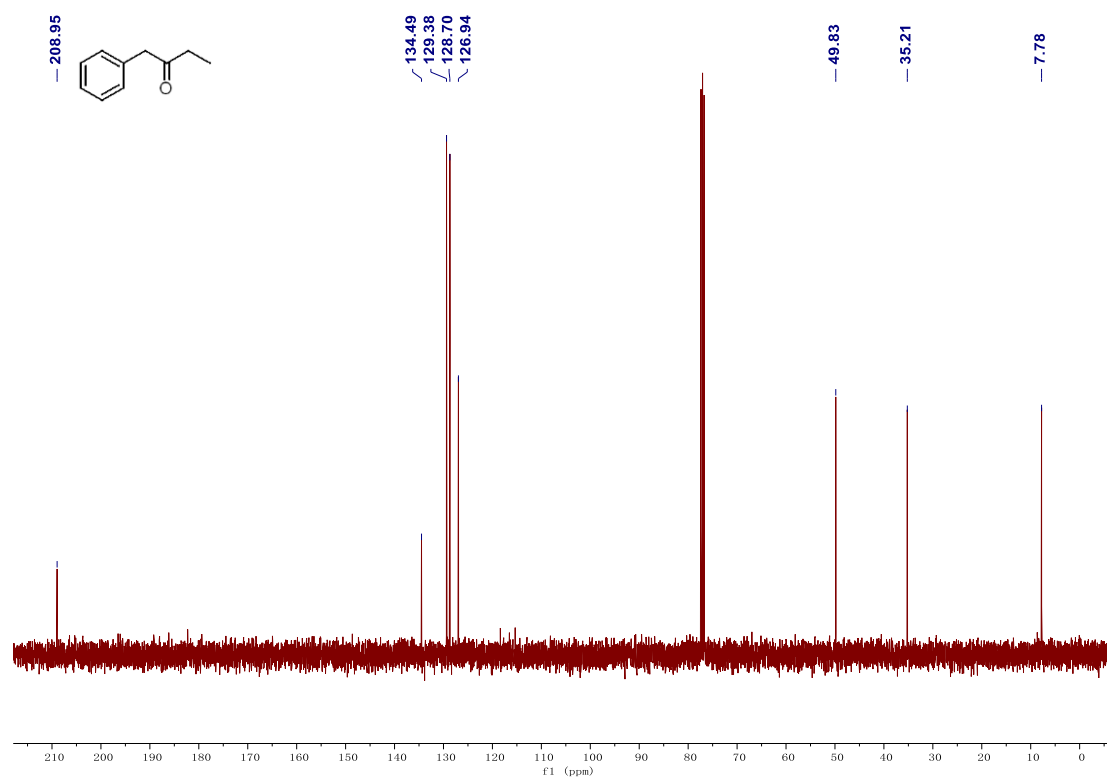
$^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of 1-(4-(methylsulfonyl)phenyl)propan-2-one (**4k**)



$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of 1-phenylbutan-2-one (**4l**)



$^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of 1-phenylbutan-2-one (**4l**)



### 3.2 $^1\text{H}$ NMR for Reaction Mixtures in Table 1

Table 1, entry 1

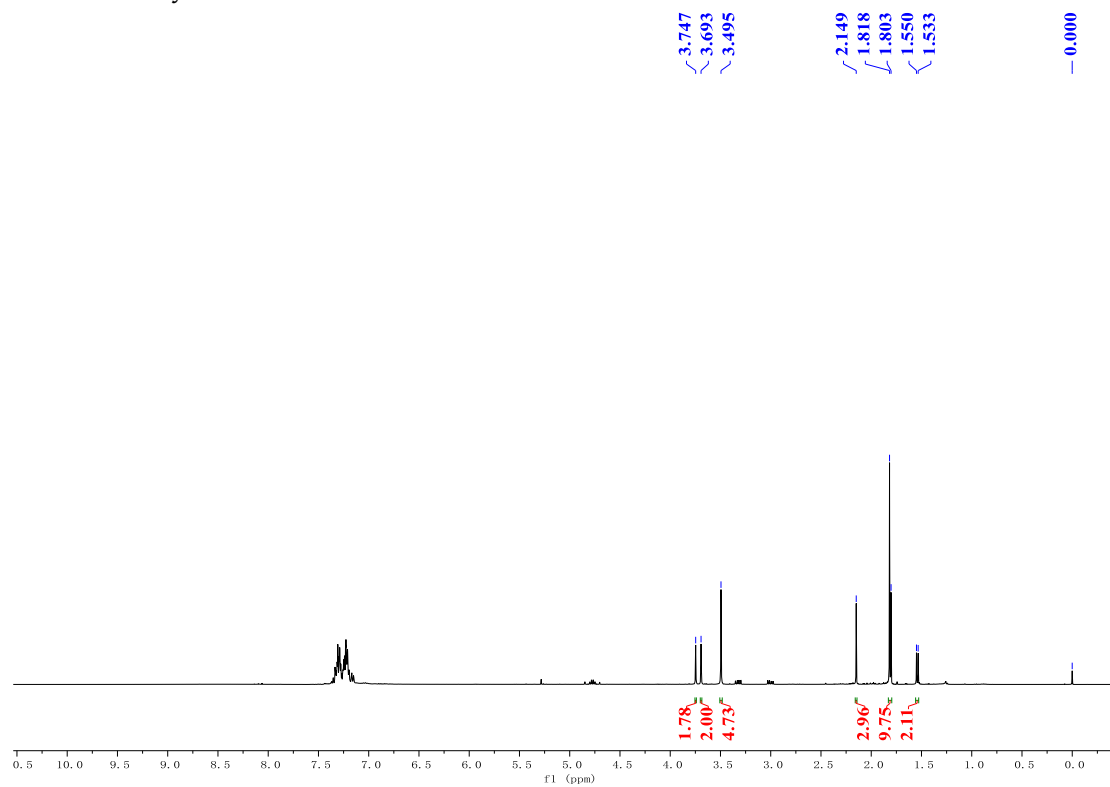


Table 1, entry 2

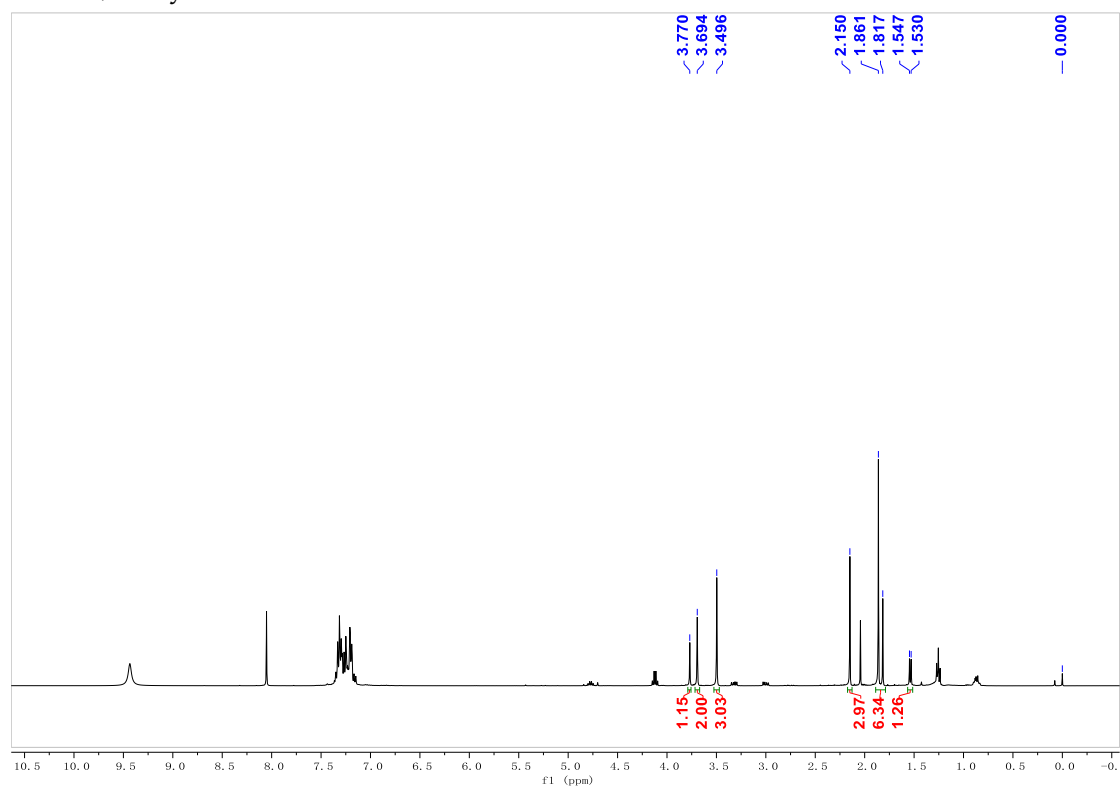


Table 1, entry 3

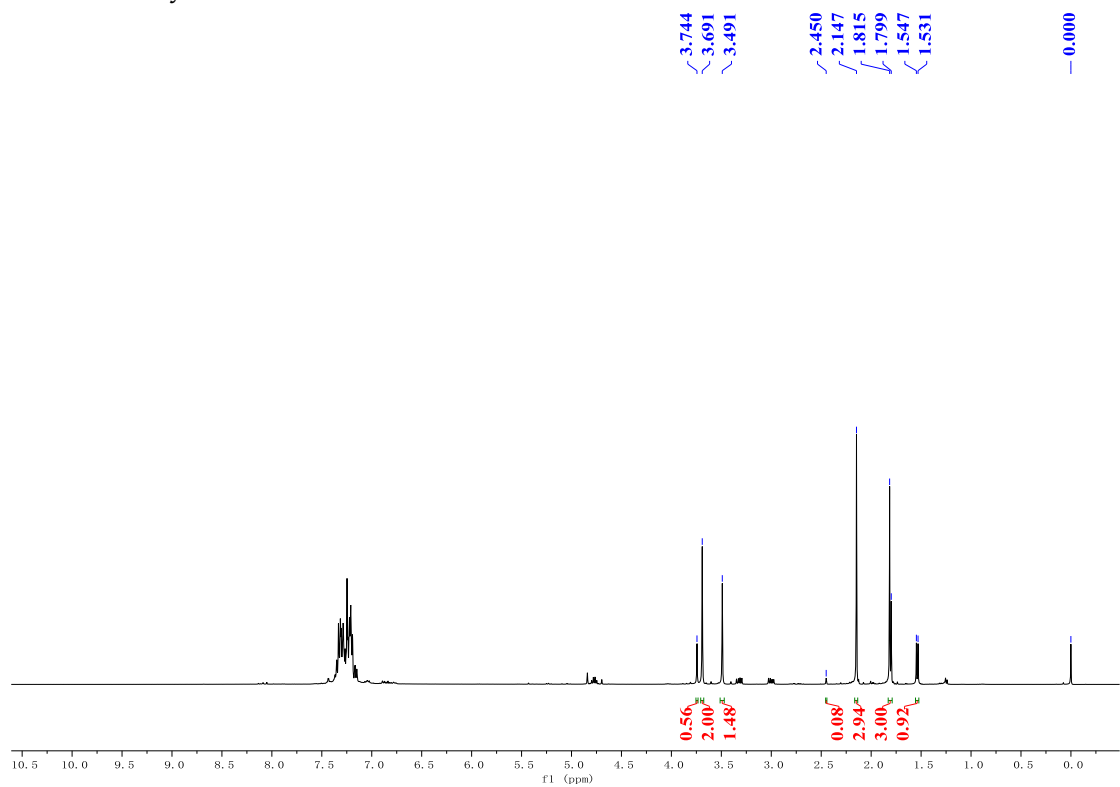


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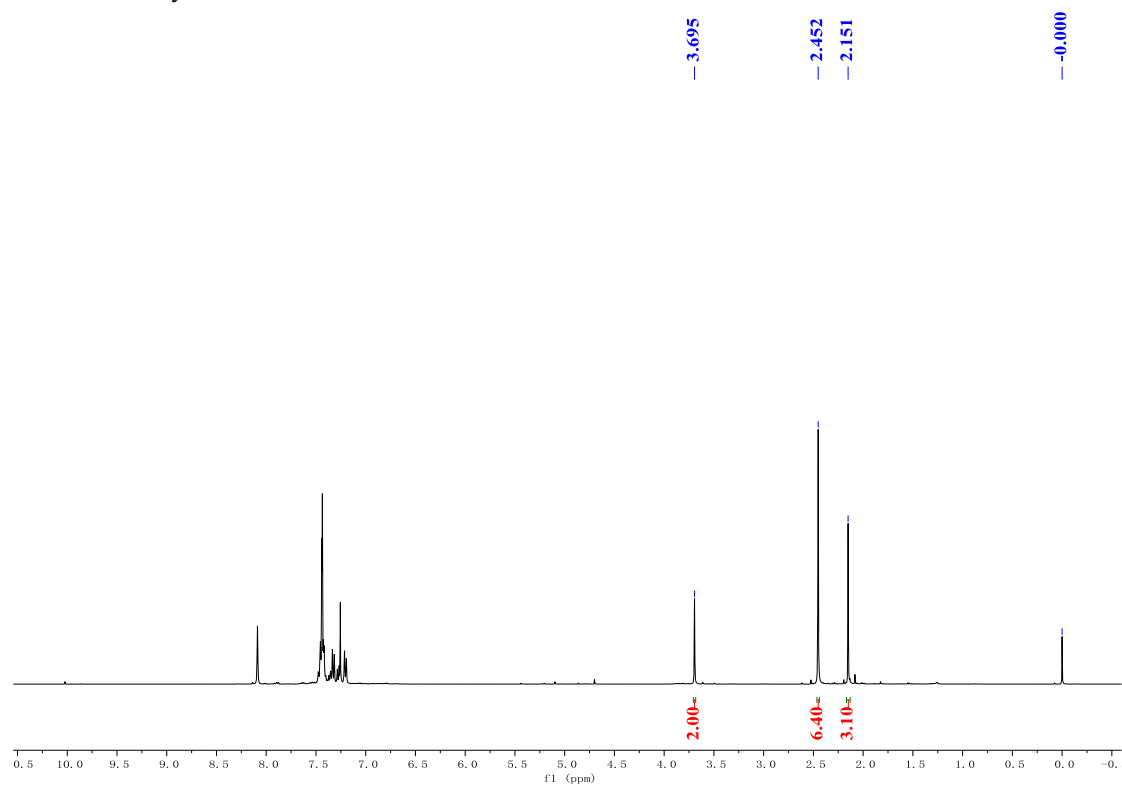


Table 1, entry 5

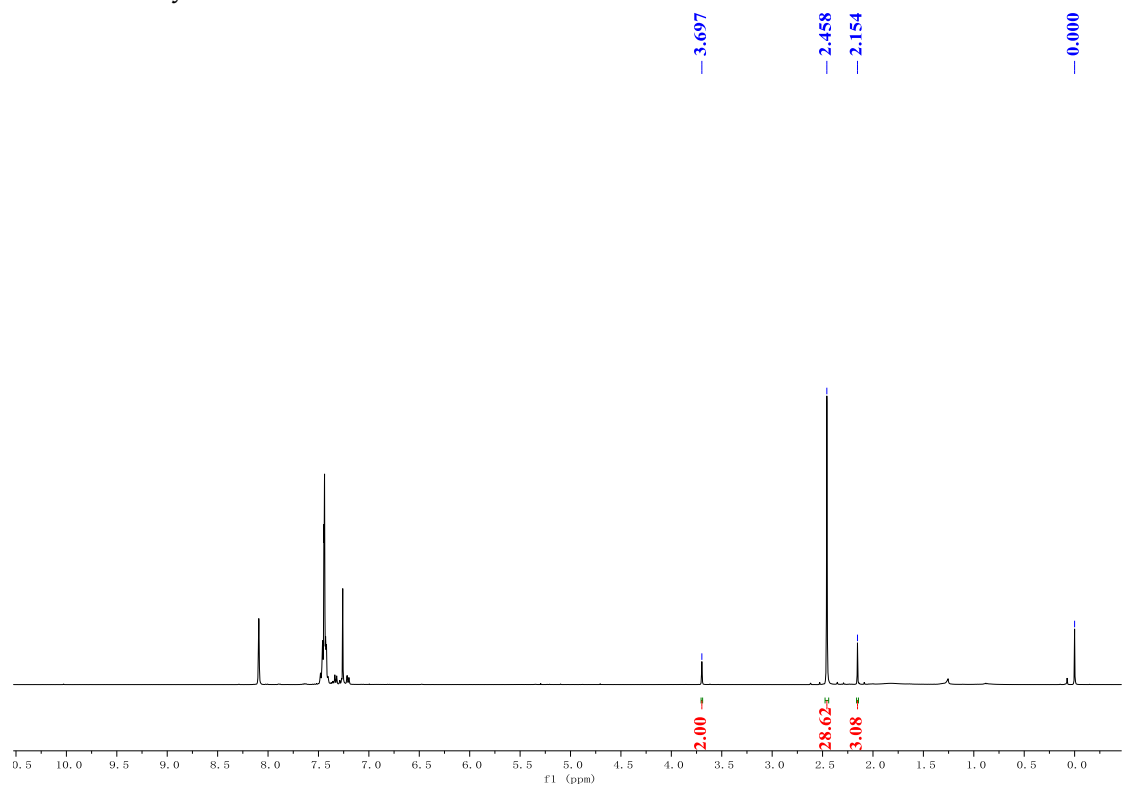


Table 1, entry 6

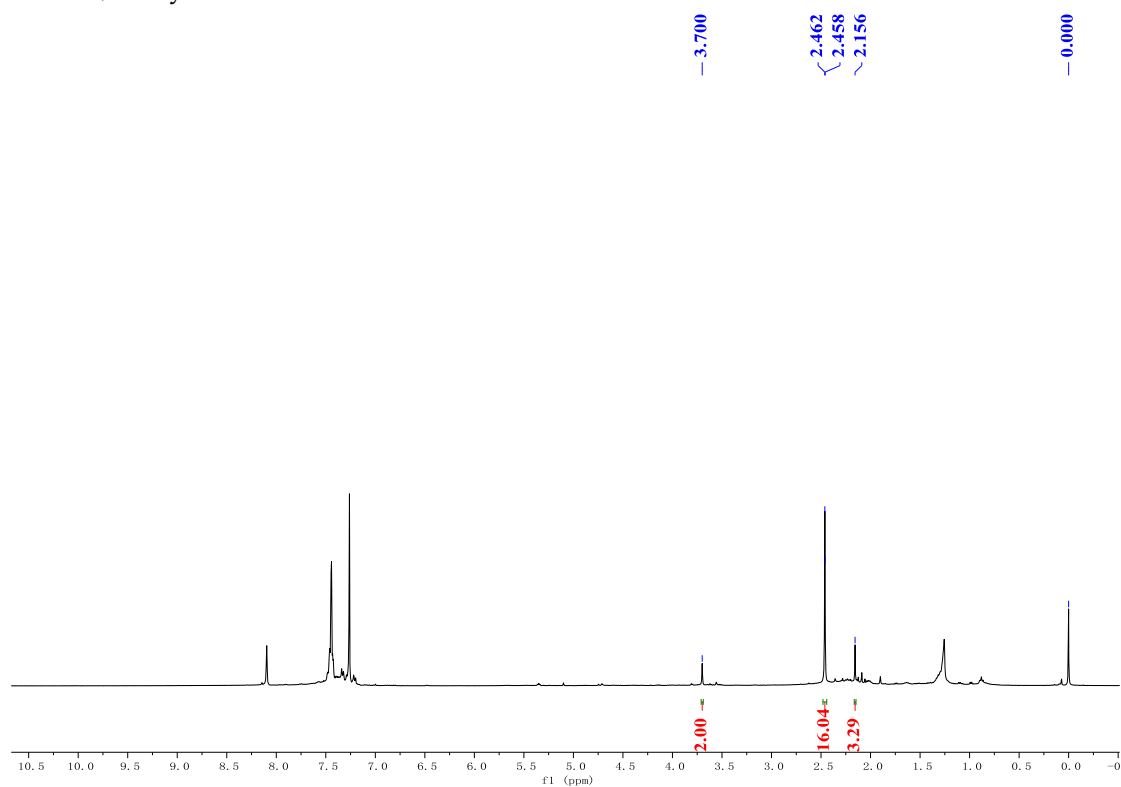


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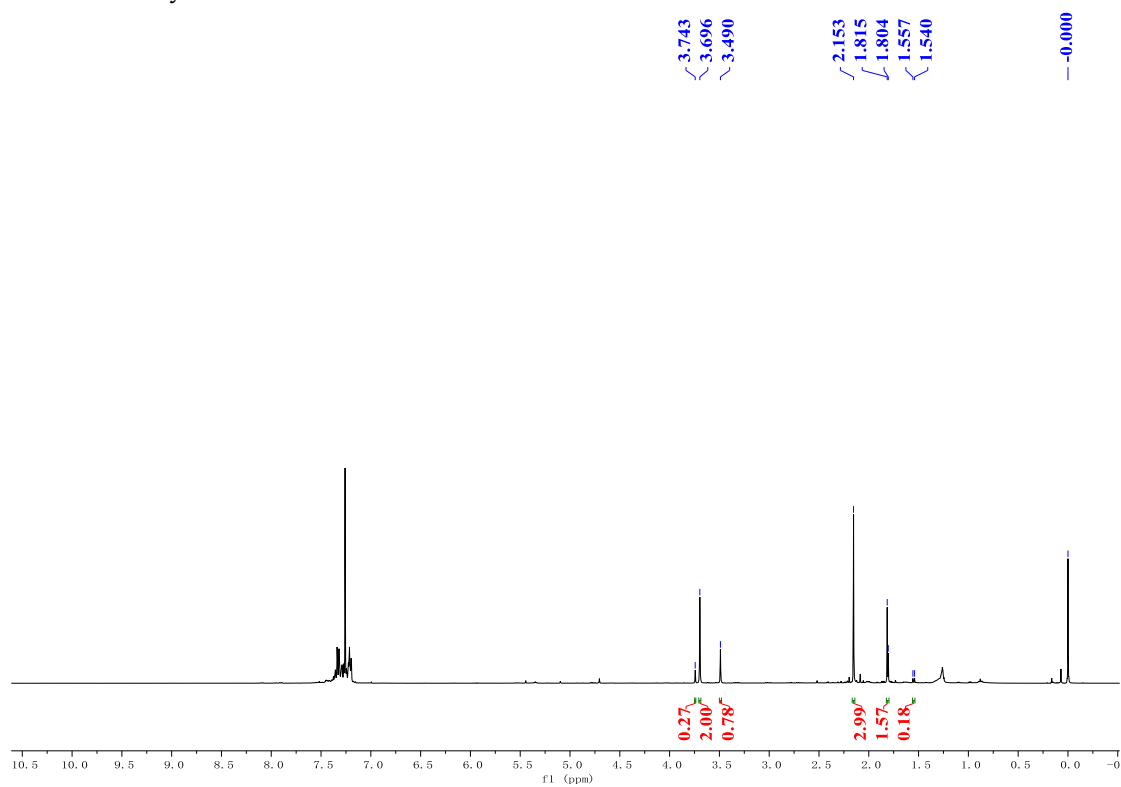


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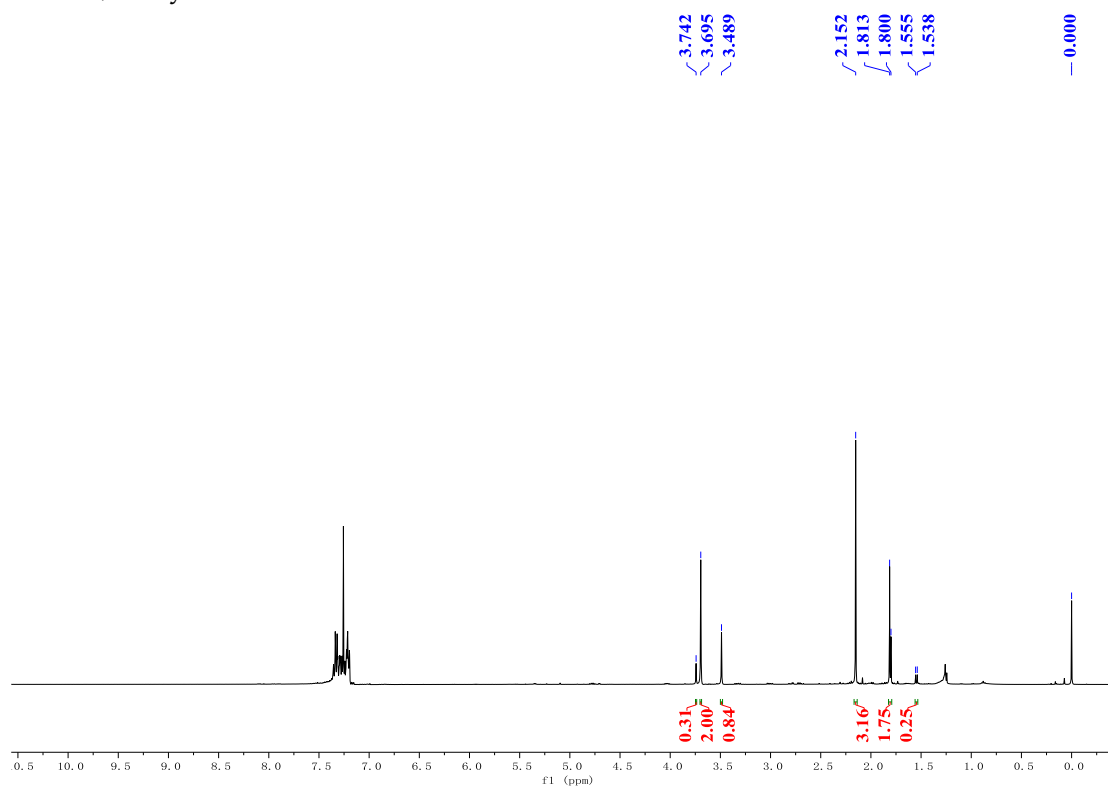


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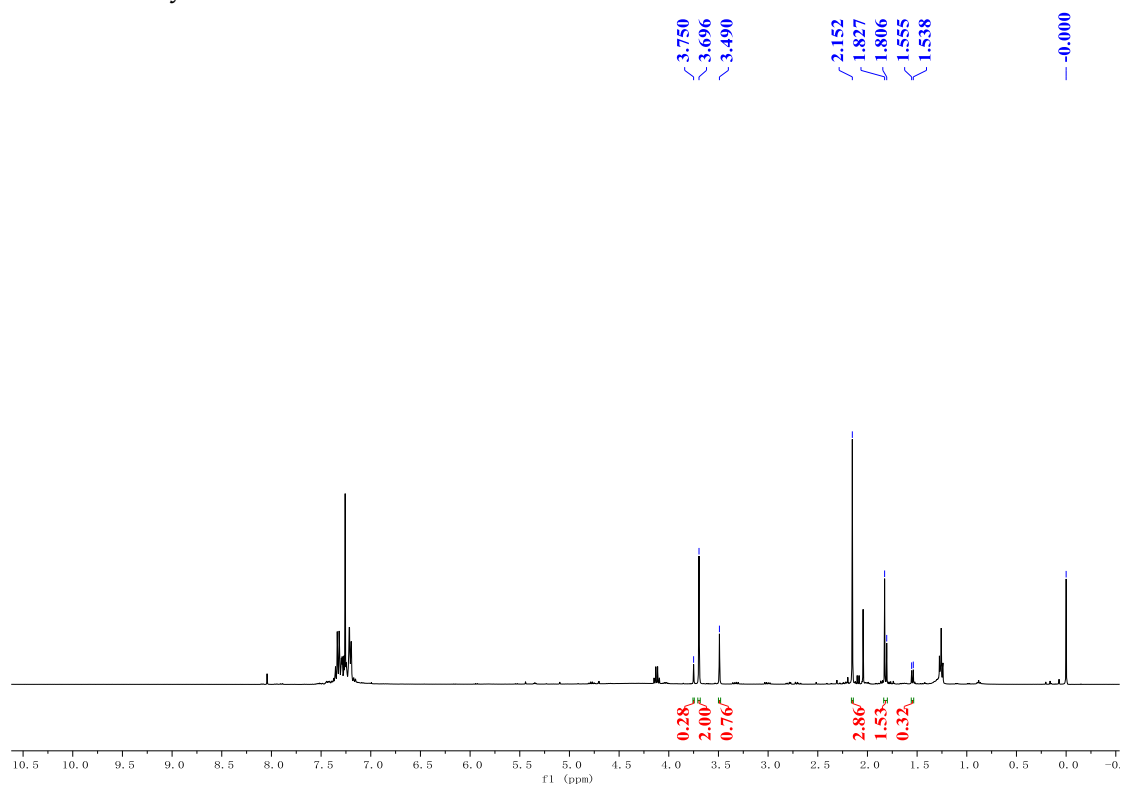


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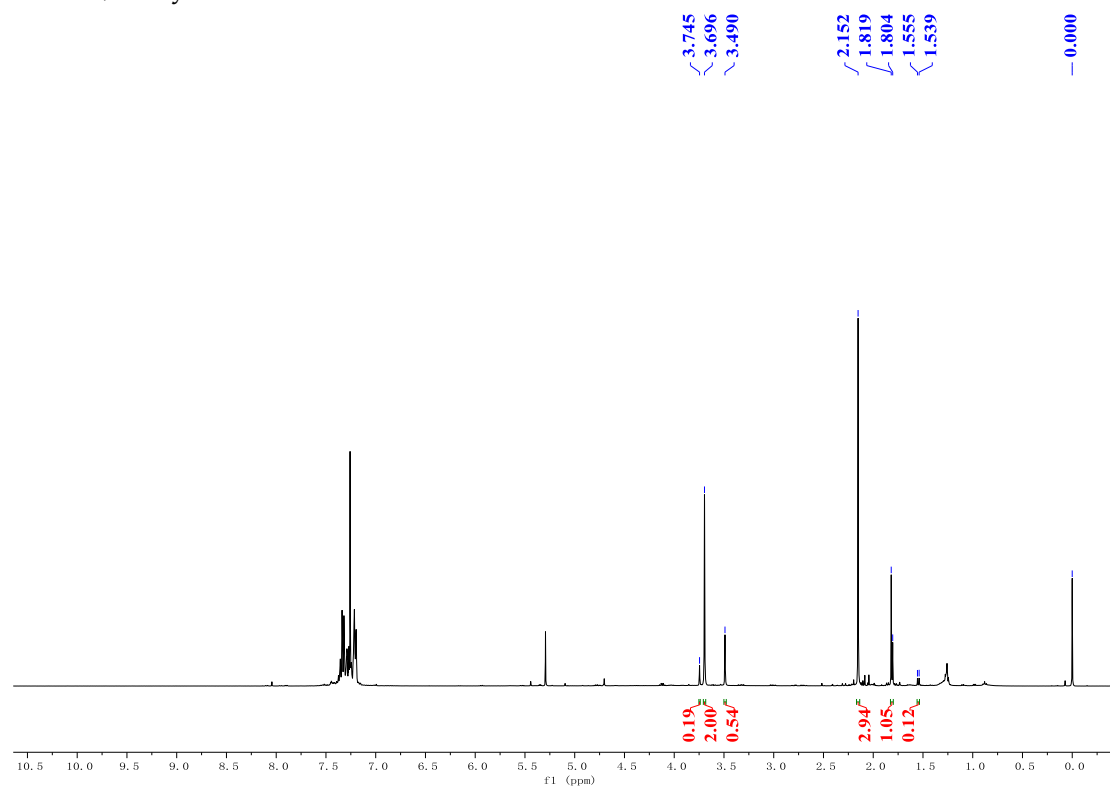


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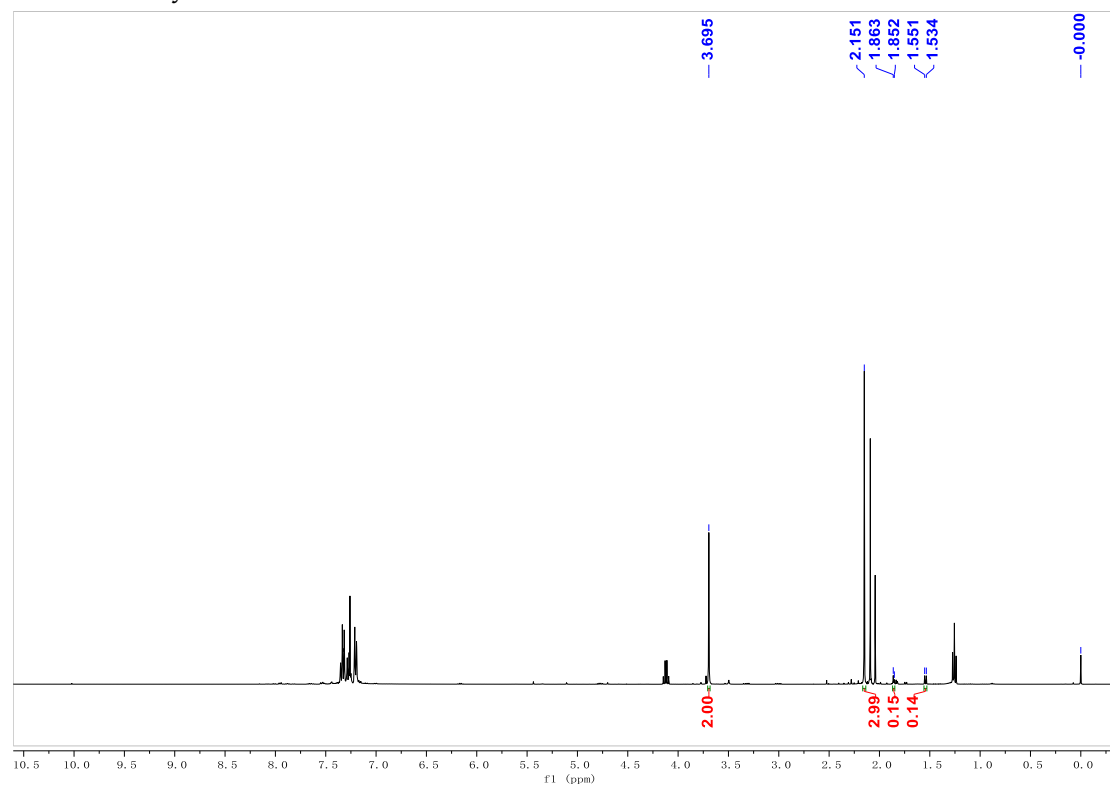




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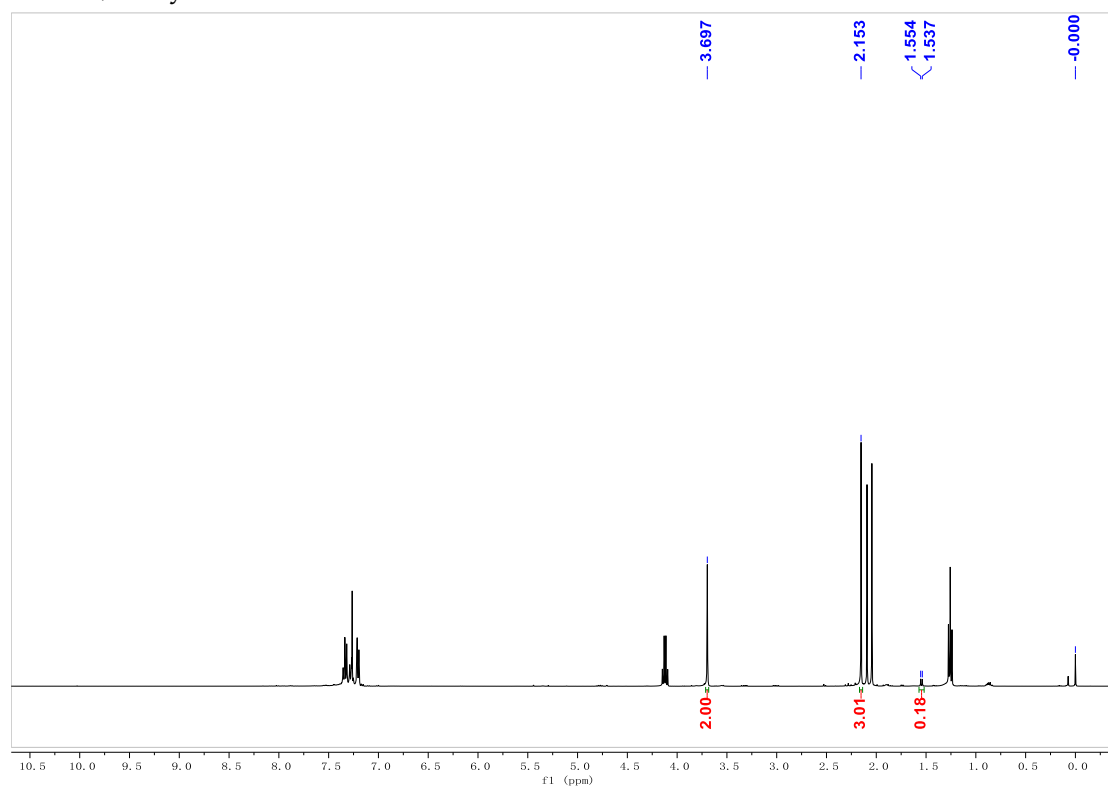


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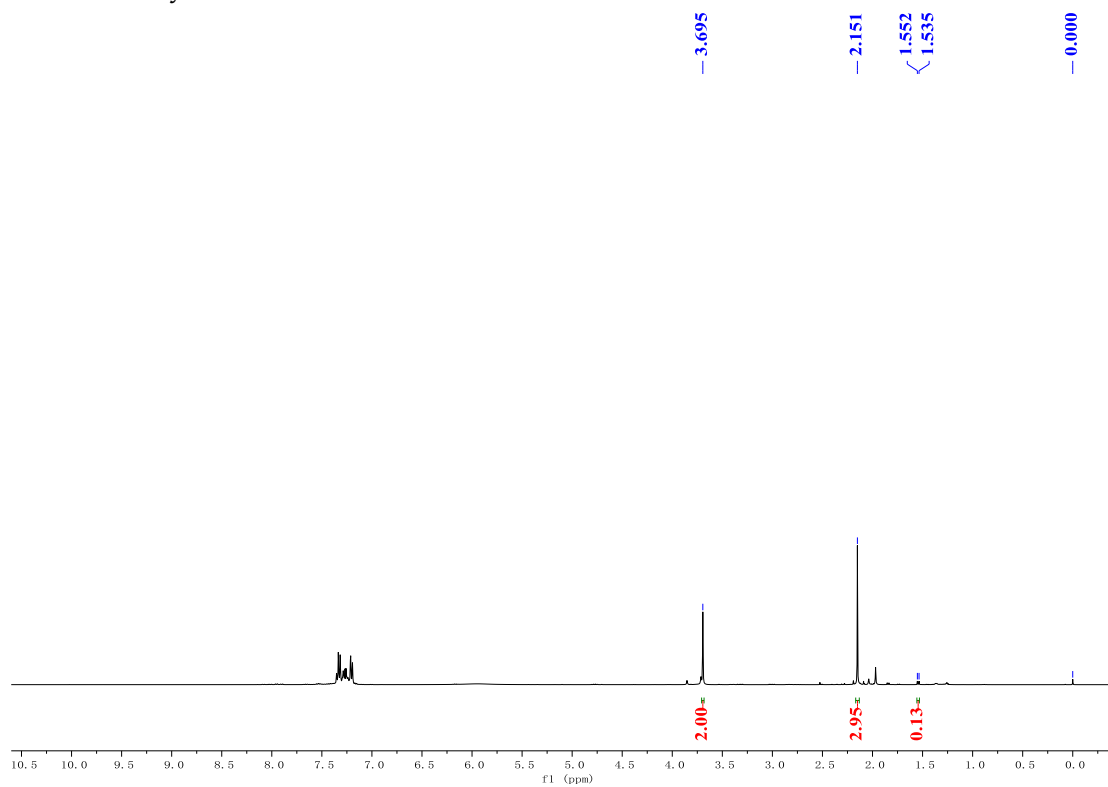


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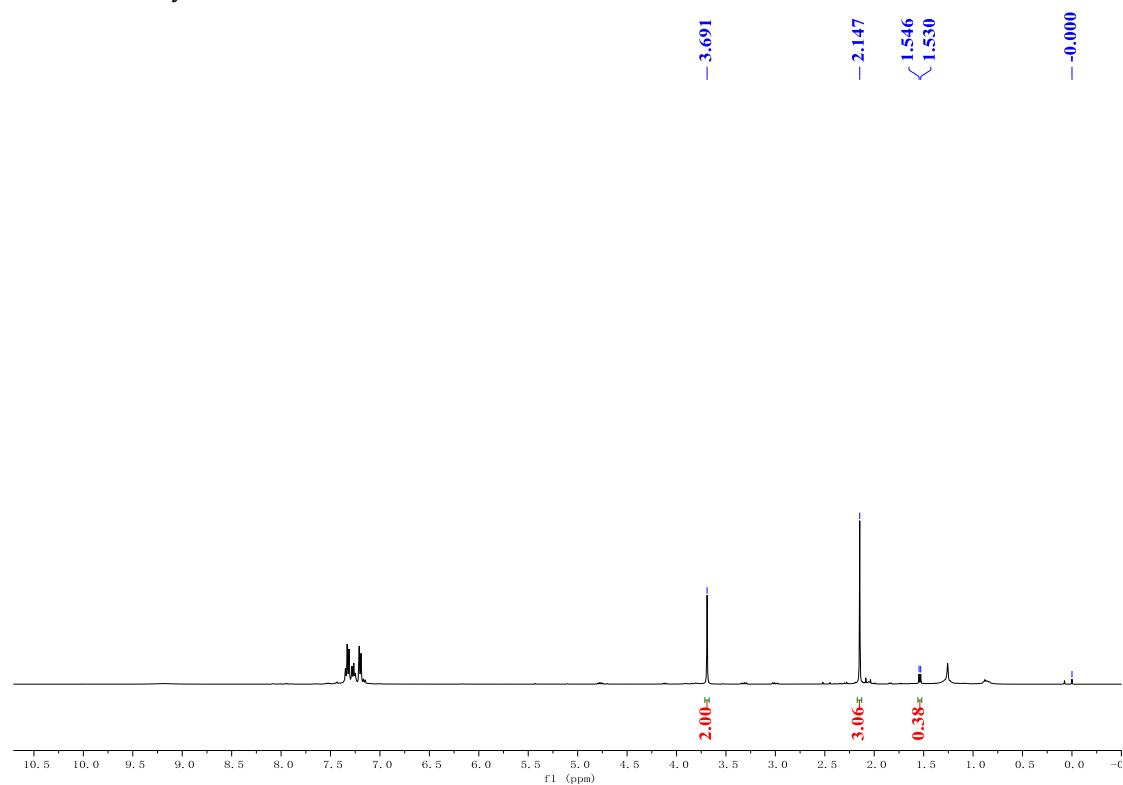


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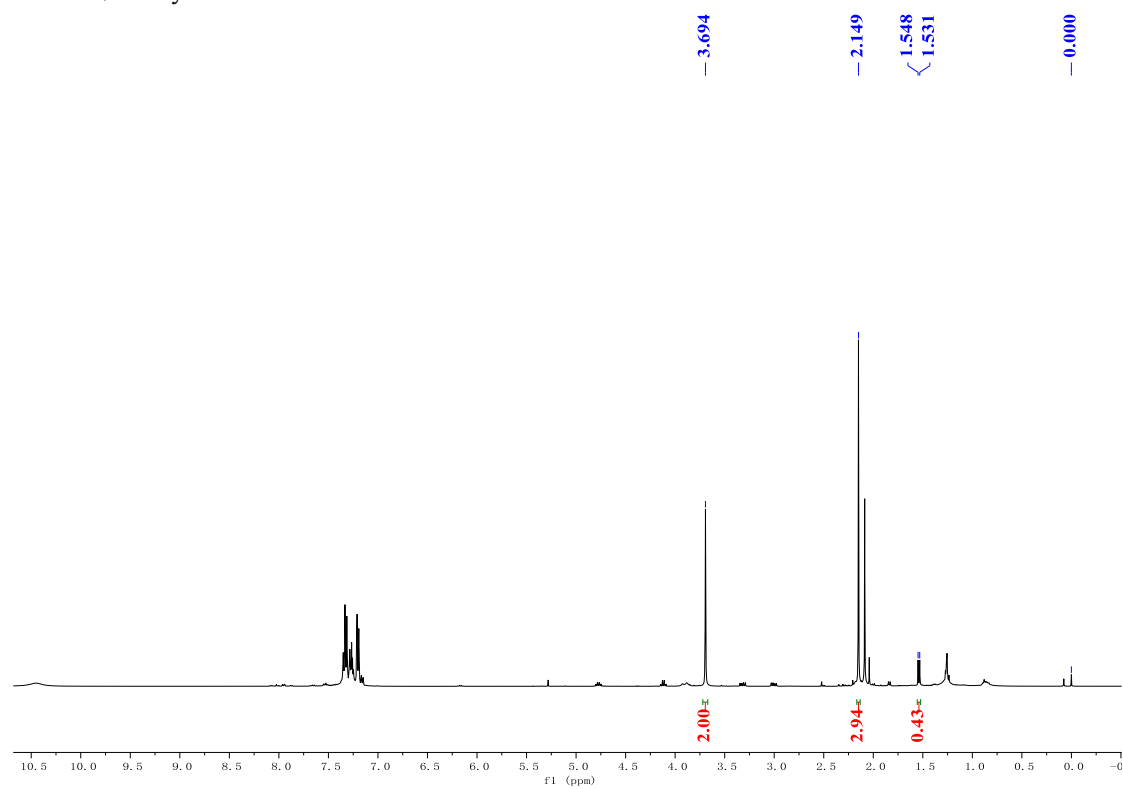


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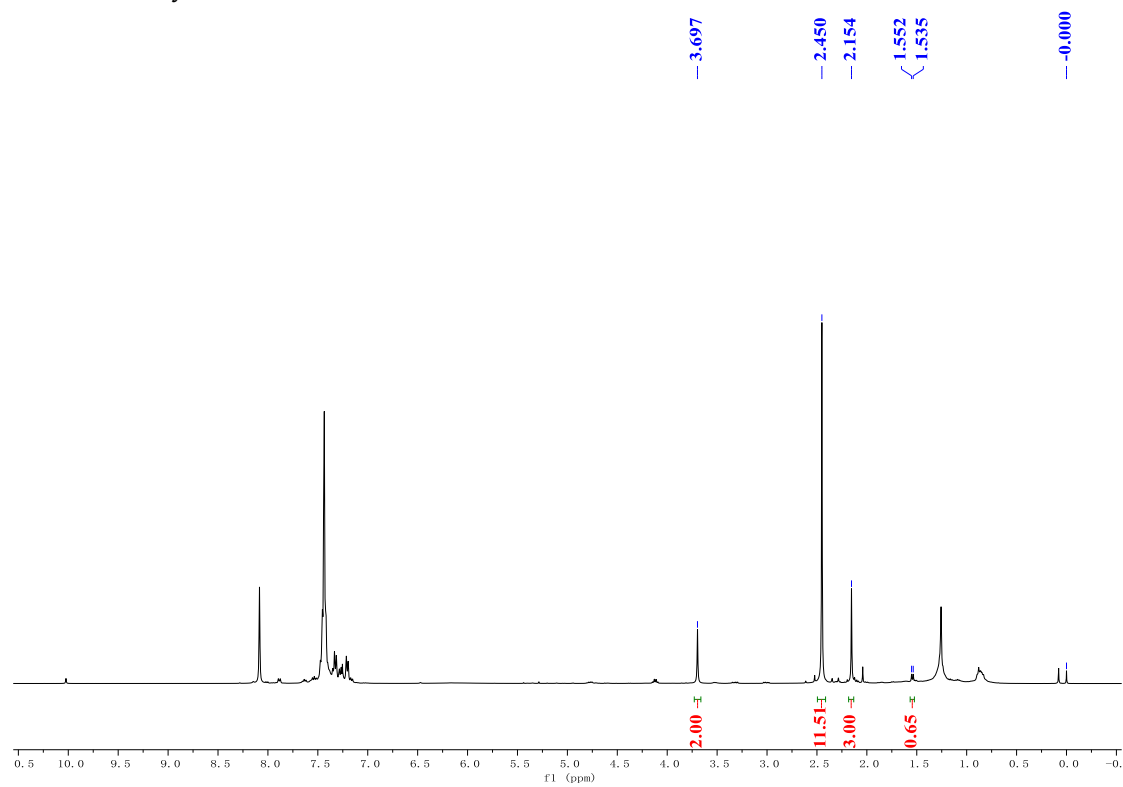


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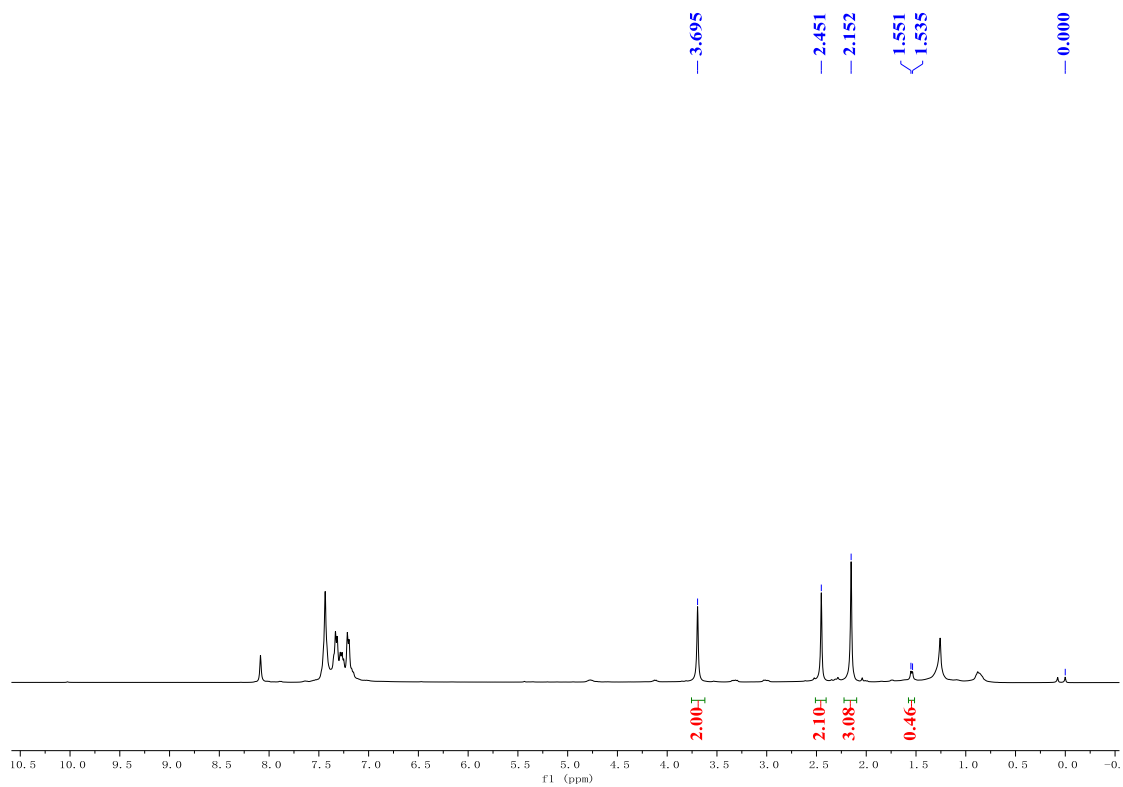


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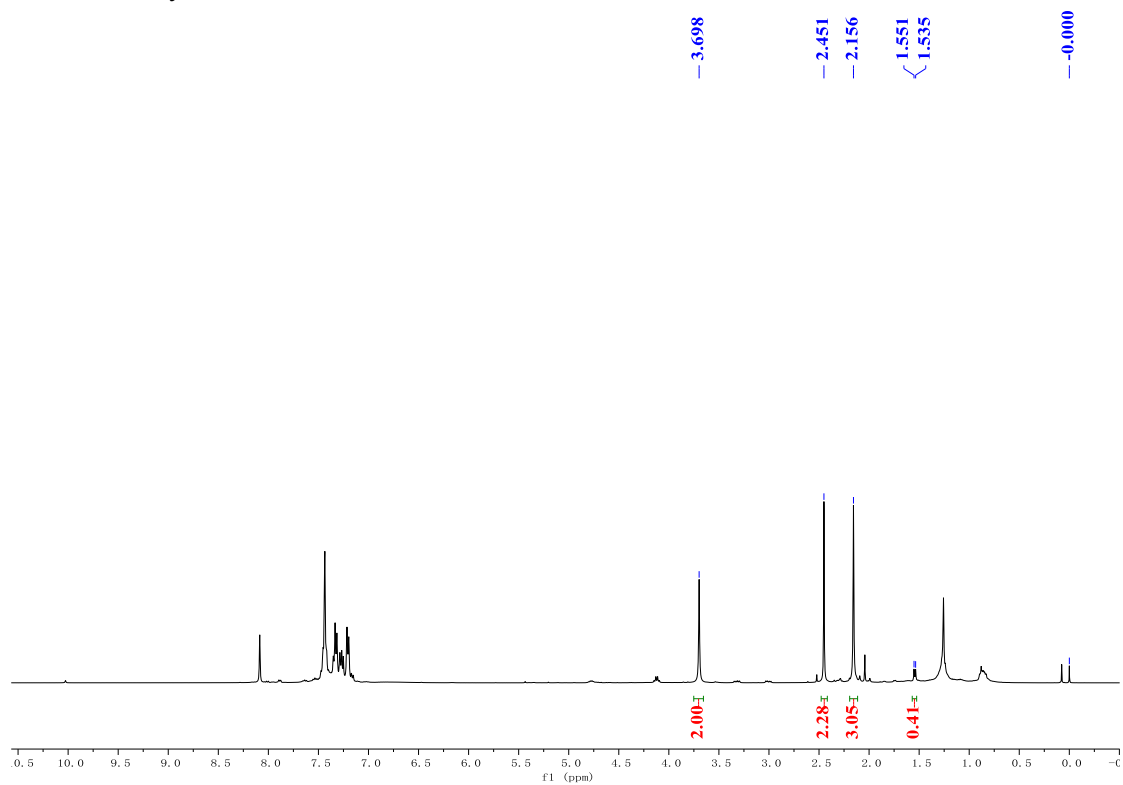


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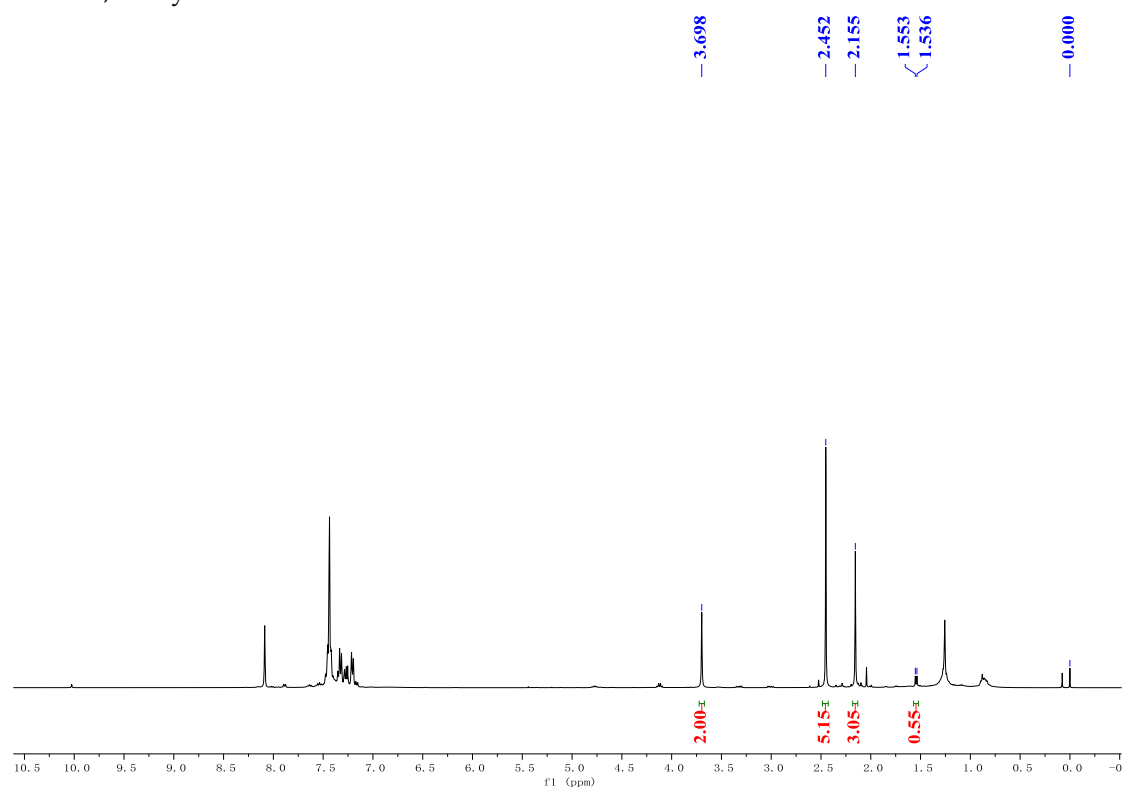


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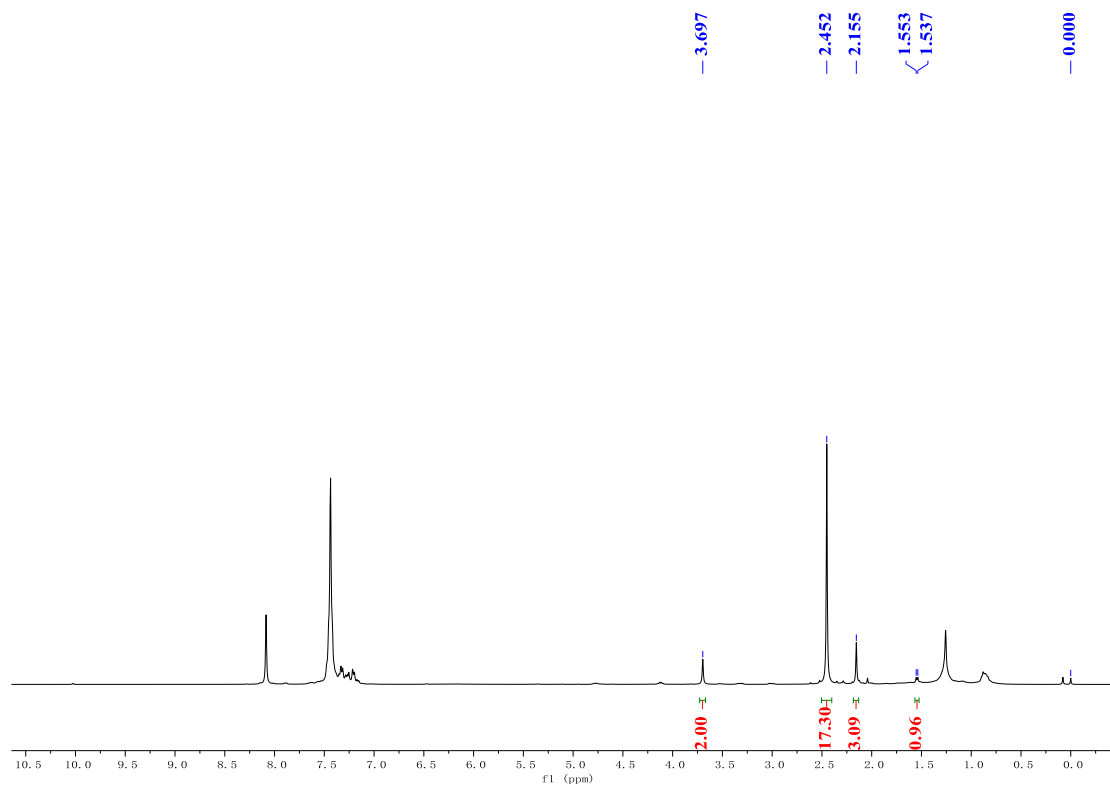


Table 1, entry 21

