# *Supporting Information*

## Visible-Light Initiated $Na_2$-Eosin Y Catalyzed Highly Regio- and Stereoselective Difunctionalization of Alkynes with Alkyl Bromides

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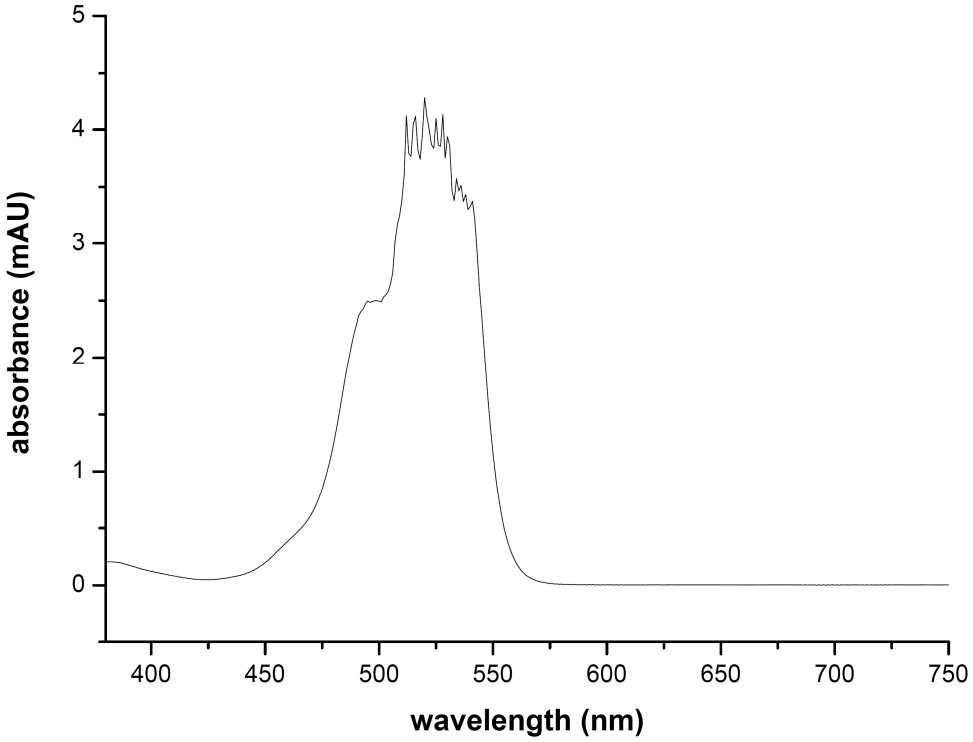
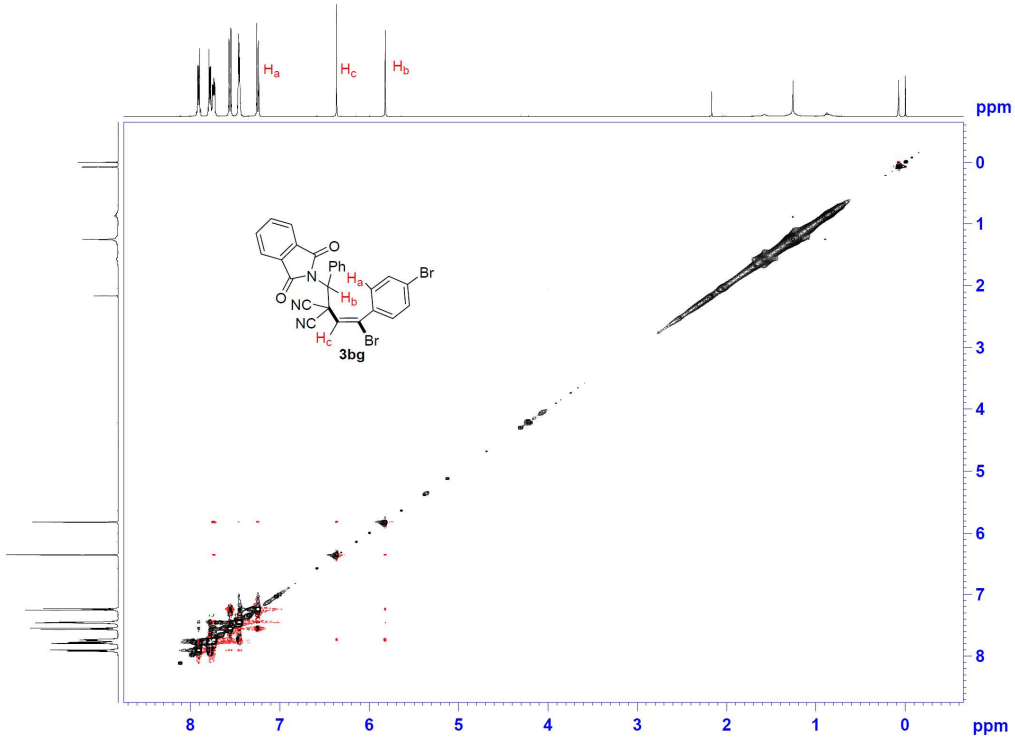
## 1. UV-Vis experiments

The UV-Vis measurement was performed with a $CH_3CN$ solution of $Na_2$-eosin Y (100 μM).



## 2. NOESY spectrum of compound 3bg

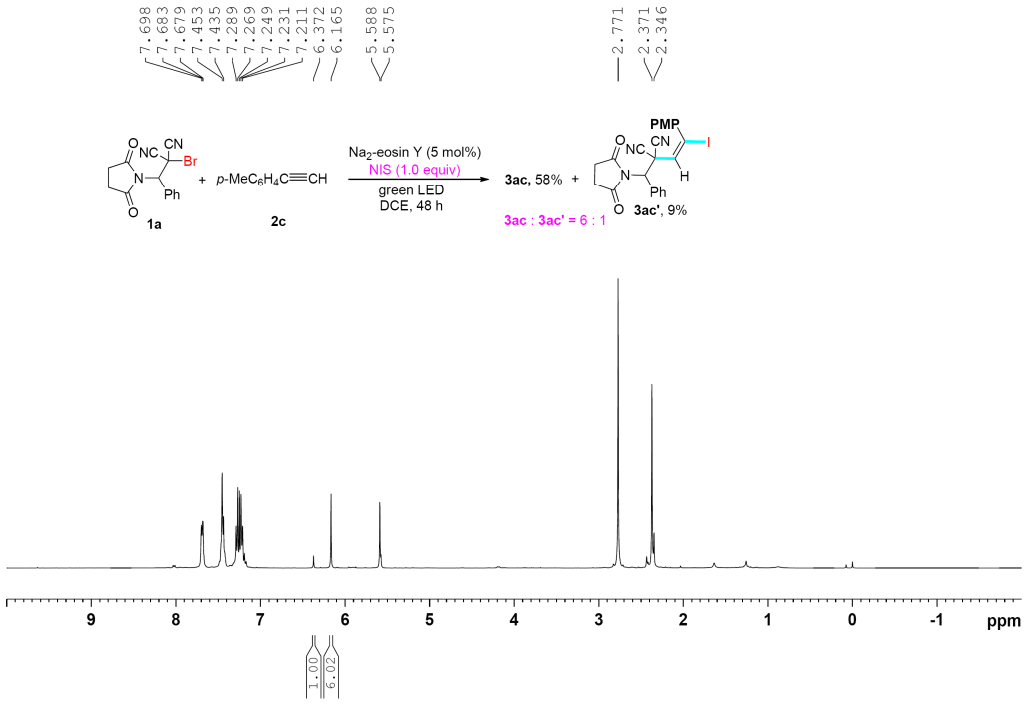


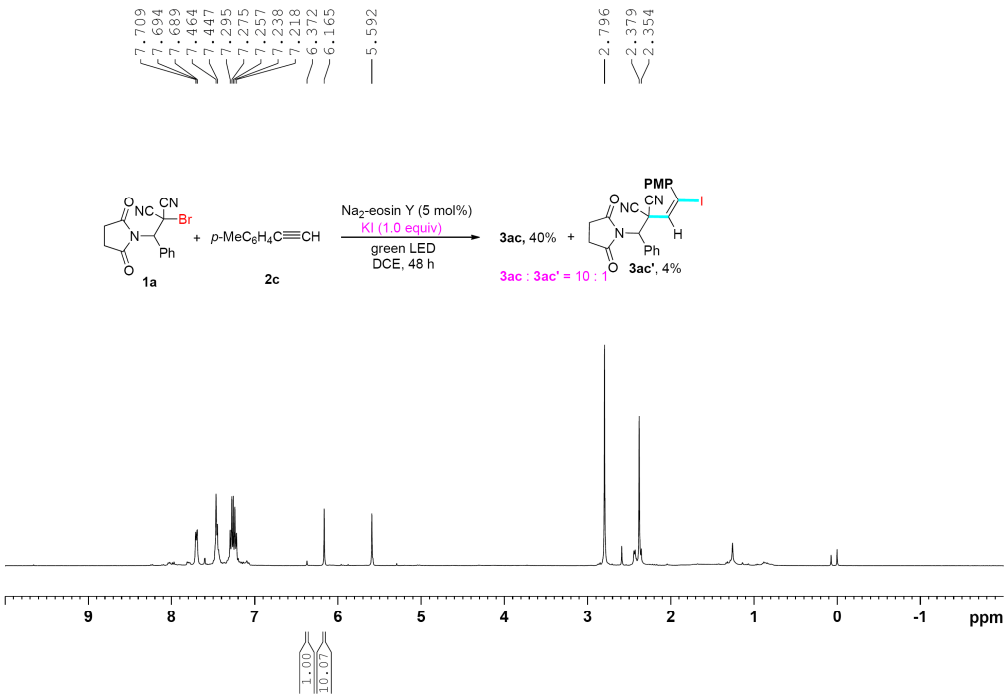

The (*E*)-configuration of the double bond can be confirmed by NOE experiments. In the NOESY spectrum of **3bg**, a cross peak of $H_a$ and $H_b$ was observed; but no NOE enhancements were appeared between $H_a$ and $H_c$, which confirmed the relationship between these substituents.

## 3. Correlative spectra of control experiments

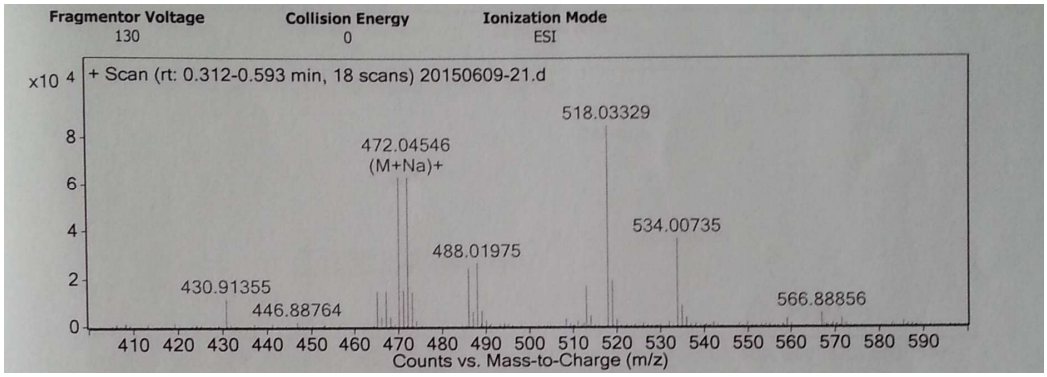
### (a) The spectra of mixture of 3ac and 3ac'

The following spectra were obtained after the reaction was stirred in the presence of NIS or KI; the yields of **3ac** and **3ac'** were calculated based on the $^{1}$H NMR spectra analysis.



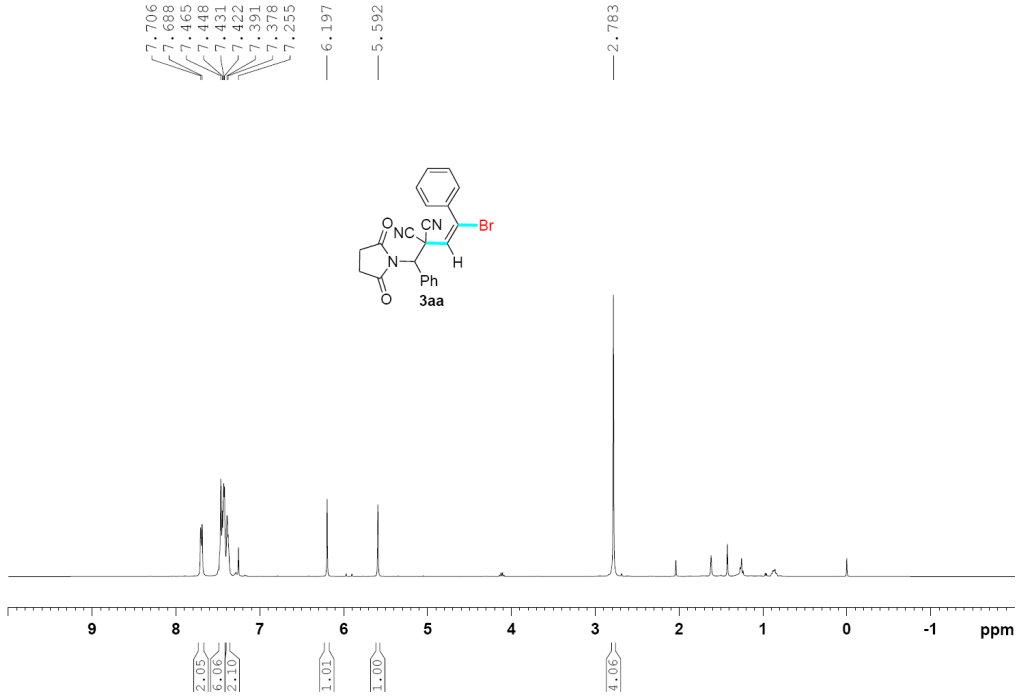
## (b) The HRMS spectra of mixture of 3ac and 3ac'

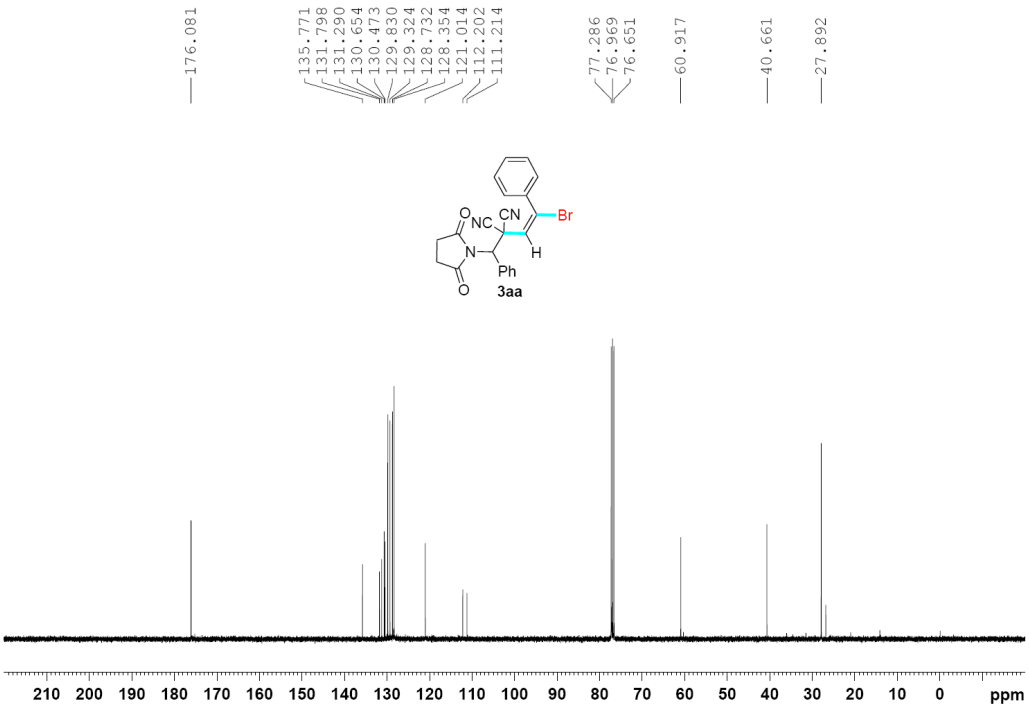


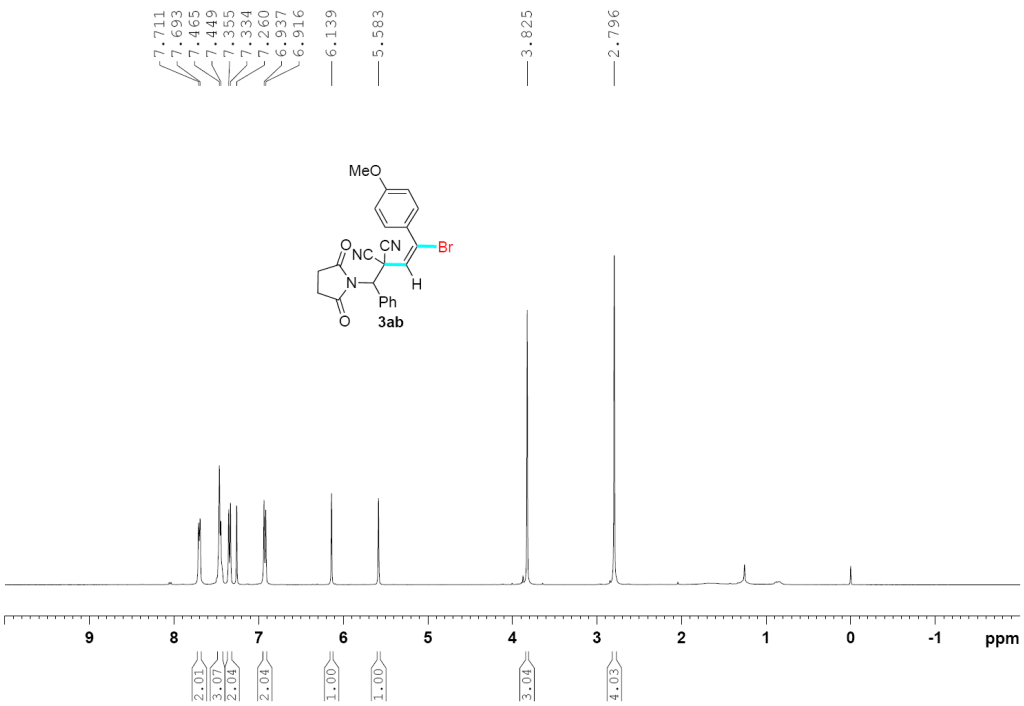

HRMS (ESI) calcd for **3ac** $C_{23}H_{18}{}^{81}BrN_3O_3Na$ $(M+Na)^+$: 472.0460; Found: 472.0455.

HRMS (ESI) calcd for **3ac'** $C_{23}H_{18}IN_3O_3Na$ $(M+Na)^+$: 518.0341; Found: 518.0333.

## 4. $^{1}$H and $^{13}$C NMR spectra of the products

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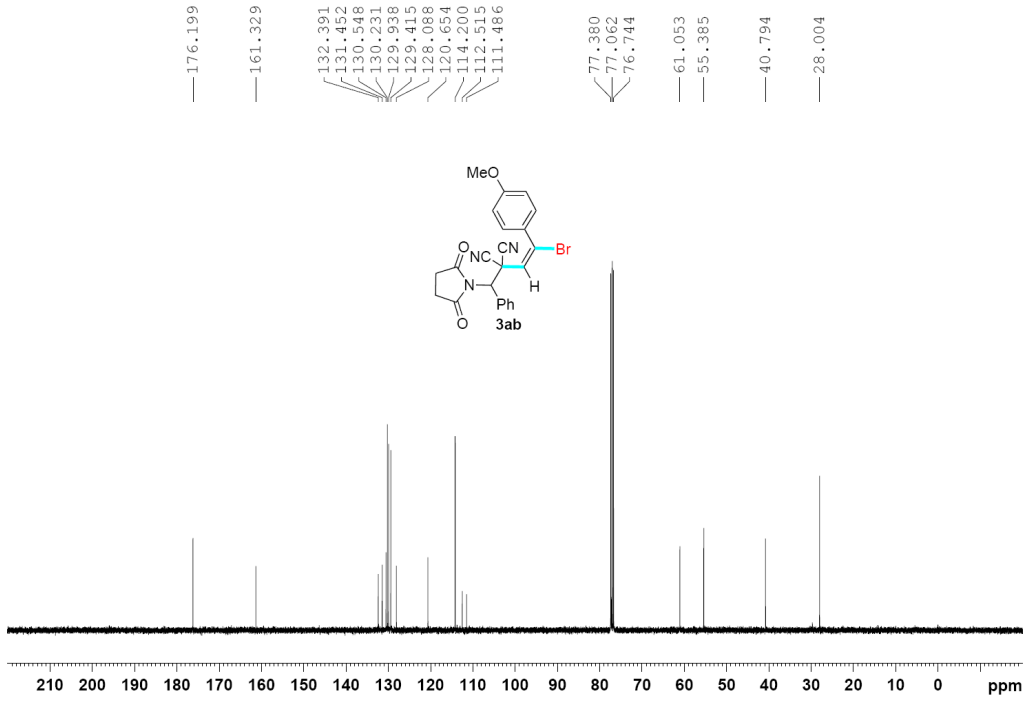
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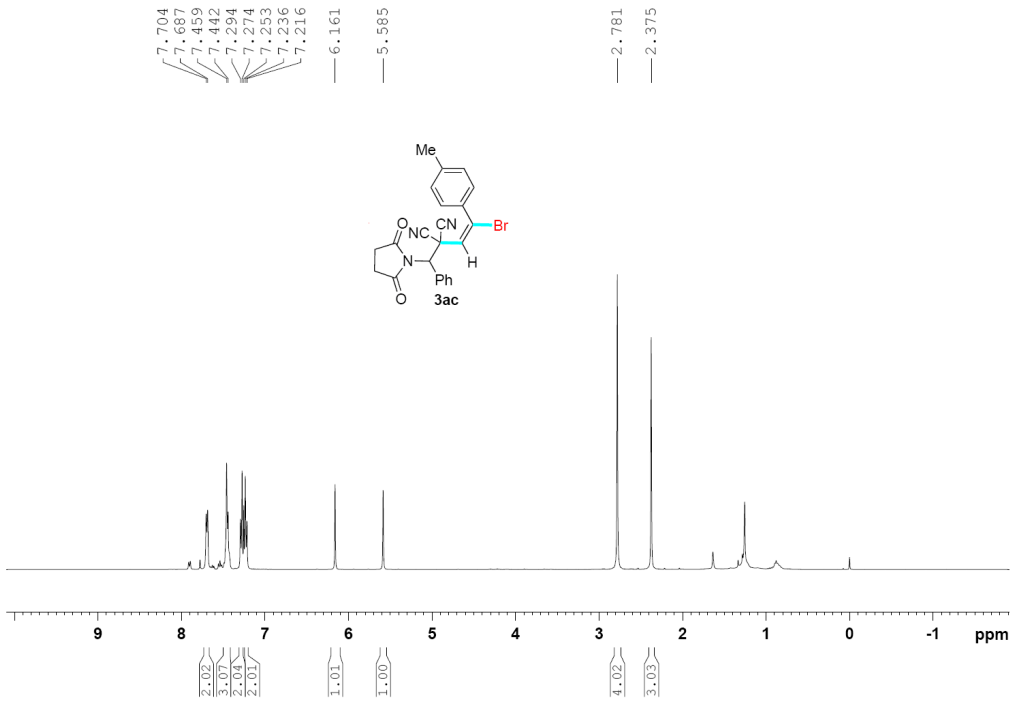
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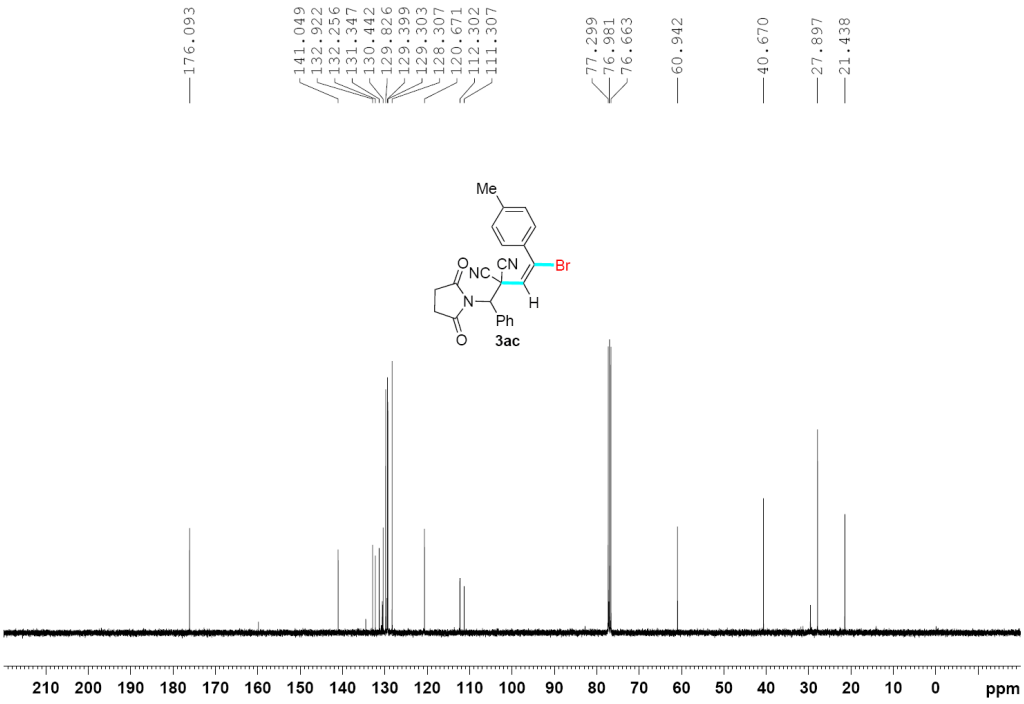
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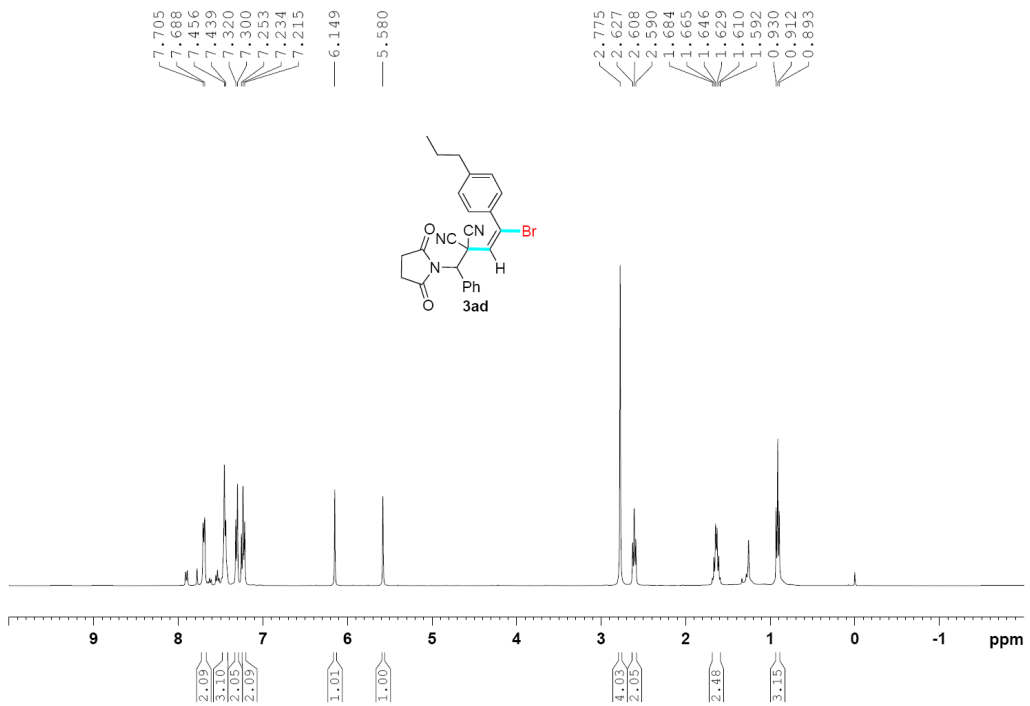
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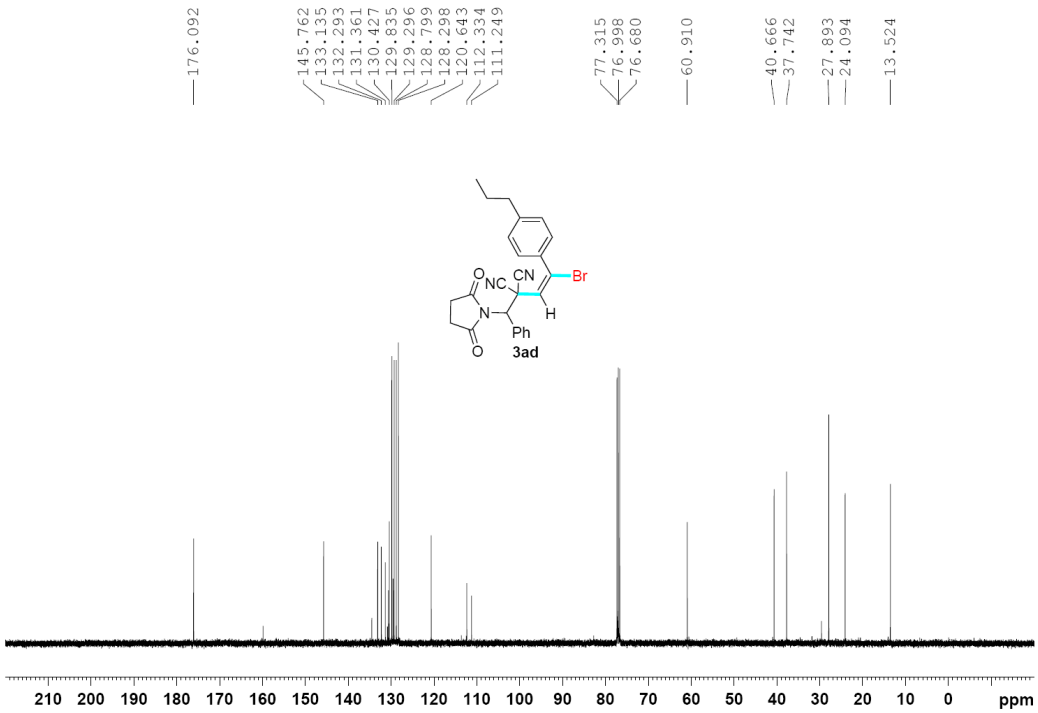
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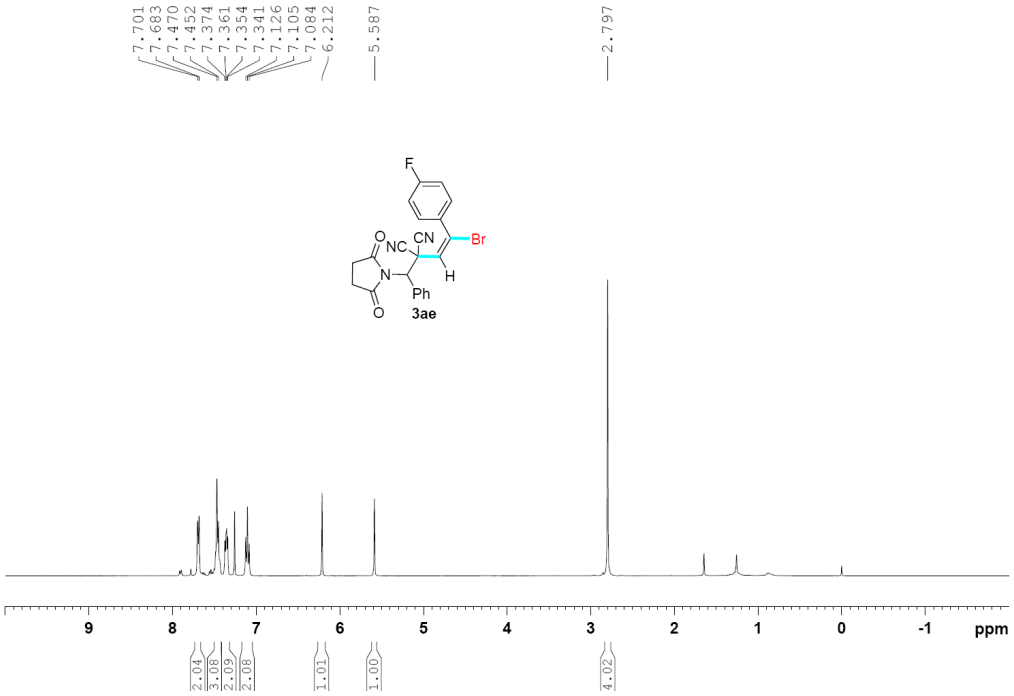
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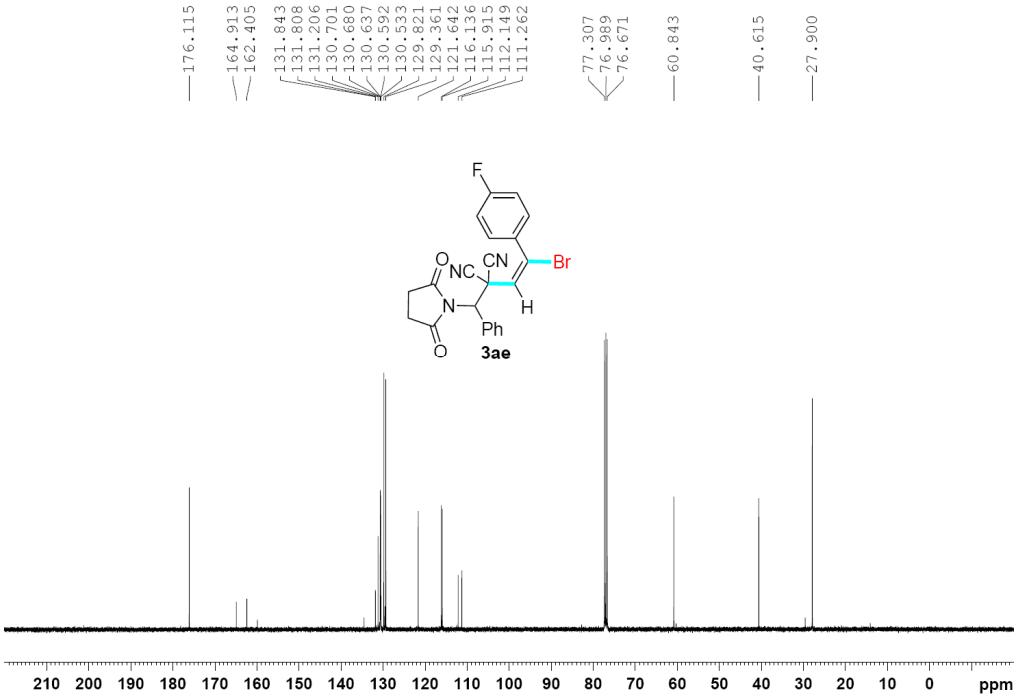
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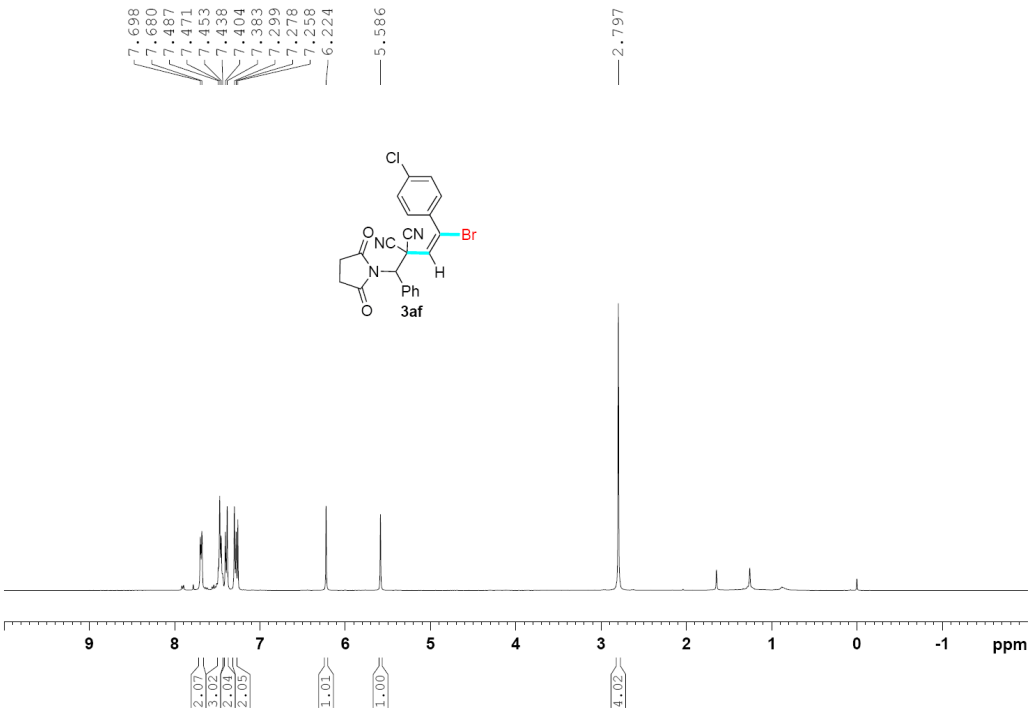
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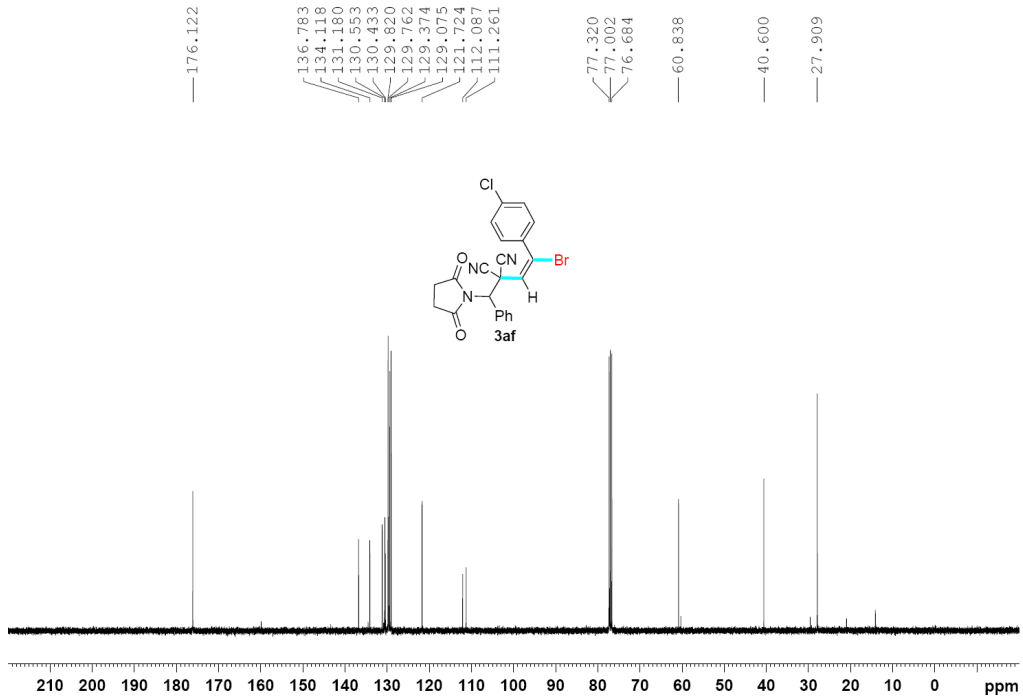
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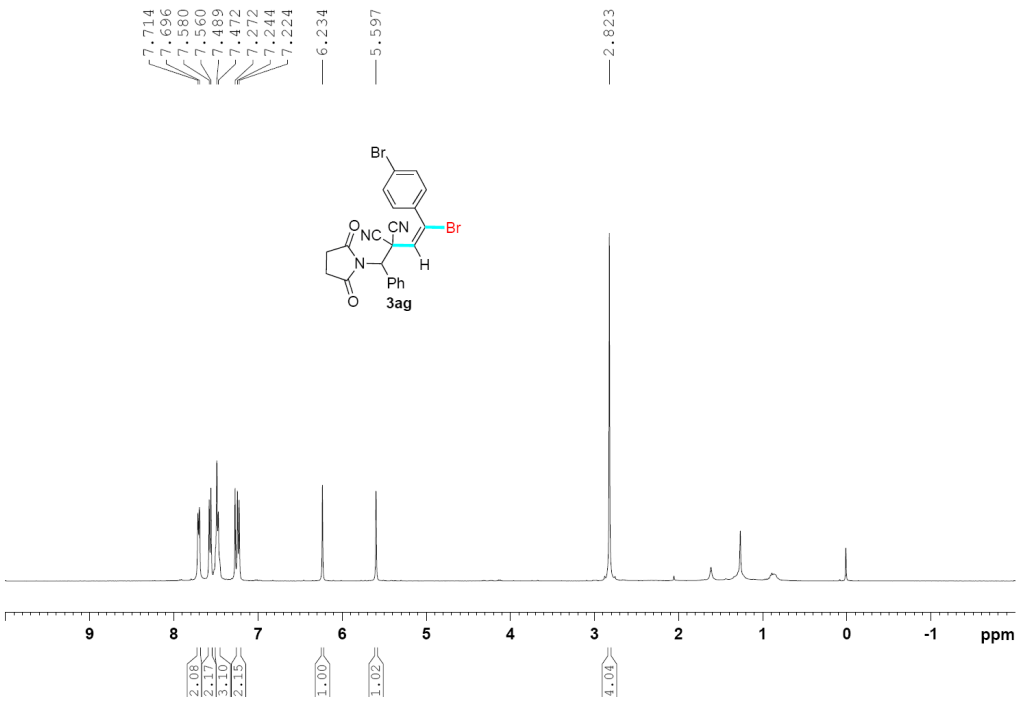
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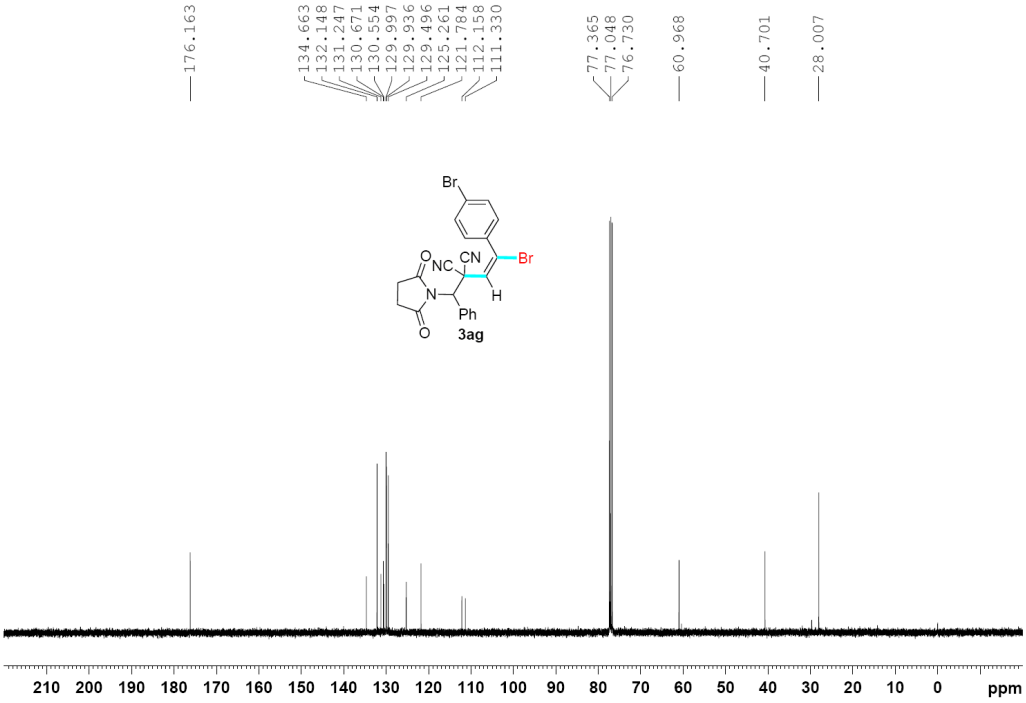
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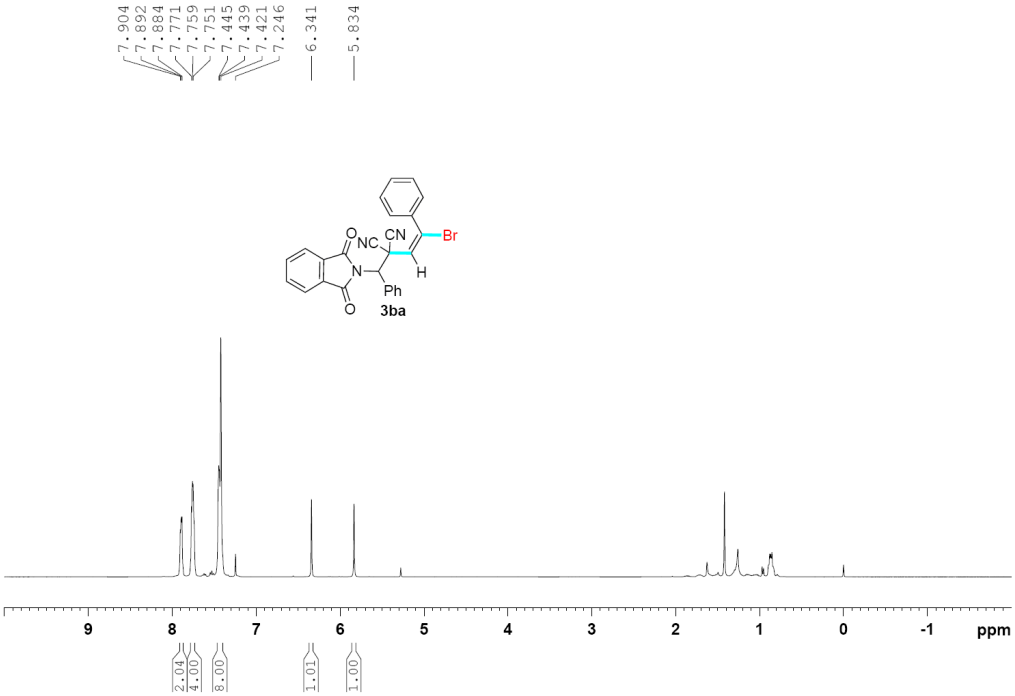
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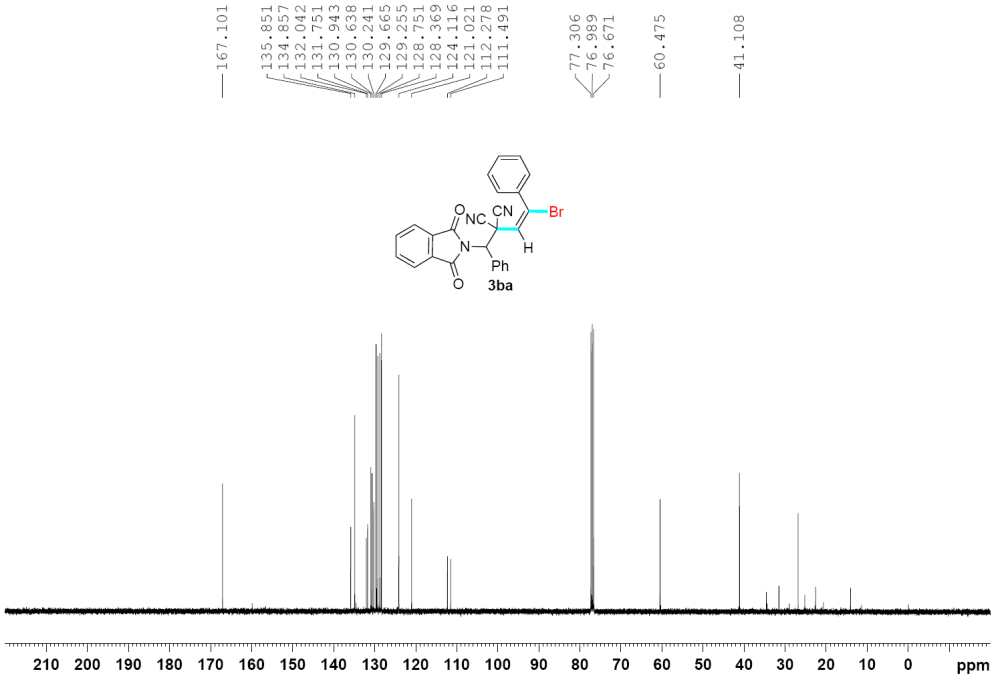
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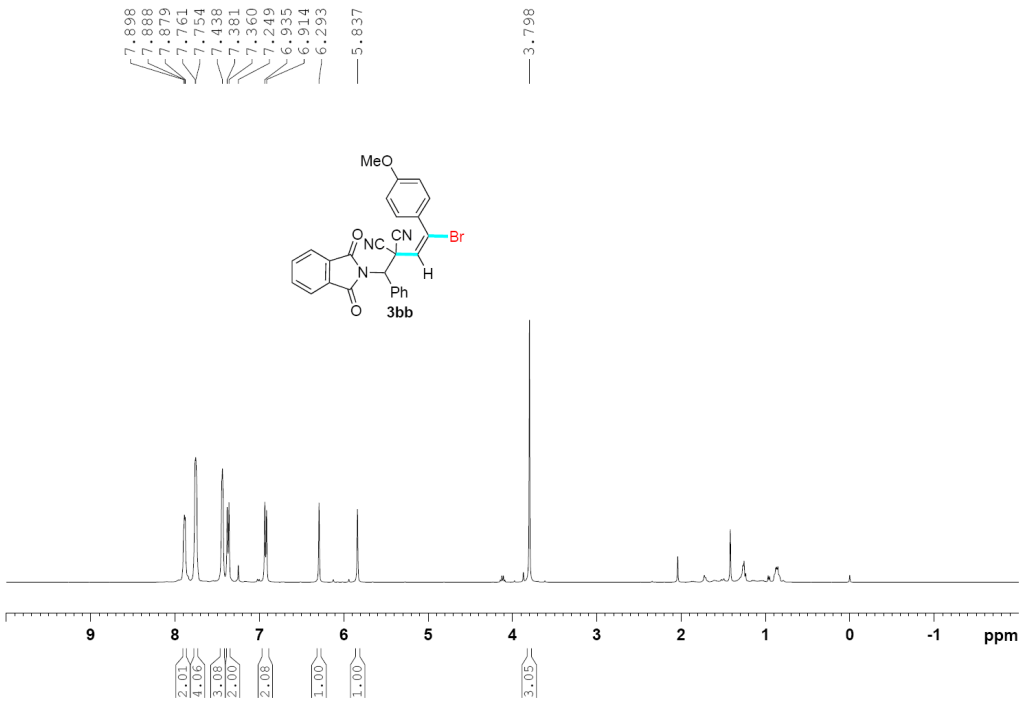
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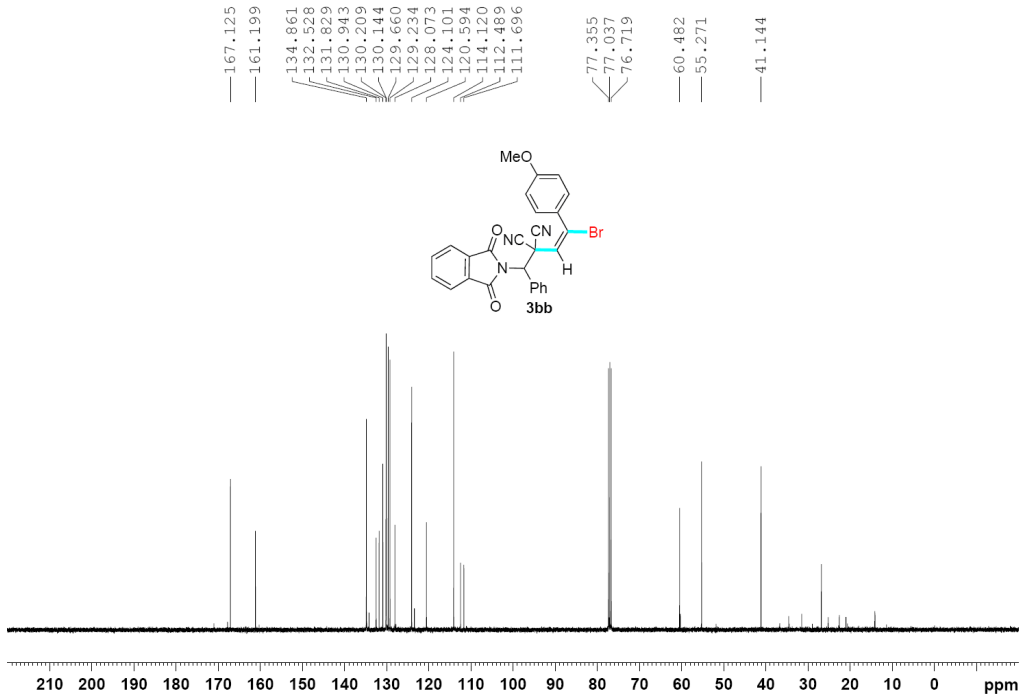
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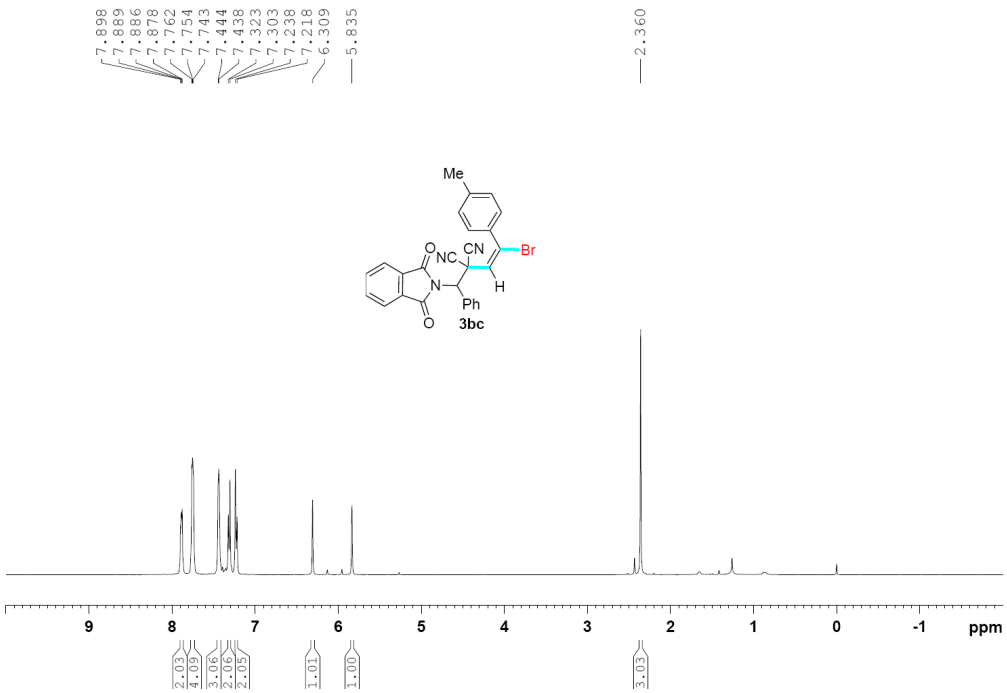
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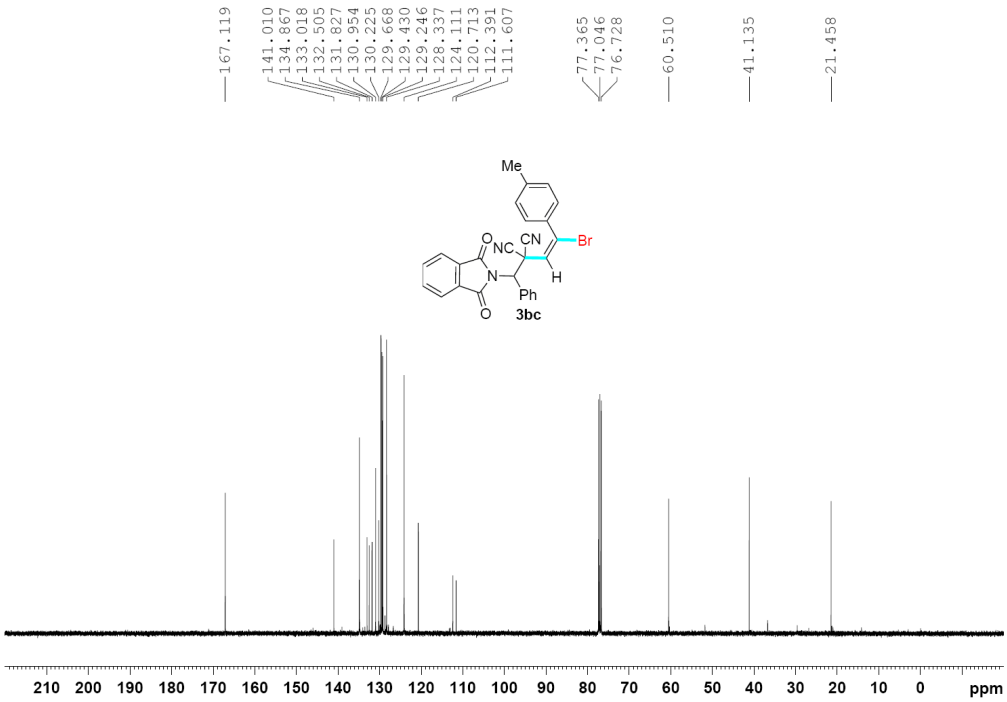
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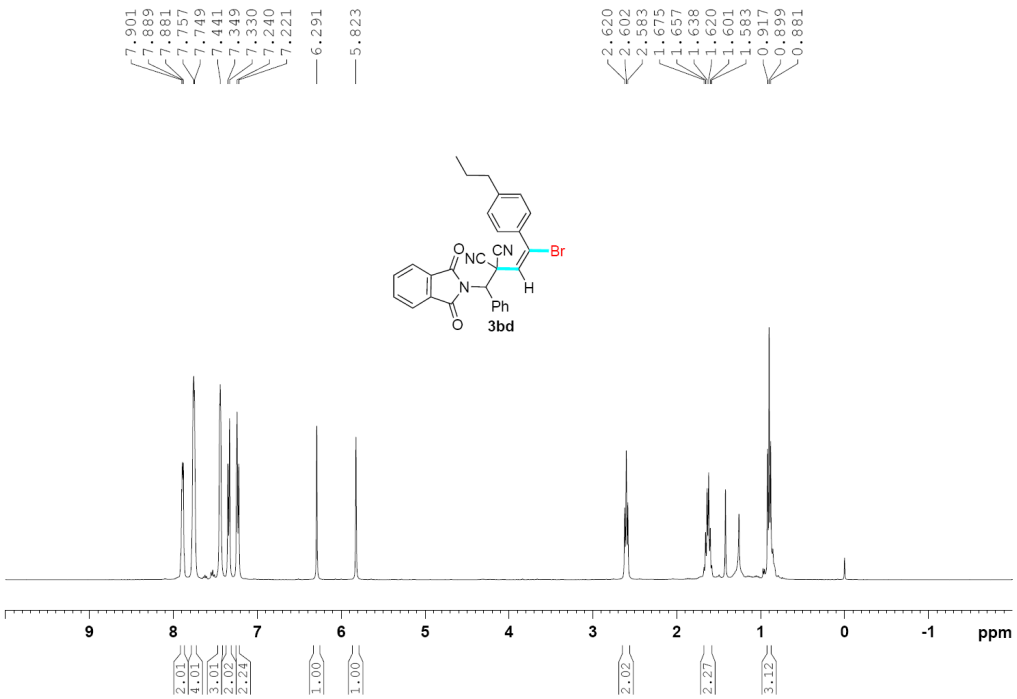
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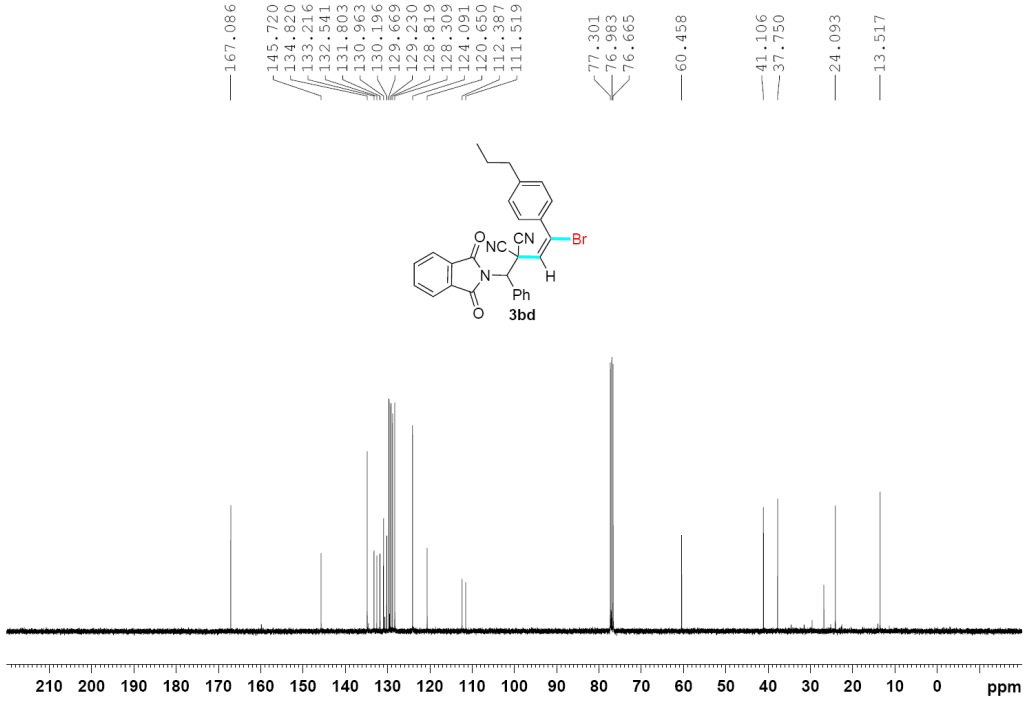
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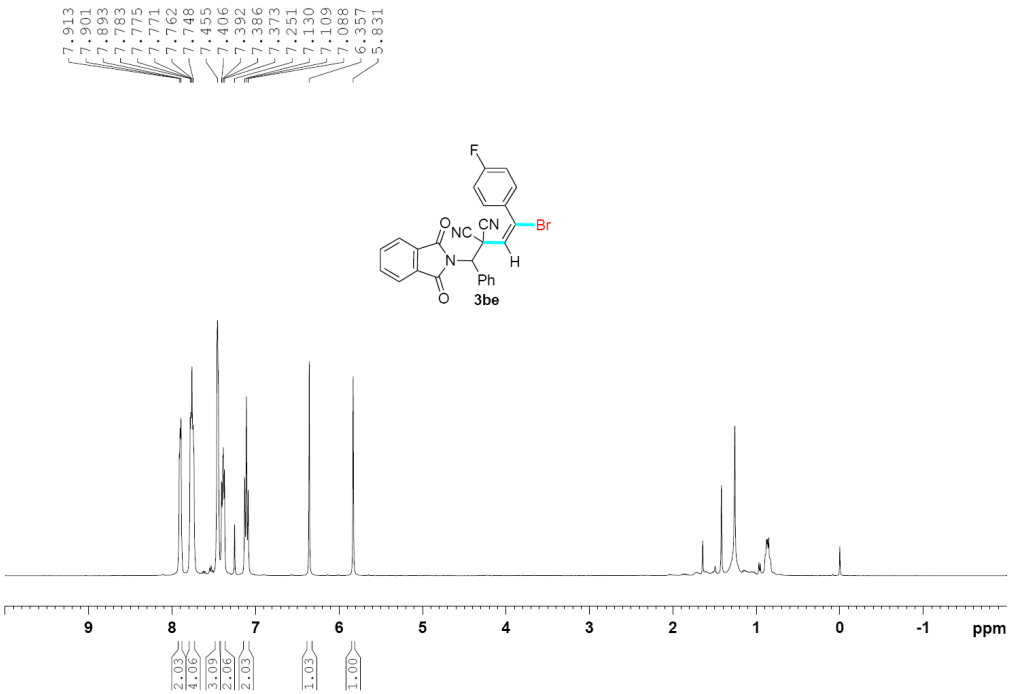
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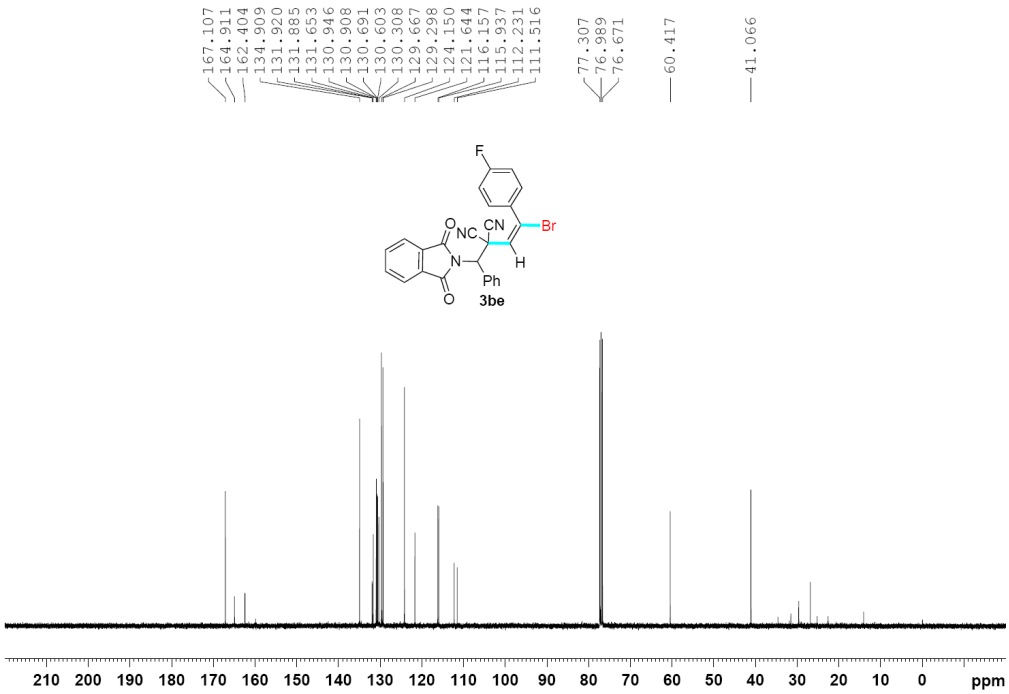
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76.671
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O
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CN
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N
H
Ph
O
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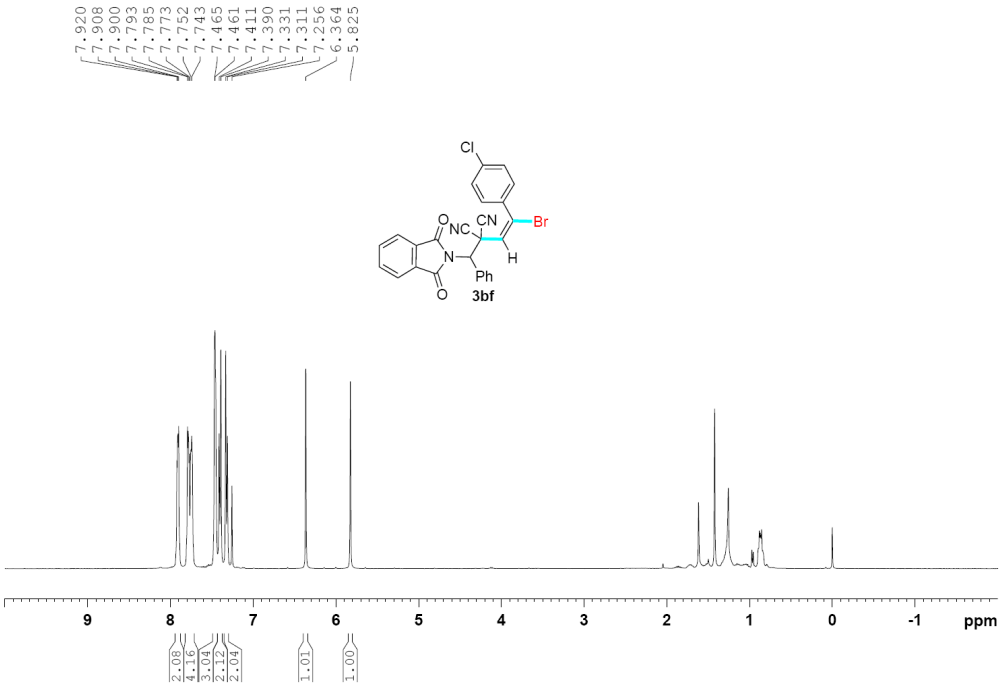
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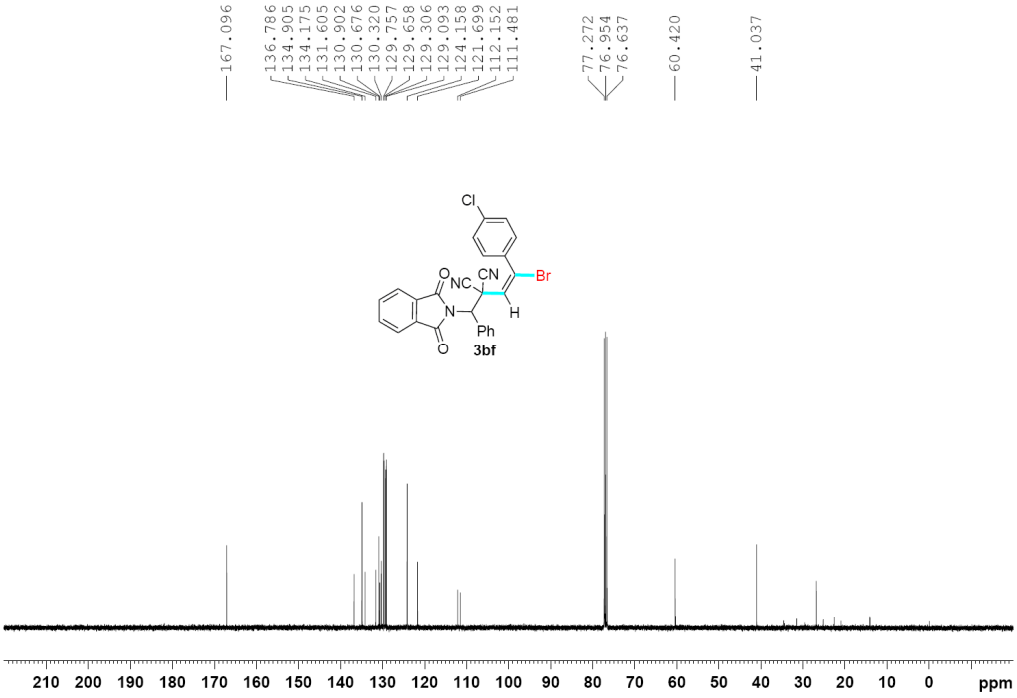
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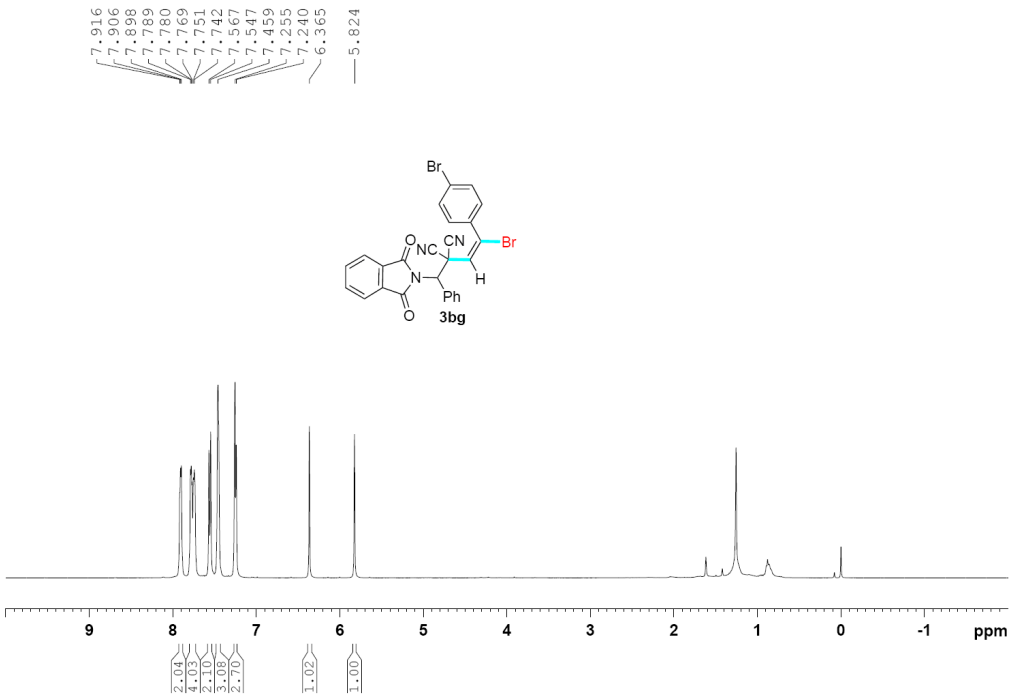
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CN
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N
H
Ph
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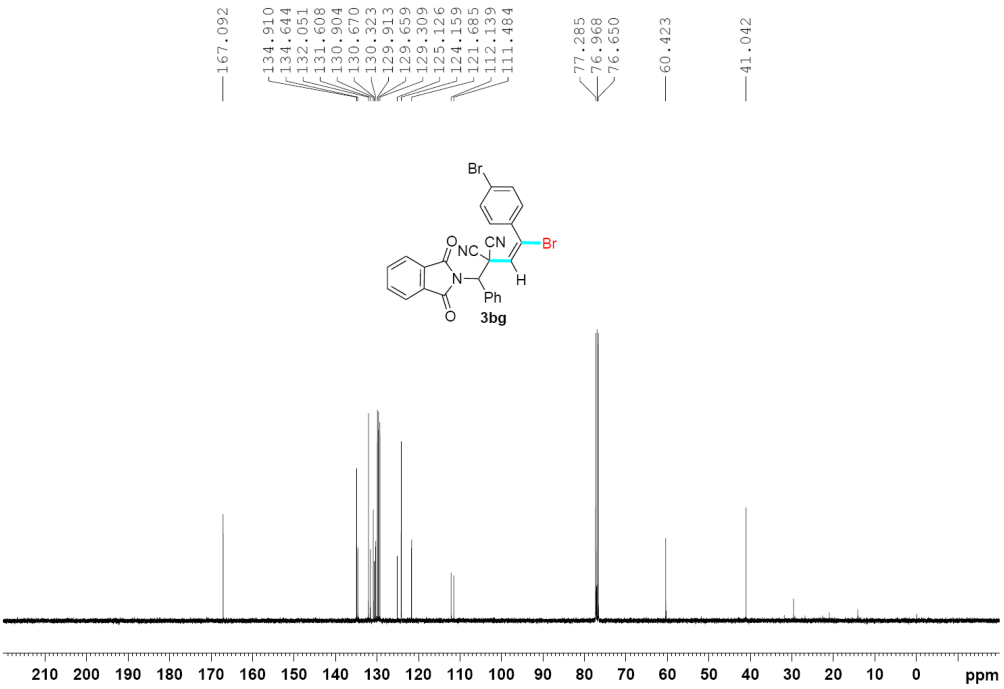
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H
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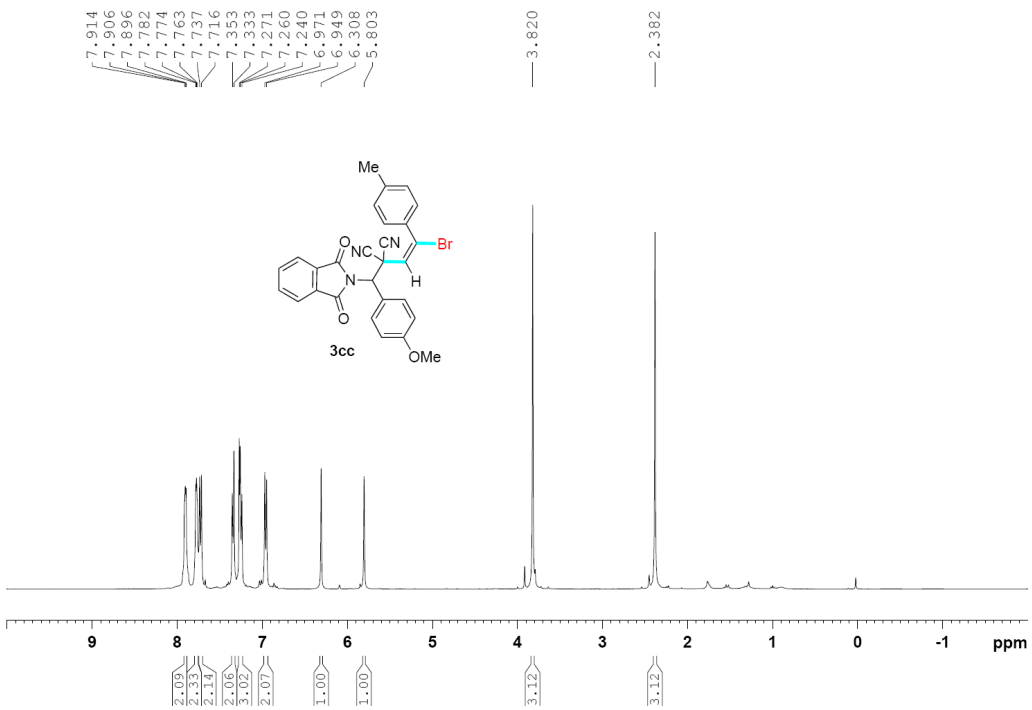
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OMe
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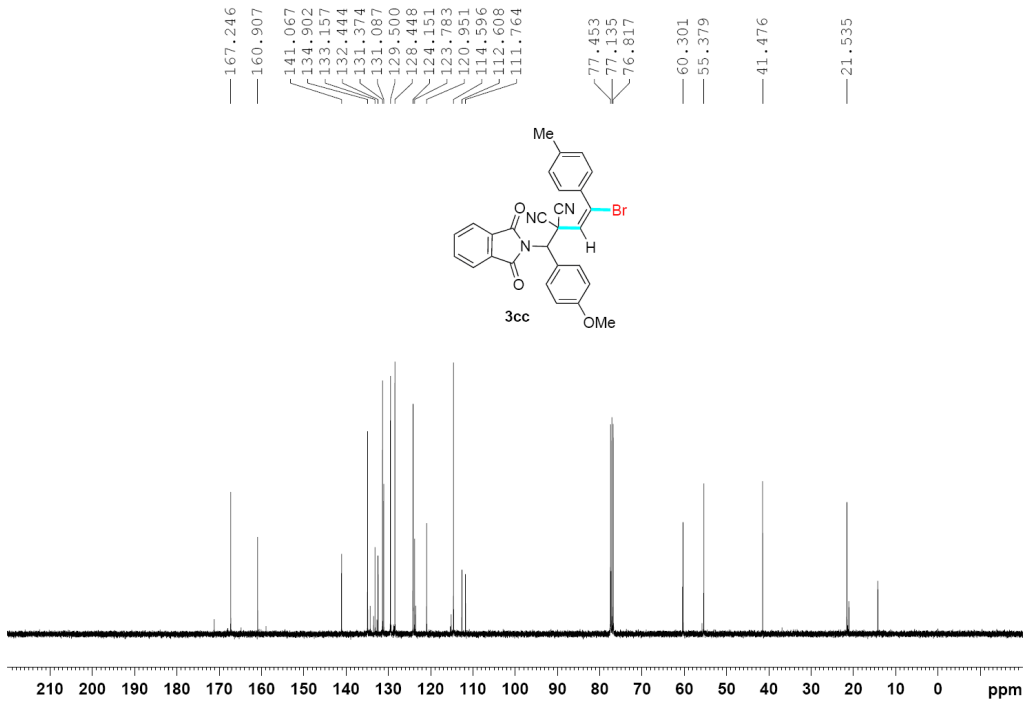
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H
O
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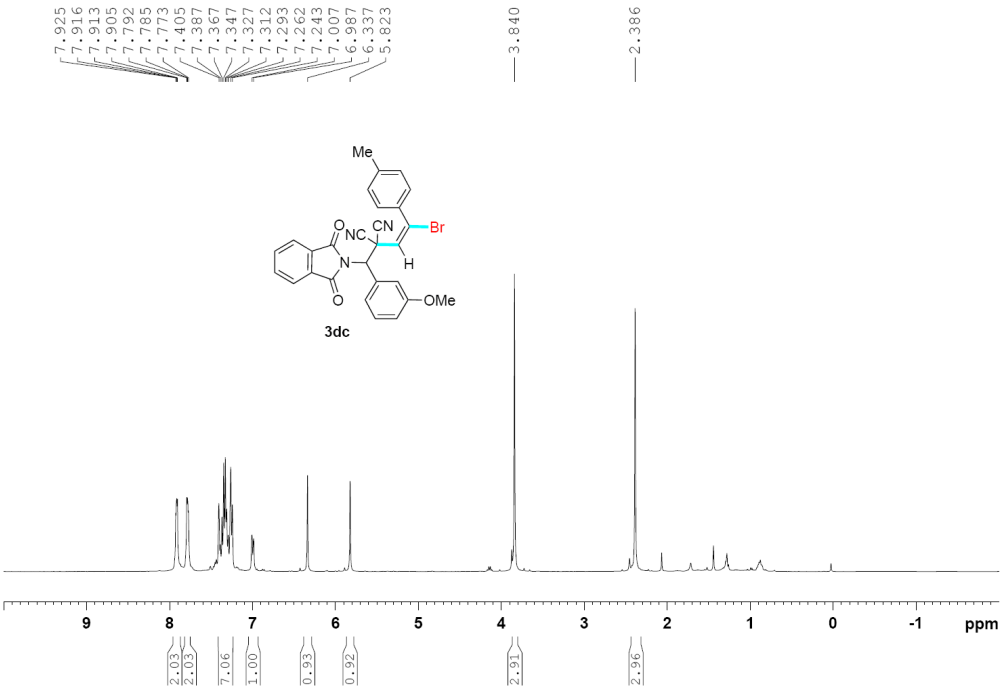
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H
OMe
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6
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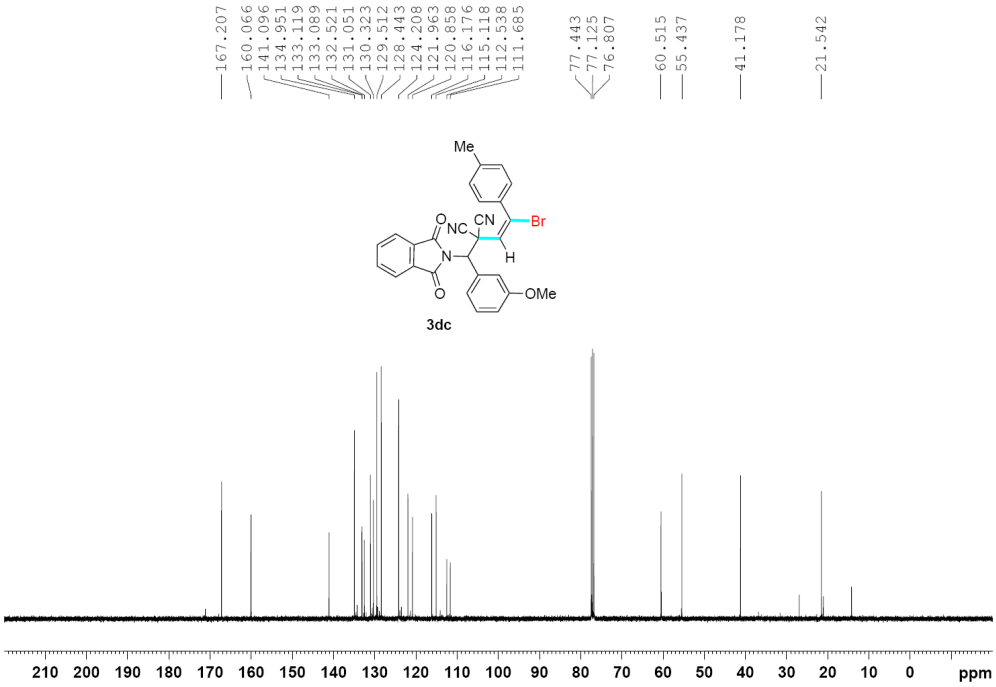
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115.118
112.538
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77.125
76.807
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55.437
41.178
21.542
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Br
CN
NC
O
N
H
OMe
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200
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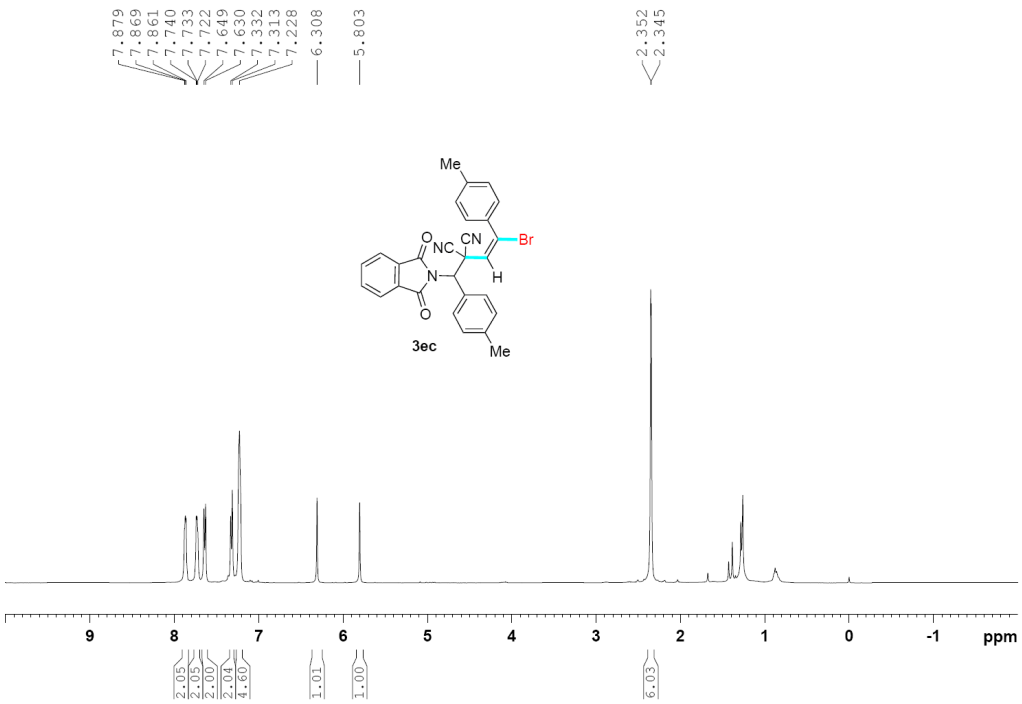
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O
NC
CN
Br
N
H
O
3ec
Me
9
8
7
6
5
4
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-1
ppm
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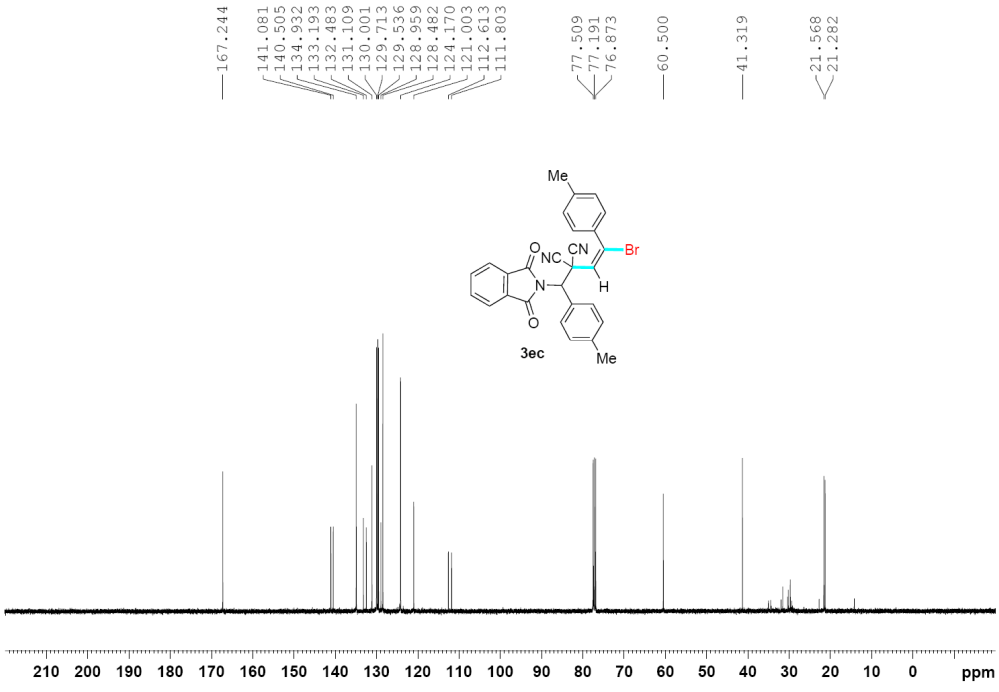
1.00
6.03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121.003
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77.191
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21.282
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O
NC
CN
Br
N
H
O
3ec
Me
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200
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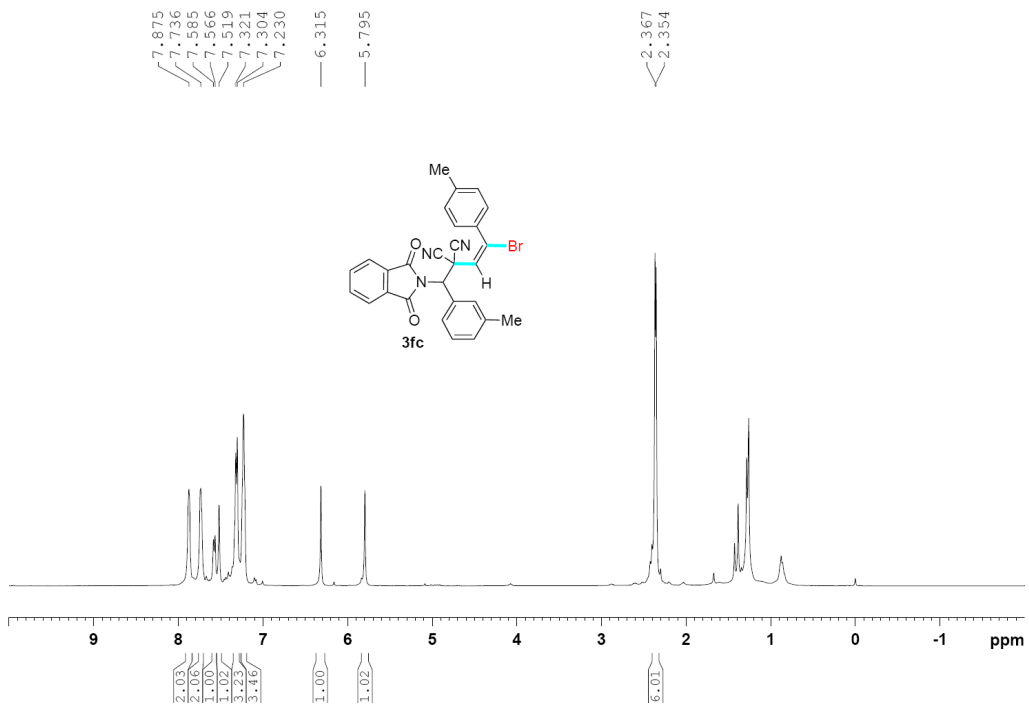
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H
O
Me
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8
7
6
5
4
3
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ppm
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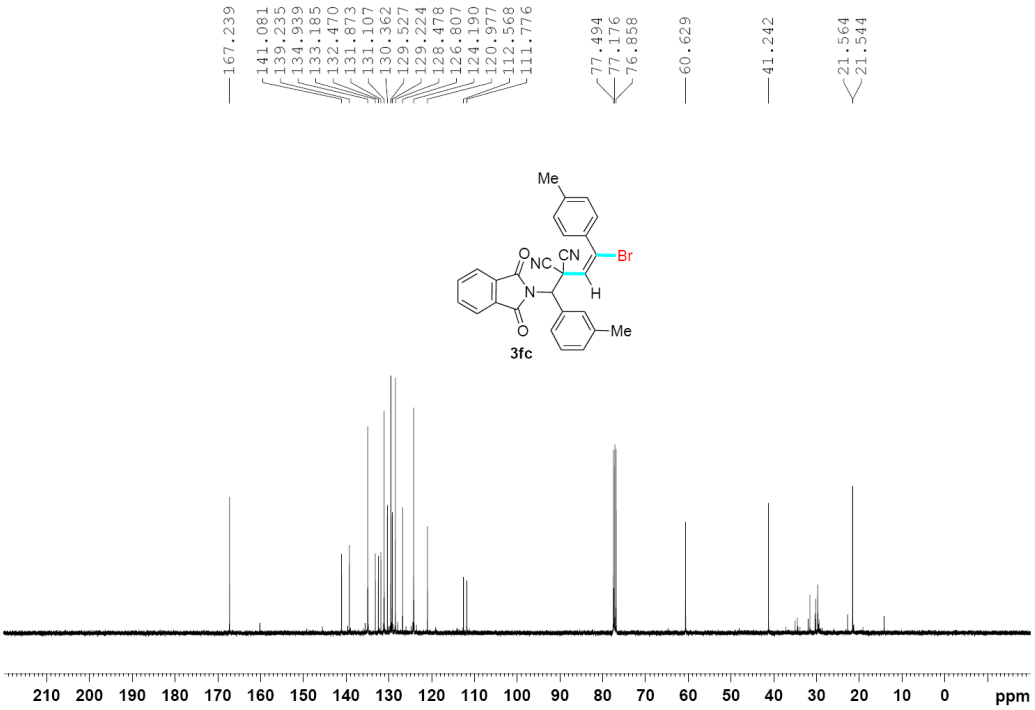
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CN
Br
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H
O
Me
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200
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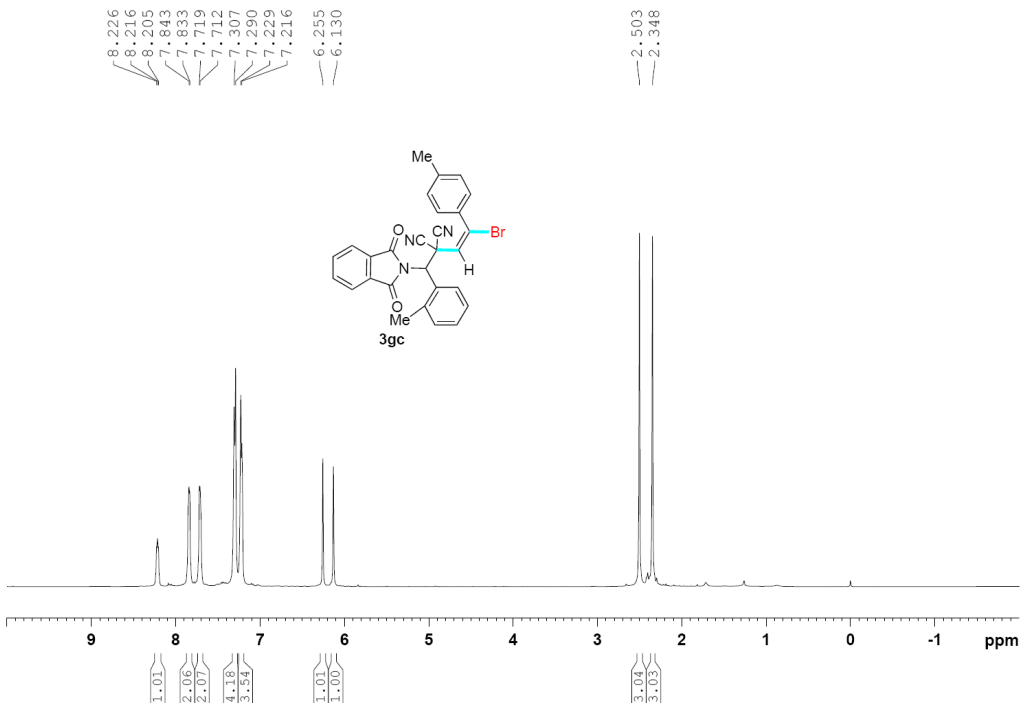
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Br
N
H
O
Me
3gc
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8
7
6
5
4
3
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ppm
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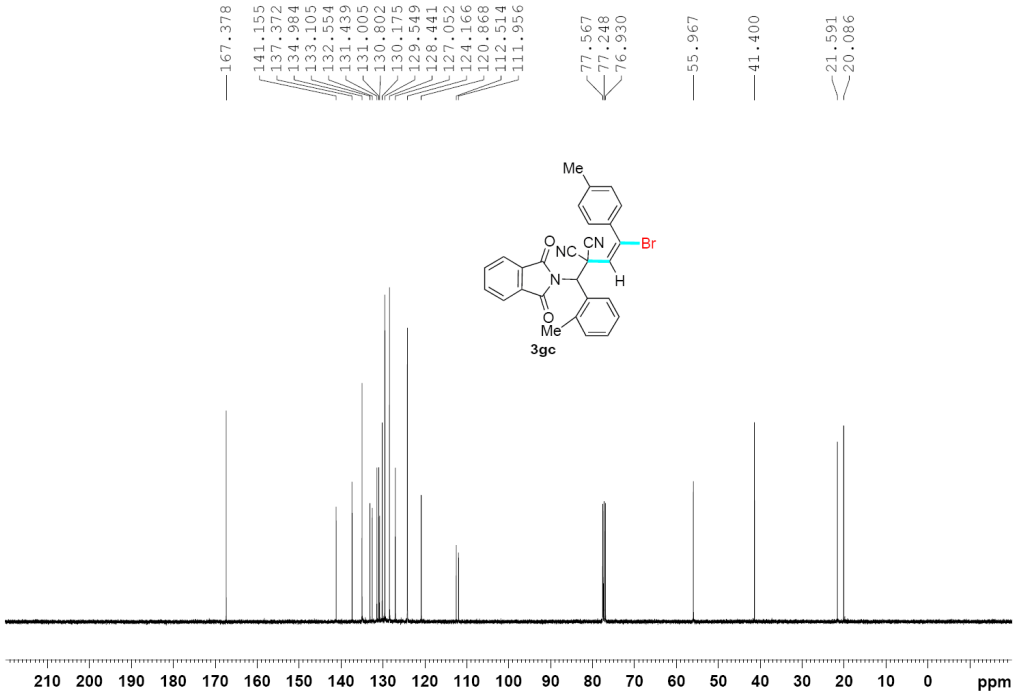
3.03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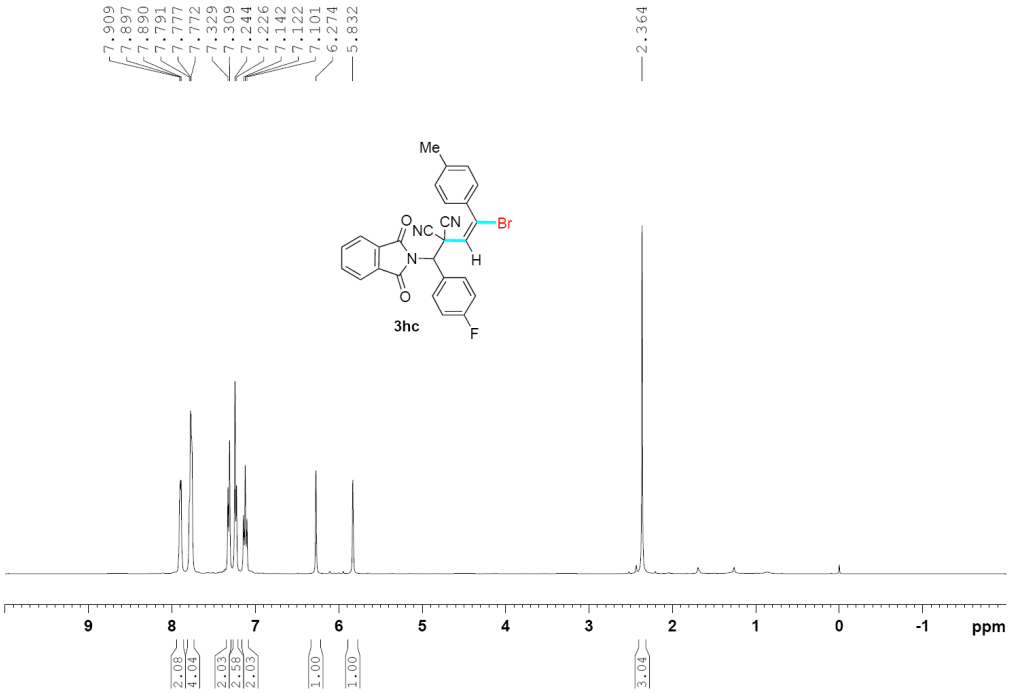
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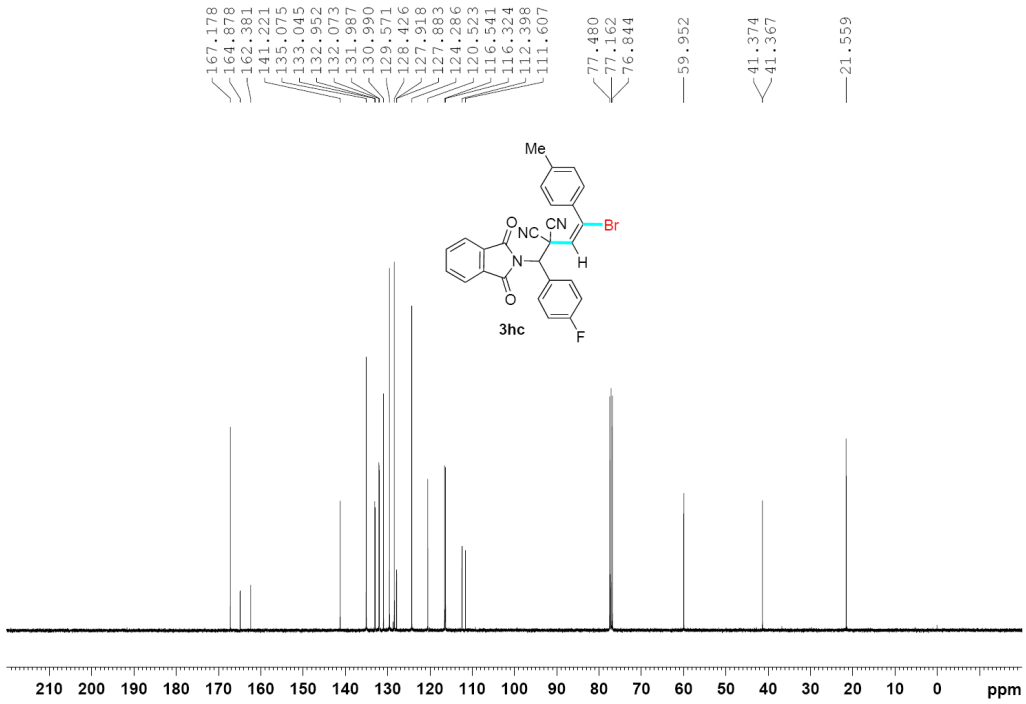
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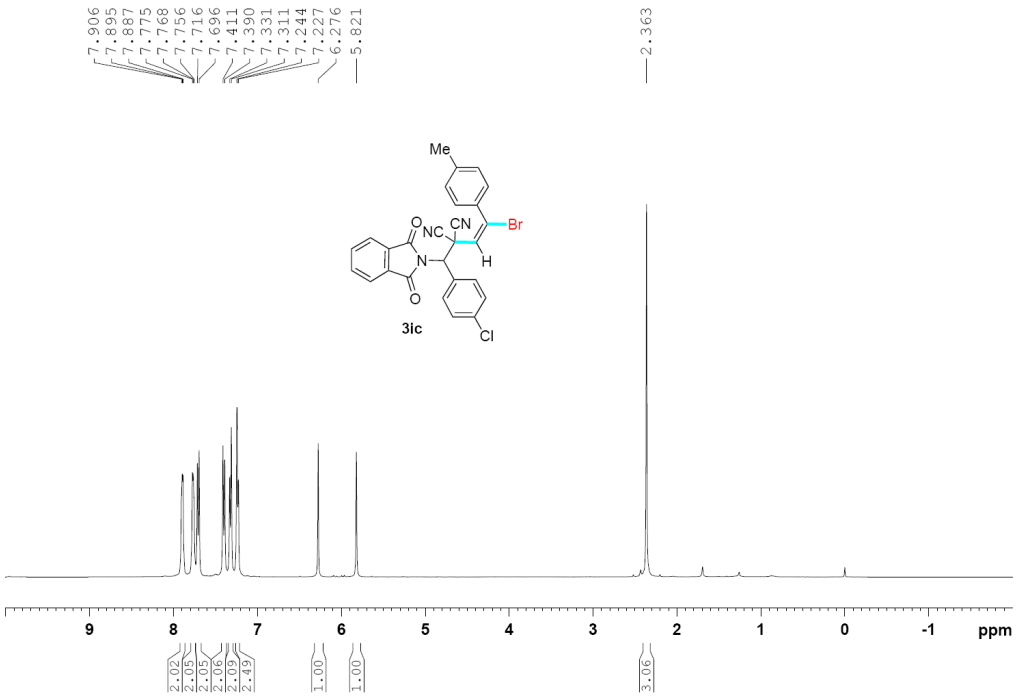
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Cl
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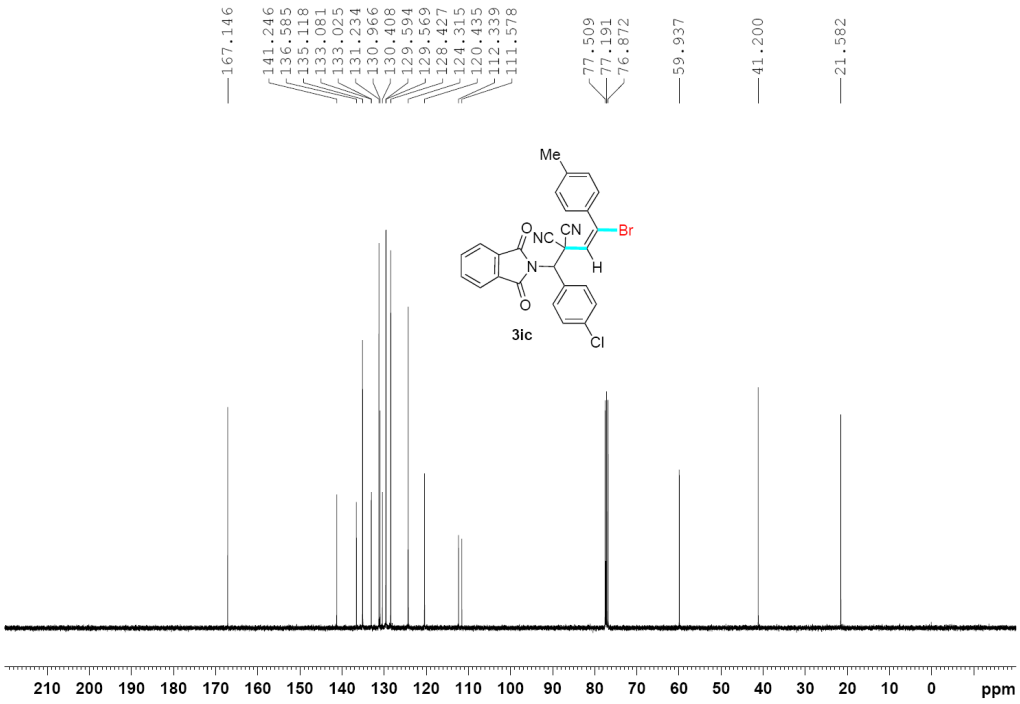
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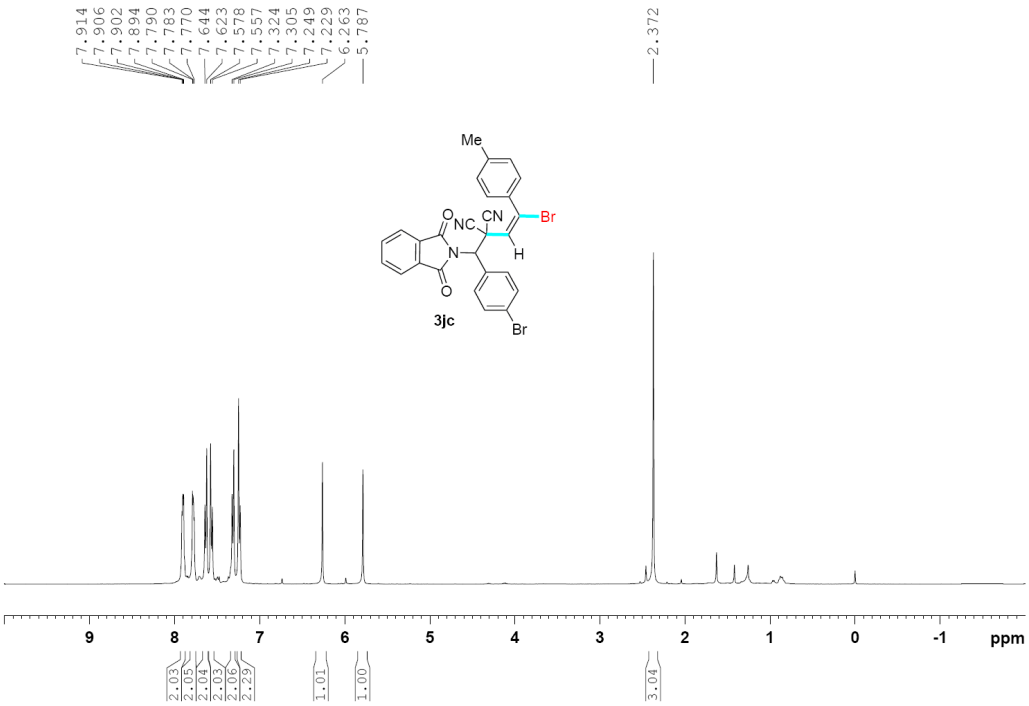
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Br
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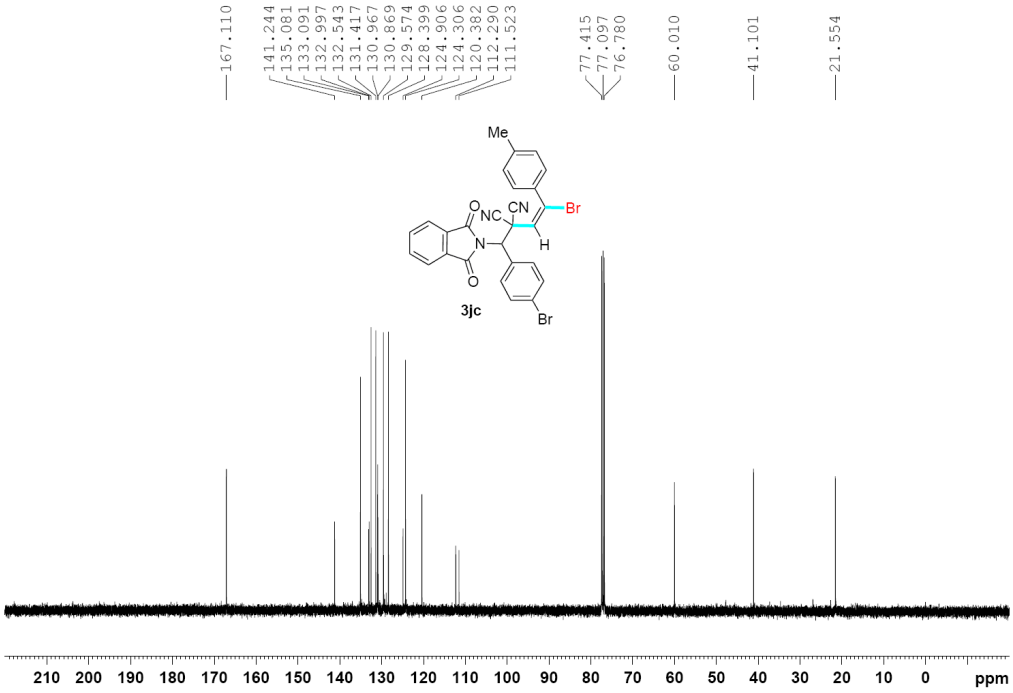
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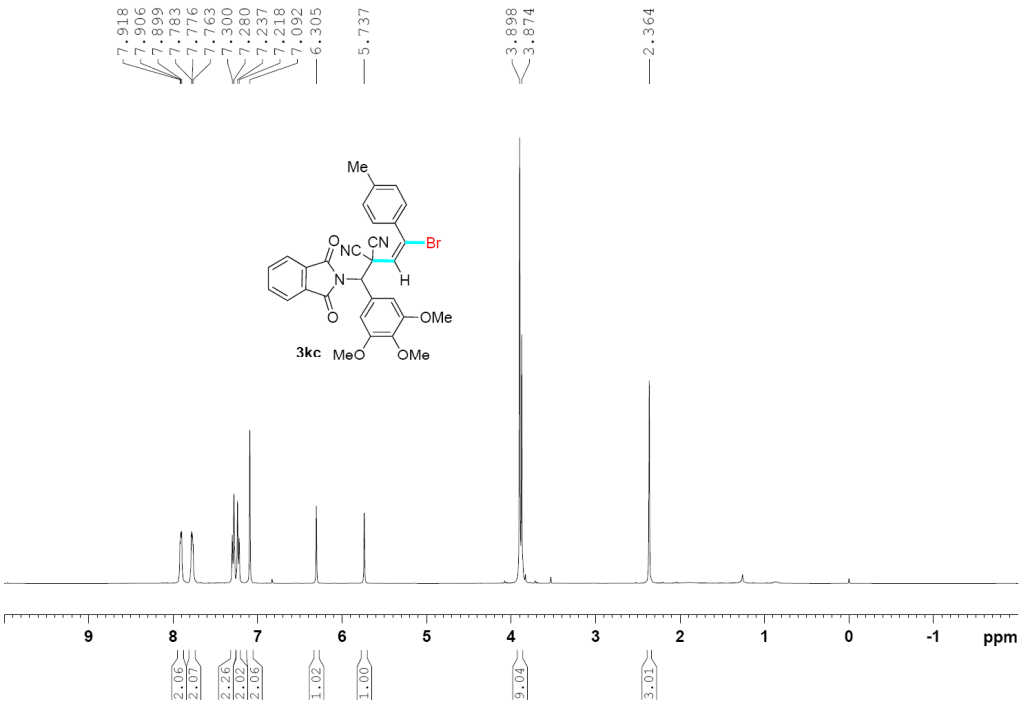
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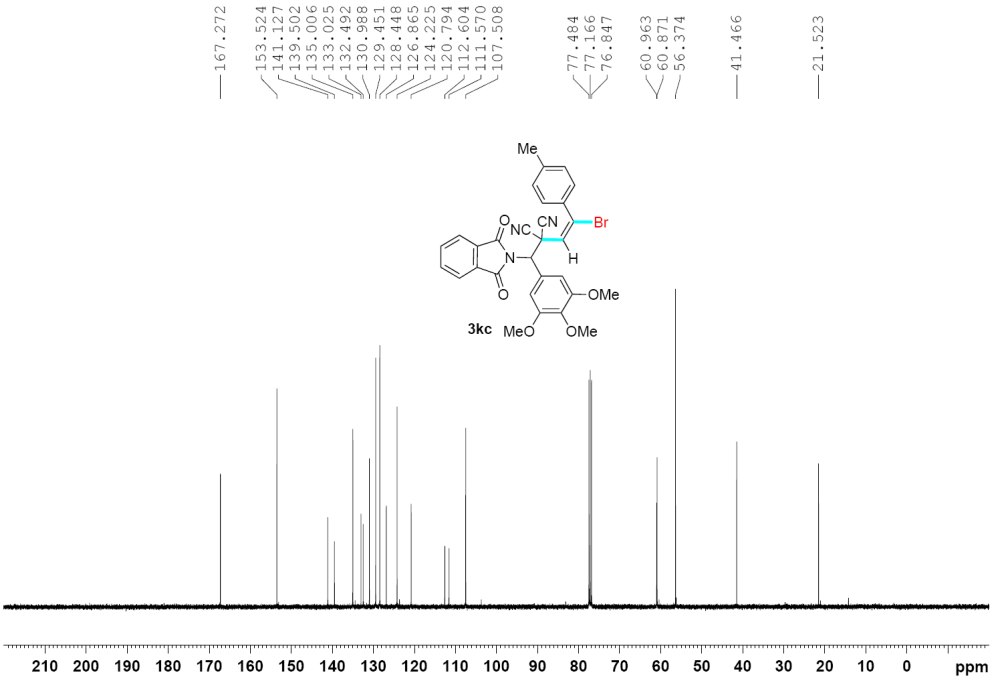
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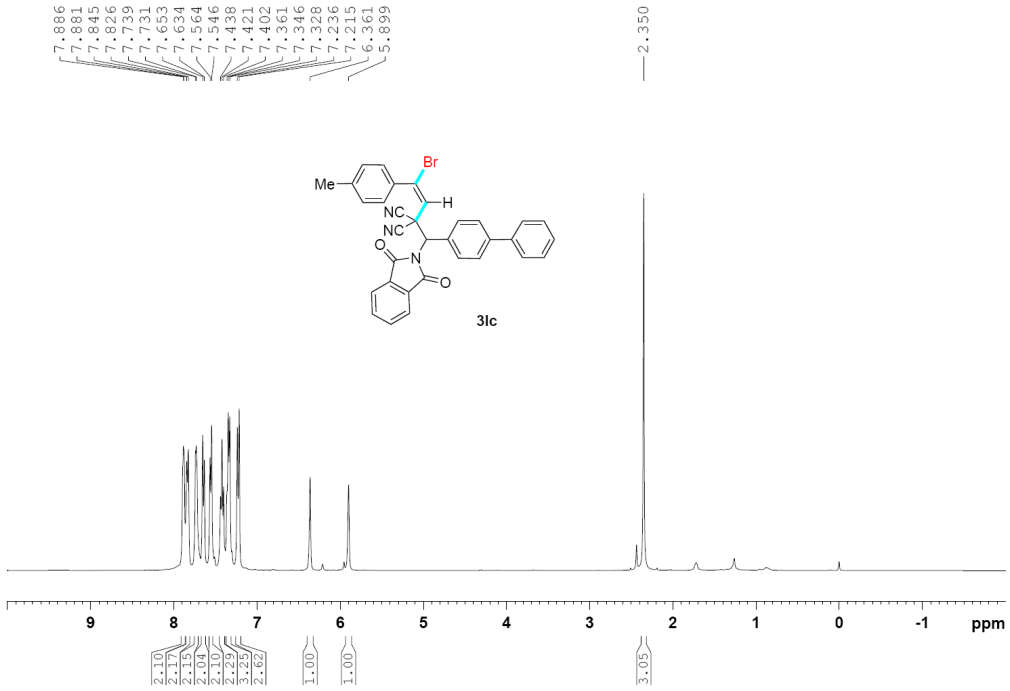
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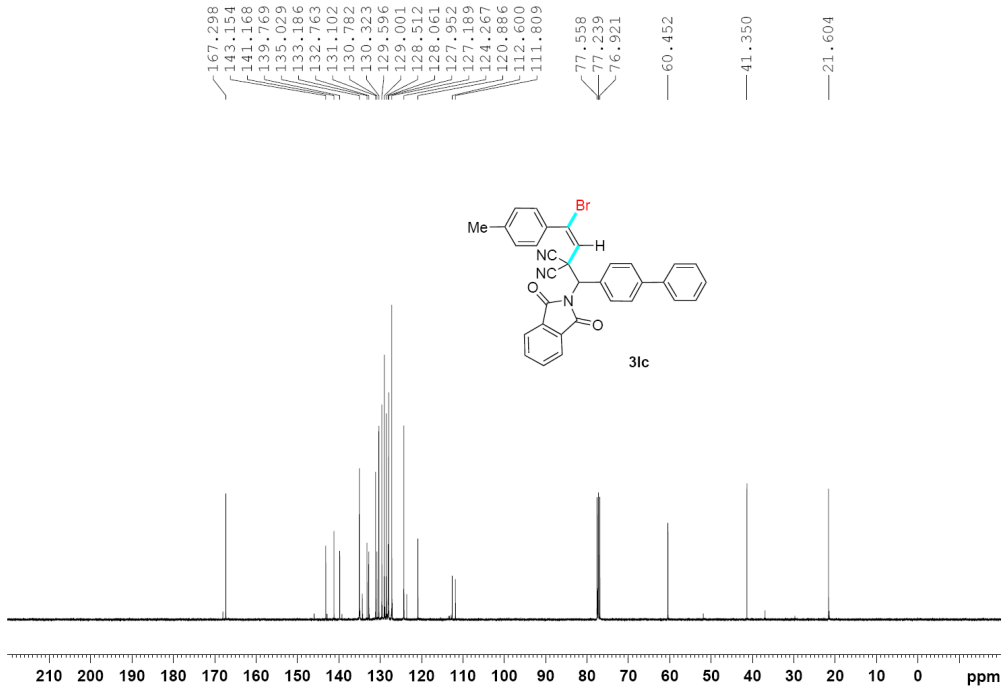
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