

# Supporting Information

## **Pd-Catalyzed Three-Component Decarboxylative Coupling Reactions Among Alkylidene Pyrazolones, Allyl Carbonates and Active Methylene Compounds**

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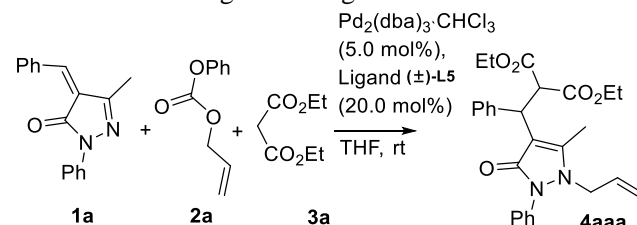
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## 1. General Information

Proton ( $^1\text{H}$ ) and carbon ( $^{13}\text{C}$ ) NMR spectra were recorded on 400 MHz instrument (400 MHz for  $^1\text{H}$  NMR, 100 MHz for  $^{13}\text{C}$  NMR) and calibrated using tetramethylsilane (TMS) as internal reference. High resolution mass spectra (HRMS) were recorded under electrospray ionization (ESI) conditions. The melting point of compounds was determined by a melting point instrument. Flash column chromatography was performed on silica gel (0.035-0.070 mm) by using compressed air. Thin layer chromatography (TLC) was carried out on 0.25 mm SDS silica gel coated glass plates (60F254). Eluted plates were visualized using a 254 nm UV lamp. Unless otherwise indicated, all reagents were commercially available and used without further purification. All solvents were distilled from the appropriate drying agents immediately before using. Alkylidene pyrazolones **1a–1g** were synthesized according to the reported procedures.<sup>1</sup> Allyl carbonates **2a–2h** were prepared according to literature procedures.<sup>2</sup>

## 2. Optimization of Coupling Reaction Conditions

**Table S1.** Screening of loading ratios of **1a/2a/3a**<sup>a</sup>



The reaction scheme shows the coupling of alkylidene pyrazolone **1a**, allyl carbonate **2a**, and diethyl malonate **3a** to form product **4aaa**. The reaction conditions are  $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$  (5.0 mol%), Ligand ( $\pm$ )-**L5** (20.0 mol%), THF, and room temperature (rt).

Entry	Ratio <b>1a</b> / <b>2a/3a</b> (mmol/mmol/mmol)	Time(h)	Yield <b>4aaa</b> <sup>b</sup> (%)
1	1:1:1	2	72
2	1:1:2	2	80
3	1:1.5:1	2	90
4	1:1.5:2	2	99
5	1:1.5:3	2	87

<sup>a</sup>Reactions were carried out with **1a**, **2a**, **3a**,  $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$  (0.005 mmol), ligand ( $\pm$ )-**L5** (0.02 mmol) in THF (1.5 mL) at the indicated loading ratios of **1a/2a/3a** at room temperature. <sup>b</sup>Isolated yield.

Under the reaction conditions of  $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$  and ligand ( $\pm$ )-**L5** in THF at room temperature, we examined the different loading ratios of **1a/2a/3a** for their effects on the decarboxylative coupling reaction of alkylidene pyrazolone **1a**, allyl carbonate **2a** and diethyl malonate **3a** as depicted in Table S1.

## 3. Control Reactions for Preliminary Investigations on Coupling Reaction Mechanism

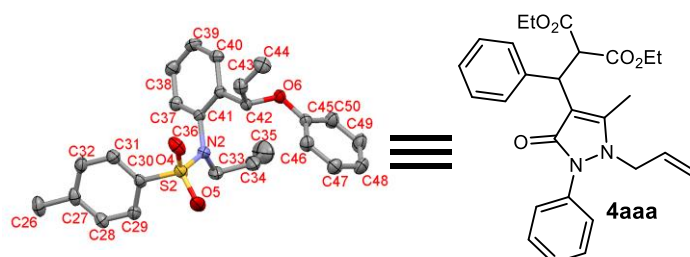
**Table S2.** Screening of allyl carbonates<sup>a</sup>

Entry	R <sup>1</sup>	Time	Yield <sup>b</sup> (%)
1	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	12 h	55
2	4-MeC <sub>6</sub> H <sub>4</sub>	8 h	73
3	4-MeOC <sub>6</sub> H <sub>4</sub>	0.5 h	83
4	Me	10 min	90

<sup>a</sup> Reactions were carried out with **1a** (0.1 mmol), **2** (0.15 mmol), **3a** (0.2 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> CHCl<sub>3</sub> (0.005 mmol), ligand (±)-**L5** (0.02 mmol) in THF ( 1.5 mL ) at room temperature. <sup>b</sup> Isolated yield.

Under the reaction conditions of Pd<sub>2</sub>(dba)<sub>3</sub> CHCl<sub>3</sub> and ligand (±)-**L5** in THF at room temperature, we explored in situ formed base R<sup>1</sup>O<sup>-</sup> for their effects on the decarboxylative coupling reaction of alkylidene pyrazolone **1a**, allyl carbonates **2** and diethyl malonate **3a** as depicted in Table S2.

#### 4. X-Ray Crystallographic Analysis of Products 4aaa

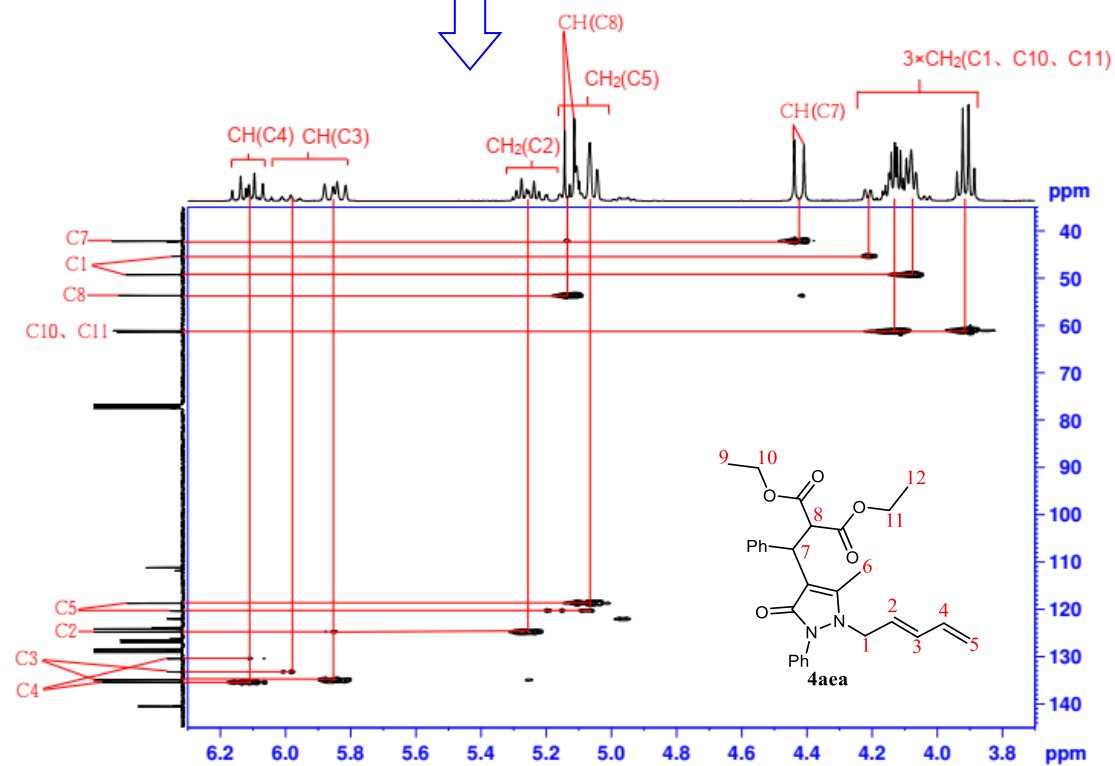
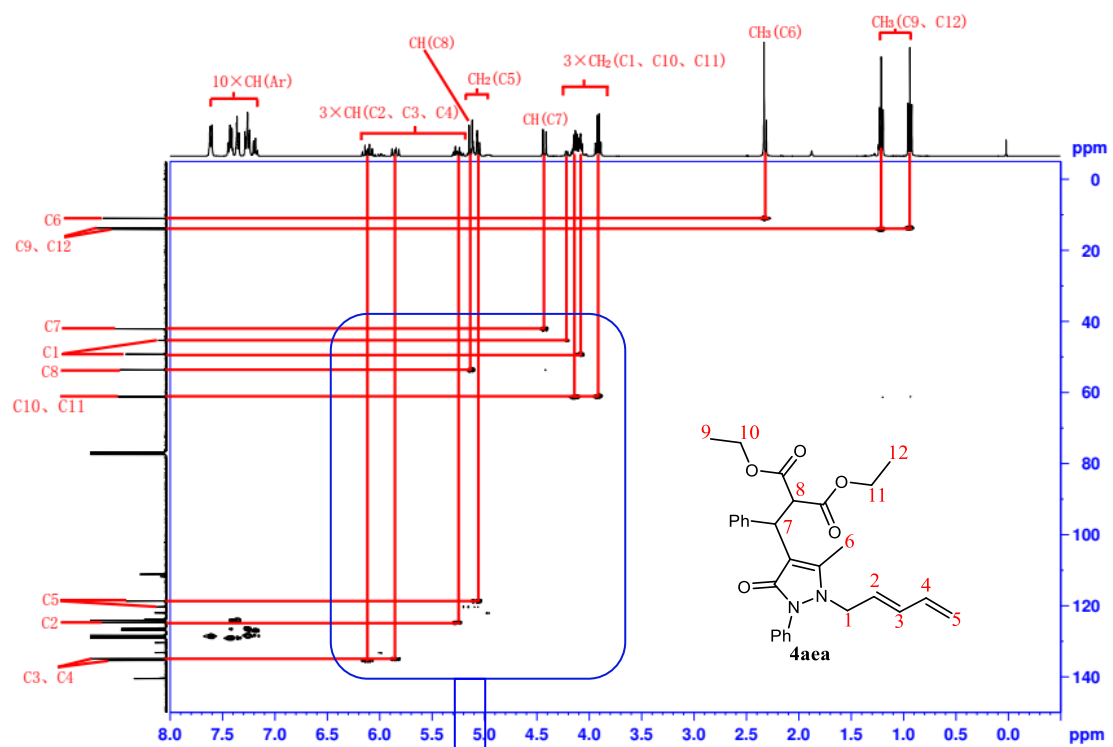


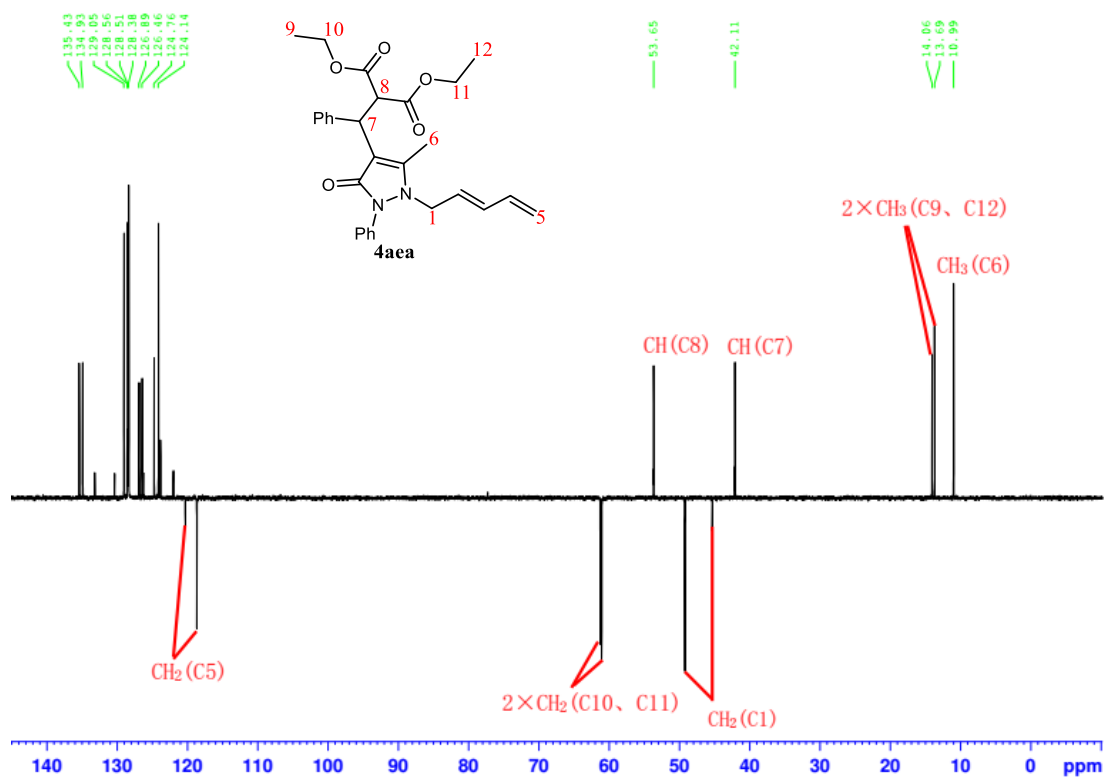
**Figure 1.** X-ray single crystal structure of **4aaa** (with thermal ellipsoids shown at the 50% probability level)

Identification code	<b>4aaa</b>
Empirical formula	C <sub>27</sub> H <sub>30</sub> N <sub>2</sub> O <sub>5</sub>
Formula weight	462.53
Temperature/K	113.15
Crystal system	monoclinic
Space group	I2/a
a/Å	22.1744(9)
b/Å	7.6768(3)
c/Å	29.6328(13)

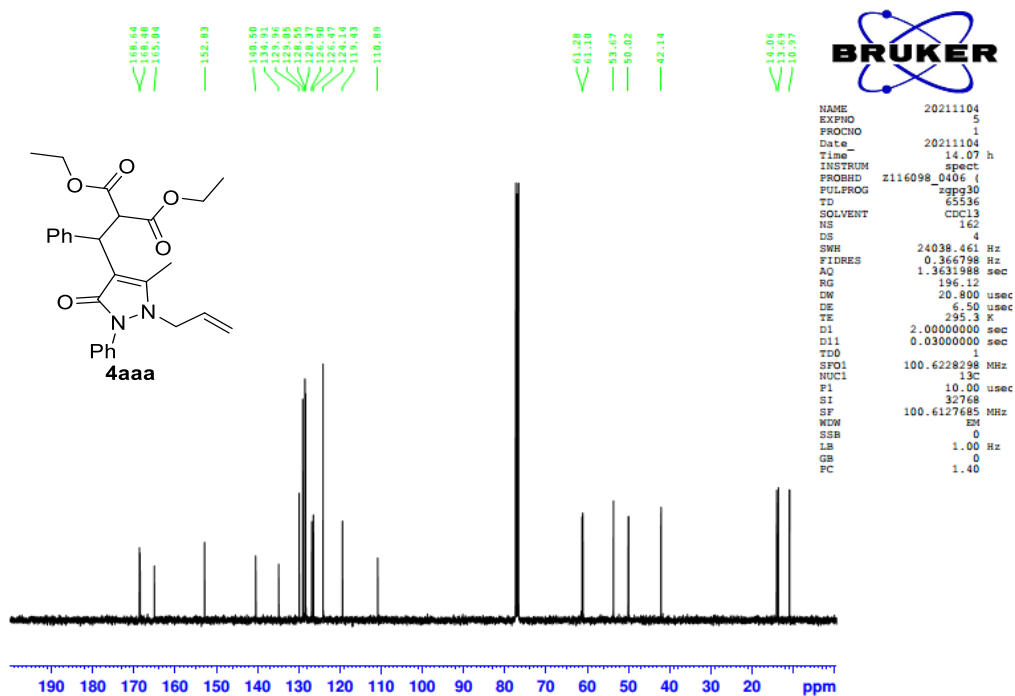
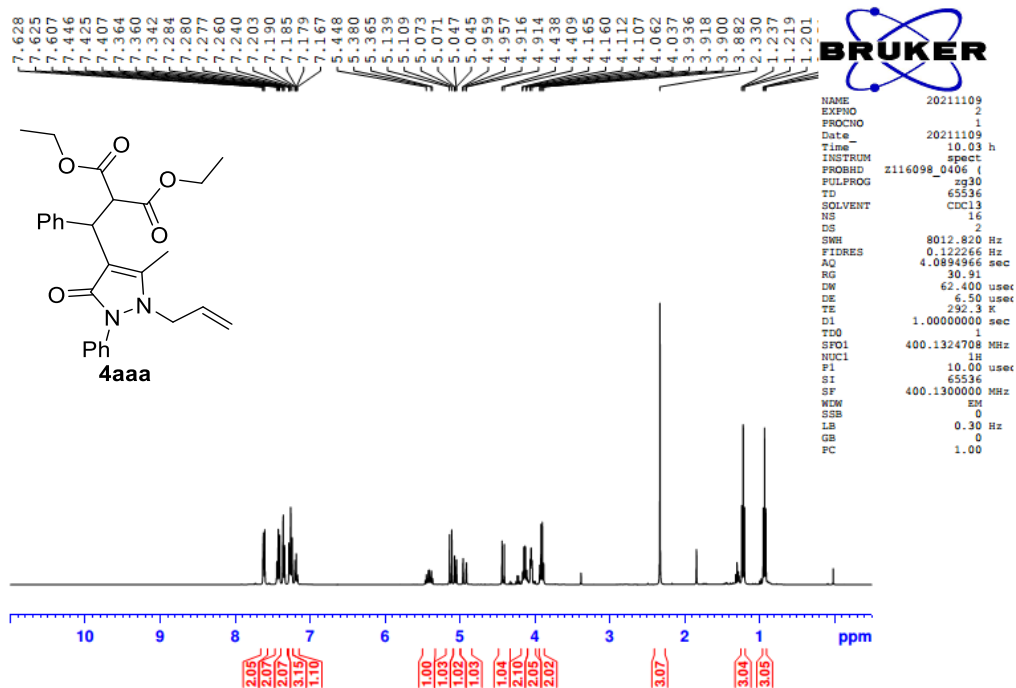
$\alpha/^\circ$	90
$\beta/^\circ$	98.428(4)
$\gamma/^\circ$	90
Volume/ $\text{\AA}^3$	4989.9(4)
Z	8
$\rho_{\text{calc}}/\text{cm}^3$	1.231
$\mu/\text{mm}^{-1}$	0.085
F(000)	1968.0
Crystal size/ $\text{mm}^3$	$0.22 \times 0.2 \times 0.16$
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ )
$2\Theta$ range for data collection/ $^\circ$	4.954 to 56.562
Index ranges	$-29 \leq h \leq 29, -9 \leq k \leq 10, -39 \leq l \leq 38$
Reflections collected	25550
Independent reflections	6133 [ $R_{\text{int}} = 0.0727, R_{\text{sigma}} = 0.0548$ ]
Data/restraints/parameters	6133/0/311
Goodness-of-fit on $F^2$	1.024
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0586, wR_2 = 0.1347$
Final R indexes [all data]	$R_1 = 0.0878, wR_2 = 0.1531$
Largest diff. peak/hole / $e \text{\AA}^{-3}$	0.80/-0.33

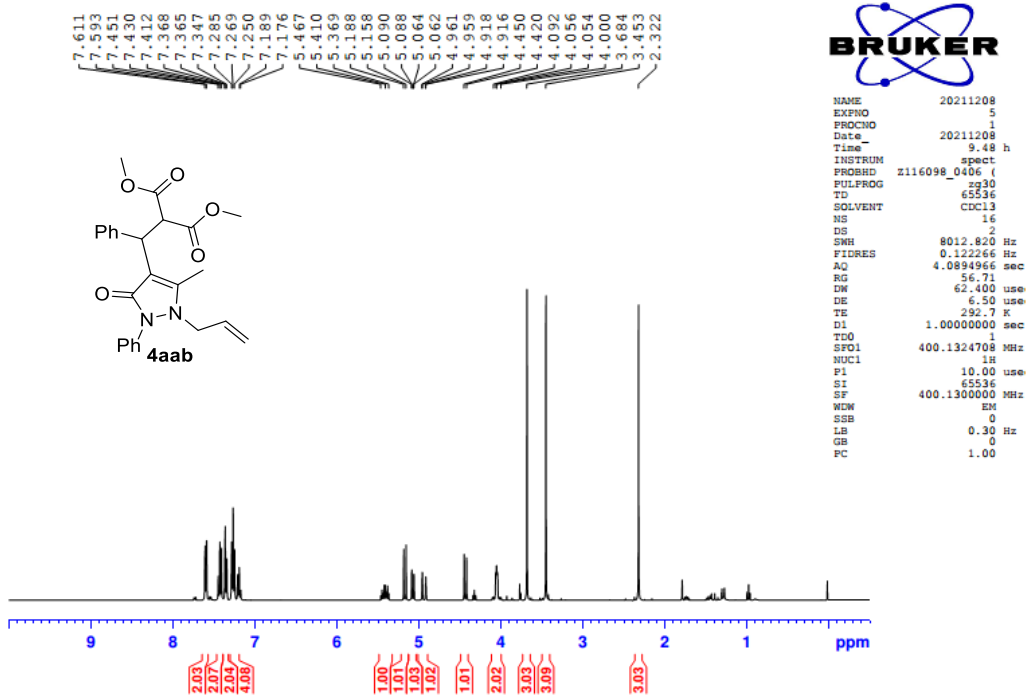
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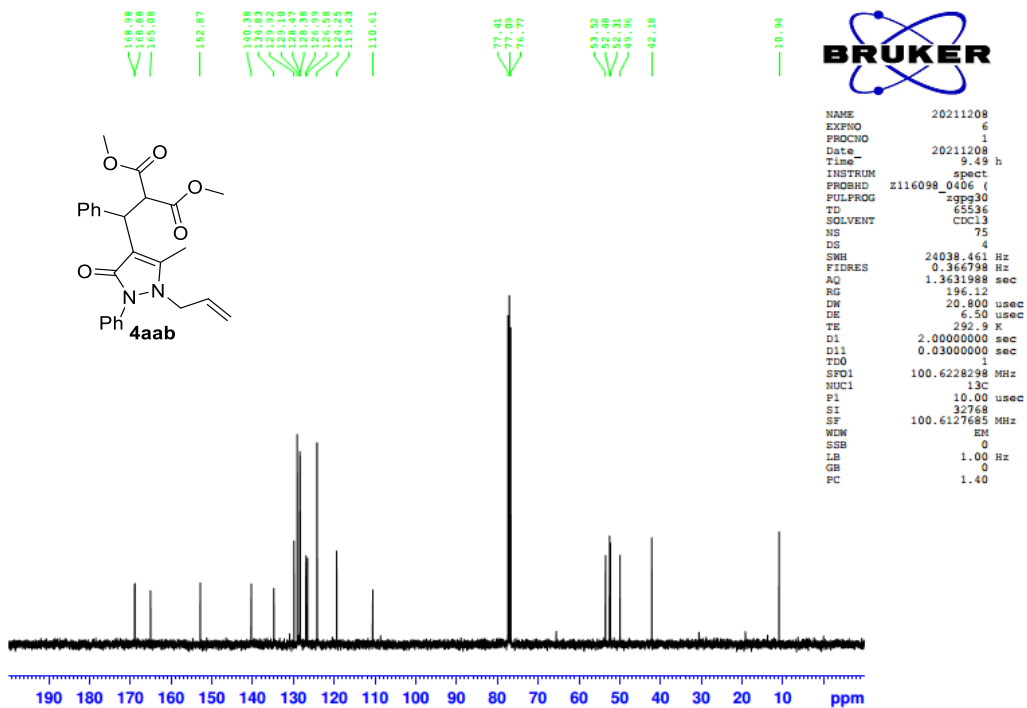
## 6. NMR Spectra of Products of 4-6





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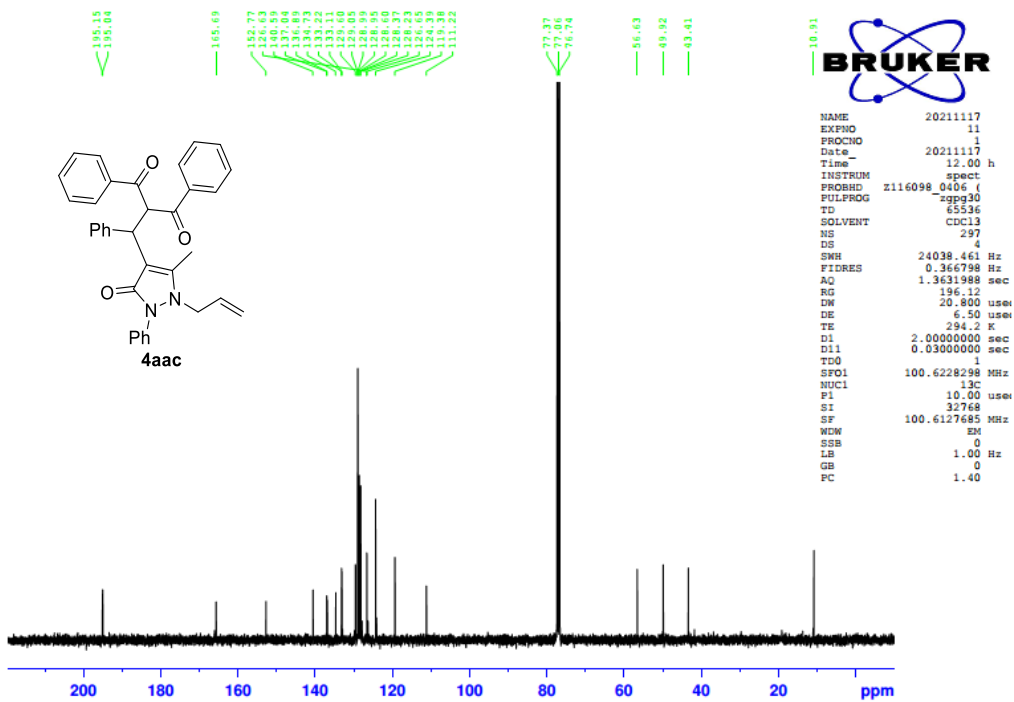
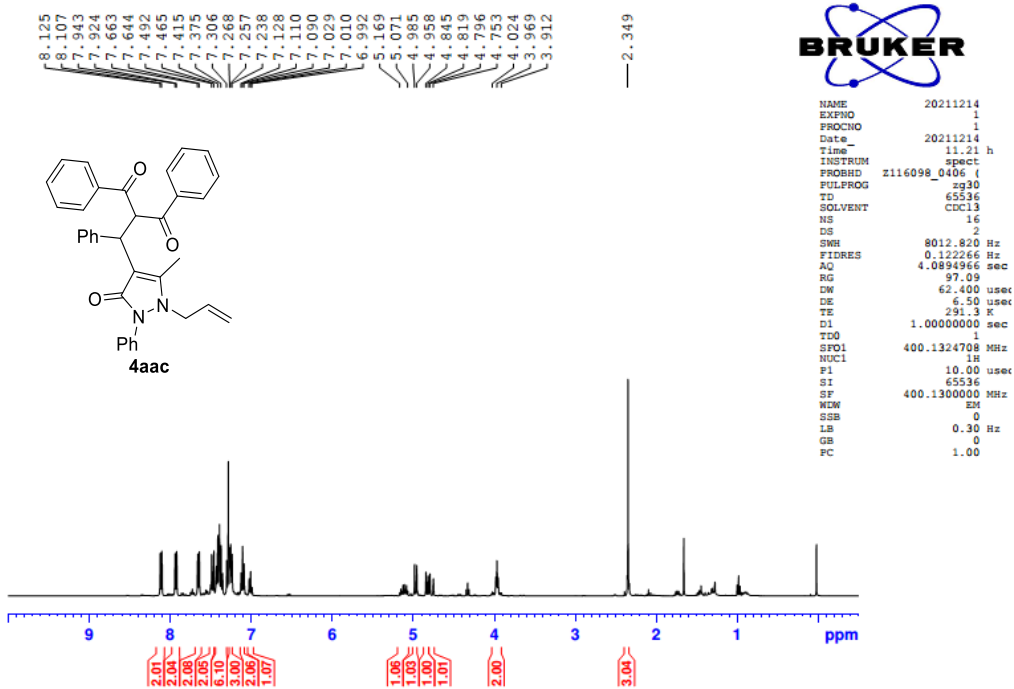
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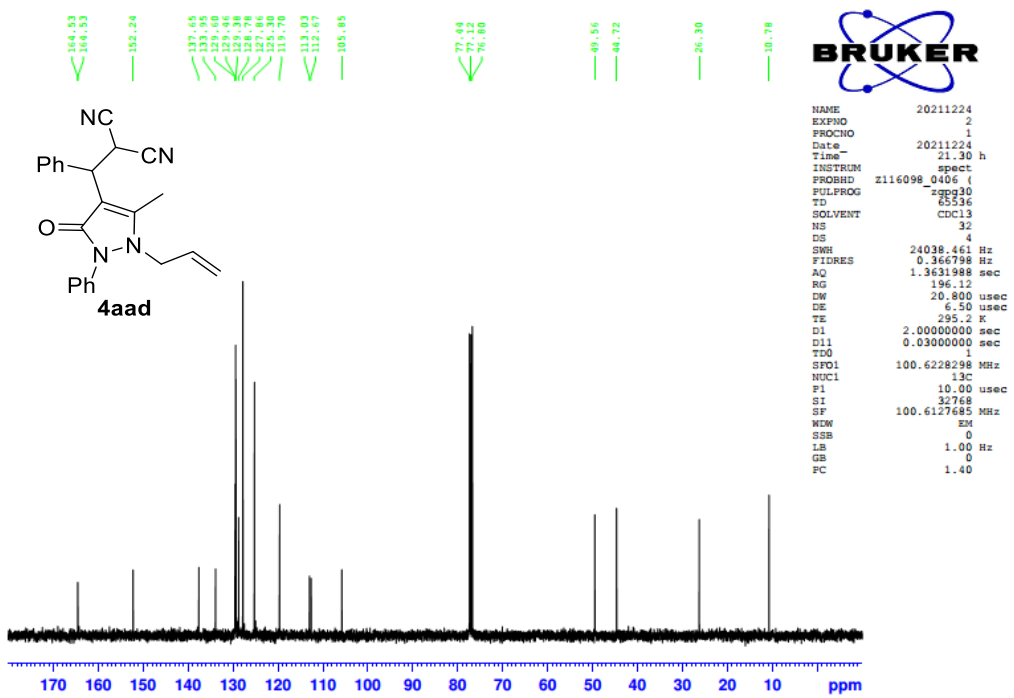
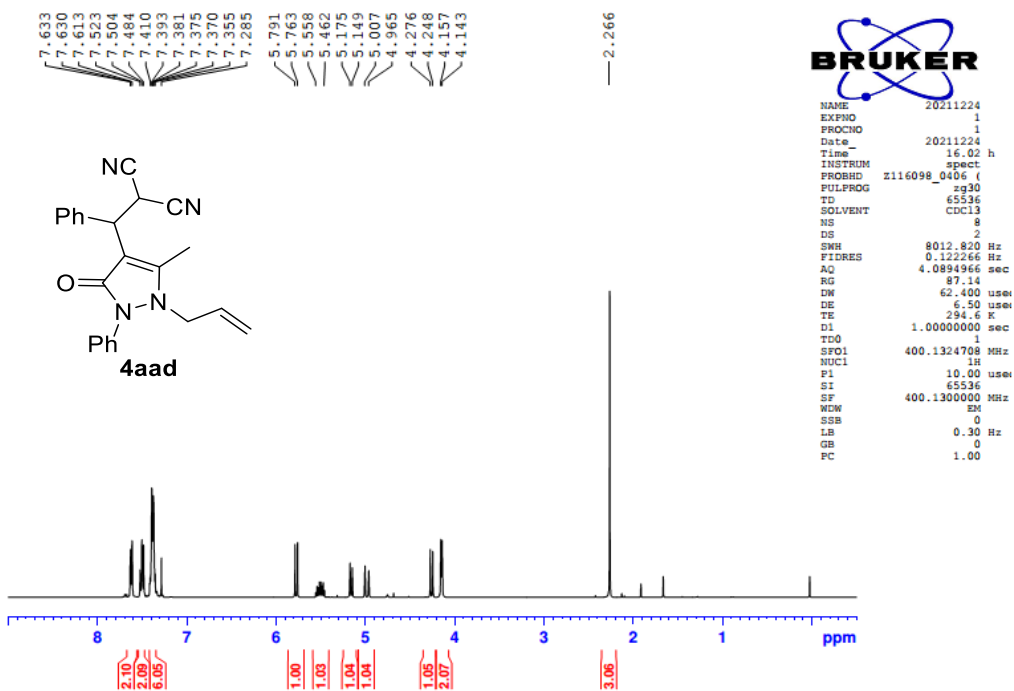


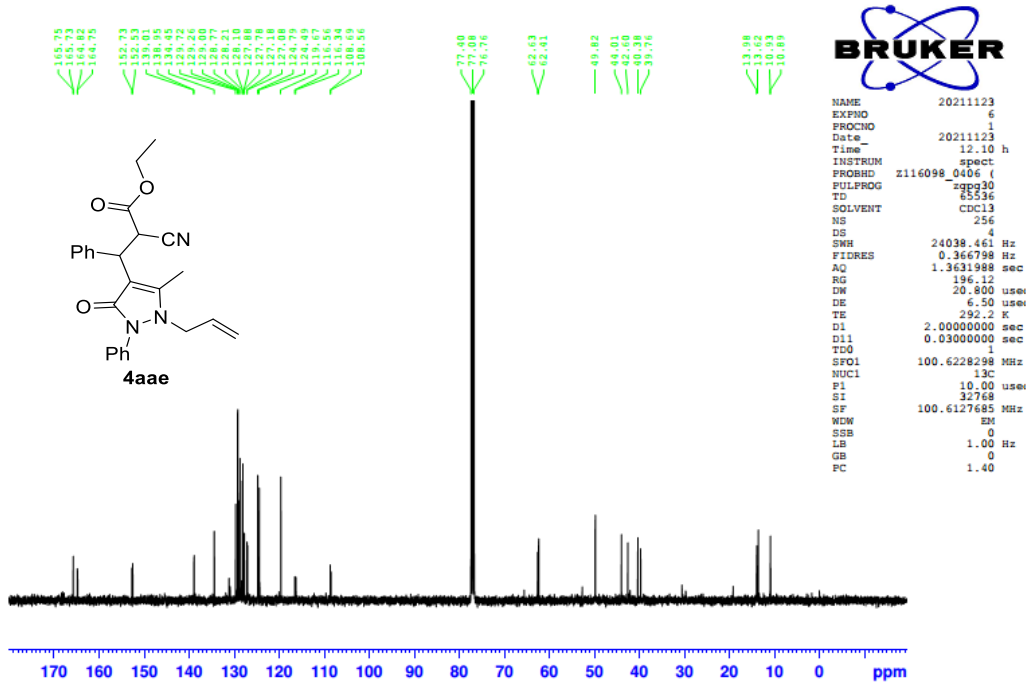
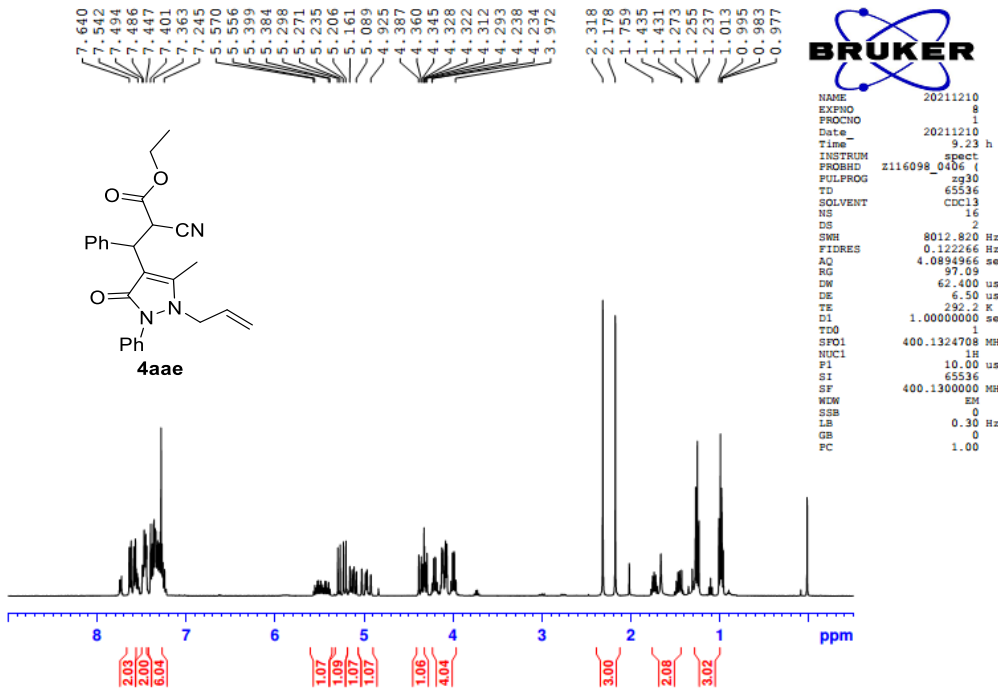
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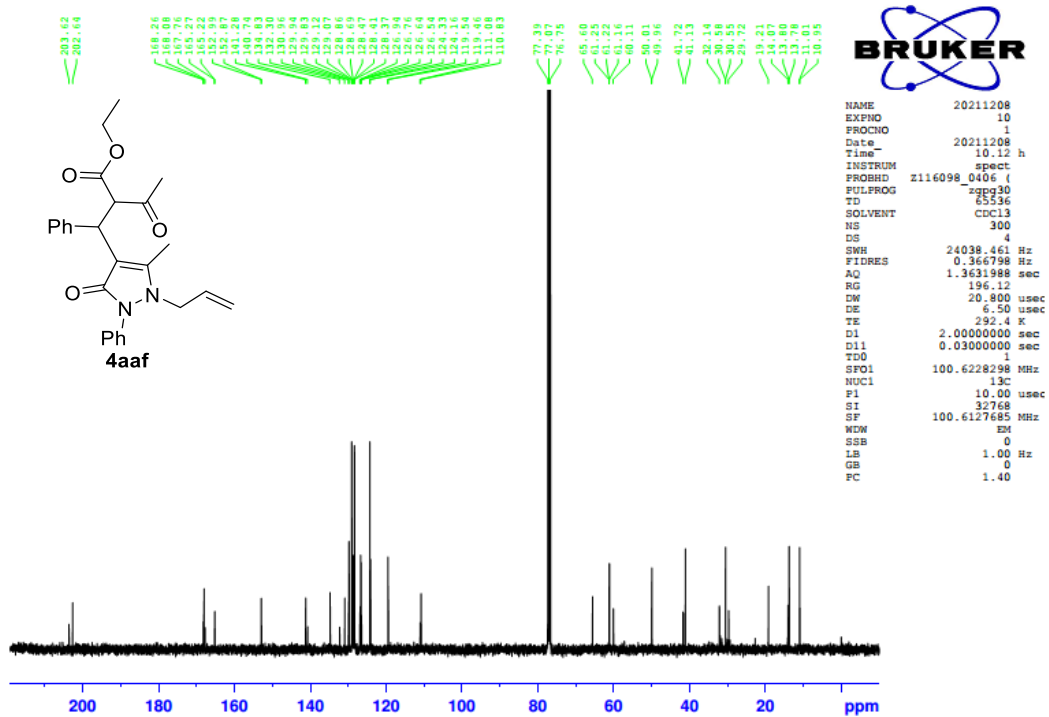
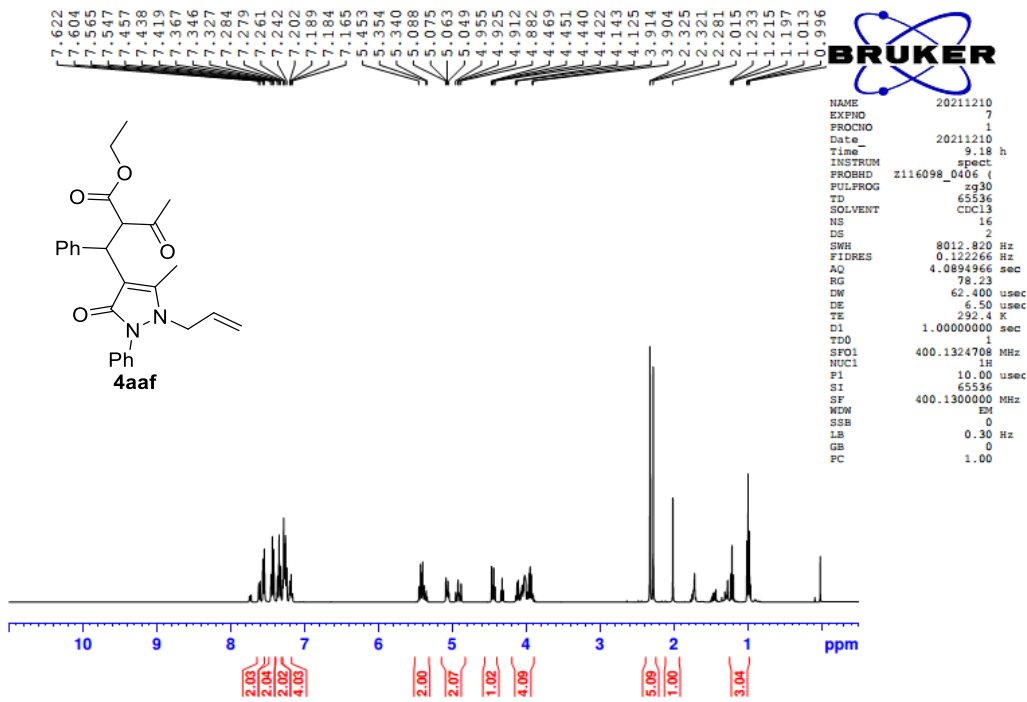
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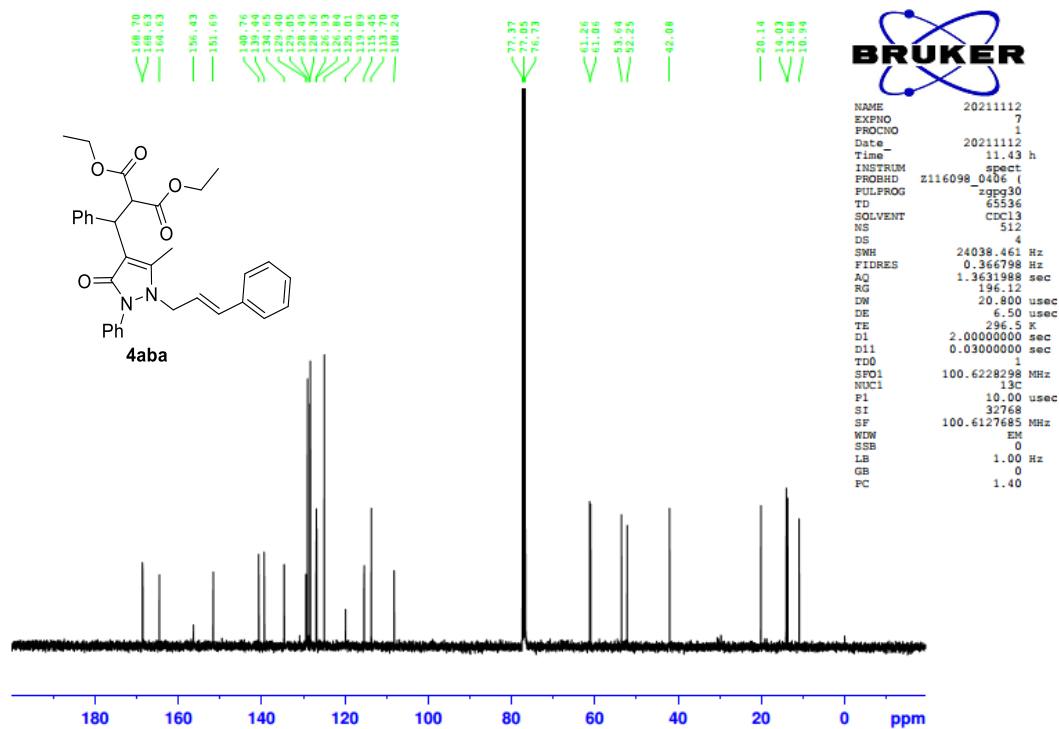
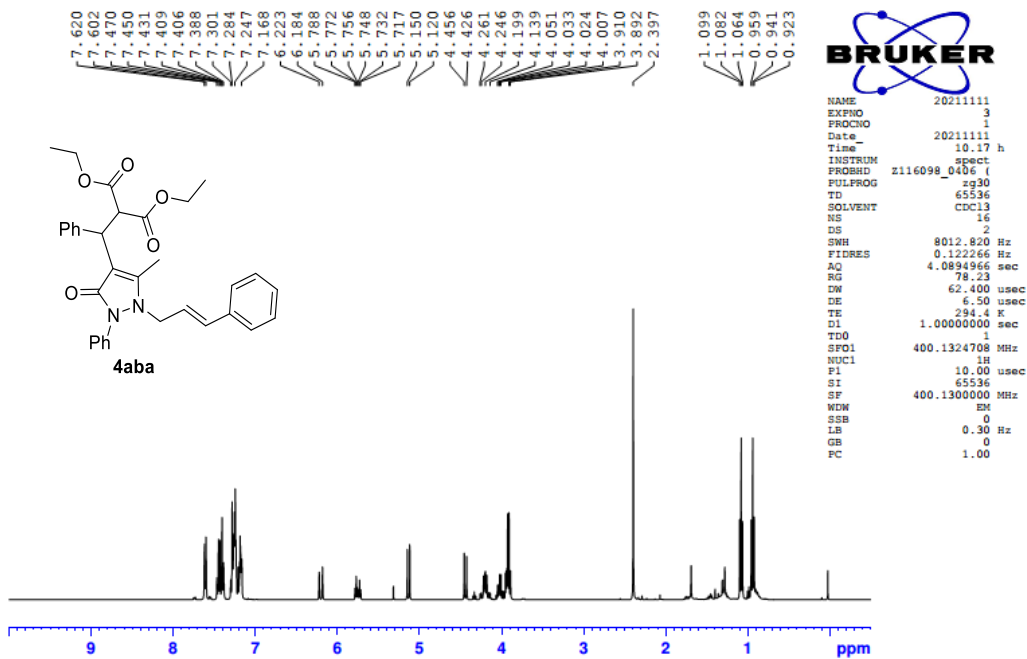


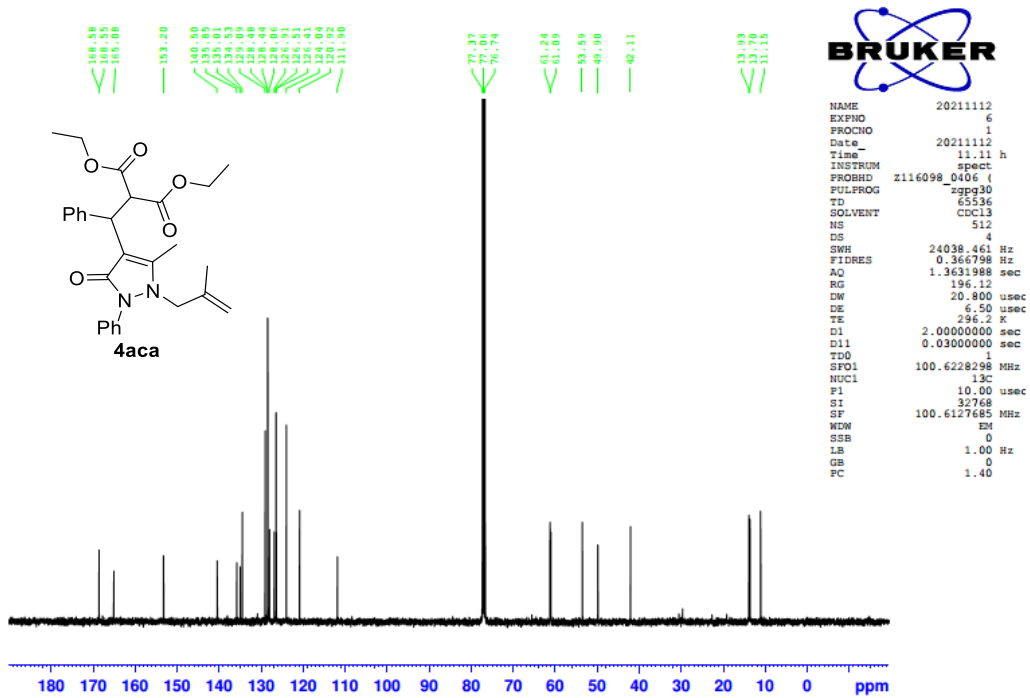
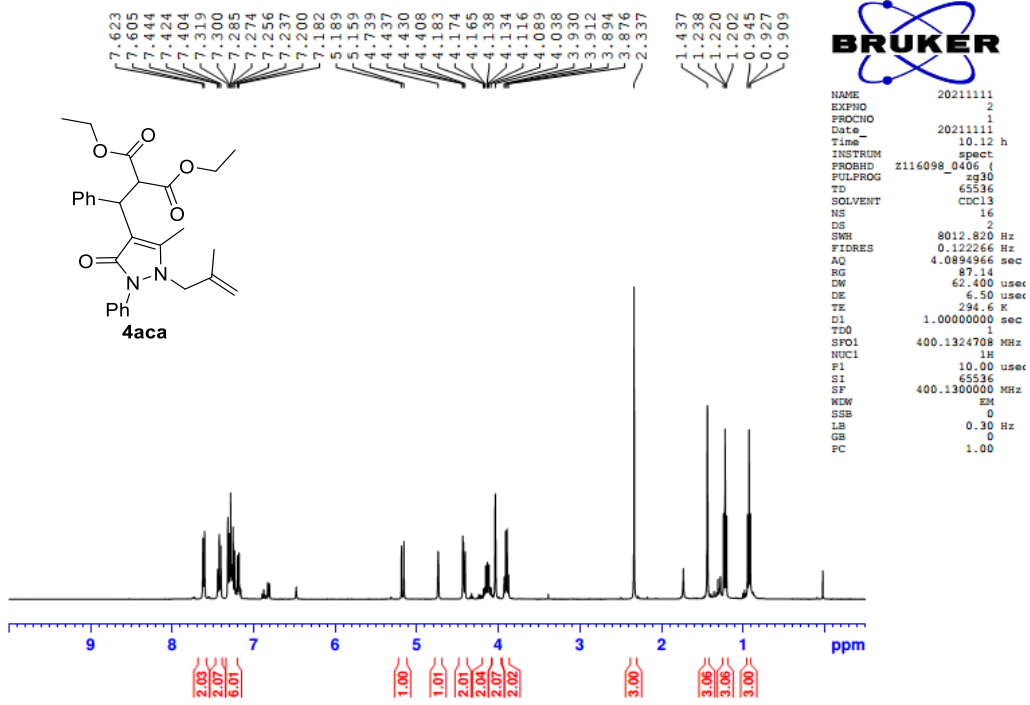


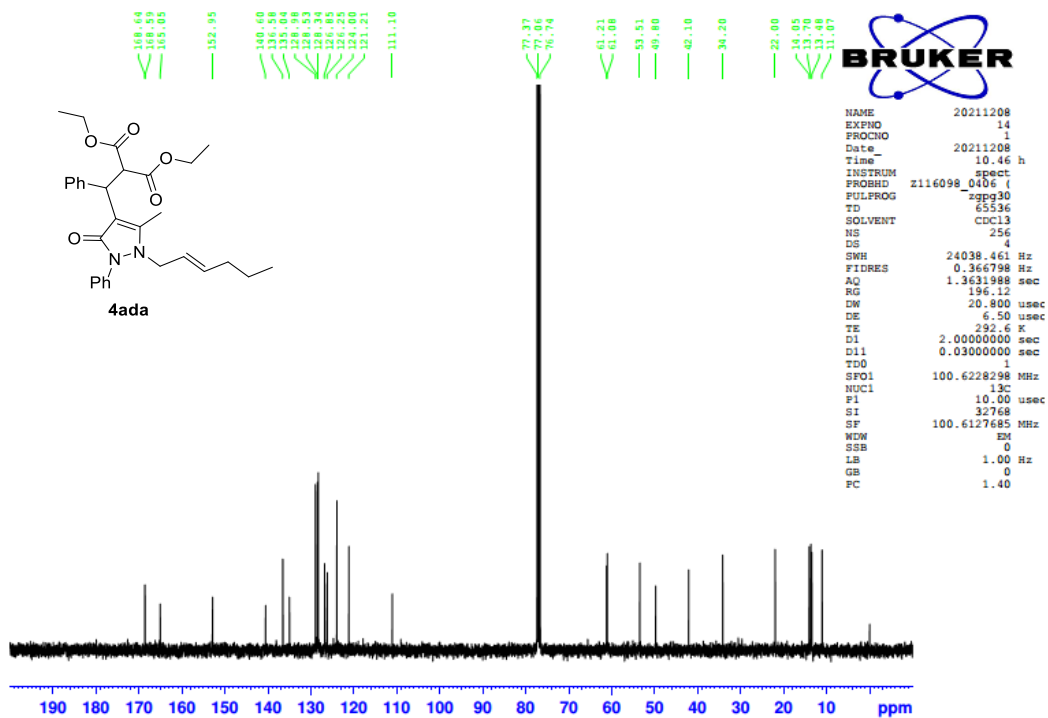
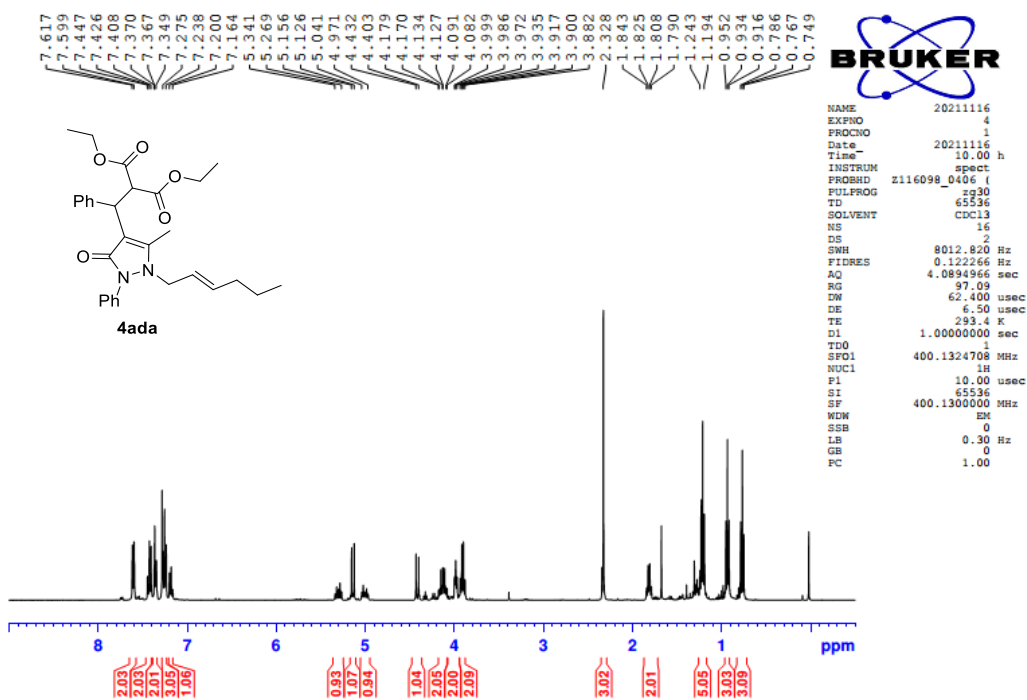


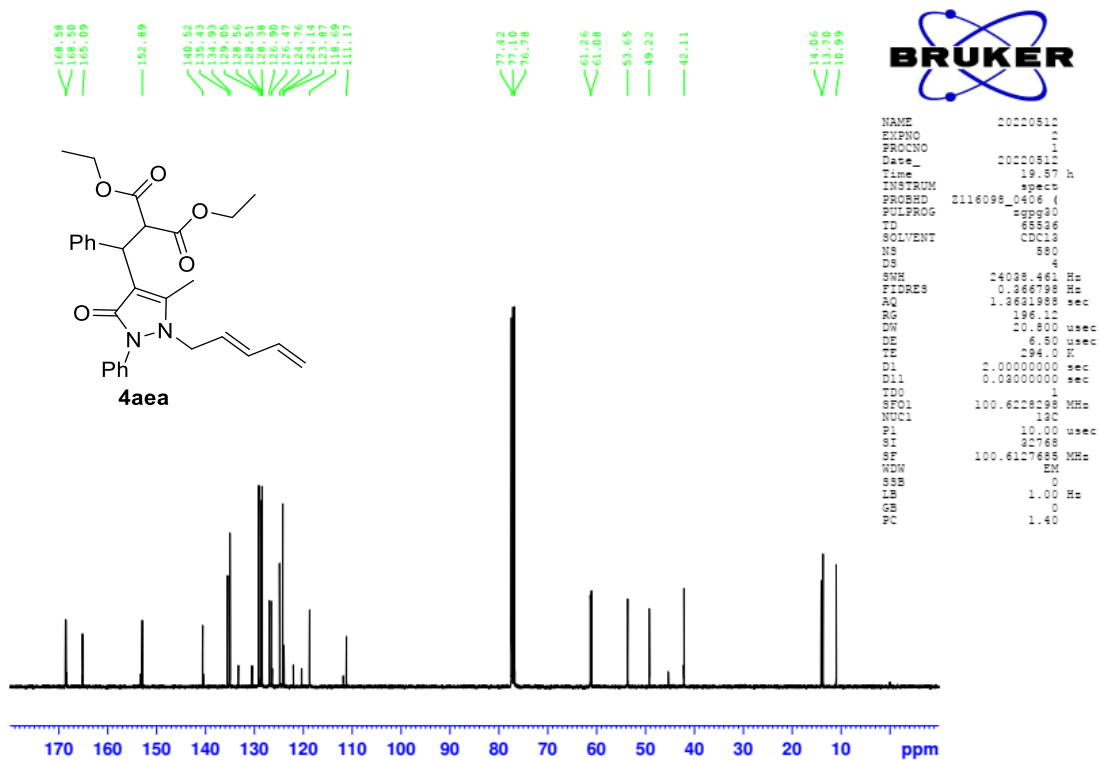
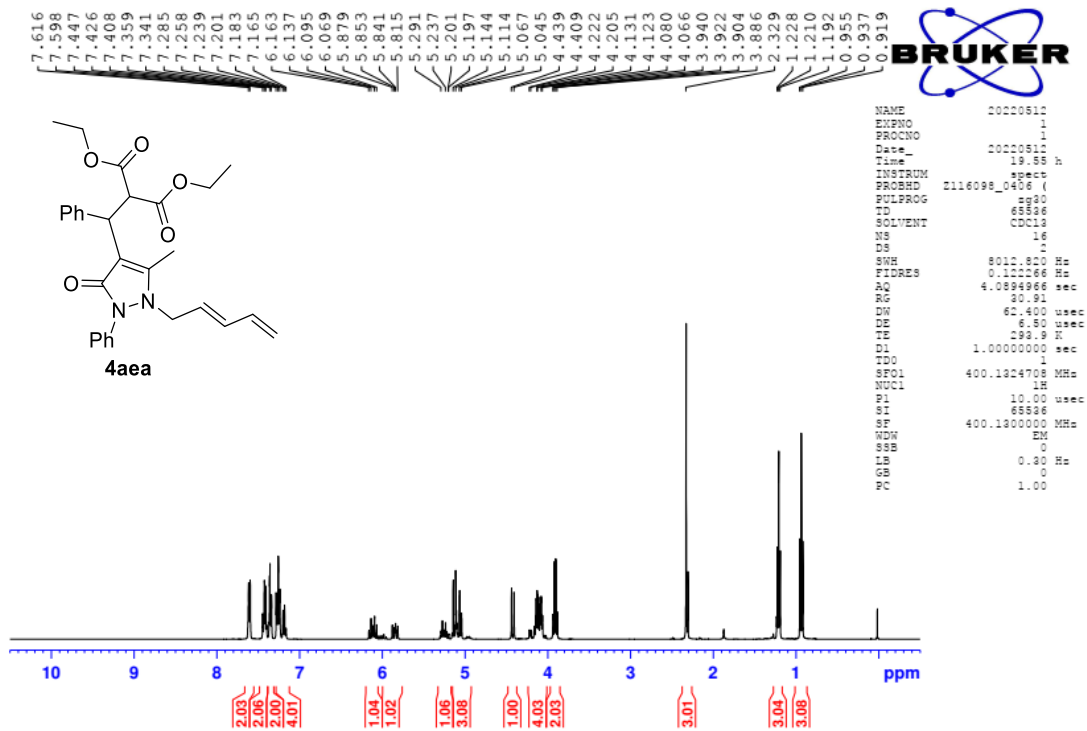




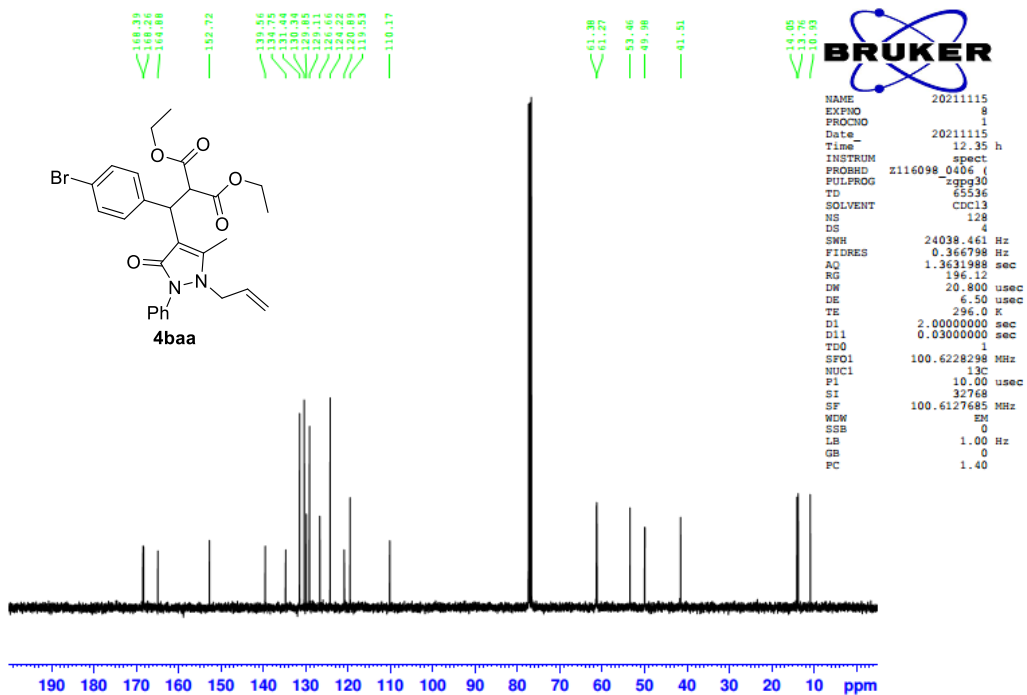
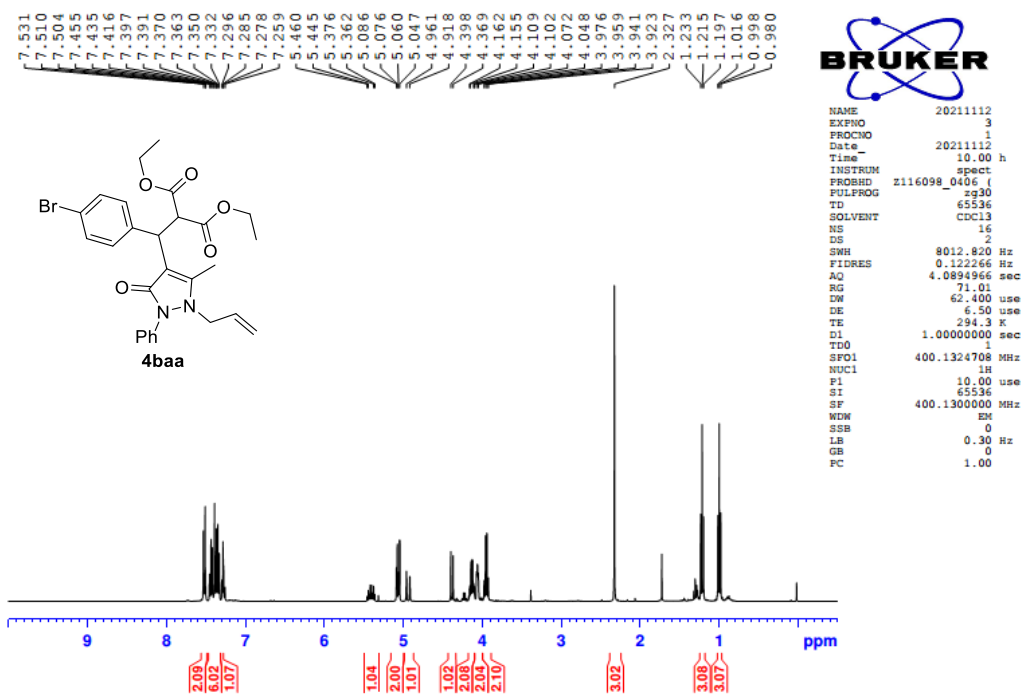


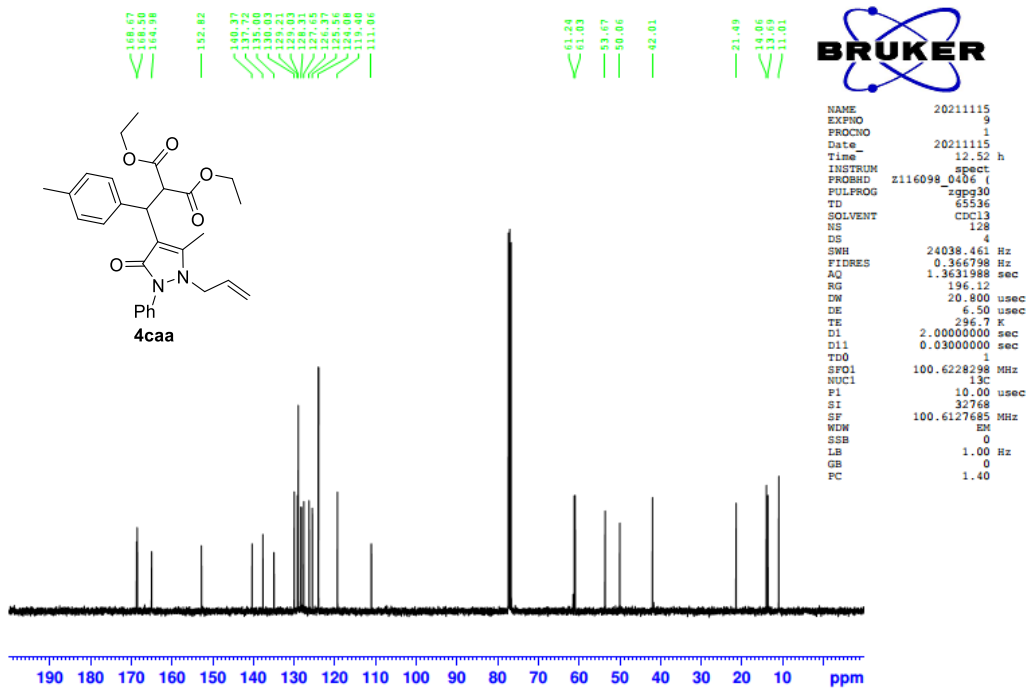
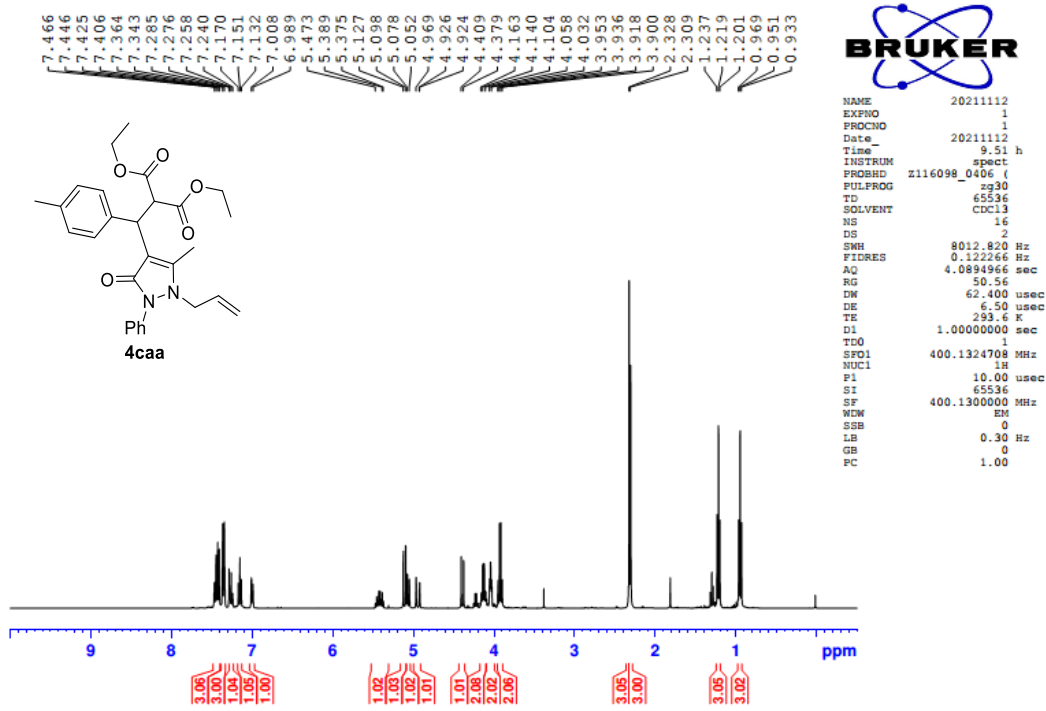


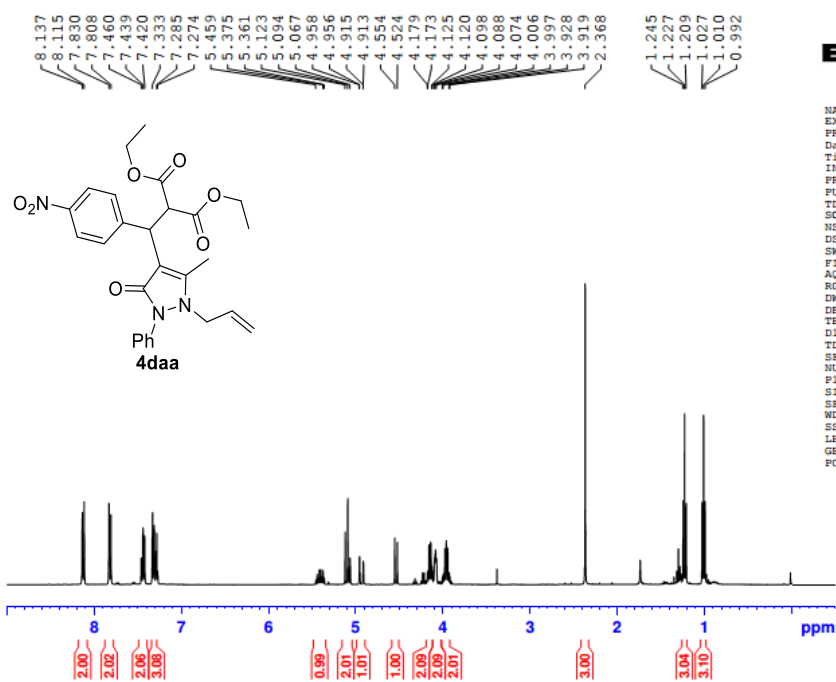






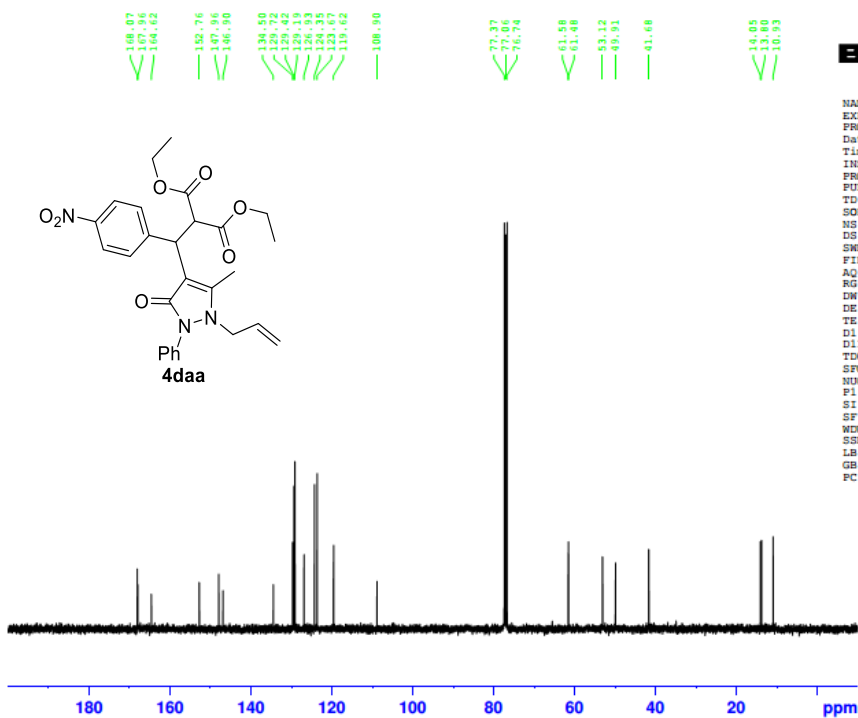






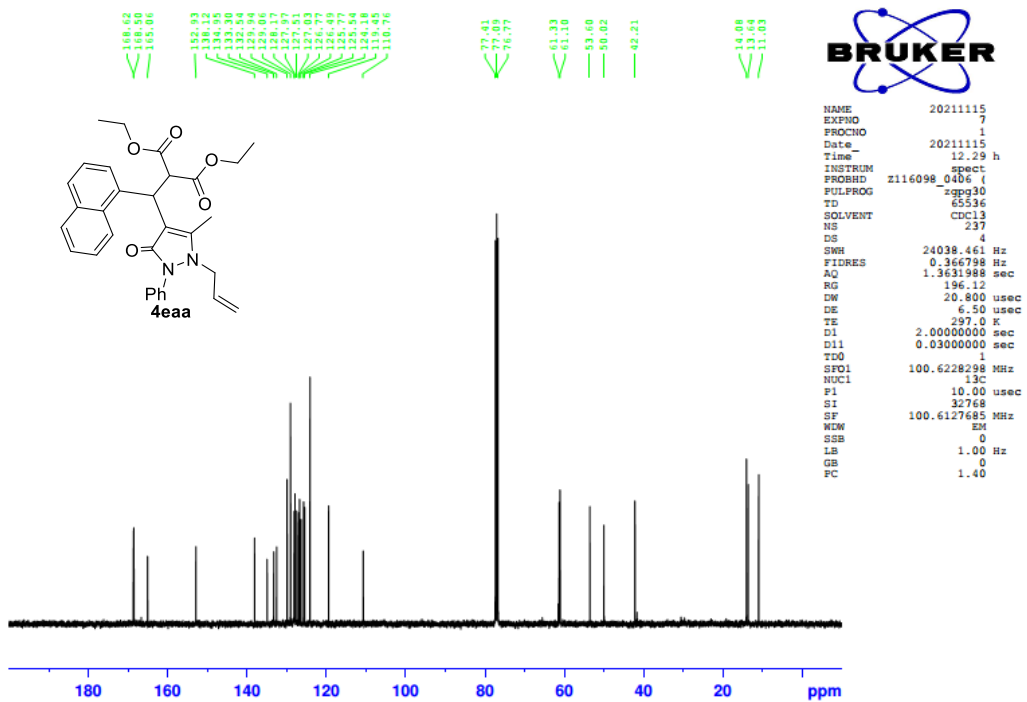
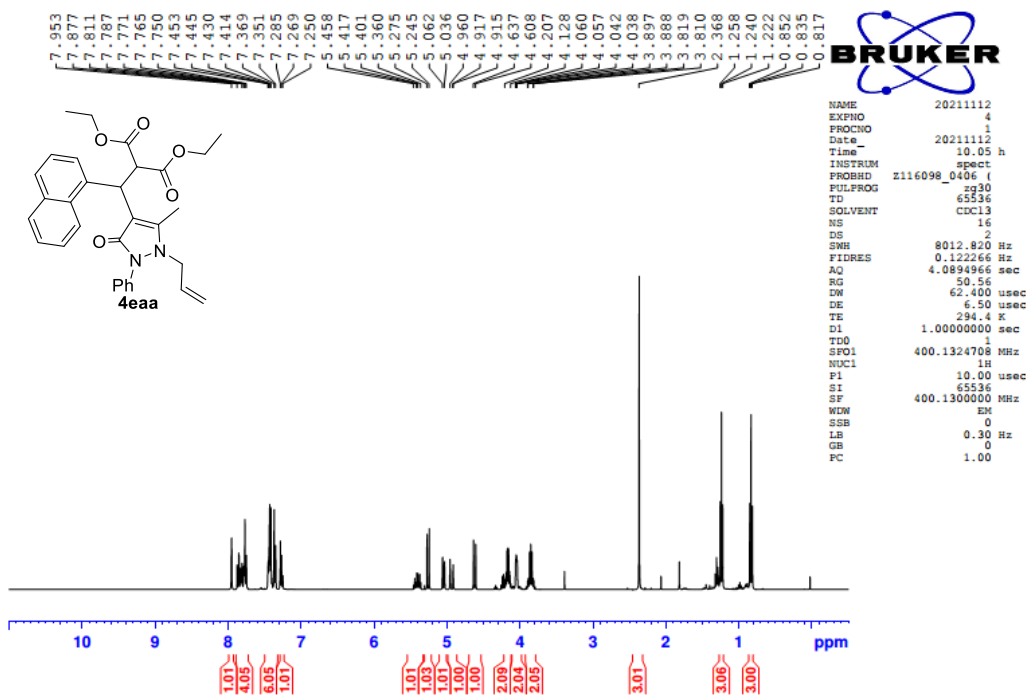
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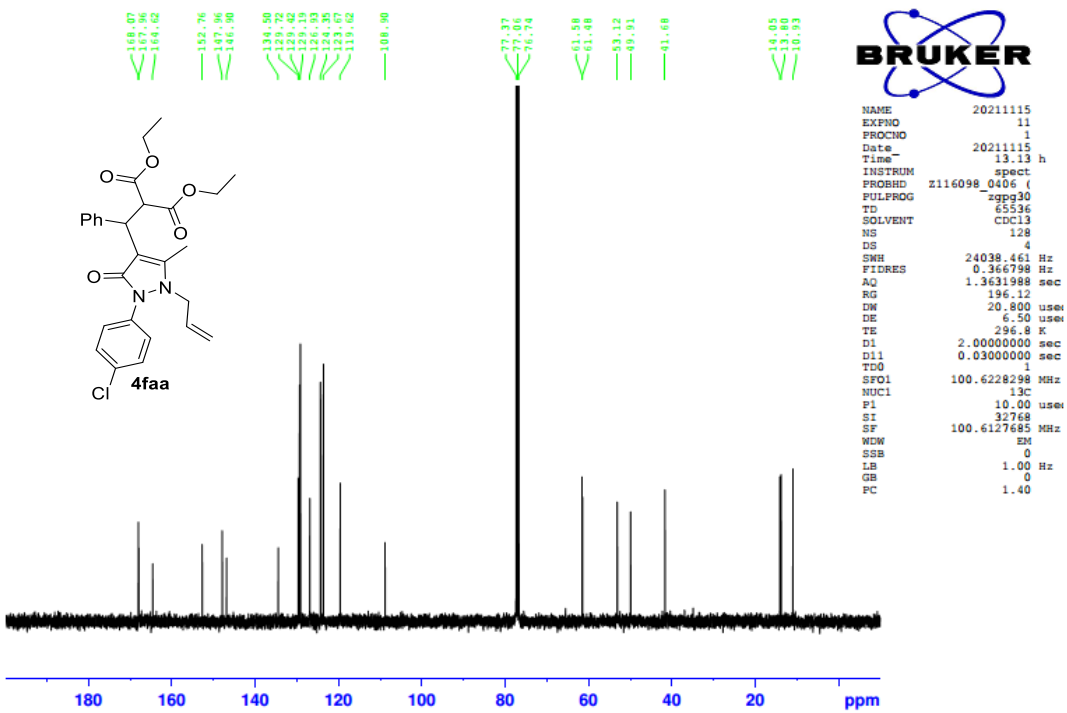
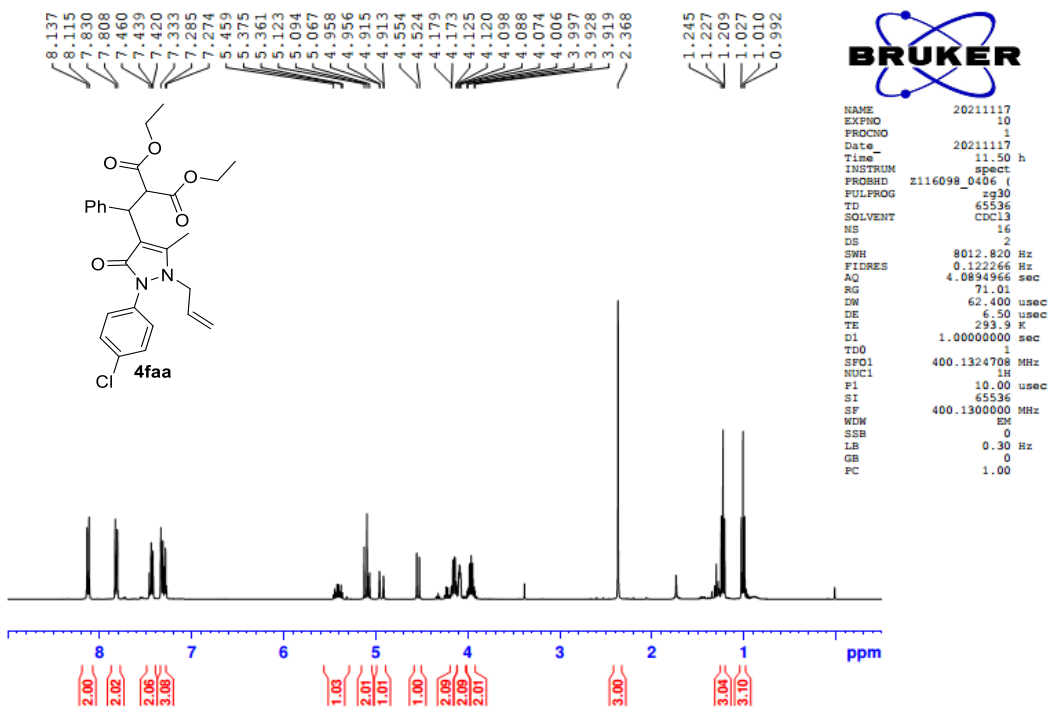
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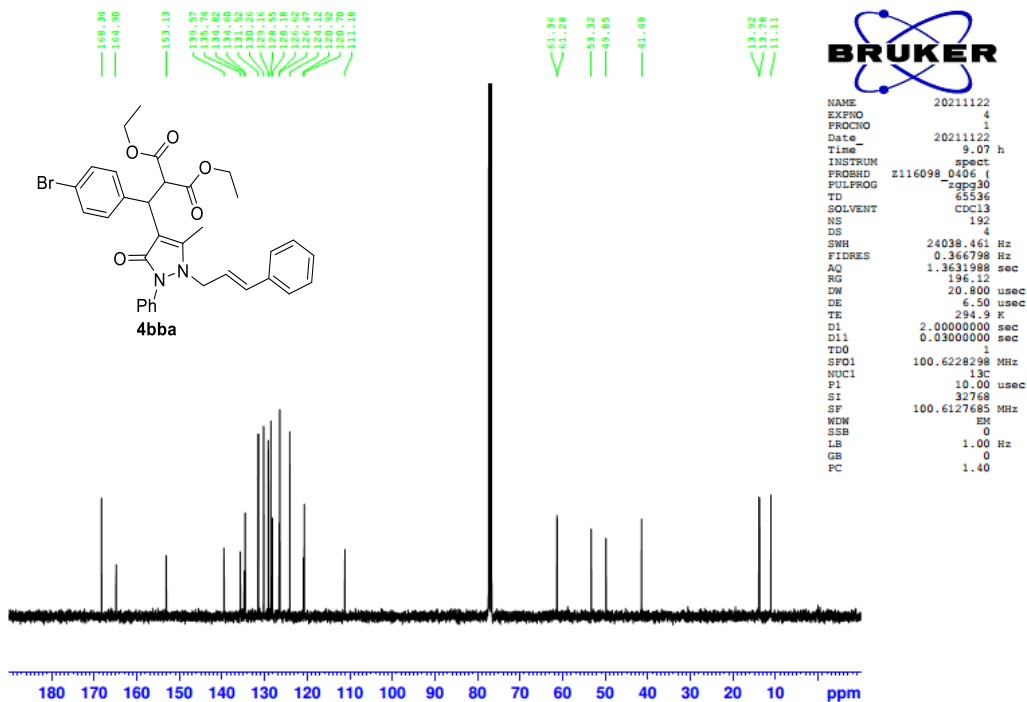
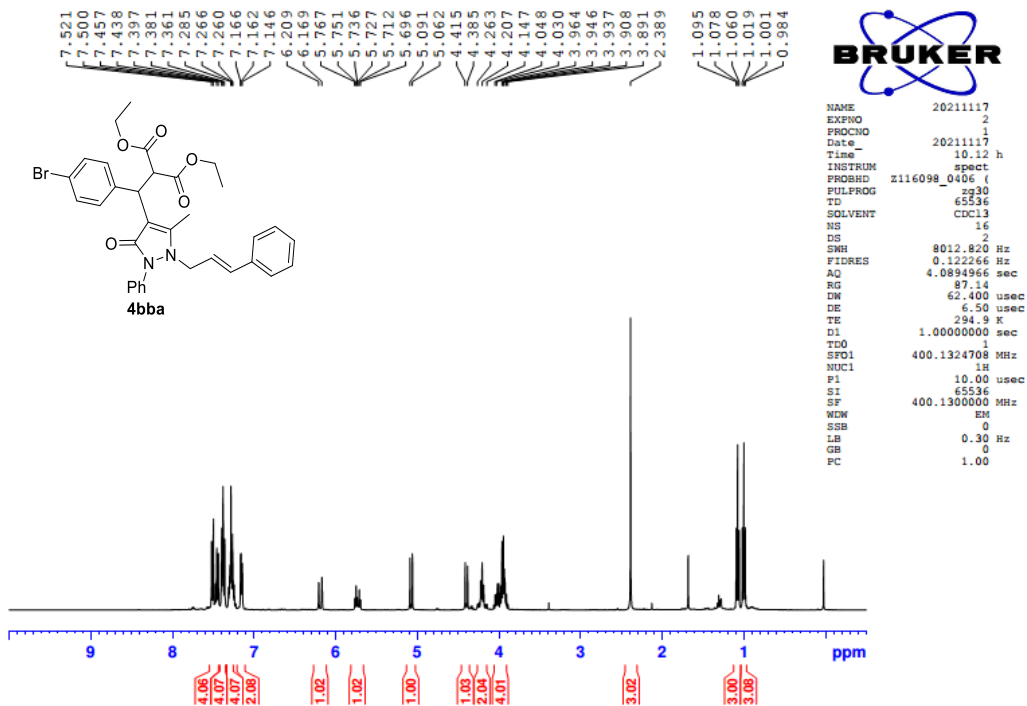


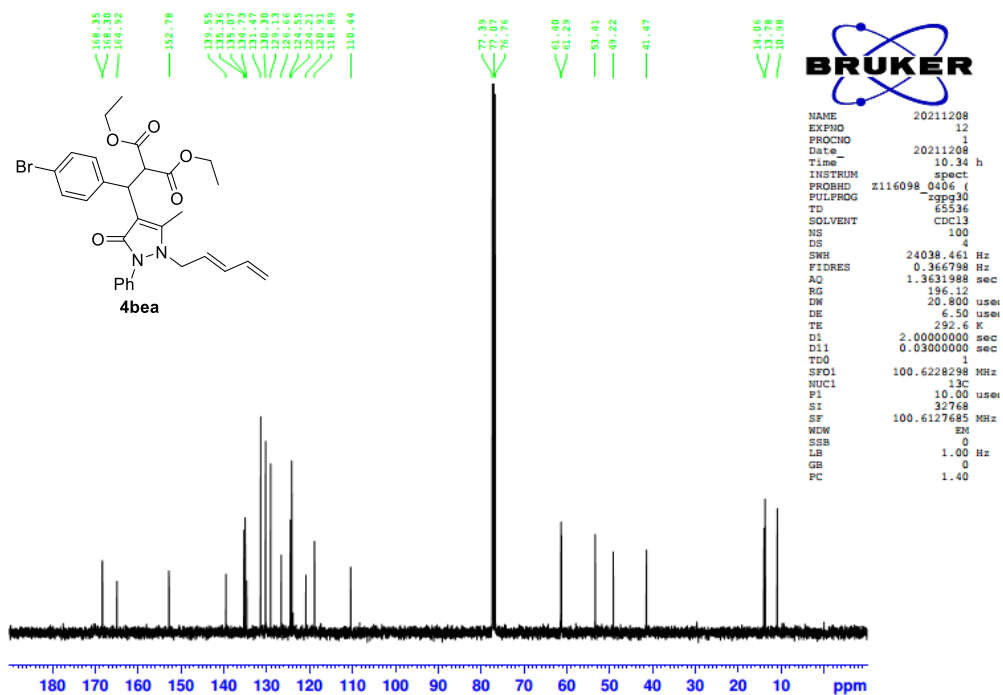
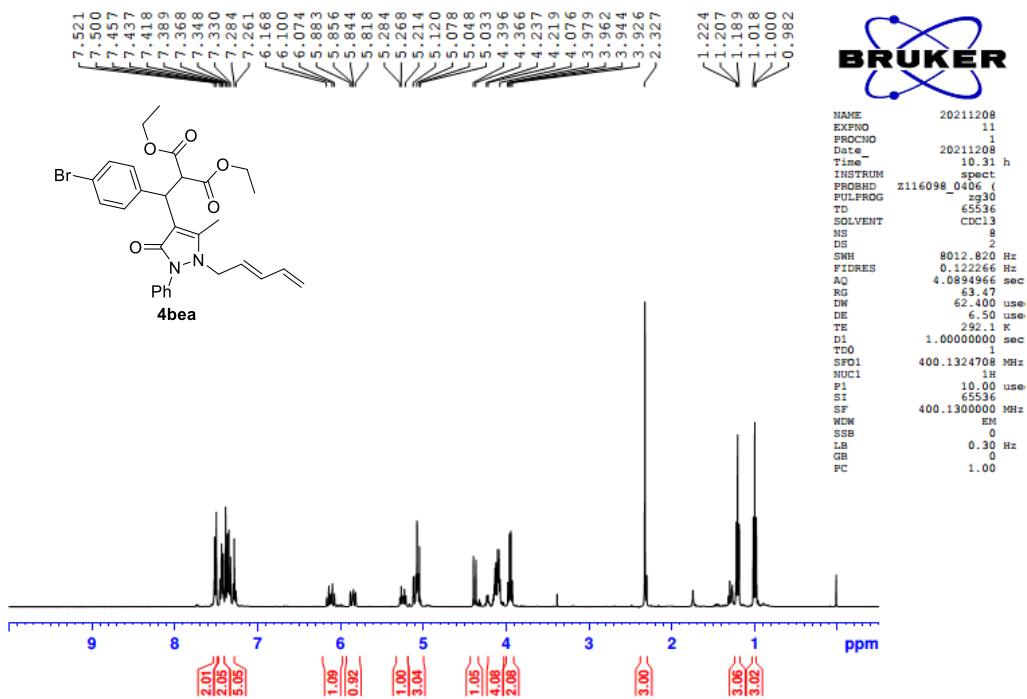
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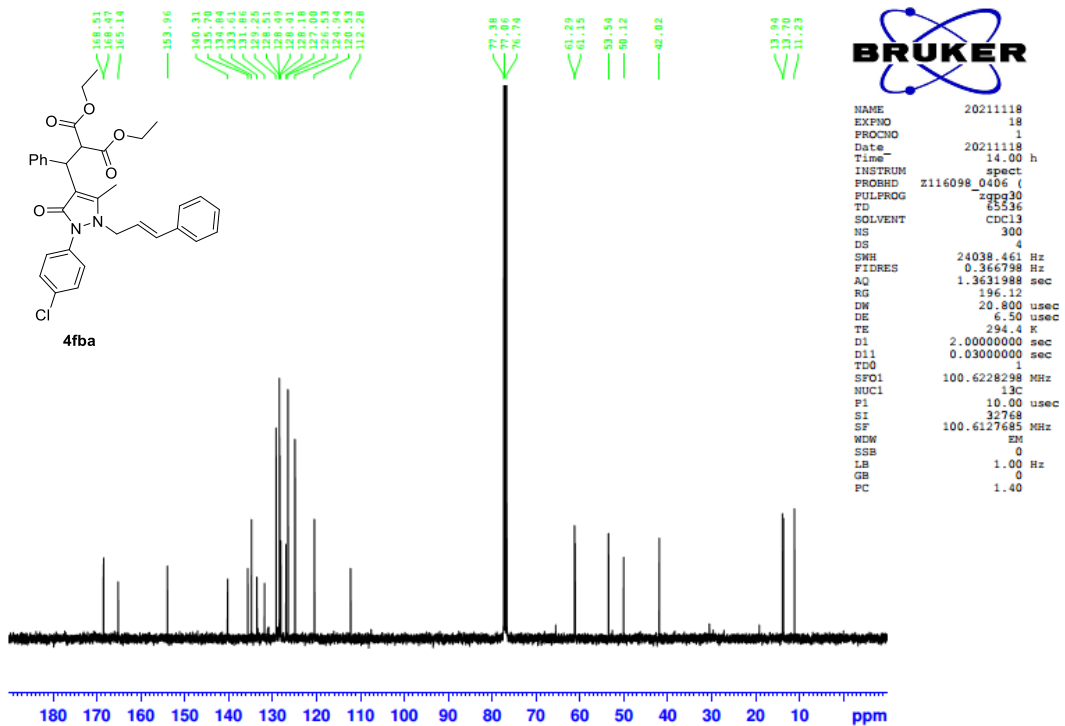
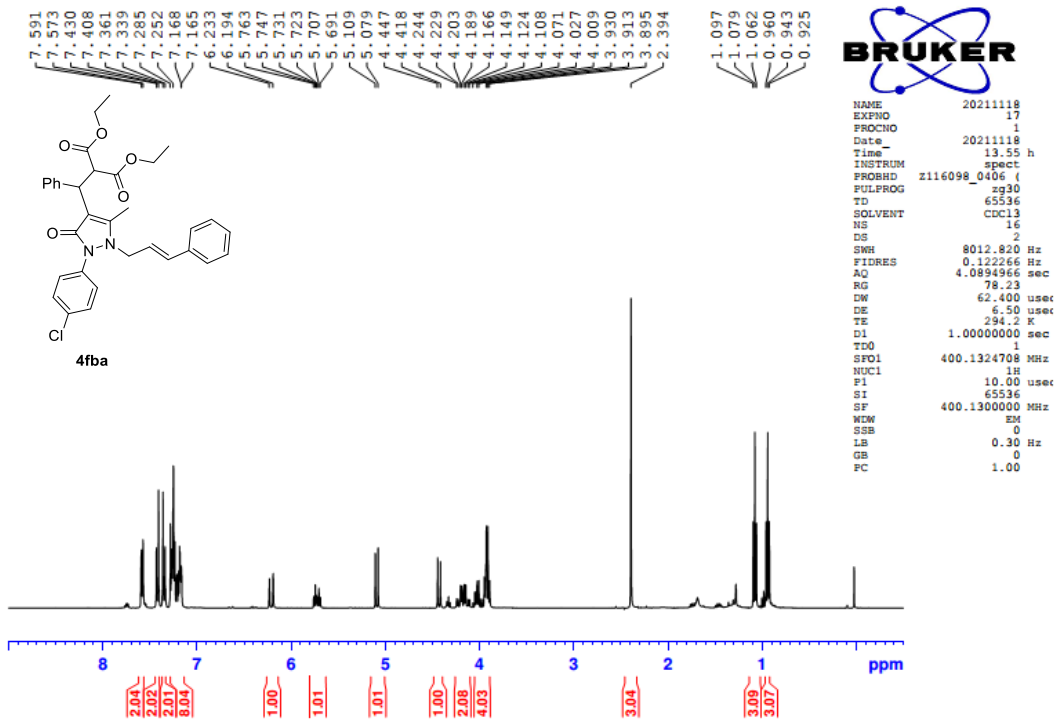
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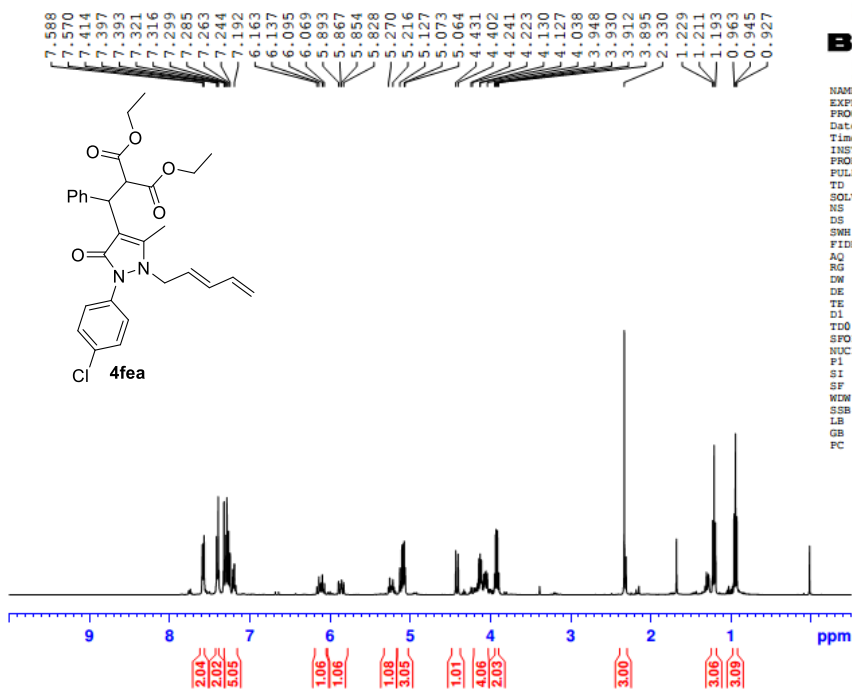








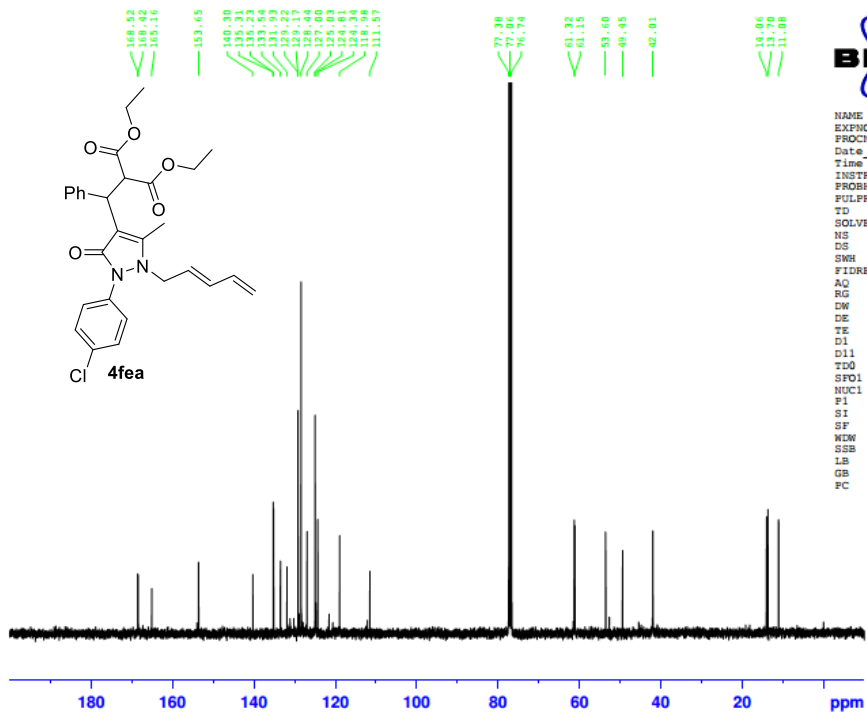




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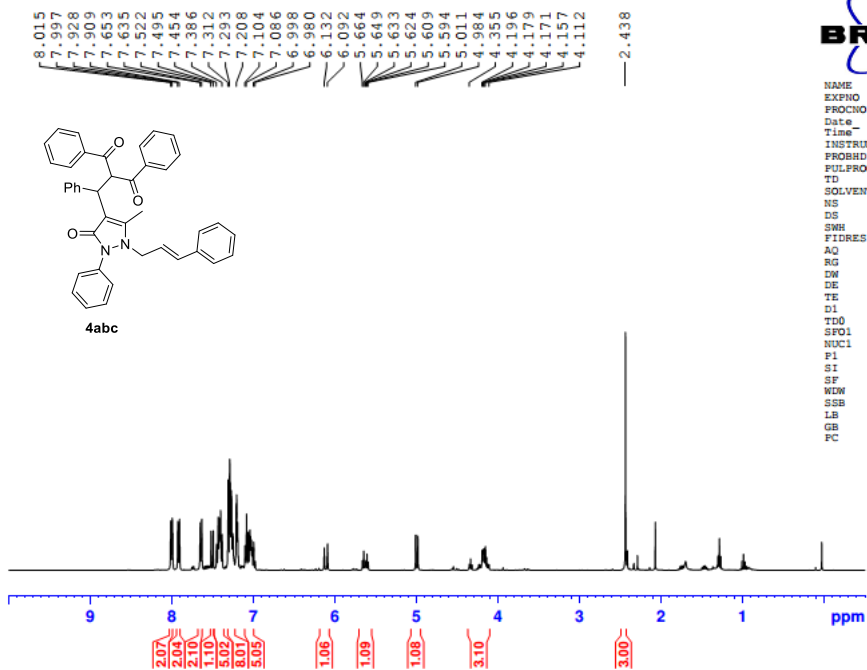
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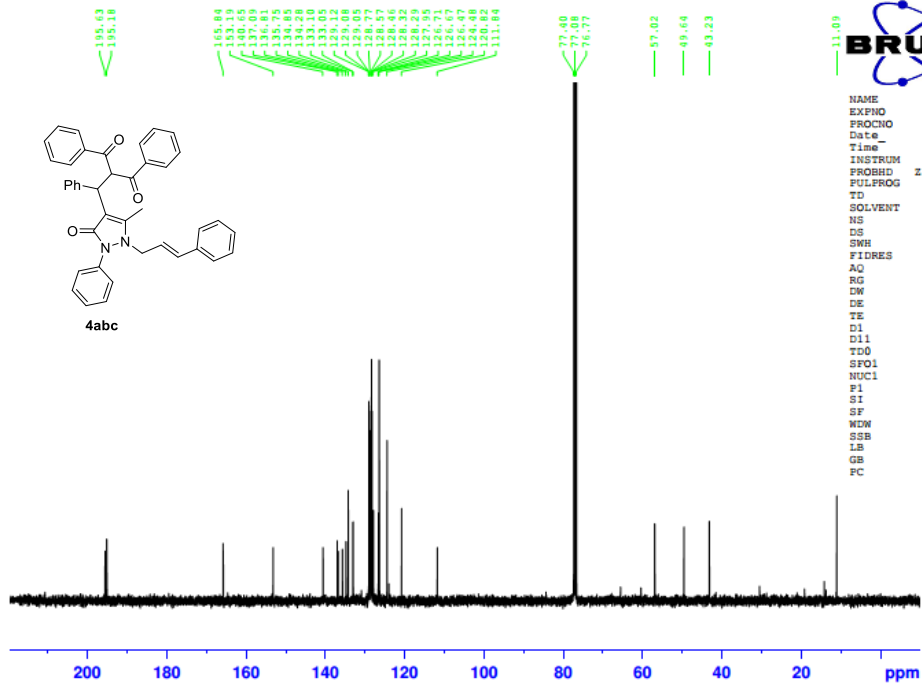
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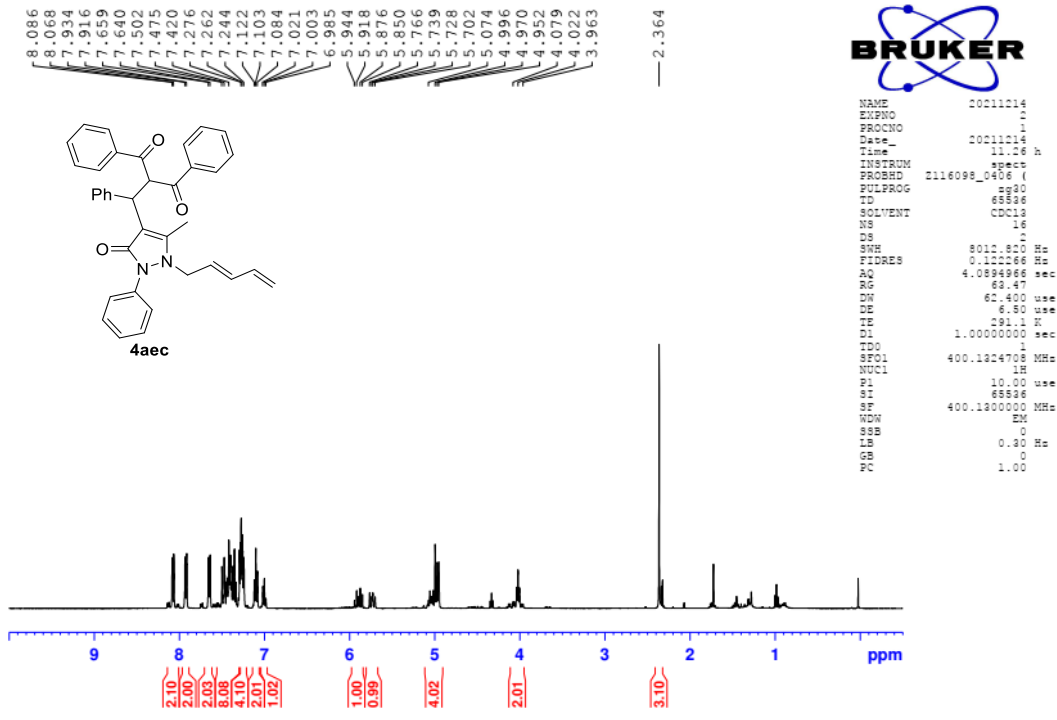
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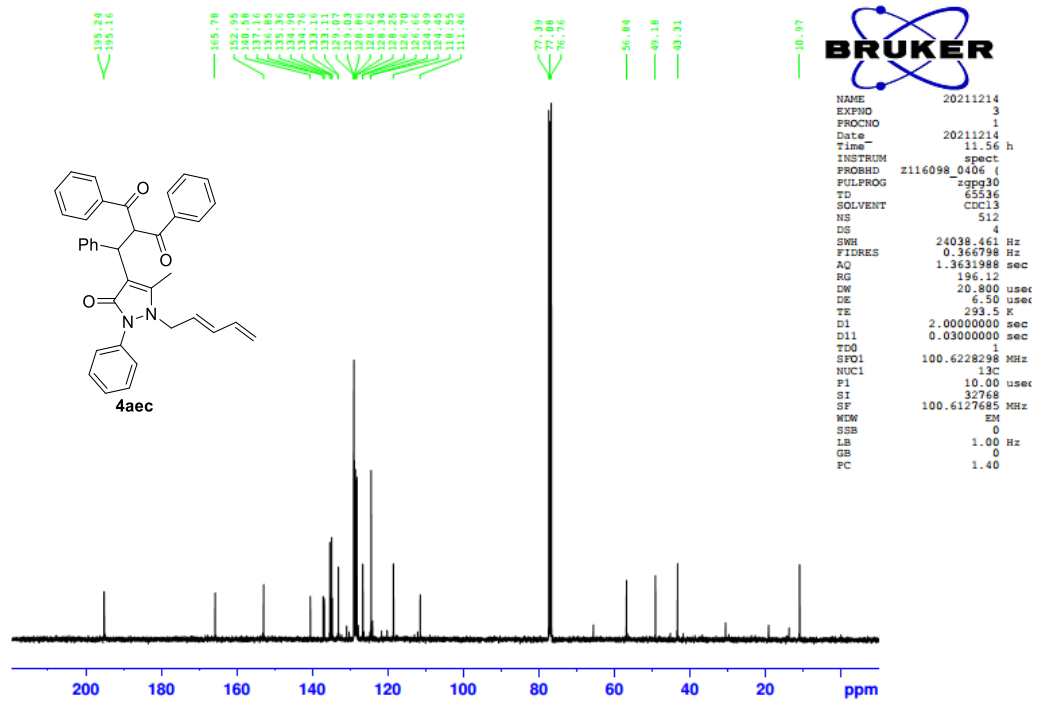
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PC         1.40
  
```



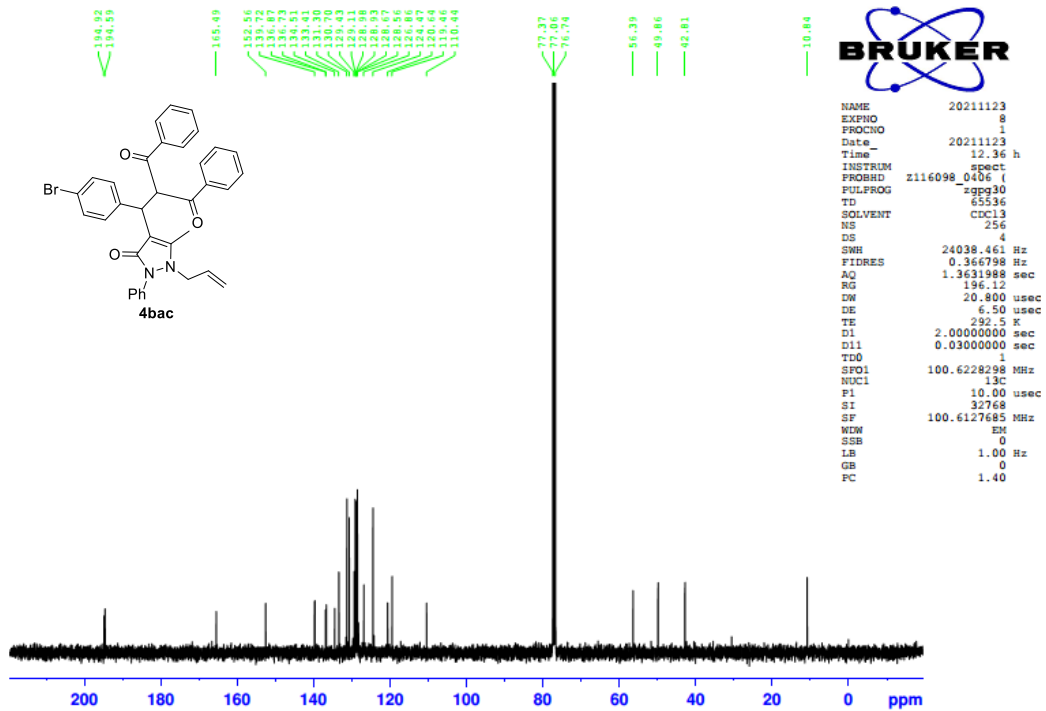
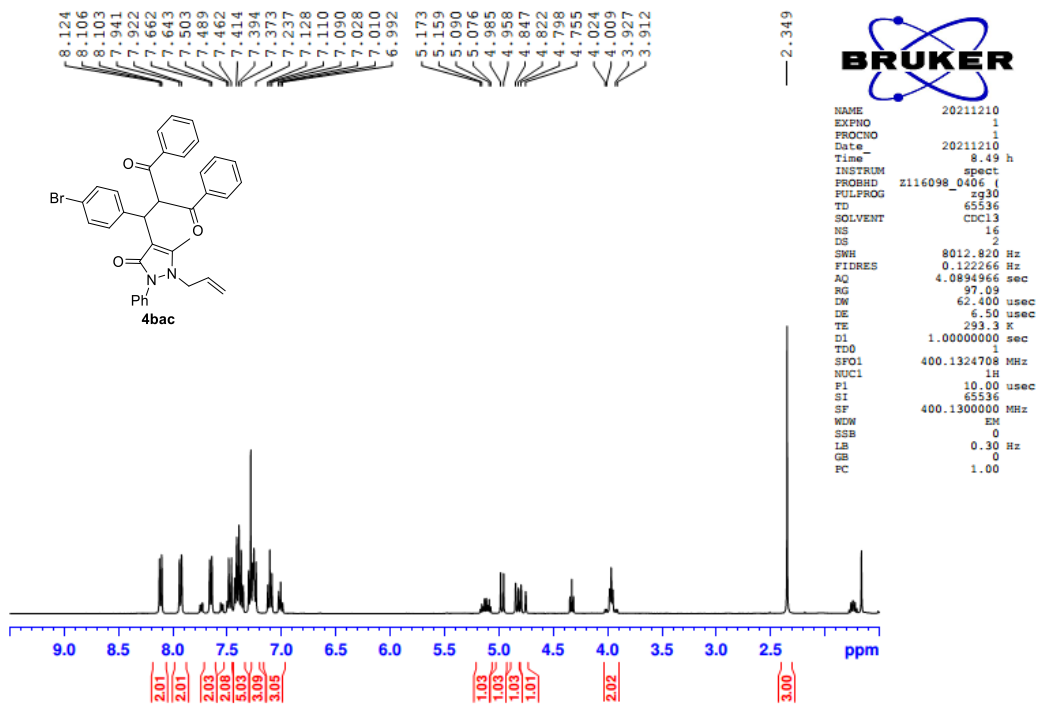
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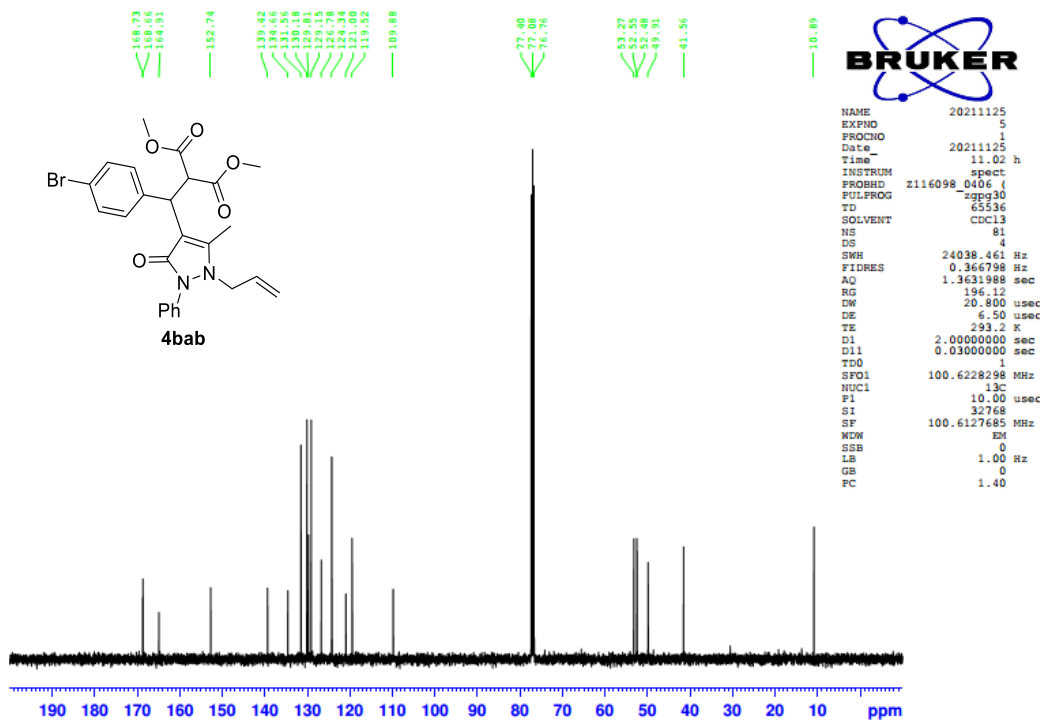
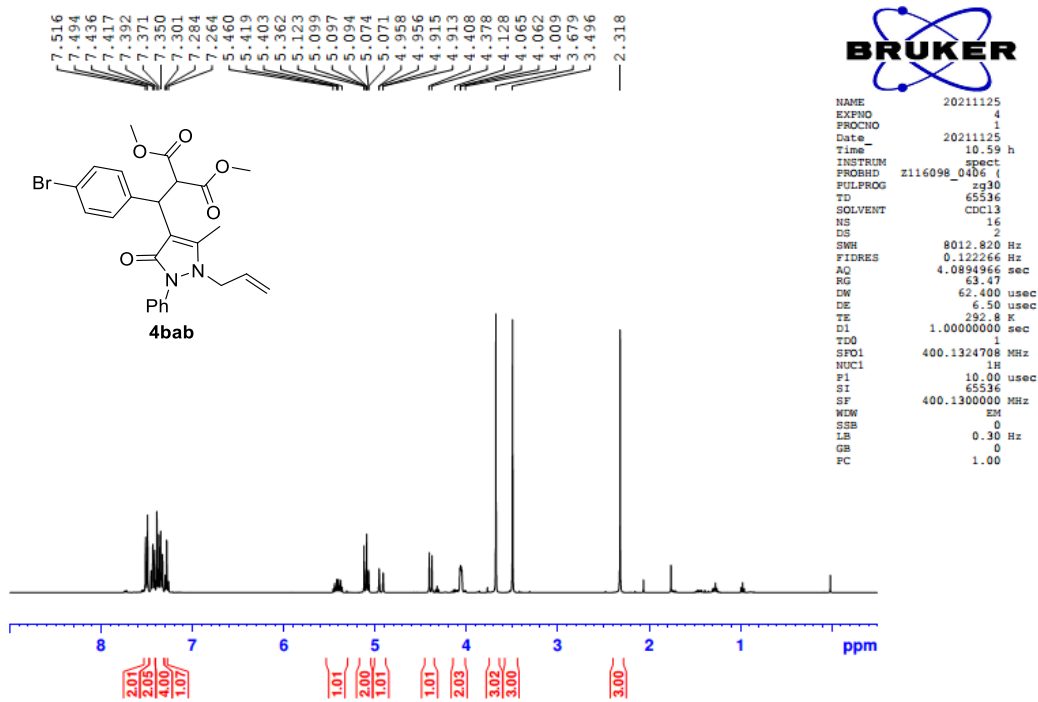
NAME      20211214
EXPNO    1
PROCNO   1
Date_    20211214
Time     11.26 h
INSTRUM  spect
PROBHD   z116098_0406 (
PULPROG  zgpg30
TD        65536
SOLVENT  CDCl3
NS        4
DS        2
SWH       8011.820 Hz
FIDRES    0.102866 Hz
AQ        4.0884966 sec
RG         62.47
DM         62.400 usec
DE         6.50 usec
TE        291.1 K
D1        1.00000000 sec
TD0       1
SFO1     400.1824701 MHz
NUC1      1H
P1        10.00 usec
SI        65536
SF        400.1800000 MHz
WDW       EM
SSB       0
LB        0.30 Hz
GB        0
PC        1.00
  
```

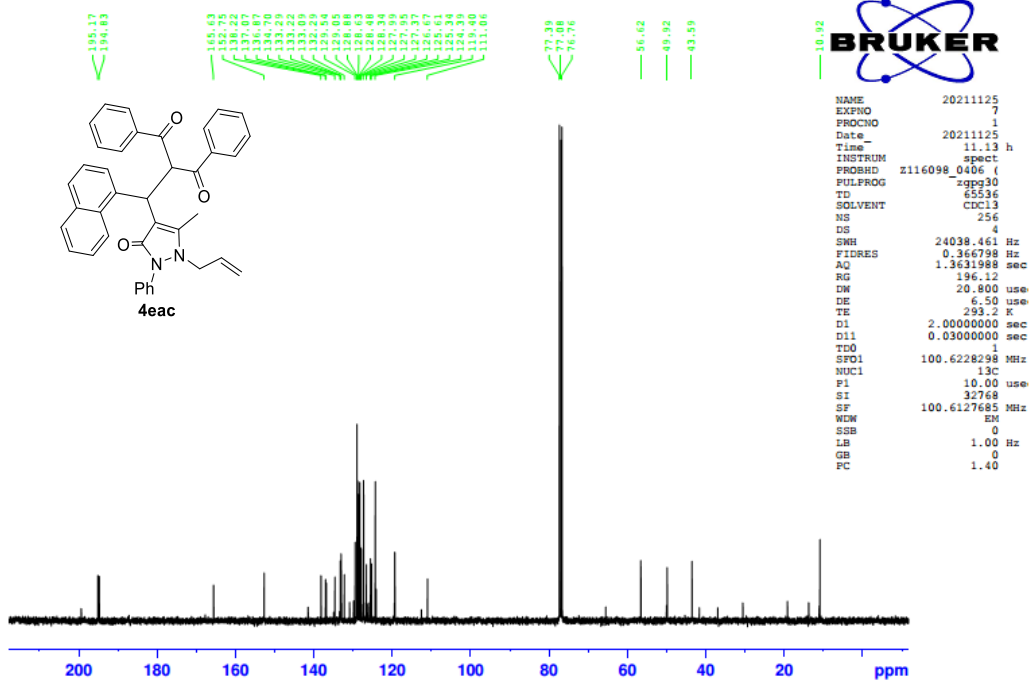
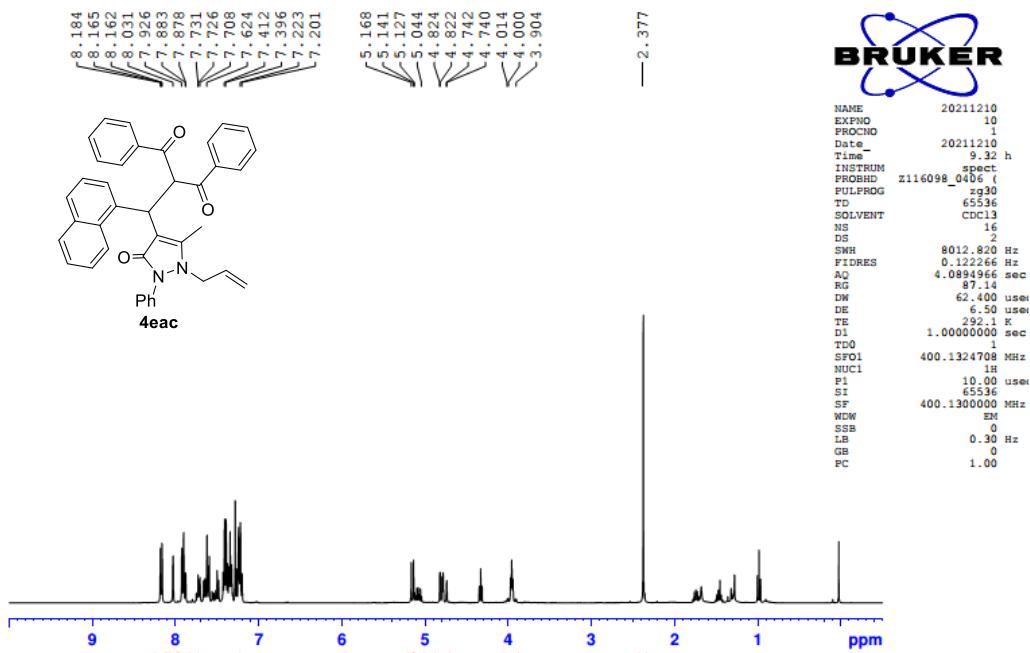


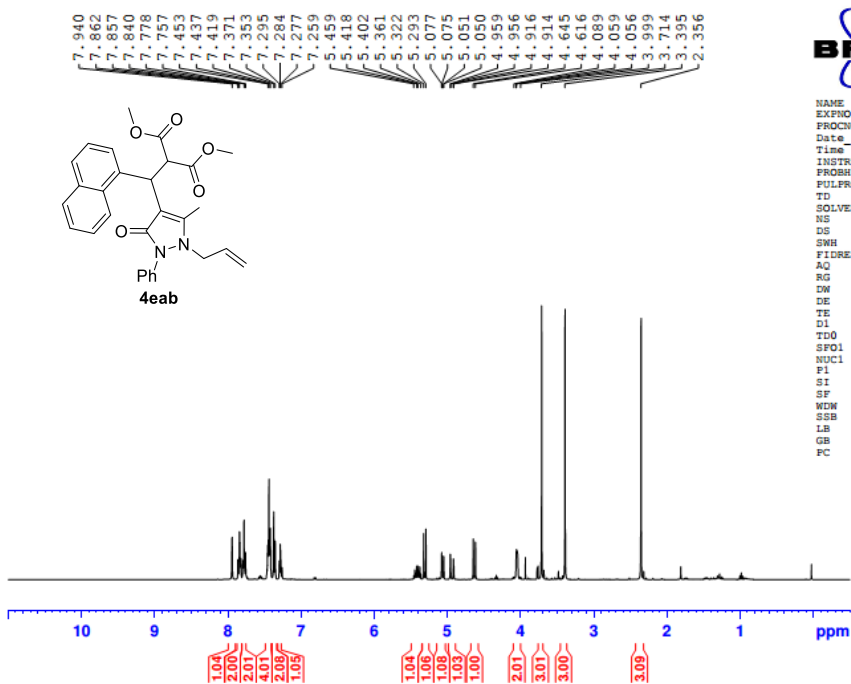
```

NAME      20211214
EXPNO    3
PROCNO   1
Date_    20211214
Time     11.56 h
INSTRUM  spect
PROBHD   z116098_0406 (
PULPROG  zgpg30
TD        65536
SOLVENT  CDCl3
NS        4
DS        4
SWH       24038.461 Hz
FIDRES    0.366798 Hz
AQ        1.3631988 sec
RG         196.12
DW         20.800 usec
DE         6.50 usec
TE        293.5 K
D1        2.00000000 sec
D11       0.03000000 sec
TD0       1
SFO1     100.6228298 MHz
NUC1      13C
P1        10.00 usec
SI        32768
SF        100.6127685 MHz
WDW       EM
SSB       0
LB        1.00 Hz
GB        0
PC        1.40
  
```



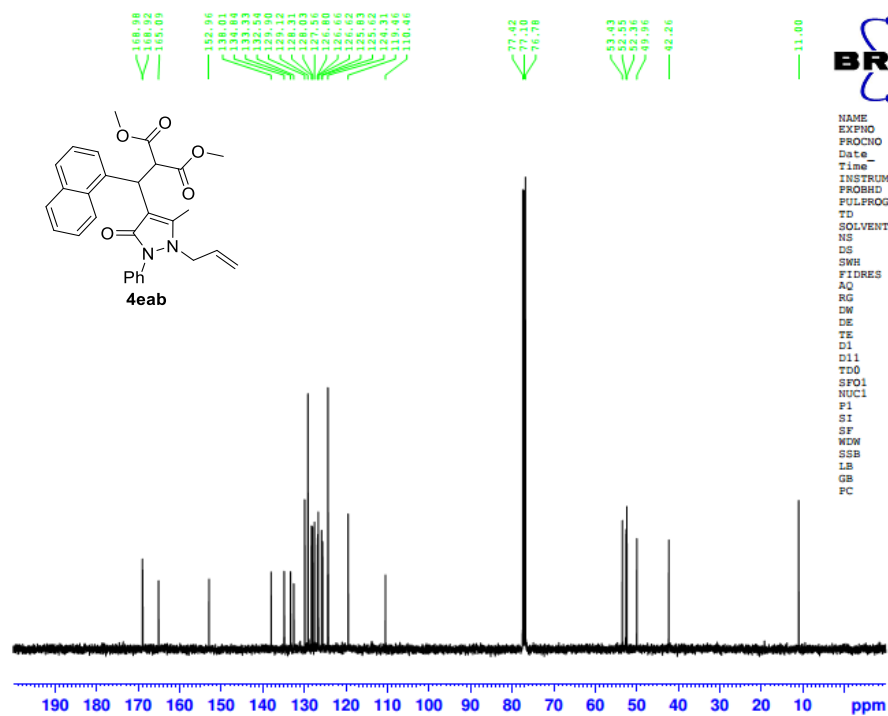






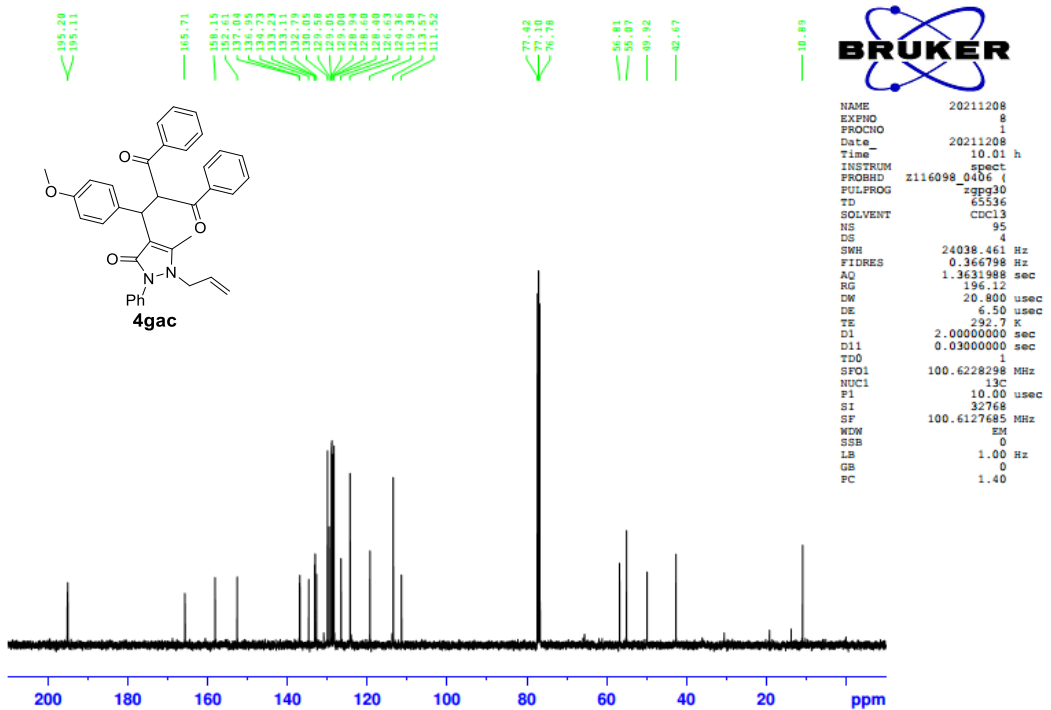
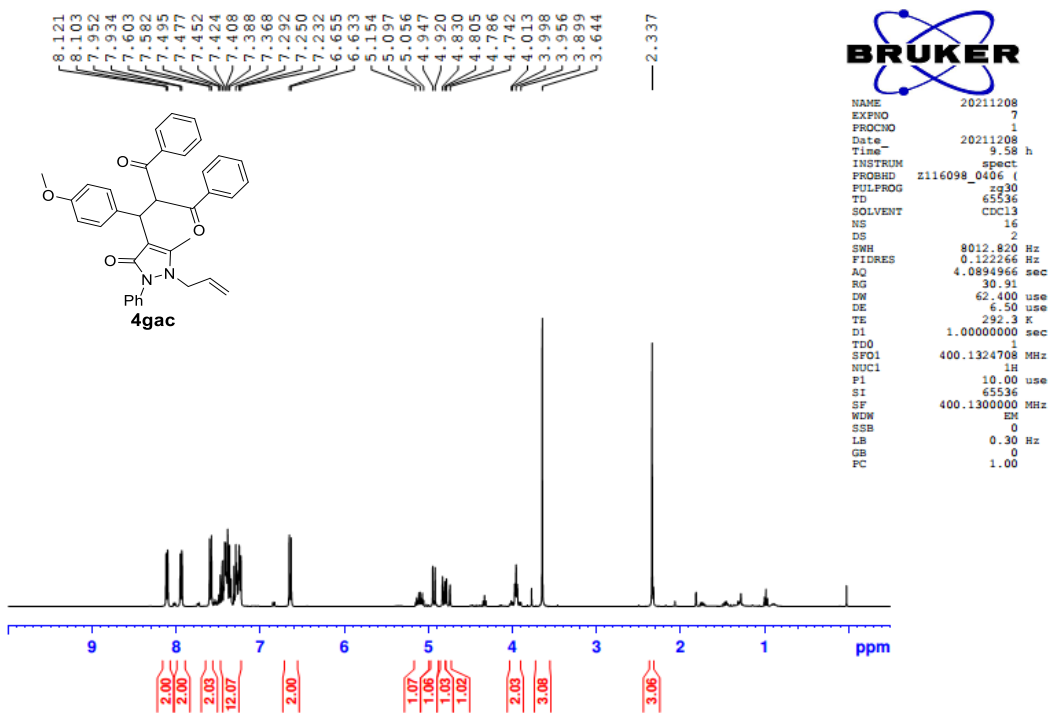
```

NAME      20211123
EXPNO    3
PROCNO   1
Date_    20211123
Time     11.43 h
INSTRUM  spect
PROBHD   Z116098_0406 (
FULPROG  zg30
TD        65536
SOLVENT  CDCl3
NS        8
DS        2
SWH      8012.820 Hz
FIDRES   0.122266 Hz
AQ        4.0894966 sec
RG        56.71
DW        62.400 usec
DE        6.50 usec
TE        292.0 K
D1        1.00000000 sec
TD0       1
SF01     400.1324708 MHz
NUC1      1H
P1        10.00 usec
SI        65536
SF        400.1300000 MHz
WDM       EM
SSB       0
LB        0.30 Hz
GB        0
PC        1.00
  
```



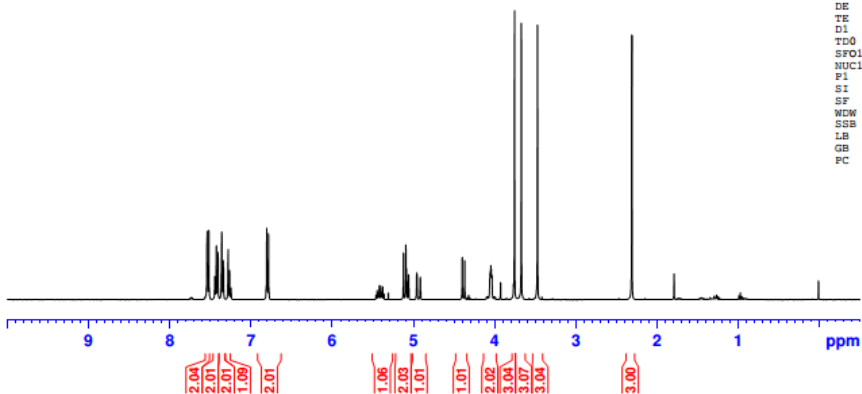
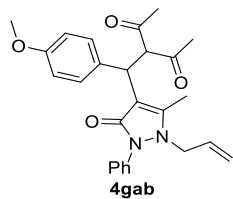
```

NAME      20211123
EXPNO    4
PROCNO   1
Date_    20211123
Time     11.45 h
INSTRUM  spect
PROBHD   Z116098_0406 (
FULPROG  zgpg30
TD        65536
SOLVENT  CDCl3
NS        128
DS        4
SWH      24038.461 Hz
FIDRES   0.366798 Hz
AQ        1.3631988 sec
RG        196.12
DW        20.800 usec
DE        6.50 usec
TE        292.5 K
D1        2.00000000 sec
D11       0.03000000 sec
TD0       1
SF01     100.6228298 MHz
NUC1      13C
P1        10.00 usec
SI        32768
SF        100.6127685 MHz
WDM       EM
SSB       0
LB        1.00 Hz
GB        0
PC        1.40
  
```



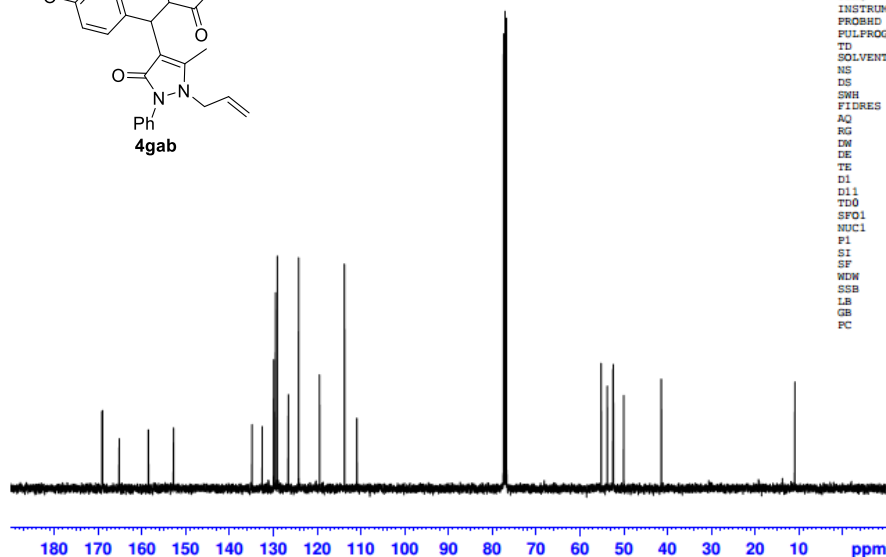
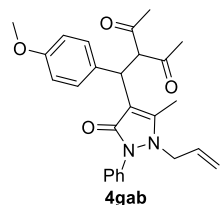


7.543  
7.522  
7.448  
7.428  
7.409  
7.365  
7.362  
7.344  
7.284  
7.267  
6.809  
6.787  
5.749  
5.438  
5.423  
5.407  
5.395  
5.381  
5.366  
5.311  
5.126  
5.096  
5.090  
5.064  
4.962  
4.919  
4.401  
4.371  
4.060  
4.050  
4.036  
3.759  
3.674  
3.476  
2.314

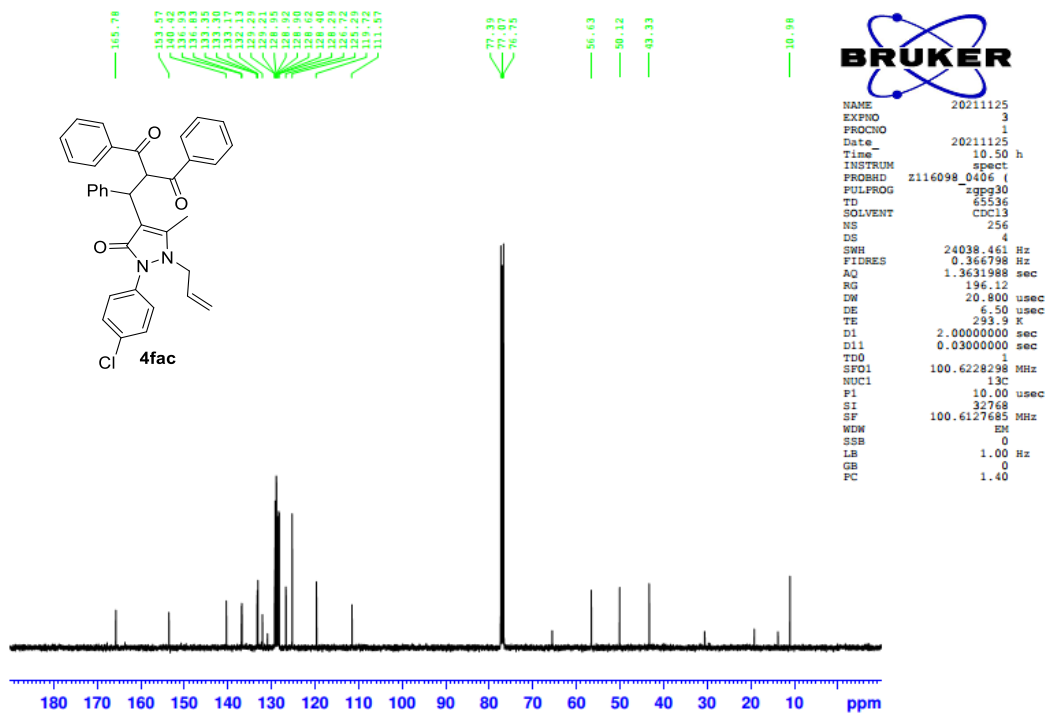
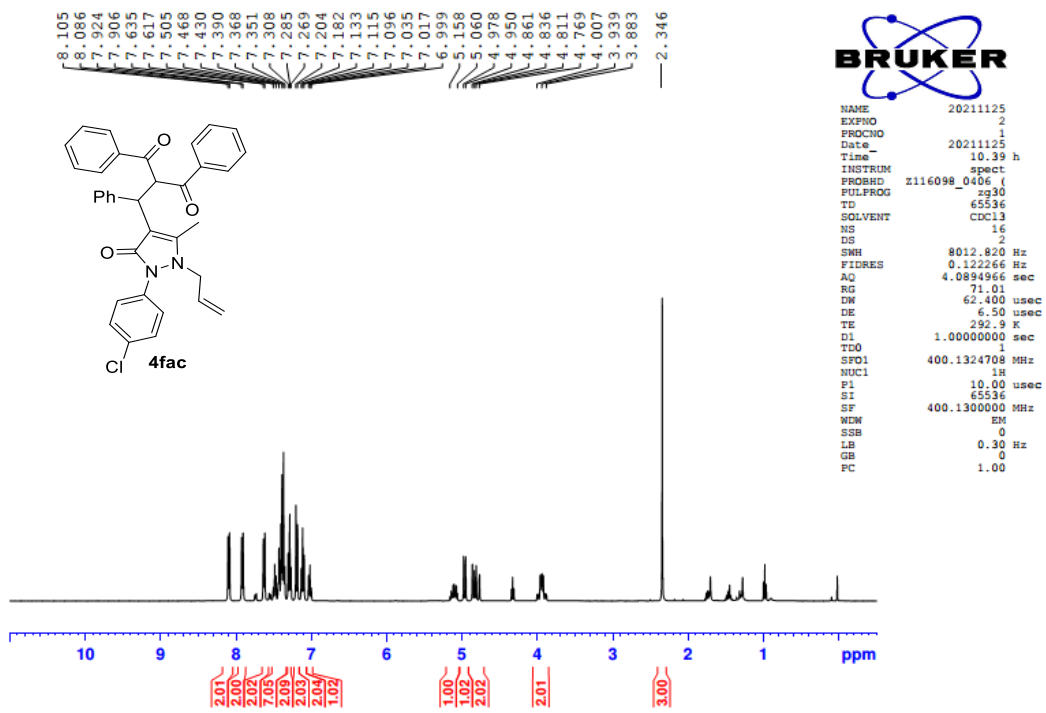


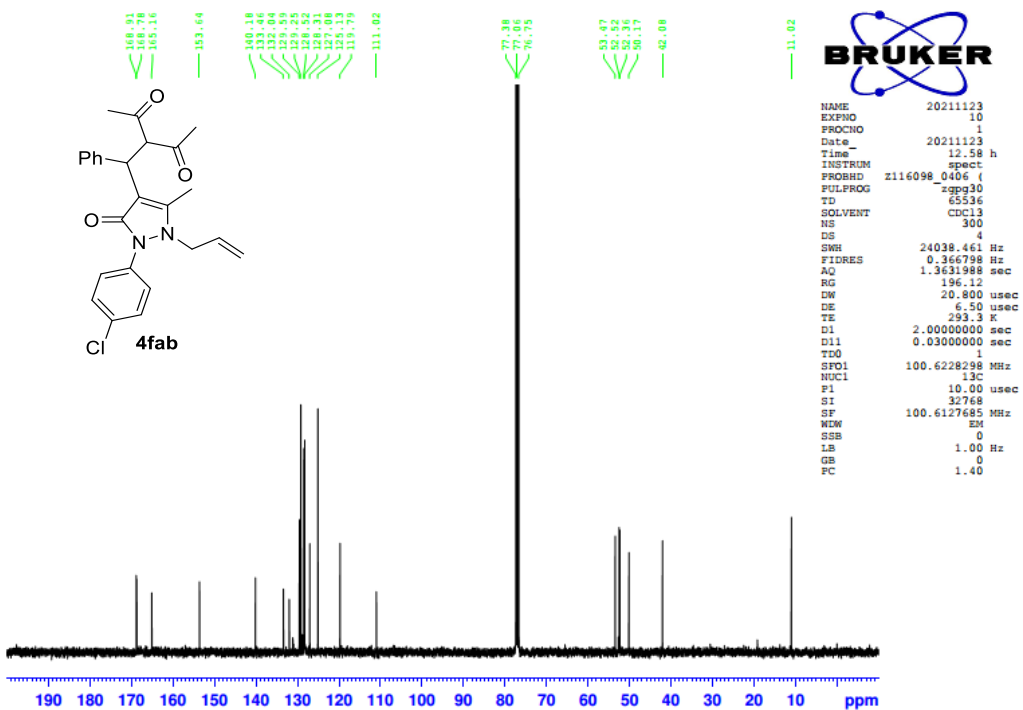
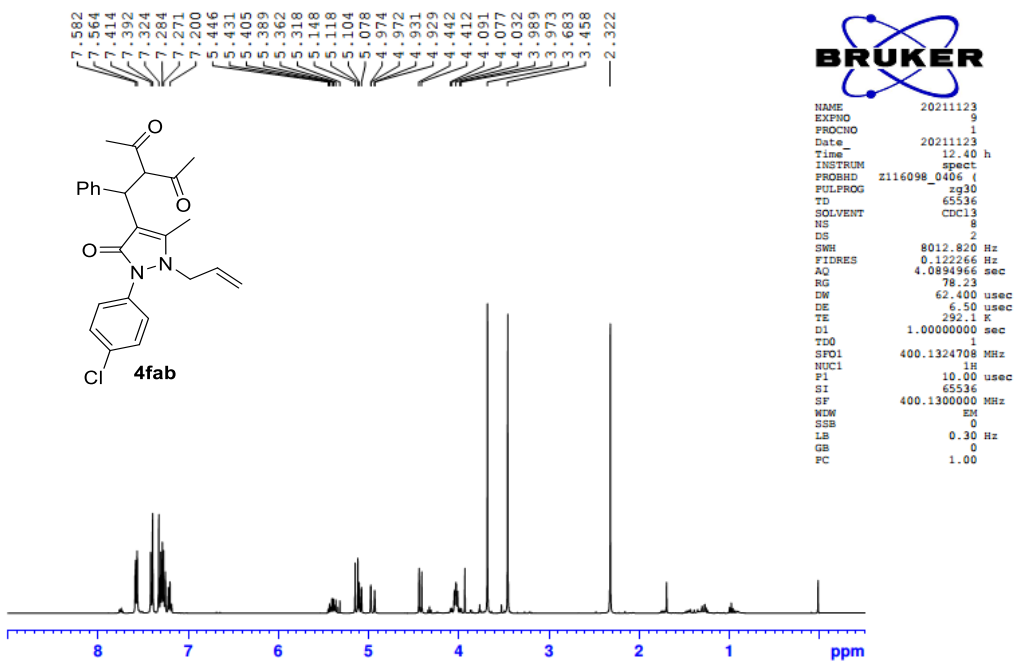
NAME 20211123  
EXPNO 1  
PROCNO 1  
Date\_ 20211123  
Time\_ 11.30 h  
INSTRUM spect  
PROBHD z116098\_0406 ( )  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 9  
DS 2  
SWH 8012.820 Hz  
FIDRES 0.122266 Hz  
AQ 4.0894966 sec  
RG 63.47  
DN 62.400 usec  
DE 6.50 usec  
TE 292.2 K  
D1 1.00000000 sec  
TDO 1  
SFO1 400.1324708 MHz  
NUC1 13C  
P1 10.00 usec  
SI 65536  
SF 400.1300000 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

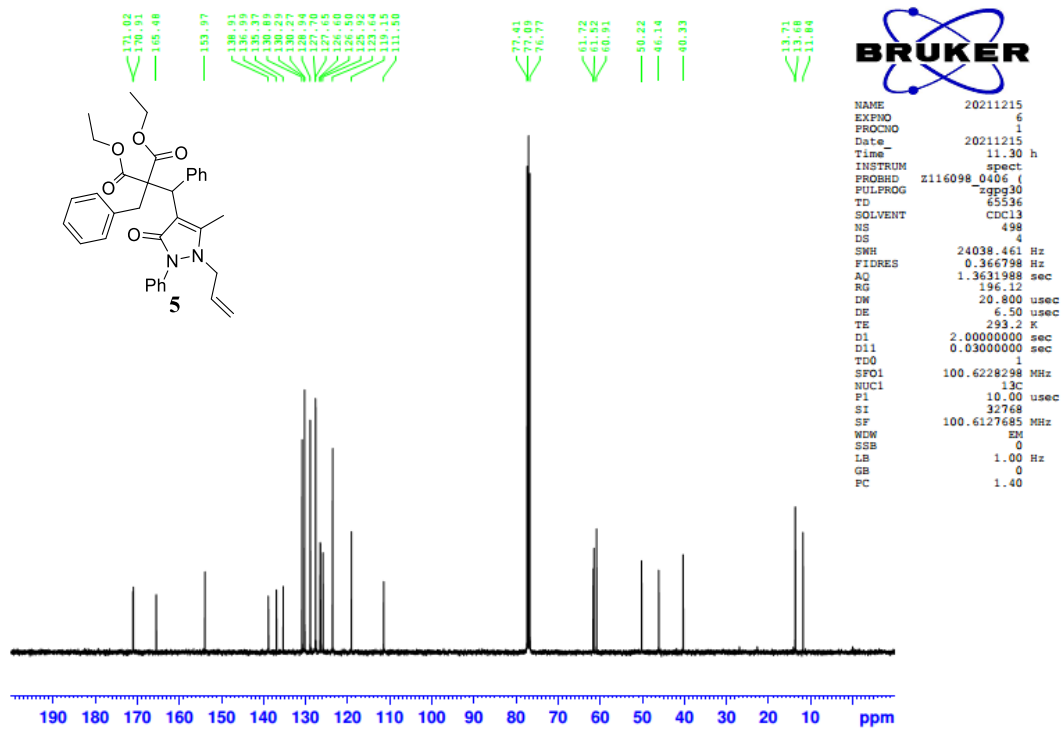
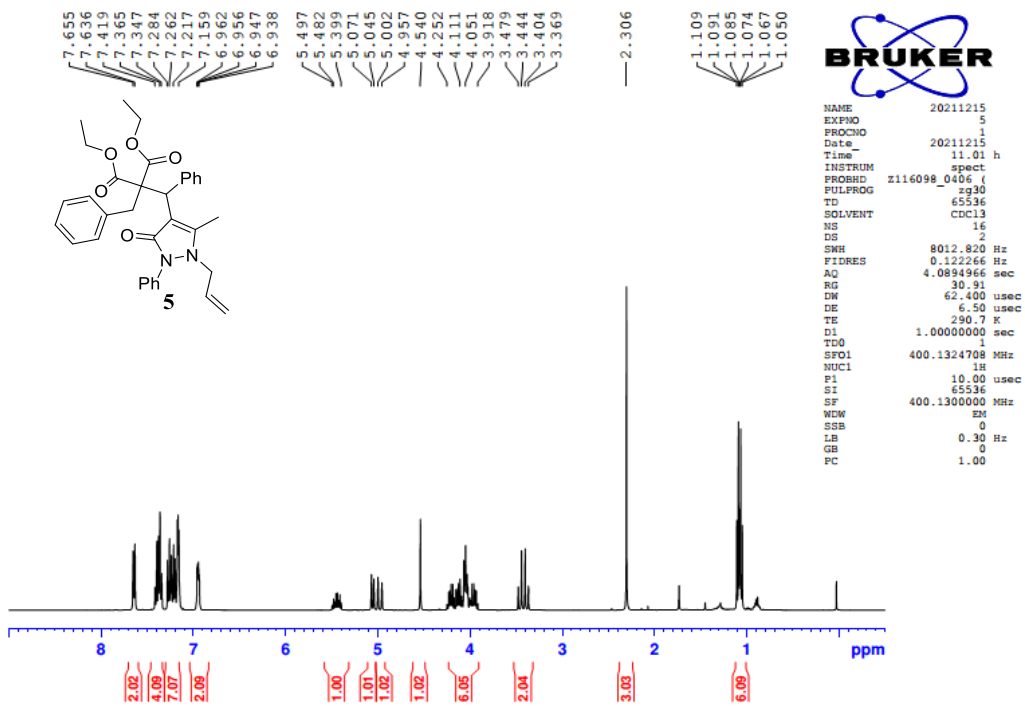
169.92  
168.91  
165.12  
158.44  
152.71  
134.85  
132.51  
129.22  
129.09  
126.55  
124.22  
119.44  
113.74  
110.91  
77.40  
77.09  
76.77  
55.13  
53.76  
52.45  
48.96  
41.40  
10.92

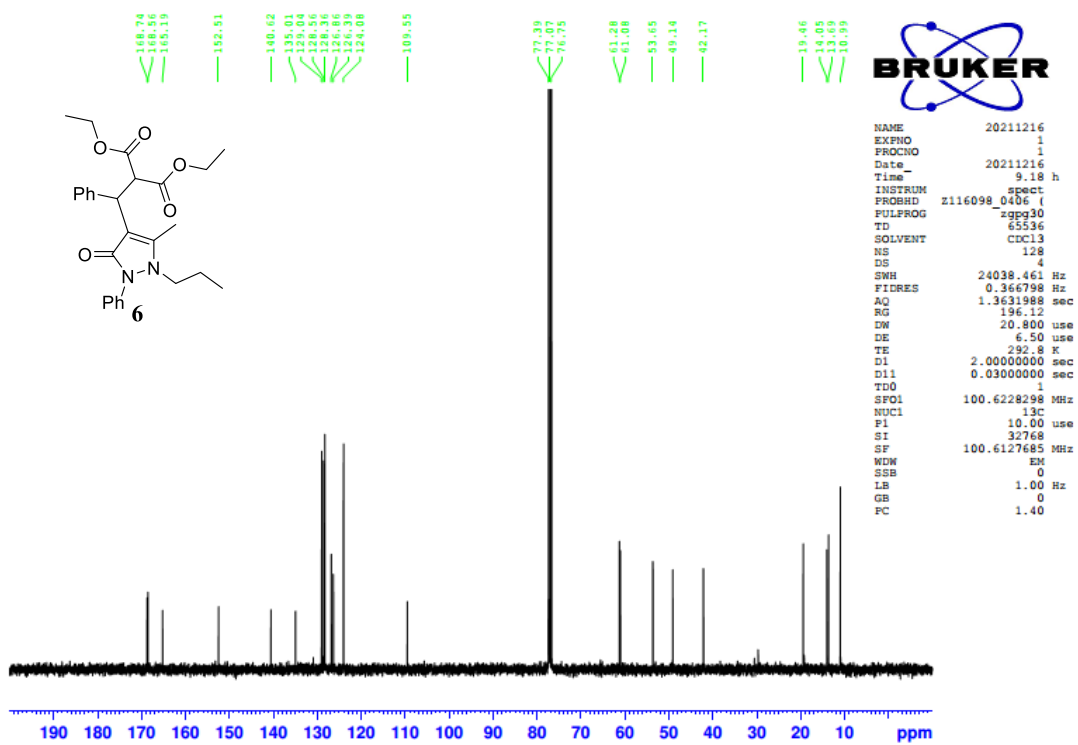
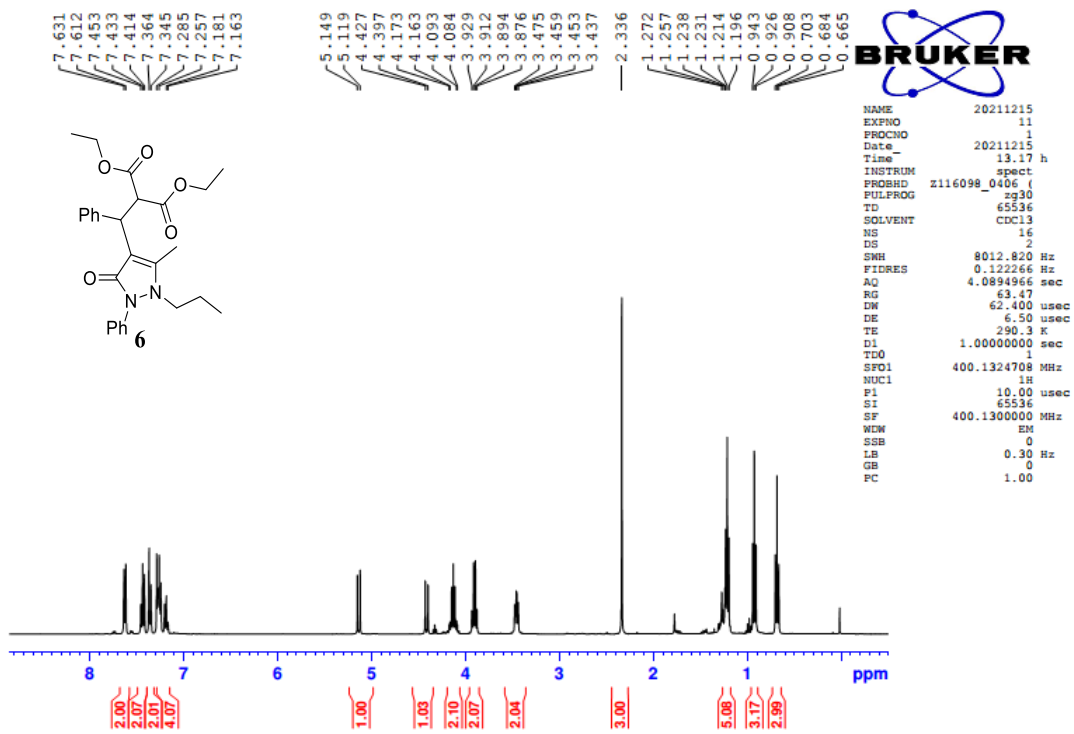


NAME 20211123  
EXPNO 2  
PROCNO 1  
Date\_ 20211123  
Time\_ 11.33 h  
INSTRUM spect  
PROBHD z116098\_0406 ( )  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 128  
DS 4  
SWH 24038.461 Hz  
FIDRES 0.366798 Hz  
AQ 1.3631988 sec  
RG 196.12  
DN 20.800 usec  
DE 6.50 usec  
TE 292.2 K  
D1 2.00000000 sec  
D11 0.03000000 sec  
TDO 1  
SFO1 100.6228298 MHz  
NUC1 13C  
P1 10.00 usec  
SI 32768  
SF 100.6127685 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40









## 7. References

- (1) (a) Shintani, R.; Fu, G. C. *J. Am. Chem. Soc.* 2003, **125**, 10778. (b) Suárez, A.; Downey, C. W.; Fu, G. C. *J. Am. Chem. Soc.* 2005, **127**, 11244. (c) Shintani, R.; Hayashi, T. *J. Am. Chem. Soc.* 2006, **128**, 6330.
- (2) (a) Chen, Q.; Liang, J.; Wang, S.; Wang, D.; Wang, R. *Chem. Commun.* 2013, **49**, 1657. (b) C. Zhao, K. Shi, G. He, Q. Gu, Z. Ru, L. Yang and G. Zhong, *Org. Lett.* 2019, **21**, 7943.