

Supporting information

**Palladium-Catalyzed α -Regioselective Allylic Amination of
Morita-Baylis-Hillman Acetates with Simple Aromatic Amines**

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1. General

2. Typical Experimental Procedures for Allylic Amination Reaction

3. The control experiment

4. NMR spectrum

1. General

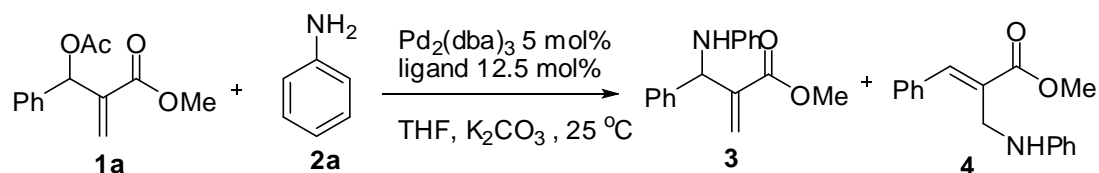
All reactions were carried out in oven dried flasks under nitrogen atmosphere under anhydrous conditions. Chemical shifts of all the ^1H and ^{13}C NMR were reported in CDCl_3 with tetramethylsilane as an internal standard. IR spectra were recorded on the infrared spectrometer. Melting points were measured without correction. HRMS spectra were recorded on GCT-Mass Micromass spectrometer. Common reagents were purchased from commercial sources and were used without further purification. Column chromatography was performed using silica gel (200-300 mesh) eluting with ethyl acetate and petroleum ether. TLC was performed on glass-backed silica plates.

2. Typical Experimental Procedures for Allylic Amination Reaction

A solution of 5 mol% $\text{Pd}_2(\text{dba})_3$ catalyst and 12.5 mol% ligand **L4** in 1 mL THF was stirred at 25 °C for 0.5 h, a solution of MBH acetates **1a** (0.2 mmol) and aniline **2a** (0.6 mmol) in 1 mL THF, and 0.6 mmol K_2CO_3 (1M) were added. The reaction mixture was stirred at 25 °C and monitored by TLC until the starting material disappeared. Then the reaction mixture was extracted by ethyl acetate. The organic phase was dried by Na_2SO_4 , filtered and evaporated to afford a mixture of the crude products. The crude product was purified by flash column chromatography over silica gel (eluent: PE/EA = 20 : 1) to give **3**.

3. The control experiment

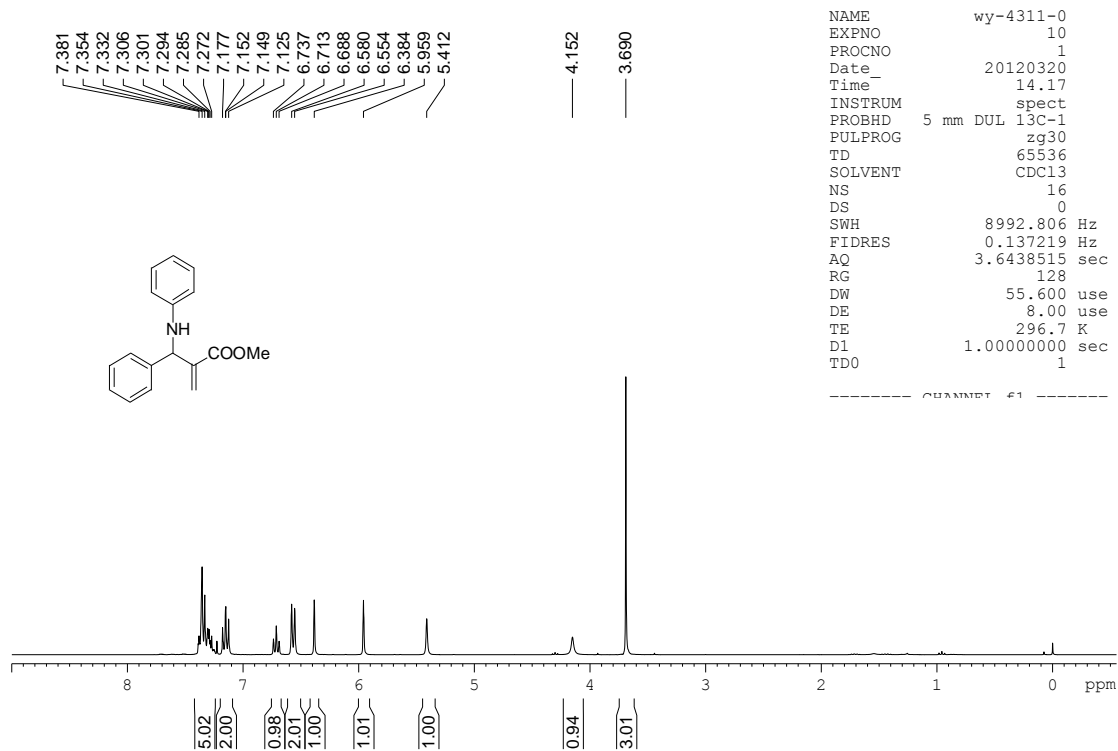
In the control experiment, we found that the ratio of α : γ -product did not change at different interval time (table 4). That demonstrated there is no conversion between the two regioselective isomers with the change of the time. The excellent regioselectivity was fully controlled by the introduction of the ligand **L4**.



Entry	t (h)	Conv. (%) ^b	3:4 ^c
1	0.25	70	21:1
2	0.5	100	21.5:1
3	1	100	22.0:1
4	2h	100	22.2:1
5	4h	100	21.7:1
6	12	100	22.5:1

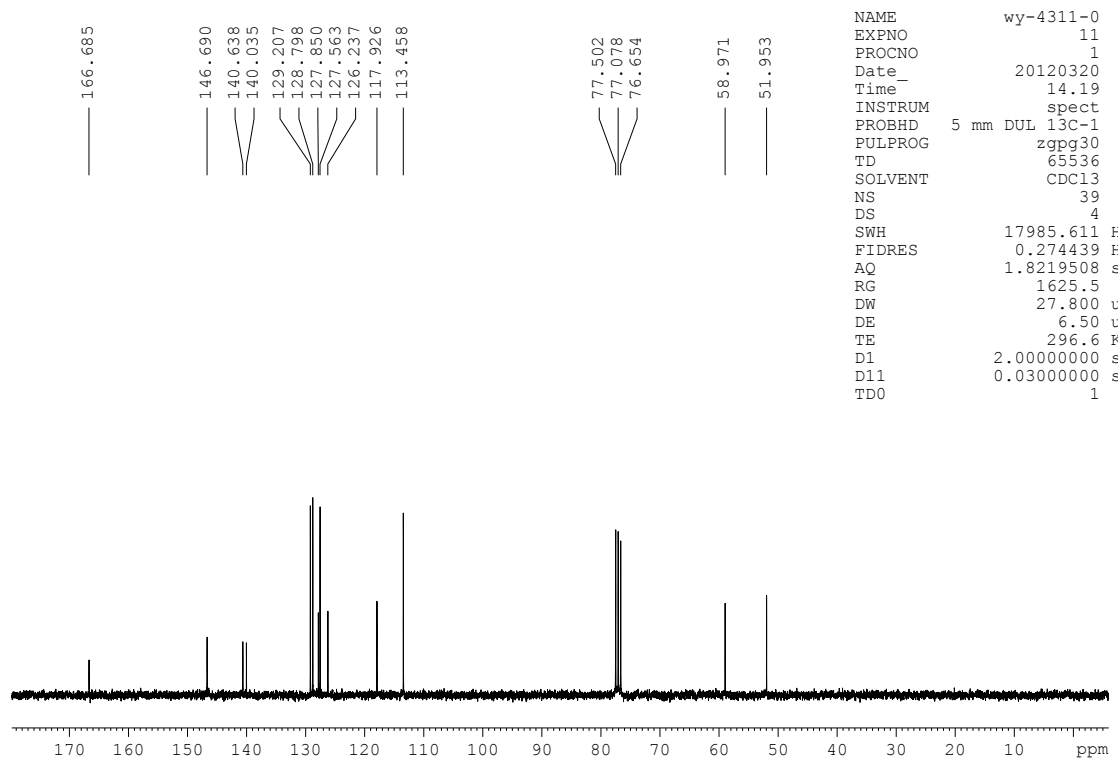
^a All reaction were performed with 0.1 mmol MBH acetates **1a**, 0.3 aniline **2a**, 0.3 mmol K₂CO₃ (1M) in 2 ml THF at 25°C in nitrogen atmosphere. 10 mol% Pd catalyst and 12.5 mol% ligand **L3** were used. ^b The conversion of the reaction was determined by ¹H NMR of the crude reaction mixture. ^c Ratio determined by ¹H NMR of the crude reaction mixture.

4. NMR spectrum



```

NAME      wy-4311-0
EXPNO    10
PROCNO   1
Date_    20120320
Time     14.17
INSTRUM  spect
PROBHD   5 mm DUL 13C-1
PULPROG  zg30
TD        65536
SOLVENT  CDCl3
NS        16
DS        0
SWH      8992.806 Hz
FIDRES   0.137219 Hz
AQ        3.6438515 sec
RG        128
DW        55.600 use
DE        8.00 use
TE        296.7 K
D1        1.00000000 sec
TD0       1
    
```



```

NAME      wy-4311-0
EXPNO    11
PROCNO   1
Date_    20120320
Time     14.19
INSTRUM  spect
PROBHD   5 mm DUL 13C-1
PULPROG  zgpg30
TD        65536
SOLVENT  CDCl3
NS        39
DS        4
SWH      17985.611 F
FIDRES   0.274439 F
AQ        1.8219508 s
RG        1625.5
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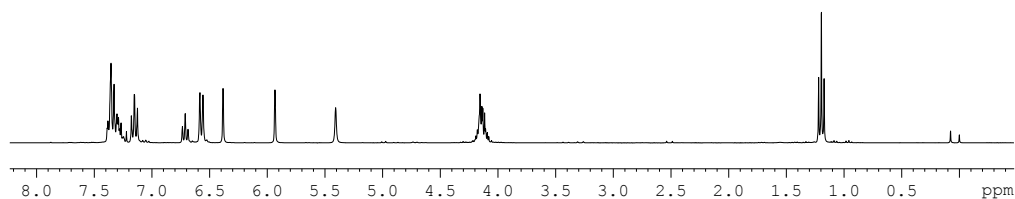
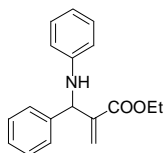
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5.932
5.407

4.191
4.178
4.155
4.139
4.131
4.115
4.107
4.092
4.079

1.219
1.196
1.172

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NAME      wy-4310-15
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PULPROG   zg30
TD         65536
SOLVENT   CDCl3
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DS         0
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AQ         3.6438515
RG         128
DW         55.600
DE         8.00
TE         295.6
    
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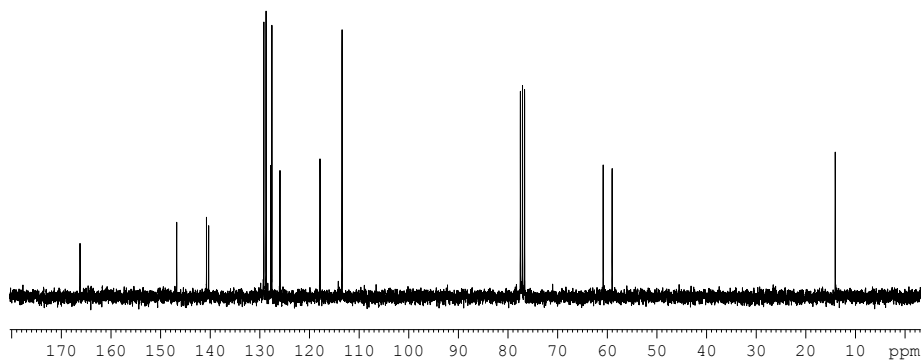
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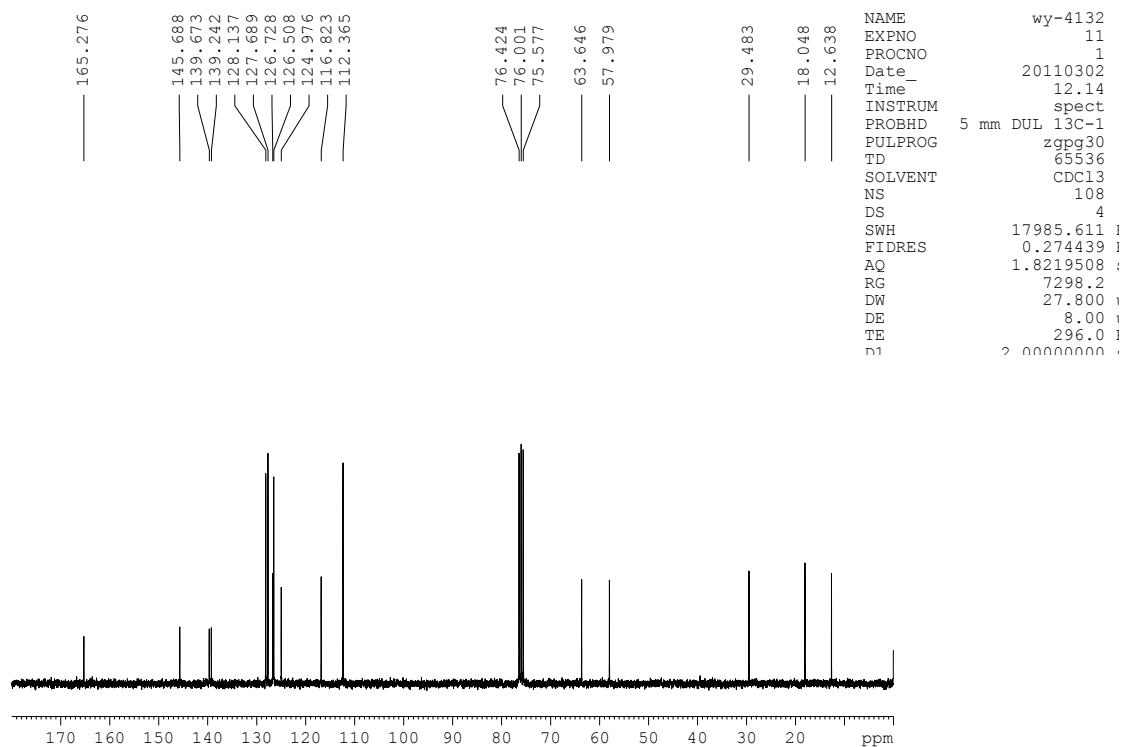
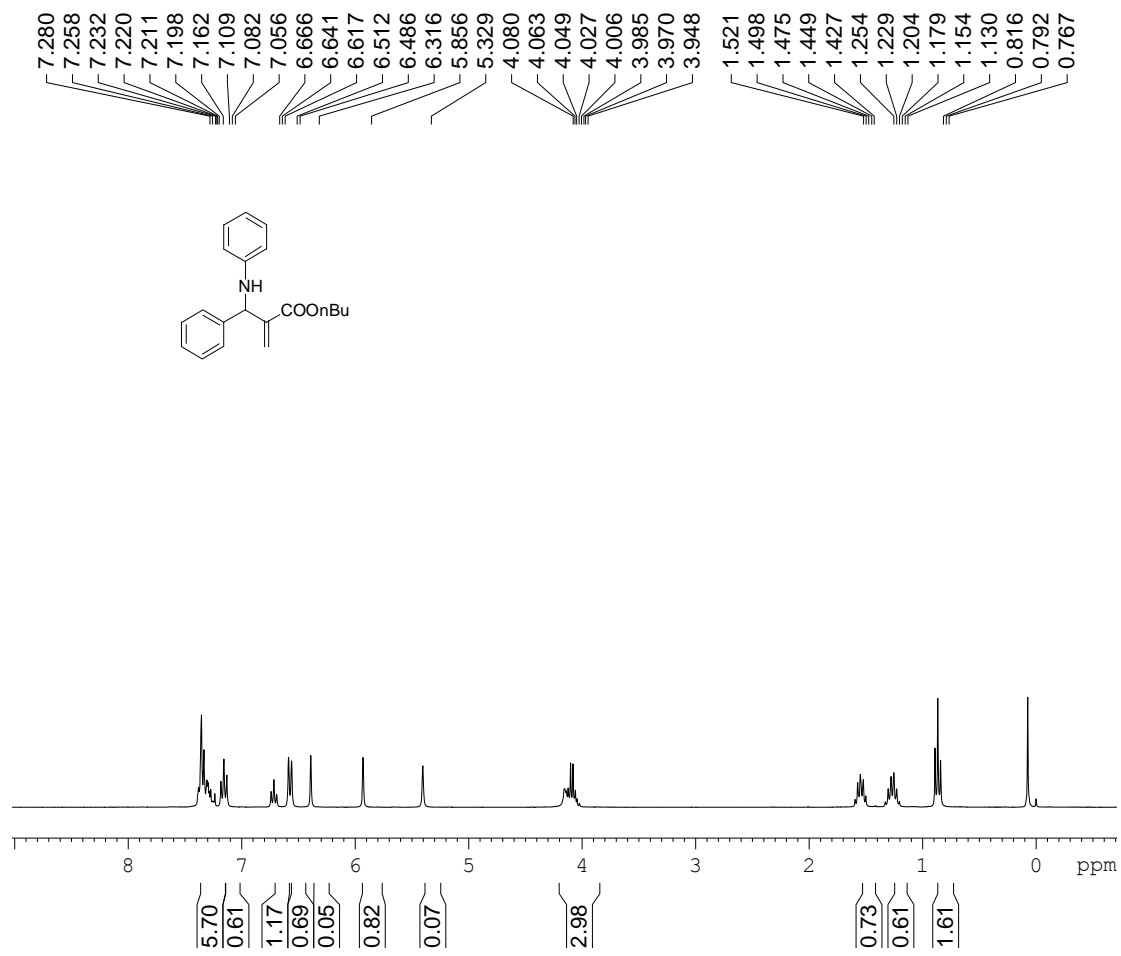
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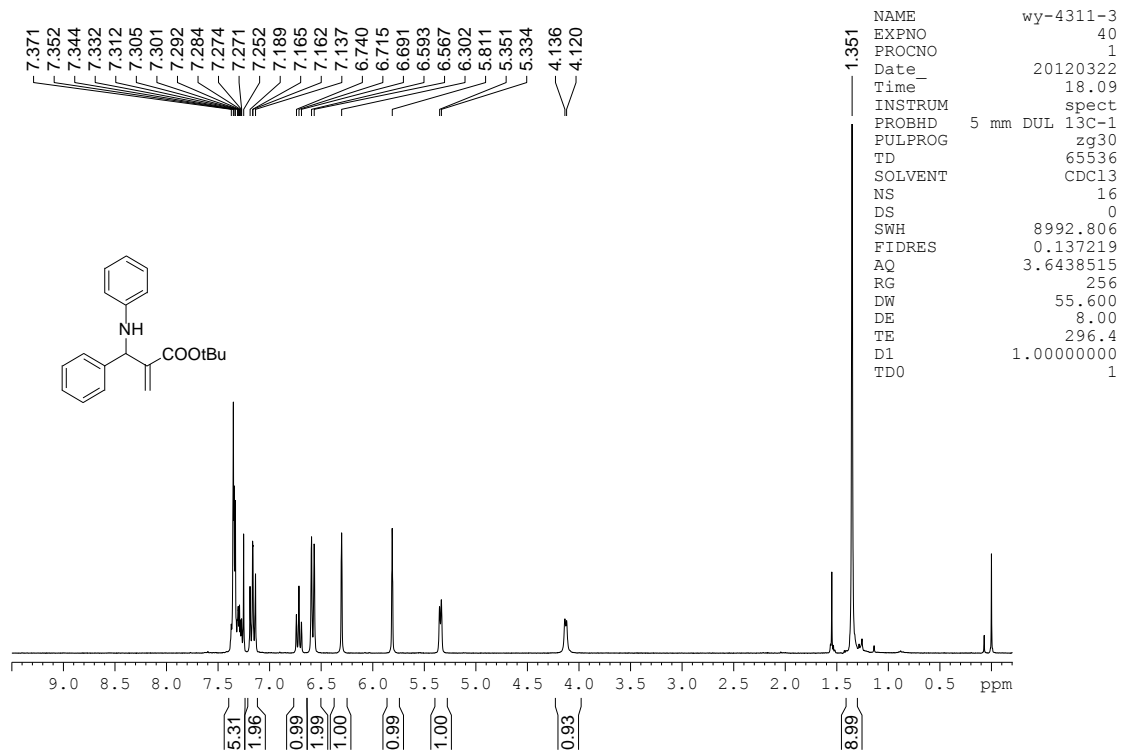
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PROCNO    1
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Time      17.55
INSTRUM   spect
PROBHD    5 mm DUL 13C-1
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         19
DS         4
SWH        17985.611
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AQ         1.8219508
RG         456.1
DW         27.800
DE         6.50
TE         295.8
    
```

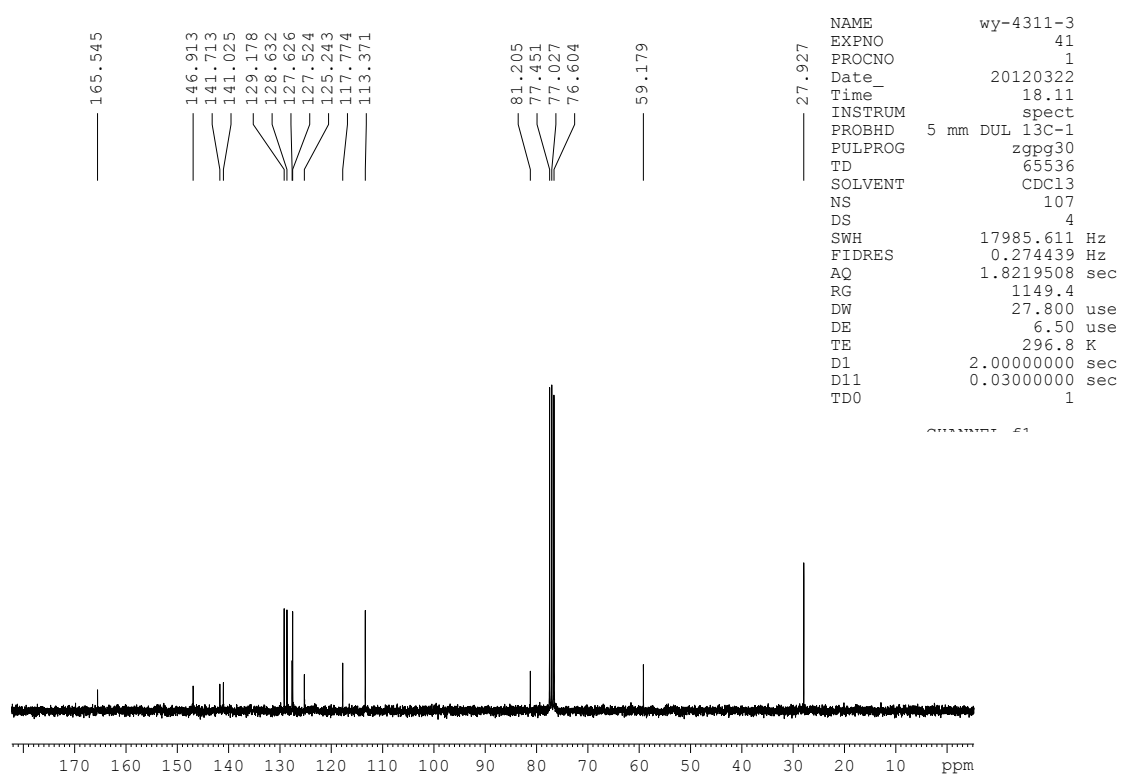






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PULPROG       zg30
TD            65536
SOLVENT       CDCl3
NS            16
DS            0
SWH           8992.806
FIDRES        0.137219
AQ            3.6438515
RG            256
DW            55.600
DE            8.00
TE            296.4
D1            1.00000000
TDO           1
    
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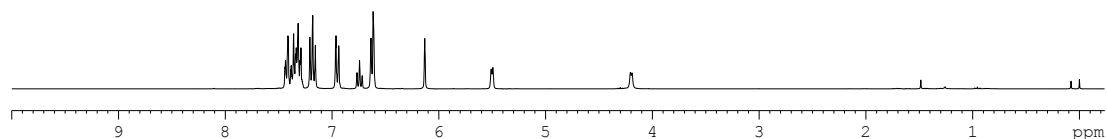
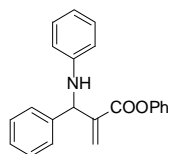
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TD            65536
SOLVENT       CDCl3
NS            107
DS            4
SWH           17985.611 Hz
FIDRES        0.274439 Hz
AQ            1.8219508 sec
RG            1149.4
DW            27.800 use
DE            6.50 use
TE            296.8 K
D1            2.00000000 sec
D11           0.03000000 sec
TDO           1
    
```

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7.341
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7.180
7.156
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6.962
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4.190

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EXPNO         30
PROCNO        1
Date_         20120319
Time_         21.49
INSTRUM       spect
PROBHD        5 mm DUL 13C-1
PULPROG       zg30
TD            65536
SOLVENT       CDCl3
NS            16
DS            0
SWH           8992.806
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AQ            3.6438515
RG            128
DW            55.600
DE            8.00
TE            296.3
    
```



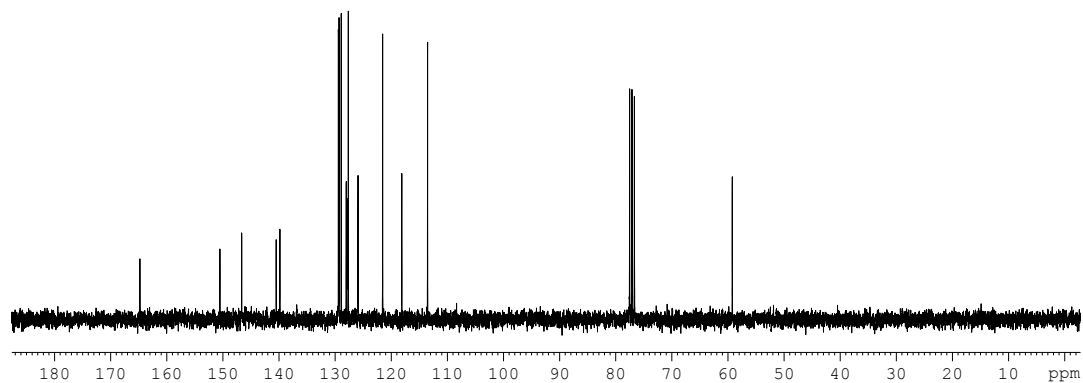
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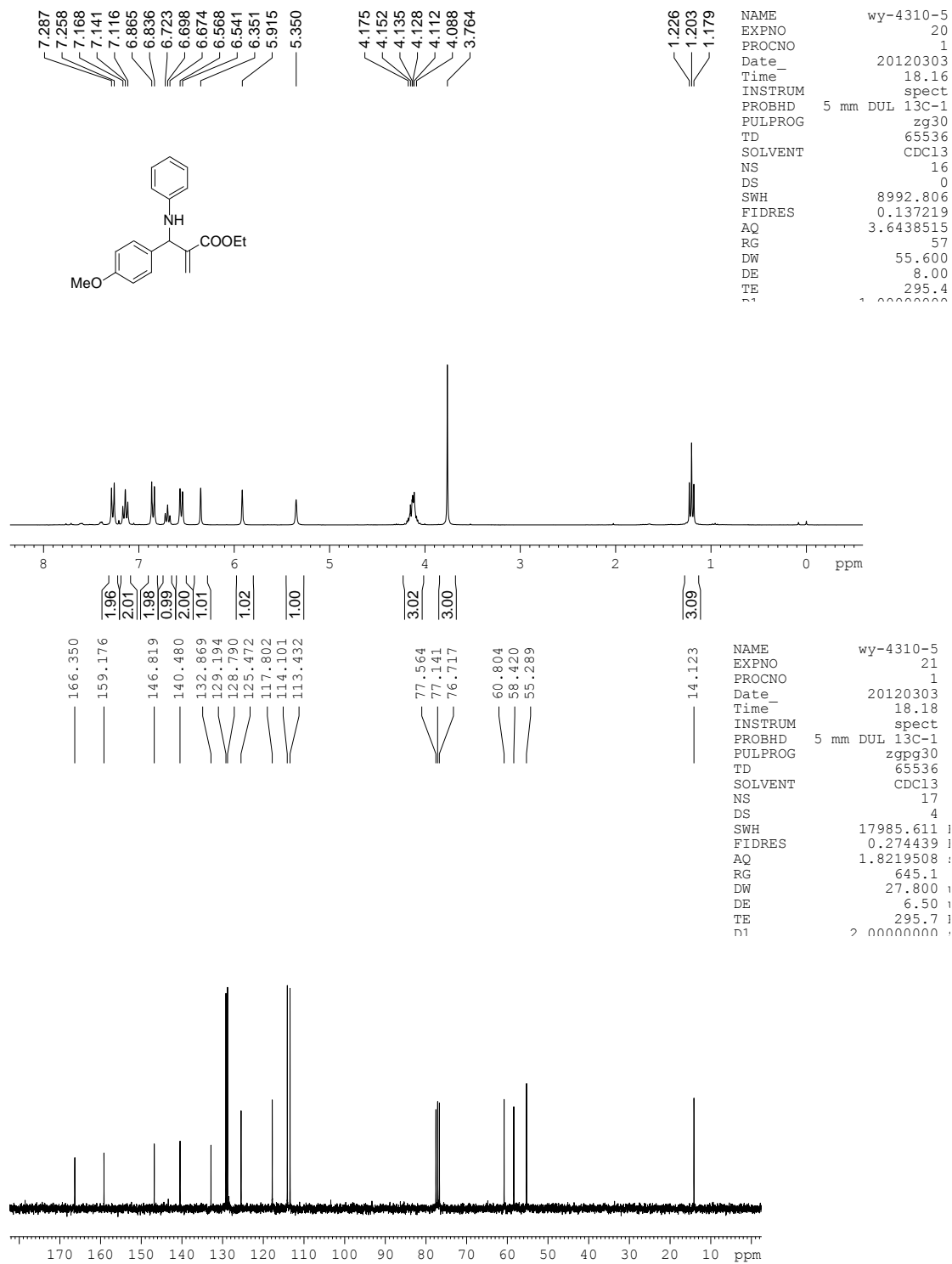
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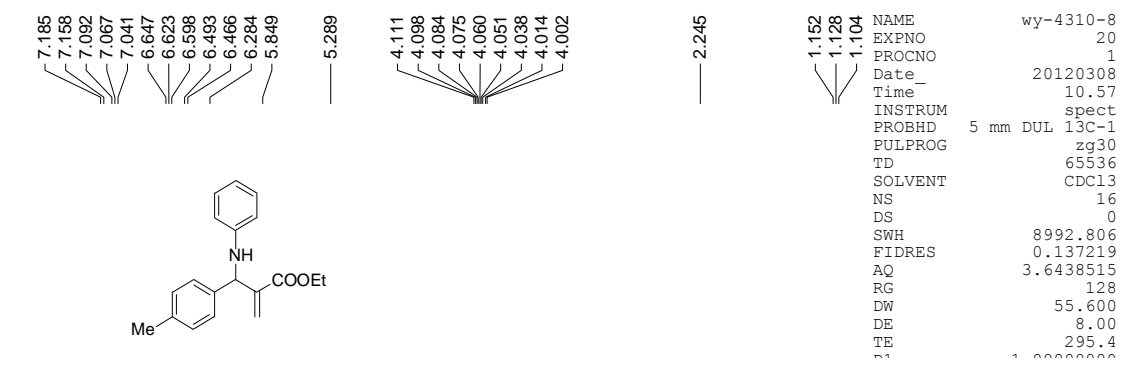
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INSTRUM       spect
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PULPROG       zgpg30
TD            65536
SOLVENT       CDCl3
NS            21
DS            4
SWH           17985.611
FIDRES        0.274439
AQ            1.8219508
RG            574.7
DW            27.800
DE            6.50
TE            296.5
    
```

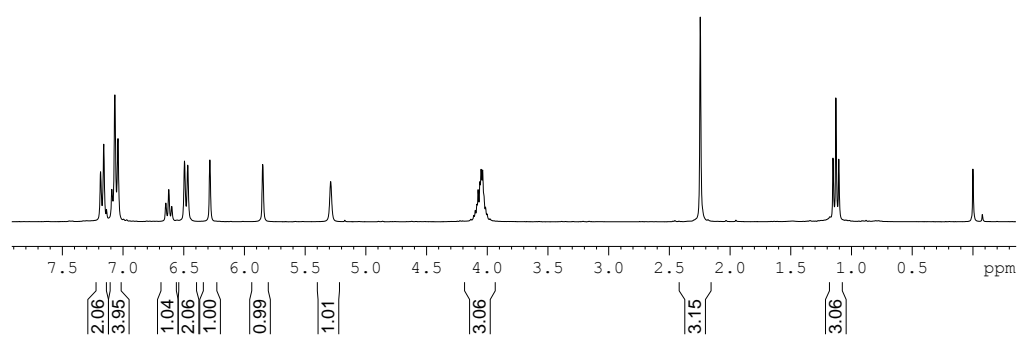






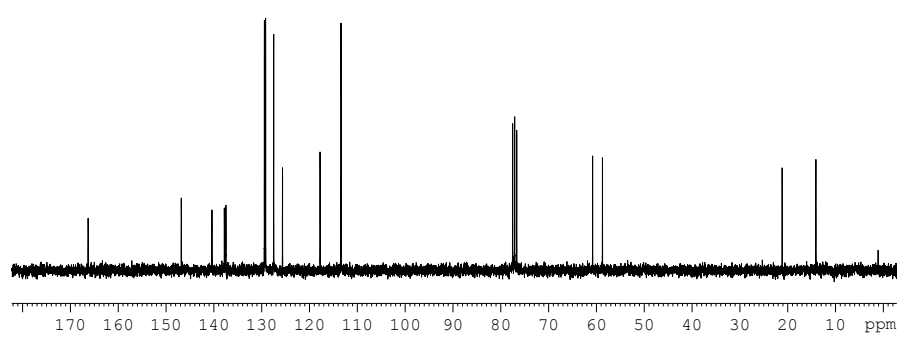
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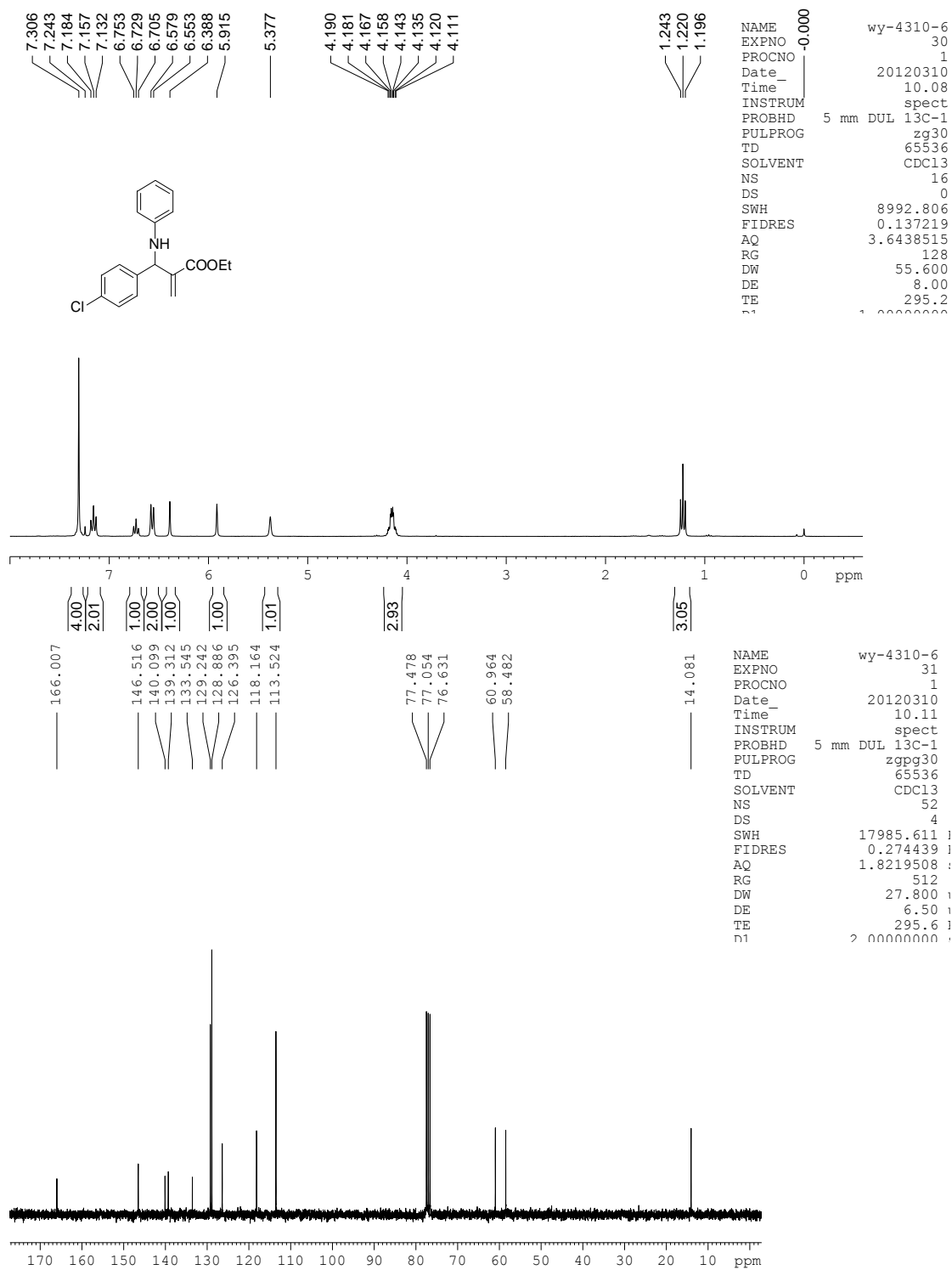
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TD         65536
SOLVENT   CDCl3
NS         16
DS         0
SWH        8992.806
FIDRES     0.137219
AQ         3.6438515
RG         128
DW         55.600
DE         8.00
TE         295.4
n1         1
    
```



```

NAME      wy-4310-8
EXPNO     21
PROCNO    1
Date_     20120308
Time      11.00
INSTRUM   spect
PROBHD    5 mm DUL 13C-1
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         25
DS         4
SWH        17985.611
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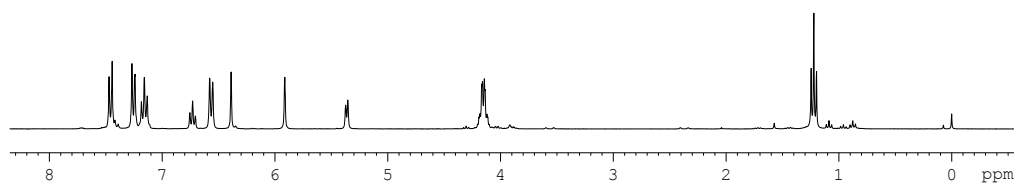
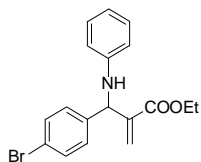


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6.388
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4.160
4.143
4.137
4.120
4.112

1.245
1.222
1.198

```

NAME      wy-4310-11
EXPNO    20
PROCNO   1
Date_    20120308
Time_    10.23
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PULPROG  zg30
TD       65536
SOLVENT  CDCl3
NS       16
DS       0
SWH      8992.806
FIDRES   0.137219
AQ       3.6438515
RG       128
DW       55.600
DE       8.00
TE       295.5
    
```



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1.01
1.98
1.03
1.00
1.02

3.00

3.05

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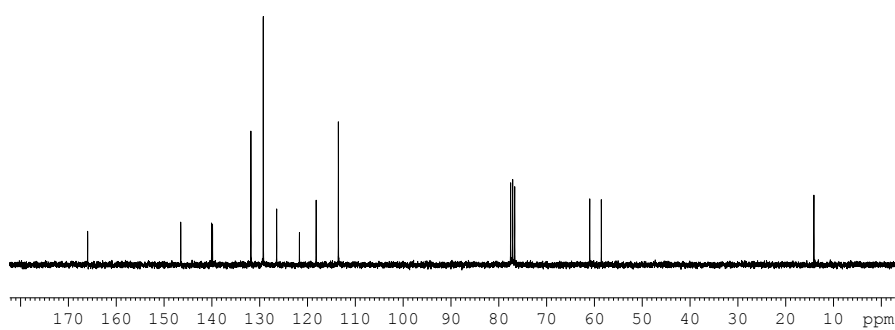
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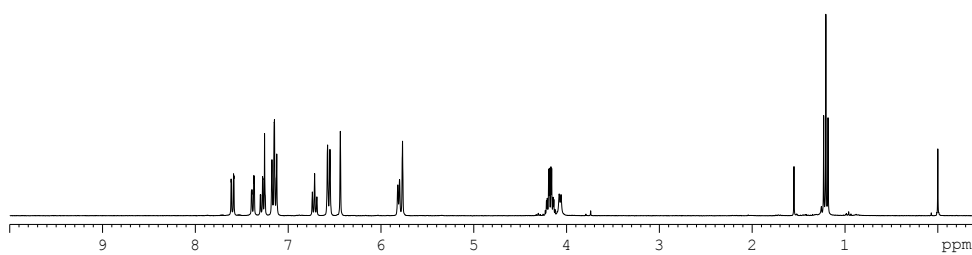
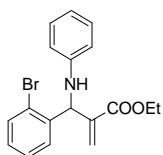
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SOLVENT  CDCl3
NS       22
DS       4
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FIDRES   0.274439
AQ       1.8219508
RG       812.7
DW       27.800
DE       6.50
TE       296.8
    
```



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7.123
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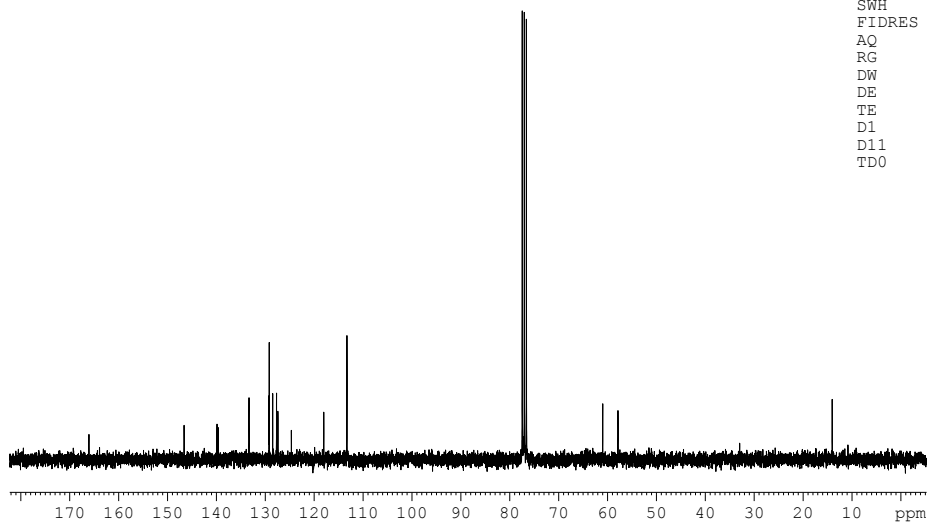
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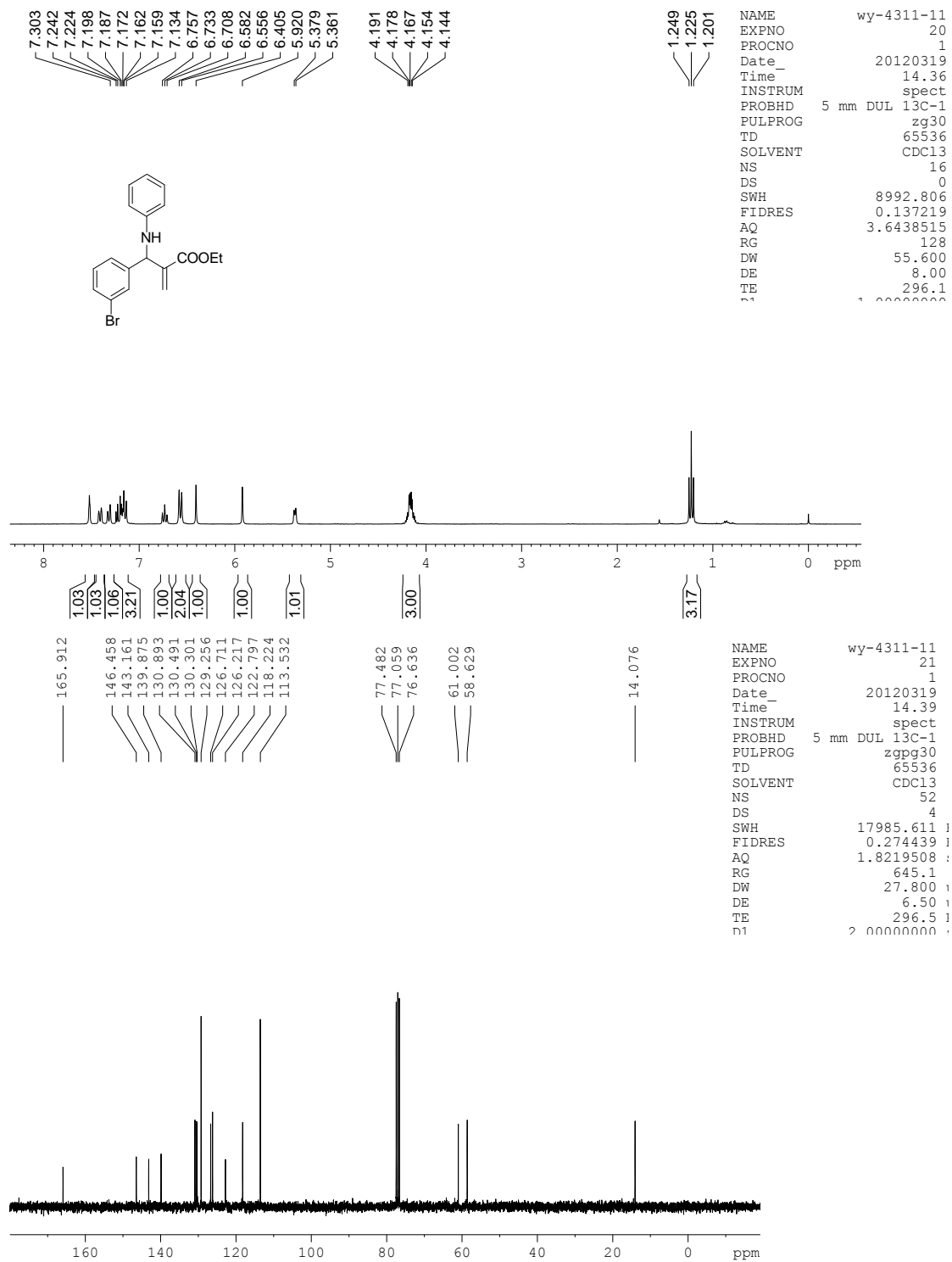
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NS	16
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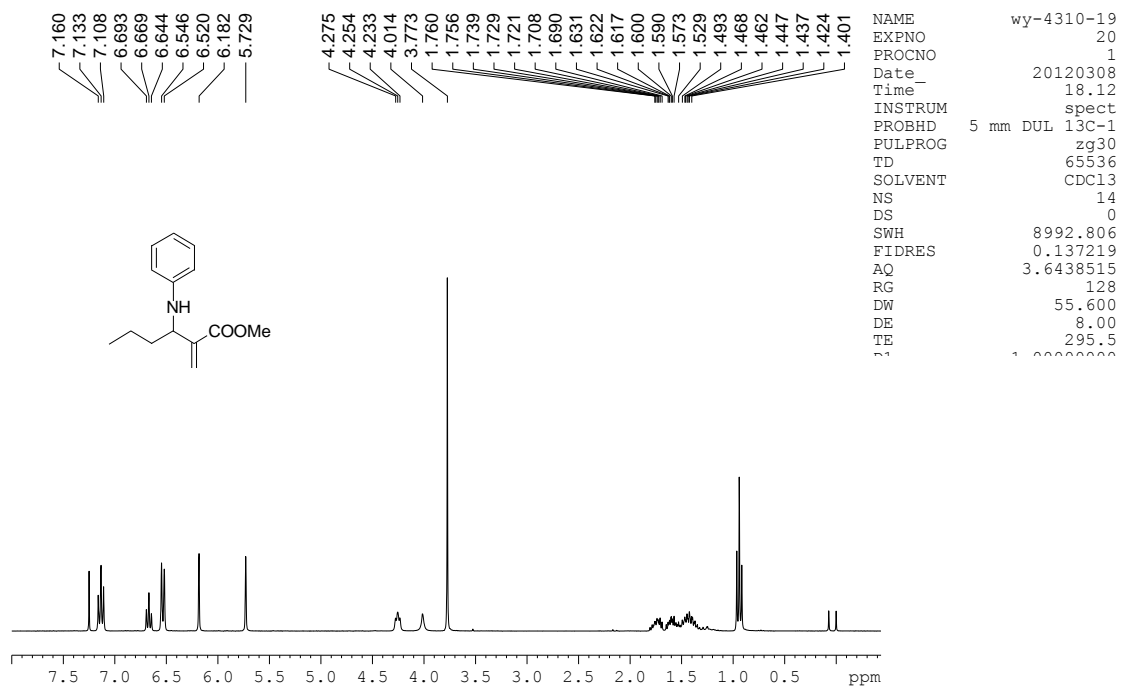


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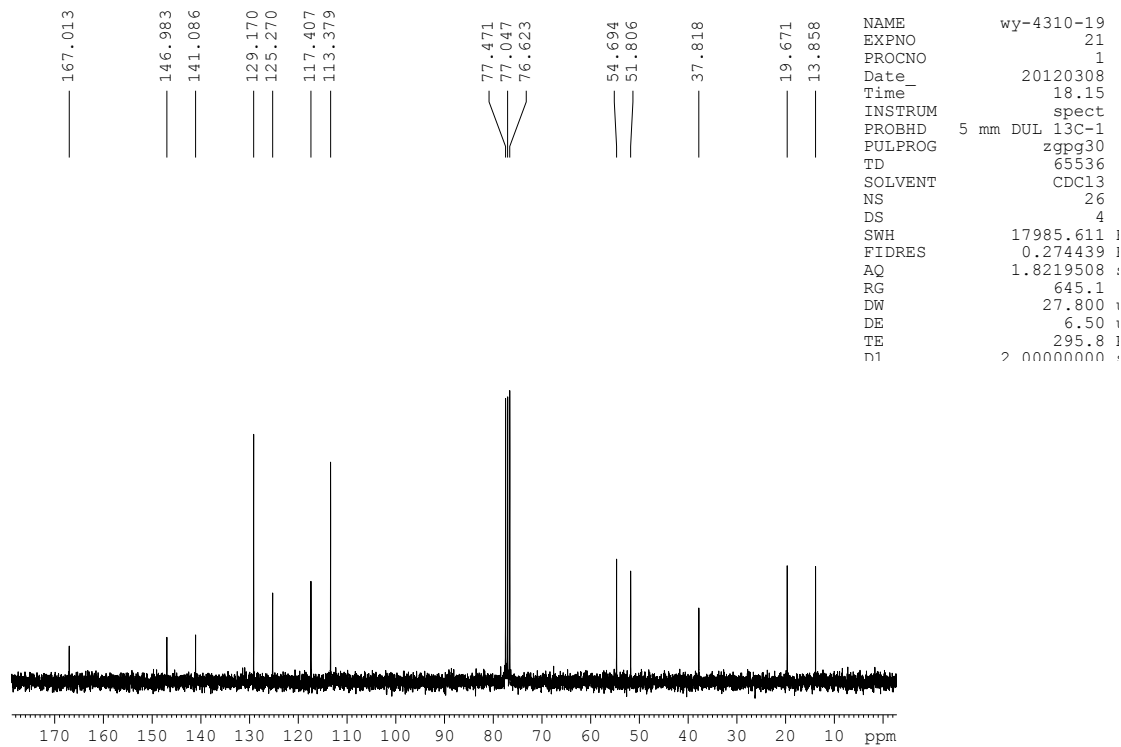
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TD	65536
SOLVENT	CDCl3
NS	84
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FIDRES	0.274439 H
AQ	1.8219508 s
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DW	27.800 u
DE	6.50 u
TE	296.8 K
D1	2.00000000 s
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TDO	1



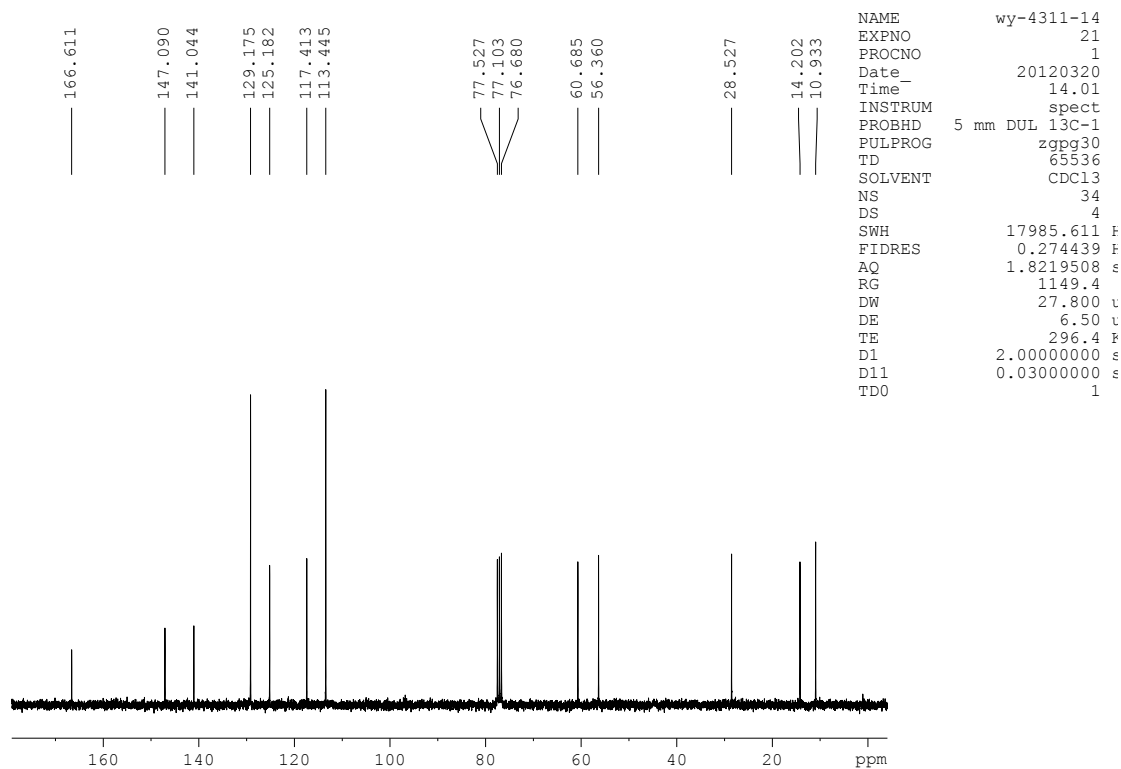
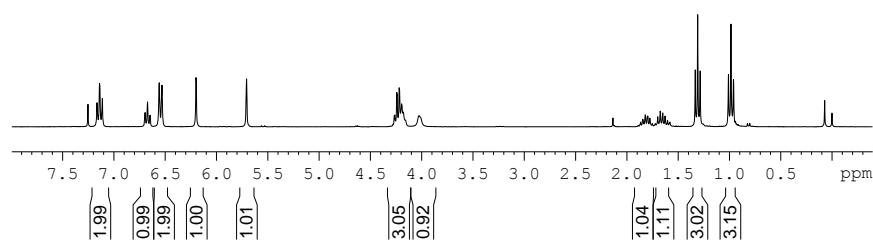
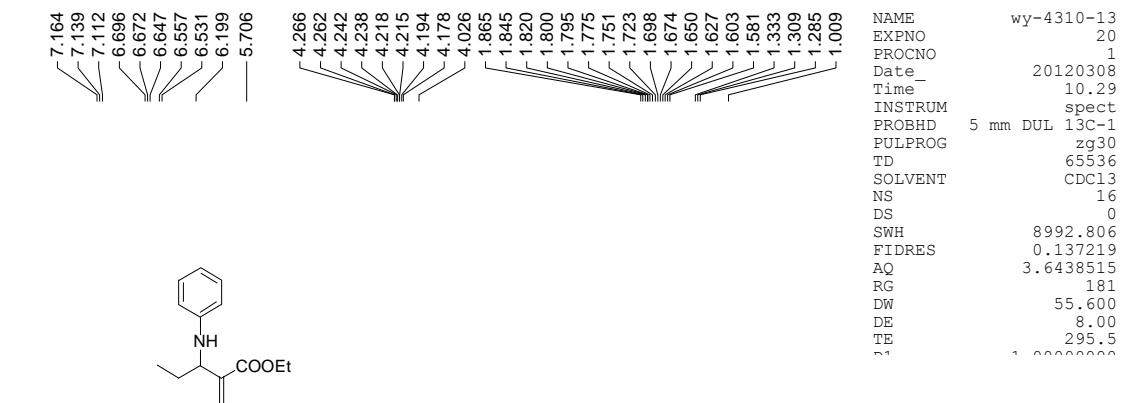


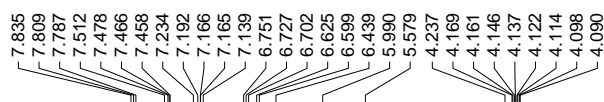


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 SOLVENT CDCl3
 NS 14
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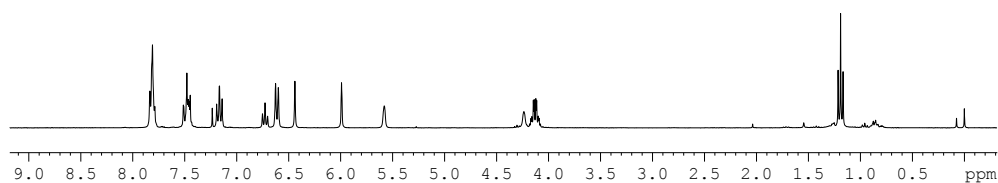
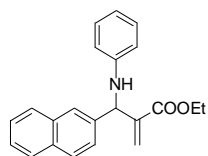
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 SOLVENT CDCl3
 NS 26
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 TE 295.8
 n1 2 000000000





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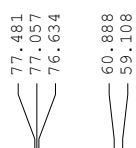
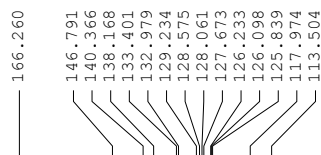
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FIDRES 0.137219
AQ 3.6438515
RG 181
DW 55.600
DE 8.00
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1.01
2.05
1.00
1.00
1.01

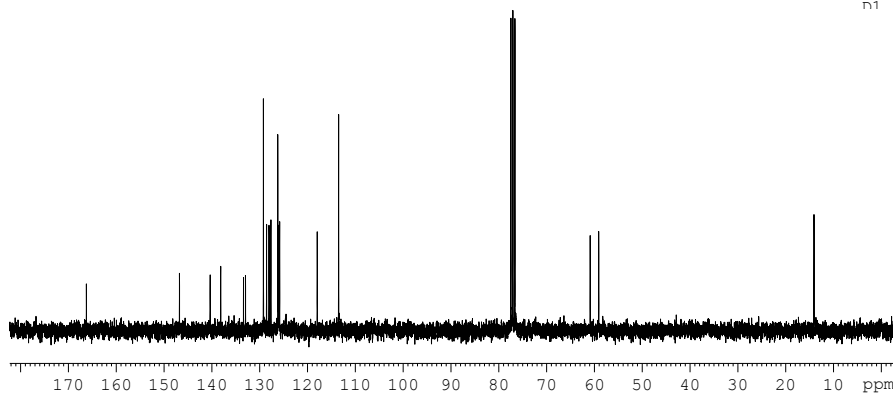
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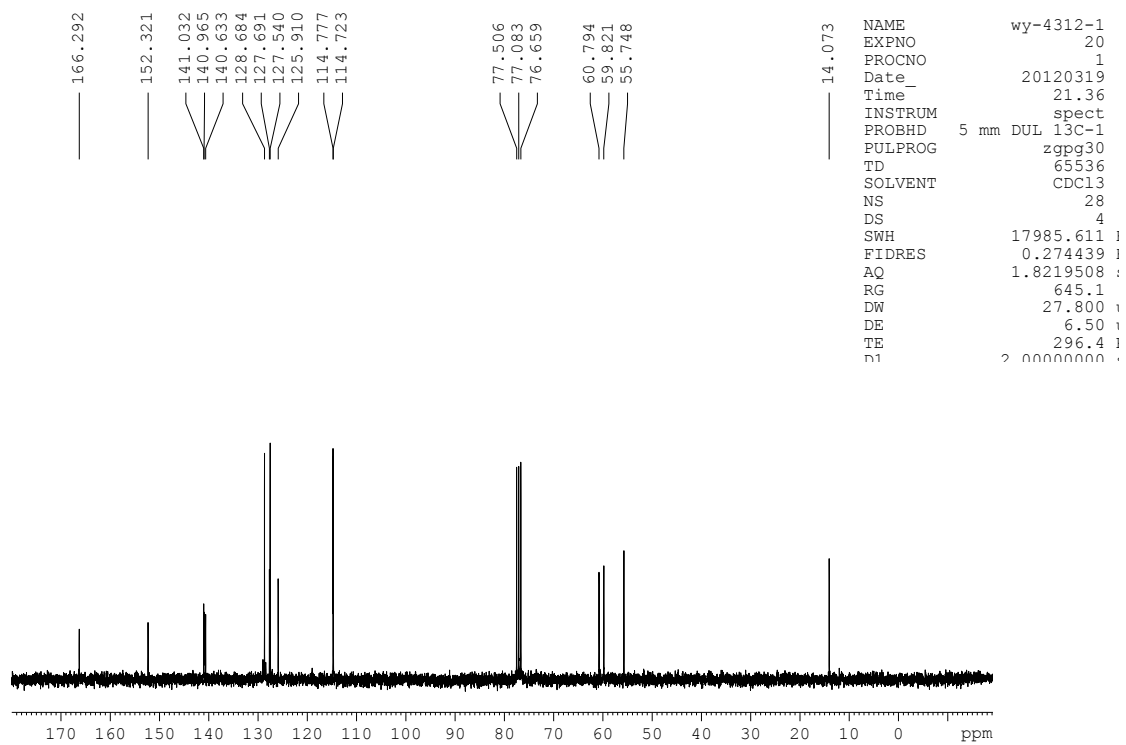
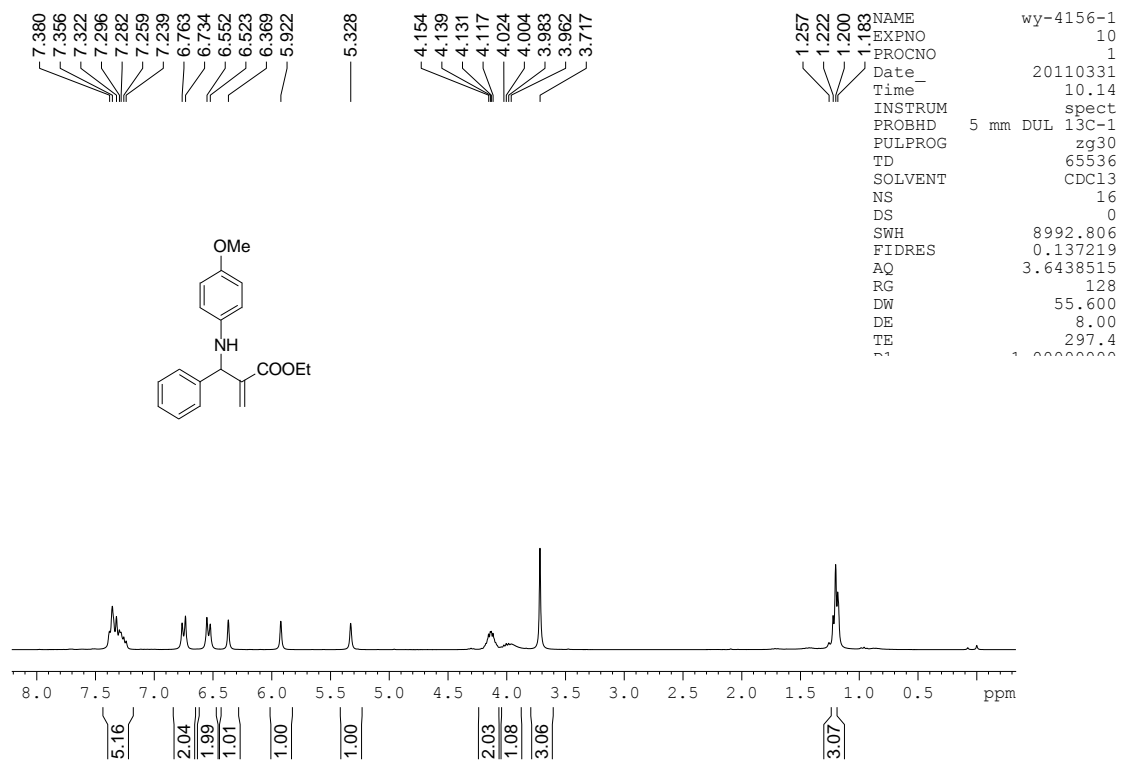
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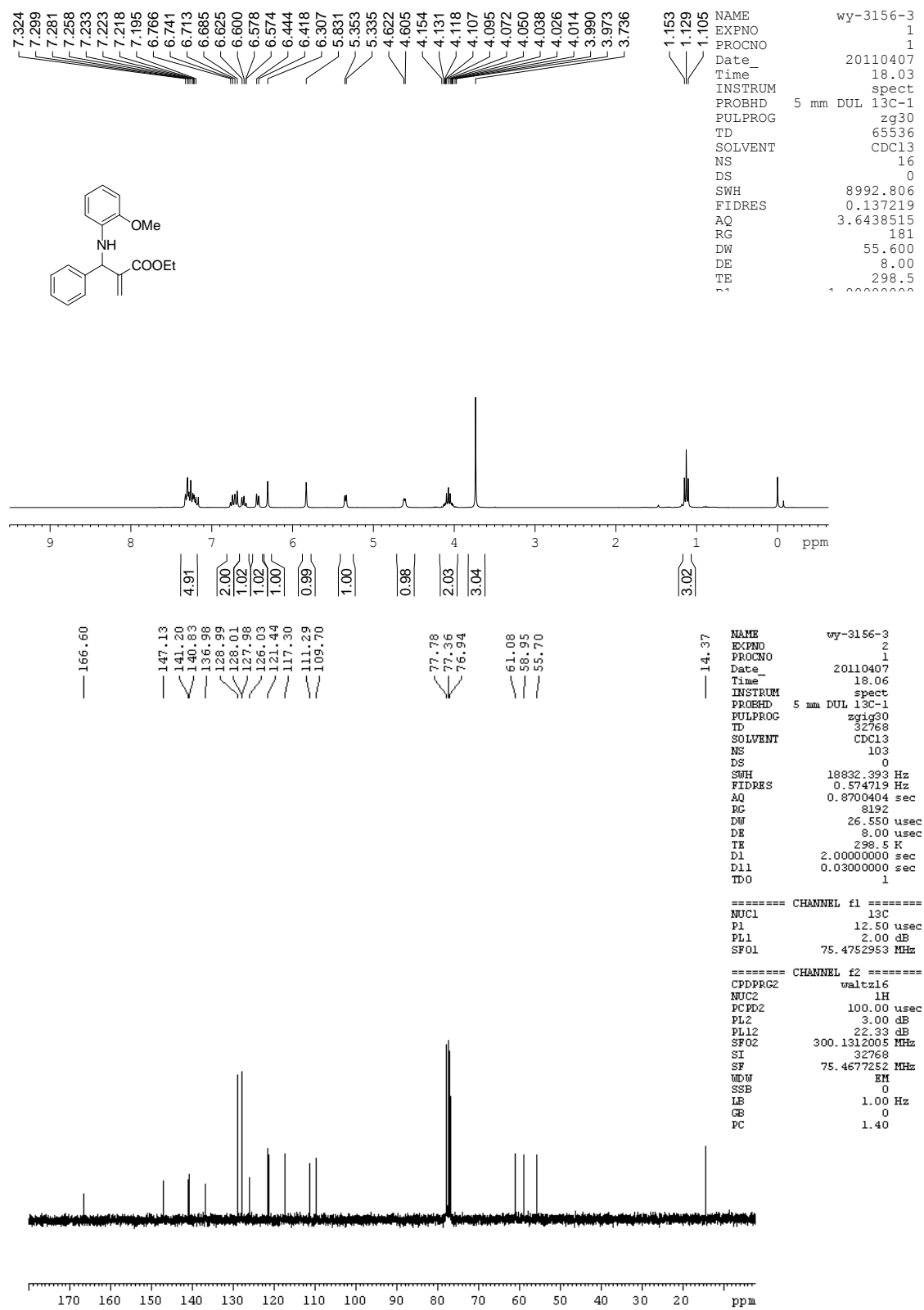


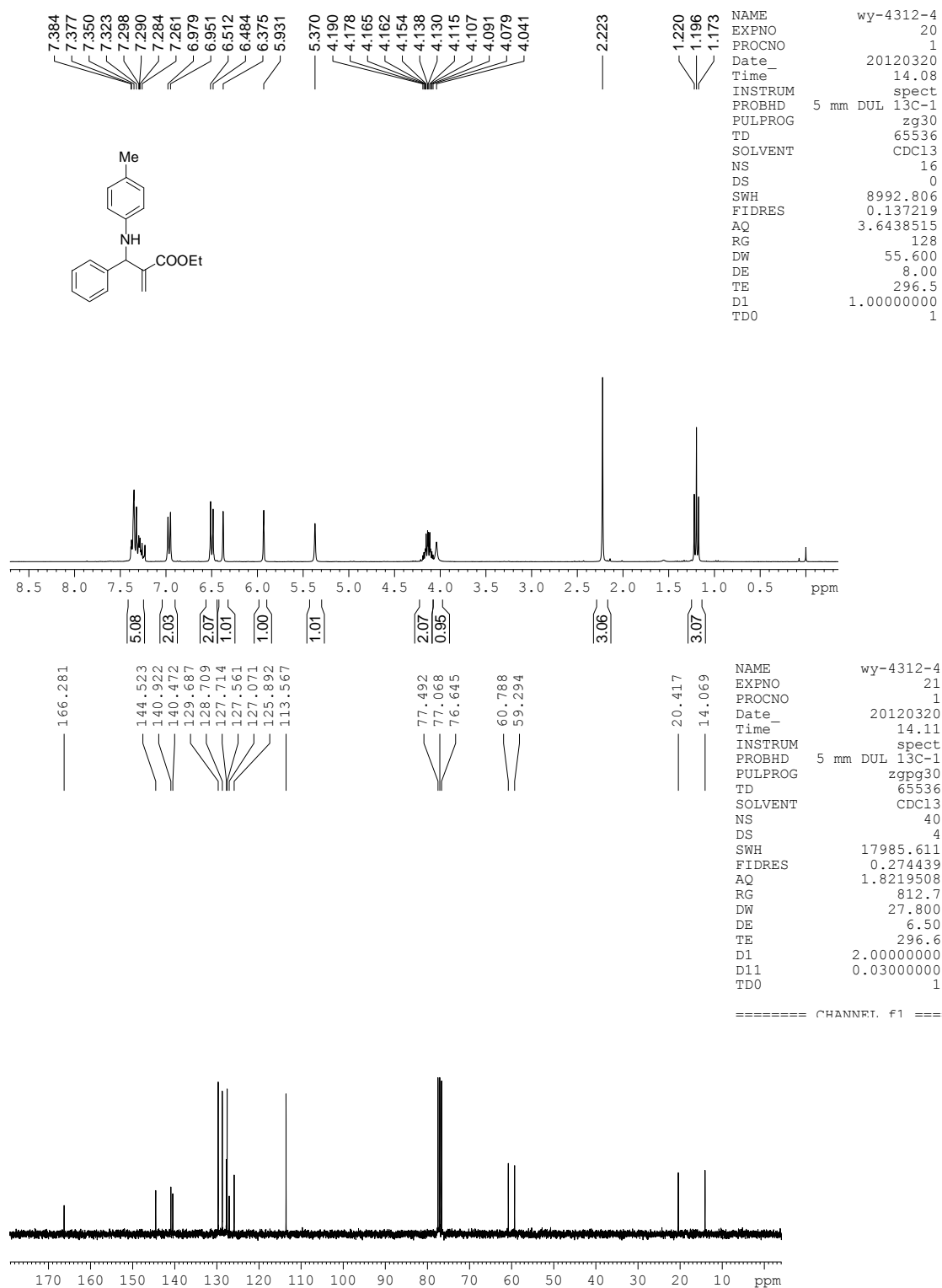
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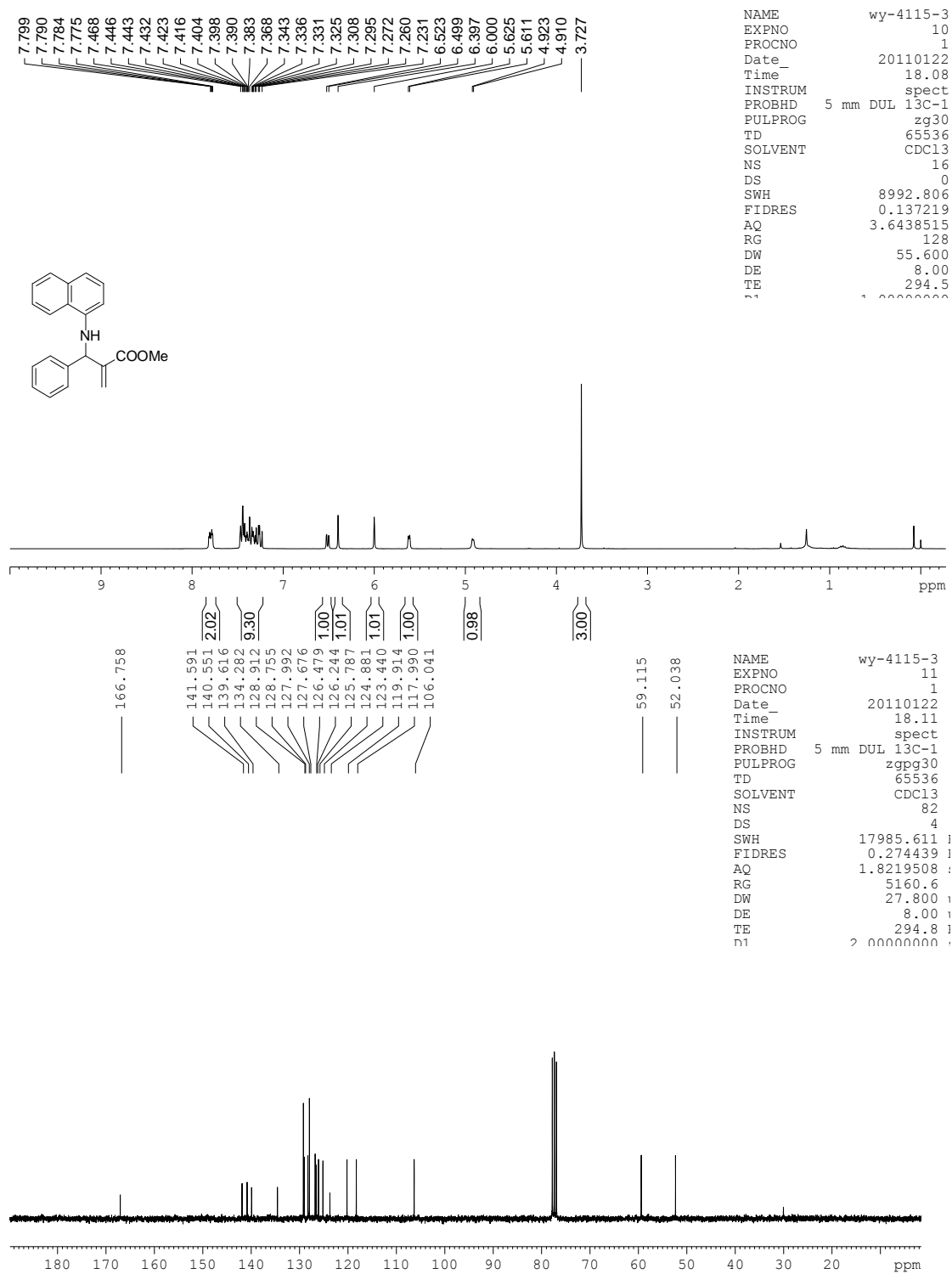
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EXPNO 21
PROCNO 1
Date_ 20120308
Time 10.37
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 43
DS 4
SWH 17985.611
FIDRES 0.274439
AQ 1.8219508
RG 574.7
DW 27.800
DE 6.50
TE 295.8
n1 2 000000000
    
```

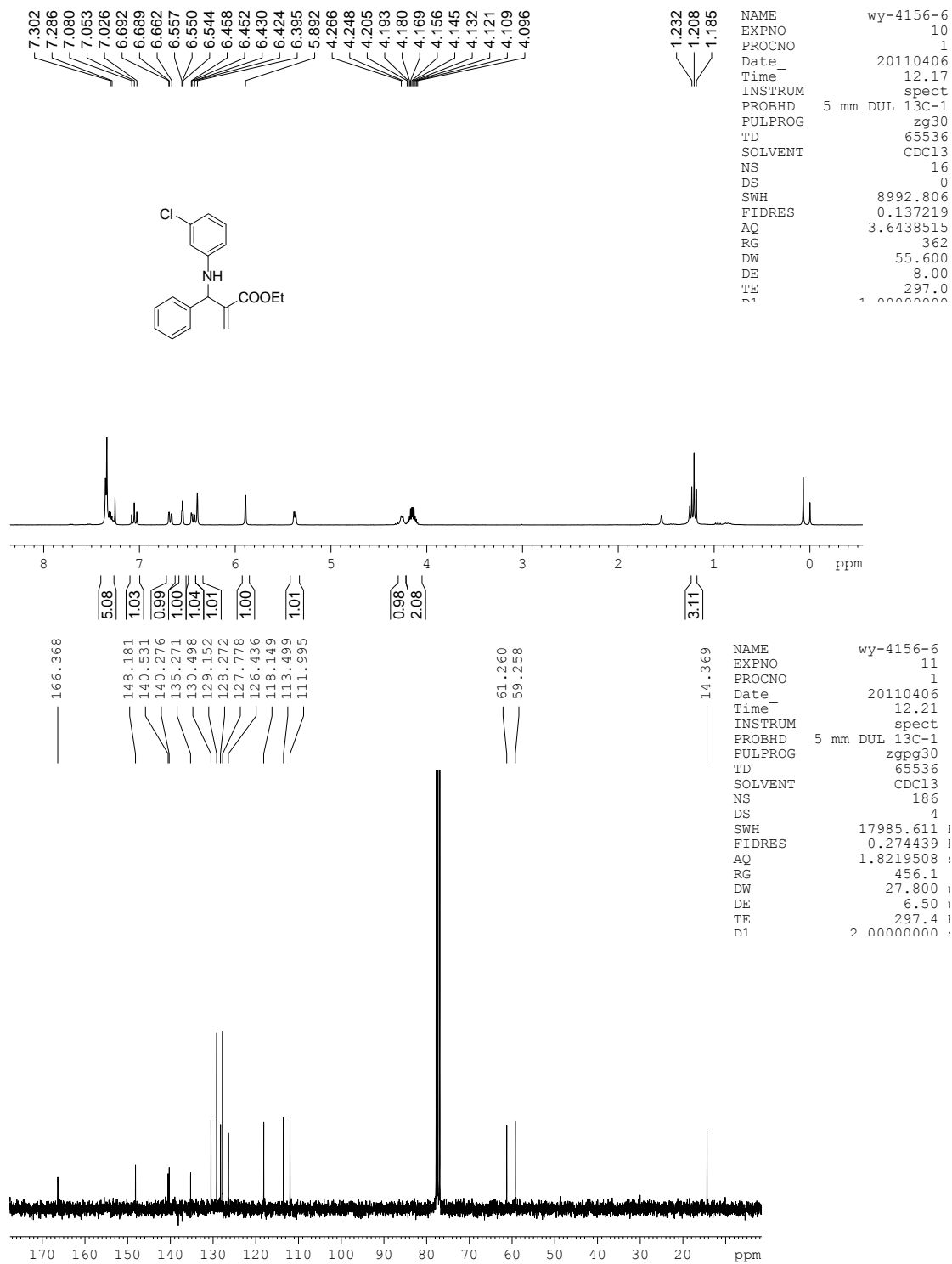


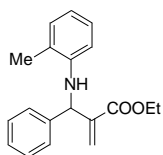
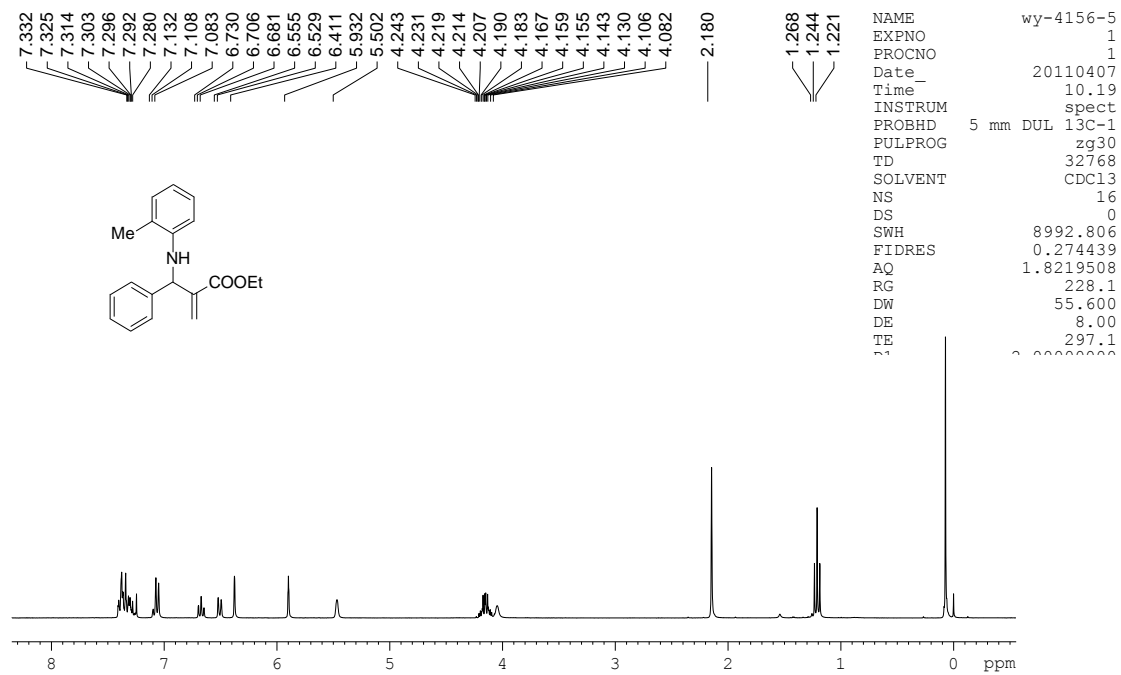






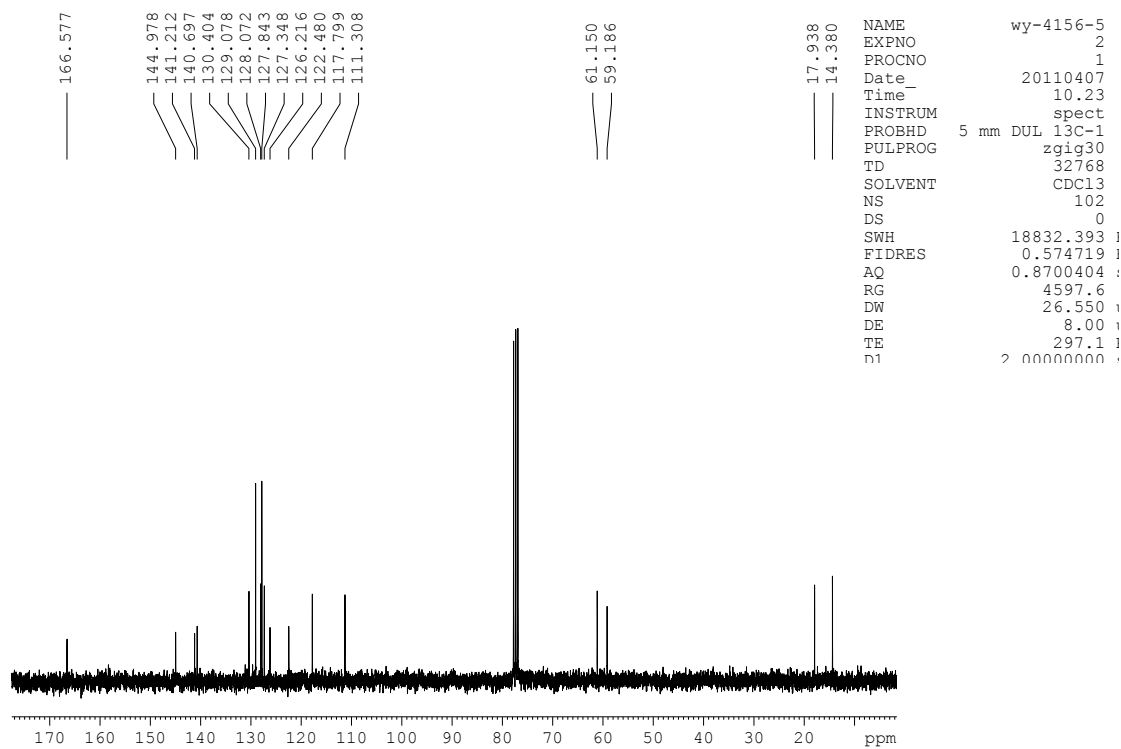






```

NAME      wy-4156-5
EXPNO     1
PROCNO    1
Date_     20110407
Time      10.19
INSTRUM   spect
PROBHD    5 mm DUL 13C-1
PULPROG   zg30
TD         32768
SOLVENT   CDCl3
NS         16
DS         0
SWH        8992.806
FIDRES     0.274439
AQ         1.8219508
RG         228.1
DW         55.600
DE         8.00
TE         297.1
    
```



```

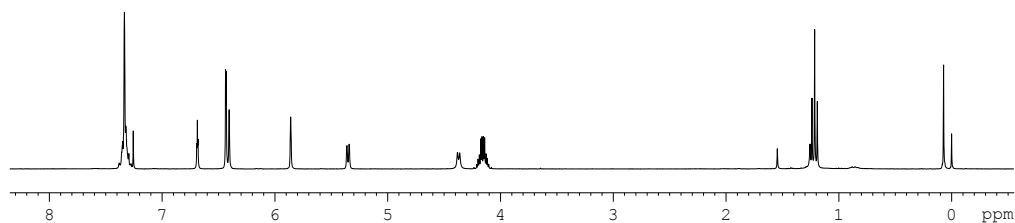
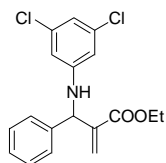
NAME      wy-4156-5
EXPNO     2
PROCNO    1
Date_     20110407
Time      10.23
INSTRUM   spect
PROBHD    5 mm DUL 13C-1
PULPROG   zgig30
TD         32768
SOLVENT   CDCl3
NS         102
DS         0
SWH        18832.393
FIDRES     0.574719
AQ         0.8700404
RG         4597.6
DW         26.550
DE         8.00
TE         297.1
    
```

7.358
7.350
7.334
7.322
7.295
6.692
6.687
6.681
6.437
6.431
6.405
5.860
5.361
5.341
4.381
4.361
4.211
4.198
4.187
4.175
4.164
4.151
4.140
4.127
4.116
4.104

1.238
1.214
1.190

```

NAME          wy-4156-8
EXPNO         10
PROCNO        1
Date_         20110408
Time_         18.15
INSTRUM       spect
PROBHD        5 mm DUL 13C-1
PULPROG       zg30
TD            65536
SOLVENT       CDCl3
NS            16
DS            0
SWH           8992.806
FIDRES        0.137219
AQ            3.6438515
RG            322.5
DW            55.600
DE            8.00
TE            298.2
    
```



5.00
0.95
1.95
1.04
1.00
1.01

0.98
2.03

3.07

165.855
148.311
139.665
139.582
135.438
128.901
128.103
127.338
126.285
117.713
111.588

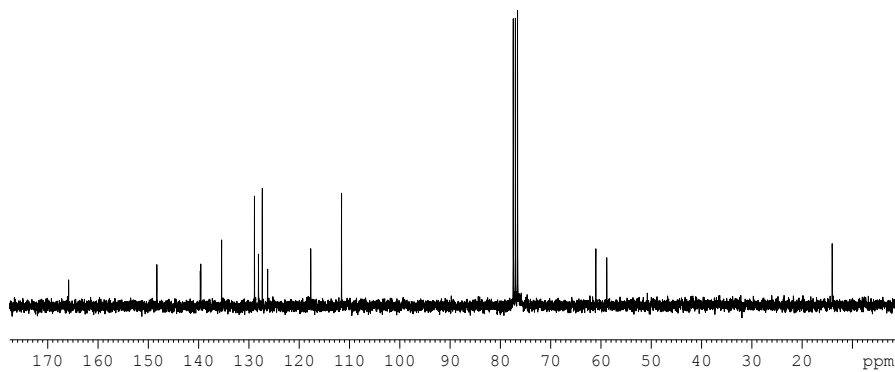
77.442
77.019
76.595

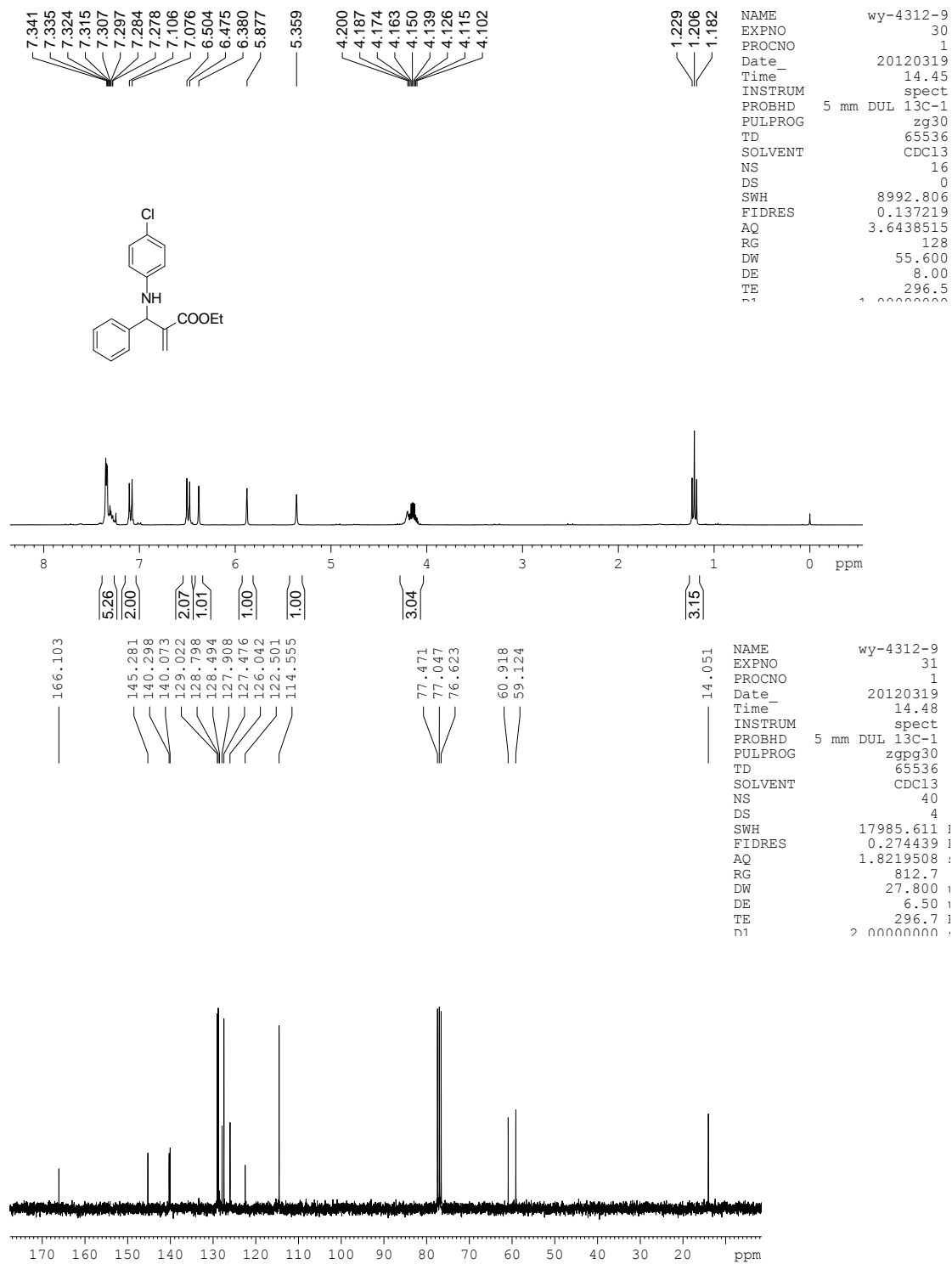
61.029
58.854

14.019

```

NAME          wy-4156-8
EXPNO         11
PROCNO        1
Date_         20110408
Time_         18.19
INSTRUM       spect
PROBHD        5 mm DUL 13C-1
PULPROG       zgig30
TD            32768
SOLVENT       CDCl3
NS            124
DS            0
SWH           18832.393
FIDRES        0.574719
AQ            0.8700404
RG            6502
DW            26.550
DE            8.00
TE            298.3
    
```



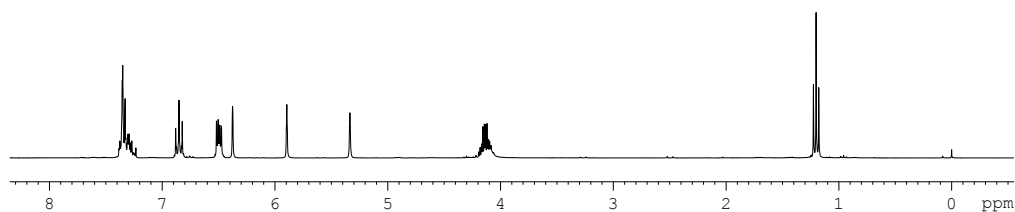
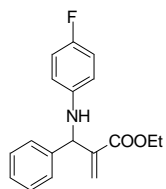


7.322
7.309
7.303
7.298
7.291
7.282
7.269
6.880
6.851
6.822
6.518
6.503
6.496
6.488
6.473
6.375
5.894
5.335
4.181
4.168
4.157
4.144
4.133
4.120
4.109
4.096
4.084

1.225
1.201
1.177

```

NAME      wy-4312-10
EXPNO     20
PROCNO    1
Date_     20120316
Time_     18.05
INSTRUM   spect
PROBHD    5 mm DUL 13C-1
PULPROG   zg30
TD        65536
SOLVENT   CDCl3
NS         16
DS         0
SWH       8992.806
FIDRES    0.137219
AQ         3.6438515
RG         128
DW         55.600
DE         8.00
TE         295.5
    
```



5.21
1.97
2.10
1.00
1.00
1.00

3.02

3.09

166.197
157.565
154.444
143.138
143.113
140.588
140.344
129.278
128.761
128.465
127.837
127.513
125.993
115.766
115.471
114.363
114.265

77.501
77.078
76.654

60.884
59.608

14.059

```

NAME      wy-4312-10
EXPNO     21
PROCNO    1
Date_     20120316
Time_     18.08
INSTRUM   spect
PROBHD    5 mm DUL 13C-1
PULPROG   zgpg30
TD        65536
SOLVENT   CDCl3
NS         51
DS         4
SWH       17985.611
FIDRES    0.274439
AQ         1.8219508
RG         2580.3
DW         27.800
DE         6.50
TE         295.9
    
```

