

Supporting Information

Cu(II)-Catalyzed and Acid-Promoted Highly Regioselective Oxidation of Tautomerizable C(sp³)-H Bonds Adjacent to 3,4-Dihydroisoquinolines Using Air (O₂) as a Clean Oxidant

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Engineering Research Center of Pharmaceutical Process Chemistry of the Ministry of Education, School of Pharmacy, East China University of Science and Technology, Shanghai 200237, People's Republic of China

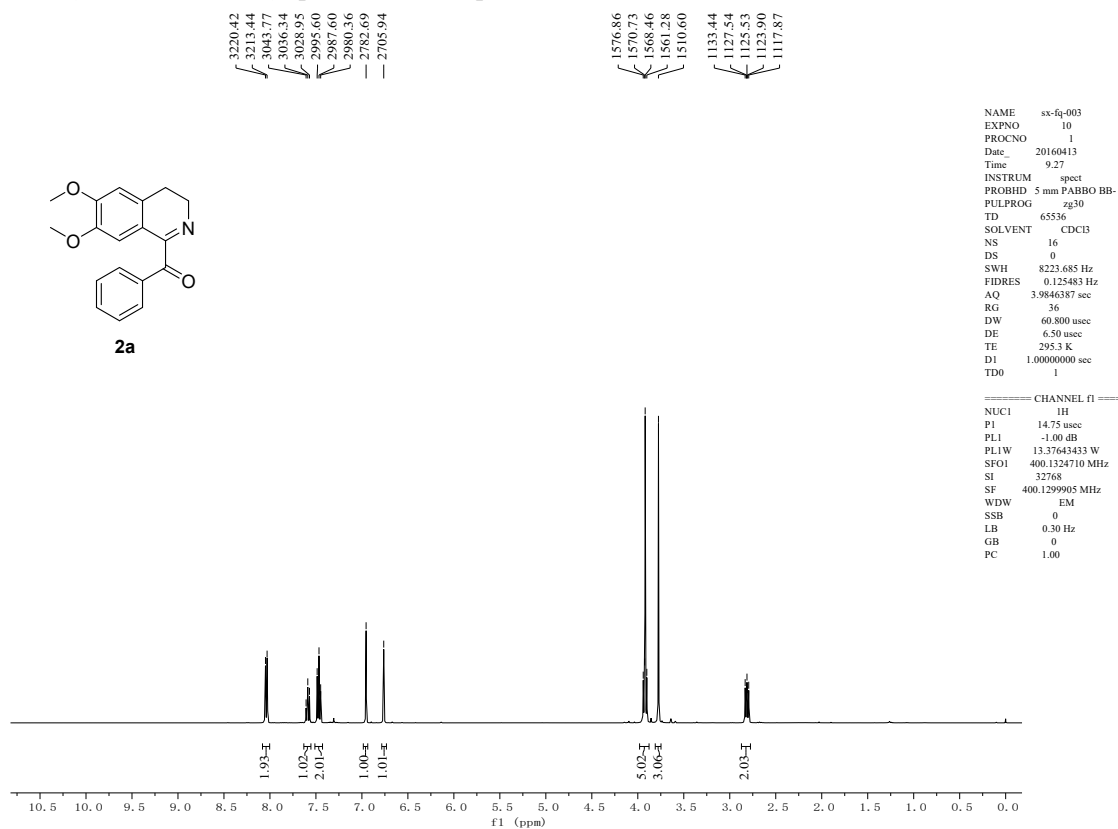
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¹H and ¹³C NMR Spectra of Compounds 2a-2t, 4-8 and 10

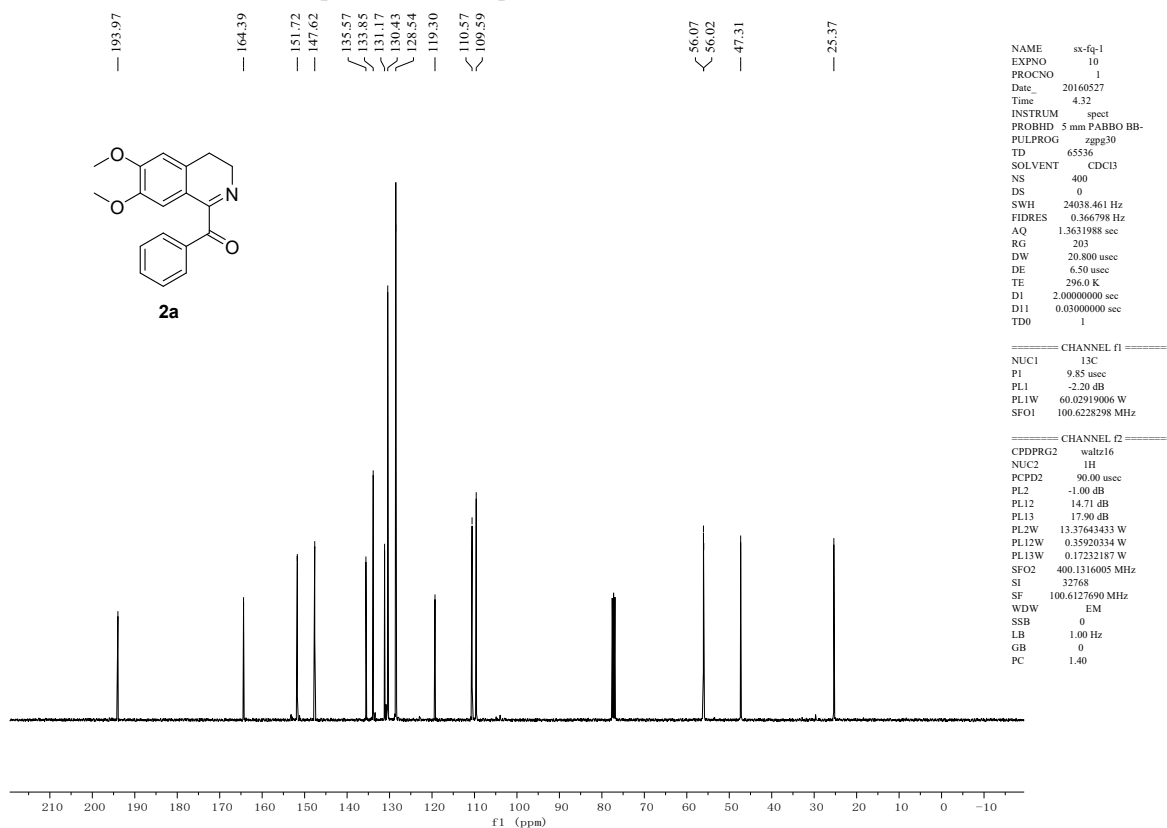
¹H NMR (CDCl₃, 400 MHz) spectrum of compound 2a:



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NAME      sx-fq-003
EXPNO     10
PROCNO    1
Date_     20160413
Time      9.27
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zg30
TD         65536
SOLVENT   CDCl3
NS         16
DS         0
SWH        8223.685 Hz
FIDRES     0.125483 Hz
AQ         3.9846387 sec
RG         36
DW         60.800 usec
DE         6.50 usec
TE         295.3 K
D1         1.00000000 sec
TD0        1
===== CHANNEL f1 =====
NUC1       1H
P1         14.75 usec
PL1        -1.00 dB
PL1W       13.37643433 W
SFO1       400.1324710 MHz
SI         32768
SF         400.1299905 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00
    
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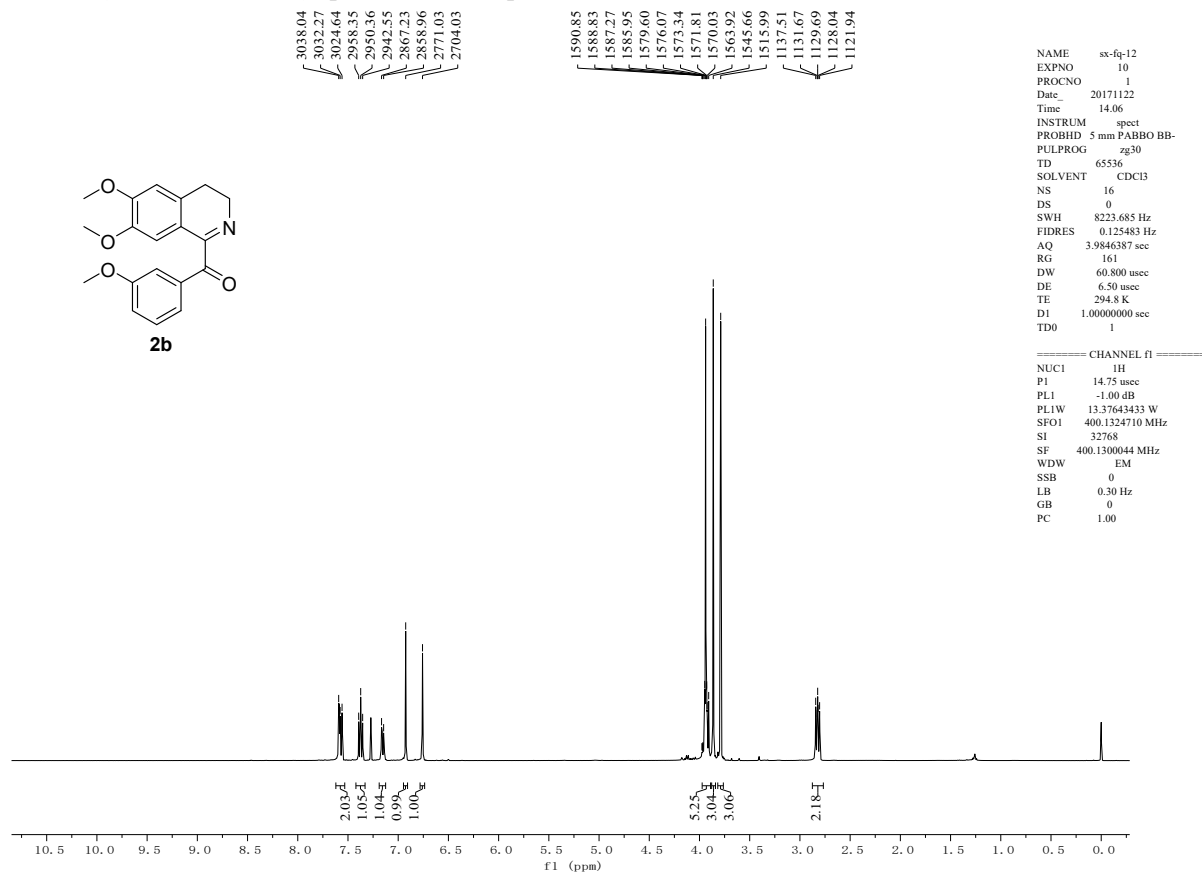
¹³C NMR (CDCl₃, 100 MHz) spectrum of compound 2a:



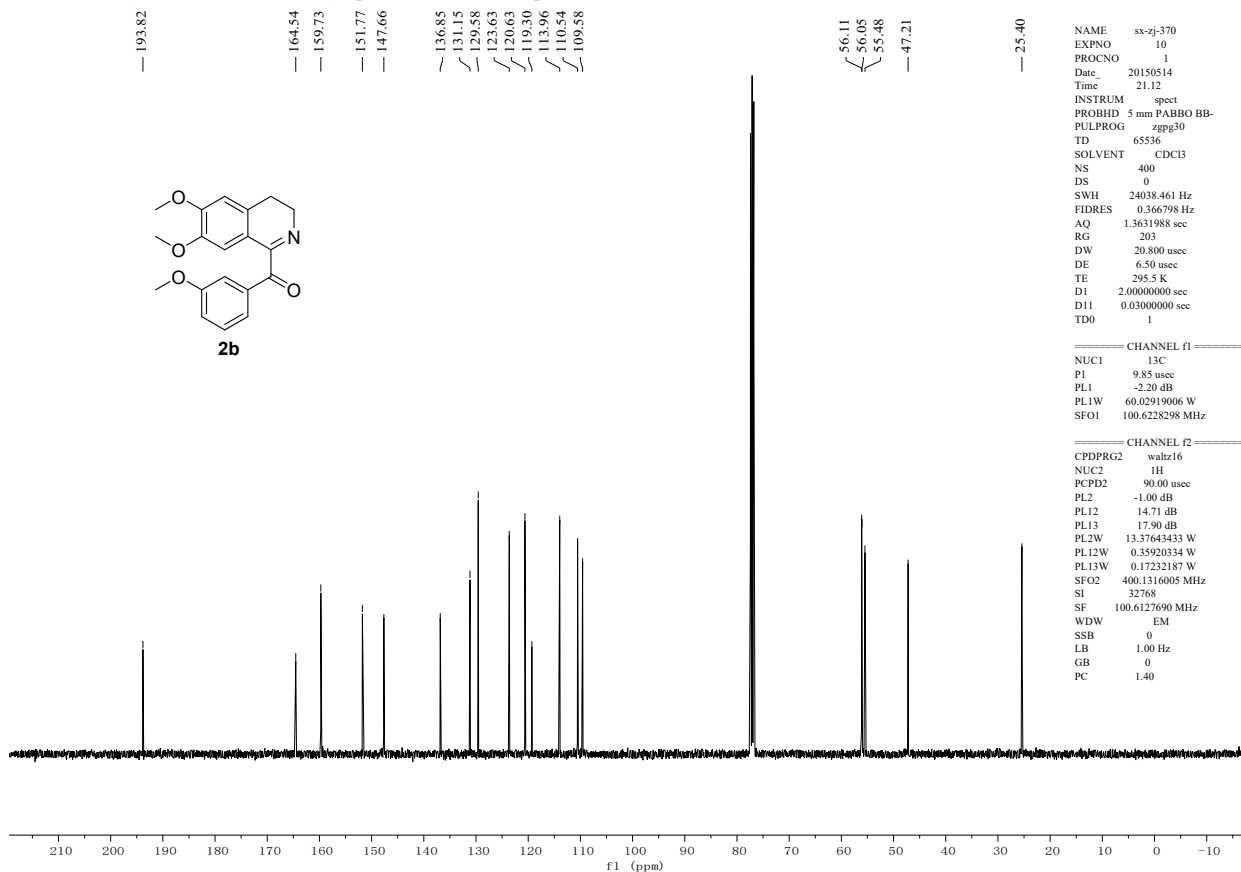
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EXPNO     10
PROCNO    1
Date_     20160527
Time      4.32
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         400
DS         0
SWH        24038.461 Hz
FIDRES     0.366798 Hz
AQ         1.3631988 sec
RG         203
DW         20.800 usec
DE         6.50 usec
TE         296.0 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0        1
===== CHANNEL f1 =====
NUC1       13C
P1         9.85 usec
PL1        -2.20 dB
PL1W       60.02919006 W
SFO1       100.6228298 MHz
===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2       1H
PCPD2     90.00 usec
PL2        -1.00 dB
PL12       14.71 dB
PL13       17.90 dB
PL2W       13.37643433 W
PL12W     0.35920334 W
PL13W     0.17232187 W
SFO2       400.1316005 MHz
SI         32768
SF         100.6127690 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
    
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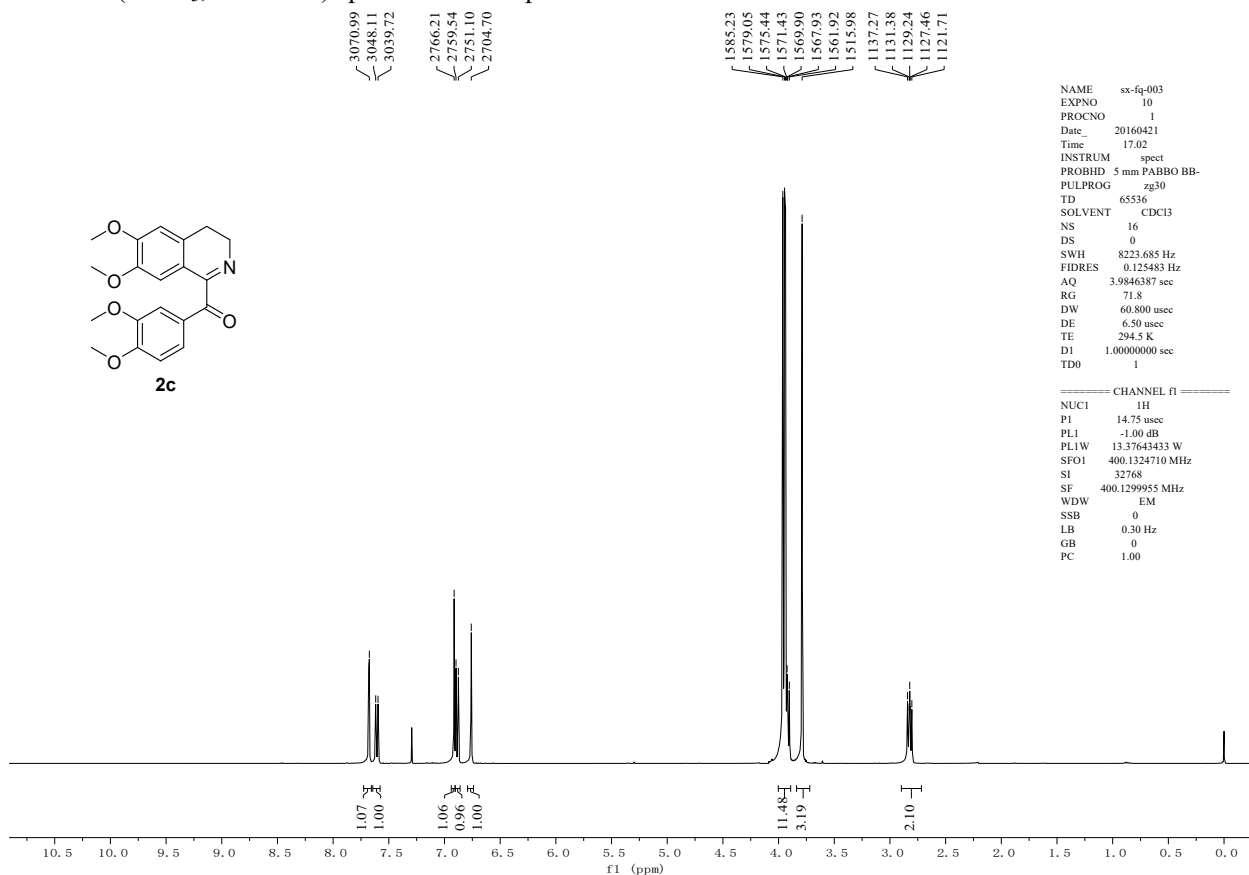
¹H NMR (CDCl₃, 400 MHz) spectrum of compound **2b**:



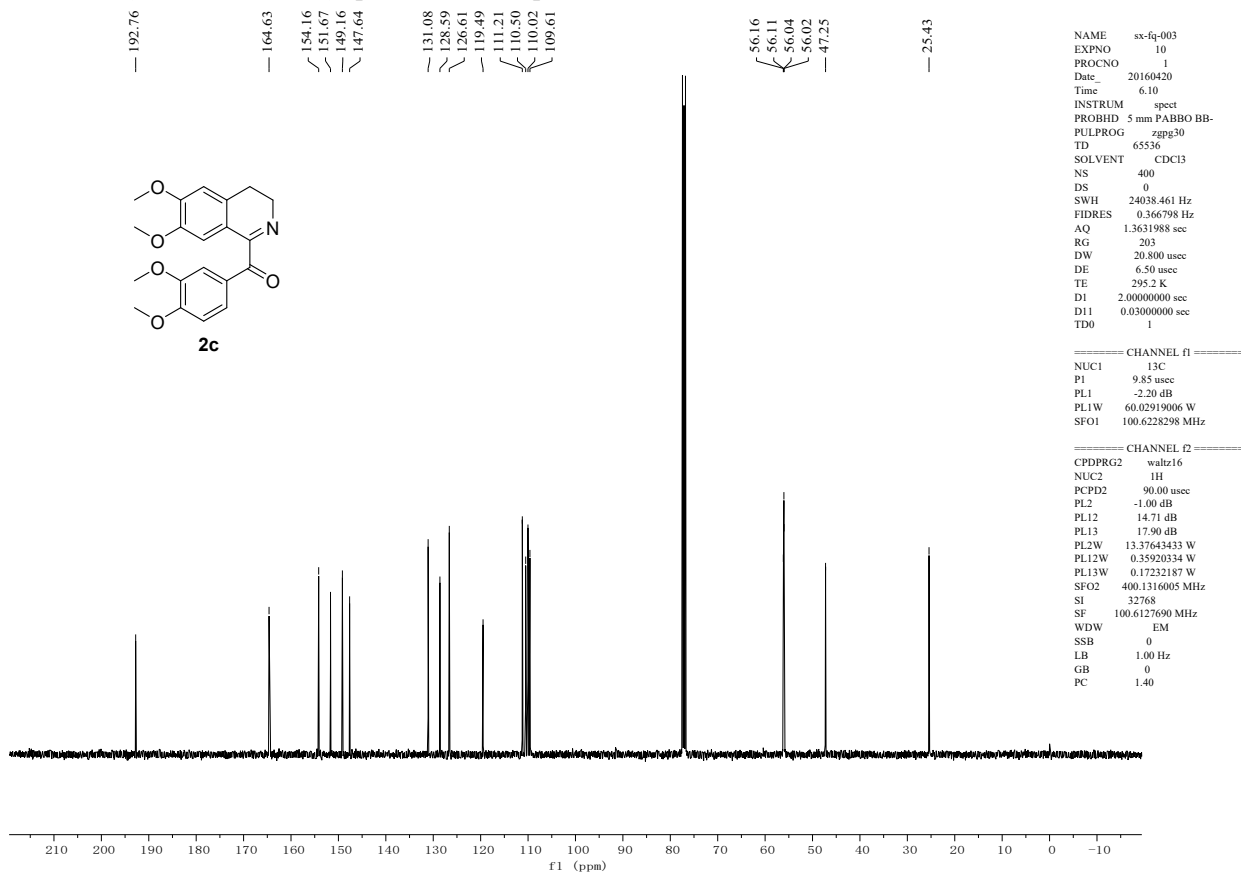
¹³C NMR (CDCl₃, 100 MHz) spectrum of compound **2b**:



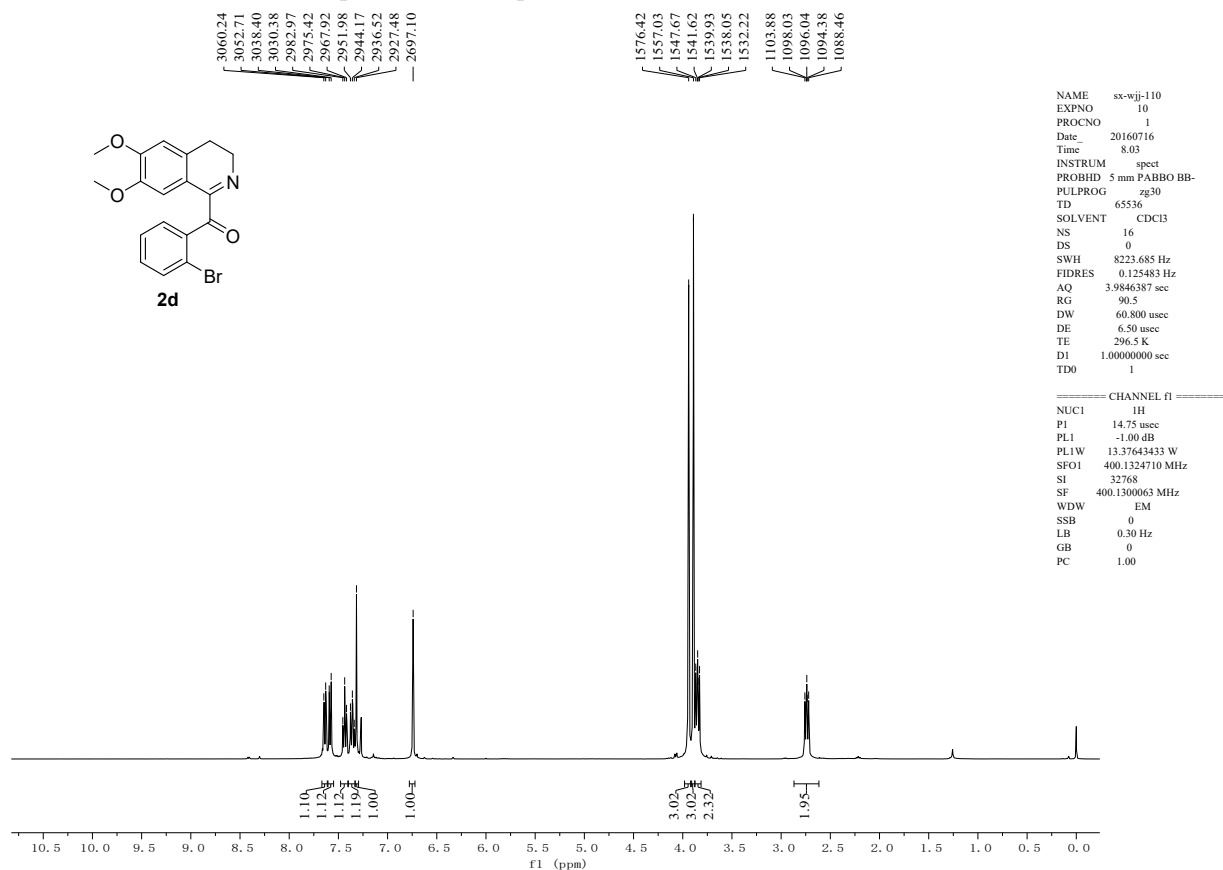
¹H NMR (CDCl₃, 400 MHz) spectrum of compound **2c**:



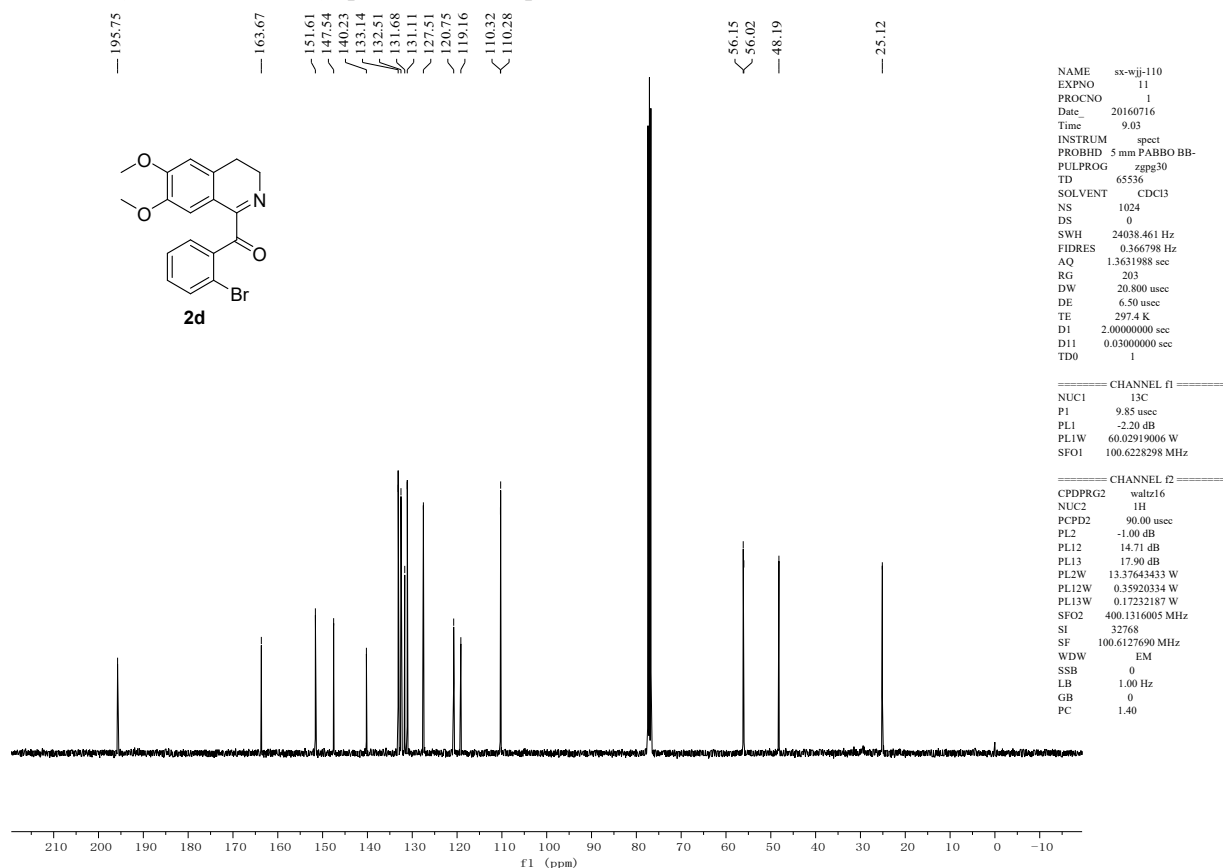
¹³C NMR (CDCl₃, 100 MHz) spectrum of compound **2c**:



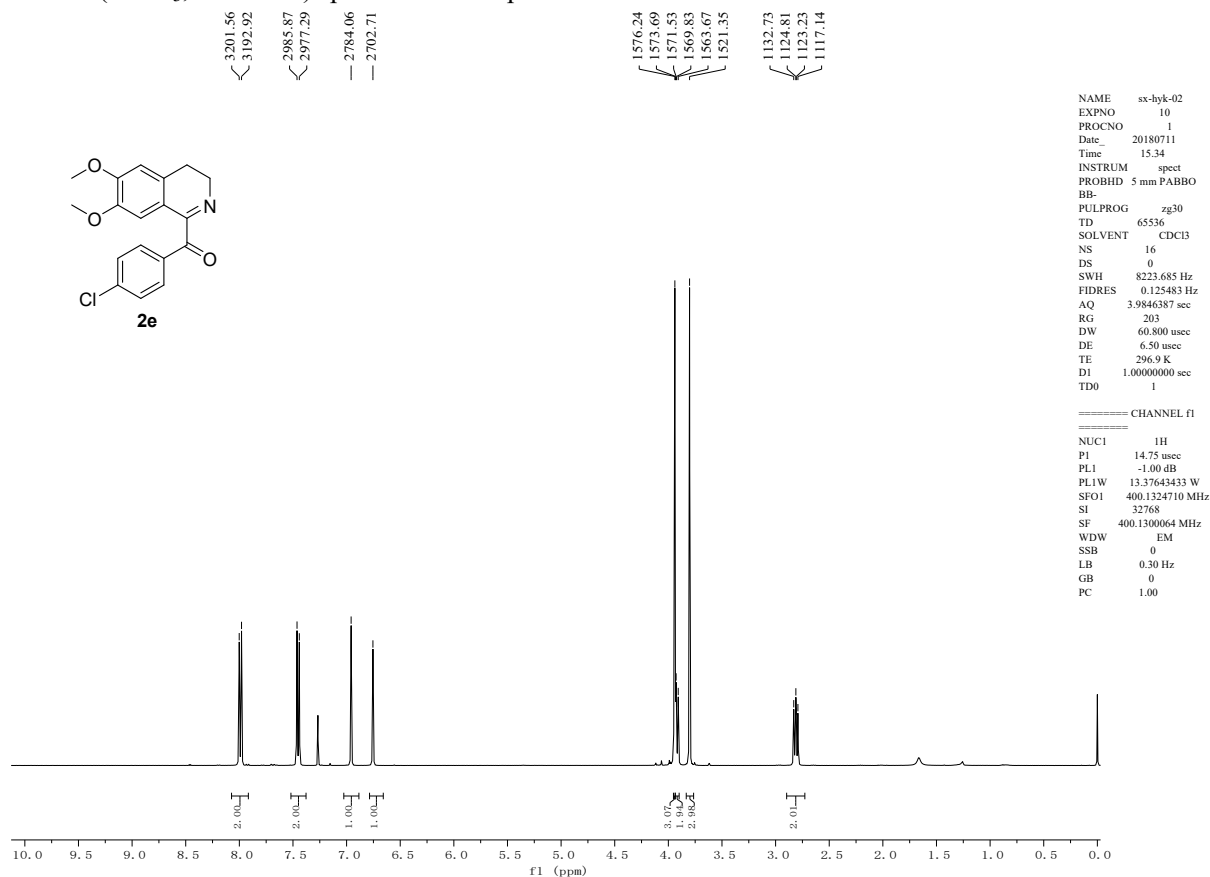
¹H NMR (CDCl₃, 400 MHz) spectrum of compound **2d**:



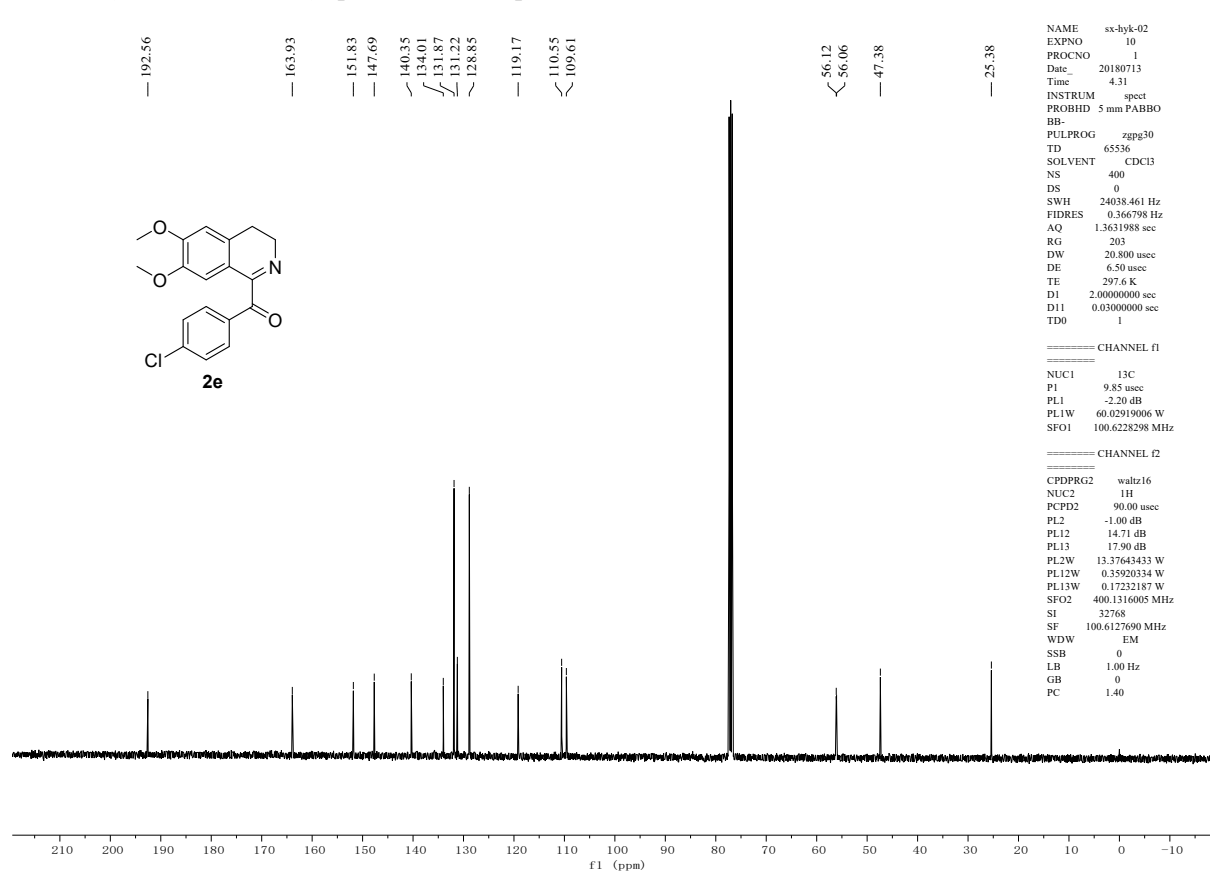
¹³C NMR (CDCl₃, 100 MHz) spectrum of compound **2d**:



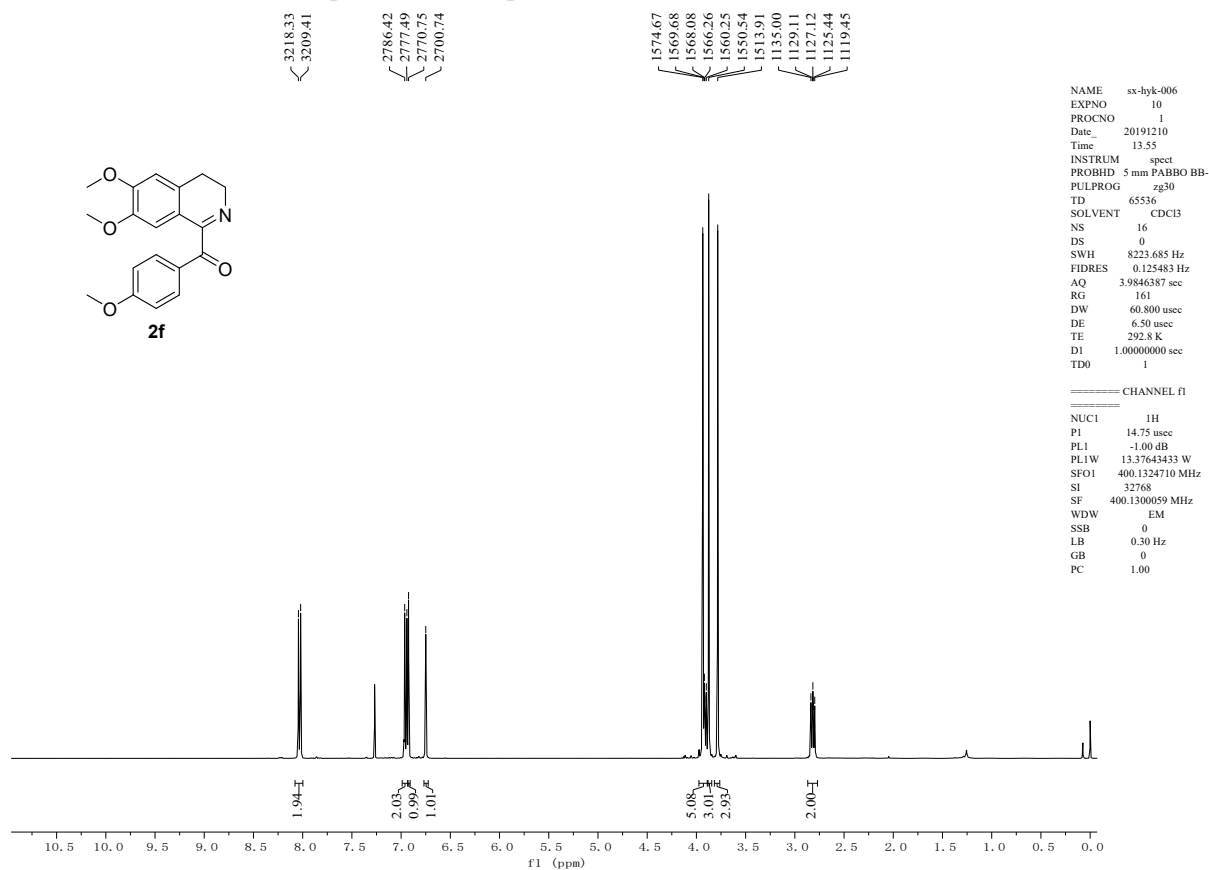
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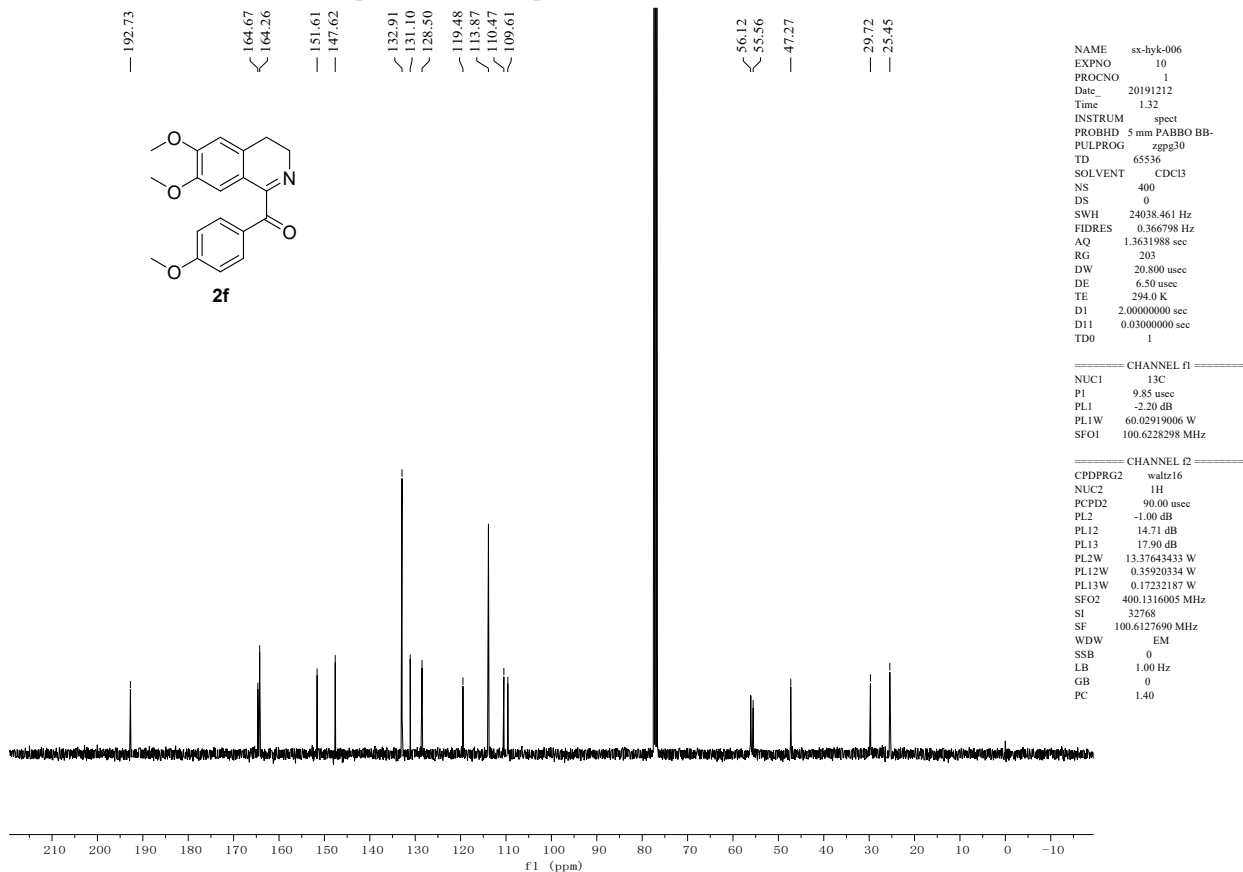
¹³C NMR (CDCl₃, 100 MHz) spectrum of compound **2e**:



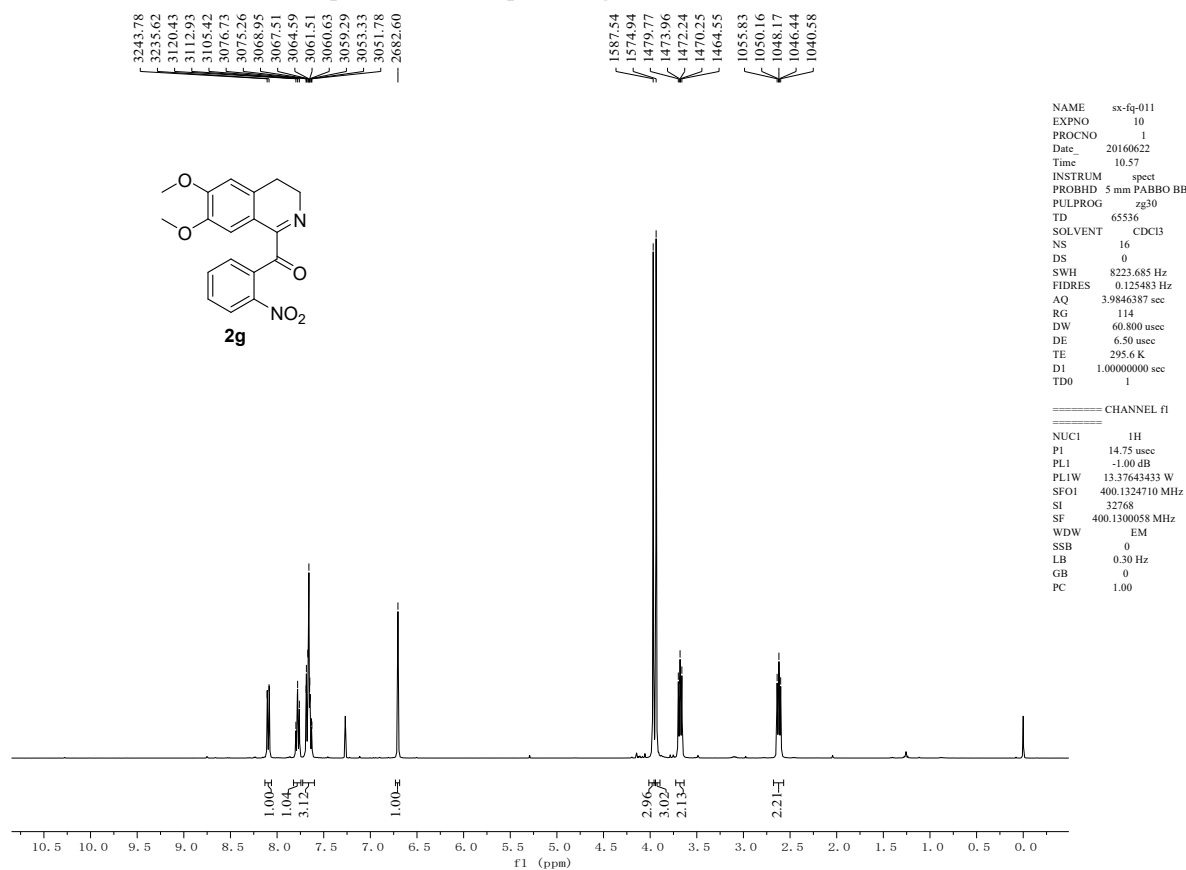
¹H NMR (CDCl₃, 400 MHz) spectrum of compound **2f**:



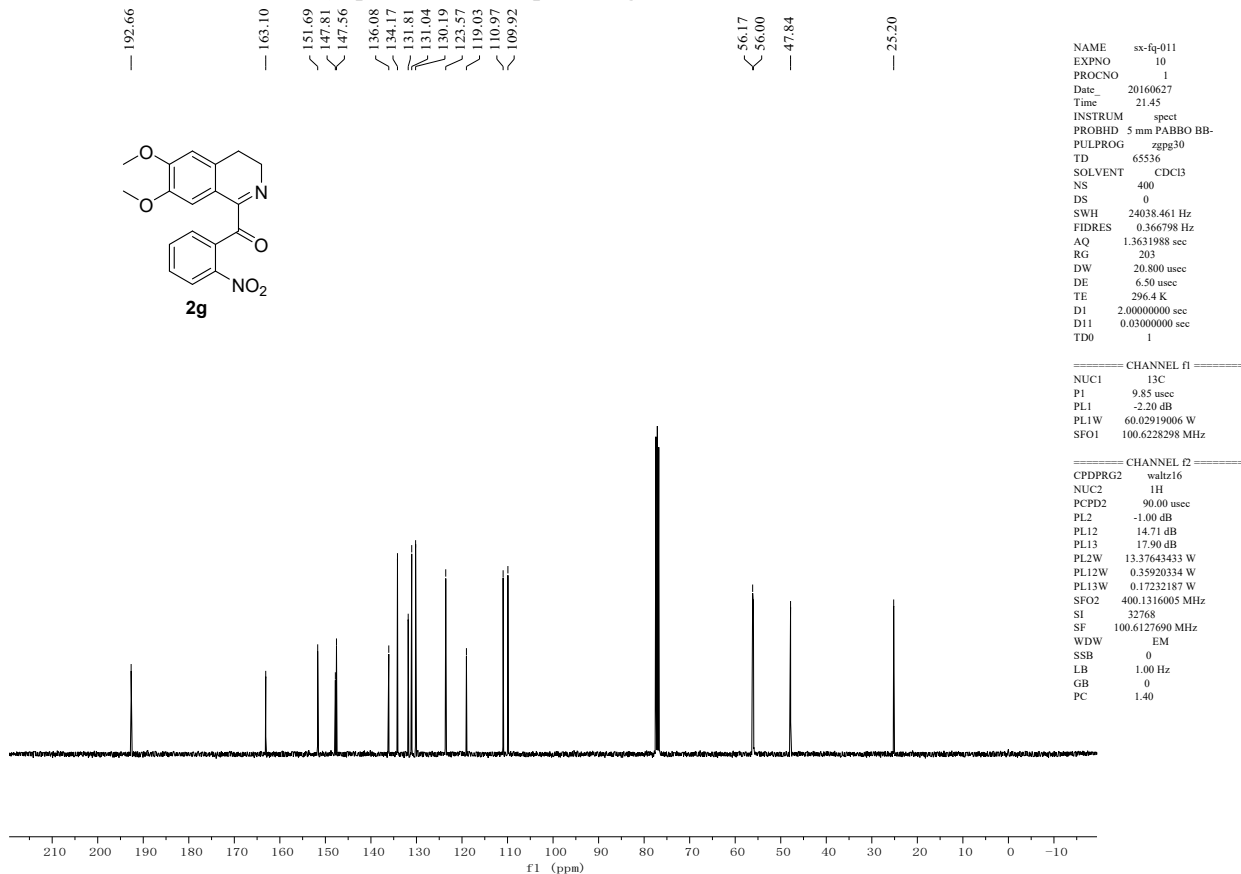
¹³C NMR (CDCl₃, 100 MHz) spectrum of compound **2f**:



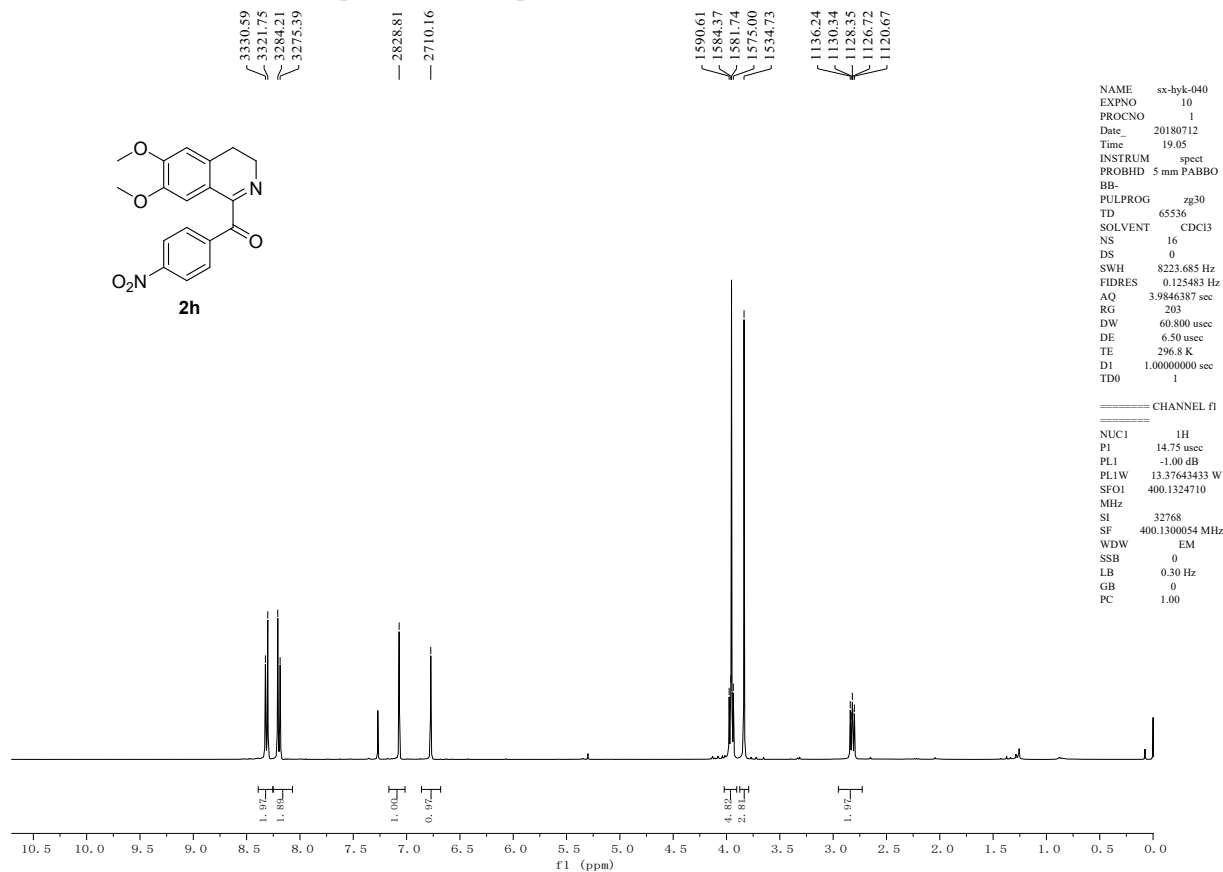
¹H NMR (CDCl₃, 400 MHz) spectrum of compound **2g**:



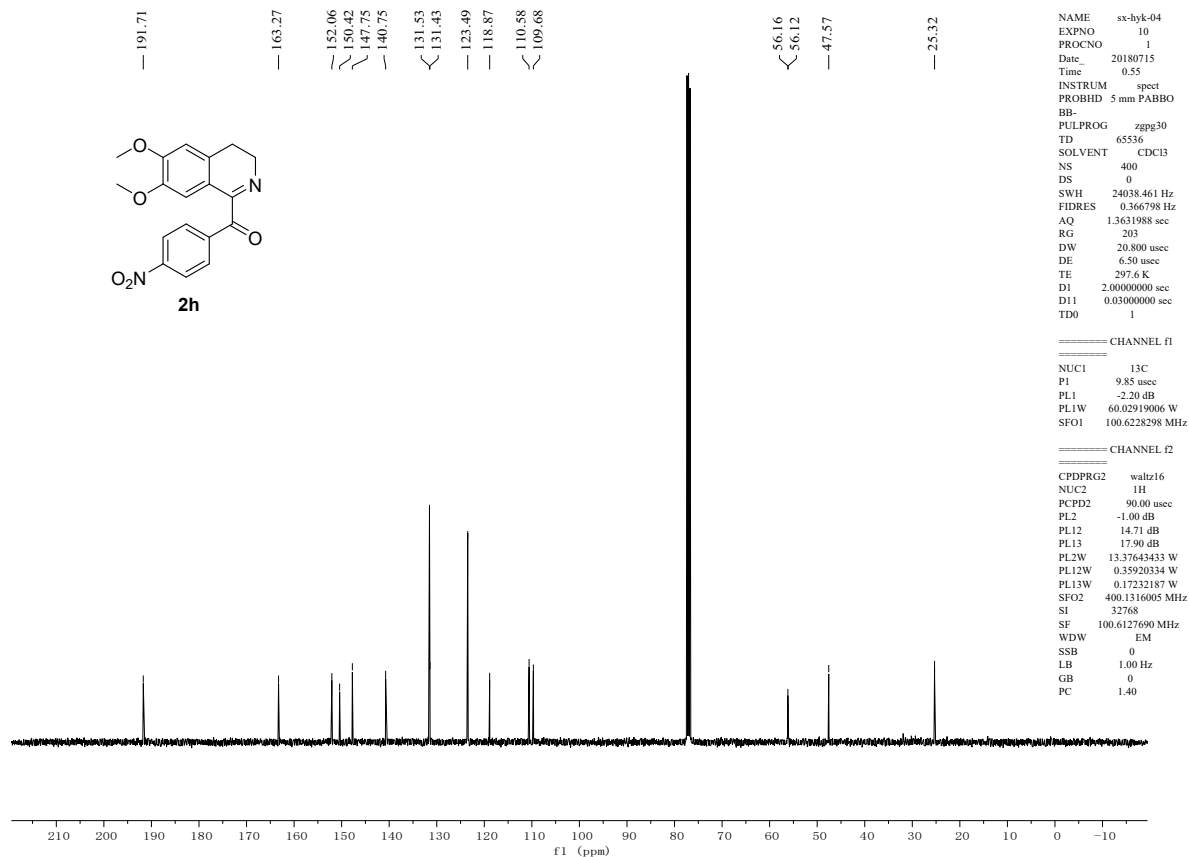
¹³C NMR (CDCl₃, 100 MHz) spectrum of compound **2g**:



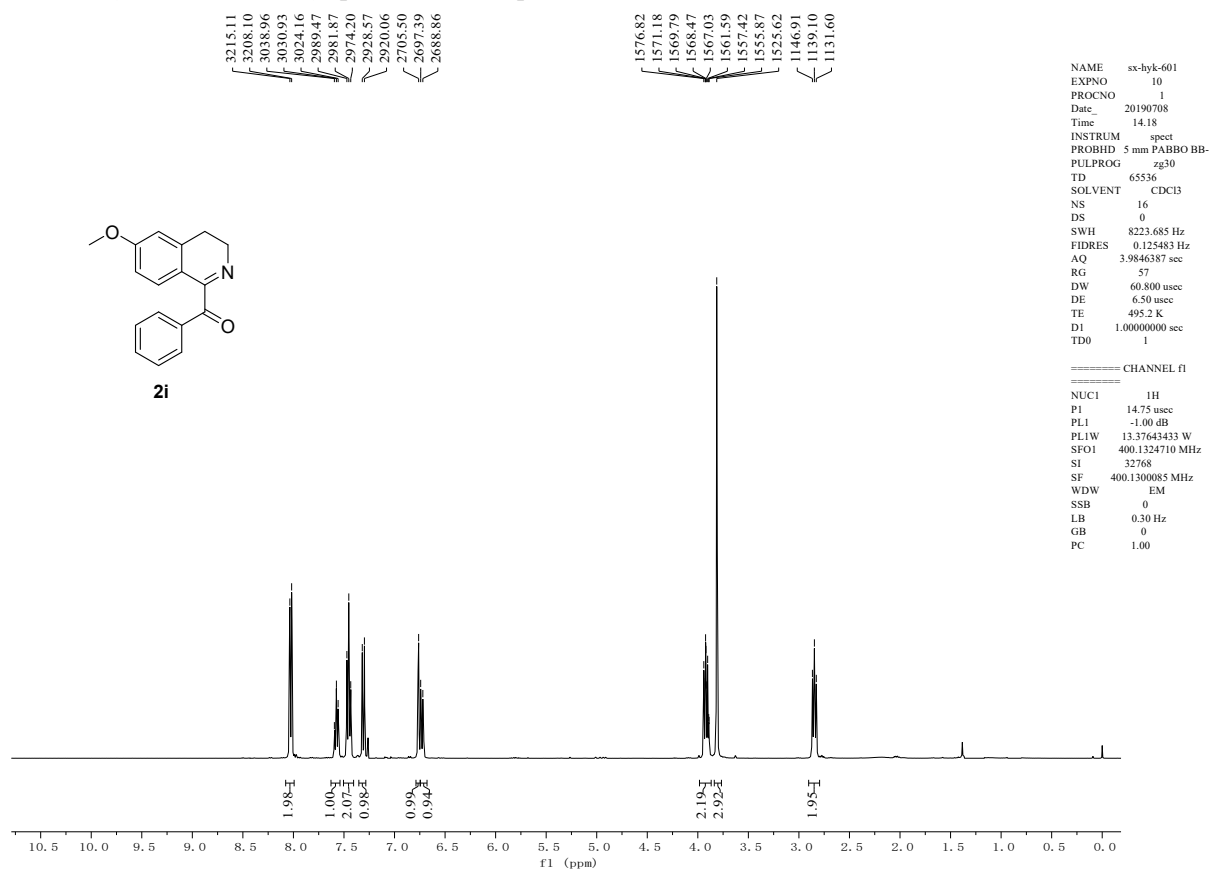
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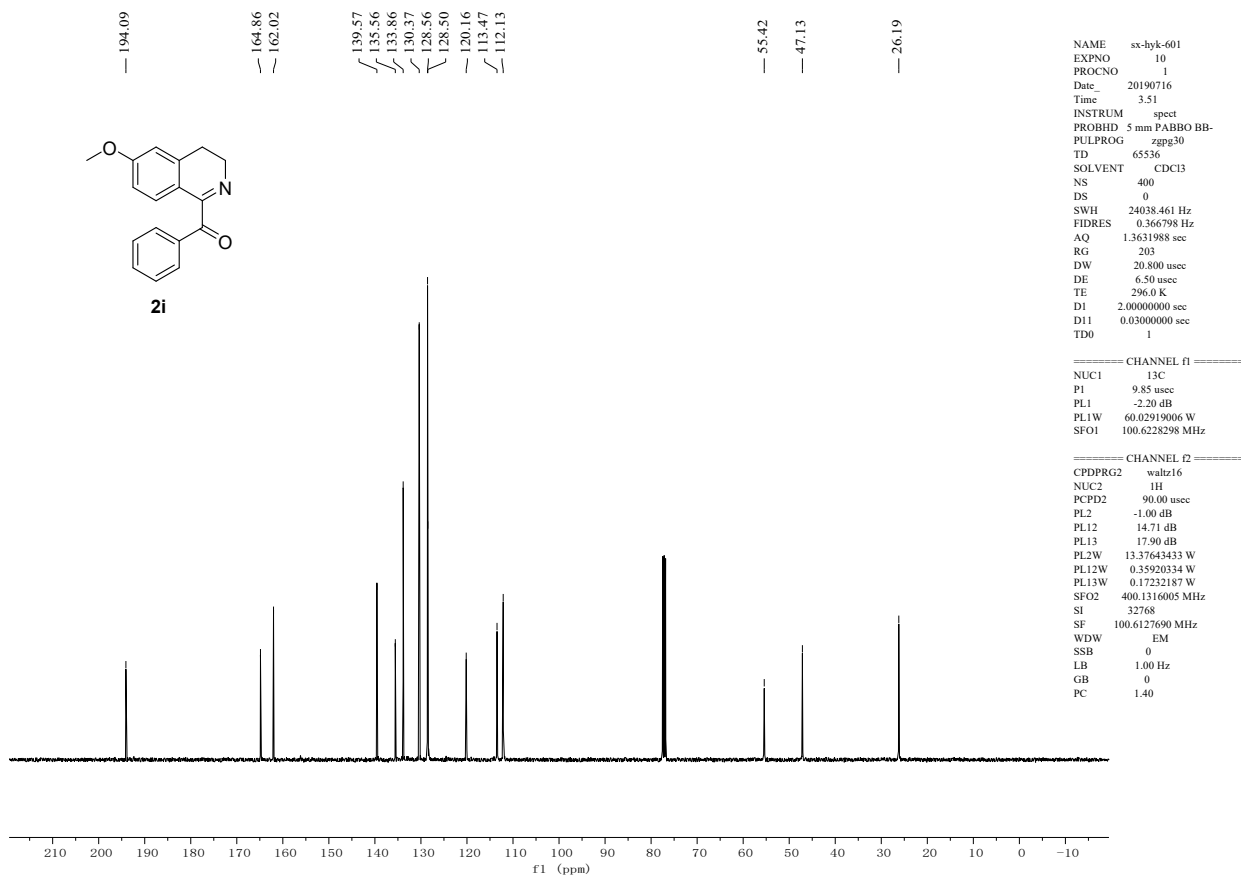
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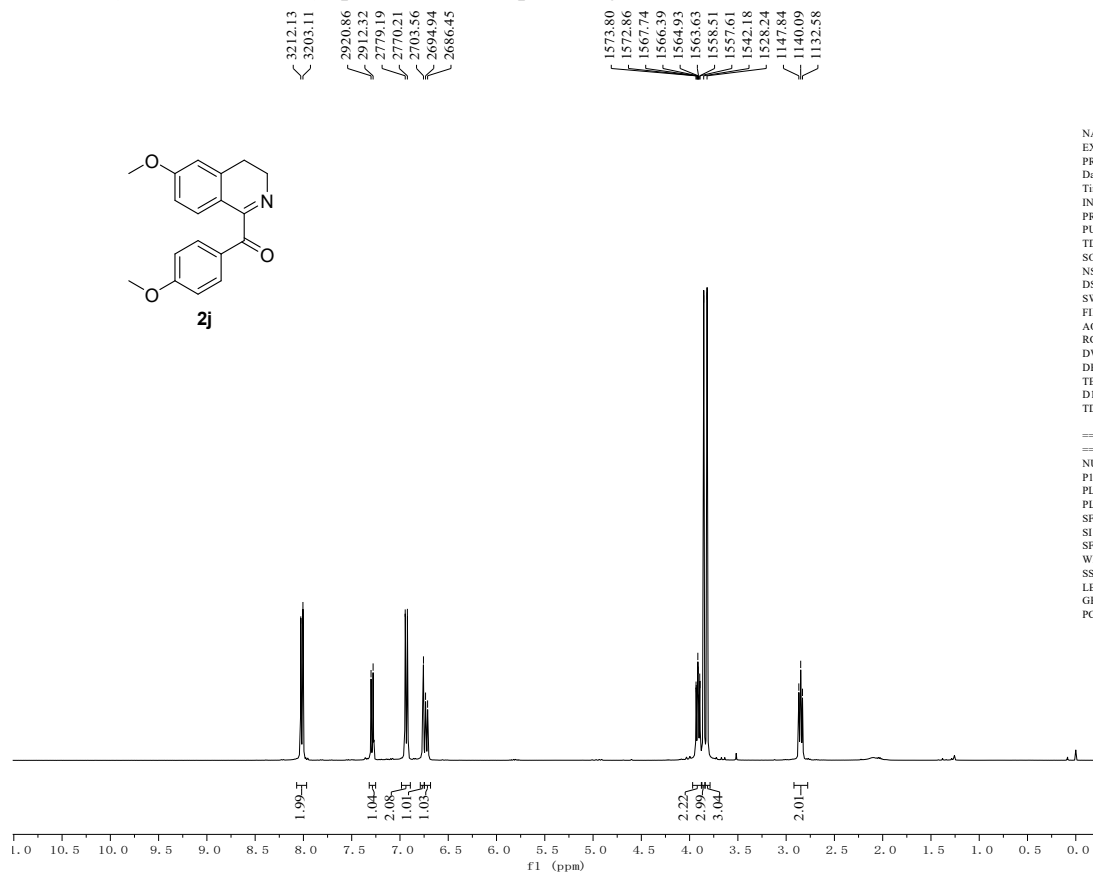
¹H NMR (CDCl₃, 400 MHz) spectrum of compound **2i**:



¹³C NMR (CDCl₃, 100 MHz) spectrum of compound **2i**:



¹H NMR (CDCl₃, 400 MHz) spectrum of compound **2j**:

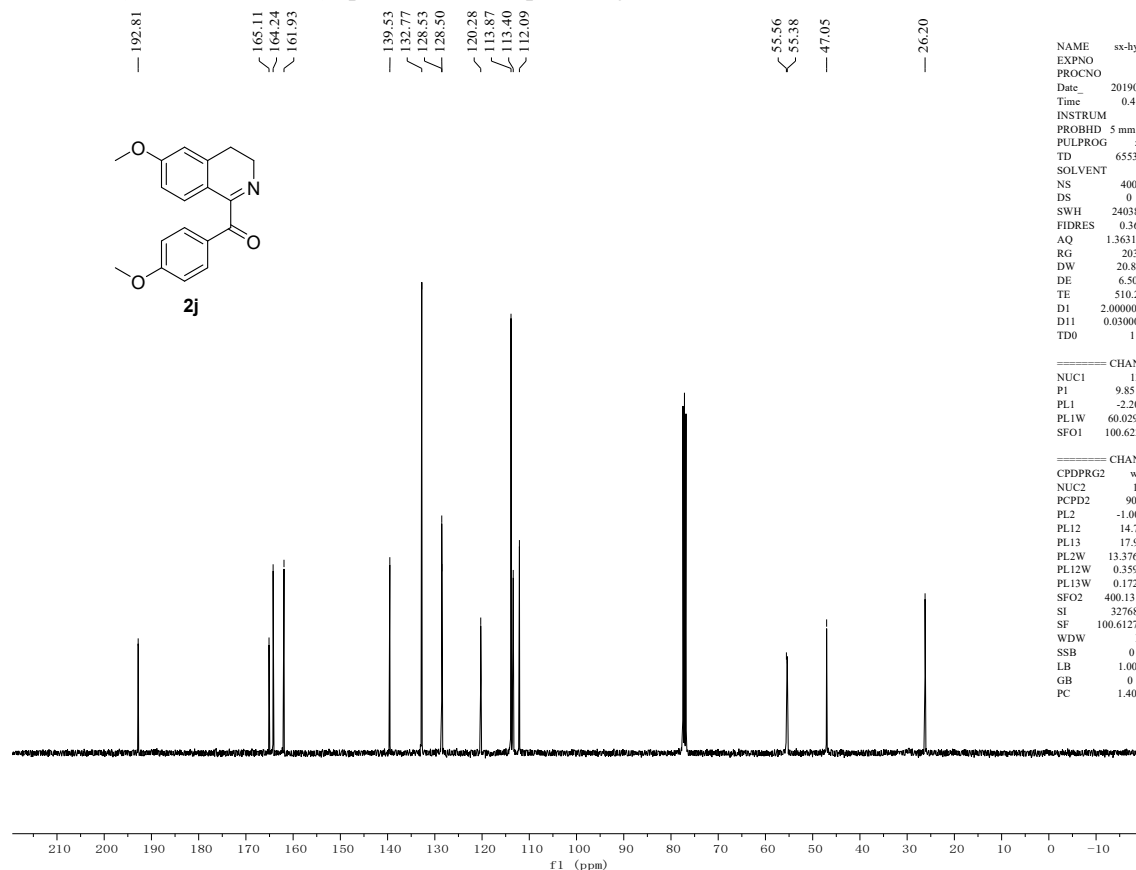


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EXPNO     10
PROCNO    1
Date_     20190705
Time      16.14
INSTRUM   spect
PROBHHD   5 mm PABBO BB-
PULPROG   zg30
TD         65536
SOLVENT   CDCl3
NS         16
DS         0
SWH        8223.685 Hz
FIDRES     0.125483 Hz
AQ         3.9846387 sec
RG         64
DW         60.800 usec
DE         6.50 usec
TE         491.2 K
D1         1.00000000 sec
TD0        1

===== CHANNEL f1 =====
NUC1       1H
P1         14.75 usec
PL1        -1.00 dB
PL1W       13.37643433 W
SFO1       400.1324710 MHz
SI         32768
SF         400.1300046 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00
    
```

¹³C NMR (CDCl₃, 100 MHz) spectrum of compound **2j**:



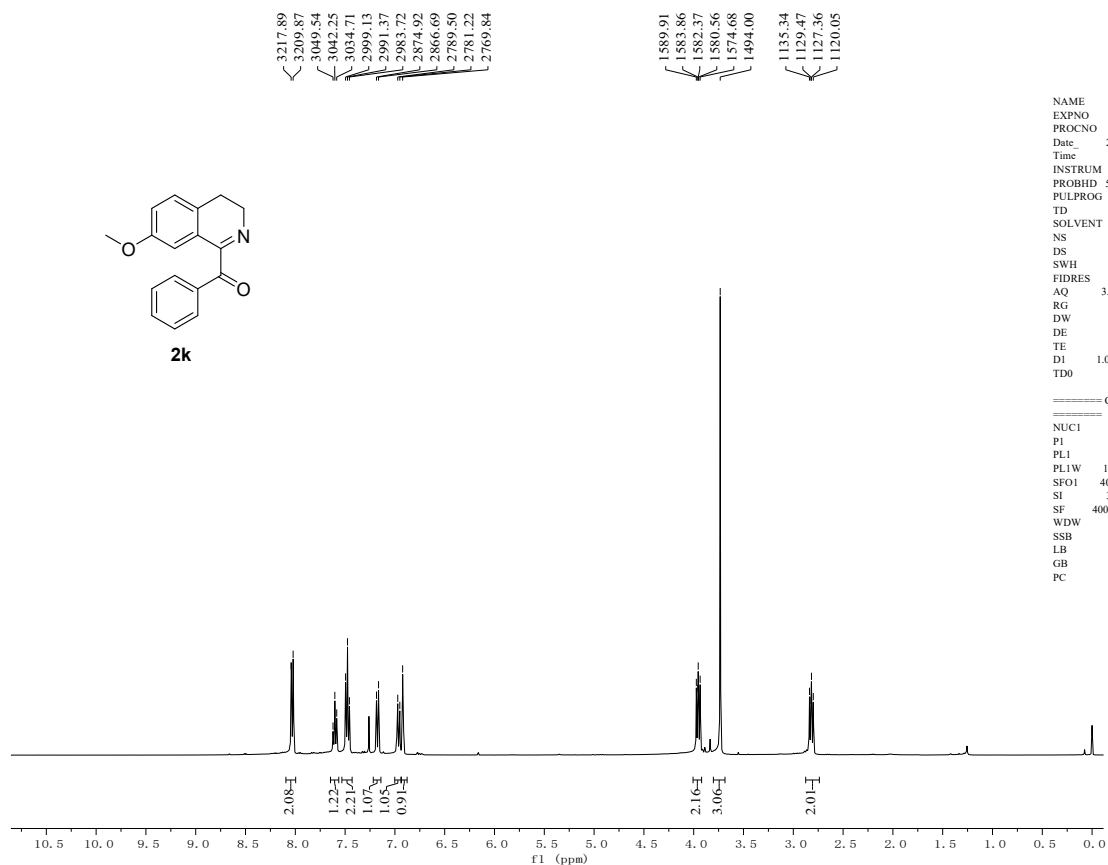
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EXPNO     10
PROCNO    1
Date_     20190709
Time      0.41
INSTRUM   spect
PROBHHD   5 mm PABBO BB-
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         400
DS         0
SWH        24038.461 Hz
FIDRES     0.366798 Hz
AQ         1.3631988 sec
RG         203
DW         20.800 usec
DE         6.50 usec
TE         510.2 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0        1

===== CHANNEL f1 =====
NUC1       13C
P1         9.85 usec
PL1        -2.20 dB
PL1W       60.02919006 W
SFO1       100.6228298 MHz

===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2       1H
PCPD2     90.00 usec
PL2        -1.00 dB
PL12       14.71 dB
PL13       17.90 dB
PL2W       13.37643433 W
PL12W     0.35920334 W
PL13W     0.17232187 W
SFO2       400.1316005 MHz
SI         32768
SF         100.6127690 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
    
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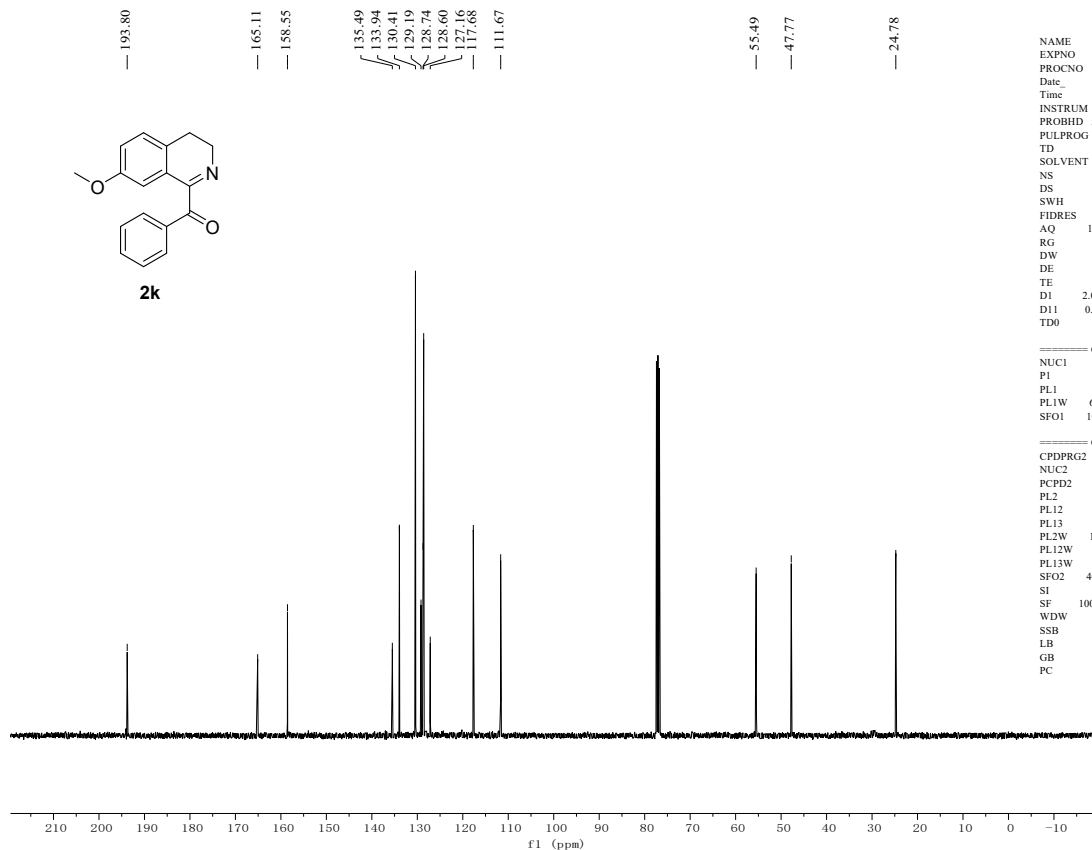
¹H NMR (CDCl₃, 400 MHz) spectrum of compound **2k**:



```

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EXPNO     10
PROCNO    1
Date_     20160622
Time      10.52
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zg30
TD         65536
SOLVENT   CDCl3
NS         16
DS         0
SWH        8223.685 Hz
FIDRES     0.125483 Hz
AQ         3.9846387 sec
RG         181
DW         60.800 usec
DE         6.50 usec
TE         295.7 K
D1         1.00000000 sec
TD0        1
===== CHANNEL f1 =====
NUC1       1H
P1         14.75 usec
PL1        -1.00 dB
PL1W       13.37643433 W
SFO1       400.1324710 MHz
SI         32768
SF         400.1300087 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00
    
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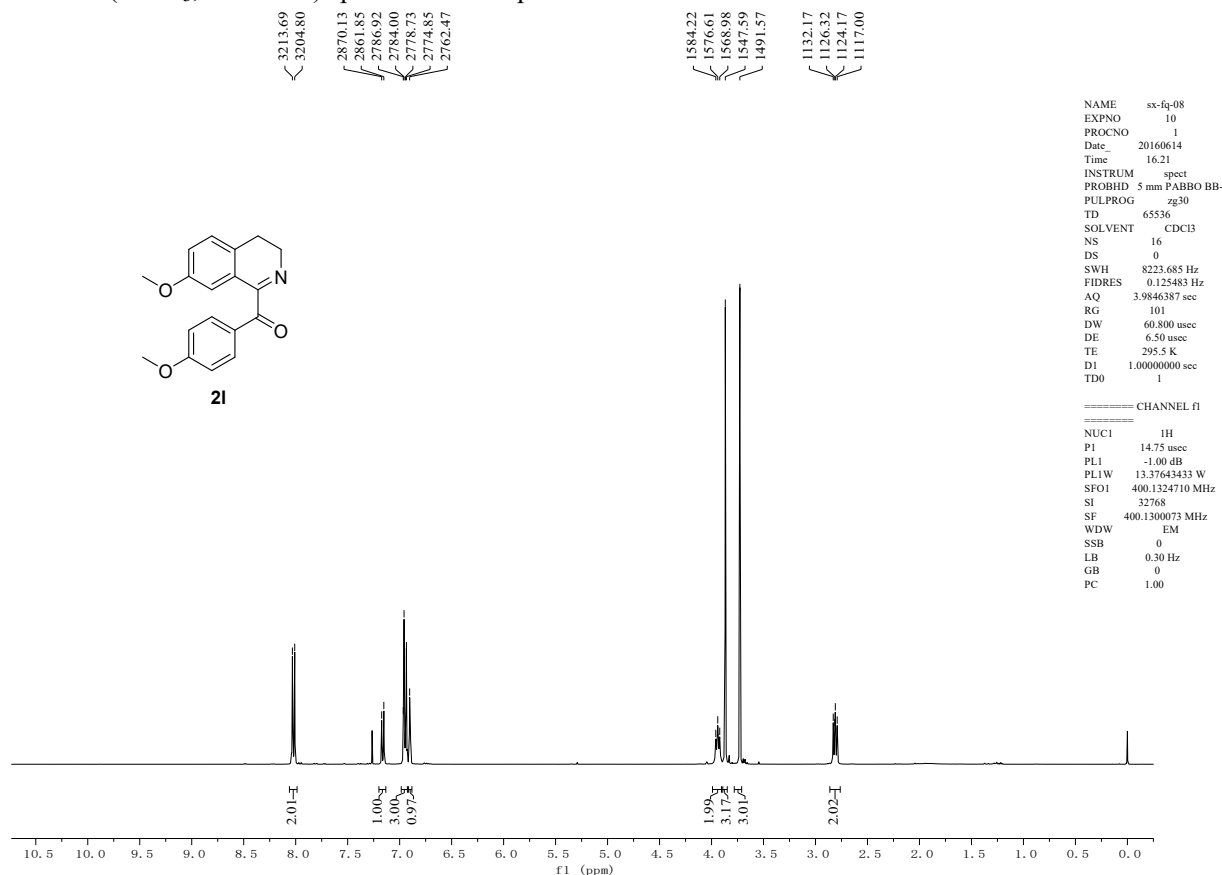
¹³C NMR (CDCl₃, 100 MHz) spectrum of compound **2k**:



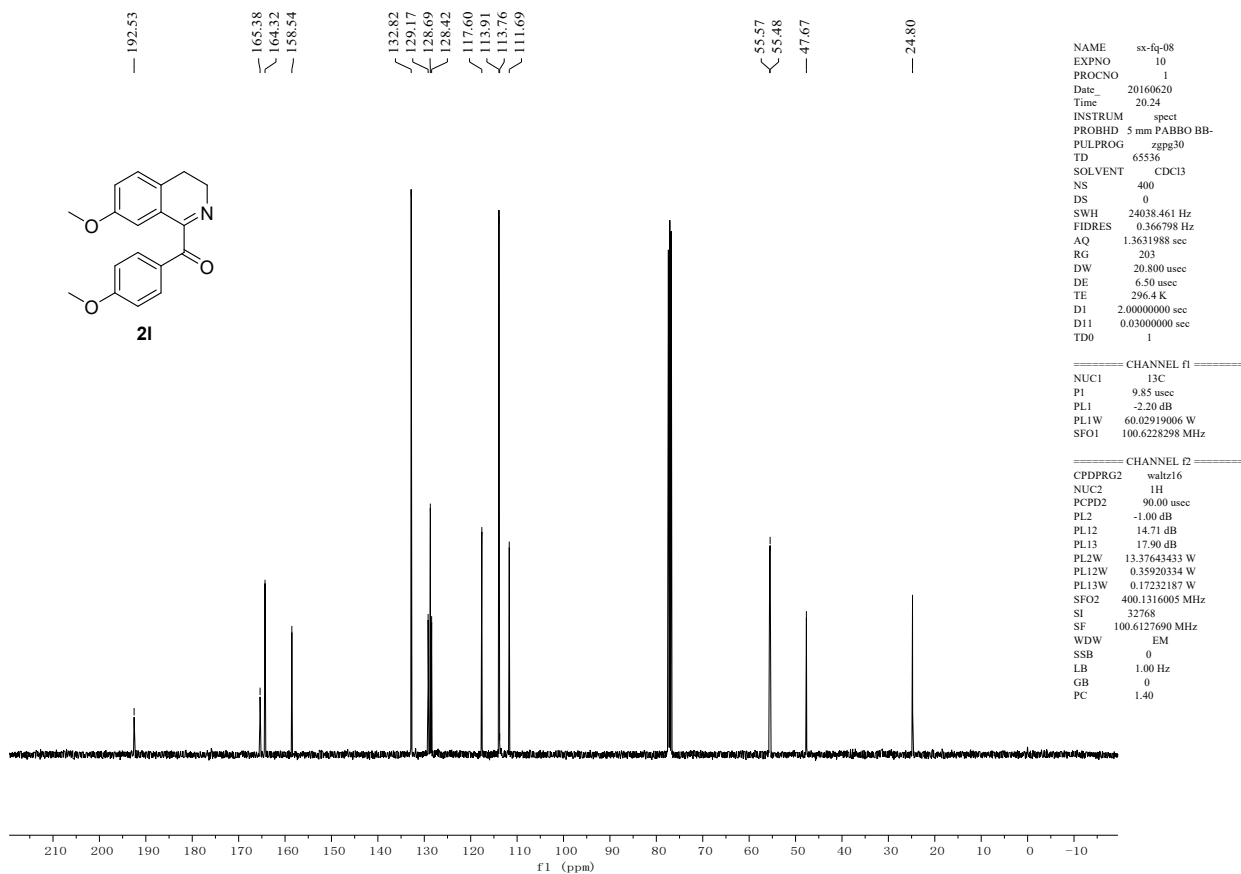
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EXPNO     11
PROCNO    1
Date_     20160625
Time      6.32
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         400
DS         0
SWH        24038.461 Hz
FIDRES     0.366798 Hz
AQ         1.3631988 sec
RG         203
DW         20.800 usec
DE         6.50 usec
TE         296.6 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0        1
===== CHANNEL f1 =====
NUC1       13C
P1         9.85 usec
PL1        -2.20 dB
PL1W       60.02919006 W
SFO1       100.6228298 MHz
===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2       1H
P2         90.00 usec
PL2        -1.00 dB
PL12       14.71 dB
PL13       17.90 dB
PL2W       13.37643433 W
PL12W      0.35920334 W
PL13W      0.17232187 W
SFO2       400.1316005 MHz
SI         32768
SF         100.6127690 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
    
```

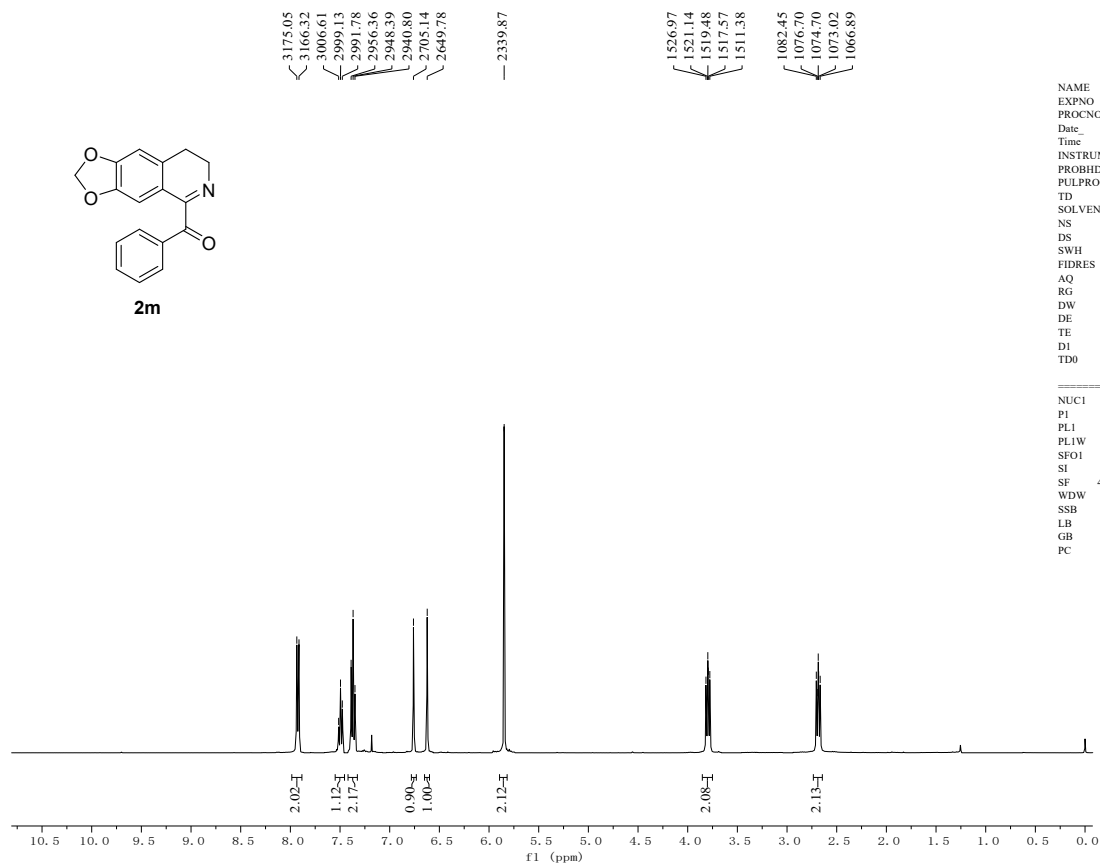
¹H NMR (CDCl₃, 400 MHz) spectrum of compound **21**:



¹³C NMR (CDCl₃, 100 MHz) spectrum of compound **21**:



¹H NMR (CDCl₃, 400 MHz) spectrum of compound **2m**:



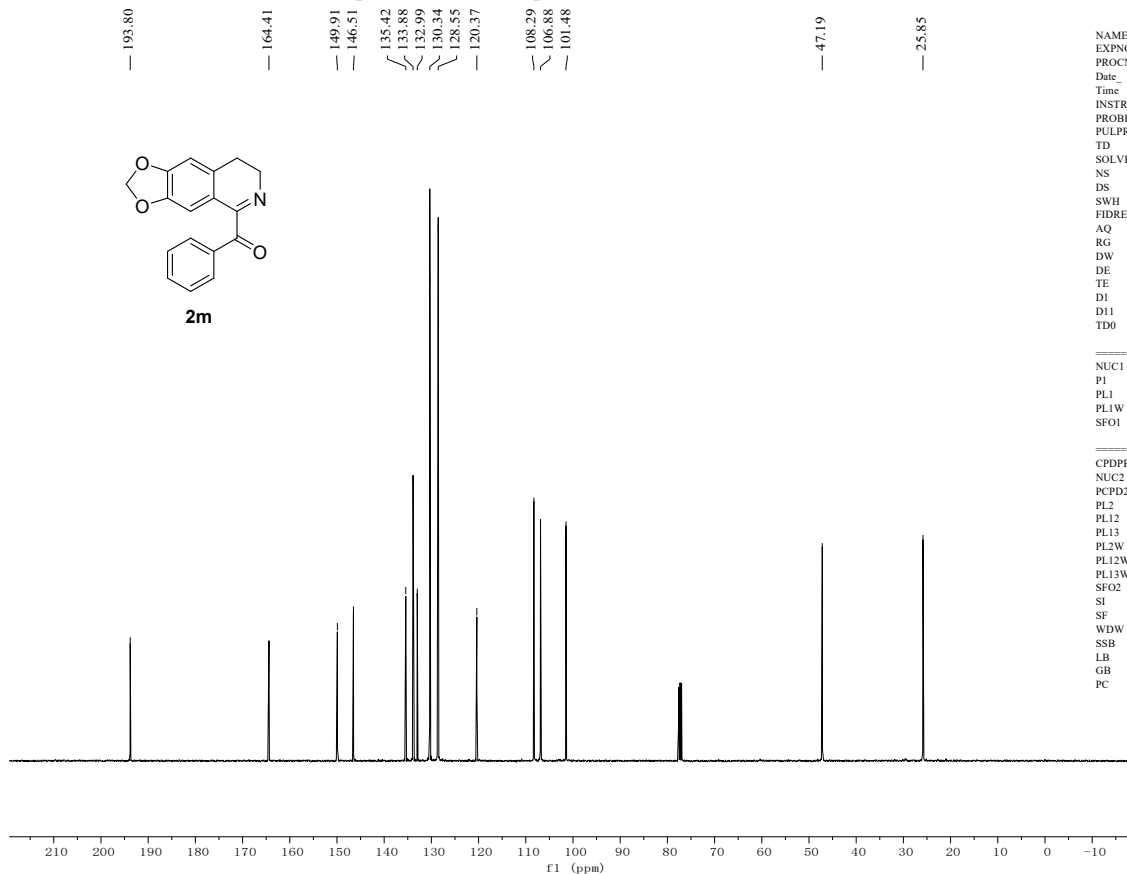
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EXPNO     10
PROCNO    1
Date_     20160517
Time      19.25
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zg30
TD         65536
SOLVENT   CDCl3
NS         16
DS         0
SWH        8223.685 Hz
FIDRES     0.125483 Hz
AQ         3.9846387 sec
RG         57
DW         60.800 usec
DE         6.50 usec
TE         294.7 K
D1         1.00000000 sec
TD0        1
    
```

```

===== CHANNEL f1 =====
NUC1      1H
P1         14.75 usec
PL1        -1.00 dB
PL1W       13.37643433 W
SFO1      400.1324710 MHz
SI         32768
SF         400.1300408 MHz
WDW        EM
SSB         0
LB         0.30 Hz
GB         0
PC         1.00
    
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¹³C NMR (CDCl₃, 100 MHz) spectrum of compound **2m**:



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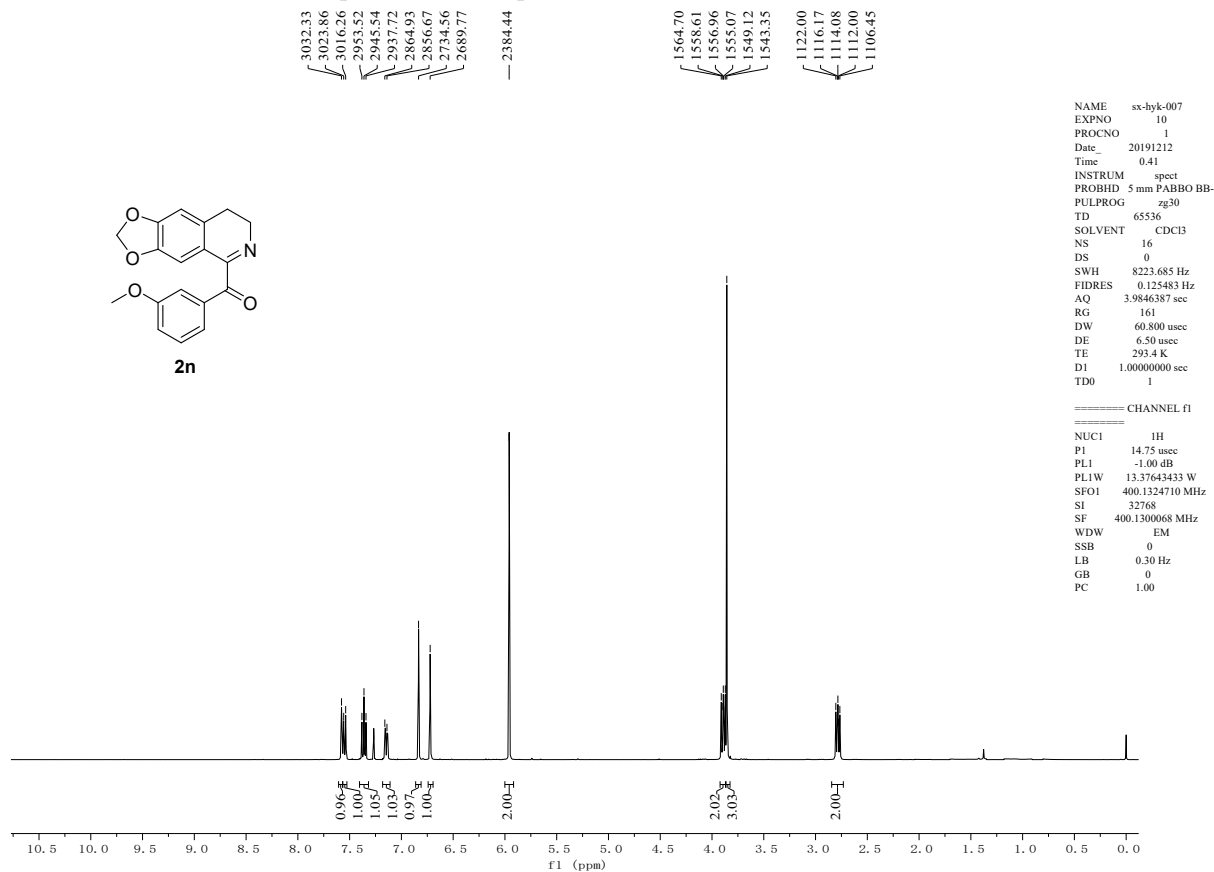
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PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         400
DS         4
SWH        24038.461 Hz
FIDRES     0.366798 Hz
AQ         1.3631988 sec
RG         203
DW         20.800 usec
DE         6.50 usec
TE         297.0 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0        1
    
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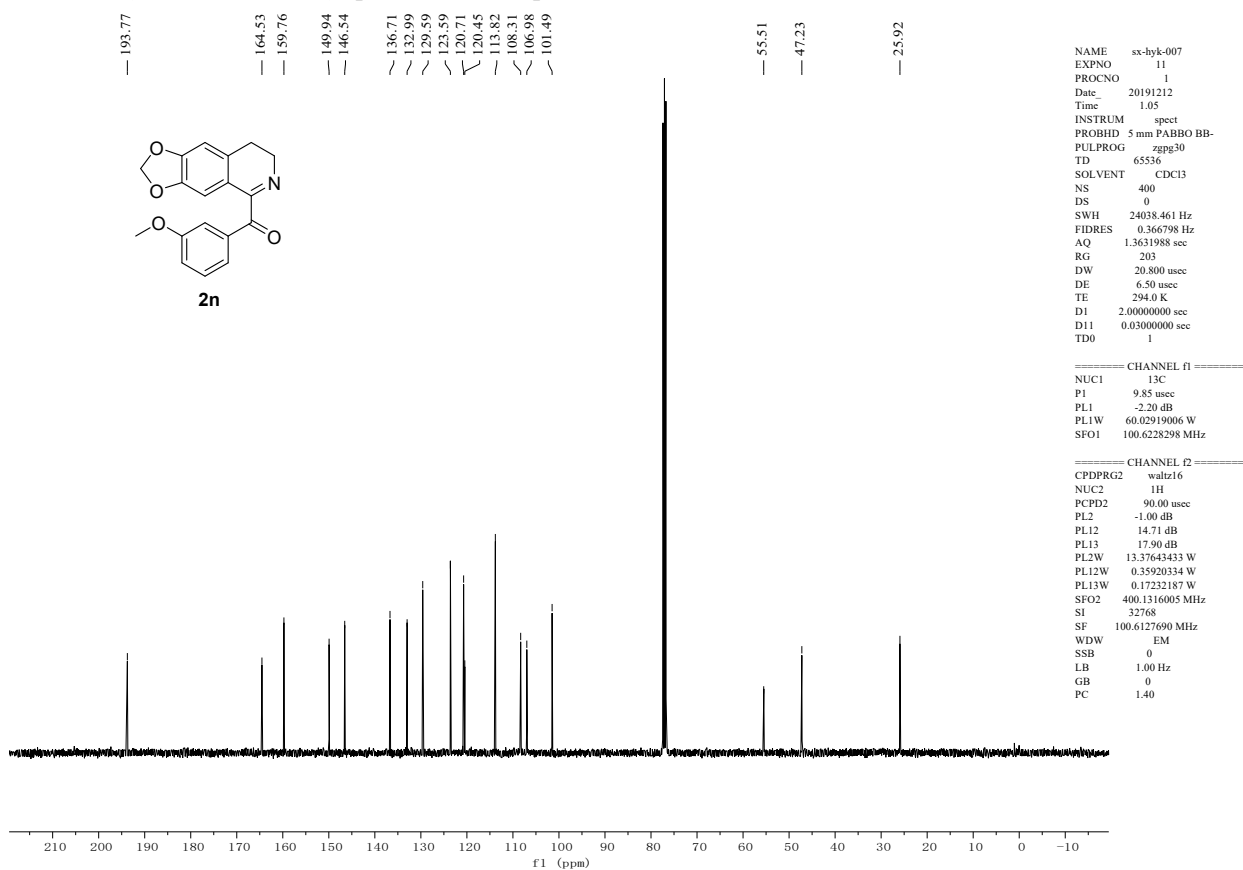
===== CHANNEL f1 =====
NUC1      13C
P1         9.85 usec
PL1        -2.20 dB
PL1W       60.02919006 W
SFO1      100.6228298 MHz

===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2      1H
PCPD2     90.00 usec
PL2        -1.00 dB
PL12       14.71 dB
PL13       17.90 dB
PL2W       13.37643433 W
PL12W     0.35920334 W
PL13W     0.17232187 W
SFO2      400.1316005 MHz
SI         32768
SF         100.6127690 MHz
WDW        EM
SSB         0
LB         1.00 Hz
GB         0
PC         1.40
    
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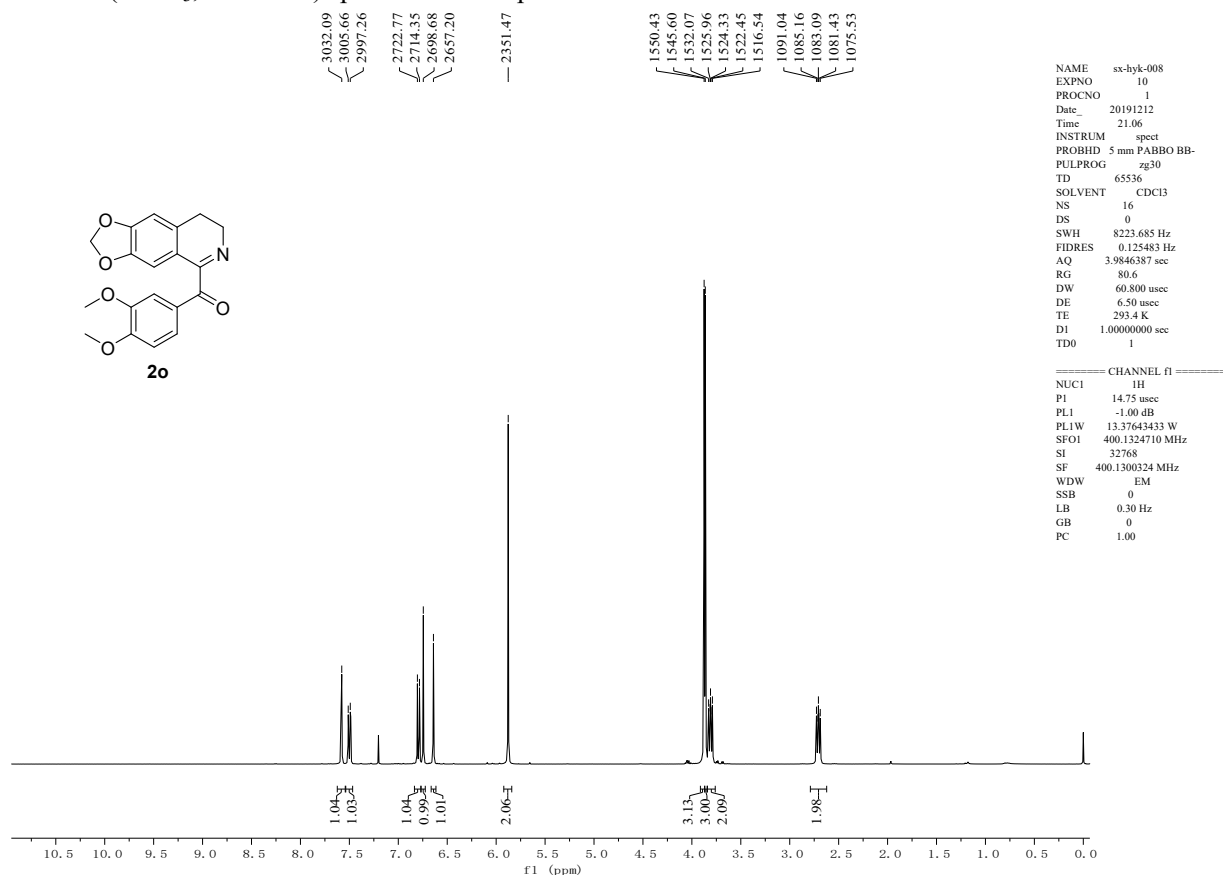
¹H NMR (CDCl₃, 400 MHz) spectrum of compound **2n**:



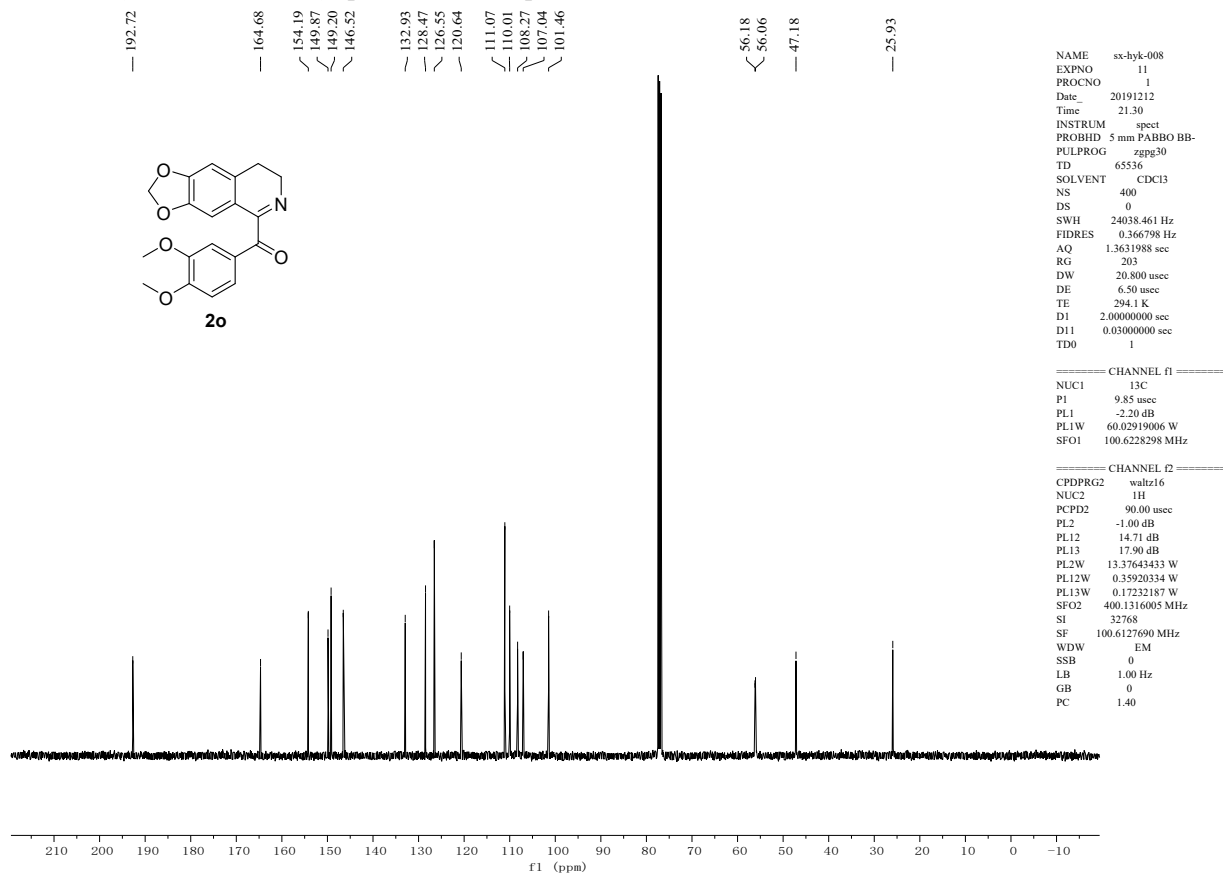
¹³C NMR (CDCl₃, 100 MHz) spectrum of compound **2n**:



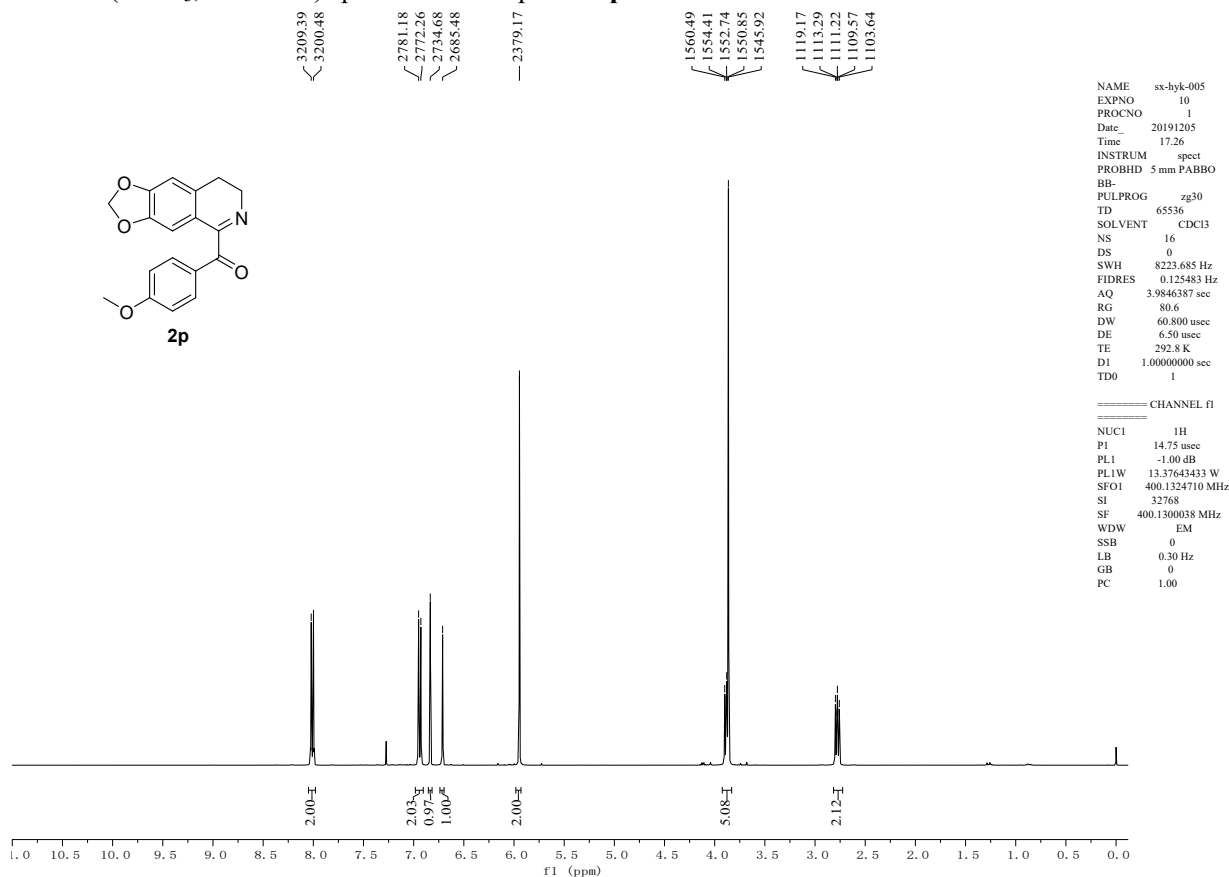
¹H NMR (CDCl₃, 400 MHz) spectrum of compound **2o**:



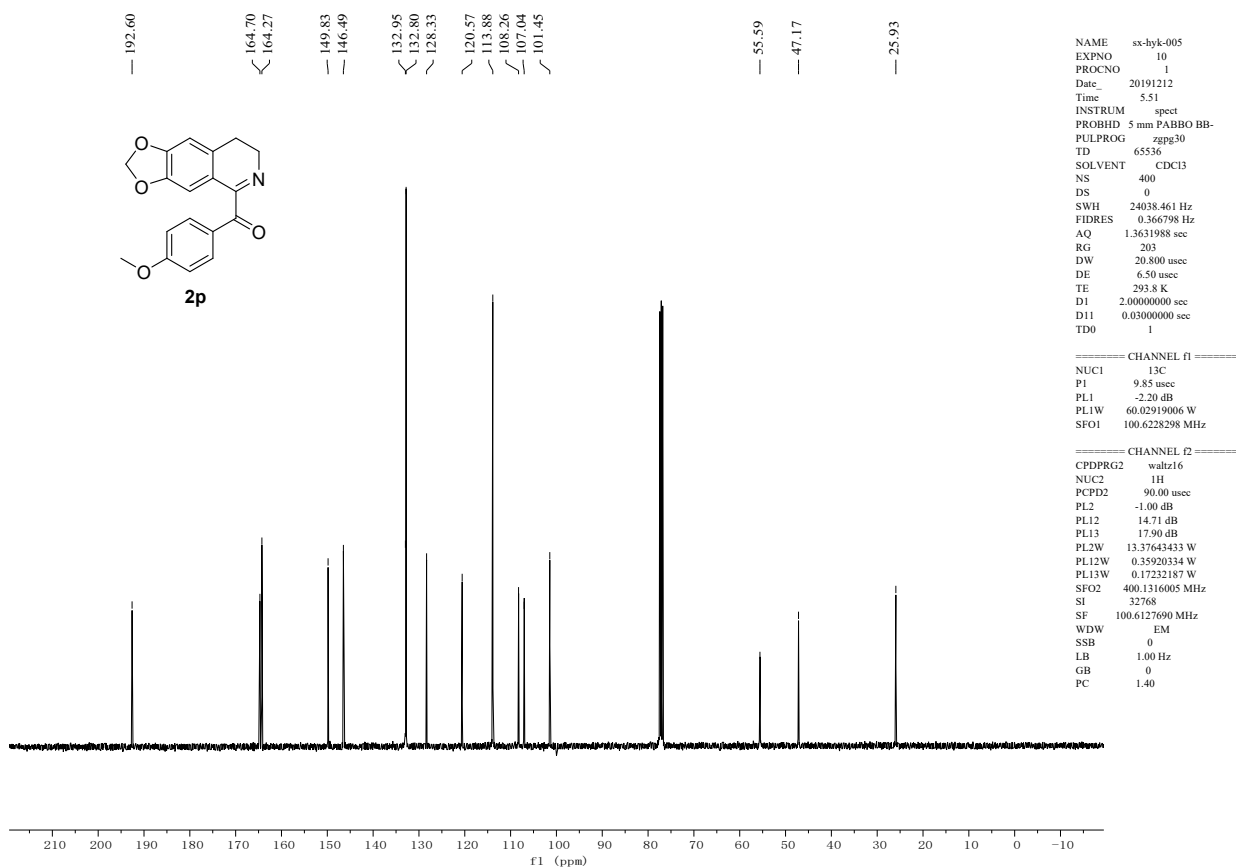
¹³C NMR (CDCl₃, 100 MHz) spectrum of compound **2o**:



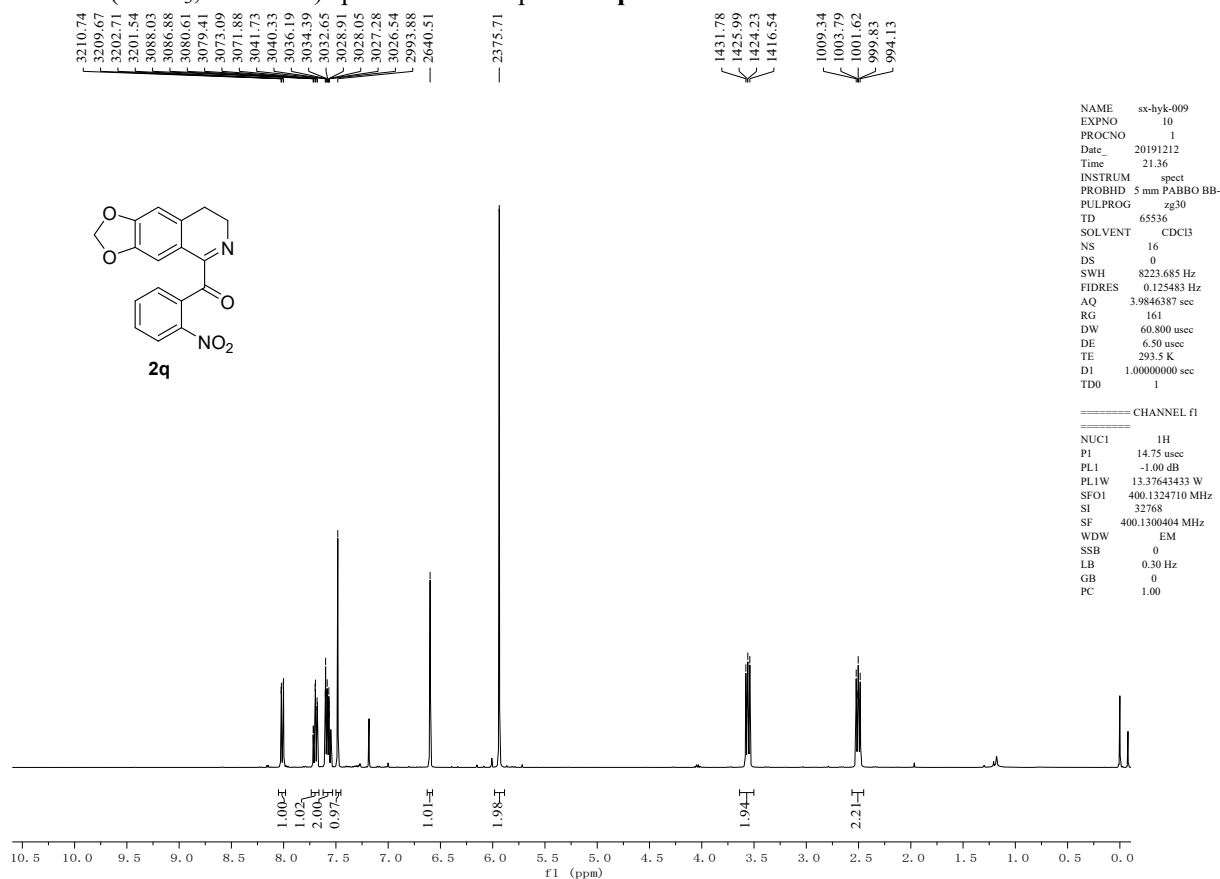
¹H NMR (CDCl₃, 400 MHz) spectrum of compound **2p**:



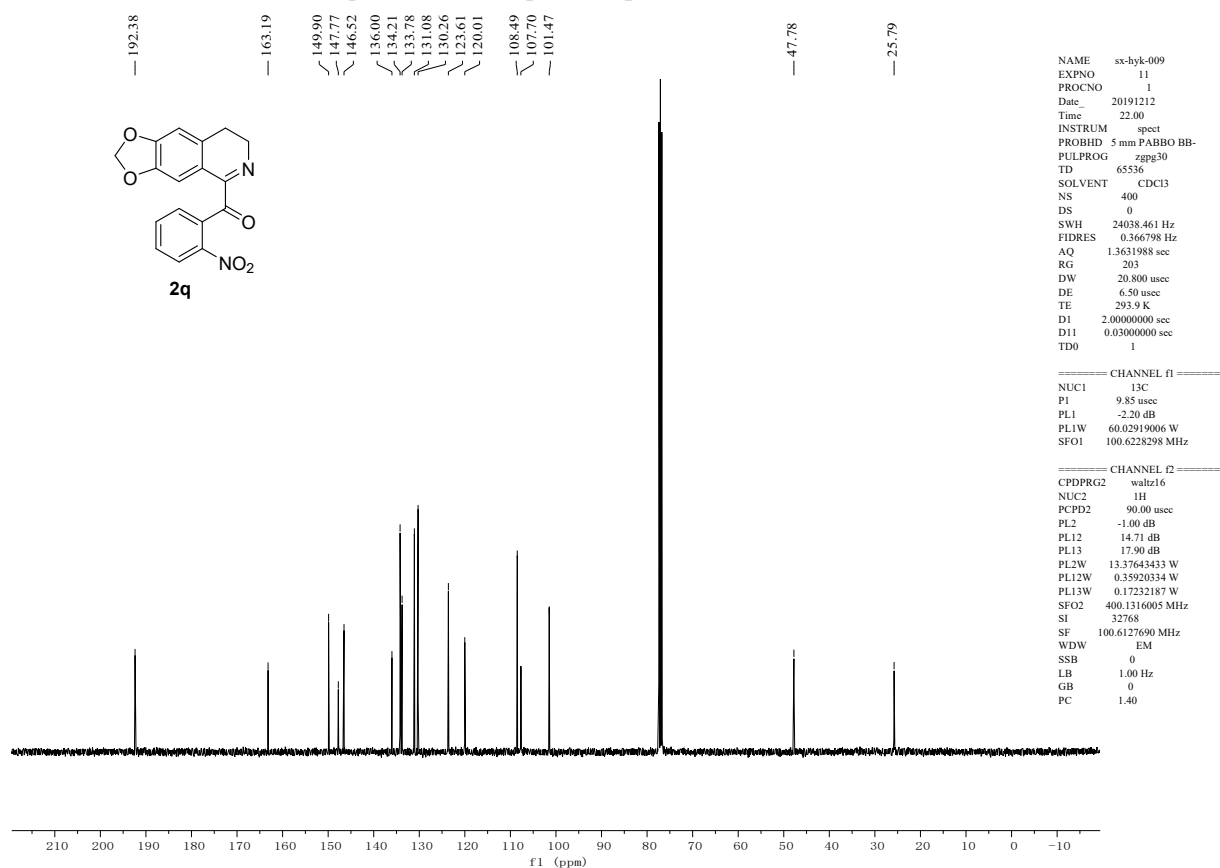
¹³C NMR (CDCl₃, 100 MHz) spectrum of compound **2p**:



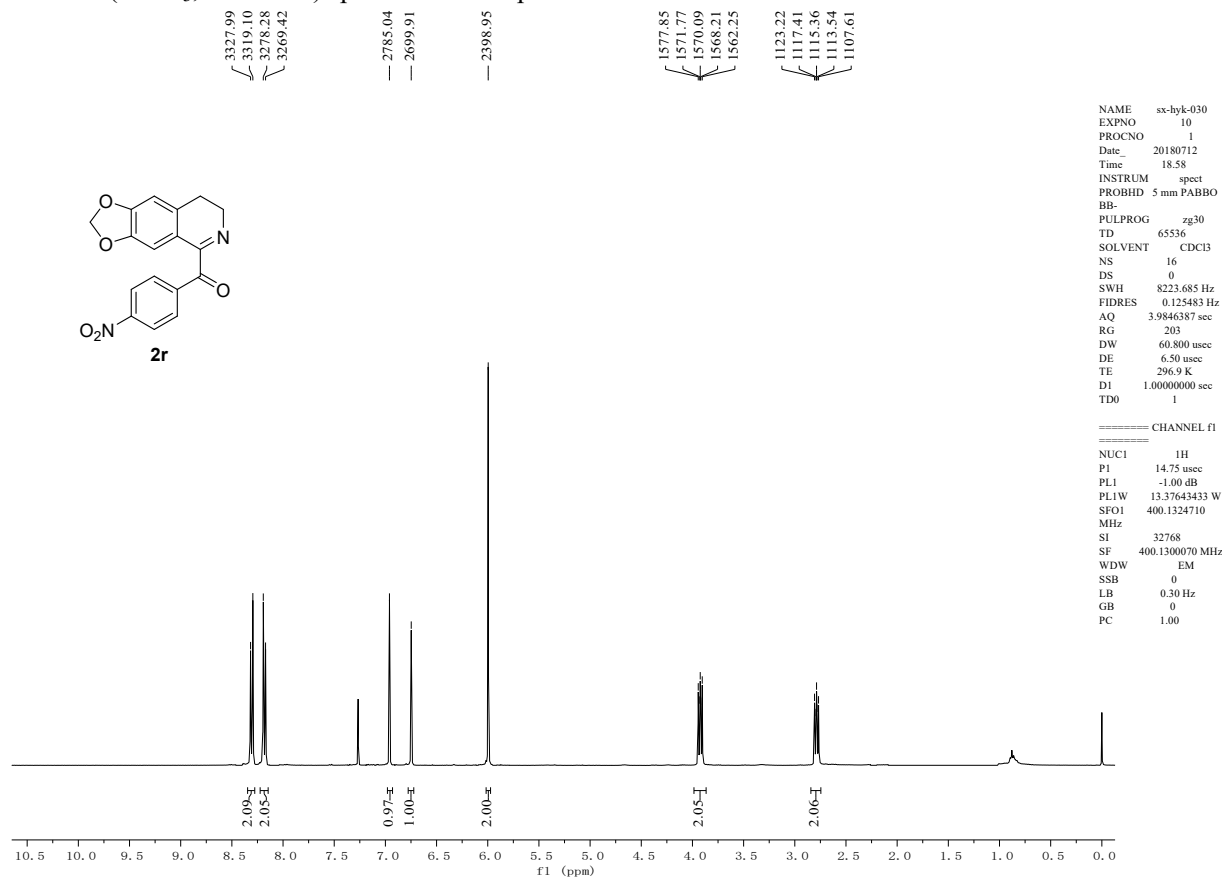
¹H NMR (CDCl₃, 400 MHz) spectrum of compound **2q**:



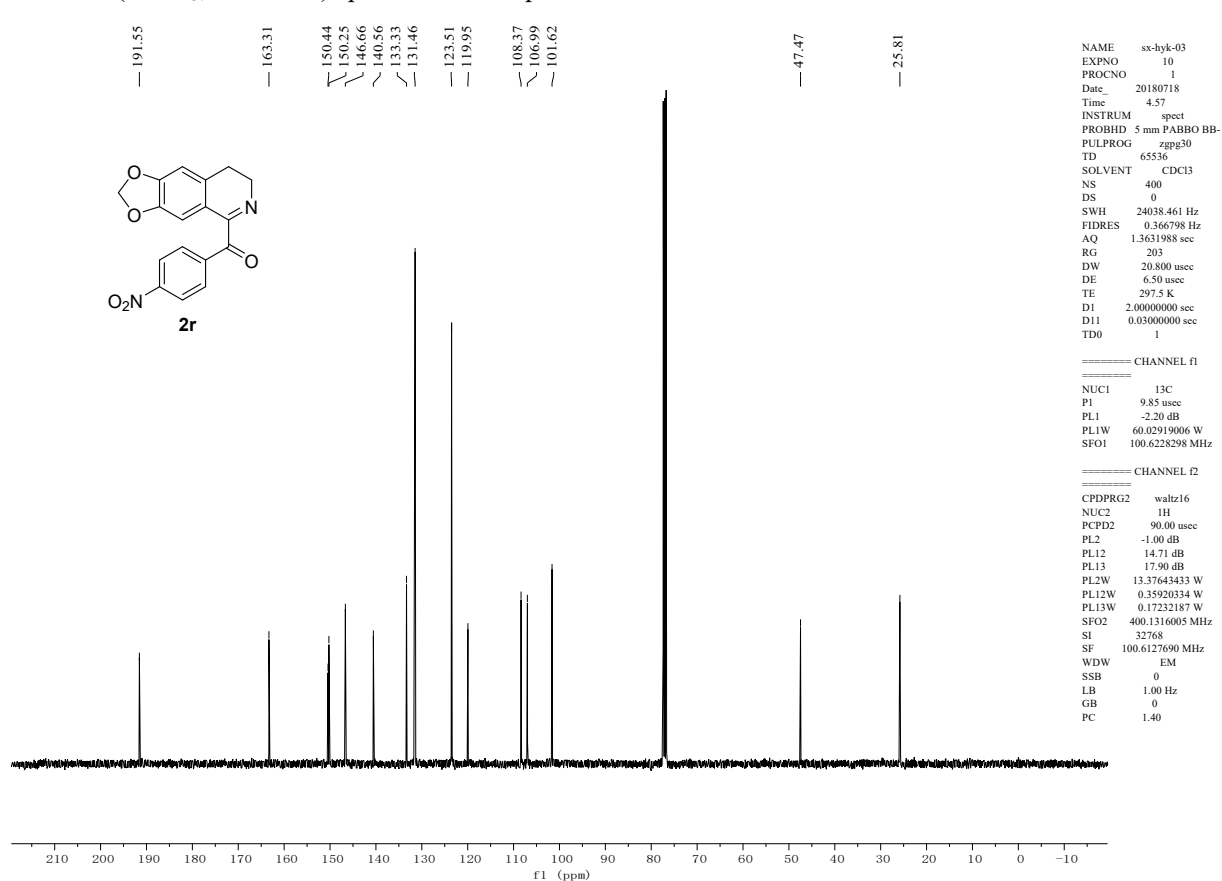
¹³C NMR (CDCl₃, 100 MHz) spectrum of compound **2q**:



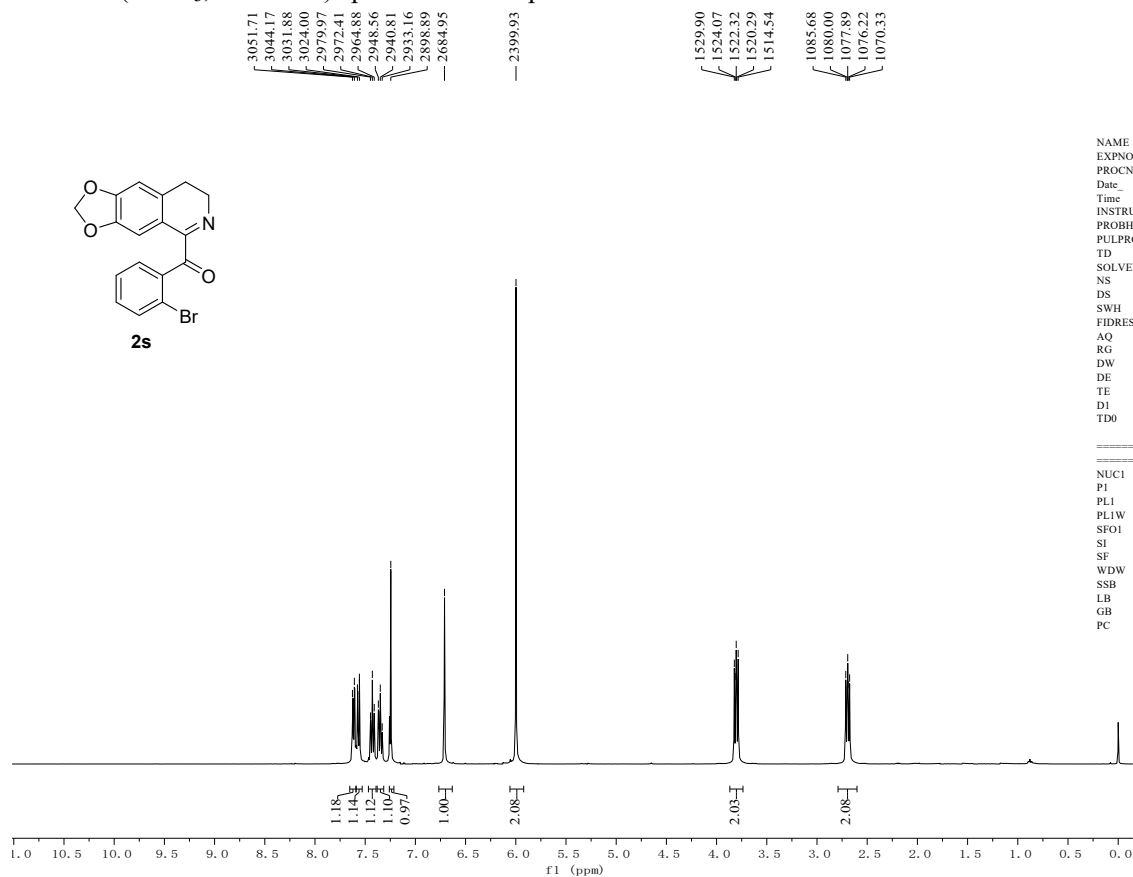
¹H NMR (CDCl₃, 400 MHz) spectrum of compound **2r**:



¹³C NMR (CDCl₃, 100 MHz) spectrum of compound **2r**:



¹H NMR (CDCl₃, 400 MHz) spectrum of compound **2s**:

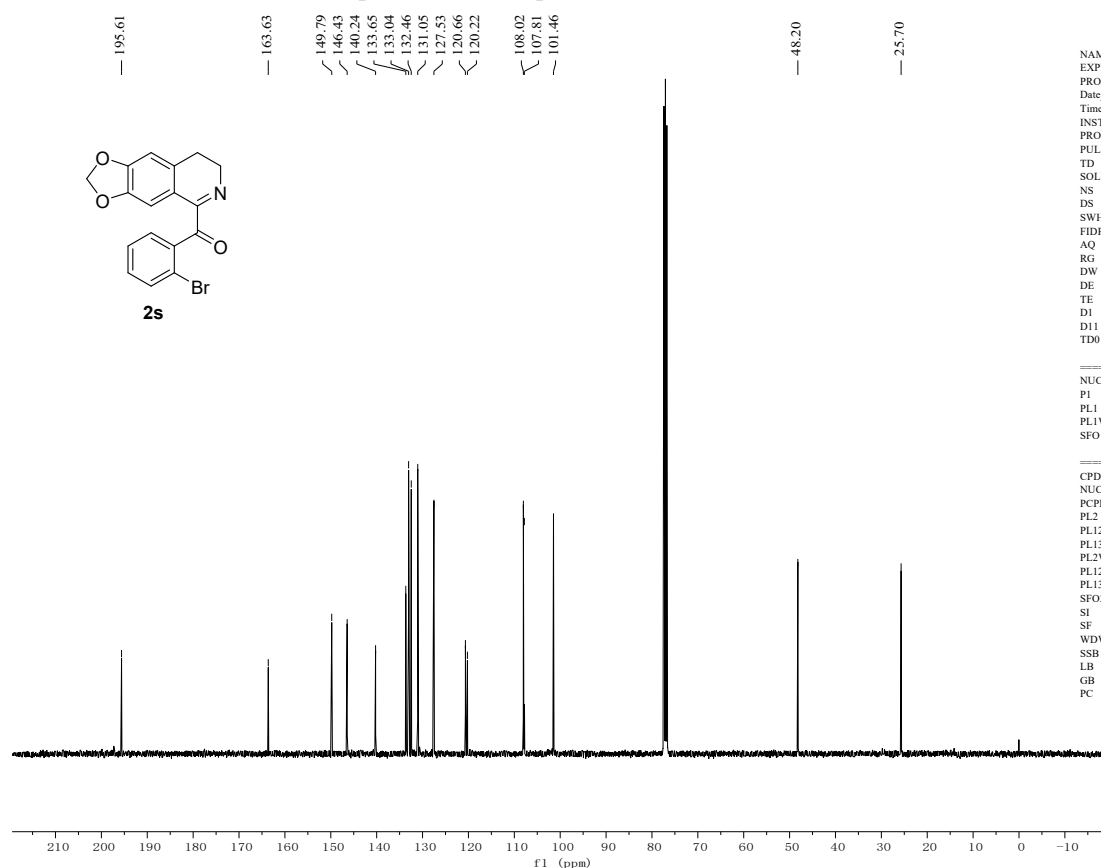


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EXPNO     10
PROCNO    1
Date_     20160716
Time      6.58
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PULPROG   zg30
TD         65536
SOLVENT   CDCl3
NS         16
DS         0
SWH        8223.685 Hz
FIDRES     0.125483 Hz
AQ         3.9846387 sec
RG         114
DW         60.800 usec
DE         6.50 usec
TE         296.5 K
D1         1.00000000 sec
TD0        1

===== CHANNEL f1 =====
NUC1       1H
P1         14.75 usec
PL1        -1.00 dB
PL1W       13.37643433 W
SFO1       400.1324710 MHz
SI         32768
SF         400.1300103 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00
    
```

¹³C NMR (CDCl₃, 100 MHz) spectrum of compound **2s**:



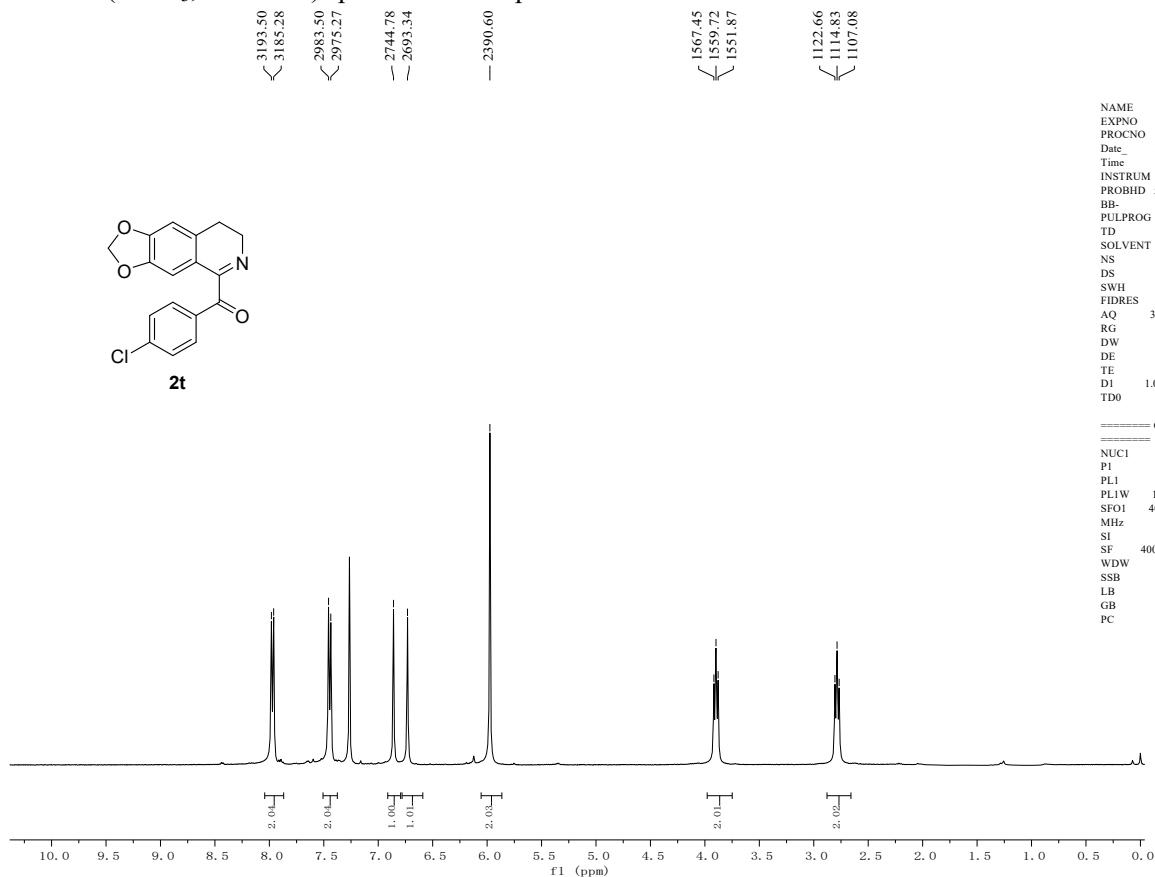
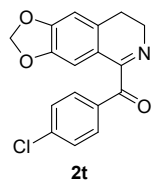
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EXPNO     11
PROCNO    1
Date_     20160716
Time      7.57
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         1024
DS         0
SWH        24038.461 Hz
FIDRES     0.366798 Hz
AQ         1.3631988 sec
RG         203
DW         20.800 usec
DE         6.50 usec
TE         297.3 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0        1

===== CHANNEL f1 =====
NUC1       13C
P1         9.85 usec
PL1        -2.20 dB
PL1W       60.02919006 W
SFO1       100.6228298 MHz

===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2       1H
PCPD2     90.00 usec
PL2        -1.00 dB
PL12      14.71 dB
PL13      17.90 dB
PL2W      13.37643433 W
PL12W     0.35920334 W
PL13W     0.17232187 W
SFO2      400.1316005 MHz
SI         32768
SF         100.6127690 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
    
```

¹H NMR (CDCl₃, 400 MHz) spectrum of compound **2t**:



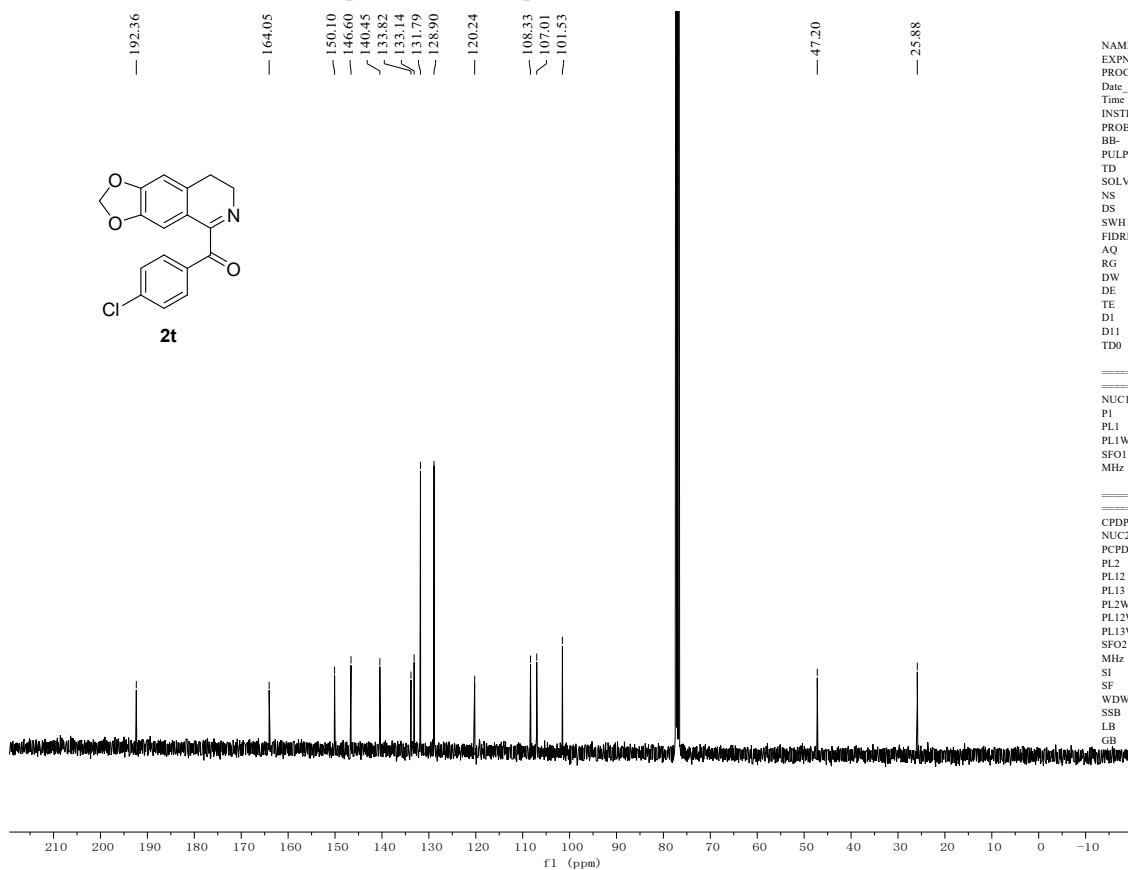
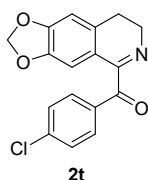
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EXPNO     10
PROCNO    1
Date_     20180712
Time      18.50
INSTRUM   spect
PROBHD    5 mm PABBO
BB-
PULPROG   zg30
TD         65536
SOLVENT   CDCl3
NS         16
DS         0
SWH        8223.685 Hz
FIDRES     0.125483 Hz
AQ         3.9846387 sec
RG         203
DW         60.800 usec
DE         6.50 usec
TE         296.9 K
D1         1.00000000 sec
TD0        1
    
```

```

===== CHANNEL f1
=====
NUC1       1H
P1         14.75 usec
PL1        -1.00 dB
PL1W       13.37643433 W
SFO1       400.1324710
MHz
SI         32768
SF         400.1300071 MHz
WDW         EM
SSB         0
LB         0.30 Hz
GB         0
PC         1.00
    
```

¹³C NMR (CDCl₃, 100 MHz) spectrum of compound **2t**:



```

NAME      sx-hyk-01
EXPNO     10
PROCNO    1
Date_     20180715
Time      0.28
INSTRUM   spect
PROBHD    5 mm PABBO
BB-
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         400
DS         0
SWH        24038.461 Hz
FIDRES     0.366798 Hz
AQ         1.3631988 sec
RG         203
DW         20.800 usec
DE         6.50 usec
TE         297.6 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0        1
    
```

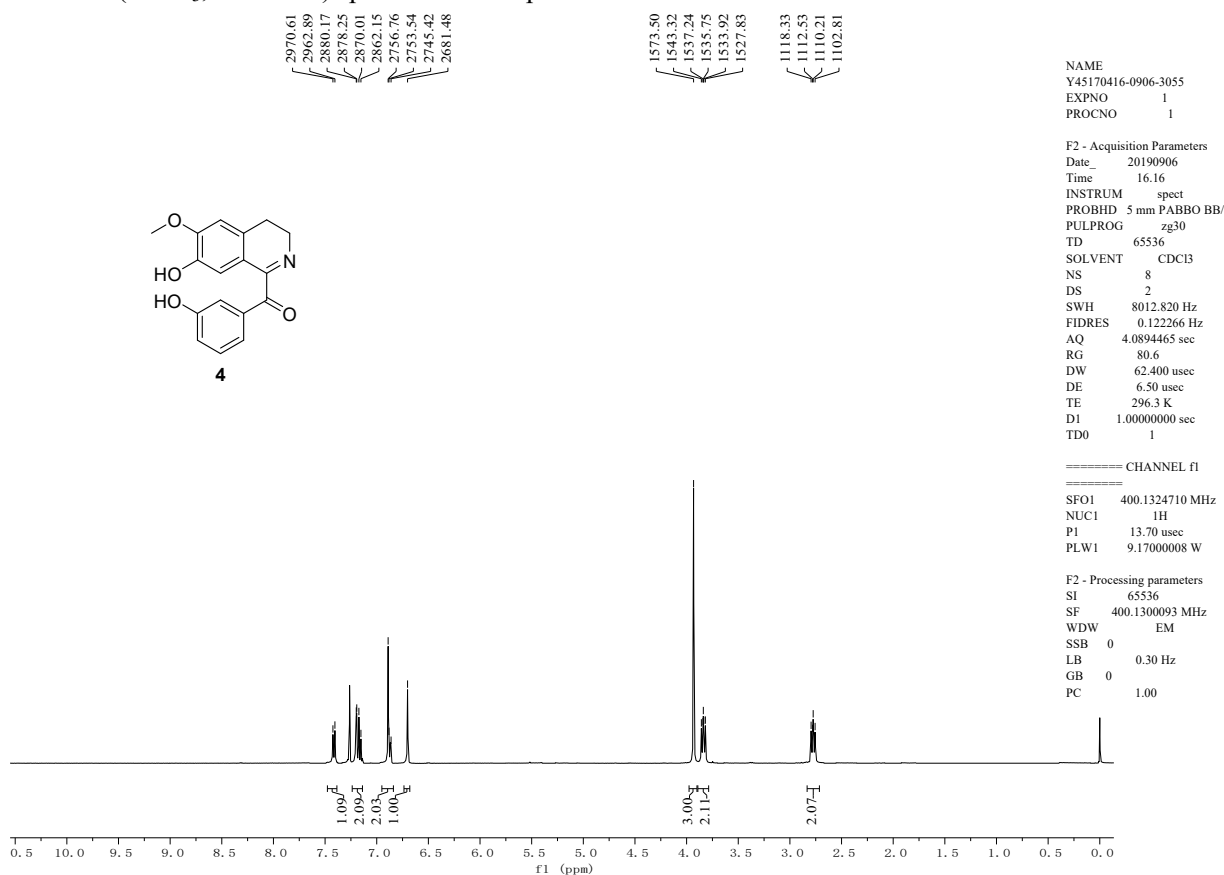
```

===== CHANNEL f1
=====
NUC1       13C
P1         9.85 usec
PL1        -2.20 dB
PL1W       60.02919006 W
SFO1       100.6228298
MHz
    
```

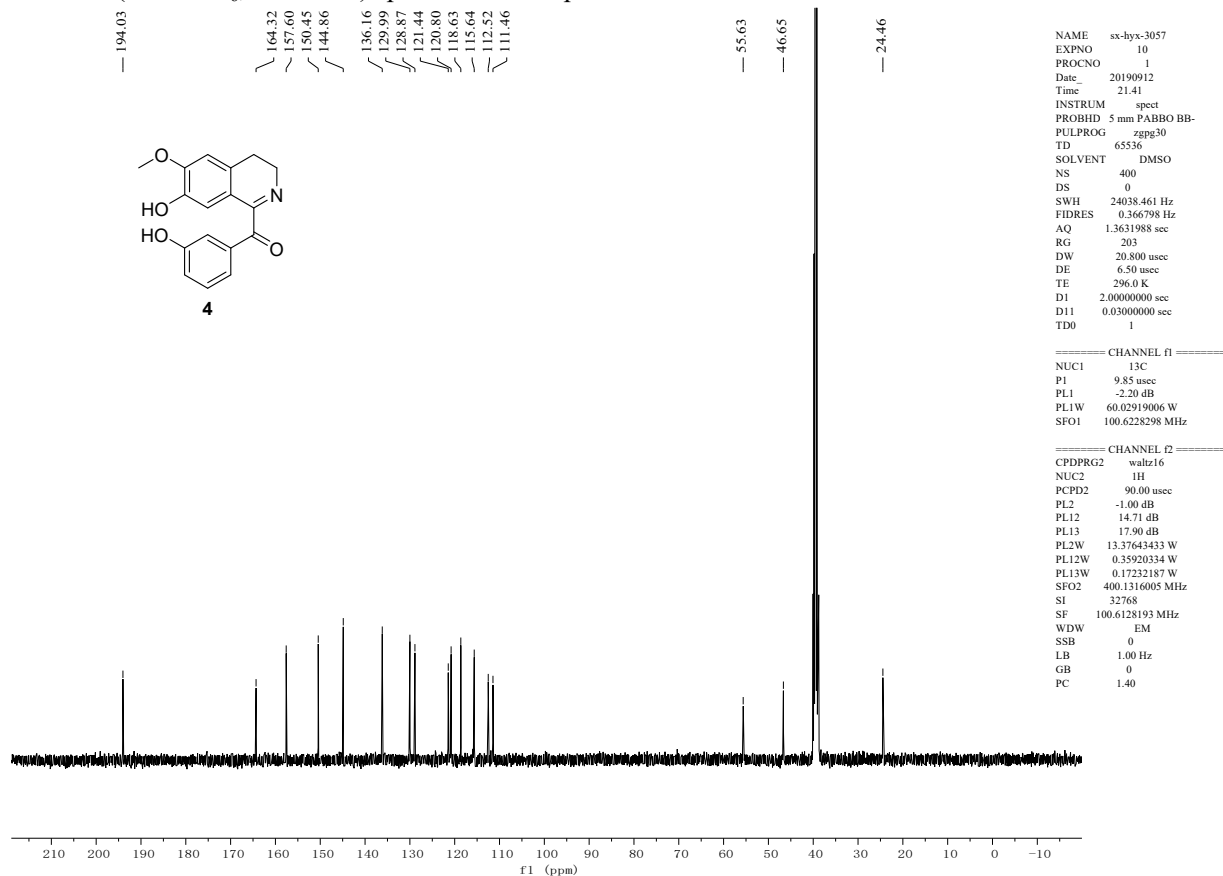
```

===== CHANNEL f2
=====
CPDPRG2    waltz16
NUC2       1H
PCPD2      90.00 usec
PL2        -1.00 dB
PL12       14.71 dB
PL13       17.90 dB
PL2W       13.37643433 W
PL12W      0.35920334 W
PL13W      0.17232187 W
SFO2       400.1316005
MHz
SI         32768
SF         100.6127690 MHz
WDW         EM
SSB         0
LB         1.00 Hz
GB         0
PC         1.40
    
```

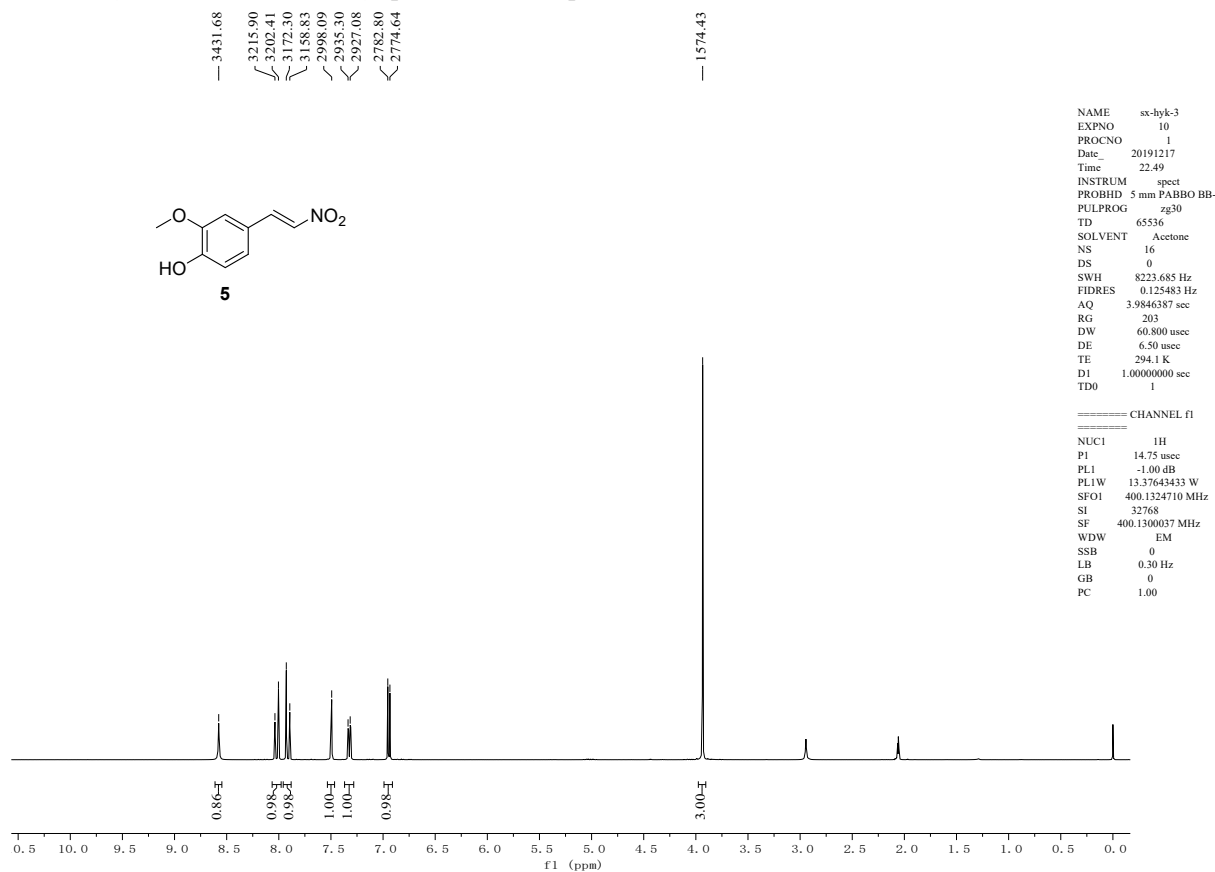
¹H NMR (CDCl₃, 400 MHz) spectrum of compound Canelillinoxine 4:



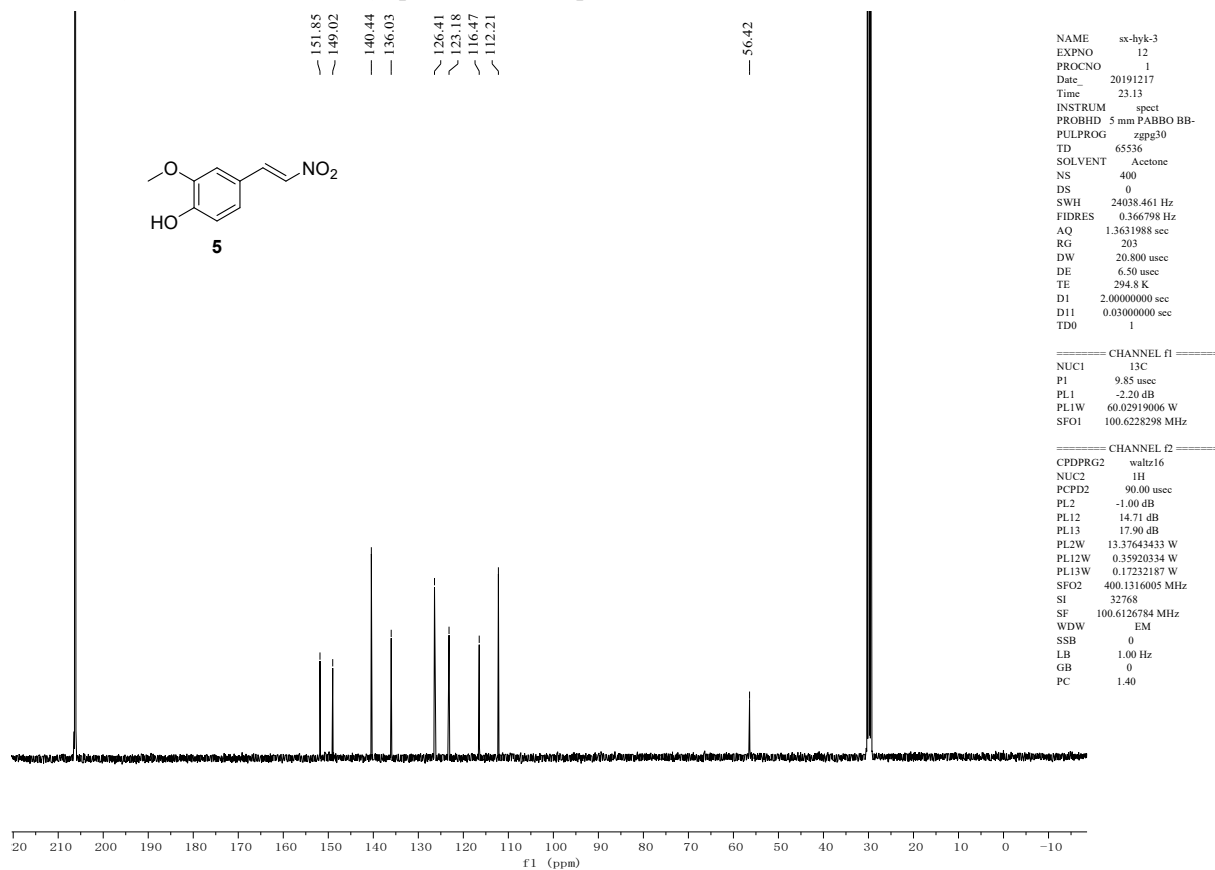
¹³C NMR (DMSO-d₆, 100 MHz) spectrum of compound Canelillinoxine 4:



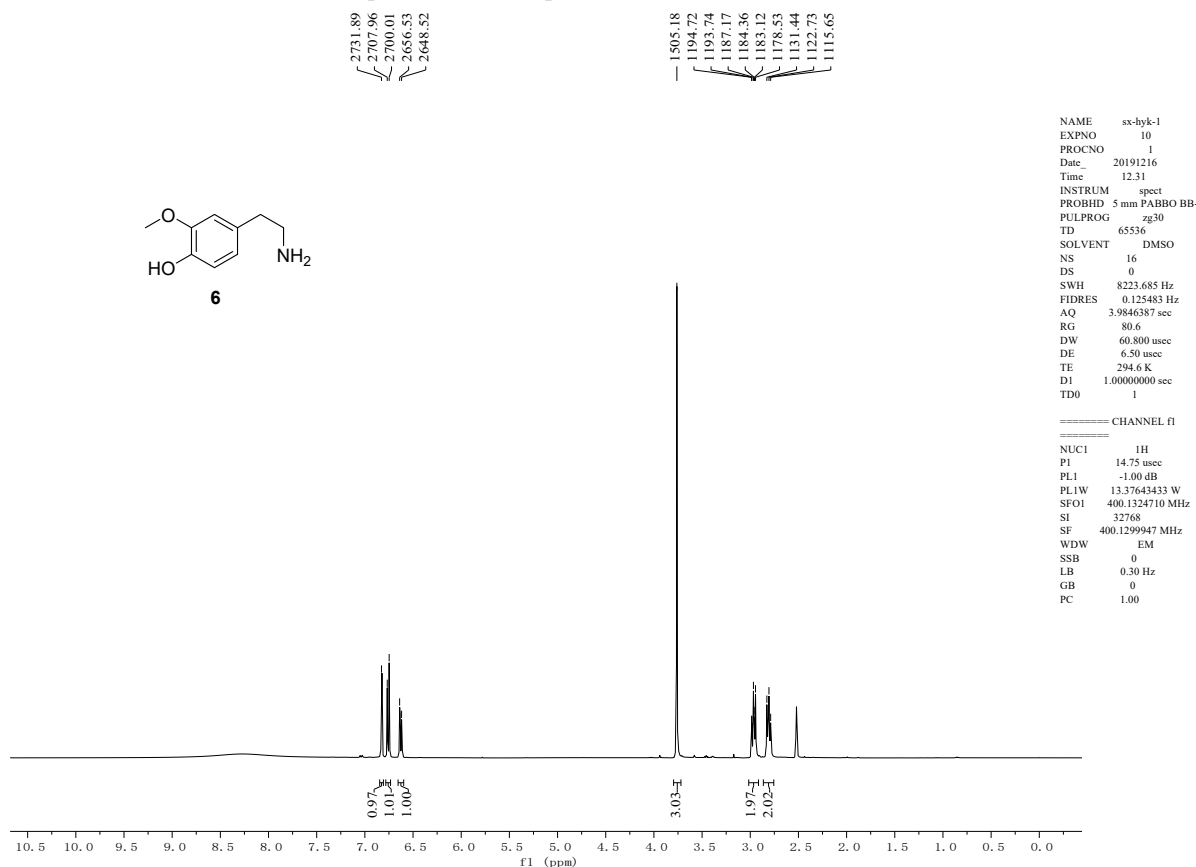
¹H NMR (Acetone-d₆, 400 MHz) spectrum of compound **5**:



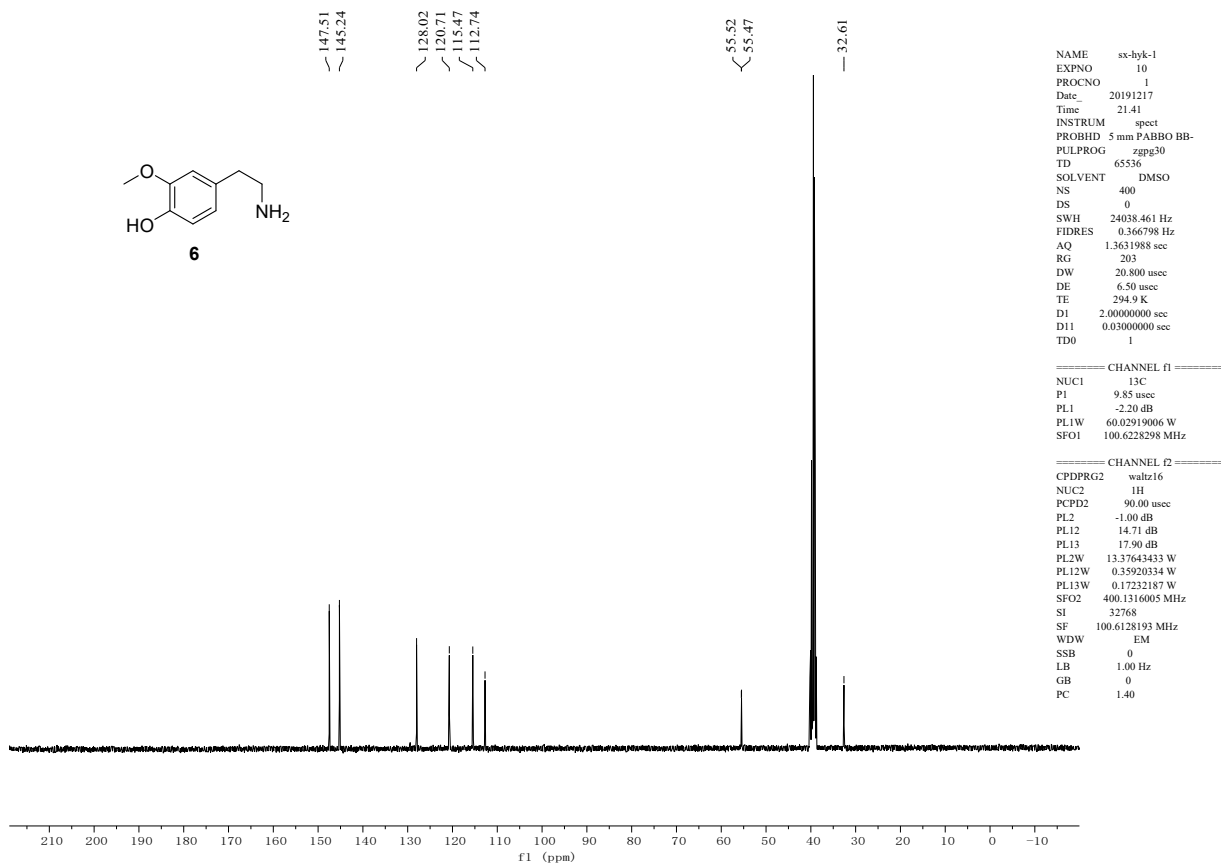
¹³C NMR (Acetone-d₆, 100 MHz) spectrum of compound **5**:



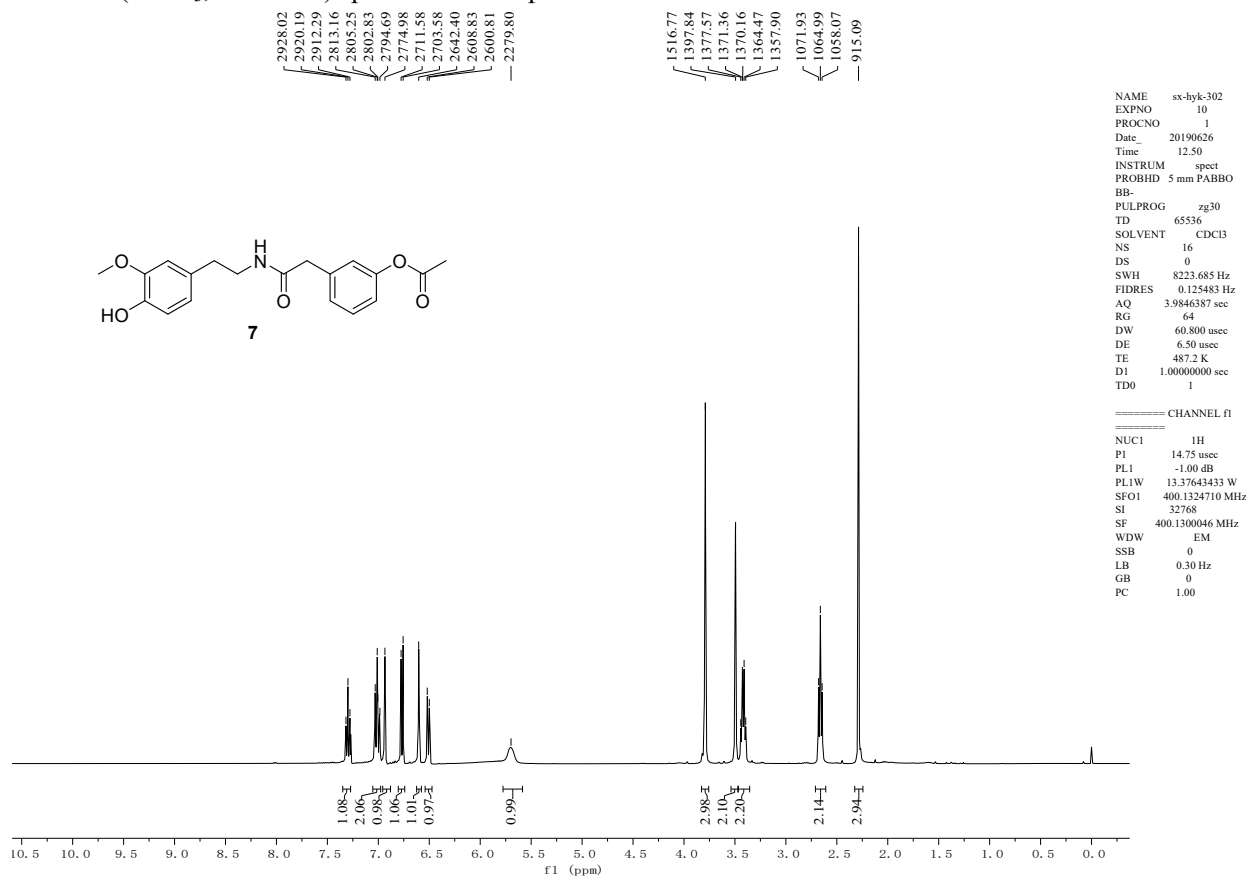
¹H NMR (DMSO-*d*₆, 400 MHz) spectrum of compound 6:



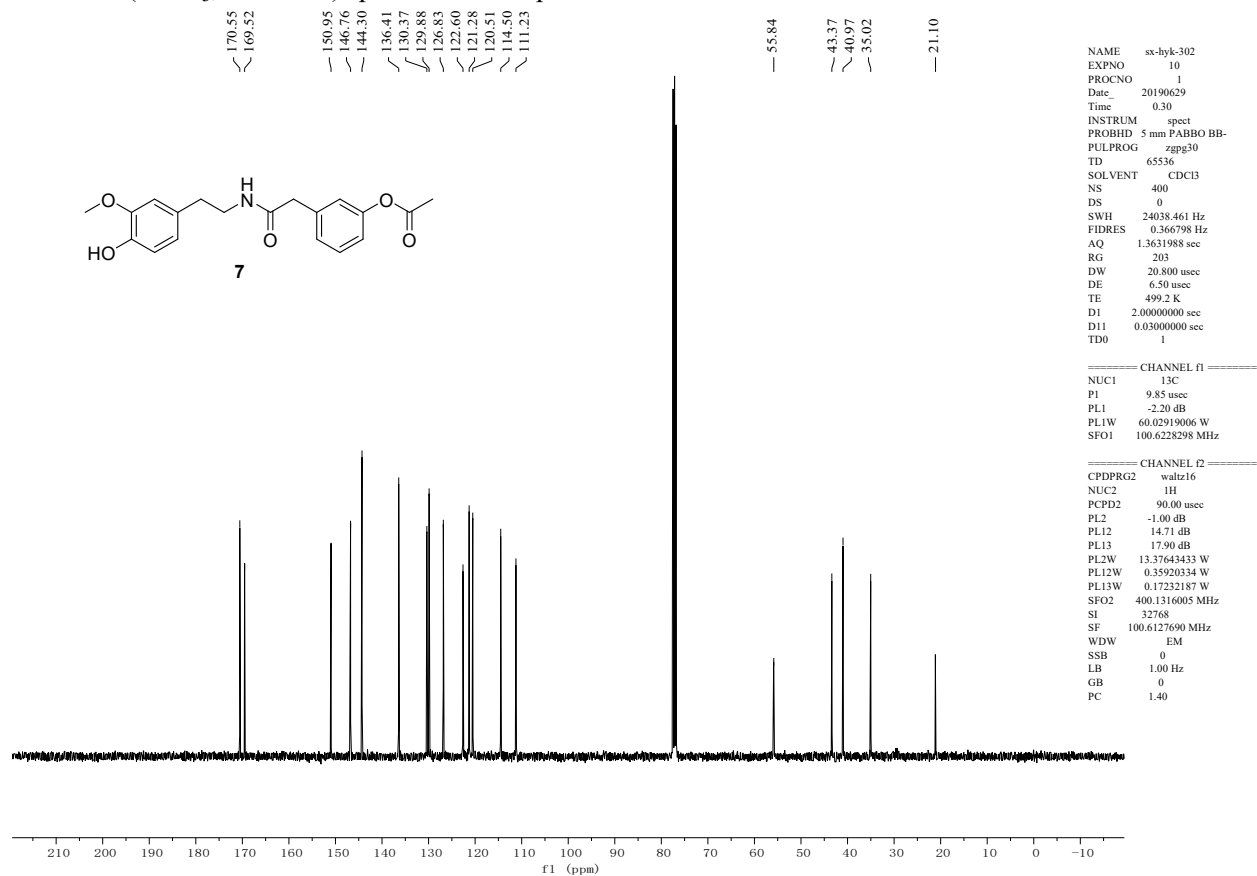
¹³C NMR (DMSO-*d*₆, 100 MHz) spectrum of compound 6:



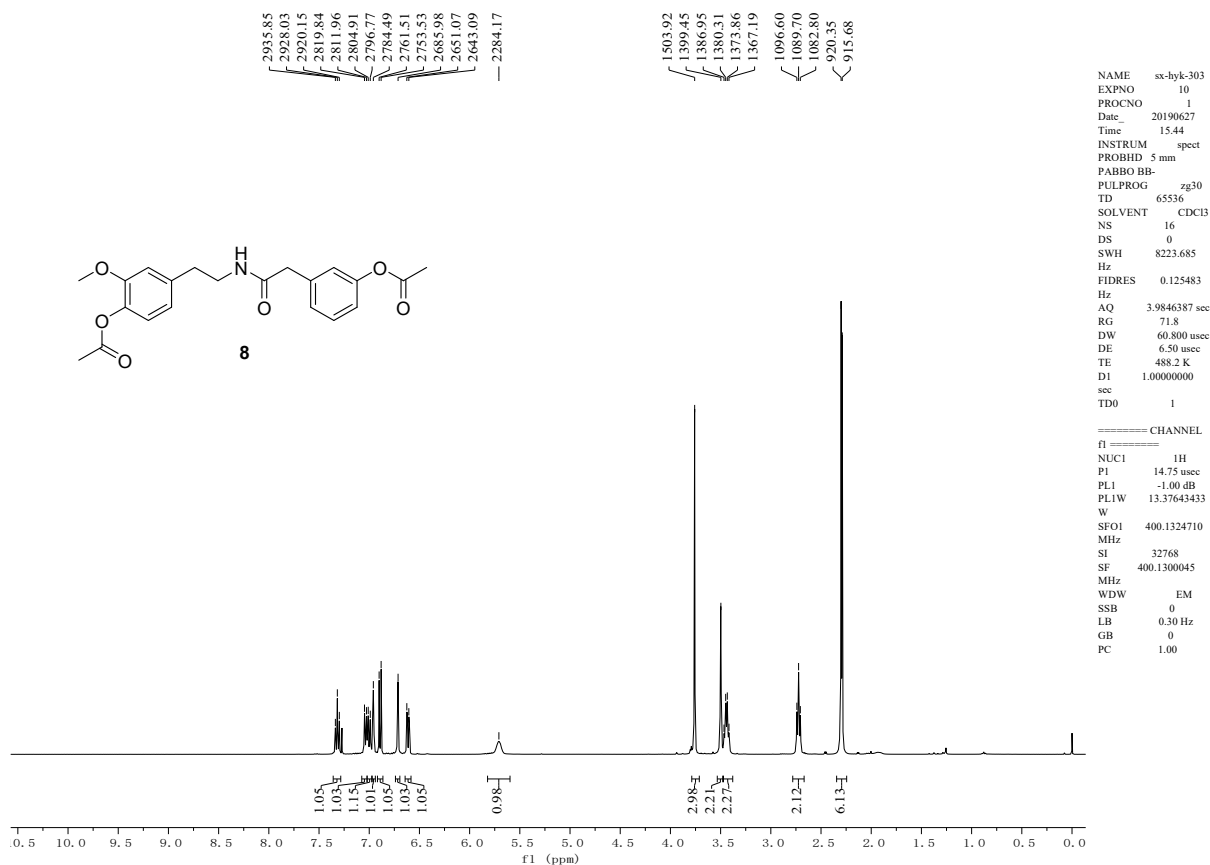
¹H NMR (CDCl₃, 400 MHz) spectrum of compound 7:



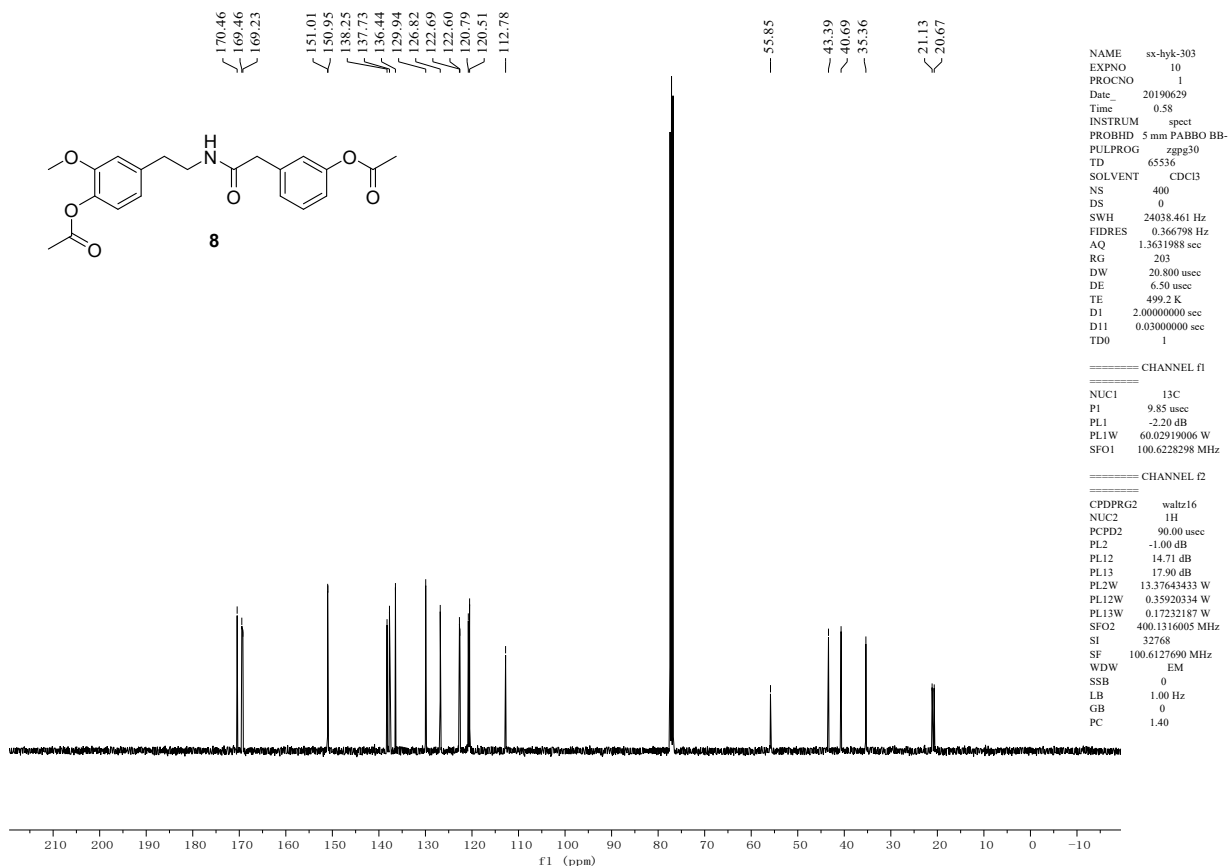
¹³C NMR (CDCl₃, 100 MHz) spectrum of compound 7:



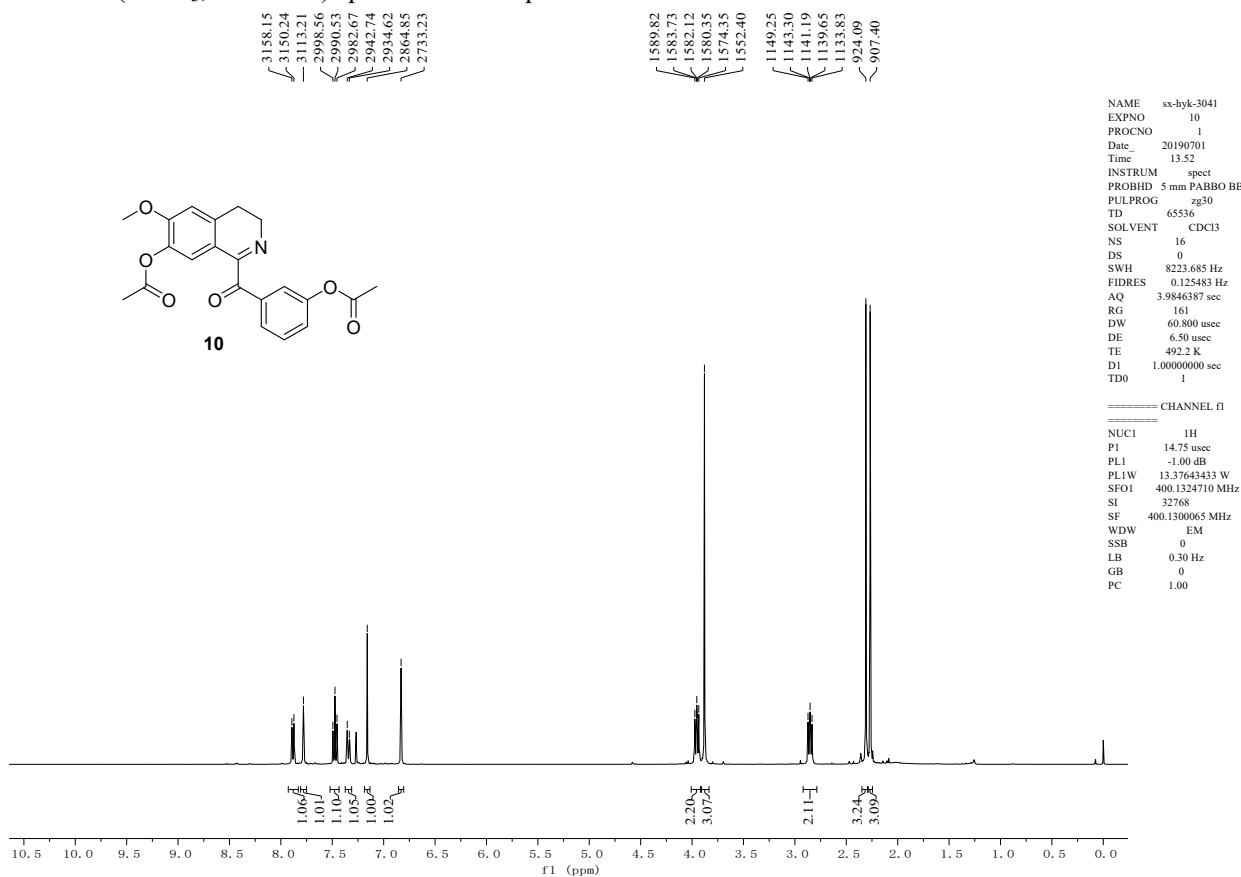
¹H NMR (CDCl₃, 400 MHz) spectrum of compound **8**:



¹³C NMR (CDCl₃, 100 MHz) spectrum of compound **8**:



¹H NMR (CDCl₃, 400 MHz) spectrum of compound 10:



¹³C NMR (CDCl₃, 100 MHz) spectrum of compound 10:

