

Supporting Information

Novel Total Syntheses of Oxoaporphine Alkaloids Enabled by Mild Cu-Catalyzed Tandem Oxidation/Aromatization of 1-Bn-DHIQs

Bo Zheng, Hui-Ya Qu, Tian-Zhuo Meng, Xia Lu, Jie Zheng, Yun-Gang He, Qi-Qi Fan, Xiao-Xin Shi*

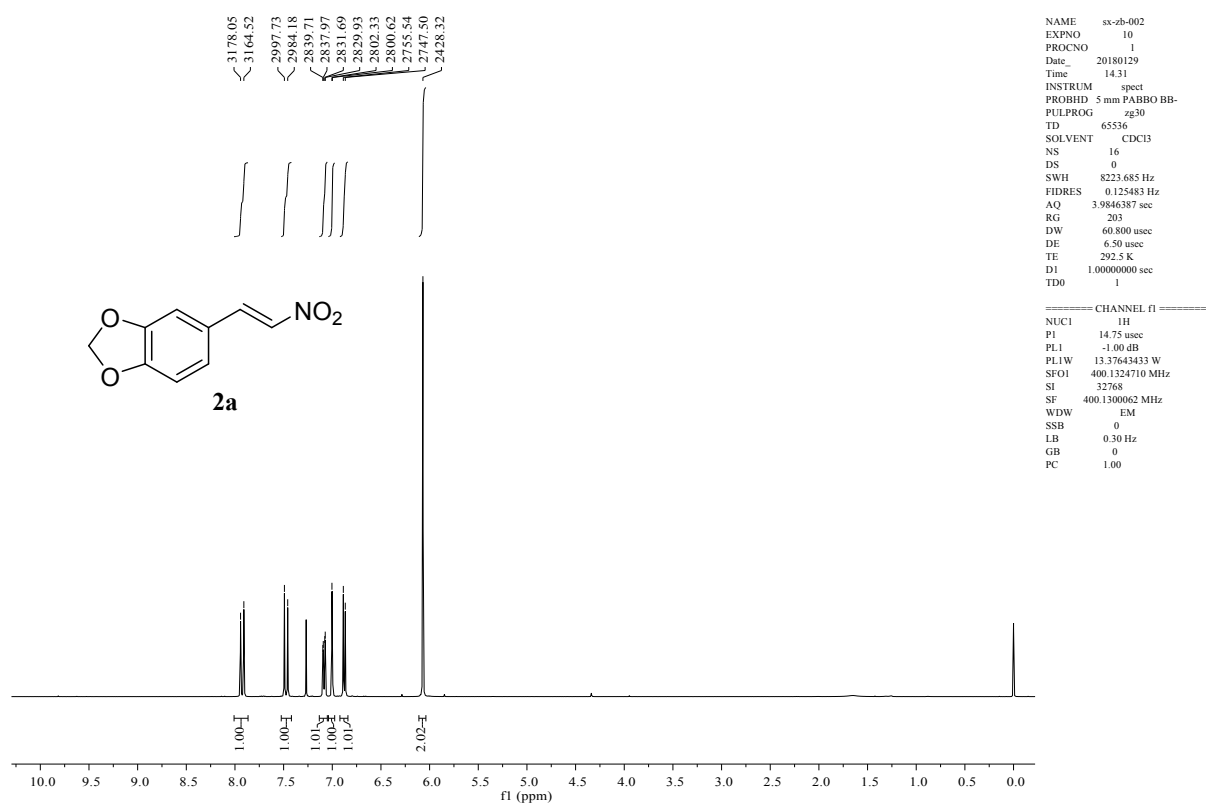
Shanghai Key Laboratory of Chemical Biology and Department of Pharmaceutical Engineering, School of
Pharmacy, East China University of Science and Technology, 130 Mei-Long Road, Shanghai 200237, P. R. China
E-mail: xxshi@ecust.edu.cn

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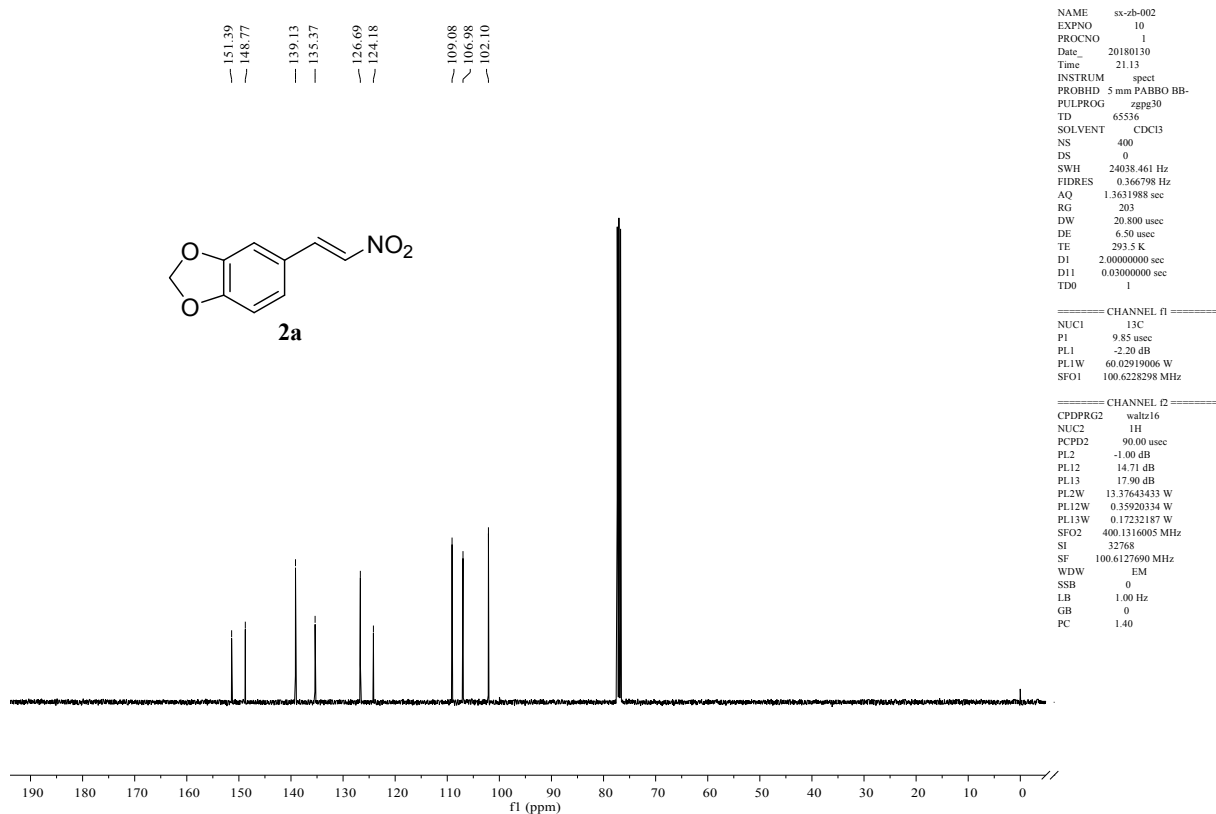
¹ H and ¹³ C NMR Spectra of All Compounds.....	S2-S45
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¹H and ¹³C NMR Spectra of All Compounds:

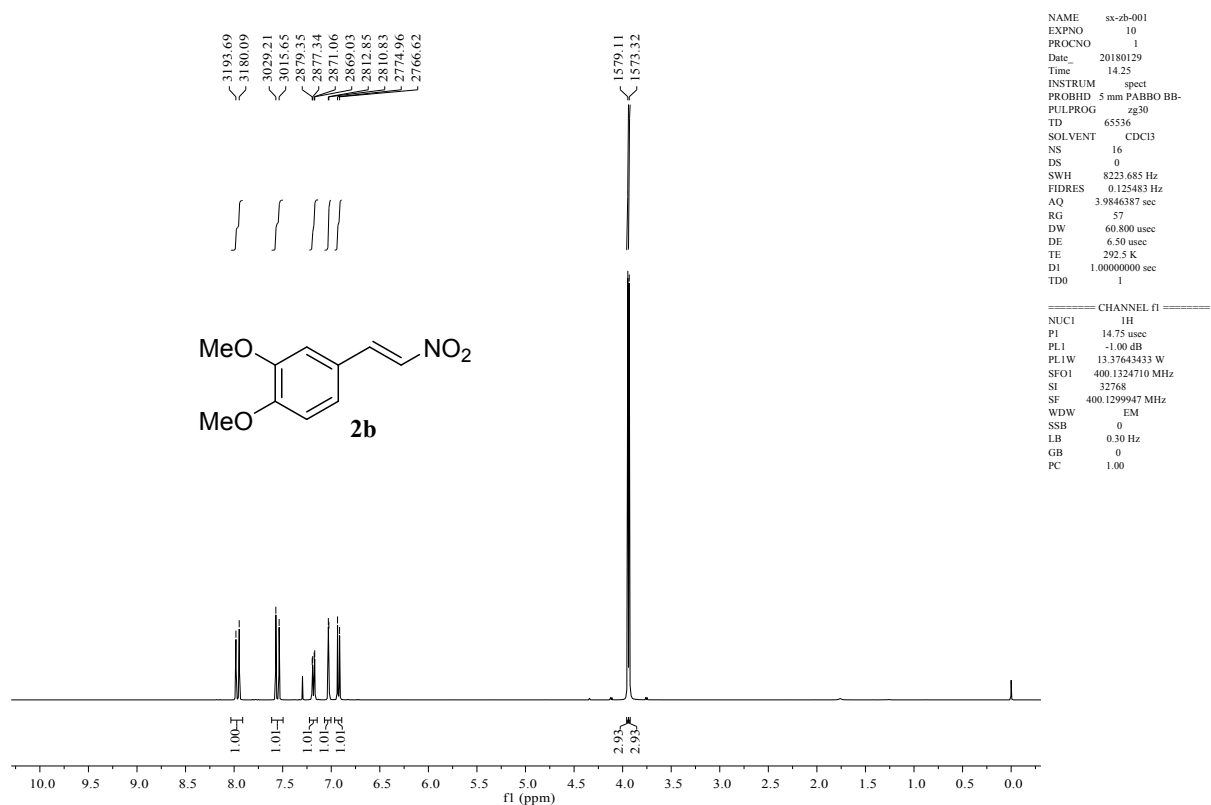
¹H NMR (CDCl₃, 400 MHz) spectrum of compound **2a**:



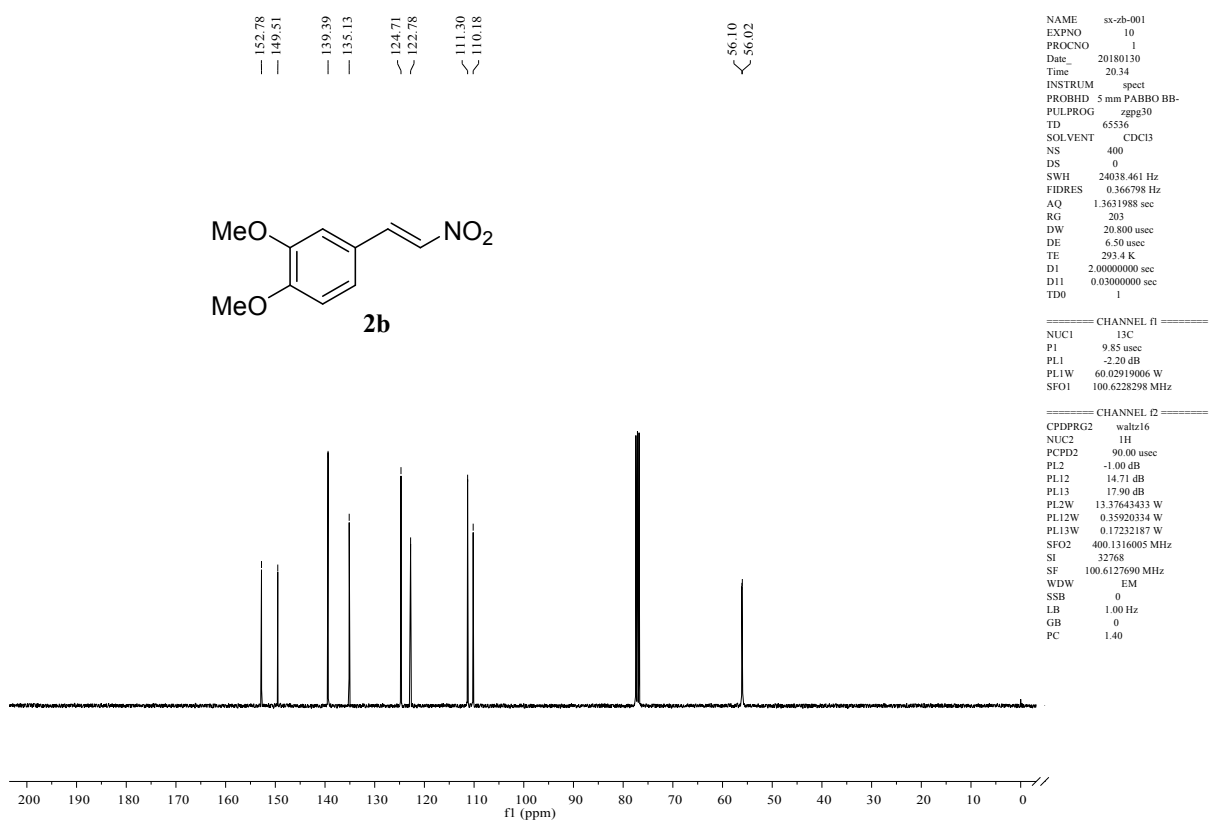
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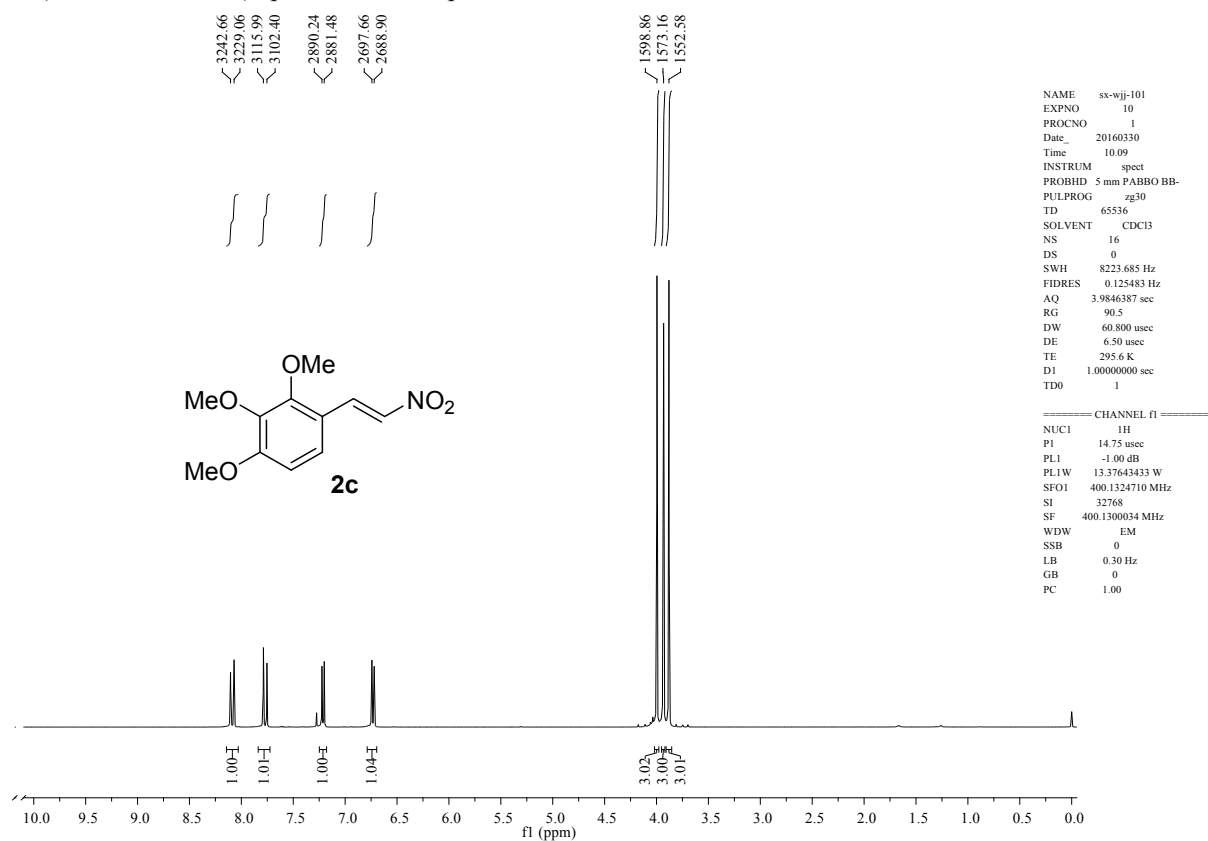
^1H NMR (CDCl_3 , 400 MHz) spectrum of compound **2b**:



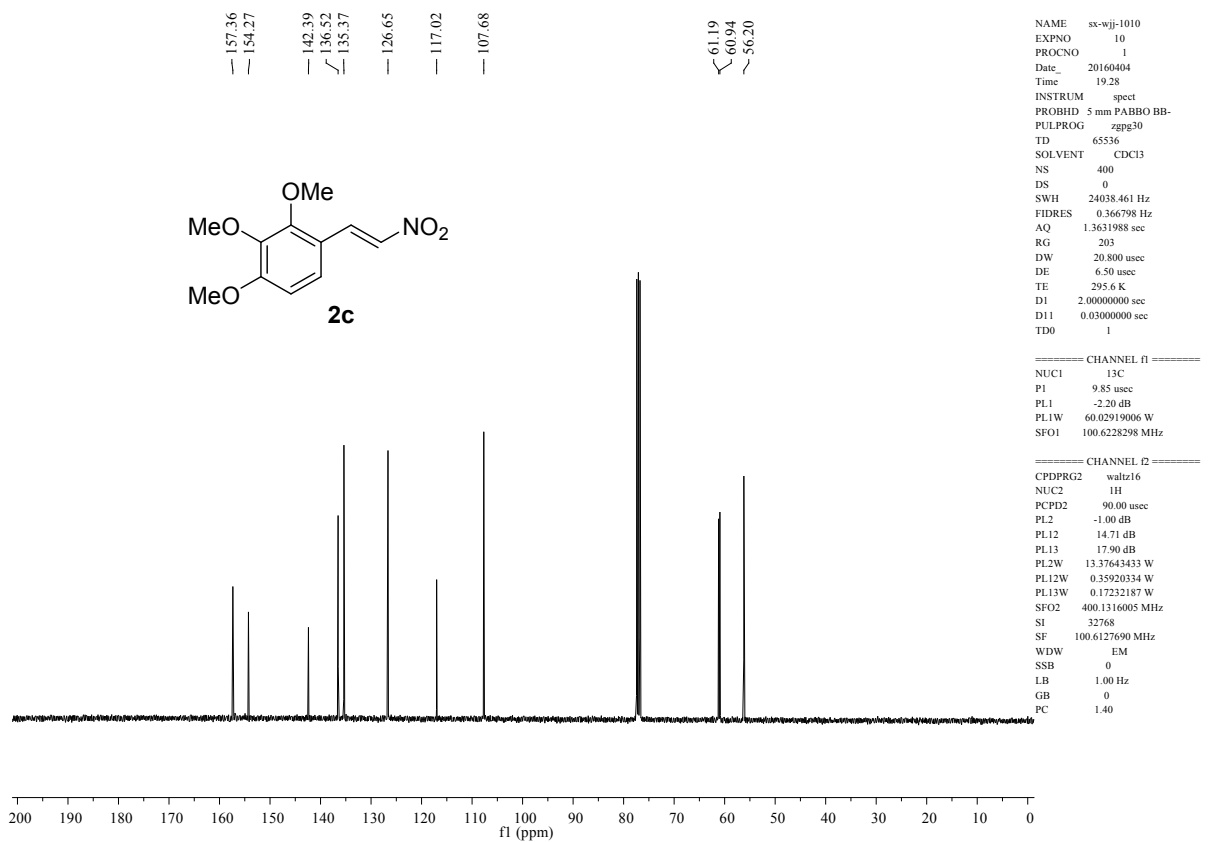
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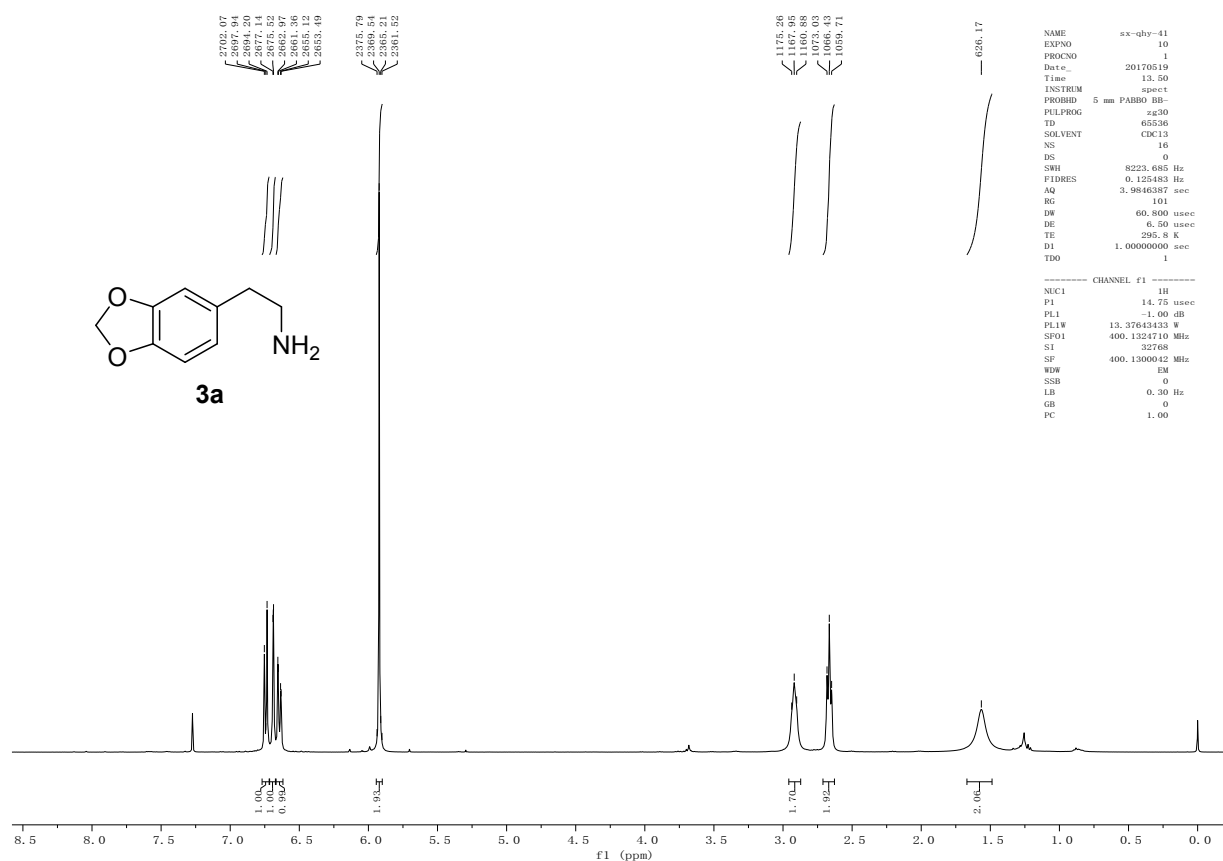
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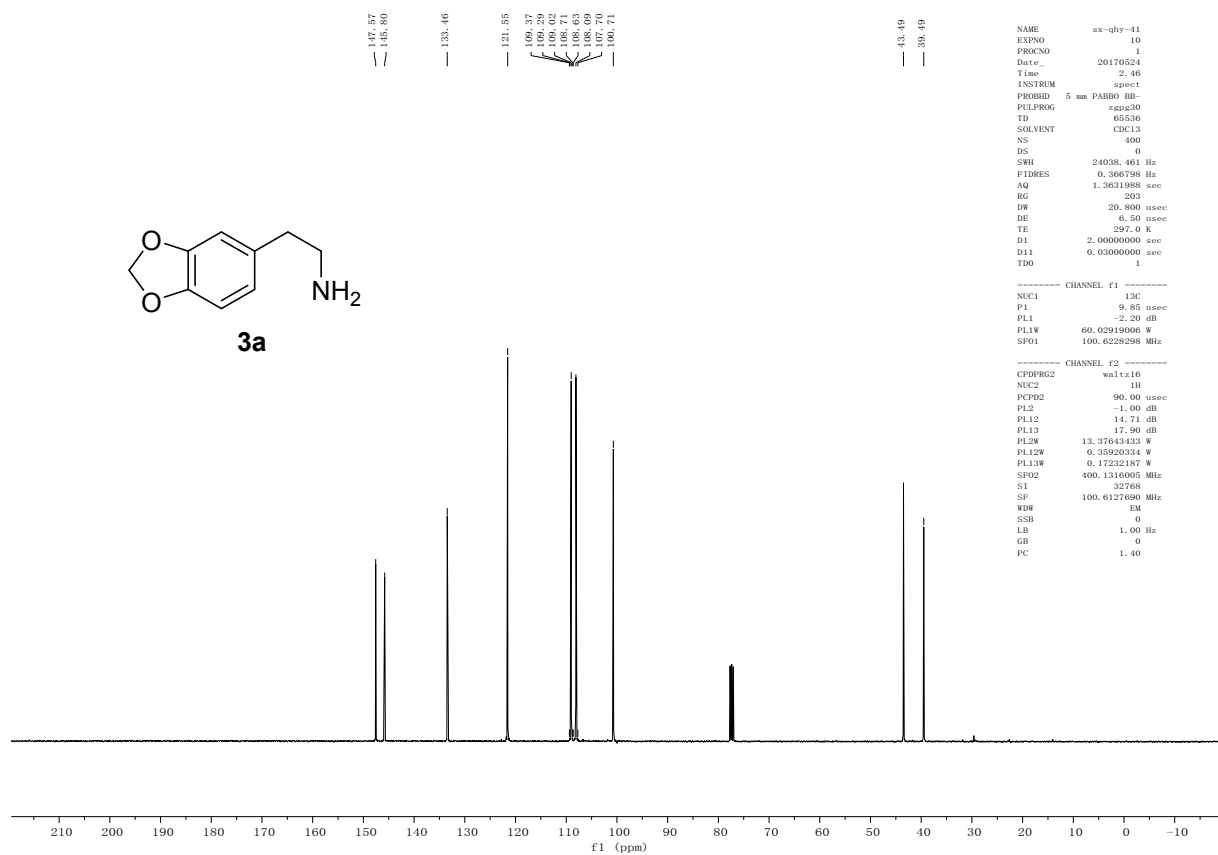
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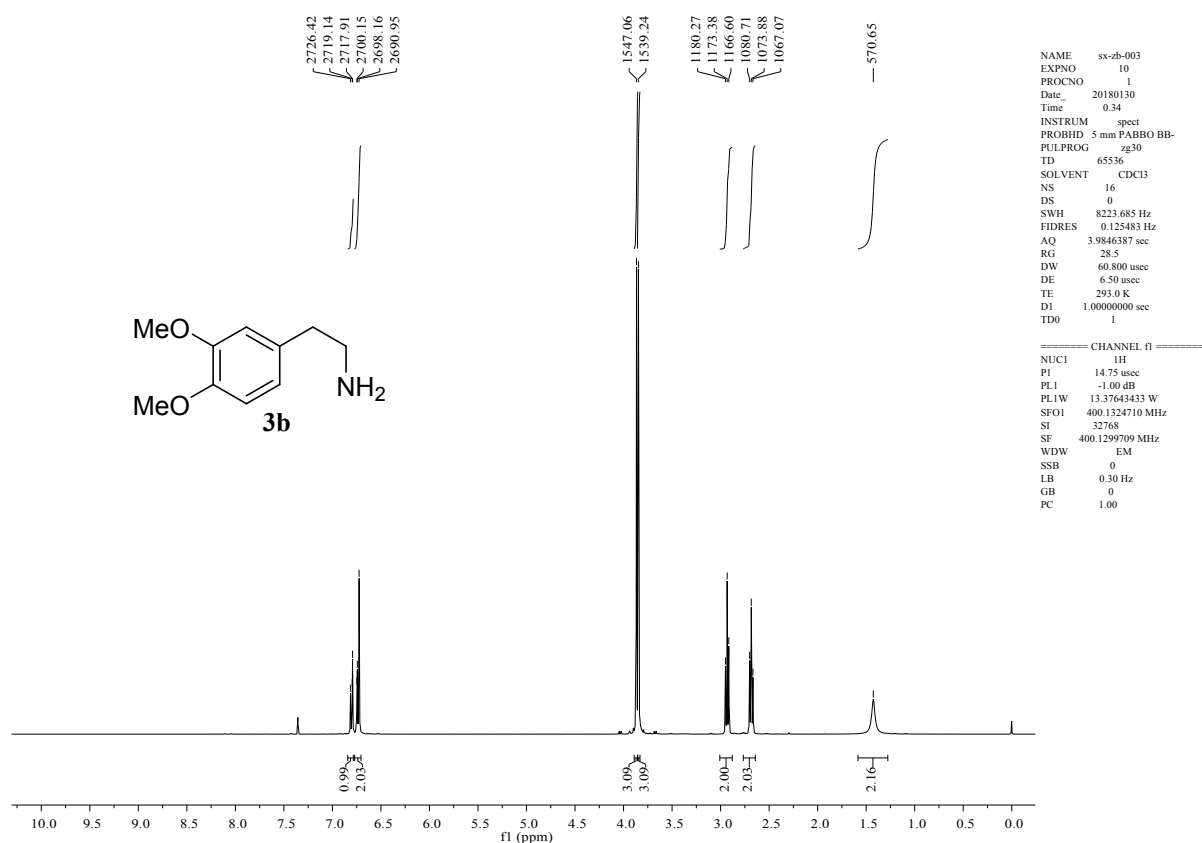
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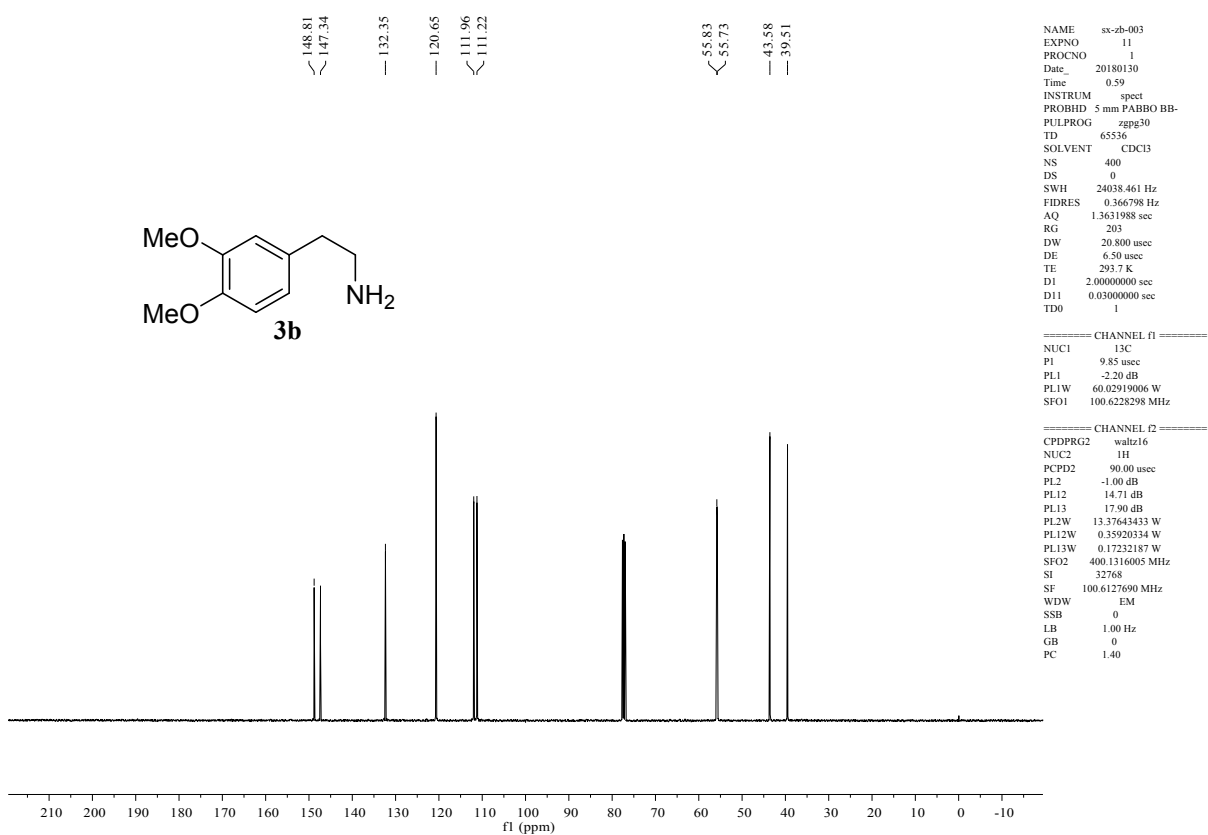
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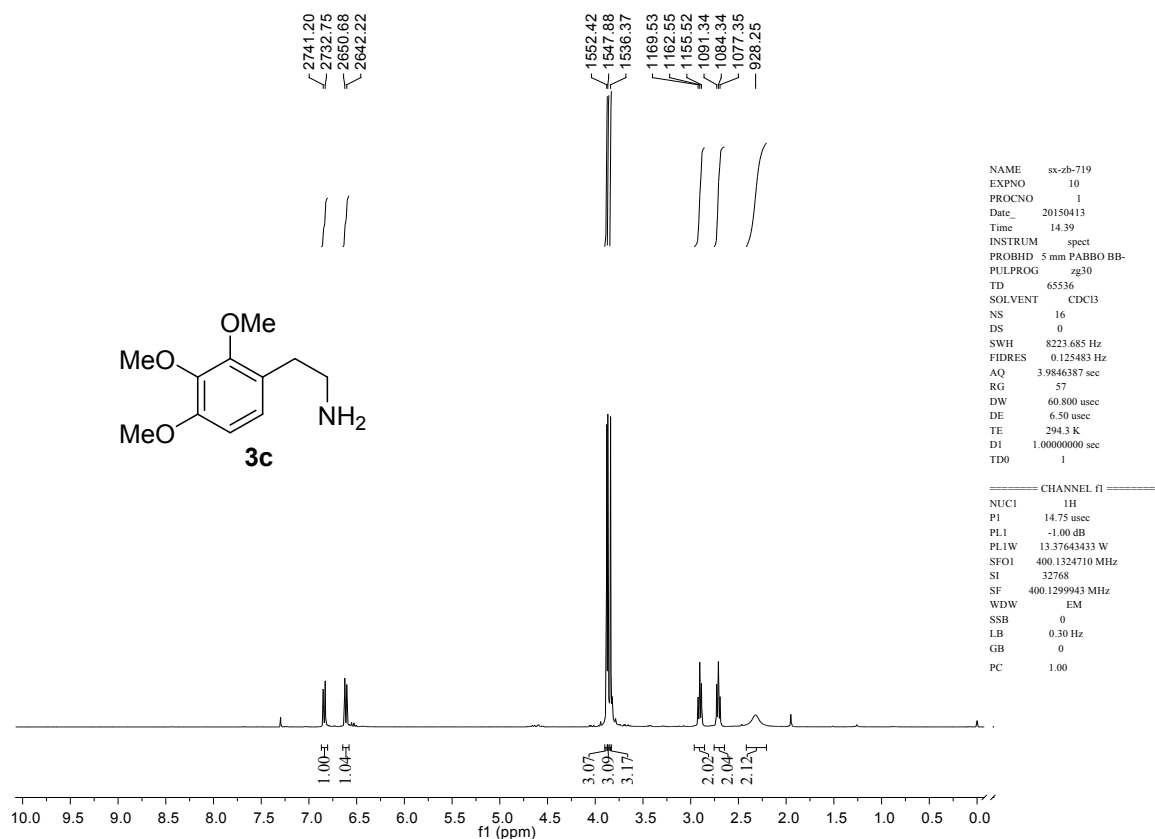
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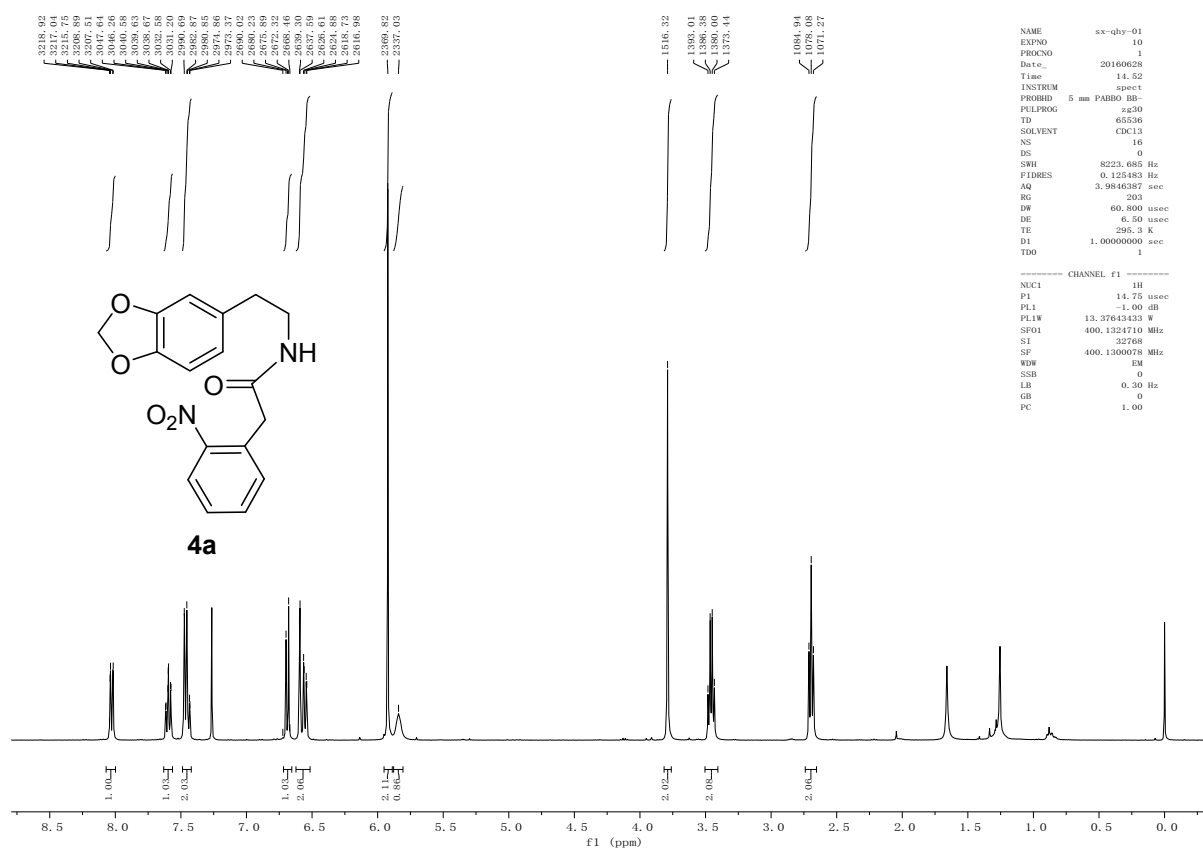
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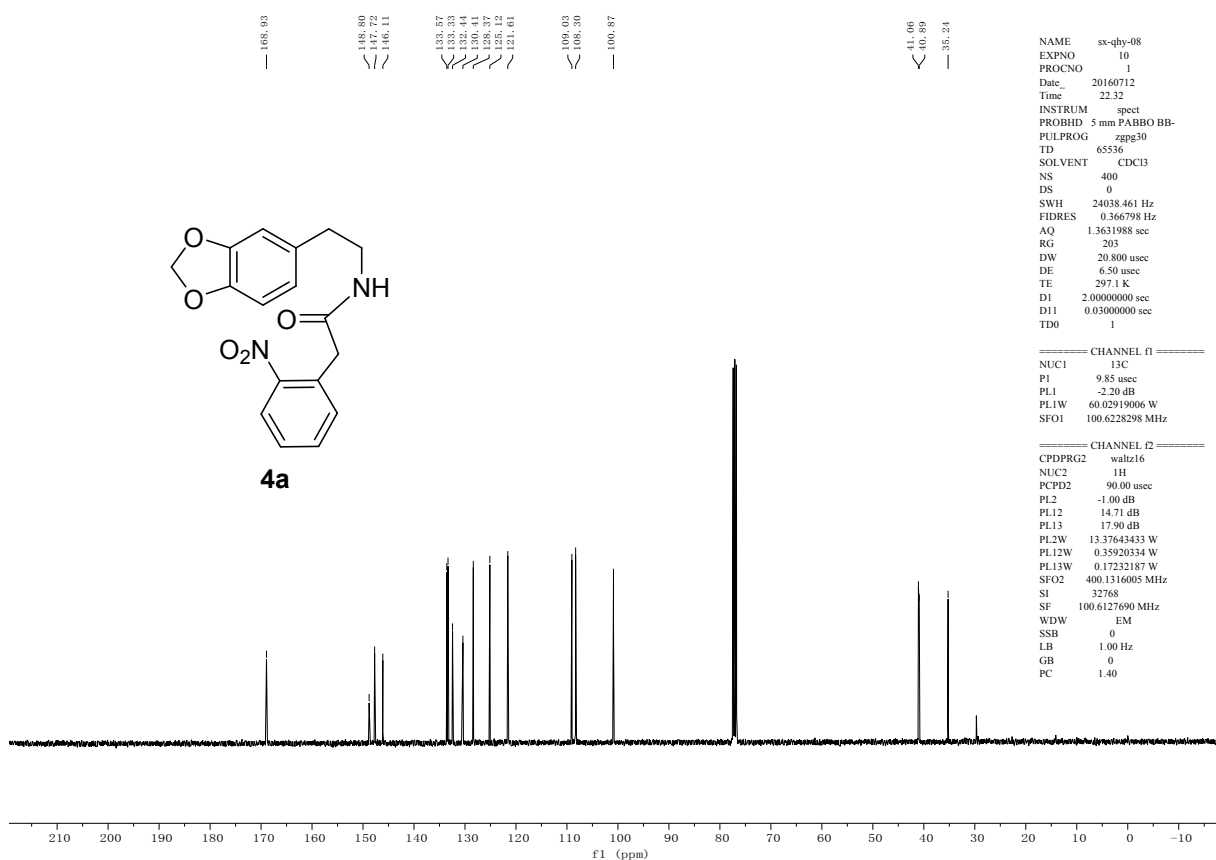
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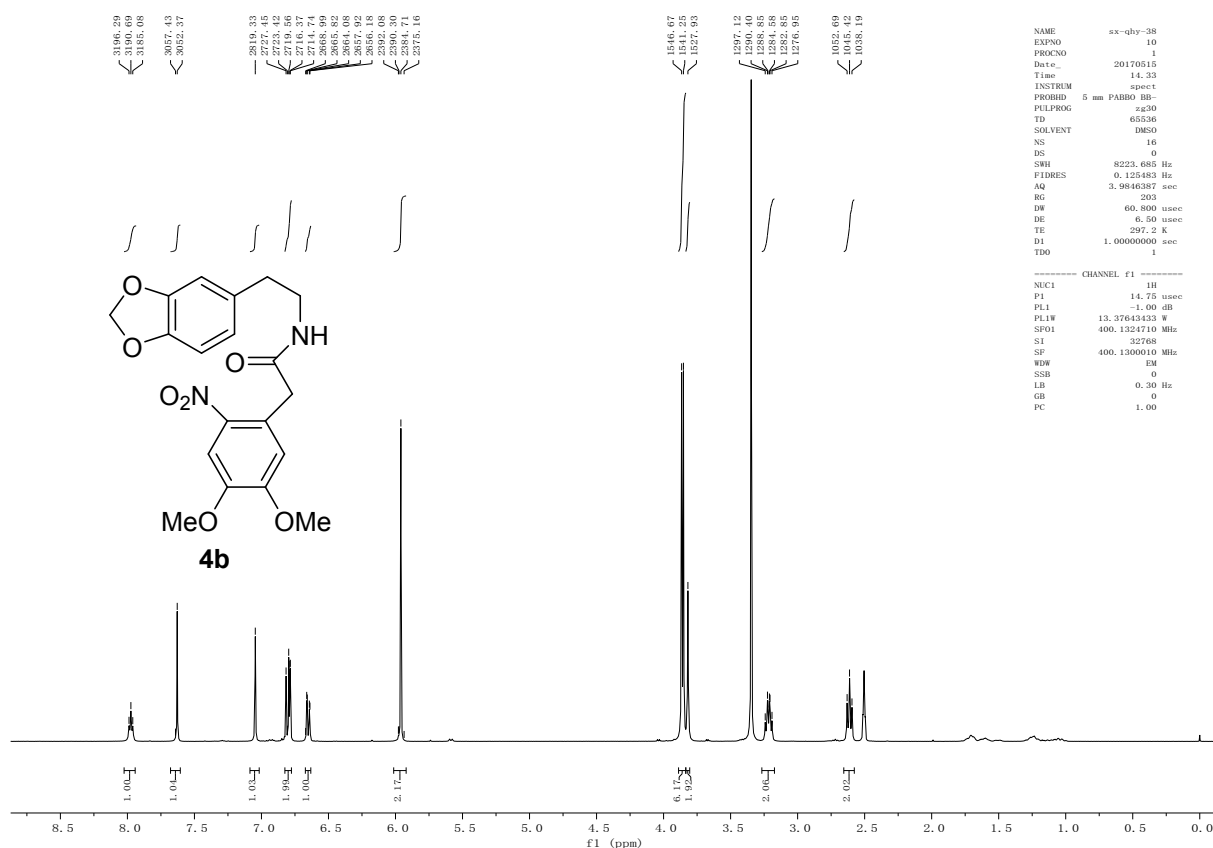
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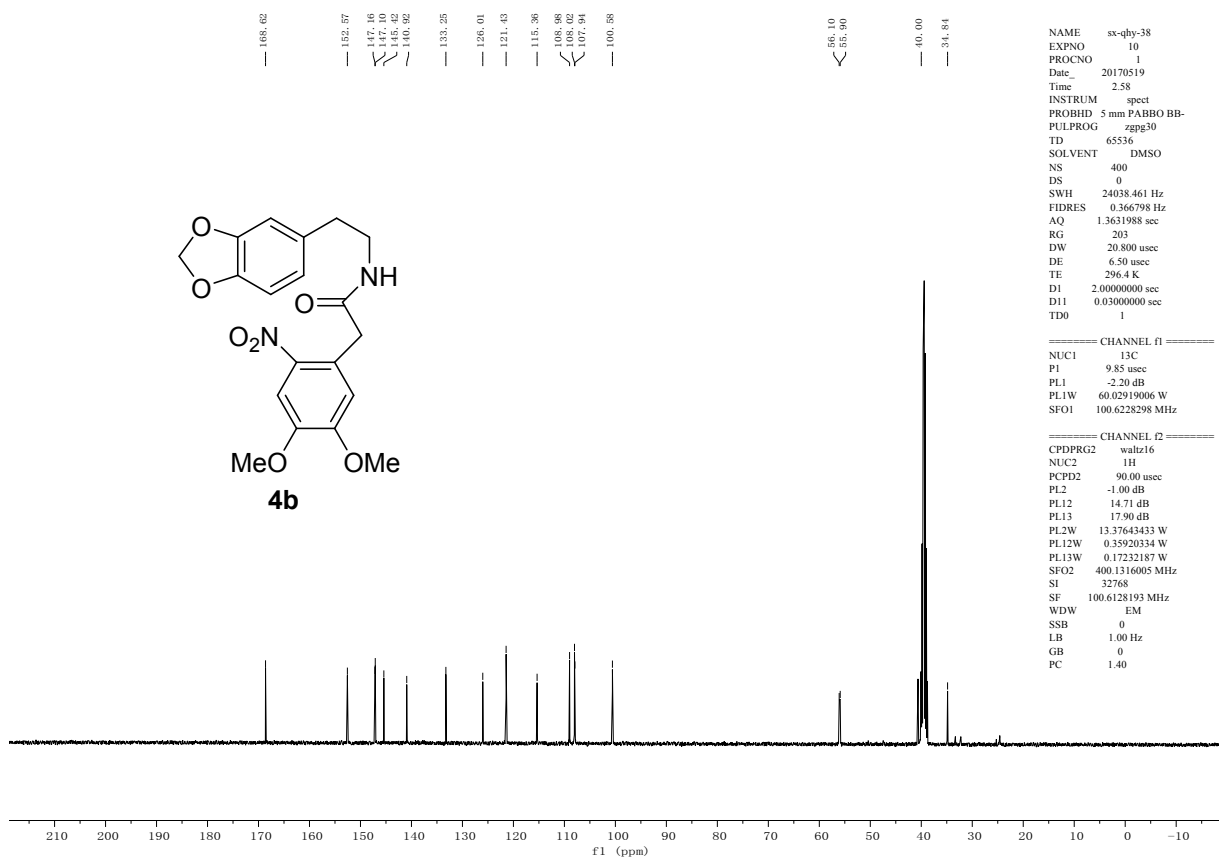
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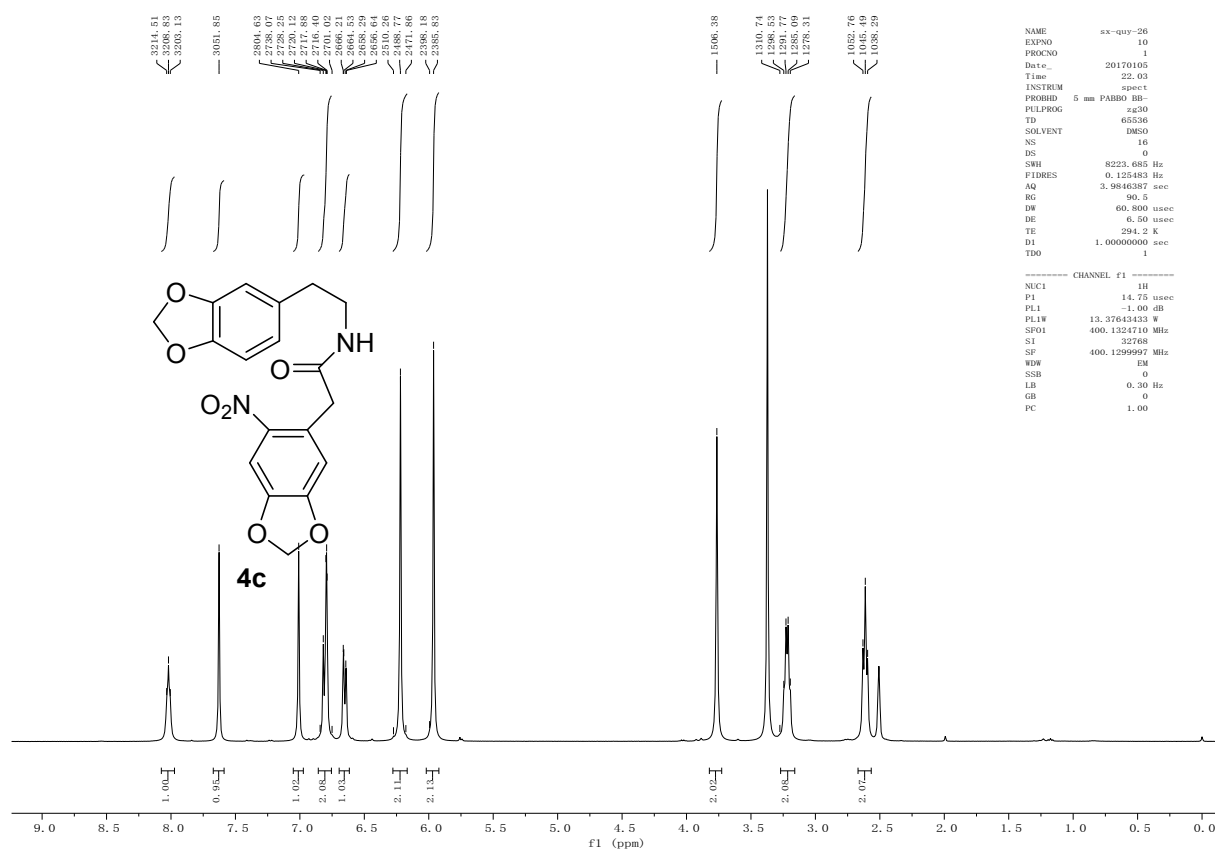
¹H NMR (DMSO-*d*₆, 400 MHz) spectrum of compound **4b**:



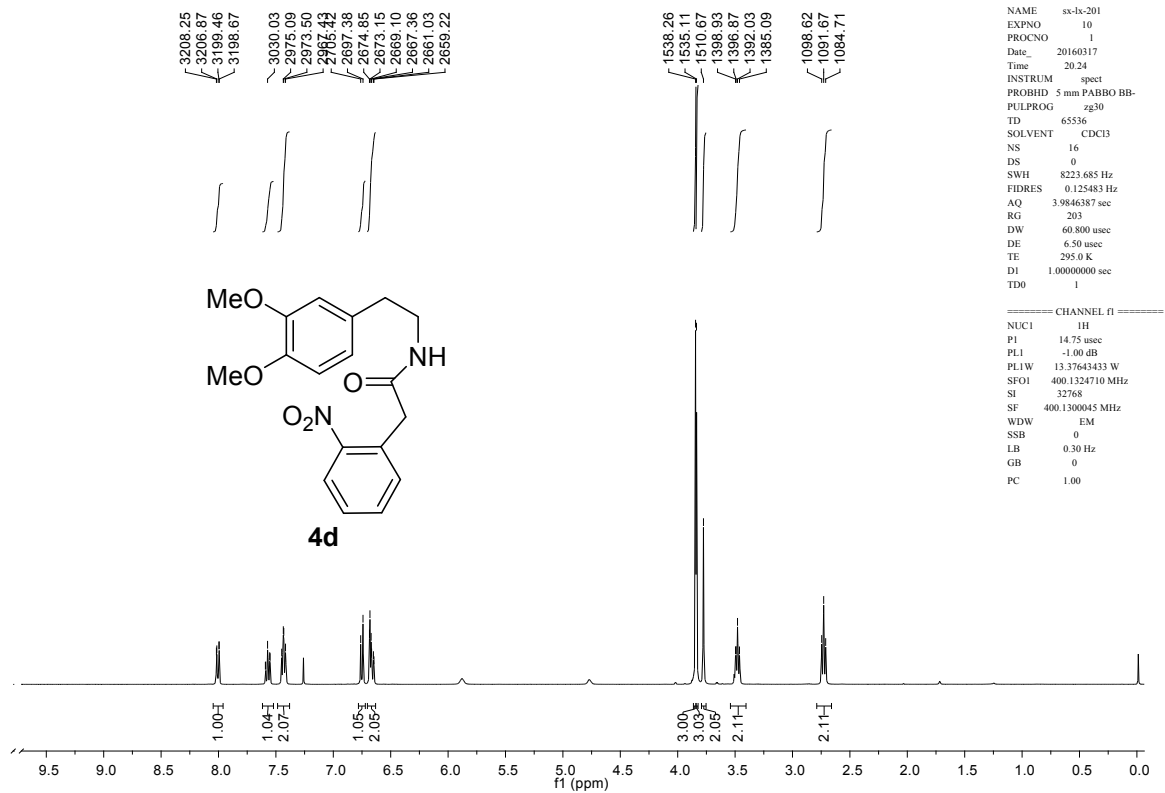
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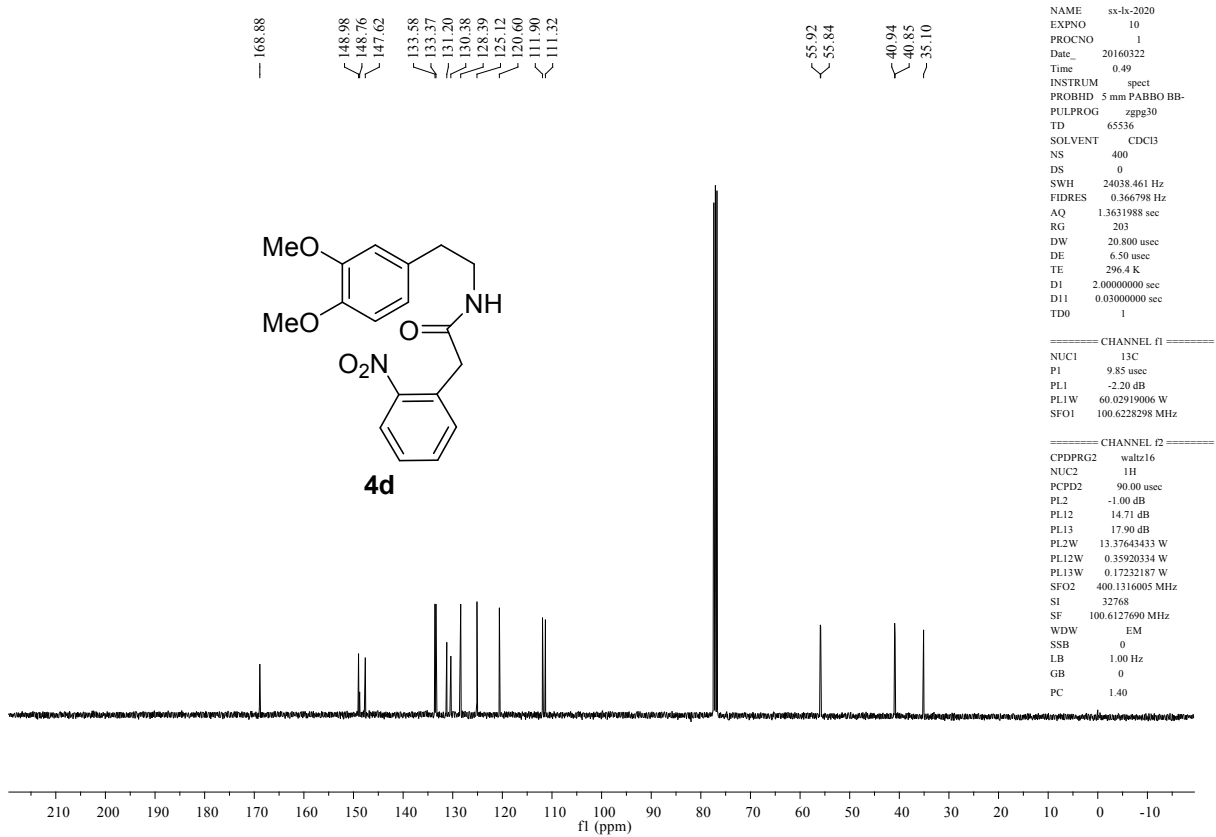
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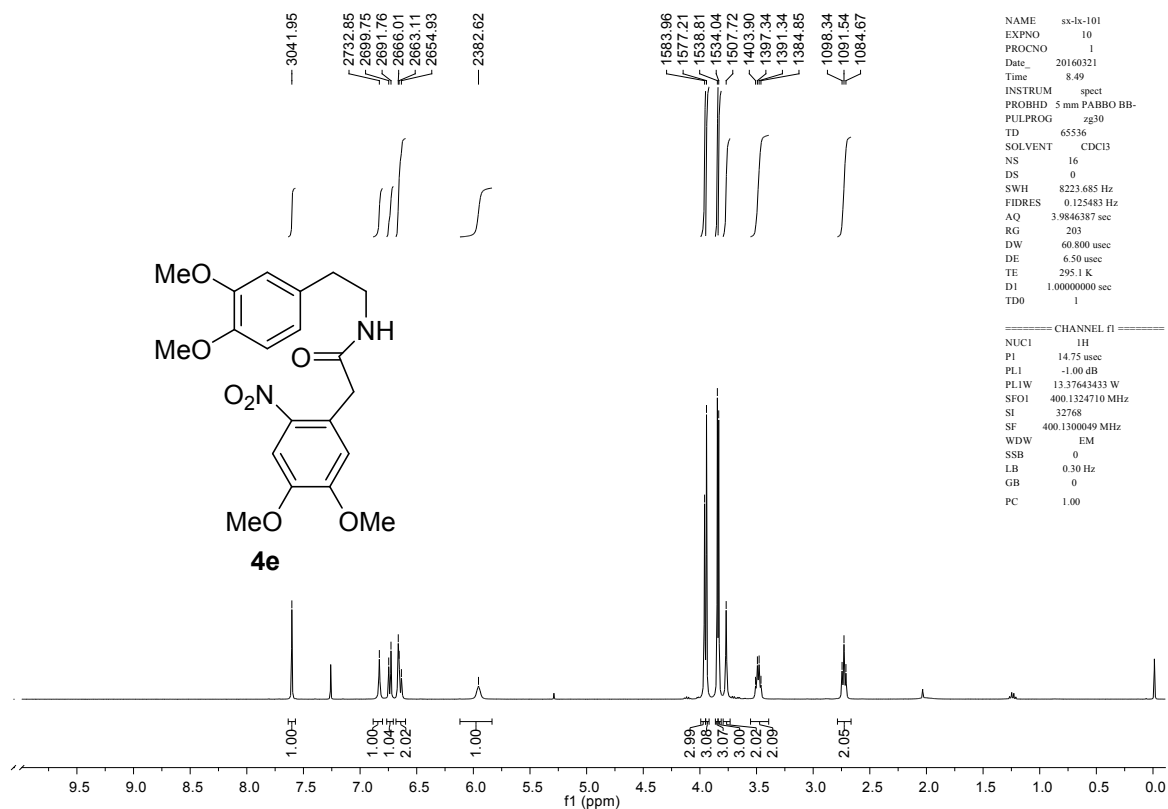
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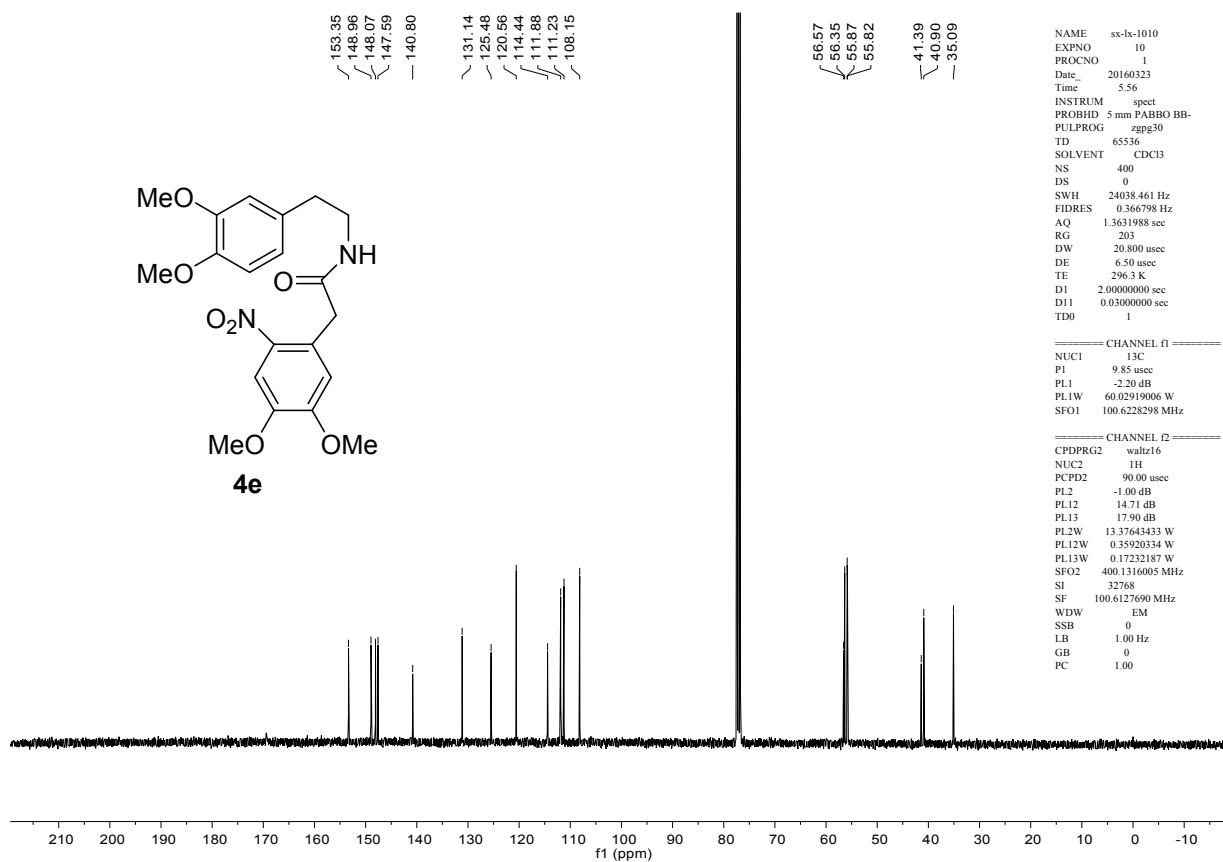
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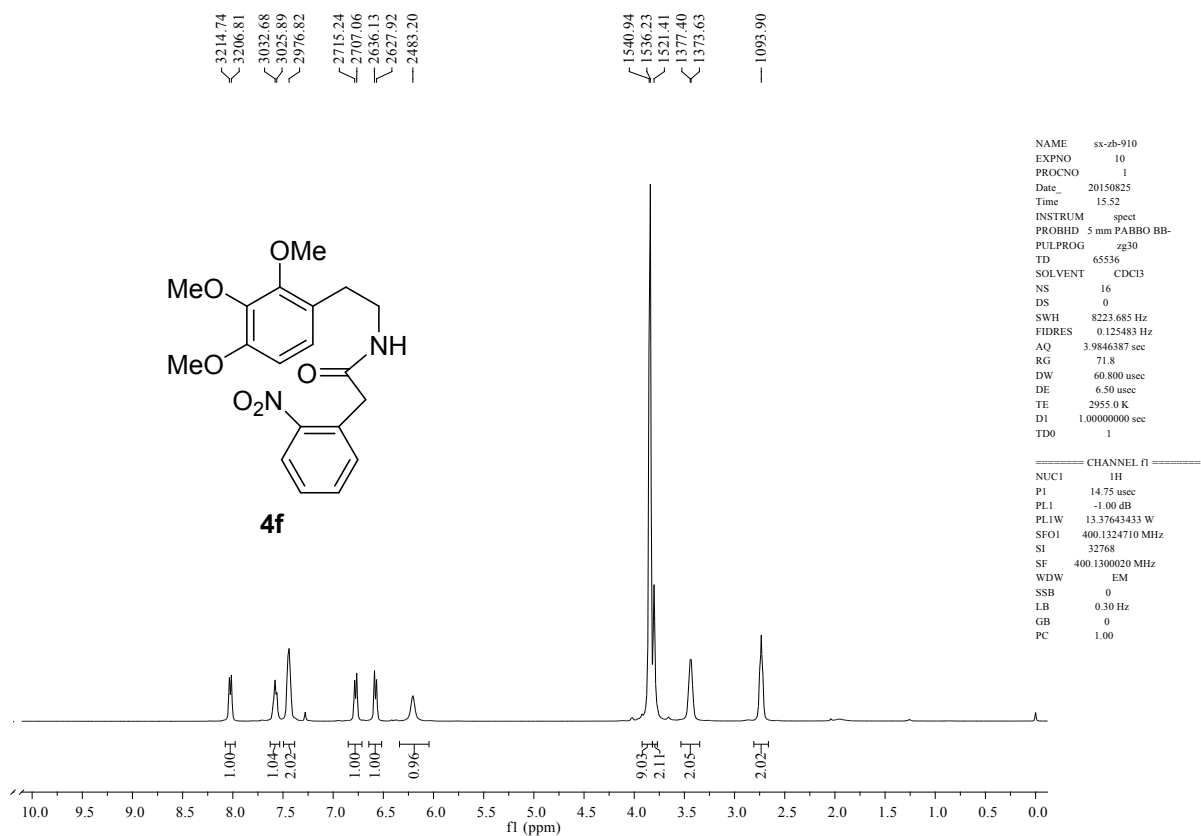
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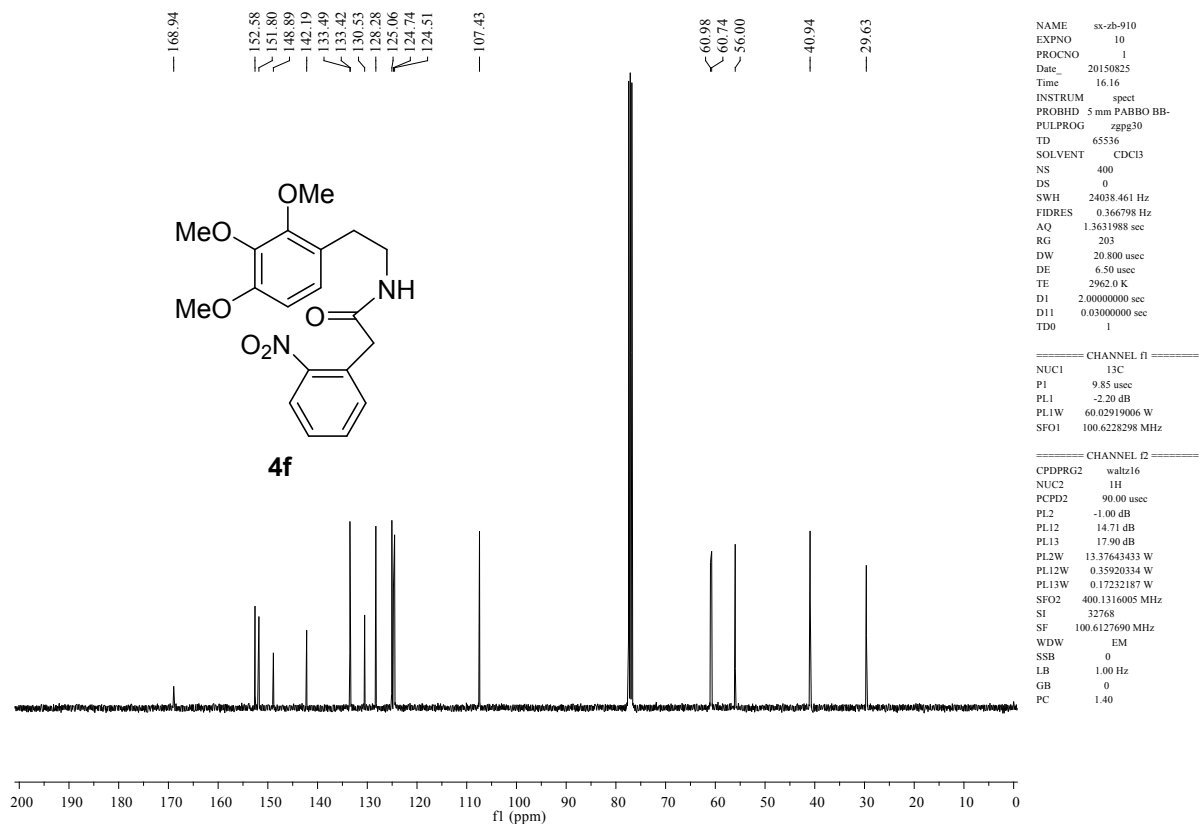
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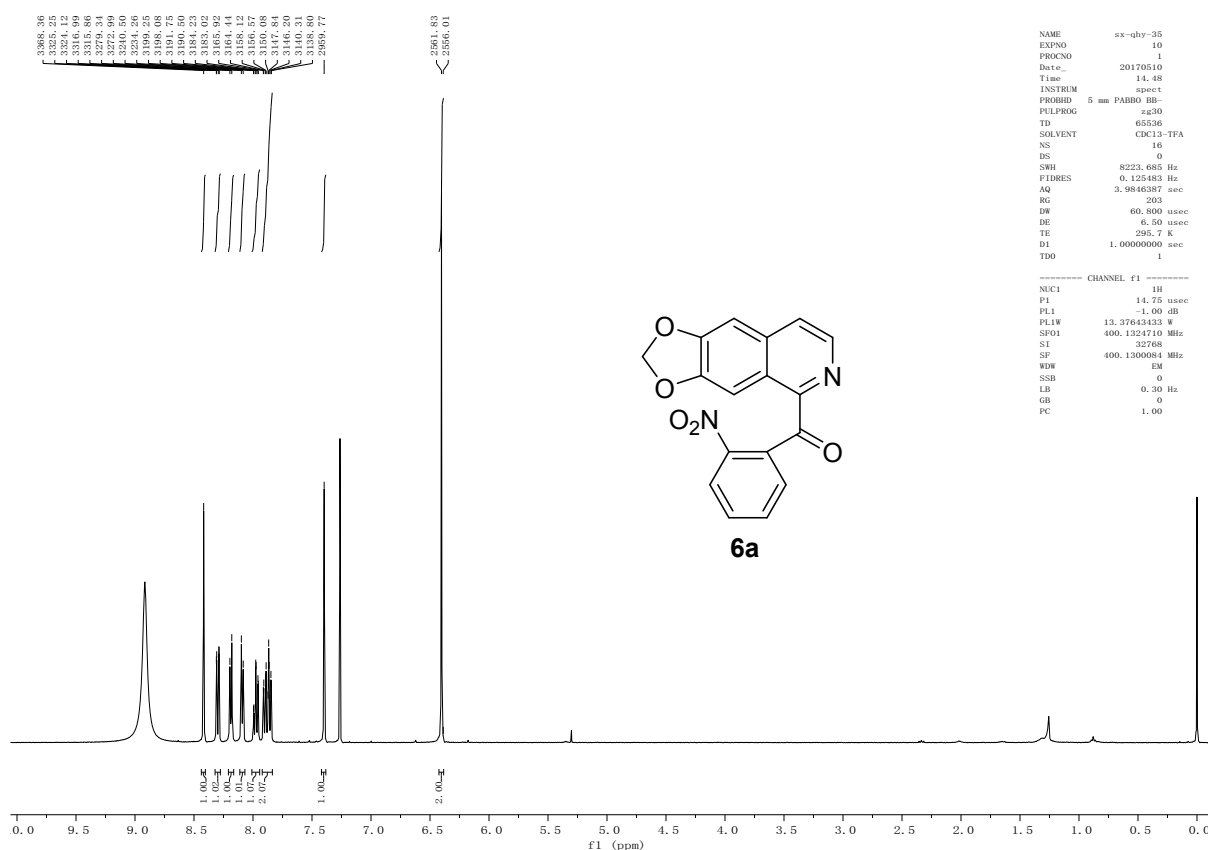
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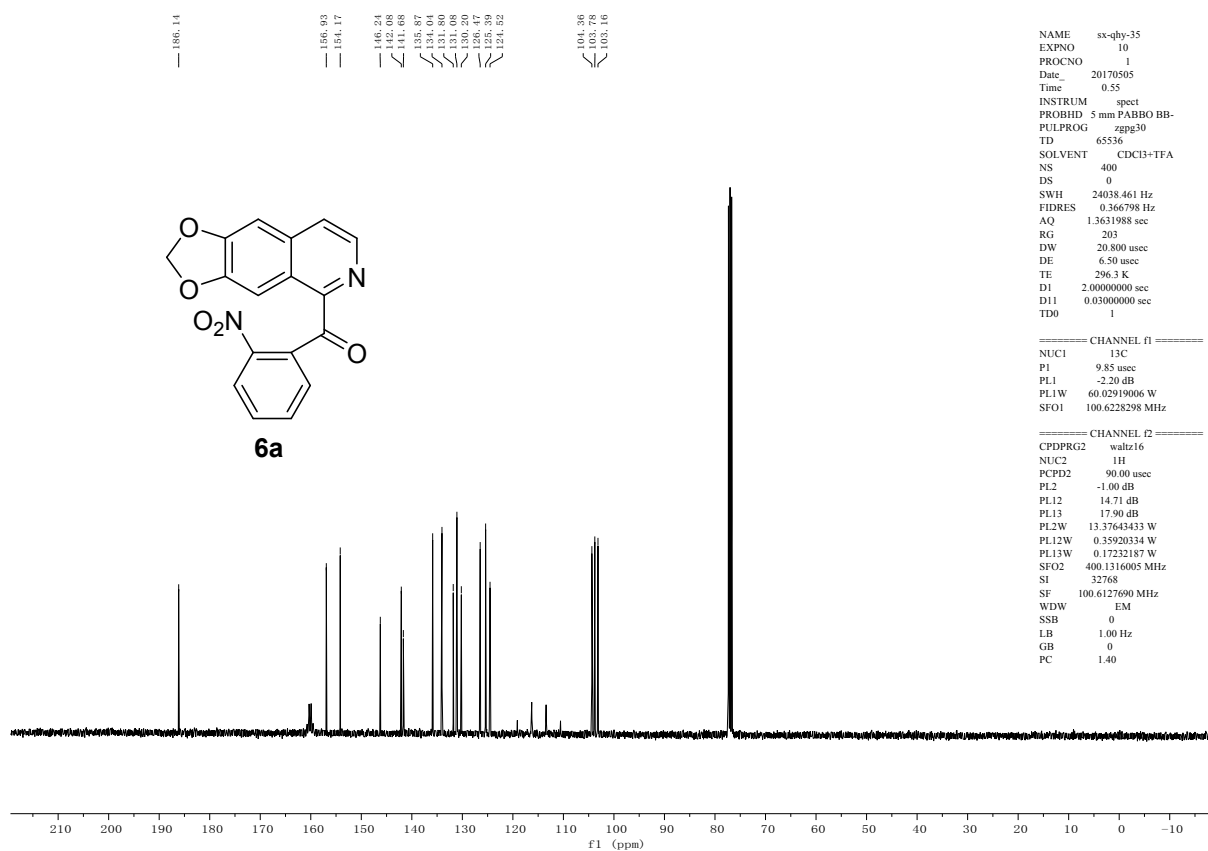
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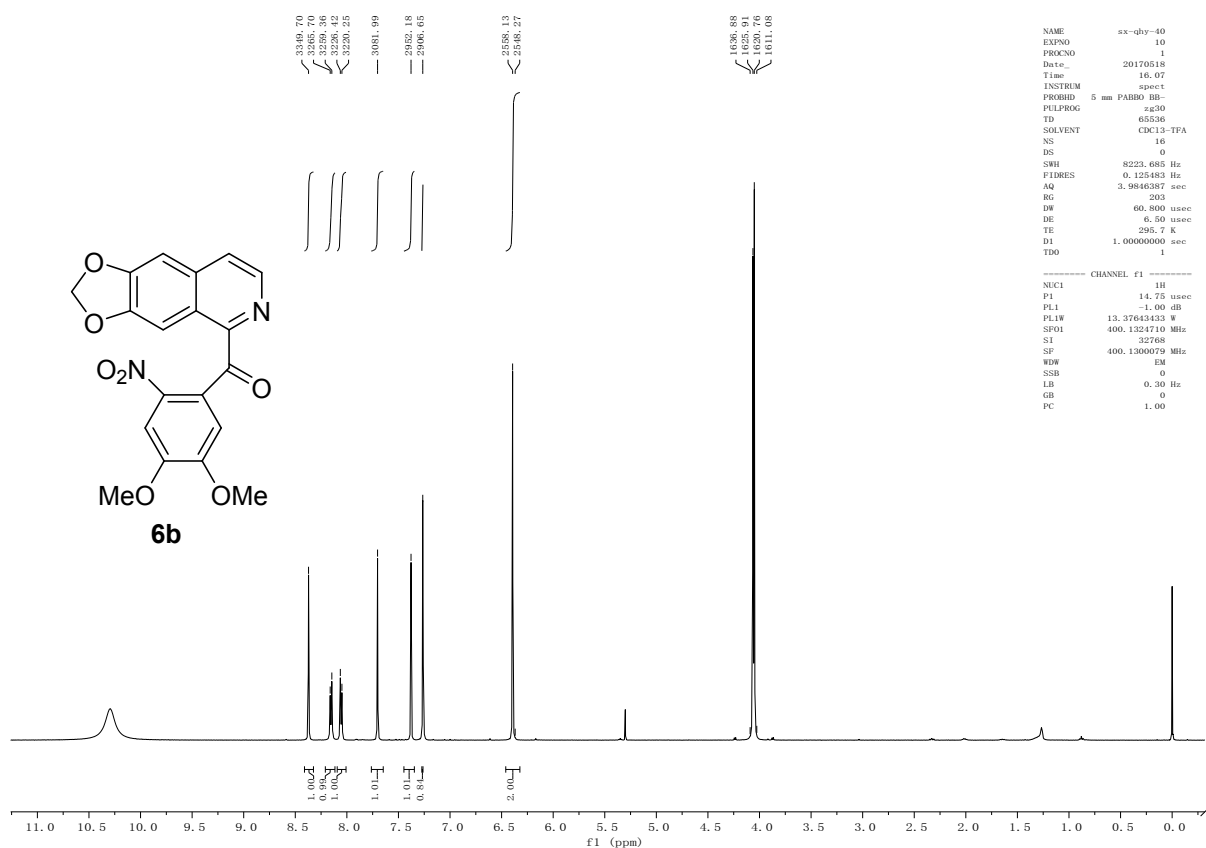
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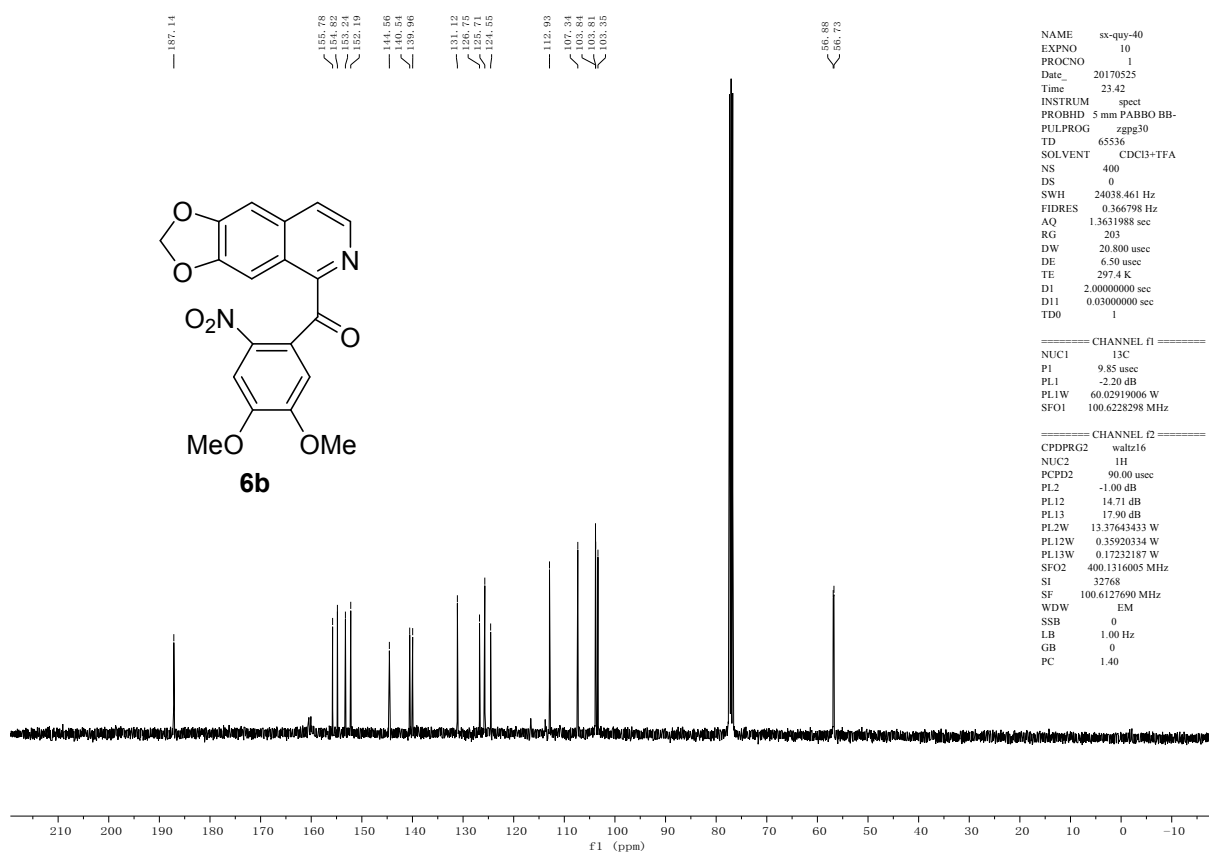
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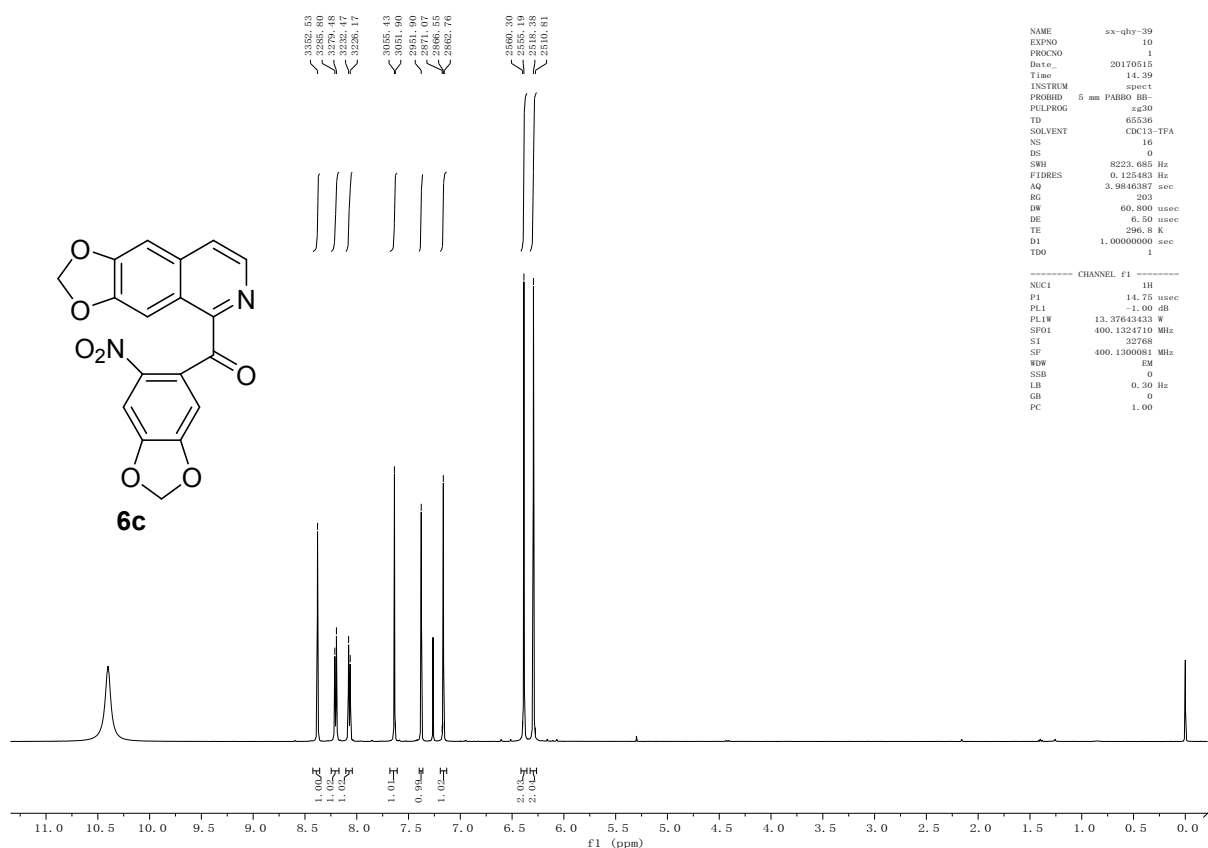
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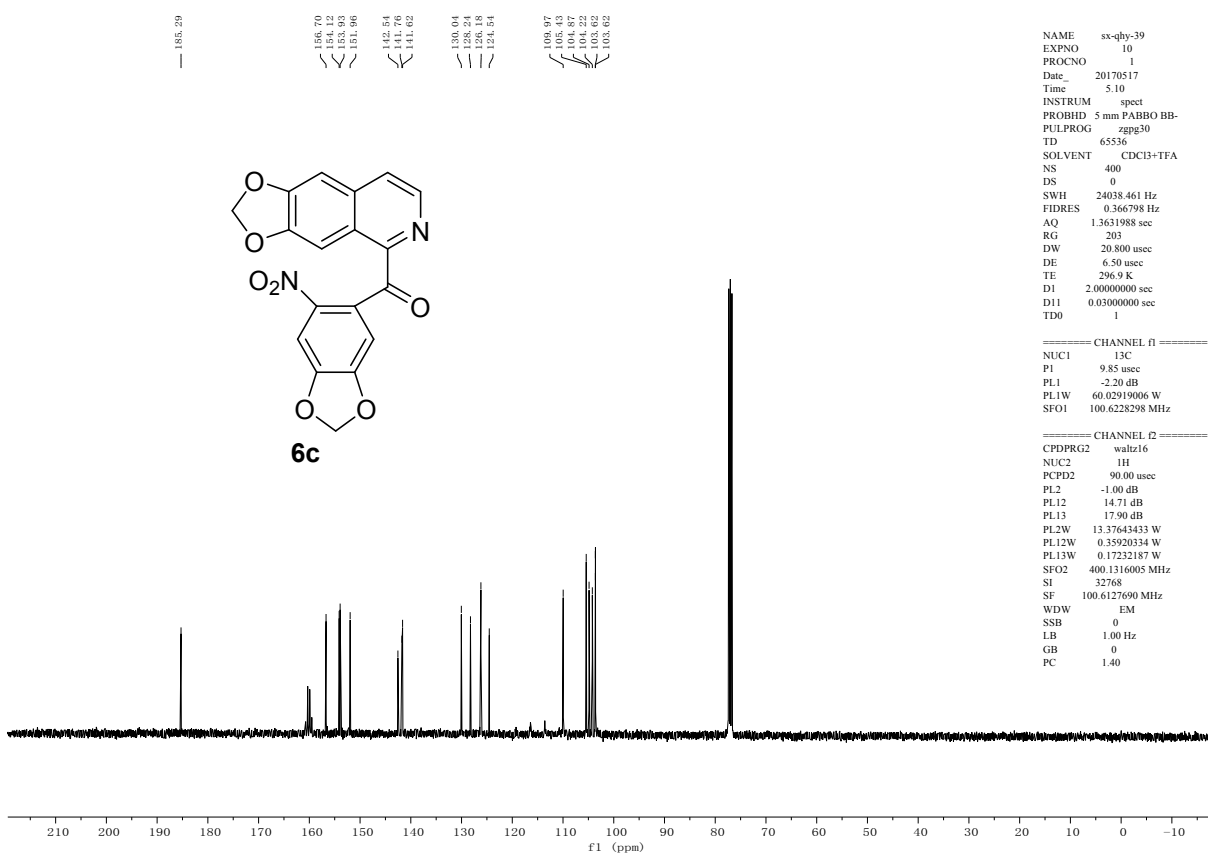
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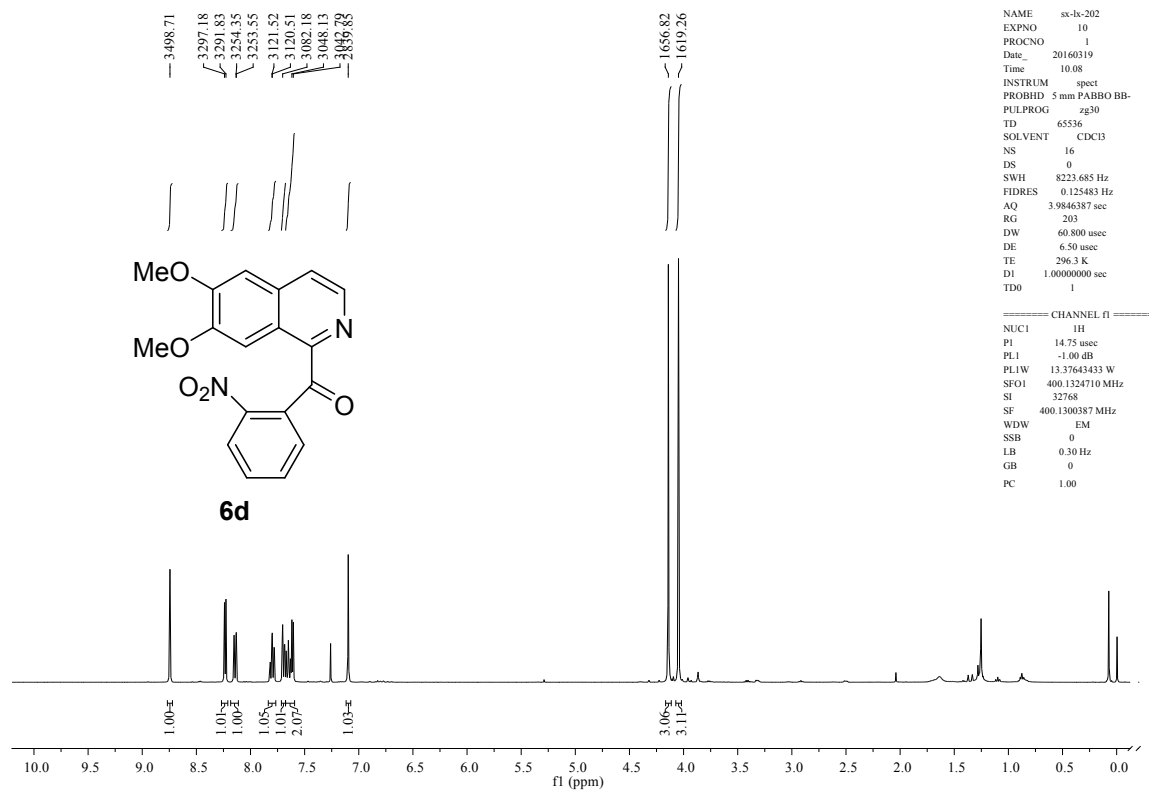
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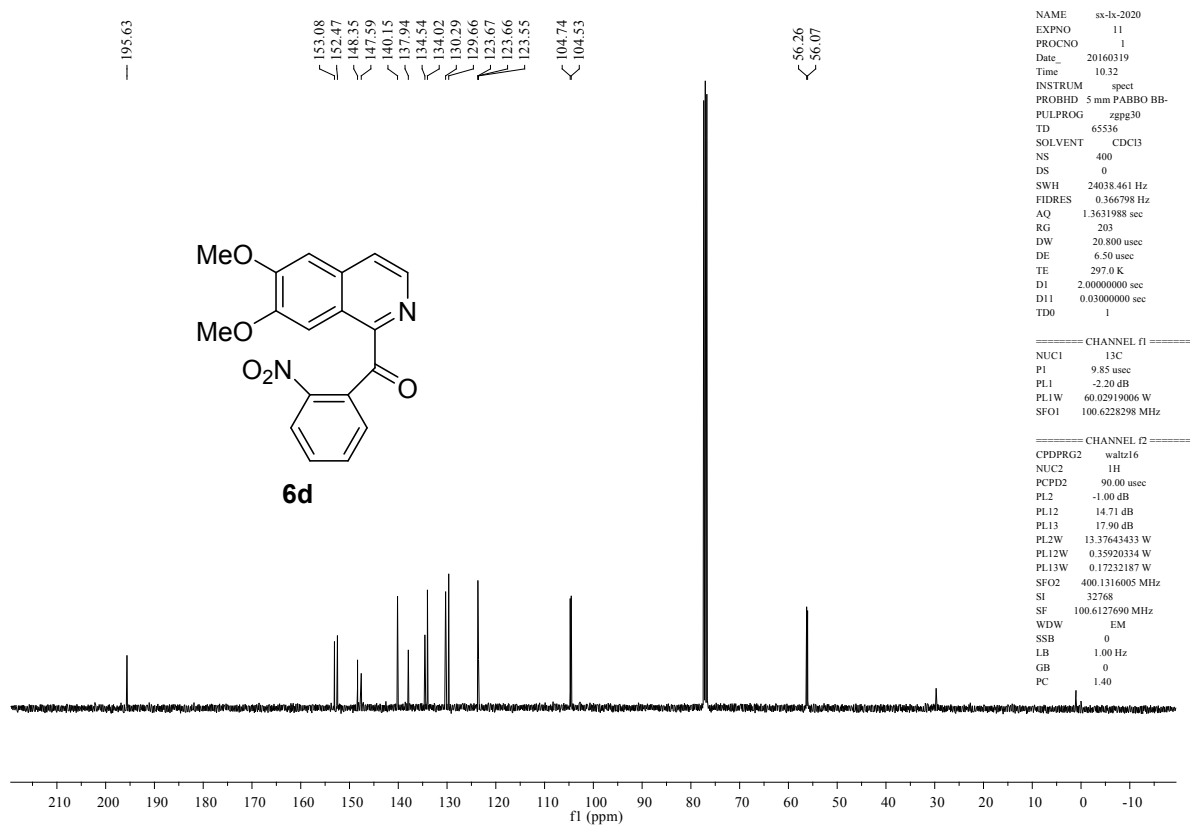
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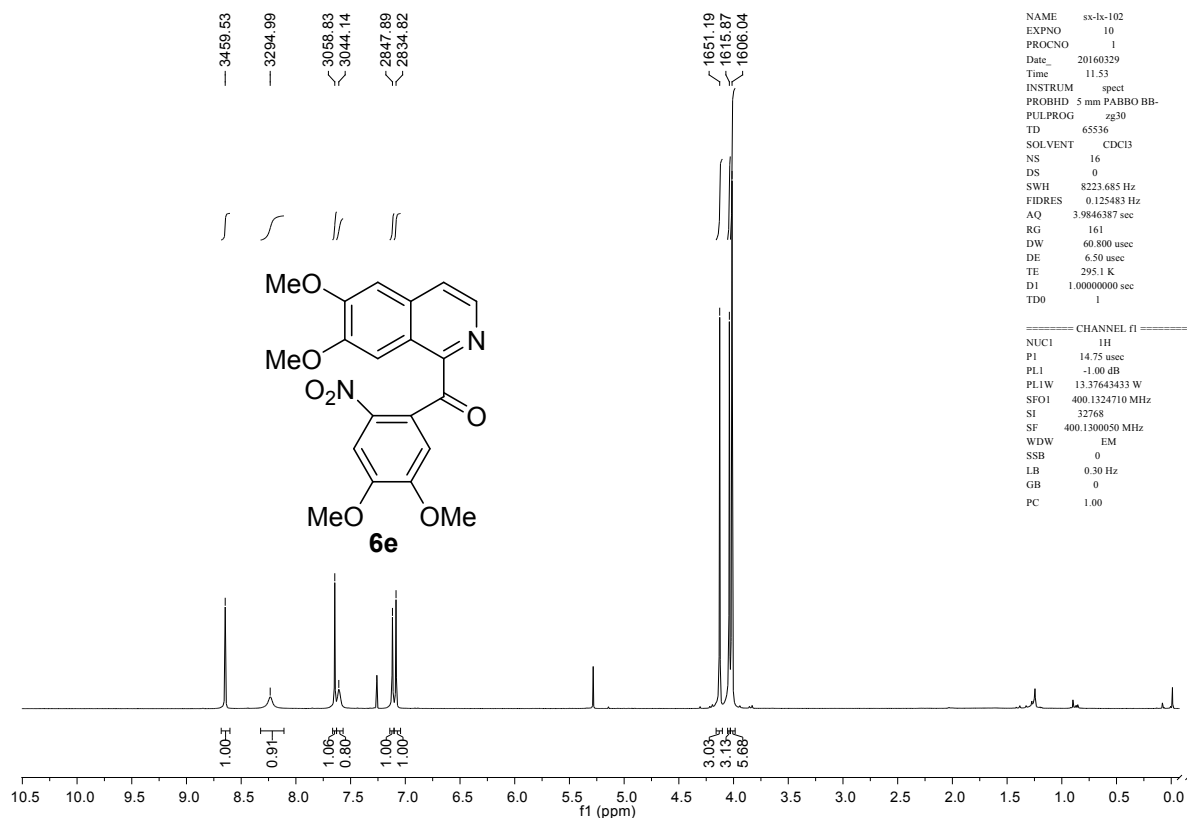
¹H NMR (CDCl₃, 400 MHz) spectrum of compound **6d**:



¹³C NMR (CDCl₃, 100 MHz) spectrum of compound **6d**:



¹H NMR (CDCl₃, 400 MHz) spectrum of compound **6e**:

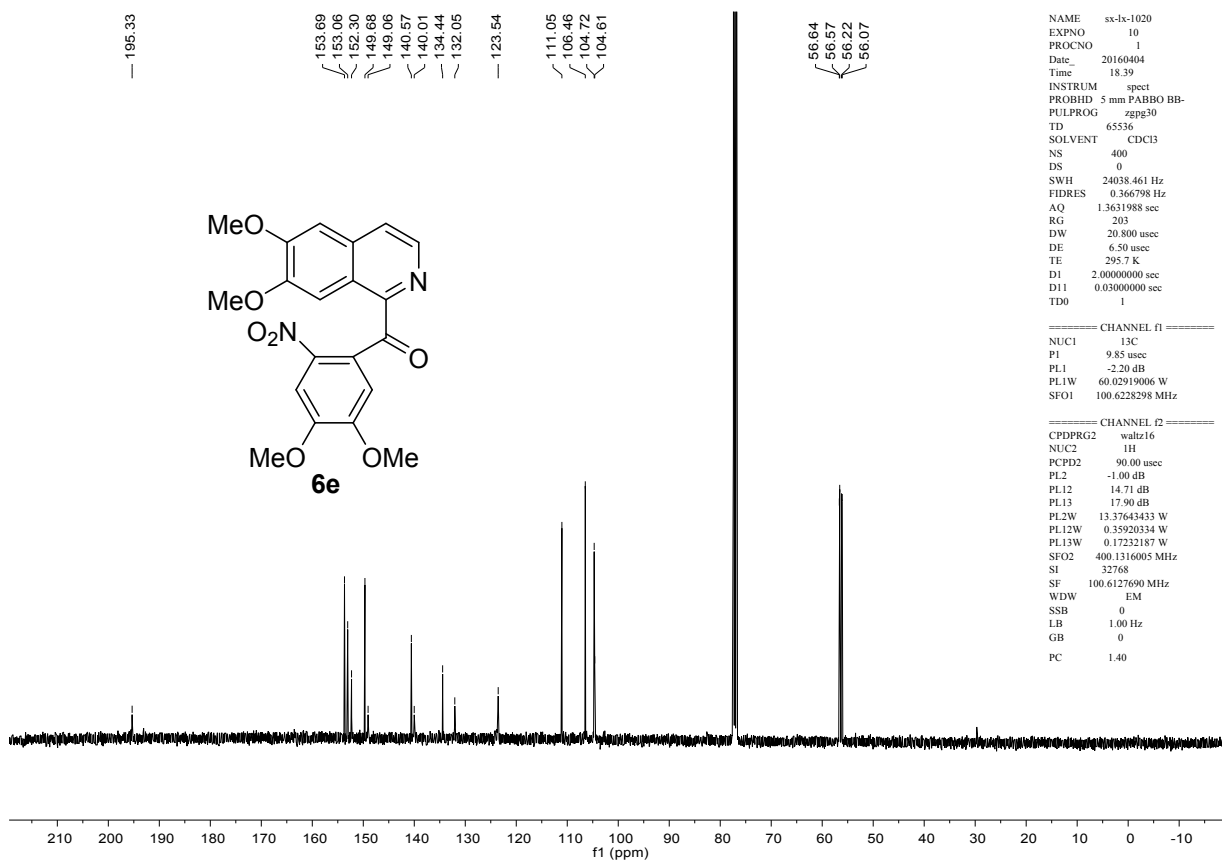


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FIDRES     0.125483 Hz
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RG         161
DW         60.800 usec
DE         6.50 usec
TE         295.1 K
D1         1.00000000 sec
TD0        1

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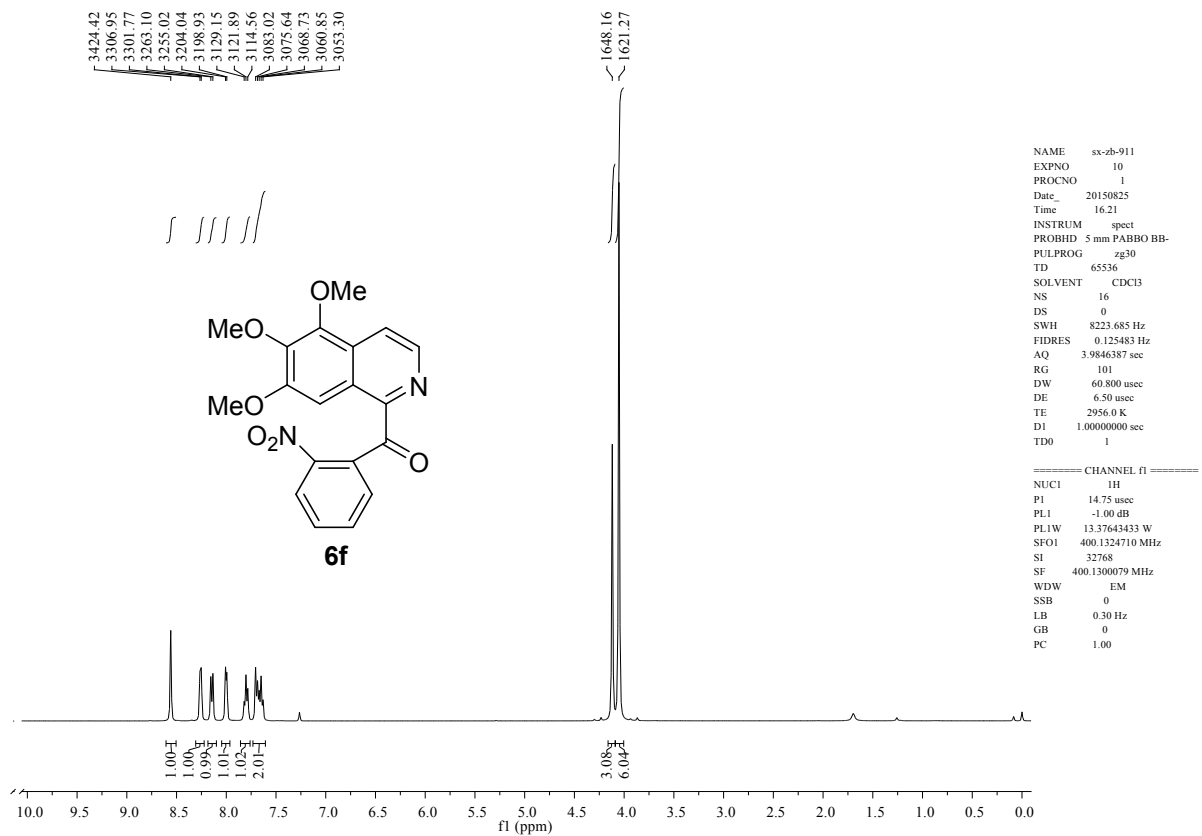
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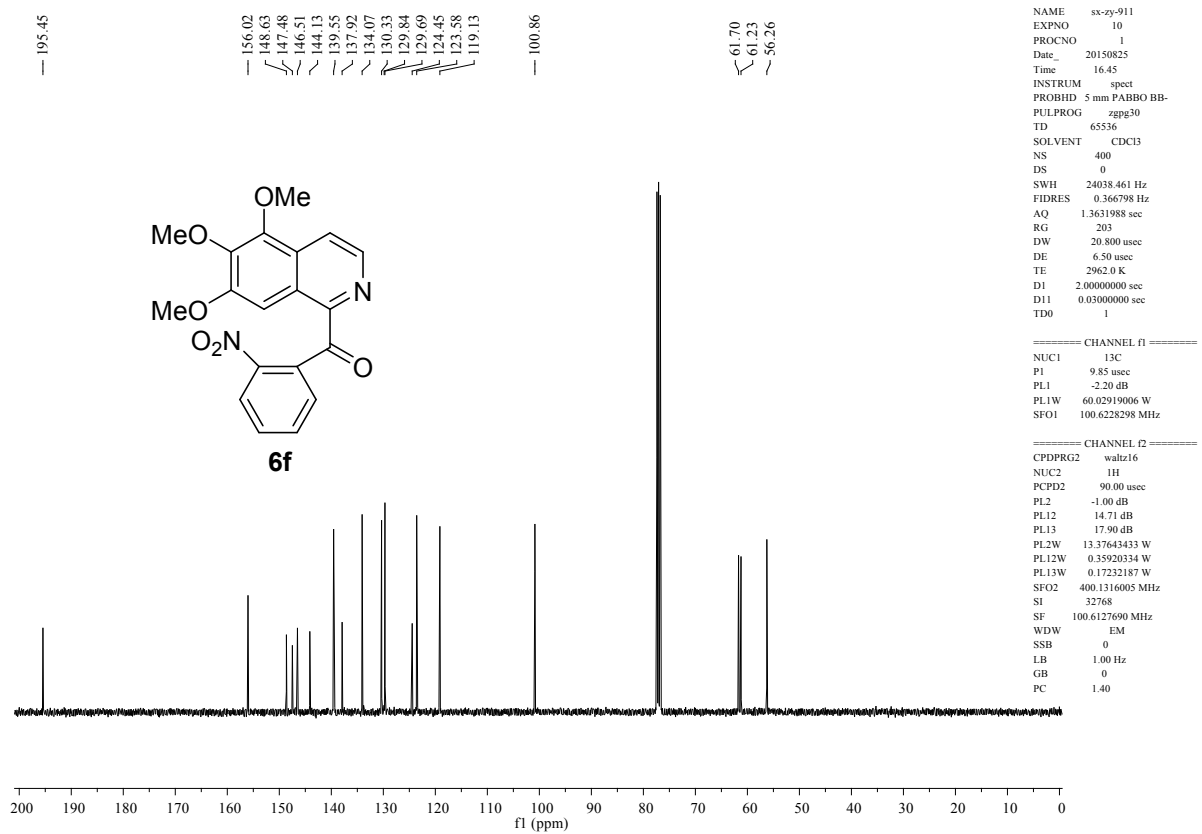
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SFO1       100.6228298 MHz

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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
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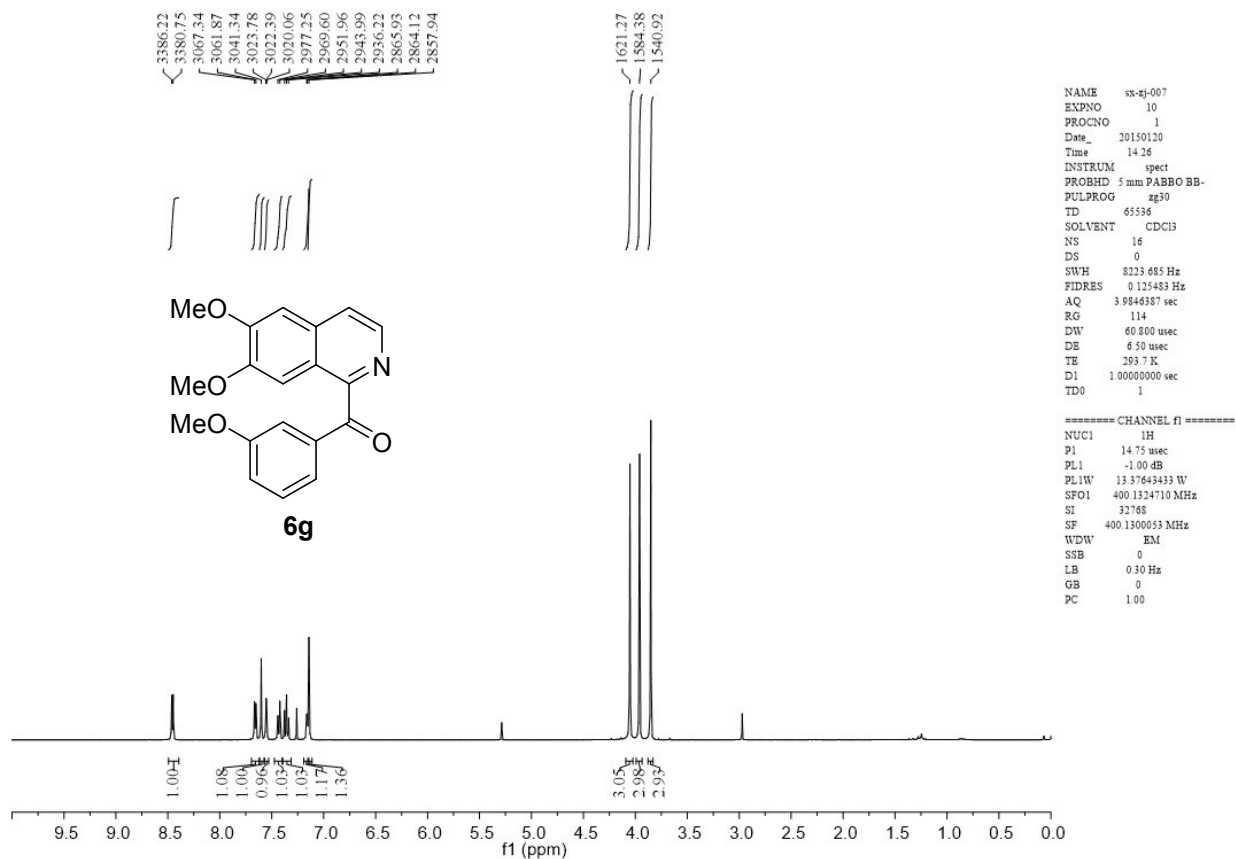
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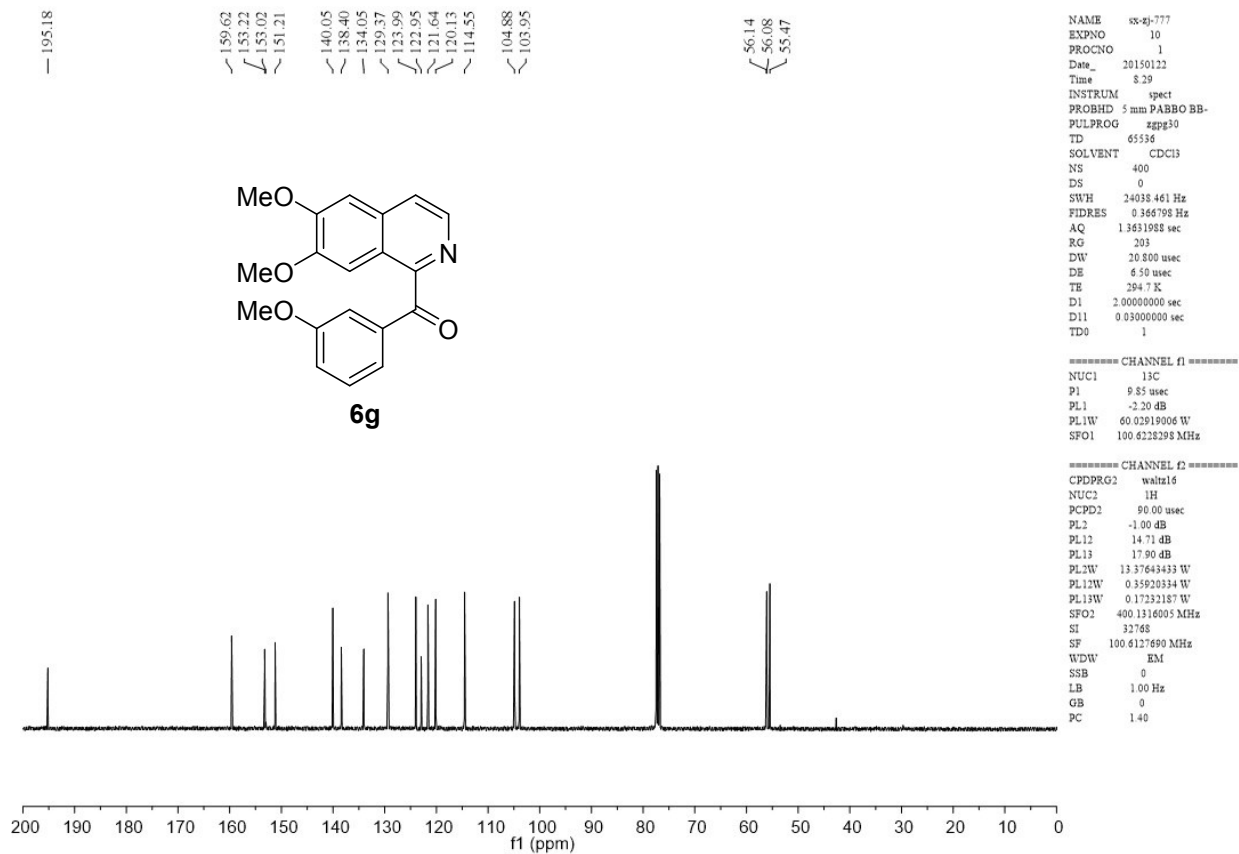
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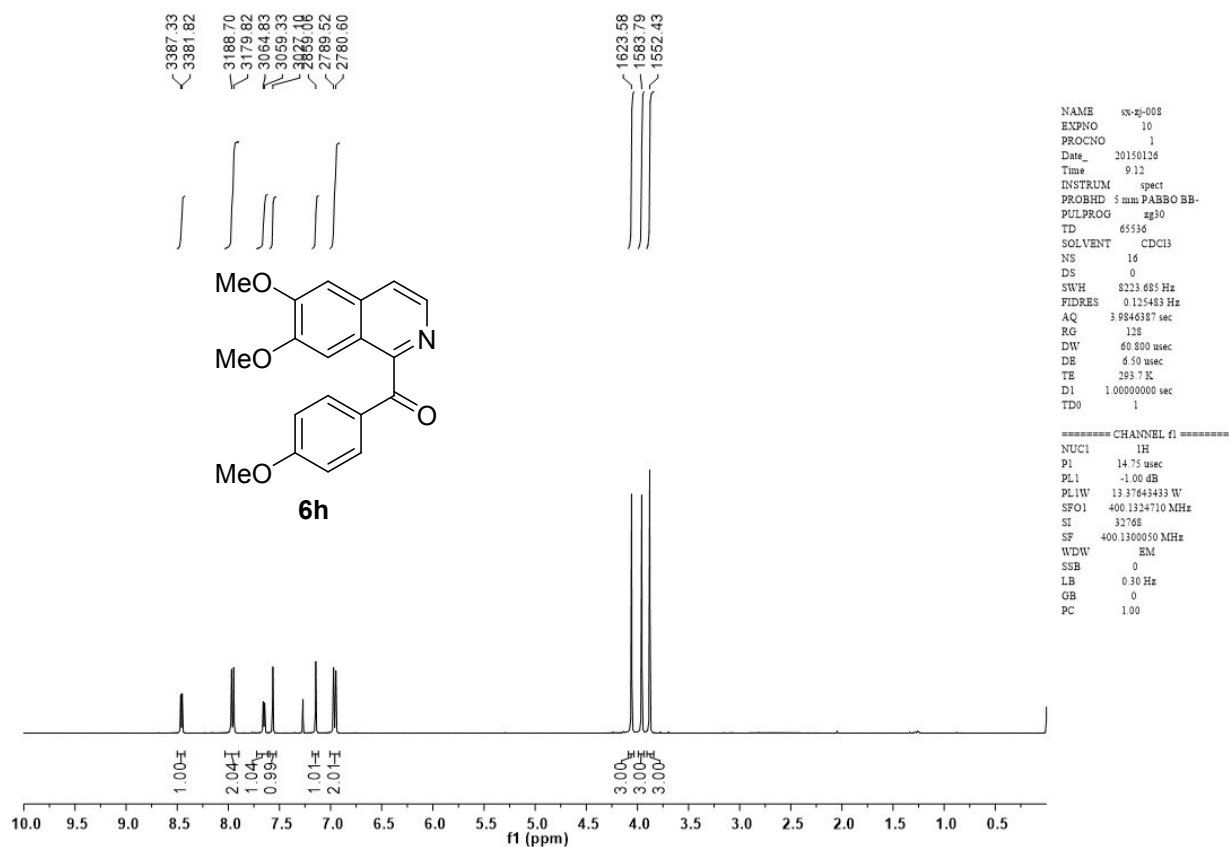
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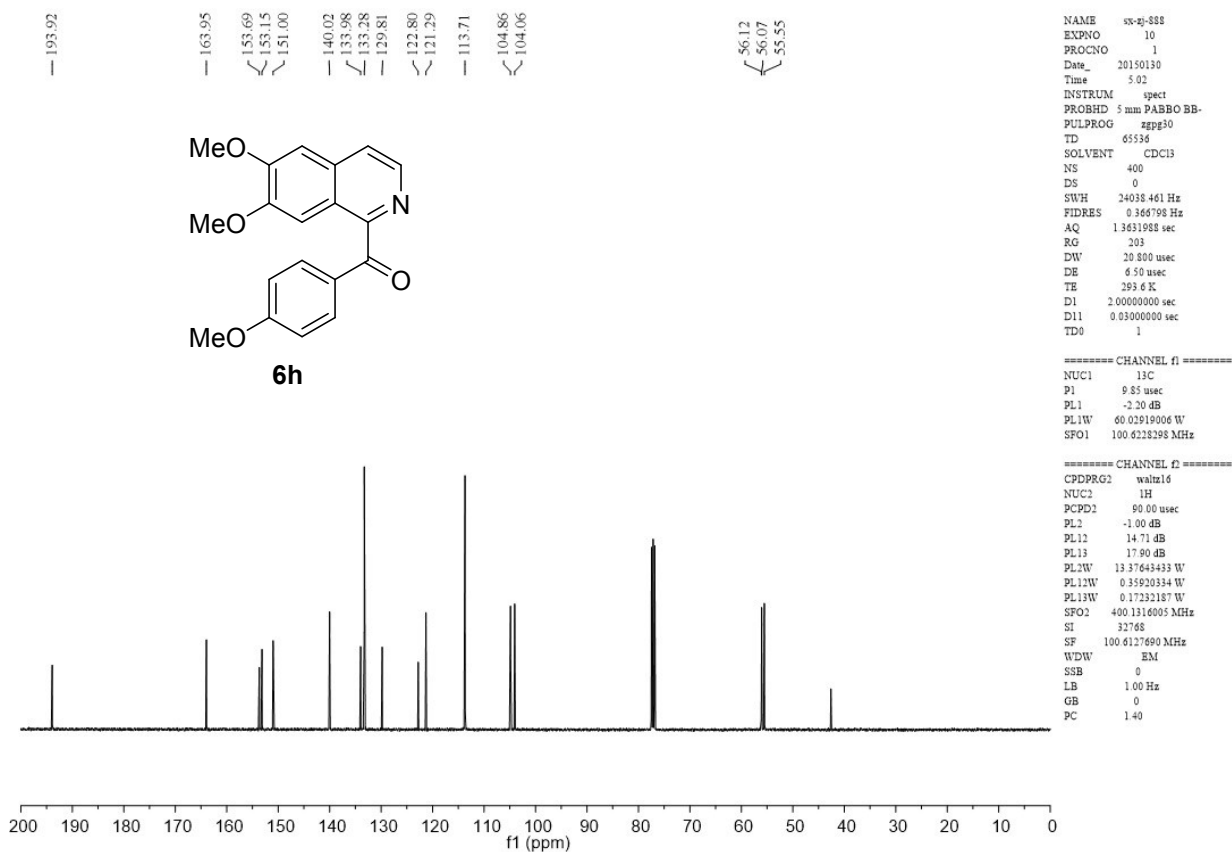
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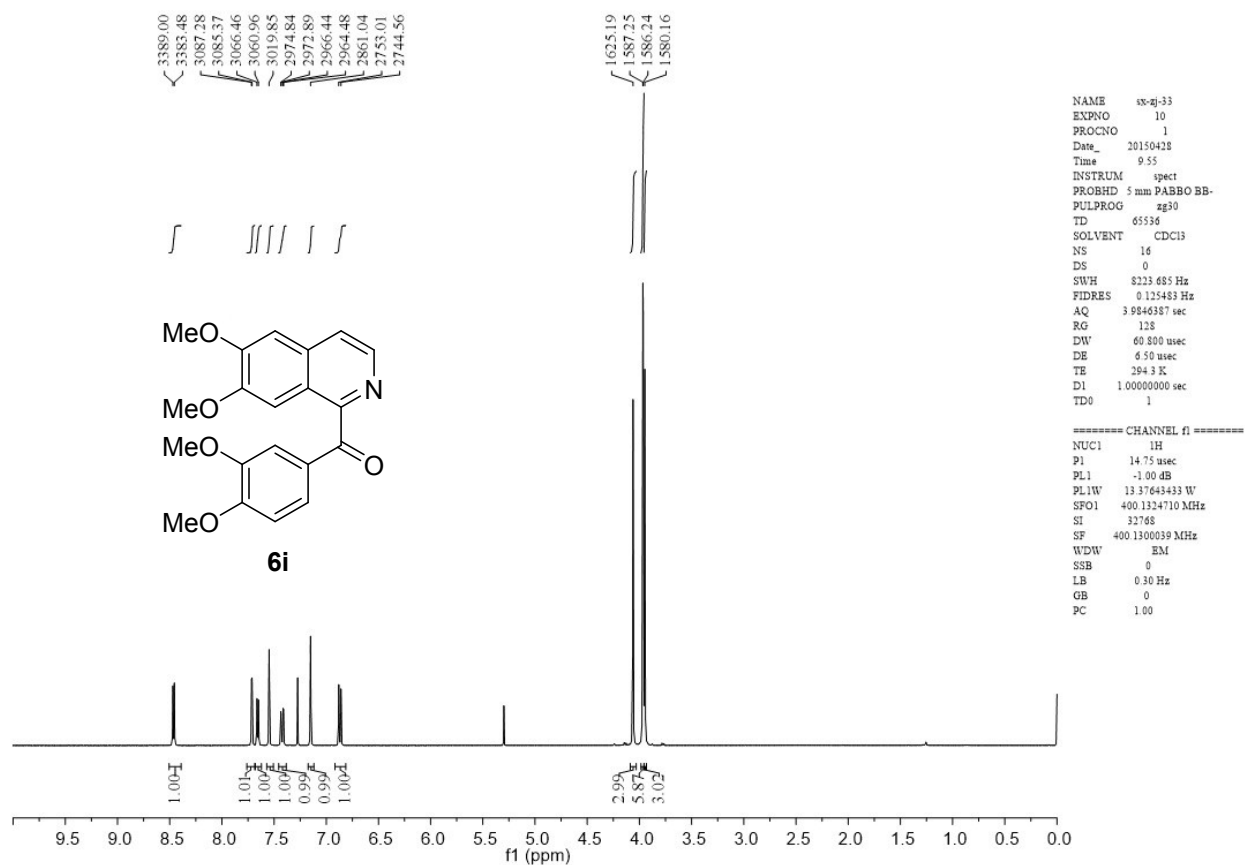
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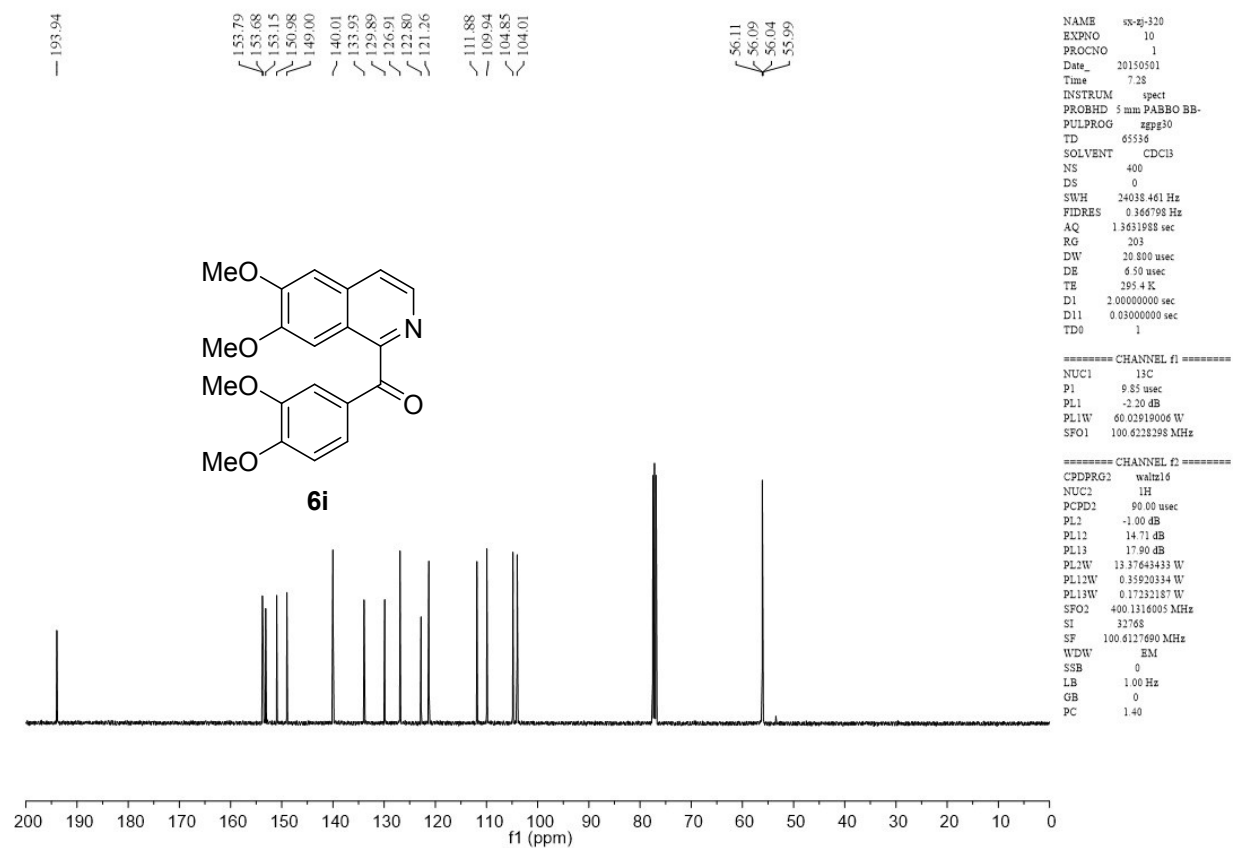
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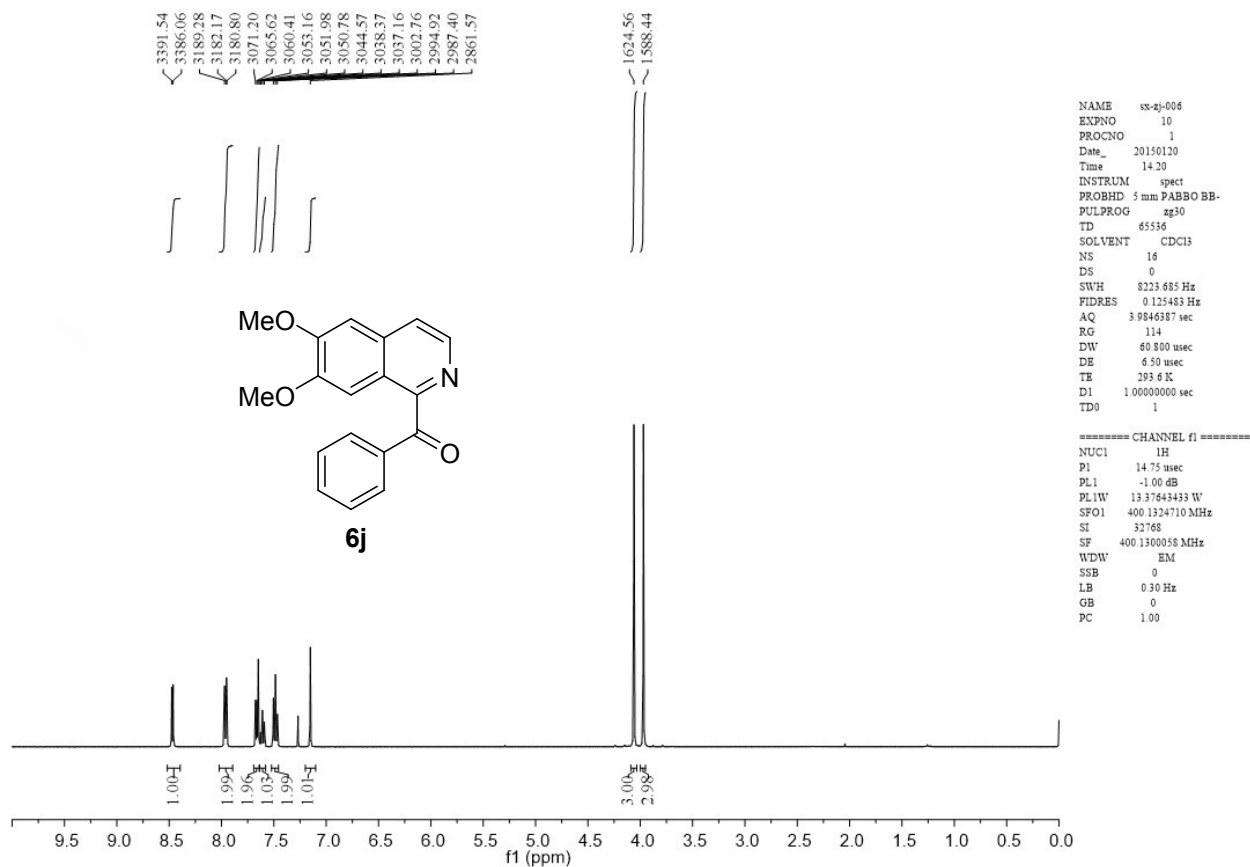
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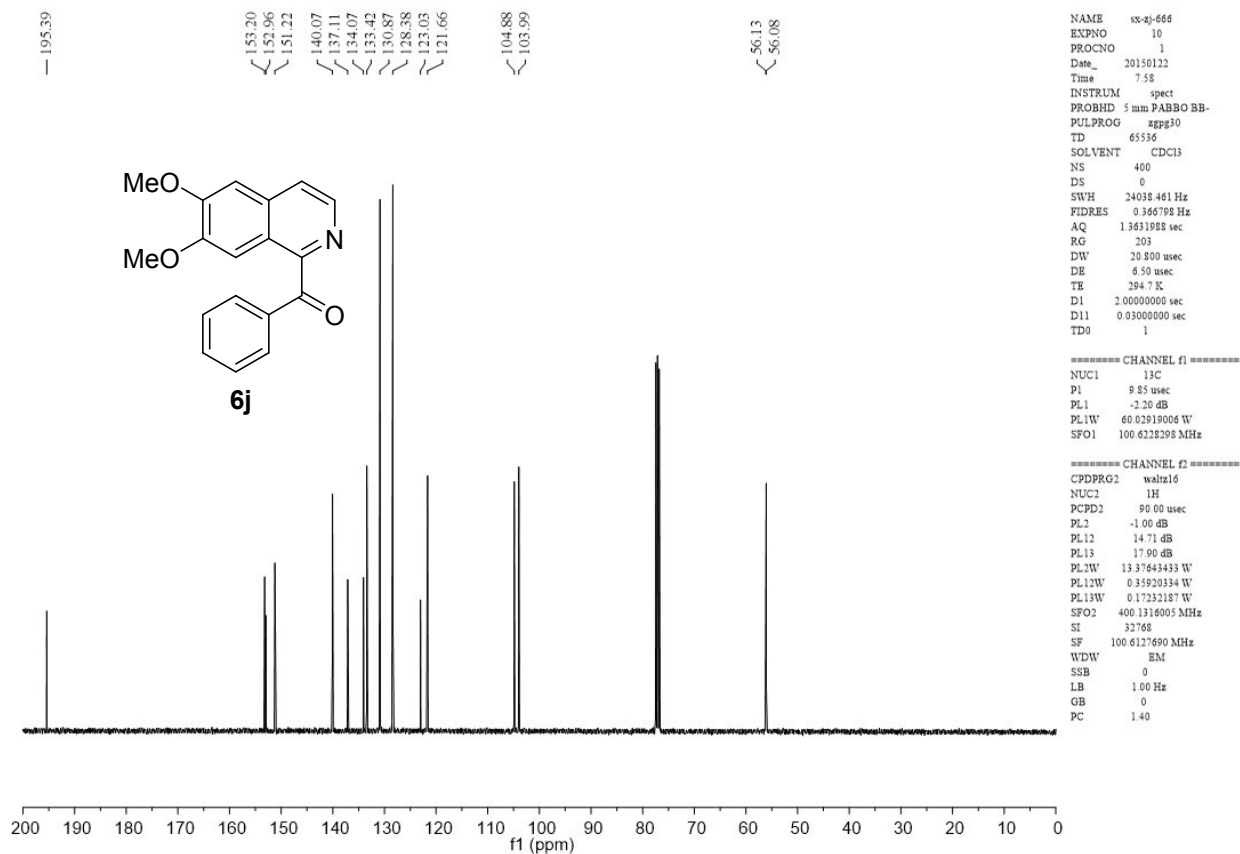
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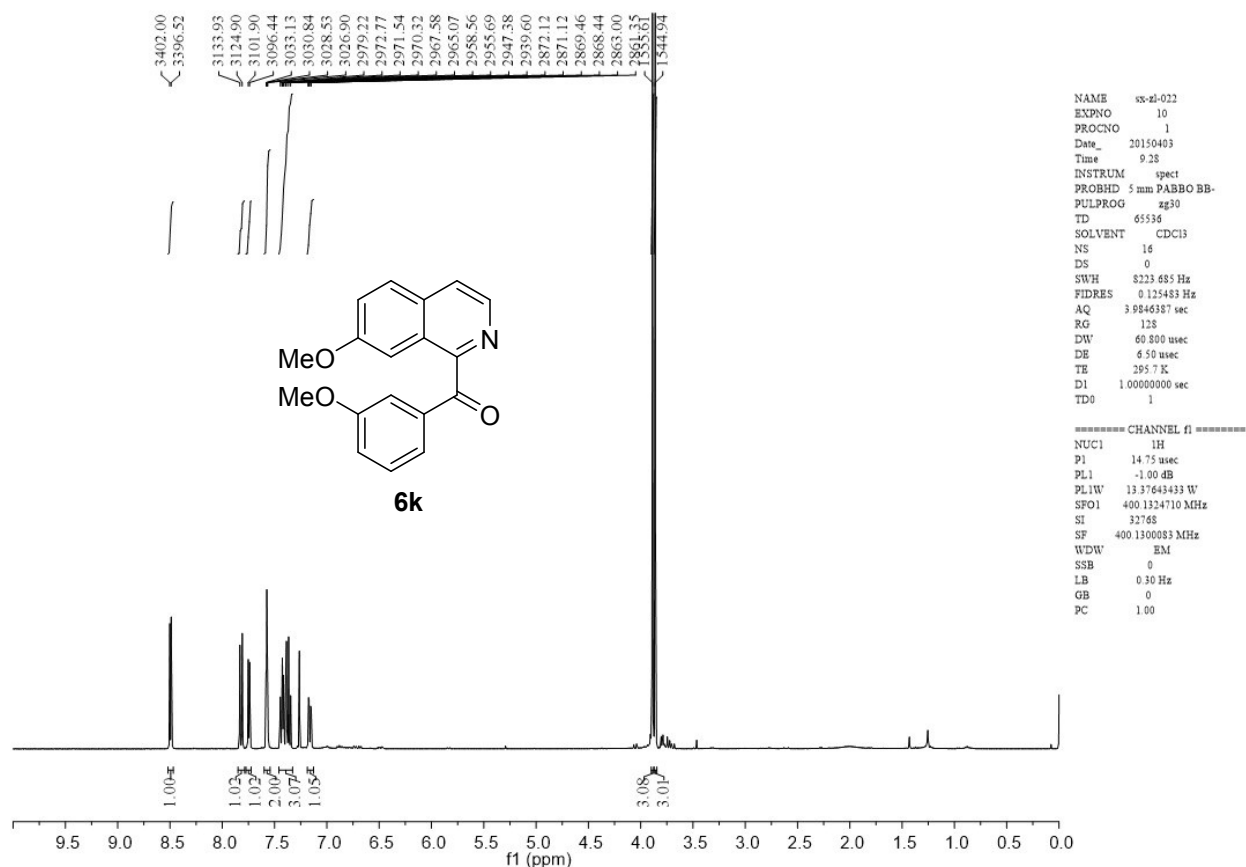
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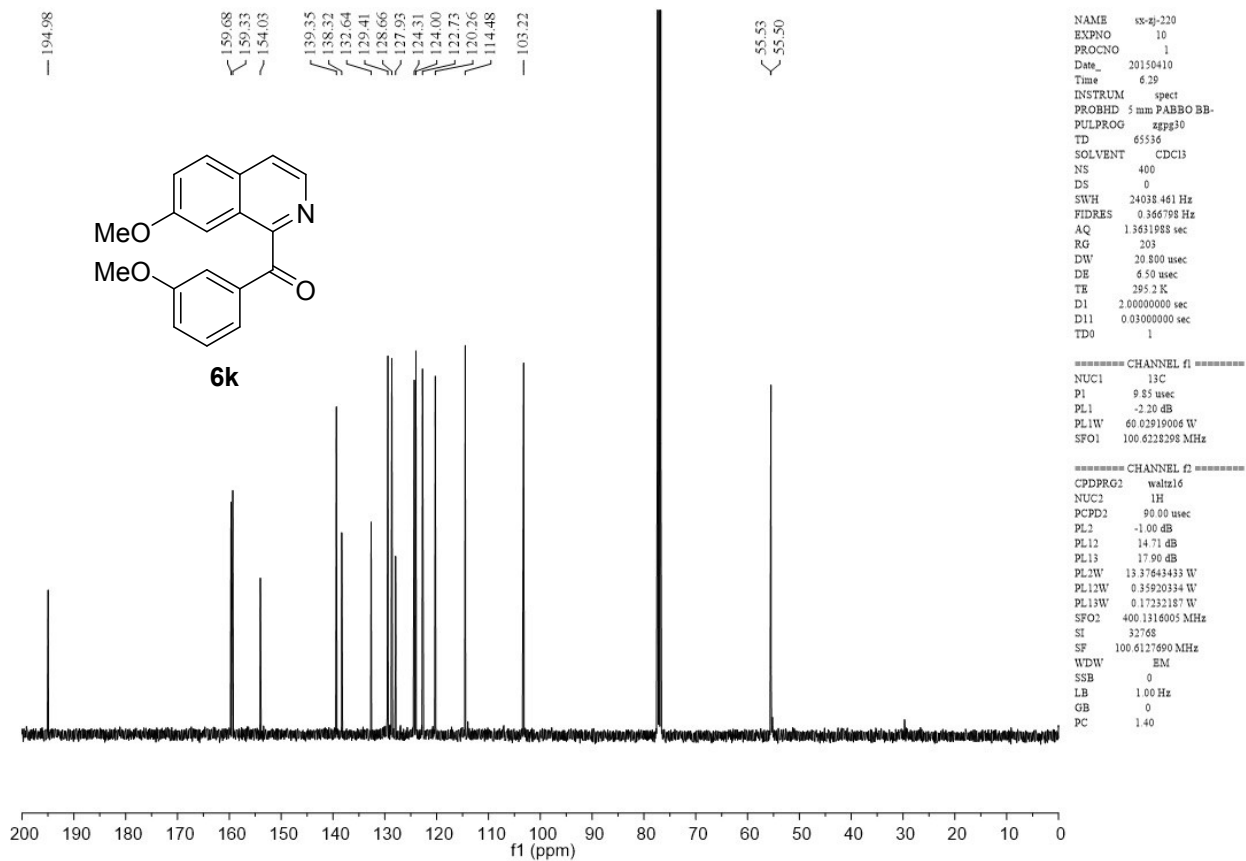
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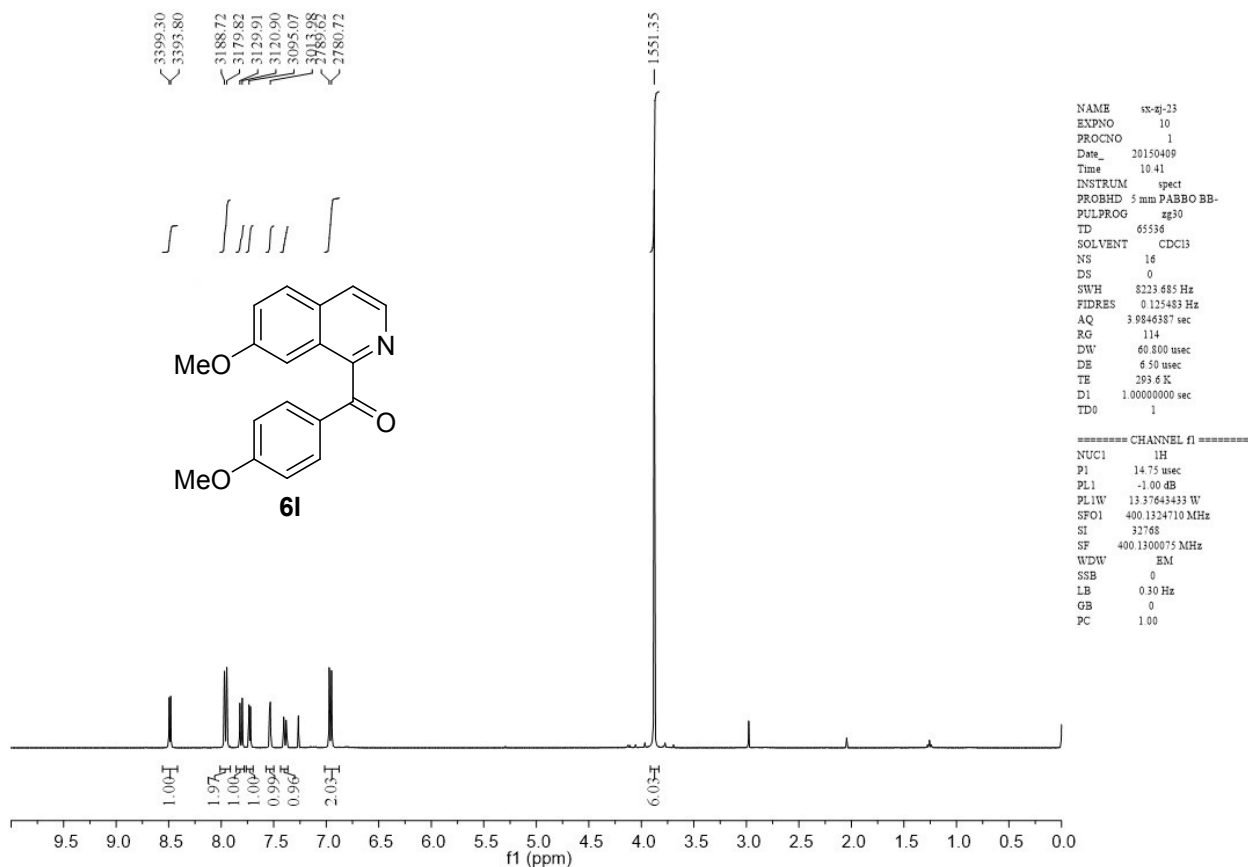
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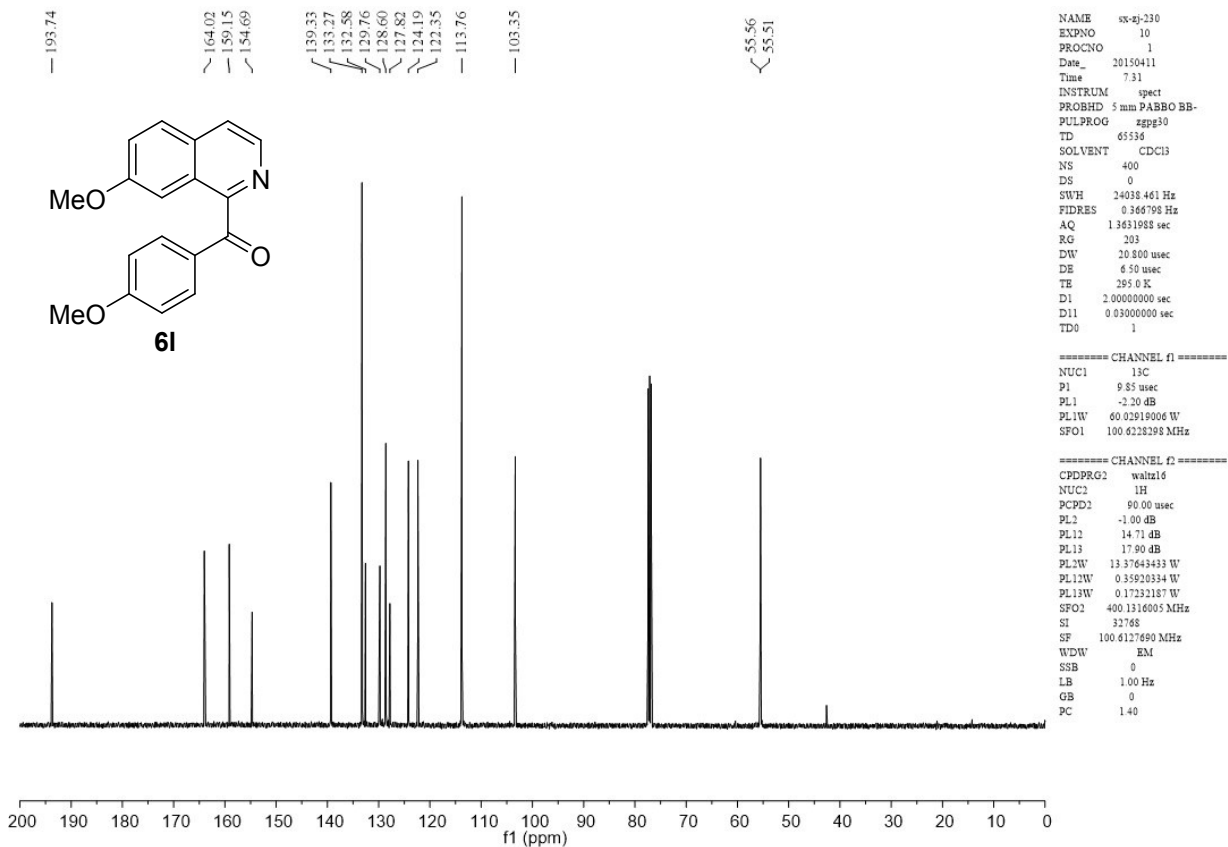
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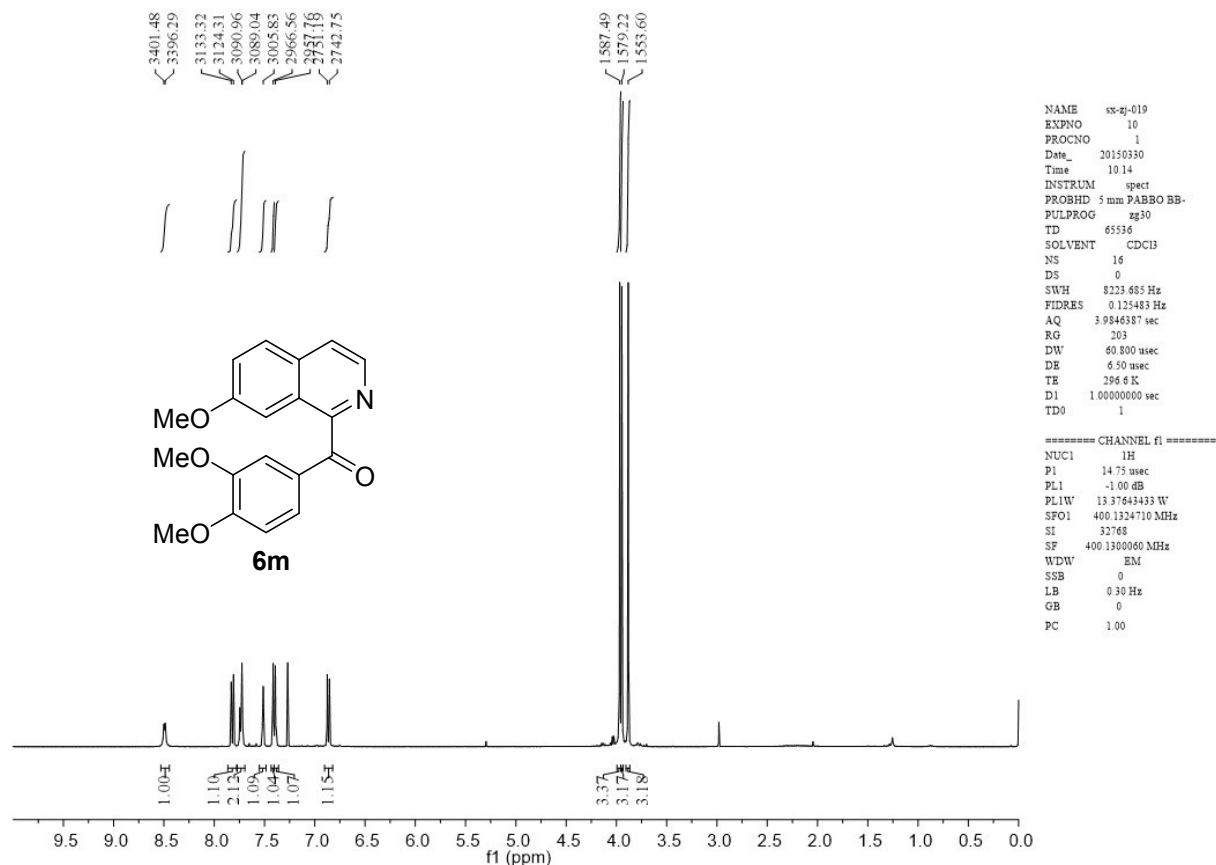
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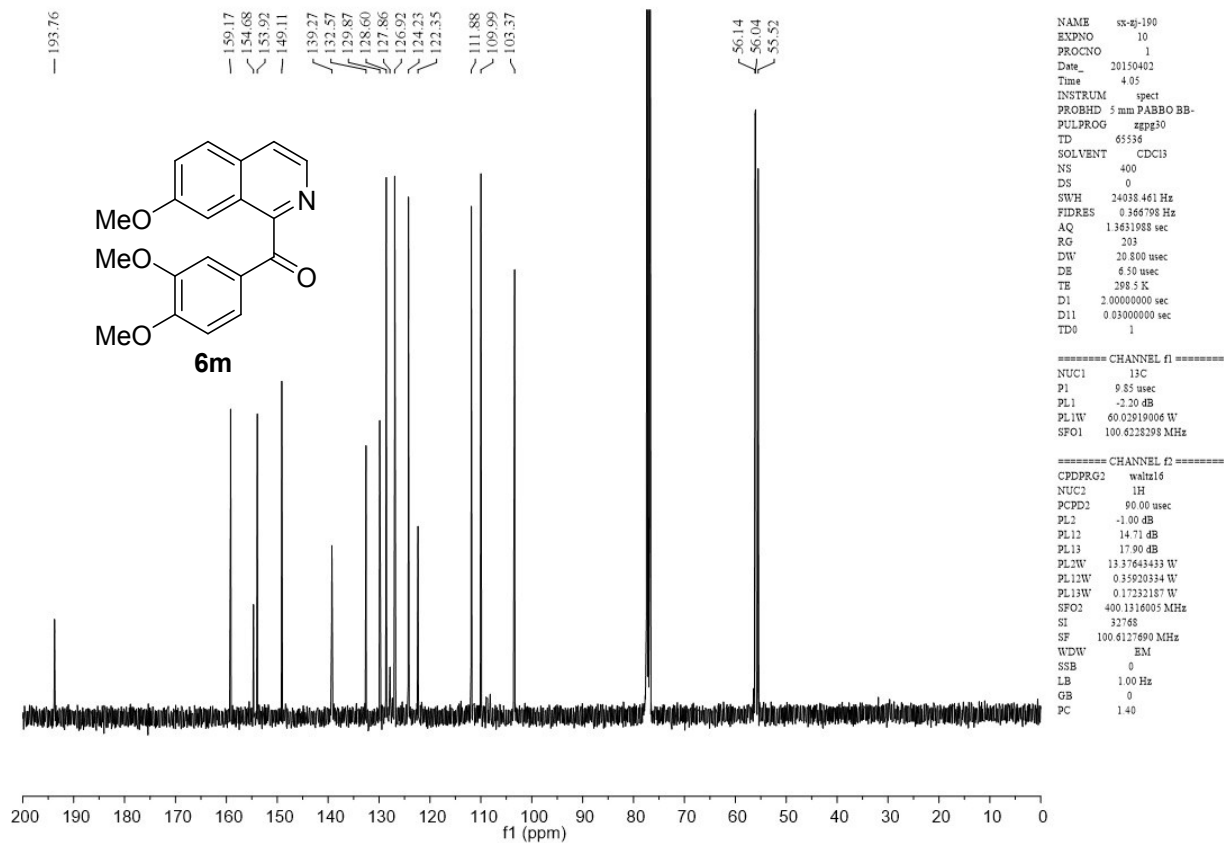
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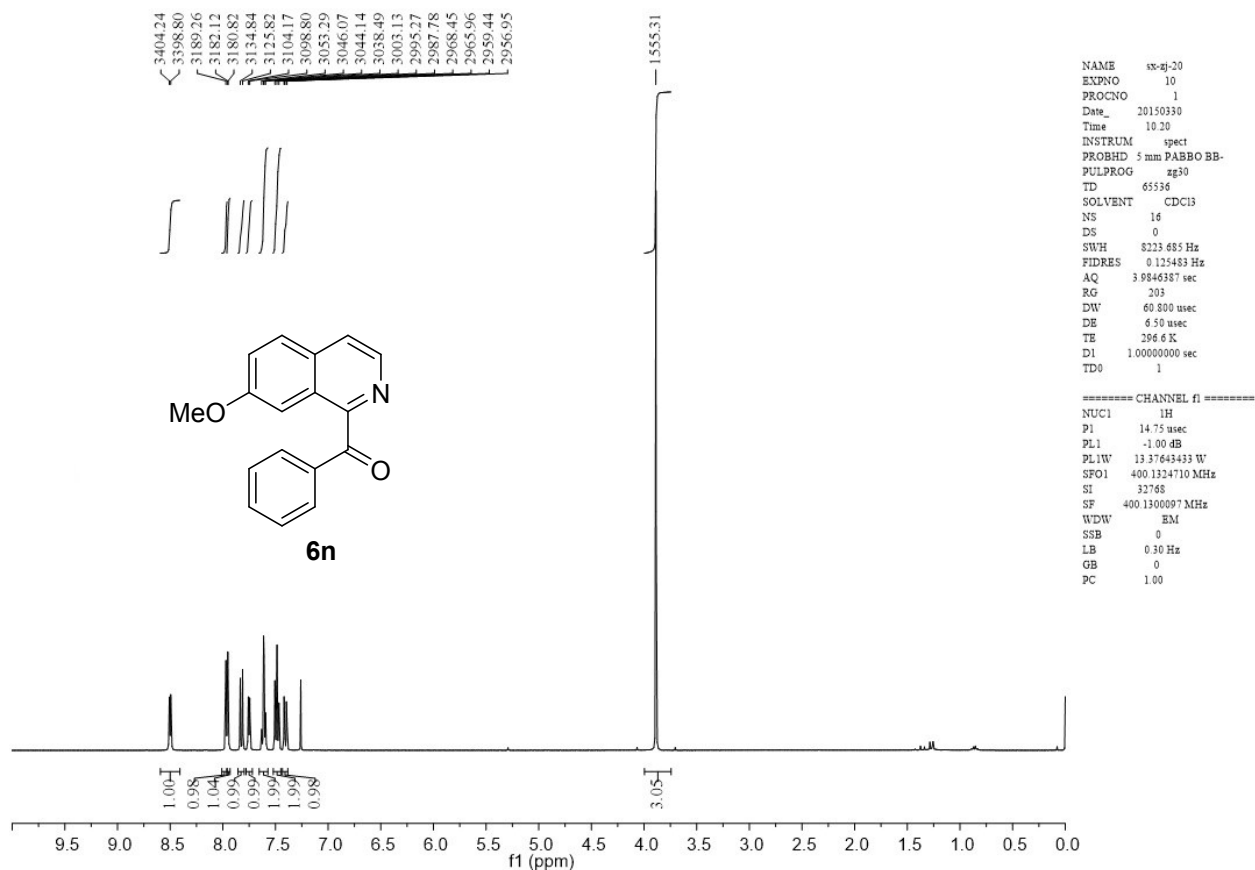
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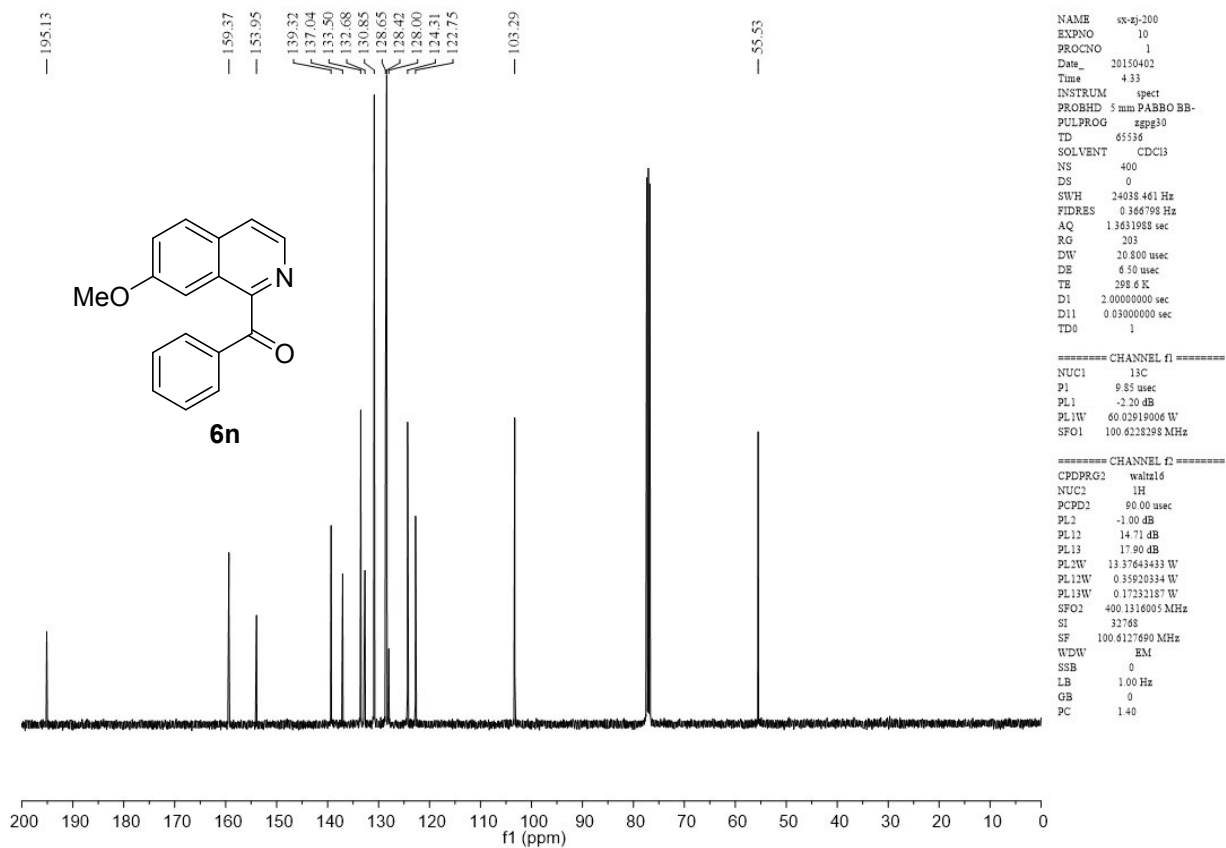
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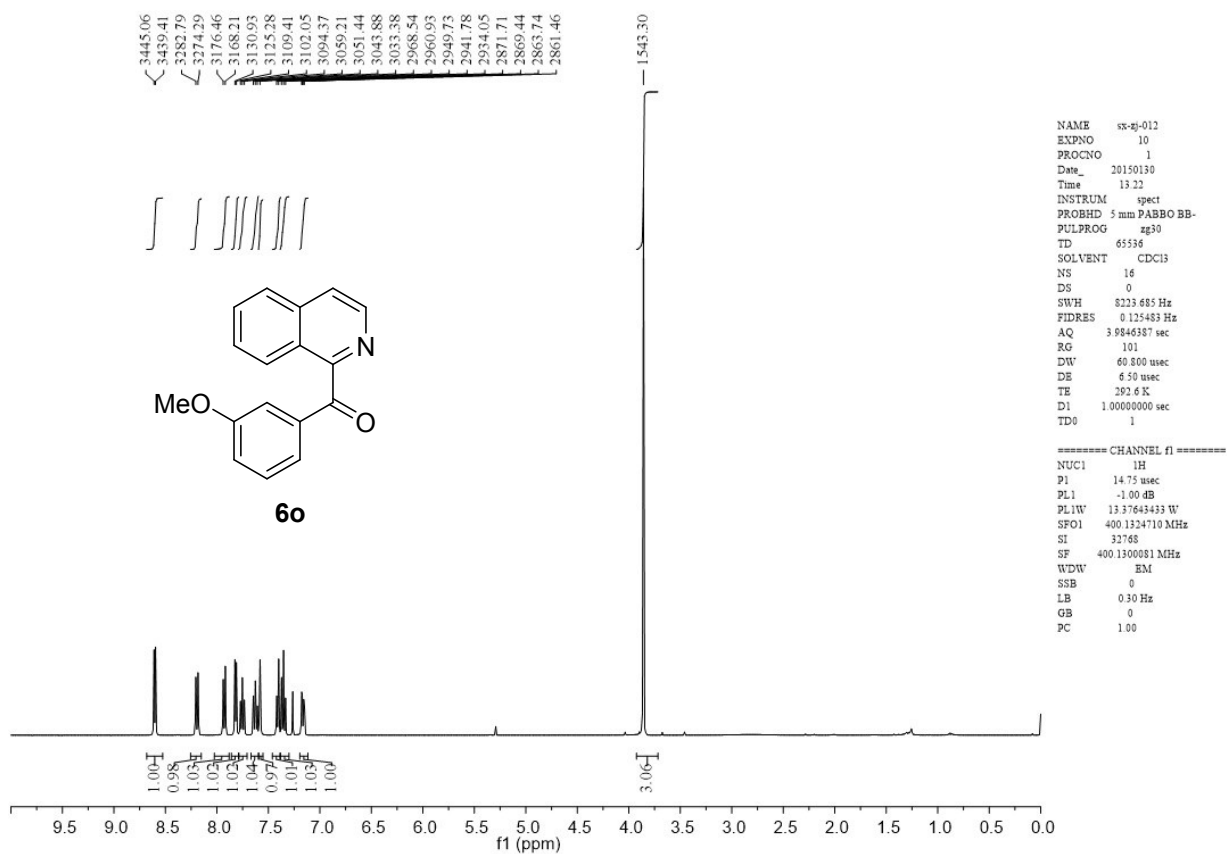
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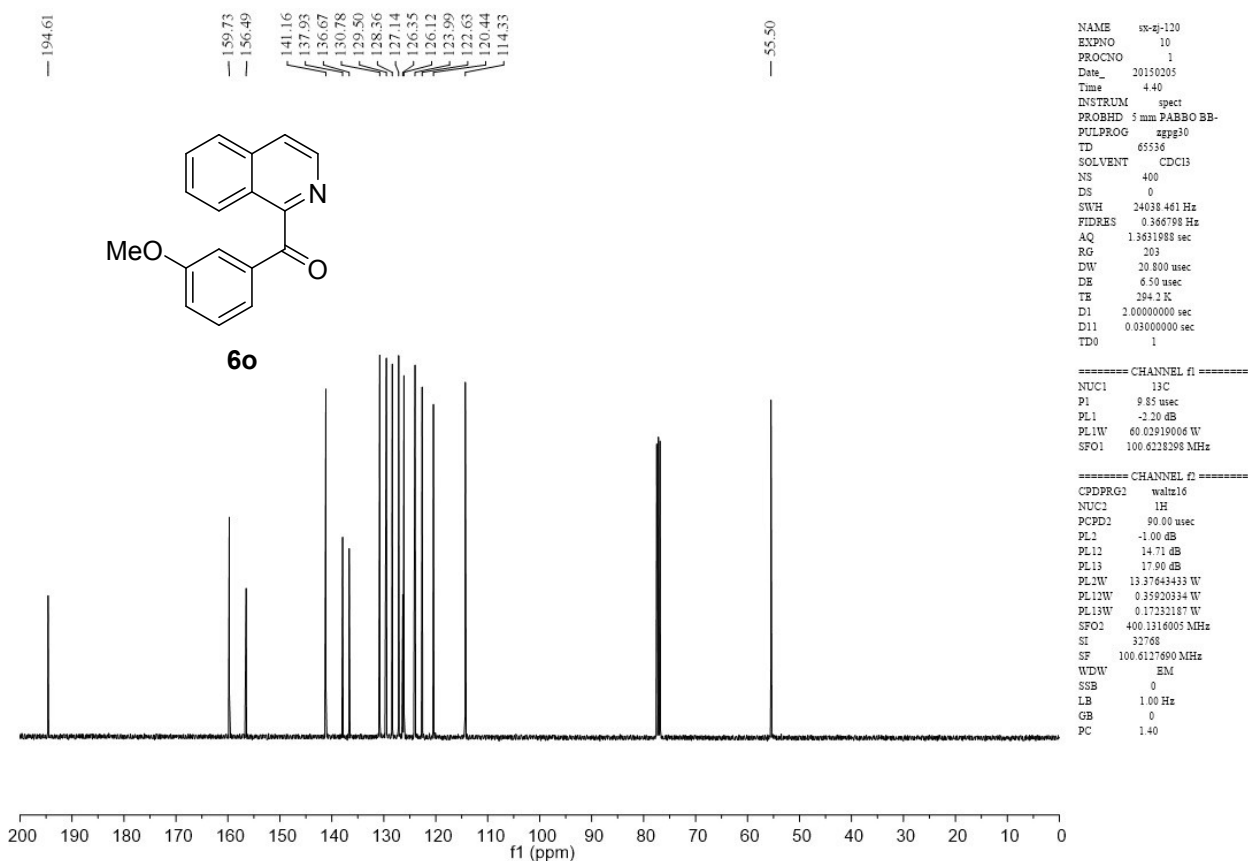
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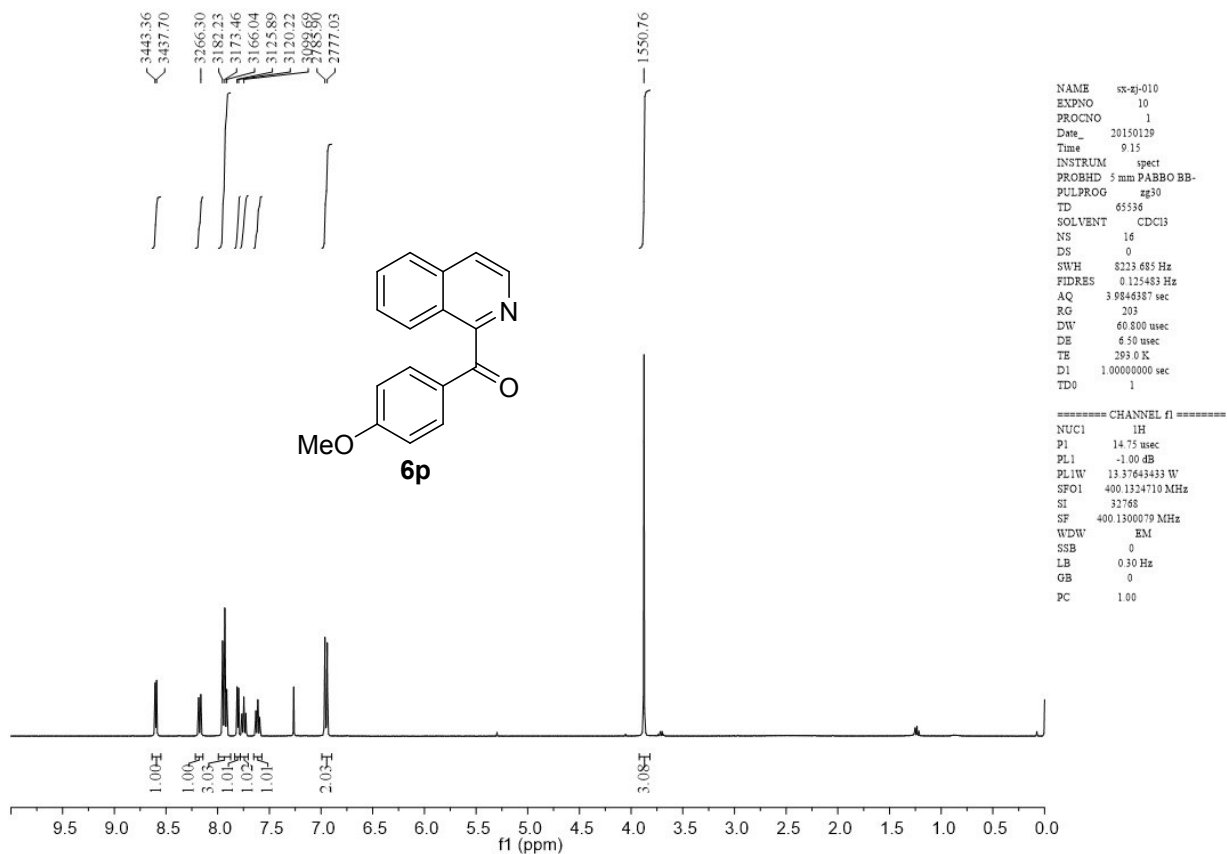
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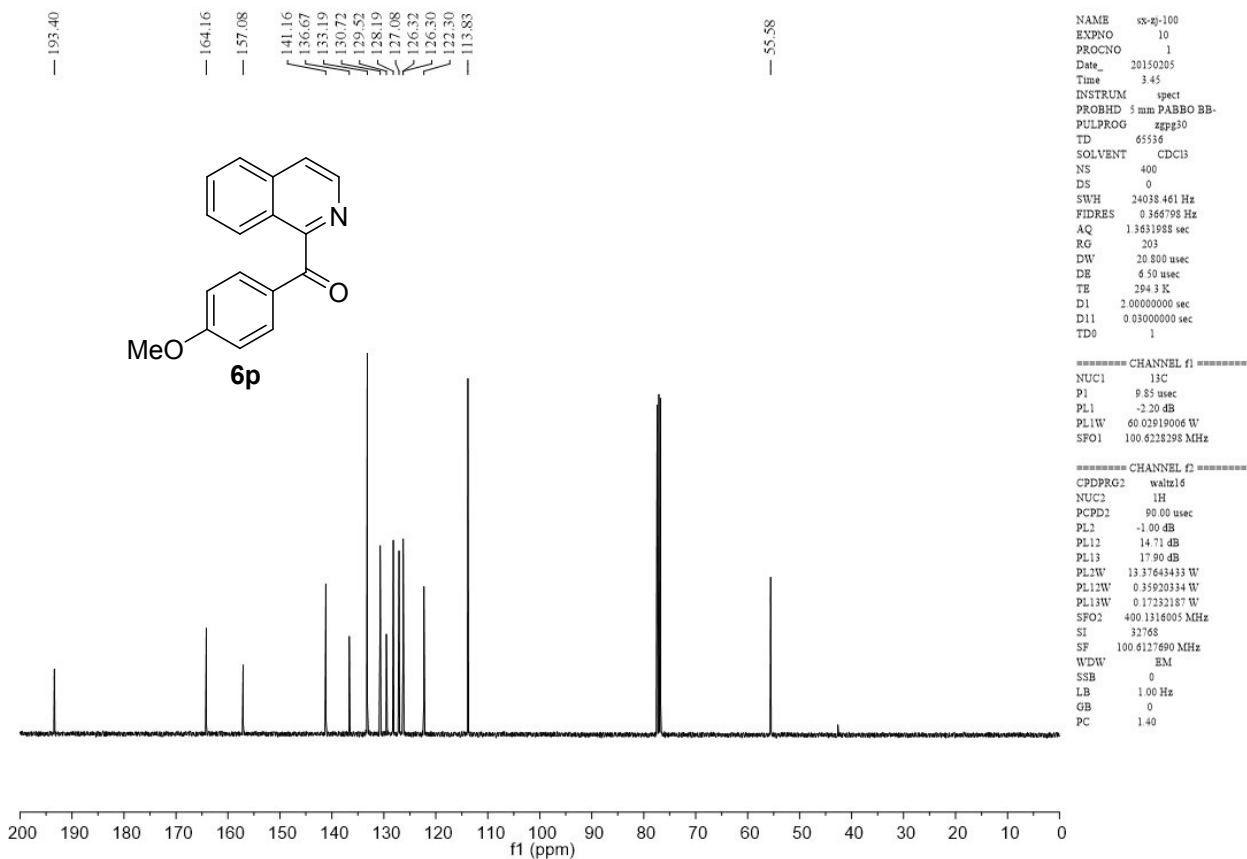
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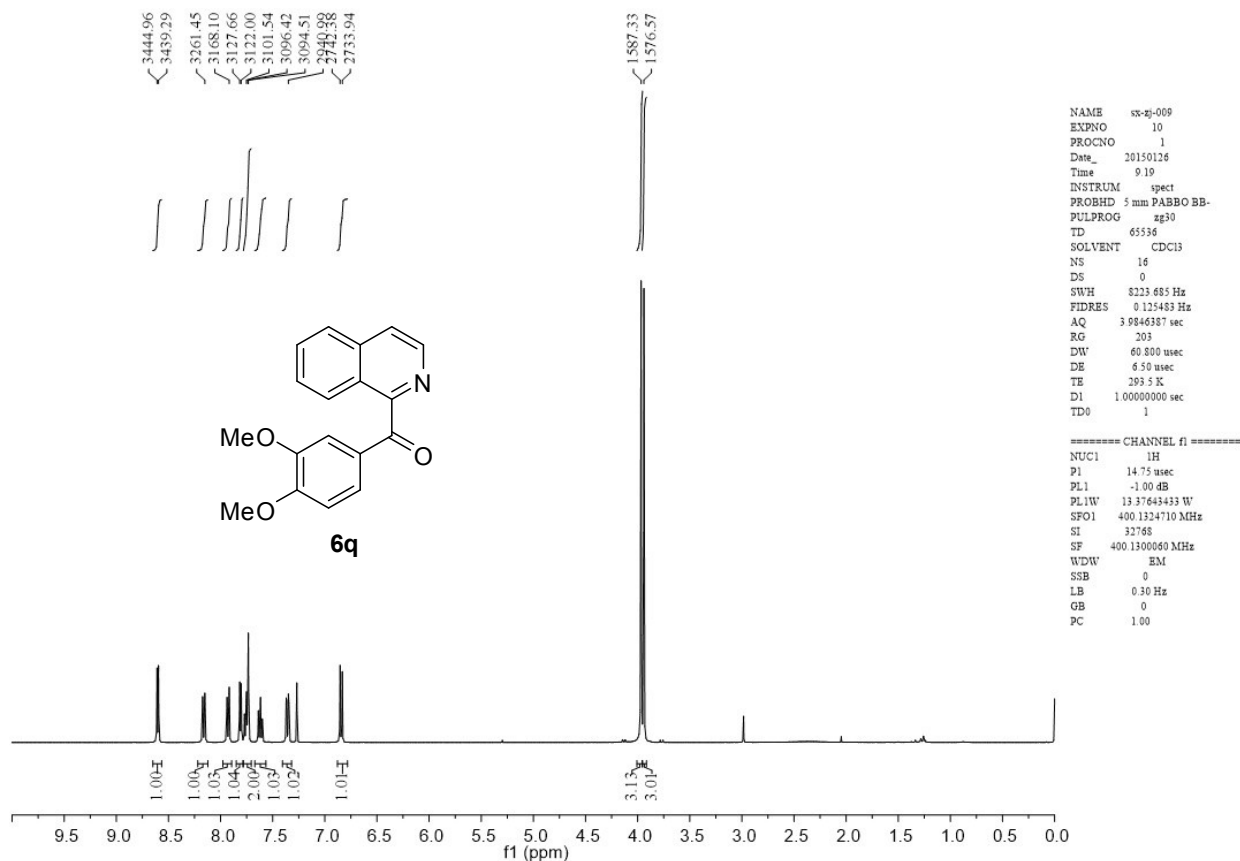
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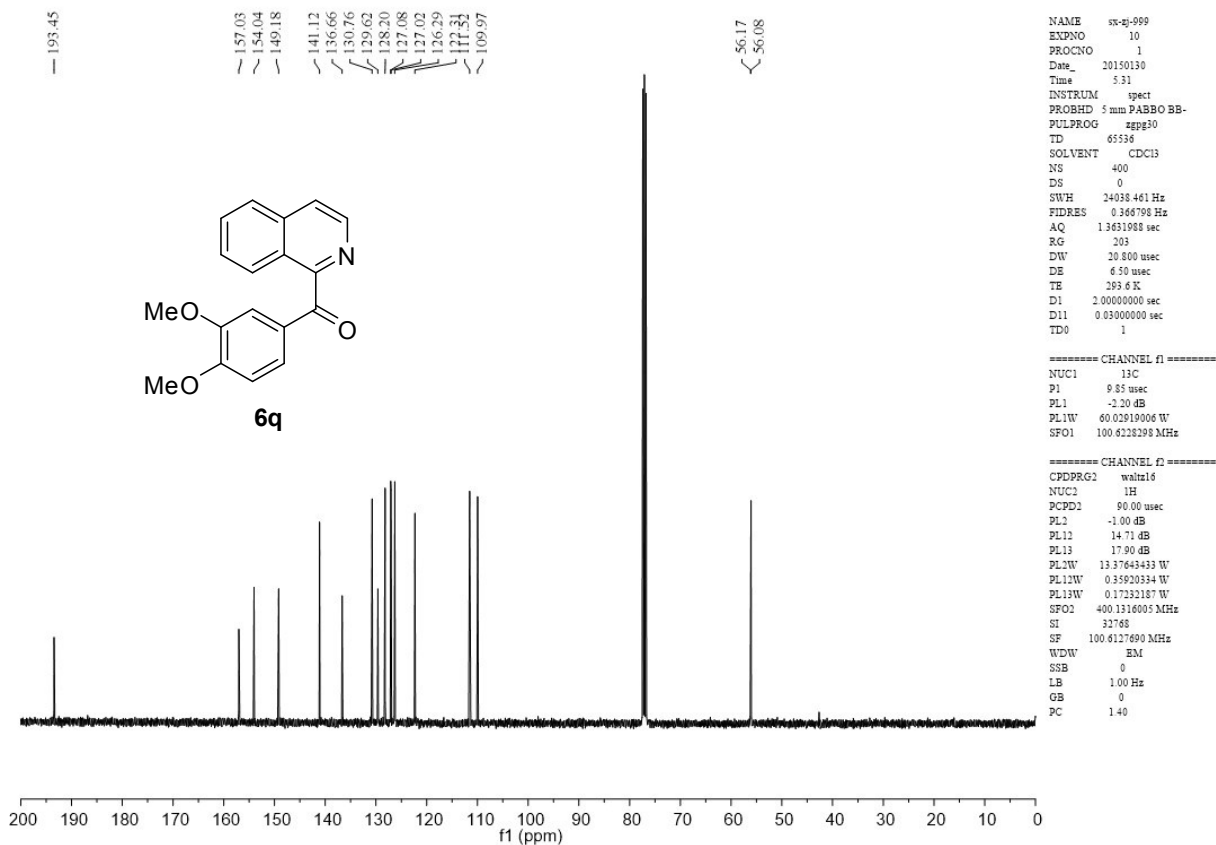
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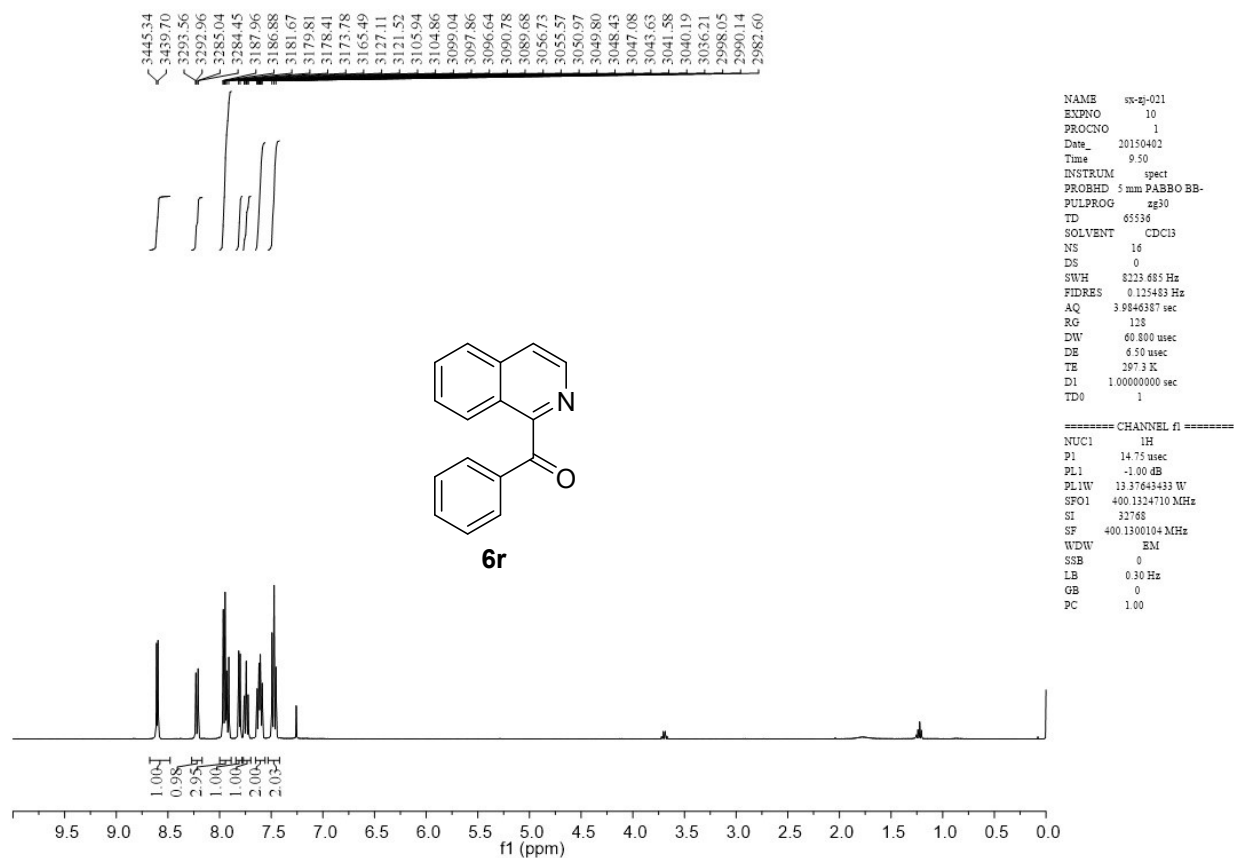
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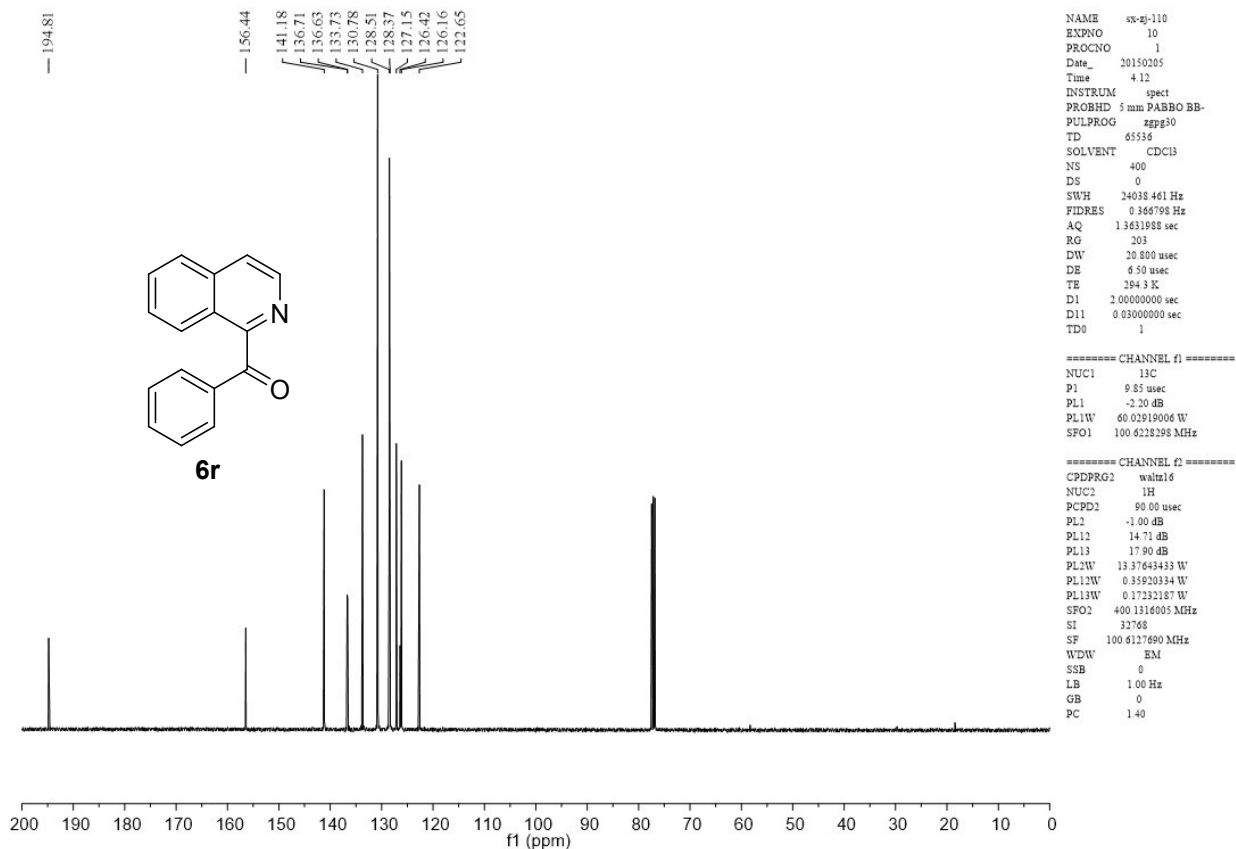
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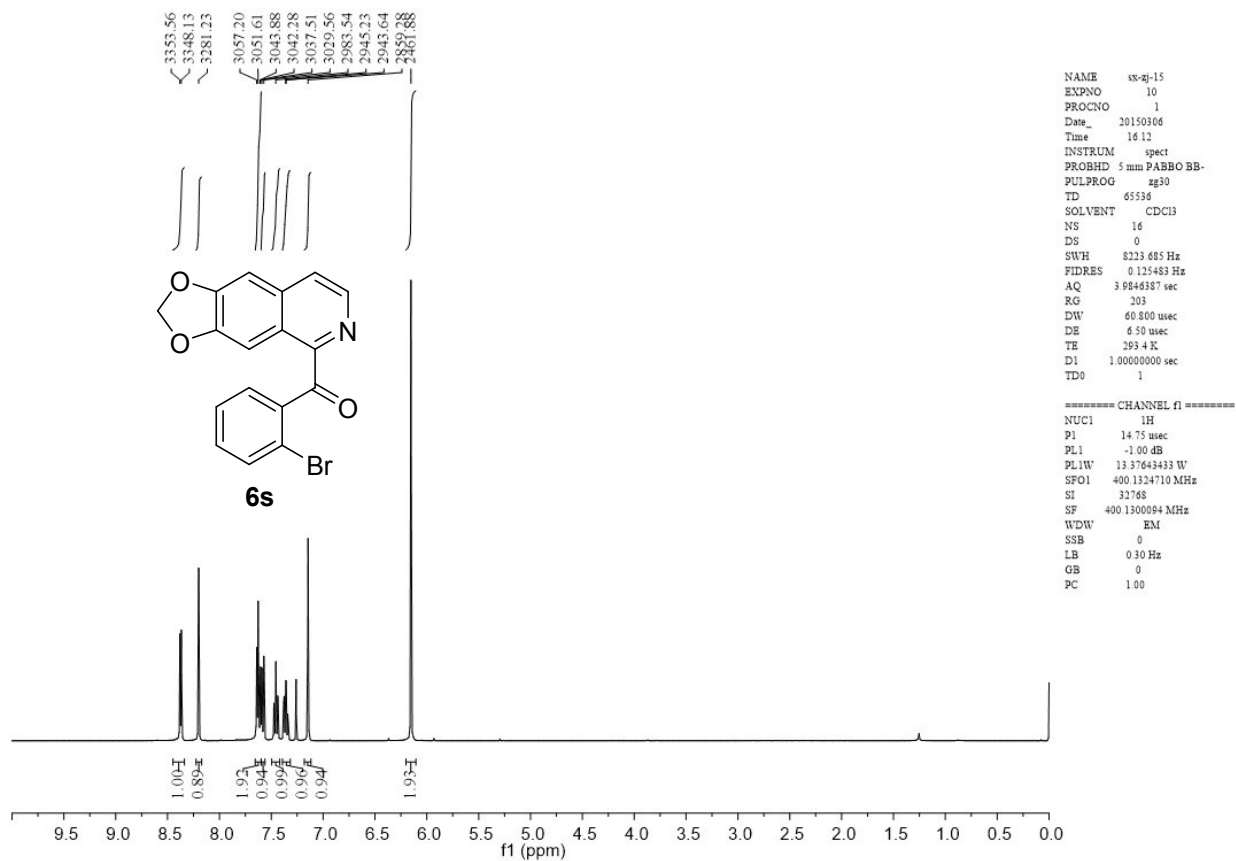
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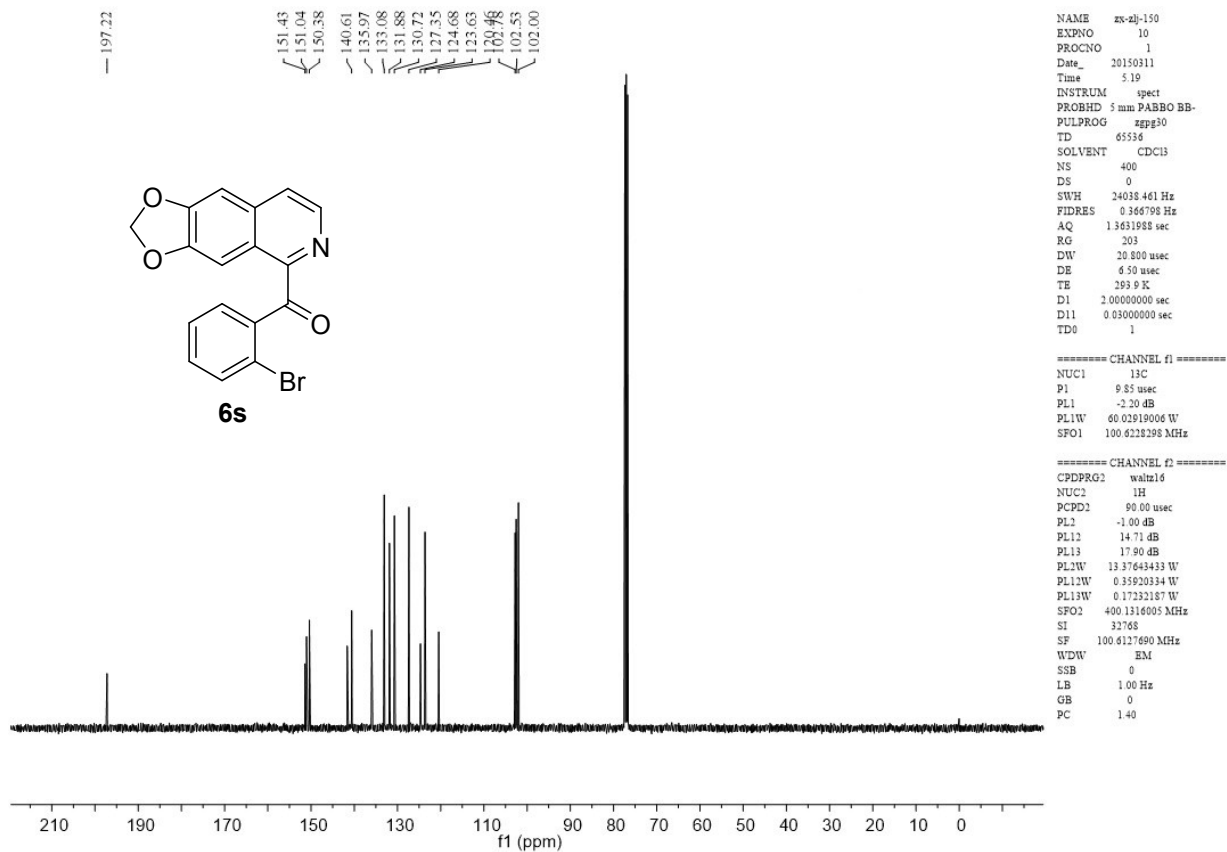
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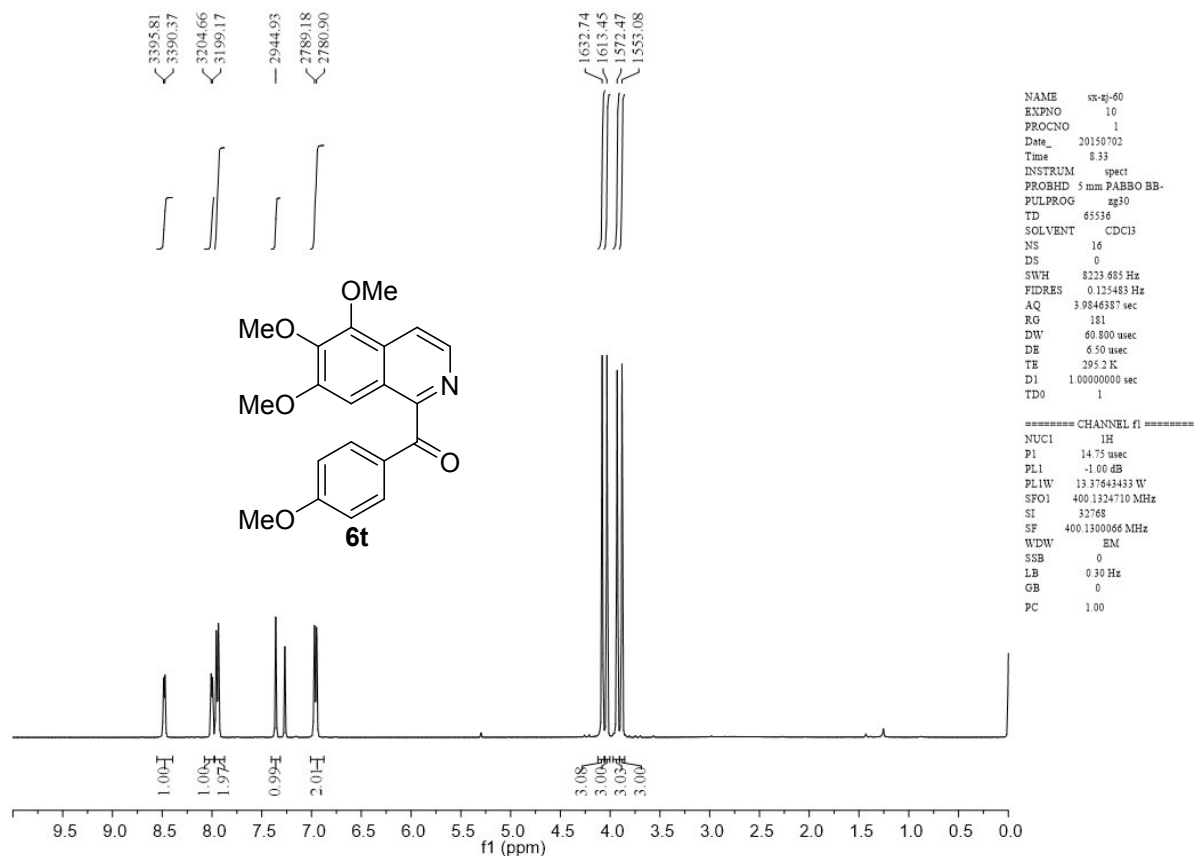
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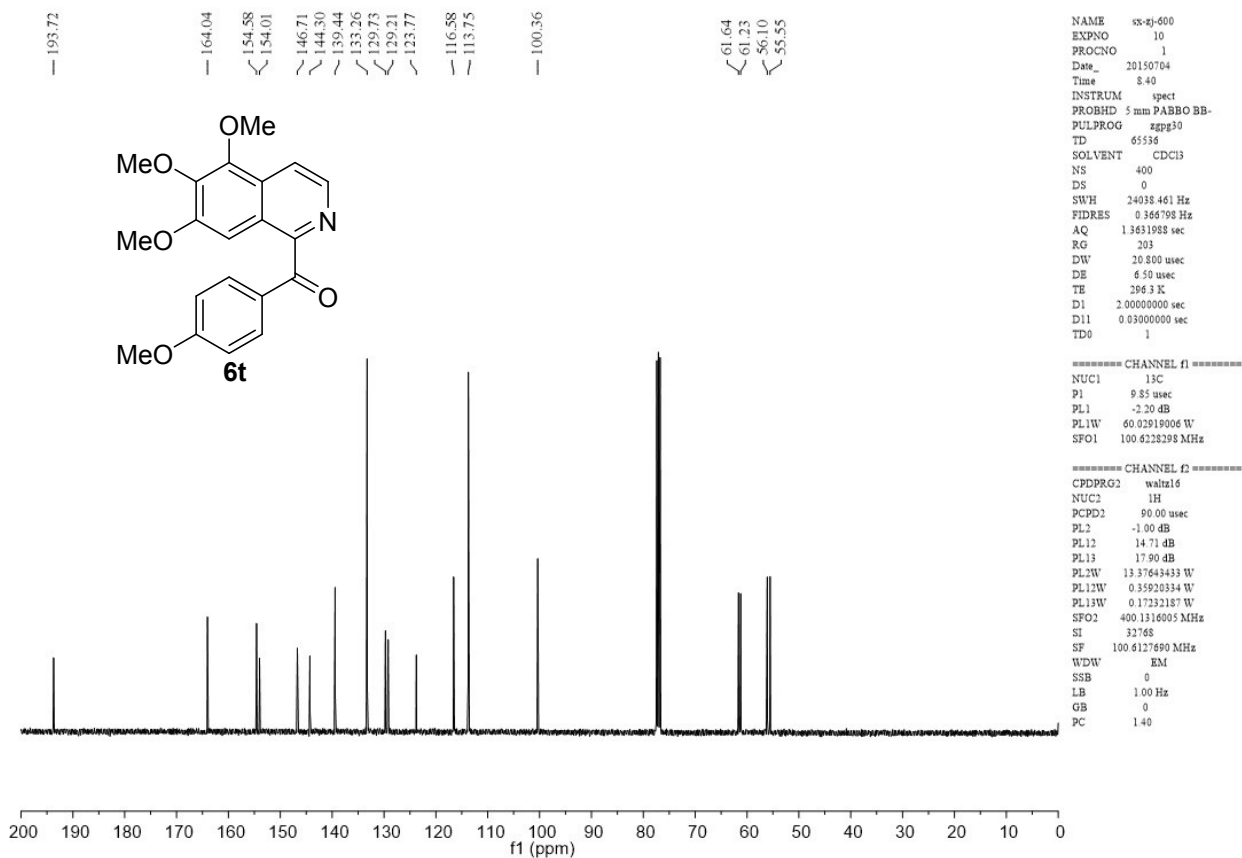
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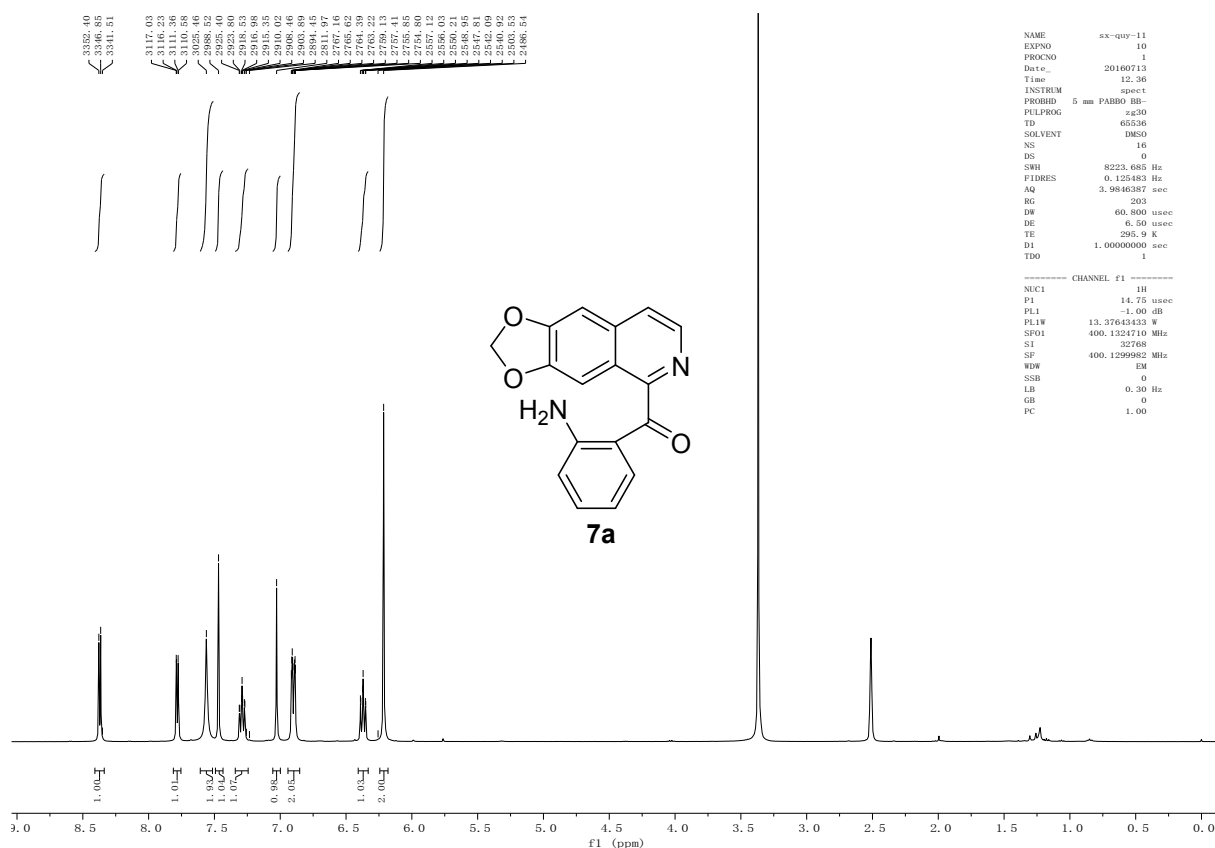
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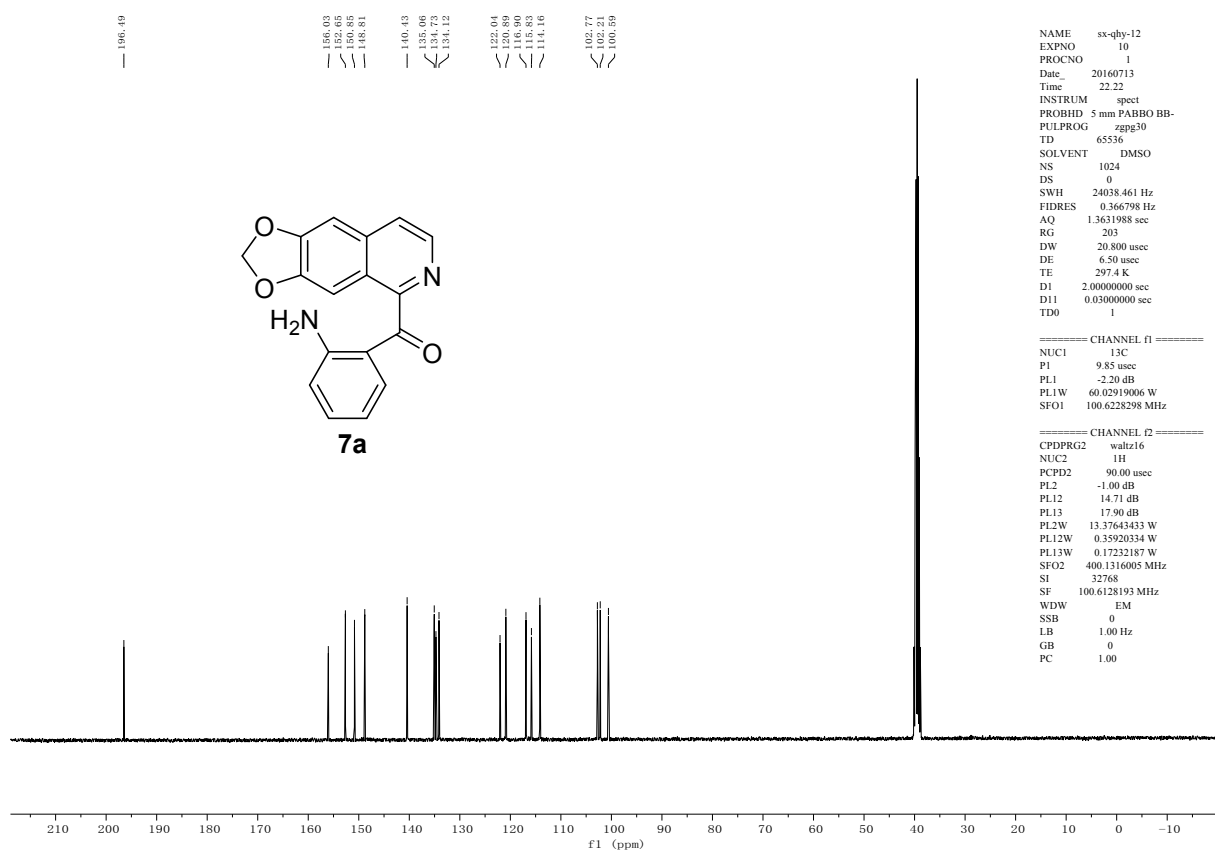
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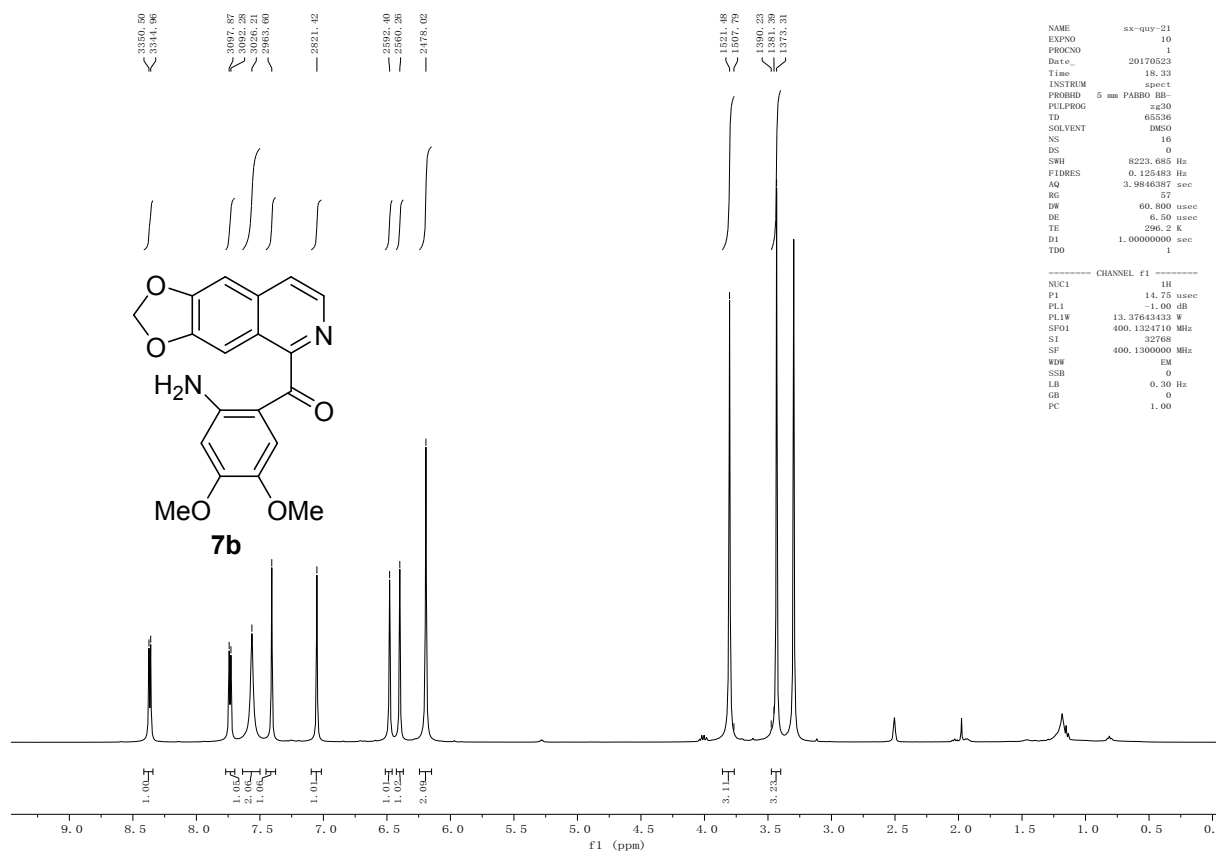
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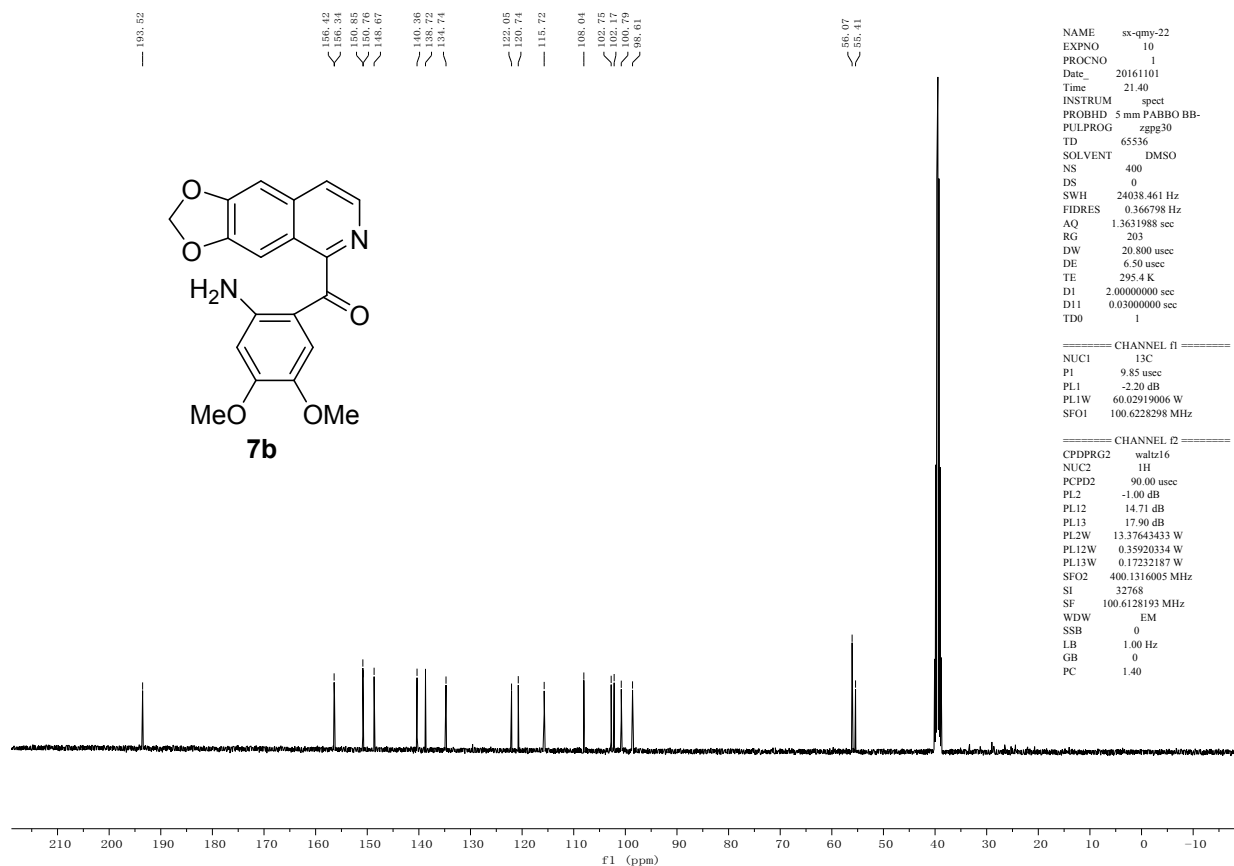
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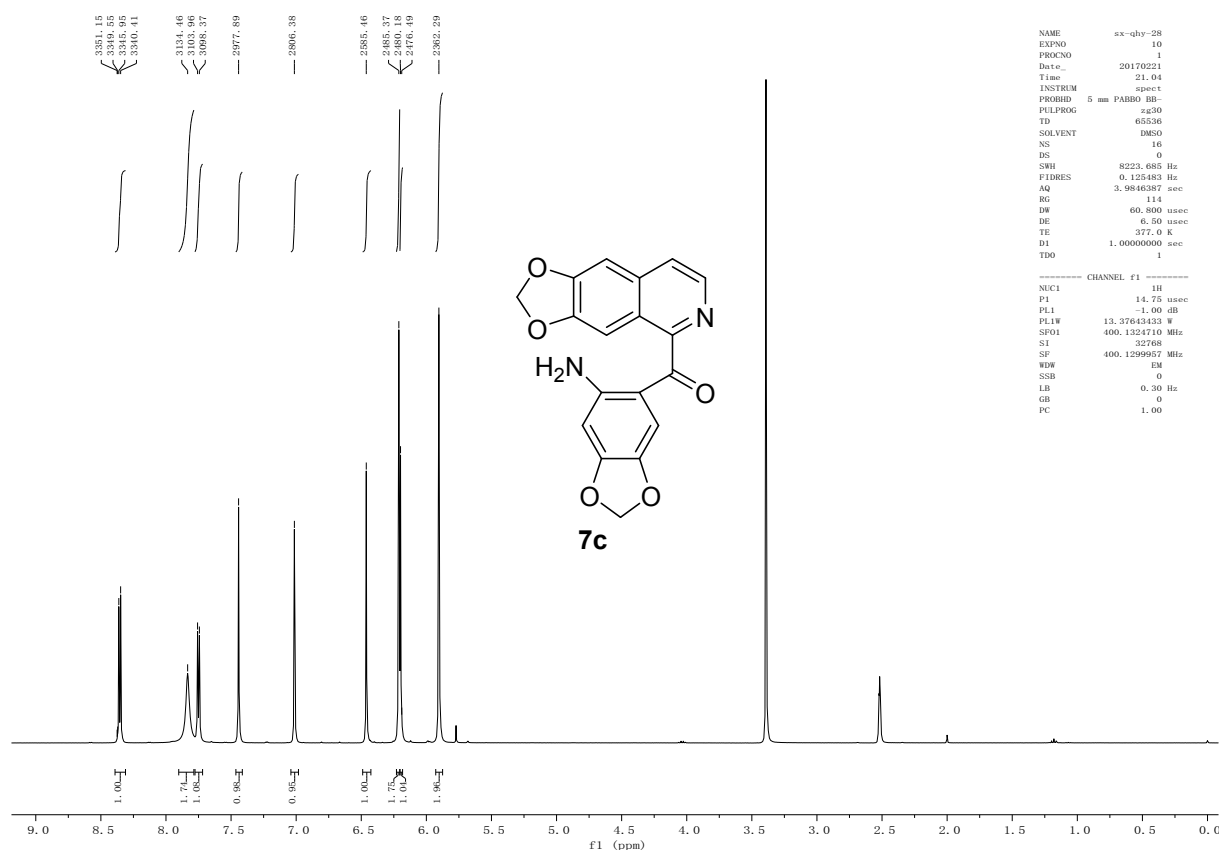
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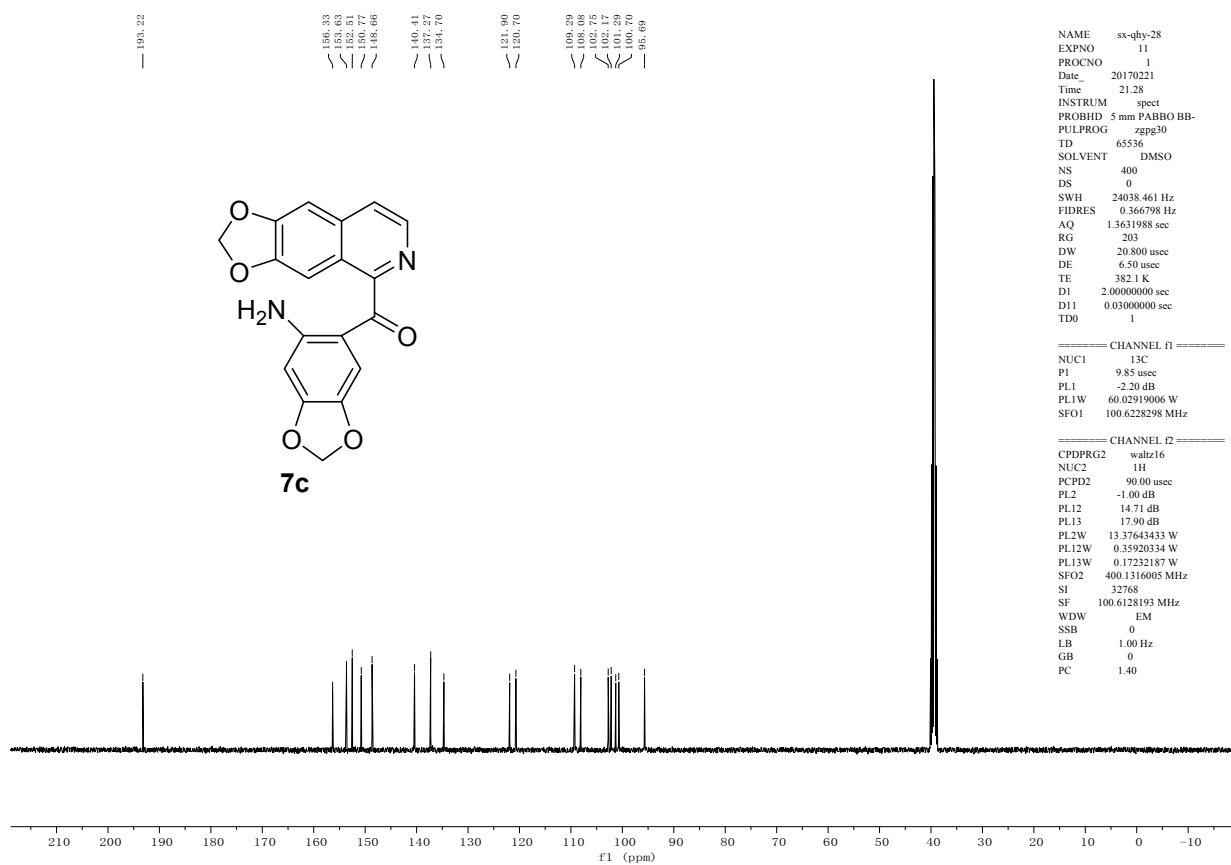
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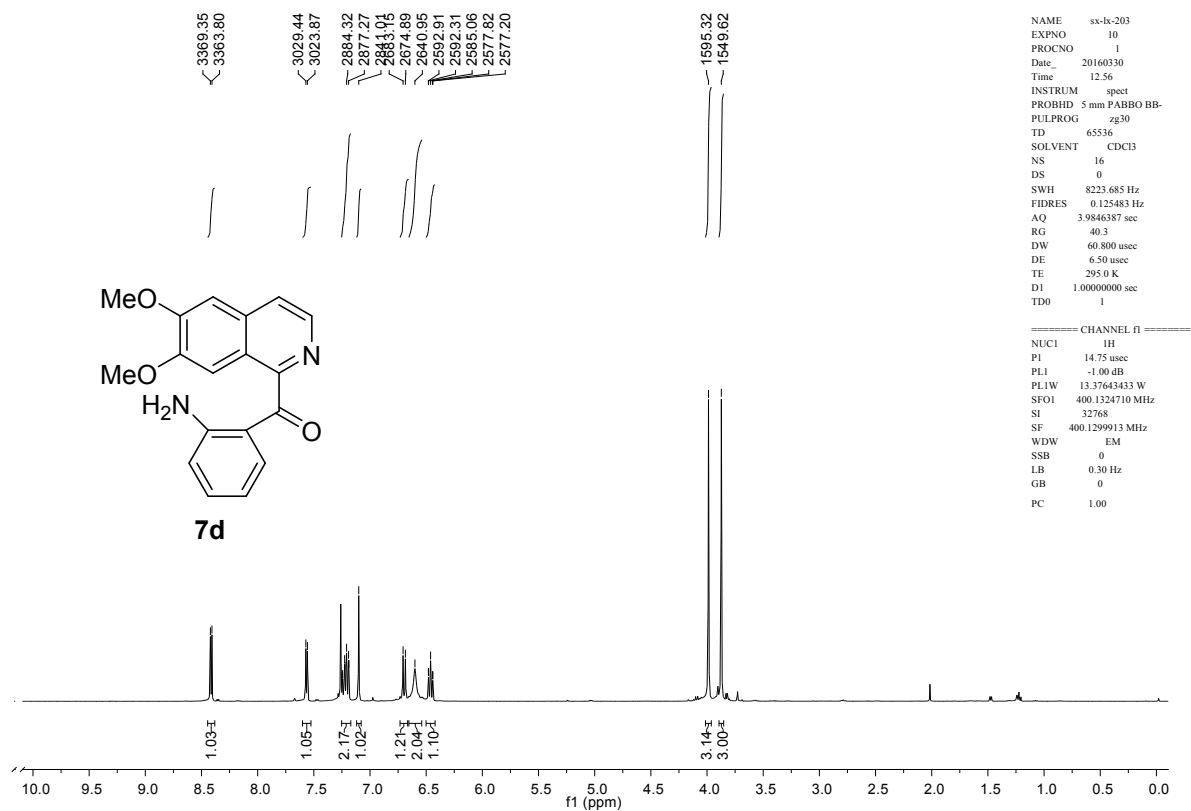
¹H NMR (DMSO-d₆, 400 MHz) spectrum of compound **7c**:



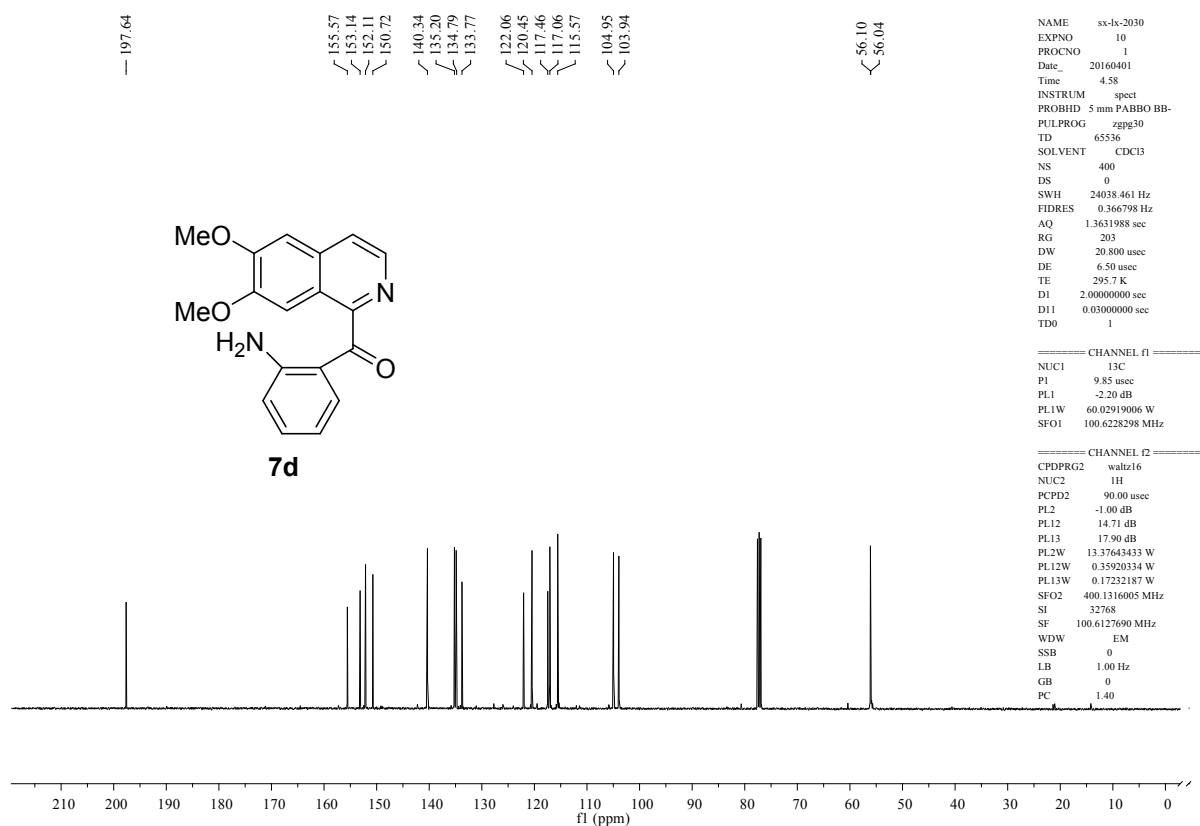
¹³C NMR (DMSO-d₆, 100 MHz) spectrum of compound **7c**:



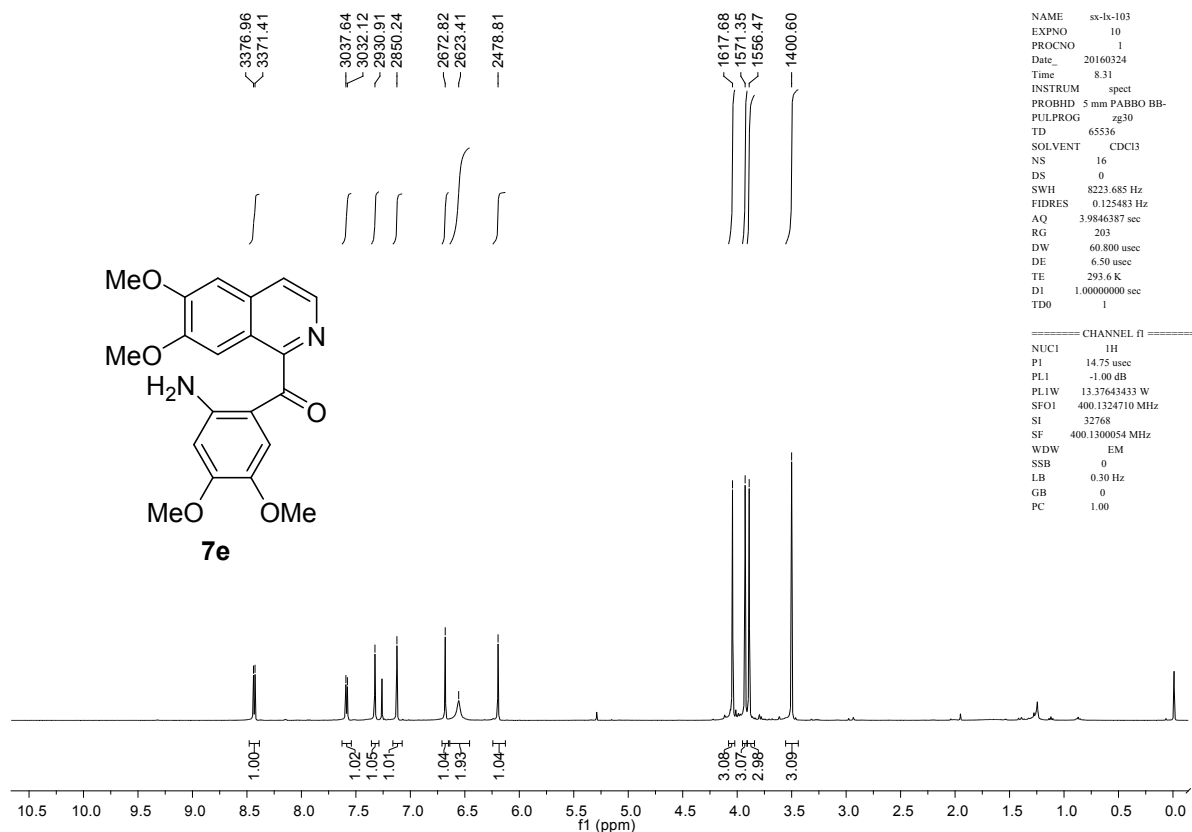
¹H NMR (CDCl₃, 400 MHz) spectrum of compound **7d**:



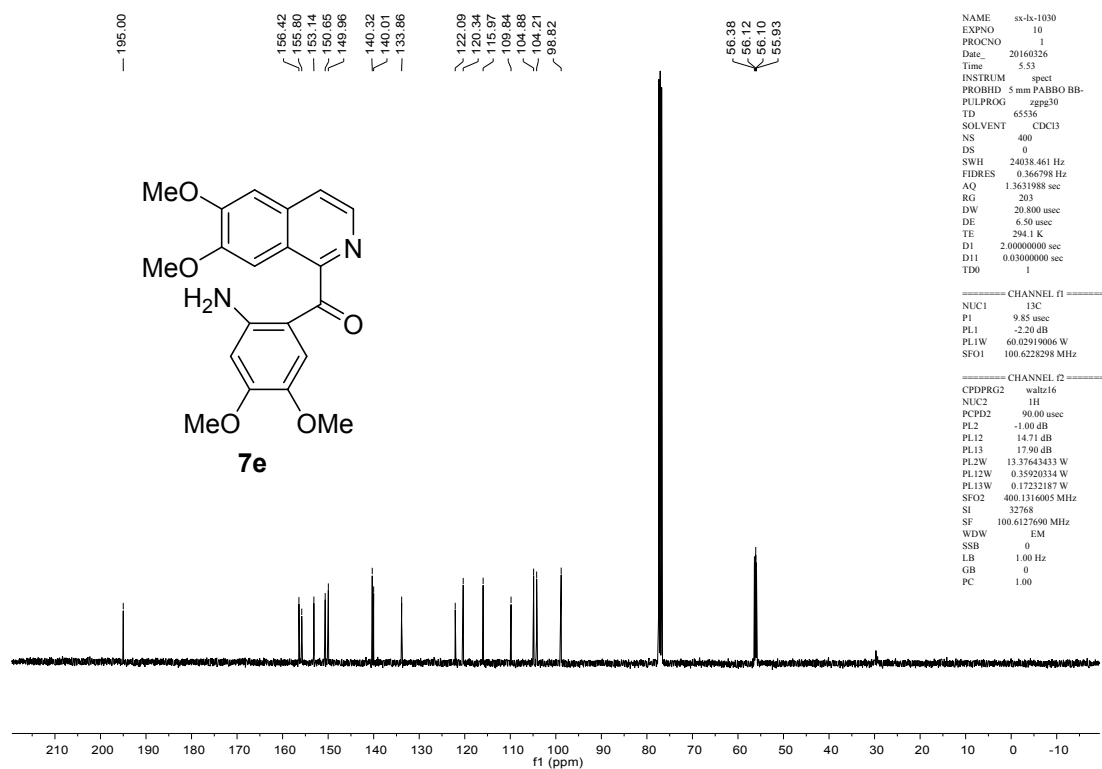
¹³C NMR (CDCl₃, 100 MHz) spectrum of compound **7d**:



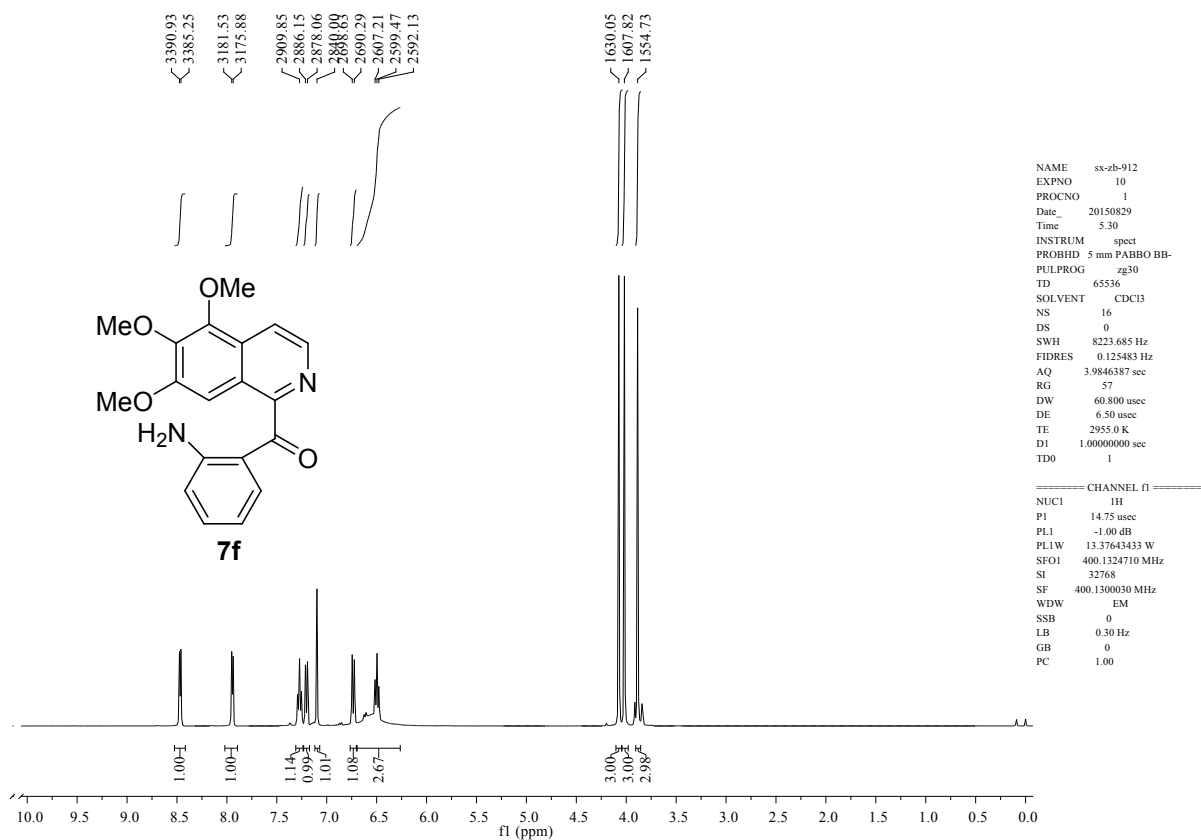
^1H NMR (CDCl_3 , 400 MHz) spectrum of compound **7e**:



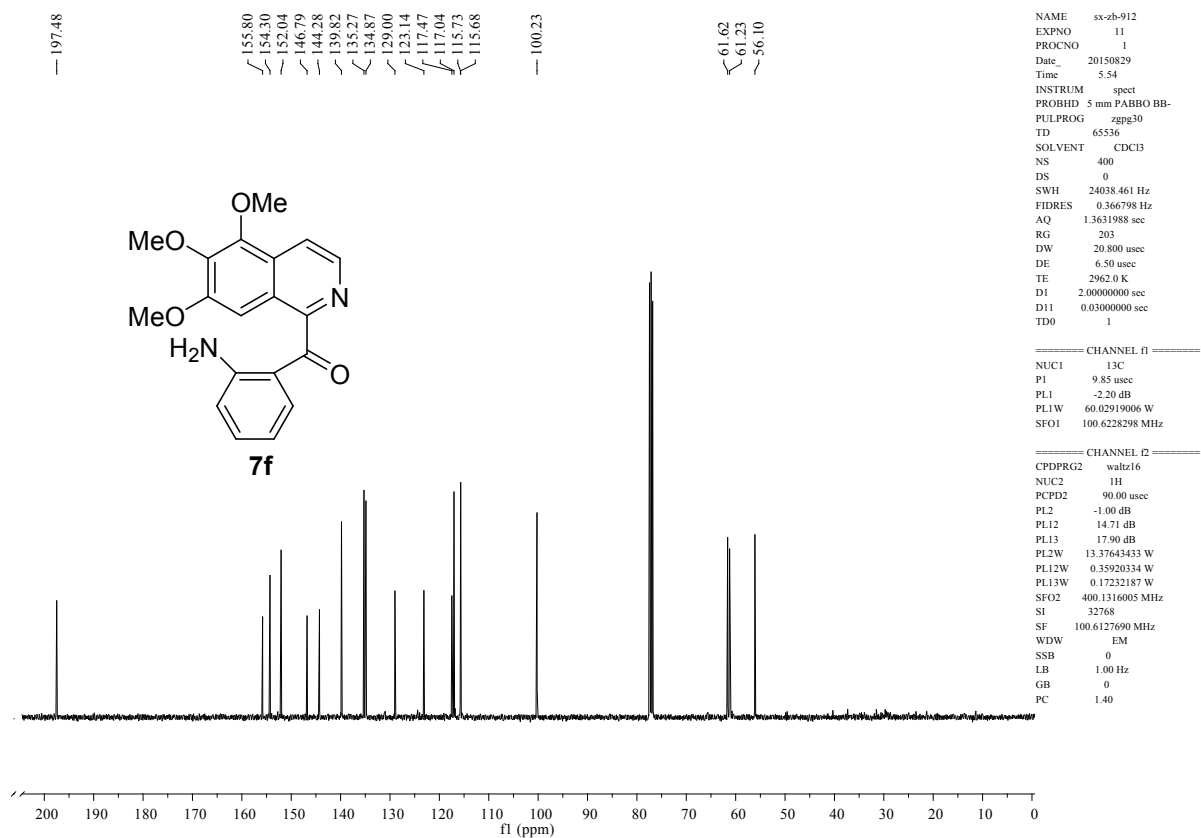
^{13}C NMR (CDCl_3 , 100 MHz) spectrum of compound **7e**:



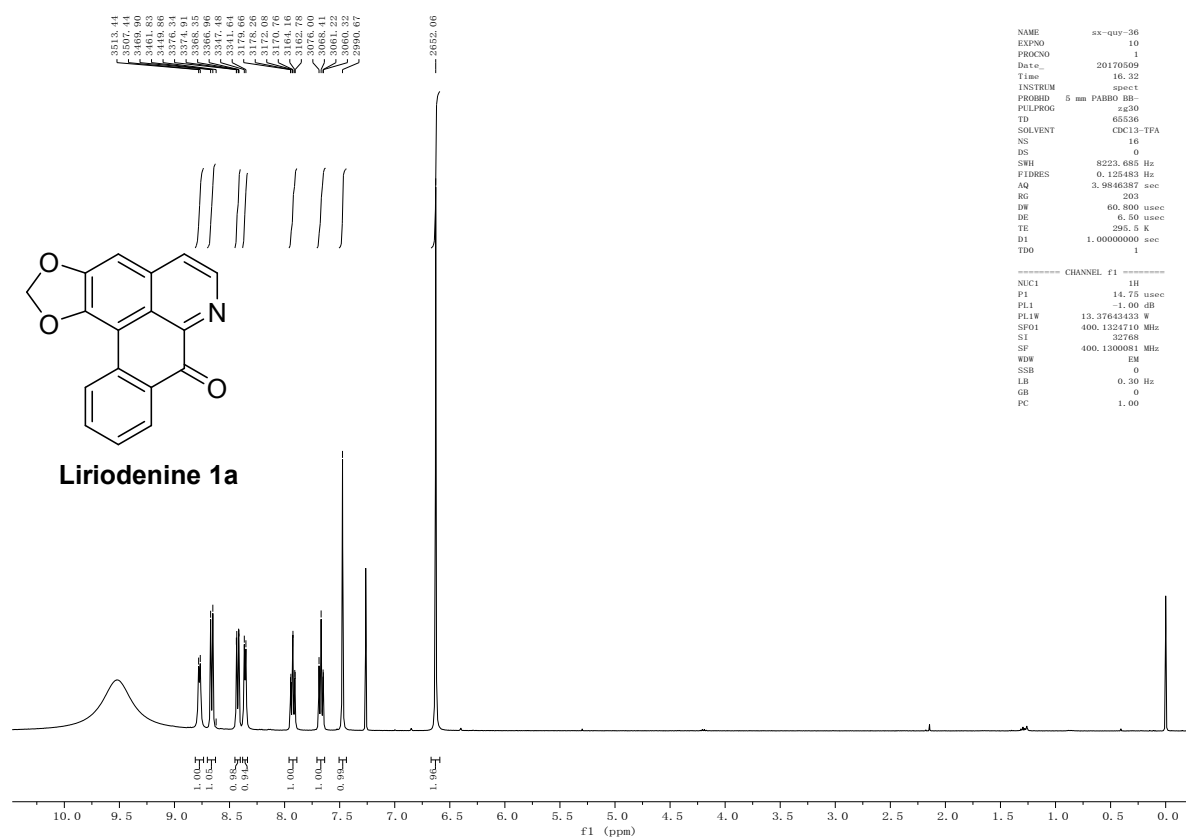
^1H NMR (CDCl_3 , 400 MHz) spectrum of compound **7f**:



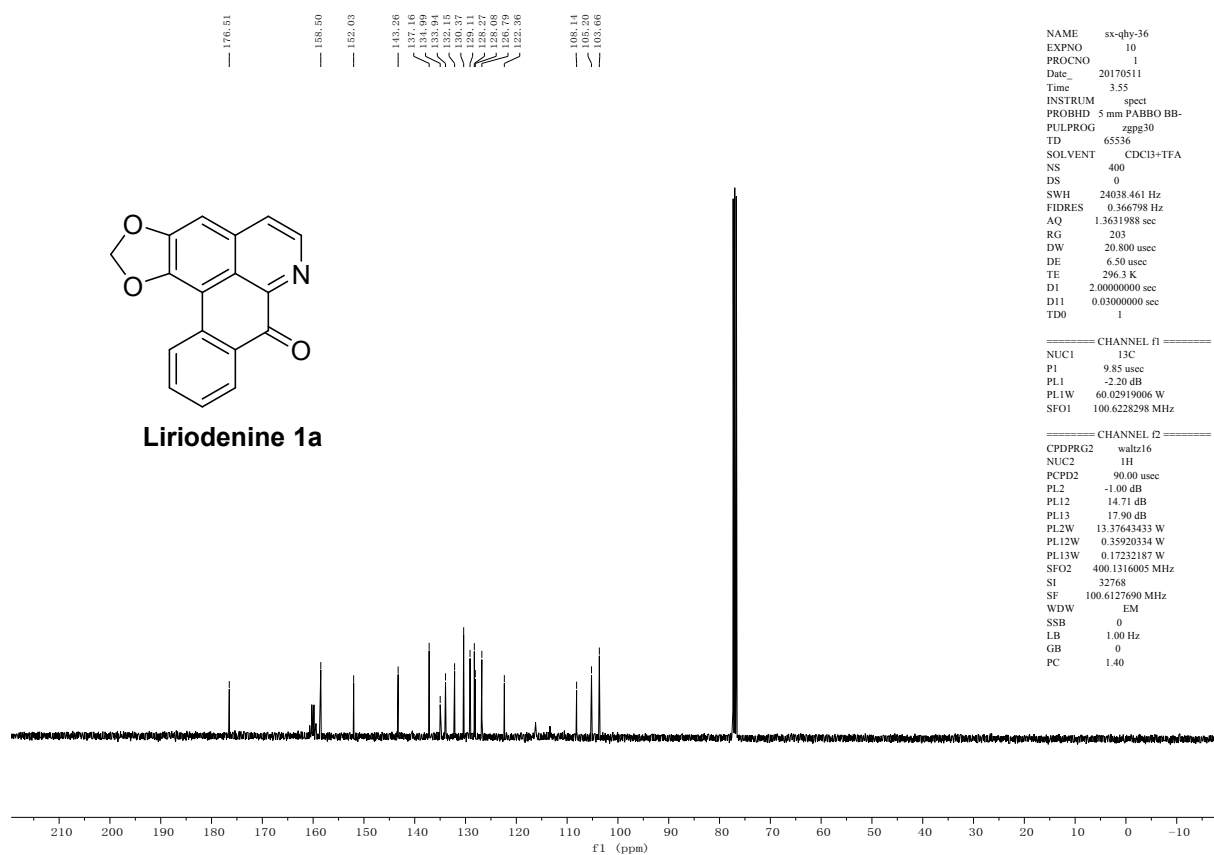
^{13}C NMR (CDCl_3 , 100 MHz) spectrum of compound **7f**:



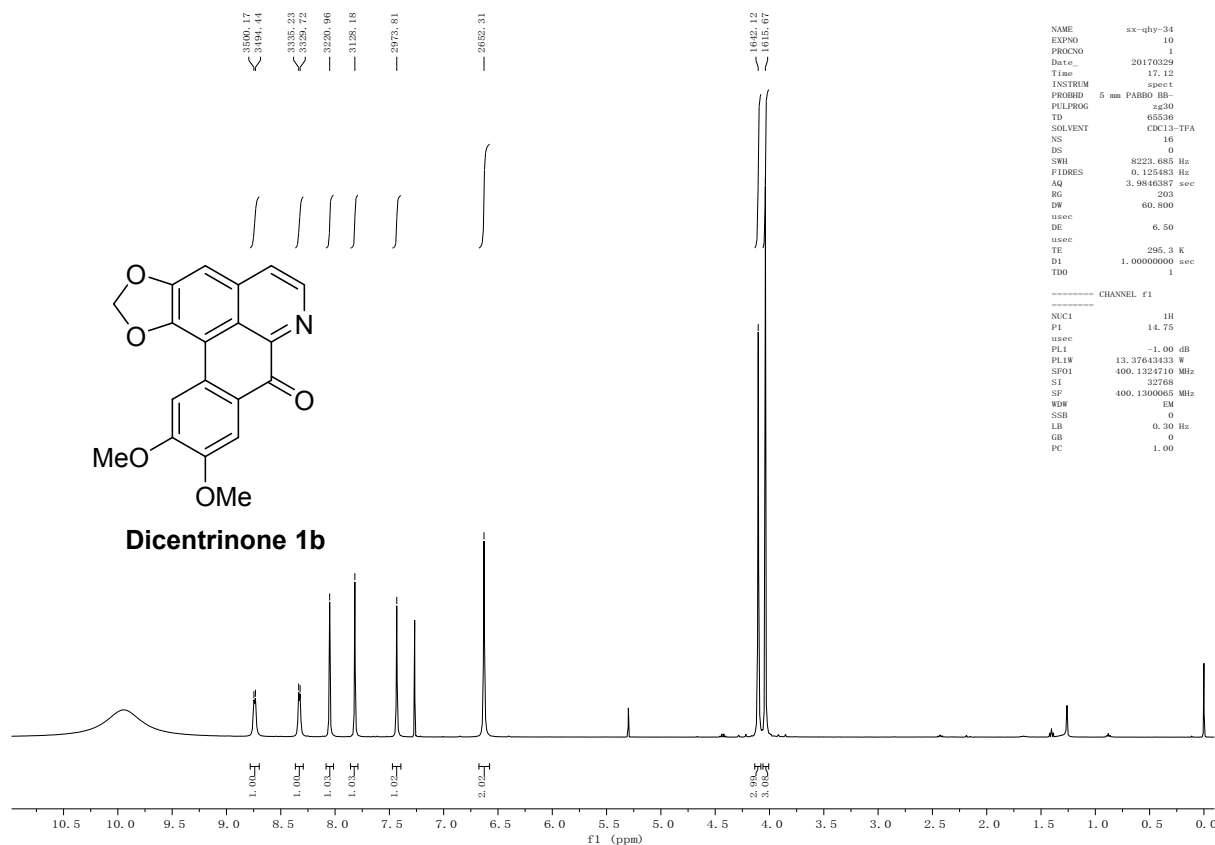
¹H NMR (CDCl₃-TFA, 400 MHz) spectrum of compound **1a**:



¹³C NMR (CDCl₃-TFA, 100 MHz) spectrum of compound **1a**:



¹H NMR (CDCl₃-TFA, 400 MHz) spectrum of compound **1b**:



```

NAME      sx-qhy-34
EXPNO     10
PROCNO    1
Date_     20170329
Time      17.12
INSTRUM    spect
PROBHD     5 mm PABBO BB-
PULPROG    zg30
TD          65536
SOLVENT    CDCl3-TFA
NS          16
DS          0
SWH         8223.685 Hz
FIDRES      0.125483 Hz
AQ          3.9846387 sec
RG          203
DW          60.800
DE          6.50
TE          295.3 K
D1          1.00000000 sec
D10         1

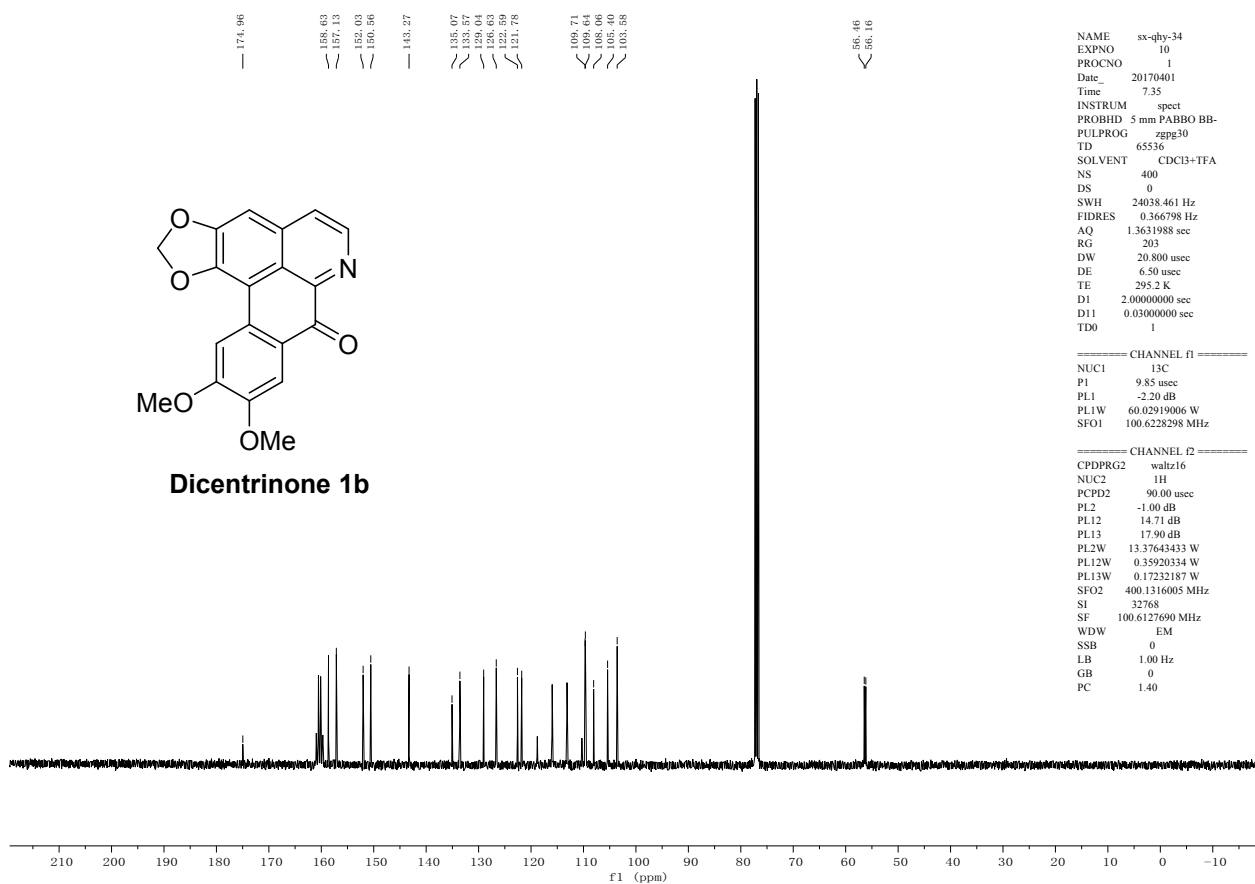
```

```

===== CHANNEL f1 =====
NUC1       1H
P1         14.75
uS         -1.00 dB
PL1        13.37643433 W
SFO1       400.1324710 MHz
SI         32768
SF         400.1300065 MHz
WDW        EM
SSB         0
LB          0.30 Hz
GB          0
PC          1.00

```

¹³C NMR (CDCl₃-TFA, 100 MHz) spectrum of compound **1b**:



```

NAME      sx-qhy-34
EXPNO     10
PROCNO    1
Date_     20170401
Time      7.35
INSTRUM    spect
PROBHD     5 mm PABBO BB-
PULPROG    zgpg30
TD          65536
SOLVENT    CDCl3-TFA
NS          400
DS          0
SWH         24038.461 Hz
FIDRES      0.366798 Hz
AQ          1.3631988 sec
RG          203
DW          20.800 uS
DE          6.50 uS
TE          295.2 K
D1          2.00000000 sec
D11         0.03000000 sec
D10         1

```

```

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

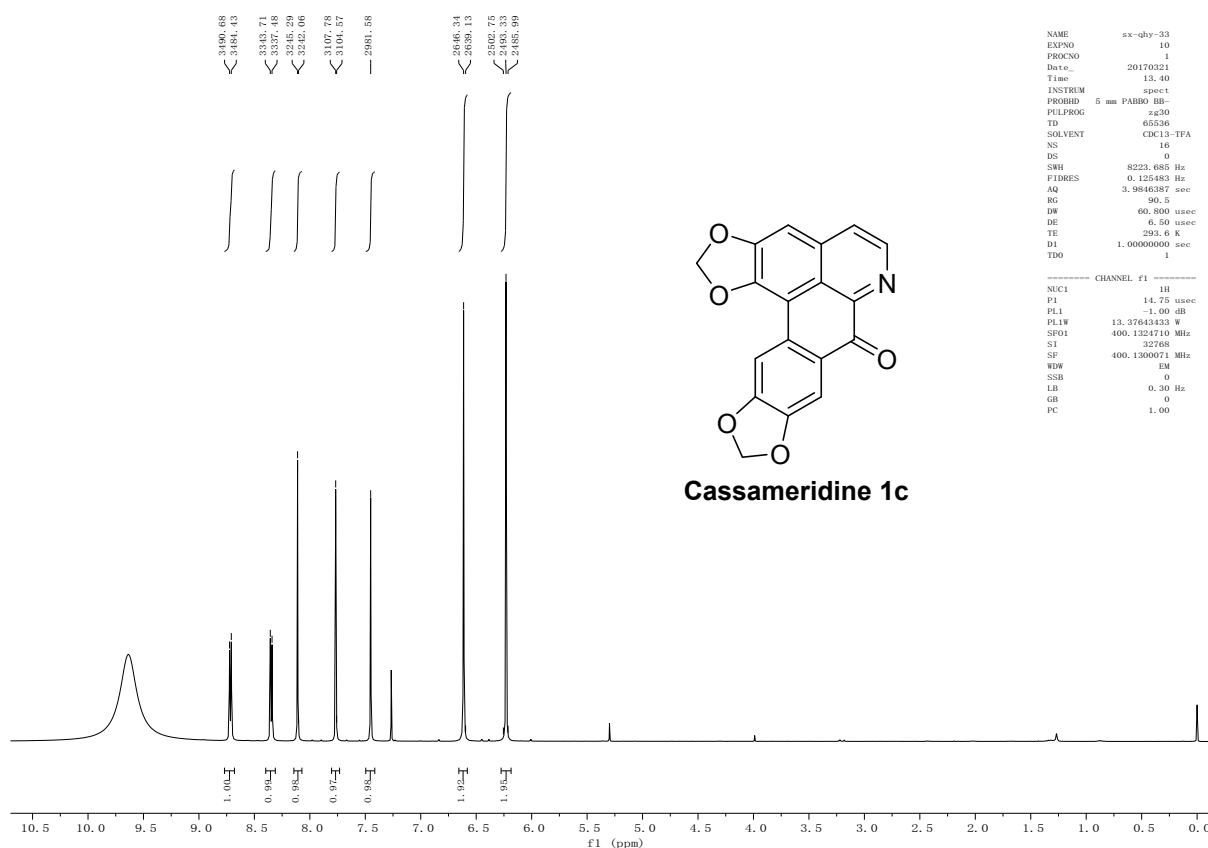
```

```

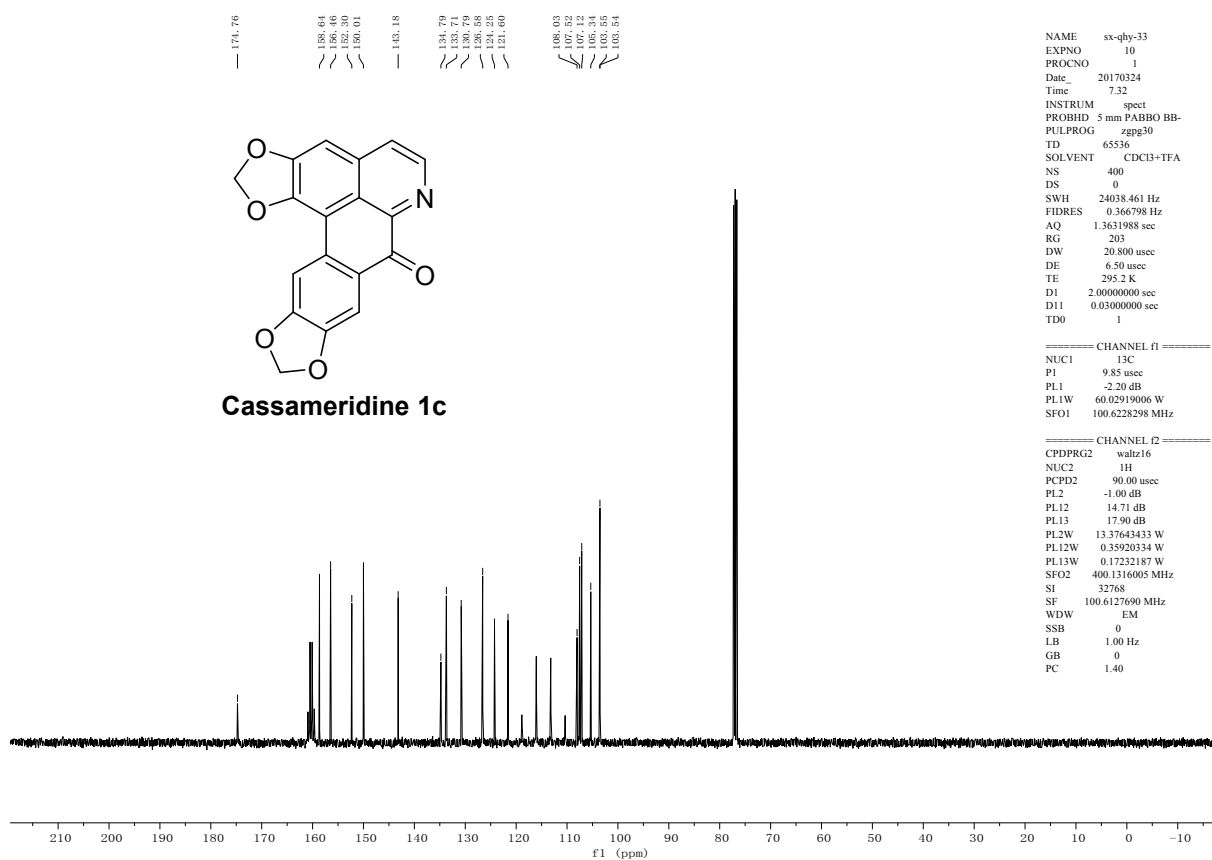
===== CHANNEL f2 =====
CPDPRG2    waltz16
NUC2       1H
PCPD2      90.00 uS
PL2        -1.00 dB
PL12       14.71 dB
PL13       17.90 dB
PL2W       13.37643433 W
PL12W      0.35920334 W
PL13W      0.17232187 W
SFO2       400.1316005 MHz
SI         32768
SF         100.6127690 MHz
WDW        EM
SSB   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

```

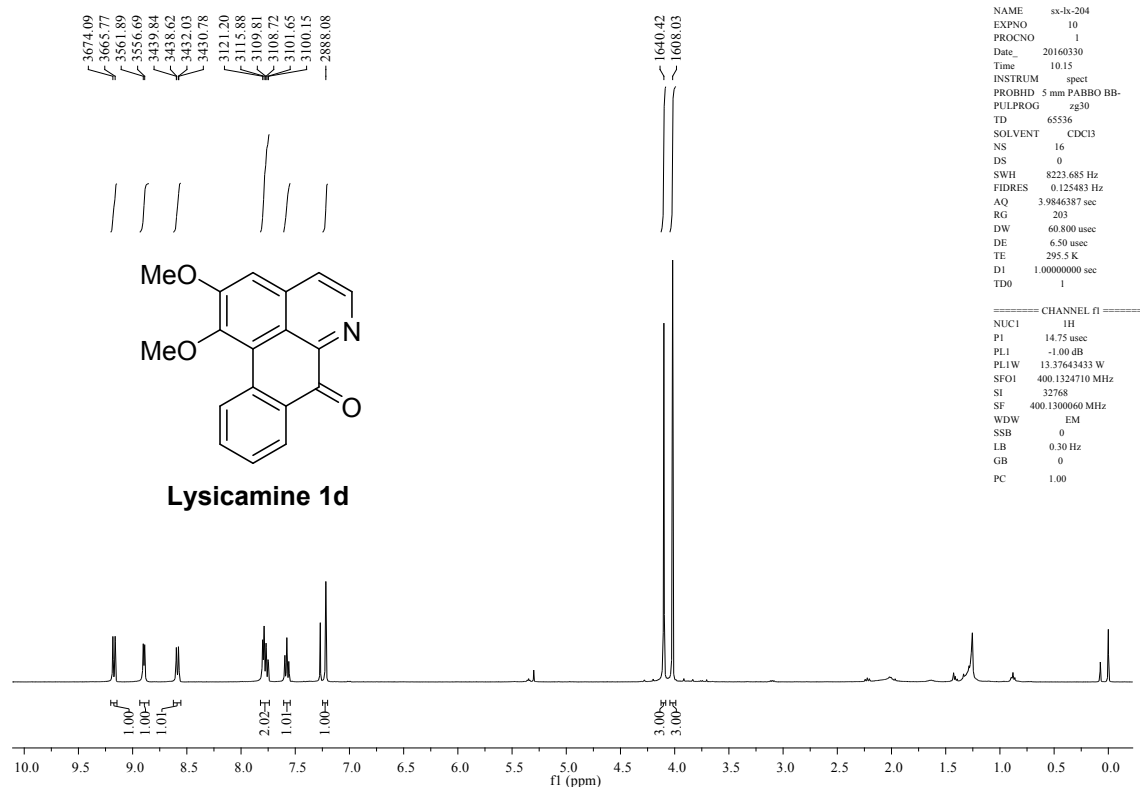
¹H NMR (CDCl₃-TFA, 400 MHz) spectrum of compound **1c**:



¹³C NMR (CDCl₃-TFA, 100 MHz) spectrum of compound **1c**:



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

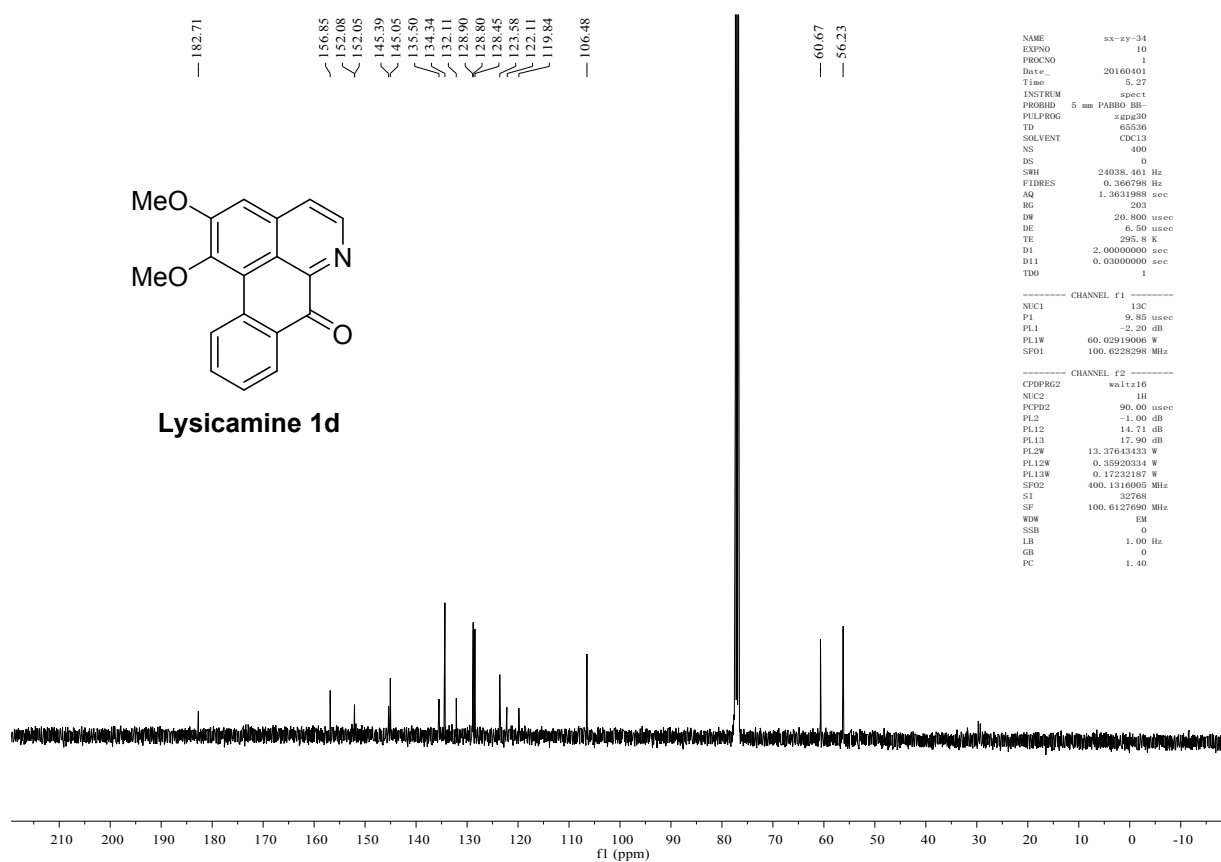


```

NAME      sx-bv-204
EXPNO     10
PROCNO    1
Date_     20160330
Time      10.15
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         295.5 K
D1         1.00000000 sec
D10        1
===== CHANNEL f1 =====
NUC1       1H
P1         14.75 usec
PL1        -1.00 dB
PL1W       13.37643433 W
SFO1       400.1324710 MHz
SI         32768
SF         400.1300060 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00

```

¹³C NMR (CDCl₃, 100 MHz) spectrum of compound **1d**:

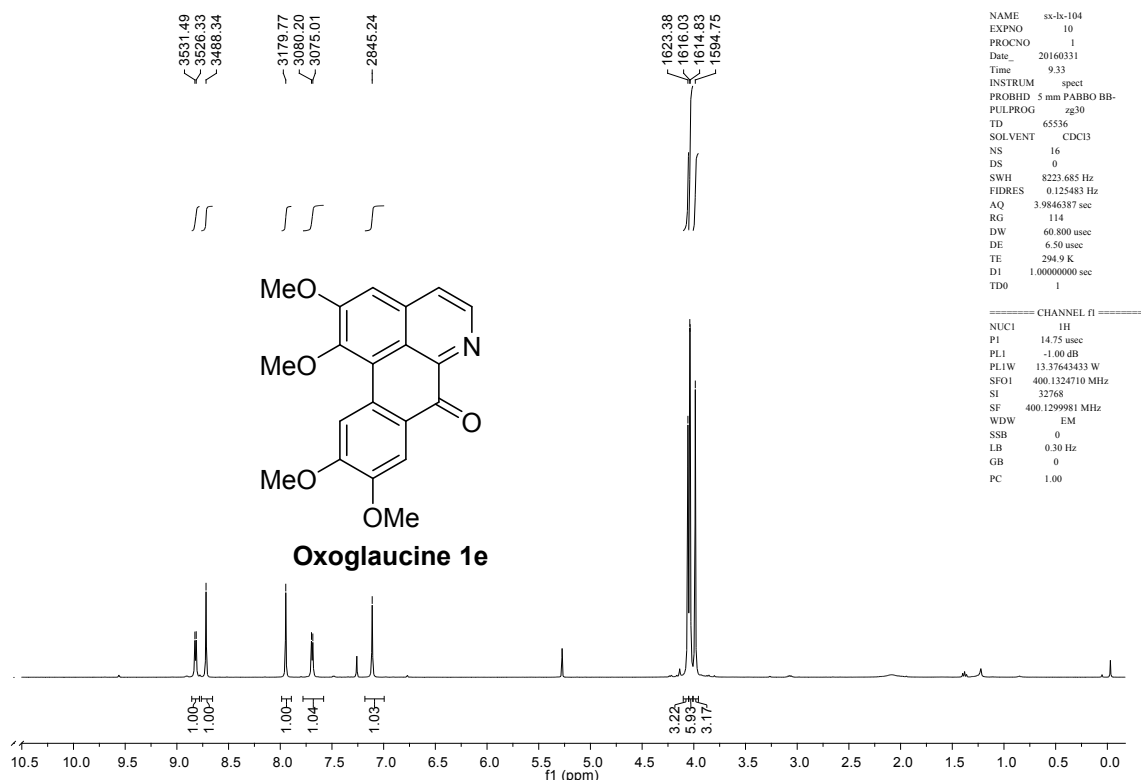


```

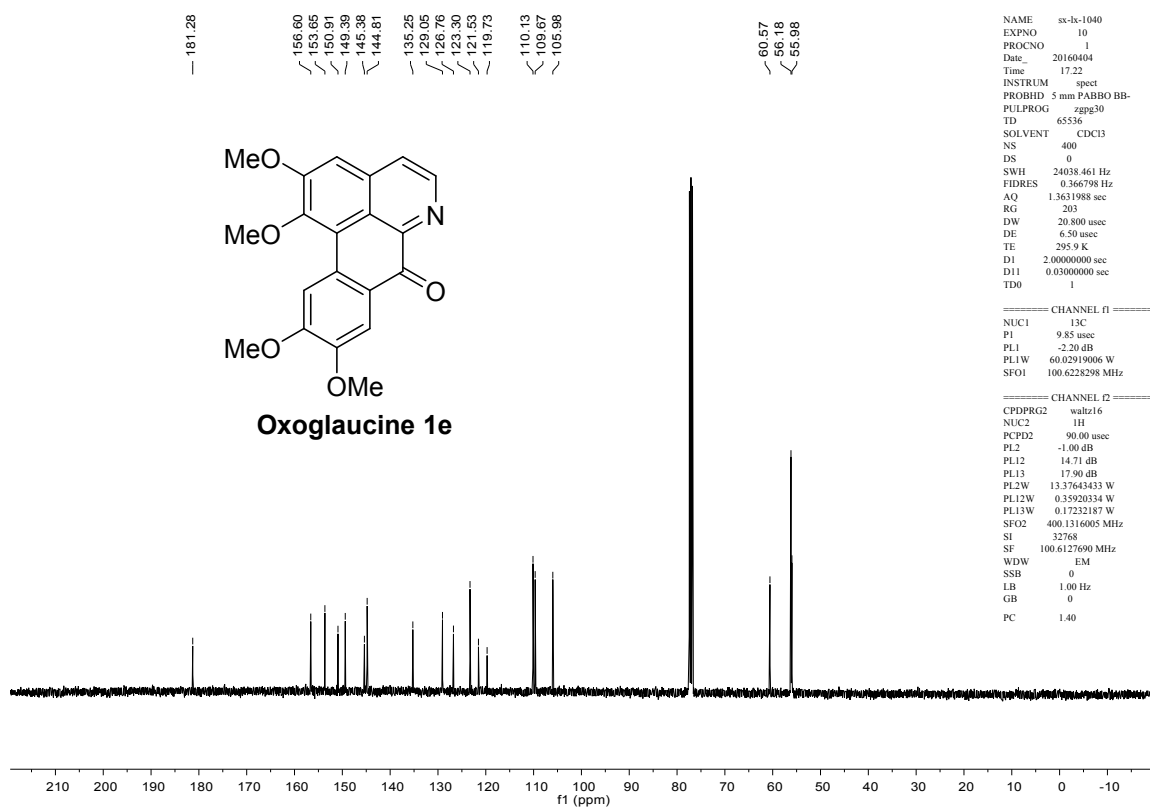
NAME      sx-zy-34
EXPNO     10
PROCNO    1
Date_     20160401
Time      5.27
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         400
DS         0
SWH        24038.461 Hz
FIDRES     0.366798 Hz
AQ         1.3631988 sec
RG         203
DW         20.800 usec
DE         6.50 usec
TE         295.5 K
D1         2.00000000 sec
D11        0.03000000 sec
D10        1
===== CHANNEL f1 =====
NUC1       13C
P1         9.35 usec
PL1        -2.20 dB
PL1W       60.02919006 W
SFO1       100.62282998 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

```

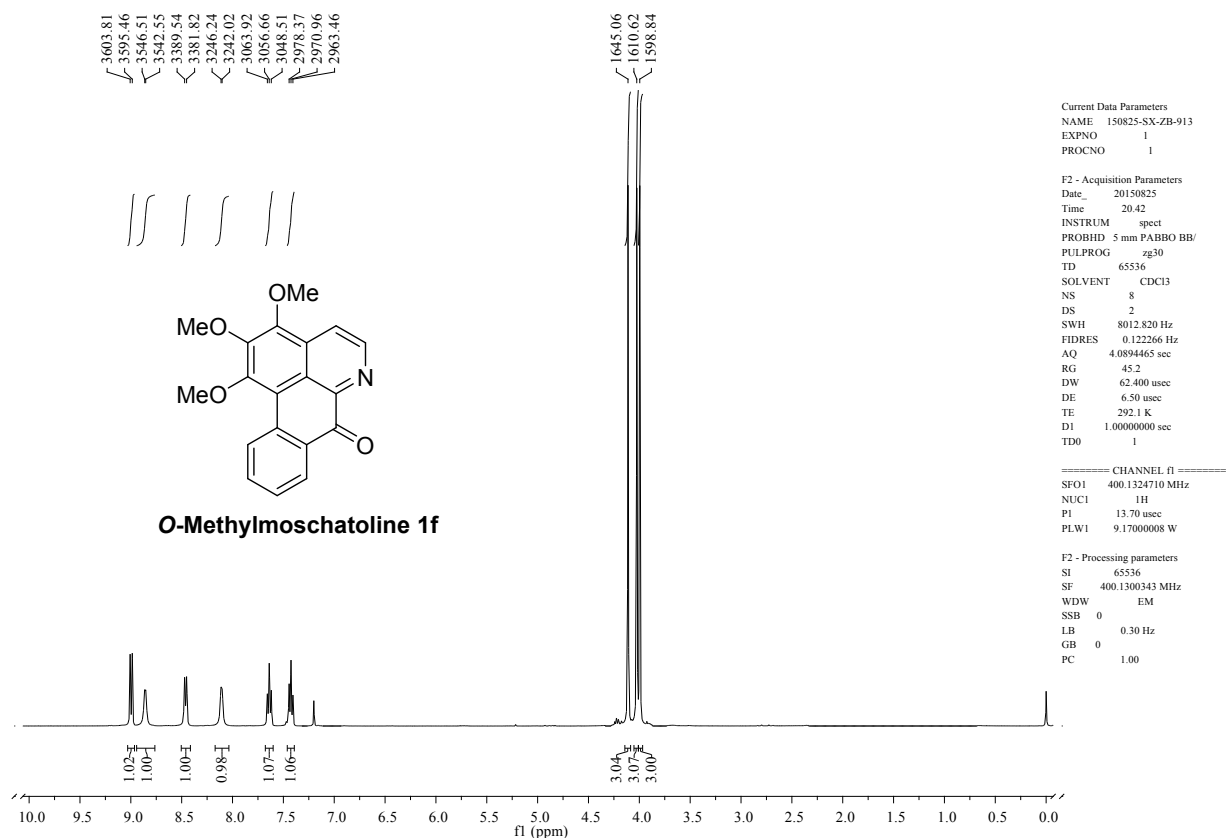
¹H NMR (CDCl₃, 400 MHz) spectrum of compound **1e**:



¹³C NMR (CDCl₃, 100 MHz) spectrum of compound **1e**:



^1H NMR (CDCl_3 , 400 MHz) spectrum of compound **1f**:



^{13}C NMR (CDCl_3 , 100 MHz) spectrum of compound **1f**:

