

Supporting information

Oxygen Free Csp³-H Oxidation of Pyridin-2-yl-methanes to Pyridin-2-yl-methanones with Water by Copper Catalysis

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Deng-Zhao Jiang ^{1,4} and Jin-Jing Li ^{2,*}

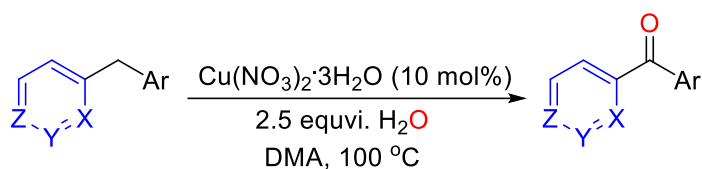
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2-pyridyl
3-pyridyl
4-pyridyl

Ar = Benzyl, thiophenyl,
thiazolyl, pyridyl, triazine

16 examples

Yield up to 92%

- O₂ free
- H₂O as oxygen source
- Mild conditions

We describe an efficient copper catalyzed synthesis of pyridin-2-yl-methanones from pyridin-2-yl-methanes by direct Csp³-H oxidation approach with water under mild conditions. Pyridin-2-yl-methanes with aromatic rings such as substituted benzene, thiophene, thiazole, pyridine, triazine, undergo the reaction well to obtain the corresponding products in moderate to good yields. Several controlled experiments are operated for the mechanism exploration, indicating that water participates in the oxidation process and it is the single oxygen source in this transformation. The current work provides a new sight for water involved oxidation reactions.

Contents

Figures	NMR spectra	Pages
1	¹ H NMR spectra of 2a	S1
2	¹³ C NMR spectra of 2a	S2
3	¹ H NMR spectra of 2b	S3
4	¹³ C NMR spectra of 2b	S4
5	¹ H NMR spectra of 2c	S5
6	¹³ C NMR spectra of 2c	S6
7	¹ H NMR spectra of 2d	S7
8	¹³ C NMR spectra of 2d	S8
9	¹ H NMR spectra of 2e	S9
10	¹³ C NMR spectra of 2e	S10
11	¹⁹ F NMR spectra of 2e	S11
12	¹ H NMR spectra of 2f	S12
13	¹³ C NMR spectra of 2f	S13
14	¹ H NMR spectra of 2g	S14
15	¹³ C NMR spectra of 2g	S15
16	¹ H NMR spectra of 2h	S16
17	¹³ C NMR spectra of 2h	S17
18	¹ H NMR spectra of 2i	S18
19	¹³ C NMR spectra of 2i	S19
20	¹ H NMR spectra of 2j	S20
21	¹³ C NMR spectra of 2j	S21
22	¹ H NMR spectra of 2k	S22
23	¹³ C NMR spectra of 2k	S23
24	¹ H NMR spectra of 2l	S24
25	¹³ C NMR spectra of 2l	S25
26	¹ H NMR spectra of 2m	S26
27	¹³ C NMR spectra of 2m	S27
28	¹ H NMR spectra of 2n	S28
29	¹³ C NMR spectra of 2n	S29
30	¹ H NMR spectra of 2o	S30
31	¹³ C NMR spectra of 2o	S31
32	¹ H NMR spectra of 2p	S32
33	¹³ C NMR spectra of 2p	S33
34	¹ H NMR spectra of 2r	S34
35	¹³ C NMR spectra of 2r	S35

8.7121 8.7103 8.7081 8.7001 8.6984 8.6962
8.0588 8.0570 8.0392 8.0358 8.0300 8.0102
7.5949 7.5926 7.5896 7.5792 7.5783 7.5739 7.5696 7.5579 7.5557 7.5525 7.4870 7.4835 7.4813 7.4782 7.4674 7.4627 7.4592 7.4491 7.4474 7.2502

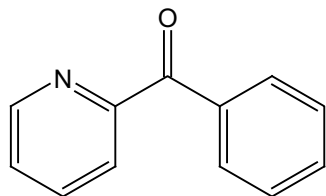
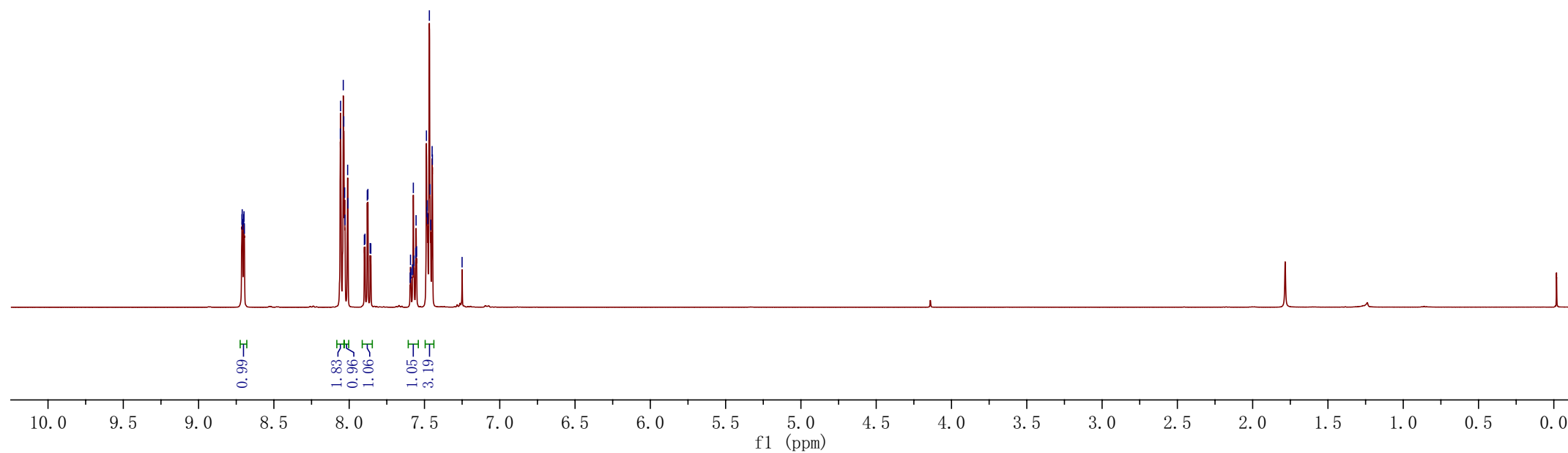


Figure S1. ^1H spectrum of **2a** in CDCl_3



193.8876

155.1326

148.5673

137.0542

136.2912

132.9260

130.9929

128.1718

126.1595

124.6247

2

77.3729

77.0553

76.7376

S2

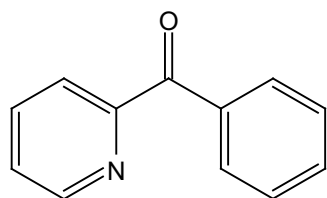
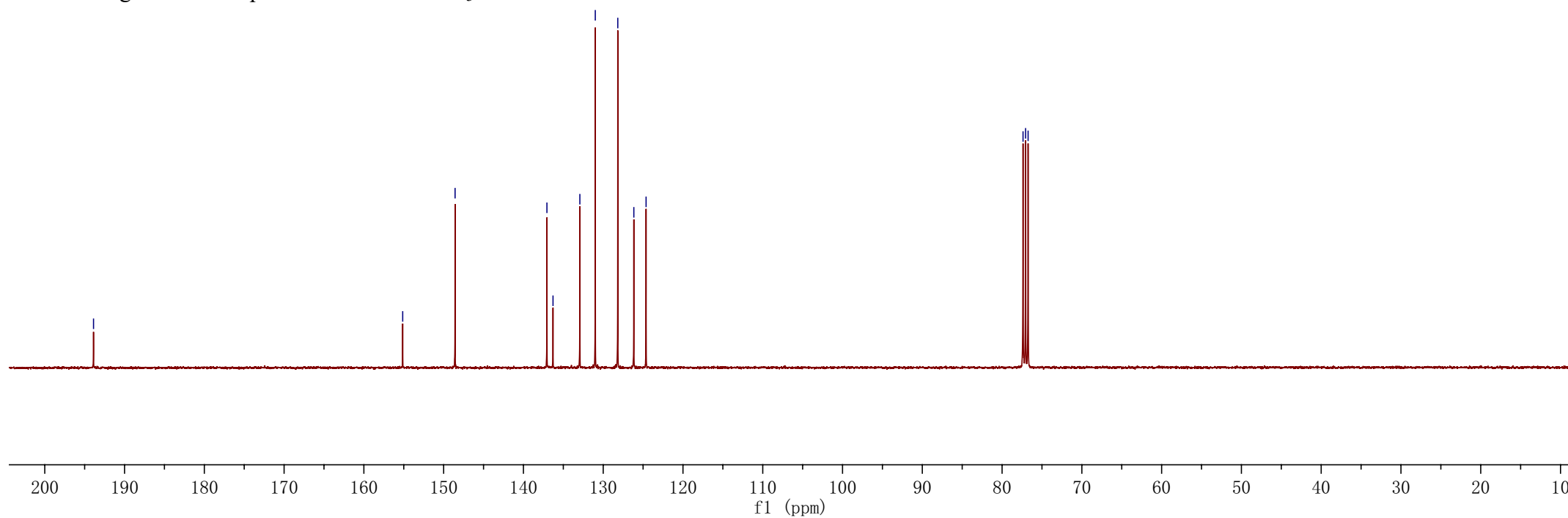


Figure S2. ^{13}C spectrum of **2a** in CDCl_3



8.7501
8.7485
8.7466
8.7382
8.7367
8.0539
8.0482
8.0434
8.0347
8.0318
8.0266
7.9082
7.5364
7.5318
7.5196
7.5149
7.5104
7.4984
7.4956
7.4917
7.4888
7.4795
7.4768
7.2817

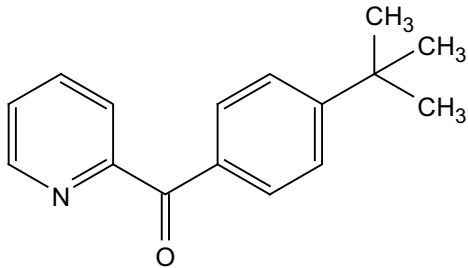
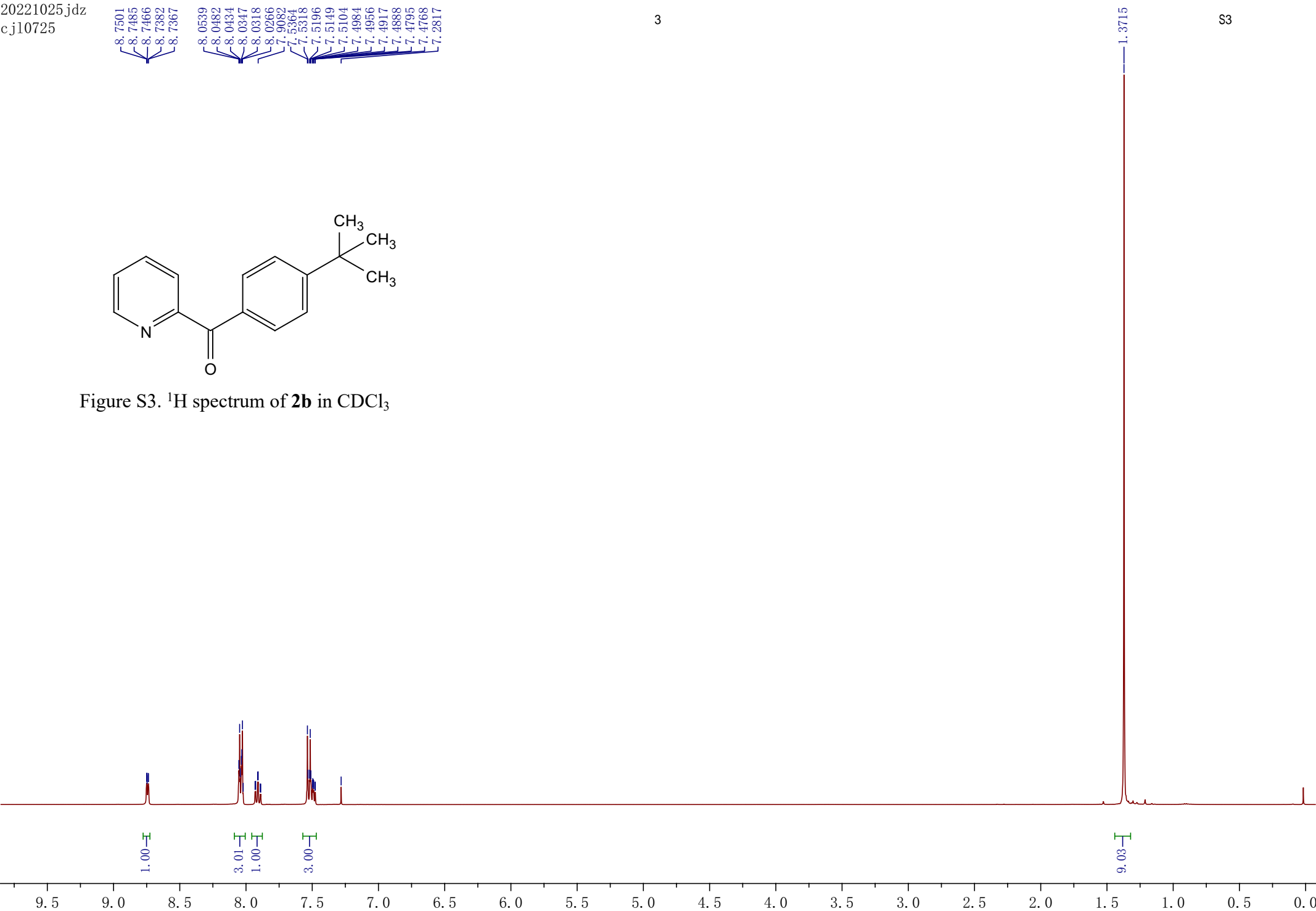


Figure S3. ¹H spectrum of **2b** in CDCl₃



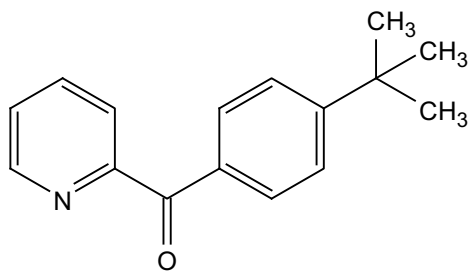
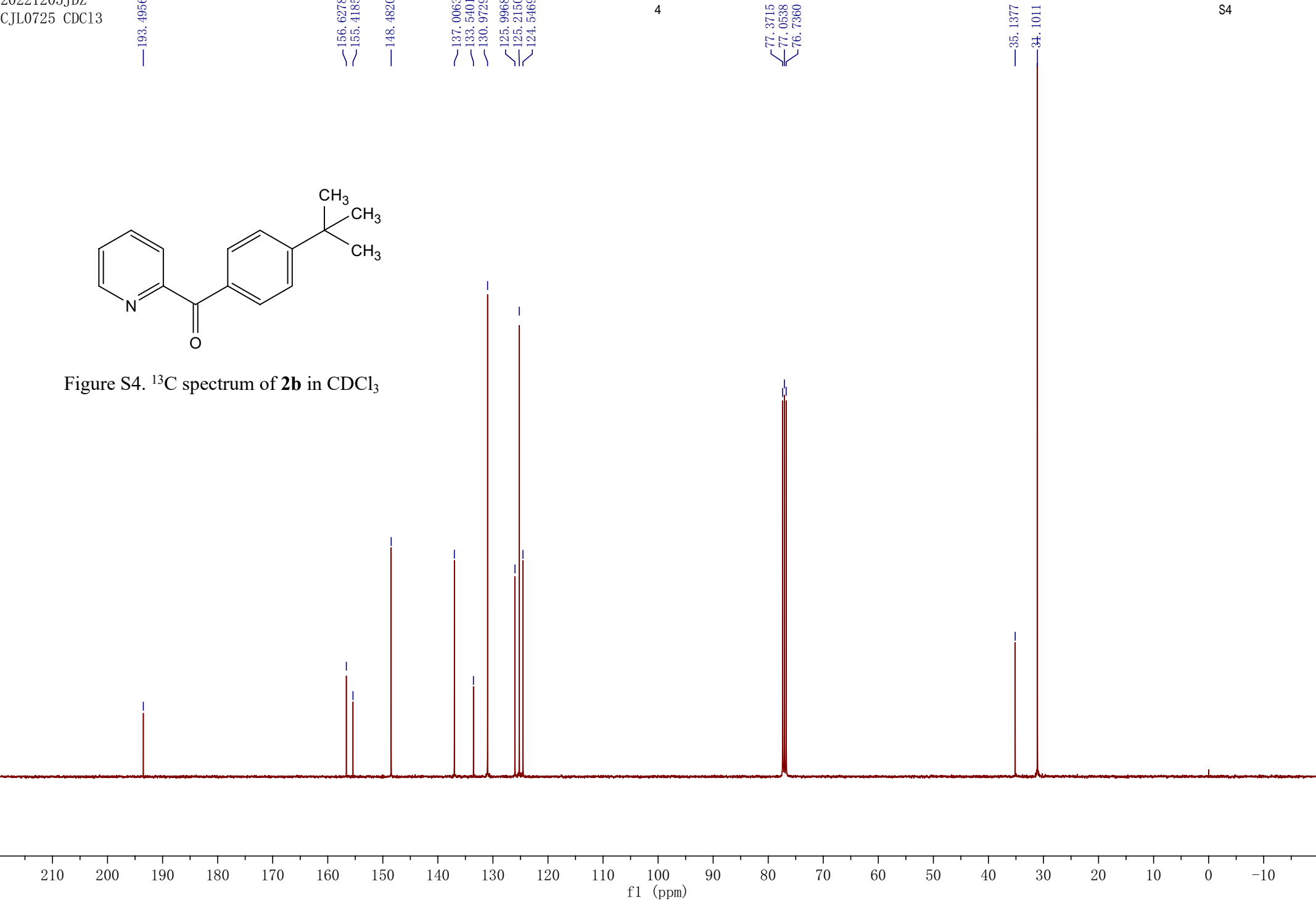


Figure S4. ¹³C spectrum of **2b** in CDCl₃



8.7257
 8.7244
 8.7140
 8.1866
 7.9528
 7.9330
 7.7328
 7.7302
 7.5689
 7.5643
 7.5559
 7.5486
 7.5400
 7.5310
 7.2817

1.5975

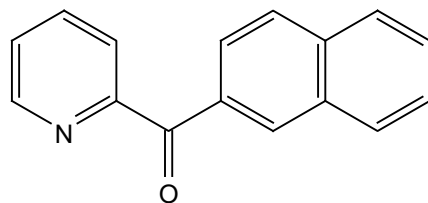
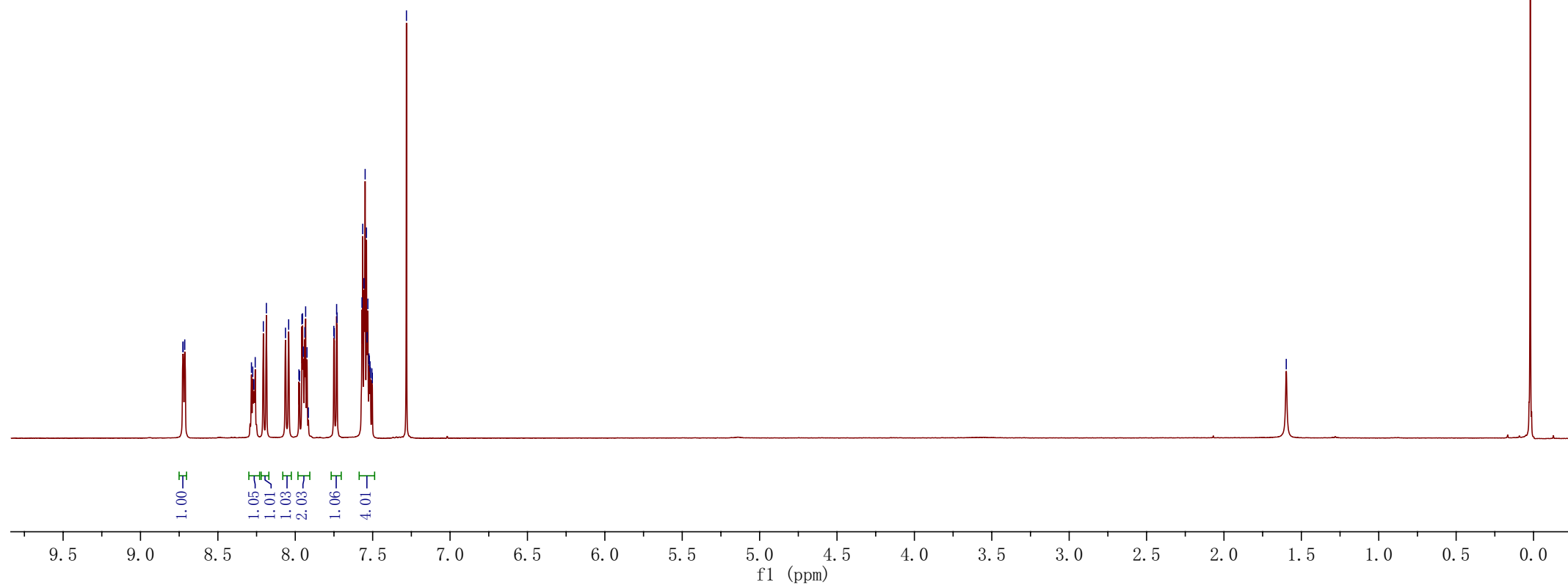


Figure S5. ¹H spectrum of **2c** in CDCl₃



— 196.5869

— 155.5215

— 149.1930

— 137.0035

— 134.7019

— 133.8449

— 132.2412

— 131.2772

— 129.9458

— 128.4813

— 127.4439

— 126.5374

— 126.3179

— 125.6869

— 124.6193

— 124.1878

6

S6

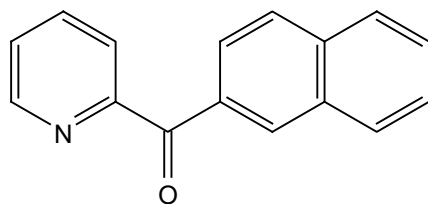
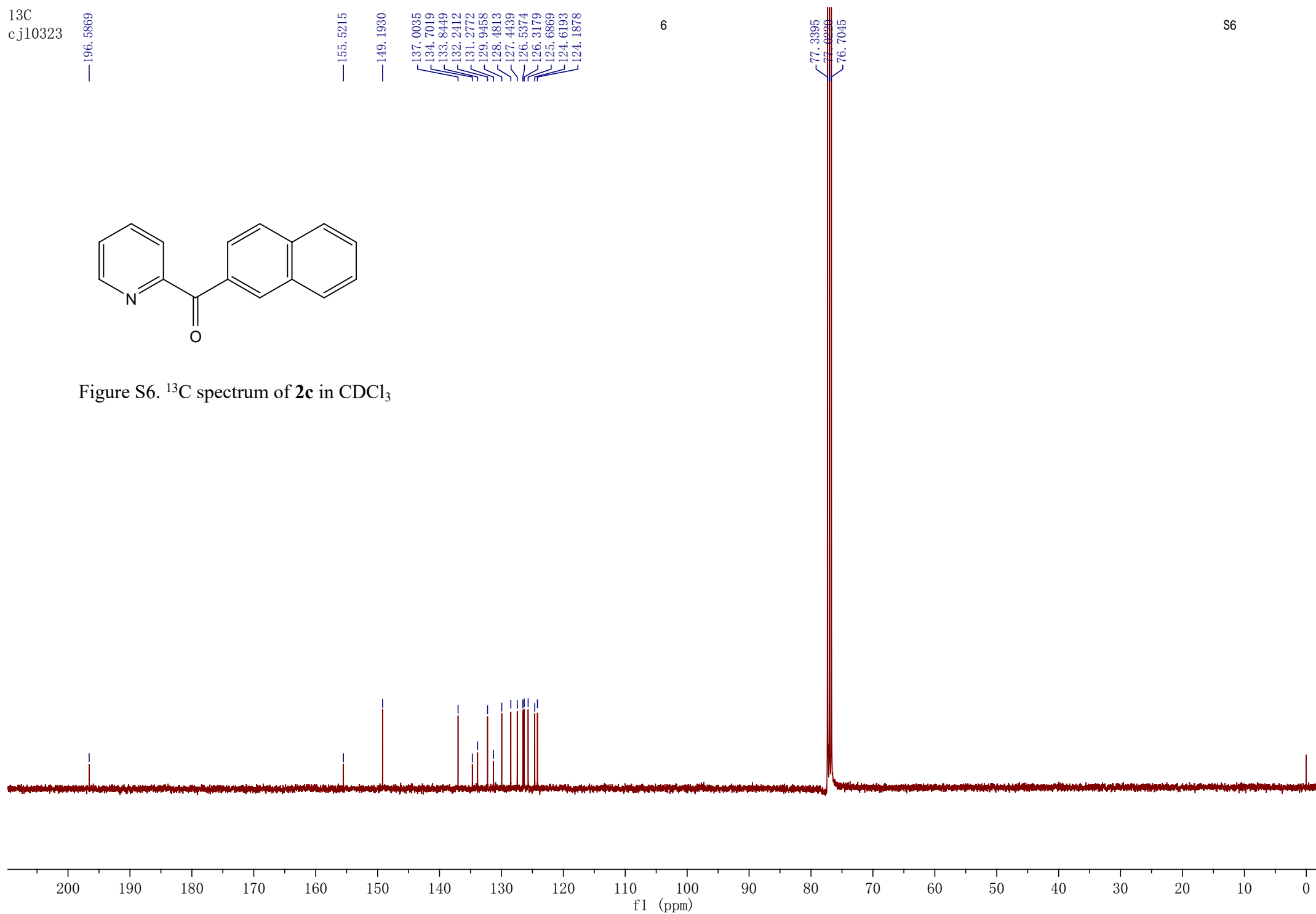


Figure S6. ¹³C spectrum of **2c** in CDCl₃



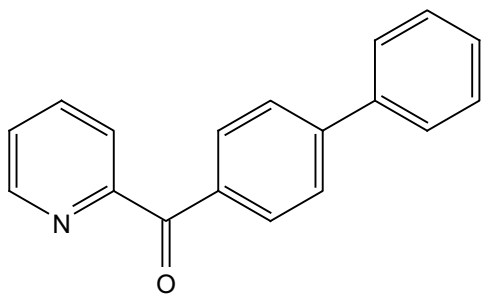
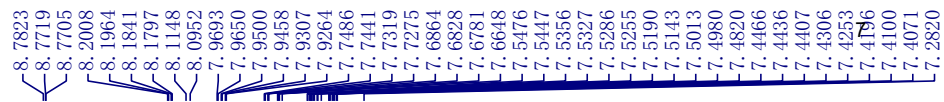
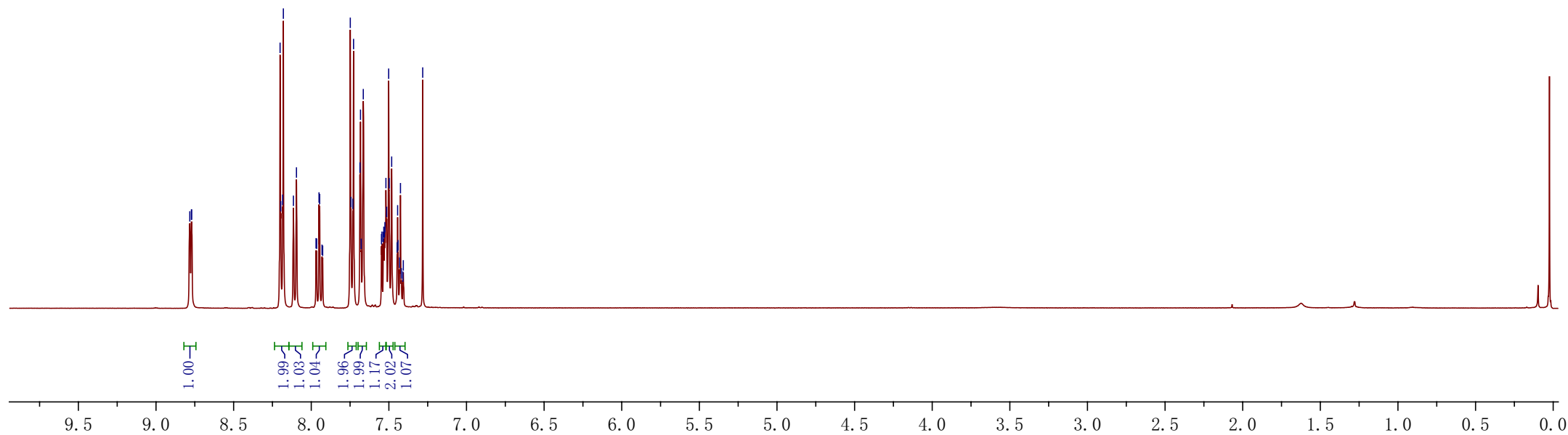
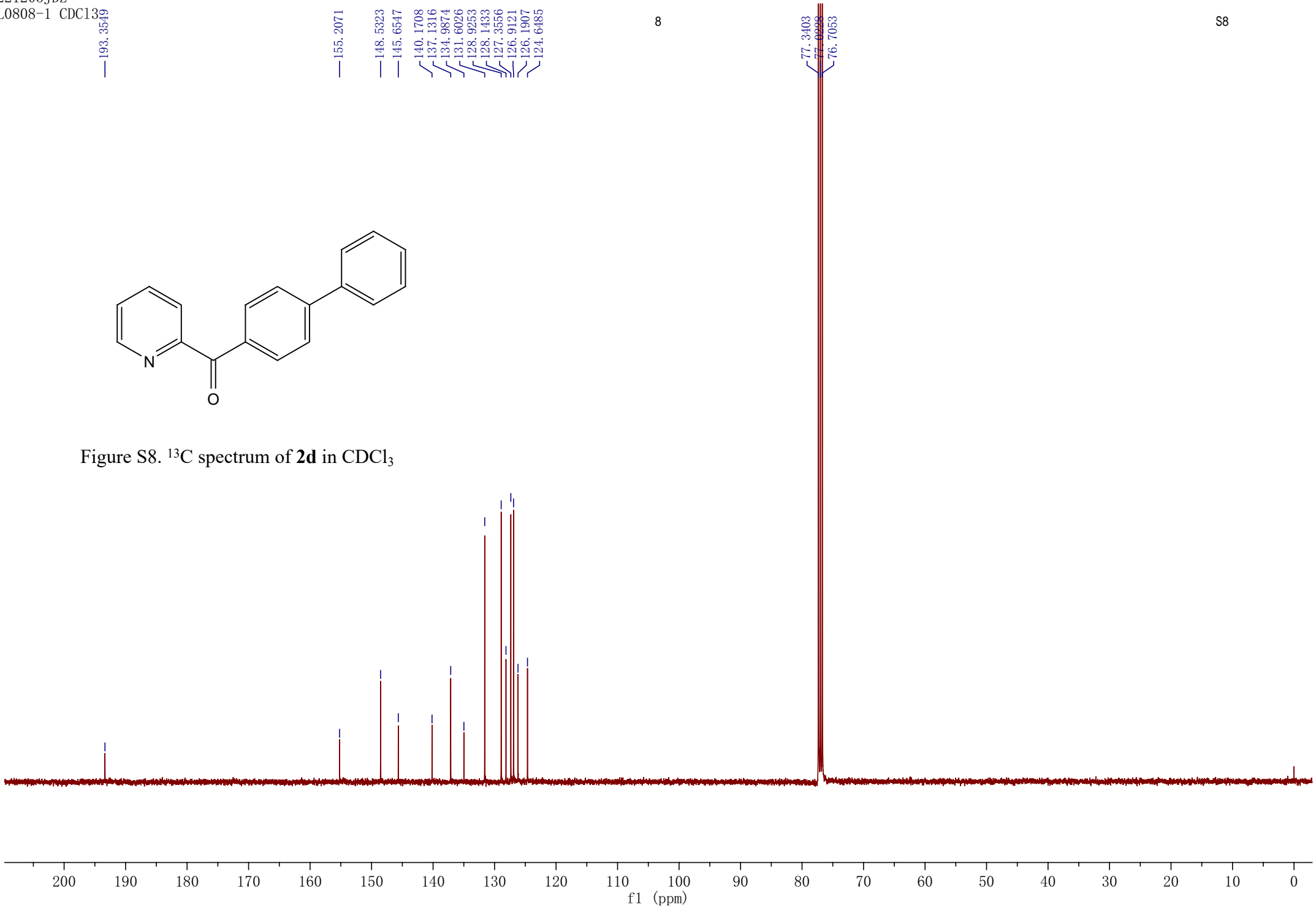
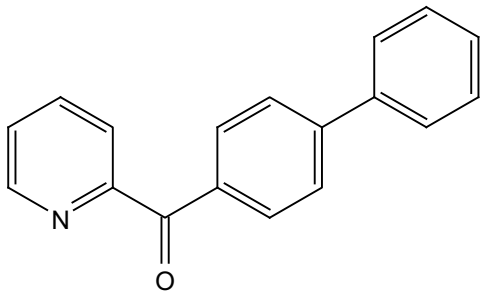


Figure S7. ^1H spectrum of **2d** in CDCl_3





8.7390
8.7375
8.7272
8.7257
8.1102
8.0906
8.0733
8.0541
8.0154
7.9272
7.9230
7.5503
7.5363
7.5303
7.5245
7.5215
7.5173
7.5142
7.5107
7.5054
7.5025
7.4635
7.4608
7.4580
7.4430
7.4402
7.4375

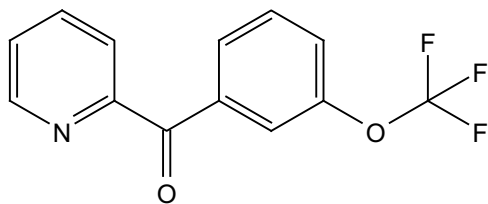
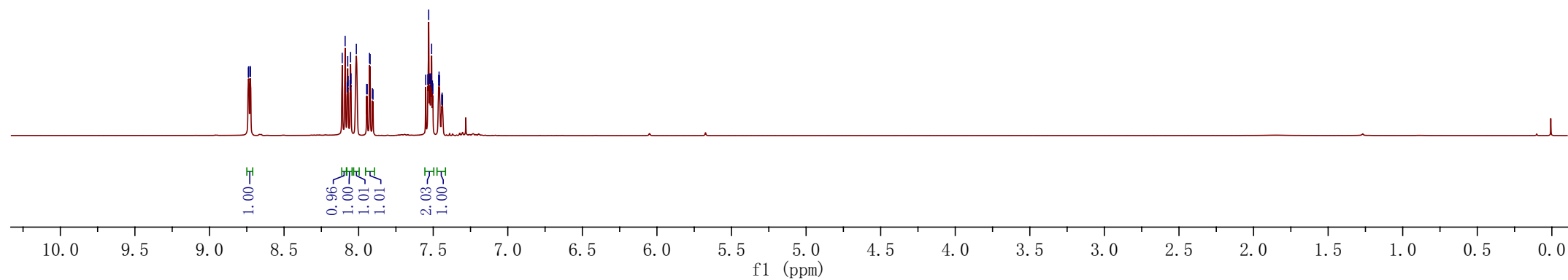


Figure S9. ^1H spectrum of **2e** in CDCl_3



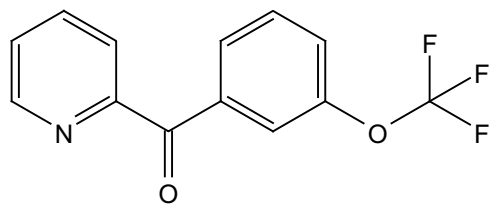
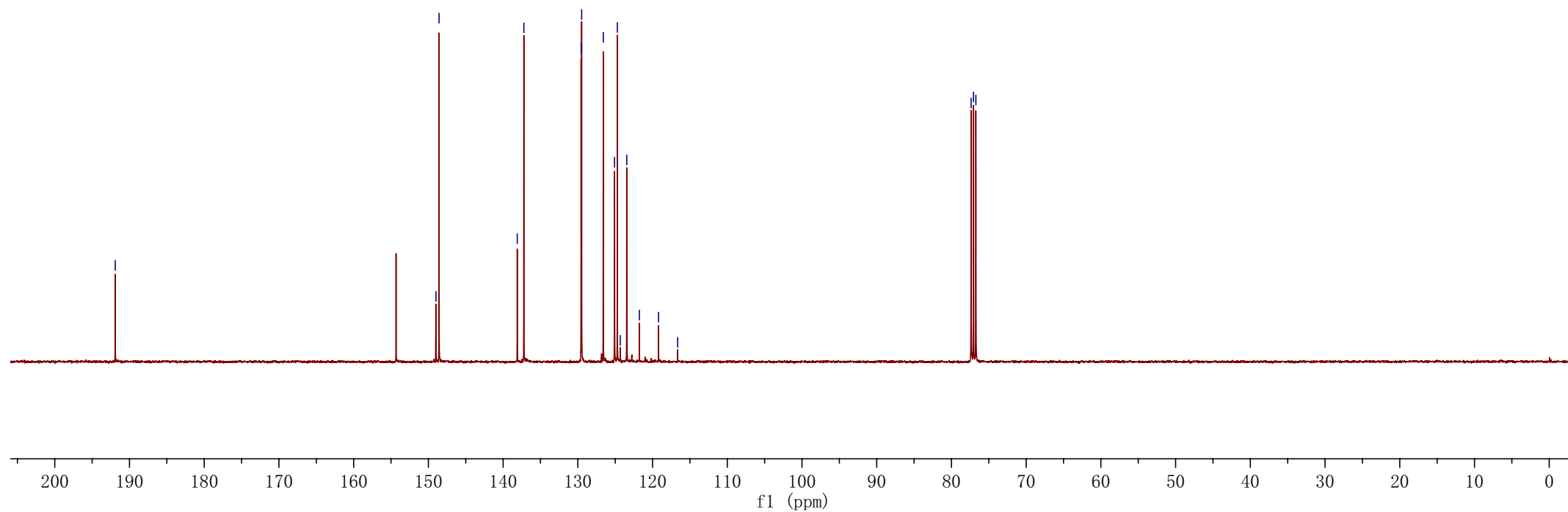
—191.9073

148.9825
148.5722138.1087
137.2210129.5600
129.4882
126.5948
125.0864
124.7120
124.3226
123.4499
121.7605
119.1984
116.6362

10

77.3654
77.0475
76.7296

S10

Figure S10. ^{13}C spectrum of **2e** in CDCl_3 

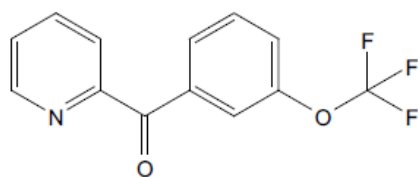
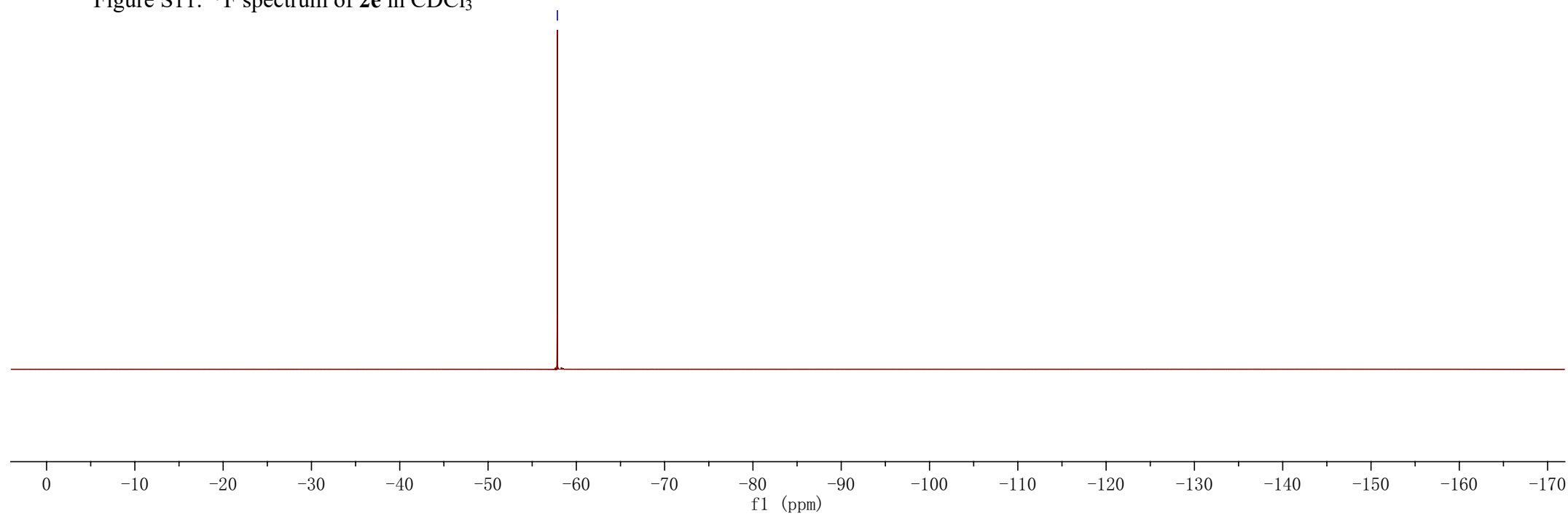


Figure S11. ¹⁹F spectrum of **2e** in CDCl₃



8.7515
8.7495
8.7411
8.7396
8.1058
8.0993
8.0946
8.0865
8.0831
8.0777
7.9451
7.5526
7.5497
7.5407
7.5377
7.5337
7.5308
7.5217
7.5188
7.5056
7.4997
7.4951
7.4830
7.4782
7.4725
7.2821

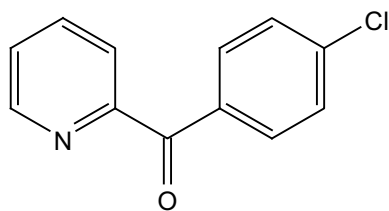
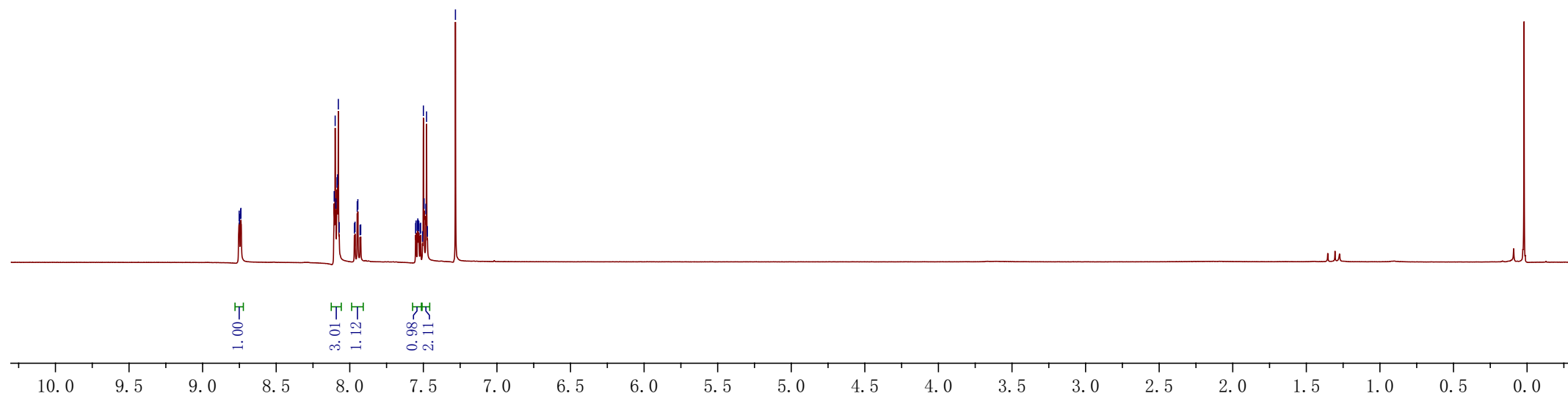


Figure S12. ^1H spectrum of **2f** in CDCl_3



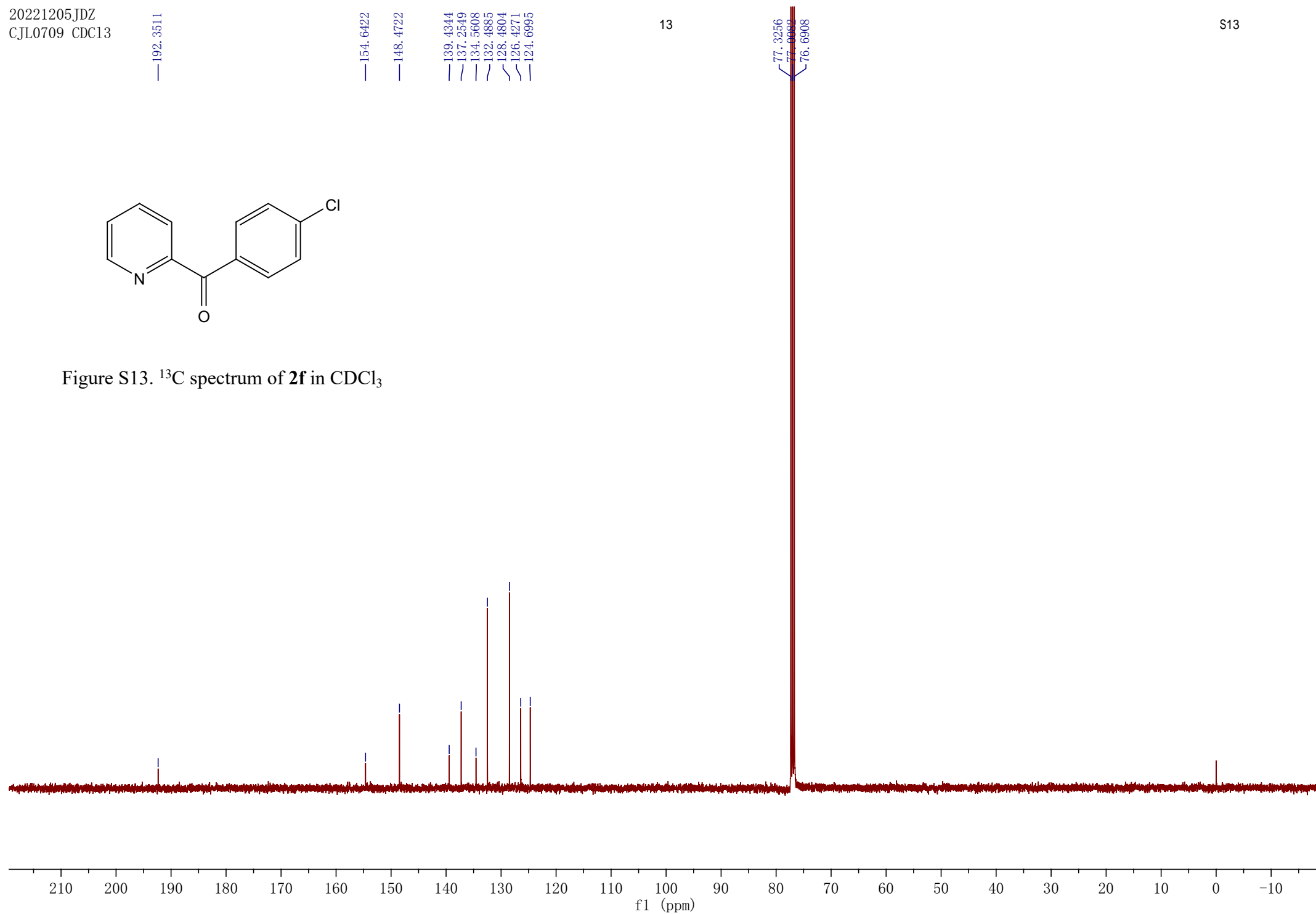
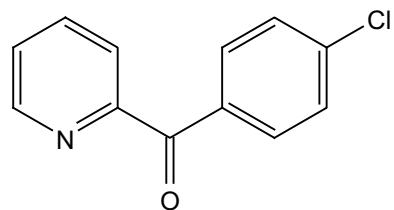


Figure S13. ¹³C spectrum of **2f** in CDCl₃

8.7636
8.7619
8.7598
8.7517
8.7500
8.1082
8.1048
8.1002
8.0881
7.9935
7.9468
7.5997
7.5971
7.5946
7.5919
7.5797
7.5771
7.5746
7.5719
7.5661
7.5532
7.5442
7.5412
7.5372
7.5342
7.5252
7.5223
7.4740
7.4544
7.4346
7.2819

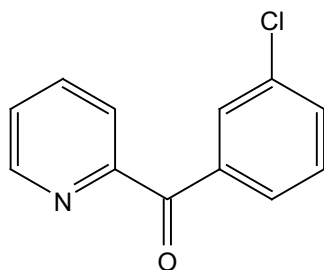
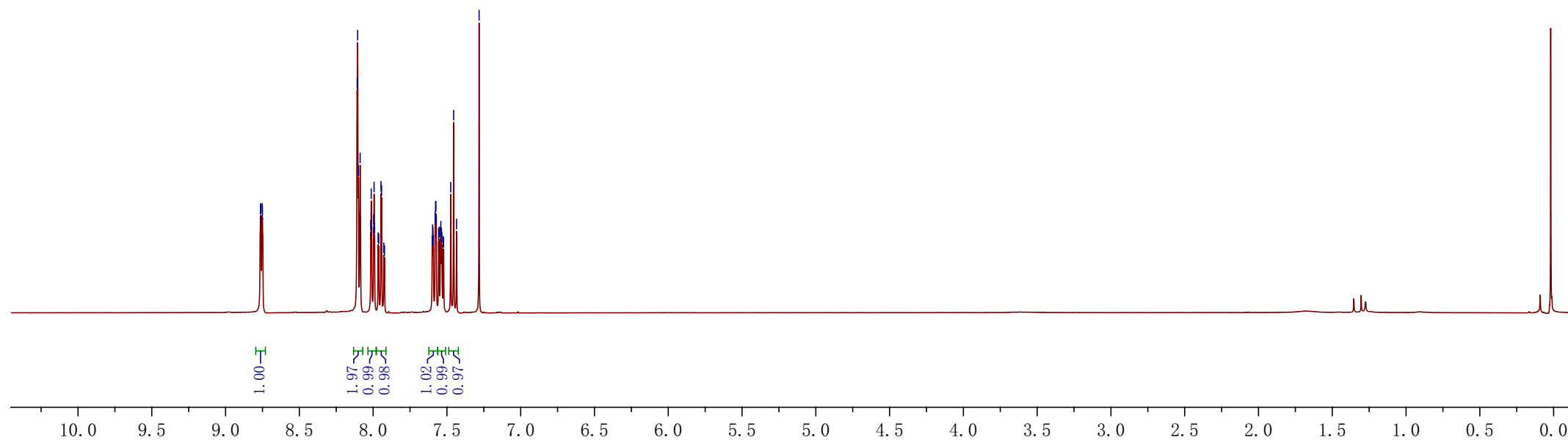


Figure S14. ^1H spectrum of **2g** in CDCl_3



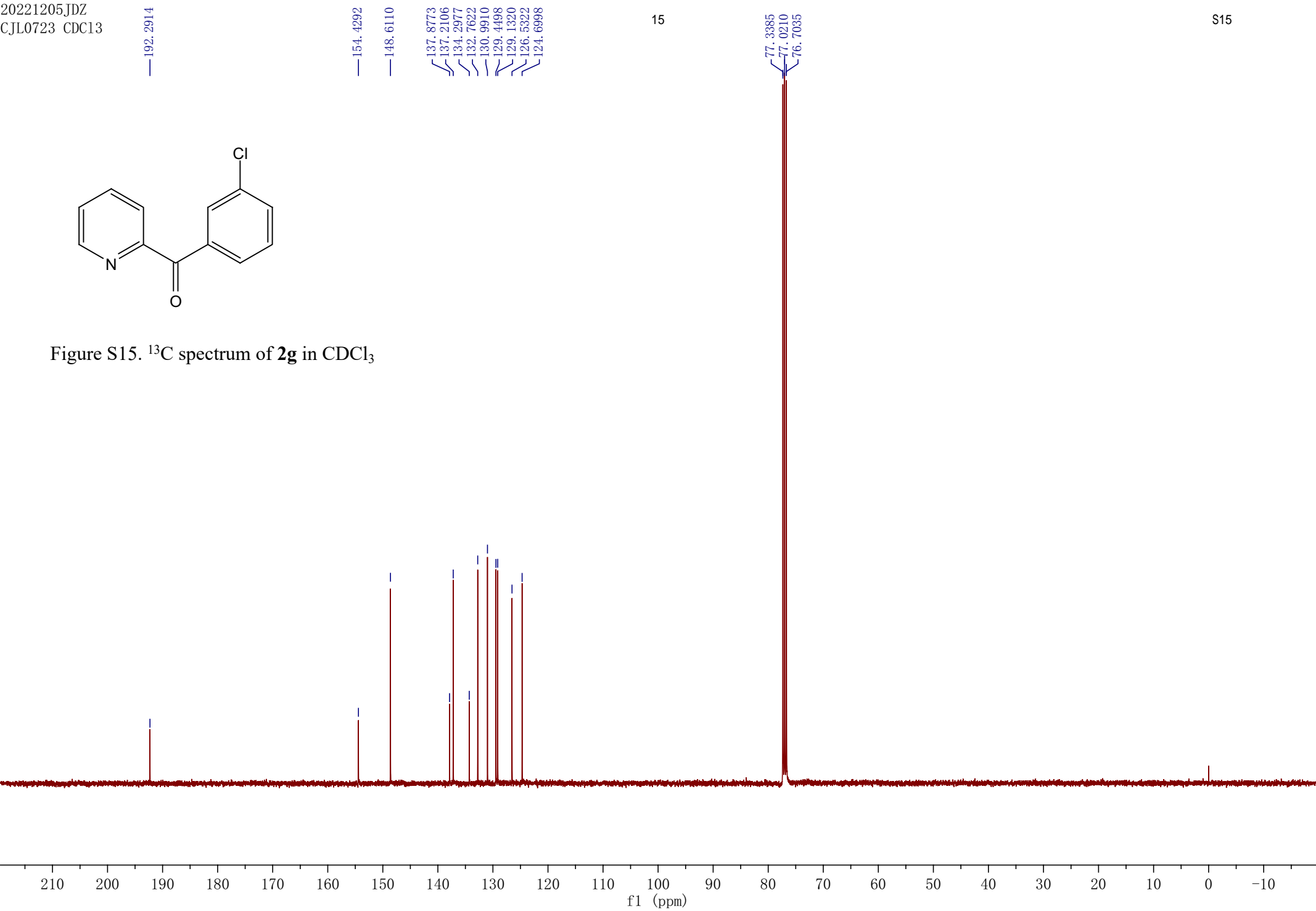


Figure S15. ¹³C spectrum of **2g** in CDCl₃

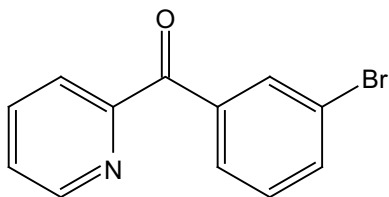
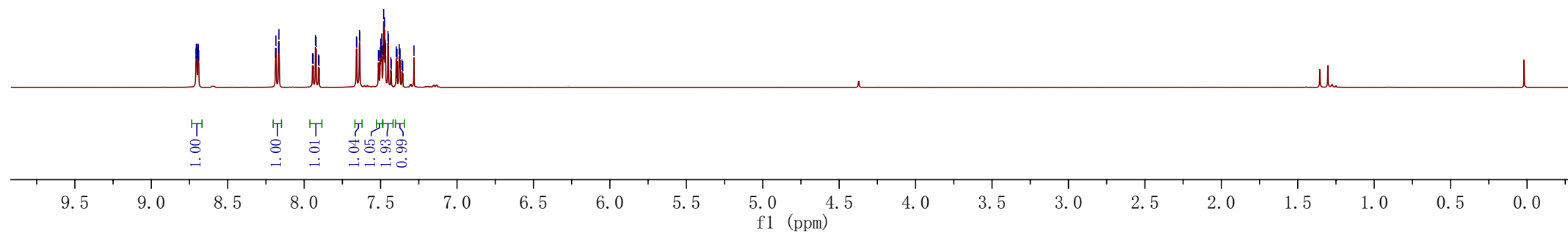


Figure S16. ^1H spectrum of **2h** in CDCl_3



195.7834

153.5043

149.3512

140.3254

137.0321

133.0437

131.5105

129.8470

127.0835

126.9667

123.9374

120.0884

17

77.3563

77.0386

76.7210

S17

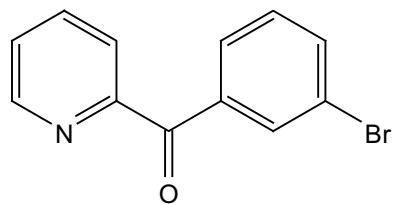
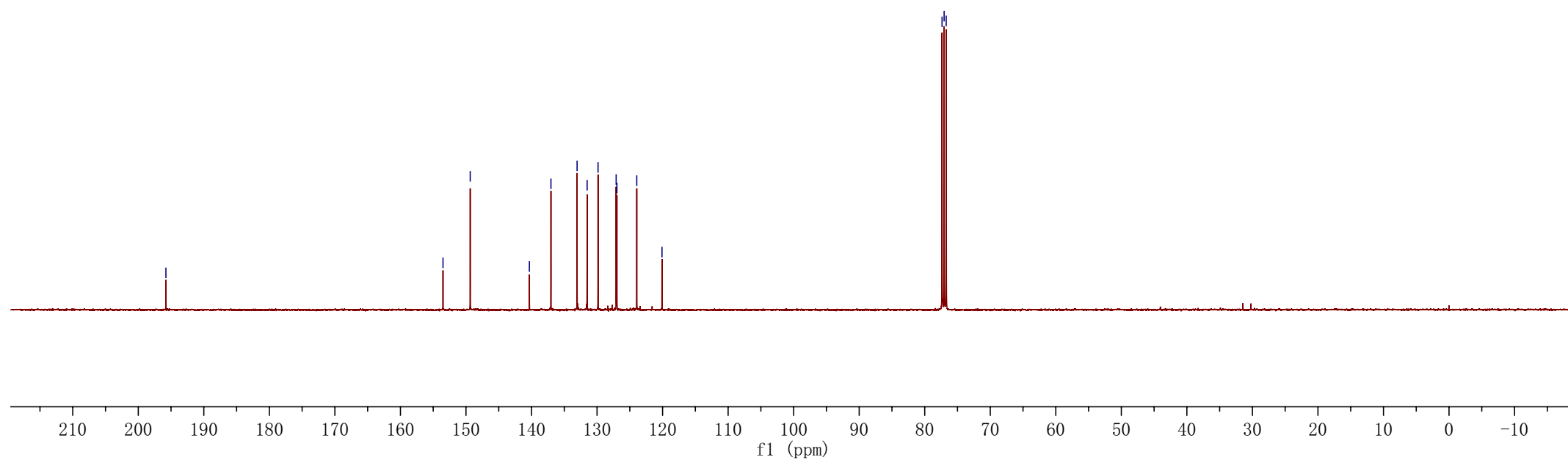


Figure S17. ¹³C spectrum of **2h** in CDCl₃



8.7550
8.7445
8.7433
8.6703
8.6664
8.6627
8.3187
8.2994
8.1406
8.1210
7.9579
7.9537
7.6399
7.6205
7.6011
7.5467
7.2819

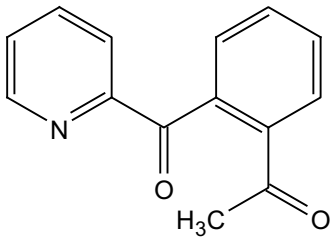
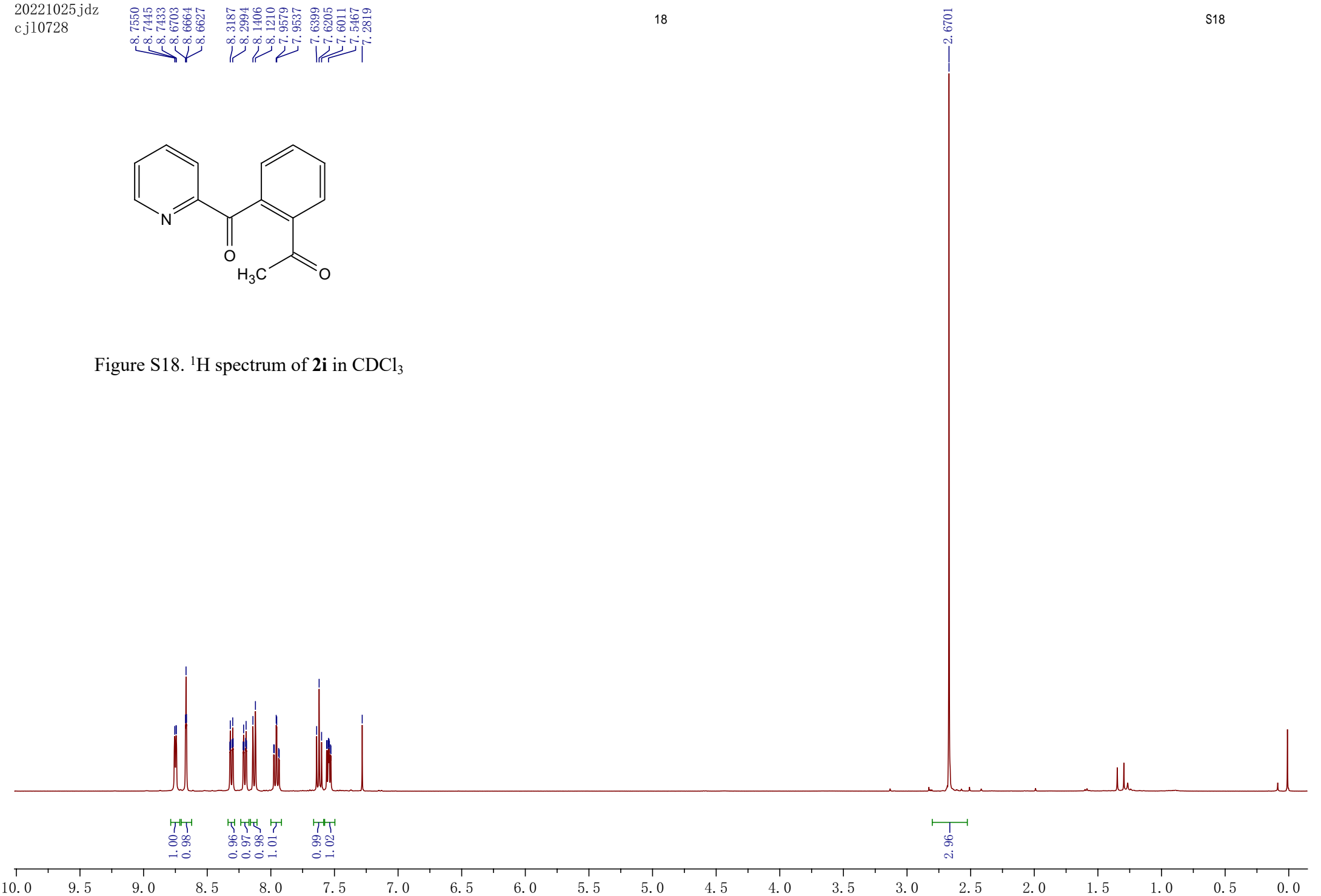


Figure S18. ¹H spectrum of **2i** in CDCl₃



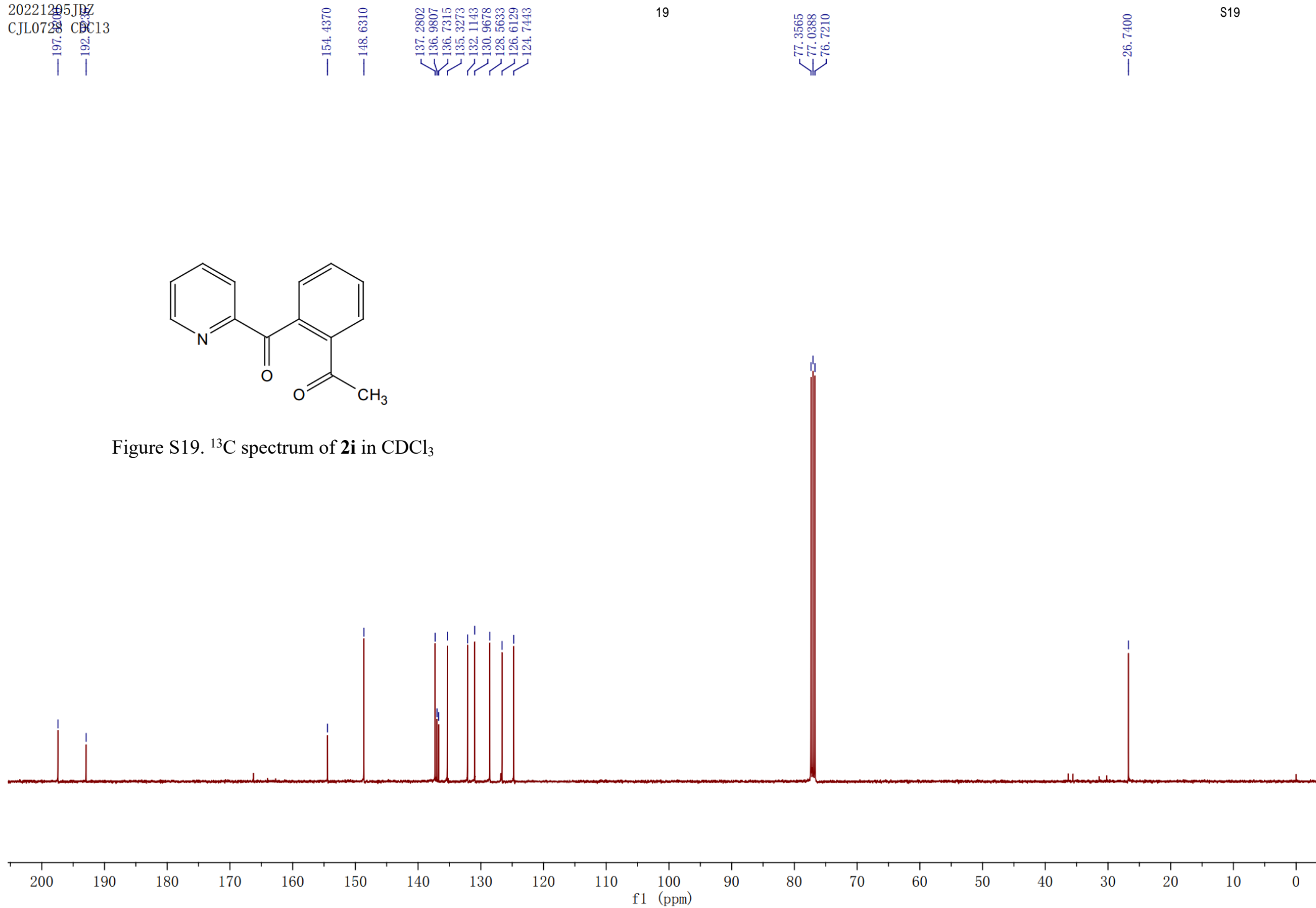


Figure S19. ¹³C spectrum of **2i** in CDCl₃

8.7589
8.7471
8.1654
8.1599
8.1501
8.1340
8.1312
8.1146
7.9537
7.9494
7.5591
7.5472
7.5442
7.2819

3.9780

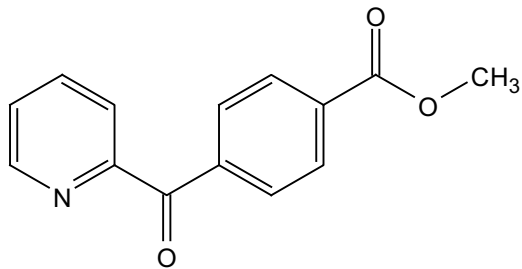
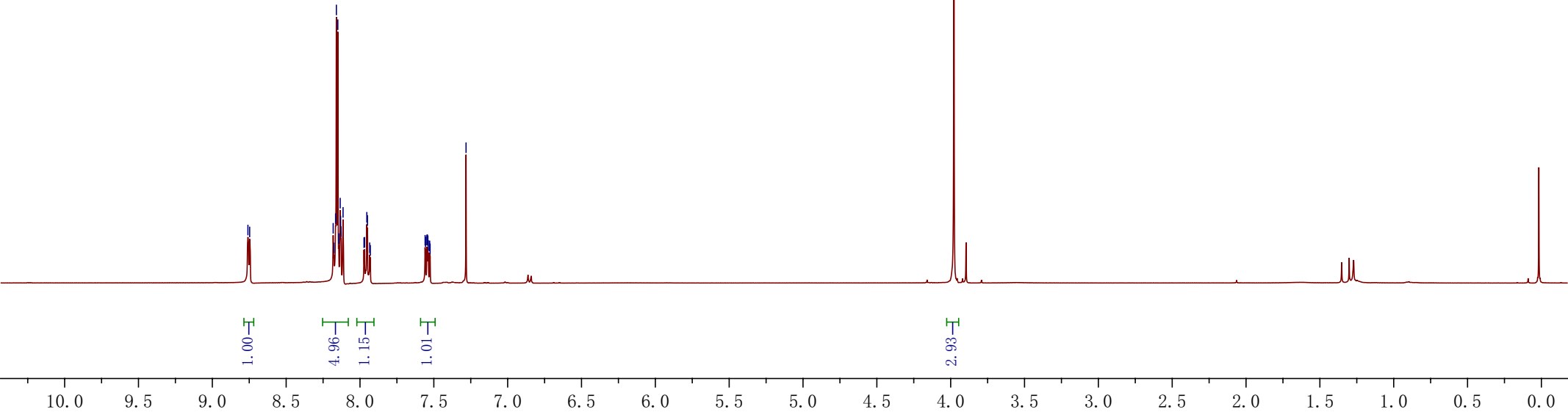


Figure S20. ¹H spectrum of **2j** in CDCl₃



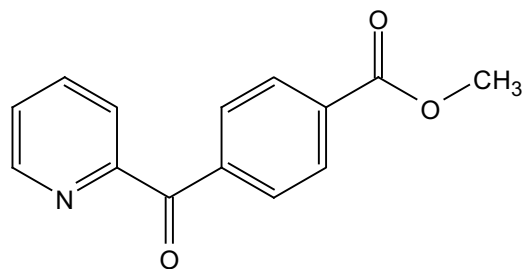
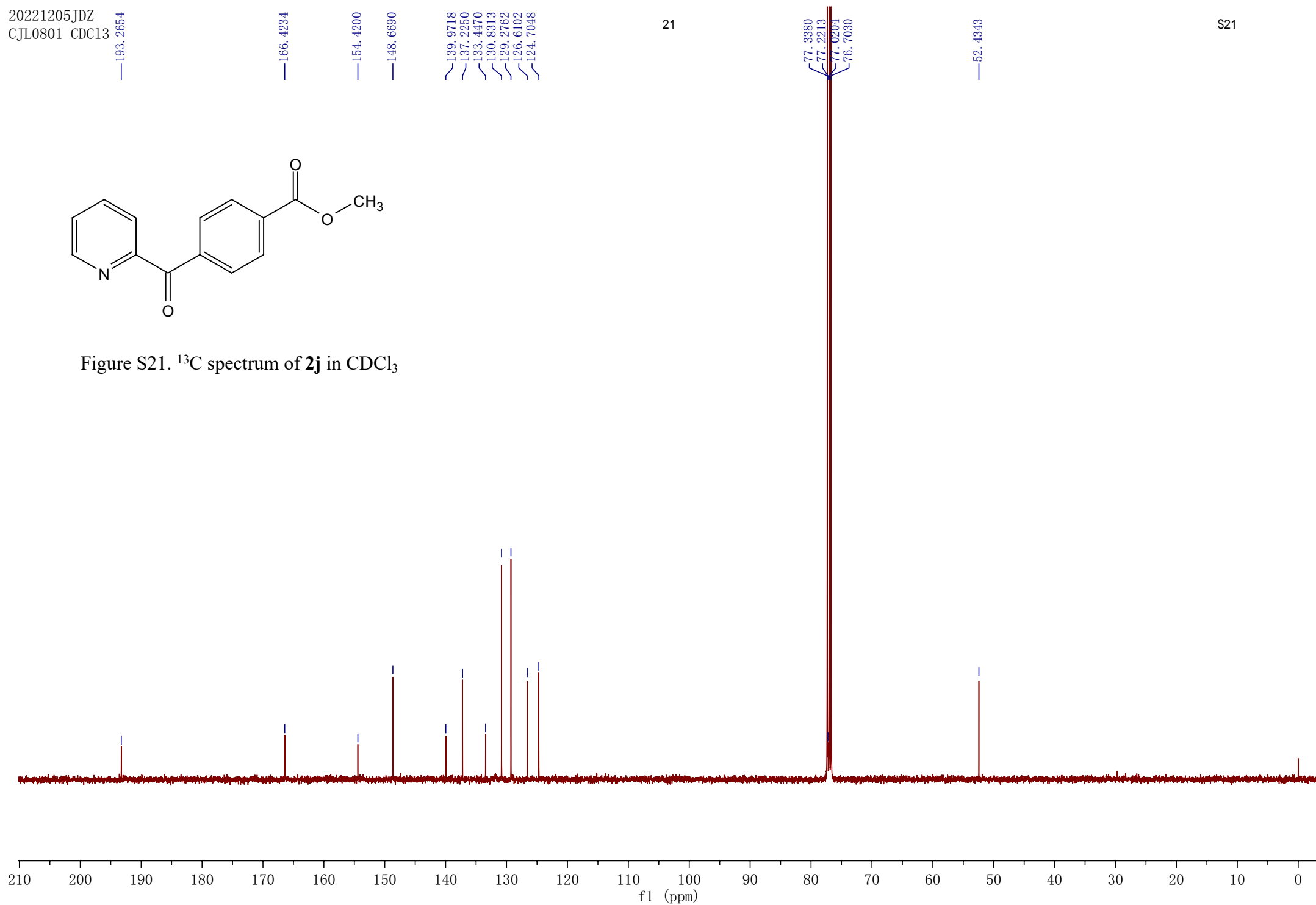


Figure S21. ^{13}C spectrum of **2j** in CDCl_3



8.7675
8.7569
8.5080
8.5044
8.5011
8.3962
8.3764
8.1808
8.1611
7.9785
7.9743
7.8940
7.8747
7.6507
7.2821

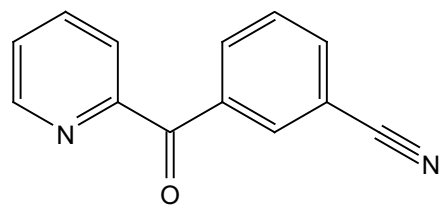
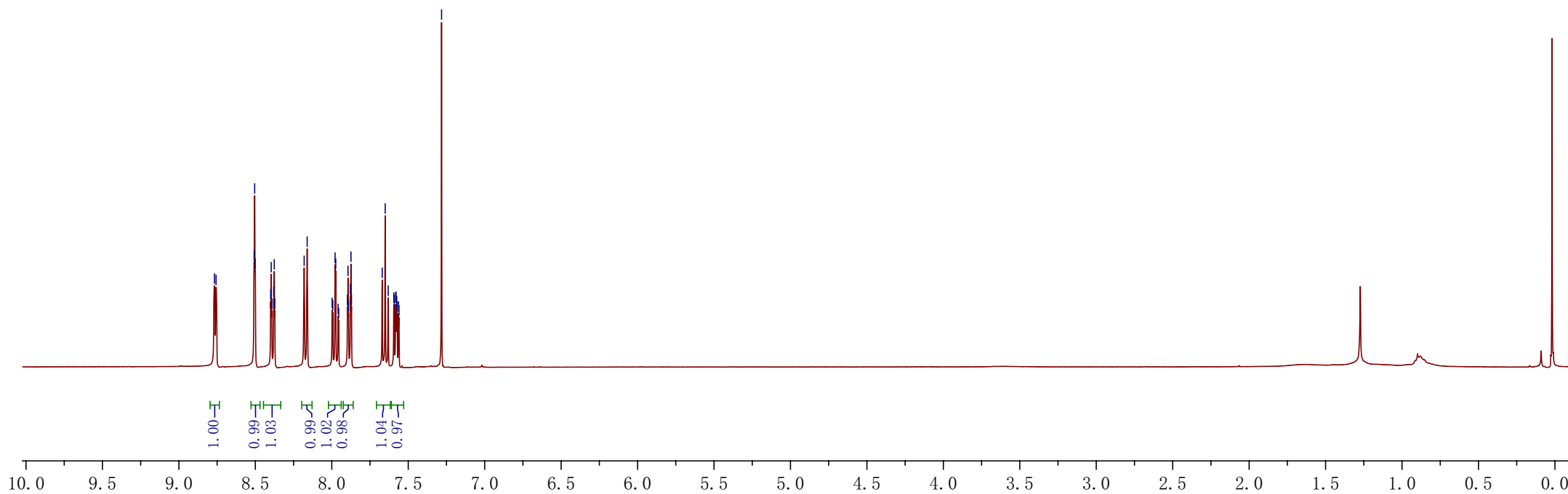


Figure S22. ^1H spectrum of **2k** in CDCl_3



191.2240

153.7692

148.6548

137.4266

137.2203

135.5768

135.0479

134.9101

129.1031

126.9666

124.8411

118.2302

112.5022

23

77.3355

77.0180

76.7005

S23

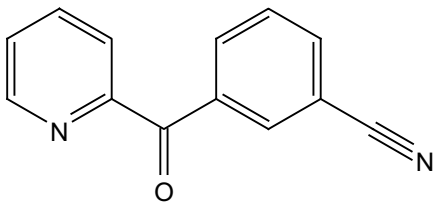
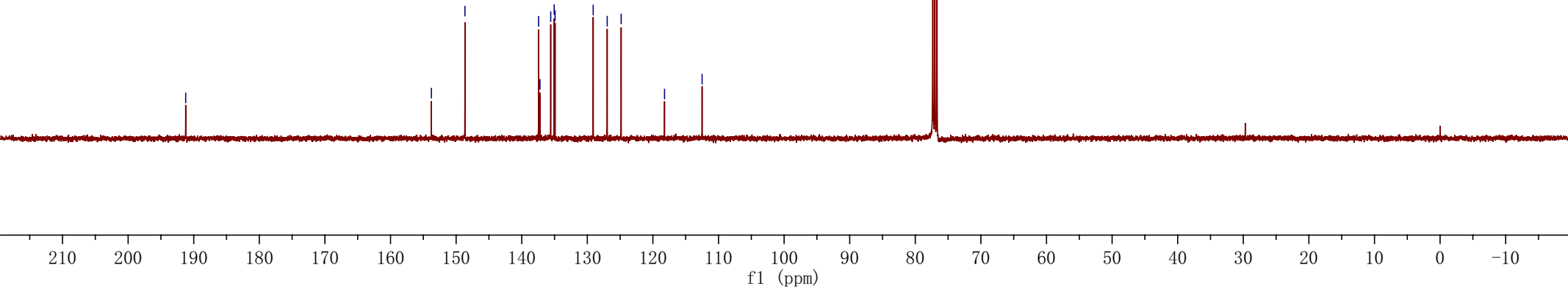


Figure S23. ¹³C spectrum of **2k** in CDCl₃



9.0326
9.0280
9.0237
8.7814
8.7797
8.4889
8.4851
8.2128
8.1932
7.9945
7.9903
7.7412
7.7214
7.7013
7.5926
7.2824

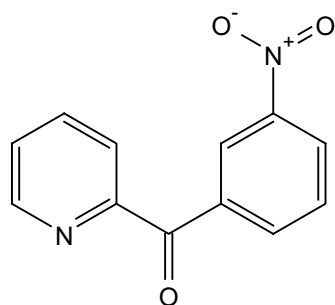
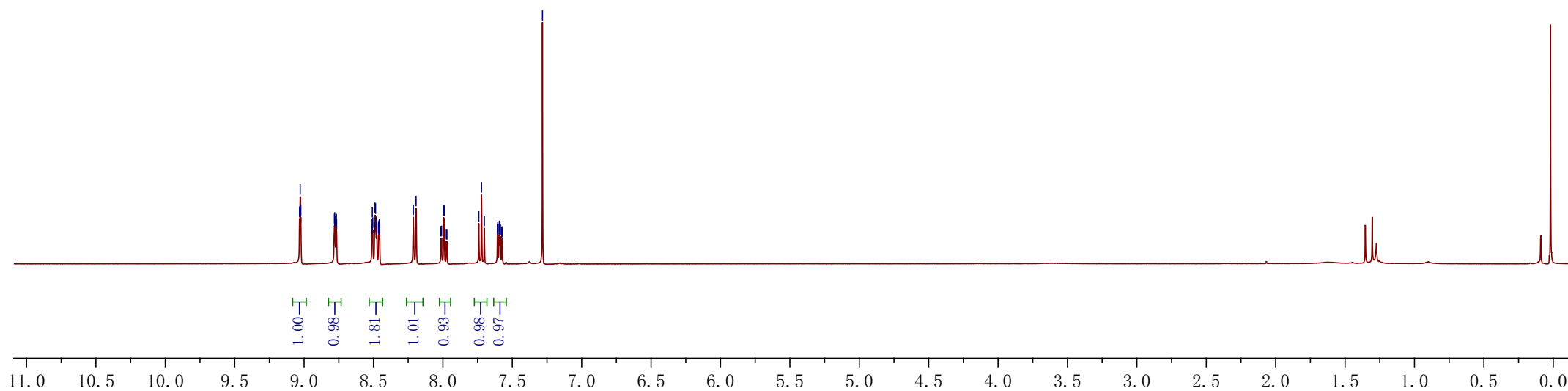


Figure S24. ^1H spectrum of **2I** in CDCl_3



20221205JDZ
CJL0705 CDCl3
—191.0732

—153.6800
—148.7131
—147.9103
—137.6754
—137.4694
—136.5606
—129.2679
—127.0535
—126.9708
—126.2444
—124.8708

25

77.3376
77.0198
76.7019

S25

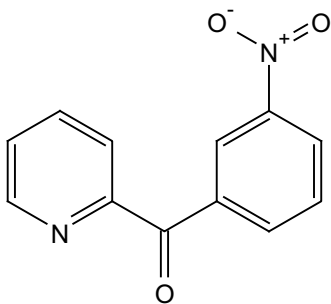
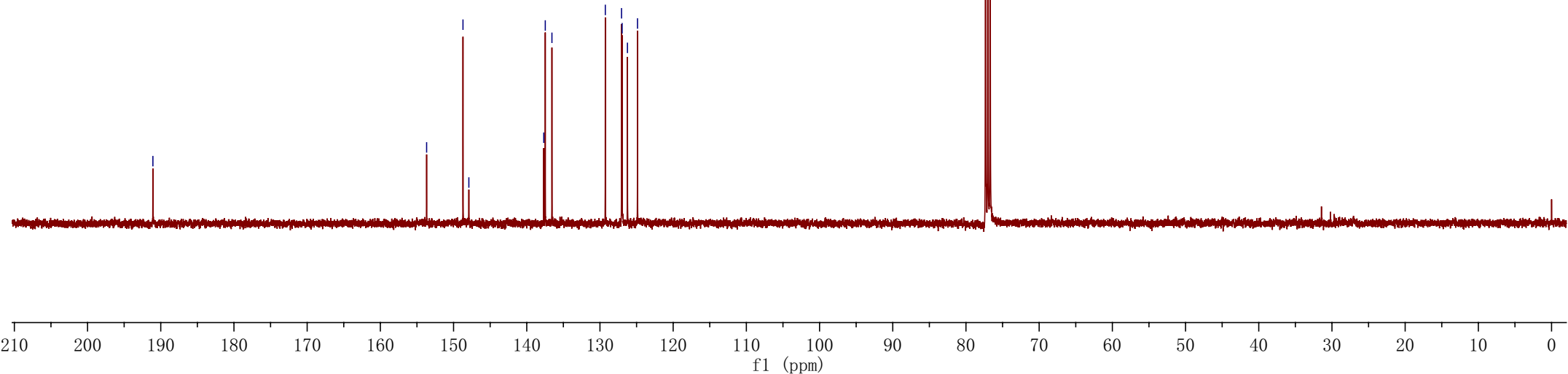


Figure S25. ¹³C spectrum of **2l** in CDCl₃



8.7694
8.7674
8.7655
8.7634
8.7576
8.7555
8.7537
8.7516
8.4154
8.4087
8.1994
8.1797
7.7718
7.7687
7.7594
7.7564
7.5126
7.5096
7.2814
7.2119
7.2022
7.1996
7.1899

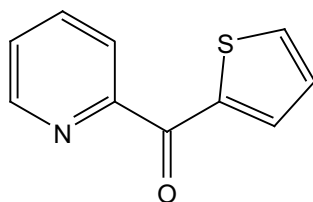
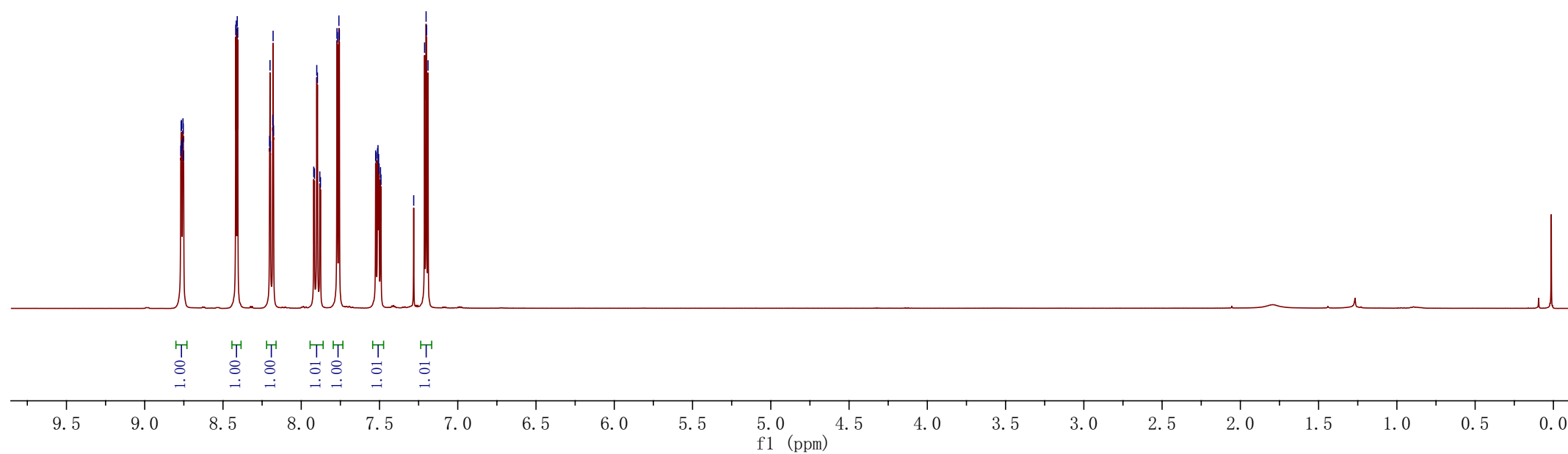


Figure S26. ^1H spectrum of **2m** in CDCl_3



183.5436

154.0169

148.2598

140.0115

137.0986

136.6988

136.3153

127.5908

126.6786

123.7974

27

77.3668

77.0492

76.7315

S27

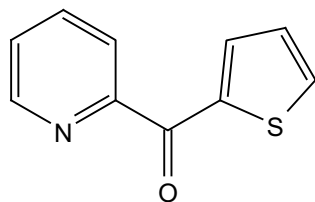
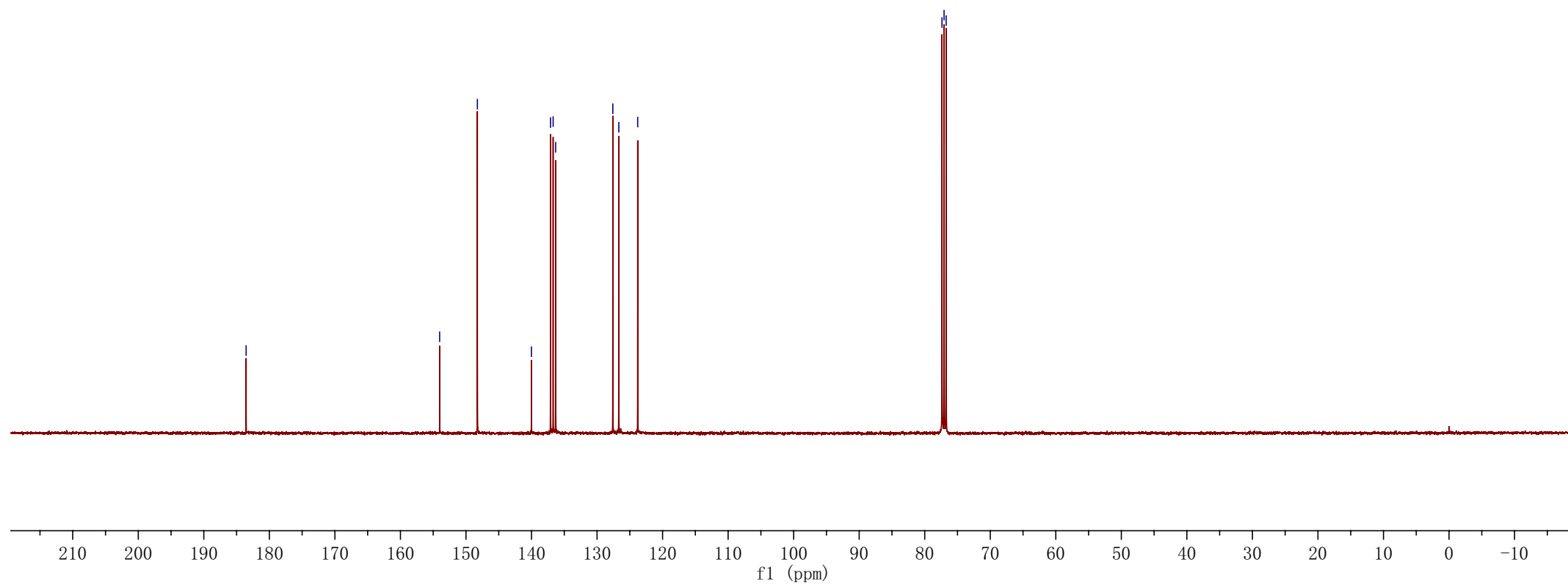


Figure S27. ¹³C spectrum of **2m** in CDCl₃



8.8570
 8.8463
 8.3780
 8.3584
 8.2218
 8.2143
 7.9648
 7.9607
 7.8043
 7.7968
 7.6014
 7.5922
 7.5894
 7.2820

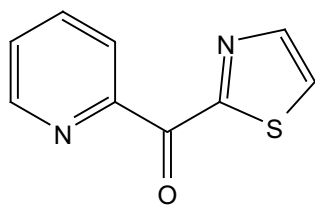
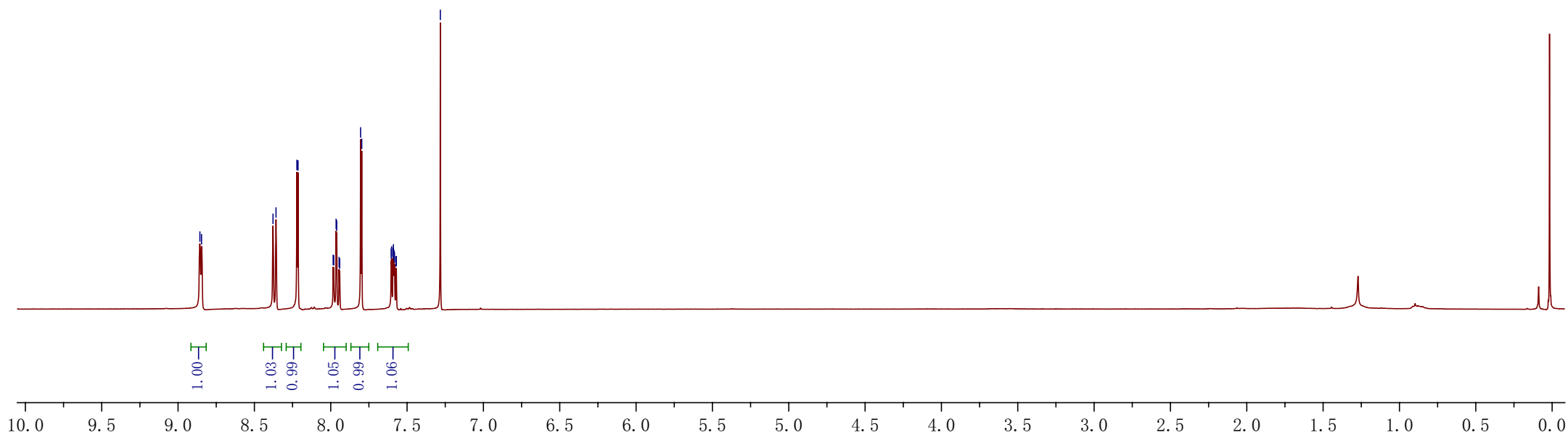
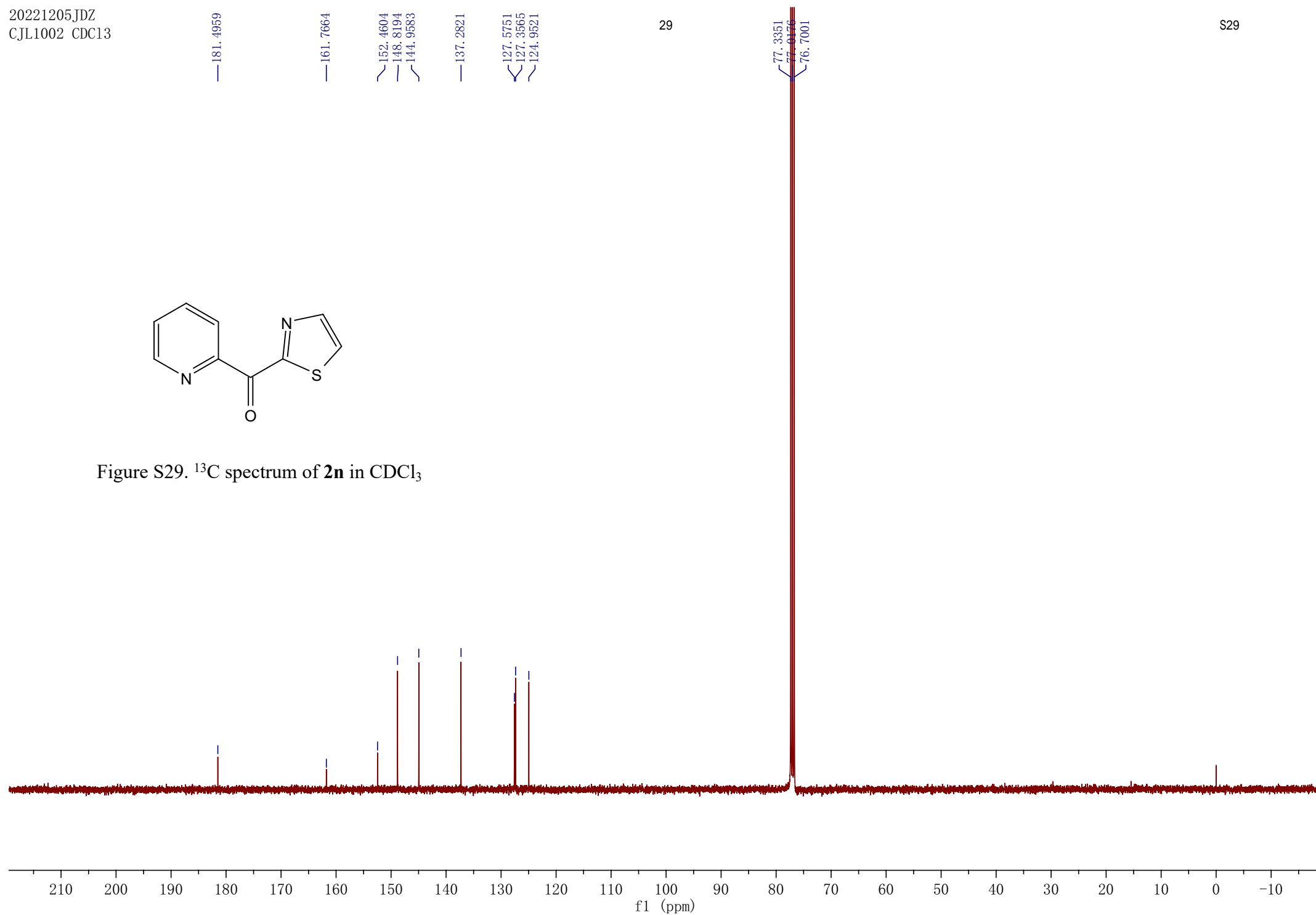
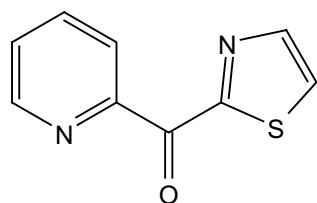


Figure S28. ^1H spectrum of **2n** in CDCl_3





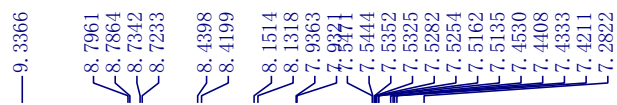
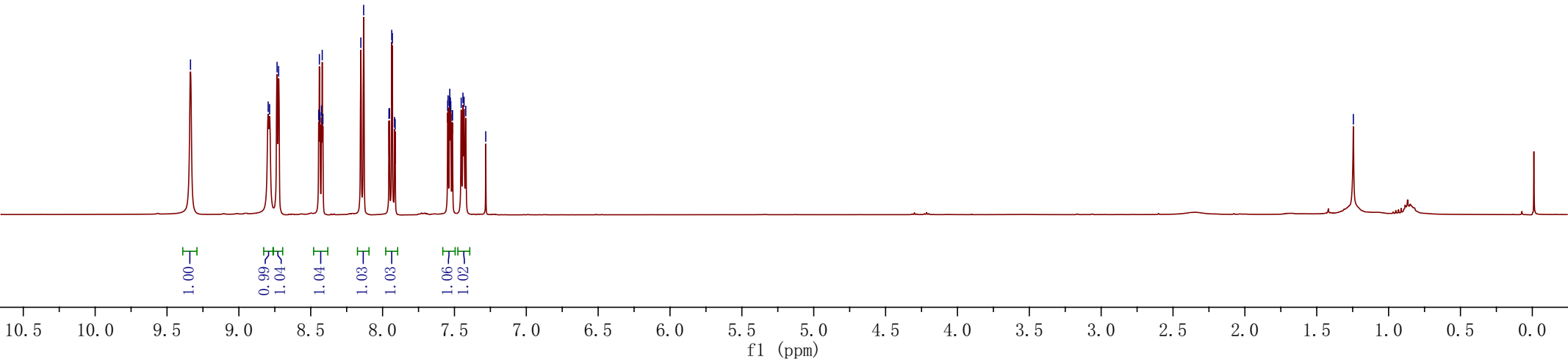


Figure S30. ¹H spectrum of **20** in CDCl₃



192.0858

20231009ZM
CJL231003 CDC13

153.9676

152.8340

152.1749

148.6444

138.2443

137.2913

132.0128

126.8503

124.5520

123.0527

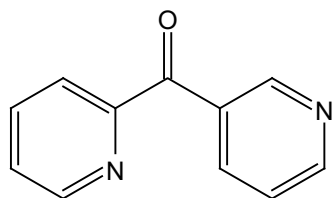
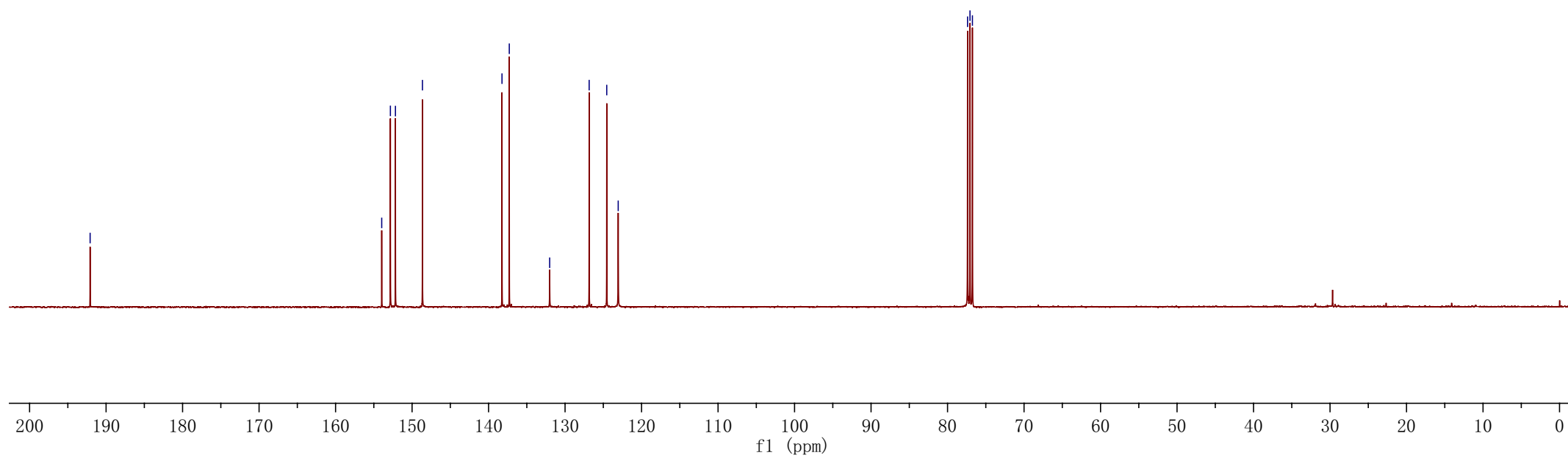
31

77.3847

77.0668

76.7490

S31

Figure S31. ^1H spectrum of **2o** in CDCl_3 

8.8452
 8.8335
 7.8536
 7.8349
 7.6899
 7.6716
 7.6528
 7.6141
 7.5996
 7.5597
 7.5403
 7.5210
 7.2819

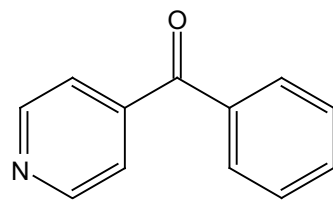
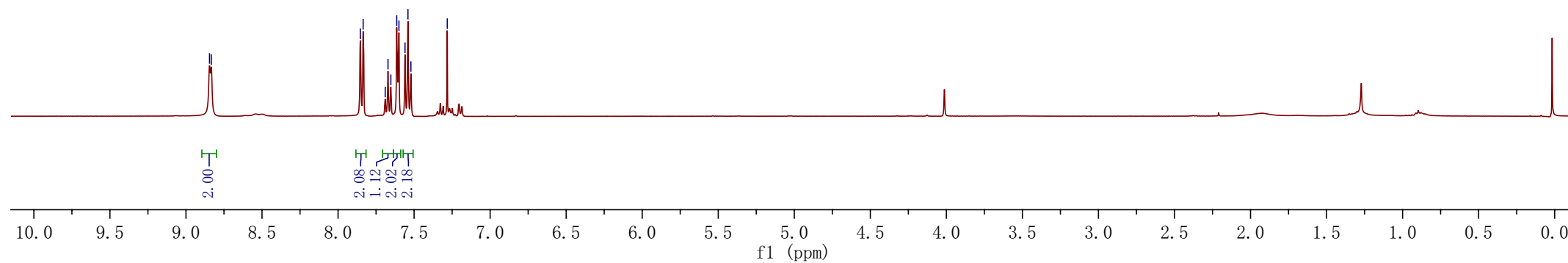


Figure S32. ^1H spectrum of **2p** in CDCl_3



— 195.1838

20231103zm
cjl-1030-1

— 150.3717

— 144.4062

— 135.9193

— 133.5538

— 130.1535

— 128.8684

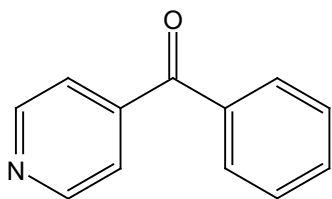
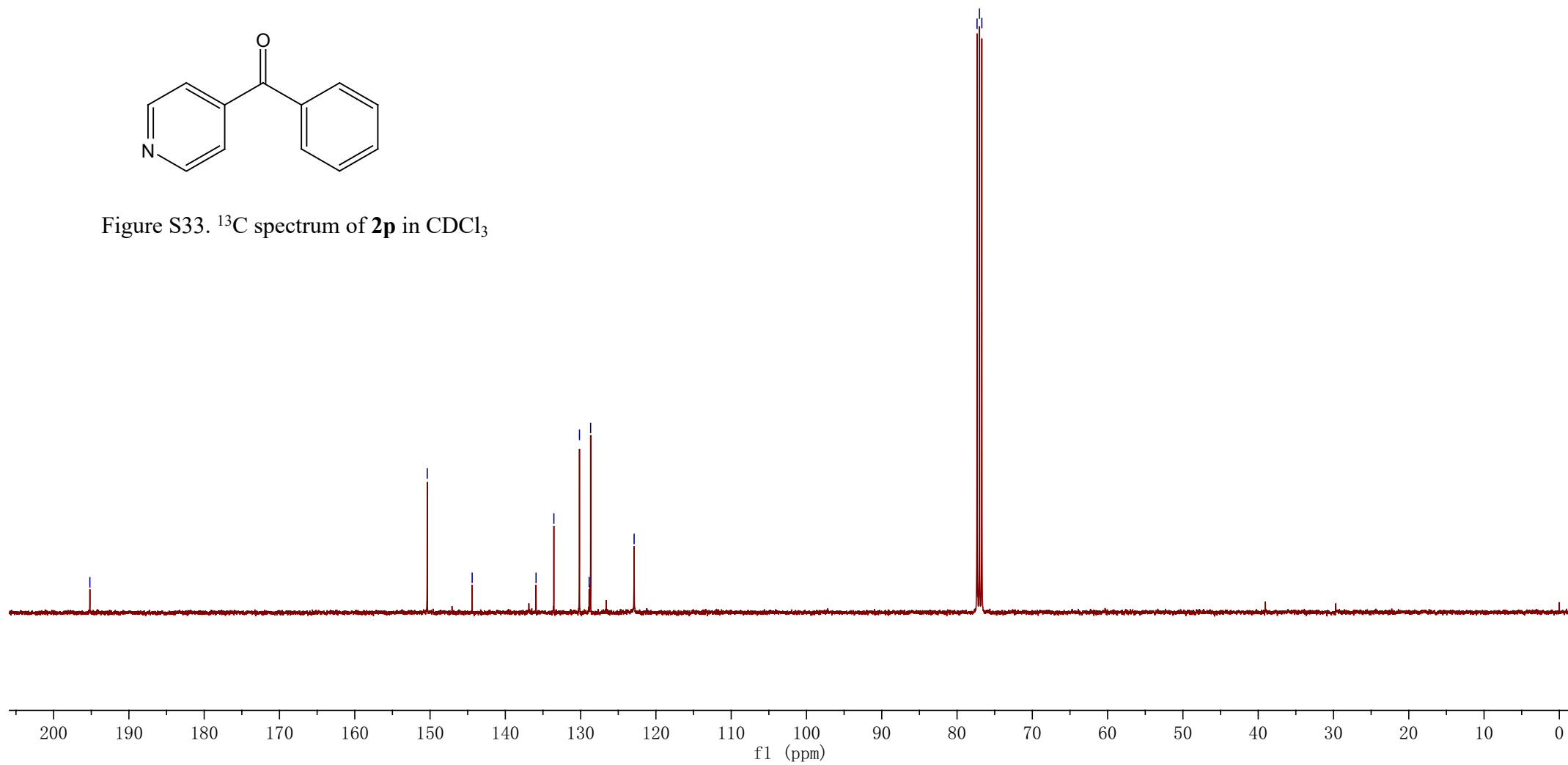
— 128.6718

— 122.8942

33

77.3428
77.0252
76.7077

S33

Figure S33. ^{13}C spectrum of **2p** in CDCl_3 

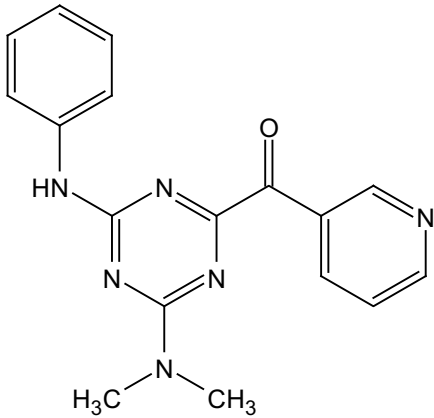
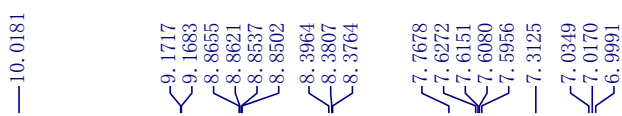
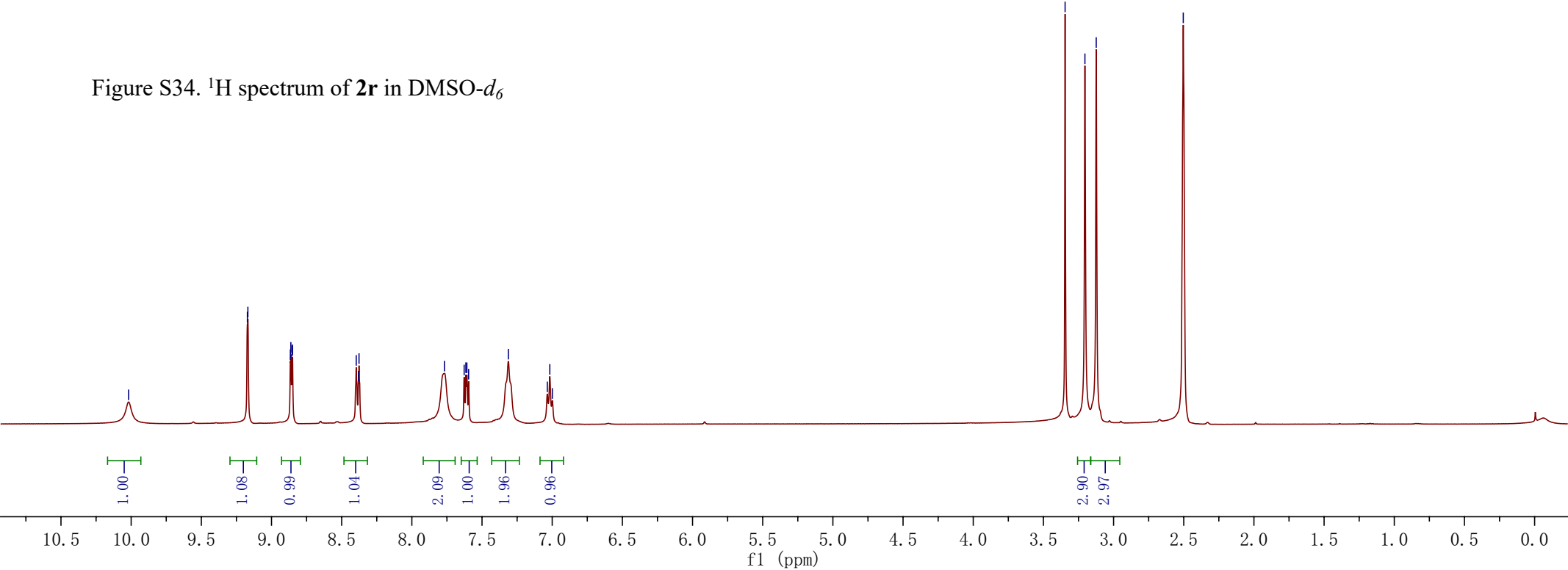
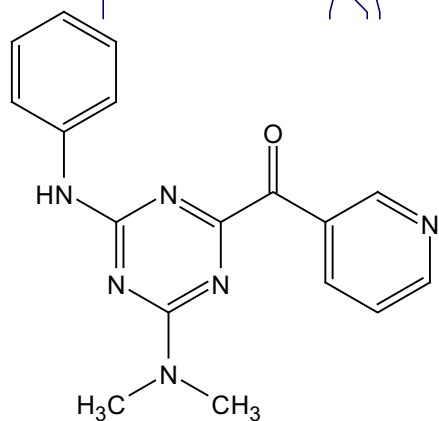


Figure S34. ¹H spectrum of **2r** in DMSO-*d*₆





35

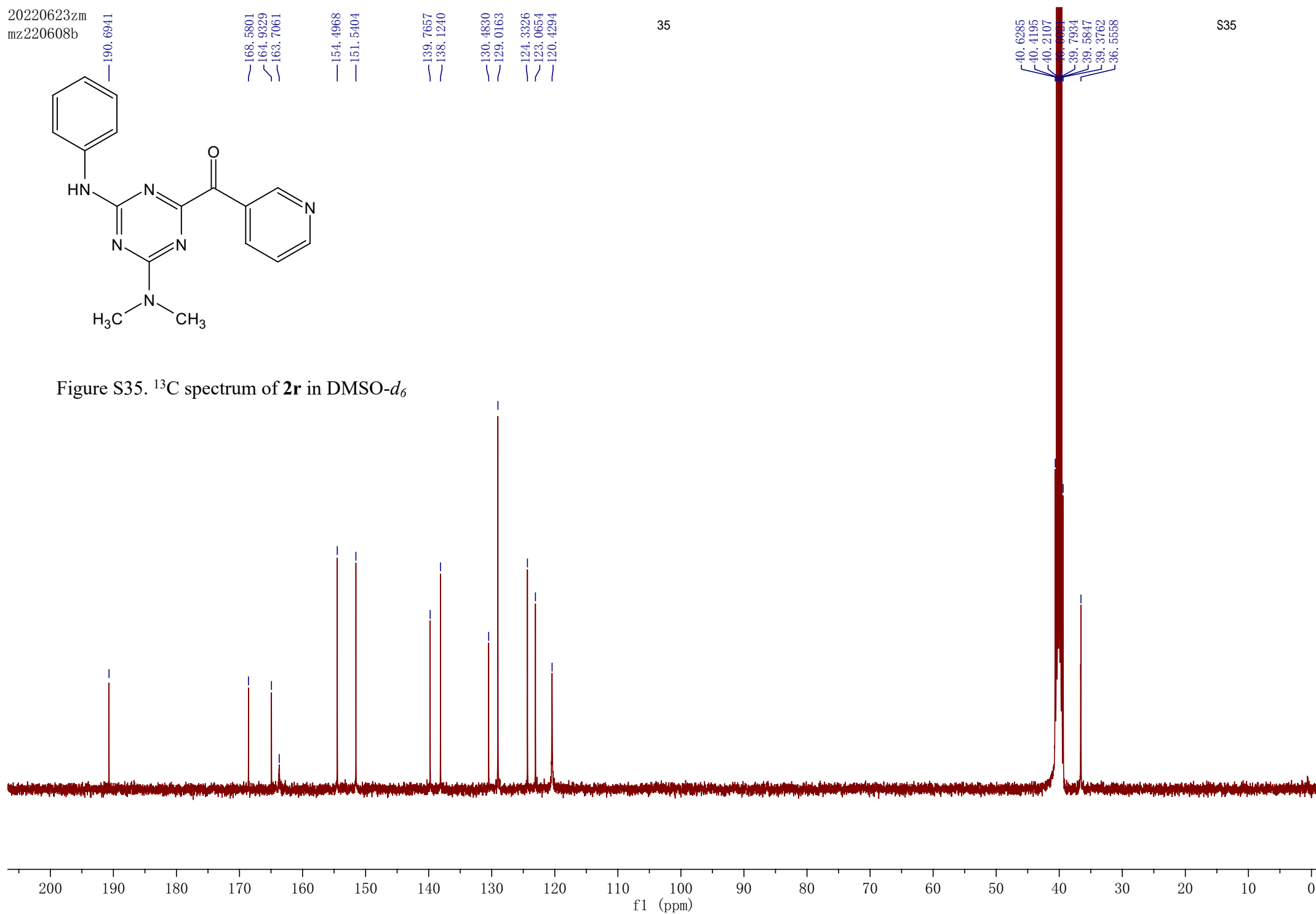


Figure S35. ^{13}C spectrum of **2r** in $\text{DMSO-}d_6$