One-Pot Synthesis of Diarylamines from Two Aromatic Amines via Oxidative Dearomatization-Imino Exchange-Reductive Aromatization

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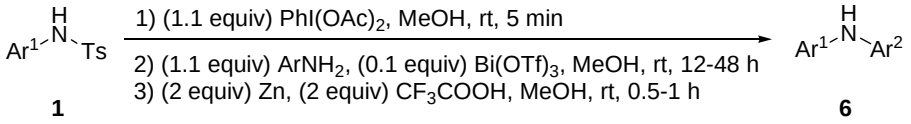
Supporting Information

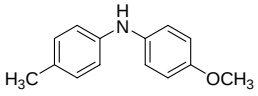
1. General Information

All reactions were performed in Schlenk tubes under nitrogen atmosphere. Flash column chromatography was performed using silica gel (60-Å pore size, 32–63 μm, standard grade). Analytical thin–layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~20 Torr (house vacuum) at 25–35 °C. Commercial reagents and solvents were used as received. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale.

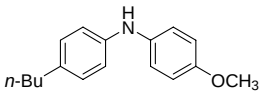
2. General Procedure and Spectral Data of Products



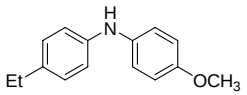
$PhI(OAc)_2$ (0.22 mmol) was added into the solution of compound **1** (0.2 mmol) in MeOH (2 mL) at 25 °C. After 5 min, aromatic amine **2** (0.22 mmol) and $Bi(OTf)_3$ (0.02 mmol) were added. The resulting reaction mixture was stirred at 25 °C until the consumption of *N*-sulfonyl cyclohexadienimine determined by TLC. The reaction mixture was treated with Zn dust (0.22 mmol) and CF_3COOH (0.22 mmol). Upon completion determined by TLC, The reaction mixture was passed through a short silica gel column and then concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 10:1) to afford the pure product **6.**



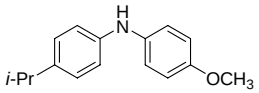
4-methoxy-N-(p-tolyl)aniline 6aa[1]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96-7.05 (m, 4 H), 6.79-6.86 (m, 4 H), 5.38 (s, 1 H), 3.77 (s, 3 H), 2.27 (s, 3 H).



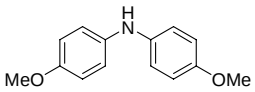
4-butyl-N-(4-methoxyphenyl)aniline 6ba[2]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97-7.07 (m, 4 H), 6.80-6.88 (m, 4 H), 5.39 (s, 1 H), 3.77 (s, 3 H), 2.52 (t, J = 7.6 Hz, 2 H), 1.48-1.60 (m, 2 H), 1.25-1.40 (m, 2 H), 0.92 (t, J = 7.4 Hz, 3 H).



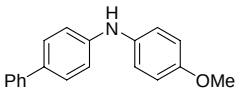
4-ethyl-N-(4-methoxyphenyl)aniline 6ca[3]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97-7.07 (m, 4 H), 6.80-6.88 (m, 4 H), 5.39 (s, 1 H), 3.77 (s, 3 H), 2.57 (t, J = 15.2 Hz, 7.6 Hz, 2 H), 1.20 (t, J = 7.6 Hz, 3 H).



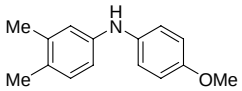
4-isopropyl-N-(4-methoxyphenyl)aniline 6da[4]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, J = 8.3 Hz, 2 H), 7.02 (d, J = 8.7 Hz, 2 H), 6.86 (d, J = 8.4 Hz, 2 H), 6.83 (d, J = 8.8 Hz, 2 H), 5.41 (s, 1 H), 3.77 (s, 3 H), 2.79-2.87 (m, 1 H), 1.20-1.23 (m, 6 H).



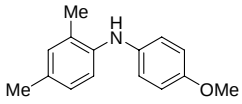
bis(4-methoxyphenyl)amine 6ea[5]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90-6.97 (m, 4 H), 6.78-6.84 (m, 4 H), 5.28 (s, 1 H), 3.77 (s, 6 H).



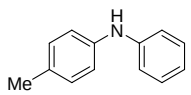
N-(4-methoxyphenyl)-[1,1'-biphenyl]-4-amine 6fa[6]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.56 (m, 2 H), 7.34-7.47 (m, 4 H), 7.09-7.10 (m, 1 H), 7.05-7.12 (m, 2 H), 6.91-6.97 (m, 2 H), 6.84-6.89 (m, 2 H), 5.55 (s, 1 H), 3.78 (s, 3 H).



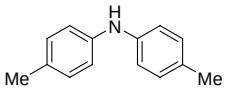
N-(4-methoxyphenyl)-3,4-dimethylaniline 6ga[7]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92-7.04 (m, 3 H), 6.79-6.86 (m, 2 H), 6.64-6.76 (m, 2 H), 5.34 (s, 1 H), 3.77 (s, 3 H), 2.19 (s, 3 H), 2.18 (s, 3 H).



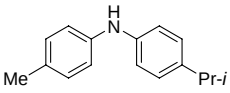
N-(4-methoxyphenyl)-2,4-dimethylaniline 6ha: brown oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80-7.25 (m, 7 H), 5.12 (s, 1 H), 3.78 (s, 3 H), 2.15-2.30 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 140.4, 137.4, 131.6, 137.4, 130.2, 127.3, 120.8, 117.1, 114.7, 55.7, 20.6, 11.8; HRMS m/z calcd for $C_{15}H_{18}NO$ ($[M+H]^+$): 228.1383, found 228.1397.



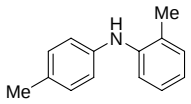
4-methyl-N-phenylaniline 6ab[8]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.25 (m, 2 H), 7.07 (d, J = 8.3 Hz, 2 H), 6.95-7.02 (m, 4 H), 6.84-6.90 (m, 1 H), 5.56 (s, 1 H), 2.29 (s, 3 H).



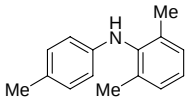
di-p-tolylamine 6ac[8]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, J = 8.2 Hz, 4 H), 6.93 (d, J = 8.4 Hz, 4 H), 5.47 (s, 1 H), 2.28 (s, 6 H).



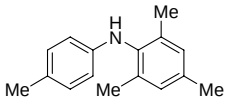
4-isopropyl-N-(p-tolyl)aniline 6ad[9]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, J = 8.0 Hz, 2 H), 7.05 (d, J = 8.0 Hz, 2 H), 6.92-6.98 (m, 4 H), 5.50 (s, 1 H), 2.79-2.88 (m,1 H), 2.28 (s, 3 H), 1.20-1.24 (m, 6 H).



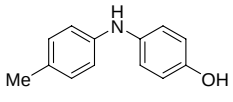
2-methyl-N-(p-tolyl)aniline 6ae[1]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04-7.20 (m, 5 H), 6.82-6.92 (m, 3 H), 5.27 (s, 1 H), 2.29 (s, 3 H), 2.23 (s, 3 H).



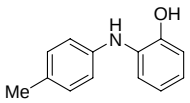
2,6-dimethyl-N-(p-tolyl)aniline 6af[10]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03-7.12 (m, 3 H), 6.96 (d, J = 8.2 Hz, 2 H), 6.43 (d, J = 8.3 Hz, 2 H), 5.08 (s, 1 H), 2.24 (s, 3 H), 2.20 (s, 6 H).



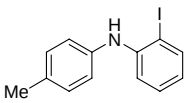
2,4,6-trimethyl-N-(p-tolyl)aniline 6ag[10]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92-6.97 (m, 4 H), 6.41 (s, 1 H), 6.39 (s, 1 H), 5.00 (s, 1 H), 2.29 (s, 3 H), 2.23 (s, 3 H), 2.16 (s, 6 H).



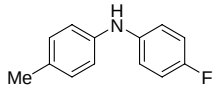
4-(p-tolylamino)phenol 6ah[11]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, J = 8.1 Hz, 2 H), 6.96 (d, J = 8.7 Hz, 2 H), 6.84 (d, J = 8.2Hz, 2 H), 6.75 (d, J = 8.6 Hz, 2 H), 5.02 (s, 2 H), 2.27 (s, 3 H).



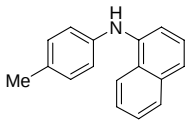
2-(p-tolylamino)phenol 6ai[8]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, J = 7.4 Hz, 1 H), 7.00-7.06 (m, 3 H), 6.95 (d, J = 7.8 Hz, 1 H), 6.86 (t, J = 7.4 Hz, 1 H), 6.70 (d, J = 8.1 Hz, 2 H), 5.42 (s, 2 H), 2.26 (s, 3 H).



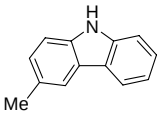
2-iodo-N-(p-tolyl)aniline 6aj[12]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.8 Hz, 1 H), 7.02-7.18 (m, 6 H), 6.56 (t, J = 7.0 Hz, 1 H), 5.84 (s, 1 H), 2.32 (s, 3 H).



4-fluoro-N-(p-tolyl)aniline 6ak[1]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, J = 8.0 Hz, 2 H), 6.86-7.00 (m, 6 H), 5.46 (s, 1 H), 2.28 (s, 3 H).



N-(p-tolyl)naphthalen-1-amine 6al[10]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.99 (m, 1 H), 7.80-7.84 (m, 1 H), 7.40-7.50 (m, 3 H), 7.30-7.36 (m, 1 H), 7.24-7.27 (m, 1 H), 7.04-7.09 (m, 2 H), 6.89-6.94 (m, 2 H), 5.84 (s, 1 H), 2.29 (s, 3 H).



3-methyl-9H-carbazole 7[13]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 7.7 Hz, 1 H), 7.93 (s, 1 H), 7.87 (s, 1 H), 7.36-7.42 (m, 2 H), 7.26-7.34 (m, 1 H), 7.16-7.26 (m, 2 H), 2.53 (s, 3 H).

Reference:

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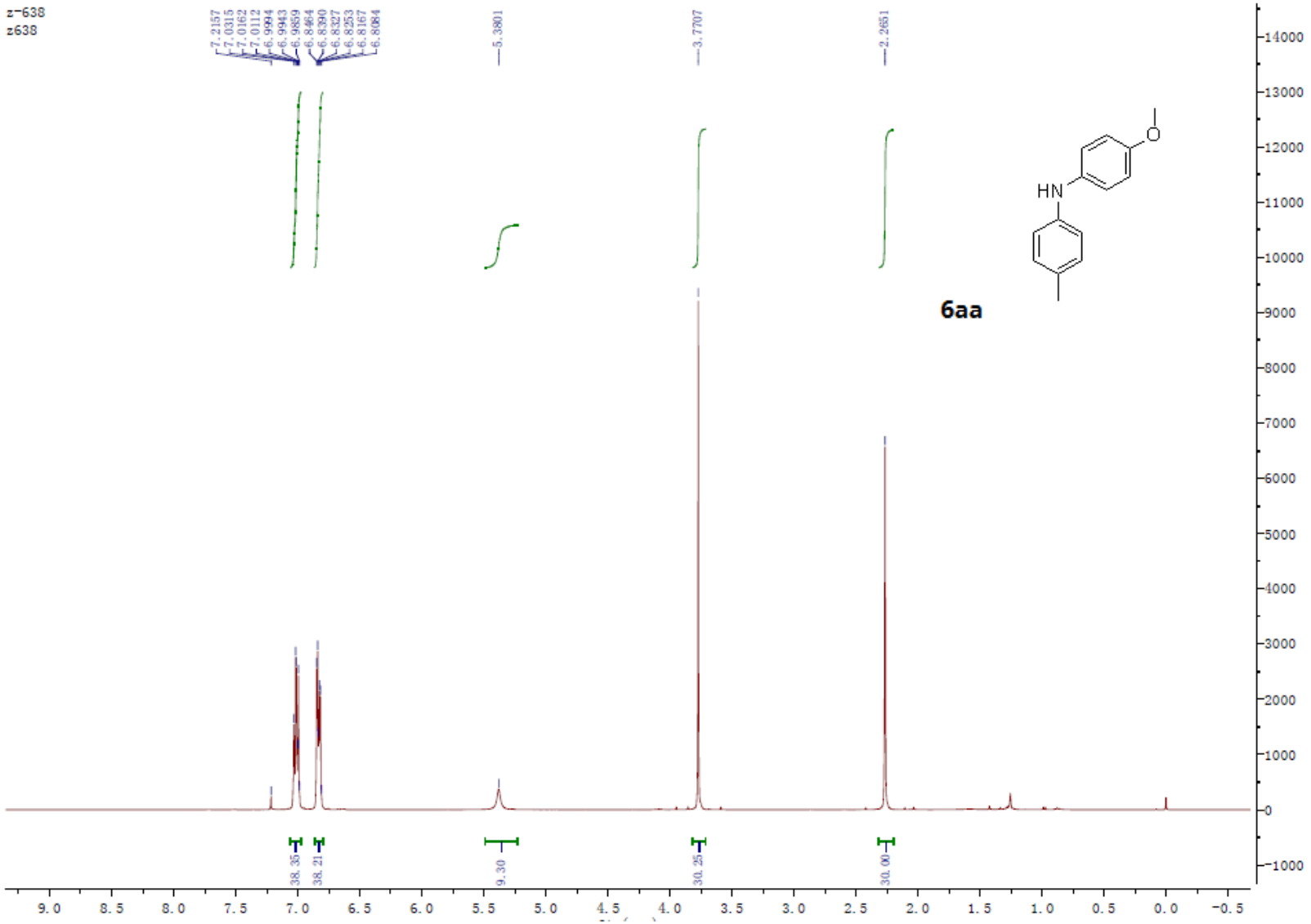
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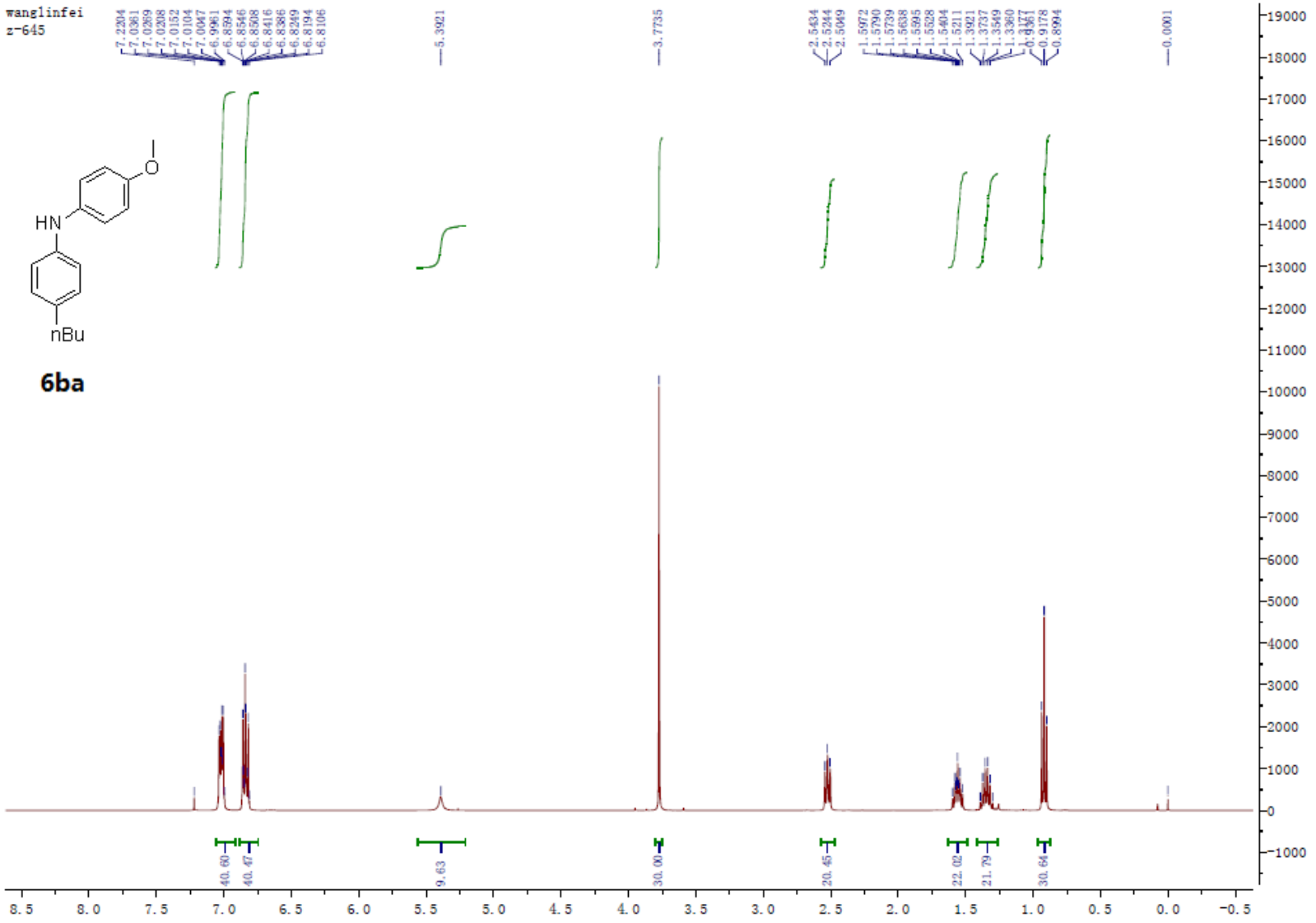
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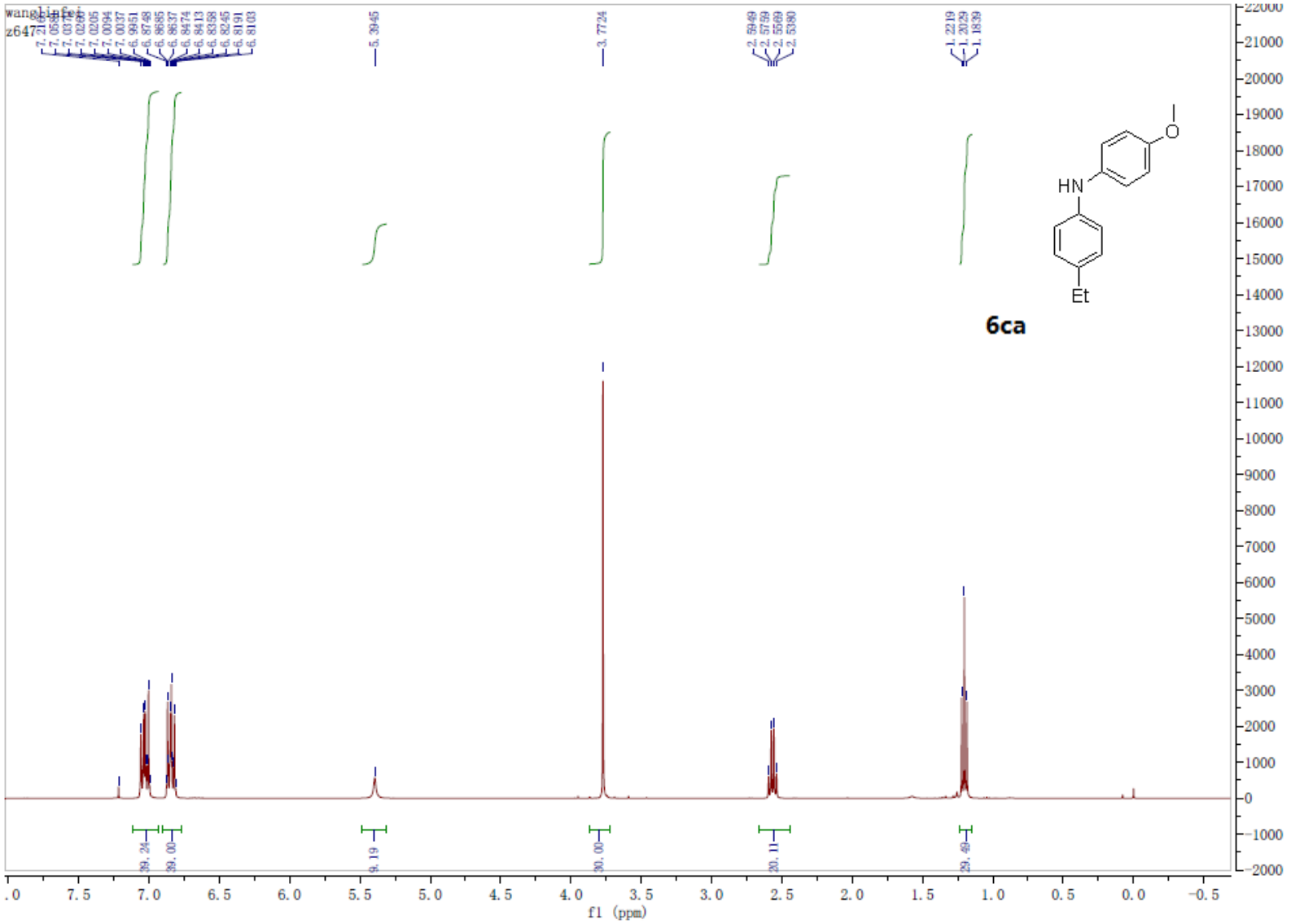
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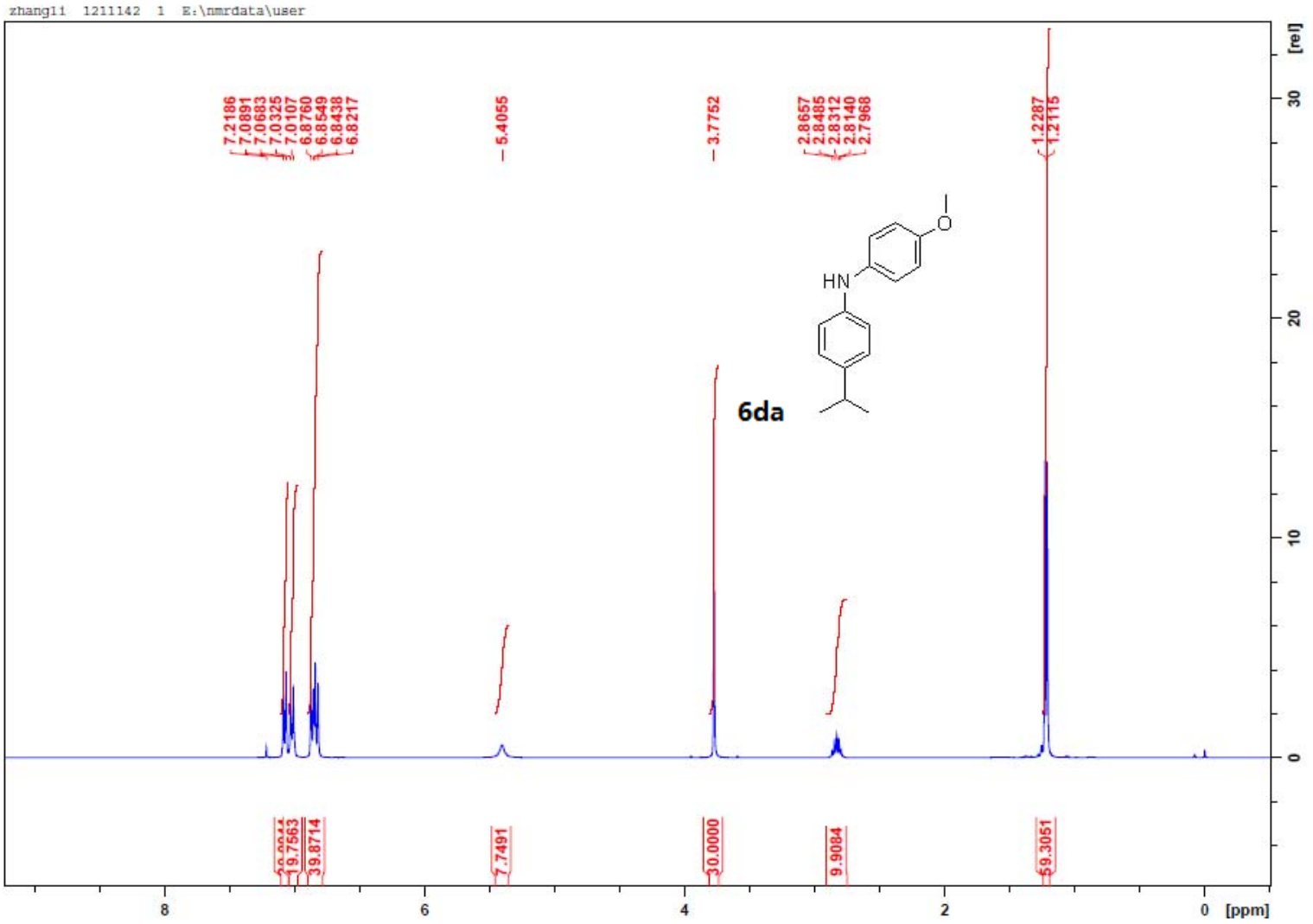
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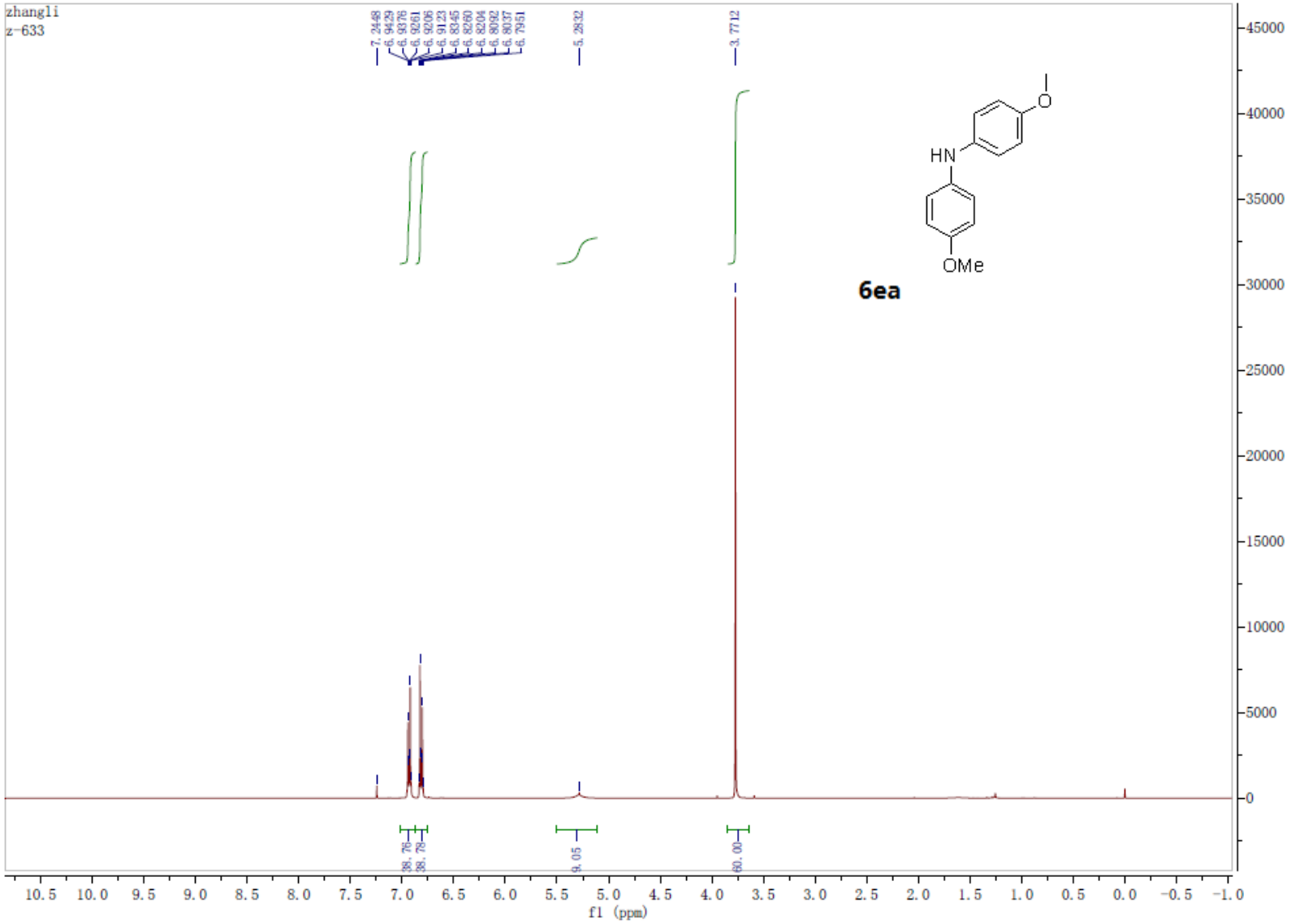
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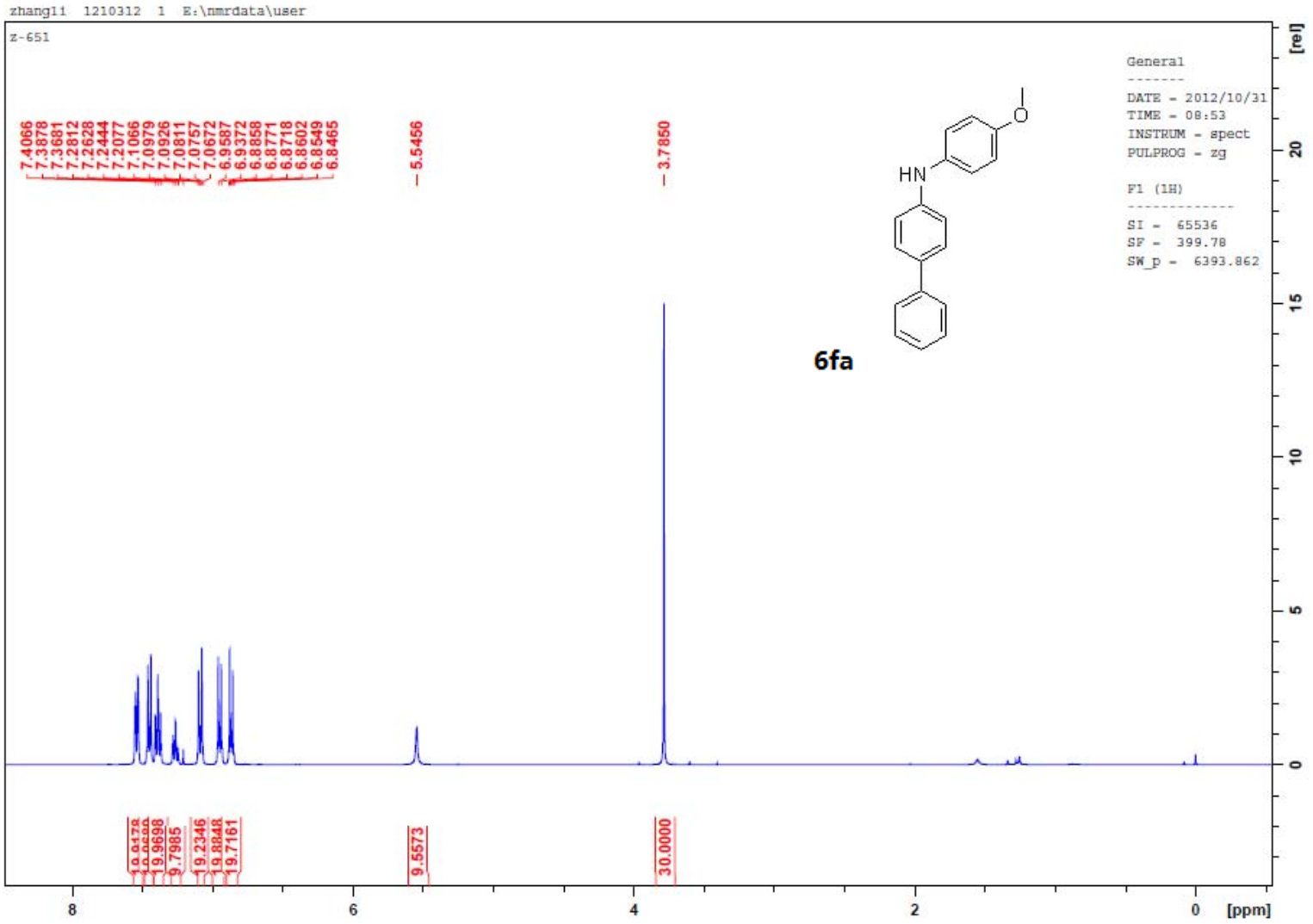
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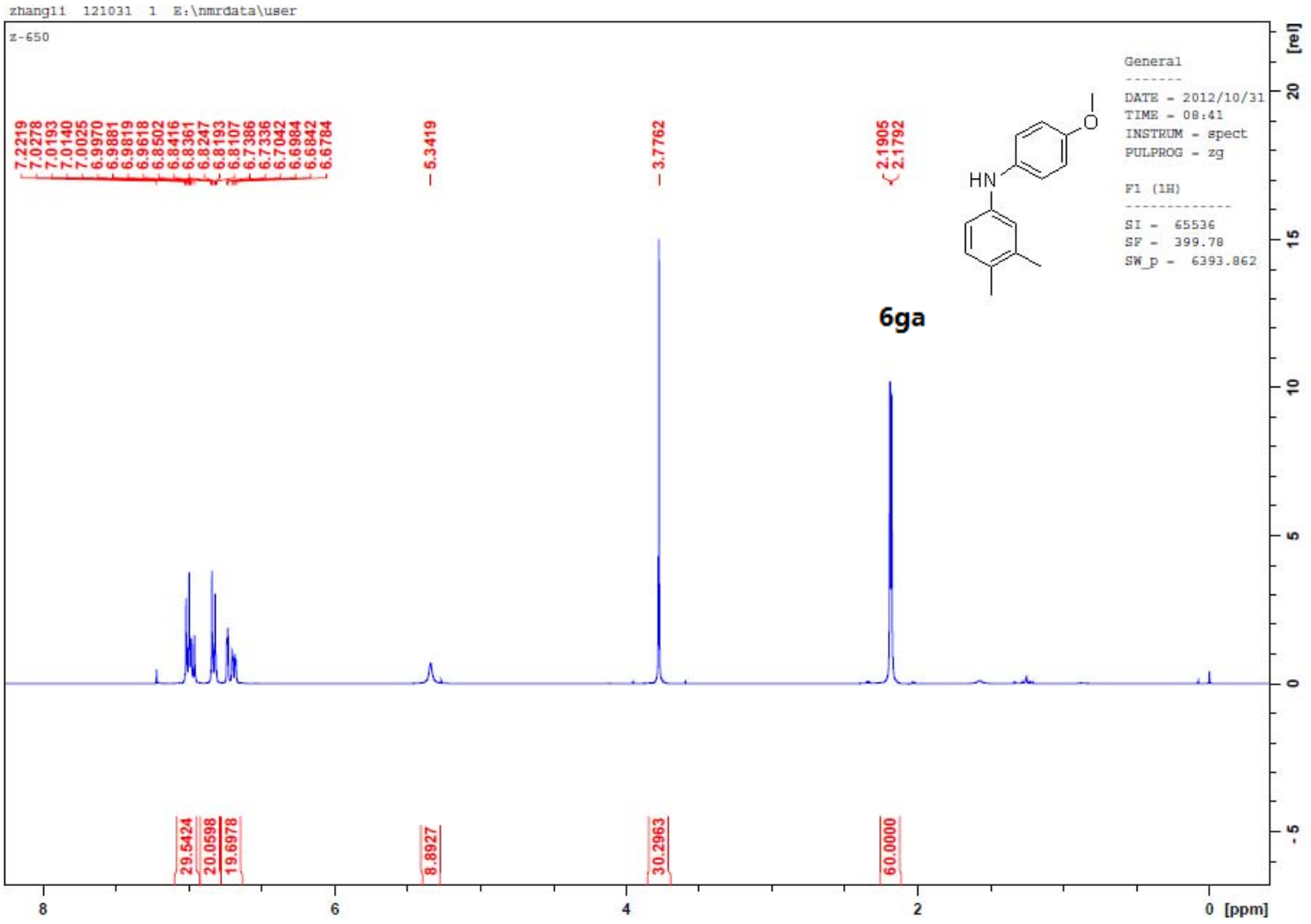
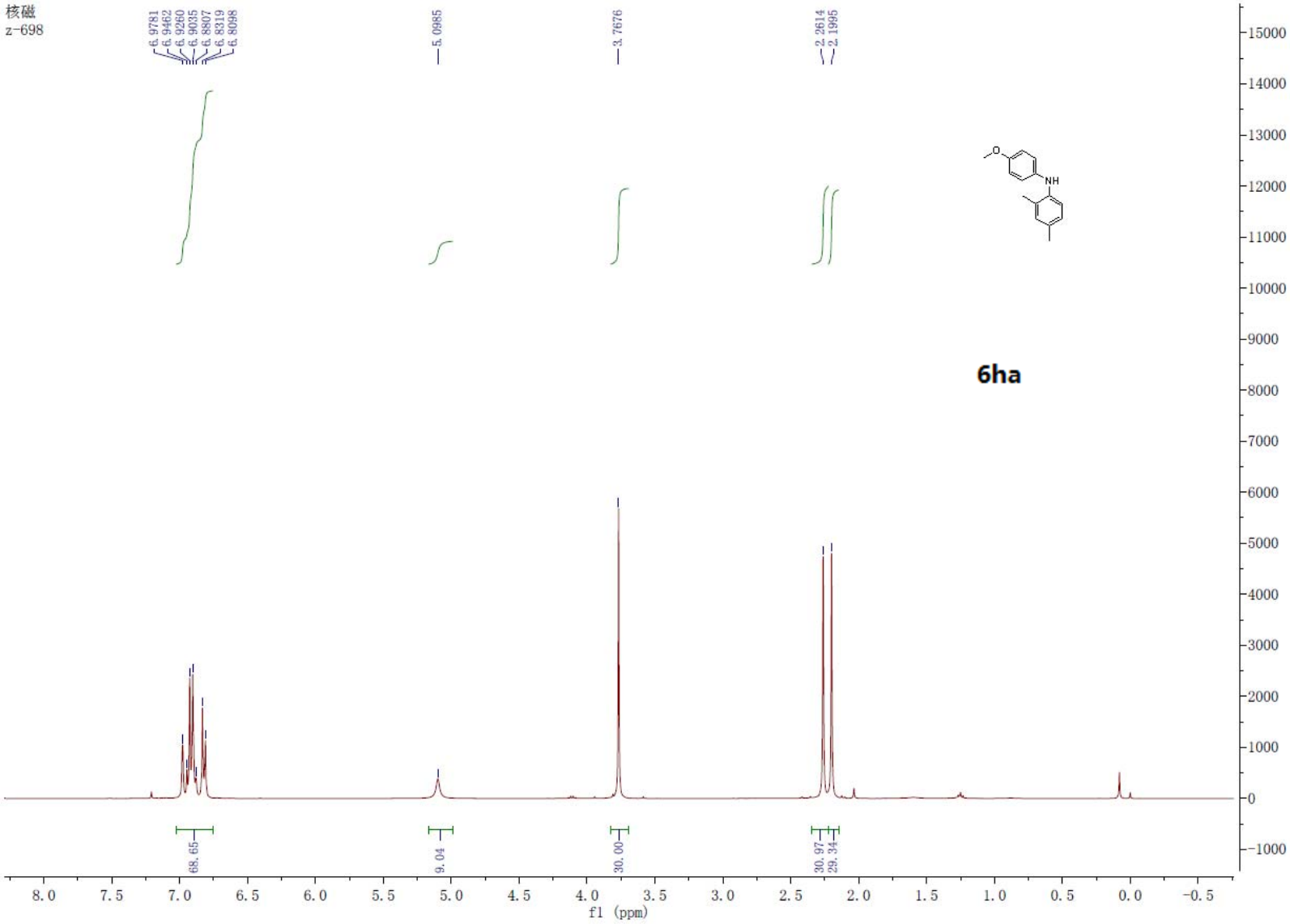
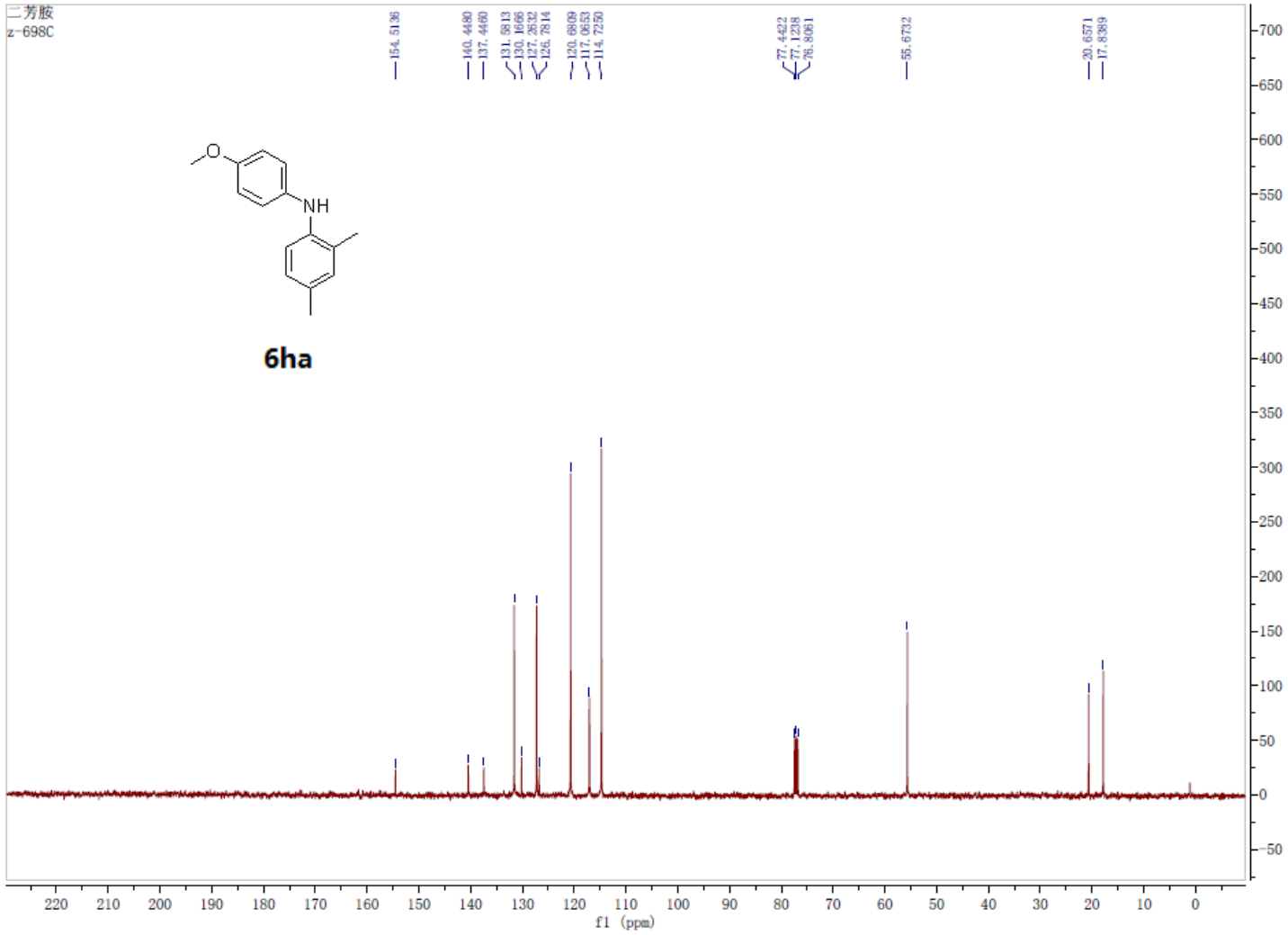
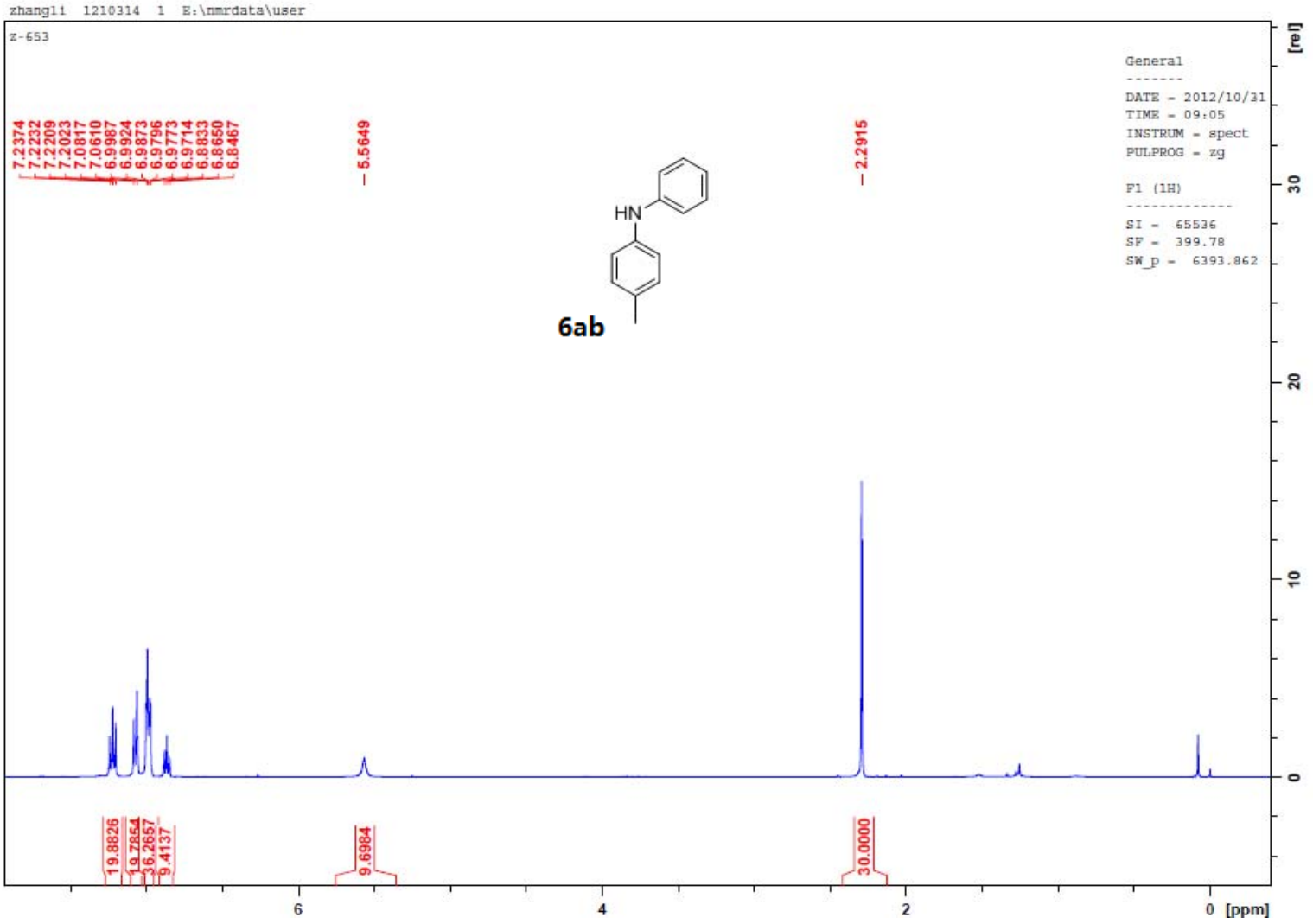
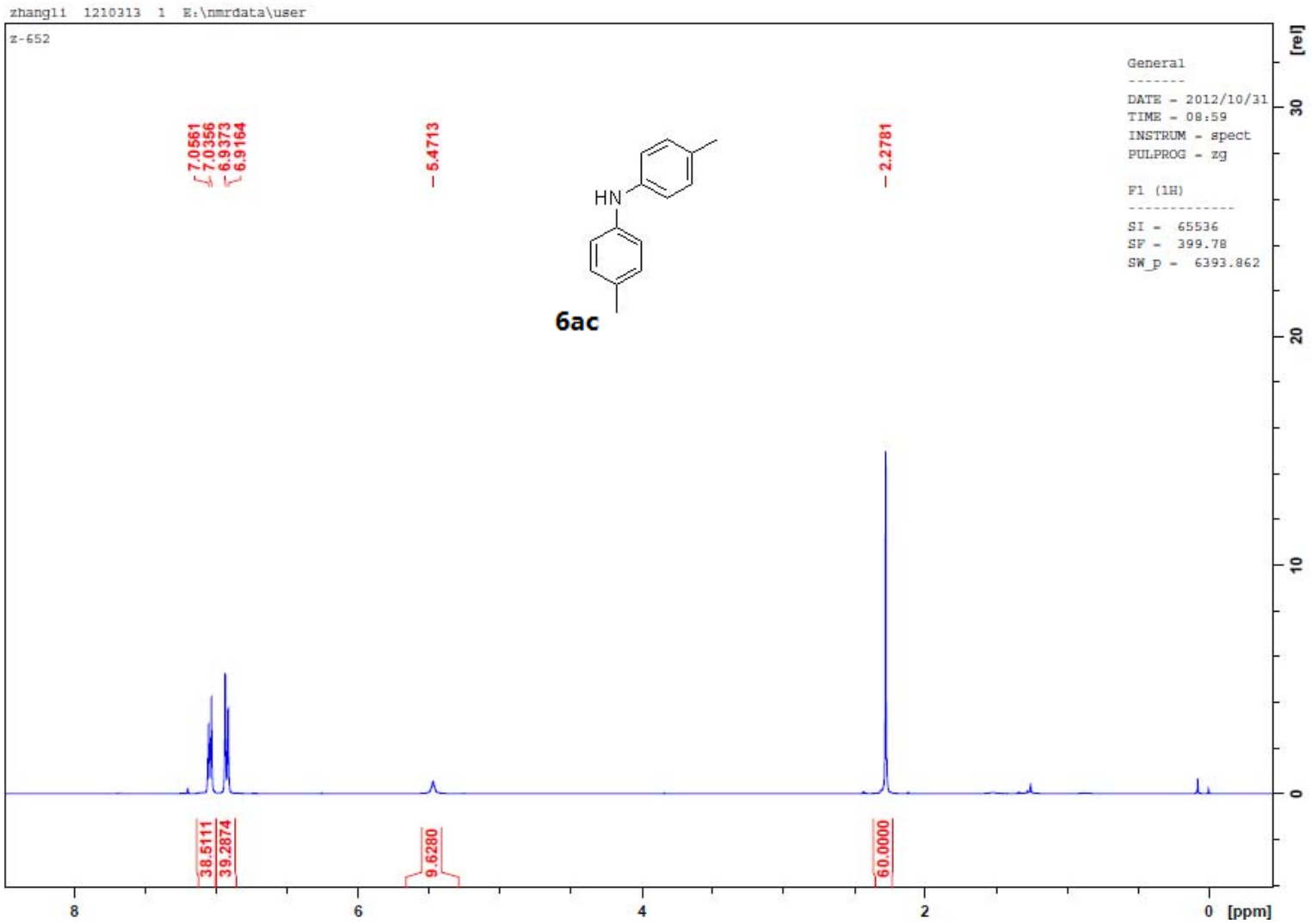
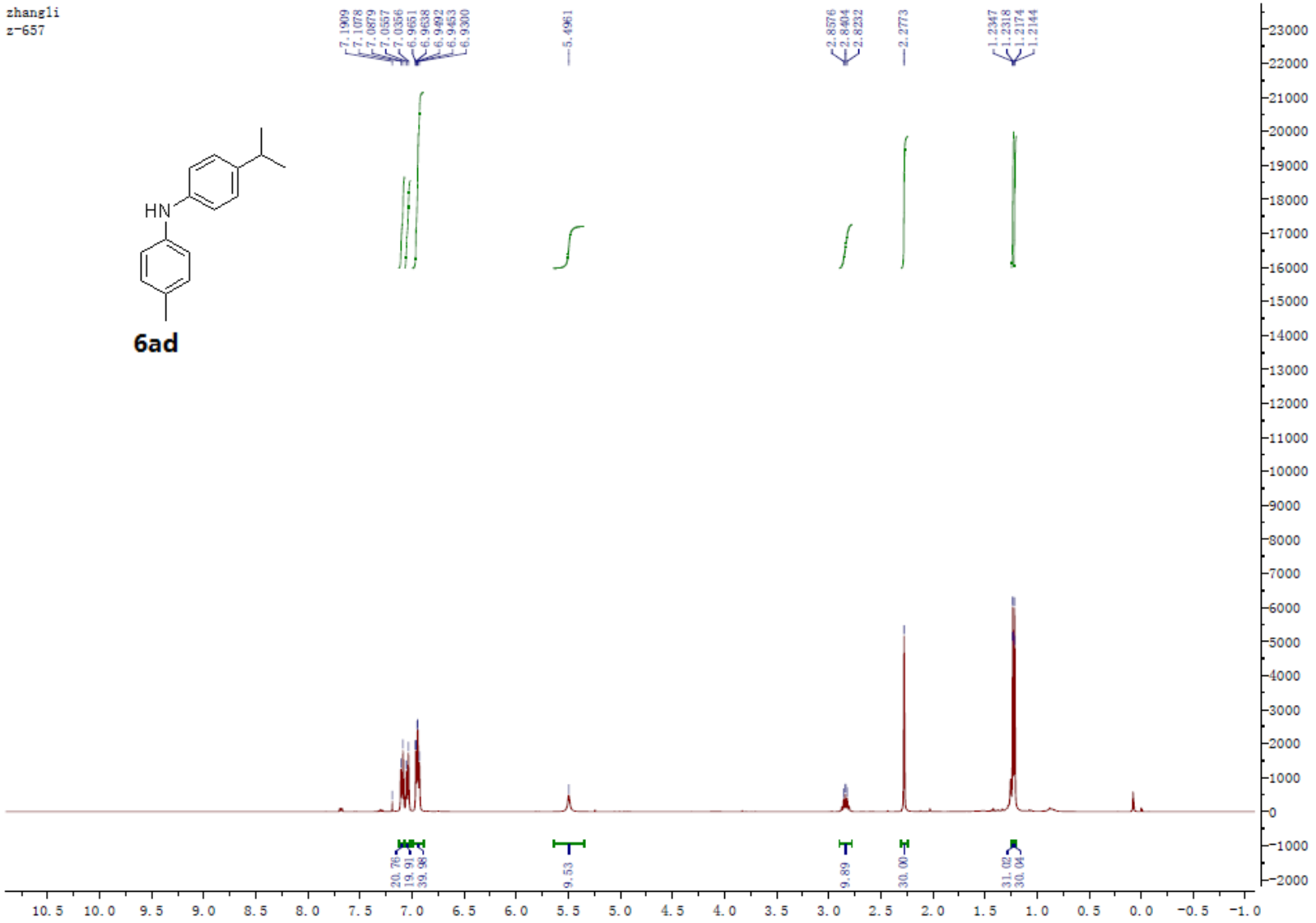

zhangli 121031 1 E:\nmrdata\user
z-650
7.2219
7.0278
7.0193
7.0140
7.0025
6.9970
6.9881
6.9819
6.9618
6.8502
6.8416
6.8361
6.8247
6.8193
6.8107
6.7386
6.7336
6.7042
6.6984
6.6842
6.6784
5.3419
3.7762
2.1905
2.1792
General
DATE = 2012/10/31
TIME = 08:41
INSTRUM = spect
PULPROG = zg
F1 (1H)
SI = 65536
SF = 399.78
SW_p = 6393.862
HN
O
6ga
29.5424
20.0598
19.6978
8.8927
30.2963
60.0000
8
6
4
2
0 [ppm]
[rel]
20
15
10
5
0
-5

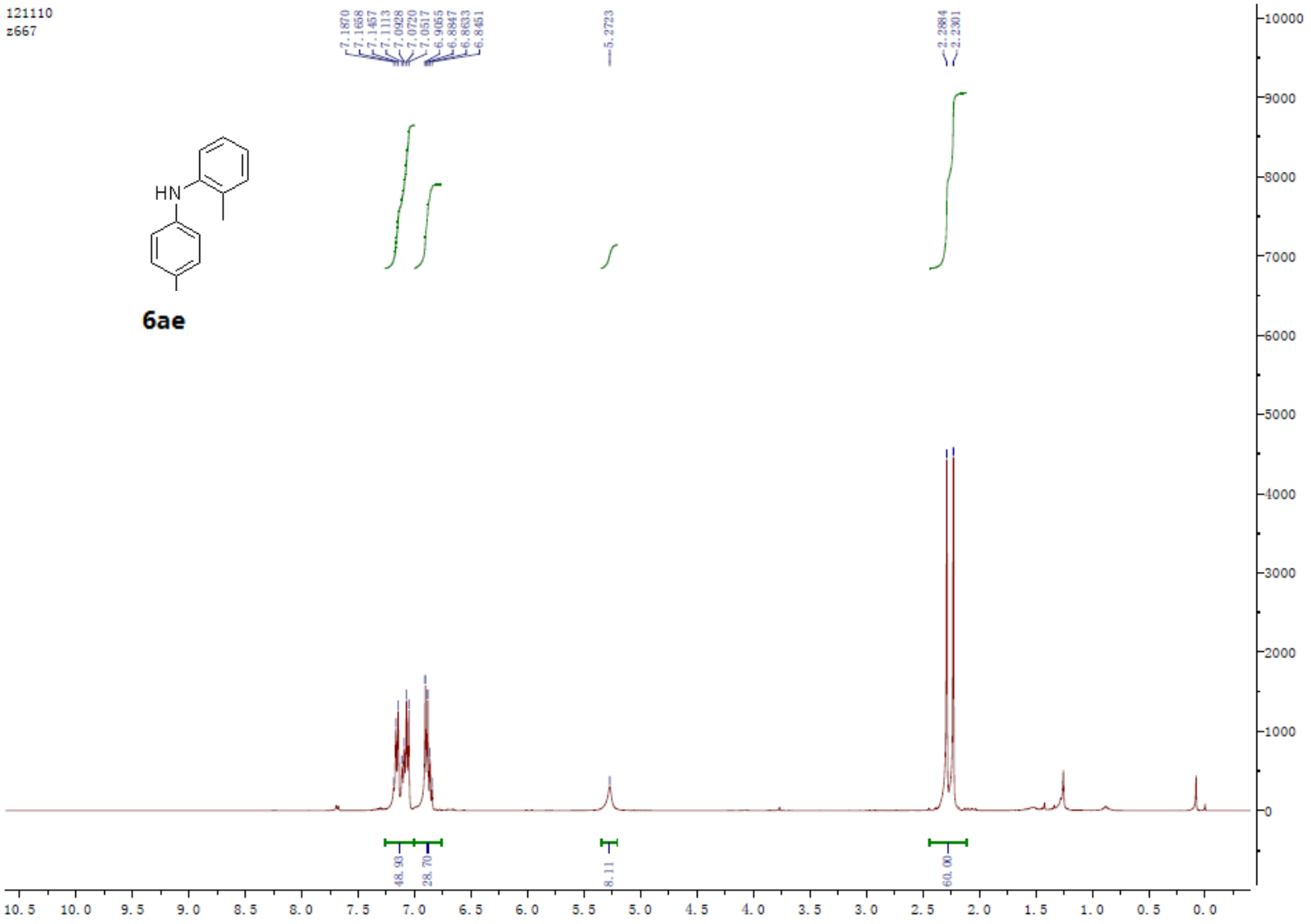

核磁
z-698
6.9781
6.9462
6.9260
6.9035
6.8807
6.8319
6.8098
5.0985
3.7676
2.2614
2.1995
6ha
68.65
9.04
30.00
30.97
29.34
f1 (ppm)

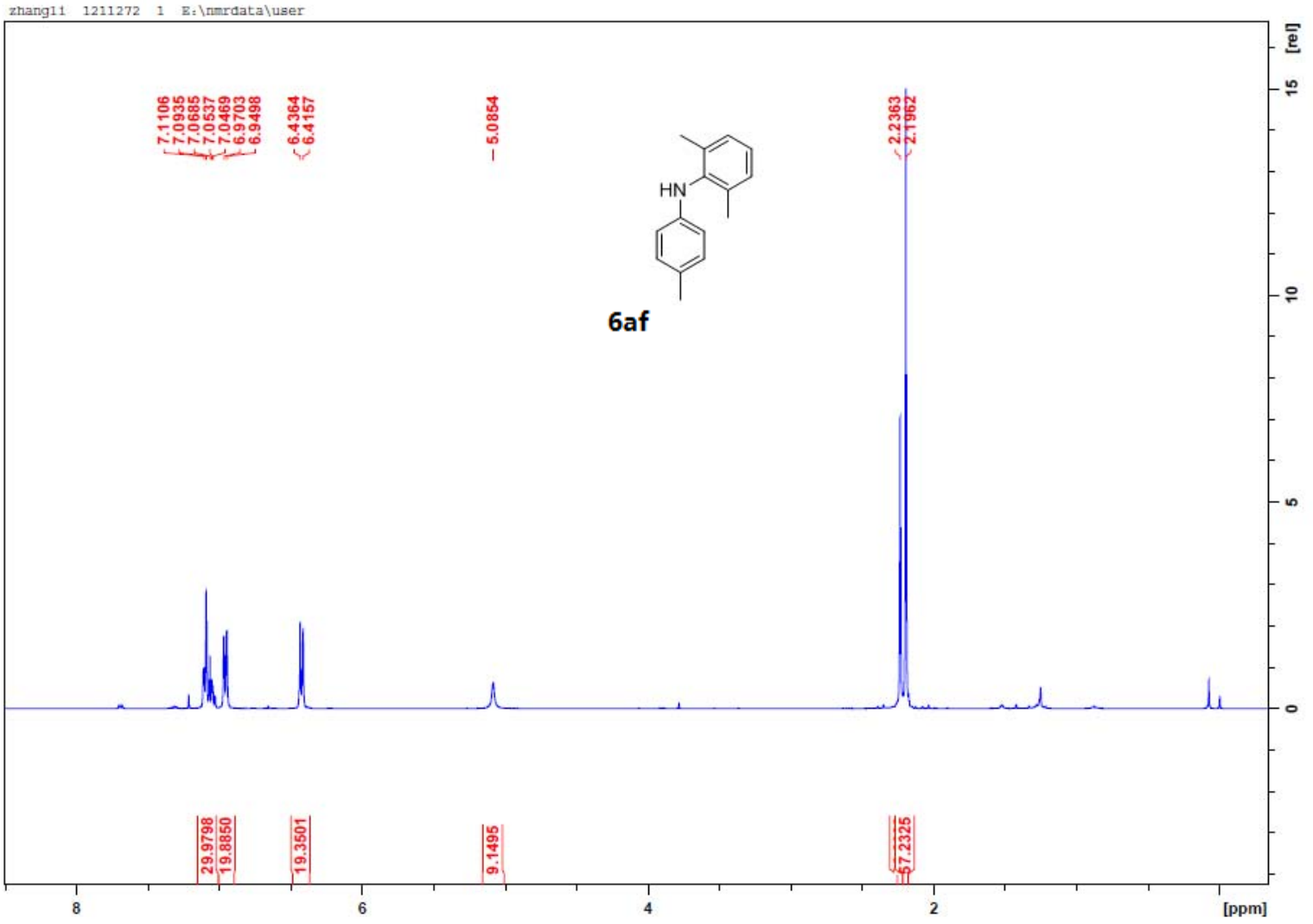

二芳胺
z-698C
154.5136
140.4480
137.4460
131.5813
130.1666
127.2532
126.7814
120.6809
117.0653
114.7250
77.4422
77.1238
76.8061
55.6732
20.6571
17.8389
O
NH
6ha
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

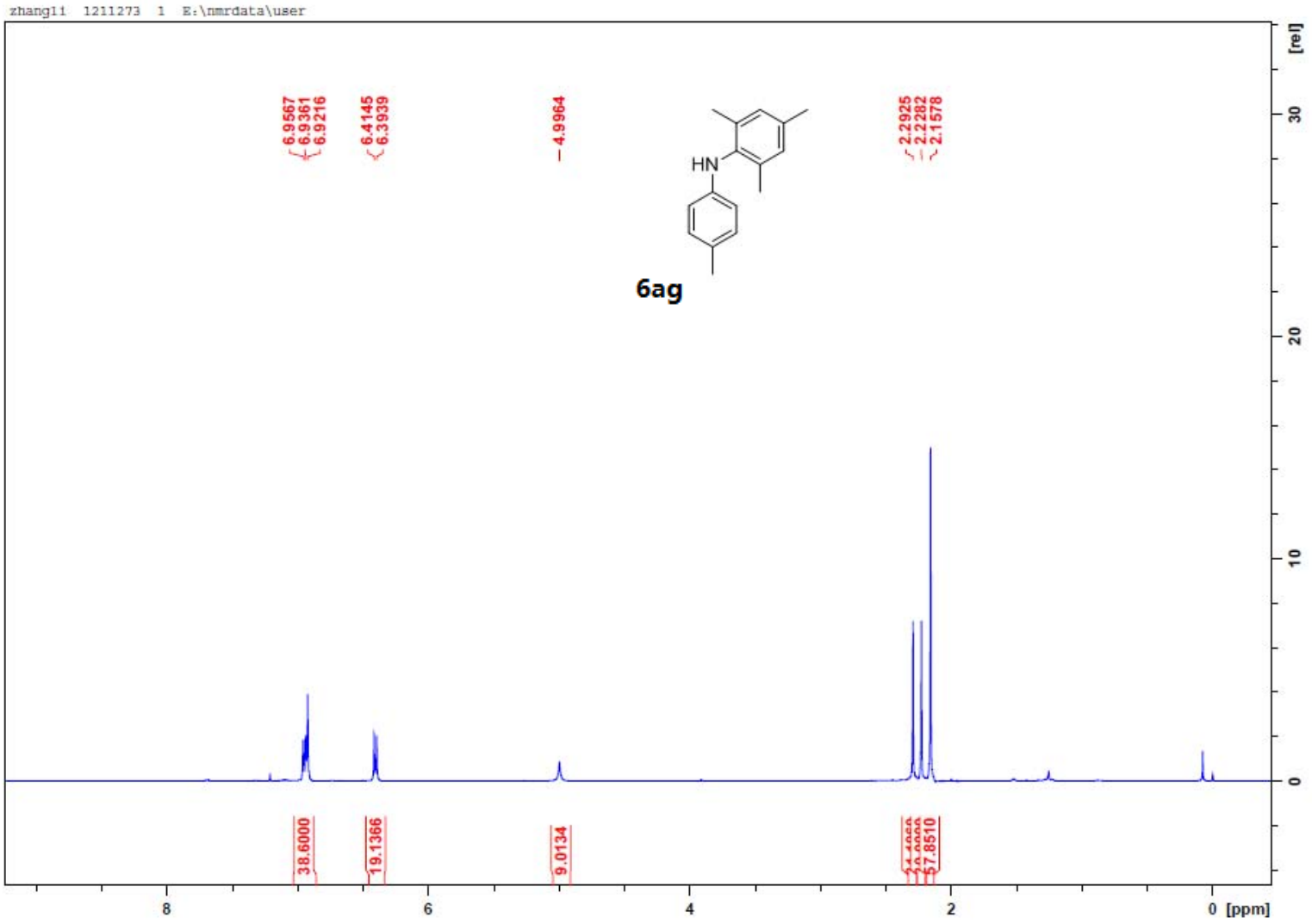

zhang11 1210314 1 E:\nmrdata\user
z-653
7.2374
7.2232
7.2209
7.2023
7.0817
7.0610
6.9987
6.9924
6.9873
6.9796
6.9773
6.9714
6.8833
6.8650
6.8467
5.5649
2.2915
HN
6ab
General
DATE = 2012/10/31
TIME = 09:05
INSTRUM = spect
PULPROG = zg
F1 (1H)
SI = 65536
SF = 399.78
SW_p = 6393.862
19.8826
19.7854
36.2657
9.4137
9.6984
30.0000
6
4
2
0 [ppm]
[rel]
30
20
10
0

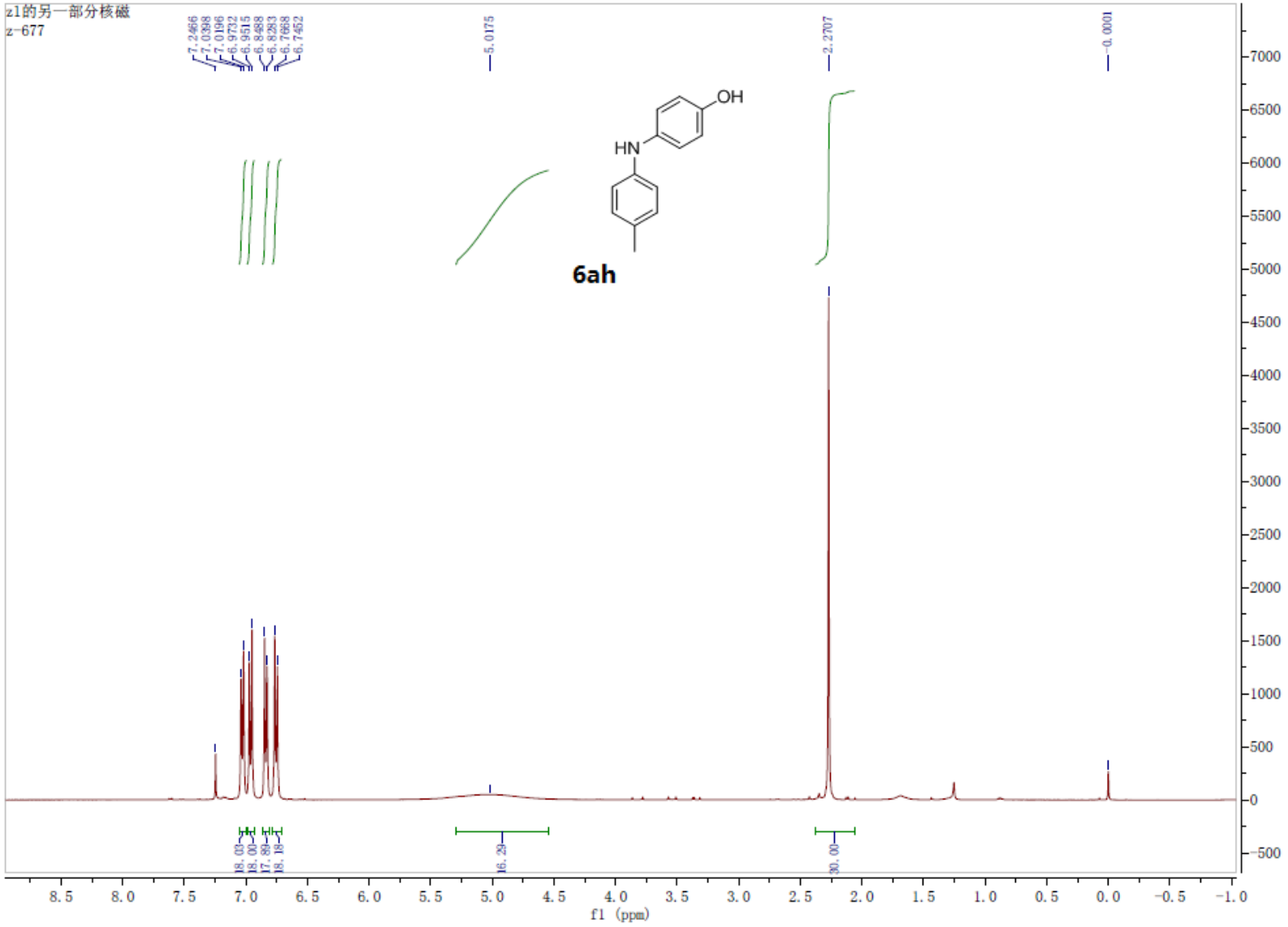

zhang11 1210313 1 E:\nmrdata\user
z-652
7.0561
7.0356
6.9373
6.9164
5.4713
2.2781
HN
6ac
General
DATE = 2012/10/31
TIME = 08:59
INSTRUM = spect
PULPROG = zg
F1 (1H)
SI = 65536
SF = 399.78
SW_p = 6393.862
38.5111
39.2874
9.6280
60.0000
8
6
4
2
0 [ppm]
[rel]
30
20
10
0

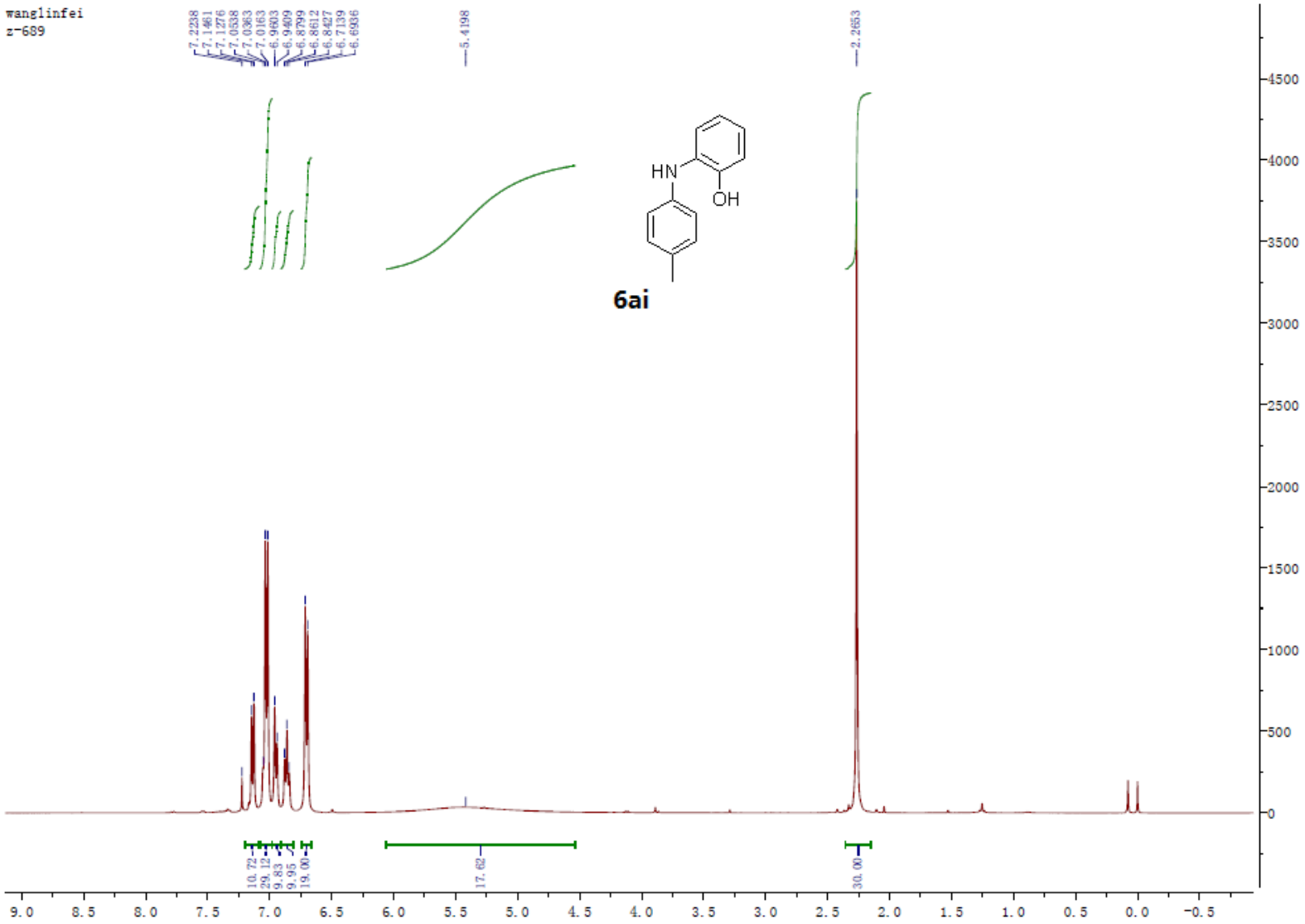

zhangli
z-657
7.1909
7.1078
7.0879
7.0557
7.0356
6.9651
6.9638
6.9492
6.9453
6.9300
5.4961
2.8576
2.8404
2.8232
2.2773
1.2347
1.2318
1.2174
1.2144
HN
6ad
20.76
19.91
39.98
9.53
9.89
30.00
31.02
30.04

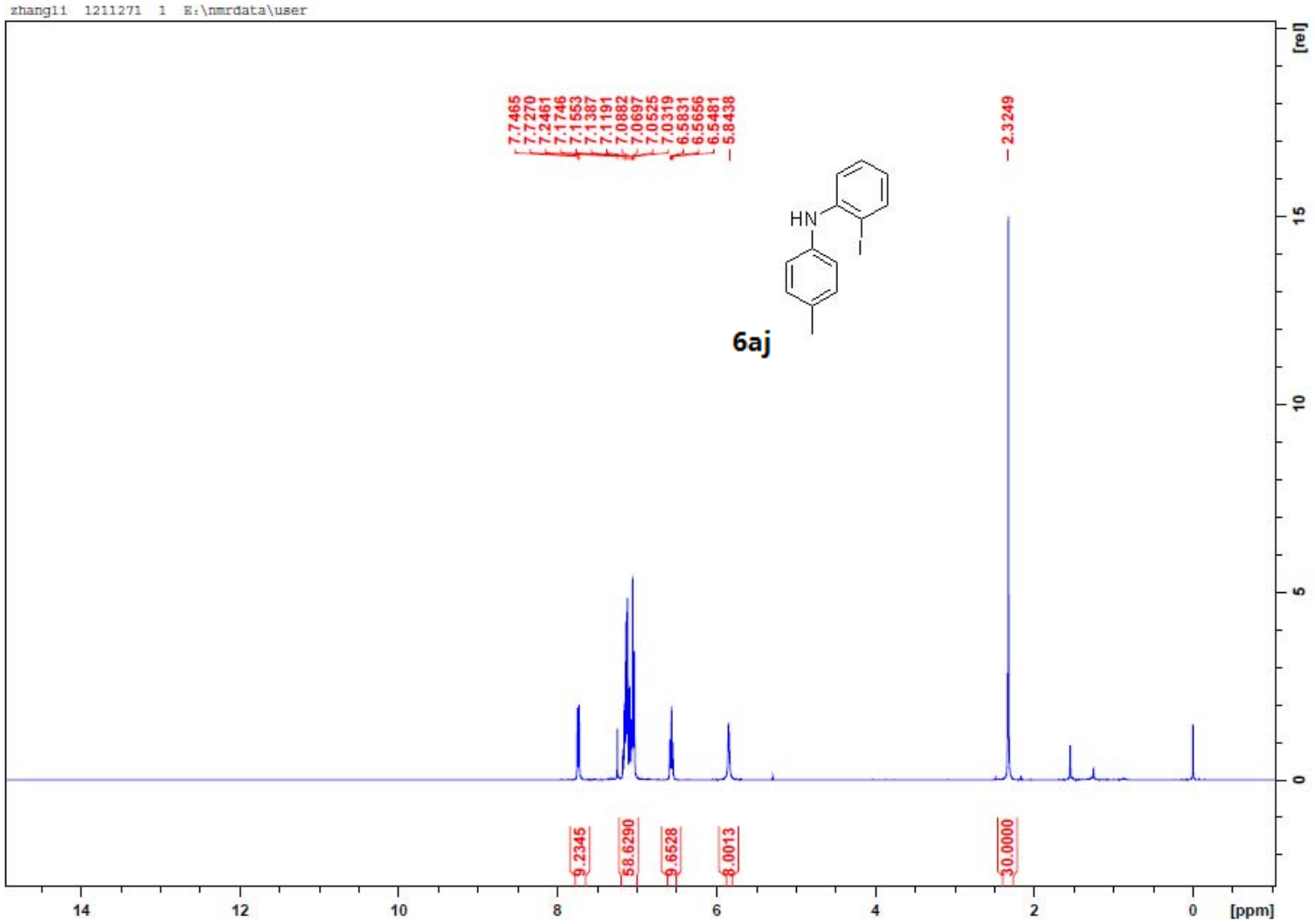

121110
z667
7.1870
7.1658
7.1457
7.1113
7.0928
7.0720
7.0517
6.9065
6.8847
6.8633
6.8451
5.2723
2.2884
2.2301
HN
6ae
48.93
28.70
8.11
60.00

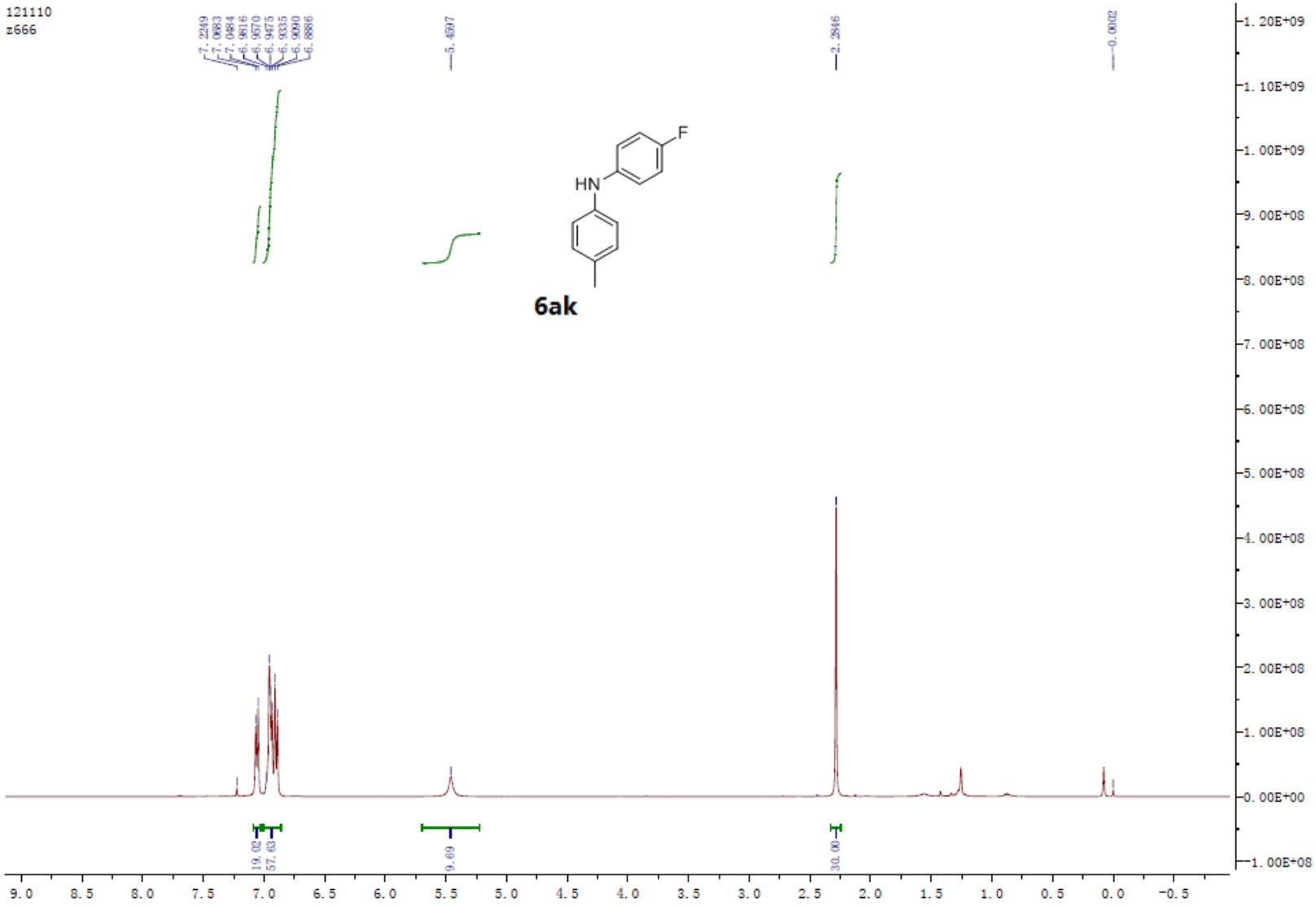

zhangli 1211272 1 E:\nmrdata\user
7.1106
7.0935
7.0685
7.0537
7.0469
6.9703
6.9498
6.4364
6.4157
5.0854
2.2363
2.1962
HN
6af
29.9798
19.8850
19.3501
9.1495
57.2325
8
6
4
2
[ppm]
15
10
5
0
[rel]

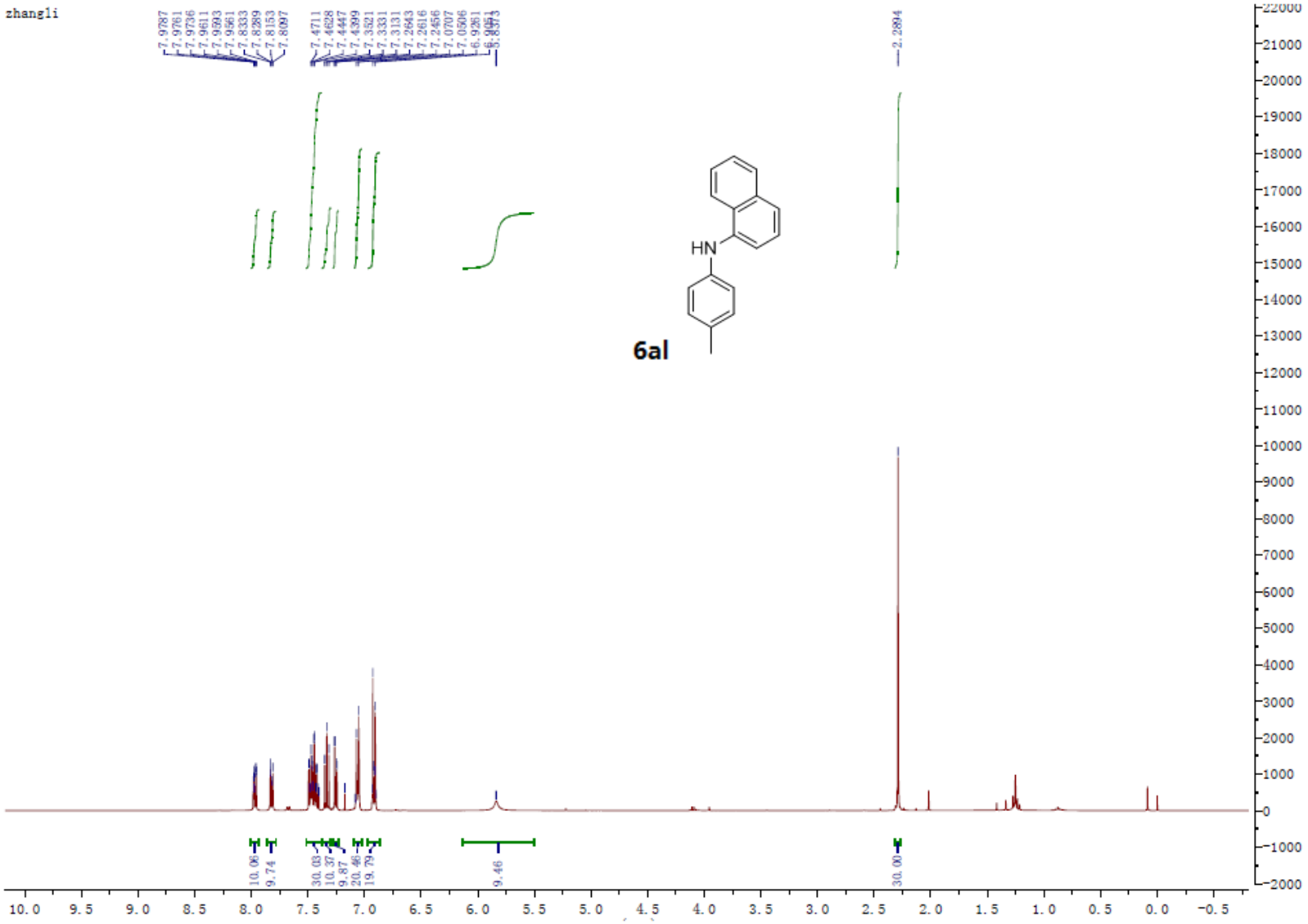

zhangli 1211273 1 E:\nmrdata\user
6.9567
6.9361
6.9216
6.4145
6.3939
4.9964
2.2925
2.2282
2.1578
HN
6ag
38.6000
19.1366
9.0134
57.8510
[rel]
30
20
10
0
8
6
4
2
0 [ppm]

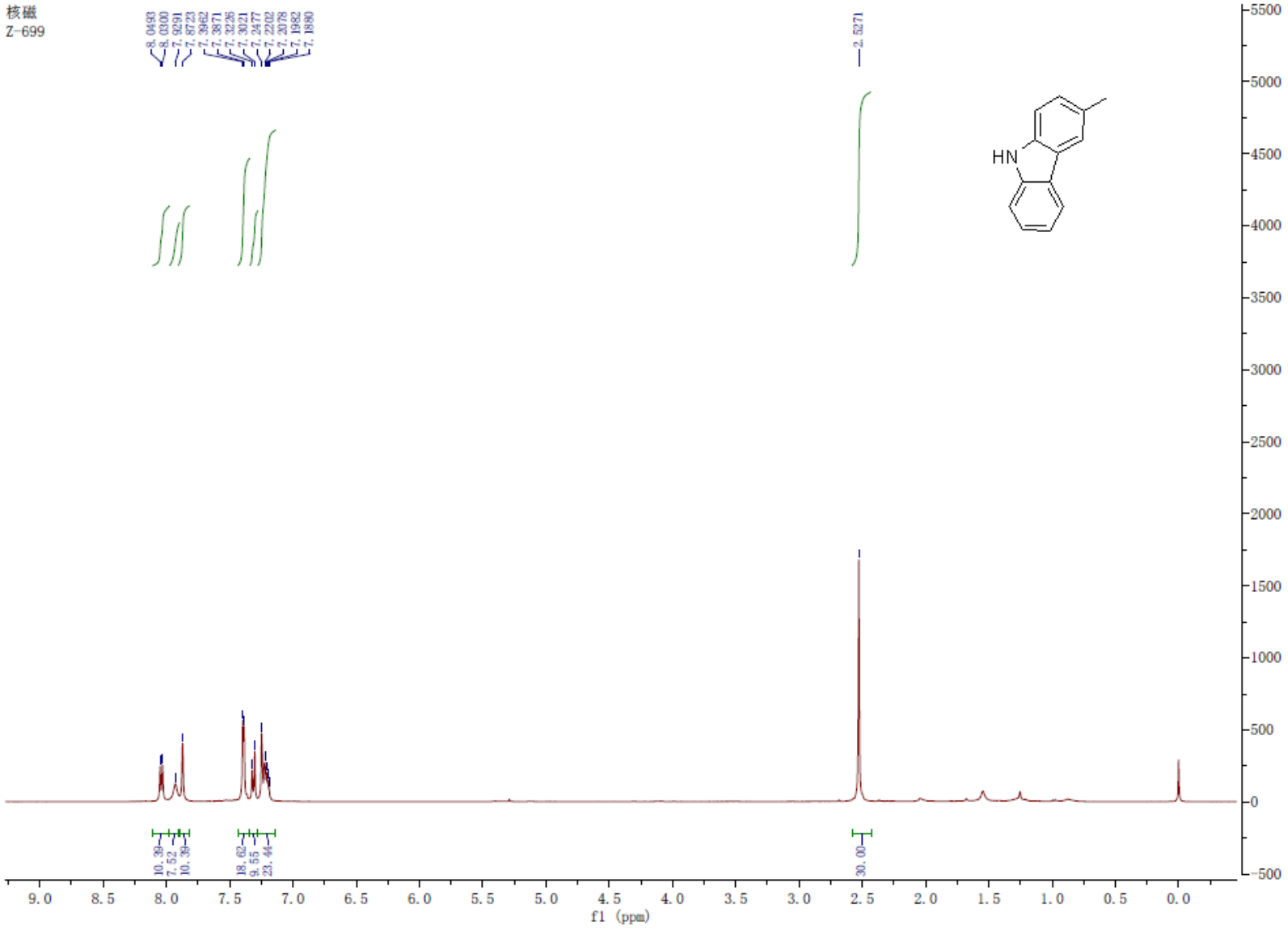

z1的另一部分核磁
z-677
7.2466
7.0398
7.0196
6.9732
6.9515
6.8498
6.8293
6.7668
6.7452
5.0175
2.2707
0.0001
OH
HN
6ah
18.03
18.00
17.89
18.18
16.29
30.00
f1 (ppm)


wanglinfei
z-689
7.2238
7.1461
7.1276
7.0538
7.0363
7.0163
6.9603
6.9409
6.8799
6.8612
6.8427
6.7139
6.6936
5.4198
2.2653
HN
OH
6ai
10.72
29.12
9.83
9.95
19.00
17.62
30.00


zhangli 1211271 1 E:\nmrdata\user
7.7465
7.7270
7.2461
7.1746
7.1553
7.1387
7.1191
7.0882
7.0697
7.0525
7.0319
6.5831
6.5656
6.5481
5.8438
2.3249
HN
I
6aj
9.2345
58.6290
9.6528
6.0013
30.0000
[rel]
[ppm]


121110
z666
7.2269
7.0883
7.0804
6.9816
6.9570
6.9475
6.9335
6.9090
6.8886
5.4697
2.2846
0.0002
HN
F
6ak
19.02
57.63
9.69
30.00
1.20E+09
1.10E+09
1.00E+09
9.00E+08
8.00E+08
7.00E+08
6.00E+08
5.00E+08
4.00E+08
3.00E+08
2.00E+08
1.00E+08
0.00E+00
-1.00E+08
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


zhangli
HN
6al


核磁
Z-699
8.0493
8.0300
7.9291
7.8723
7.3962
7.3871
7.3235
7.3021
7.2477
7.2202
7.2078
7.1982
7.1880
2.5271
HN
10.39
7.52
10.39
18.62
9.55
23.44
30.00
f1 (ppm)