Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

For

Direct Cleavage of N=N Bond of Azobenzenes by MeOTf Leading to *N*-Arylbenzimidazoles

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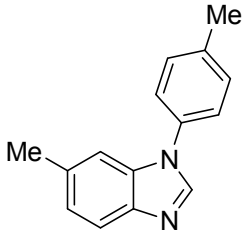
General Considerations

All manipulations were conducted in sealed tubes under an atmosphere of dinitrogen. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Substituted azobenzenes were prepared according to literature (**1b**[1], **1j**[3], **1l**[4], and others[2]). DCE was dried by 4Å molecule sieves. ^{1}H NMR and ^{13}C NMR spectra were recorded on 400M and 600M NMR spectrometer with TMS as internal standard. GC-MS spectra were recorded on Hewlett Packard GC-MS system.

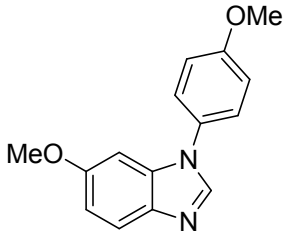
Experimental Procedures

Typical procedure for reaction of azobenzenes with MeOTf. To a 25 mL tube charged with nitrogen, was added azobenzene **1a** (0.2 mmol), TCQ (0.24 mmol), MeOTf (0.3 mmol), DCE 1 mL. The tube was sealed and stirred for 4 h at 140^{o}C. Removing the solvent of reaction mixture and subsequent purification by column chromatography on silica gel (petroleum ether/ethyl acetate/triethylamine: 1/1/0.05) afforded **2a** (39 mg, 87% isolated yield) as a colorless oil.



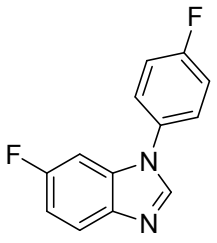
2a

87% yield. Rf = 0.35. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.99 (s, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.38 – 7.31 (m, 4H), 7.28 (s, 1H), 7.13 (d, *J* = 8.2 Hz, 1H), 2.46 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 142.2, 142.1, 138.1, 134.2, 134.0, 133.7, 130.6, 124.4, 124.2, 120.1, 110.4, 21.9, 21.3. HRMS (ESI mode) calcd for $C_{15}H_{14}N_2$+H^+ 223.1230, found 223.1232.



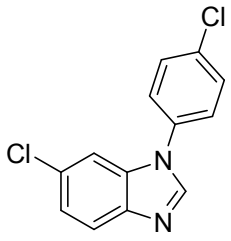
2b

Colorless oil, 35 mg (70% yield). Rf = 0.21 (PE/EA/TEA: 1/1/0.05). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.94 (s, 1H), 7.73 (d, *J* = 8.8 Hz, 1H), 7.43 – 7.37 (m, 2H), 7.10 – 7.05 (m, 2H), 6.96 (dd, *J* = 8.8, 2.2 Hz, 1H), 6.88 (d, *J* = 2.2 Hz, 1H), 3.89 (s, 3H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 159.5, 157.4, 142.0, 138.4, 135.1, 129.3, 125.9, 121.1, 115.3, 112.2, 93.8, 56.0, 55.8. HRMS (ESI mode) calcd for $C_{15}H_{14}O_2N_2$+H^+ 255.1128, found 255.1133.



2c

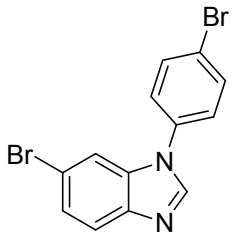
Colorless oil, 36 mg (78% yield). Rf = 0.33 (PE/EA/TEA: 1/1/0.05). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.05 (s, 1H), 7.80 (dd, *J* = 8.8, 4.8 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.32 – 7.25 (m, 2H), 7.16 – 7.06 (m, 2H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 162.2 (d, *J* = 249.2 Hz), 160.4 (d, *J* = 240.9 Hz), 142.92, 140.34, 134.1 (d, *J* = 13.3 Hz), 132.1, 126.1 (d, *J* = 8.6 Hz), 121.6 (d, *J* = 10.1 Hz), 117.3 (d, *J* = 23.0 Hz), 111.5 (d, *J* = 25.2 Hz), 97.0 (d, *J* = 28.2 Hz). HRMS (ESI mode) calcd for $C_{13}H_8F_2N_2$+H^+ 231.0728, found 231.0729.



2d

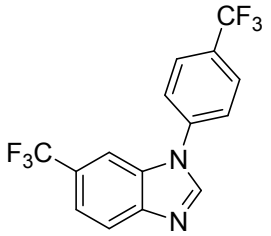
Colorless oil, 38 mg (73% yield). Rf = 0.36 (PE/EA/TEA: 1/1/0.05). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.06 (s, 1H), 7.77 (d, *J* = 8.6 Hz, 1H), 7.57 – 7.54 (m, 2H), 7.48 – 7.40 (m, 3H), 7.30 (dd, *J* = 8.6, 1.9 Hz, 1H). ^{13}C NMR (101 MHz,

CHLOROFORM-D) δ 142.8, 142.7, 134.4, 134.2, 130.5, 129.9, 125.4, 123.8, 121.7, 110.5. HRMS (ESI mode) calcd for $C_{13}H_8Cl_2N_2$+H^+ 263.0137, found 263.0135.



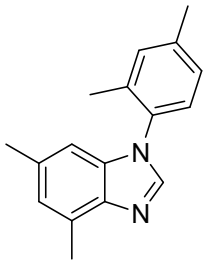
2e

Colorless oil, 49 mg (69% yield). Rf = 0.33 (PE/EA/TEA: 1/1/0.05). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.05 (s, 1H), 7.77 – 7.69 (m, 3H), 7.63 (d, *J* = 1.8 Hz, 1H), 7.45 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.41 – 7.35 (m, 2H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 143.1, 142.7, 134.9, 134.7, 133.6, 126.6, 125.8, 122.3, 122.1, 117.5, 113.5. HRMS (ESI, positive mode) calcd for $C_{13}H_8Br_2N_2$+H^+ 352.9112, found 352.9109.



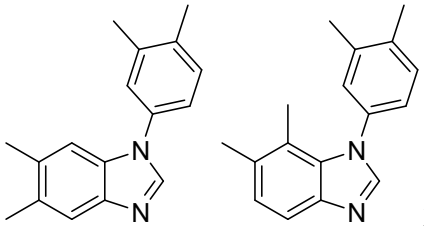
2f

Colorless oil, 16 mg (24% yield). Rf = 0.39 (PE/EA/TEA: 1/1/0.05). ^{1}H NMR (600 MHz, CHLOROFORM-D) δ 8.26 (s, 1H), 7.98 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 8.3 Hz, 2H), 7.80 (s, 1H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.63 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (151 MHz, CHLOROFORM-D) δ 146.4, 144.2, 138.7, 132.9, 130.9 (q, *J* = 33.5 Hz), 127.8 (q, *J* = 2.9 Hz), 126.7 (q, *J* = 32.7 Hz), 124.5 (q, *J* = 272.6 Hz), 124.4, 123.6 (q, *J* = 272.1 Hz), 121.6, 120.4 (q, *J* = 3.4 Hz), 108.17 (q, *J* = 4.1 Hz). HRMS (ESI mode) calcd for $C_{15}H_8F_6N_2$+H^+ 331.0664, found 331.0669.



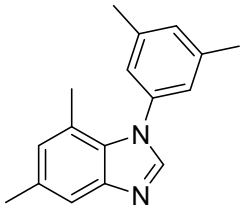
2g

Colorless oil, 26 mg (53% yield). Rf = 0.44 (PE/EA/TEA: 1/1/0.05). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.85 (s, 1H), 7.22 (s, 1H), 7.19 – 7.12 (m, 2H), 6.95 (s, 1H), 6.74 (s, 1H), 2.70 (s, 3H), 2.43 (s, 3H), 2.39 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 141.9, 140.8, 139.3, 135.2, 134.8, 133.5, 132.5, 132.1, 129.7, 127.8, 127.6, 124.6, 107.9, 21.8, 21.2, 17.6, 16.7. HRMS (ESI mode) calcd for $C_{17}H_{18}N_2$+H^+ 251.1543, found 251.1549.



2h

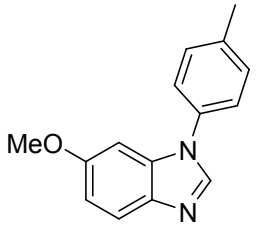
Colorless oil, 42 mg (85% yield) in 4:1 ratio. Rf = 0.39 (PE/EA/TEA: 1/1/0.05). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.96 (s), 7.79 (s), 7.61 (s), 7.58 (s), 7.37 – 7.08 (m), 2.39 – 2.33 (m). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 142.7, 141.8, 138.6, 137.7, 136.6, 134.5, 132.8, 132.5, 131.6, 131.0, 130.2, 125.2, 125.0, 121.4, 120.5, 117.4, 110.7, 20.7, 20.4, 20.1, 20.0, 19.7, 19.6. HRMS (ESI mode) calcd for $C_{17}H_{18}N_2$+H^+ 251.1543, found 251.1544.



2i

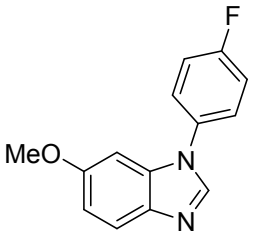
Colorless oil, 6 mg (12% yield). Rf = 0.40 (PE/EA/TEA: 1/1/0.05). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.84 (s, 1H), 7.49 (s, 1H), 7.13 (s, 1H), 7.01 (s, 2H), 6.86 (s, 1H), 2.45 (s, 3H), 2.39 (s, 6H), 2.05 (s, 3H). ^{13}C NMR (101 MHz,

CHLOROFORM-D) δ 144.2, 143.9, 139.0, 137.3, 132.4, 131.6, 130.6, 127.3, 125.4, 121.6, 117.9, 21.5, 21.3, 18.7. HRMS (ESI mode) calcd for $C_{17}H_{18}N_2$+H^+ 251.1543, found 251.1545.



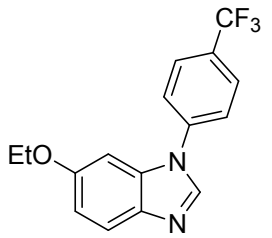
2j

Colorless oil, 34 mg (71% yield). Rf = 0.33 (PE/EA/TEA: 1/1/0.05). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.98 (s, 1H), 7.74 (d, *J* = 8.6 Hz, 1H), 7.38 (s, 4H), 7.00 – 6.92 (m, 2H), 3.82 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 157.4, 141.8, 138.2, 134.7, 134.0, 130.7, 124.2, 121.1, 112.2, 94.0, 56.0, 21.3. HRMS (ESI mode) calcd for $C_{15}H_{14}ON_2$+H^+ 239.1179, found 239.1178.



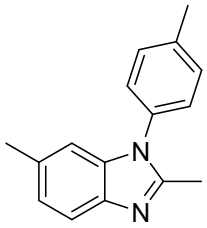
2k

Colorless oil, 17 mg (35% yield). Rf = 0.29 (PE/EA/TEA: 1/1/0.05). ^{1}H NMR (600 MHz, CHLOROFORM-D) δ 7.94 (s, 1H), 7.73 (d, *J* = 8.9 Hz, 1H), 7.49 – 7.44 (m, 2H), 7.29 – 7.24 (m, 2H), 6.97 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.88 (d, *J* = 2.3 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (151 MHz, CHLOROFORM-D) δ 162.1 (d, *J* = 248.6 Hz), 157.5, 141.6, 138.4, 134.7, 132.6, 126.2 (d, *J* = 8.6 Hz), 121.2, 117.1 (d, *J* = 22.9 Hz), 112.3, 93.7, 56.0. HRMS (ESI mode) calcd for $C_{14}H_{11}OFN_2$+H^+ 243.0928, found 243.0926.



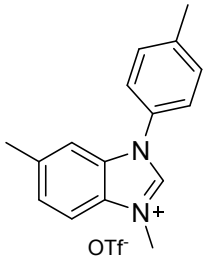
2l

Colorless solid, 20 mg (32% yield). Rf = 0.34 (PE/EA/TEA: 1/1/0.05). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.01 (s, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 9.5 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.01 – 6.94 (m, 2H), 4.04 (q, *J* = 7.0 Hz, 2H), 1.42 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 157.05, 141.05, 139.58, 138.61, 133.95, 130.0 (q, *J* = 33.2 Hz), 127.5(q, *J* = 3.5 Hz), 123.95, 123.7 (q, *J* = 272.3 Hz), 121.41, 112.93, 94.78, 64.35, 14.94. HRMS (ESI mode) calcd for $C_{16}H_{13}F_3ON_2$+H^+ 307.1053, found 307.1055.



2m

Colorless oil, 30 mg (64% yield). Rf = 0.34 (PE/EA/TEA: 1/1/0.05). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.61 (d, *J* = 8.2 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 1H), 6.90 (s, 1H), 2.48 (s, 3H), 2.47 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 138.9, 133.7, 132.6, 130.6, 127.0, 123.8, 118.6, 110.0, 21.8, 21.4, 14.5. HRMS (ESI mode) calcd for $C_{16}H_{16}N_2$+H^+ 237.1386, found 237.1389.



3a

Colorless solid, 76 mg (99% yield). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 9.65 (s, 1H), 7.74 (d, *J* = 8.6 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 8.6 Hz, 1H), 7.43 (d, *J* = 7.7 Hz, 2H), 7.42 (s, 1H), 4.23 (s, 3H), 2.53 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 141.2, 141.2, 138.9, 131.7, 131.2, 130.3, 129.4, 124.7, 120.6 (q, *J* = 320.4 Hz), 112.9, 112.9, 33.8, 21.8, 21.3. HRMS (ESI mode) calcd for $C_{16}H_{17}N_2$ 237.1386, found 237.1385.

Reference:

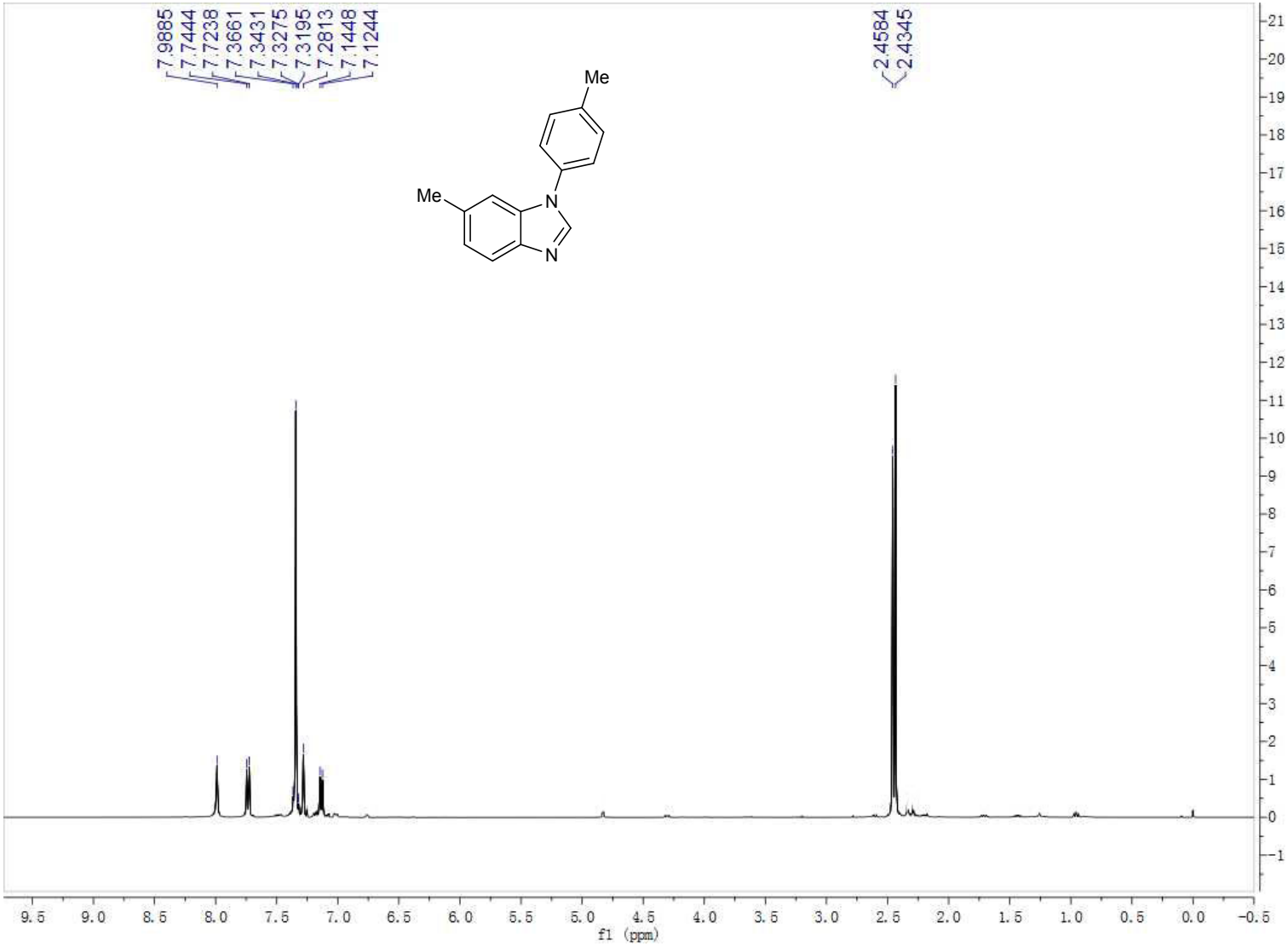
(1) Lu, W.; Xi, C. *Tetrahedron Lett.* **2008**, *49*, 4011.

(2) Zhang, C.; Jiao, N. *Angew. Chem. Int. Ed.* **2010**, *49*, 6174.

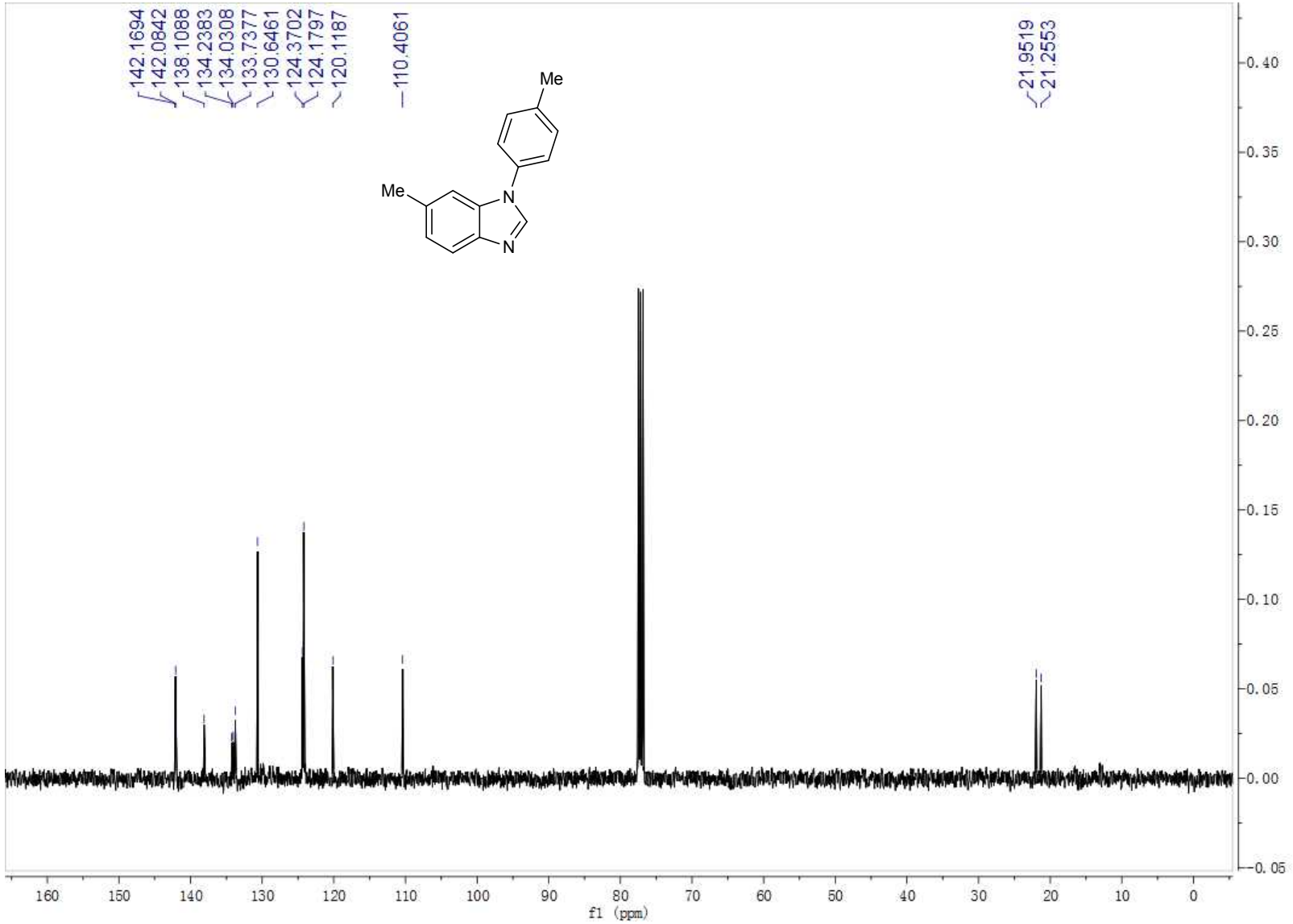
(3) Takeda, Y.; Okumura, S.; Minakata, S. *Angew. Chem. Int. Ed.* **2012**, *51*, 7804.

(4) Haghbeen, K.; Tan, E. W. *J. Org. Chem.* **1998**, *63*, 4503.

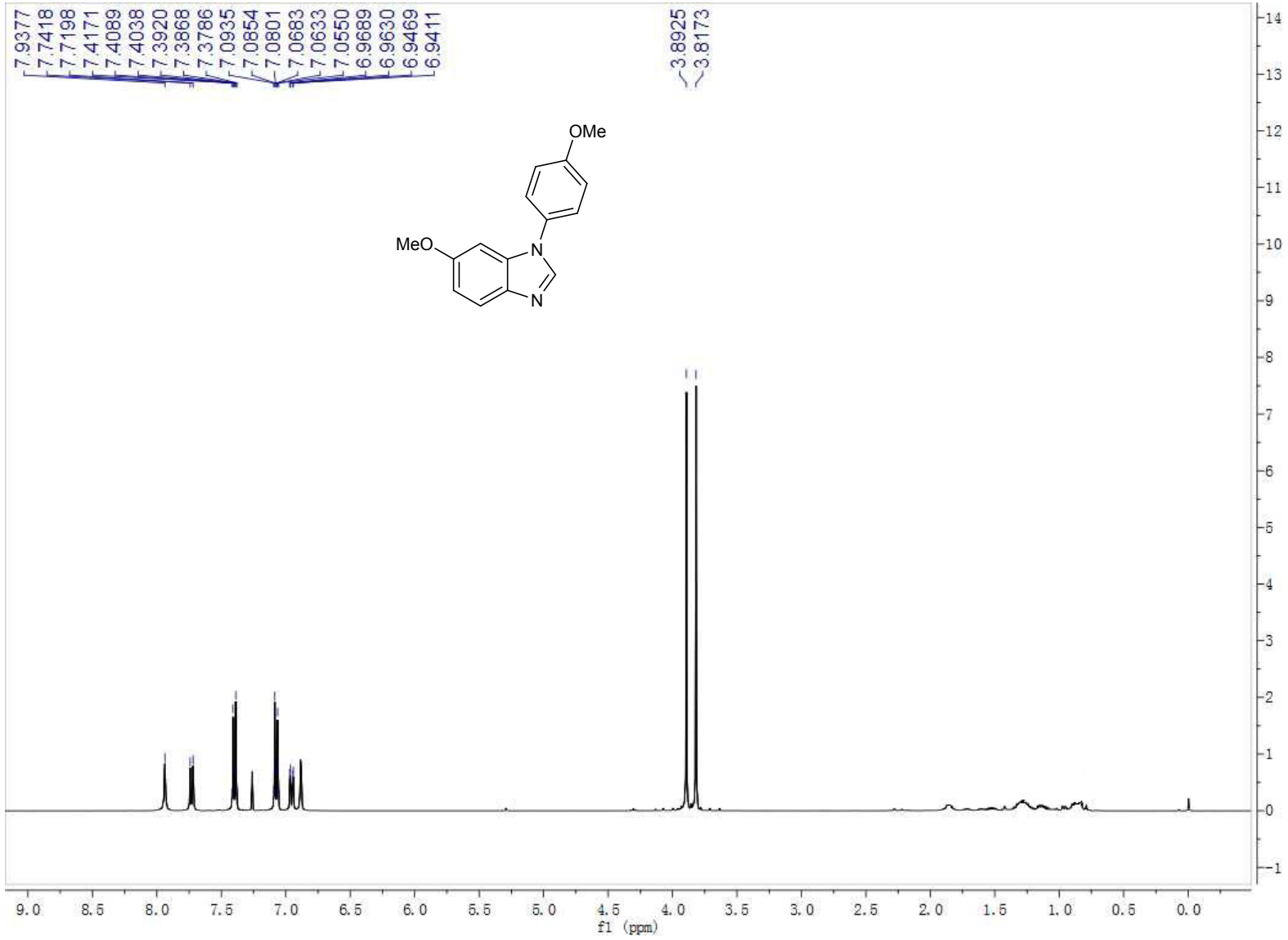
Copies of ^{1}H and ^{13}C NMR Spectra



^{1}H NMR for compound **2a**



^{13}C NMR for compound **2a**


7.9377
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7.0683
7.0633
7.0550
6.9689
6.9630
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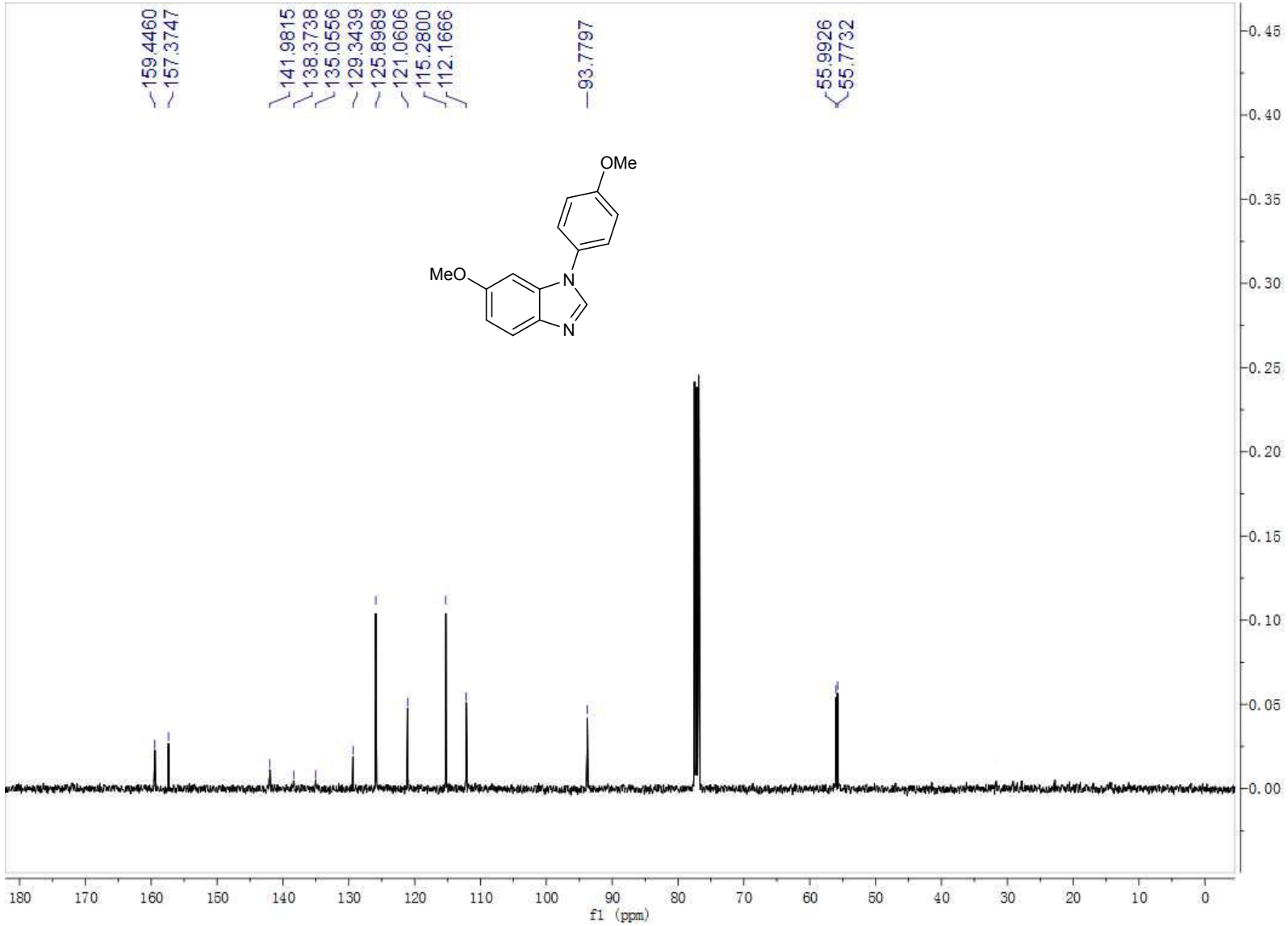
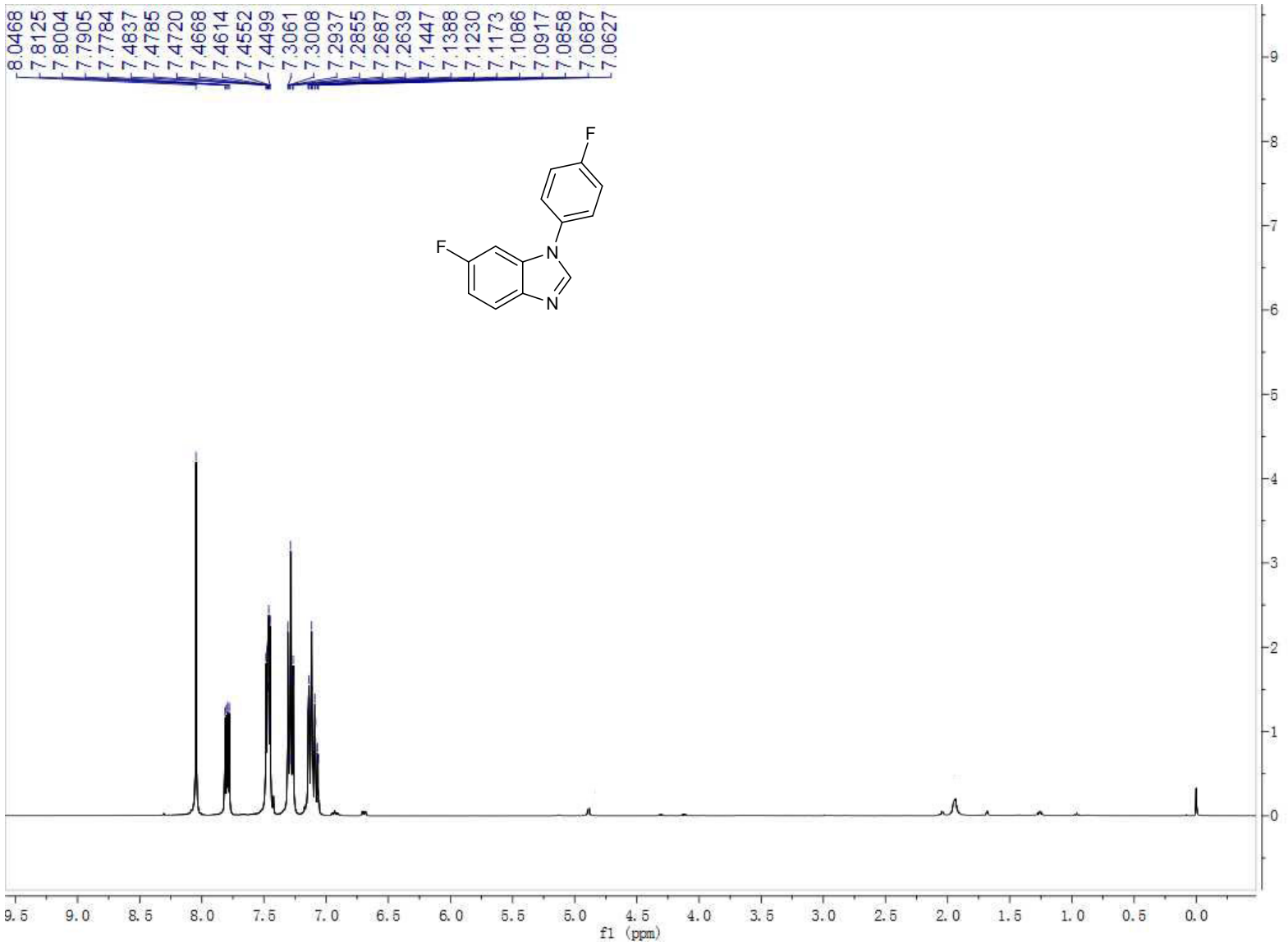
OMe
MeO
N
N
f1 (ppm)

^{1}H NMR for compound **2b**



^{13}C NMR for compound **2b**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7.7905
7.7784
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7.4785
7.4720
7.4668
7.4614
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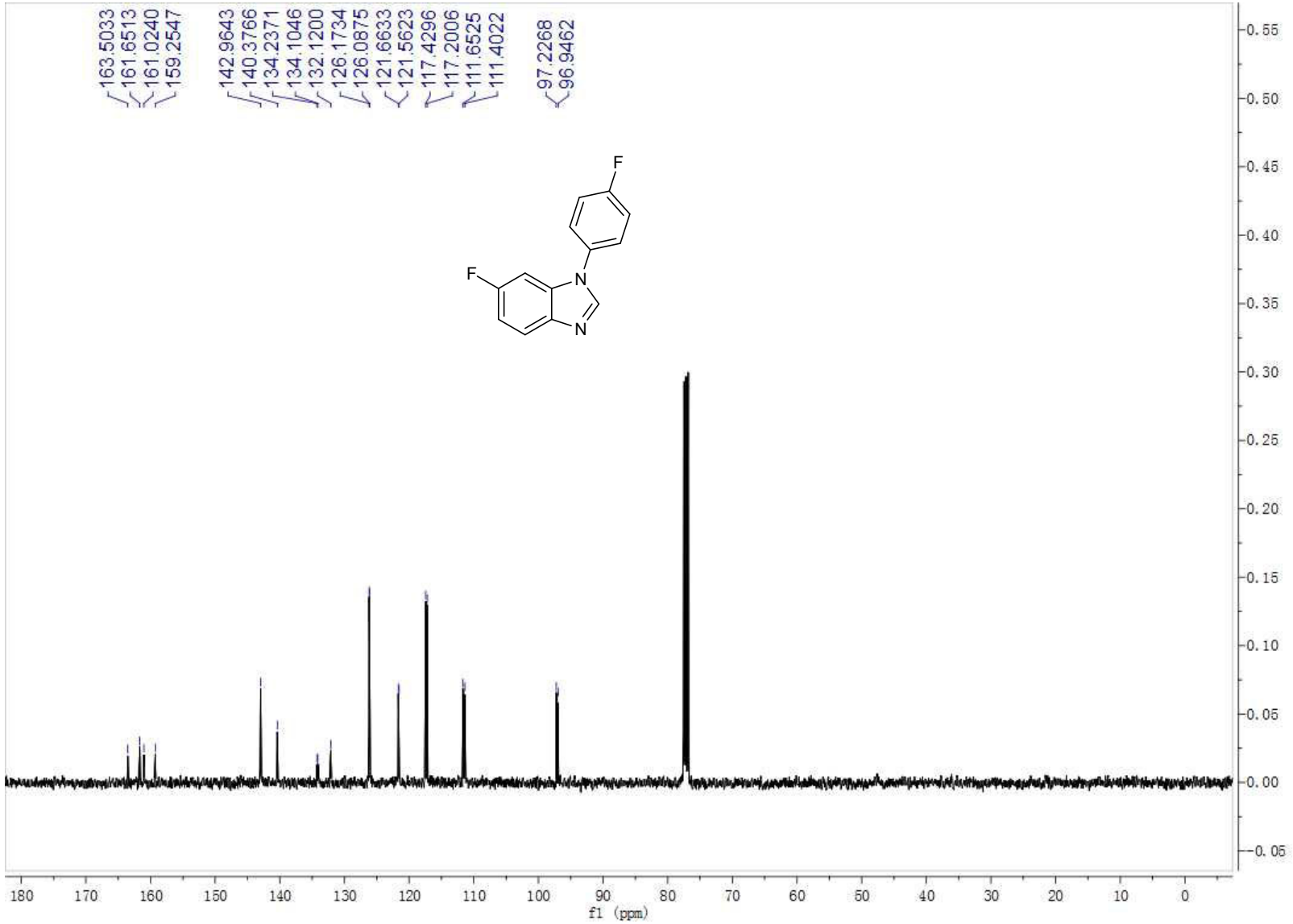
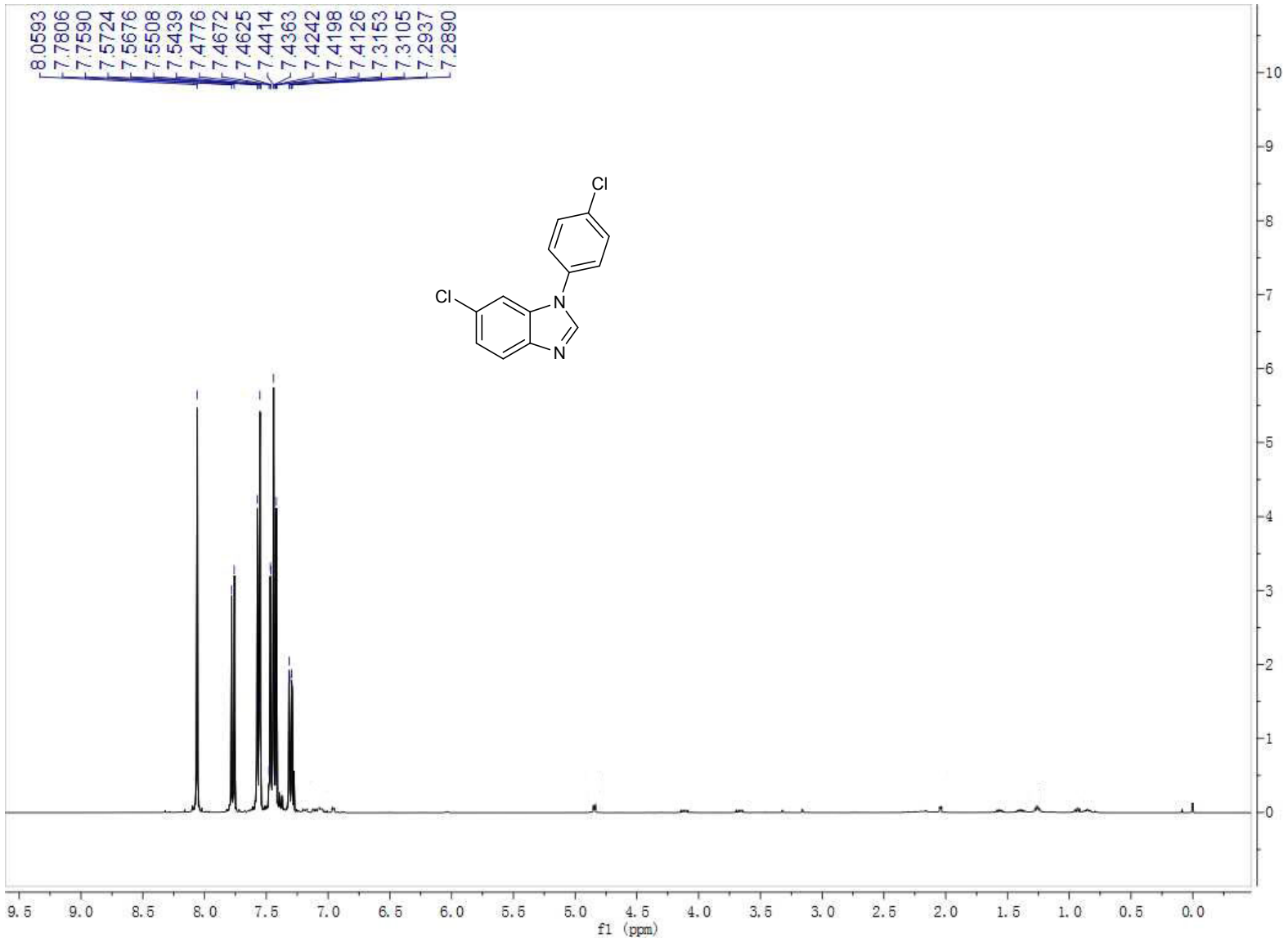
7.4499
7.3061
7.3008
7.2937
7.2855
7.2687
7.2639
7.1447
7.1388
7.1230
7.1173
7.1086
7.0917
7.0858
7.0687
7.0627
F
F
N
N
f1 (ppm)

^{1}H NMR for compound **2c**



^{13}C NMR for compound **2c**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7.4242
7.4198
7.4126
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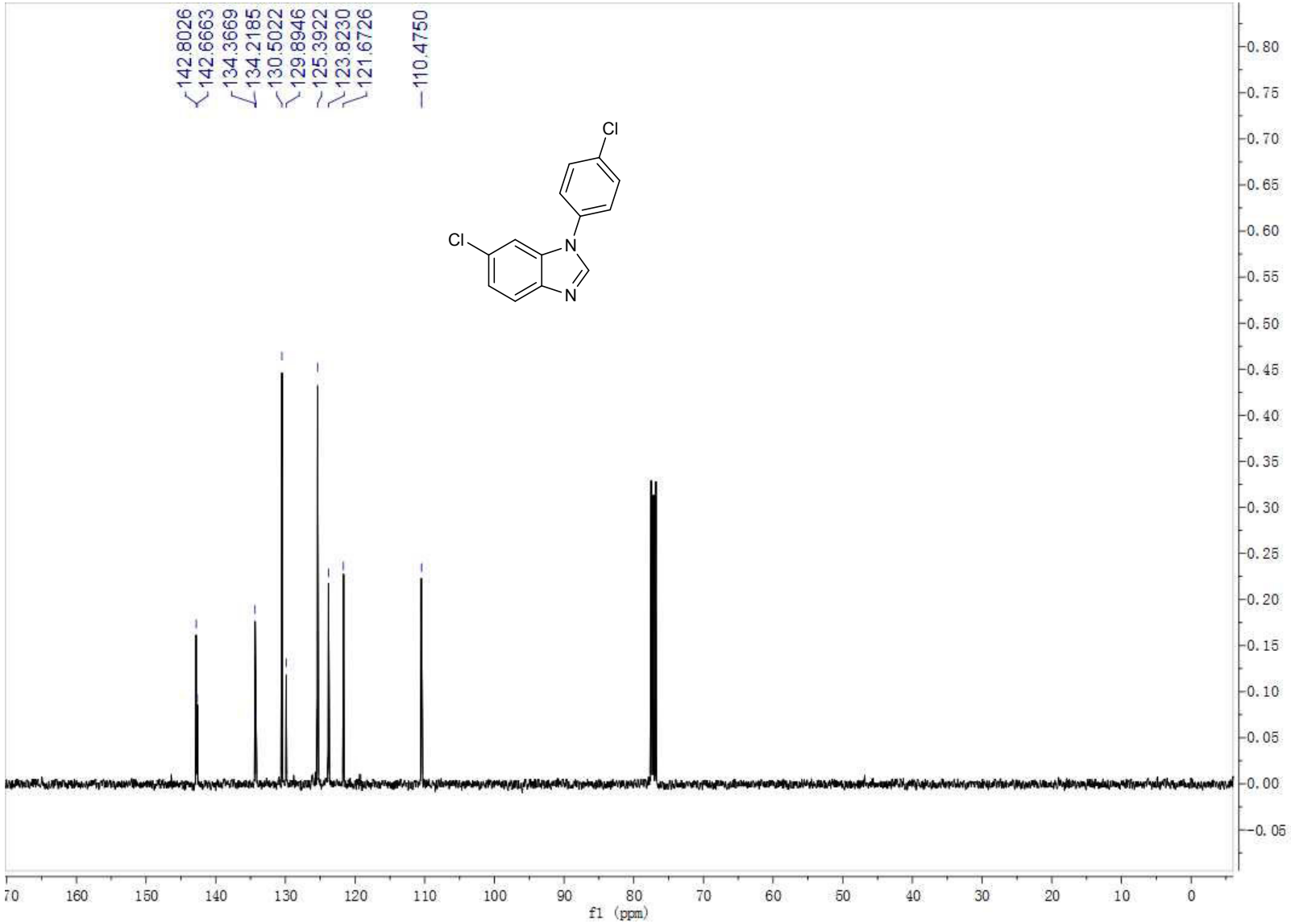
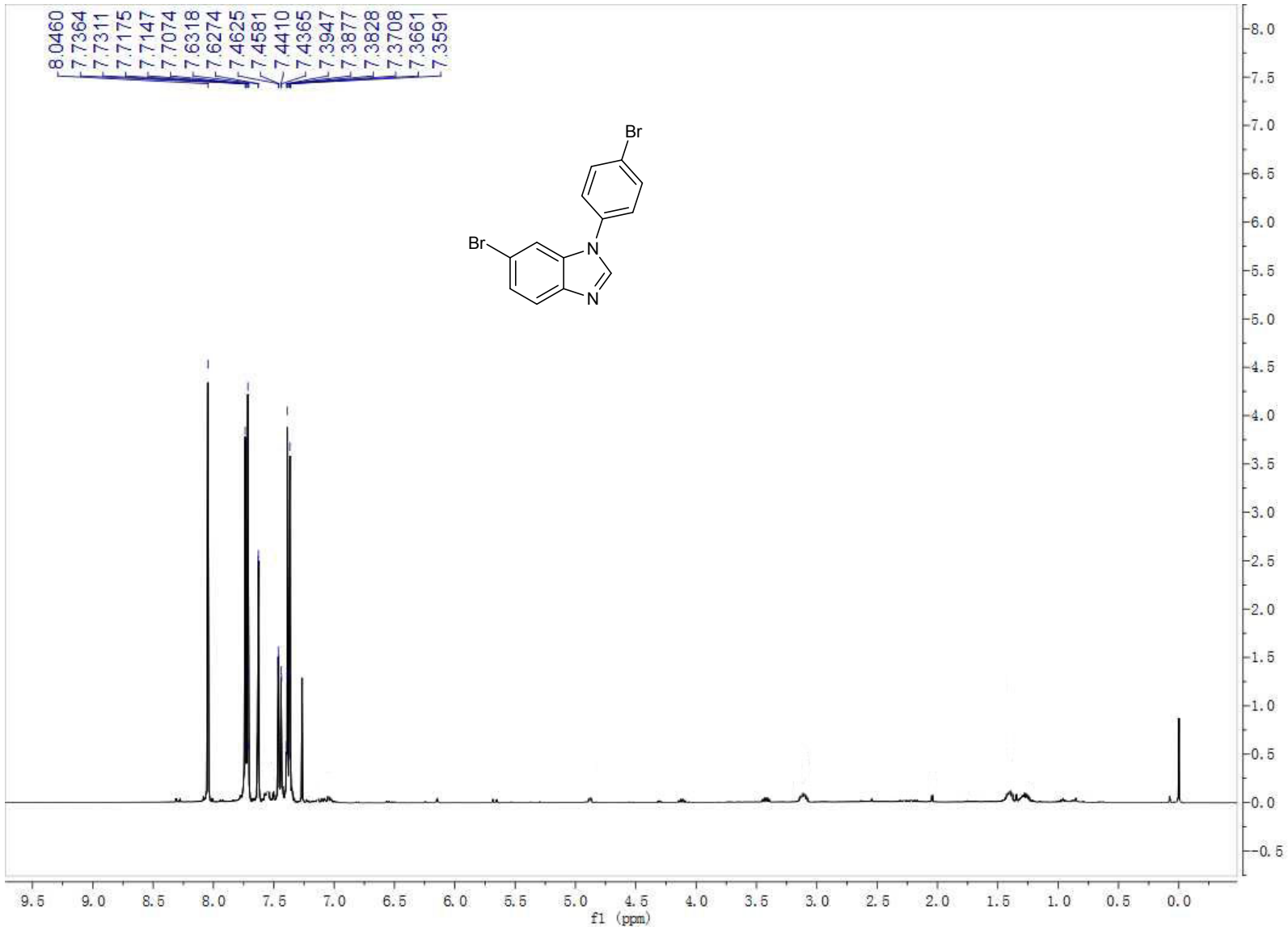
7.2937
7.2890
Cl
Cl
N
N
f1 (ppm)

^{1}H NMR for compound **2d**



^{13}C NMR for compound **2d**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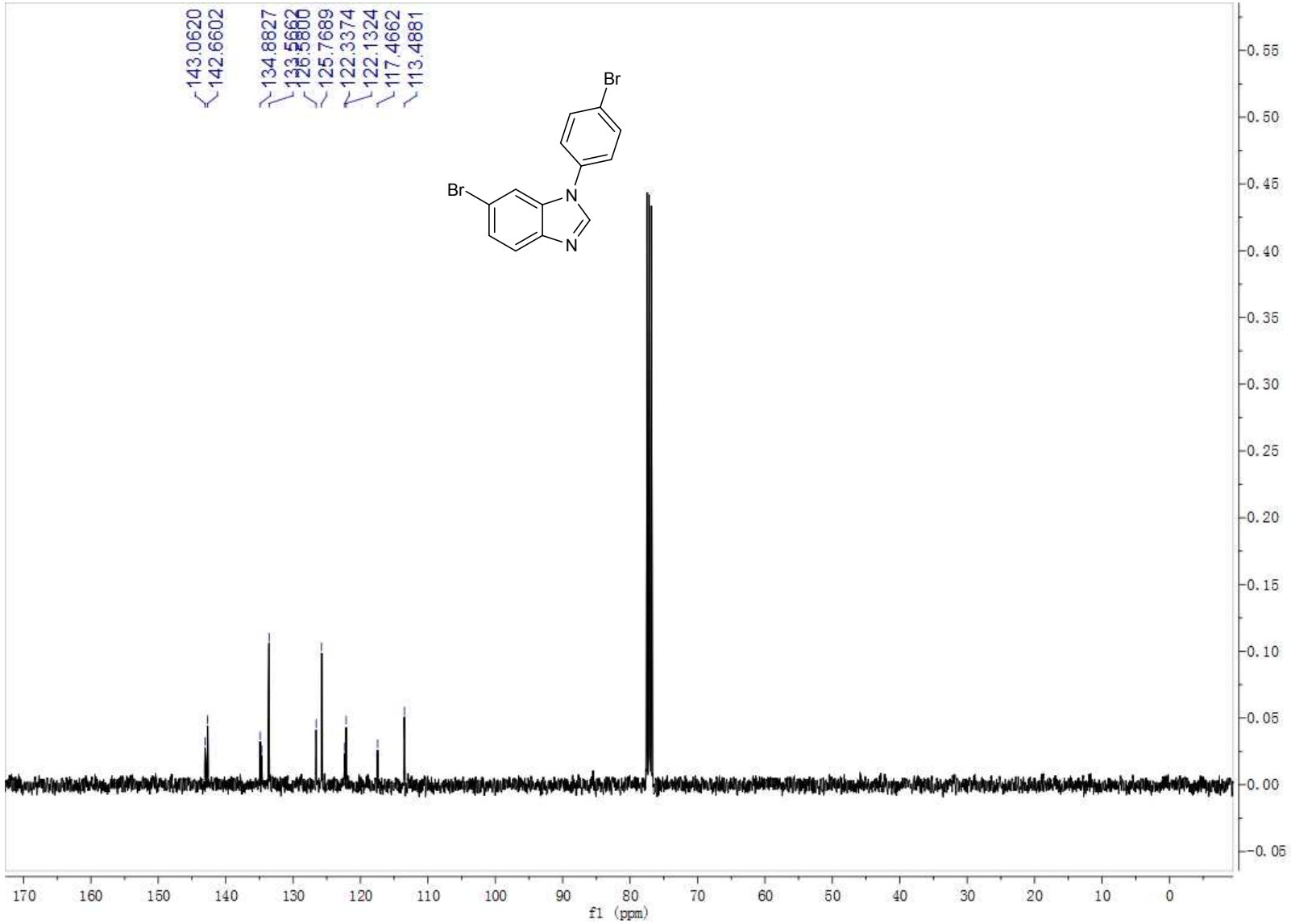
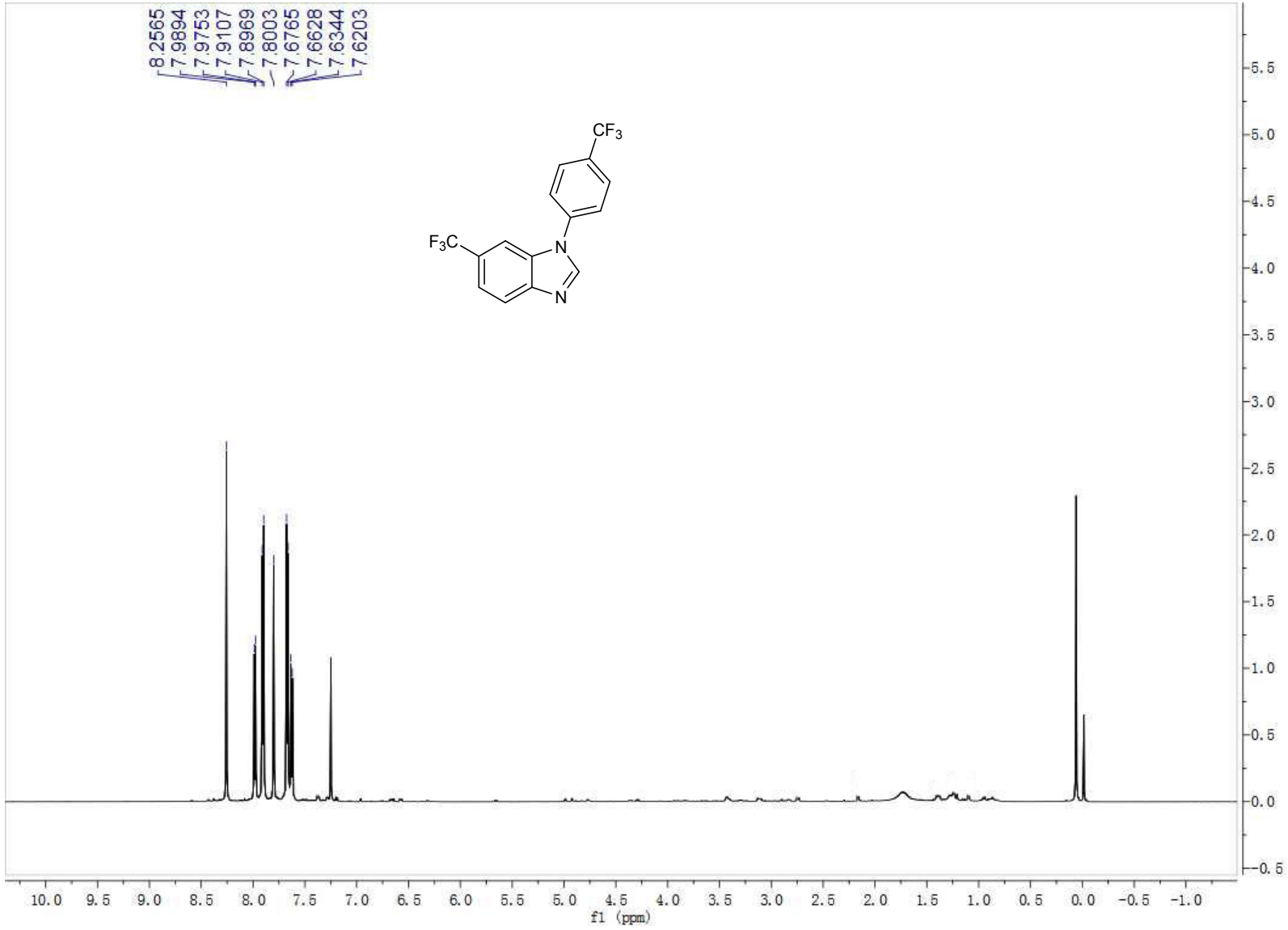
7.4365
7.3947
7.3877
7.3828
7.3708
7.3661
7.3591
Br
Br
N
N
f1 (ppm)

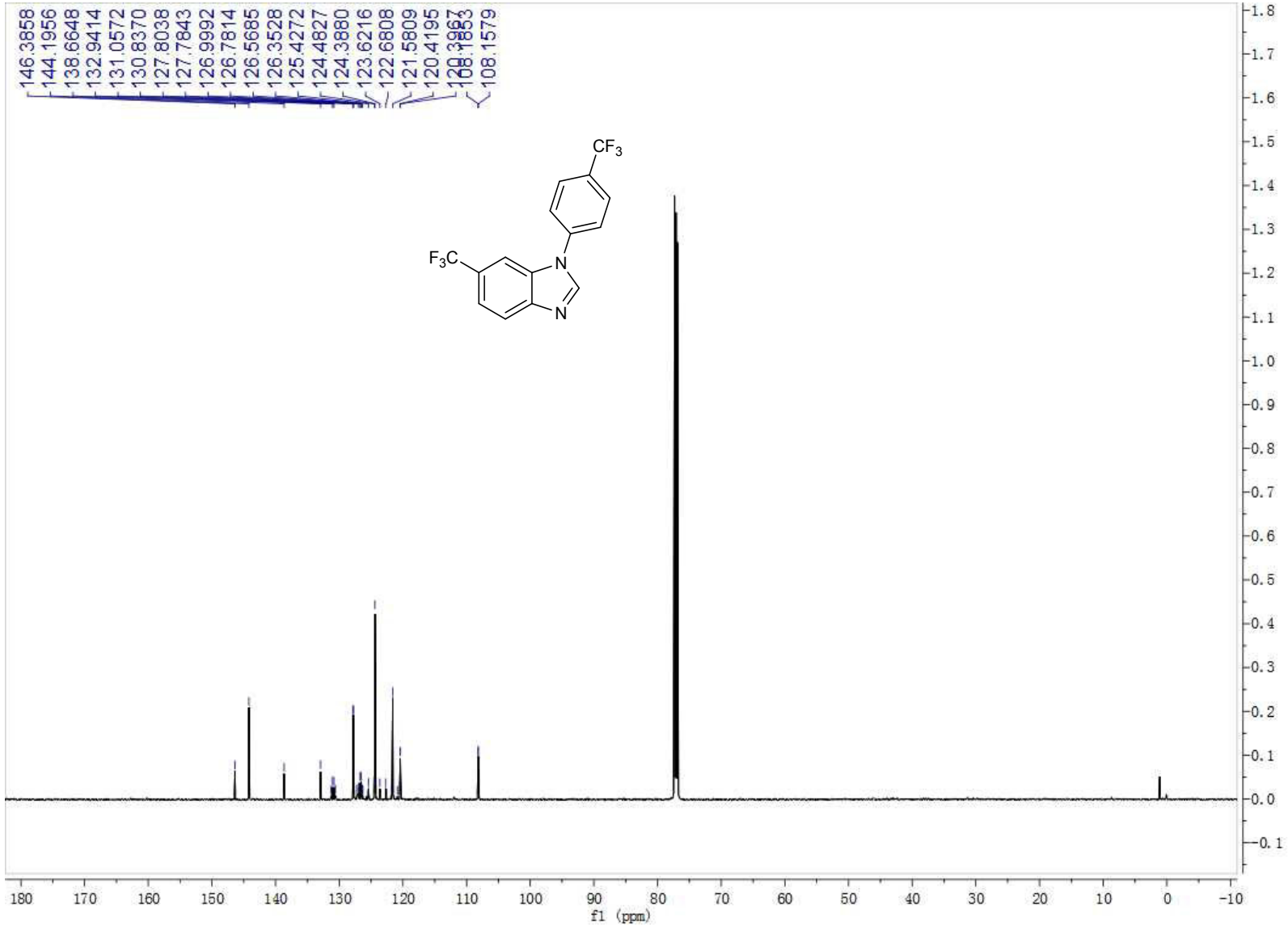
^{1}H NMR for compound **2e**



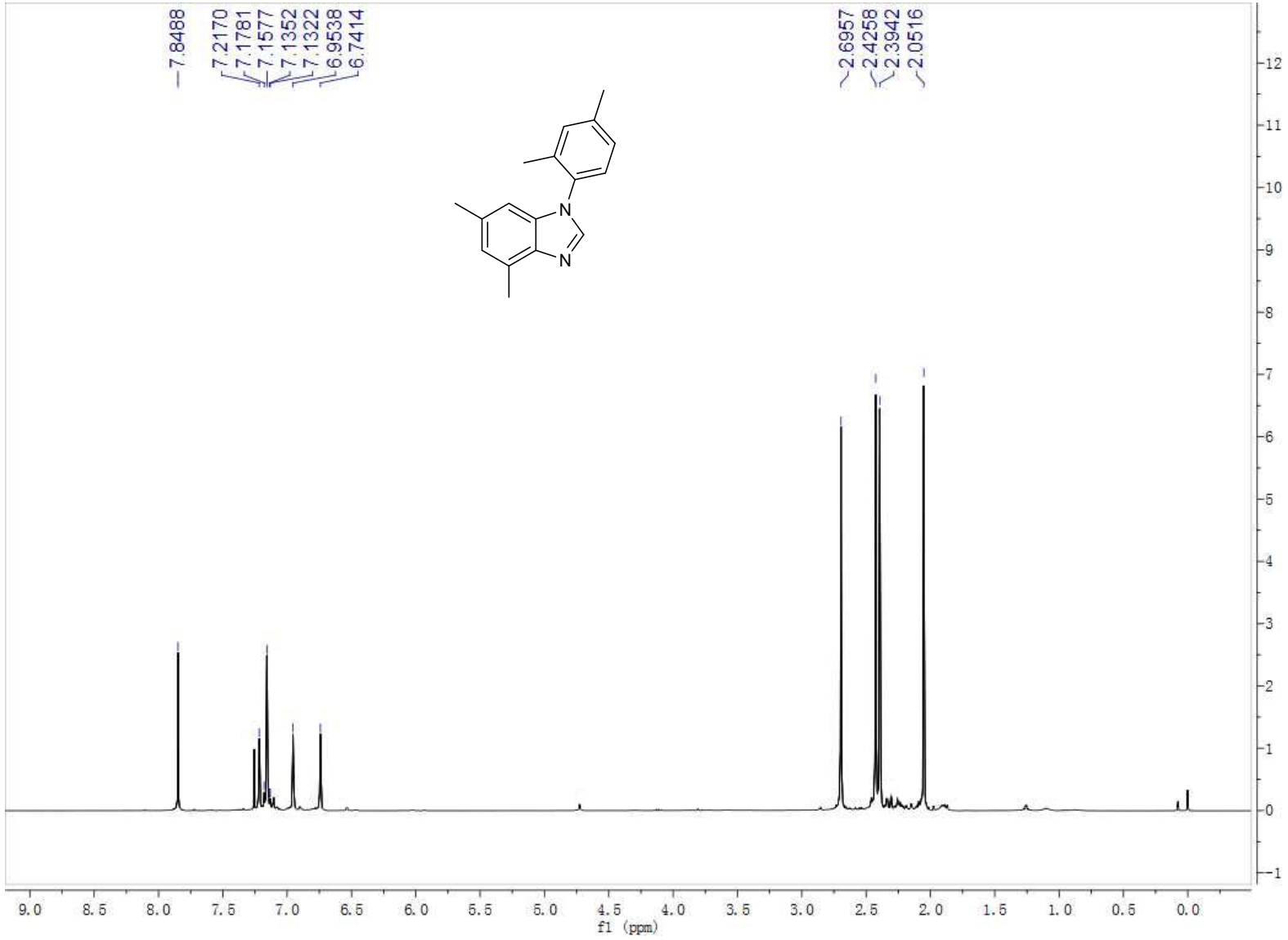
^{13}C NMR for compound **2e**


8.2565
7.9894
7.9753
7.9107
7.8969
7.8003
7.6765
7.6628
7.6344
7.6203
CF3
F3C
N
N
f1 (ppm)

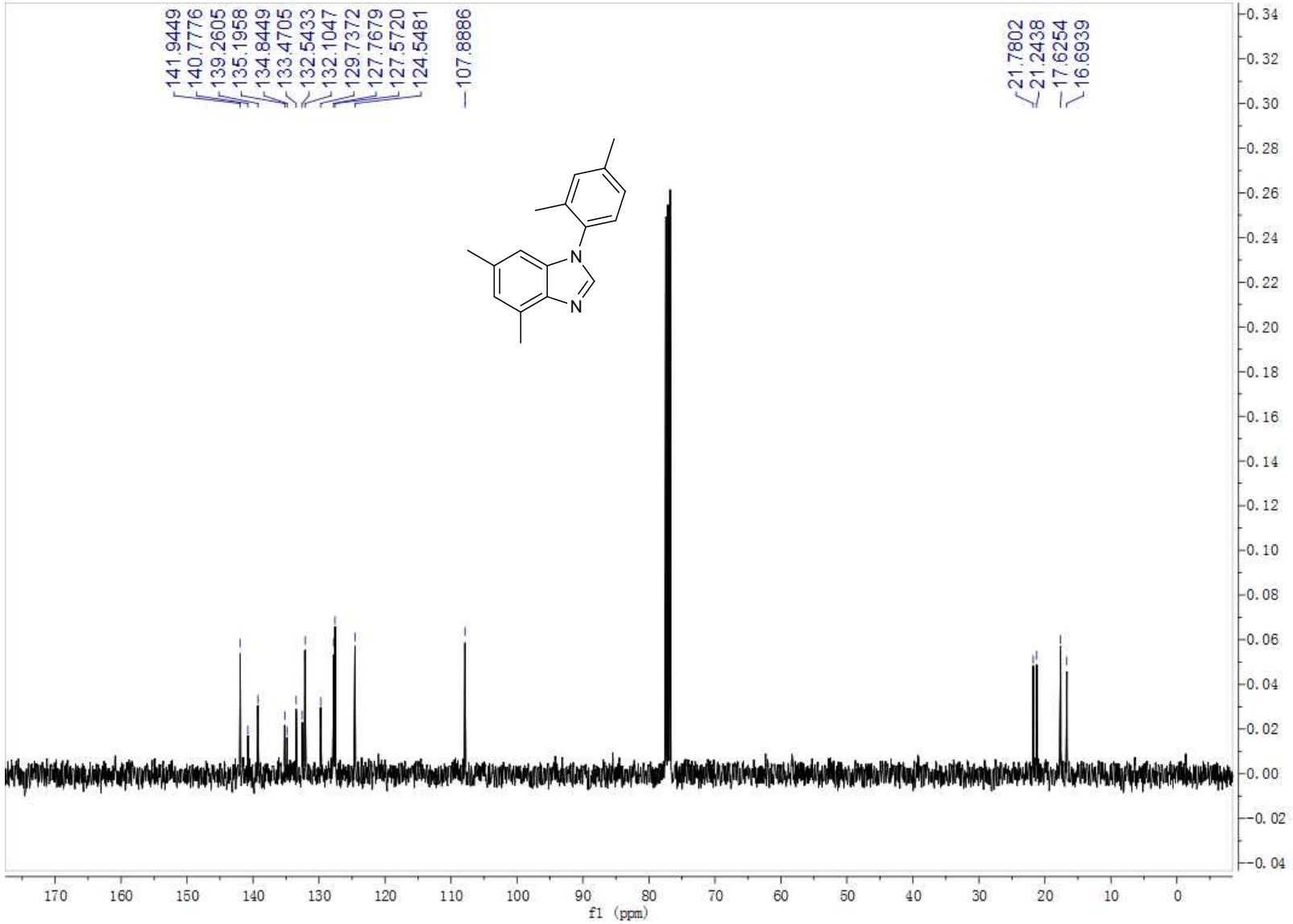
^{1}H NMR for compound **2f**



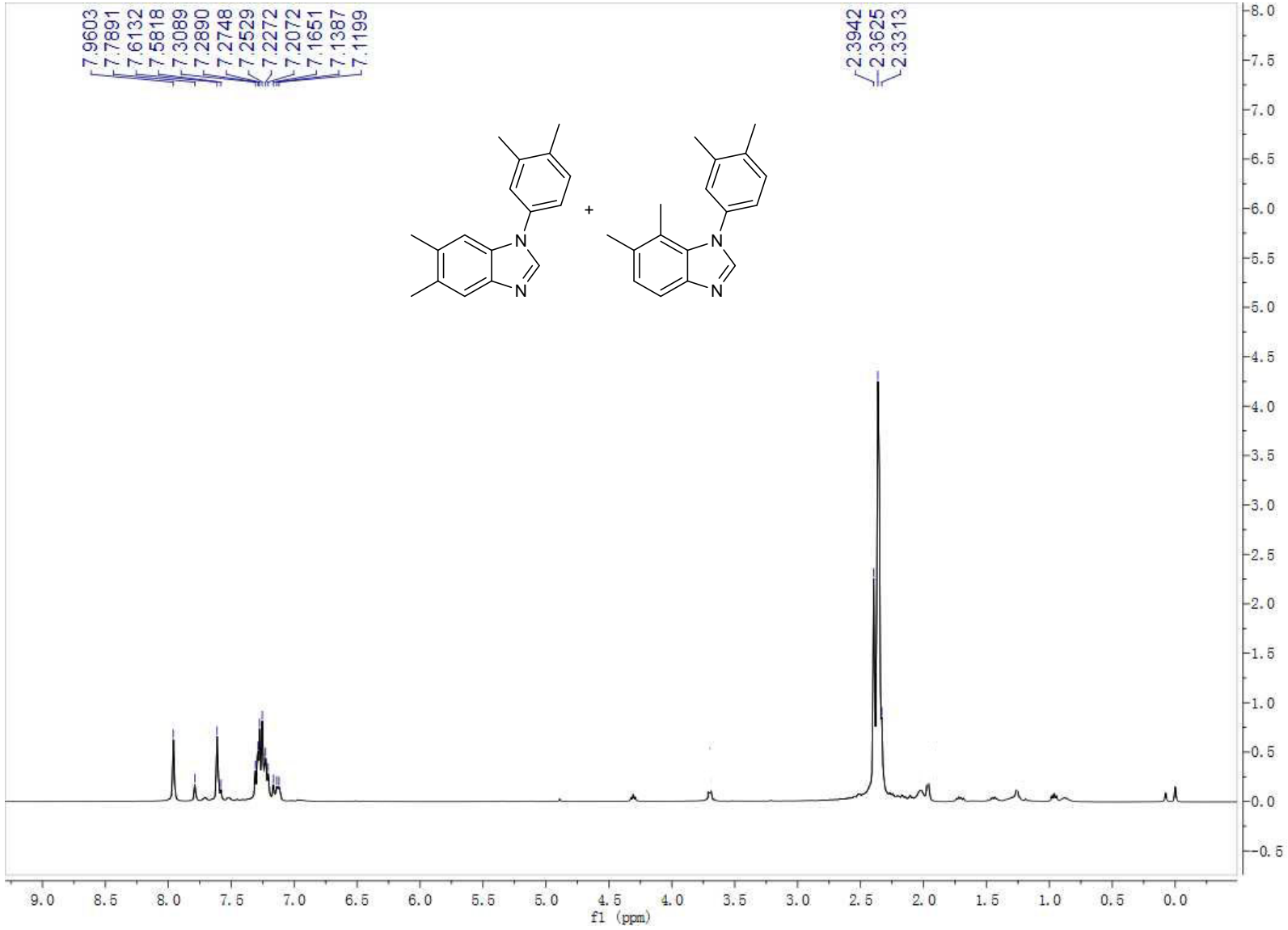
^{13}C NMR for compound **2f**


7.8488
7.2170
7.1781
7.1577
7.1352
7.1322
6.9538
6.7414
2.6957
2.4258
2.3942
2.0516
N
N
f1 (ppm)

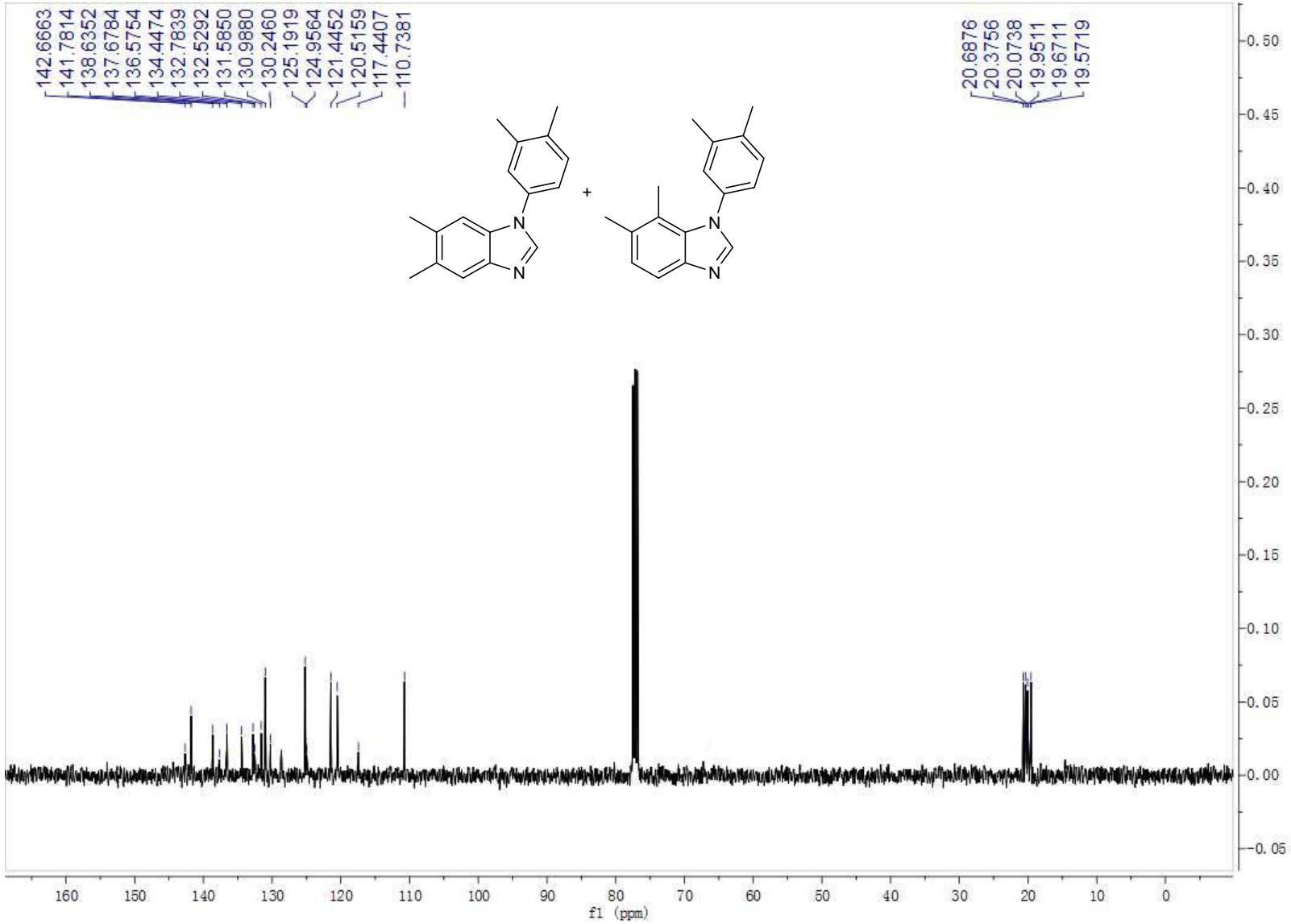
^{1}H NMR for compound **2g**



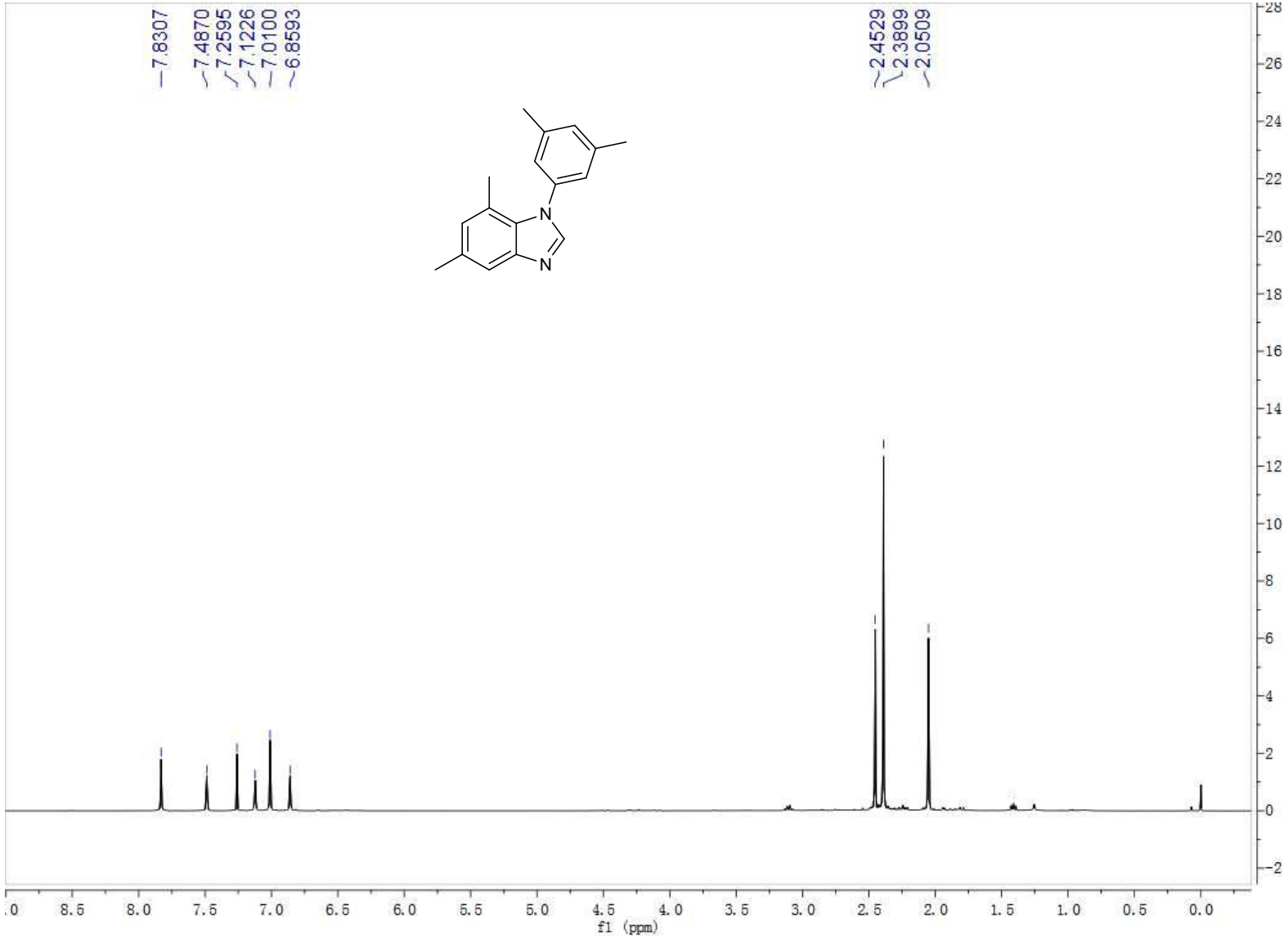
^{13}C NMR for compound **2g**


7.9603
7.7891
7.6132
7.5818
7.3089
7.2890
7.2748
7.2529
7.2272
7.2072
7.1651
7.1387
7.1199
2.3942
2.3625
2.3313
+
N
N
N
N
f1 (ppm)

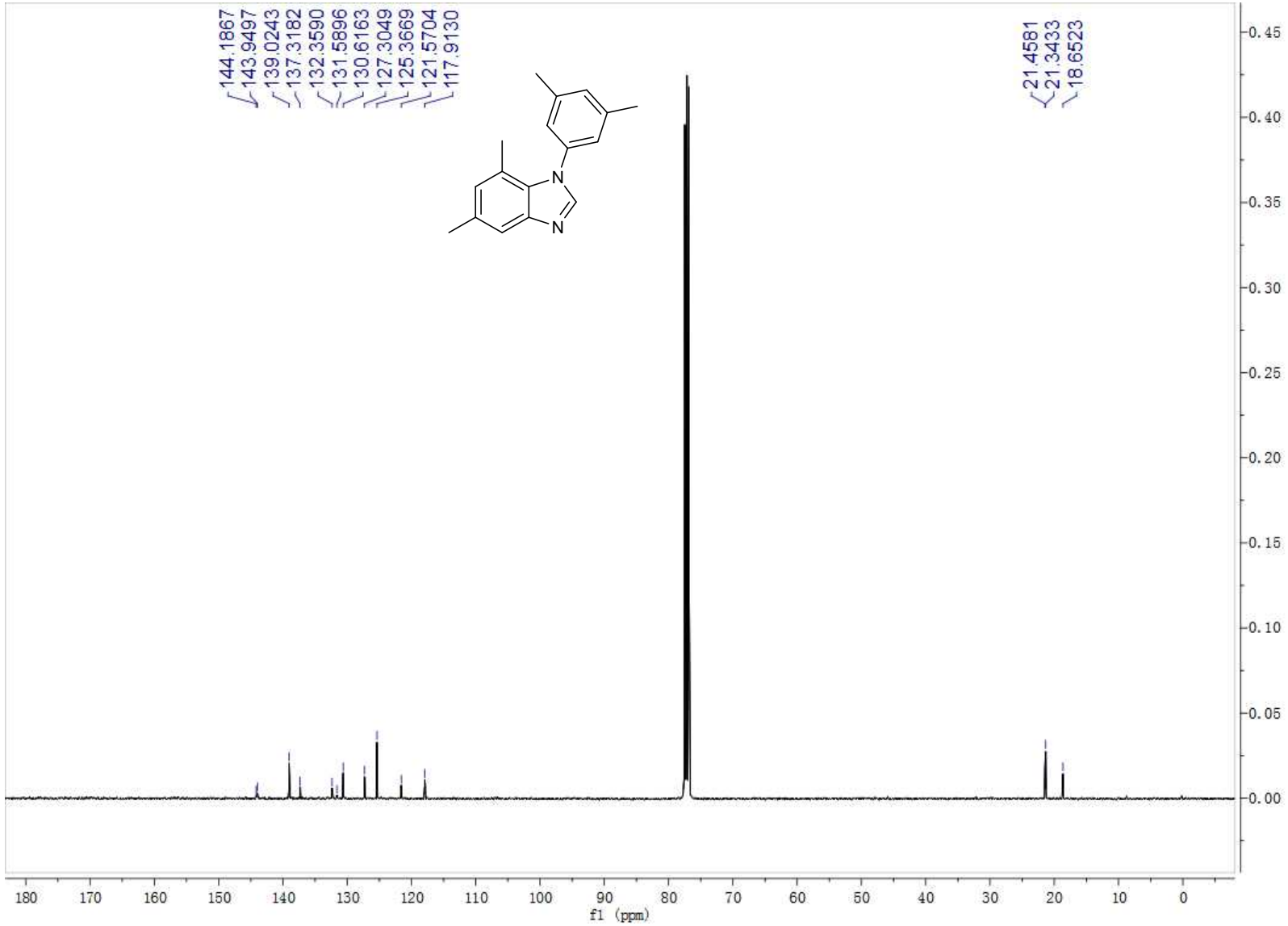
^{1}H NMR for compound **2h**



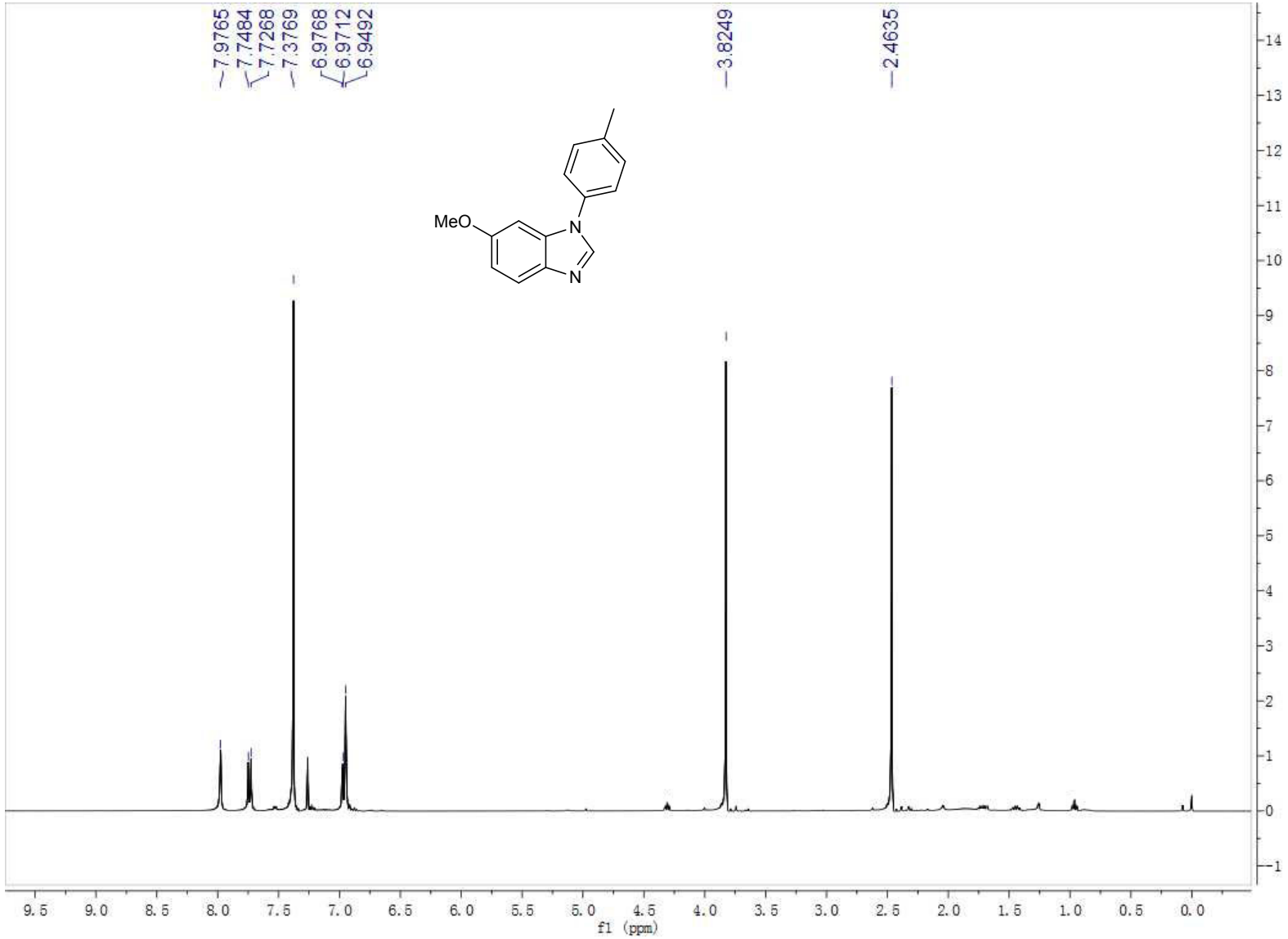
^{13}C NMR for compound **2h**


7.8307
7.4870
7.2595
7.1226
7.0100
6.8593
2.4529
2.3899
2.0509
N
N
f1 (ppm)

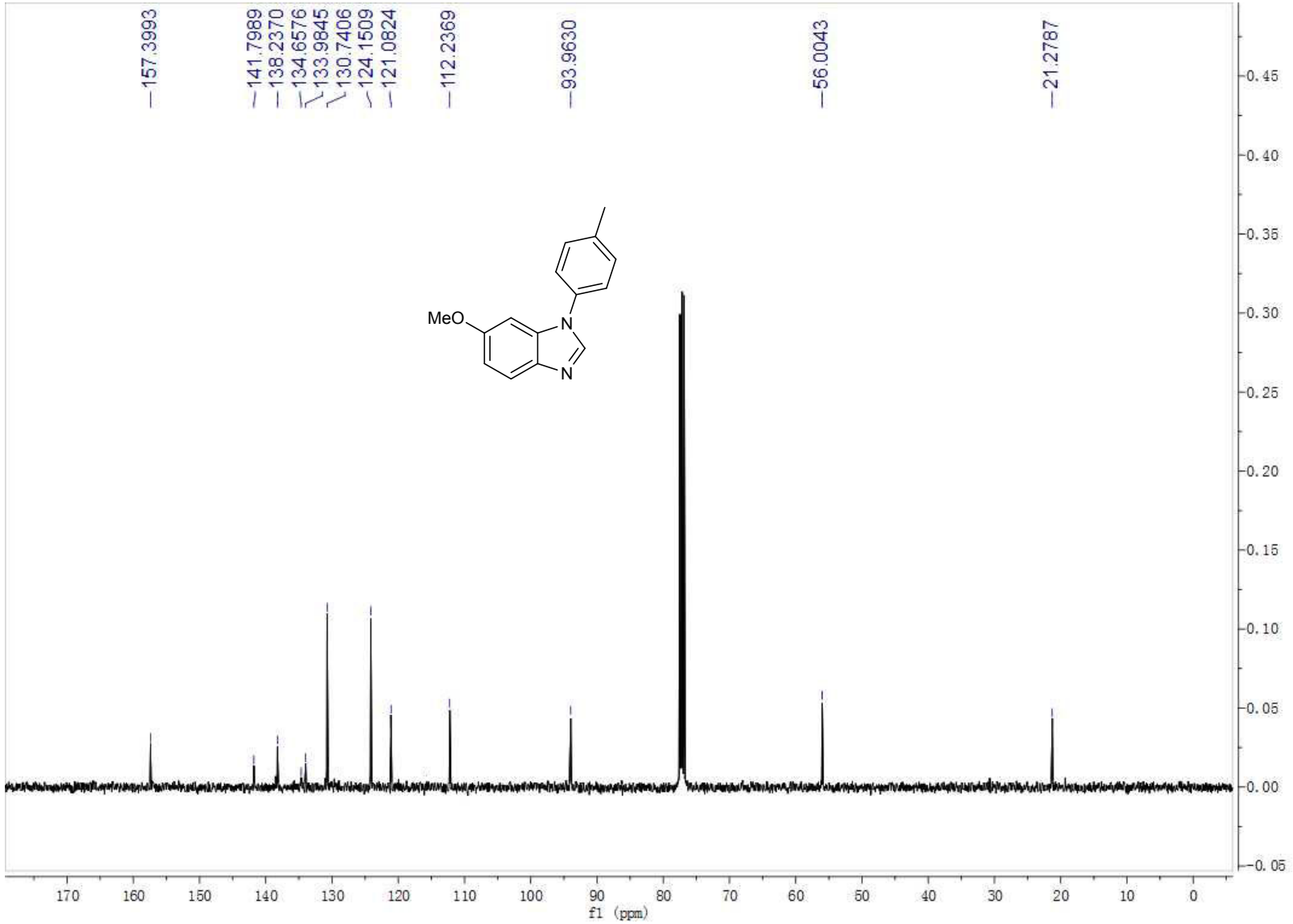
^{1}H NMR for compound **2i**



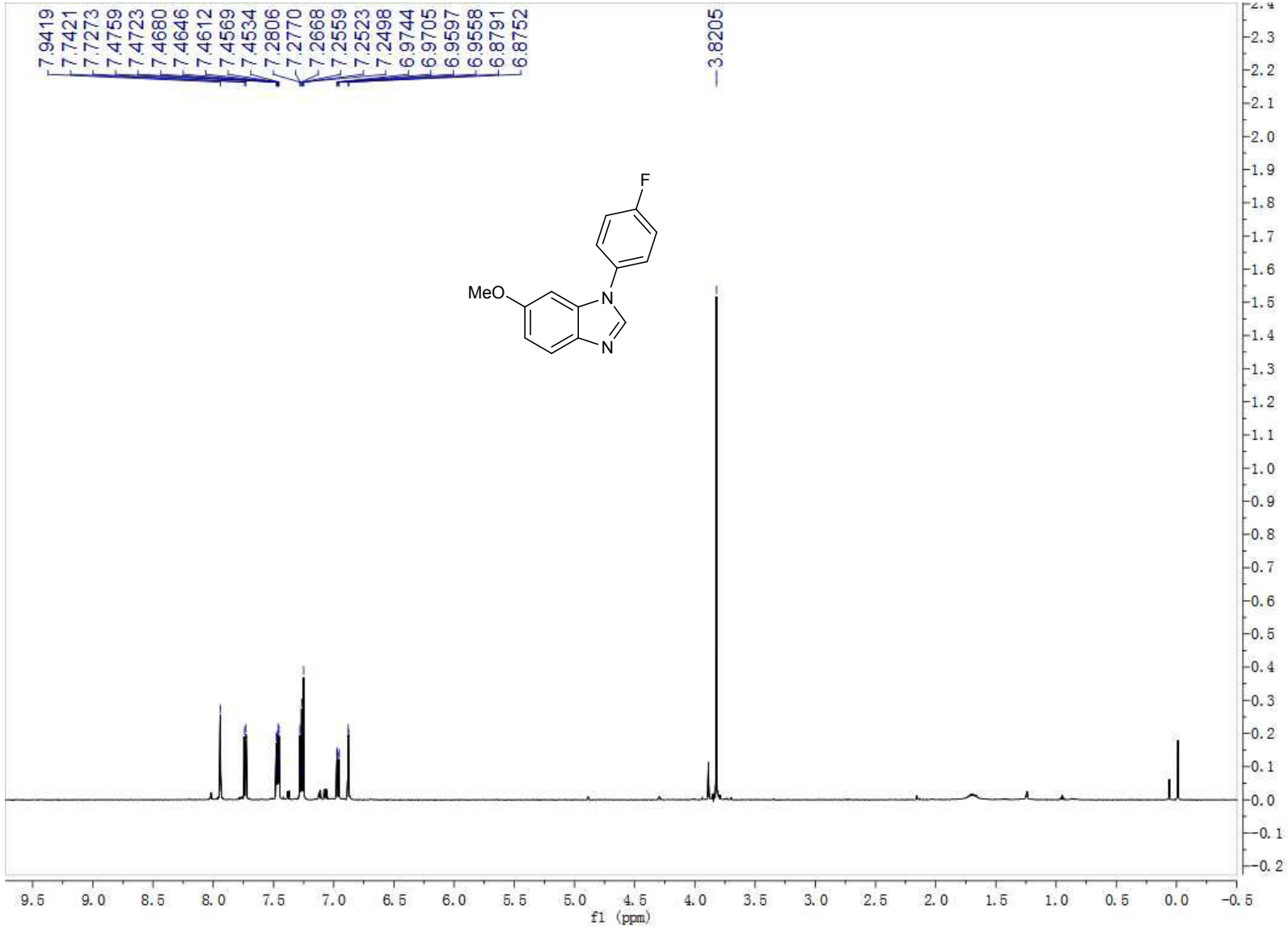
^{13}C NMR for compound **2i**


7.9765
7.7484
7.7268
7.3769
6.9768
6.9712
6.9492
3.8249
2.4635
MeO
N
N
f1 (ppm)

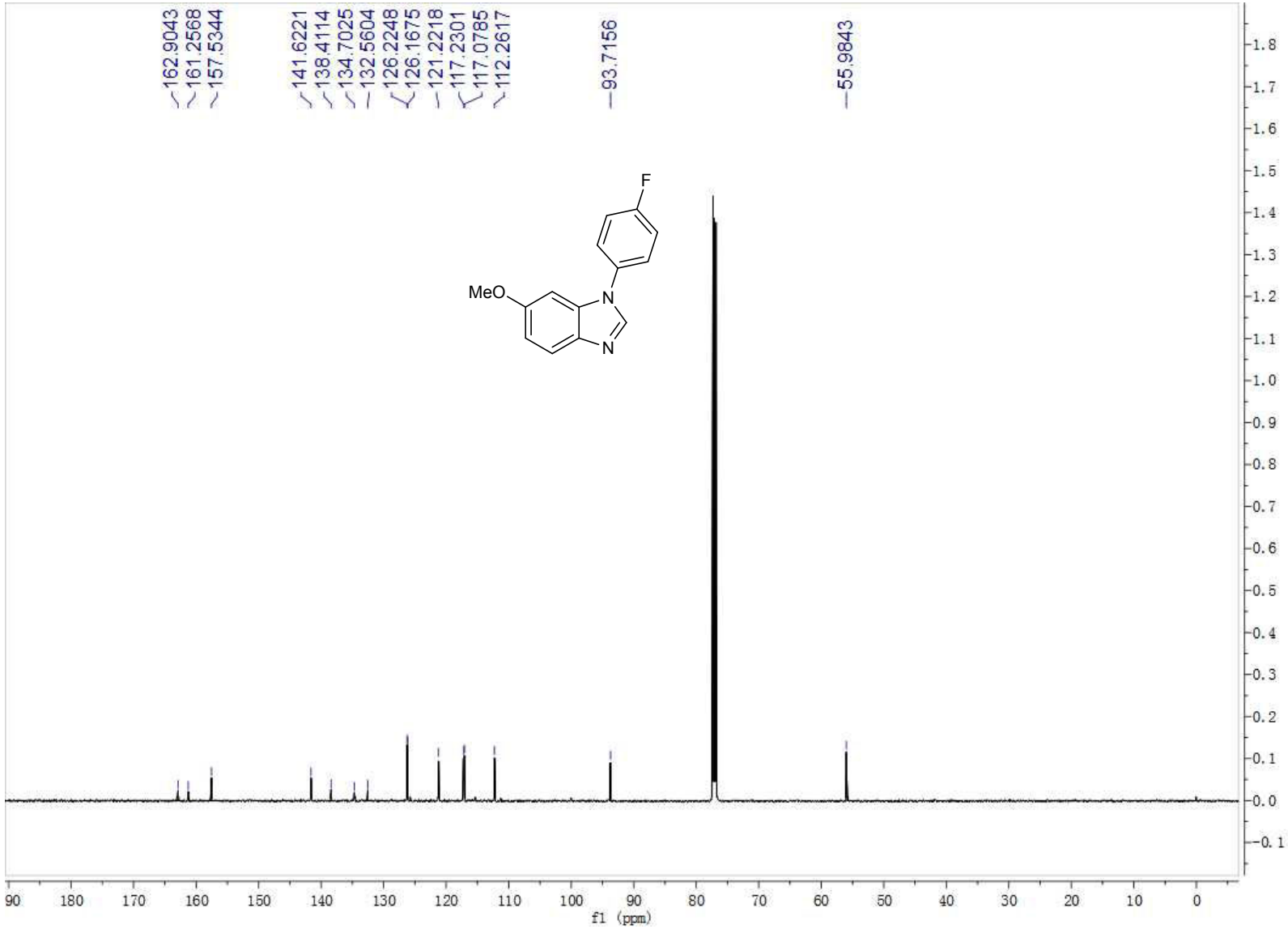
^{1}H NMR for compound **2j**



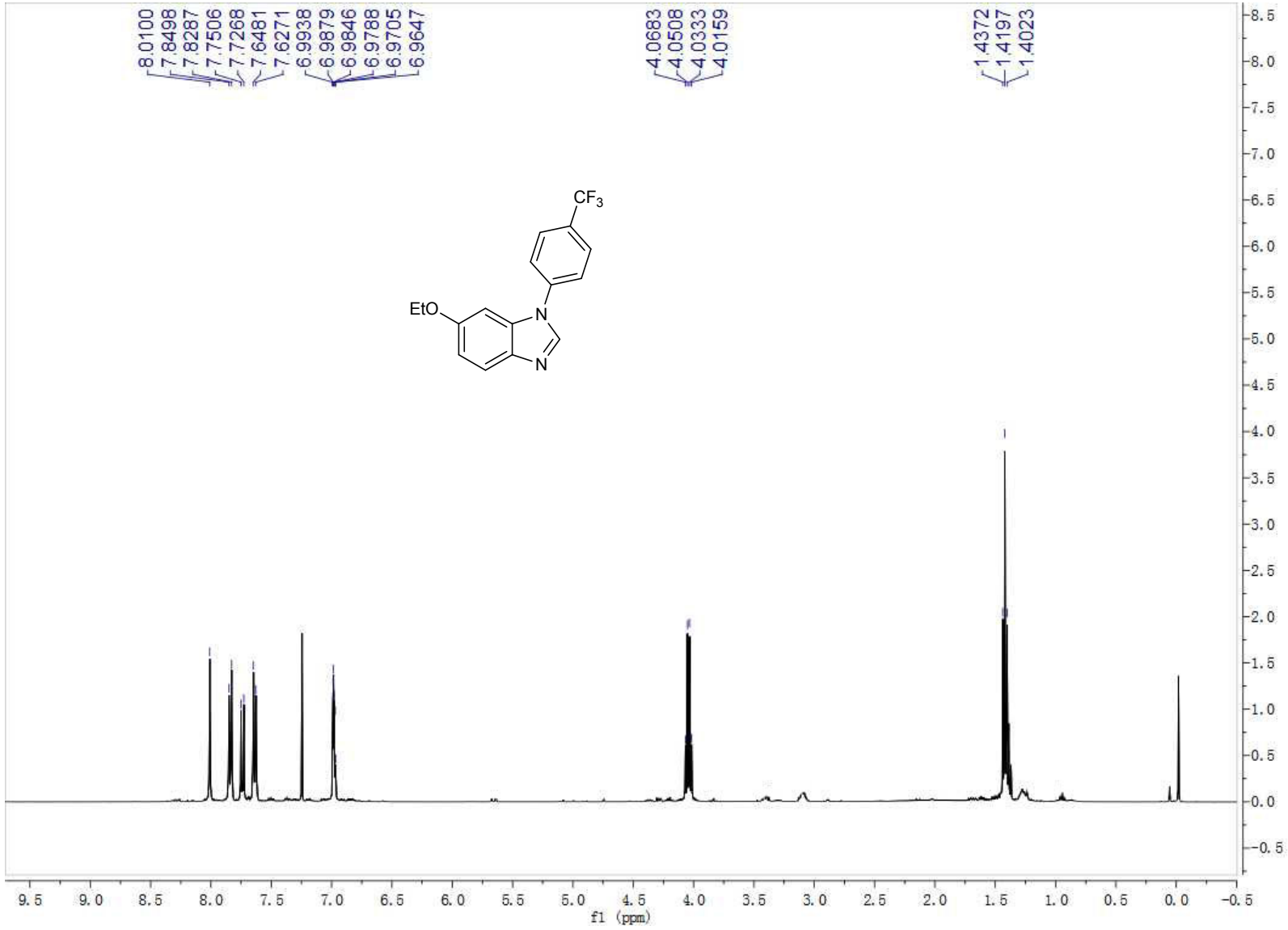
^{13}C NMR for compound **2j**


7.9419
7.7421
7.7273
7.4759
7.4723
7.4680
7.4646
7.4612
7.4569
7.4534
7.2806
7.2770
7.2668
7.2559
7.2523
7.2498
6.9744
6.9705
6.9597
6.9558
6.8791
6.8752
3.8205
F
MeO
N
N
f1 (ppm)

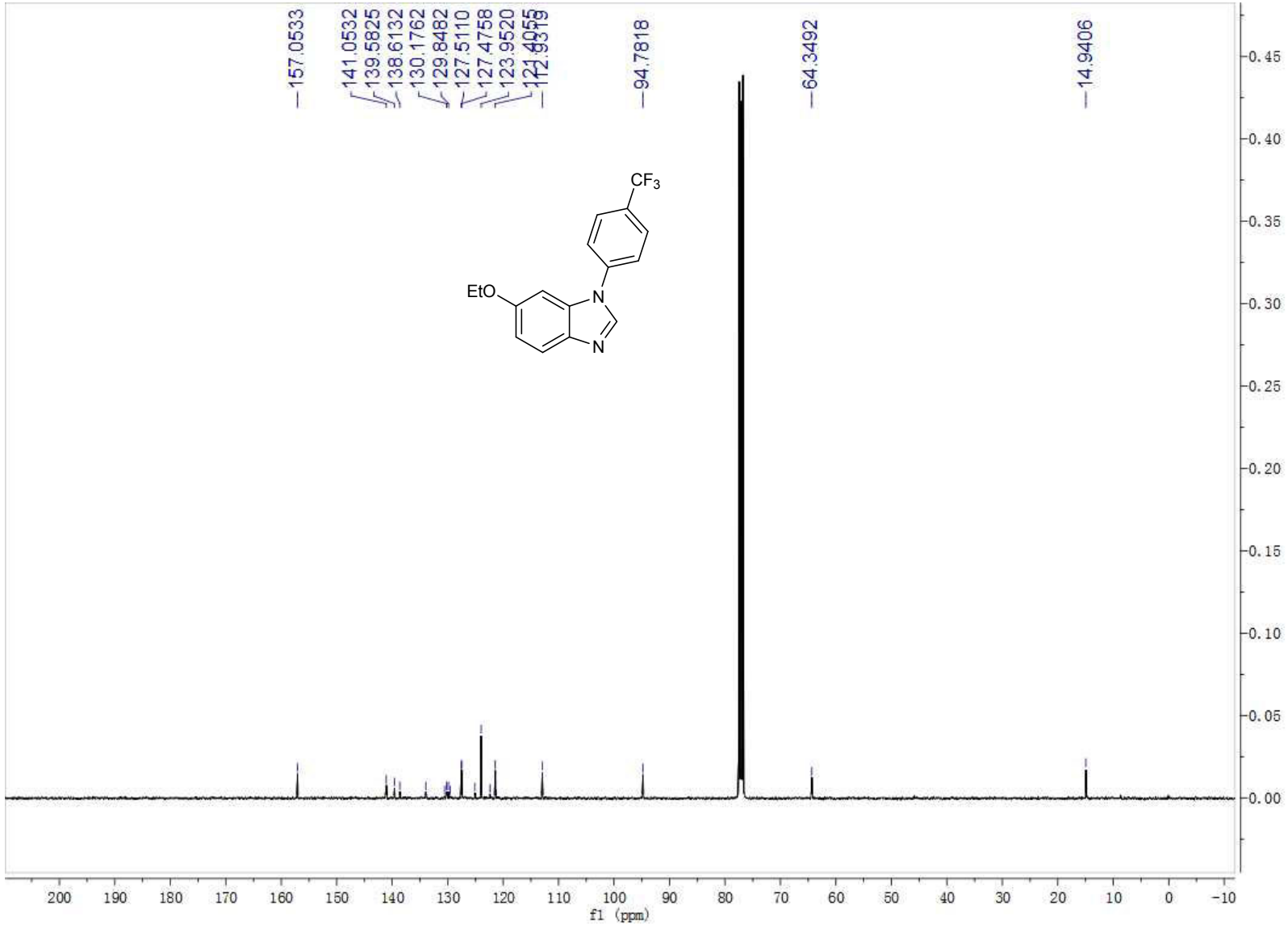
^{1}H NMR for compound **2k**



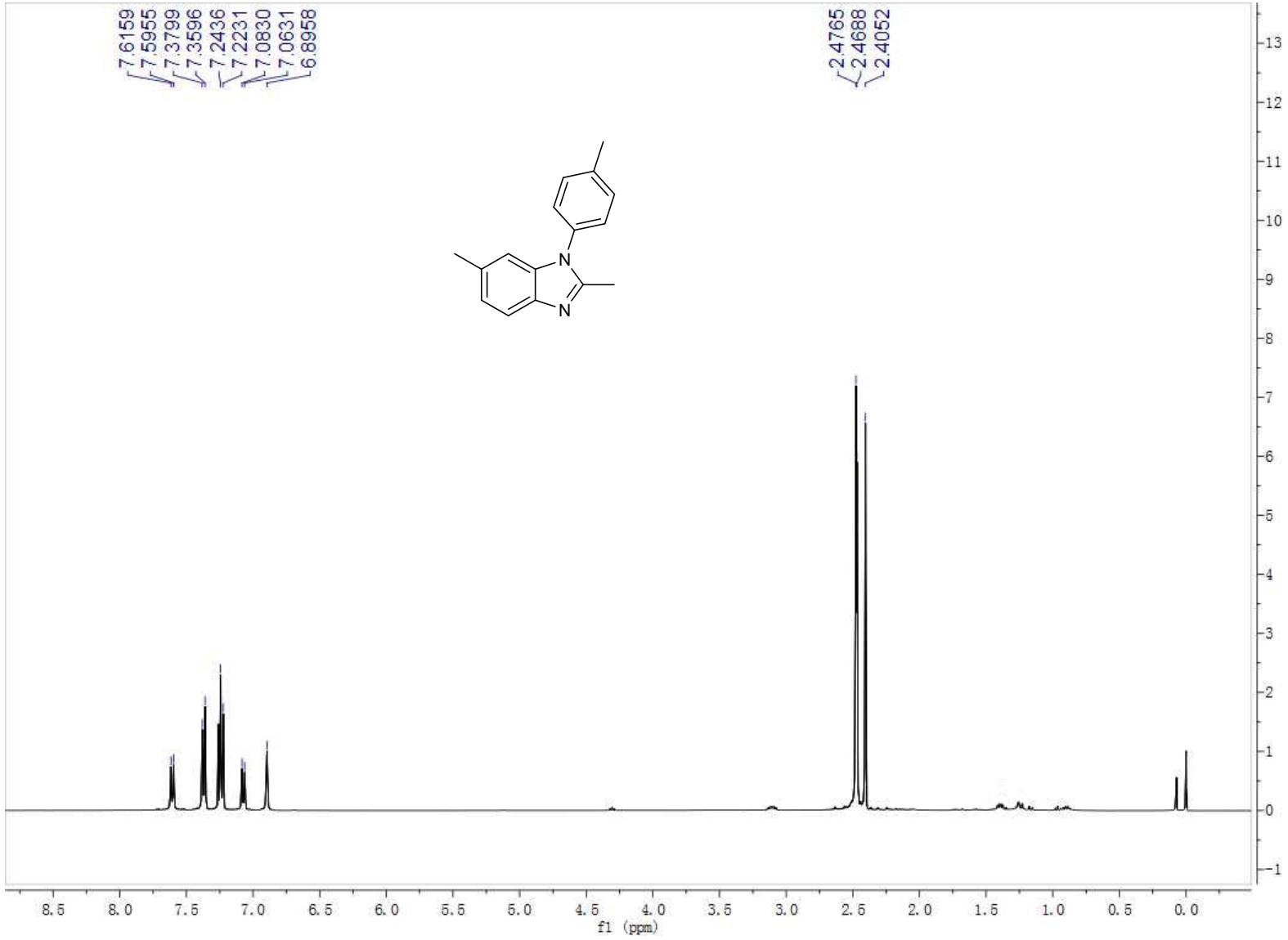
^{13}C NMR for compound **2k**


8.0100
7.8498
7.8287
7.7506
7.7268
7.6481
7.6271
6.9938
6.9879
6.9846
6.9788
6.9705
6.9647
4.0683
4.0508
4.0333
4.0159
1.4372
1.4197
1.4023
CF3
EtO
N
N
f1 (ppm)

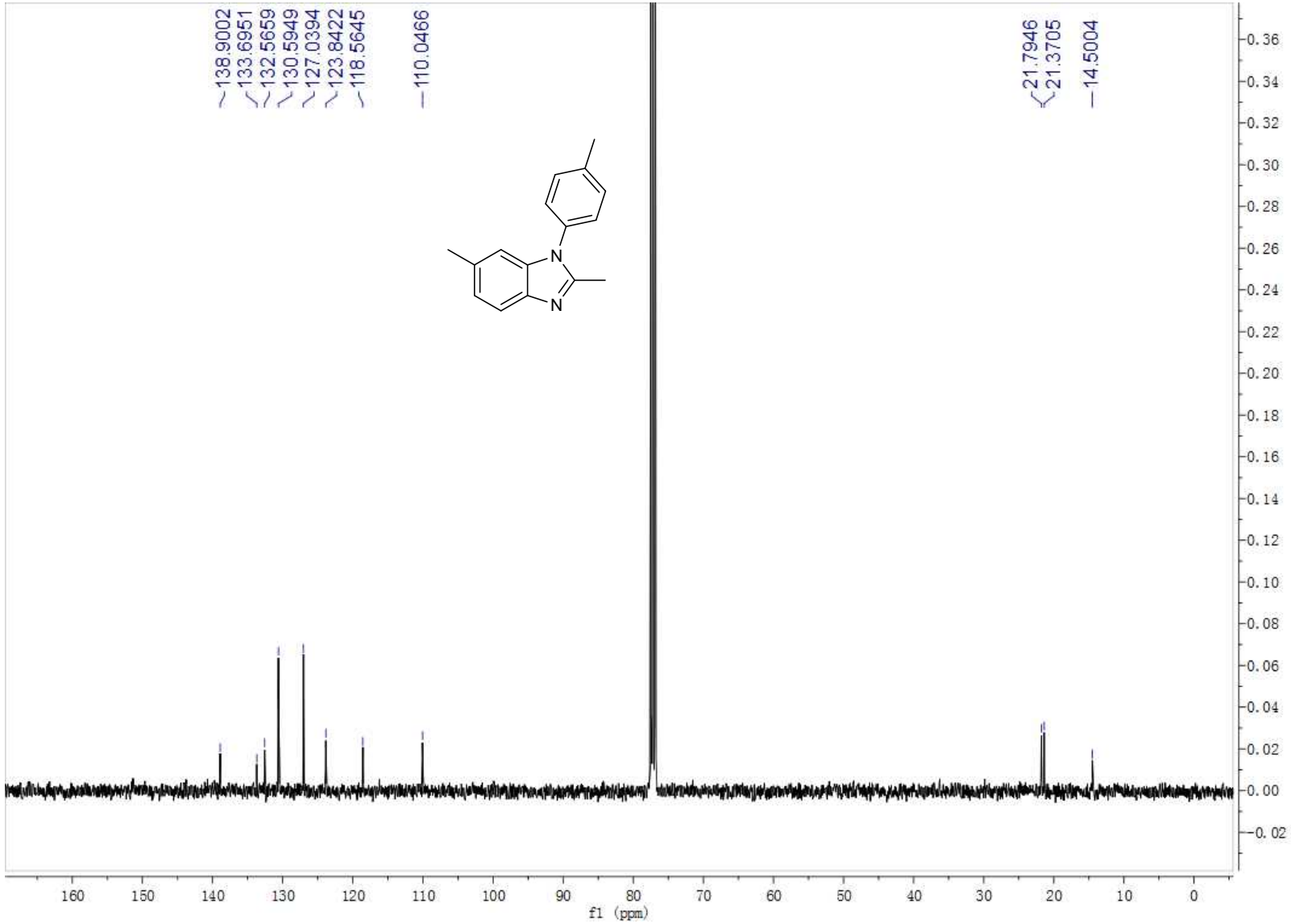
^{1}H NMR for compound **2l**



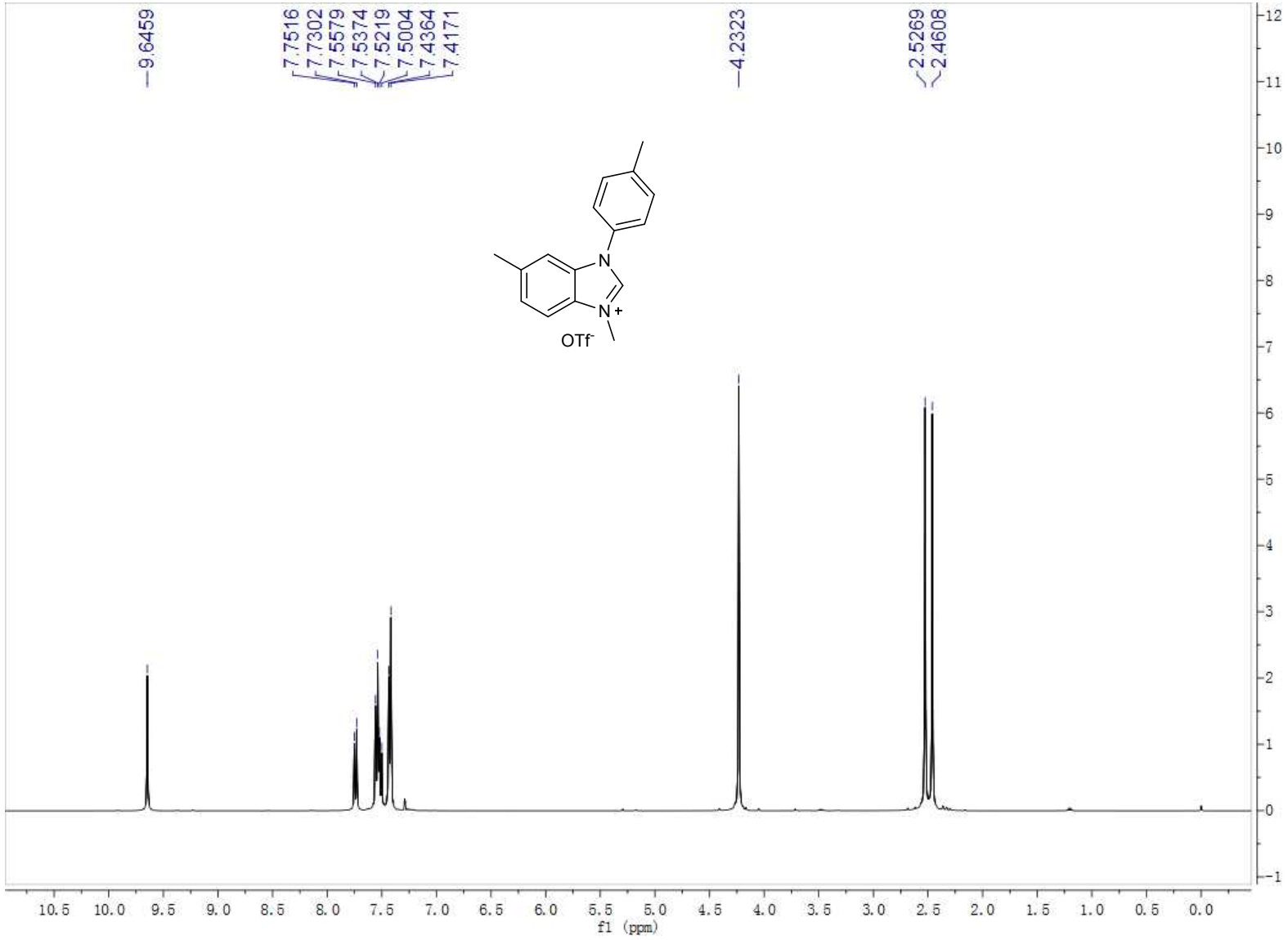
^{13}C NMR for compound **2l**


7.6159
7.5955
7.3799
7.3596
7.2436
7.2231
7.0830
7.0631
6.8958
2.4765
2.4688
2.4052
N
N
f1 (ppm)

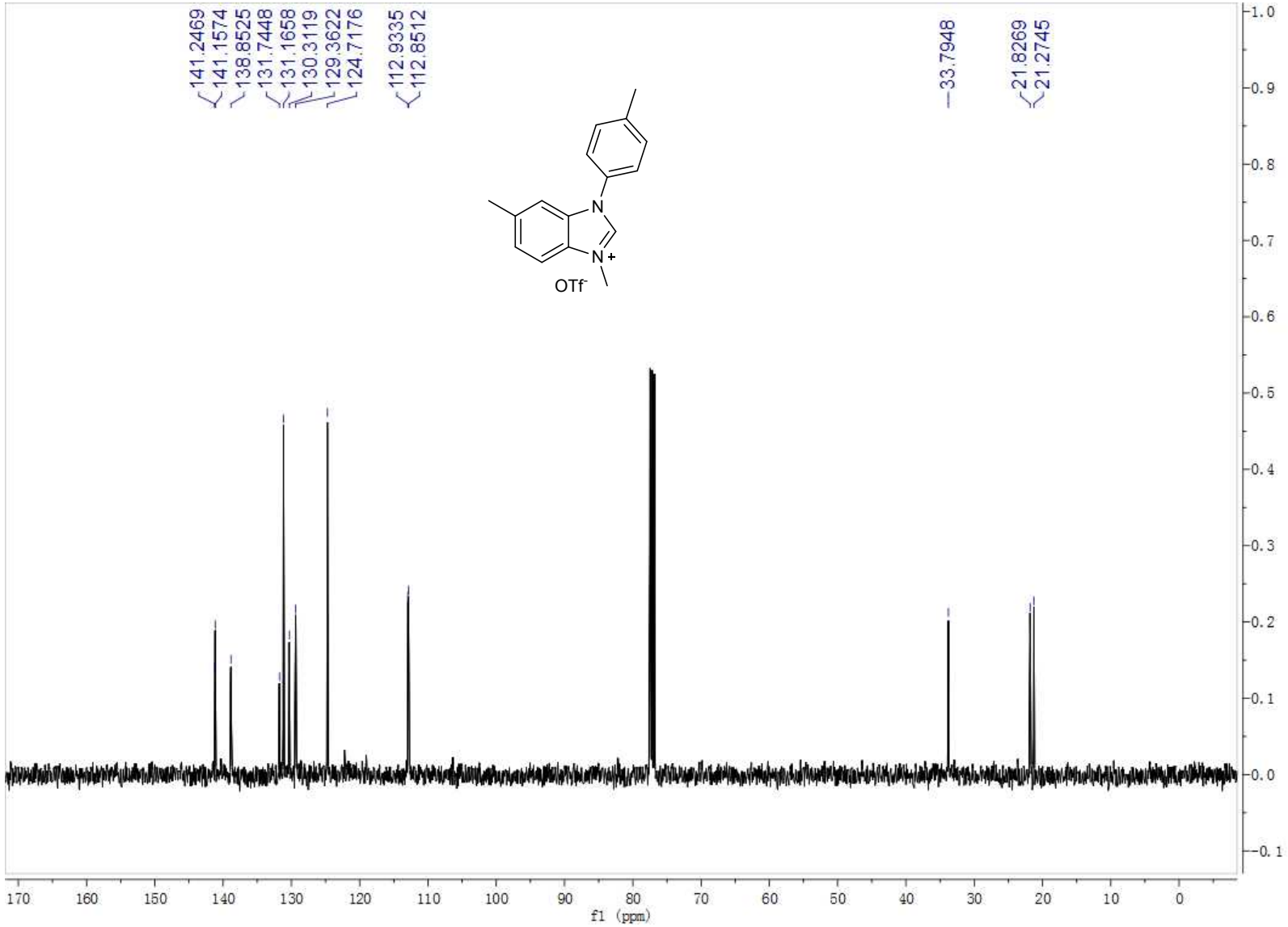
^{1}H NMR for compound **2m**



^{13}C NMR for compound **2m**


9.6459
7.7516
7.7302
7.5579
7.5374
7.5219
7.5004
7.4364
7.4171
4.2323
2.5269
2.4608
N
N+
OTf-
f1 (ppm)

^{1}H NMR for compound **3a**



^{13}C NMR for compound **3a**