

Supporting Information

Copper-Catalyzed Cyanation of Disulfides by Azobisisobutyronitrile

Leading to Thiocyanates

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1. General Considerations

All chemicals were used as received without further purification unless stated otherwise. ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded at ambient temperature on a 300, 400 or 500 MHz spectrometer (75 or 100 MHz for ^{13}C NMR, and 470 MHz for ^{19}F NMR). NMR experiments are reported in δ units, parts per million (ppm), and were referenced to CDCl_3 (δ 7.26 or 77.0 ppm) as the internal standard. The coupling constants J are given in Hz. Column chromatography was performed using EM Silica gel 60 (300-400 meshes).

2. Experimental Procedures.

Under O_2 , a 20 mL of Schlenk tube equipped with a stir bar was charged with ArSSAr (0.1 mmol), AIBN (0.15 mmol, 24.6 mg), CuI (0.01 mmol, 1.9 mg), KHCO_3 (0.1 mmol, 10.0 mg) and CH_3CN (2 mL). The tube was sealed with a Teflon lined cap. The reaction mixture was stirred at 100 °C for 12 h. After the completion of the reaction (monitored by TLC), the solvent was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-ethyl acetate as the eluent to give the desired product.

3. Research on the Mechanism

3.1 The detection of CN^- by indicator paper

The combination of CN^- and acids produces hydrocyanic acid, which reacts with picric acid to show rose-red colour.

A picric acid test strip was fixed on a Teflon lined cap, and saturated sodium carbonate solution was dropped on to make it wet. Then, 0.2 g of tartrate and 3.0 mL of the reaction solution were added to Schlenk tube, which was sealed with this Teflon lined cap, immediately. The tube was heated in the oil bath under 80 °C for 15 minutes. The test paper appeared rose-red proved the existence of CN^- .



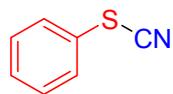
Fig. S1 Results of detecting cyanide anion

3.2 Preparation of CuSPh

To an ice-cold mixture of 12.5 mL of conc. aq. NH_3 and 50 mL H_2O was added $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (3.13 g, 12.5 mmol) forming a royal blue-colored solution. $\text{NH}_2\text{OH} \cdot \text{HCl}$ (1.94 g, 28.0 mmol) was added portionwise in 45 min. Then stirred overnight at 25 °C, under N_2 , produced a colorless solution of $[\text{Cu}(\text{NH}_3)_2]^+$. A solution of PhSH (1.42 g, 12.9 mmol) in 80 mL of EtOH was added through syringe. A yellow solid formed immediately. The solid product was collected via filtration and was sequentially washed with H_2O , EtOH and ether in succession and vacuum-dried.

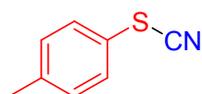
4. Characterization Data for the Products

Thiocyanatobenzene (3a):¹



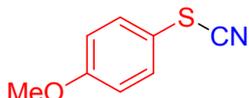
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 80) give the product (17.5 mg, 65% yield) as a colorless liquid. ¹H NMR (CDCl₃, 400 MHz) δ 7.41-7.46 (m, 3H), 7.51-7.54 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 110.5, 124.4, 129.5, 130.0, 130.2.

4-Methylphenyl thiocyanate (3b):¹



Flash column chromatography on a silica gel (petroleum ether) give the product (16.4 mg, 55% yield) as a yellowish liquid. ¹H NMR (CDCl₃, 400 MHz) δ 2.37 (s, 3H), 7.22-7.26 (m, 2H), 7.41-7.44 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 21.1, 111.0, 120.5, 130.7, 130.9, 140.2.

4-Methoxyphenyl thiocyanate (3c):¹



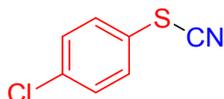
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 80) give the product (26.7 mg, 81% yield) as a white solid. ¹H NMR (CDCl₃, 300 MHz) δ 3.82 (s, 3H), 6.92-6.97 (m, 2H), 7.47-7.51 (m, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 55.5, 111.6, 113.7, 115.8, 133.8, 161.2.

2-Fluorophenyl thiocyanate (3d):



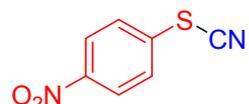
Flash column chromatography on a silica gel (petroleum ether) give the product (22.3 mg, 73% yield) as a colorless liquid. ¹H NMR (CDCl₃, 400 MHz) δ 7.18-7.28 (m, 2H), 7.42-7.48 (m, 1H), 7.61-7.65 (m, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 109.0, 111.8 (d, *J*_{C-F} = 17.4 Hz), 116.7 (d, *J*_{C-F} = 20.6 Hz), 125.7 (d, *J*_{C-F} = 3.8 Hz), 132.0 (d, *J*_{C-F} = 7.8 Hz), 132.2, 160.3 (d, *J*_{C-F} = 248.9 Hz); ¹⁹F NMR (470 MHz, CDCl₃): δ -107.9 (s, 1F). MS (EI): 153 (M⁺); HRMS (ESI) *m/z* calcd for C₇H₅FNS (M+H)⁺ 154.0121, found 154.0120.

4-Chlorophenyl thiocyanate (3e):¹



Flash column chromatography on a silica gel (petroleum ether) give the product (22.6 mg, 67 % yield) as a white solid. ¹H NMR (CDCl₃, 400 MHz) δ 7.42 (d, *J* = 8.7 Hz, 2H), 7.47 (d, *J* = 8.7 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 110.0, 122.7, 130.4, 131.4, 136.2.

4-Nitrophenyl thiocyanate (3f):²



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give the product (27.4 mg, 76% yield) as a white solid. ¹H NMR (CDCl₃, 400 MHz) δ 7.67 (d, *J* = 8.9 Hz,

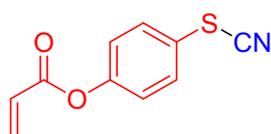
2H), 8.30 (d, $J = 8.9$ Hz, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 108.0, 125.0, 128.7, 133.3, 147.9.

Methyl 2-thiocyanatobenzoate (3g):³



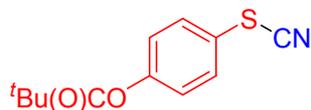
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 100) give the product (20.1 mg, 52% yield) as a yellowish liquid. ^1H NMR (CDCl_3 , 400 MHz) δ 3.95 (s, 3H), 7.39-7.43 (m, 1H), 7.61-7.66 (m, 1H), 7.90-7.92 (m, 1H), 8.10-8.12 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 52.9, 111.5, 126.1, 127.5, 127.8, 130.8, 131.6, 134.1, 166.4.

4-Thiocyanatophenyl acrylate (3h):



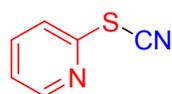
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 40) give the product (20.5 mg, 50% yield) as a colorless liquid. ^1H NMR (CDCl_3 , 400 MHz) δ 6.05-6.08 (m, 1H), 6.28-6.35 (m, 1H), 6.61-6.66 (m, 1H), 7.23-7.26 (m, 2H), 7.57-7.59 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 110.4, 121.2, 123.6, 127.3, 131.8, 133.5, 151.7, 163.9. MS (EI): 205 (M^+); HRMS (ESI) m/z calcd for $\text{C}_{10}\text{H}_8\text{NO}_2\text{S}$ ($\text{M}+\text{H}$)⁺ 206.0260, found 206.0270. IR: 3094, 3070, 3040, 2955, 2924, 2850, 2158, 1743, 1633, 1205, 1146.

4-Thiocyanatophenyl pivalate (3i):



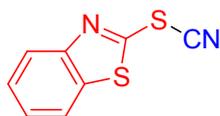
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 60) give the product (34.3 mg, 73% yield) as a colorless liquid. ^1H NMR (CDCl_3 , 400 MHz) δ 1.35 (s, 9H), 7.15 (d, $J = 8.7$ Hz, 2H), 7.55 (d, $J = 8.7$ Hz, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 27.0, 39.1, 110.4, 120.8, 123.5, 131.8, 152.3, 176.5. MS (EI): 235 (M^+); HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_{14}\text{N}_2\text{O}_2\text{S}$ ($\text{M}+\text{H}$)⁺ 236.0740, found 236.0740. IR: 3093, 3068, 2975, 2956, 2908, 2874, 2158, 1753, 1205, 1109.

2-Thiocyanatopyridine (3j):



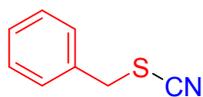
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether: triethylamine, 10: 100: 1) give the product (20.9 mg, 77% yield) as a yellowish liquid. ^1H NMR (CDCl_3 , 300 MHz) δ 7.26-7.29 (m, 1H), 7.59-7.61 (m, 1H), 7.74-7.79 (m, 1H), 8.51-8.52 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 108.9, 122.0, 122.7, 138.4, 149.9, 150.5. MS (EI): 136 (M^+); HRMS (ESI) m/z calcd for $\text{C}_6\text{H}_4\text{N}_2\text{S}$ ($\text{M}+\text{H}$)⁺ 137.0172, found 137.0168.

2-Thiocyanatobenzo[d]thiazole (3k):⁴



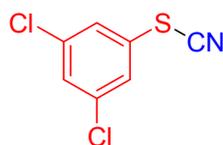
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 100) give the product (14.2 mg, 37% yield) as a white solid. ^1H NMR (CDCl_3 , 400 MHz) δ 7.44-7.48 (m, 1H), 7.51-7.55 (m, 1H), 7.87 (d, $J = 8.1$ Hz, 1H), 8.00 (d, $J = 8.1$ Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 106.9, 121.3, 123.1, 126.3, 127.1, 136.4, 152.9, 153.3.

(Thiocyanatomethyl)benzene (3l):⁵



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 60) give the product (16.7 mg, 56% yield) as a colorless liquid. ^1H NMR (CDCl_3 , 300 MHz) δ 4.16 (s, 2H), 7.36-7.42 (m, 5H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 38.3, 111.9, 128.9, 128.9, 129.1, 134.3.

3,5-Dichlorophenyl thiocyanate (3m):⁶



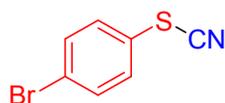
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 125) give the product (23.5 mg, 58% yield) as a yellowish liquid. ^1H NMR (CDCl_3 , 400 MHz) δ 7.40-7.41 (m, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 108.6, 127.3, 127.5, 129.8, 136.6.

3-Nitrophenyl thiocyanate (3n):⁶



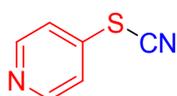
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 80) give the product (31.3 mg, 87% yield) as a white solid. ^1H NMR (CDCl_3 , 400 MHz) δ 7.66-7.70 (m, 1H), 7.87-7.89 (m, 1H), 8.27-8.29 (m, 1H), 8.39-8.40 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 108.6, 124.2, 124.2, 127.2, 131.2, 134.9, 148.8.

4-Bromophenyl thiocyanate (3o):²



Flash column chromatography on a silica gel (petroleum ether) give the product (19.0 mg, 49% yield) as a yellowish liquid. ^1H NMR (CDCl_3 , 400 MHz) δ 7.39 (t, $J = 4.3$ Hz, 2H), 7.56 (t, $J = 4.2$ Hz, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 109.8, 123.4, 124.1, 131.5, 133.4.

4-Thiocyanatopyridine (3p):⁷



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether: triethylamine, 10: 100: 1) give the product (16.3 mg, 60% yield)

as a white solid. ^1H NMR (CDCl_3 , 400 MHz) δ 7.38-7.39 (m, 2H), 8.62-8.63 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 107.3, 121.5, 136.7, 150.6.

2-Nitrophenyl thiocyanate (3q):⁶



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 50) give the product (28.9 mg, 80% yield) as a white solid. ^1H NMR (CDCl_3 , 400 MHz) δ 7.56-7.60 (m, 1H), 7.79-7.83 (m, 1H), 8.04-8.07 (m, 1H), 8.39-8.42 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 110.1, 126.3, 126.5, 128.8, 129.0, 135.5, 144.5.

1-Thiocyanatooctane (3r):⁸



Flash column chromatography on a silica gel (petroleum ether) give the product (17.8 mg, 52% yield) as a colorless liquid. ^1H NMR (CDCl_3 , 400 MHz) δ 0.86-0.89 (m, 3H), 1.27-1.33 (m, 8H), 1.39-1.46 (m, 2H), 1.81 (p, $J = 7.4$ Hz, 2H), 2.93 (t, $J = 7.3$ Hz, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 14.0, 22.5, 27.9, 28.8, 28.9, 29.8, 31.6, 34.0, 112.3.

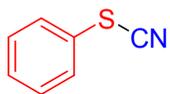
5. References

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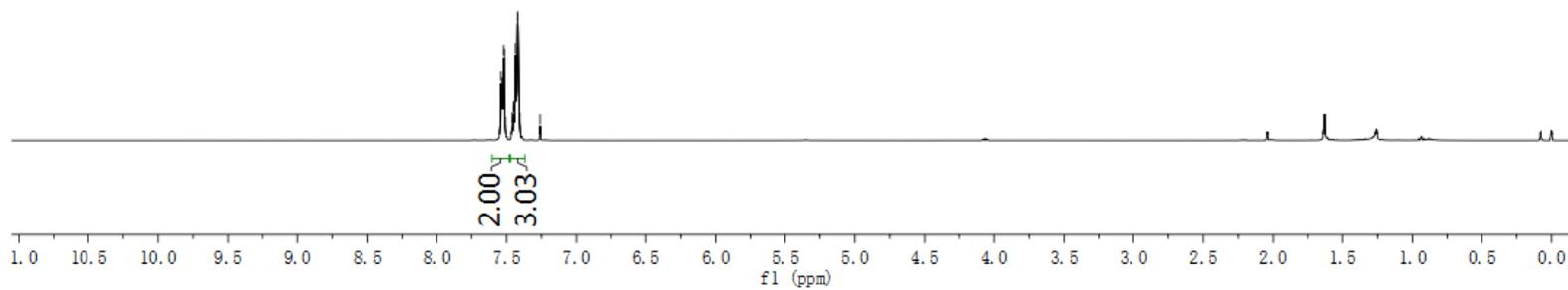
6. Copies of the ^1H NMR and ^{13}C NMR Spectra

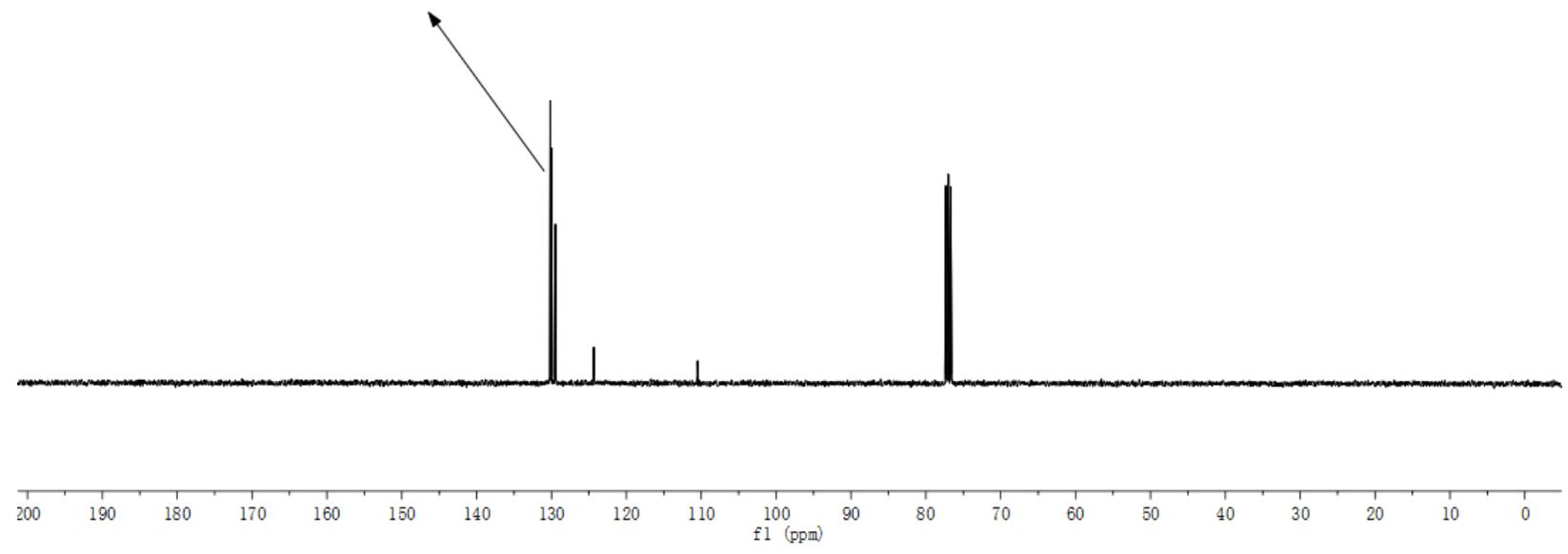
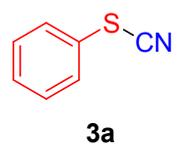
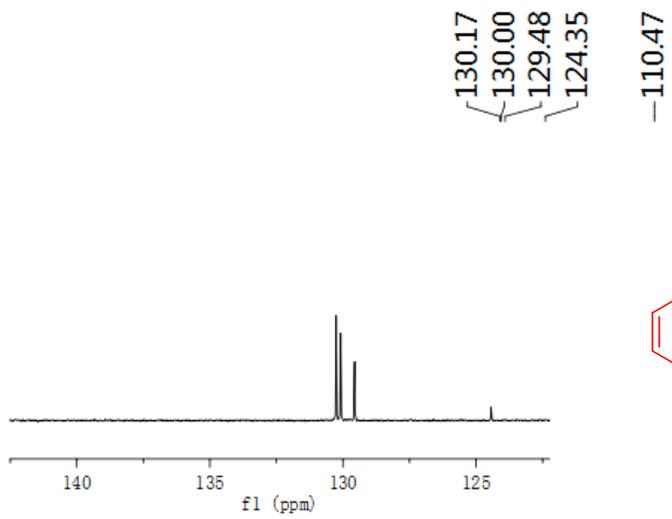
Thiocyanatobenzene (3a)

7.5404
7.5350
7.5304
7.5249
7.5203
7.5164
7.5083
7.4597
7.4557
7.4499
7.4458
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7.4328
7.4283
7.4222
7.4186
7.4109
7.4060
7.2597



3a

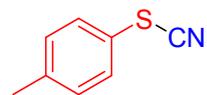




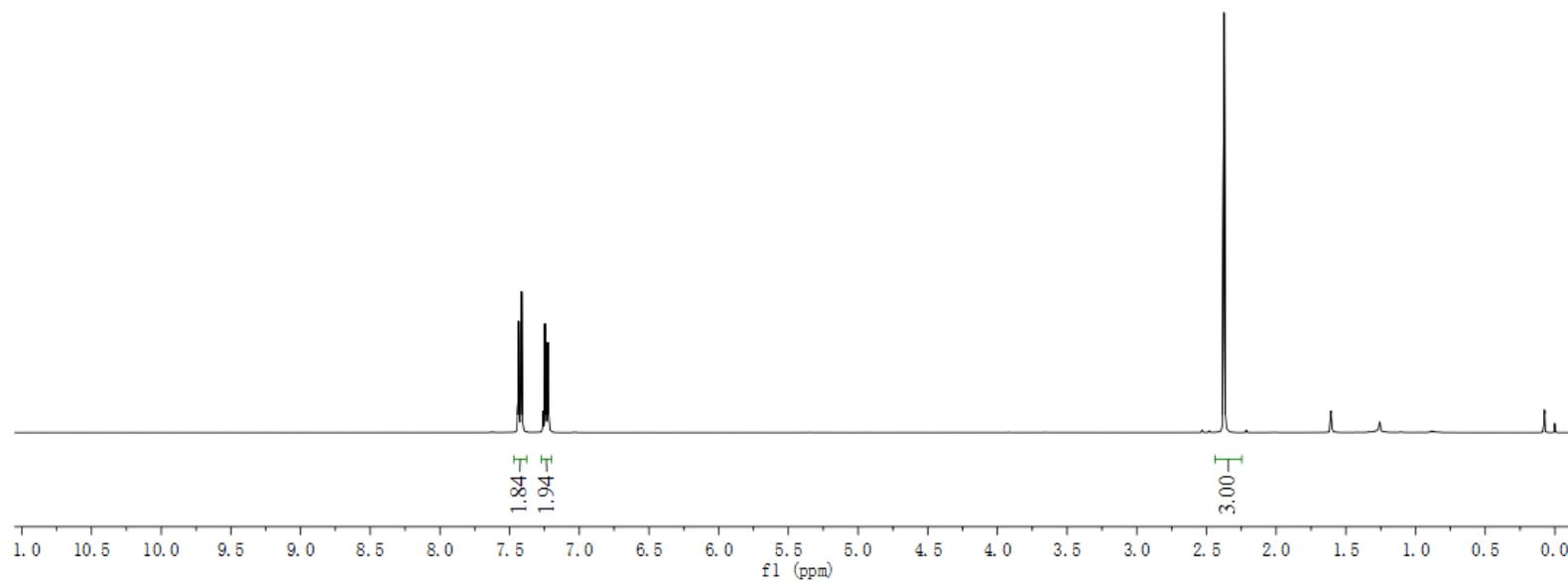
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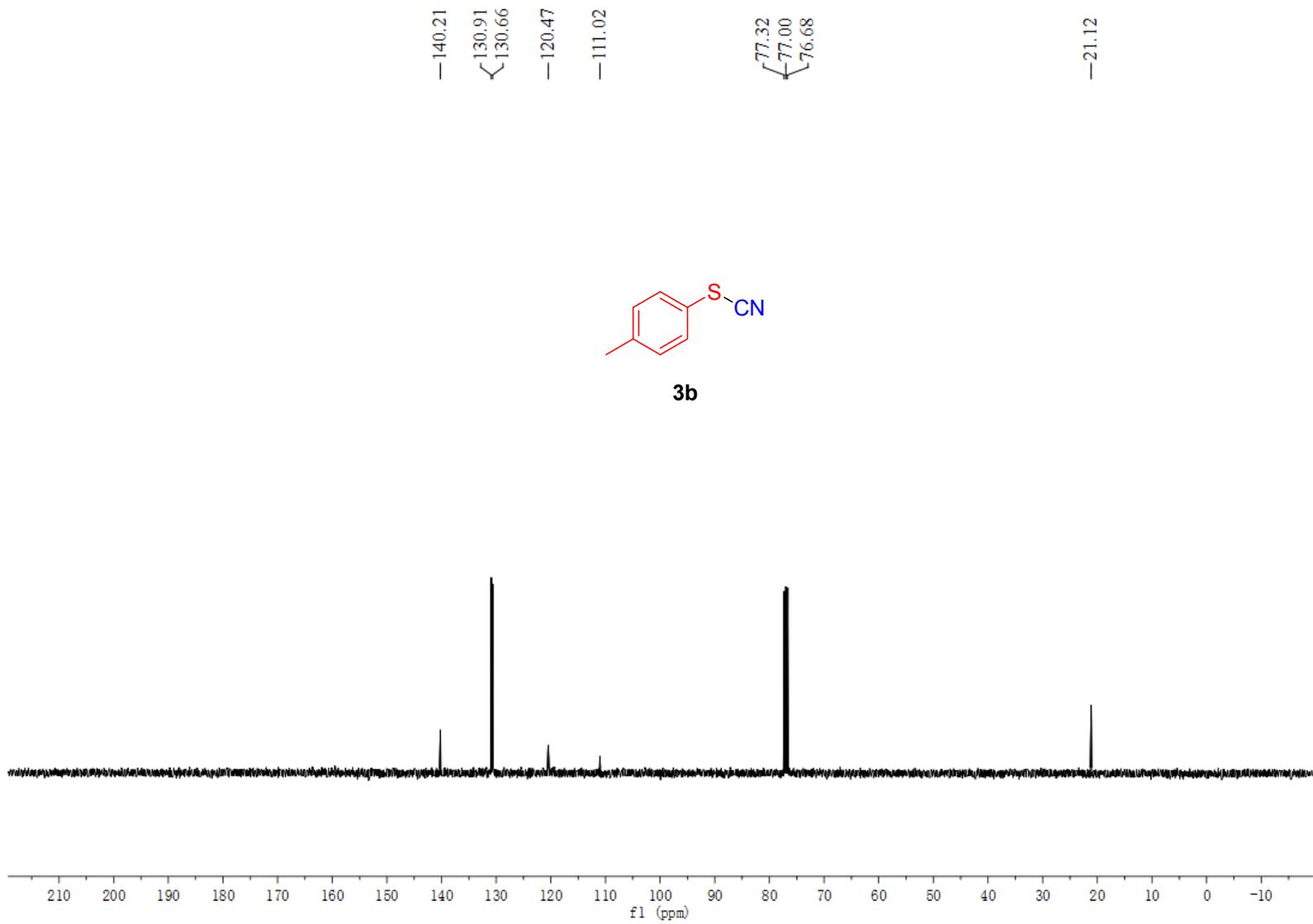
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7.2257

2.3746



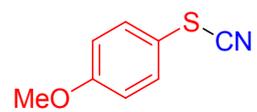
3b



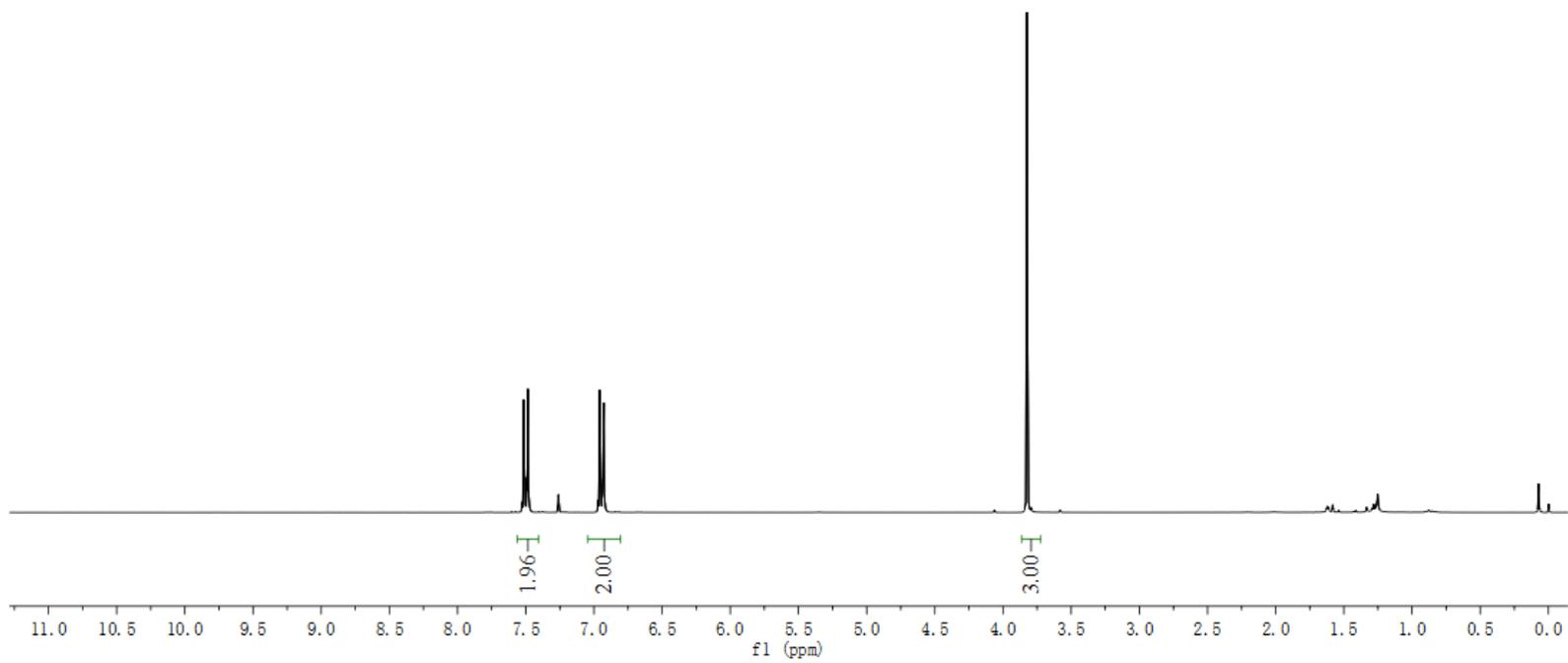


4-Methoxyphenyl thiocyanate (3c)

7.5147
7.5075
7.4922
7.4849
7.4742
7.2602
6.9688
6.9582
6.9509
6.9355
6.9283
6.9176
3.8243



3c



—161.25

—133.78

—115.78

—113.70

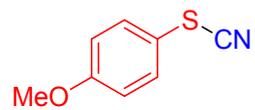
—111.60

—77.42

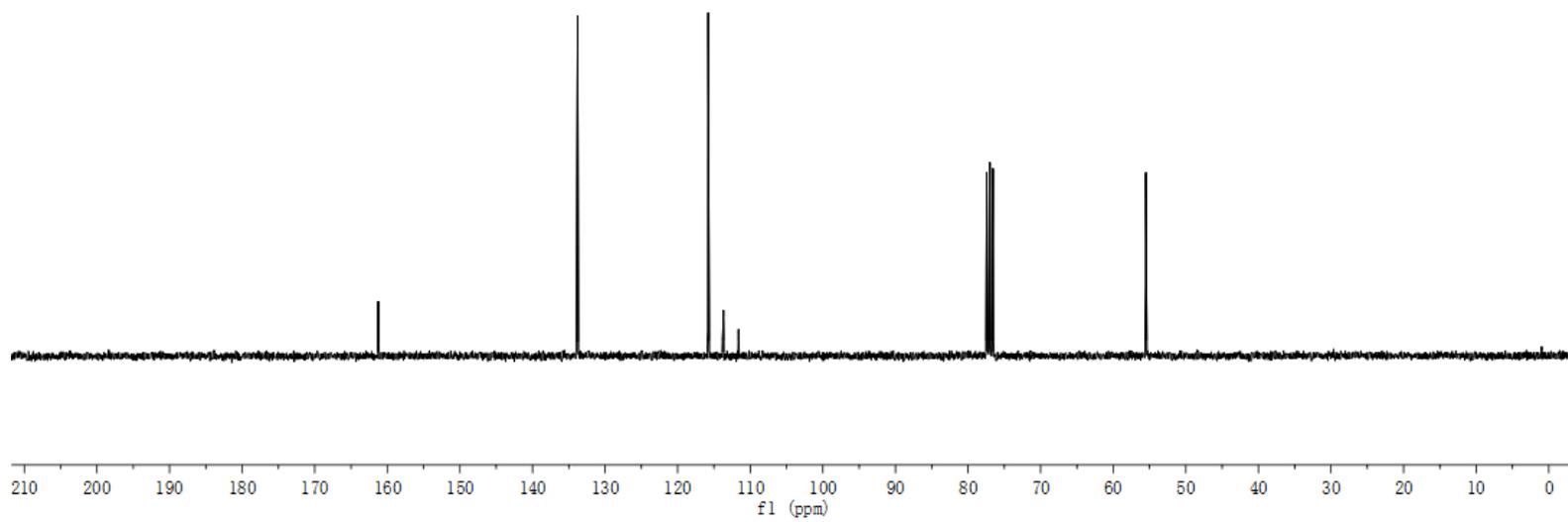
—77.00

—76.58

—55.49

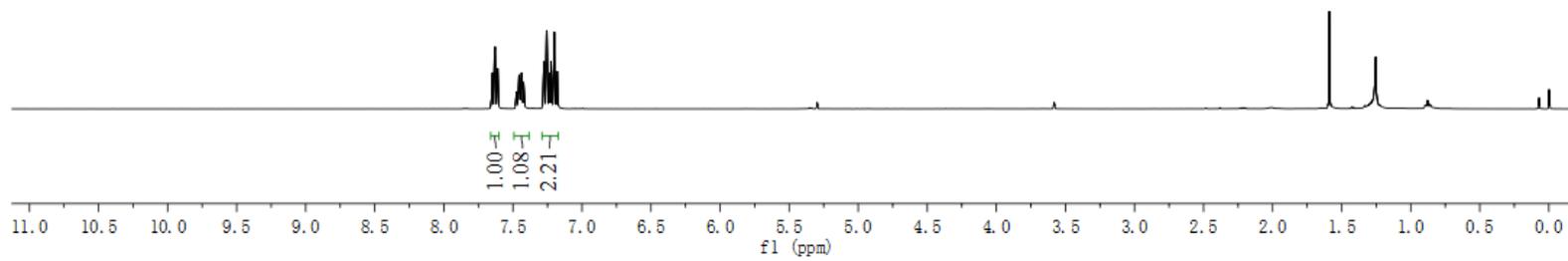
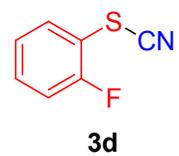


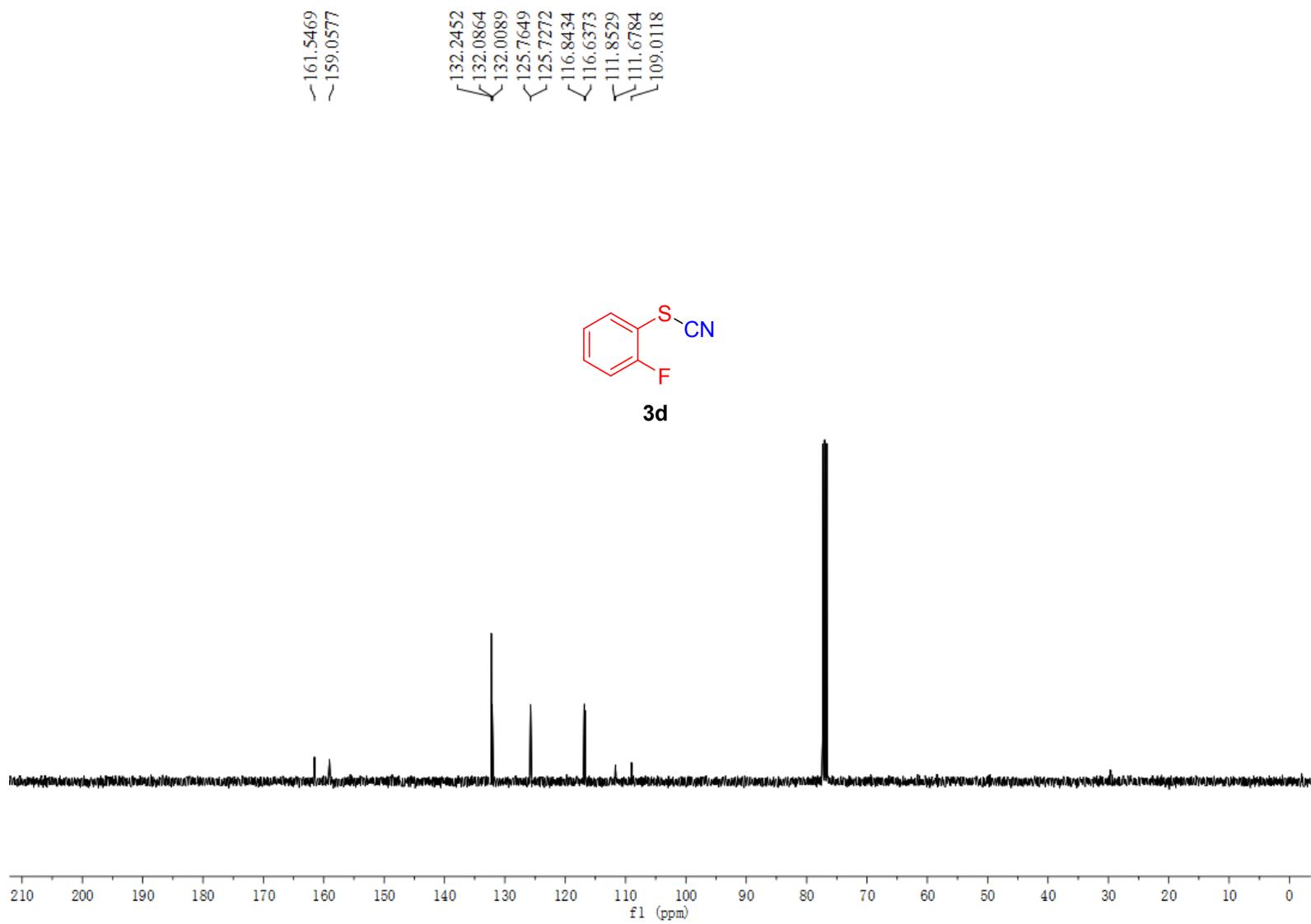
3c

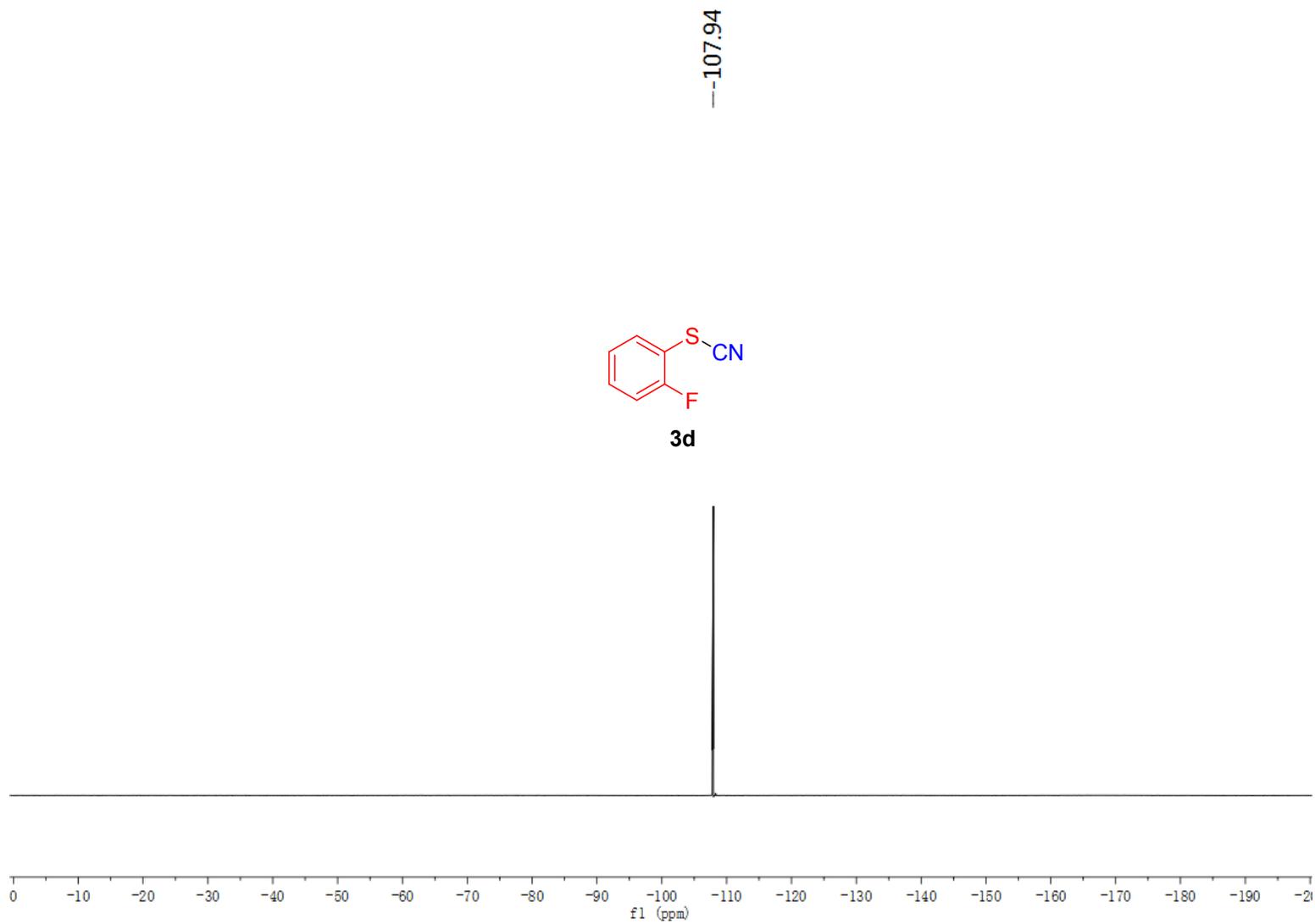


2-Fluorophenyl thiocyanate (3d)

7.6513
7.6473
7.6321
7.6286
7.6135
7.6095
7.4750
7.4709
7.4622
7.4561
7.4546
7.4520
7.4416
7.4390
7.4370
7.4363
7.4315
7.4227
7.4186
7.2767
7.2739
7.2604
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7.2353
7.2239
7.2211
7.2007
7.1802
7.1772

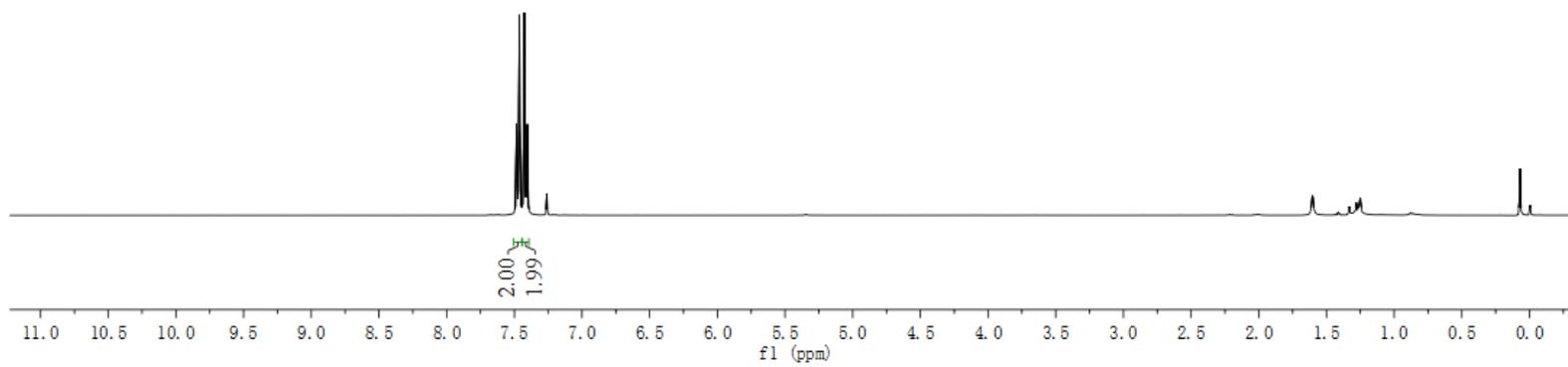
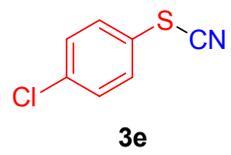




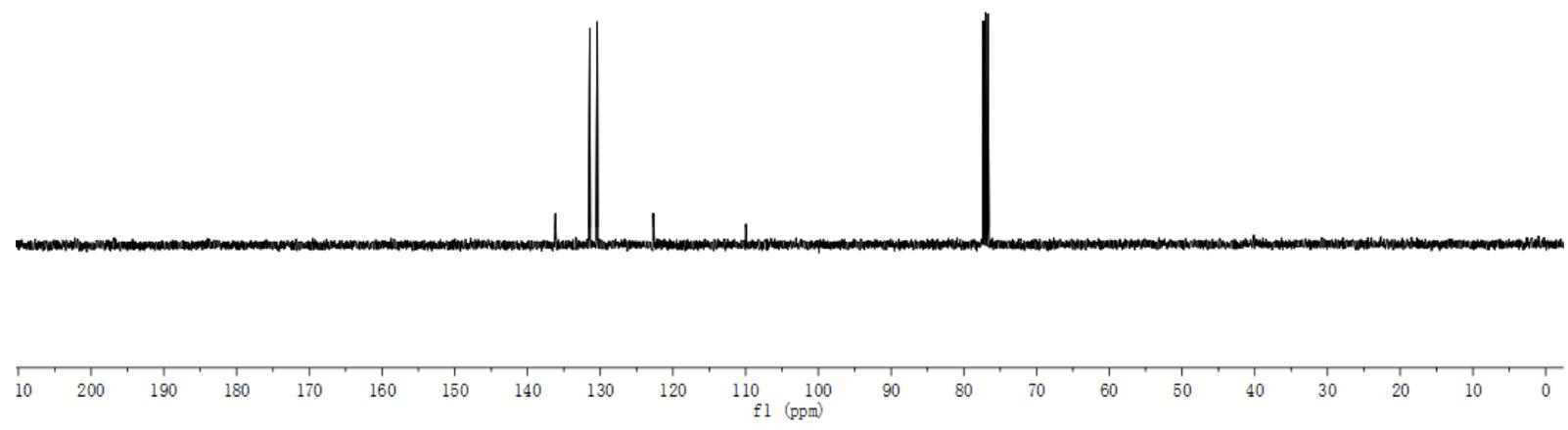
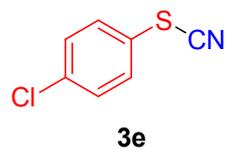


4-Chlorophenyl thiocyanate (3e)

7.4841
7.4623
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7.4047
7.2596

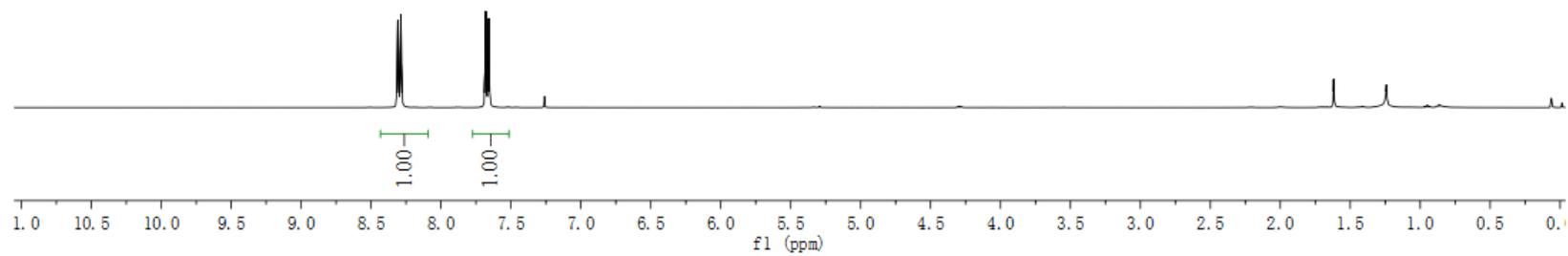
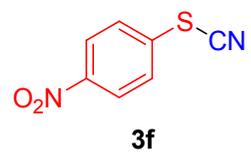


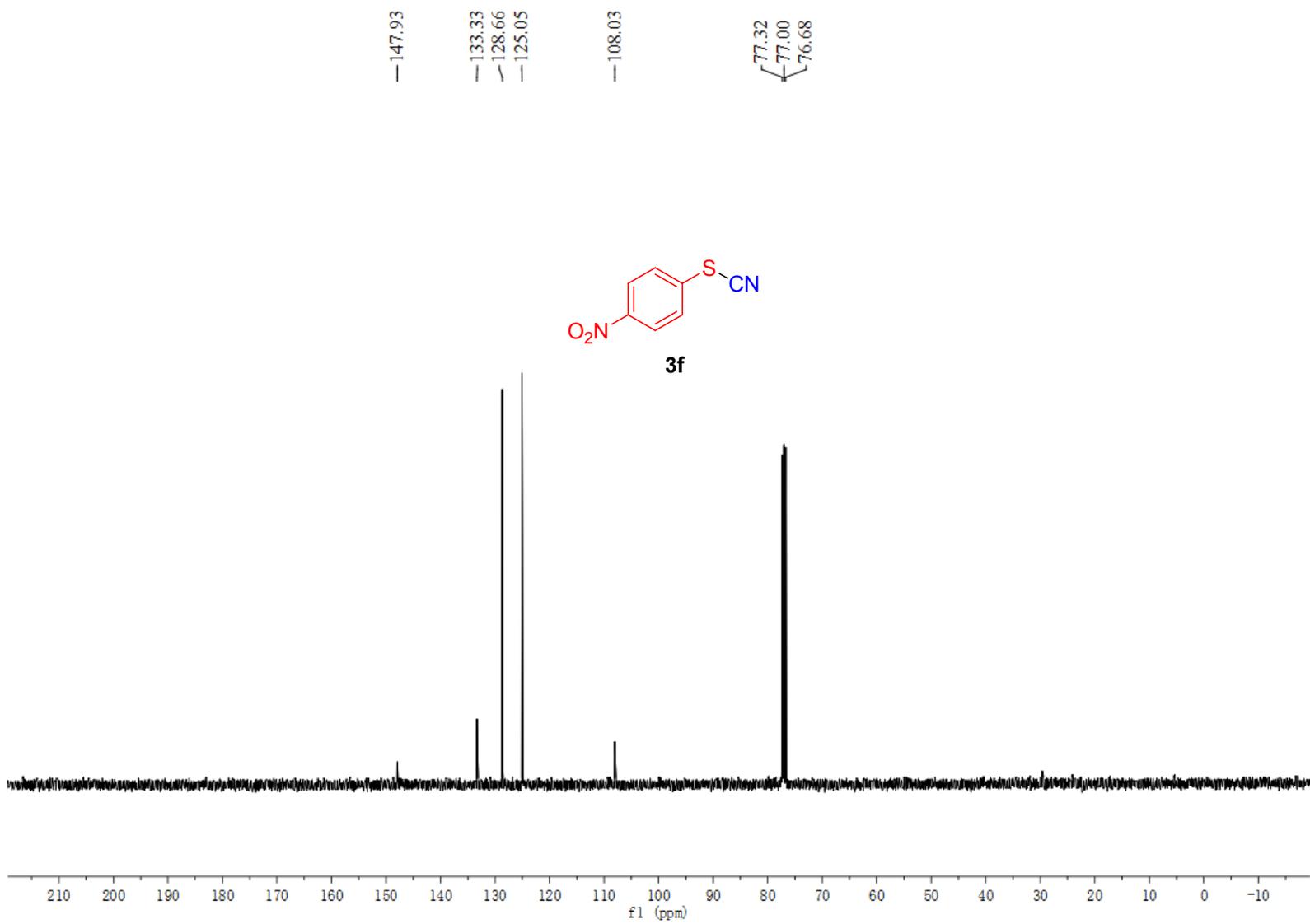
136.15
131.43
130.42
122.68
109.95
77.32
77.00
76.68



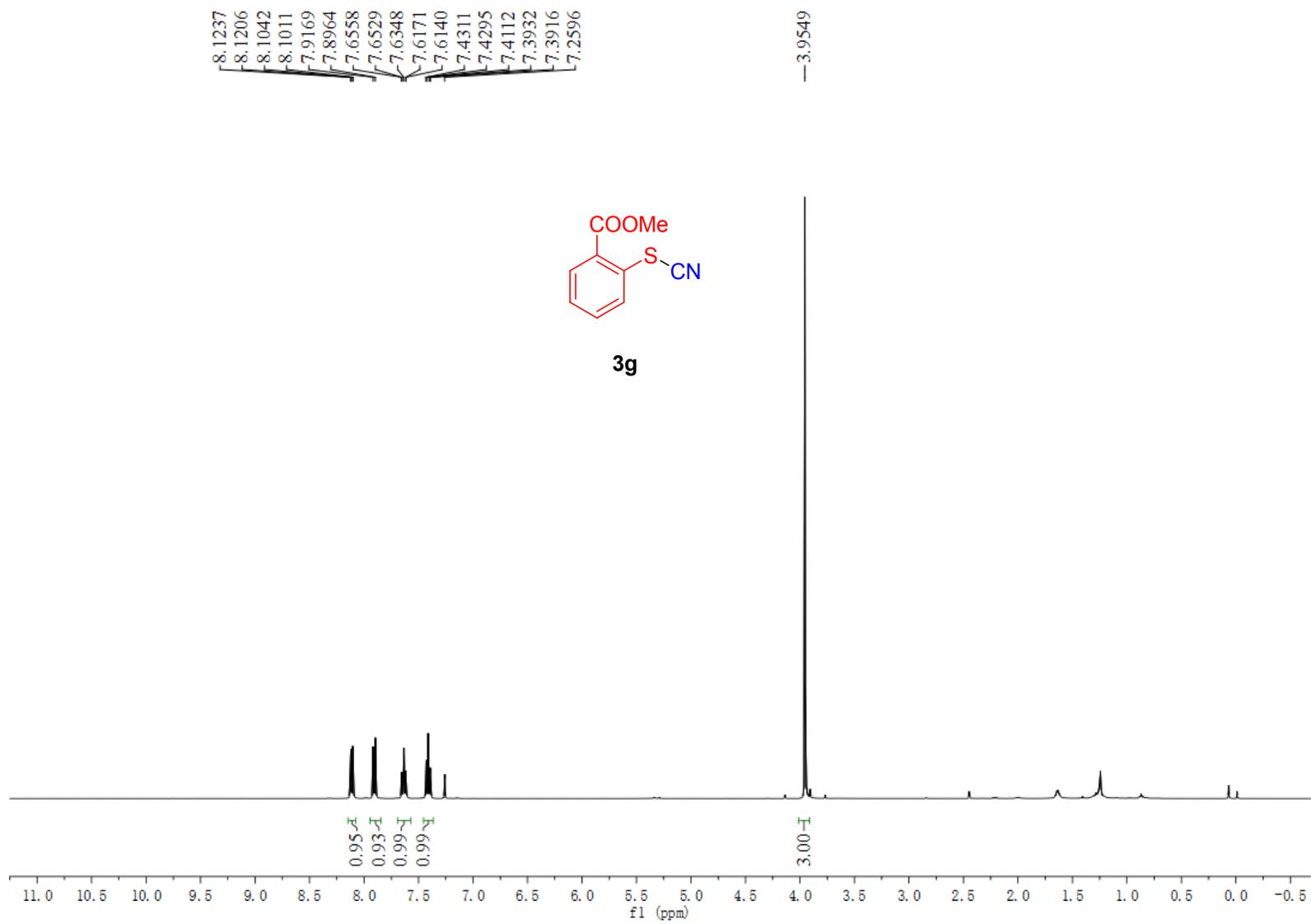
4-Nitrophenyl thiocyanate (3f)

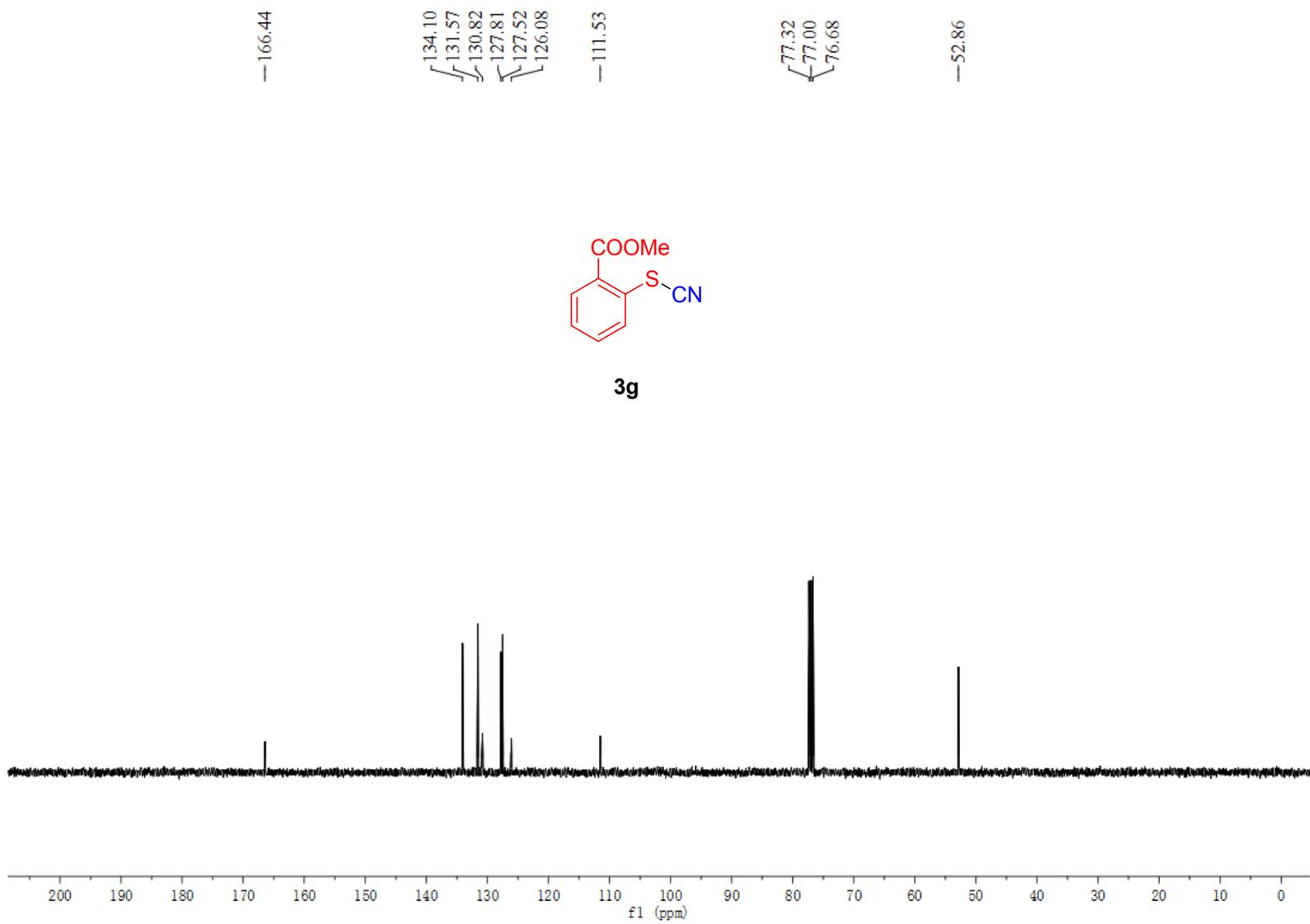
8.3083
8.2860
7.6806
7.6583
7.2597





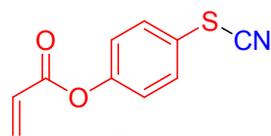
Methyl 2-thiocyanatobenzoate (3g)



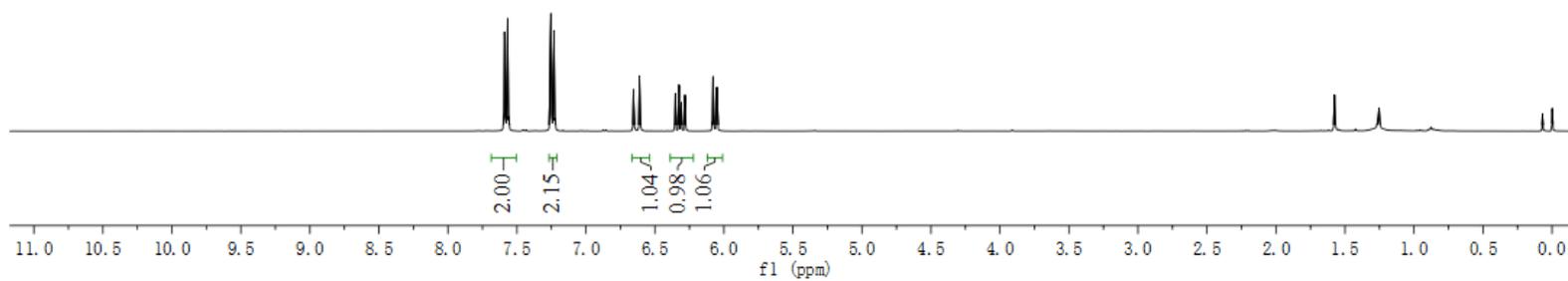


4-Thiocyanatophenyl acrylate (3h)

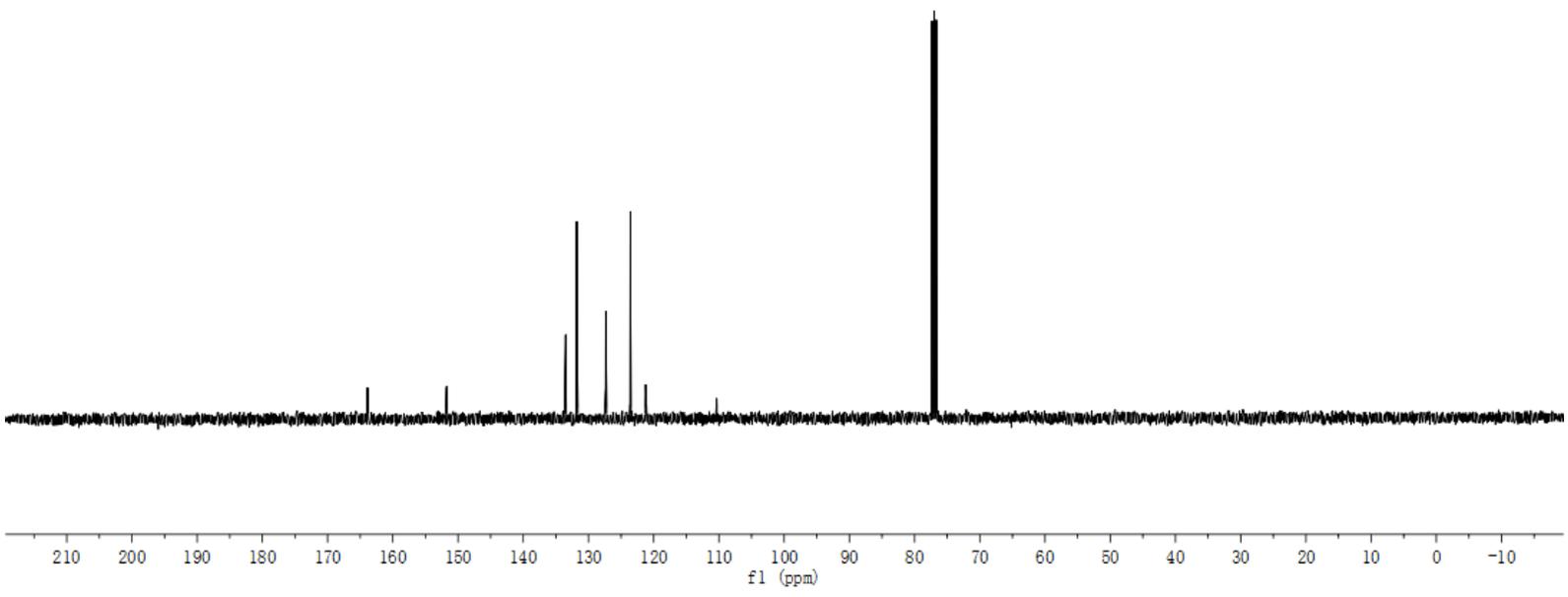
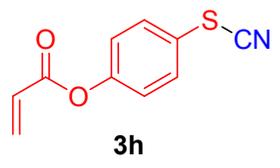
7.5894
7.5843
7.5726
7.5675
7.2597
7.2534
7.2481
7.2365
7.2315
6.6552
6.6526
6.6120
6.6094
6.3519
6.3258
6.3087
6.2826
6.0791
6.0766
6.0530
6.0505



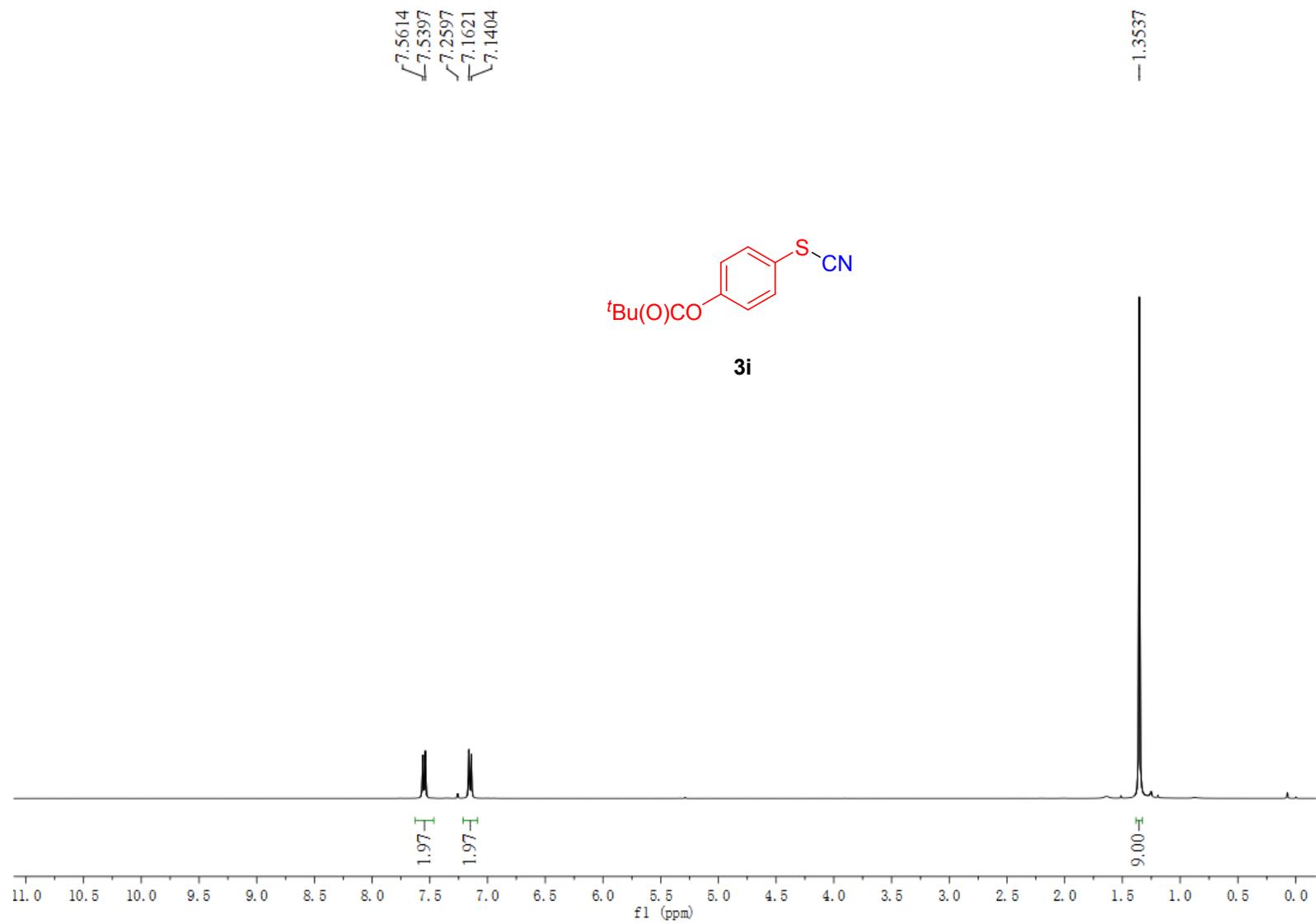
3h

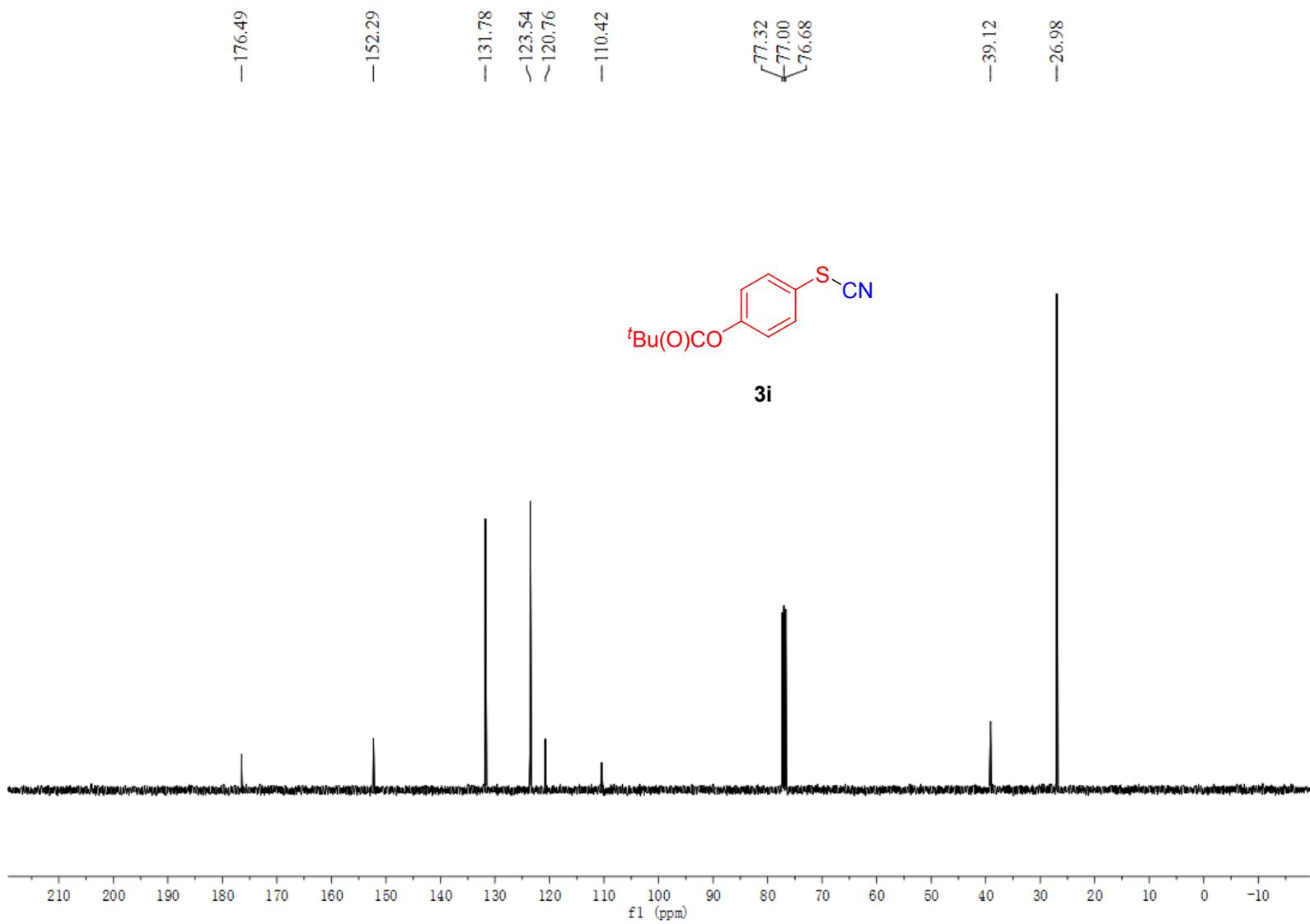


— 163.90
— 151.74
/ 133.49
~ 131.81
— 127.33
~ 123.58
/ 121.21
— 110.35
/ 77.32
/ 77.00
/ 76.68



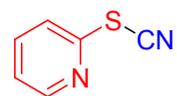
4-Thiocyanatophenyl pivalate (3i)



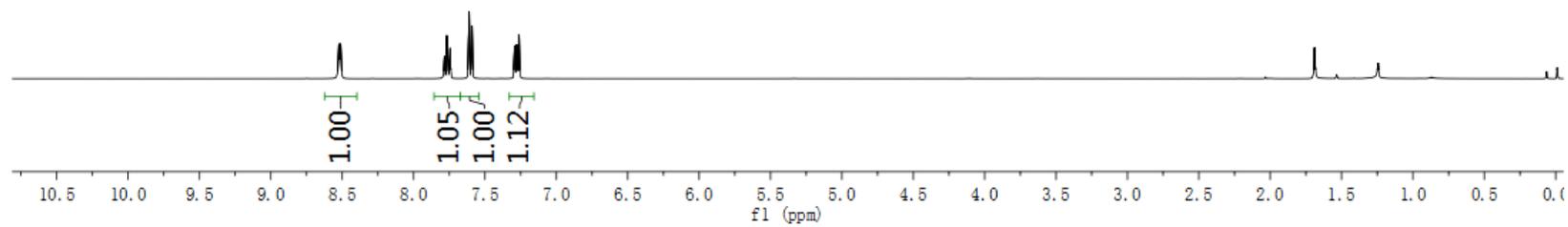


2-Thiocyanatopyridine (3j)

8.5254
8.5231
8.5135
8.5112
7.7878
7.7831
7.7680
7.7635
7.7487
7.7441
7.6116
7.5914
7.2926
7.2907
7.2804
7.2785
7.2738
7.2719
7.2622
7.2599



3j



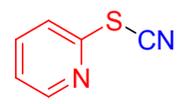
150.48
149.87

138.41

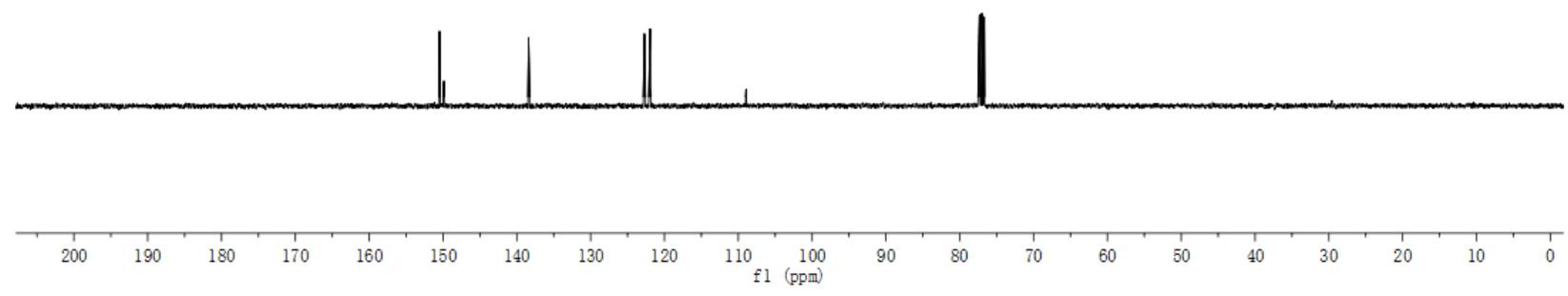
122.72
121.95

108.94

77.32
77.00
76.68

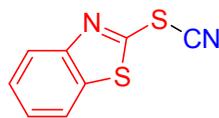


3j

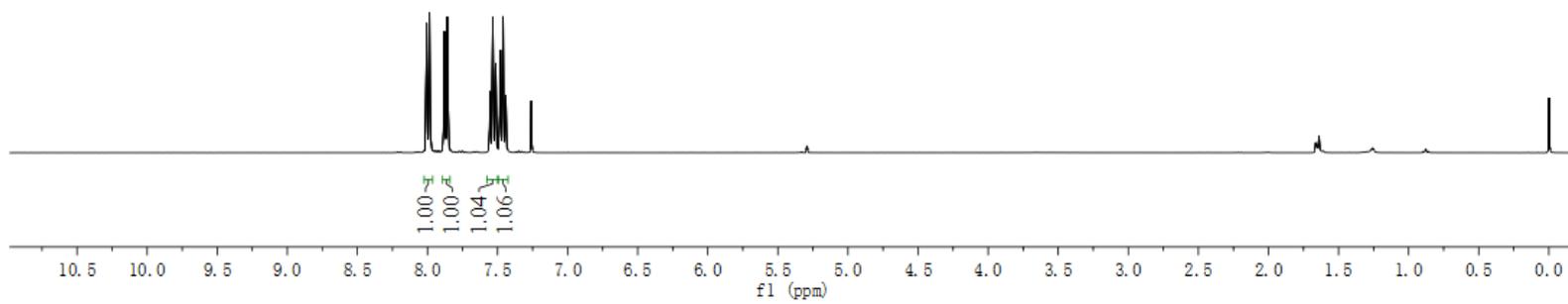


2-Thiocyanatobenzo[d]thiazole (3k)

8.0057
7.9854
7.8791
7.8589
7.5520
7.5339
7.5149
7.5134
7.4797
7.4613
7.4417
7.2597



3k



153.29
152.88

136.40

127.10

126.30

123.12

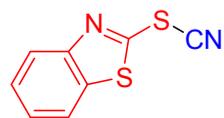
121.34

106.92

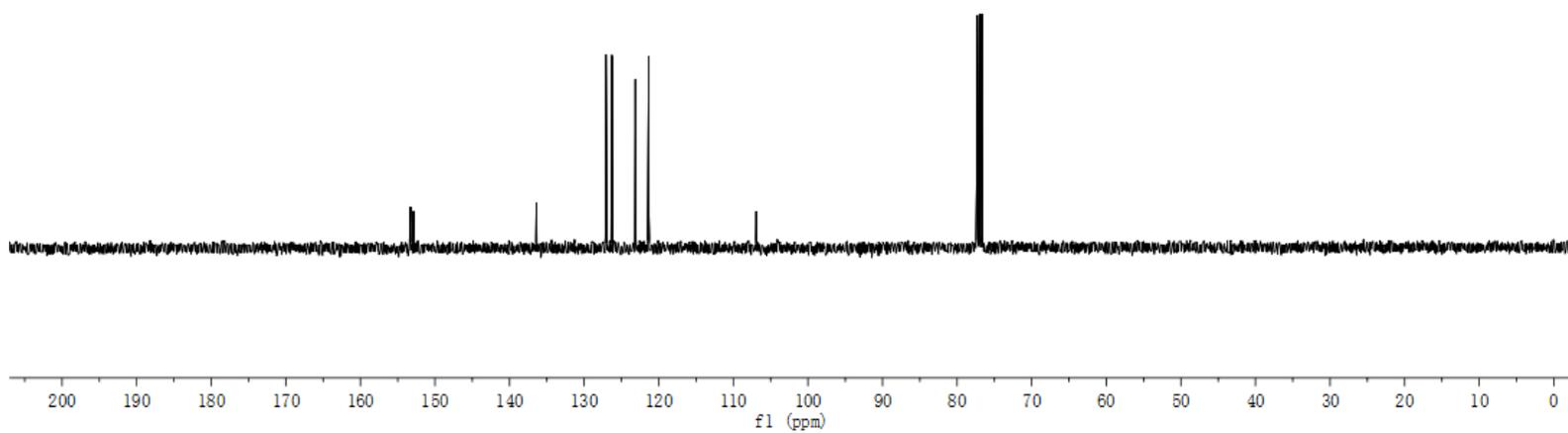
77.32

77.00

76.68



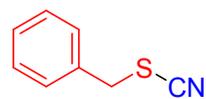
3k



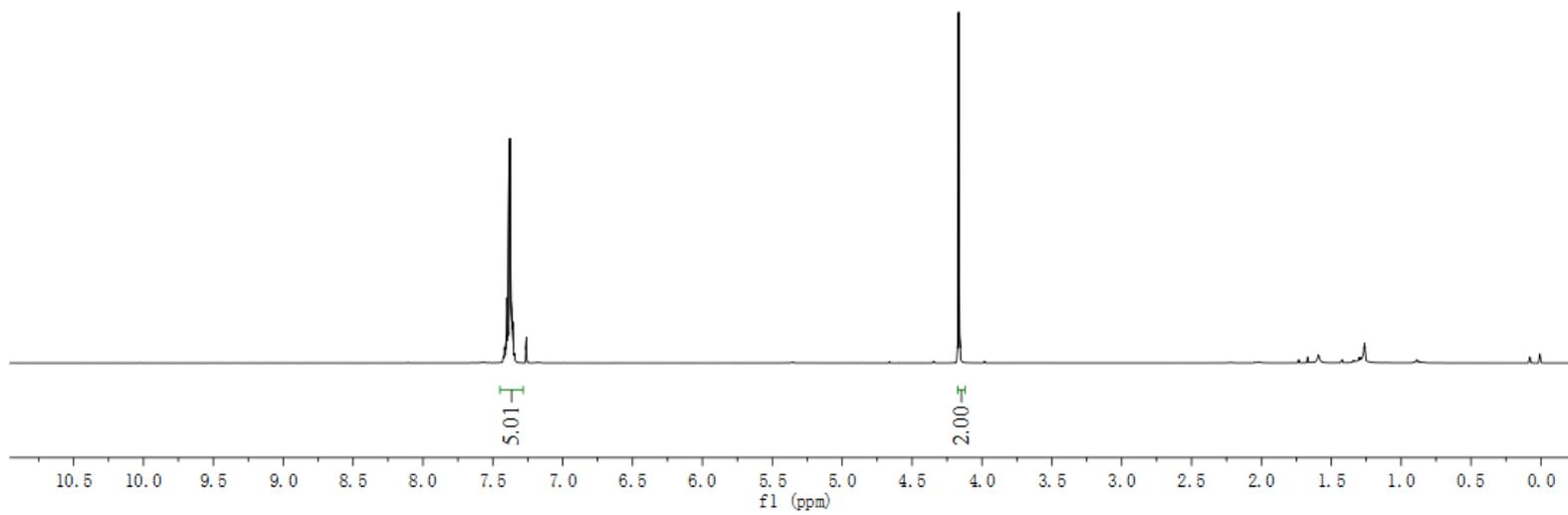
(Thiocyanatomethyl)benzene (3I)

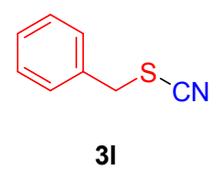
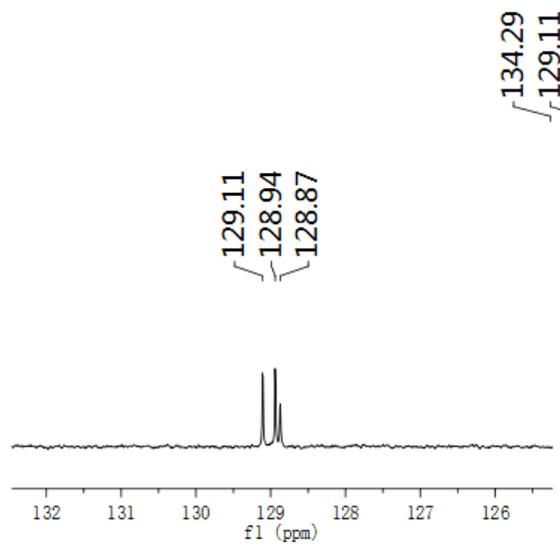
7.4160
7.4018
7.3967
7.3841
7.3763
7.3669
7.3587
7.2597

4.1659



3I



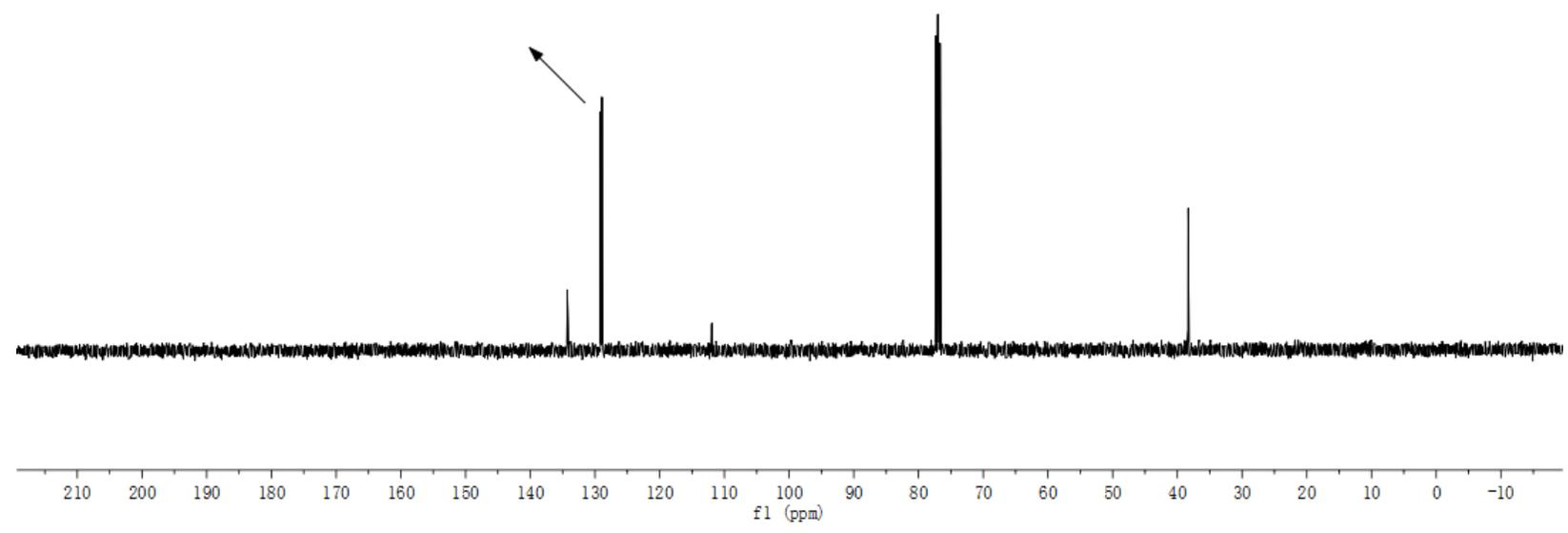


134.29
129.11
128.94
128.87

-111.93

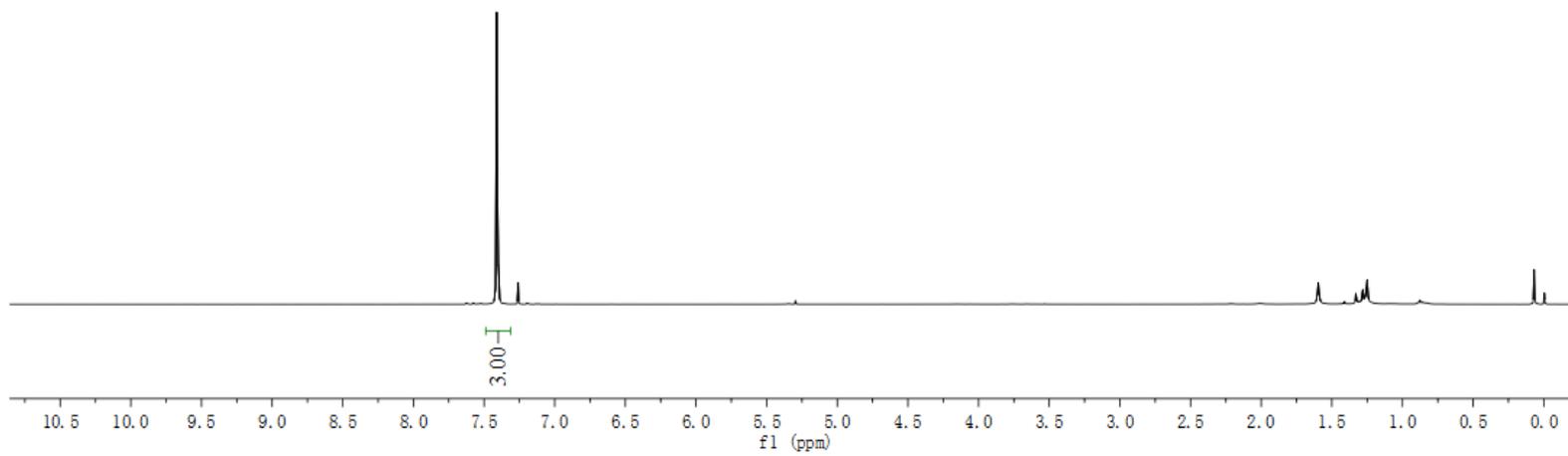
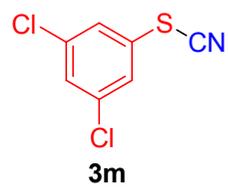
77.32
77.00
76.68

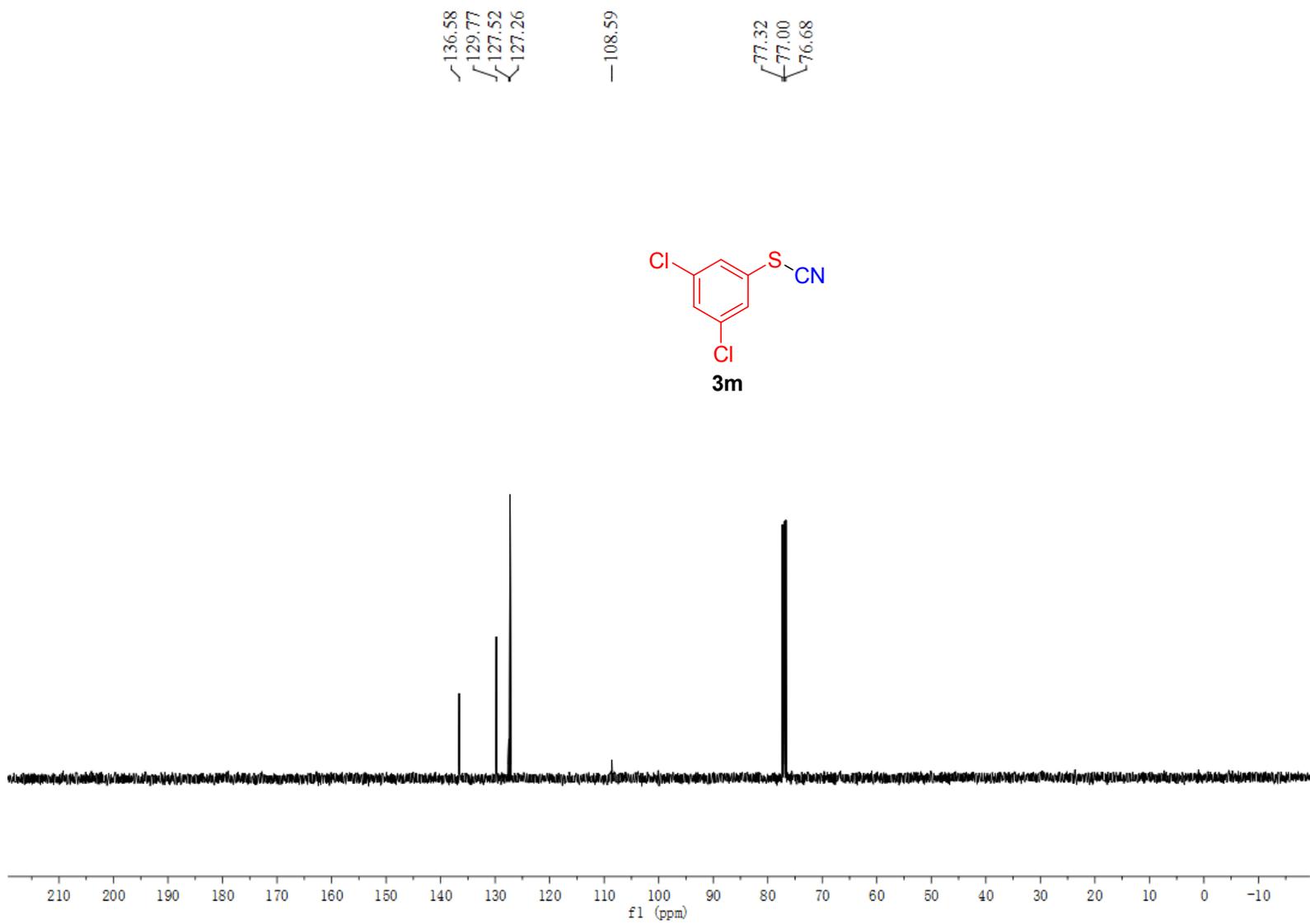
-38.32



3, 5-Dichlorophenyl thiocyanate (3m)

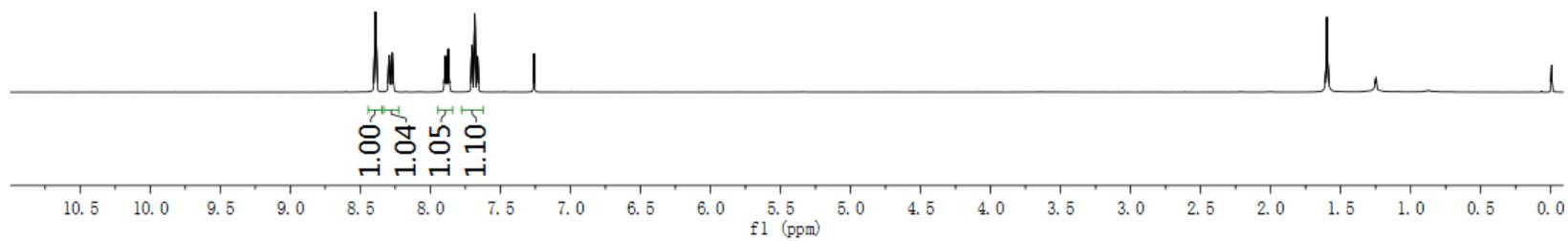
7.4140
7.4109
7.4070
7.4040
7.2599

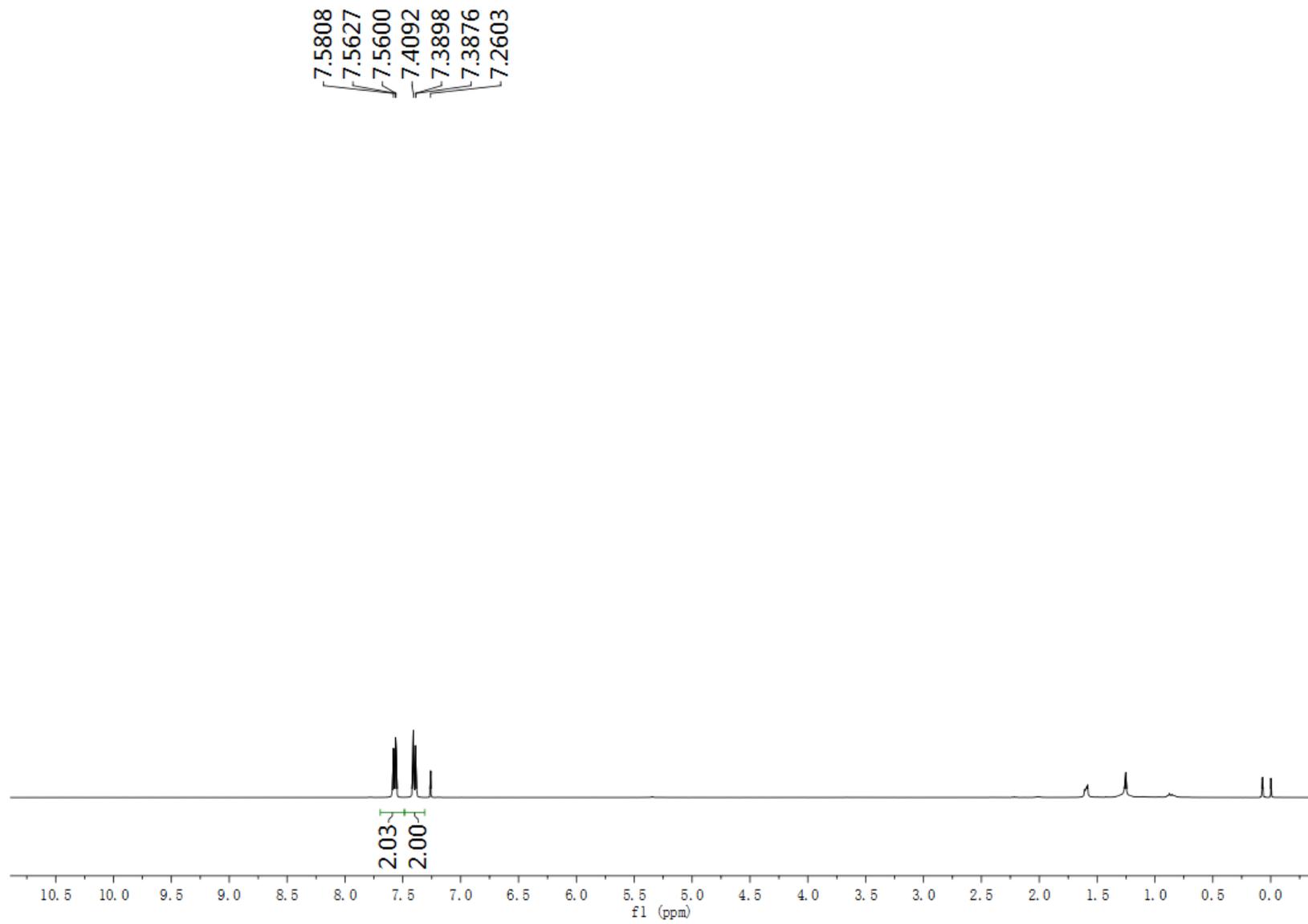




3-Nitrophenyl thiocyanate (3n)

8.3958
8.3911
8.3864
8.2926
8.2896
8.2721
8.2690
7.8925
7.8907
7.8727
7.8709
7.7021
7.6818
7.6616

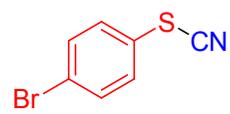




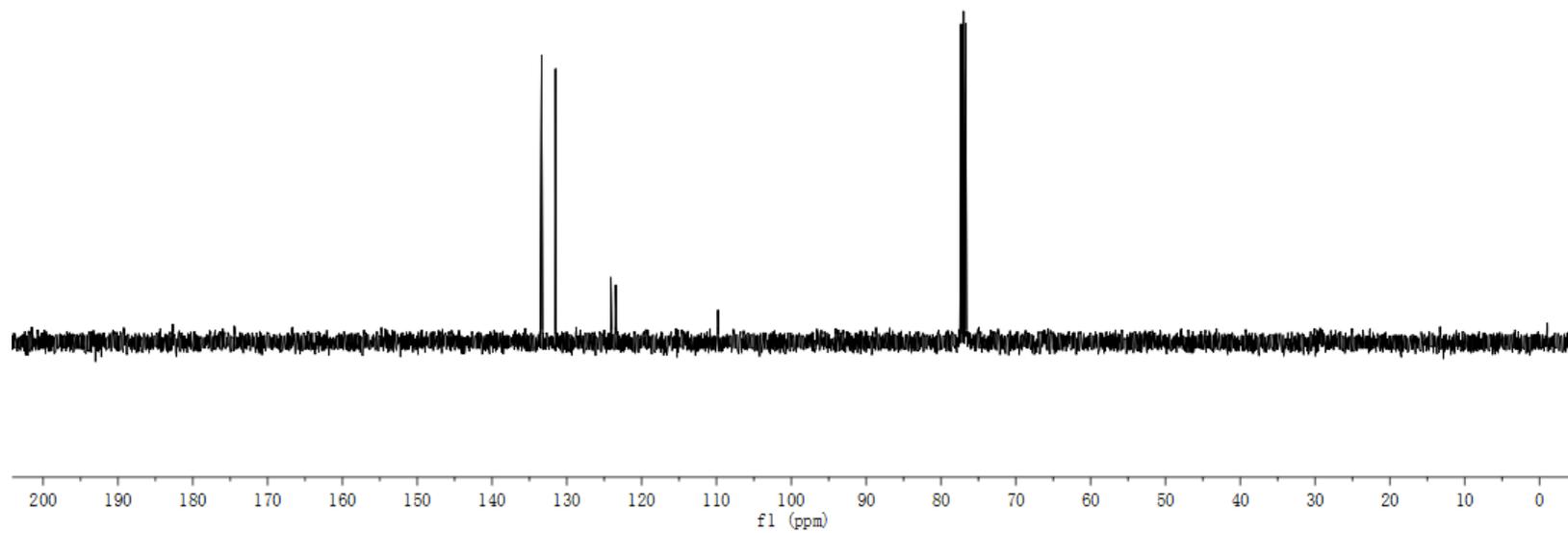
133.38
131.49
124.12
123.45

109.80

77.32
77.00
76.68

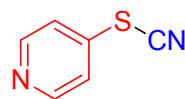


3o

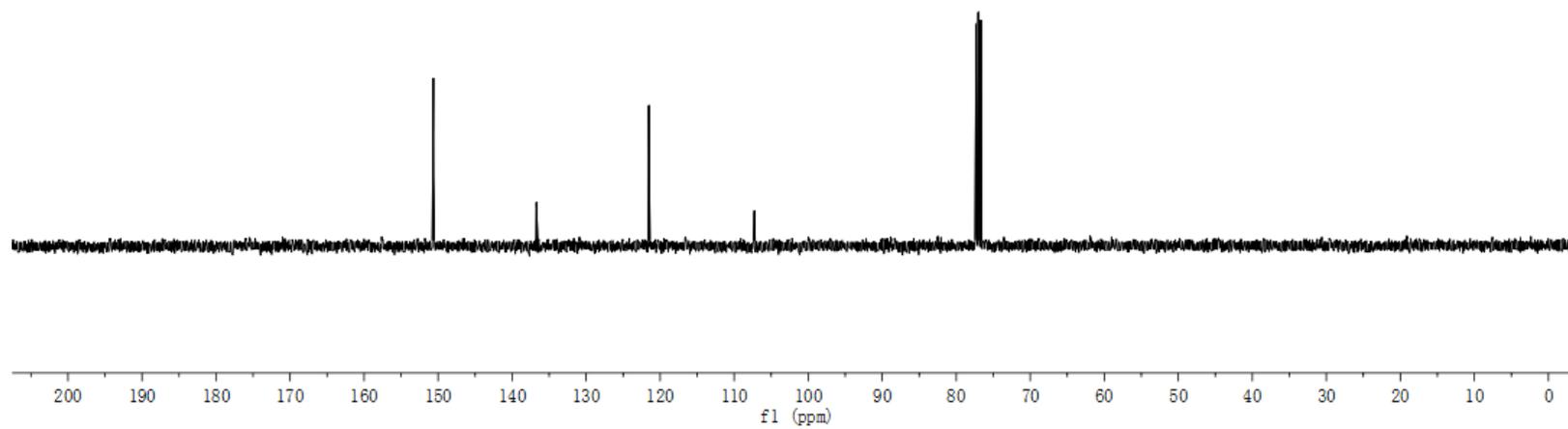


4-Thiocyanatopyridine (3p)

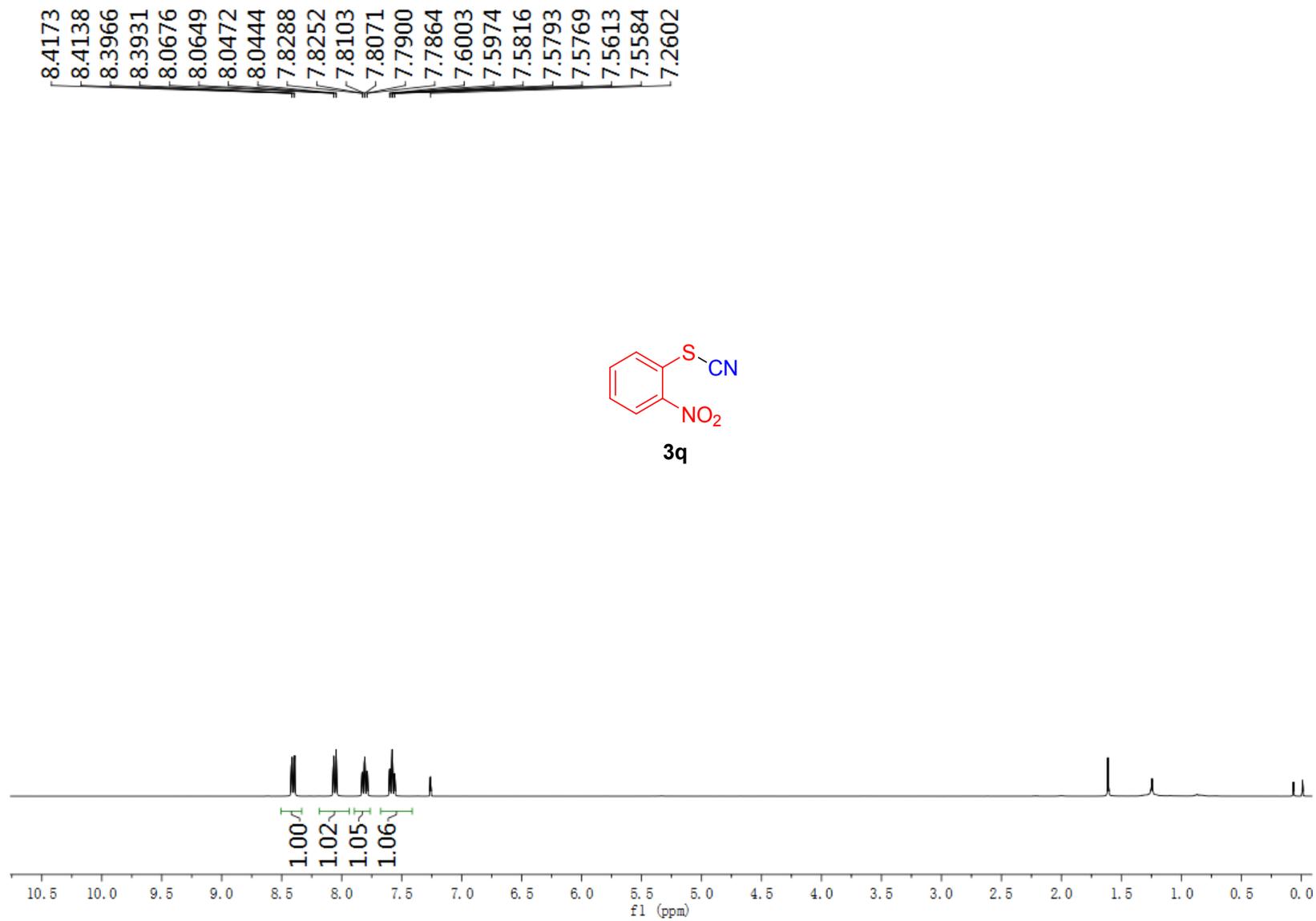
-150.65
-136.71
-121.52
-107.26
77.32
77.00
76.68

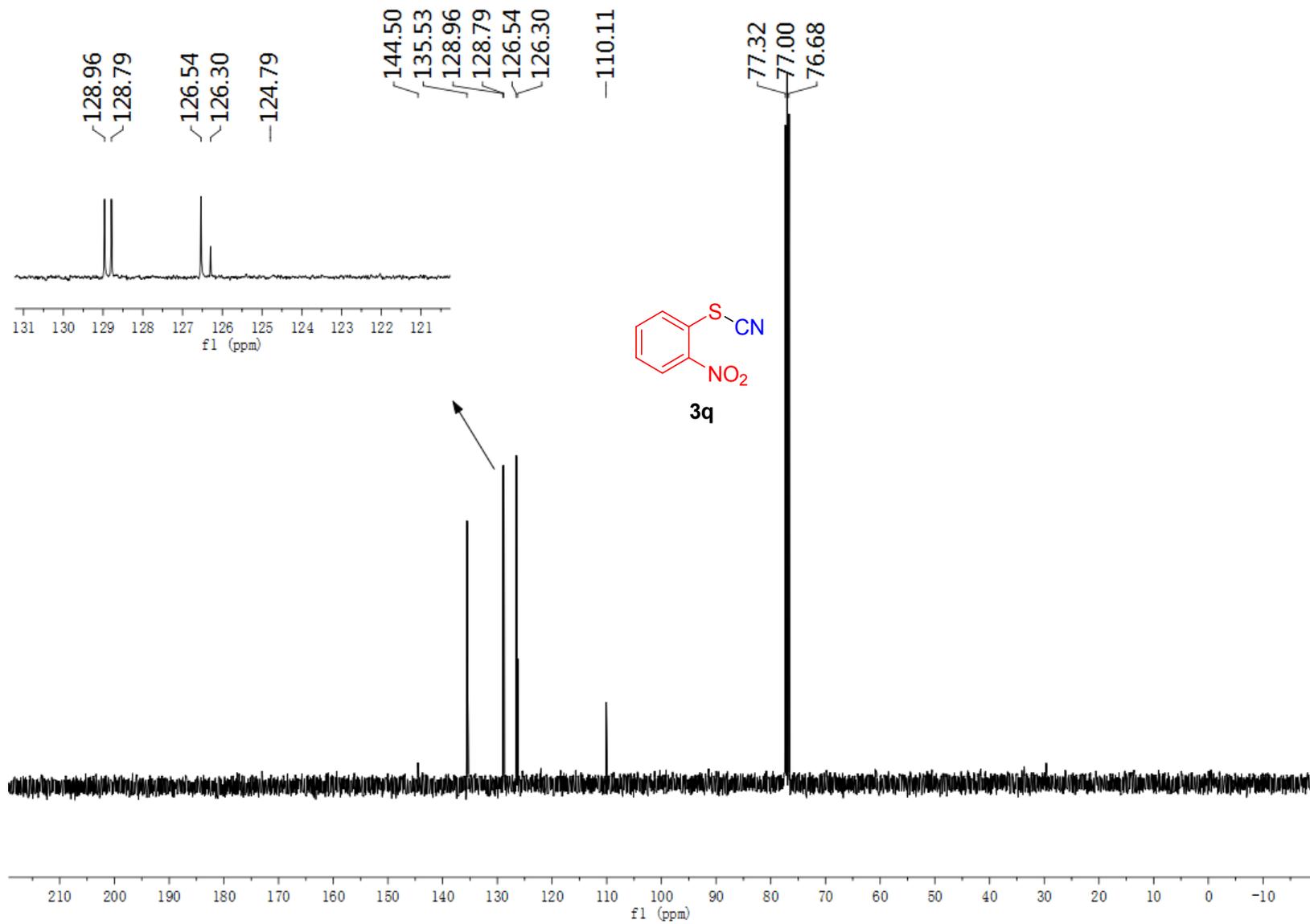


3p



2-Nitrophenyl thiocyanate (3q)





1-Thiocyanatooctane (3r)

-7.2602

2.9514
2.9332
2.9149
1.8450
1.8269
1.8083
1.7897
1.7711
1.4622
1.4445
1.4273
1.4077
1.3902
1.3283
1.3183
1.3123
1.2909
1.2843
1.2702
0.8906
0.8738
0.8562

