Supporting Information

The palladium-catalyzed desulfitative cyanation of arenesulfonyl chlorides and sodium sulfinates

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1. General experimental details:

Chemicals were either purchased or purified by standard techniques without special instructions. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker 500 MHz spectrometer (^{1}H 500 MHz and ^{13}C 125 MHz), using $CDCl_3$ or DMSO-d_6 as the solvent at room temperature. Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet. Coupling constants *J*, were reported in hertz unit (Hz). Chemical shifts (in ppm) were referenced to tetramethylsilane (δ = 0 ppm) in $CDCl_3$ as an internal standard. ^{13}C NMR spectra were obtained by using the same NMR spectrometers and chemical shifts were reported in ppm referenced to the center line of a triplet at 77.0 ppm of $CDCl_3$ or 39.5 ppm of DMSO-d_6.

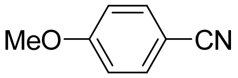
Caution: Work with cyanides is hazardous; the experiments and work-up need to be carried out in a well-ventilated fume-hood.

Dry 1,4-dioxane: After heated with sodium wire for several hours, dry 1,4-dioxane was gathered by distill.

Typical experimental procedures for the reaction of arenesulfonyl chlorides and sodium sulfinates: In a sealed tube, 2.0 mL of dry 1,4-dioxane was added to a mixture of arenesulfonyl chlorides **1** or aryl sodium sulfinates **1’** (0.2 mmol, 1.0 equiv), CuCN (18.9 mg, 0.21 mmol, 1.05 equiv), $Pd(CH_3CN)_2Cl_2$ (5.1 mg, 0.02 mmol, 0.1 equiv), $Cu(acac)_2$ (10.5 mg, 0.04 mmol, 0.2 equiv) and Na_2CO_3 (42.4 mg, 0.4 mmol, 2.0 equiv) under air. The tube was sealed with a Teflon lined cap and the reaction mixture was stirred at 130 °C for 24 h. After cooling to room temperature, the resultant mixture was evaporated with EtOAc (2 x 25 mL) under reduced pressure and the residue was purified by flash column chromatography on a silica gel to give the products.

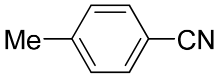
2. Spectral data for the products:

4-methoxybenzonitrile (2a)[1]



^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.58 (d, J = 9.0 Hz, 2H), 6.95 (d, J = 9.0 Hz, 2H), 3.86 (s, 3H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ 162.8, 134.0, 119.2, 114.7, 104.0, 55.5.

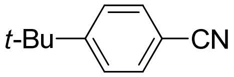
4-methylbenzonitrile (2b)[4]



^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.39 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 2.29 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 143.5, 131.7, 129.6, 118.8, 109.0, 21.5.

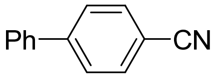
4-tert-butylbenzonitrile (2c)[5]



^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.58 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 1.32 (s, 9H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 156.6, 131.9, 126.1, 119.1, 109.2, 35.2, 30.9.

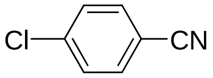
biphenyl-4-carbonitrile (2d)[1]



^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.74-7.68 (m, 4H), 7.60 (d, J = 8.0 Hz, 2H), 7.50-7.49 (m, 2H), 7.47-7.43 (m, 1H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 145.6, 139.1, 132.5, 129.1, 128.6, 127.7, 127.2, 118.9, 110.9.

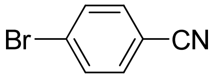
4-chlorobenzonitrile (2e)[2]



^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.59 (d, J = 8.5 Hz, 2H), 7.46 (d, J = 8.5 Hz, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 139.5, 133.3, 129.6, 117.9, 110.8.

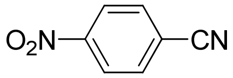
4-bromobenzonitrile (2f)[3]



^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.62 (d, J = 8.5 Hz, 2H), 7.51 (d, J = 8.5 Hz, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 133.3, 132.5, 127.9, 117.9, 111.1.

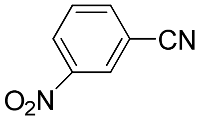
4-nitrobenzonitrile (2g)[4]



^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.36 (d, J = 8.5 Hz, 2H), 7.89 (d, J = 8.5 Hz, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 150.0, 133.5, 124.3, 118.3, 116.8.

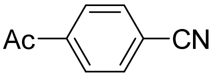
3-nitrobenzonitrile (2h^{2})



^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.54-8.53 (m, 1H), 8.53-8.47 (m, 1H), 8.01-7.99 (m, 1H), 7.76-7.73 (m, 1H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 148.3, 137.6, 130.7, 127.5, 127.2, 116.5, 114.2.

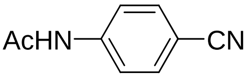
4-acetylbenzonitrile (2i)[1]



^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.03 (d, *J* = 8.5 Hz, 2H), 7.77 (d, *J* = 8.5 Hz, 2H), 2.64 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 196.5, 139.9, 132.5, 128.7, 117.9, 116.4, 26.7.

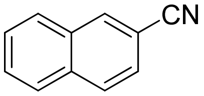
N-(4-cyanophenyl)acetamide (2j)[3]



^{1}H NMR (DMSO-d_6, 500 MHz): δ 10.42 (s, 1H), 7.72 (s, 4H), 2.07 (s, 3H).

^{13}C NMR (DMSO-d_6, 125 MHz): δ 169.8, 143.6, 133.5, 119.4, 119.3, 105.1, 24.4.

2-naphthonitrile (2k)[1]



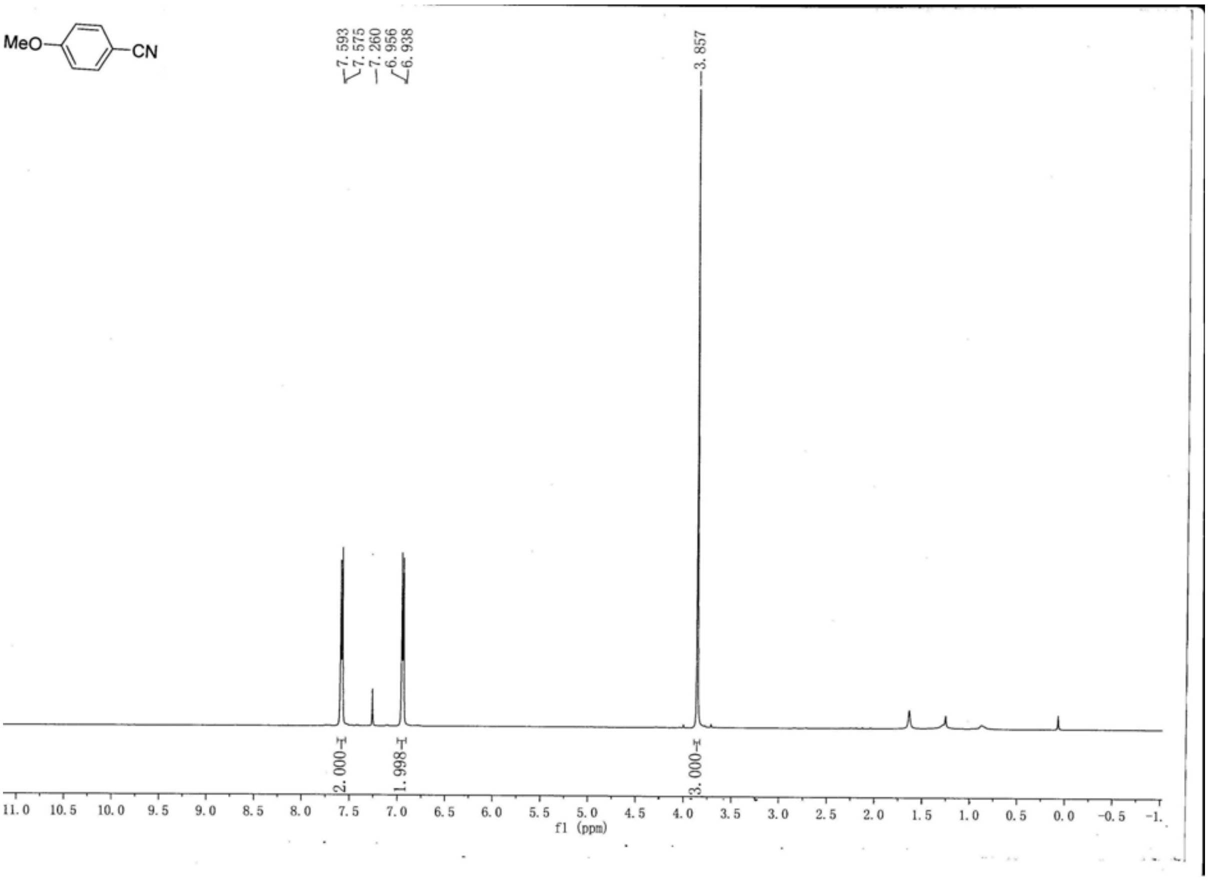
^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.23 (s 1H), 7.92-7.88 (m, 3H), 7.66-7.59 (m, 3H).

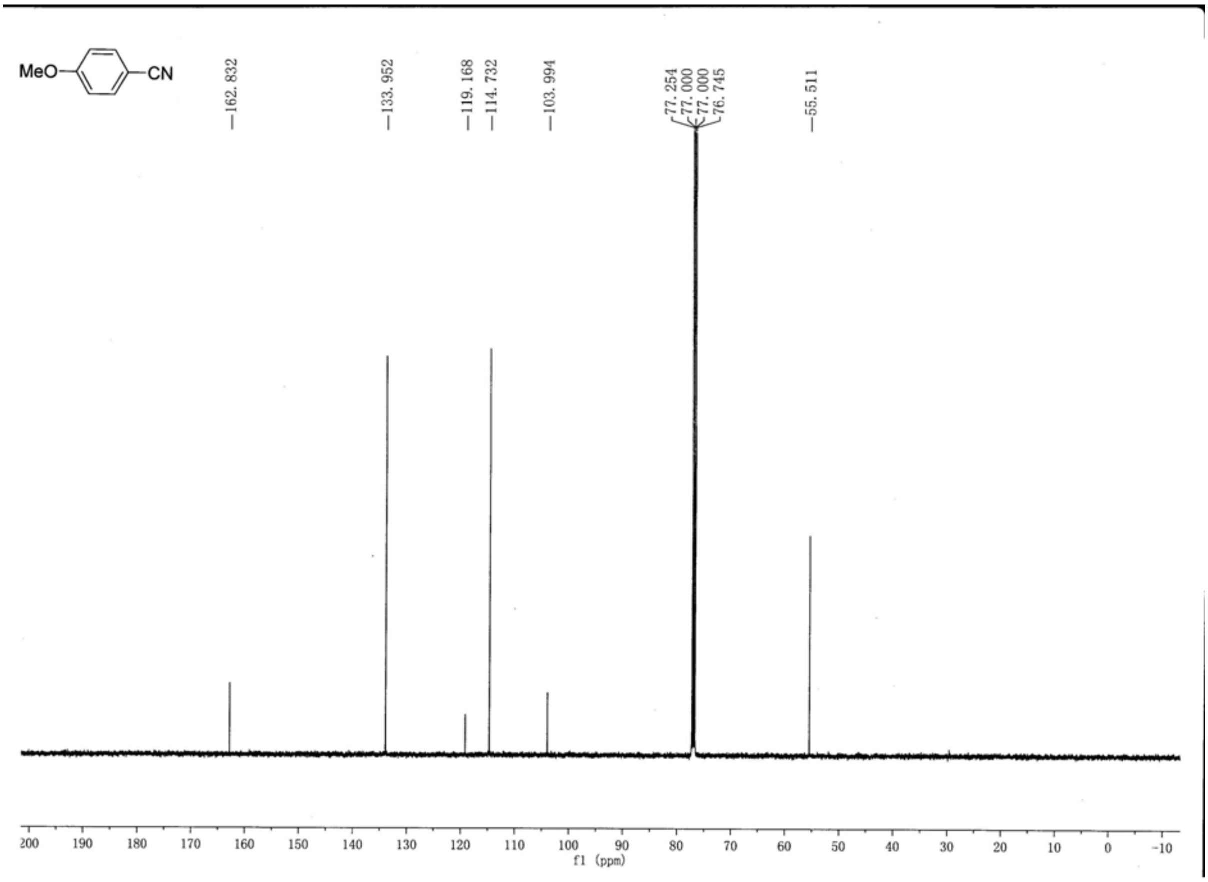
^{13}C NMR ($CDCl_3$, 125 MHz): δ 134.6, 134.1, 132.2, 129.2, 129.0, 128.4, 128.0, 127.6, 126.3, 119.2, 109.4.

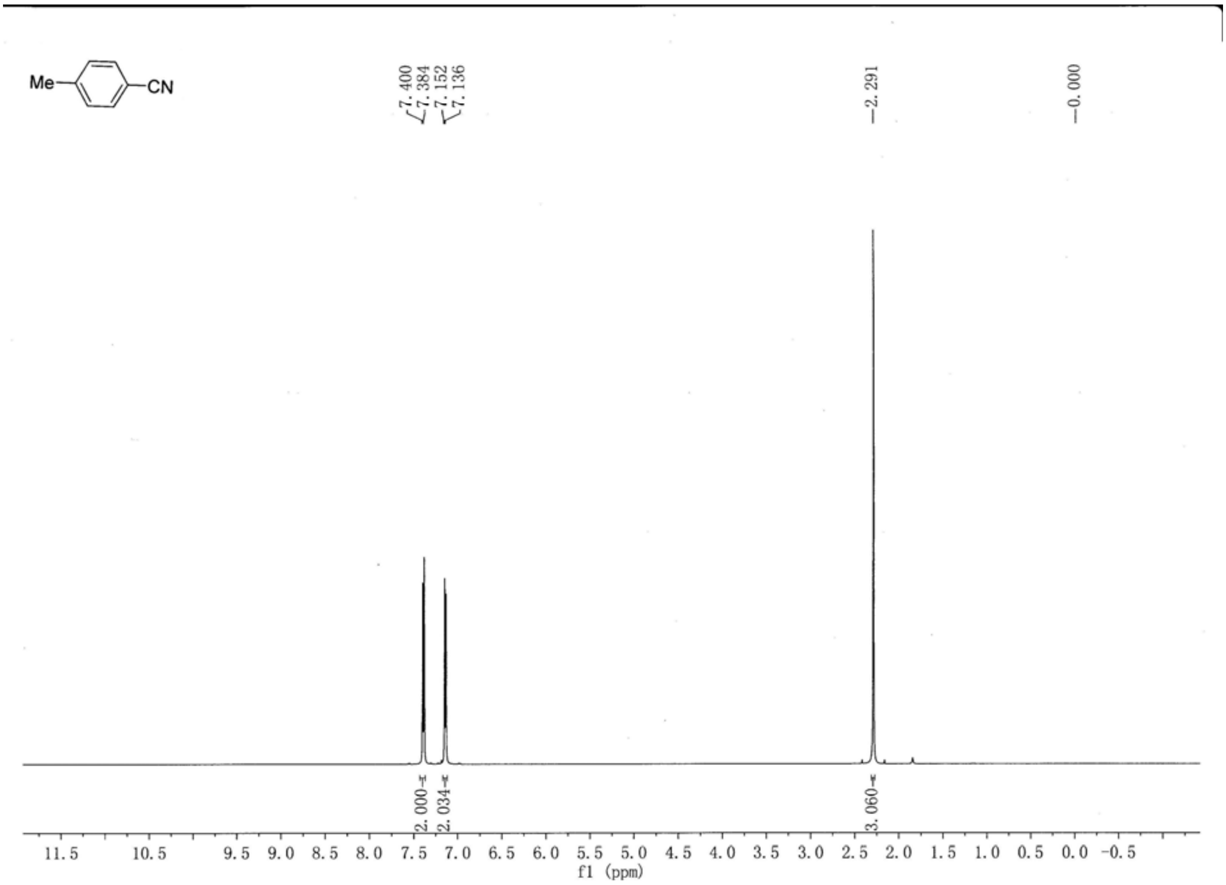
3. References:

1 O. Grossman and D. Gelman, *Org. Lett.*, 2006, **8**, 1189.
2 M. Sundermeier, A. Zapf and M.Beller, *Angew. Chem., Int. Ed.*, 2003, **42**, 1661.
3 S. Zhou, K. Junge, D. Addis, S. Das and M. Beller, *Org. Lett.*, 2009, **11**, 2461.
4 A. V. Ushkov and V. V. Grushin, *J. Am. Chem. Soc.*, 2011, **133**, 10999.
5 P. Y. Yeung, C. M. So, C. P. Lau and F. Y. Kwong, *Angew. Chem., Int. Ed.*, 2010, **49**, 8918.

4. Copies of product ^{1}H NMR and ^{13}C NMR:



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6.0
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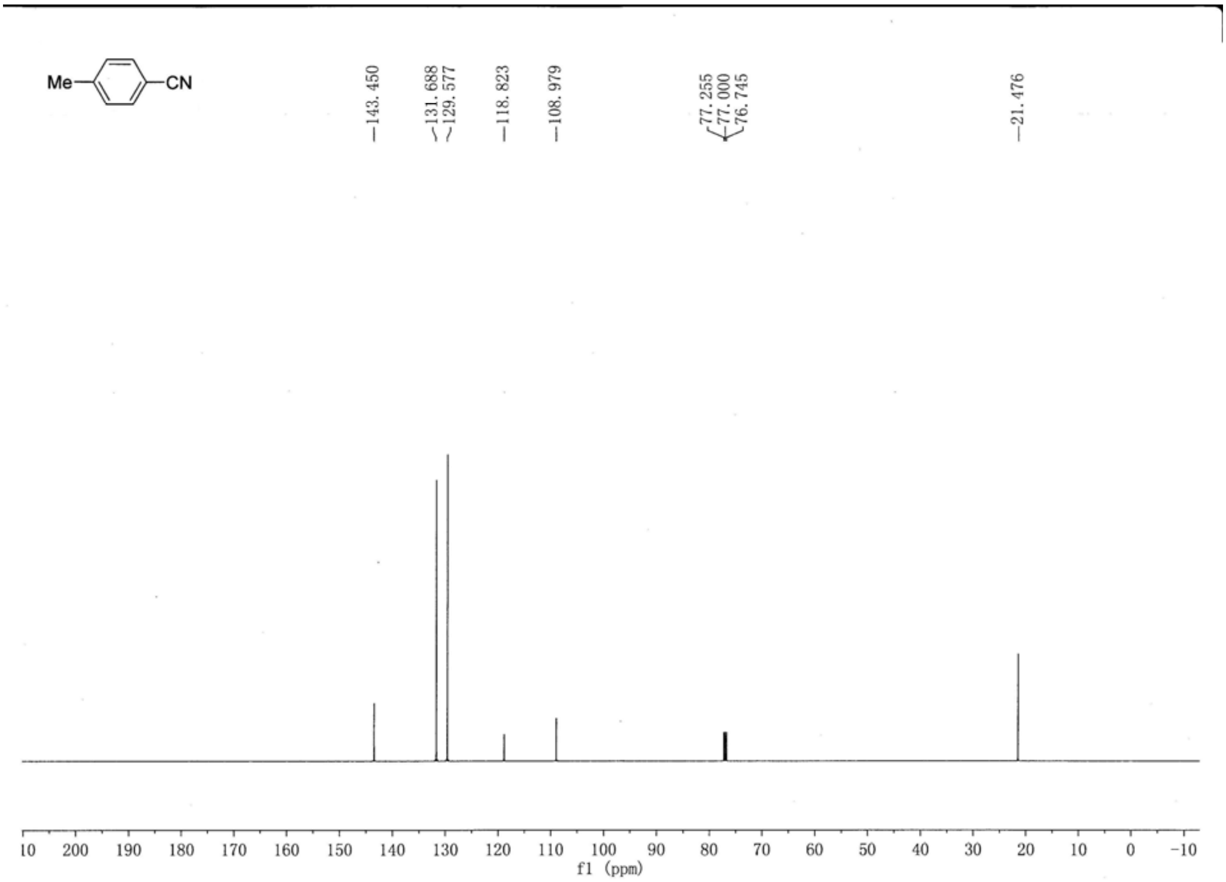
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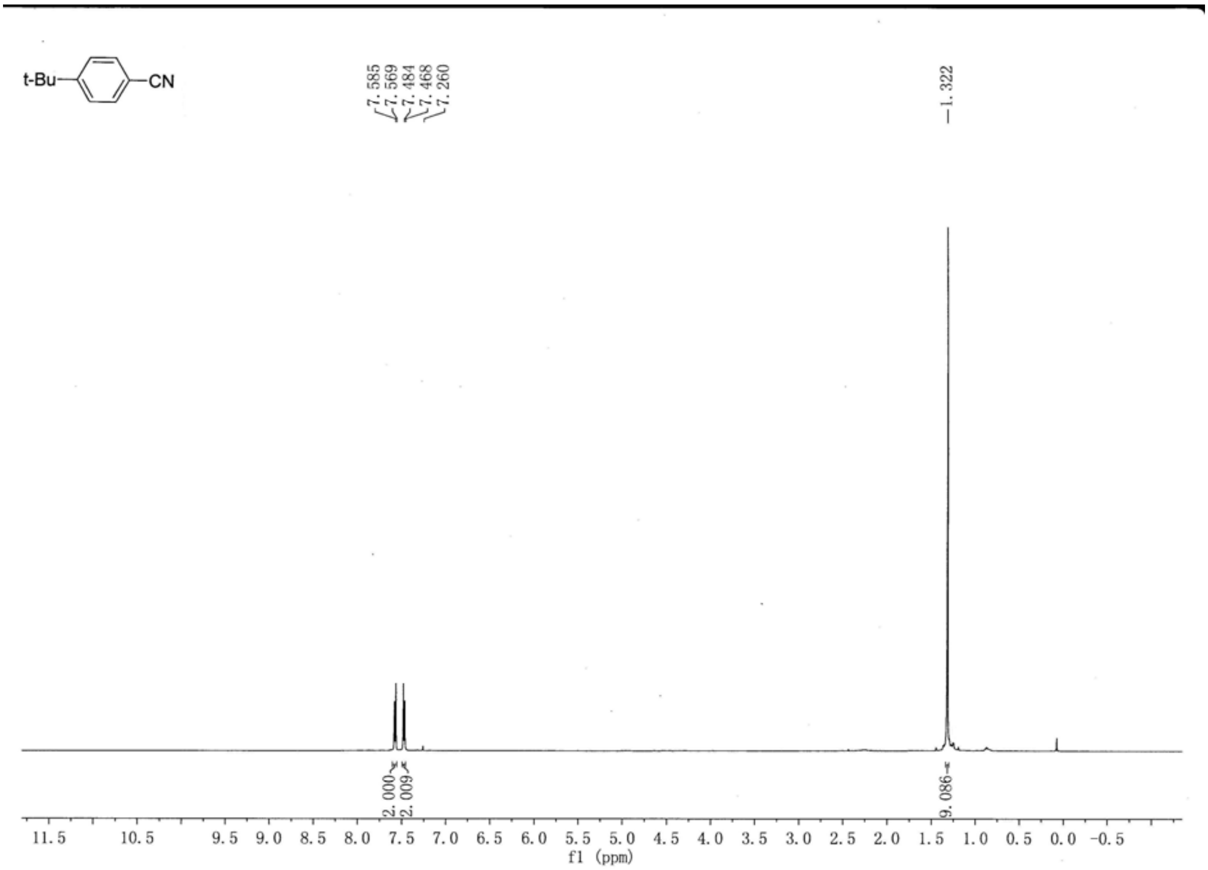
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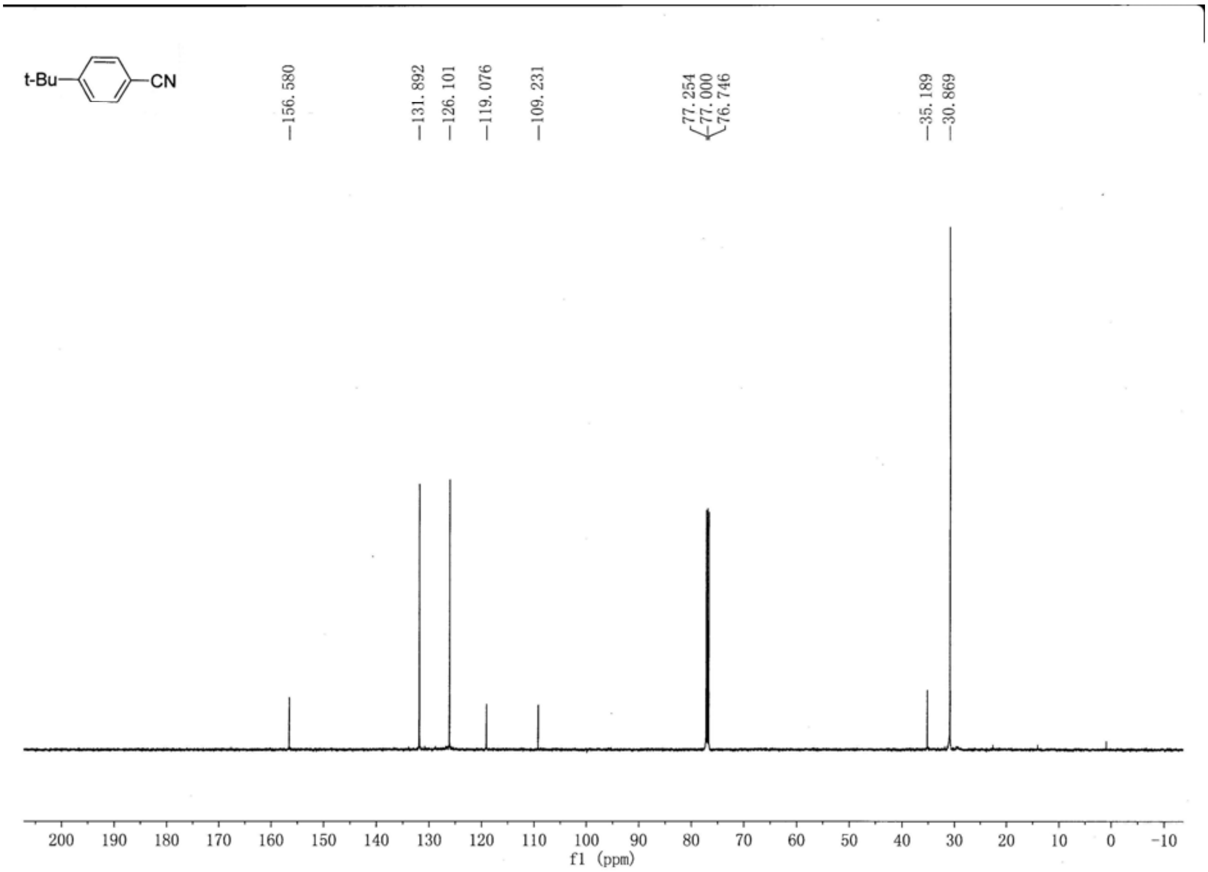
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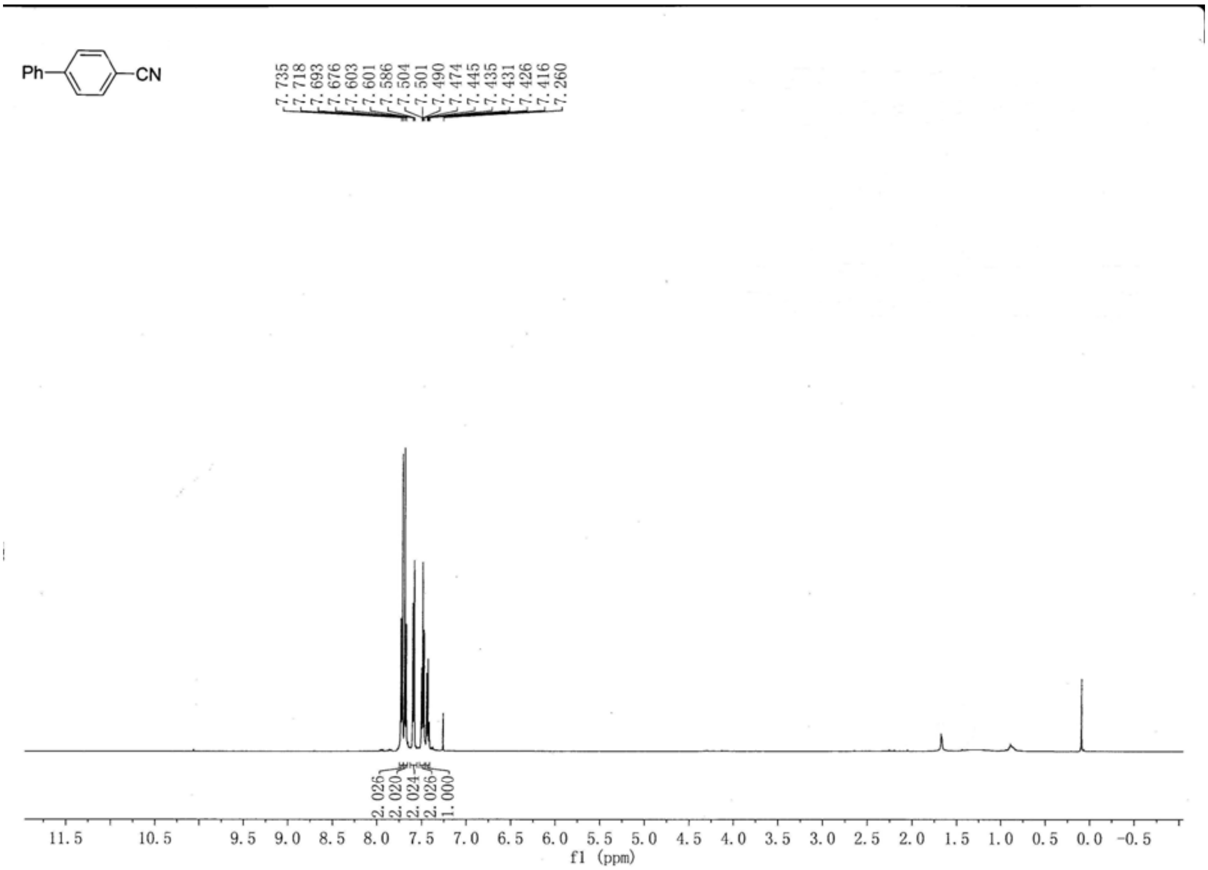
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2.024
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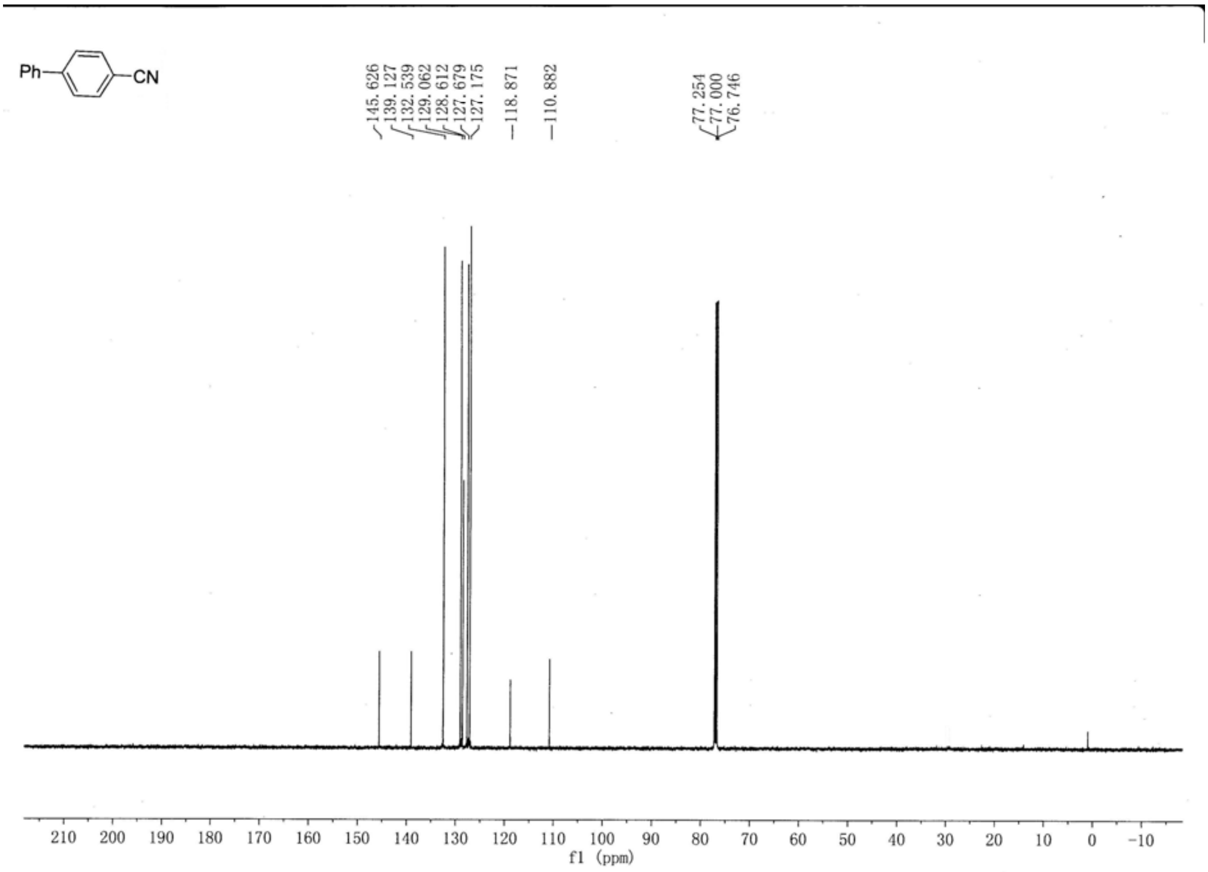
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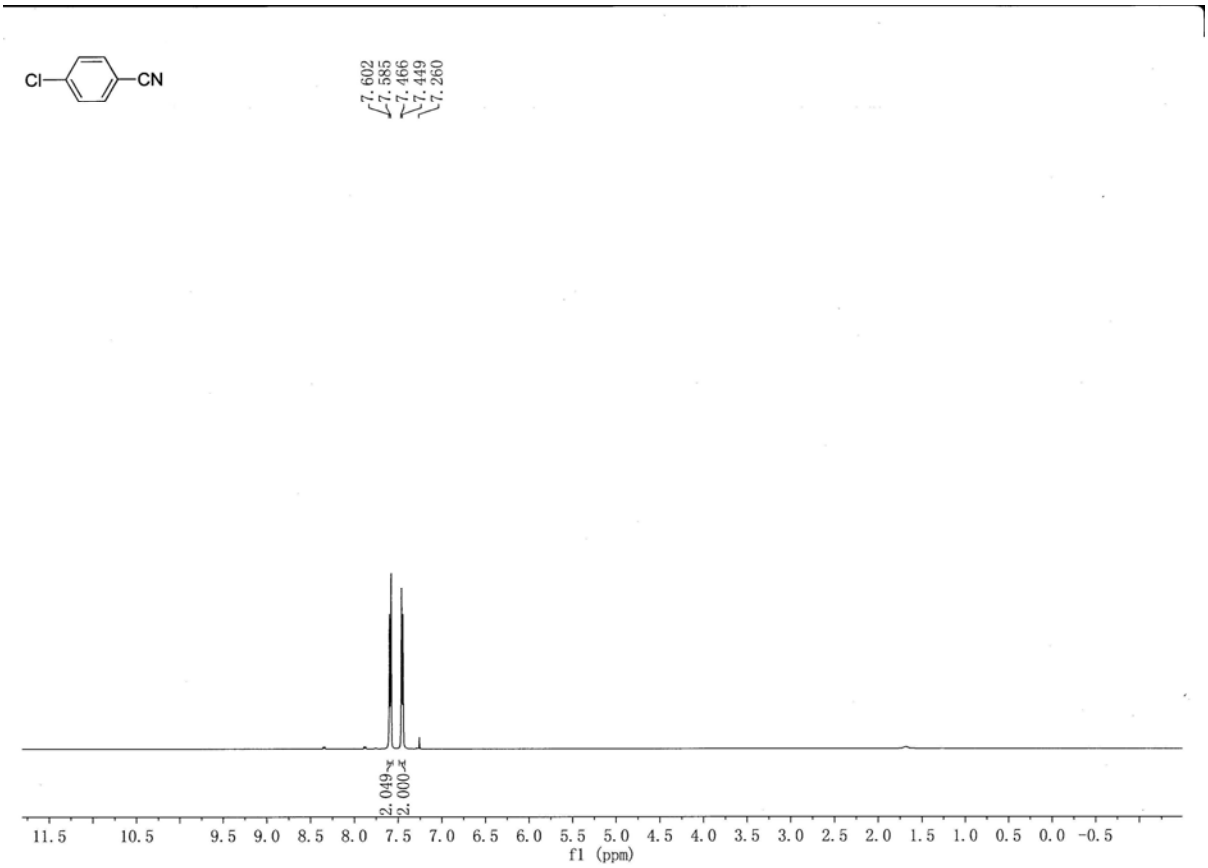
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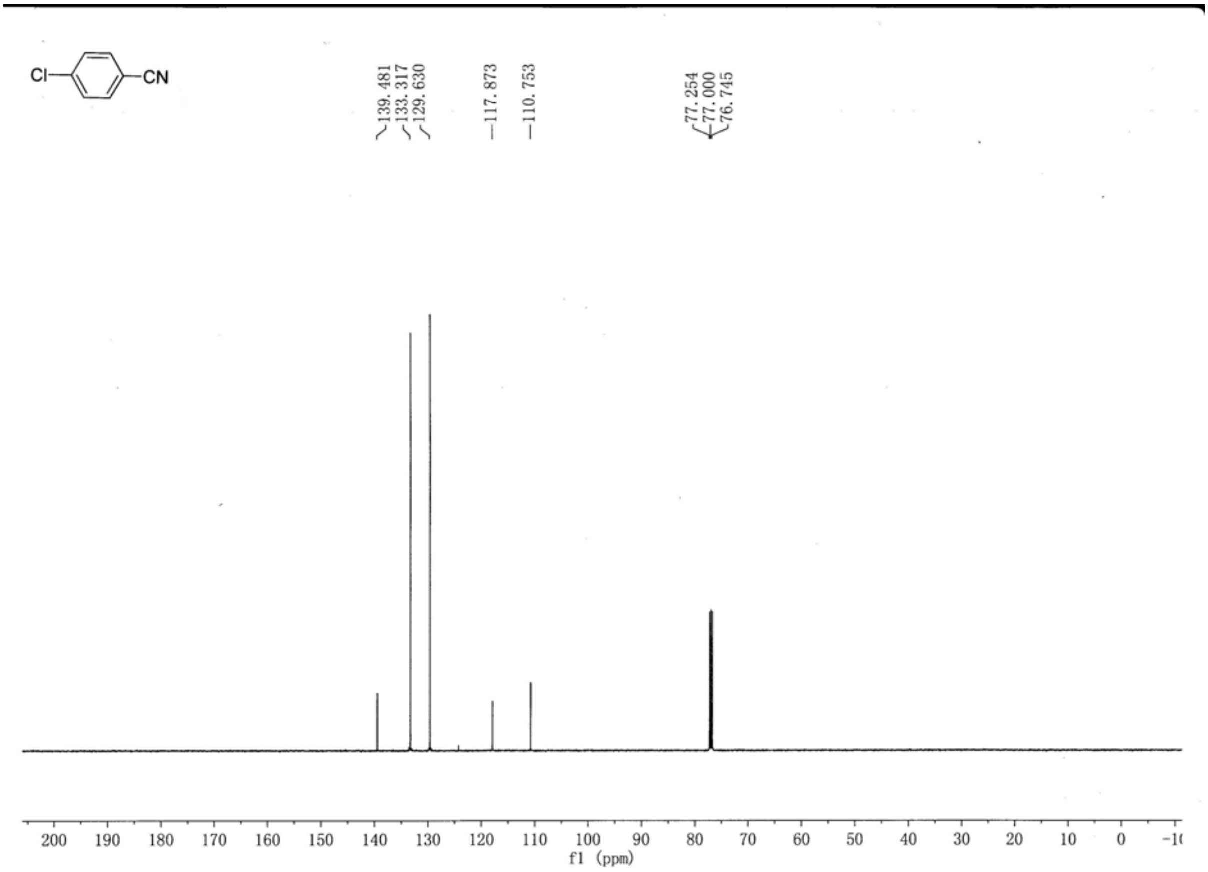
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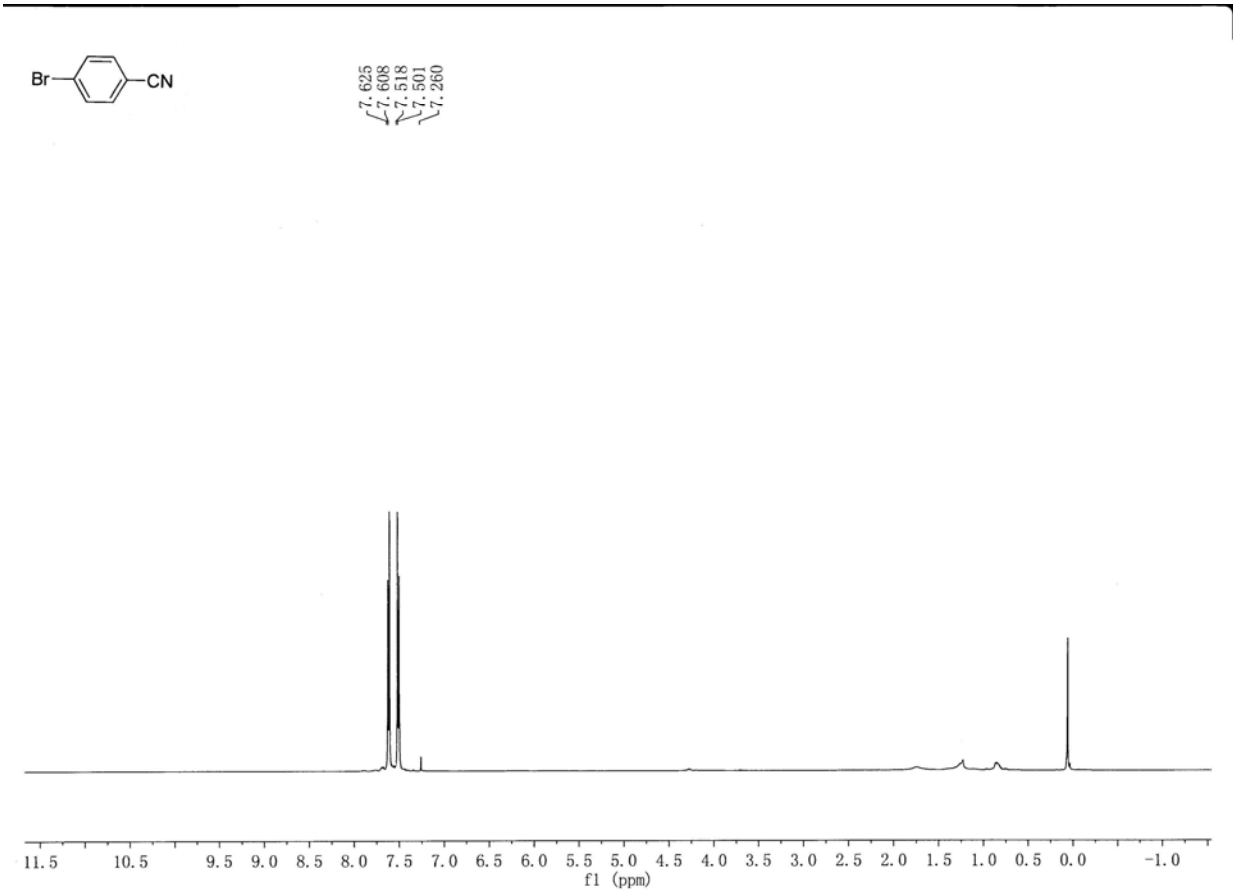
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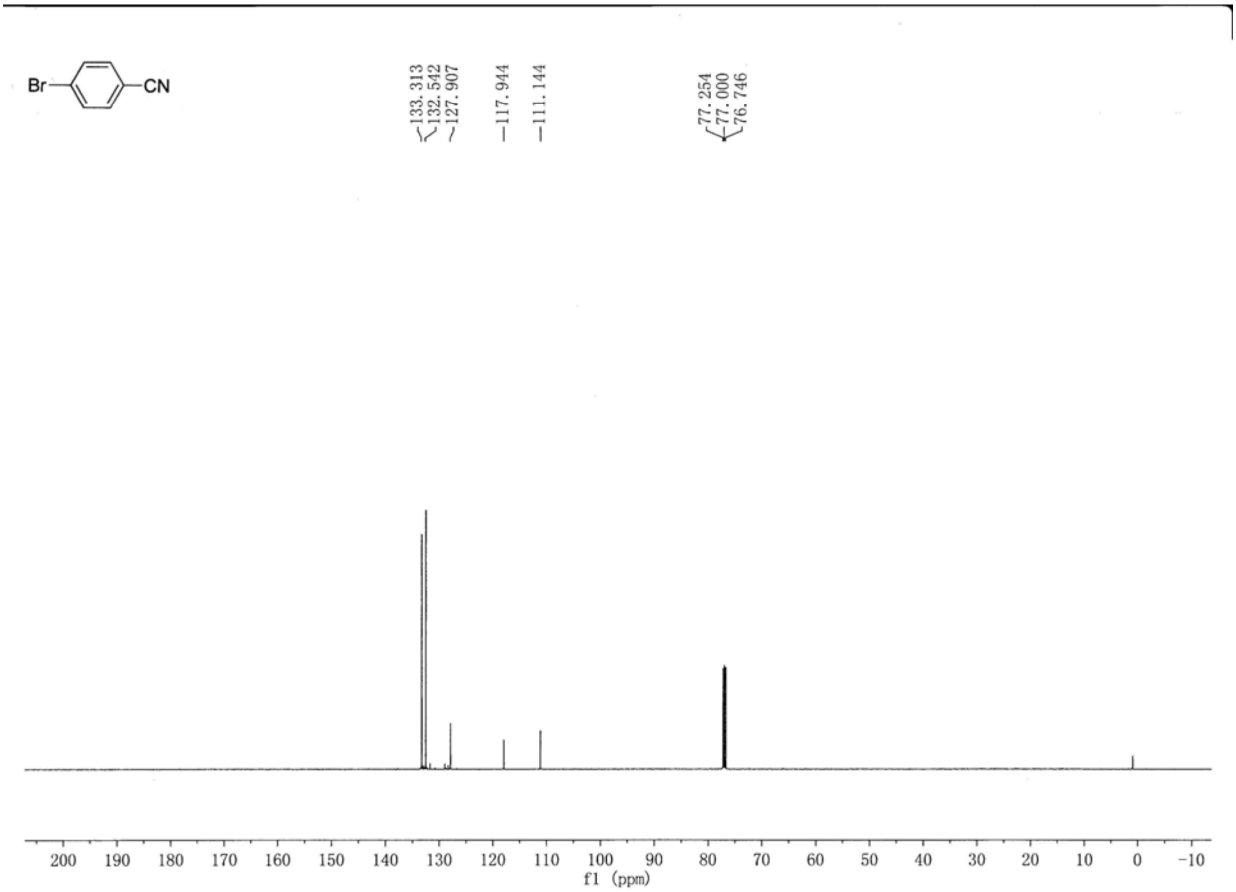
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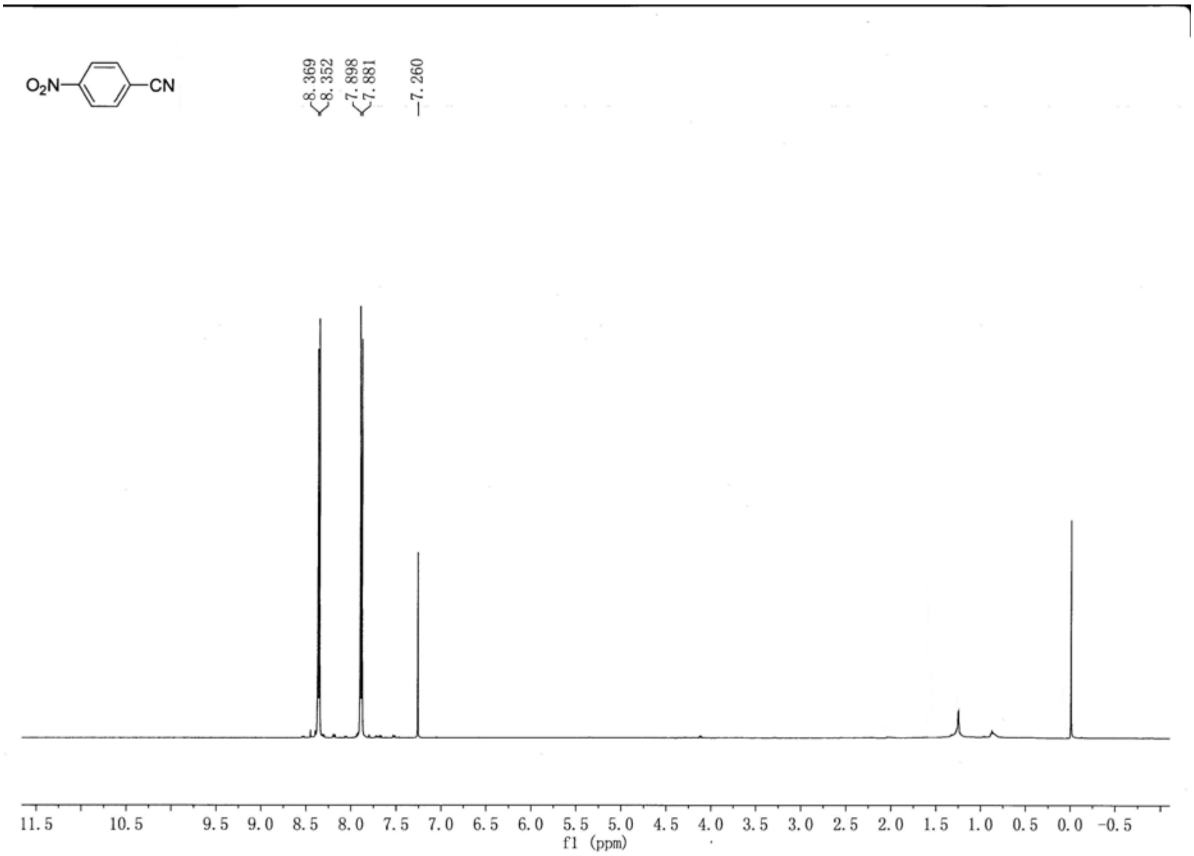
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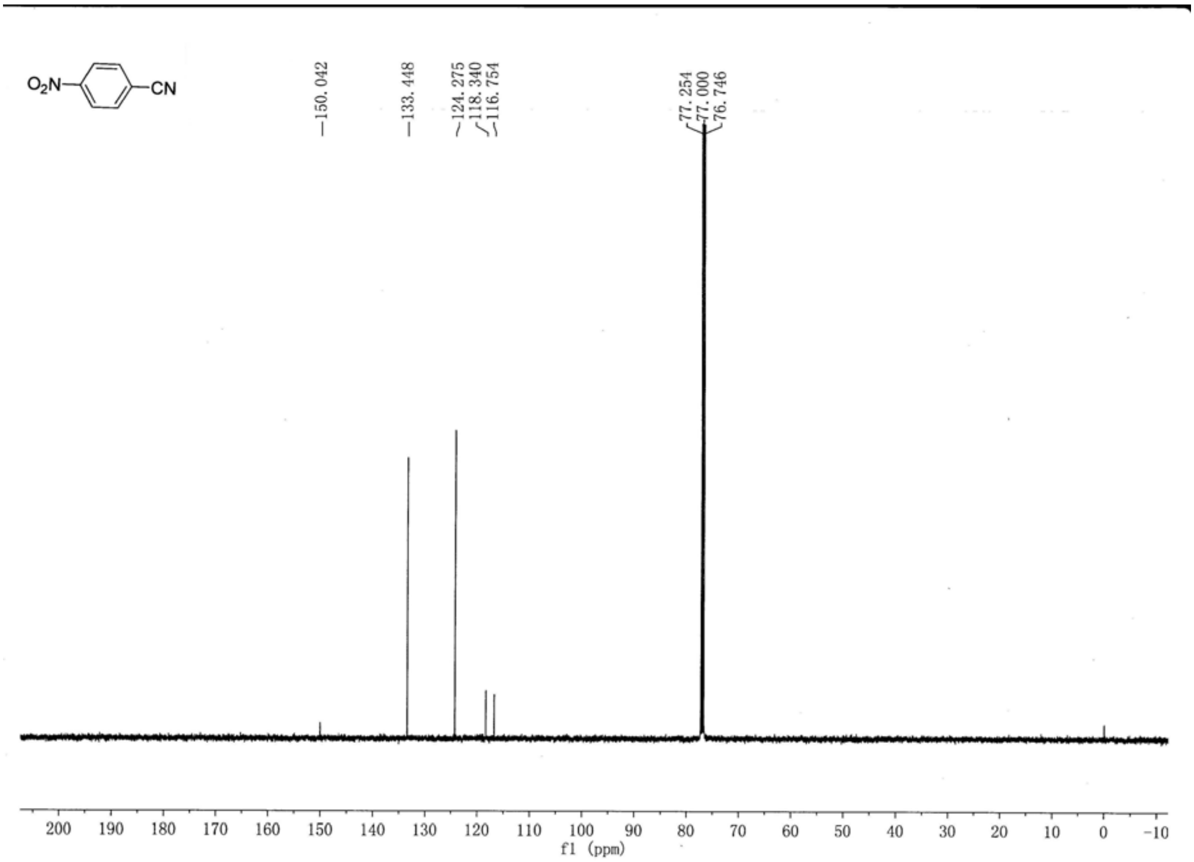
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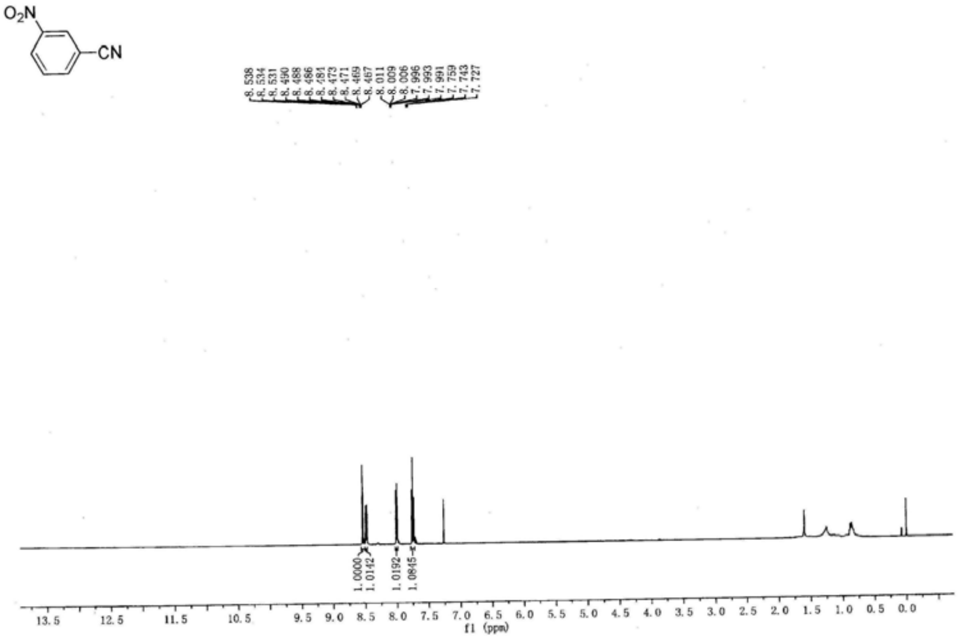
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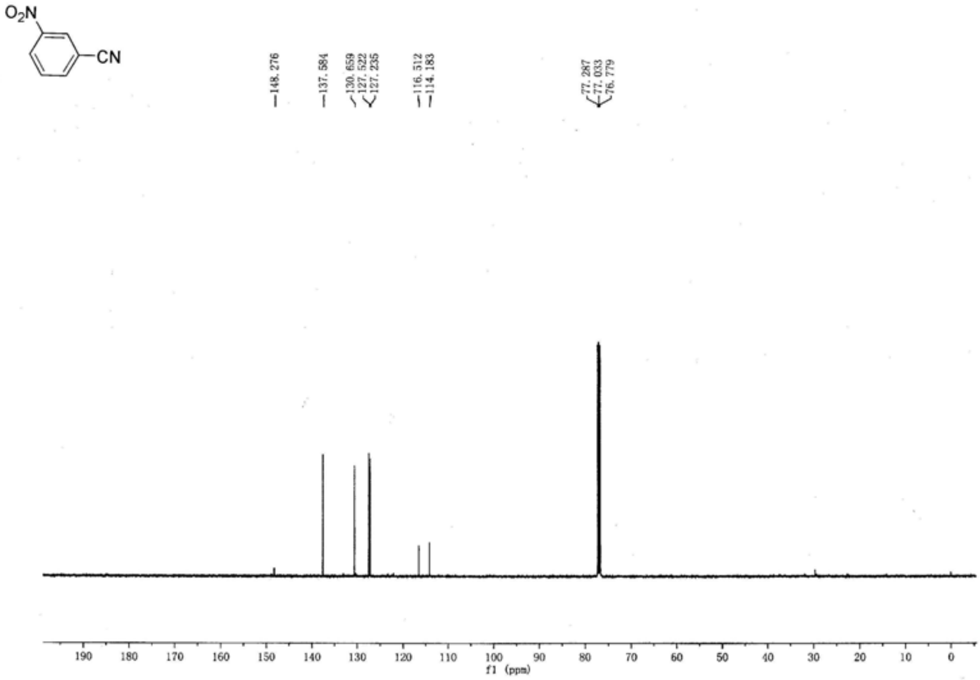
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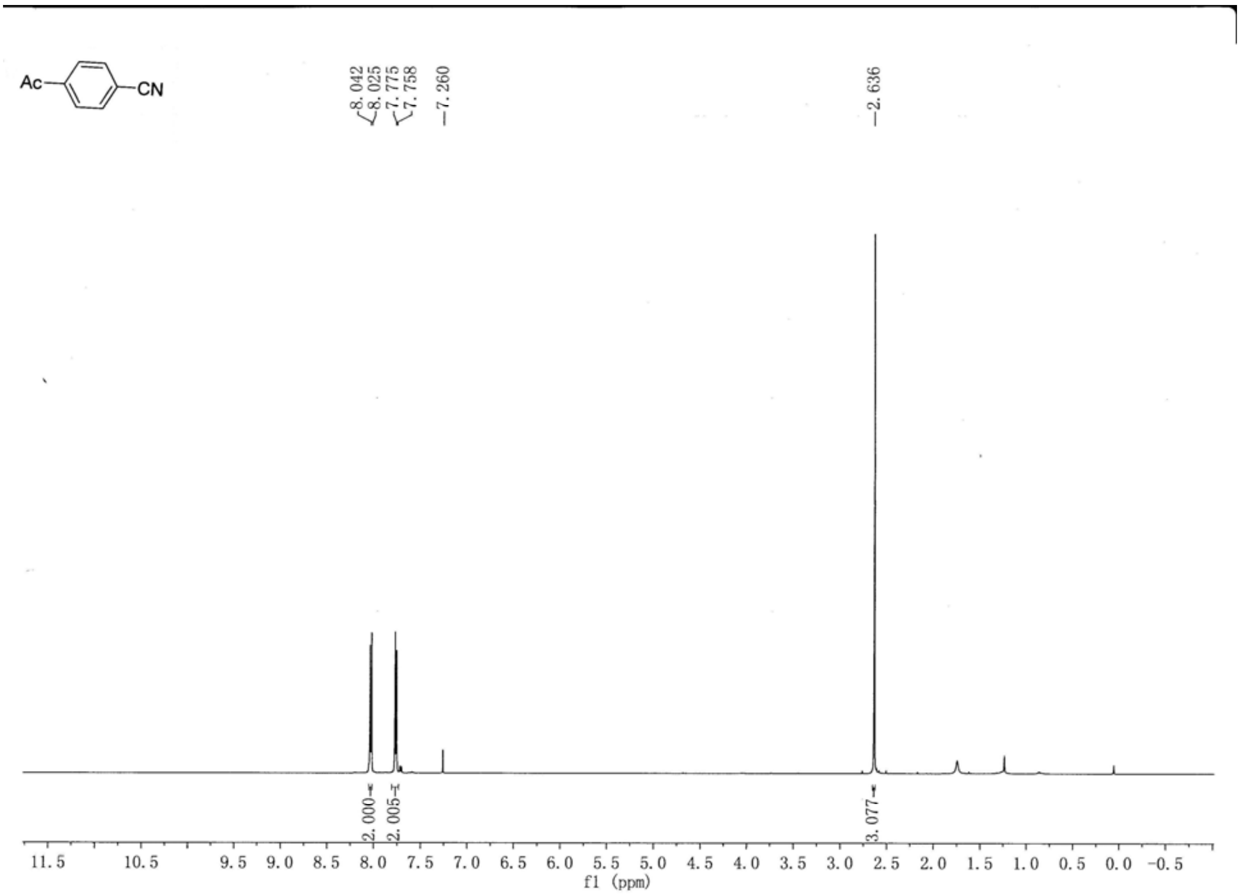
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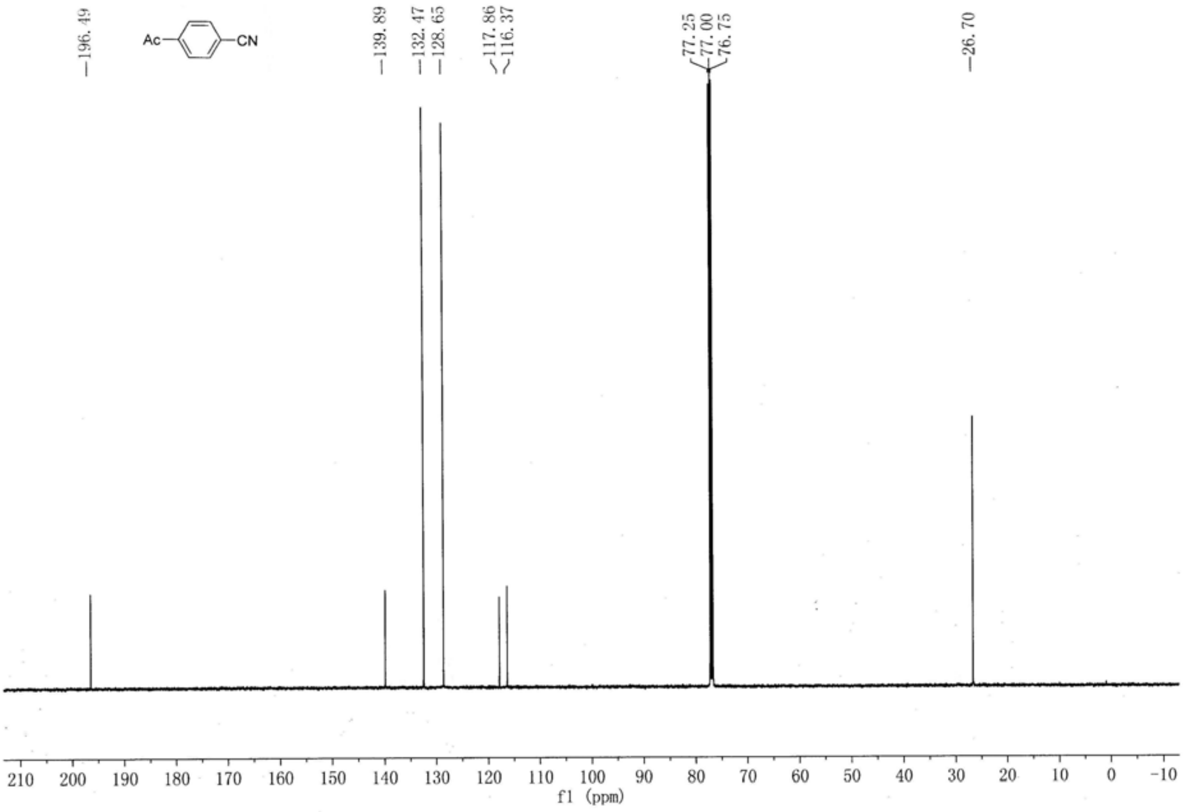
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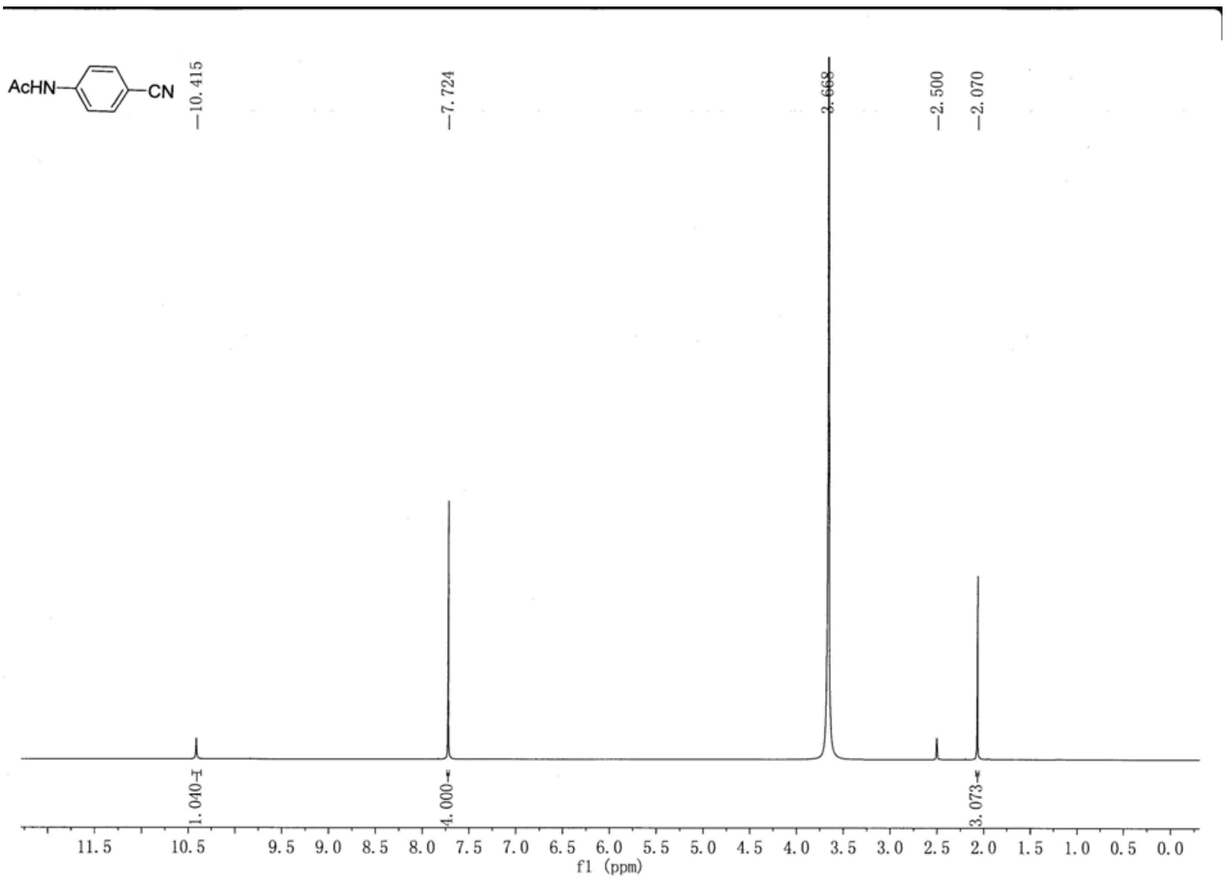
f1 (ppm)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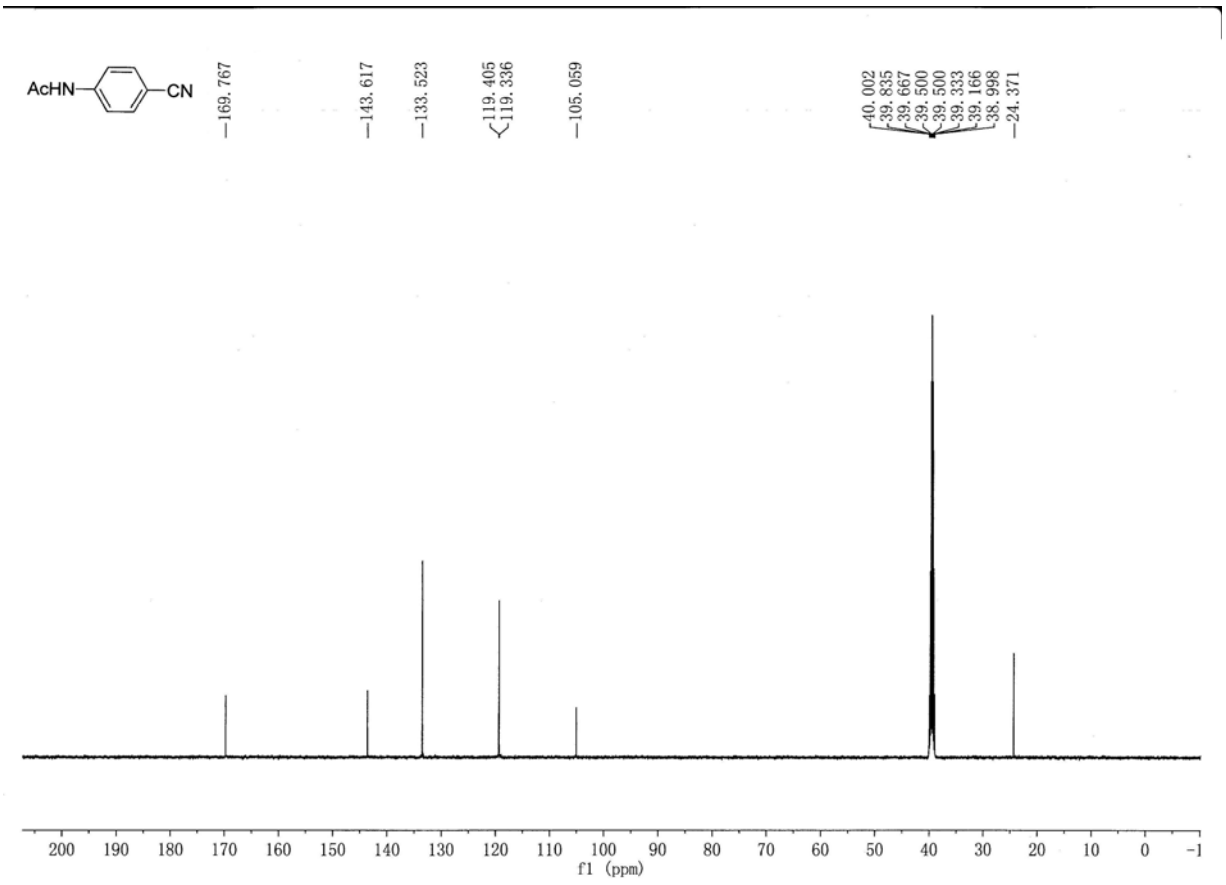
f1 (ppm)


AcHN–C6H4–CN
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100
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60
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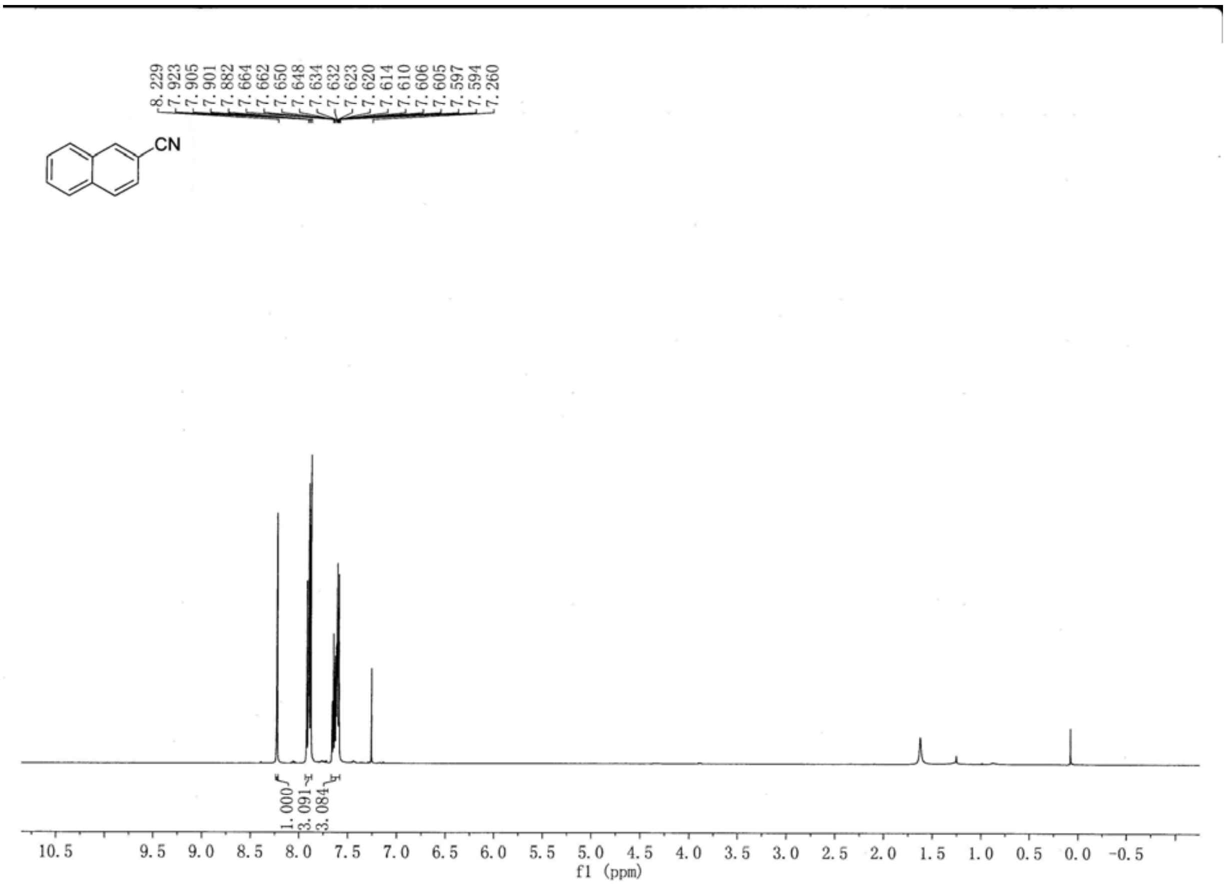
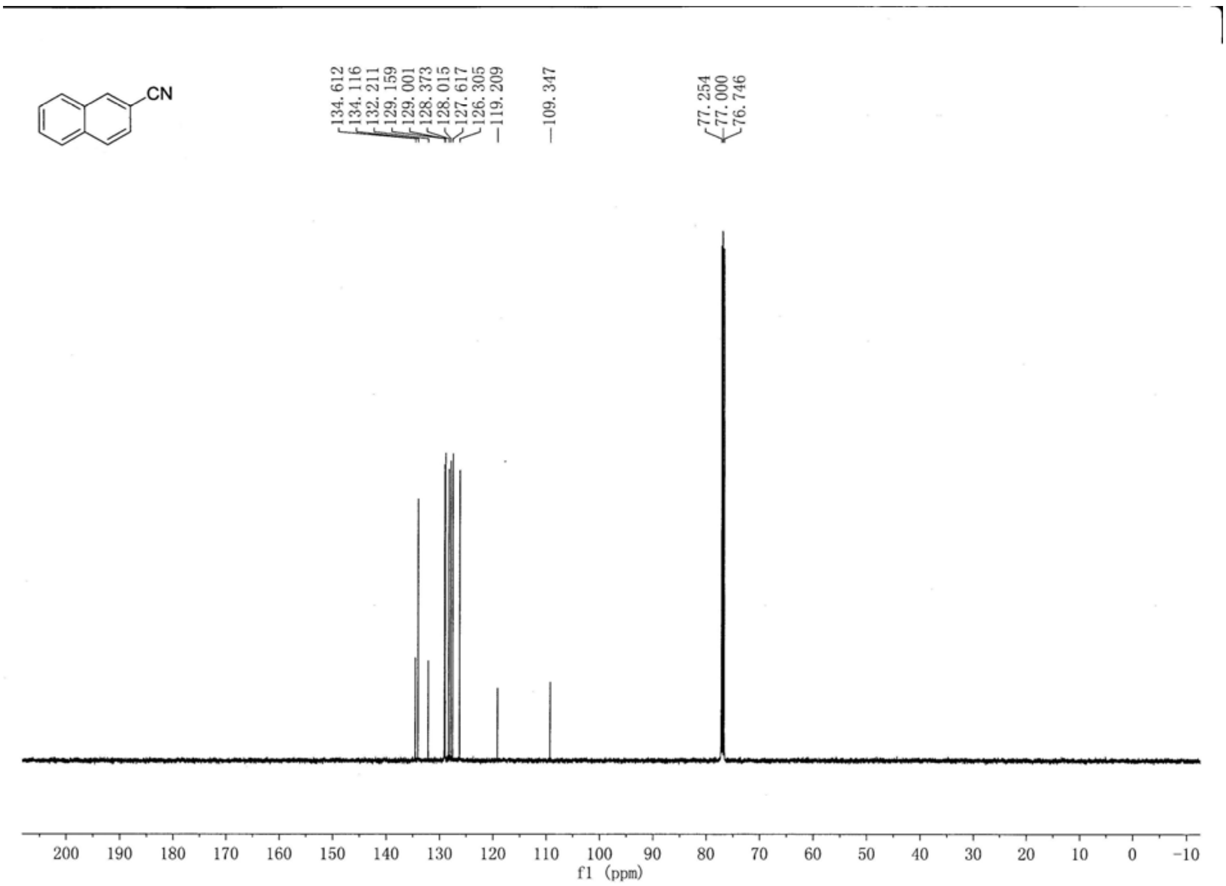
40
30
20
10
0
-1
f1 (ppm)


8.229
7.923
7.905
7.901
7.882
7.664
7.662
7.650
7.648
7.634
7.632
7.623
7.620
7.614
7.610
7.606
7.605
7.597
7.594
7.260
CN
1.000
3.091
3.084
10.5
9.5
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
f1 (ppm)


CN
134.612
134.116
132.211
129.159
129.001
128.373
128.015
127.617
126.305
119.209
109.347
77.254
77.000
76.746
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)