Common Metal of Copper (0) as An Efficient Catalyst for Preparation of Nitriles and Imines by Controlling Additives

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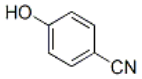
Experimental Section

1. General. The benzylamine and its derivatives were purchased from Sinopharm Chemical Reagent Co. Ltd. All materials were used without further purification. Scanning electron microscopy (SEM) measurements were performed on a Hitachi S-4700 cold field emission scanning electron microscope operated at 30 KV. The product mixtures were analyzed by GC (VARIAN CP-3800 GC, HP-5 capillary column, FID detector) and GC-MS (VARIAN 450-GC & VARIAN 240-GC) equipped with a CP8944 capillary column (30 m × 0.25 mm) and an FID detector. The NMR spectra were measured on a spectrometer at 400 MHz for ^{1}H and 100 MHz for ^{13}C in $CDCl_3$ solution.

2. Typical catalytic oxidation procedure. To a reaction tube equipped with a magnetic stirrer an appropriate amount of red copper (10 mg), NH_4Br (98 mg, 1 mmol), benzylamine (109 μL, 1 mmol), and toluene (2 mL) were added. The air in the tube was then exchanged 3 times with 1 atm of O_2. Finally, the tube was immersed in an oil bath at 100 °C in a sealed O_2 system. After stirring for 24 h at 100 °C, the mixture was cooled to room temperature. A sample of the mixture was immediately analyzed by GC and GC-MS. All the reactions were performed for at least 5 times till their differences were within an acceptable error range.

NMR data of the partial products:

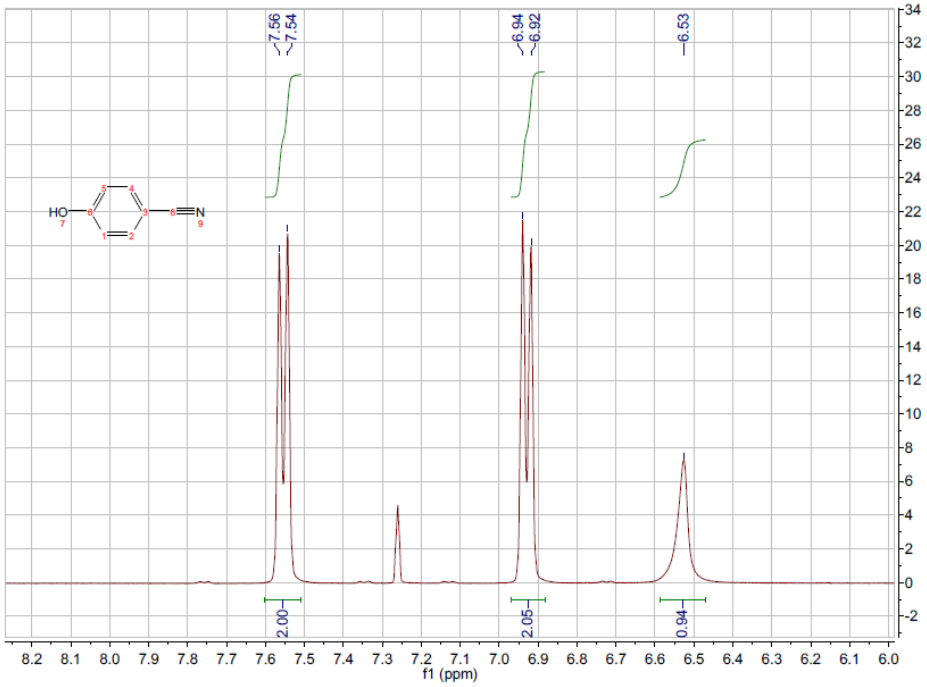
1. 4-cyanophenol



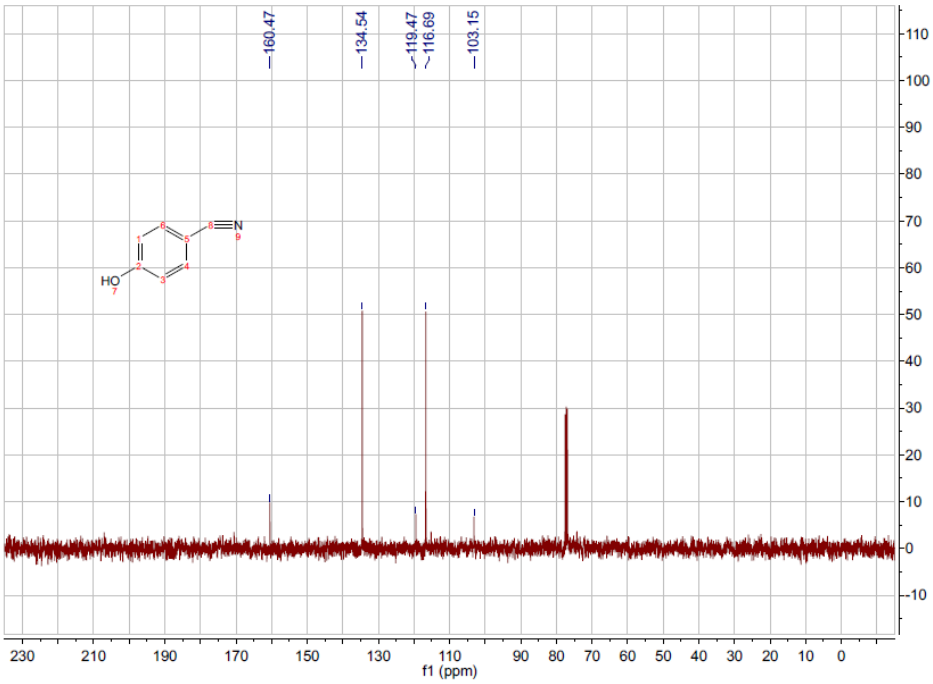
^{1}H NMR(400 MHz, $CDCl_3$):δ=7.56-7.54 (d, 2H), 6.94-6.92 (d, 2H), 6.54 (s, 1H).

^{13}C NMR(100 MHz, $CDCl_3$): δ=103.15, 116.69, 119.47, 134.54, 160.47.

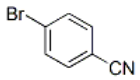
^{1}H NMR:



^{13}C NMR:



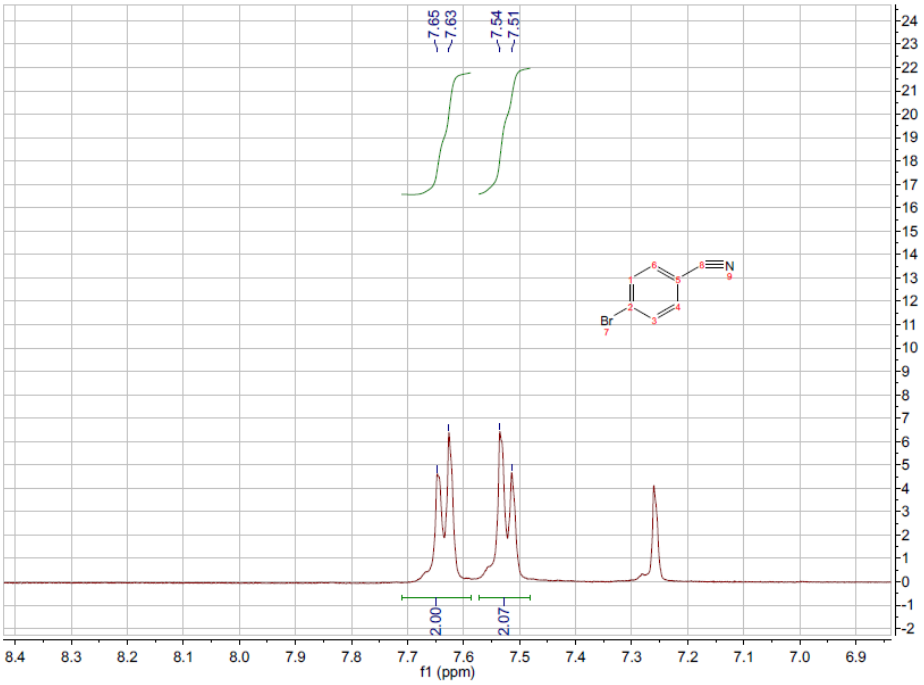
2. 4-bromobenzonitrile



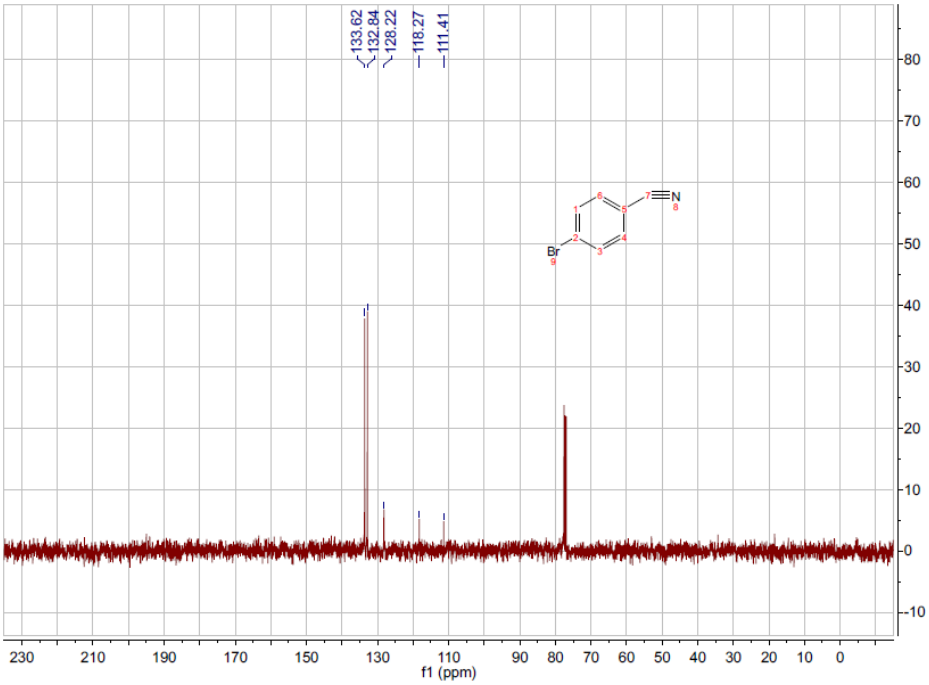
^{1}H NMR(400 MHz, $CDCl_3$):δ=7.65-7.63 (d, 2H), 7.54-7.51 (d, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 111.41, 118.27, 128.22, 132.84, 133.62.

^{1}H NMR:



^{13}C NMR:

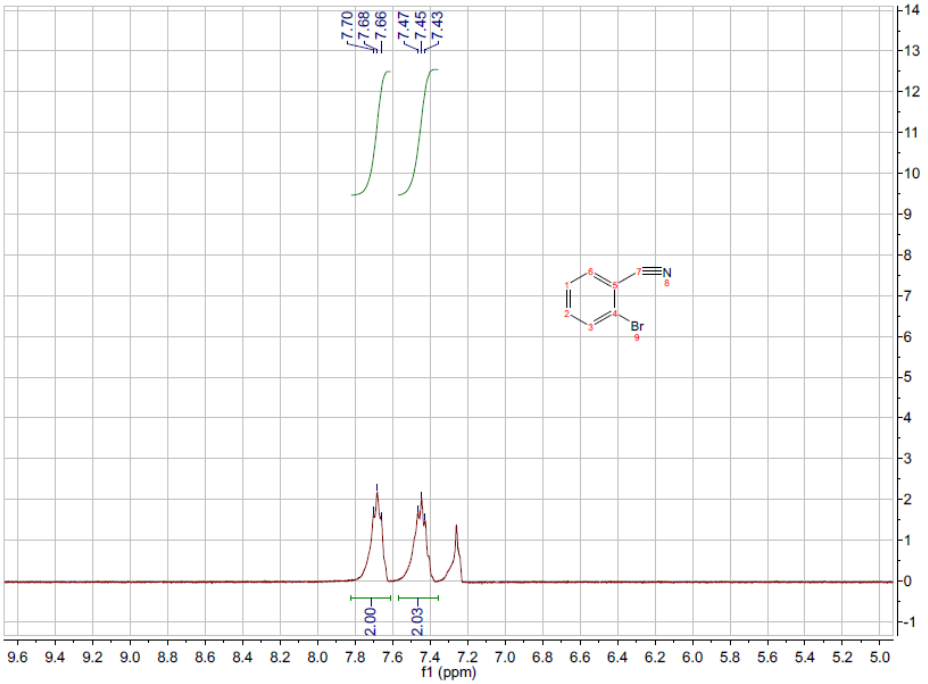


3. 2-bromobenzonitrile

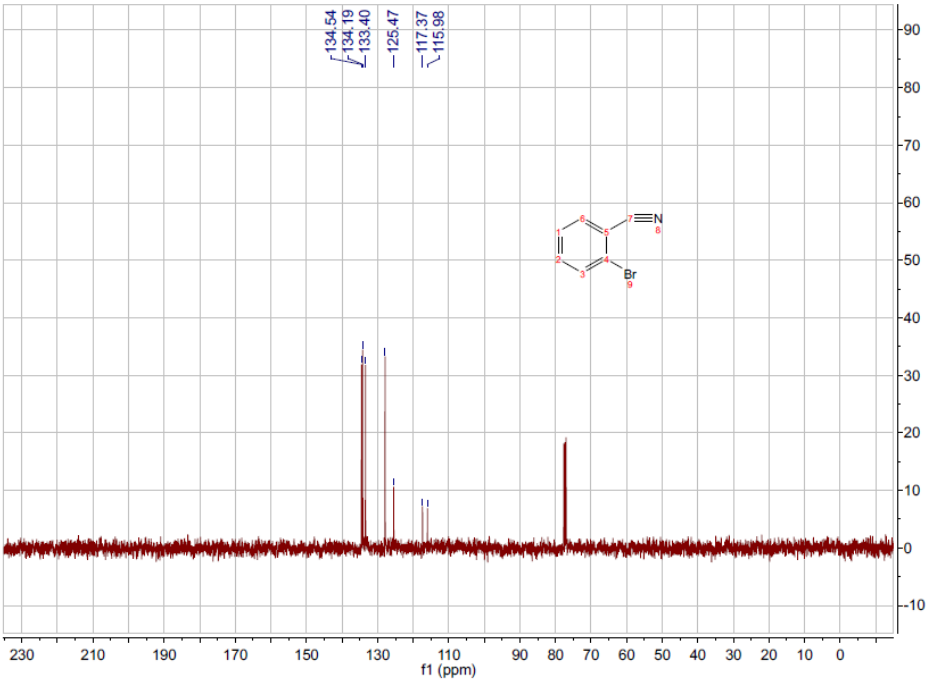
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70-7.66 (m, 2H), 7.47-7.43 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 115.98, 117.37, 125.47, 133.40, 134.19, 134.54.

^{1}H NMR:



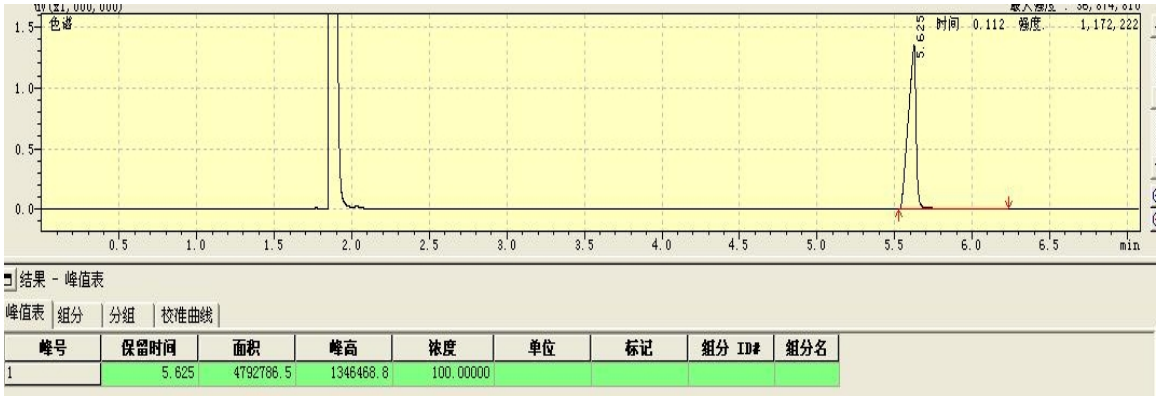
^{13}C NMR:



GC data of the partial products:

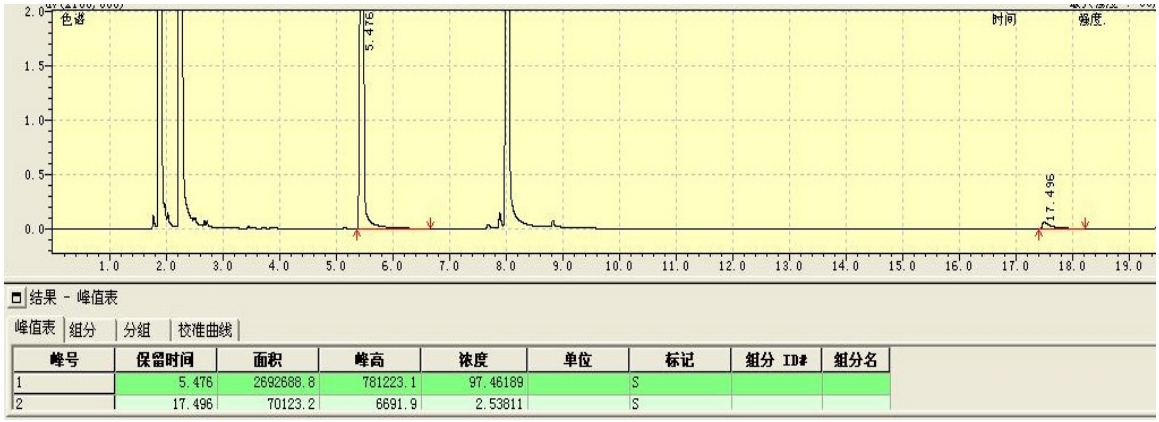
1. 4-methylbenzylamine peak position at 5.625 min
   Isoquinoline peak position at 8.043 min
   p-tolunitrile peak position at 5.476 min

4-methylbenzylamine:



峰号	保留时间	面积	峰高	浓度	单位	标记	组分 ID#	组分名
1	5.625	4792786.5	1346468.8	100.00000				

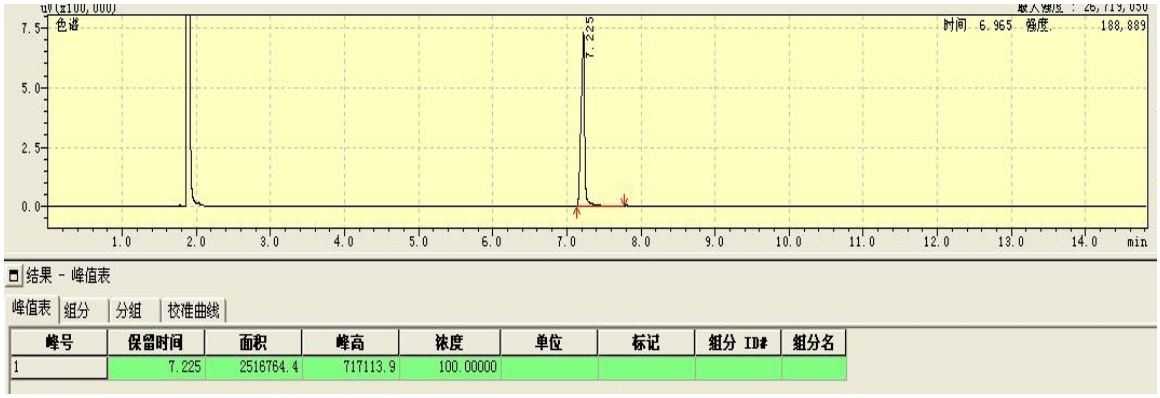
p-tolunitrile:



峰号	保留时间	面积	峰高	浓度	单位	标记	组分 ID#	组分名
1	5.476	2692888.8	781223.1	97.46189		S		
2	17.496	70123.2	6691.9	2.53811		S		

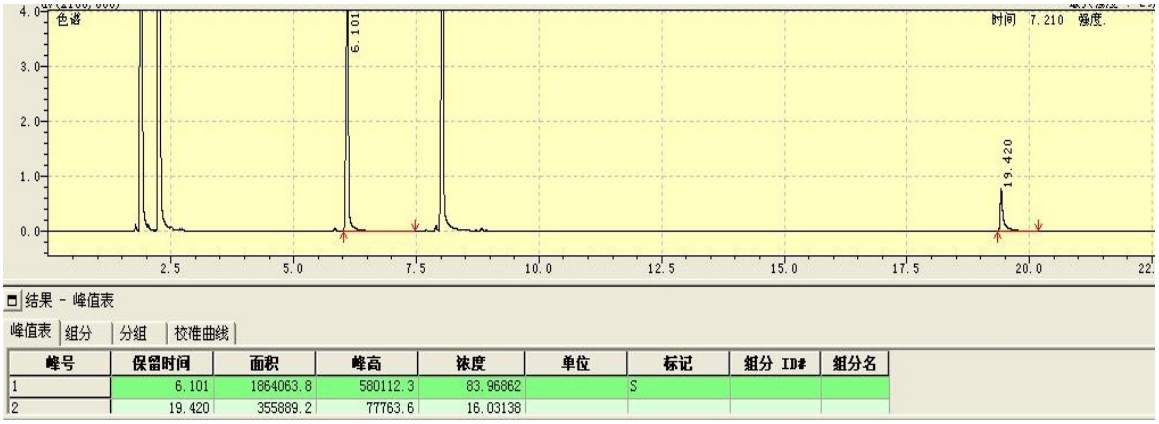
2. 4-chlorobenzylamine peak position at 7.225 min
   4-chlorobenzonitrile peak position at 6.101 min

4-chlorobenzylamine:



峰号	保留时间	面积	峰高	浓度	单位	标记	组分 ID#	组分名
1	7.225	2516764.4	717113.9	100.00000				

4-chlorobenzonitrile:

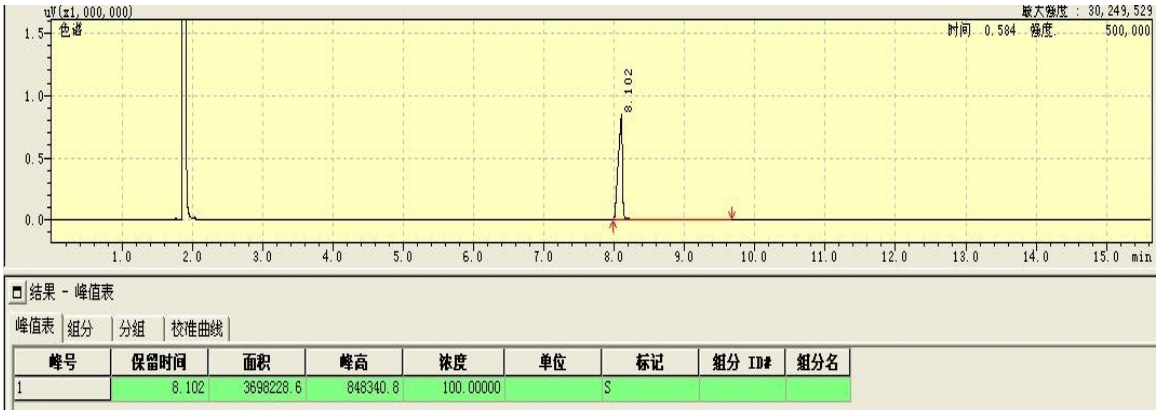


峰号	保留时间	面积	峰高	浓度	单位	标记	组分 ID#	组分名
1	6.101	1864063.8	580112.3	83.96862		S		
2	19.420	355889.2	77763.6	16.03138				

3. 4-methoxy benzylamine peak position at 8.102 min

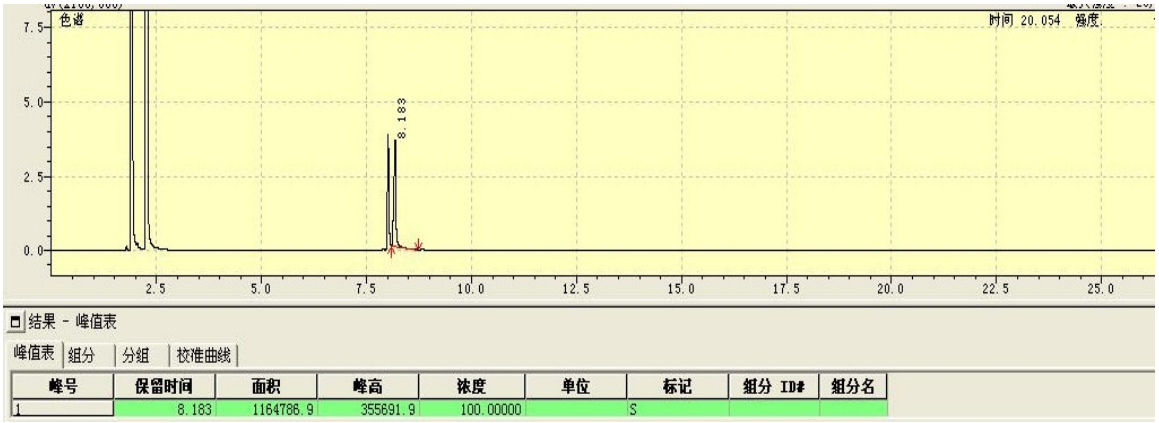
Anisonitrile peak position at 8.183 min

4-methoxy benzylamine:

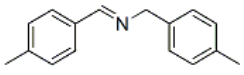


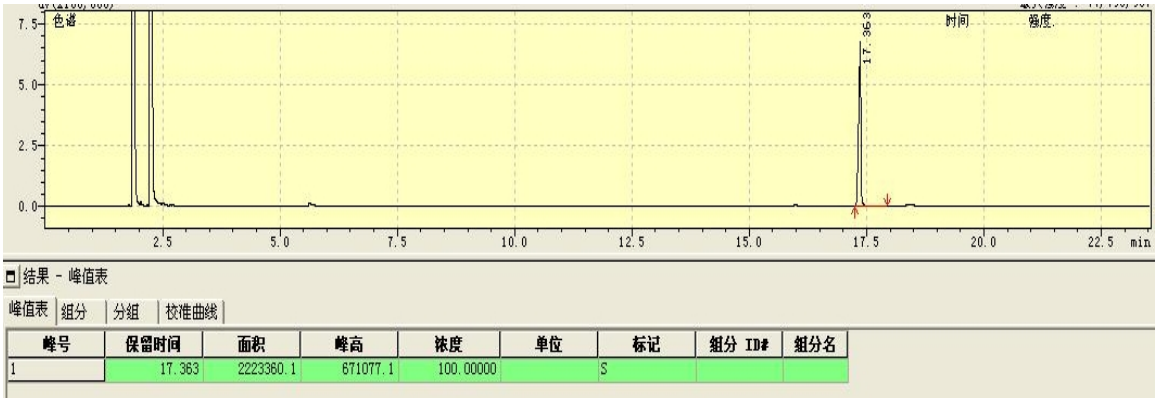
峰号	保留时间	面积	峰高	浓度	单位	标记	组分 ID#	组分名
1	8.102	3698228.6	848340.8	100.00000		S		

Anisonitrile:

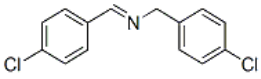


峰号	保留时间	面积	峰高	浓度	单位	标记	组分 ID#	组分名
1	8.183	1164786.9	355691.9	100.00000		S		

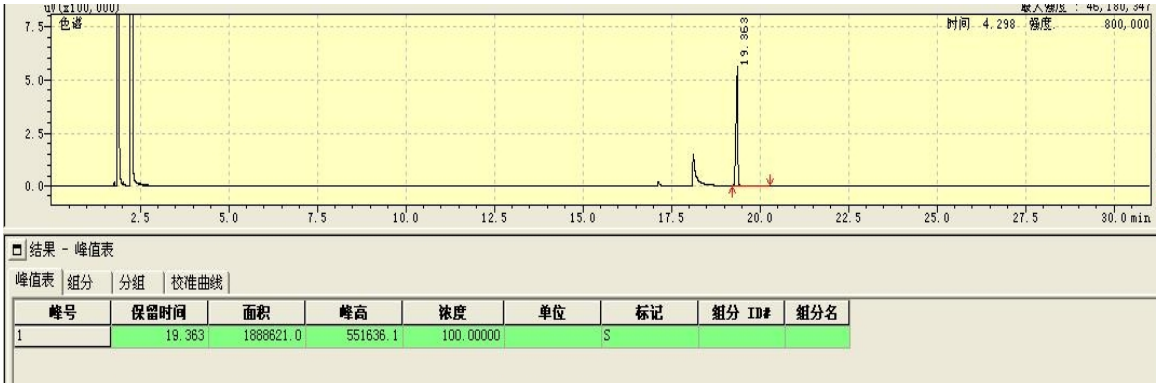
4.  peak position at 17.363 min



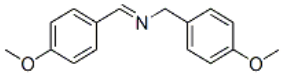
峰号	保留时间	面积	峰高	浓度	单位	标记	组分 ID#	组分名
1	17.363	2223360.1	671077.1	100.00000		S		

5.  peak position at 19.363 min

1, 10-phenanthroline peak position at 18.121 min



峰号	保留时间	面积	峰高	浓度	单位	标记	组分 ID#	组分名
1	19.363	1888621.0	551636.1	100.00000		S		

6.  peak position at 20.745 min

峰号	保留时间	面积	峰高	浓度	单位	标记	组分 ID#	组分名
1	20.745	73166.0	7738.7	100.00000		S		