Supporting Information

A Highly Efficient, Ligand-Free and Recyclable SBA-15 Supported Cu_2O Catalyzed Cyanation of Aryl Iodides with Potassium Hexacyanoferrate (Ⅱ)

Wenzhu Yin, Rui Liu, Gunagke He, Wangjie Lv Hongjun Zhu*

Department of Applied Chemistry, College of Science, Nanjing Tech University, Jiangsu Key Laboratory of Industrial Water Conservation and Emission Reduction, Nanjing 211816, P. R. China

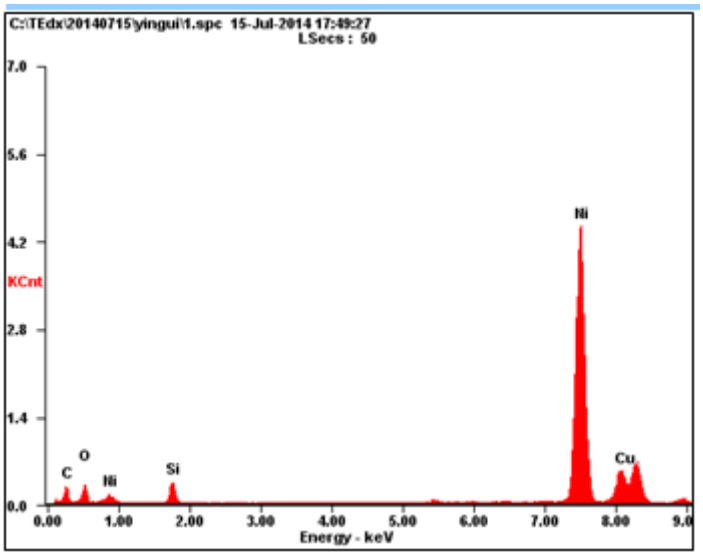


Fig. S1 TEM-EDS pattern of Cu_2O/SBA-15

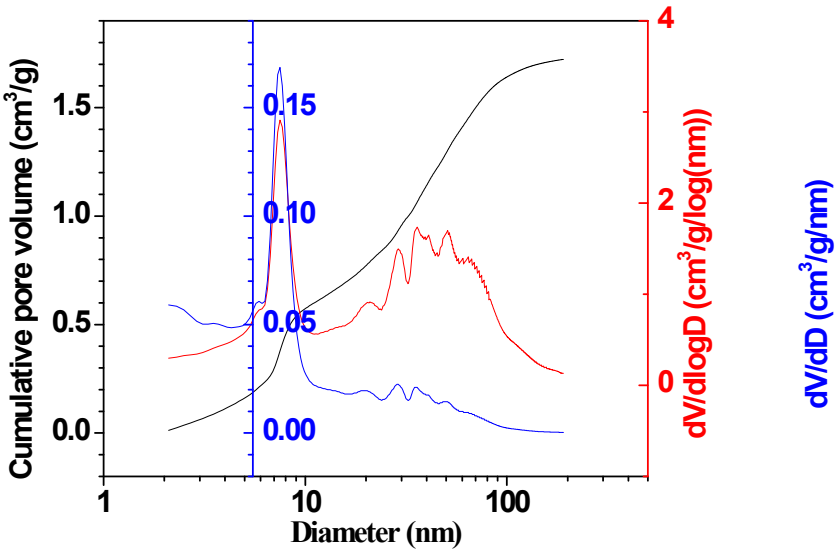


Fig. S2 The pore size distributions.

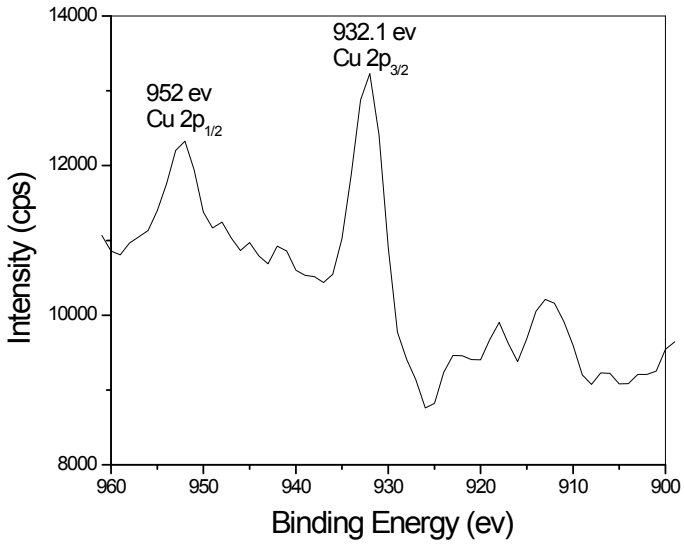


Fig. S3 XPS of Cu_2O/SBA-15

^{1}H NMR, ^{13}C NMR and GC-MS data

^{1}H NMR, ^{13}C NMR and GC-MS data

4-Nitrobenzonitrile (1a). pale yellow solid; mp 143-145 ℃;

^{1}H NMR (300 MHz, DMSO-d_6) δ 8.36 (d, *J* = 8.9 Hz, 1H), 8.16 (d, *J* = 8.9 Hz, 1H).
^{13}C NMR (75 MHz, DMSO-d_6) δ 150.39, 134.60, 124.78, 117.76, 117.65
GC-MS (EI): rt=10.450 min, m/z:148

4-Methoxybenzonitrile (**1b**). white solid; mp 57-58 ℃

^{1}H NMR (300 MHz, DMSO-d_6) δ 7.75 (d, 9.0 Hz, 2H), 7.09 (d, 9.0Hz, 2H), 3.82 (s, 3H).
^{13}C NMR (75 MHz, DMSO-d_6) δ 163.15, 134.63, 119.62, 115.56, 103.26, 56.12.
GC-MS (EI): rt=8.475 min, m/z:133

Terephthalonitrile (1c). white solid; m.p.111-114℃

^{1}H NMR (300 MHz, DMSO-d_6) δ 8.06 (s, 1H).
^{13}C NMR (75 MHz, DMSO-d_6) δ 133.67, 117.99, 116.17.
GC-MS (EI): rt=8.685 min, m/z:128

4-Fluorobenzonitrile (1d). white solid; mp 33-36 ℃

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 8.5, 5.2 Hz, 1H), 7.28 – 6.92 (m, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 166.64 (4-Ar-C, *J* =254.25 Hz), 163.25 (4-Ar-C, *J* =254.25 Hz), 134.74 (*3*-Ar-C, *J* =9.0 Hz), 134.62 (*3*-Ar-C, *J* =9.0 Hz), 117.99 (1-Ar-C), 116.94 (*2*-Ar-C, *J* =23.25 Hz), 116.63 (2-Ar-C, *J* =23.25 Hz), 108.50 (CN).
GC-MS (EI): rt=4.535 min, m/z:121

4-Bromobenzonitrile (1e). white solid; m.p.110-113 ℃

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 133.43, 132.65, 128.03, 118.07, 111.25.
GC-MS (EI): rt=8.300 min, m/z: 181, 183.

4-Phenylbenzonitrile (**1f**). white solid; mp 83-84 ℃

^{1}H NMR (300 MHz, DMSO-d_6) δ 7.90 (m, 4H), 7.73 (d, *J* = 7.2 Hz, 2H), 7.60 – 7.30 (m, 3H).
^{13}C NMR (75 MHz, DMSO-d_6) δ 145.10, 138.72, 133.32, 129.64, 129.23, 128.04, 127.55, 119.34, 110.
GC-MS (EI): rt=14.970 min, m/z:179

4,4'-Biphenyldicarbonitrile (1g). white solid; m.p.239-241℃

^{1}H NMR (300 MHz, DMSO-d_6) δ 7.97 (d, *J* = 0.6 Hz, 1H).
^{13}C NMR (75 MHz, DMSO-d_6) δ 143.14, 133.49, 128.55, 119.09, 111.76
GC-MS (EI): rt=19.230 min, EI-MS: m/z:204

4-(4-Bromophenyl)benzonitrile (1h). white solid; mp. 152-155 ℃

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.5 Hz, 2H), 7.62 (dd, *J* = 11.8, 8.5 Hz, 4H), 7.47 (d, *J*=8.5 Hz, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 144.40, 138.05, 132.74, 132.30, 128.80, 127.55, 123.19, 118.78, 111.34.
GC-MS (EI): rt=18.630 min, m/z:257, 259.

Methyl 4-cyanobenzoate (**1i**). white solid; mp 65-67 ℃

^{1}H NMR (300 MHz, DMSO-d_6) δ 8.06 (d, *J* = 8.6 Hz, 1H), 7.98 (d, *J* = 8.6 Hz, 1H), 3.88 (s, 1H).
^{13}C NMR (75 MHz, DMSO-d_6) δ 165.46, 133.94, 133.26, 130.24, 118.48, 115.93, 53.18
GC-MS (EI): rt=10.075 min, m/z:161

4-Methylbenzonitrile (1j). white solid; mp 28-30 ℃

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.9 Hz, 2H), 7.27 (d, *J* = 7.6 Hz, 2H), 2.42 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 143.74, 131.99, 129.86, 119.15, 109.24, 21.81.
GC-MS (EI): rt=6.350 min, m/z:117

3-Nitrobenzonitrile (1k). pale yellow solid; mp 114-115 ℃

^{1}H NMR (300 MHz, DMSO-d_6) δ 8.77 – 8.71 (m, 1H), 8.51 (ddd, *J* = 8.4, 2.3, 1.0 Hz, 1H), 8.38 – 8.23 (m, 1H), 7.86 (t, *J* = 8.1 Hz, 1H).
^{13}C NMR (75 MHz, DMSO-d_6) δ 148.35, 138.99, 131.67, 128.47, 127.90, 117.49, 113.30.
GC-MS (EI): rt=10.595 min, m/z:148

3-Fluorobenzonitrile (1l). white solid; mp 14-16 ℃

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50-7.47 (m, 2H), 7.39-7.32 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 163.85(*3*-Ar-C, *J*=248.25 Hz), 160.54(*3*-Ar-C, *J* =248.25 Hz), 131.25(5-Ar-C, *J*=8.25 Hz), 131.14(5-Ar-C, *J*=8.25 Hz), 128.24(6-Ar-C, *J*=3.75 Hz), 128.19 (6-Ar-C, *J*=3.75 Hz), 120.68 (4-Ar-C, *J*=21 Hz), 120.40 (4-Ar-C,

J=21 Hz), 119.31 (2-Ar-C, *J*=24 Hz), 118.99 (2-Ar-C, *J*=24 Hz), 117.53 (CN), 113.96(1-Ar-C, *J*=9 Hz), 113.84(1-Ar-C, *J*=9 Hz).
GC-MS (EI): rt=4.215 min, m/z:121

3-Bromobenzonitrile (1m). white solid; m.p.43-46℃

^{1}H NMR (300 MHz, DMSO-d_6) δ 8.15 (s, 1H), 7.90 (dd, *J* = 19.1, 7.4 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 1H).
^{13}C NMR (75 MHz, DMSO-d_6) δ 136.89, 135.03, 131.93, 131.63, 122.63, 117.88, 113.83.
GC-MS (EI): rt=8.155 min, m/z: 181, 183.

3-Methylbenzonitrile (1n). colorless liquid; b.p.212-215℃

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.7 Hz, 1H), 7.46 (td, *J* = 7.7, 1.2 Hz, 1H), 7.26 (dd, *J* = 17.9, 7.8 Hz, 1H), 2.51 (s, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 141.87, 132.67, 132.46, 130.24, 126.24, 118.12, 112.70, 20.42.
GC-MS (EI): rt=6.130 min, m/z:117

2-Nitrobenzonitrile (1o). pale yellow solid; m.p 107-109℃

^{1}H NMR (300 MHz, DMSO-d_6) δ 8.45 – 8.33 (m, 1H), 8.18 (dd, *J* = 5.9, 3.2 Hz, 1H), 7.98 (dd, *J* = 5.9, 3.4 Hz, 2H).
^{13}C NMR (75 MHz, DMSO-d_6) δ 148.65, 136.28, 135.47, 135.01, 126.19, 116.03, 107.27.
GC-MS (EI): rt=11.890 min, m/z:148

Methyl 2-cyanobenzoate (**1p**).colorless solid. m.p.48-50℃

^{1}H NMR (300 MHz, DMSO-d_6) δ 8.14 – 8.08 (m, 1H), 8.00 (dd, *J* = 5.8, 3.1 Hz, 1H), 7.87 – 7.77 (m, 1H), 3.90 (s, 2H).
^{13}C NMR (75 MHz, DMSO-d_6) δ 164.57, 135.62, 133.93, 133.81, 132.10, 131.32, 117.84, 112.07, 53.29.
GC-MS (EI): rt=10.620 min, m/z:161

2-Fluorobenzonitrile (1q). colorless liquid. b.p. 20-22℃

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 – 7.52 (m, 1H), 7.24 (dt, *J* = 17.9, 8.3 Hz, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 164.83 (2-Ar-C, *J*=257.25 Hz), 161.40 (2-Ar-C, *J*=257.25Hz), 135.24 (4-Ar-C, *J*=8.25 Hz), 135.13 (4-Ar-C, *J*=8.25 Hz), 133.54 (5-Ar-C), 124.93 (3-Ar-C, *J*=0.3 Hz), 124.89 (3-Ar-C, *J*=0.3 Hz), 116.62 (1-Ar-C, *J*=19.5 Hz), 116.36 (1-Ar-C, *J*=19.5 Hz), 113.97 (CN).
GC-MS (EI): rt=4.810 min, m/z:121

2-Chlorobenzonitrile (1r). white solid;m.p.43-46℃

^{1}H NMR (300 MHz, DMSO-d_6) δ 8.01 (t, *J* = 1.7 Hz, 1H), 7.80 (tdd, *J* = 8.3, 2.4, 1.1 Hz, 2H), 7.59 (t, *J* = 8.0 Hz, 1H).
^{13}C NMR (75 MHz, DMSO-d_6) δ 134.42, 134.03, 132.28, 131.81, 131.60, 117.98, 113.62.
GC-MS (EI): rt=6.415 min, m/z:187

2-Bromobenzonitrile (1s). white solid; m.p.54-56 ℃

^{1}H NMR (300 MHz, DMSO-d_6) δ 8.11 – 7.75 (m, 1H), 7.77 – 7.45 (m, 1H).
^{13}C NMR (75 MHz, DMSO-d_6) δ 135.56, 135.42, 133.63, 128.97, 124.93, 117.72, 114.88.
GC-MS (EI): rt=8.755 min, m/z: 181, 183.

2-Methylbenzonitrile (1t). colorless liquid; b.p.203-205℃

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 – 7.29 (m, 4H), 2.38 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.23, 133.66, 132.47, 129.26, 129.00, 119.04, 112.23, 21.15.
GC-MS (EI): rt=6.335 min, m/z:117

Benzonitrile (1u). colorless liquid. b.p.188-191℃

^{1}H NMR (300 MHz, DMSO) δ 7.85 (dt, *J* = 3.3, 1.4 Hz, 2H), 7.79 – 7.71 (m, 1H), 7.65 – 7.57 (m, 2H).
^{13}C NMR (75 MHz, DMSO-d_6) δ 133.60, 132.57, 129.80, 119.21, 111.89.
GC-MS (EI): rt=4.675 min, m/z:103

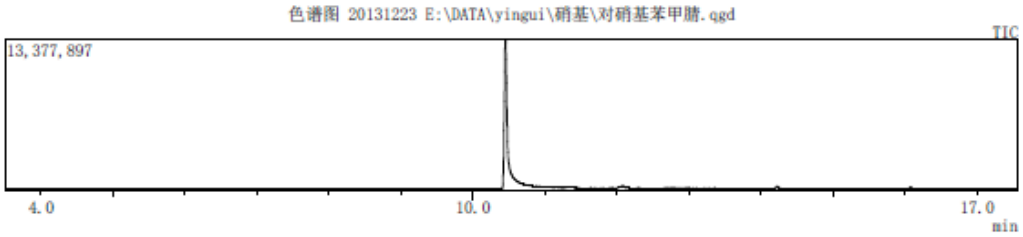
4-Cyanopyridine (1v). white solid; m.p.82-84℃

^{1}H NMR (300 MHz, DMSO-d_6) δ 8.83 (dd, *J* =8.8 Hz, 1H), 7.85 (dd, *J* =8.8 Hz, 1H).
^{13}C NMR (75 MHz, DMSO-d_6) δ 151.21, 126.08, 119.86, 117.24.
GC-MS (EI): rt=4.505 min, m/z:104

3-Cyanopyridine (1w). white solid; m.p.50-51℃

^{1}H NMR (300 MHz, DMSO-d_6) δ 9.01 (s, 1H), 8.85 (d, *J* = 3.8 Hz, 1H), 8.31 (dt, *J* = 8.0, 1.9 Hz, 1H), 7.61 (dd, *J* = 7.7, 4.8 Hz, 1H).
^{13}C NMR (75 MHz, DMSO-d_6) δ 153.72, 152.87, 140.47, 124.56, 117.45, 109.68.
GC-MS (EI): rt=4.940 min, m/z:104

4-Nitrobenzonitrile (1a)



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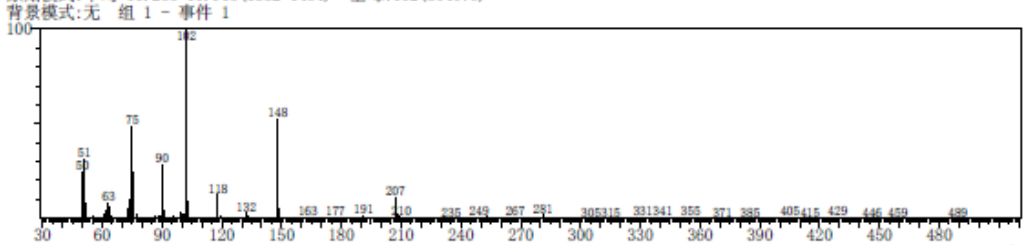

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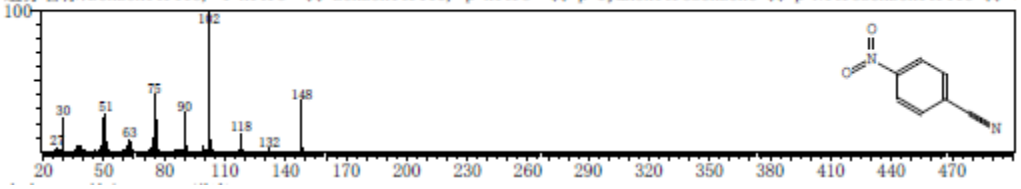
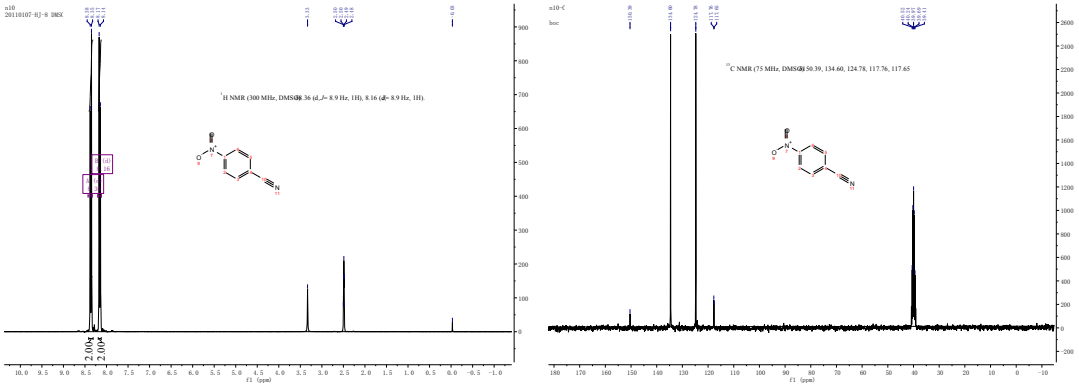
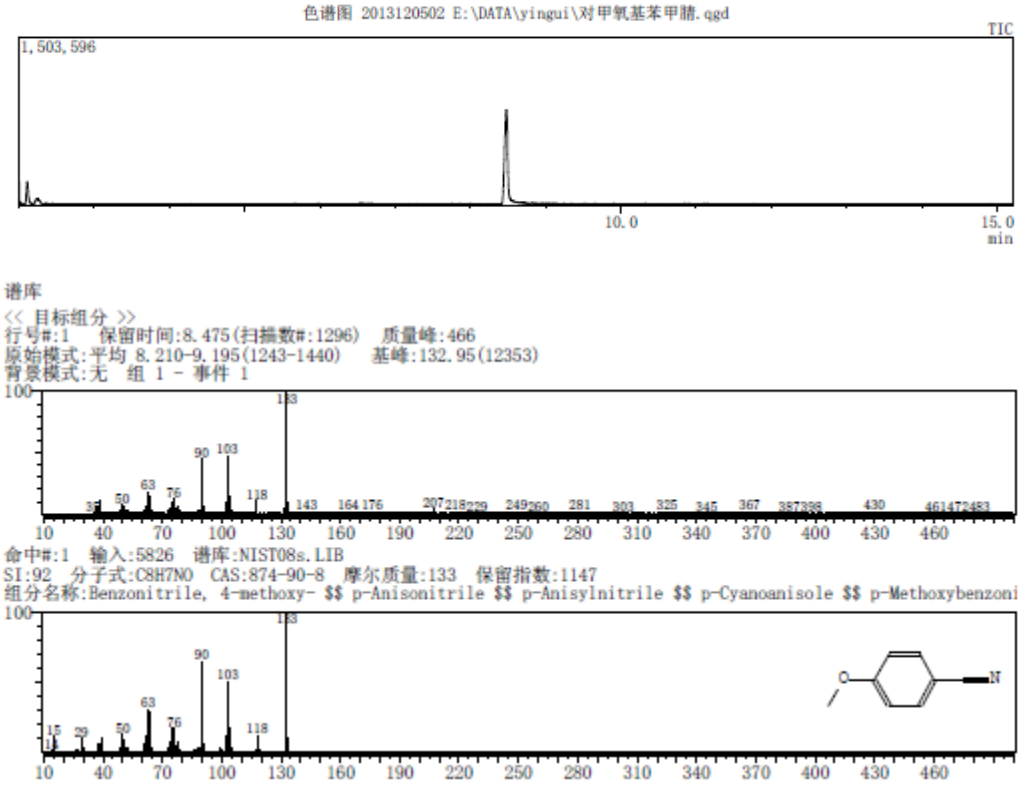
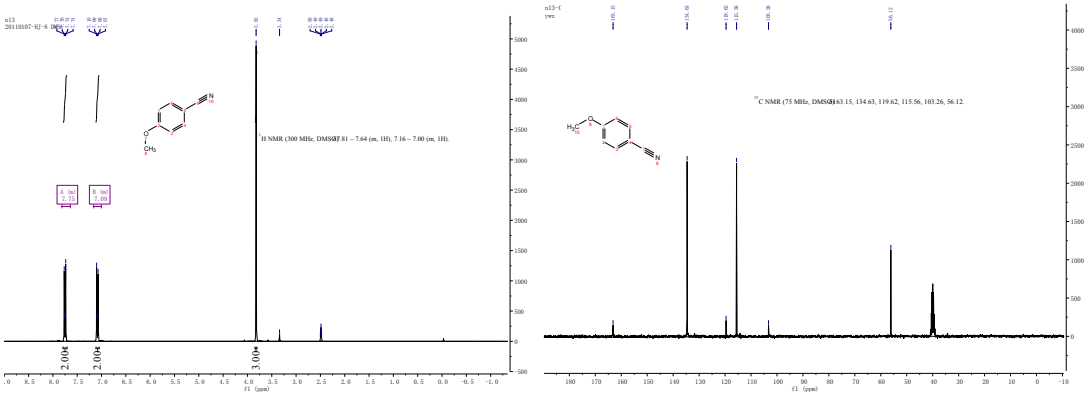


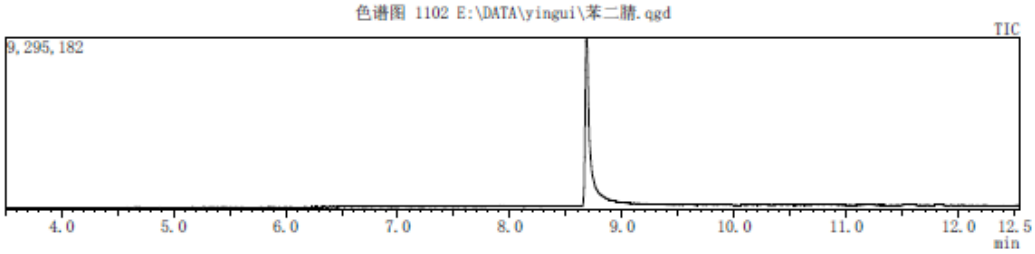


4-Methoxybenzonitrile (1b)





Terephthalonitrile (1c)



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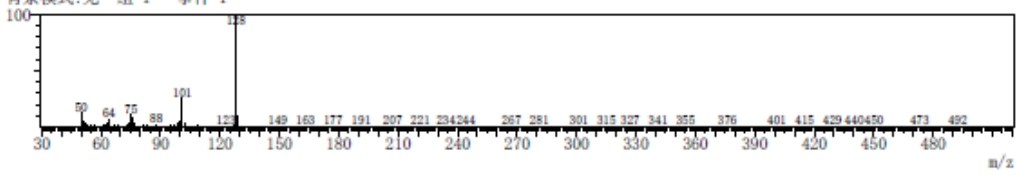

谱库

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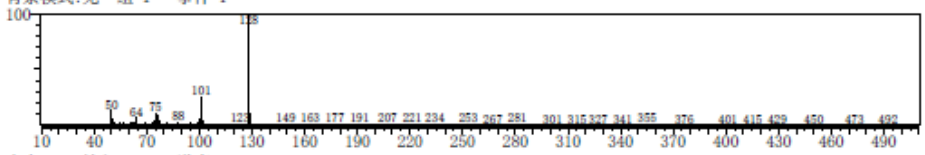

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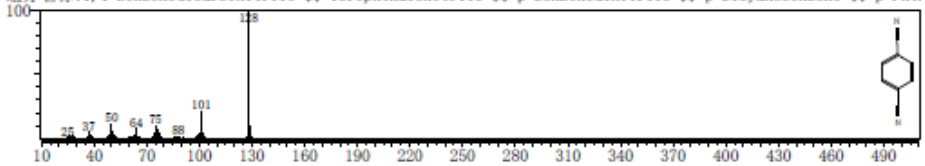
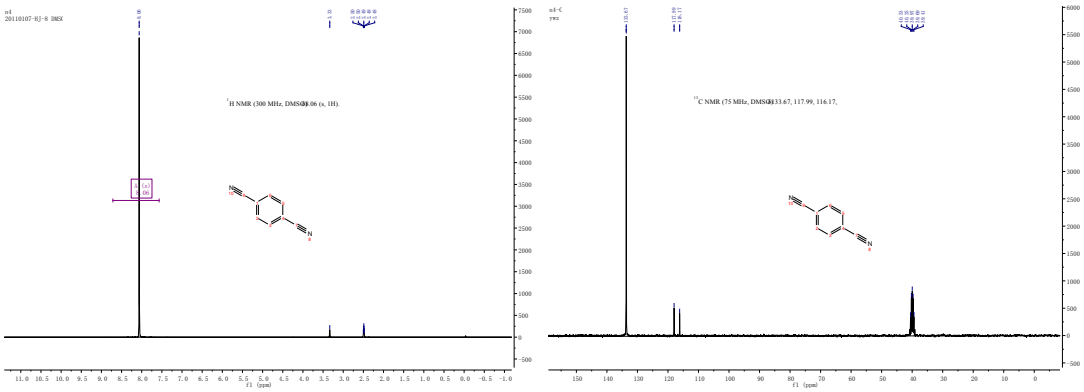
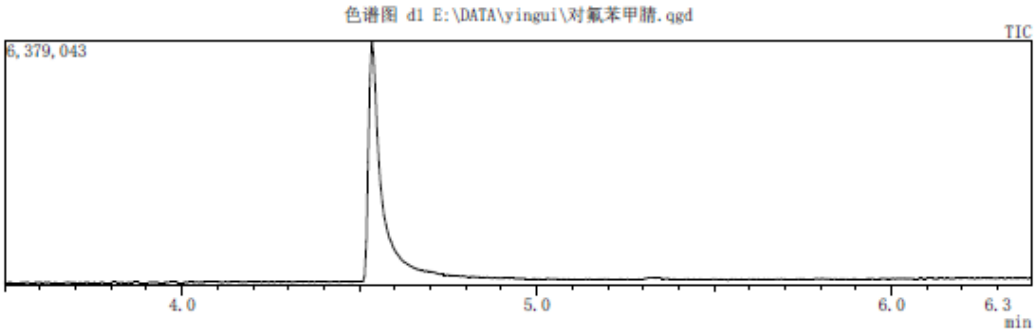
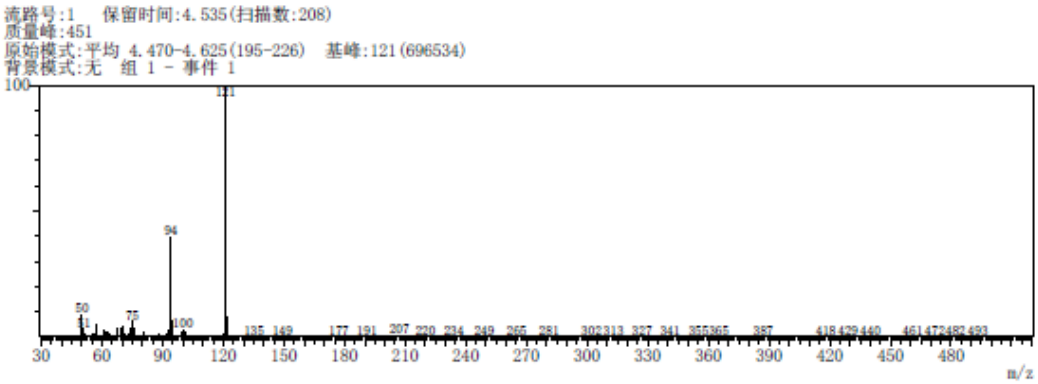


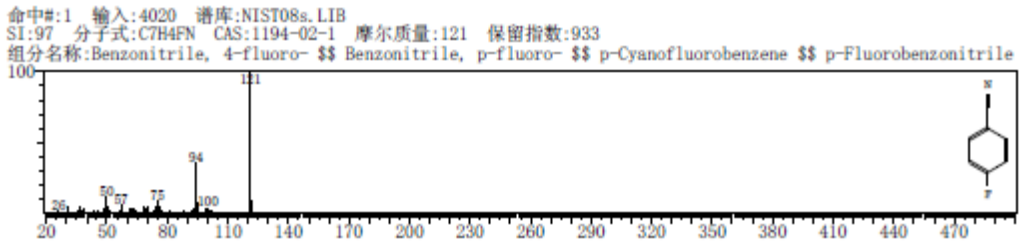


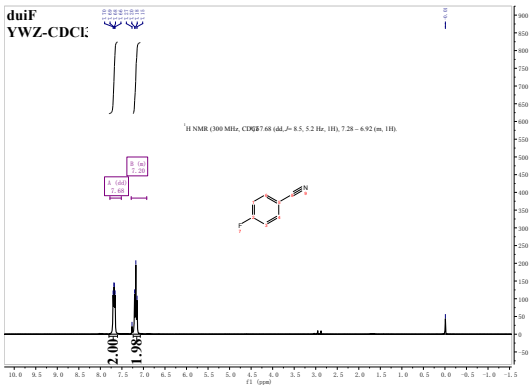
4-Fluorobenzonitrile (1d)

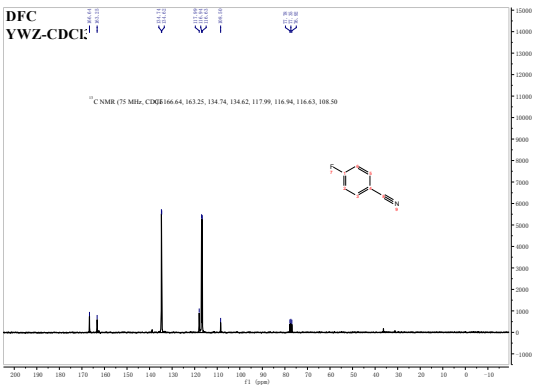


质谱

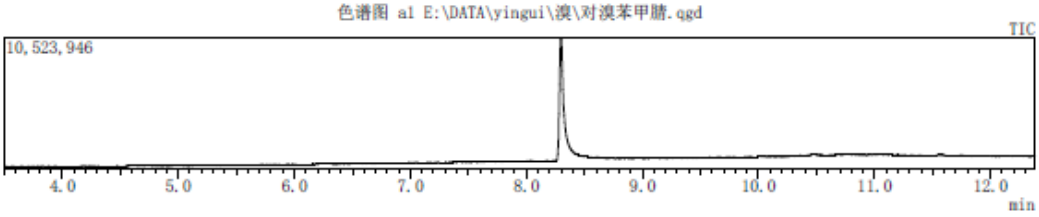








4-Bromobenzonitrile (1e)



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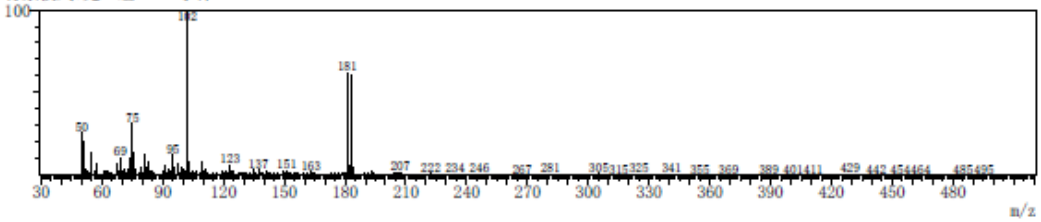

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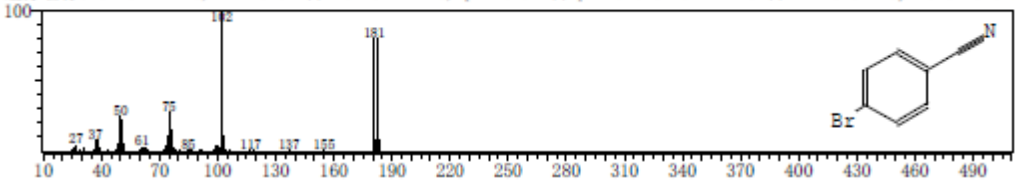
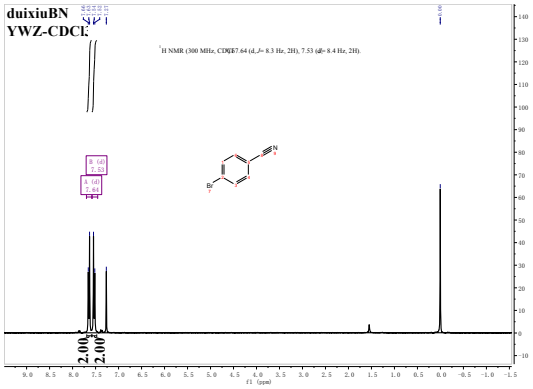
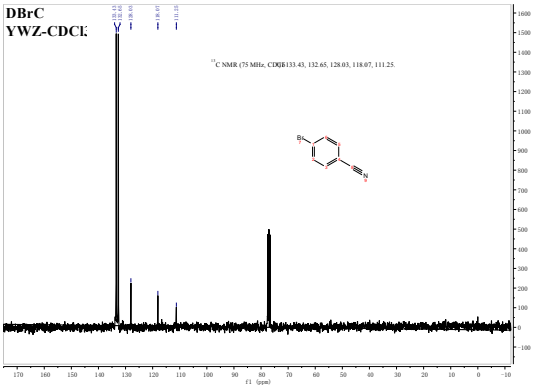
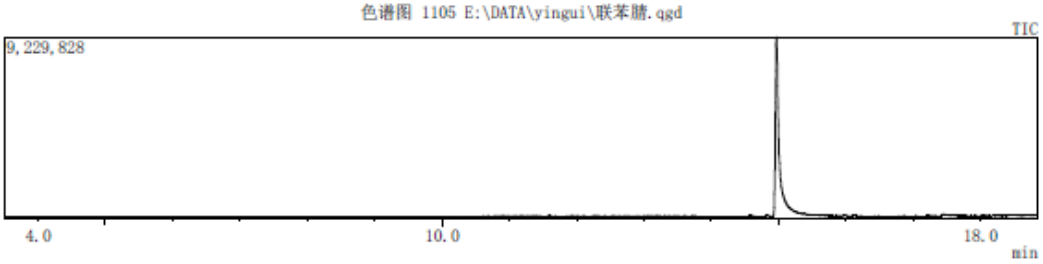




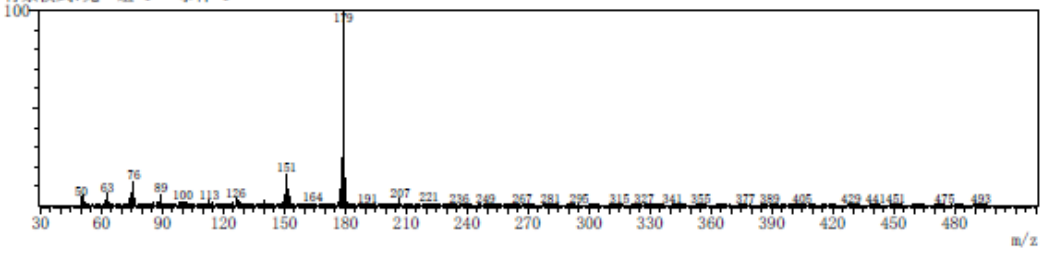


4-Phenylbenzonitrile (1f)

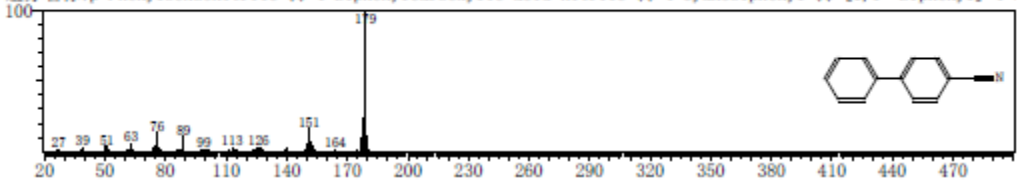


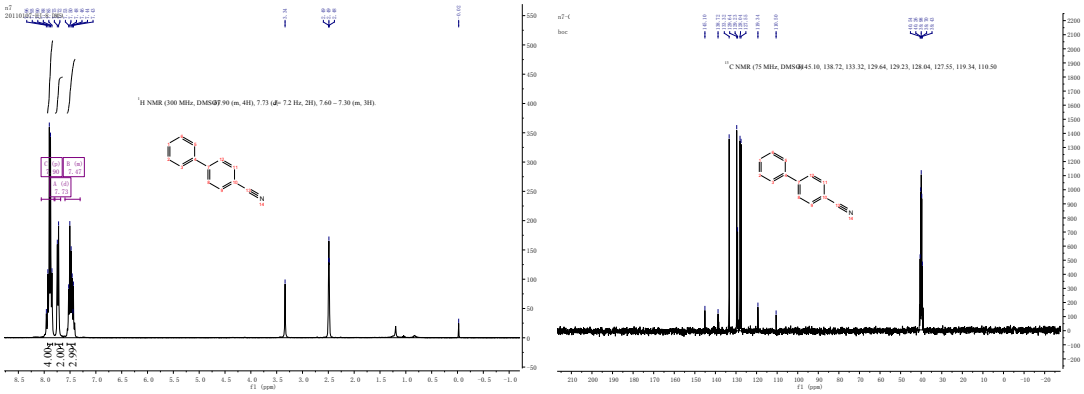
质谱

流路号:1　保留时间:14.970(扫描数:2295)
质量峰:451
原始模式:平均 14.620-15.825(2225-2466)　基峰:179(201313)
背景模式:无　组 1 - 事件 1

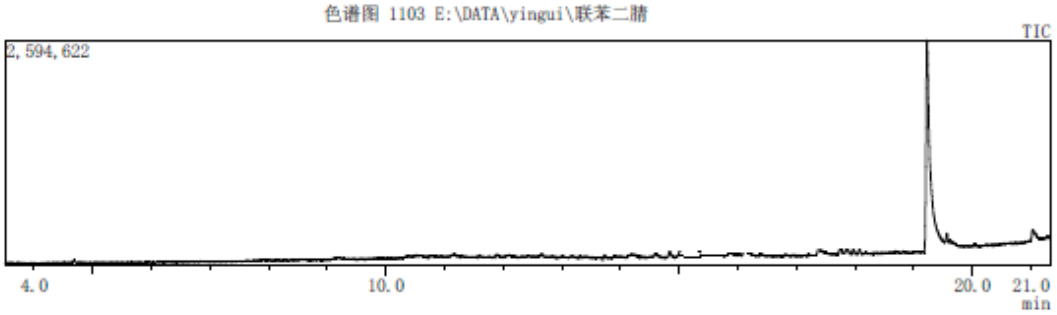


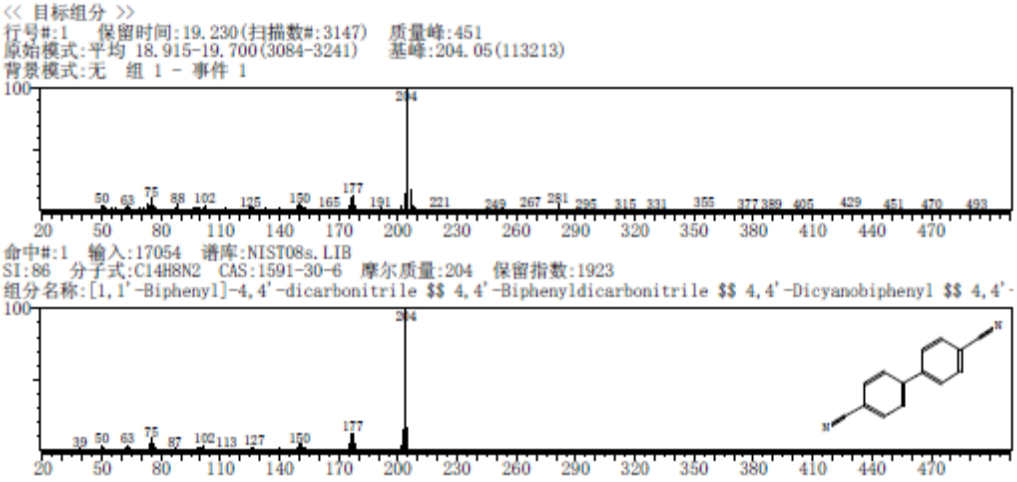
命中#:1　输入:30378　谱库:NIST08.LIB
SI:96　分子式:C13H9N　CAS:2920-38-9　摩尔质量:179　保留指数:1645
组分名称:p-Phenylbenzonitrile $$ 4-Biphenylcarboxylic acid nitrile $$ 4-Cyanobiphenyl $$ [1,1'-Biphenyl]-4-

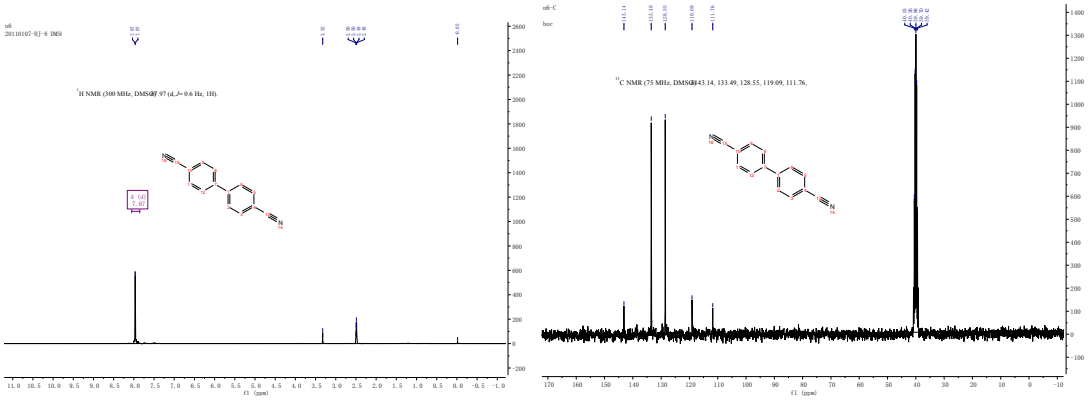




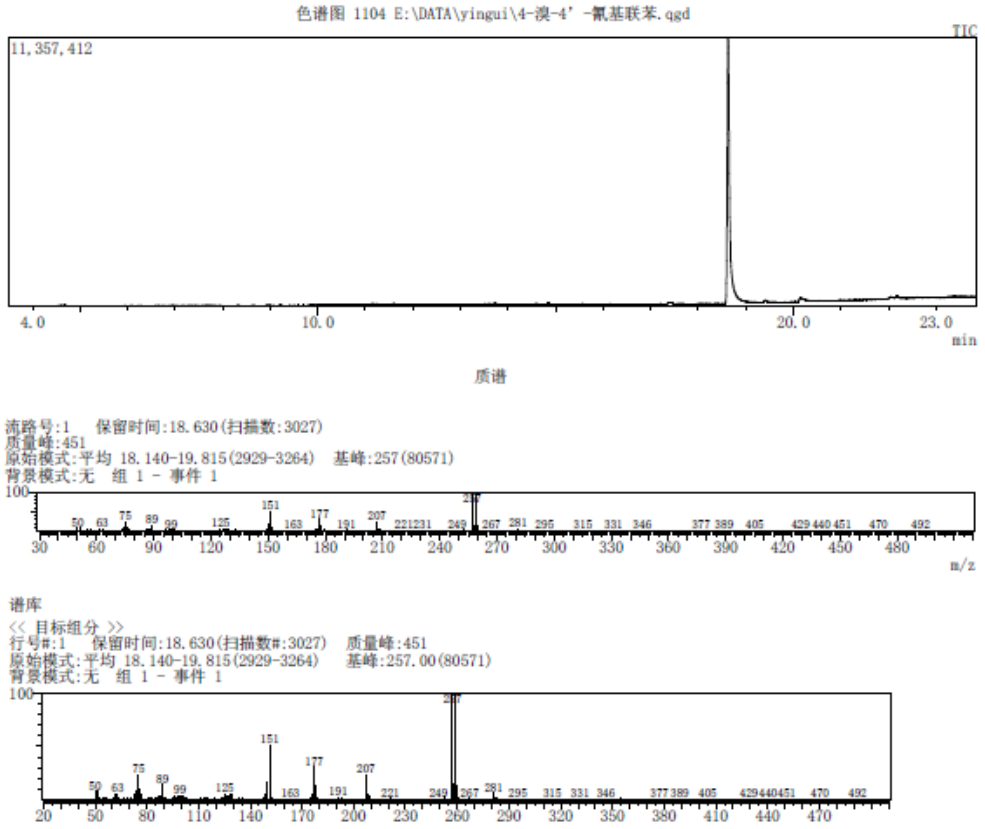
4,4'-Biphenyldicarbonitrile (1g)

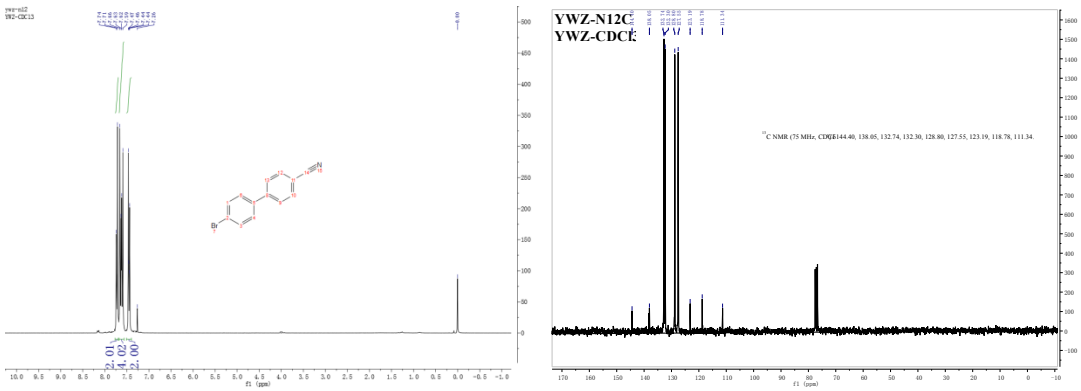




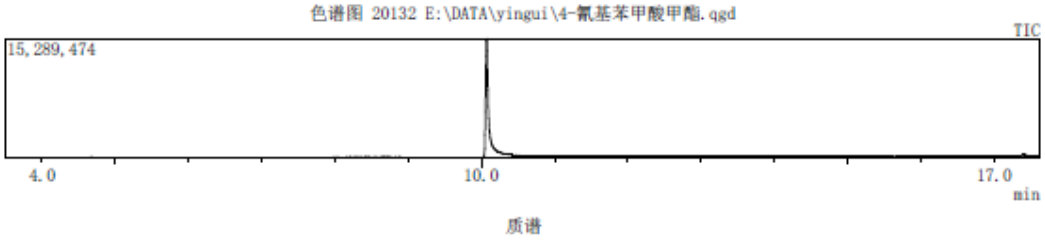


4-(p-bromophenyl)benzonitrile (1h)

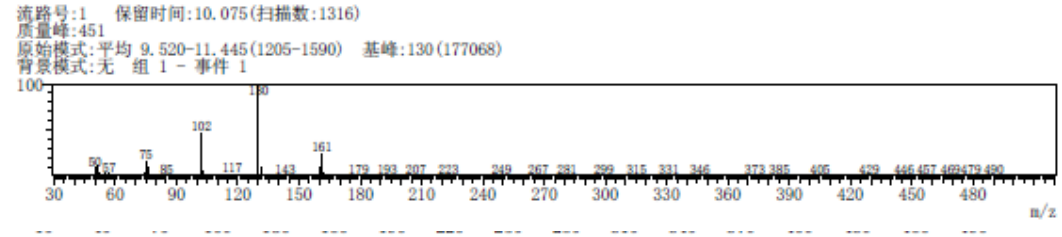


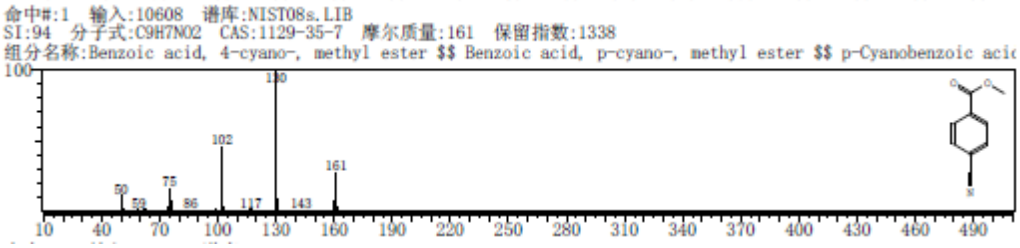


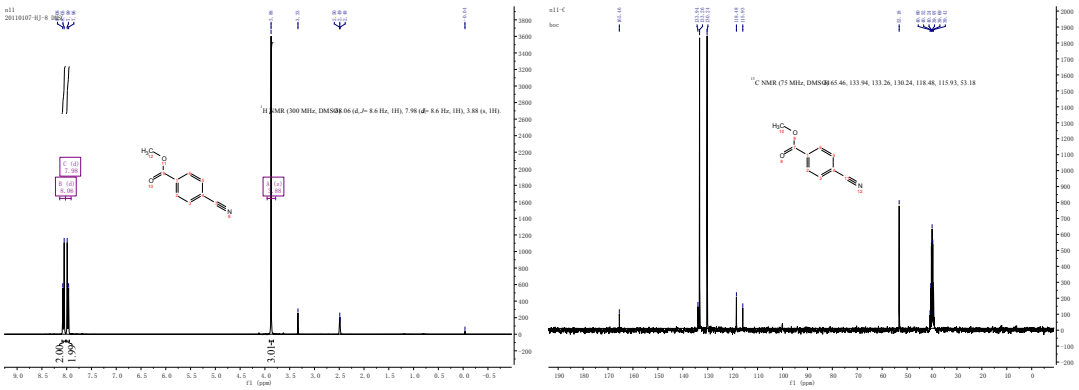
Methyl 4-cyanobenzoate (1i)



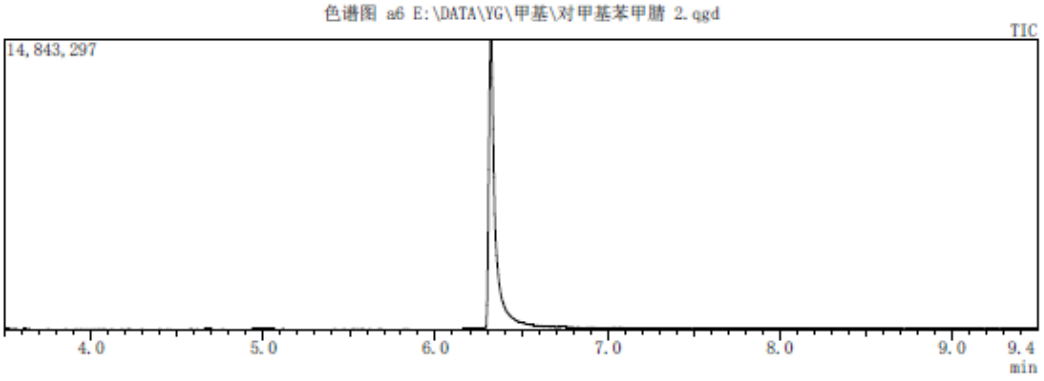
质谱



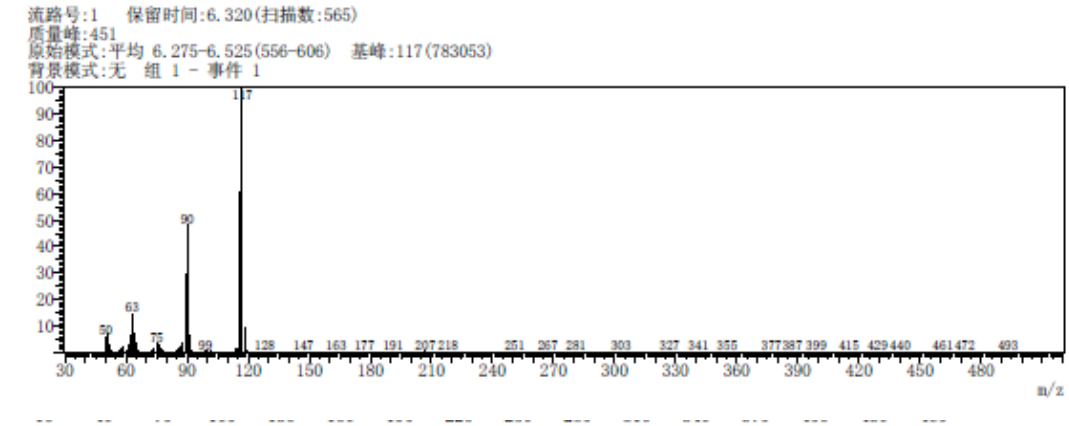


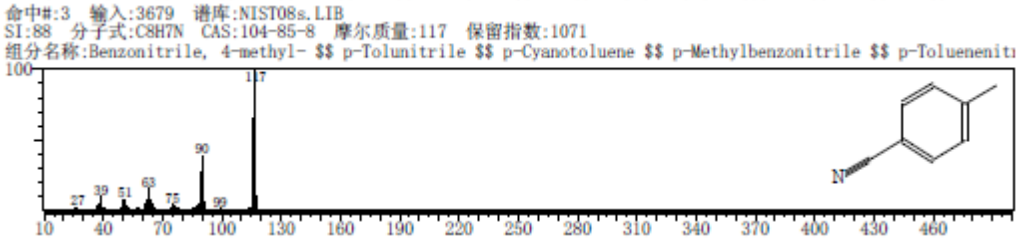


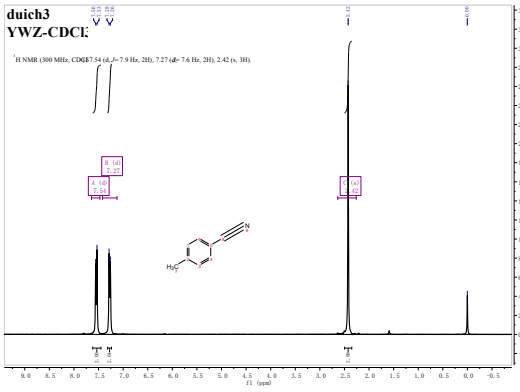
4-Methylbenzonitrile (1j)

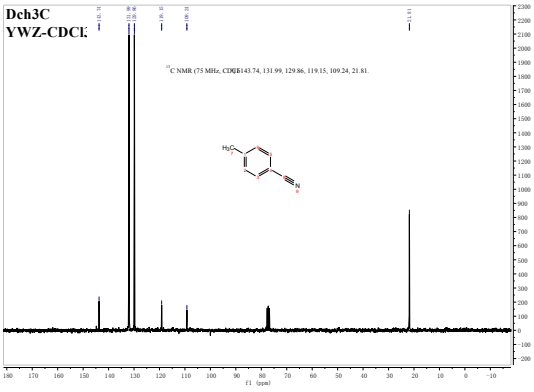


质谱

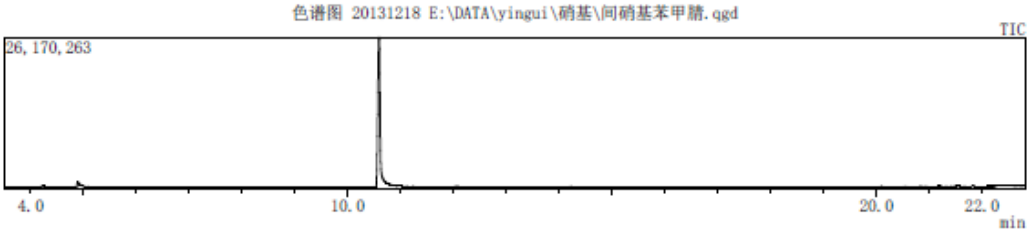




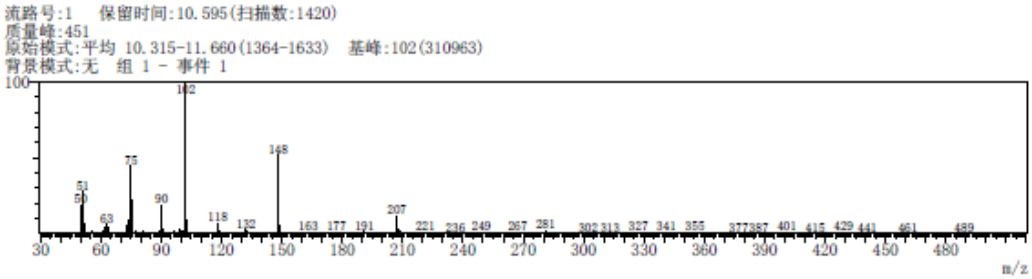


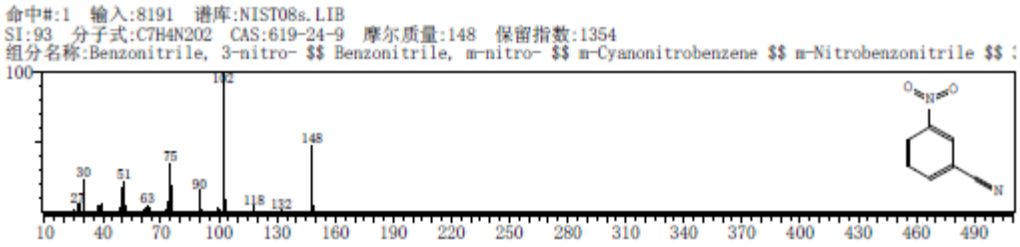


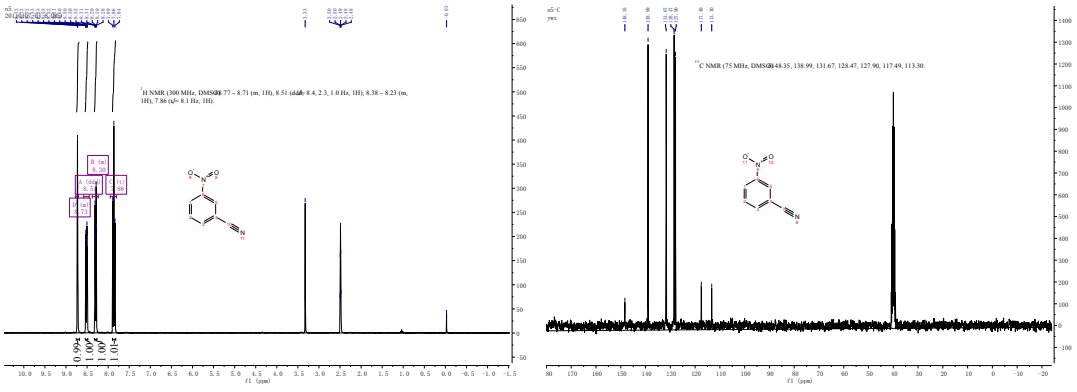
3-Nitrobenzonitrile (1k)



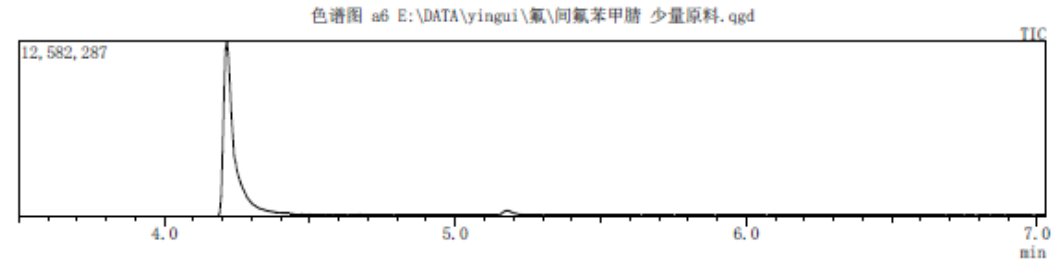
质谱





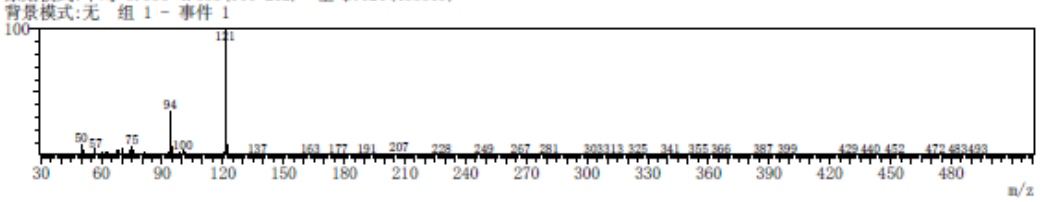


3-Fluorobenzonitrile (1l)

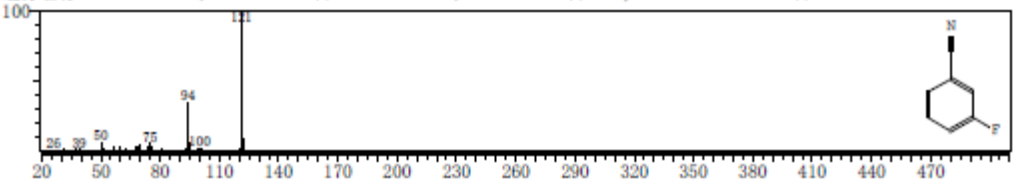


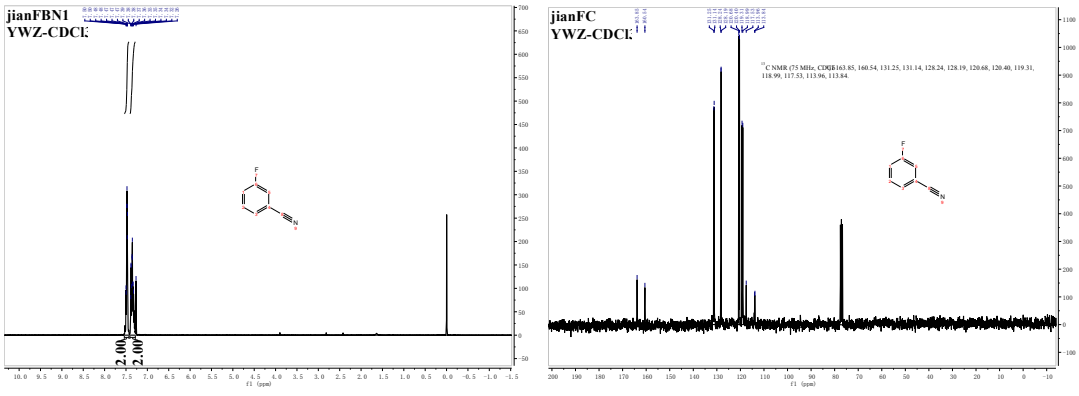
质谱

流路号:1　保留时间:4.215(扫描数:144)
质量峰:451
原始模式:平均 3.995-4.555(100-212)　基峰:121(466519)
背景模式:无　组 1 - 事件 1

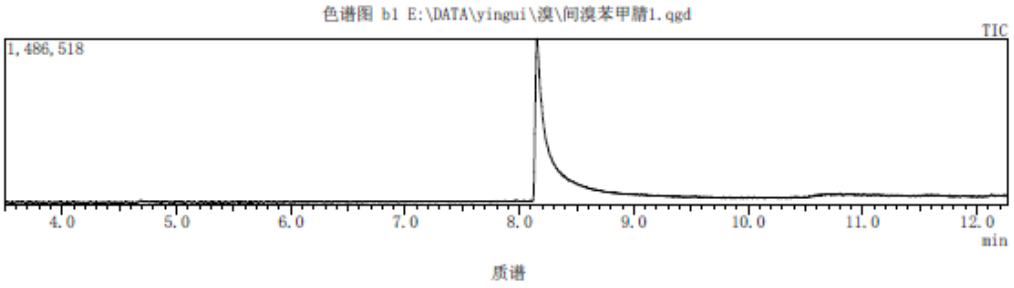


命中#:1　输入:4024　谱库:NIST08s.LIB
SI:98　分子式:C7H4FN　CAS:403-54-3　摩尔质量:121　保留指数:933
组分名称:Benzonitrile, 3-fluoro- $$ Benzonitrile, m-fluoro- $$ m-Cyanofluorobenzene $$ m-Fluorobenzonitrile



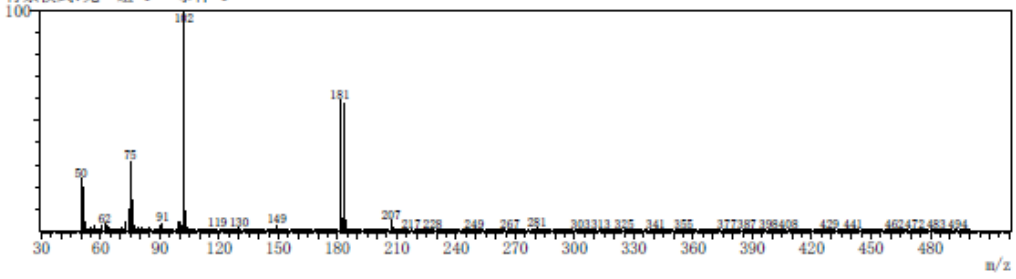


3-Bromobenzonitrile (1m)

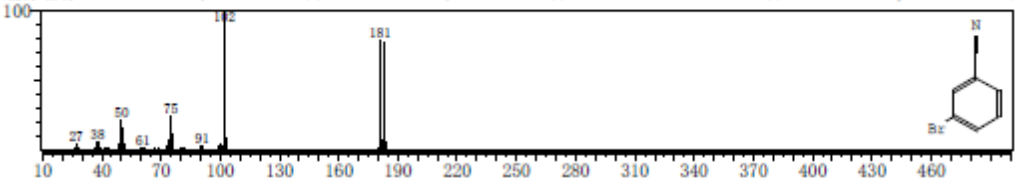


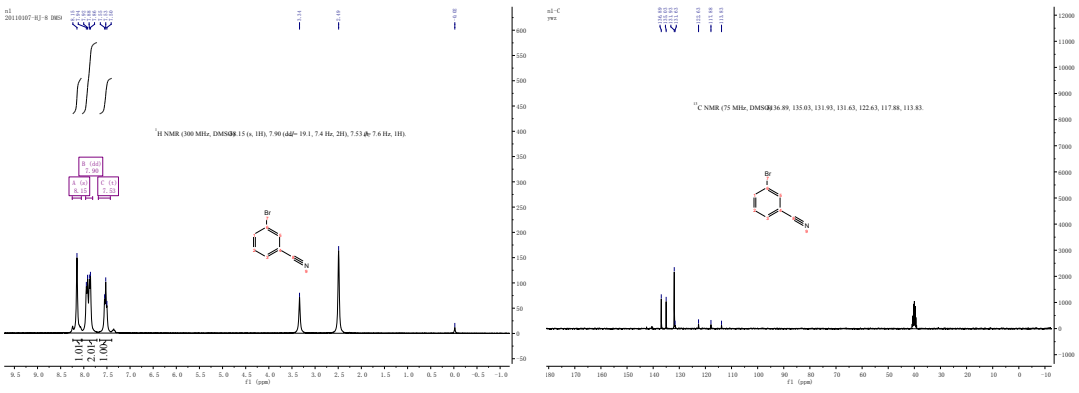
质谱

流路号:1　保留时间:8.155(扫描数:932)
质量峰:451
原始模式:平均 7.945-9.100(890-1121)　基峰:102(50611)
背景模式:无　组 1 - 事件 1

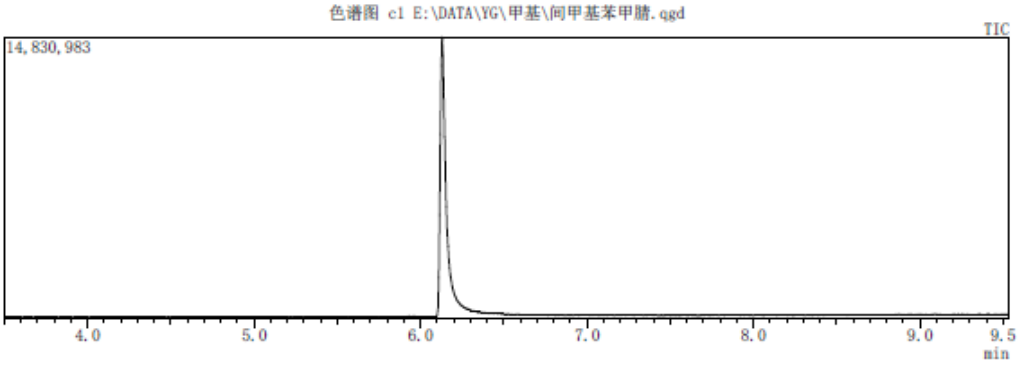


命中#:2　输入:13824　谱库:NIST08s.LIB
SI:92　分子式:C7H4BrN　CAS:6952-59-6　摩尔质量:181　保留指数:1278
组分名称:Benzonitrile, 3-bromo- $$ Benzonitrile, m-bromo- $$ m-Bromobenzonitrile $$ 1-Bromo-3-cyanobenzene

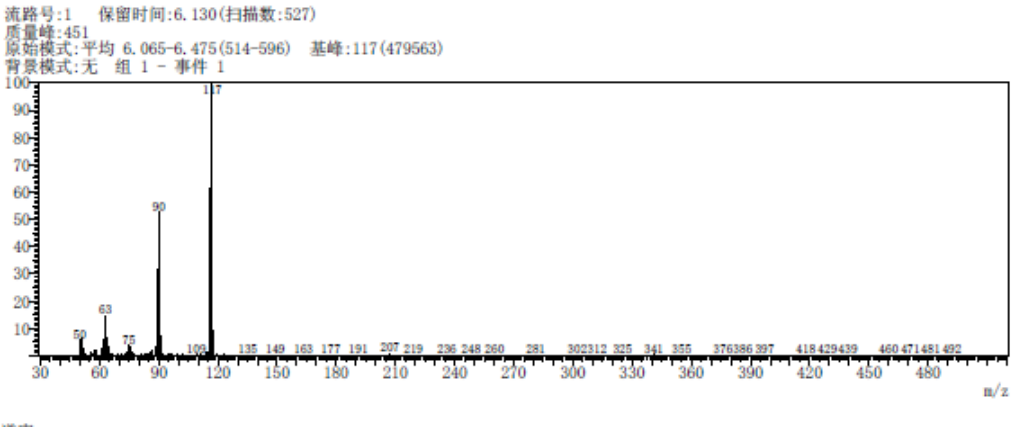


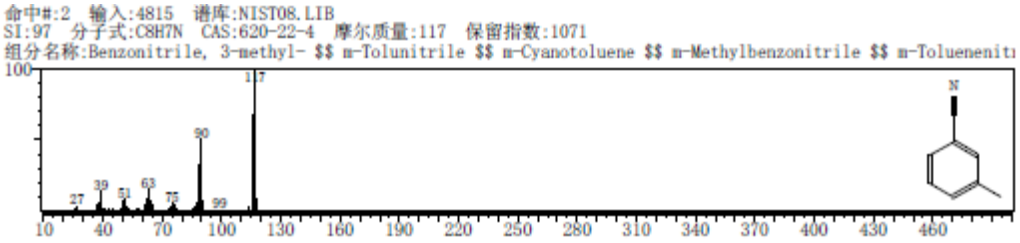


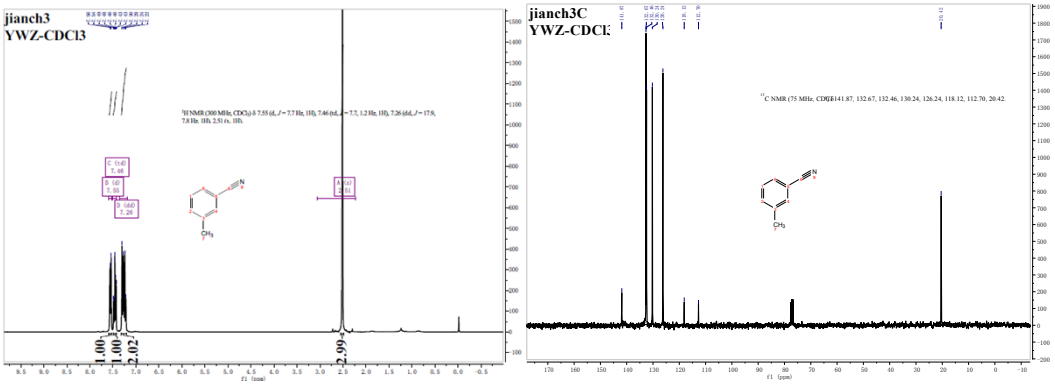
3-Methylbenzonitrile (1n)



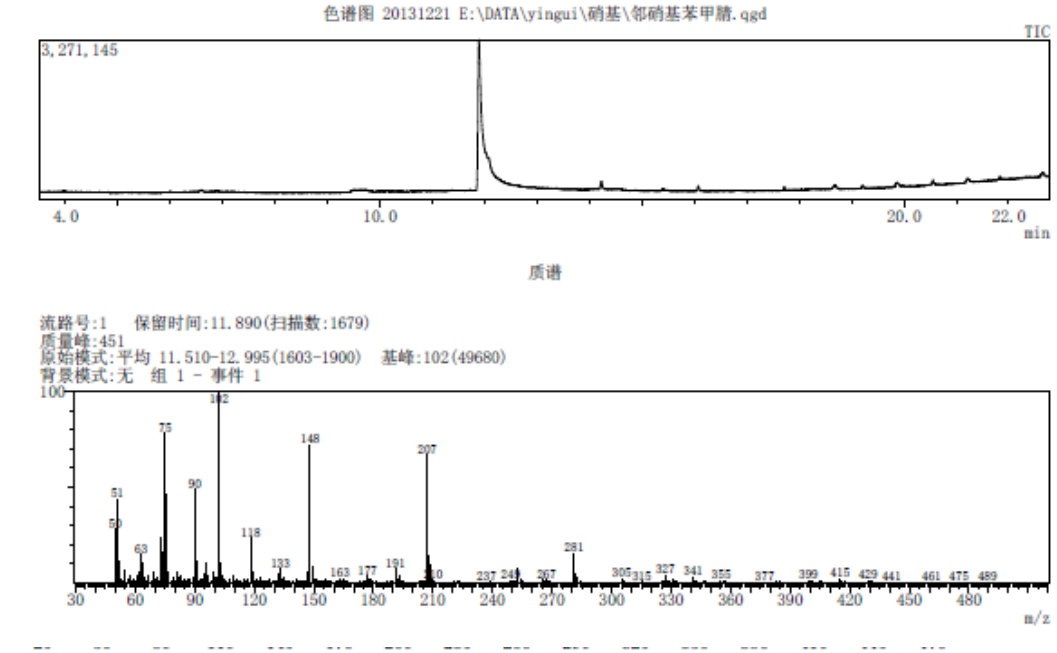
质谱

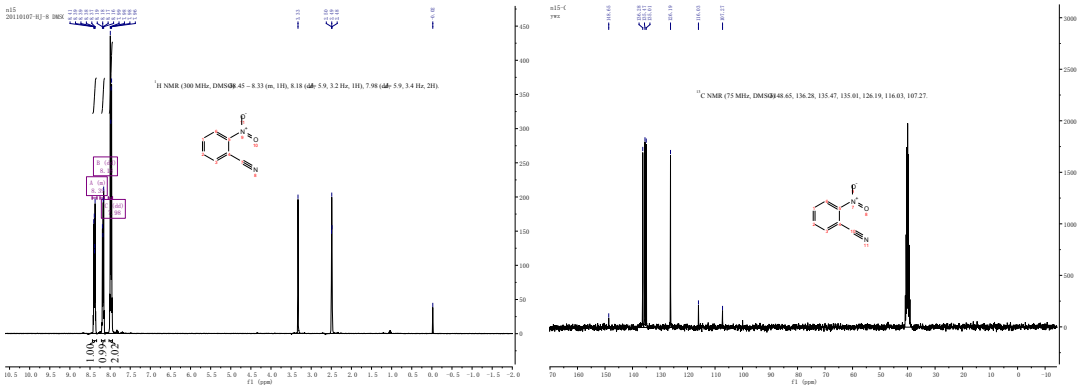




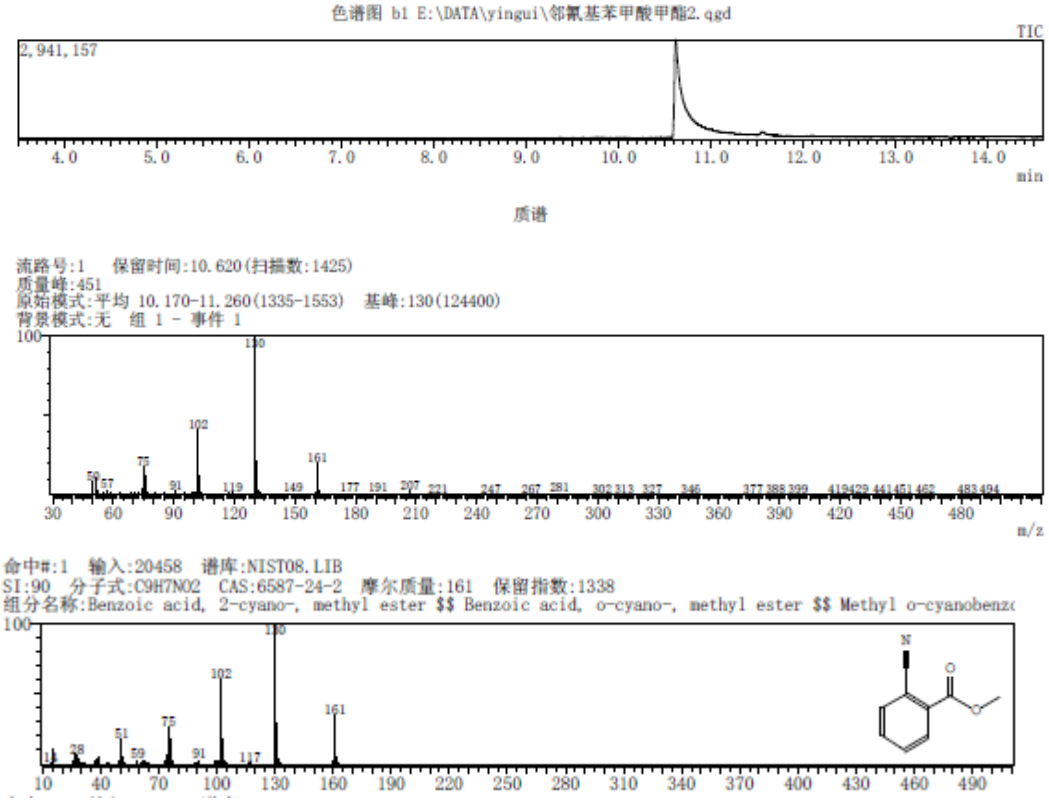


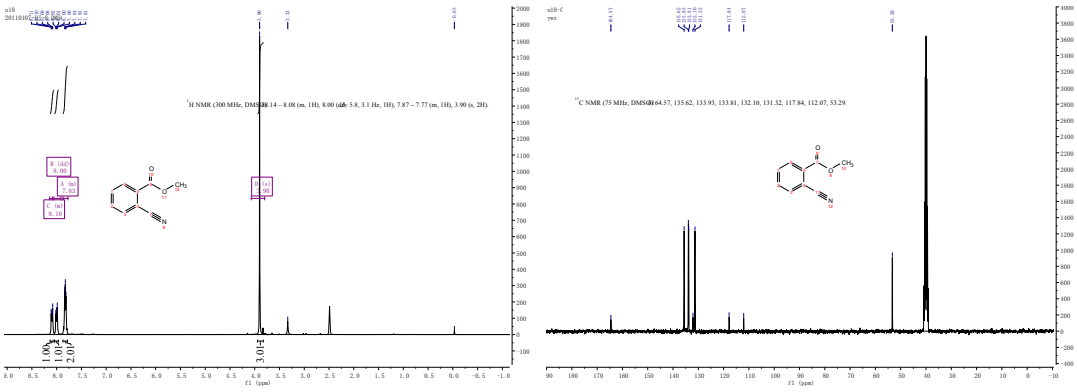
2-Nitrobenzonitrile (1o)



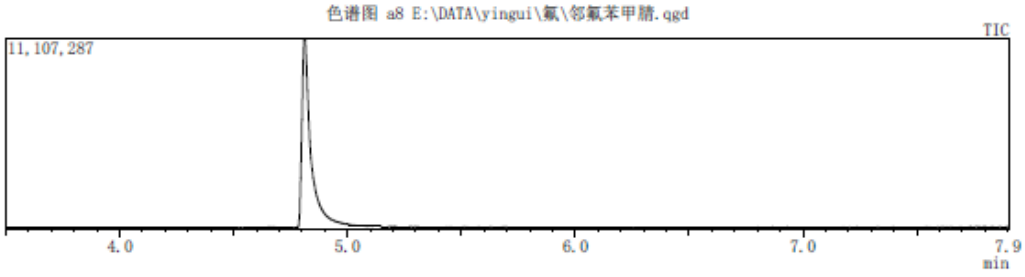


Methyl 2-cyanobenzoate (1p)



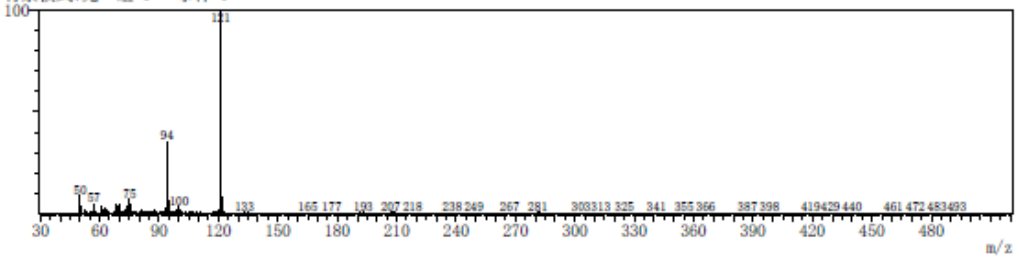


2-Fluorobenzonitrile (1q)

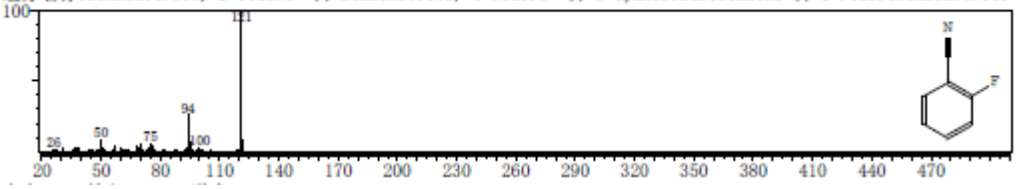


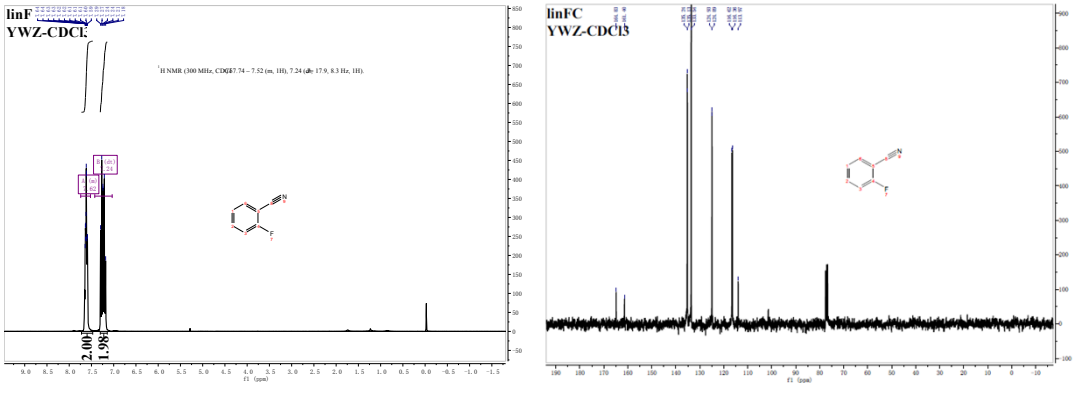
质谱

流路号:1　保留时间:4.810(扫描数:263)
质量峰:451
原始模式:平均 4.685-5.215(238-344)　基峰:121(463010)
背景模式:无　组 1 - 事件 1

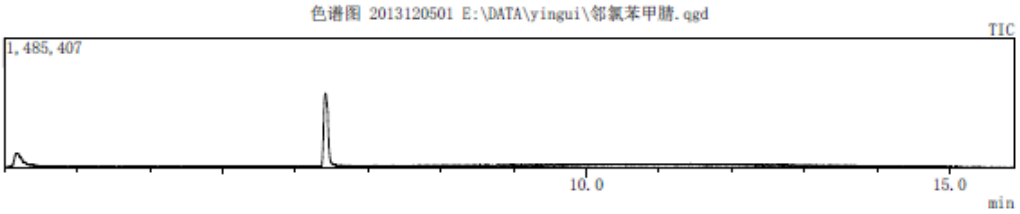


命中#:4　输入:5370　谱库:NIST08.LIB
SI:97　分子式:C7H4FN　CAS:394-47-8　摩尔质量:121　保留指数:933
组分名称:Benzonitrile, 2-fluoro- $$ Benzonitrile, o-fluoro- $$ o-Cyanofluorobenzene $$ o-Fluorobenzonitrile

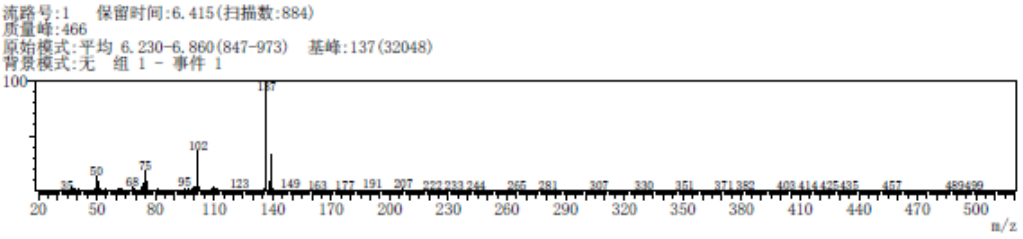


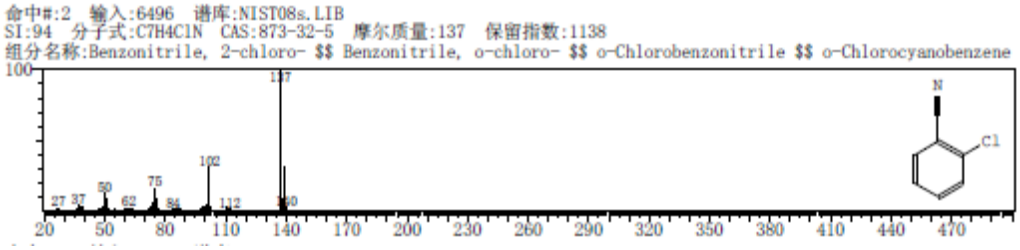


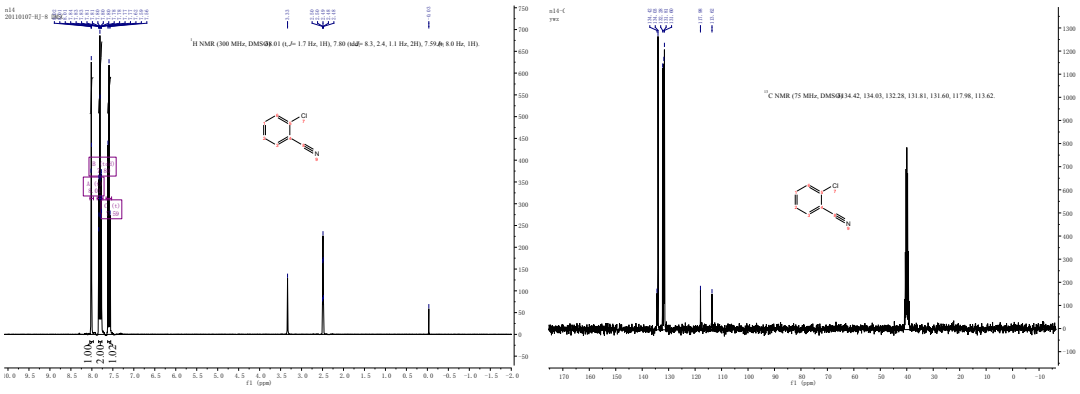
2-Chlorobenzonitrile (1r)



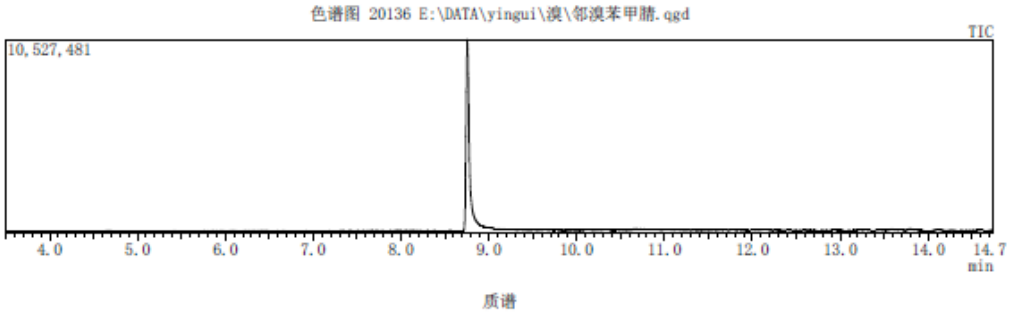
质谱



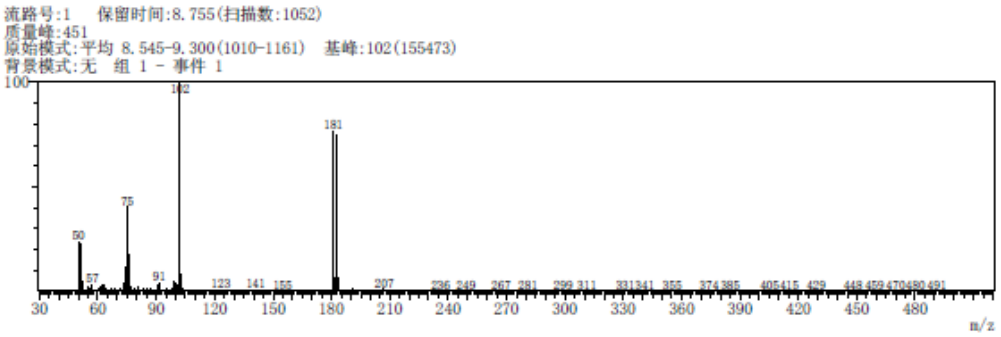


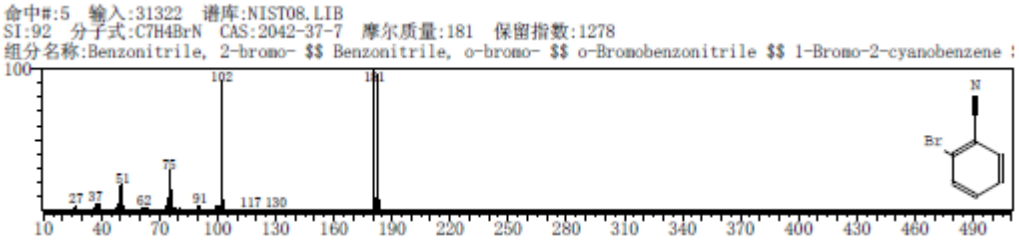


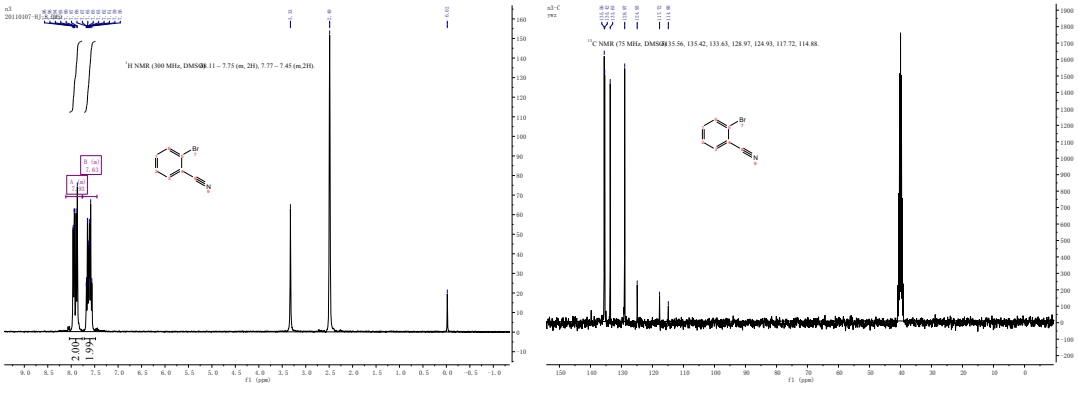
2-Bromobenzonitrile (1s)



质谱

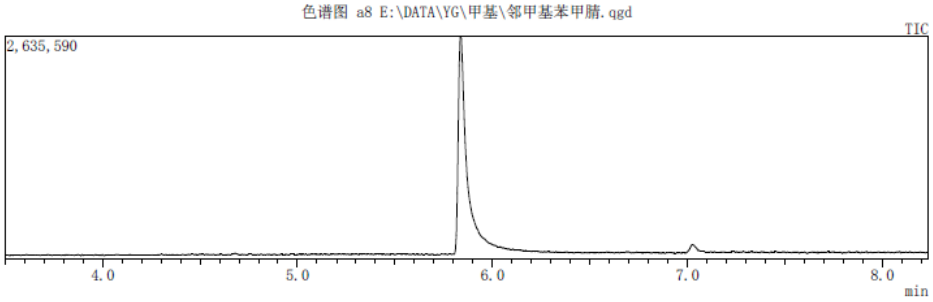






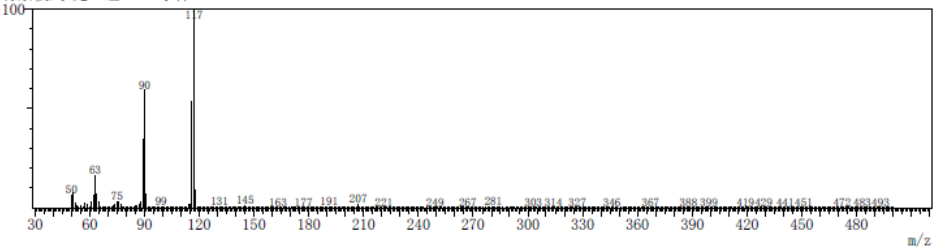
2-Methylbenzonitrile (1t)

色谱图 a8 E:\DATA\YG\甲基\邻甲基苯甲腈.qgd

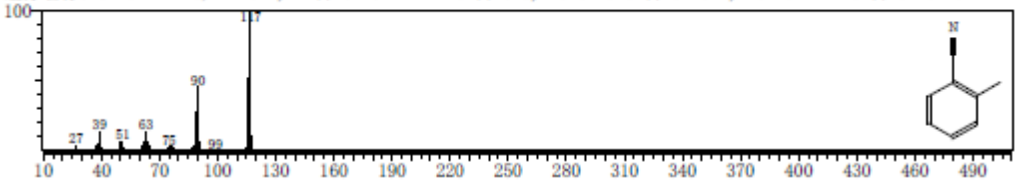


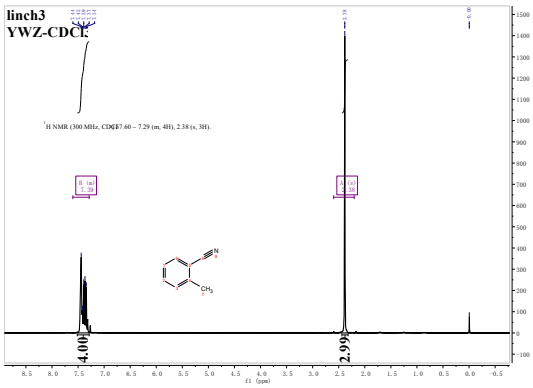
质谱

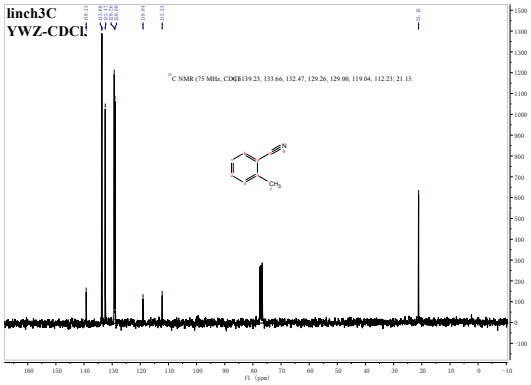
流路号:1　保留时间:5.835(扫描数:468)
质量峰:451
原始模式:平均 5.775-6.030(456-507)　基峰:117(154844)
背景模式:无　组 1 - 事件 1



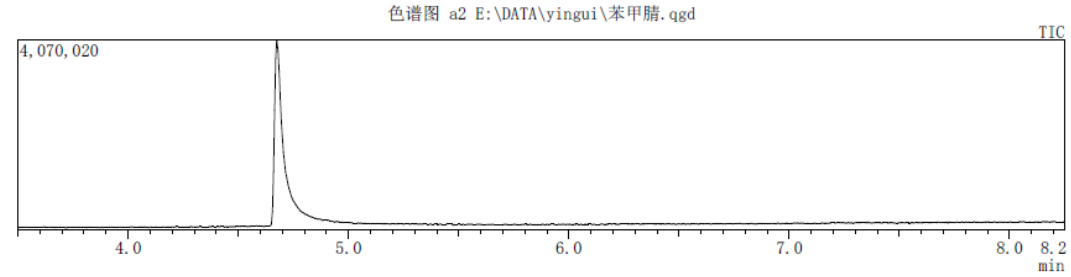
命中#:1　输入:3675　谱库:NIST08s.LIB
SI:88　分子式:C8H7N　CAS:529-19-1　摩尔质量:117　保留指数:1071
组分名称:Benzonitrile, 2-methyl- $$ o-Tolunitrile $$ o-Cyanotoluene $$ o-Methylbenzonitrile $$ o-Toluonitri



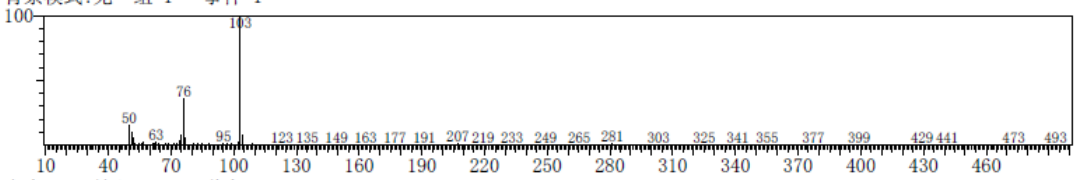




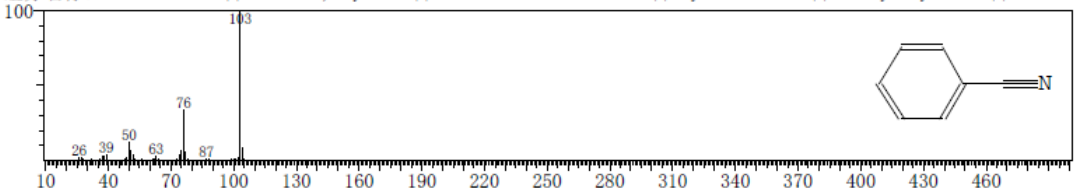
Benzonitrile (1u)

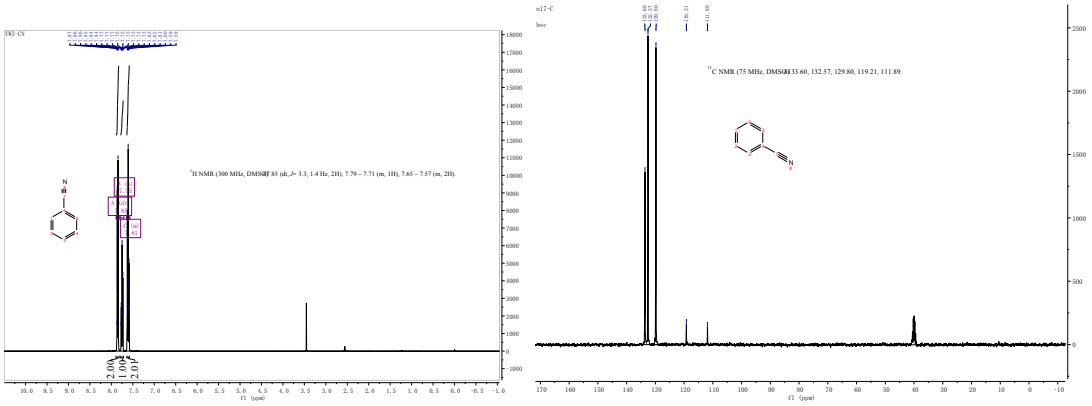


谱库
<< 目标组分 >>
行号#:1　保留时间:4.675(扫描数#:236)　质量峰:451
原始模式:平均 4.605-5.050(222-311)　基峰:103.05(241400)
背景模式:无　组 1 - 事件 1

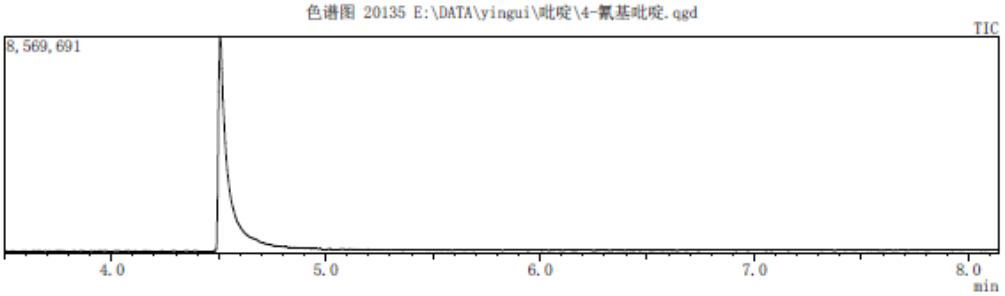


命中#:1　输入:2160　谱库:NIST08s.LIB
SI:95　分子式:C7H5N　CAS:100-47-0　摩尔质量:103　保留指数:958
组分名称:Benzonitrile $$ Benzene, cyano- $$ Benzoic acid nitrile $$ Cyanobenzene $$ Phenyl cyanide $$ Benzer



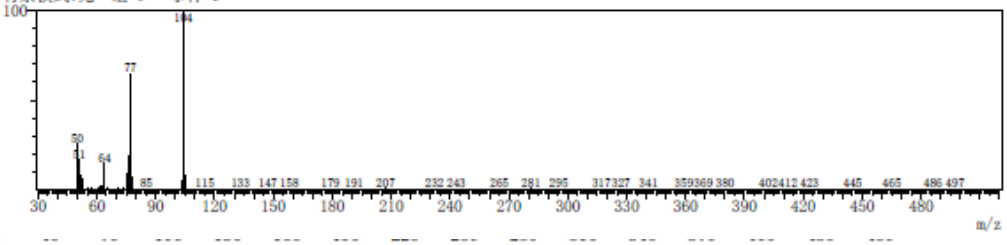


4-Cyanopyridine (1v)

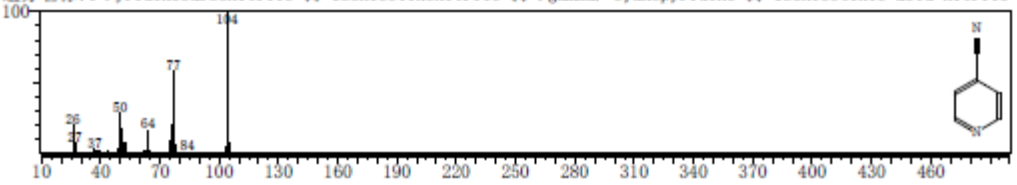


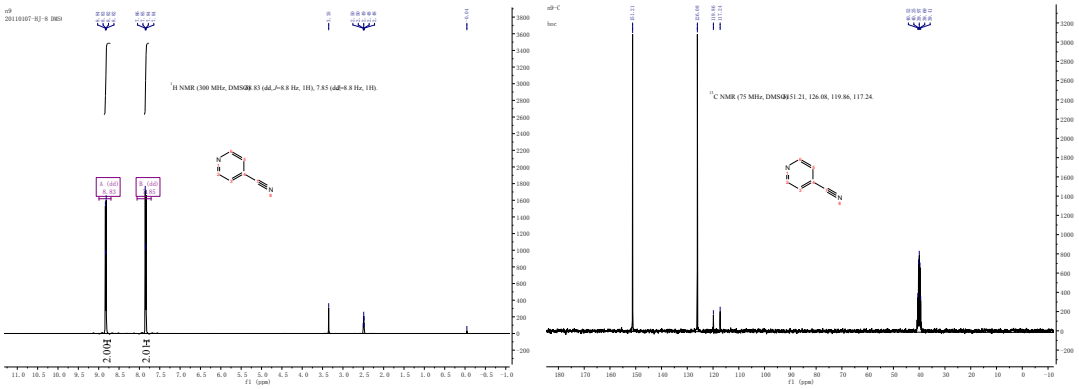
质谱

流路号:1　保留时间:4.505(扫描数:202)
质量峰:451
原始模式:平均 4.435-4.970(188-295)　基峰:104(303190)
背景模式:无　组 1 - 事件 1

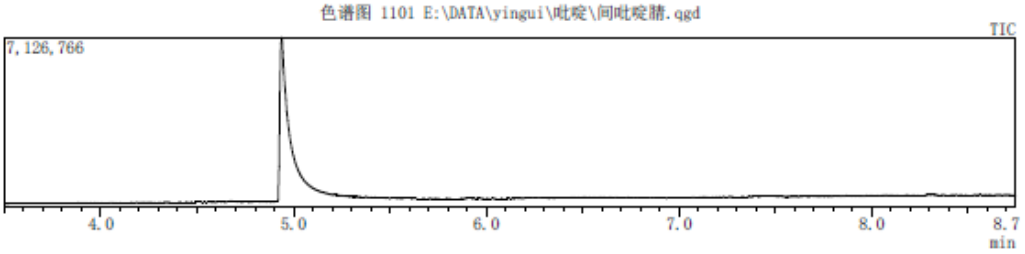


命中#:1　输入:2260　谱库:NIST08s.LIB
SI:98　分子式:C6H4N2　CAS:100-48-1　摩尔质量:104　保留指数:952
组分名称:4-Pyridinecarbonitrile $$ Isonicotinonitrile $$ .gamma.-Cyanopyridine $$ Isonicotinic acid nitrile



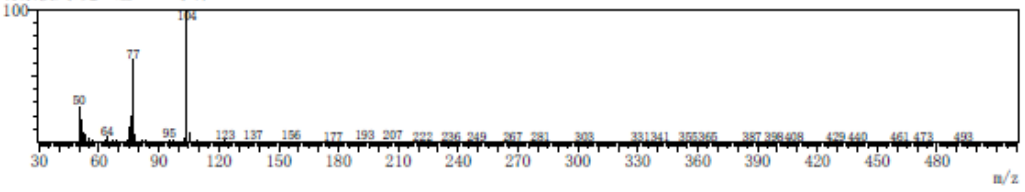


3-Cyanopyridine (1w)



质谱

流路号:1　保留时间:4.940(扫描数:289)
质量峰:451
原始模式:平均 4.840-5.230(269-347)　基峰:104(425526)
背景模式:无　组 1 - 事件 1



命中#:2　输入:2556　谱库:NIST08.LIB
SI:92　分子式:C6H4N2　CAS:100-54-9　摩尔质量:104　保留指数:952
组分名称:3-Pyridinecarbonitrile $$ Nicotinonitrile $$ Nicotinic acid nitrile $$ 3-Cyanopyridine $$ 3-Pyridyl