Electronic Supplementary Information

Syntheses and structures of copper complexes of 3-(6-(1H-pyrazol-1-yl)pyridin-2-yl)pyrazol-1-ide and their excellent performance in the syntheses of nitriles and aldehydes

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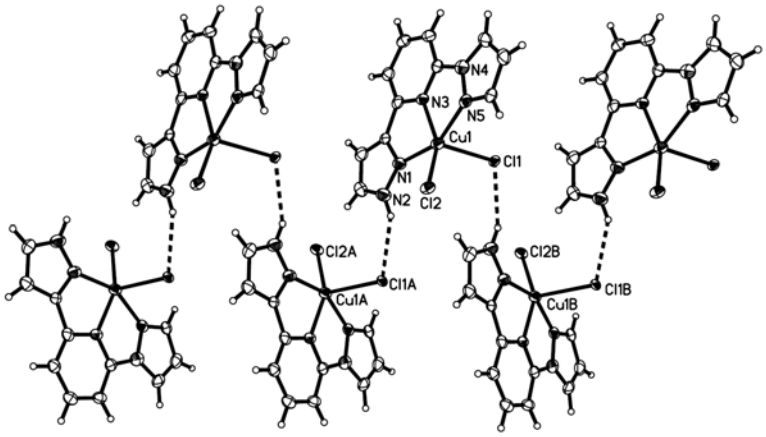


Figure S1. One-dimensional chain (extended along the *b* axis) formed *via* H-bonding interactions in **4**.

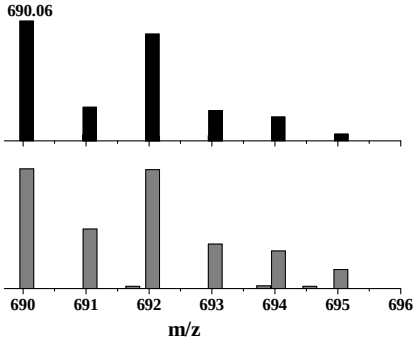


Figure S2. The calculated isotope pattern (top) and the observed patterns (below) of the $[\{(Cu(NO_3))(\mu\text{-pzpypz})\}_2 + NO_3 + 2CH_3CN]^+$ cation in the positive-ion ESI mass spectrum of **1**.

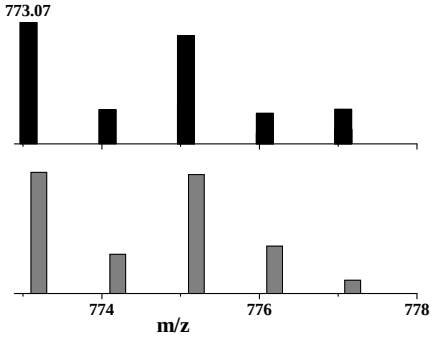


Figure S3. The calculated isotope pattern (top) and the observed patterns (below) of the $[CuClO_4(pzpypzH)CuOCH_3(pzpypz) + 3MeOH]^+$ cation in the positive-ion ESI mass spectrum of **2**.

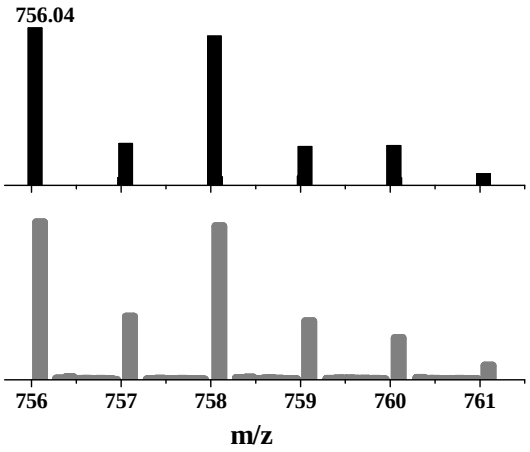


Figure S4. The calculated isotope pattern (top) and the observed patterns (below) of the $[\{Cu_2(\mu\text{-}SO_4)(\mu\text{-}pzpypz)_2\} + HSO_4 + 2MeOH + 4H_2O + CH_3CN]^+$ cation in the positive-ion ESI mass spectrum of **3**.

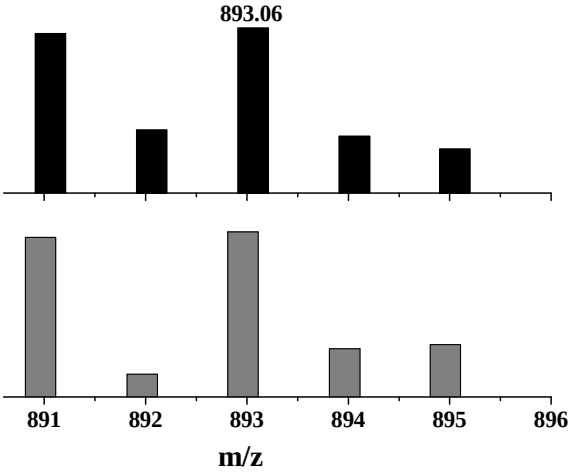


Figure S5. The calculated isotope pattern (top) and the observed patterns (below) of the $[\{(CuI)(\mu\text{-}pzpypz)\}_2 + I + 3H_2O + 4CH_3CN]^+$ cation in the positive-ion ESI mass spectrum of **5**.

benzonitrile: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.47 (t, *J* = 8.0Hz, 1H), 7.60 (d, *J* = 8.0Hz, 1H), 7.64 (d, *J* = 8.0Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 112.2, 118.6, 128.9, 132.0, 132.6.

2-methylbenzonitrile: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 2.53 (s, 3H), 7.26 (d, *J* = 8.0Hz, 1H), 7.31 (t, *J* = 8.0Hz, 1H), 7.47 (t, *J* = 8.0Hz, 1H), 7.56 (d, *J* = 8.0Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 20.2, 112.4, 117.9, 126.0, 130.0, 132.2, 132.4, 141.6.

3-methylbenzonitrile: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 2.37 (s, 3H), 7.34 (t, *J* = 8.0Hz, 1H), 7.41 (t, *J* = 8.0Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 20.8, 111.8, 118.7, 128.7, 132.1, 133.4, 138.8.

4-methylbenzonitrile: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 2.42 (s, 3H), 7.27 (d, *J* = 8.0Hz, 2H), 7.52 (d, *J* = 8.0Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 21.7, 109.1, 119.0, 129.7, 131.9, 143.6.

2-methoxybenzonitrile: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 2.53 (s, 3H), 7.27 (t, *J* = 8.0Hz, 1H), 7.31 (t, *J* = 8.0Hz, 1H), 7.48 (t, *J* = 8.0Hz, 1H), 7.57 (t, *J* = 8.0Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 20.2, 112.4, 117.9, 126.0, 130.0, 132.2, 132.4, 141.6.

3-methoxybenzonitrile: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 3.83 (s, 3H), 7.13 (d, *J* = 8.0Hz, 2H), 7.23 (d, *J* = 8.0Hz, 1H), 7.37 (t, *J* = 8.0Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 55.3, 112.9, 116.6, 118.6, 119.1, 124.2, 130.1, 159.4.

4-methoxybenzonitrile: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 3.86 (s, 3H), 6.95 (d, *J* = 8.0Hz, 2H), 7.58 (d, *J* = 8.0Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 55.5, 103.9, 114.7, 119.2, 133.9, 162.8.

4-chlorobenzonitrile: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.47 (d, *J* = 8.0Hz, 2H), 7.61 (d, *J* = 8.0Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 110.7, 117.9, 129.6, 133.3, 139.4.

4-nitrobenzonitrile: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.89 (d, *J* = 8.0Hz, 2H), 8.35 (d, *J* = 8.0Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 116.7, 118.2, 124.2, 133.4, 150.0.

3,4-(Methylenedioxy)benzonitrile: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 6.08 (s, 2H), 6.87 (d, *J* = 8.0Hz, 1H), 7.02 (s, 1H), 7.21 (d, *J* = 8.0Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 102.1, 104.8, 109.0, 111.2, 118.8, 128.0, 147.9, 151.4.

1-naphthonitrile: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.47 (t, *J* = 8.0Hz, 1H), 7.58 (t, *J* = 8.0Hz, 1H), 7.64 (t, *J* = 8.0Hz, 1H), 7.86 (t, *J* = 8.0Hz, 2H), 8.02 (d, *J* = 8.0Hz, 1H), 8.19 (d, *J* = 8.0Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 110.0, 117.8, 124.8, 127.3, 128.4, 128.5, 132.1, 132.4, 132.7, 133.1.

3-cyanopyridine: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.49 (t, *J* = 8.0Hz, 1H), 8.02 (d, *J* = 8.0Hz, 1H), 8.86 (s, 1H), 8.92 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 109.8, 116.3, 123.5, 139.1, 152.2, 152.7.

2-thiophenecarbonitrile: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$,

ppm): δ 109.2, 113.9, 127.3, 132.4, 137.1

benzaldehyde: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.50 (t, *J* = 8.0Hz, 2H), 7.60 (t, *J* = 8.0Hz, 1H), 7.86 (d, *J* = 8.0Hz, 2H), 9.99 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 129.1, 129.8, 134.6, 136.5, 192.5.

2-methylbenzaldehyde: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 2.66 (s, 3H), 7.25 (d, *J* = 8.0Hz, 1H), 7.35 (t, *J* = 8.0Hz, 1H), 7.47 (t, *J* = 8.0Hz, 1H), 7.79 (d, *J* = 8.0Hz, 1H), 10.26 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 19.9, 126.3, 131.8, 132.1, 133.7, 134.2, 140.6, 192.8.

3-methylbenzaldehyde: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 2.41 (s, 3H), 7.39 (t, *J* = 8.0Hz, 2H), 7.66 (s, 2H), 9.96 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 21.2, 127.2, 128.9, 130.0, 135.3, 136.5, 138.9, 192.6.

4-methylbenzaldehyde: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 2.44 (s, 3H), 7.33 (d, *J* = 8.0Hz, 2H), 7.77 (t, *J* = 8.0Hz, 2H), 9.96 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 21.2, 71.8, 127.9, 129.1, 135.3, 137.3.

2-methoxybenzaldehyde: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 3.89 (s, 3H), 6.95-7.01 (m, 2H), 7.53 (t, *J* = 8.0Hz, 1H), 7.80 (d, *J* = 8.0Hz, 1H), 10.45 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 55.3, 111.4, 120.3, 124.5, 128.0, 135.7, 161.5, 189.4.

3-methoxybenzaldehyde: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 3.06 (s, 3H), 7.13-7.16 (m, 1H), 7.33-7.43 (m, 3H), 9.94 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 55.3, 112.0, 121.3, 123.3, 129.9, 137.7, 160.0, 191.9.

4-methoxybenzaldehyde: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 3.73 (s, 3H), 6.86 (d, *J* = 12.0Hz, 2H), 7.69 (d, *J* = 12.0Hz, 2H), 9.73 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 55.2, 114.0, 129.6, 131.6, 164.2, 190.4.

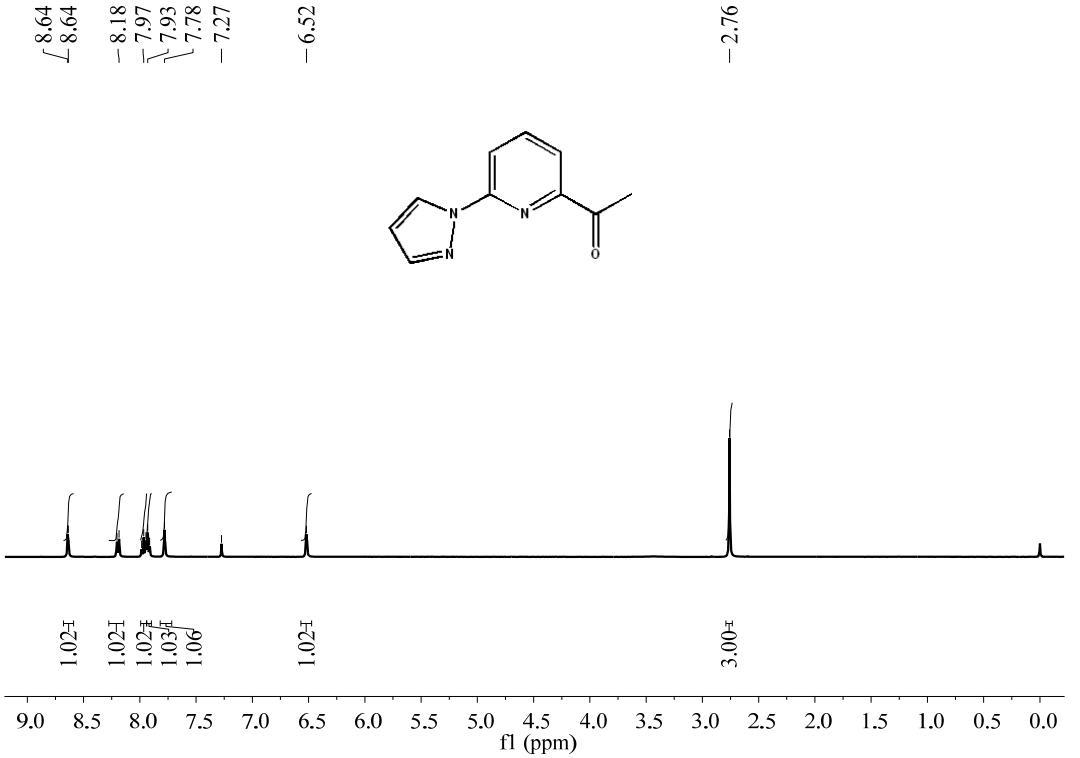
4-chlorobenzoic aldehyde: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.53 (d, *J* = 12.0Hz, 2H), 7.83 (d, *J* = 12.0Hz, 2H), 9.99 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 129.5, 130.9, 134.7, 141.0, 190.9.

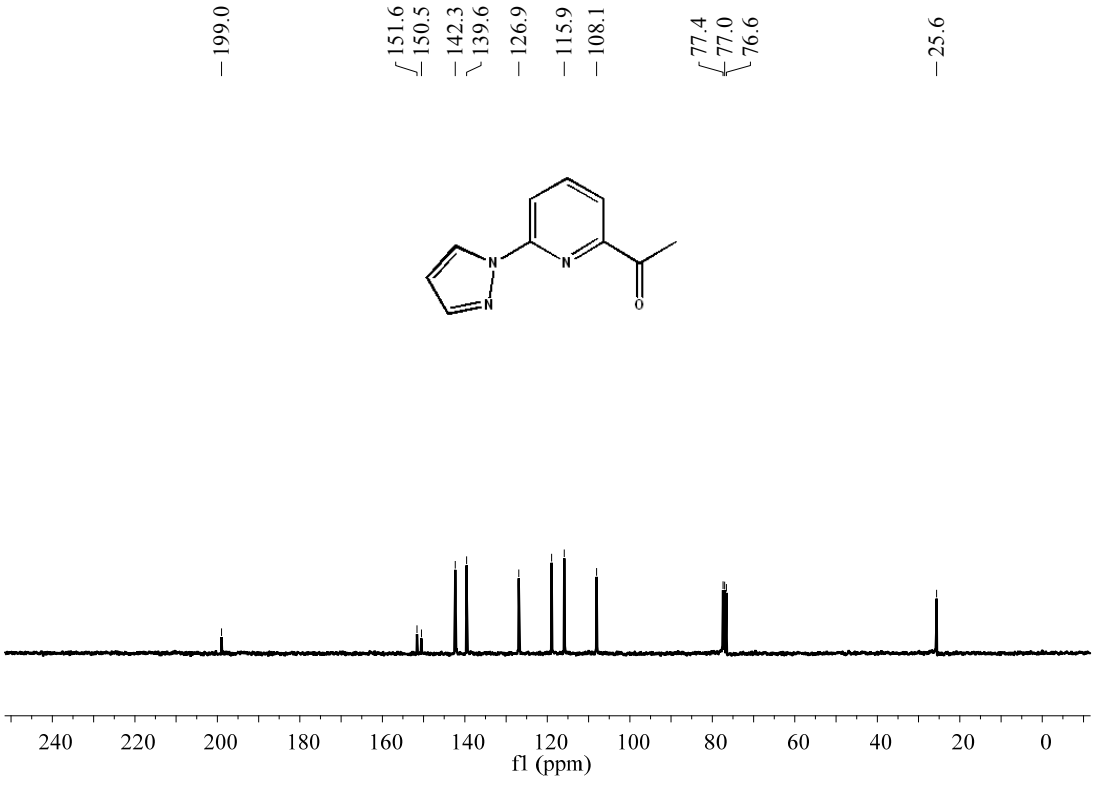
4-nitrobenzaldehyde: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.09 (d, *J* = 8.0Hz, 2H), 8.41 (d, *J* = 12.0Hz, 2H), 10.17(s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 124.3, 130.5, 140.1, 151.1, 190.4.

3-pyridinecarboxaldehyde: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.51-7.54 (m, 1H), 8.20 (d, *J* = 8.0Hz, 1H), 8.87 (d, *J* = 8.0Hz, 1H), 9.11 (d, *J* = 4.0Hz, 1H), 10.15 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 124.0, 131.3, 135.7, 151.7, 154.5, 190.8.

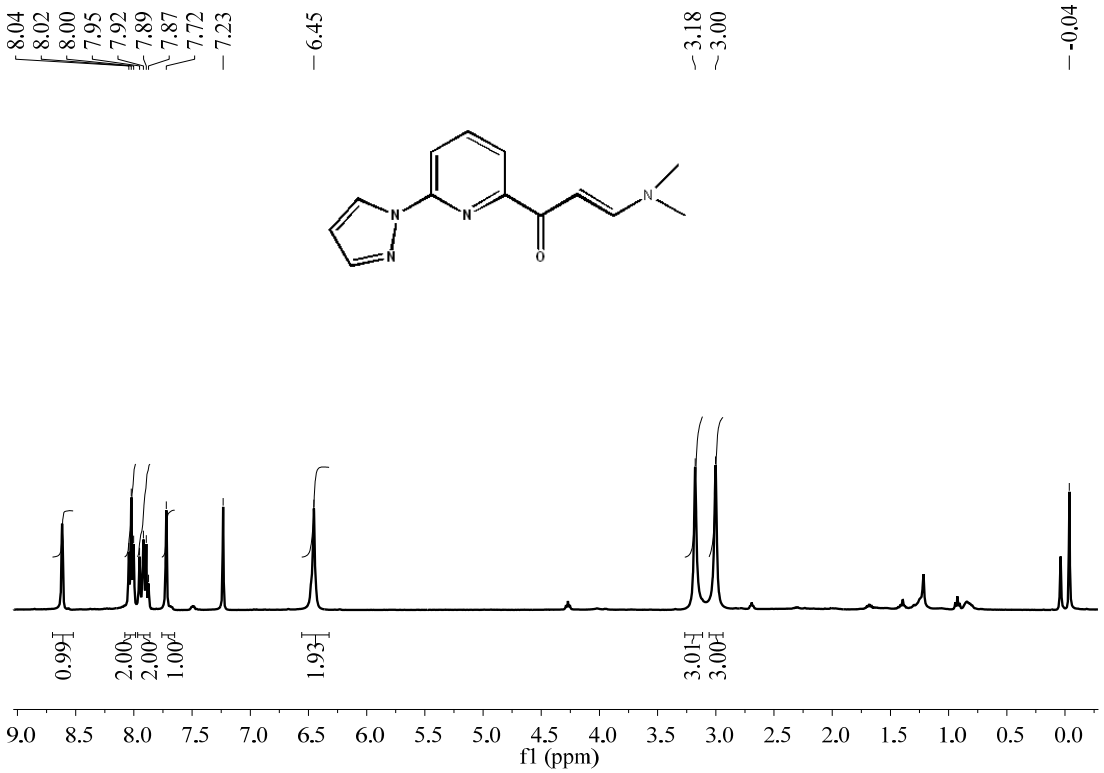
2-thenaldehyde: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.21-7.24 (m, 1H), 7.77-7.80 (m, 2H), 9.96 (d, *J* = 4.0Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 128.2, 134.9, 136.3, 143.7, 182.8.

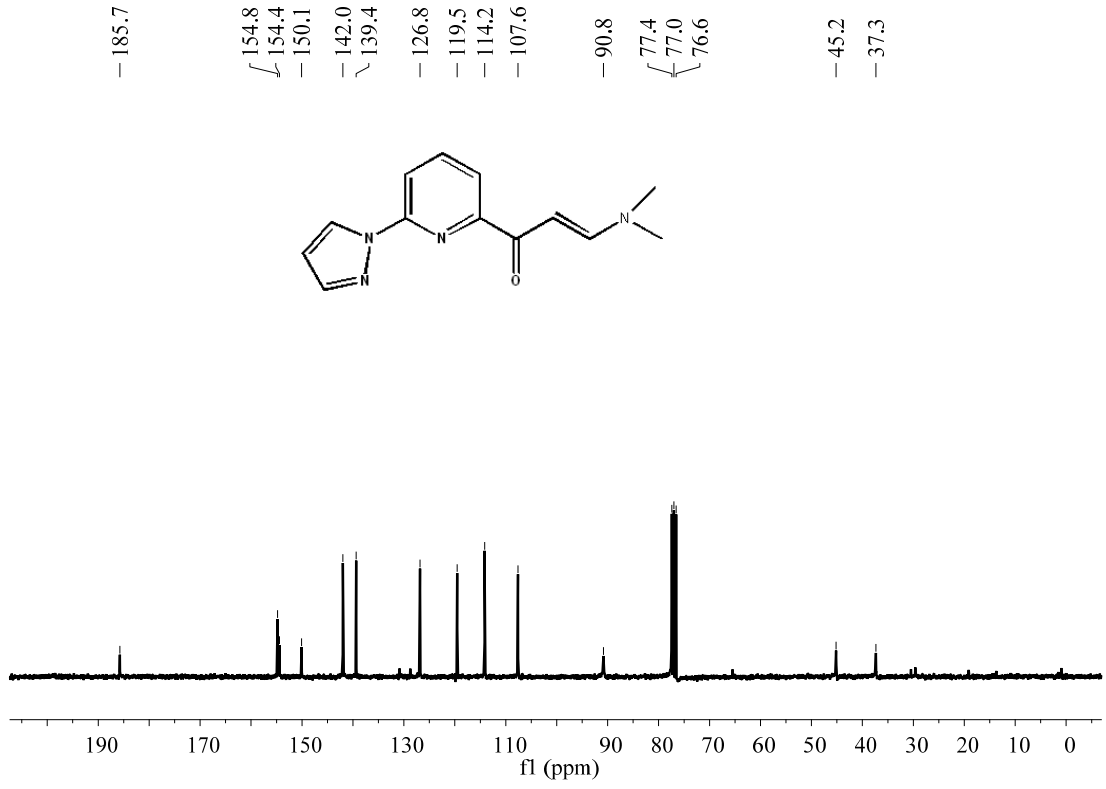
The ^{1}H and ^{13}C NMR spectra of 1-(6-(1H-pyrazol-1-yl)pyridin-2-yl)ethanone



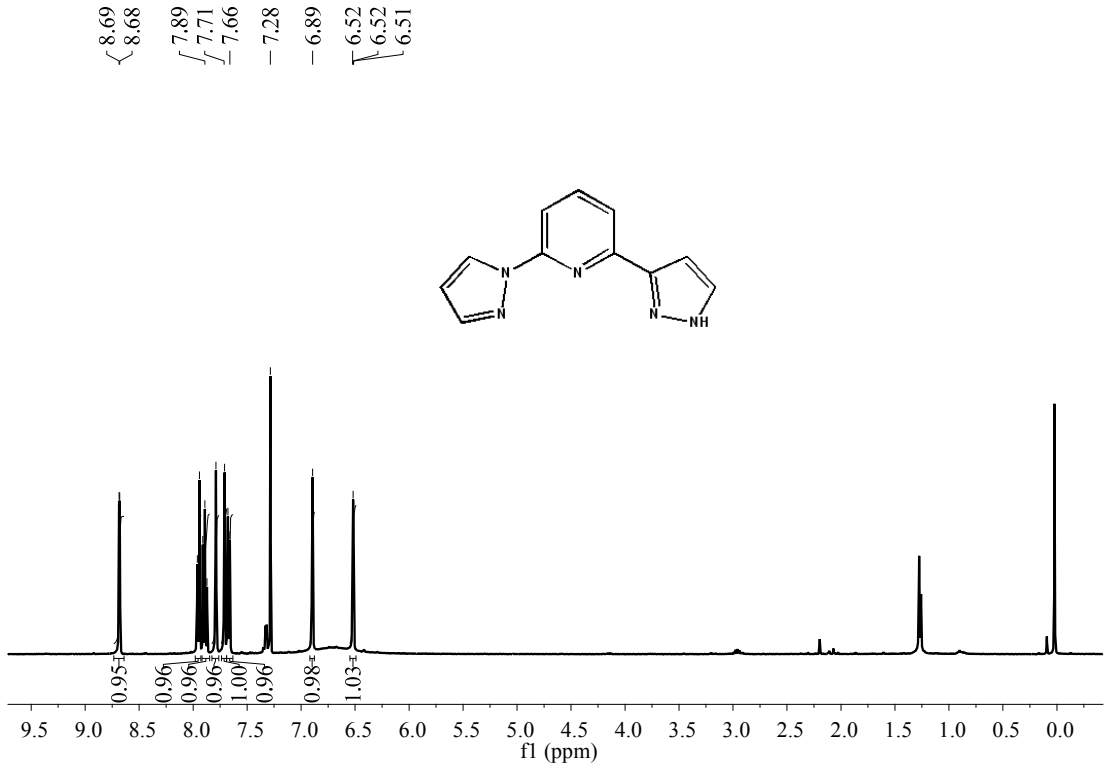


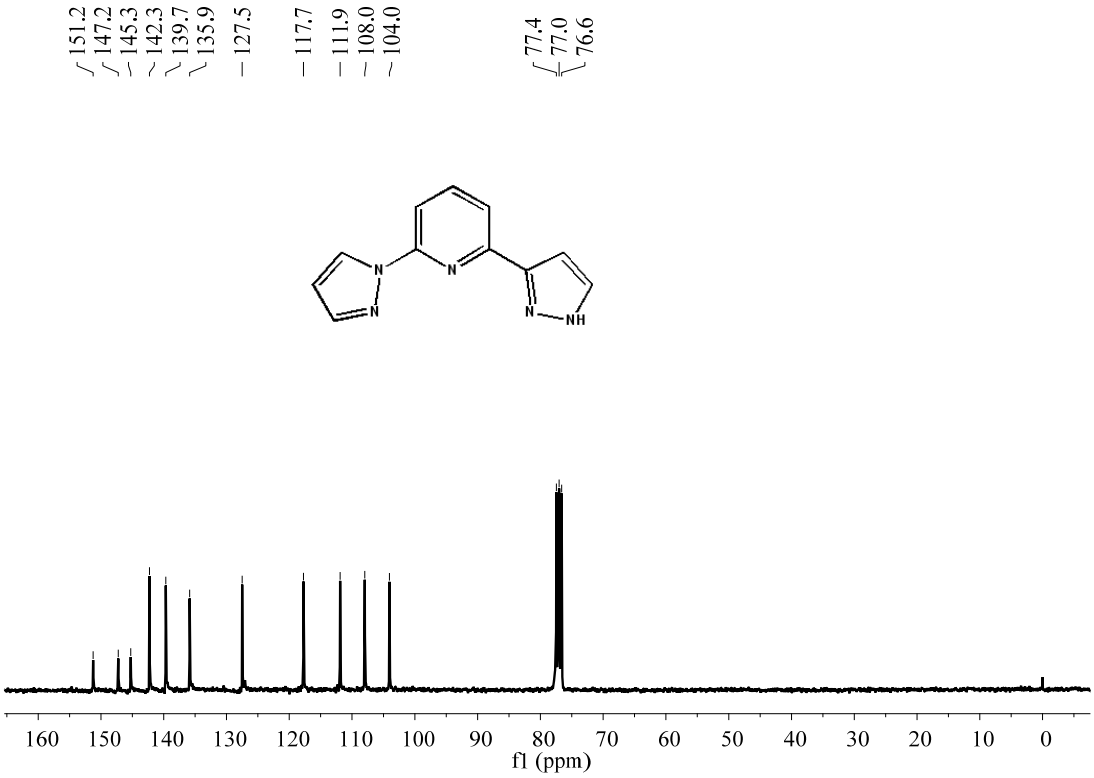
The ^{1}H and ^{13}C NMR spectra of 1-(6-(1H-pyrazol-1-yl)pyridin-2-yl)-3-(dimethylamino)prop-2-en-1-one



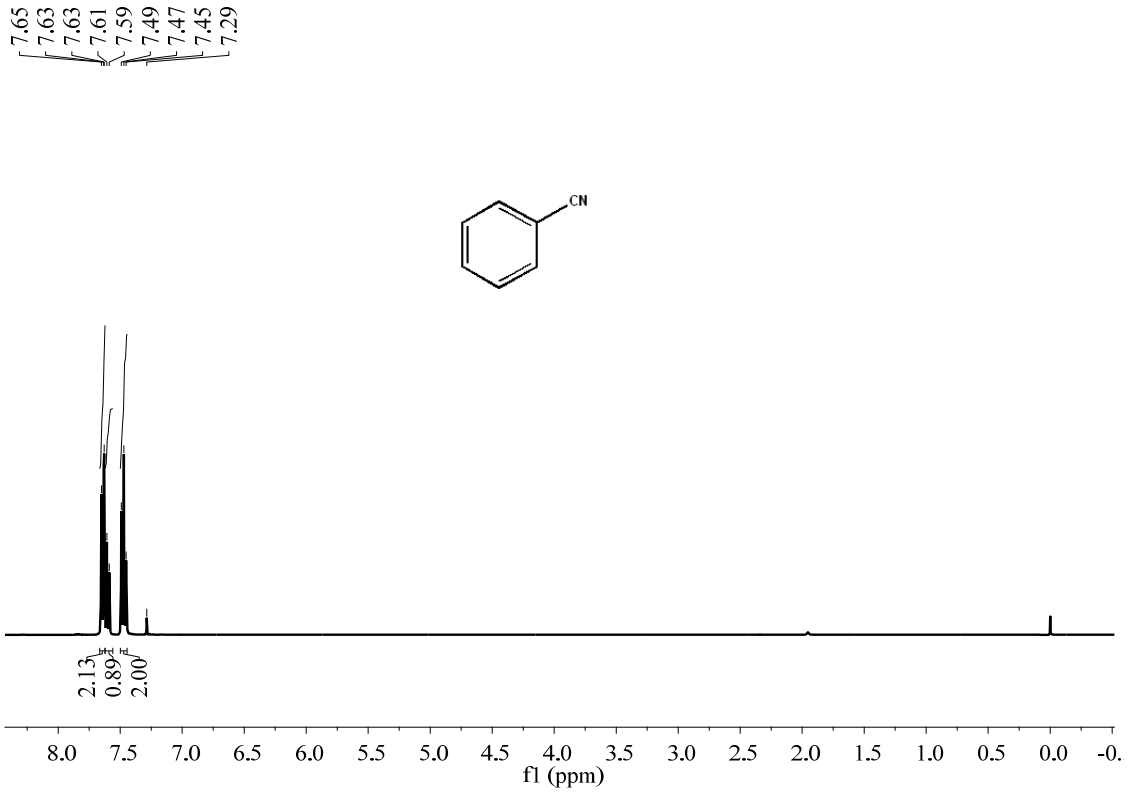


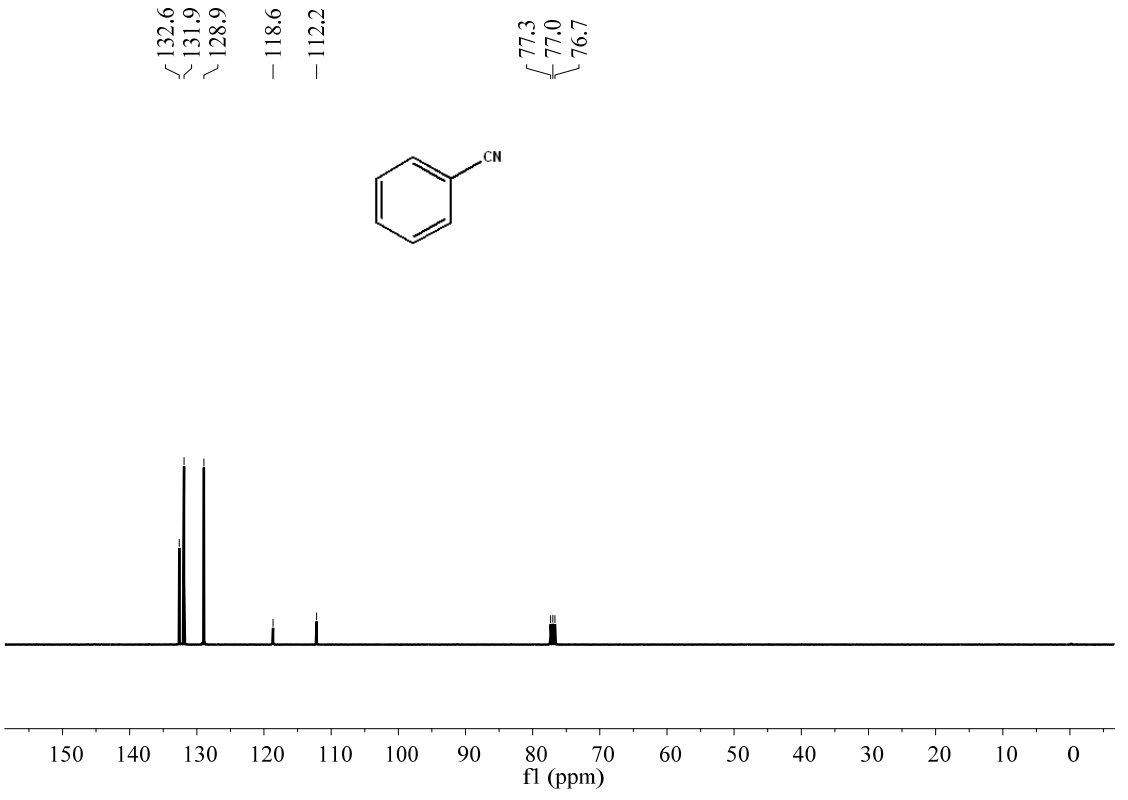
The ^{1}H and ^{13}C NMR spectra of 2-(1H-pyrazol-1-yl)-6-(1H-pyrazol-3-yl)pyridine



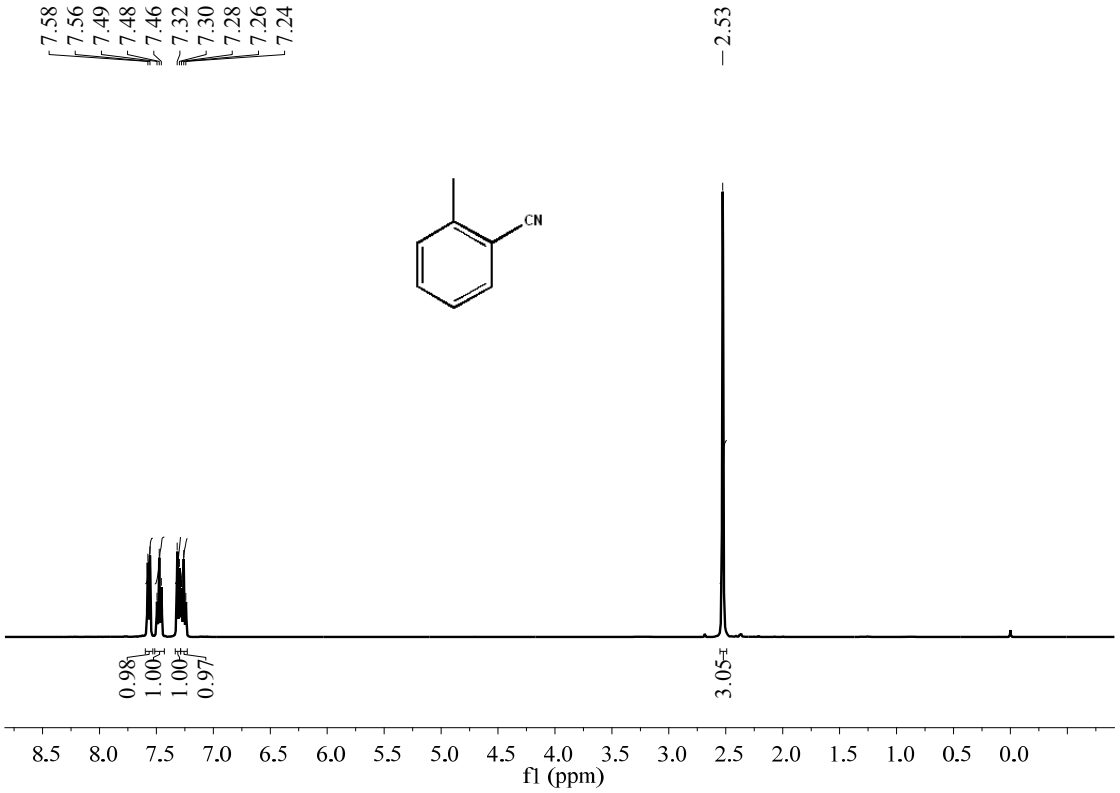


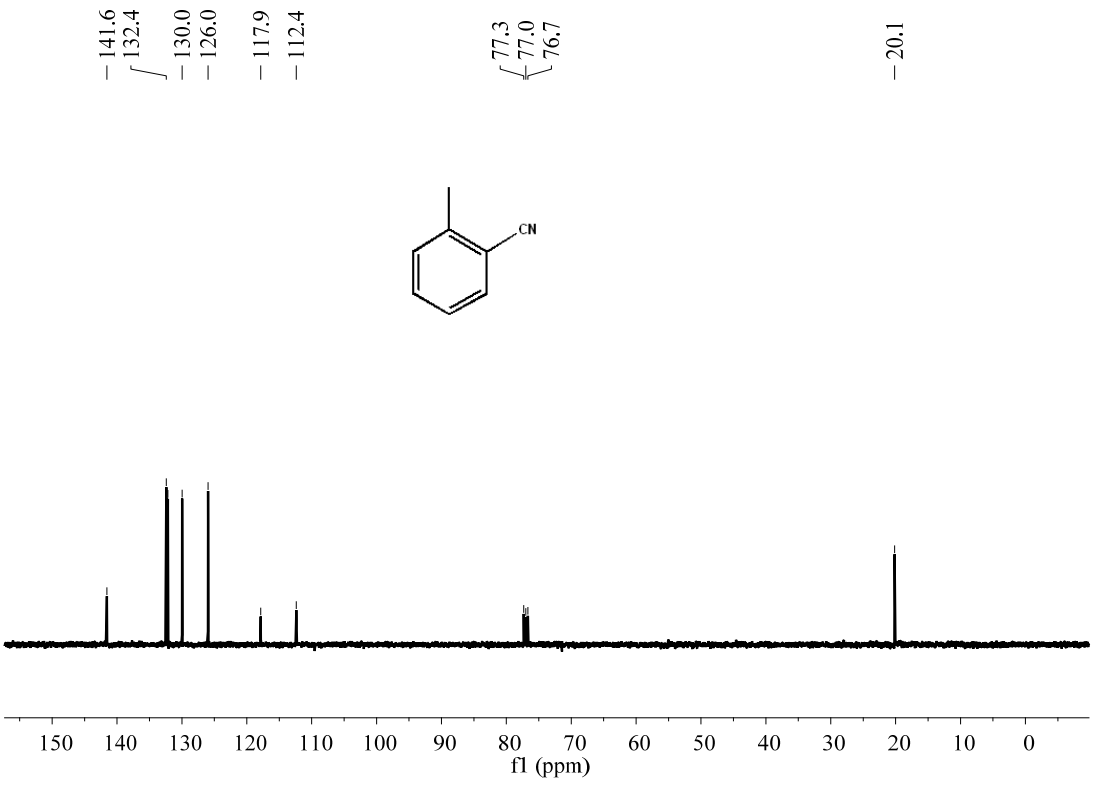
The ^{1}H and ^{13}C NMR spectra of the product benzonitrile



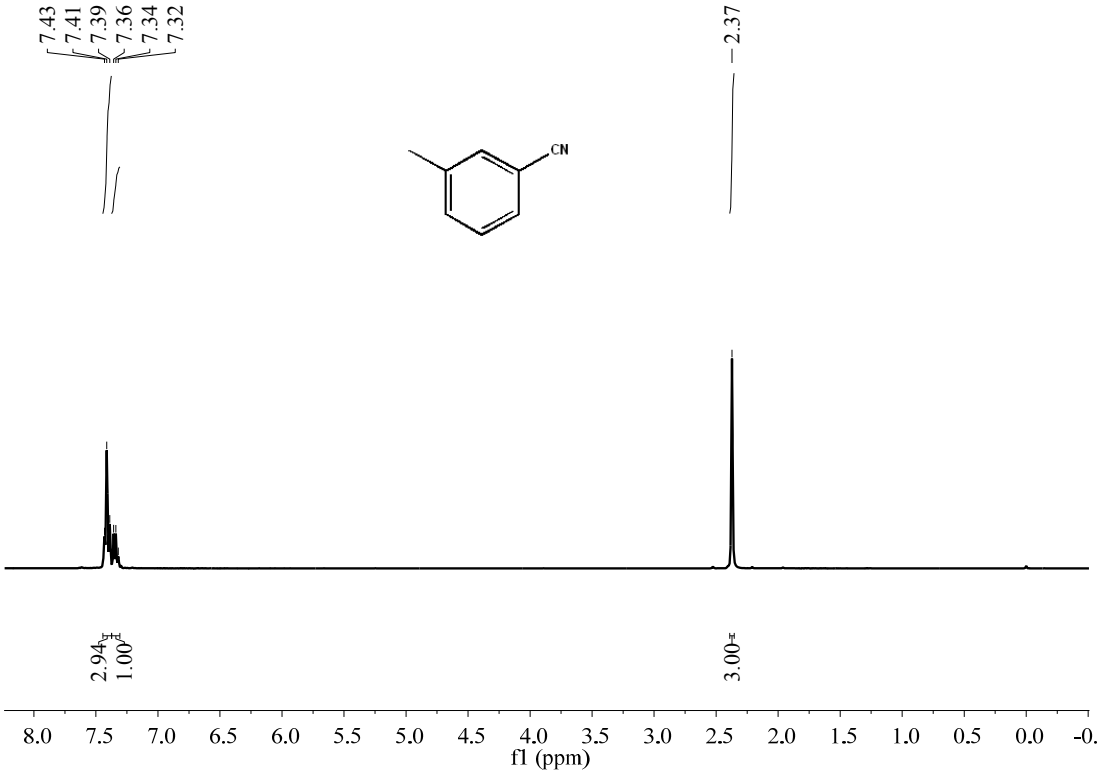


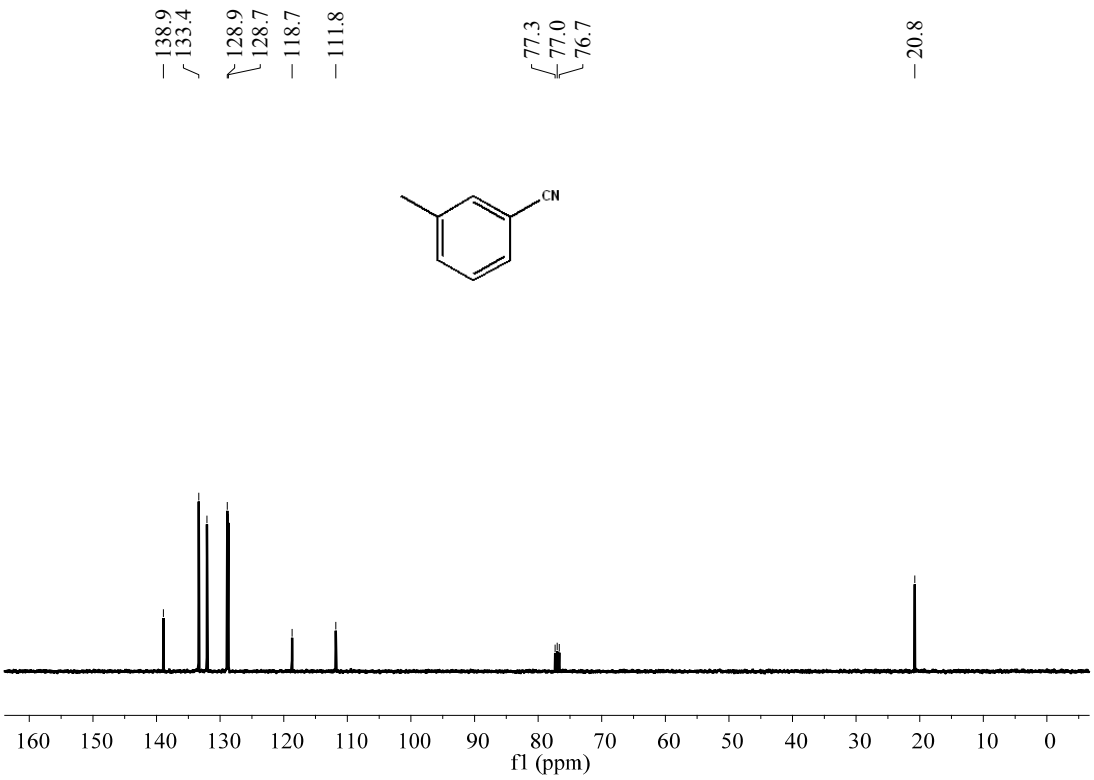
The ^{1}H and ^{13}C NMR spectra of the product 2-methylbenzonitrile



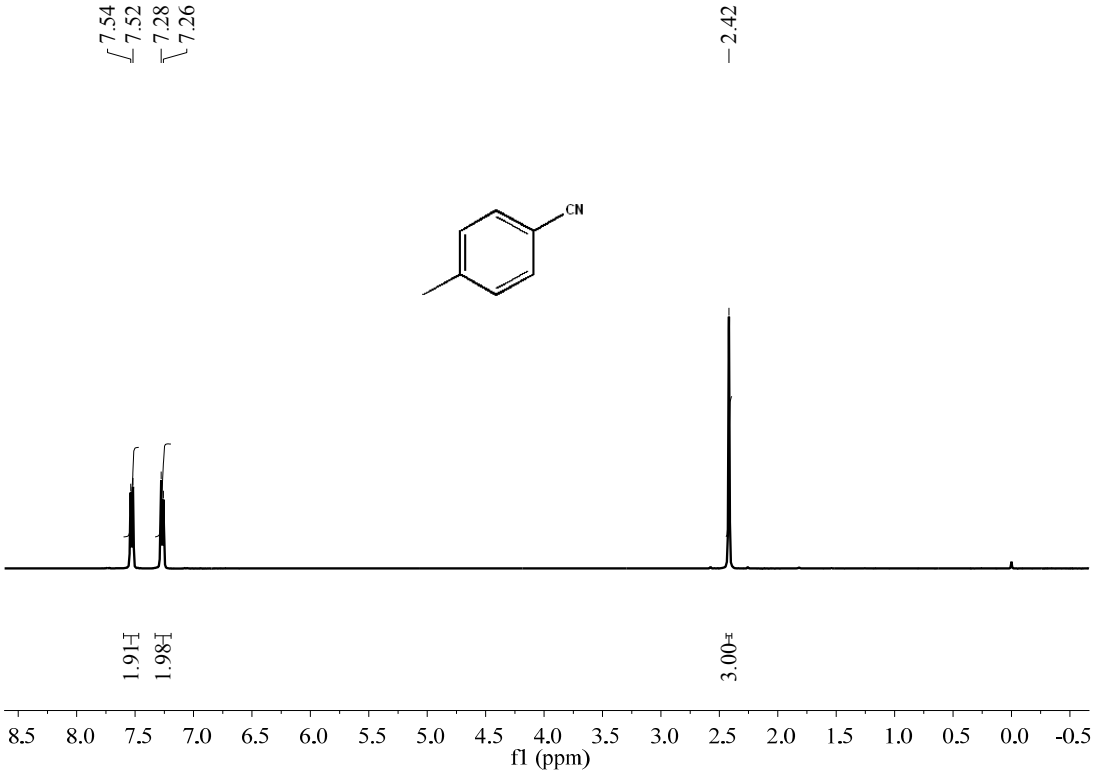


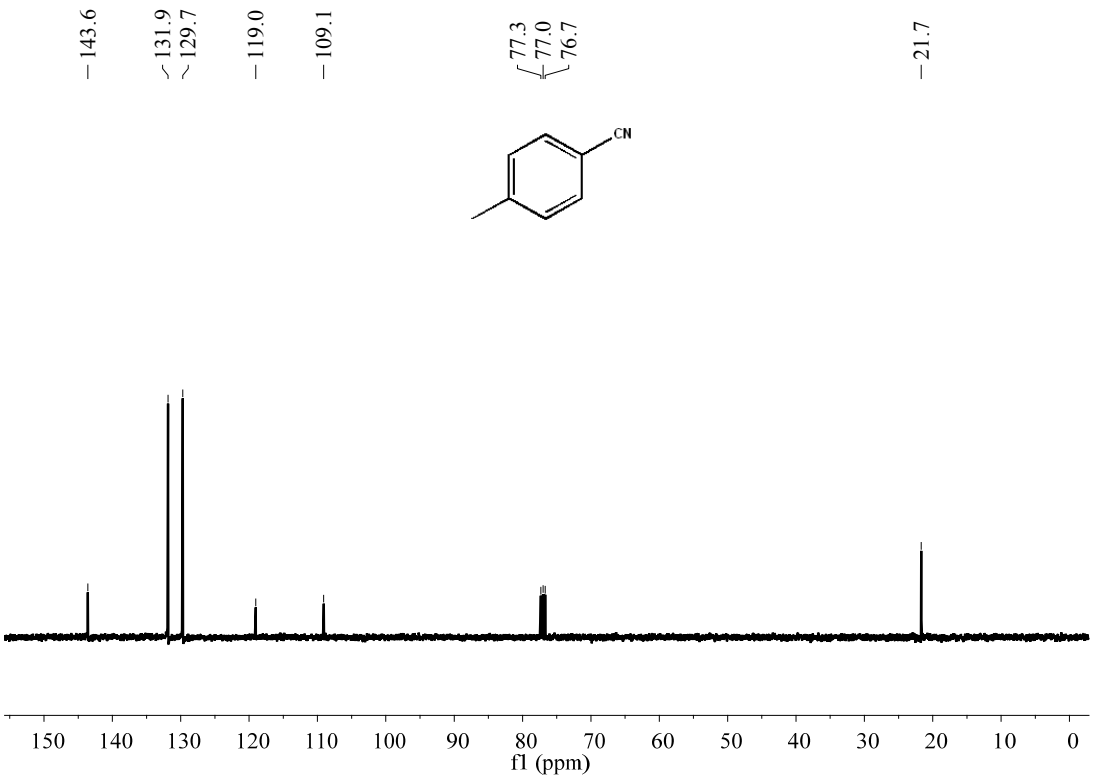
The ^{1}H and ^{13}C NMR spectra of the product 3-methylbenzonitrile



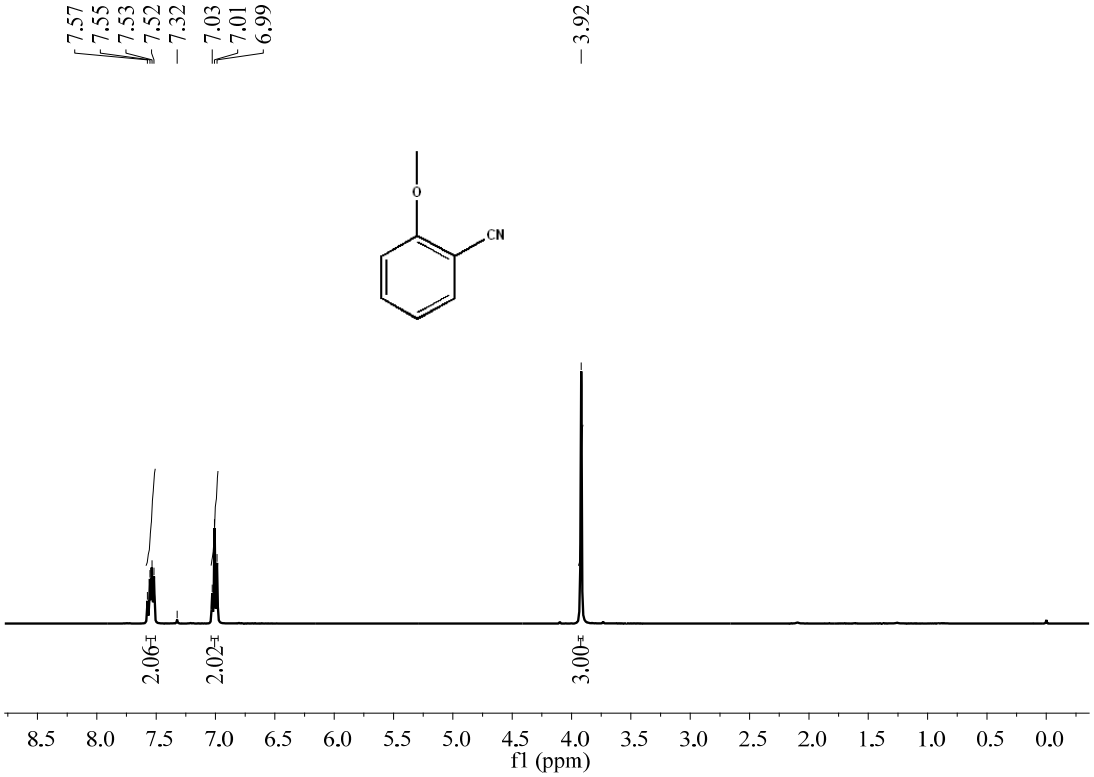


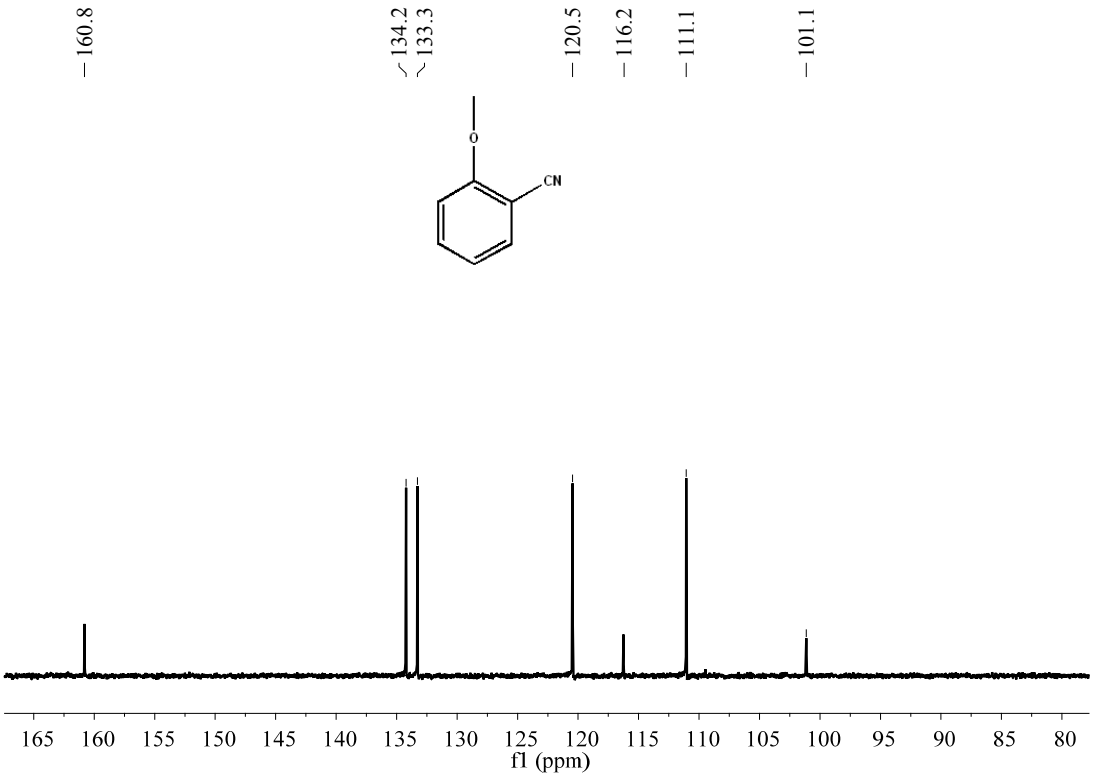
The ^{1}H and ^{13}C NMR spectra of the product 4-methylbenzonitrile



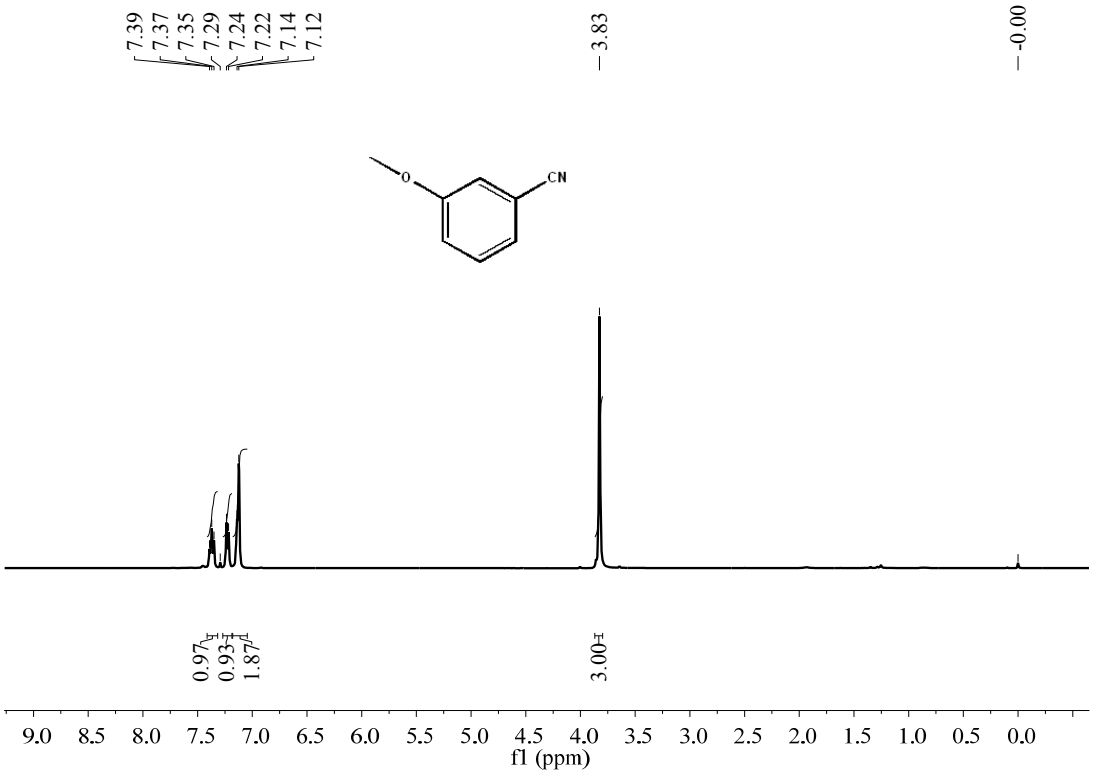


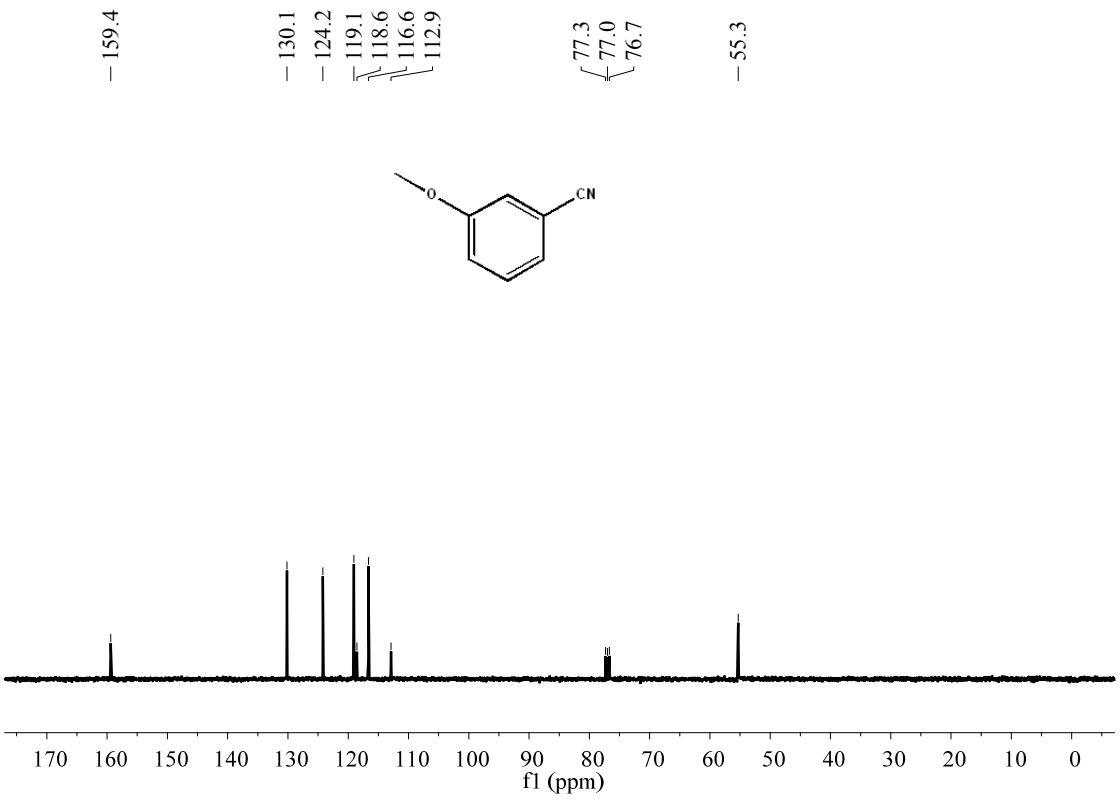
The ^{1}H and ^{13}C NMR spectra of the product 2-methoxybenzonitrile



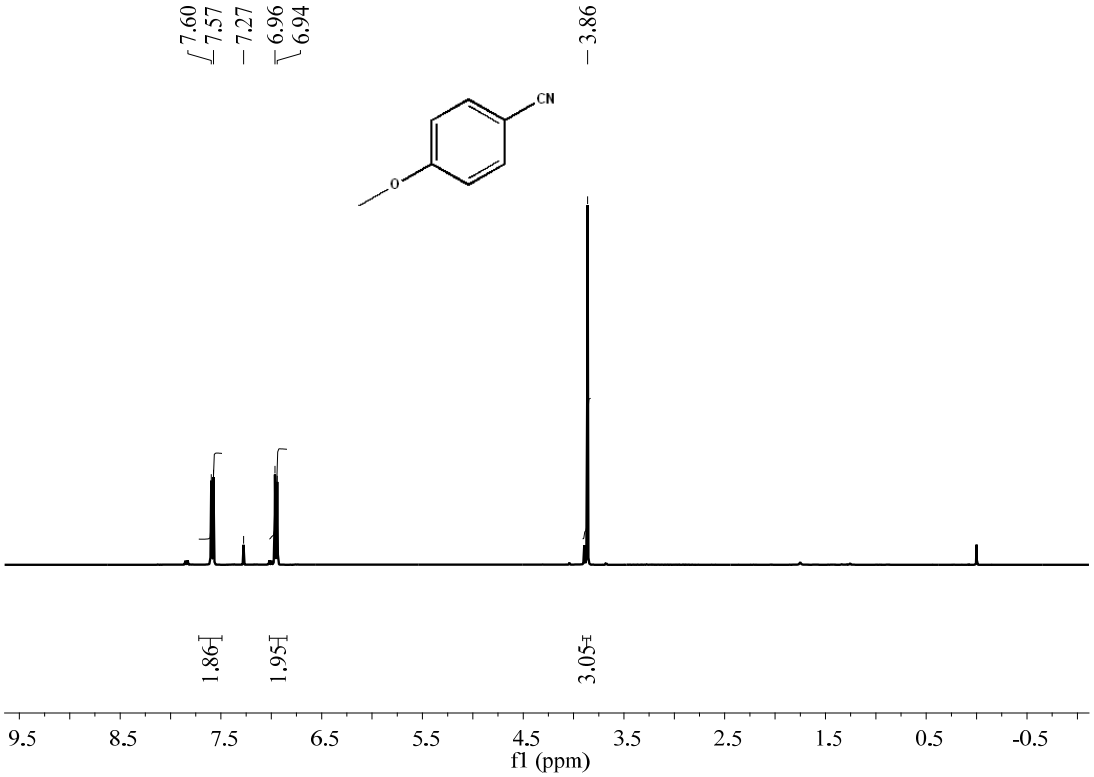


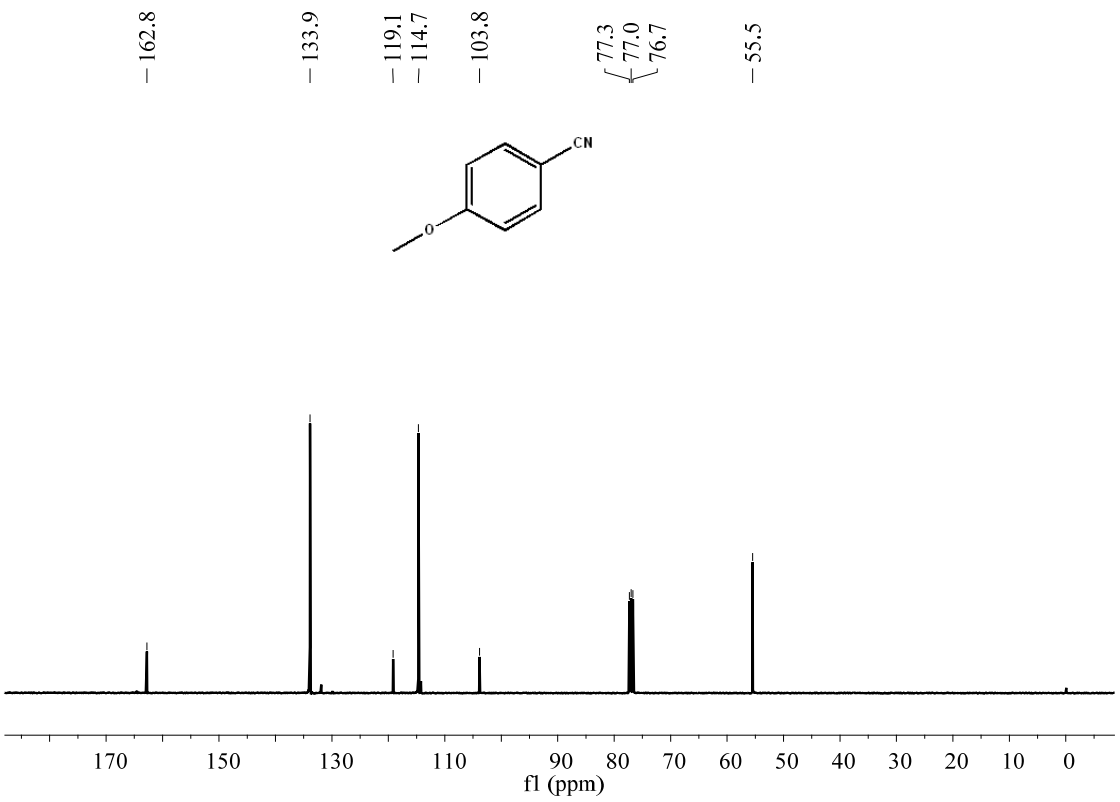
The ^{1}H and ^{13}C NMR spectra of the product 3-methoxybenzonitrile



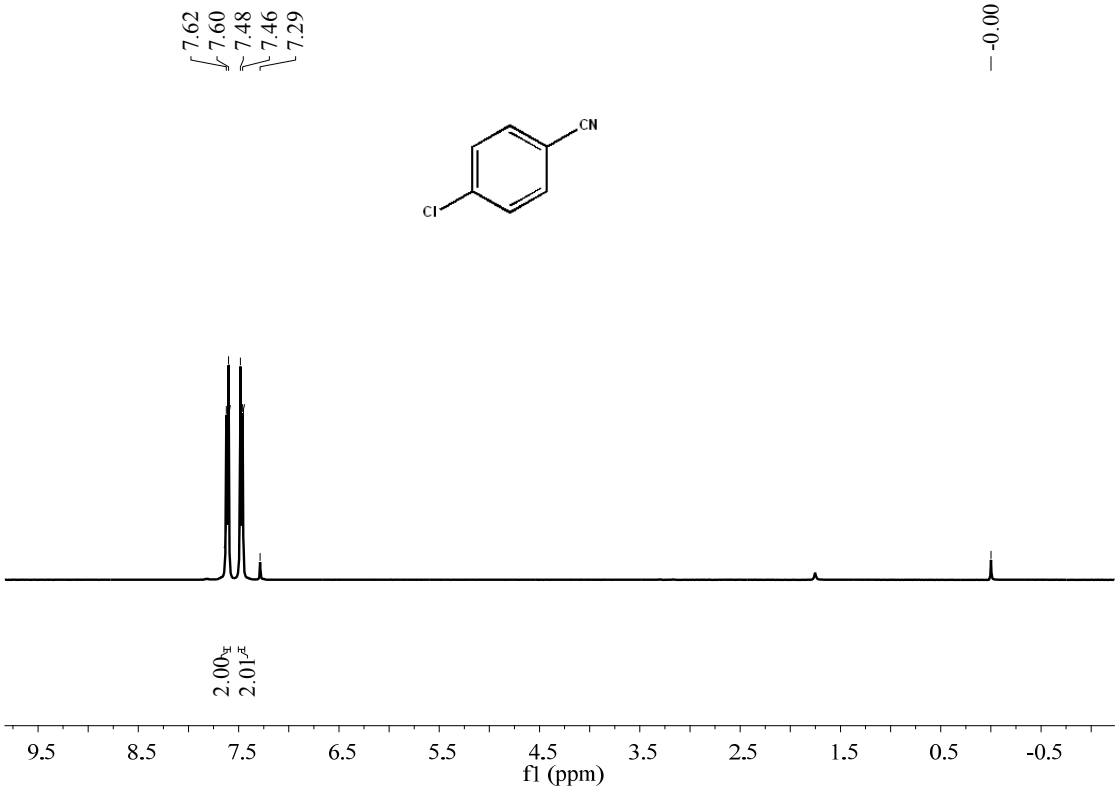


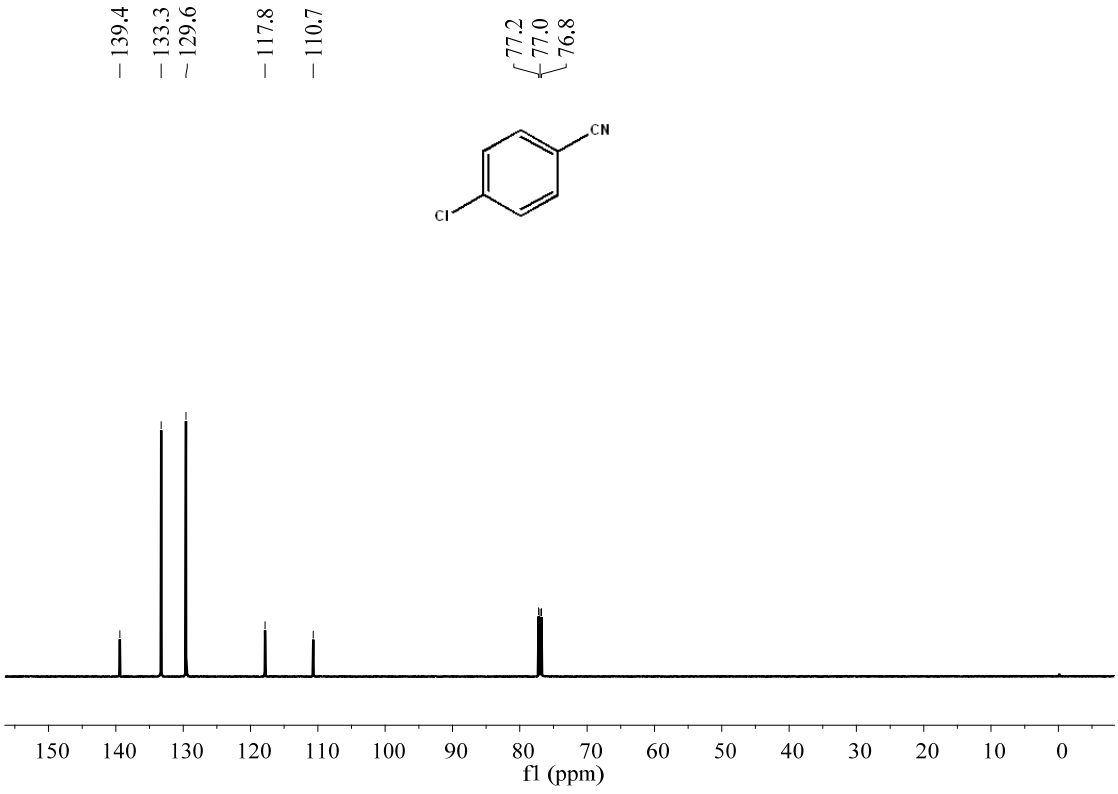
The ^{1}H and ^{13}C NMR spectra of the product 4-methoxybenzonitrile



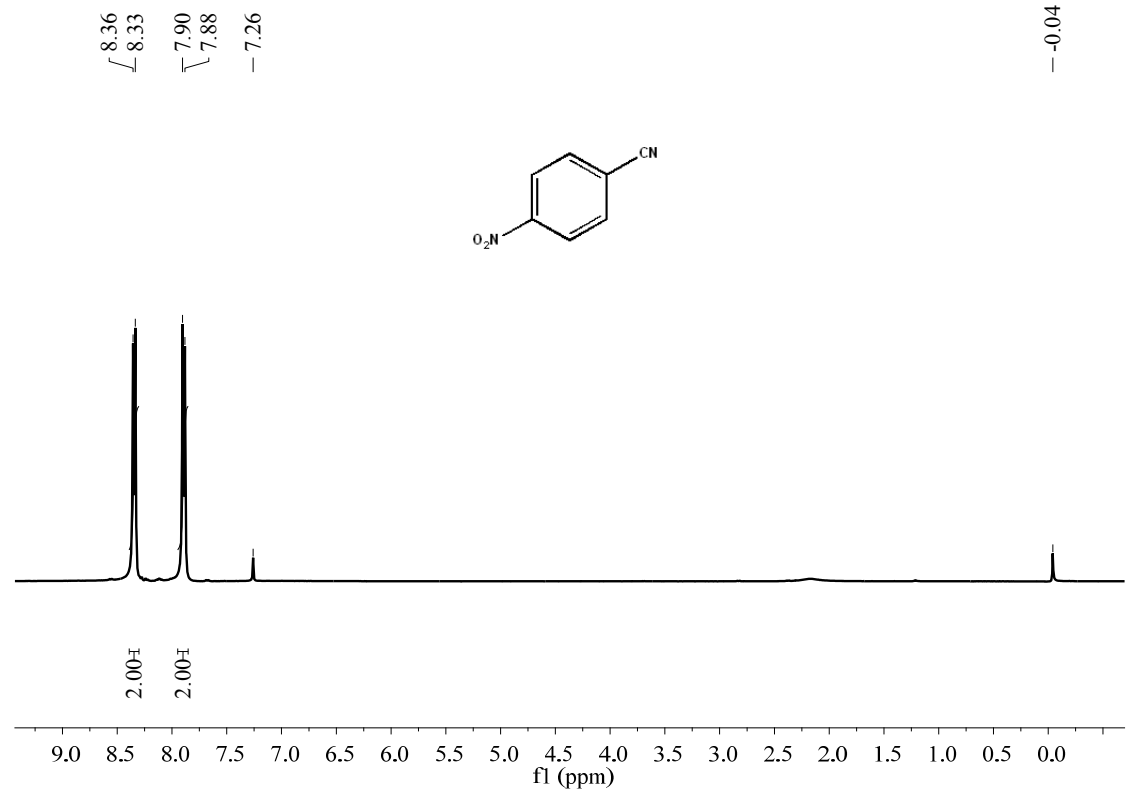


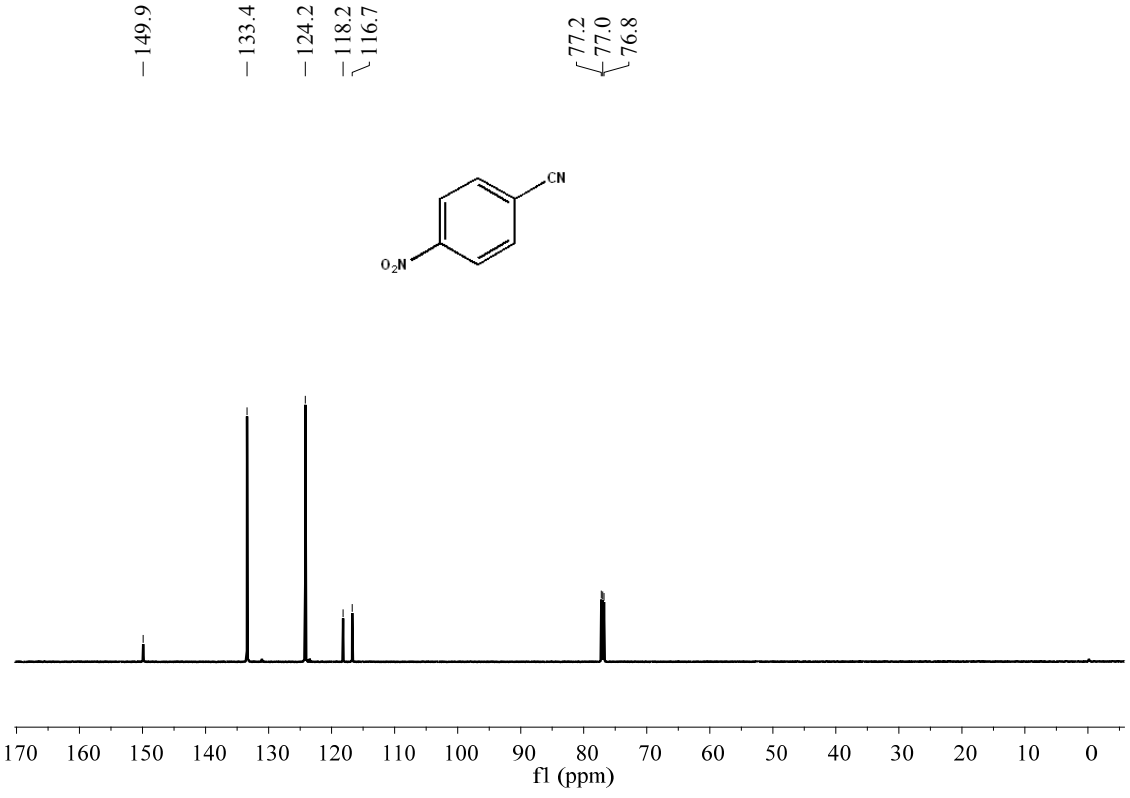
The ^{1}H and ^{13}C NMR spectra of the product 4-chlorobenzonitrile



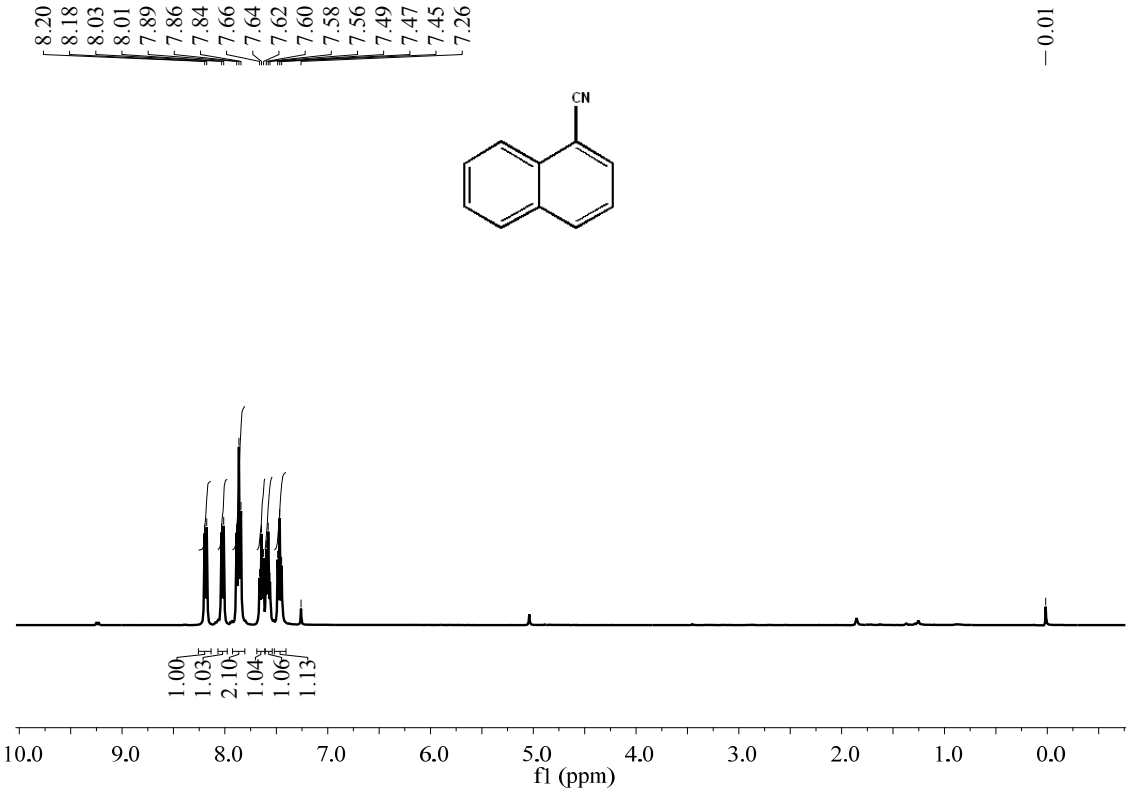


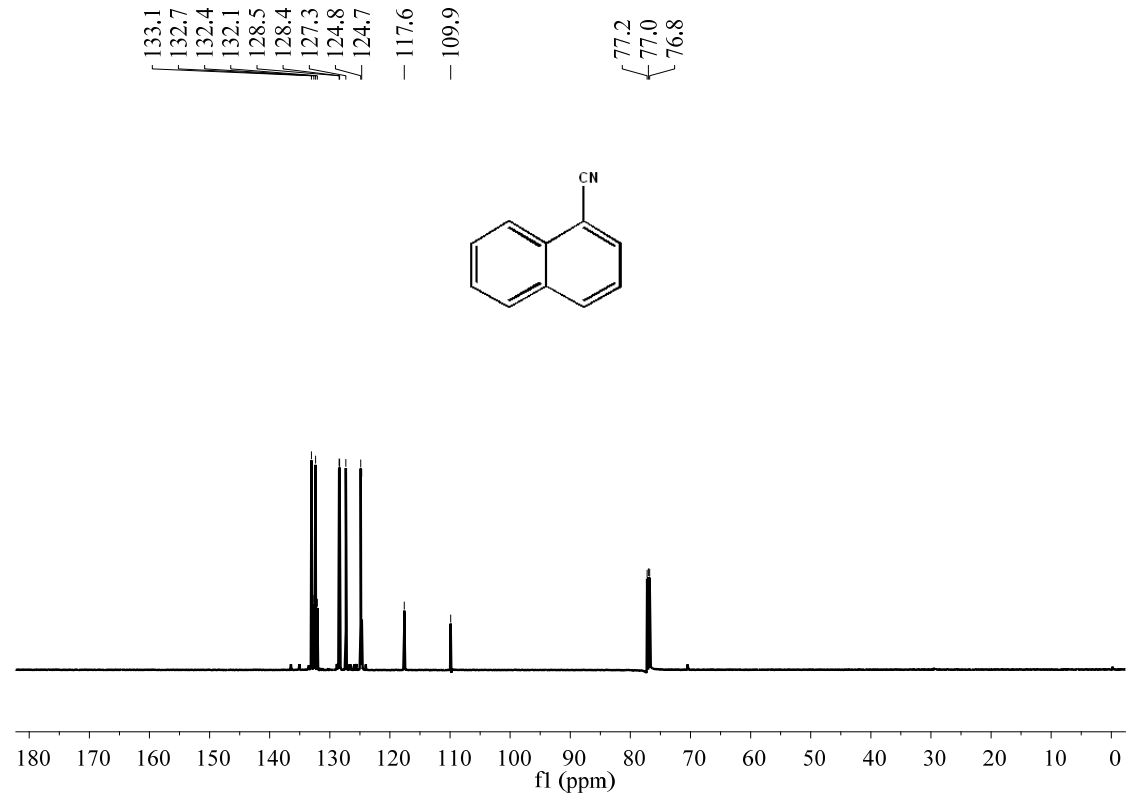
The ^{1}H and ^{13}C NMR spectra of the product 4-nitrobenzonitrile



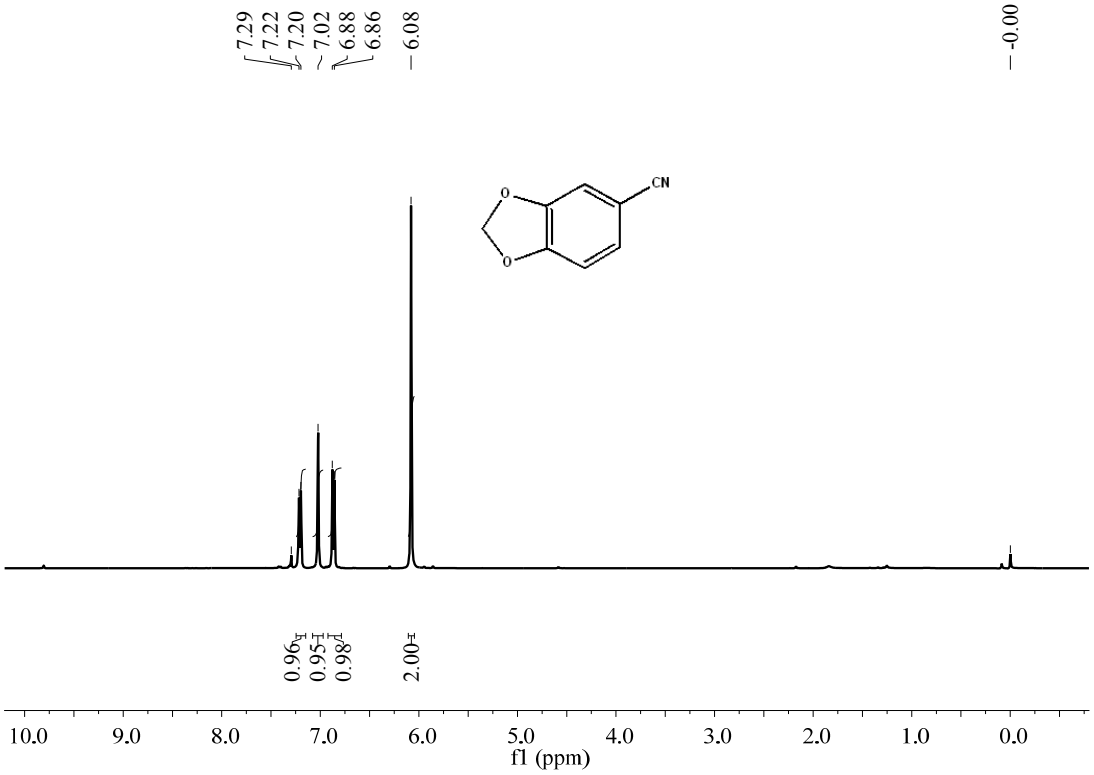


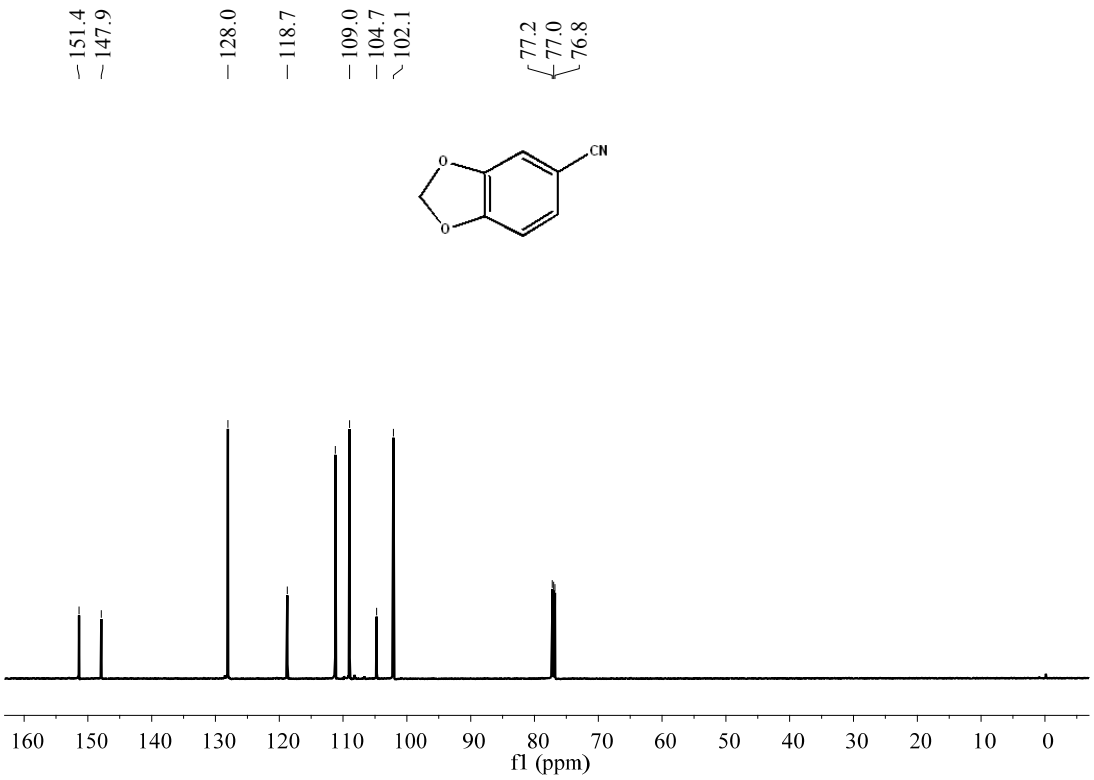
The ^{1}H and ^{13}C NMR spectra of the product 1-naphthonitrile



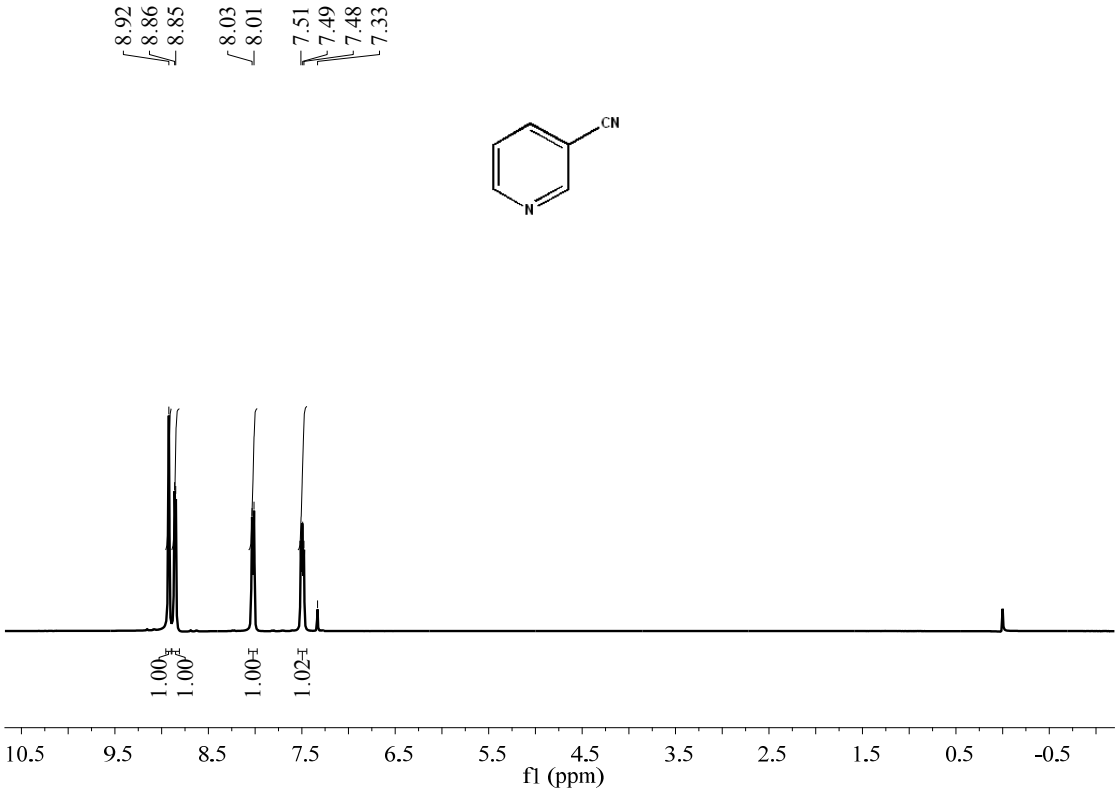


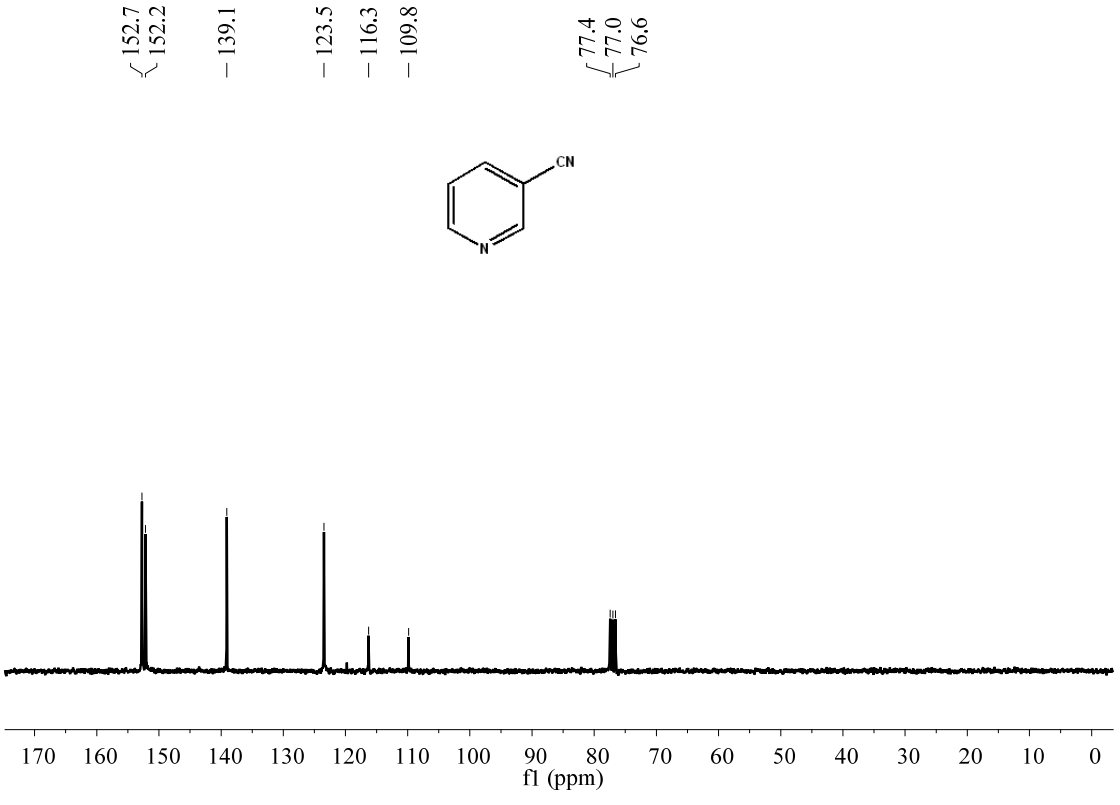
The ^{1}H and ^{13}C NMR spectra of the product 3,4-(methylenedioxy)benzonitrile



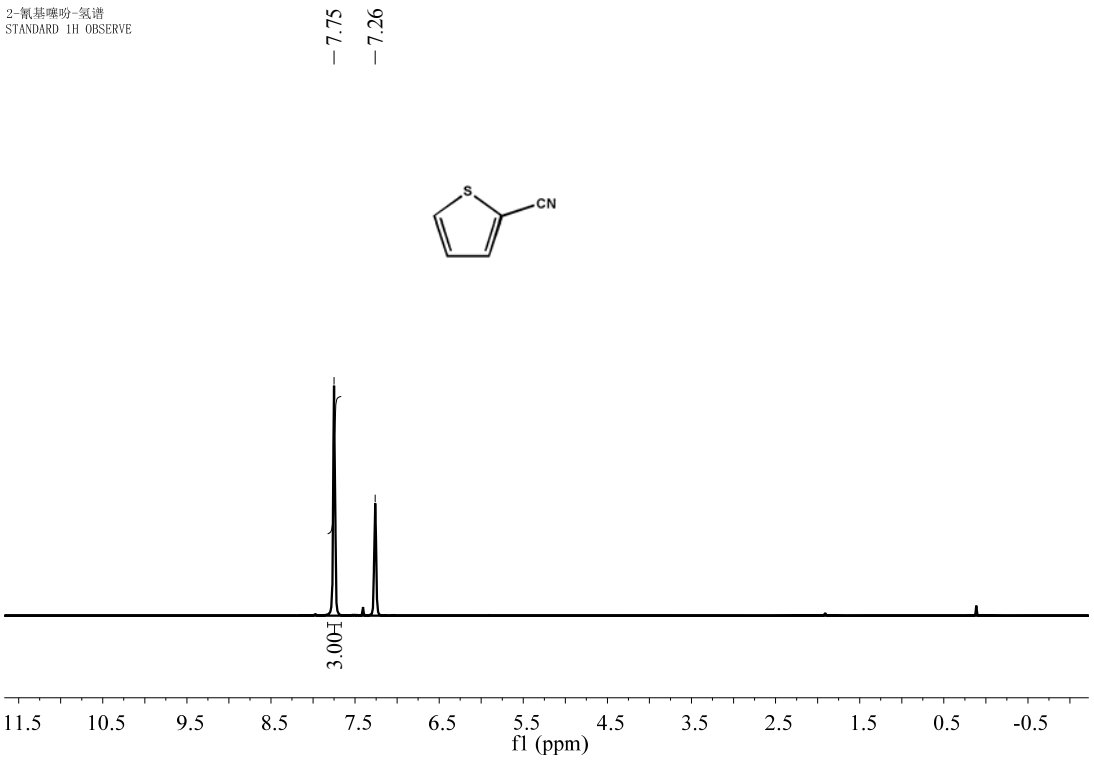


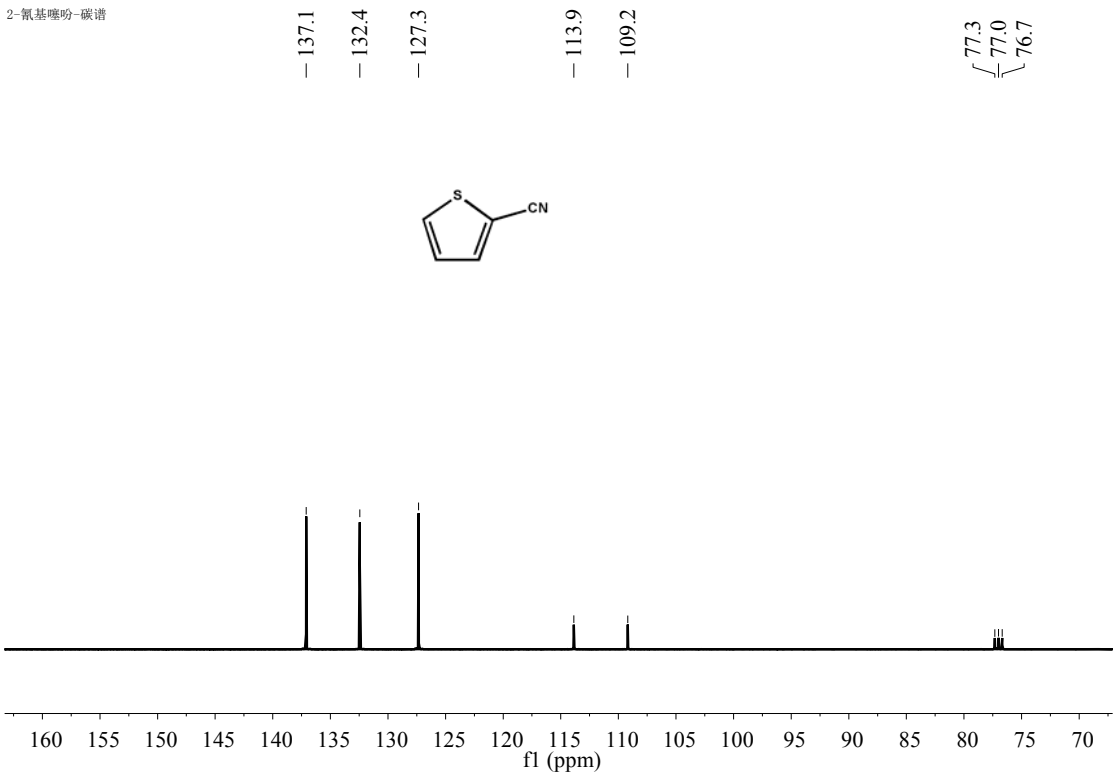
The ^{1}H and ^{13}C NMR spectra of the product 3-cyanopyridine



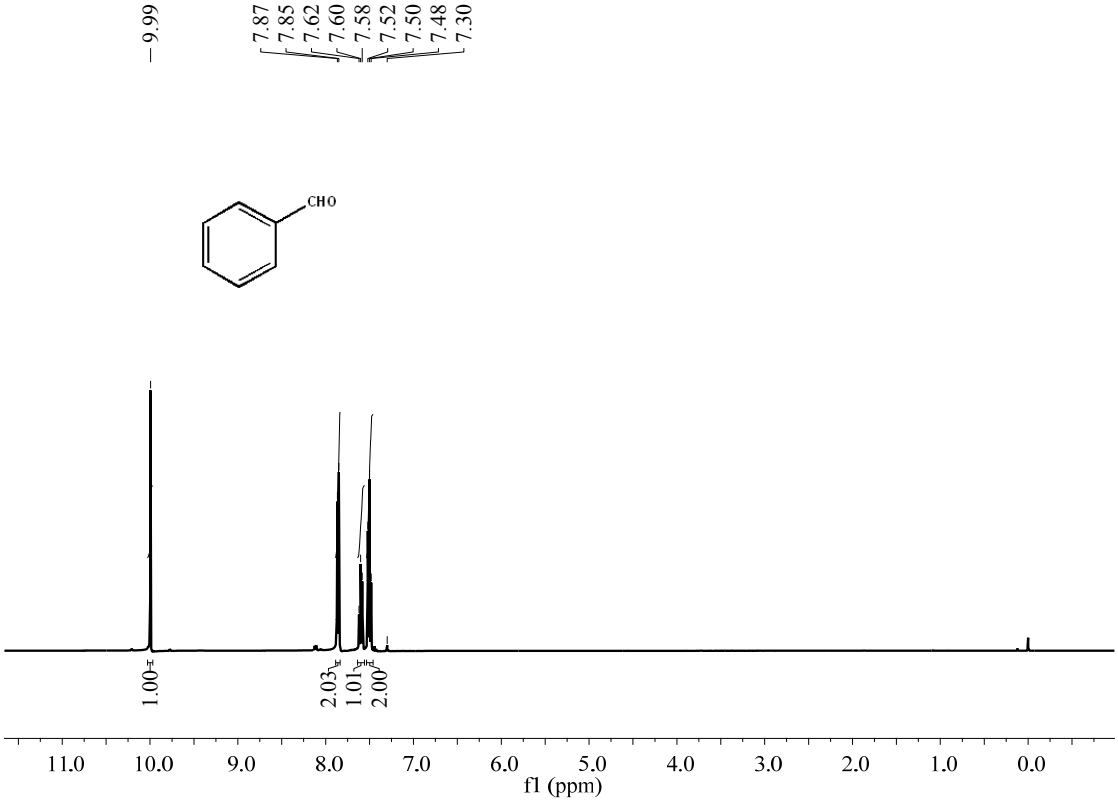


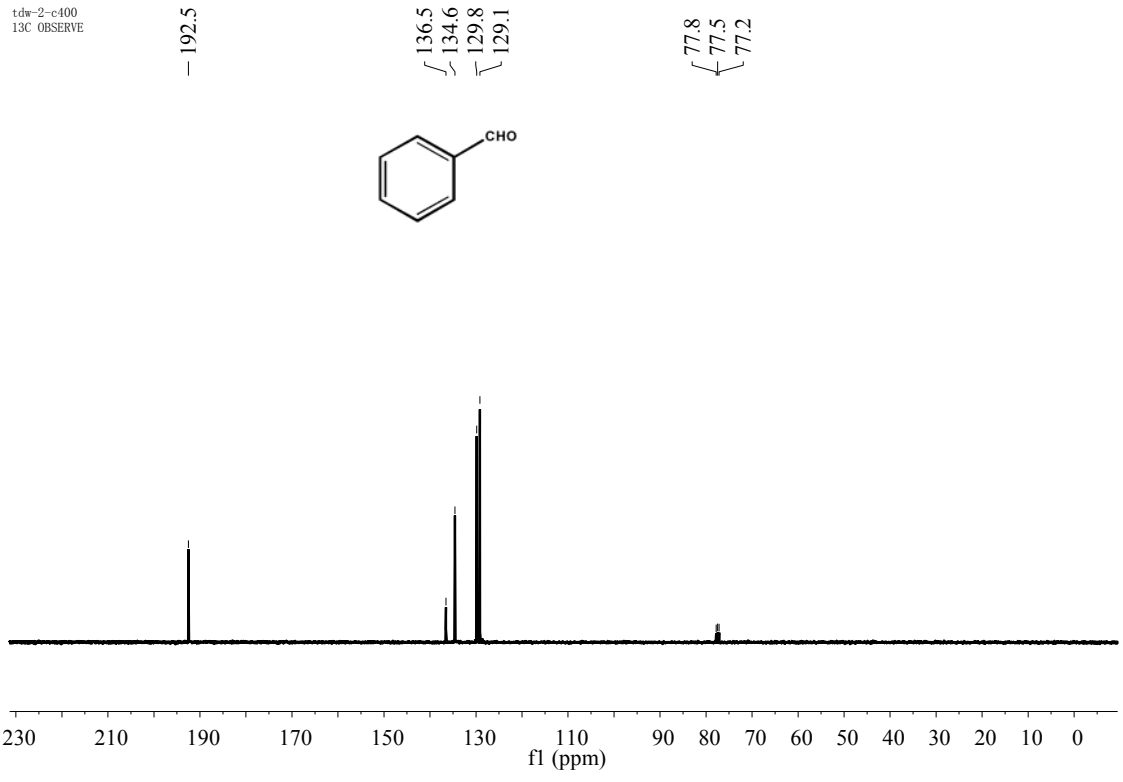
The ^{1}H and ^{13}C NMR spectra of the product 2-thiophenecarbonitrile



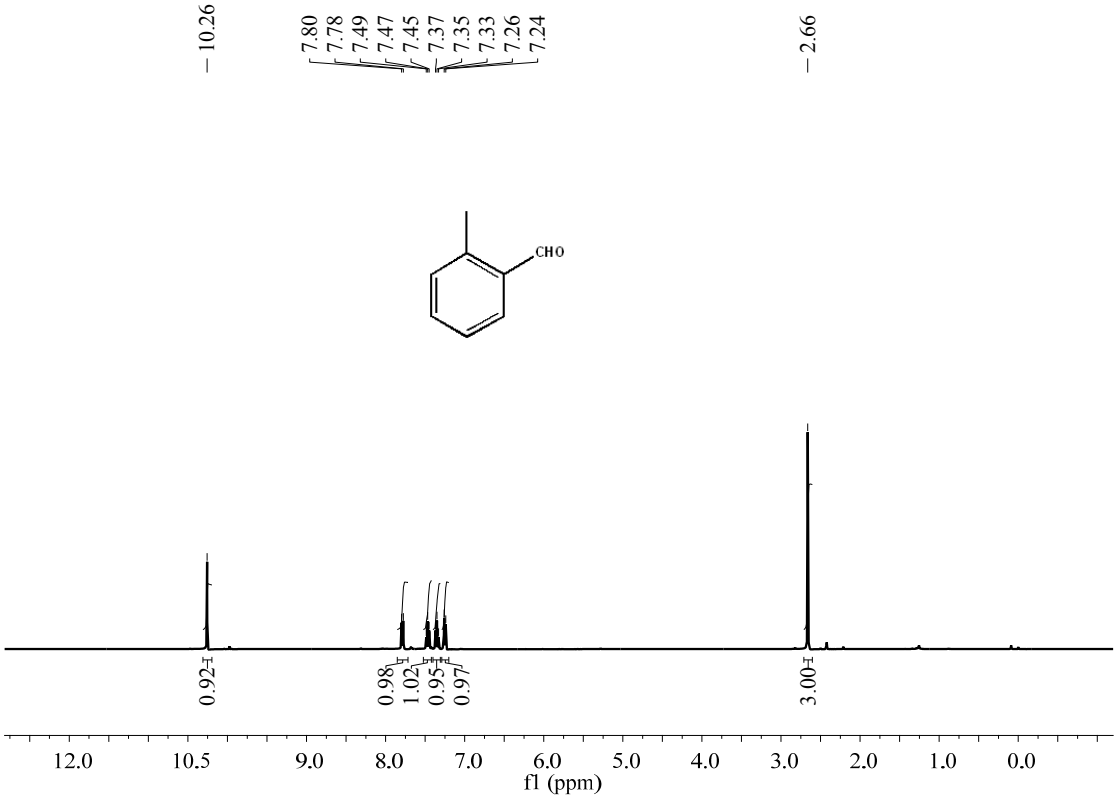


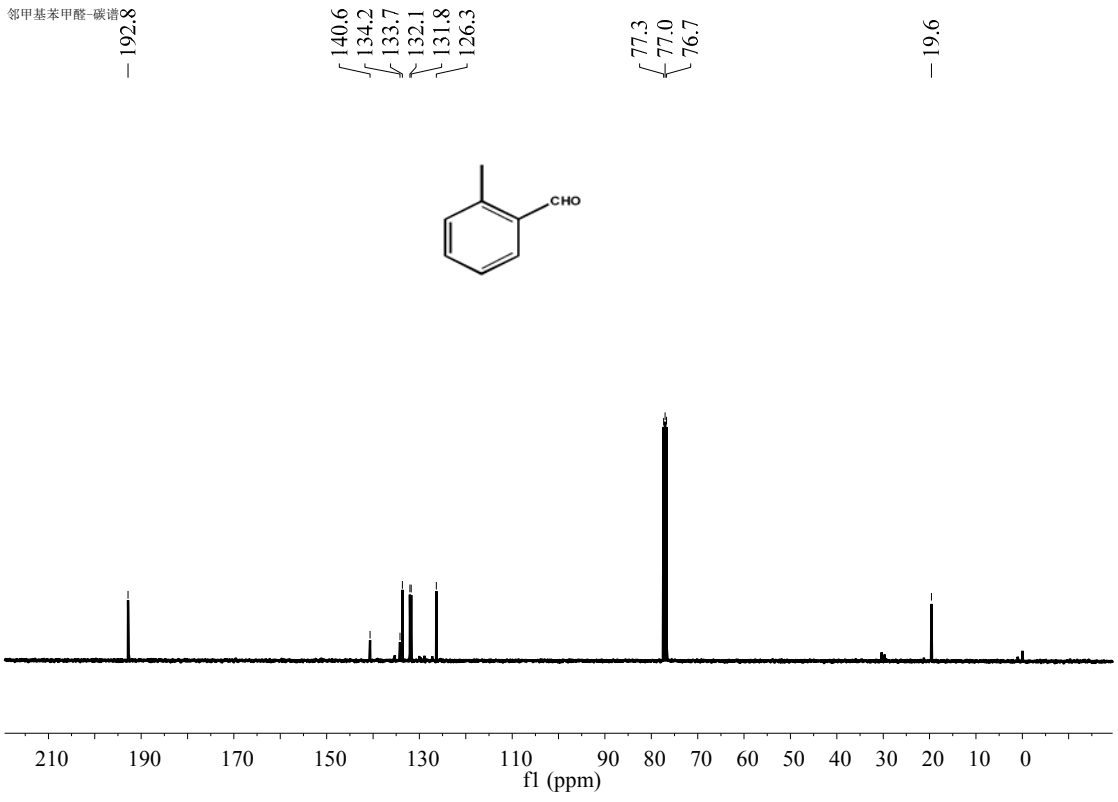
The ^{1}H and ^{13}C NMR spectra of the product benzaldehyde



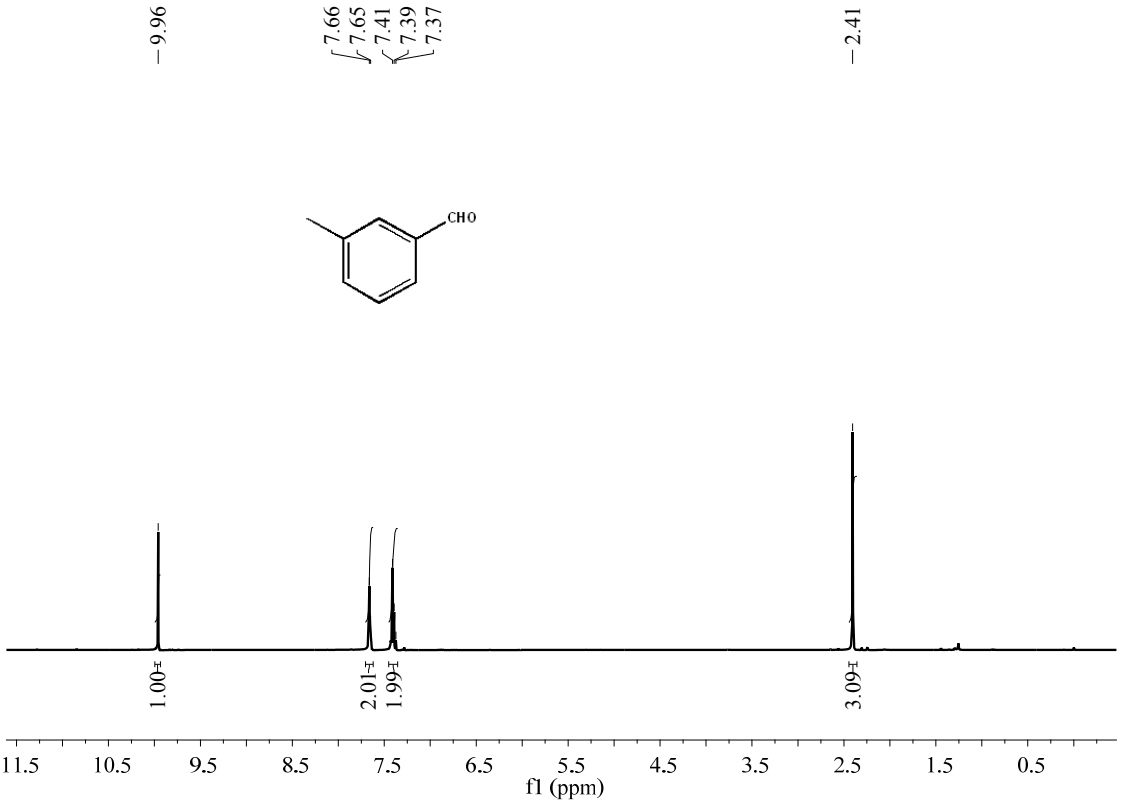


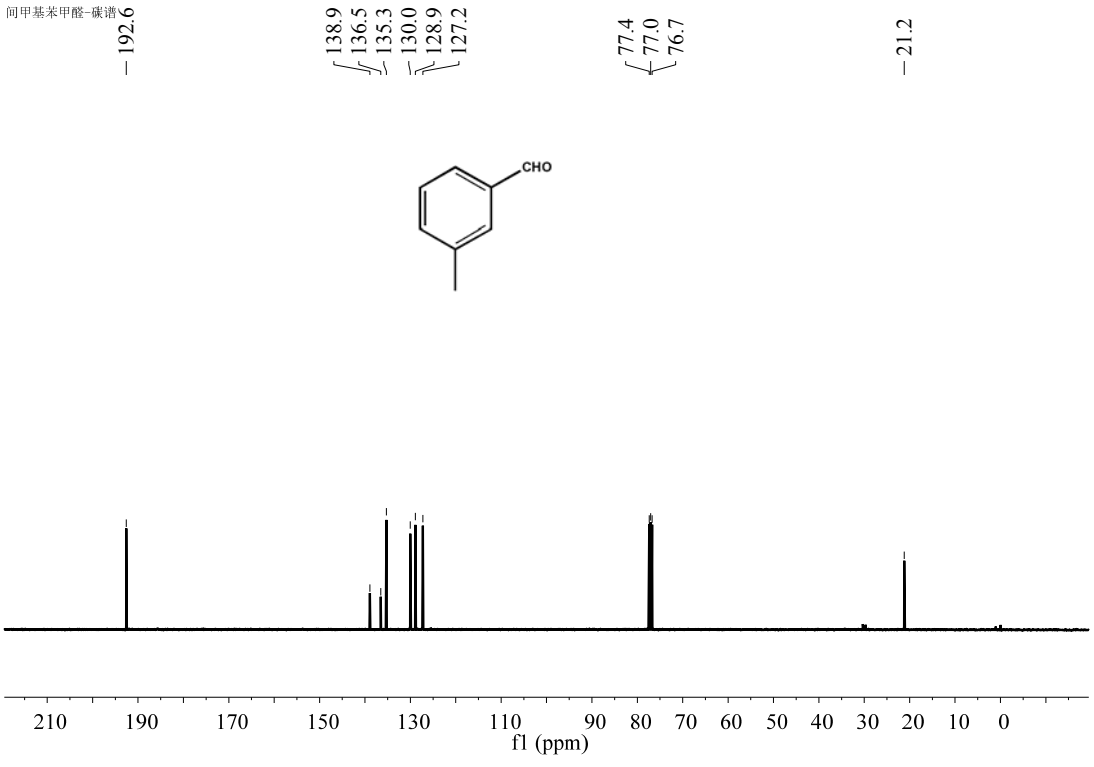
The ^{1}H and ^{13}C NMR spectra of the product 2-methylbenzaldehyde



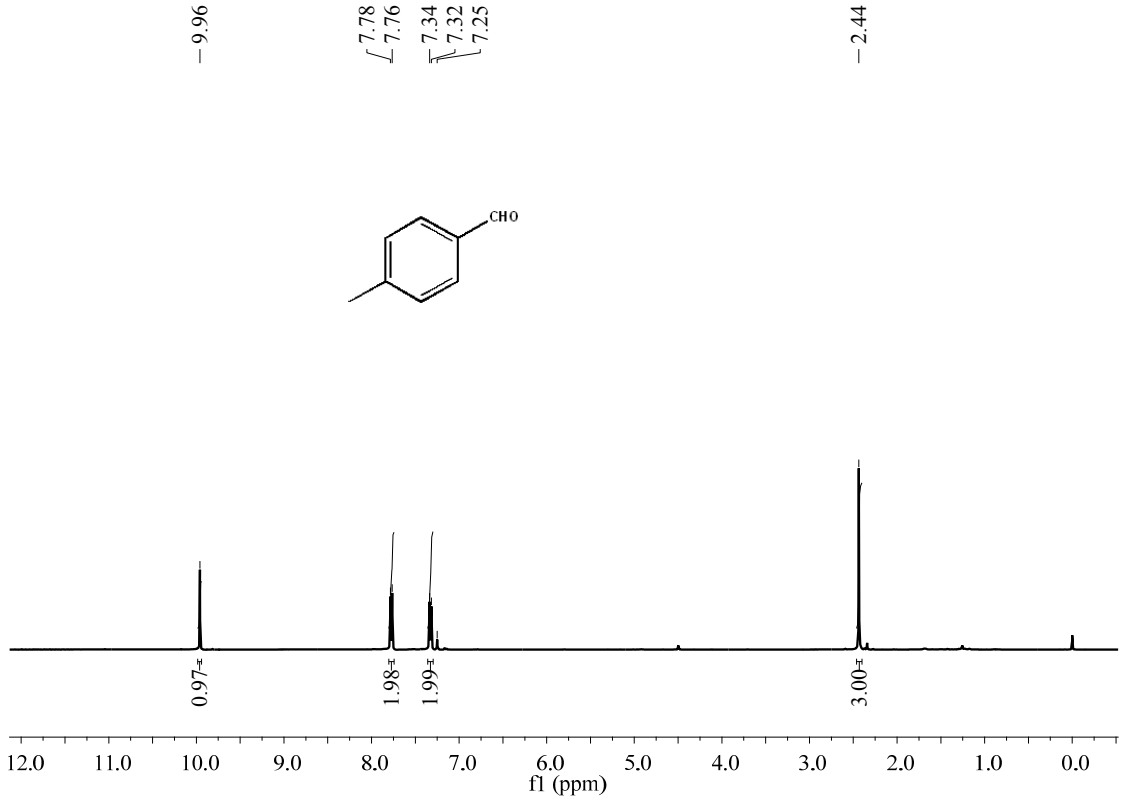


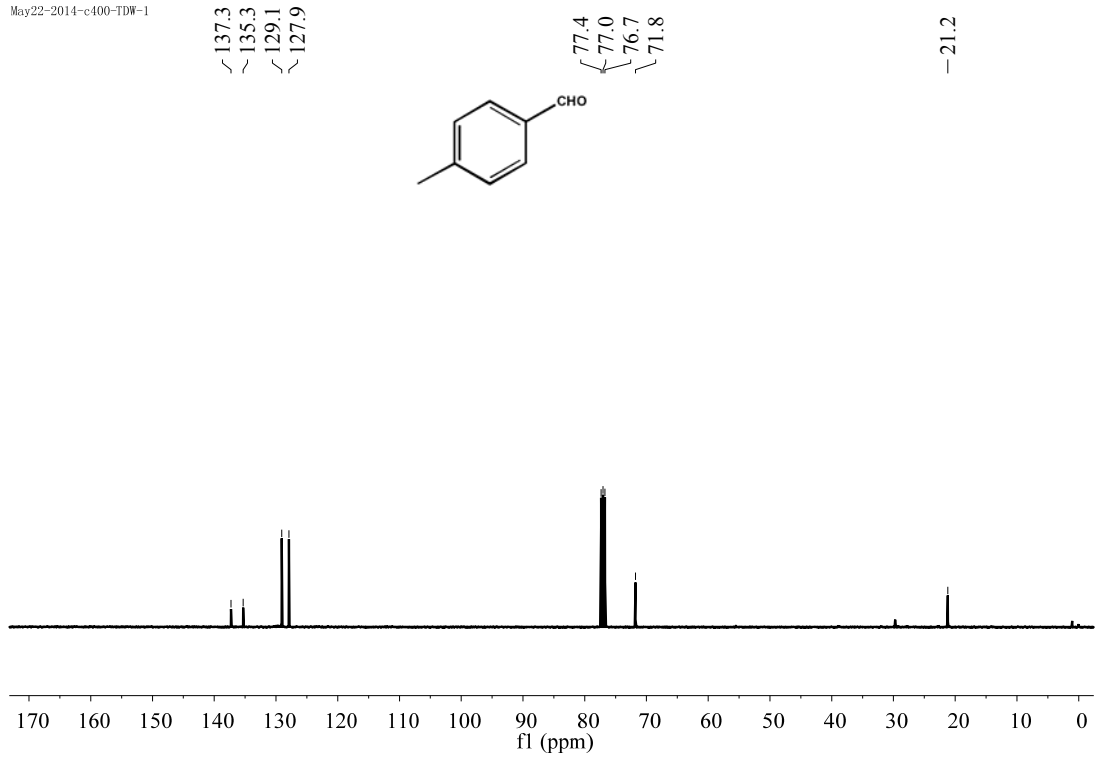
The ^{1}H and ^{13}C NMR spectra of the product 3-methylbenzaldehyde



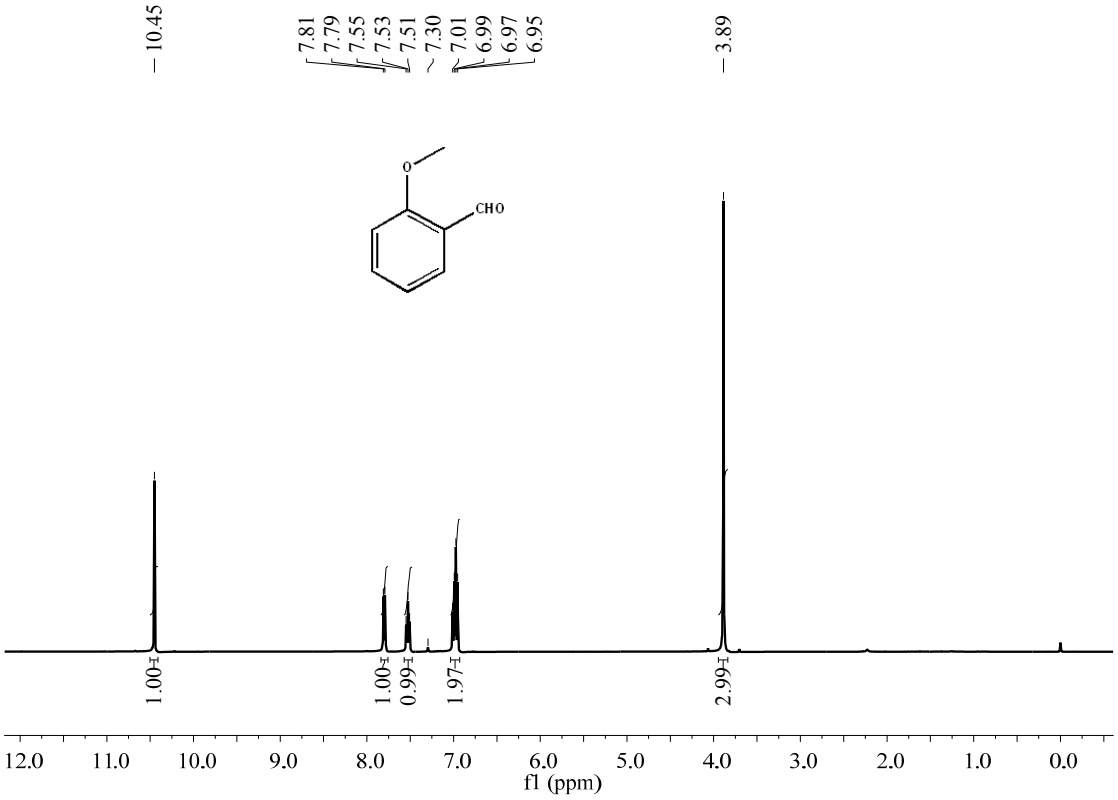


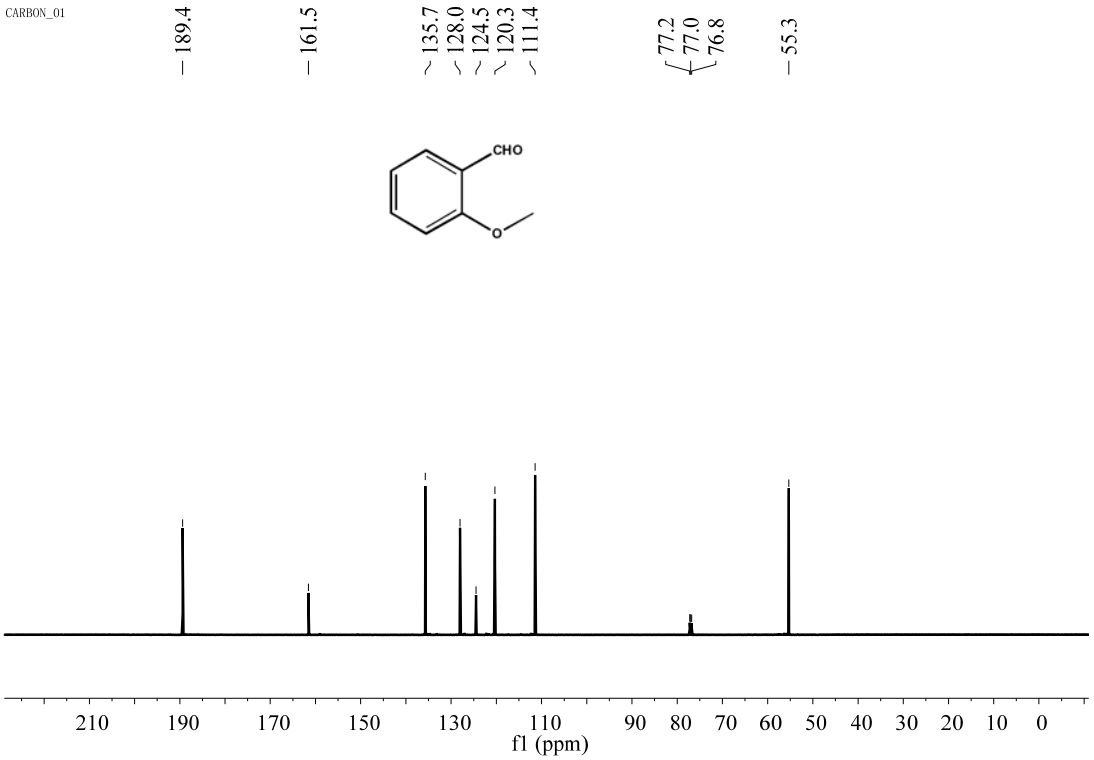
The ^{1}H and ^{13}C NMR spectra of the product 4-methylbenzaldehyde



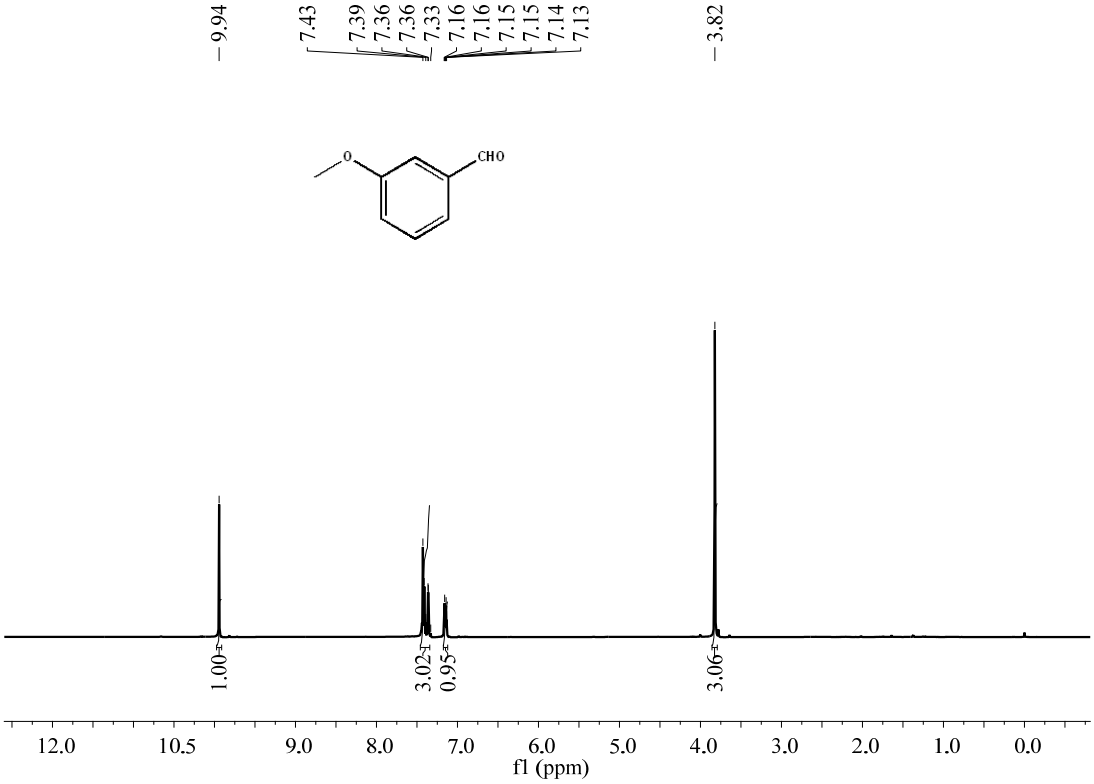


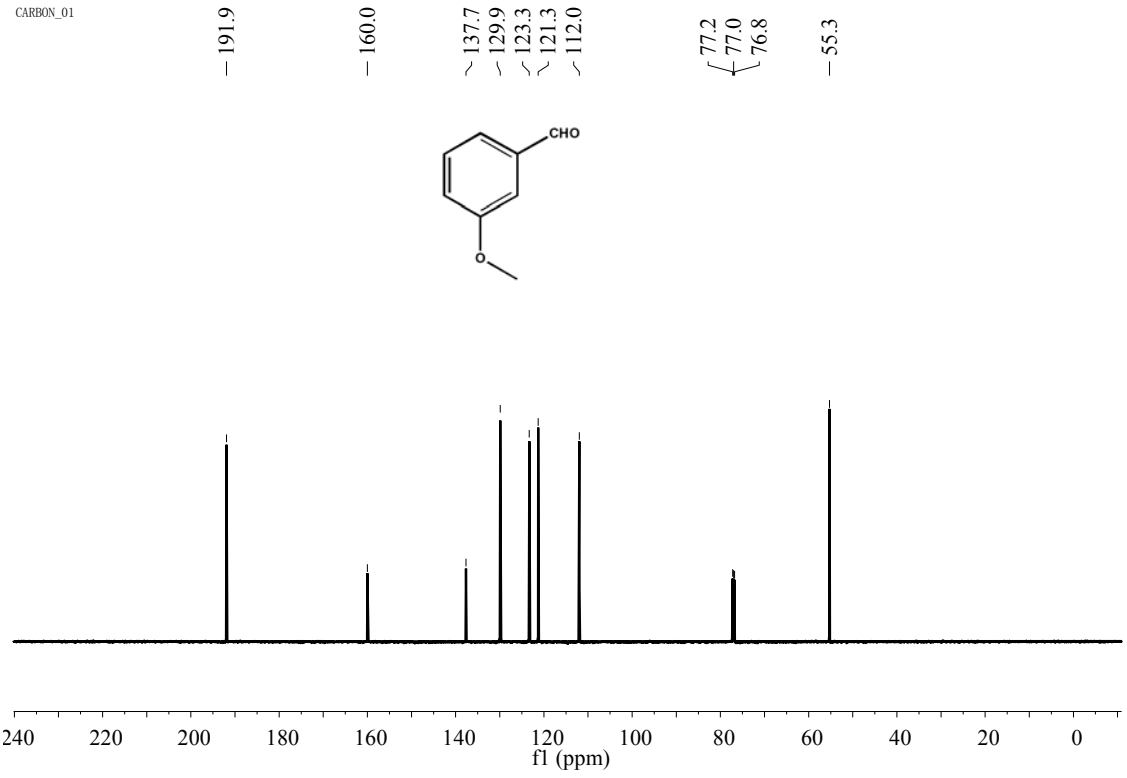
The ^{1}H and ^{13}C NMR spectra of the product 2-methoxybenzaldehyde



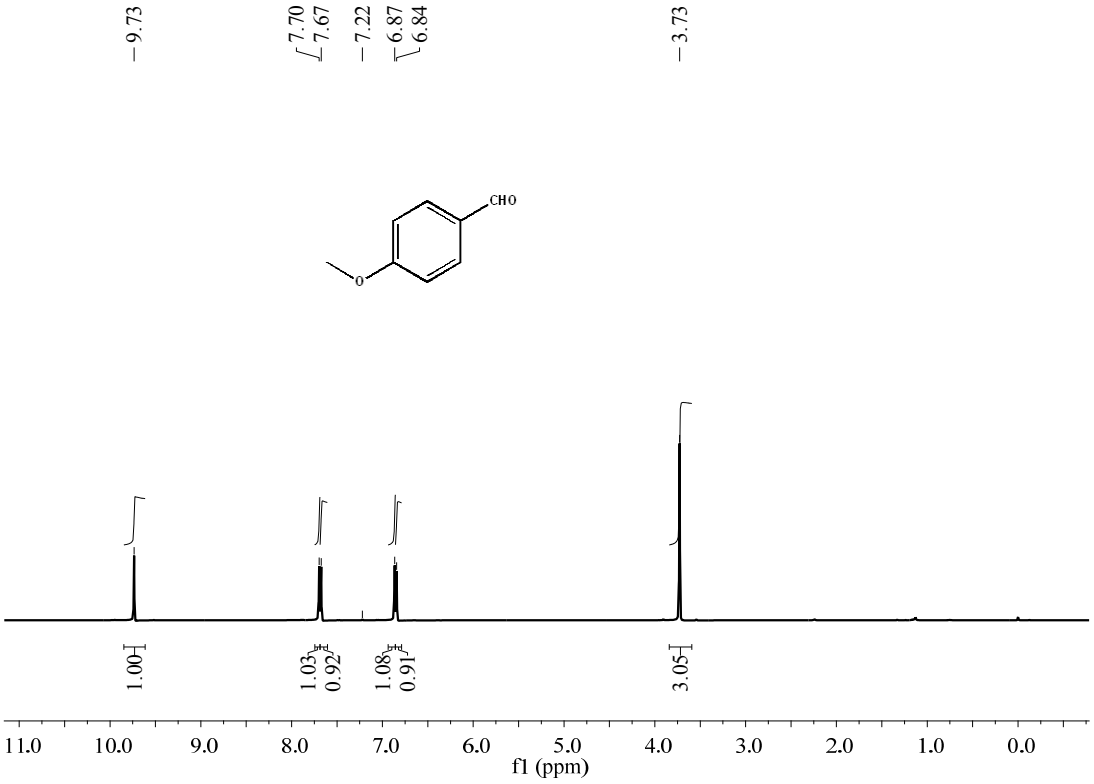


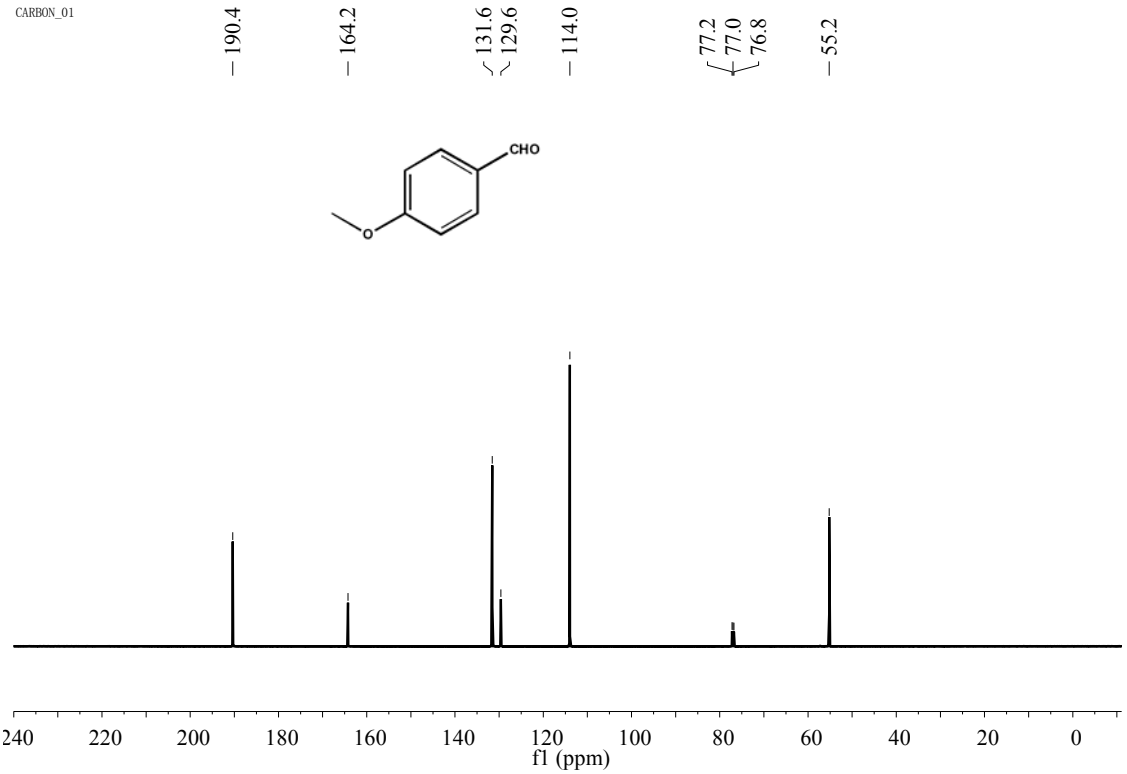
The ^{1}H and ^{13}C NMR spectra of the product 3-methoxybenzaldehyde



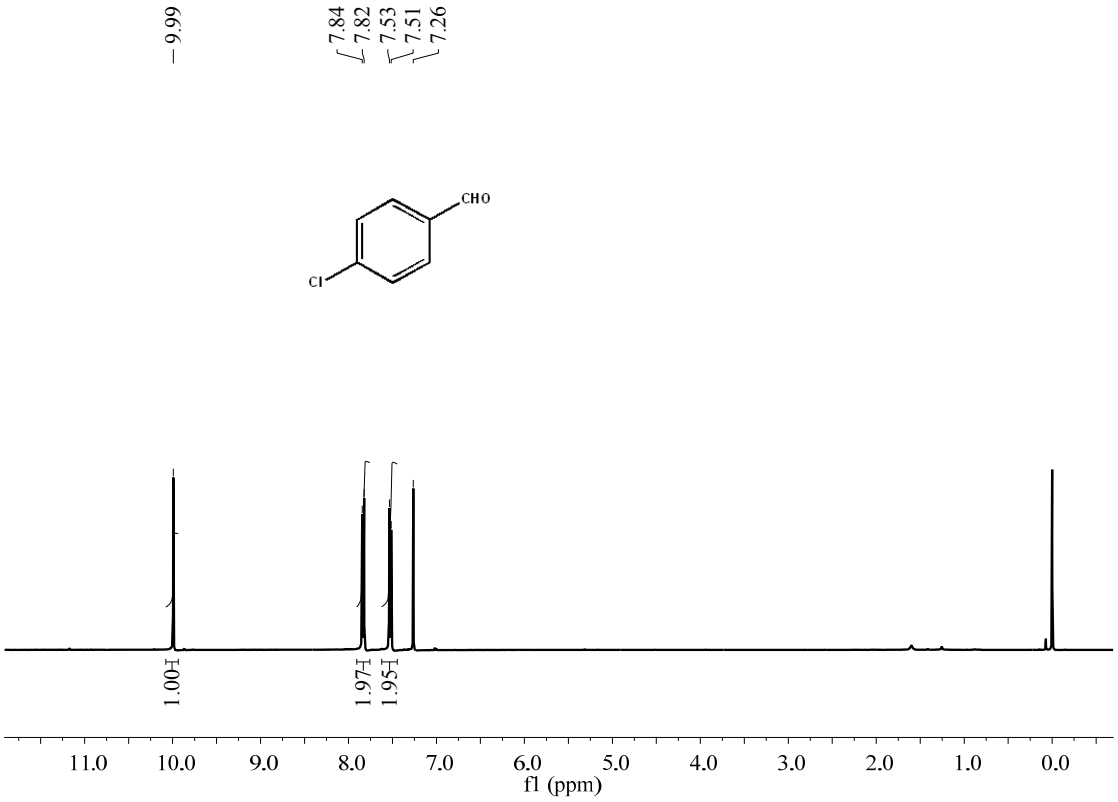


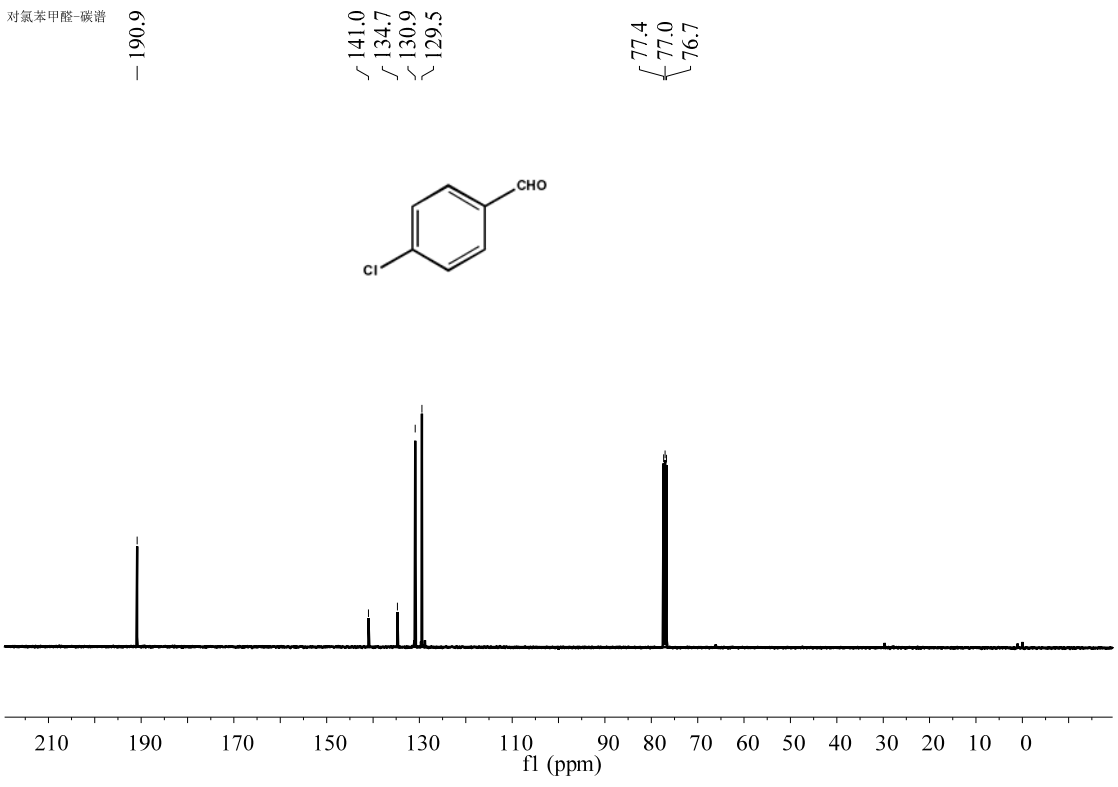
The ^{1}H and ^{13}C NMR spectra of the product 4-methoxybenzaldehyde



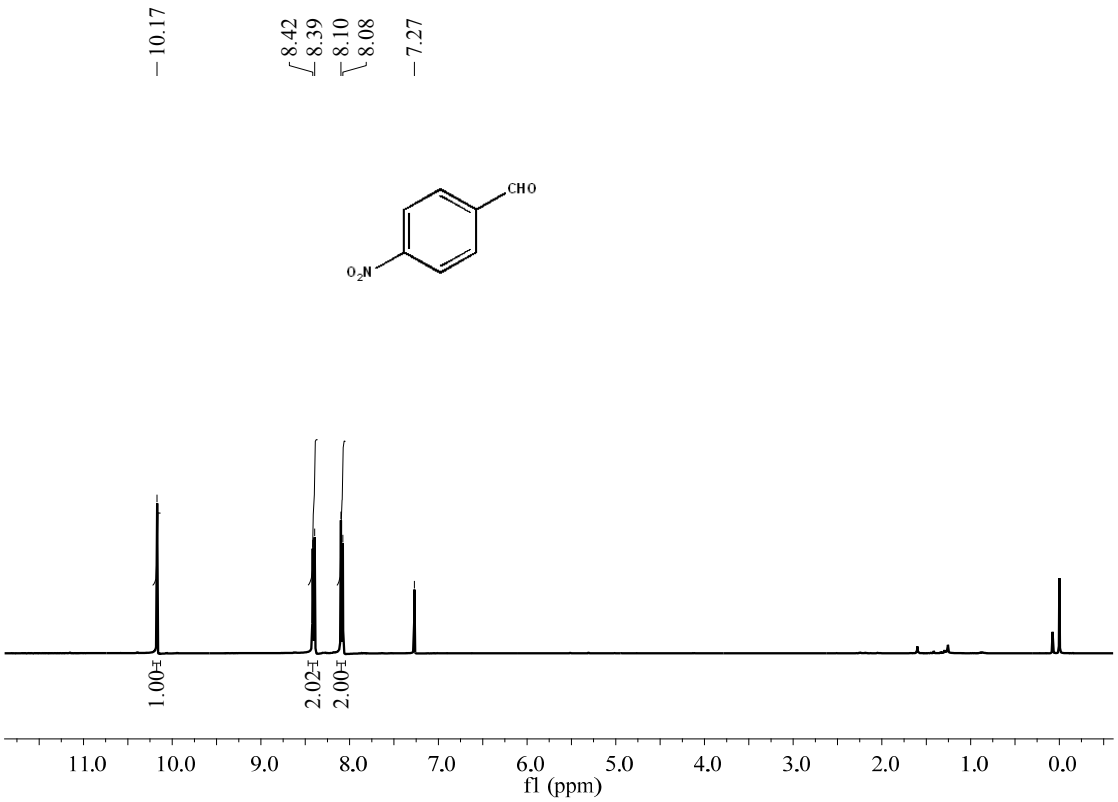


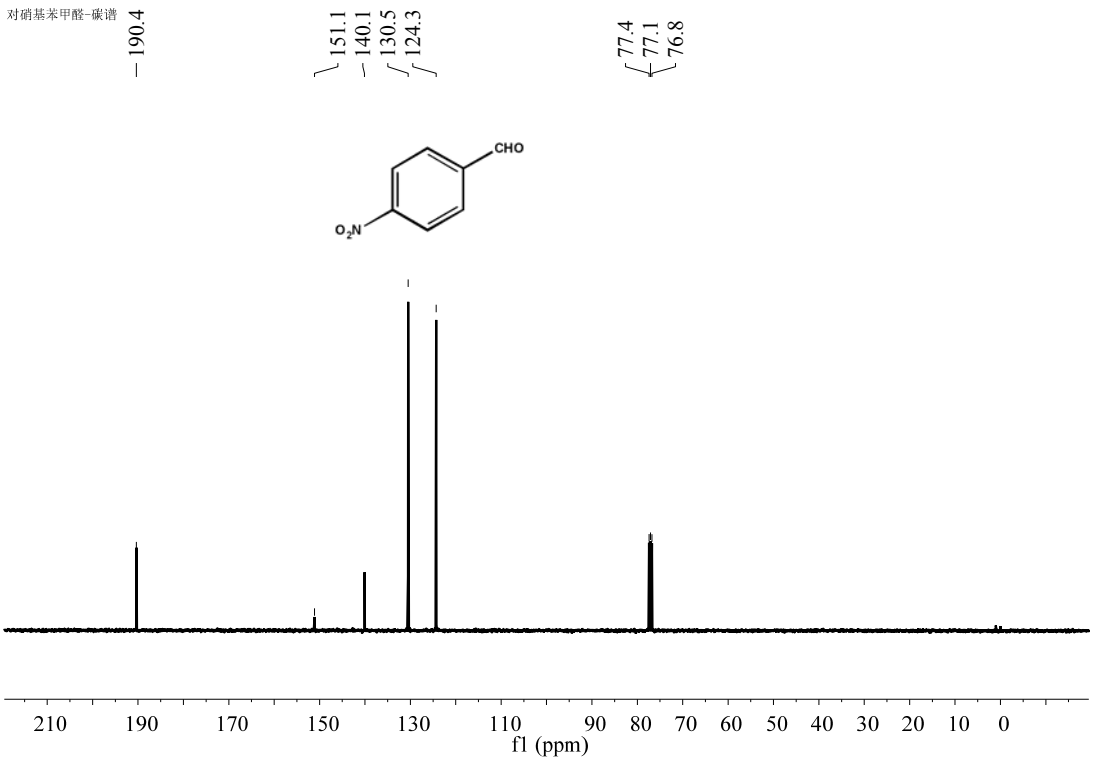
The ^{1}H and ^{13}C NMR spectra of the product 4-chlorobenzoic aldehyde



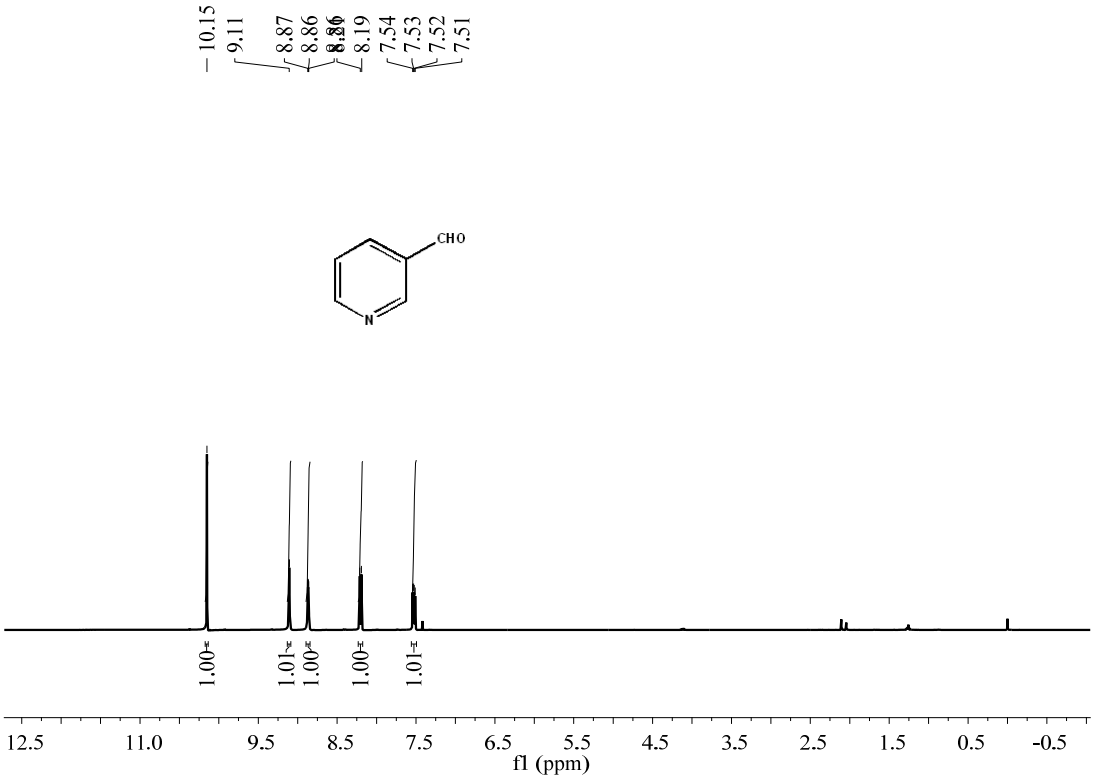


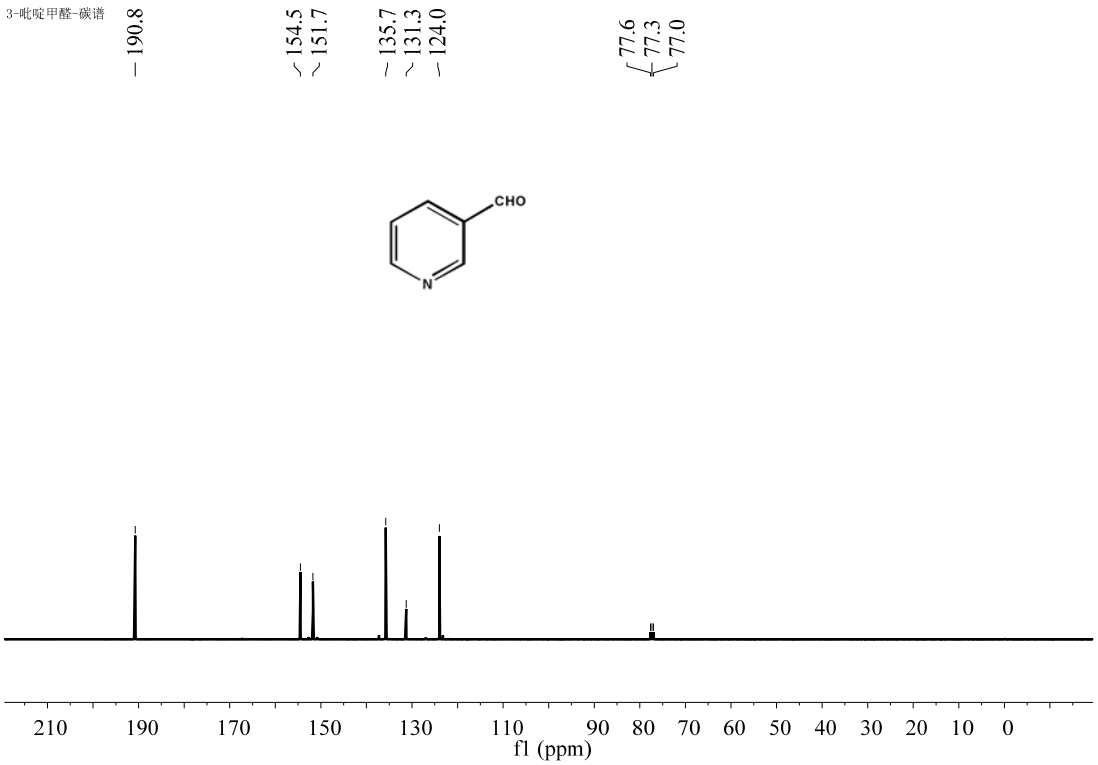
The ^{1}H and ^{13}C NMR spectra of the product 4-nitrobenzaldehyde





The ^{1}H and ^{13}C NMR spectra of the product 3-pyridinecarboxaldehyde





The ^{1}H and ^{13}C NMR spectra of the product 2-thenaldehyde