Electronic Supplementary Information

Cyanation of aromatic/vinylic boronic acids with α-cyanoacetates

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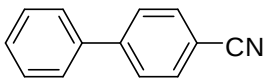
1. General experimental considerations

All the reactants and reagents were used as received commercially without further purification. All the reactions were performed under O_2 balloon. ^1H and ^{13}C NMR spectra of the products were recorded in $CDCl_3$ solvent on a Bruker Advance III HD spectrometer (400 MHz for ^1H NMR and 101 MHz for ^{13}C NMR). Chemical shifts are reported in *ppm* relative to TMS. Coupling constants are reported in Hz where applicable. Elemental analyses were performed using Elementar VARIOEL III. Infrared spectroscopy study was done on a IRTracer-100 spectrometer. The melting points were measured using SGWX-4 melting point apparatus.

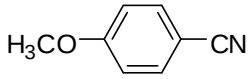
2. A typical procedure for copper-mediated aerobic cyanation of aryl/vinyl boronic acids or halides with α-cyanoacetates

Into an oven-dried Schlenk tube charged with a magnetic stir bar were added aryl/vinyl boronic acid or halide (**1**, 0.5 mmol), CuI (0.5 mmol) and PPh_3 (0.1 mmol). The tube was then sealed, evacuated and backfilled with dry O_2 using an O_2 balloon. Then, an NMP (2 mL) solution of ethyl cyanoacetate (**2**, 1.0 mmol), TBHP (1.0 mmol) and HOAC (1.0 mmol) was added by syringe. The reaction mixture was stirred under O_2 (balloon) at 130 ℃ (oil bath) for 18 hours. The reaction mixture was then cooled to room temperature, diluted by ethyl acetate (3 mL), and partitioned between ethyl acetate and saturated NH_4Cl. The organic layer was then washed with brine, dried over Na_2SO_4 and concentrated in vacuum. The residue obtained was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 20:1~10:1 (v/v)) to give products **3** or **4**.

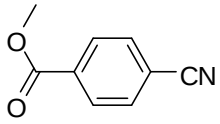


Biphenyl-4-carbonitrile (3a; 61 mg, 68%**)**.[S1] White solid; mp 85-86 ^oC. ^1H NMR (400 MHz, $CDCl_3$): δ 7.78–7.69 (m, 4H), 7.62 (d, *J* = 7.1 Hz, 2H), 7.51 (t, *J* = 7.3 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 145.7, 139.2, 132.6,

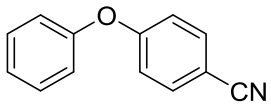
129.1, 128.7, 127.8, 127.2, 118.9, 110.9. IR (KBr, cm^{-1}): 3027, 2228, 1596, 847. Anal. Calcd for $C_{13}H_9N$: C, 87.12; H, 5.06; N, 7.82. Found: C, 87.28; H, 5.12; N, 7.76.



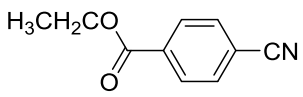
4-Methoxybenzonitrile (**3b**; 44 mg, 66%).[S1] White solid; mp 61-62 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.9, 134.0, 122.3, 114.8, 104.0, 55.5. IR (KBr, cm^{-1}): 2968, 2232, 1598, 812. Anal. Calcd for C_8H_7NO: C, 72.16; H, 5.30; N, 10.52. Found: C, 72.34; H, 5.41; N, 10.44.



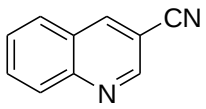
Methyl 4-cyanobenzoate (3c; 32 mg, 40%**)**.[S1] White solid; mp 65-66 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.5 Hz, 2H), 7.77 (d, *J* = 8.5 Hz, 2H), 3.98 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.4, 133.9, 132.2, 130.1, 117.9, 116.4, 52.7. IR (KBr, cm^{-1}): 2964, 2232, 1716, 788. Anal. Calcd for $C_9H_7NO_2$: C, 67.07; H, 4.38; N, 8.69. Found: C, 67.35; H, 4.50; N, 8.52.



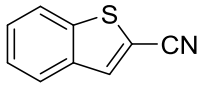
4-Phenoxybenzonitrile (3d; 50 mg, 52%**)**. [S1] Yellow solid; mp 42-43 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.9 Hz, 2H), 7.47–7.41 (m, 2H), 7.26 (t, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 7.6 Hz, 2H), 7.03 (d, *J* = 8.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.7, 154.8, 134.1, 130.2, 125.2, 120.4, 118.8, 117.9, 105.8. IR (KBr, cm^{-1}): 3054, 2232, 1598, 856. Anal. Calcd for $C_{13}H_9NO$: C, 79.98; H, 4.65; N, 7.17. Found: C, 80.15; H, 4.75; N, 7.09.



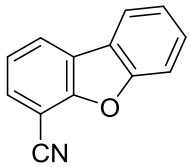
Ethyl 4-cyanobenzoate (3e; 40 mg, 46%**)**.[S2] Yellow solid; mp 52-54 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 8.5 Hz, 2H), 4.43 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.0, 128.4, 126.2, 124.1, 112.0, 110.4, 55.9, 8.3. IR (KBr, cm^{-1}): 3028, 2228, 1721, 847. Anal. Calcd for $C_{10}H_9NO_2$: C, 68.56; H, 5.18; N, 8.00. Found: C, 68.78; H, 5.29; N, 7.91.



quinoline-3-carbonitrile (**3i**; 69 mg, 89%).[S3] White solid; mp 108-110^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 (s, 1H), 8.58 (d, *J* = 1.8 Hz, 1H), 8.21 (d, *J* = 8.8 Hz, 1H), 7.93 (dd, *J* = 8.1, 6.0 Hz, 2H), 7.73 (t, *J* = 7.6 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 149.7, 148.8, 141.5, 132.8, 129.9, 128.5, 128.3, 126.3, 117.1, 106.6. IR (KBr, cm^{-1}): 3058, 2223, 1598, 786, 750. Anal. Calcd for $C_{10}H_6N_2$: C, 77.91; H, 3.92; N, 18.17. Found: C, 78.10; H, 4.08; N, 18.04.

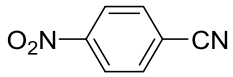


Benzo[*b*]thiophene-2-carbonitrile (3j; 34 mg, 43%**)**.[S3] Yellow solid; mp 25-26 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94–7.85 (m, 3H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3, 137.5, 135.0, 127.9, 125.7, 125.3, 122.4, 114.5, 109.7. IR (KBr, cm^{-1}): 3066, 2220, 1594, 1508, 866, 741. Anal. Calcd for C_9H_5NS: C, 67.90; H, 3.17; N, 8.80. Found: C, 67.96; H, 3.12; N, 8.74.

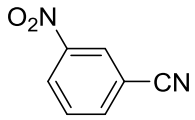


Dibenzofuran-1-carbonitrile (3k; 42 mg, 44%**)**.[S3] White solid; mp 135-136 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.00 (dd, *J* = 7.7, 0.6 Hz, 1H), 7.75 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.70 (d, *J* = 8.3 Hz, 1H), 7.58 (td, *J* = 8.0, 1.2 Hz,

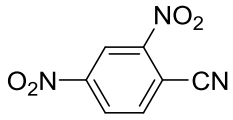
1H), 7.45 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.4, 156.2, 130.4, 128.6, 125.7, 125.4, 123.8, 123.0, 122.9, 121.0, 115.1, 112.3, 96.7. IR (KBr, cm^{-1}): 3058, 2228, 1419, 749. Anal. Calcd for $C_{13}H_7NO$: C, 80.82; H, 3.65; N, 7.25. Found: C, 80.98; H, 3.75; N, 7.18.



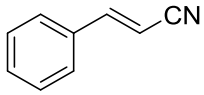
4-Nitrobenzonitrile (**3l**; 50 mg, 68%).[S1] White solid; mp 141-142 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (dt, *J* = 8.9, 2.0 Hz, 2H), 7.91 (dt, *J* = 8.9, 2.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.8, 133.5, 124.1, 118.1, 116.6. IR (KBr, cm^{-1}): 3054, 2232, 1598, 855. Anal. Calcd for $C_7H_4N_2O_2$: C, 56.76; H, 2.72; N, 18.91. Found: C, 56.85; H, 2.74; N, 18.84.



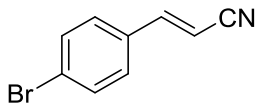
3-Nitrobenzonitrile (**3m**; 45 mg, 61%). [S1] White solid; mp 111-112 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67–8.41 (m, 2H), 8.03 (d, *J* = 7.7 Hz, 1H), 7.77 (t, *J* = 8.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.2, 137.6, 130.7, 127.5, 127.2, 116.5, 114.2. IR (KBr, cm^{-1}): 3081, 2232, 1536, 870, 786. Anal. Calcd for $C_7H_4N_2O_2$: C, 56.76; H, 2.72; N, 18.91. Found: C, 56.83; H, 2.75; N, 18.85.



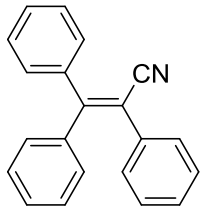
2,4-Dinitrobenzonitrile (**3n**; 72 mg, 75%).[S4] Yellow solid; mp 103 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.17 (d, *J* = 2.2 Hz, 1H), 8.70 (dd, *J* = 8.4, 2.2 Hz, 1H), 8.22 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.1, 137.3, 128.5, 120.9, 113.2. IR (KBr, cm^{-1}): 3070, 2221, 1504, 836, 753. Anal. Calcd for $C_7H_3N_3O_4$: C, 43.54; H, 1.57; N, 21.76. Found: C, 43.69; H, 1.64; N, 21.62.



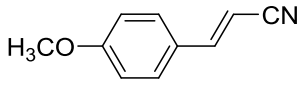
(*E*)-Cinnamonitrile (**4a**; 48 mg, 74%).[S5] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50−7.40 (dt, *J* = 22.8, 8.9 Hz, 6H), 5.91 (d, *J* = 16.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.6, 133.5, 131.2, 129.1, 127.4, 118.1, 96.4. IR (KBr, cm^{-1}): 3054, 2216, 1596, 756, 695. Anal. Calcd for C_9H_7N: C, 83.69; H, 5.46; N, 10.84. Found: C, 83.86; H, 5.52; N, 10.70.



(*E*)-3-(4-bromophenyl)acrylonitrile (**4b**; 55 mg, 56%).[S5] Yellow solid; mp 104-105 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 8.5 Hz, 2H), 7.39–7.32 (m, 3H), 5.90 (d, *J* = 16.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.2, 132.4, 128.7, 125.8, 117.9, 97.2. IR (KBr, cm^{-1}): 3054, 2216, 1598, 845. Anal. Calcd for C_9H_6BrN: C, 51.96; H, 2.91; N, 6.73. Found: C, 52.30; H, 3.04; N, 6.58.



2,3,3-Triphenylacrylonitrile (**4c**; 114 mg, 81%).[S6] White solid; mp 165-166 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (s, 5H), 7.25 (d, *J* = 43.7 Hz, 8H), 7.03 (d, *J* = 7.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.8, 139.1, 130.8, 129.9–129.0, 128.5–128.2, 120.1, 111.7. IR (KBr, cm^{-1}): 3058, 2216, 1598, 762. Anal. Calcd for $C_{21}H_{15}N$: C, 89.65; H, 5.37; N, 4.98. Found: C, 89.73; H, 5.42; N, 4.86.



(*E*)-3-(4-methoxyphenyl)acrylonitrile (**4d**; 48 mg, 60%).[S5] Yellow solid; mp 62-63 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.8 Hz, 1H), 7.42 (d, *J* = 8.8 Hz, 2H),

7.35 (d, J = 16.6 Hz, 1H), 7.04 (s, 1H), 6.94 (d, J = 8.8 Hz, 2H), 5.74 (d, J = 16.6 Hz, 1H), 3.88 (s, 1H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.1, 150.0, 129.1, 126.4, 118.7, 114.6, 93.4, 55.5. IR (KBr, cm^{-1}): 3062, 2213, 1598, 1508, 800. Anal. Calcd for $C_{10}H_9NO$: C, 75.45; H, 5.70; N, 8.80. Found: C, 75.51; H, 5.62; N, 8.73.

References

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(S2) A. V. Ushkov and V. V. Grushin, *J. Am. Chem. Soc.* 2011, 133, 10999.

(S3) U. Dutta, D. W. Lupton and D. Maiti, *Org. Lett.* 2016, 18, 860.

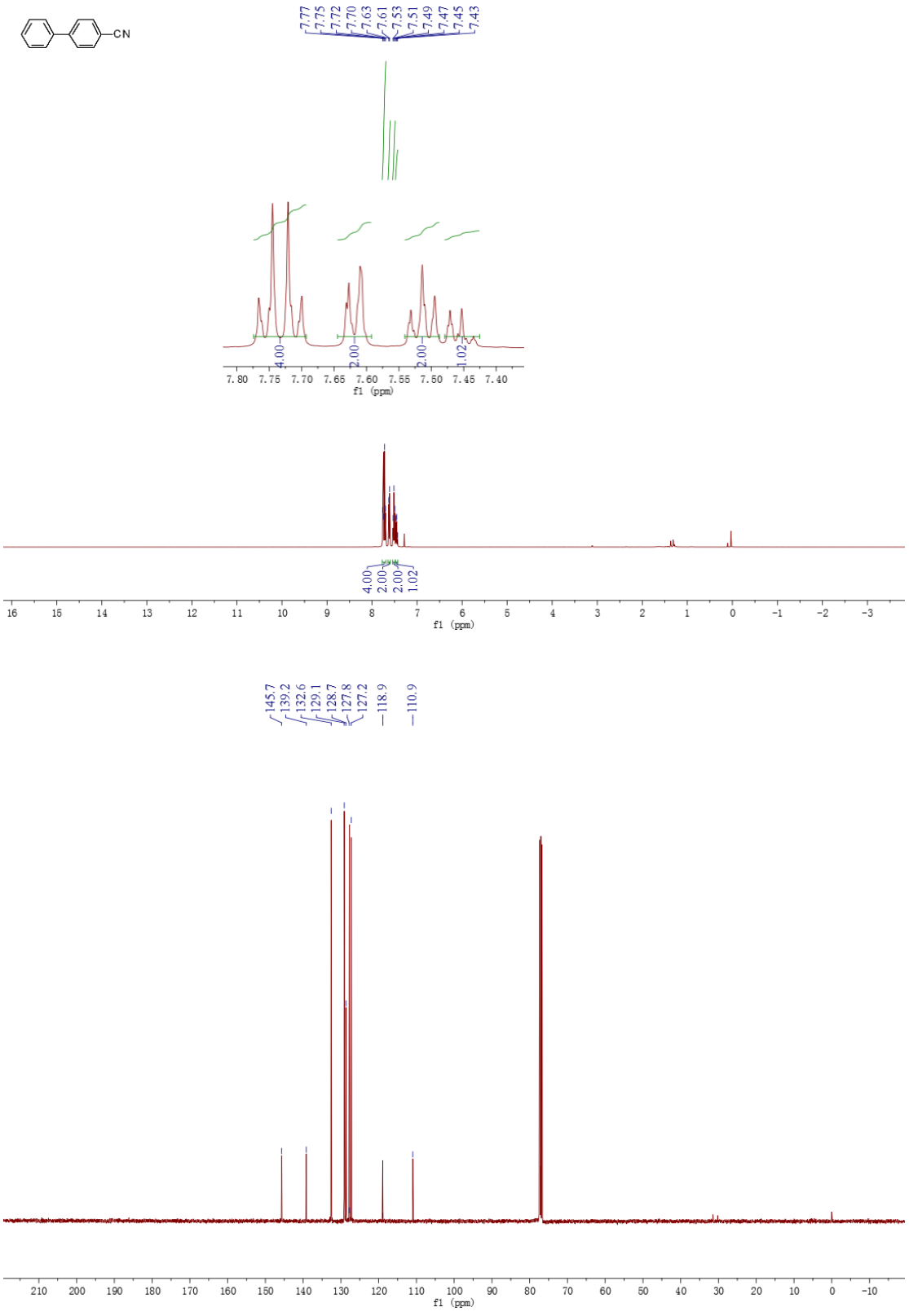
(S4) Q. Wu, Y. Luo, A. Lei and J. You, *J. Am. Chem. Soc.* 2016, 138, 2885.

(S5) J. Ruan, X. Li, O. Saidi and J. Xiao, *J. Am. Chem. Soc.* 2008, 130, 2424.

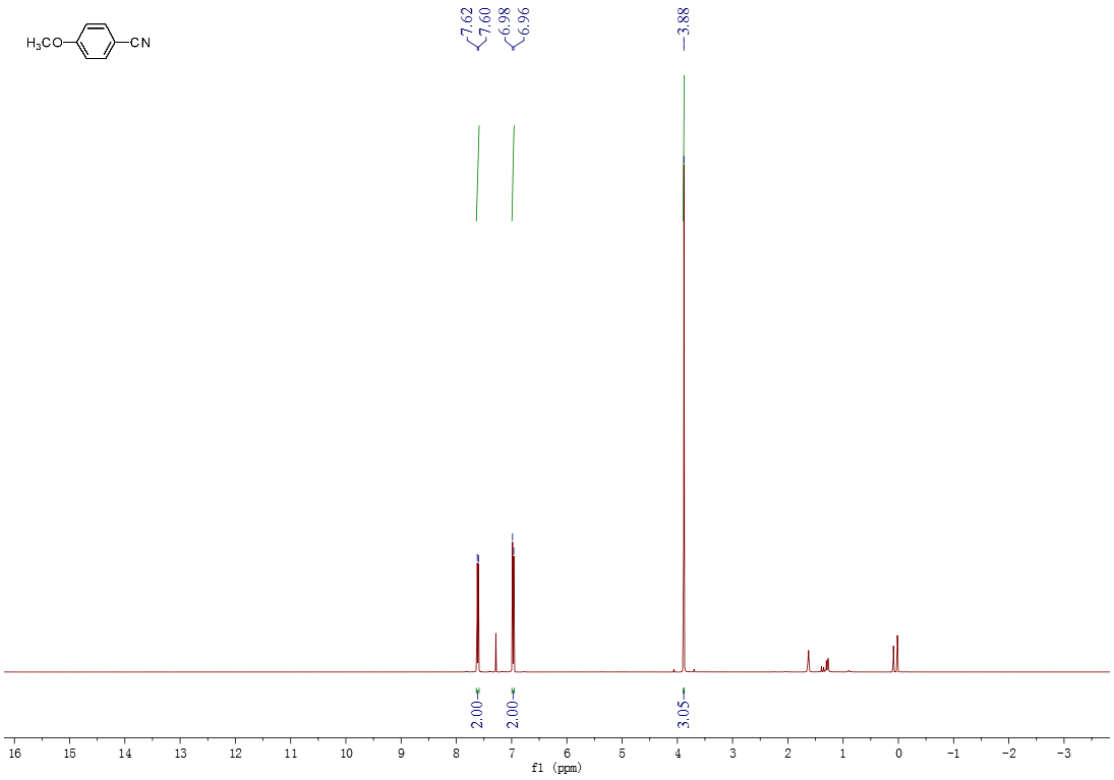
(S6) Y. Cheng, Z. Duan, L. Yu, Z. Li, Y. Zhu and Y. Wu, *Org. Lett.* 2008, 10, 901.

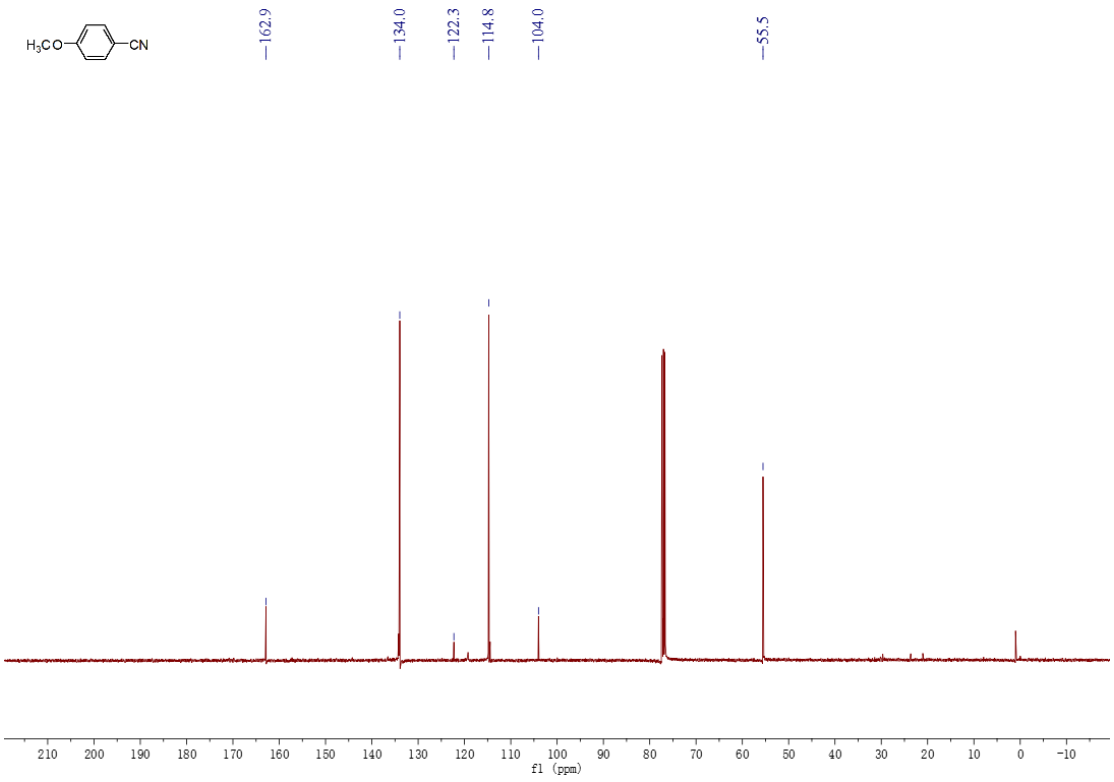
3. ^{1}H and ^{13}C NMR spectra for all the products

Biphenyl-4-carbonitrile (**3a**. ^{1}H NMR 400 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)

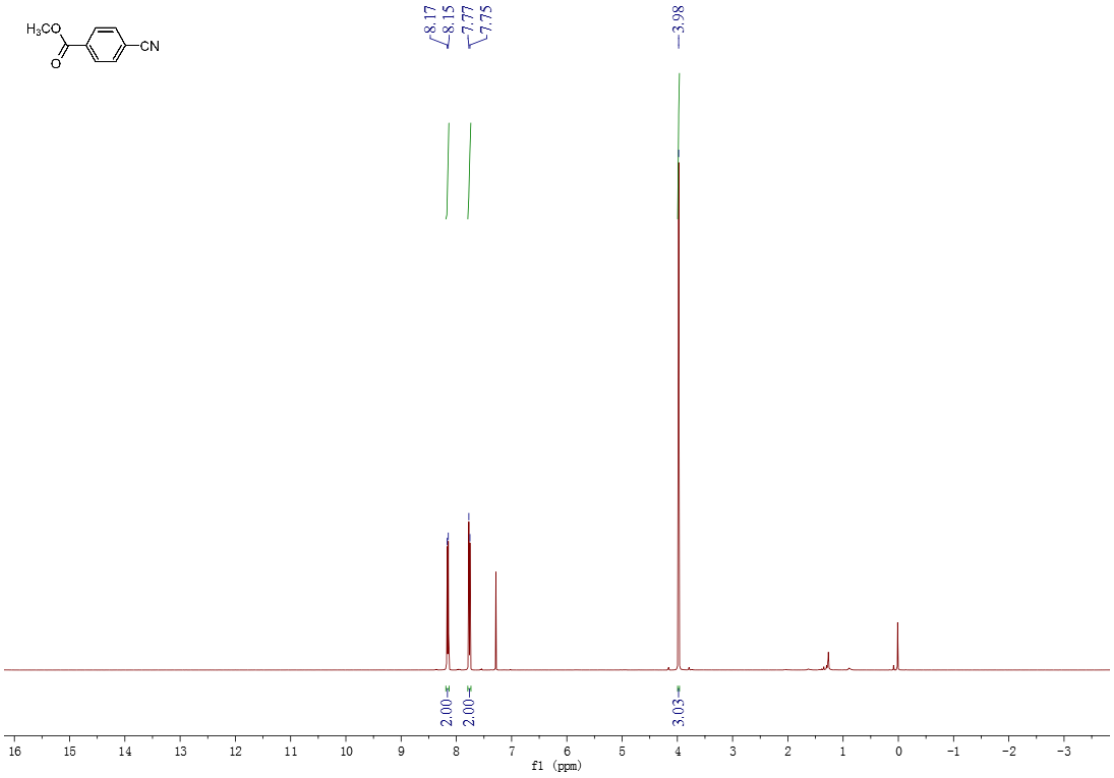


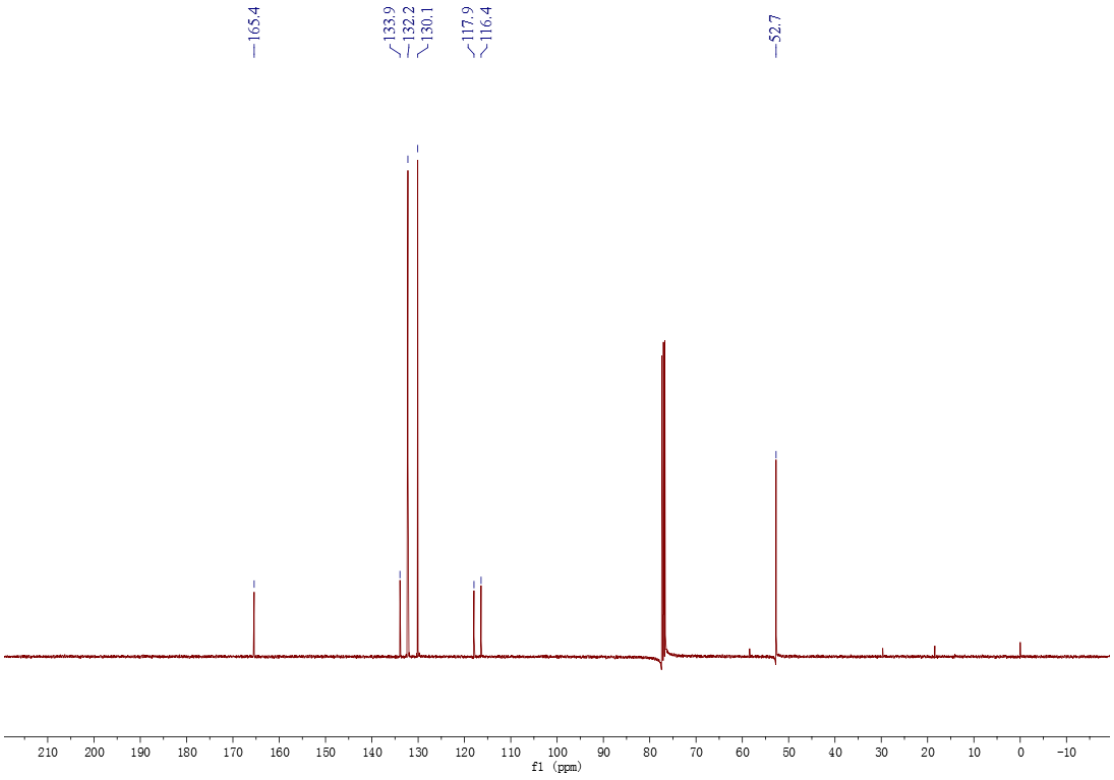
4-Methoxybenzonitrile (**3b**. ^{1}H NMR 400 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)



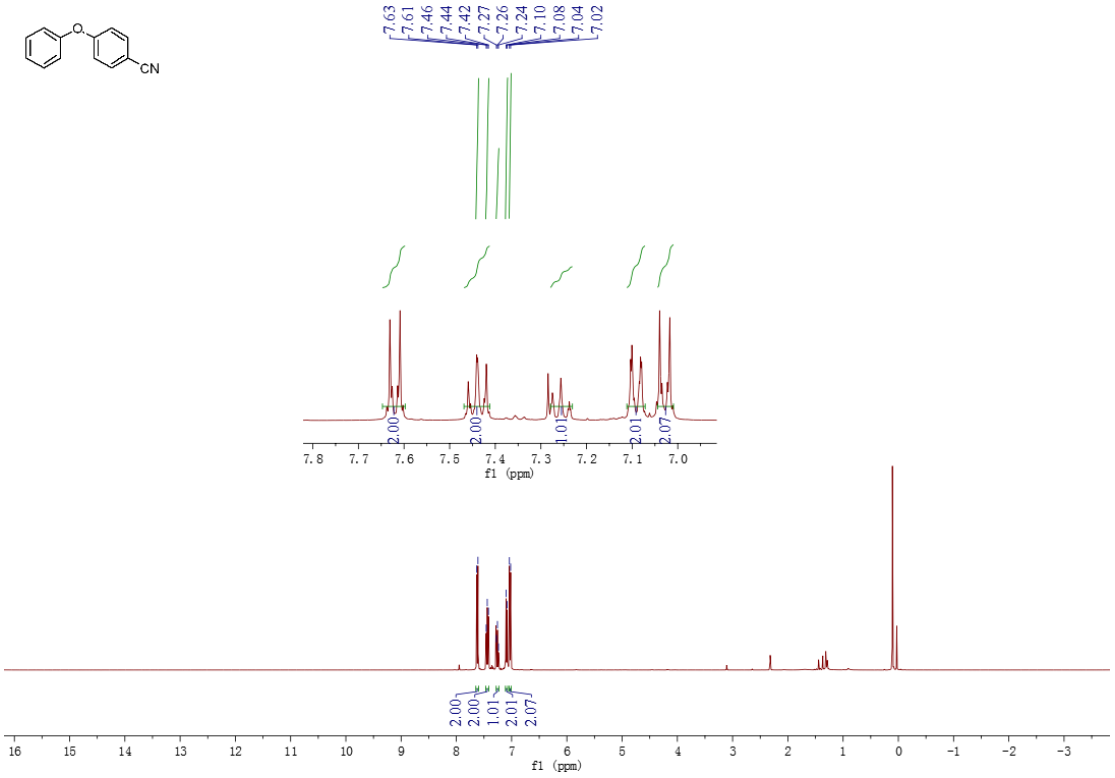


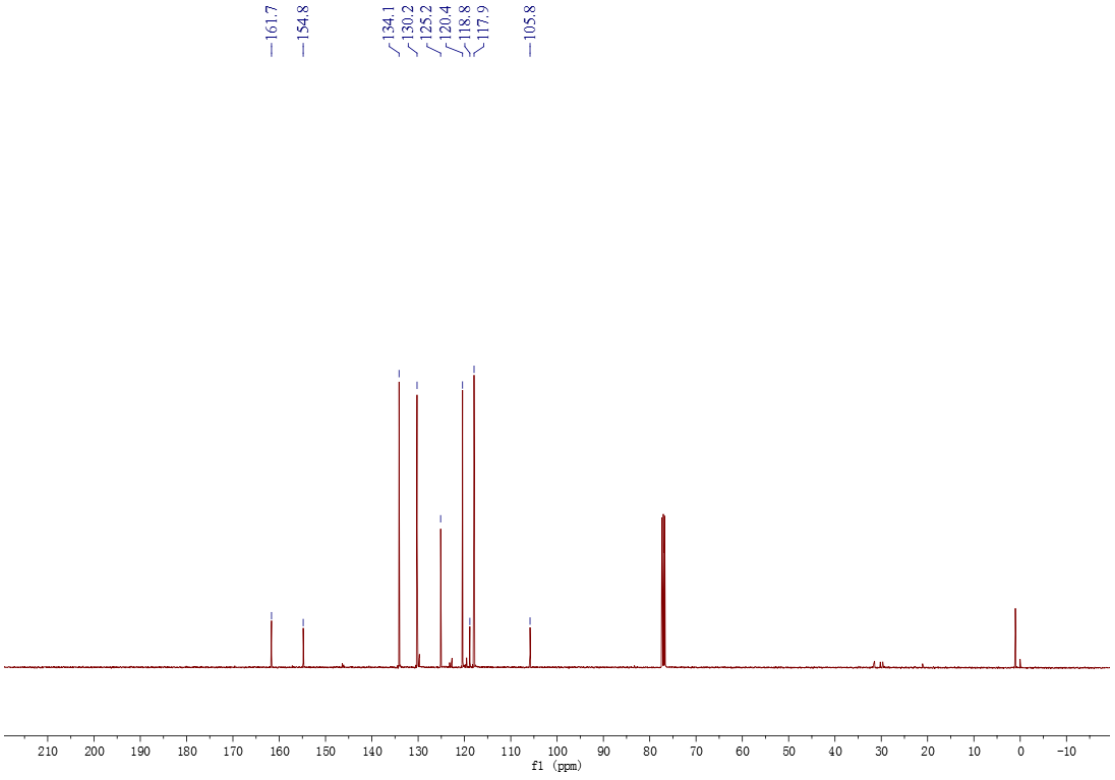
Methyl 4-cyanobenzoate (**3c**. ^{1}H NMR 400 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)



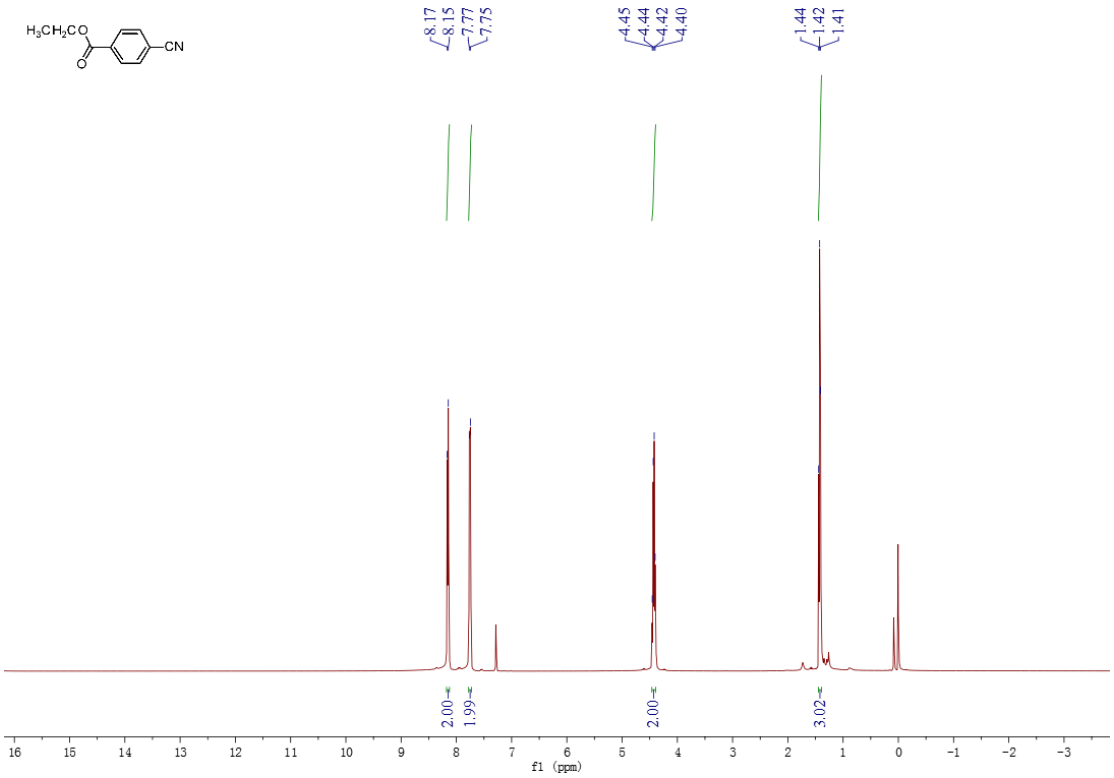


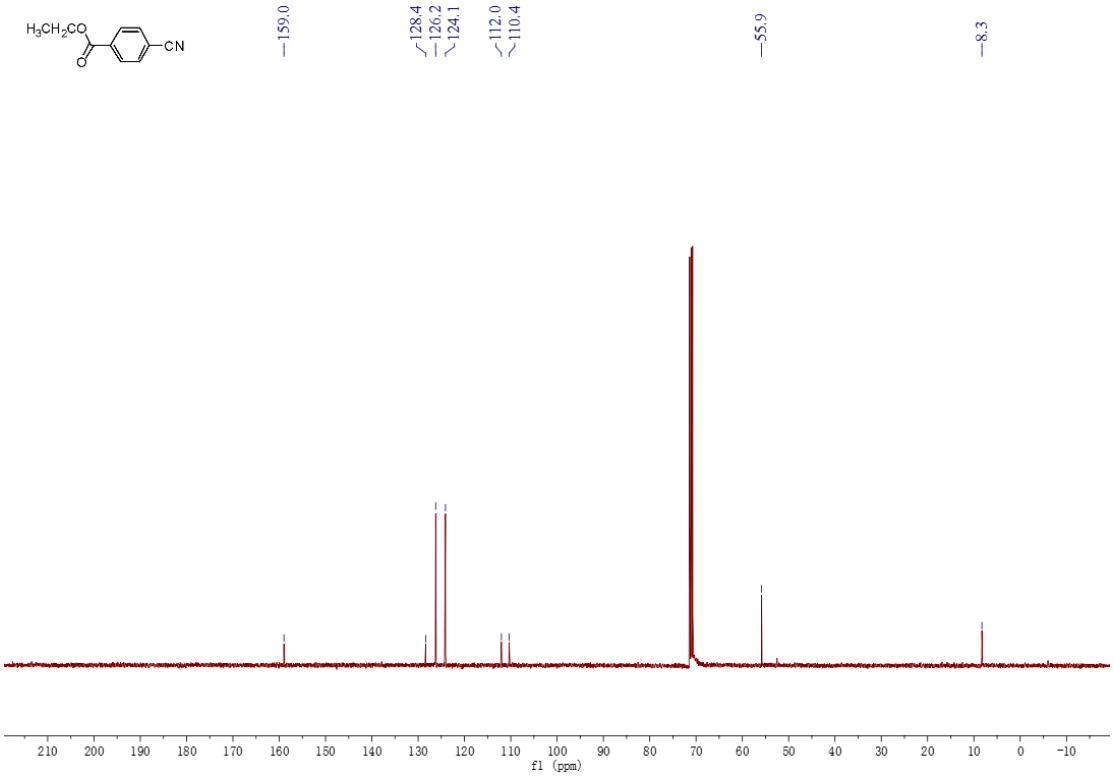
4-phenoxybenzonitrile (**3d**. ^{1}H NMR 400 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)



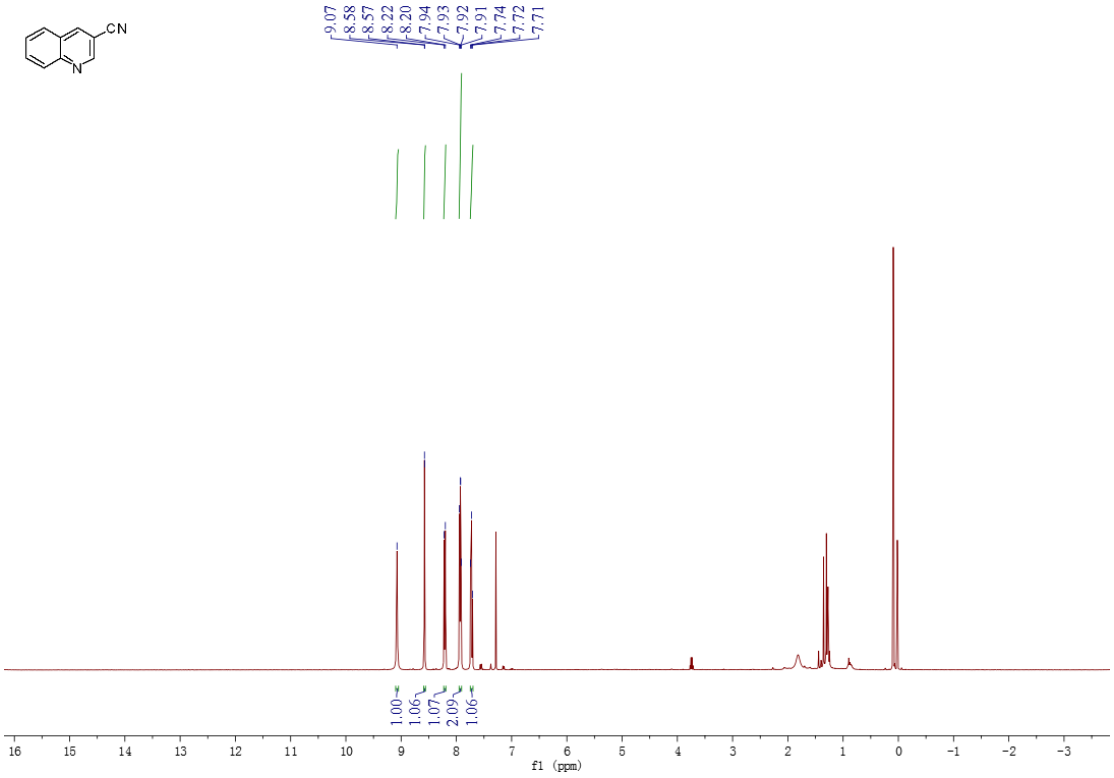


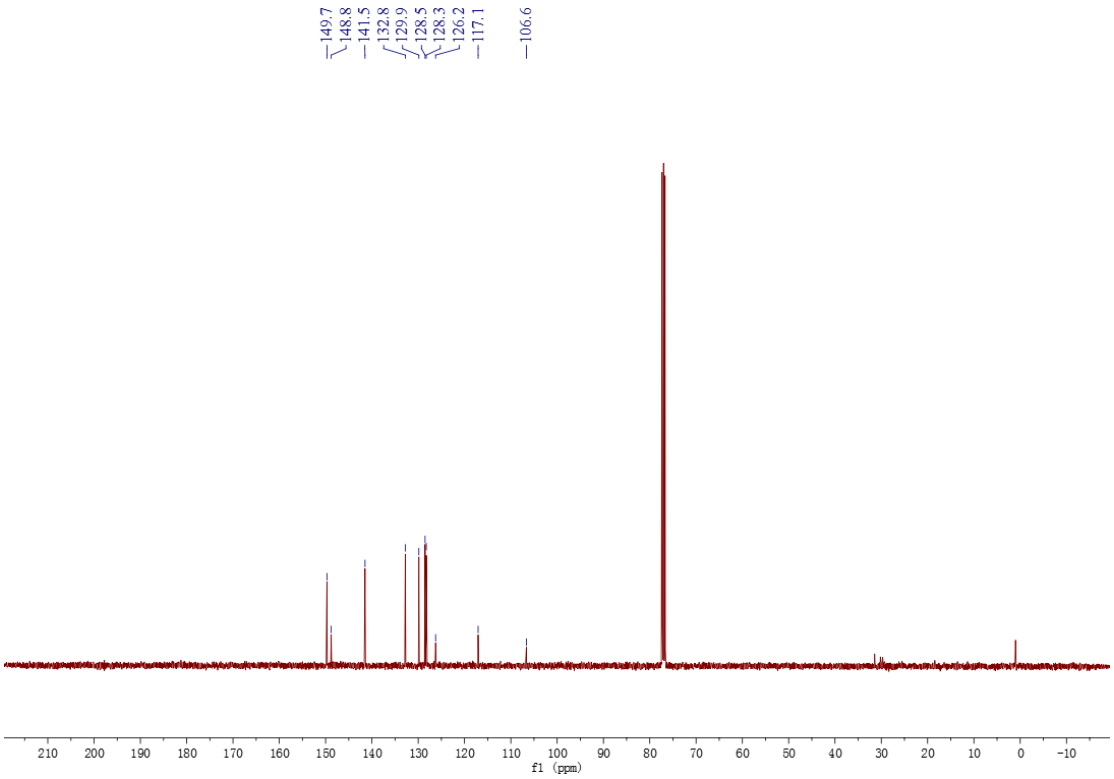
Ethyl 4-cyanobenzoate (**3e**. ^{1}H NMR 400 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)



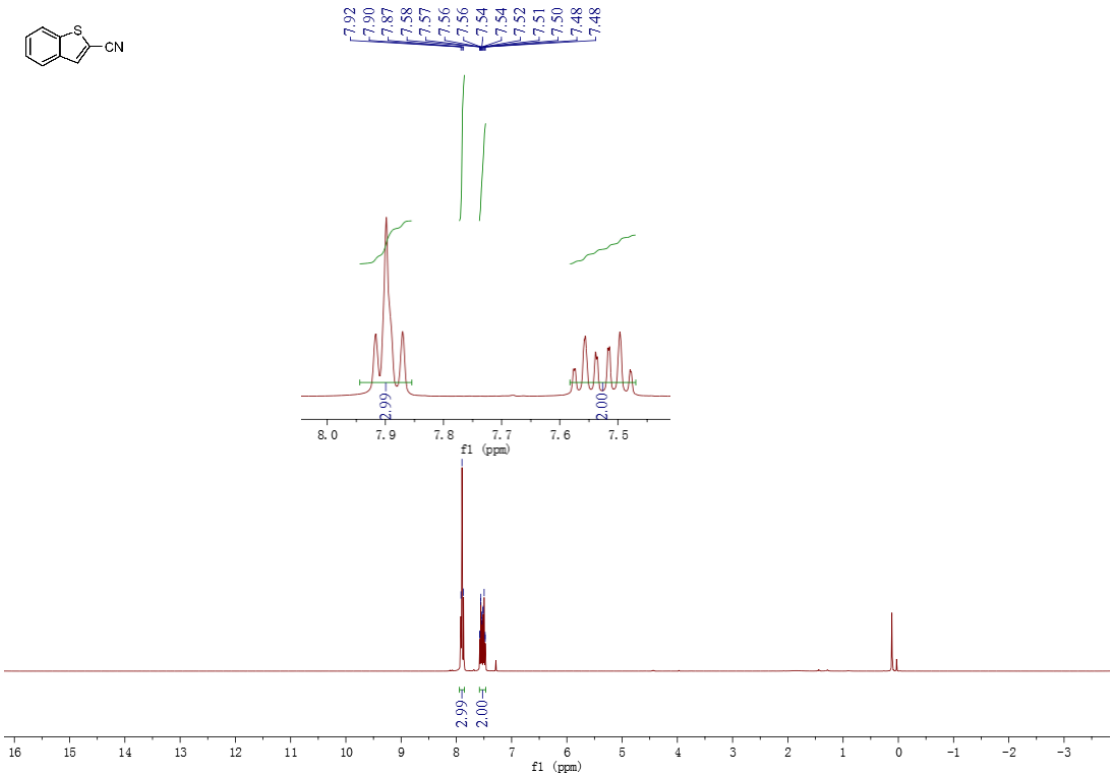


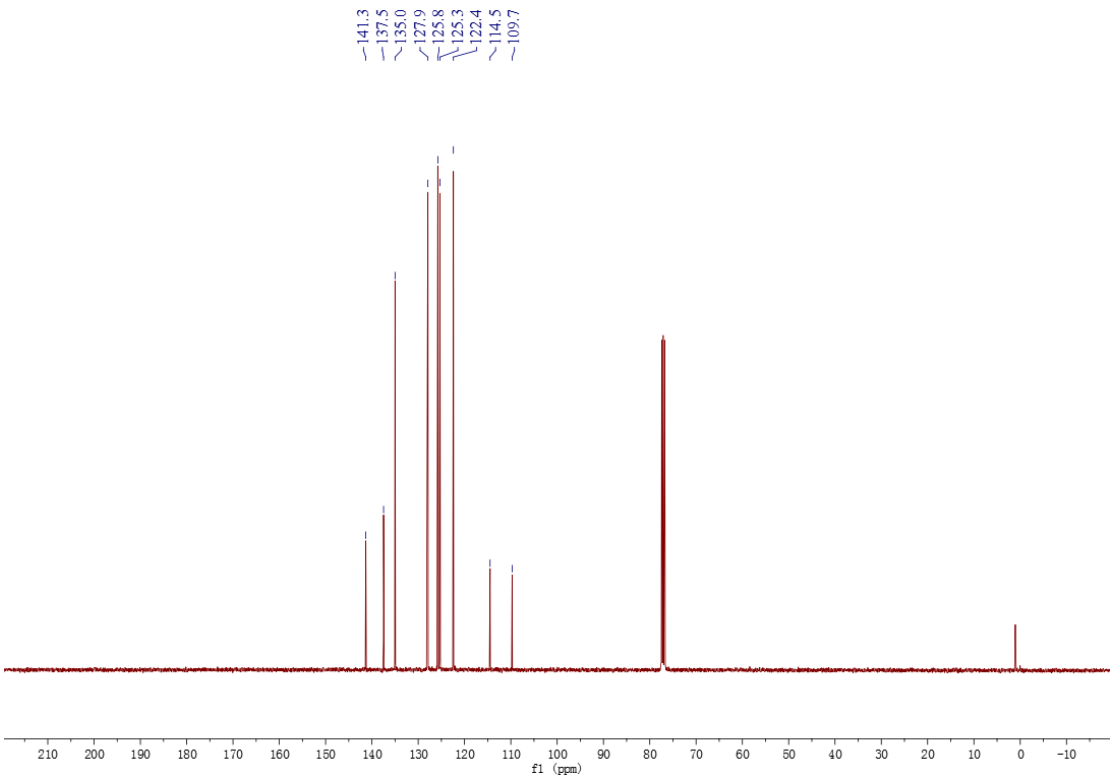
Quinoline-3-carbonitrile (**3i.** ^{1}H NMR 400 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$).



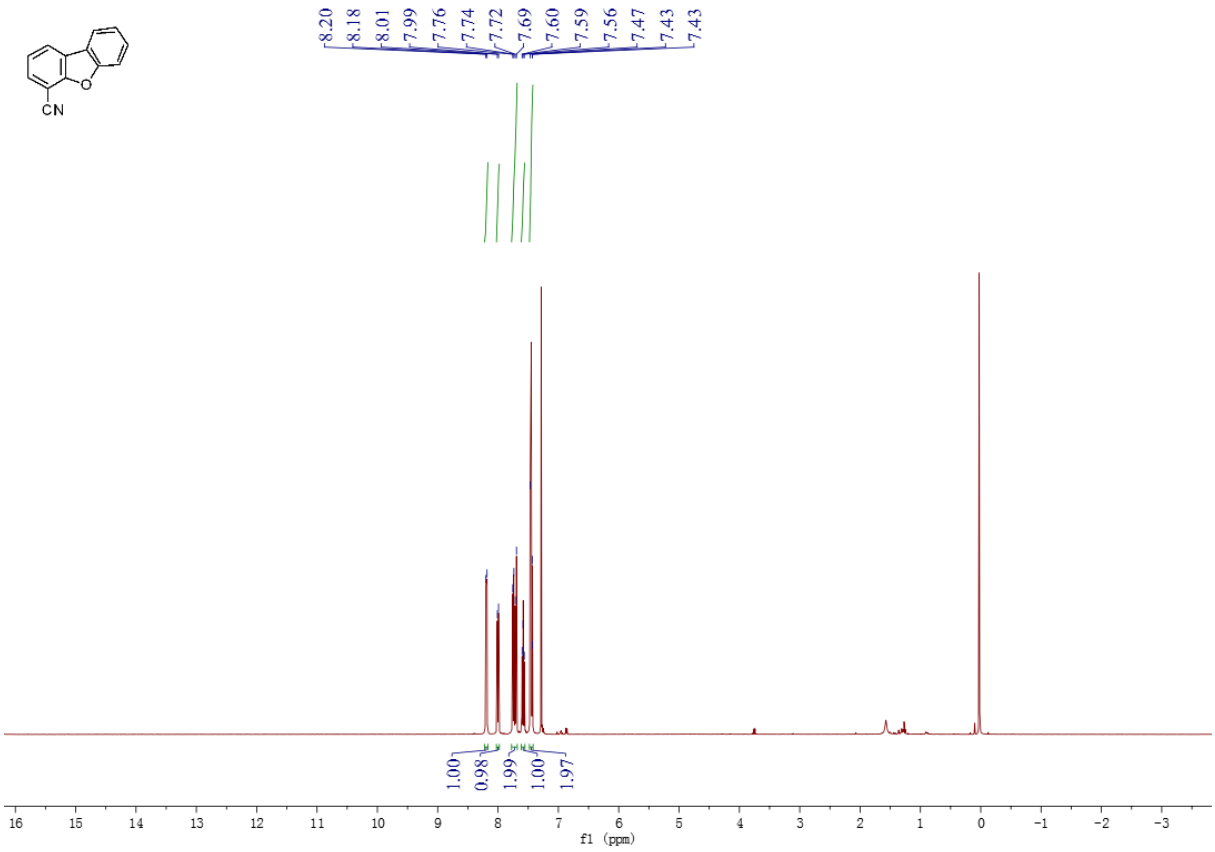


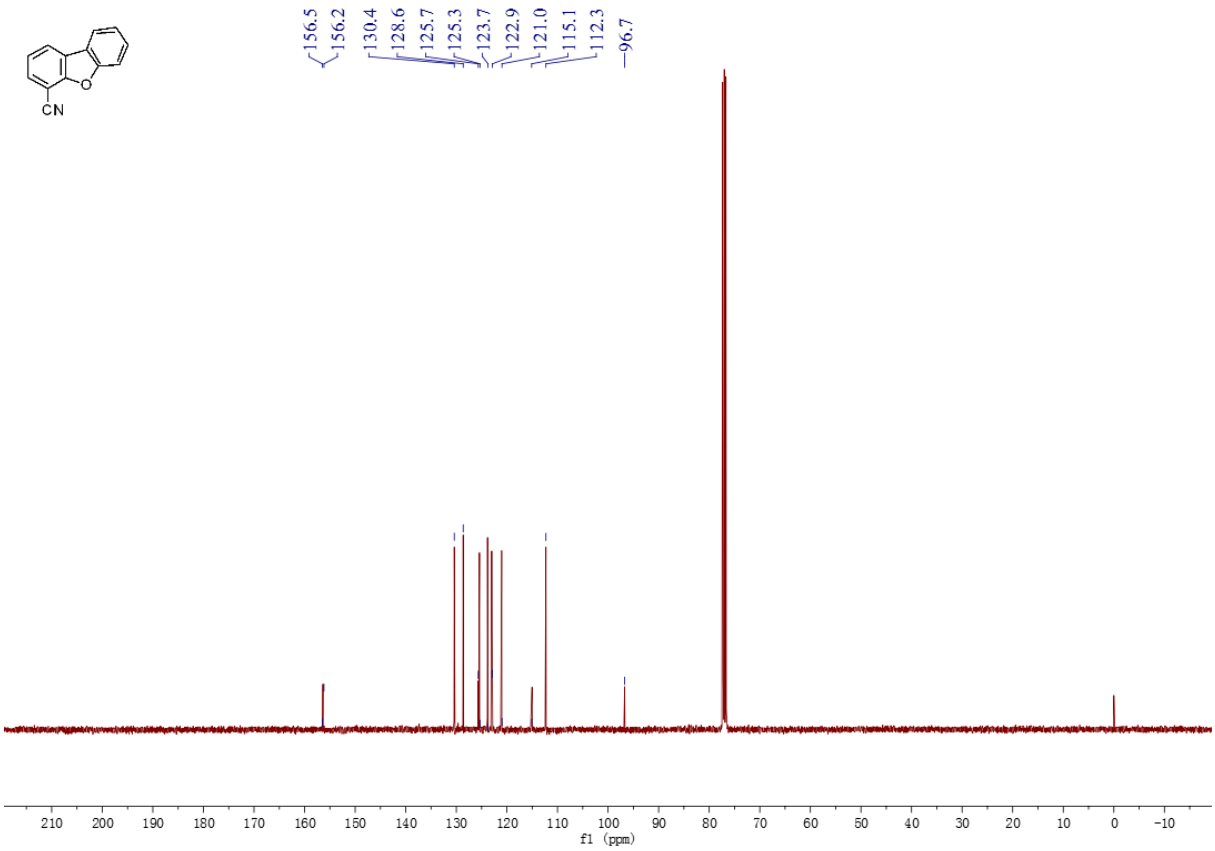
Benzo[*b*]thiophene-2-carbonitrile (**3j**. ^{1}H NMR 400 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)



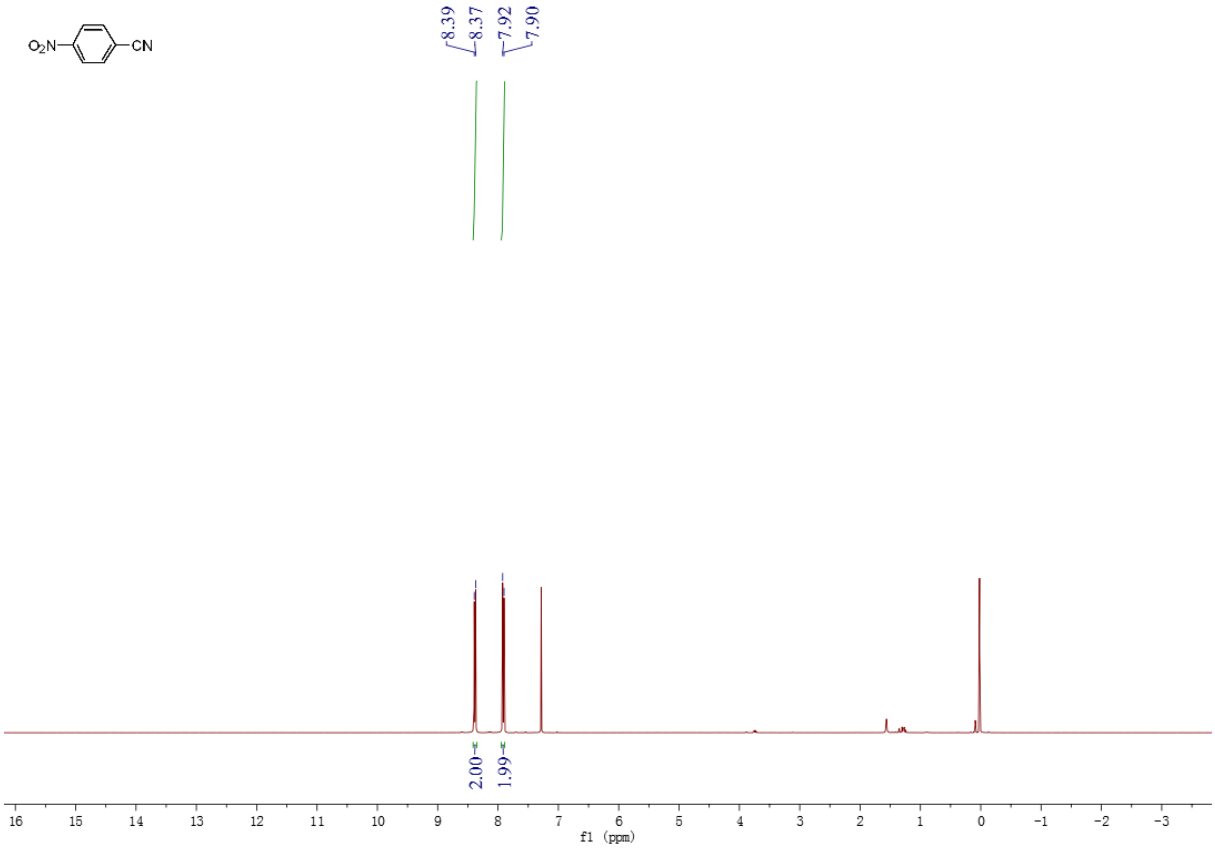


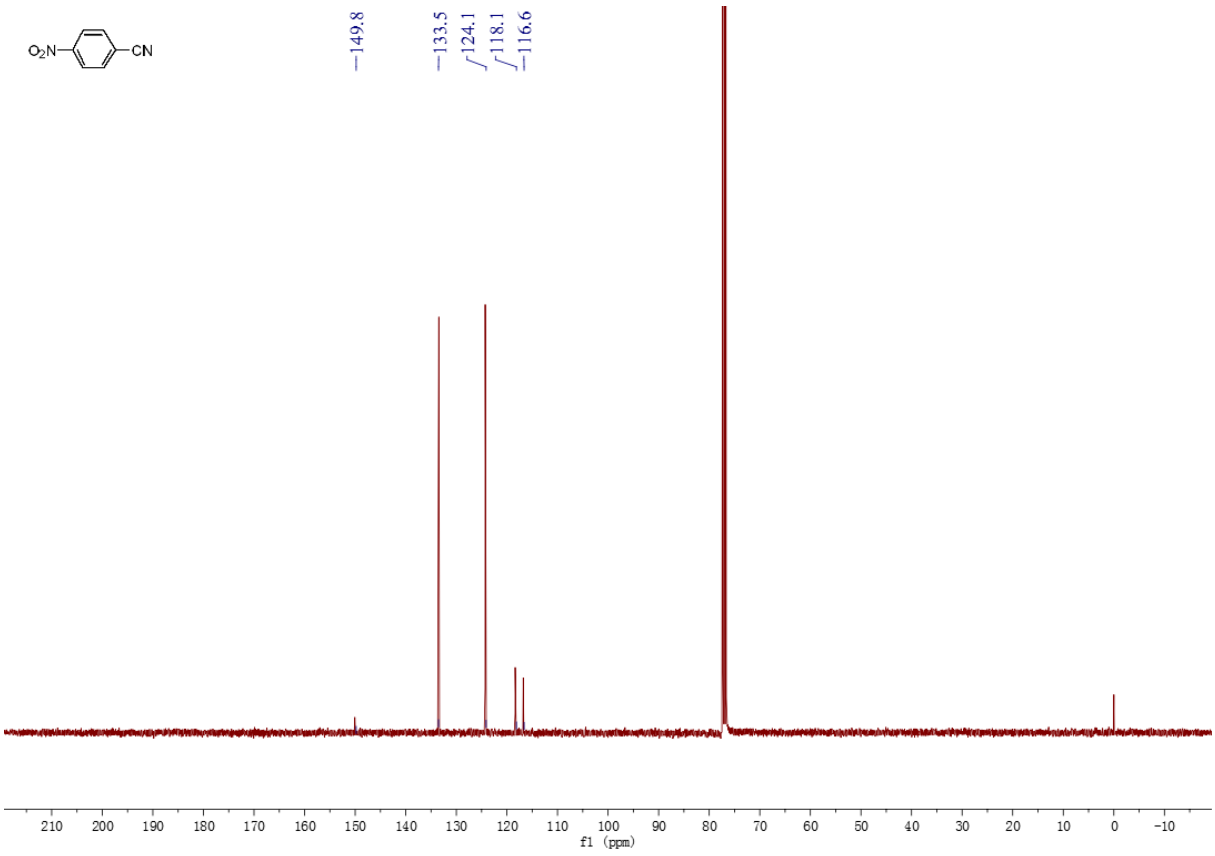
Dibenzofuran-1-carbonitrile (**3k**. ^{1}H NMR 400 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)



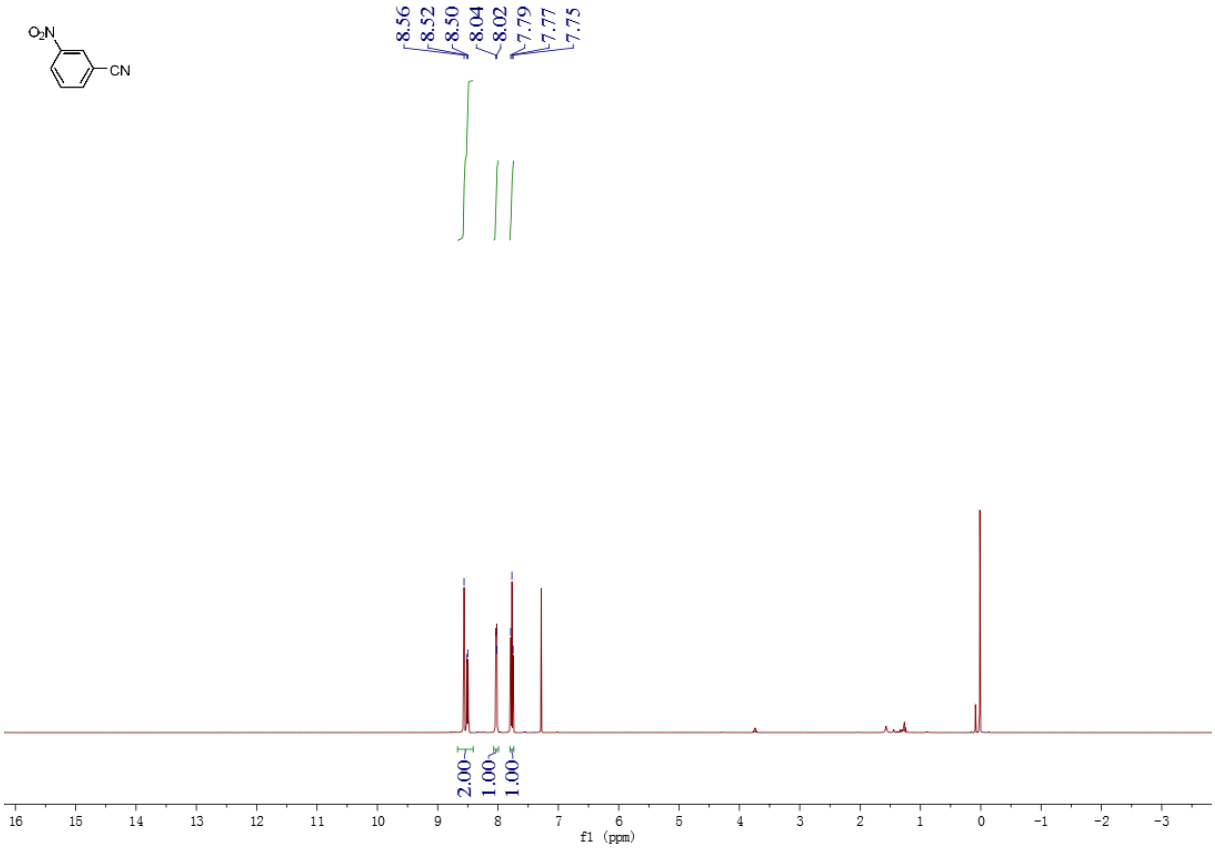


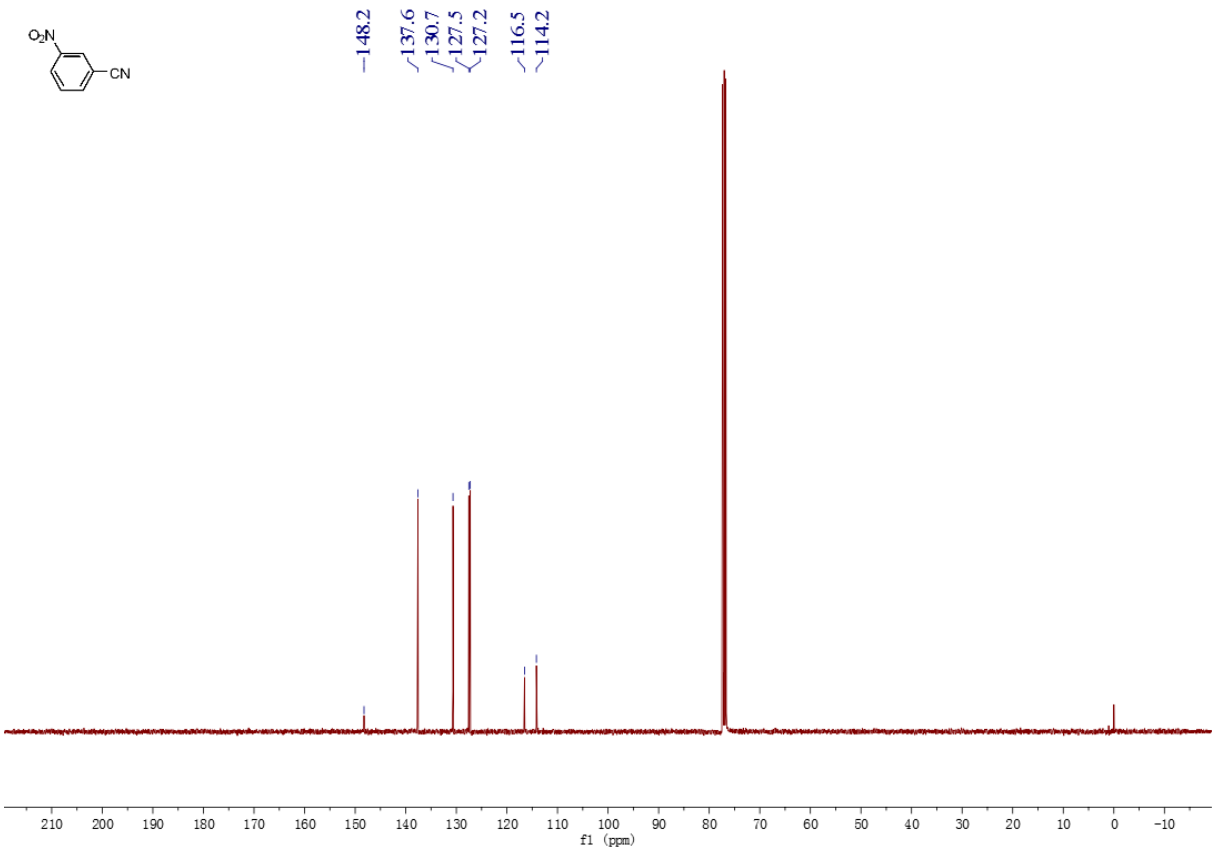
4-Nitrobenzonitrile (**3l**. ^{1}H NMR 400 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)



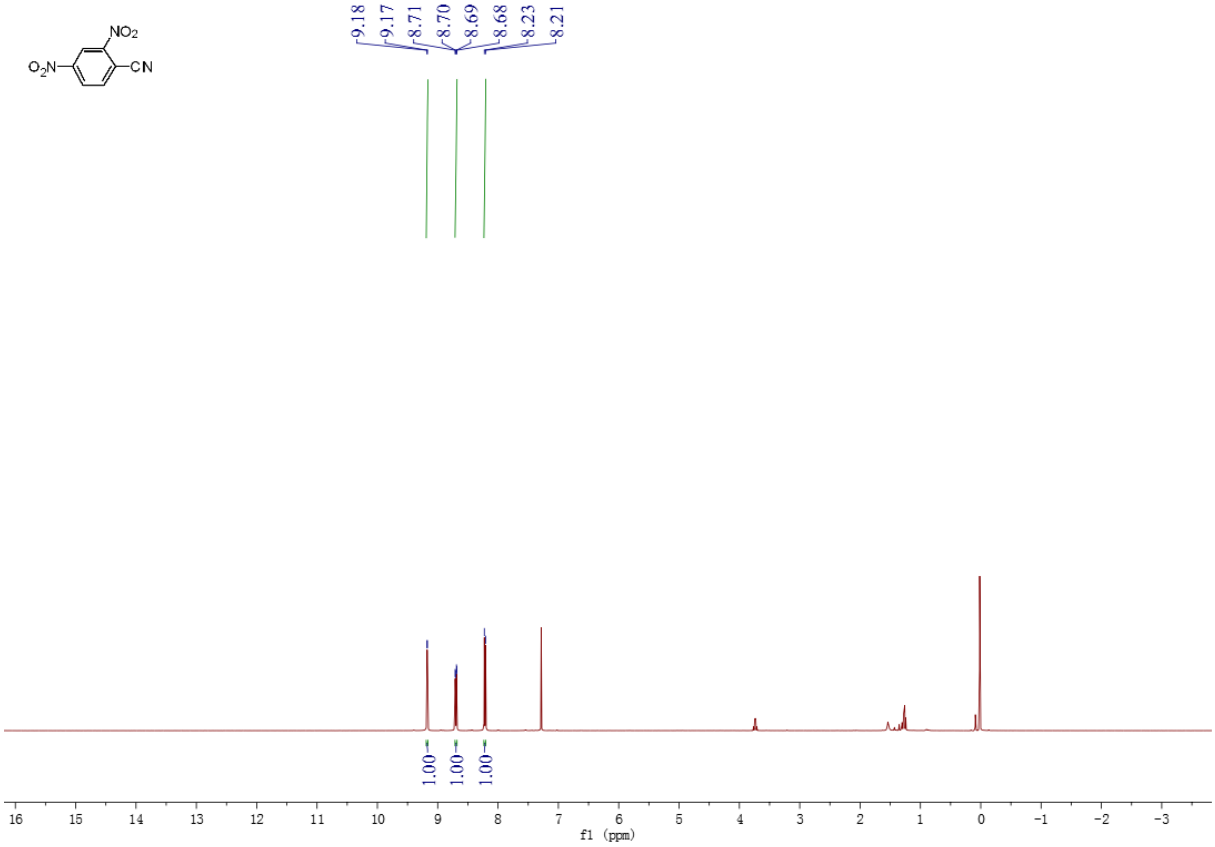


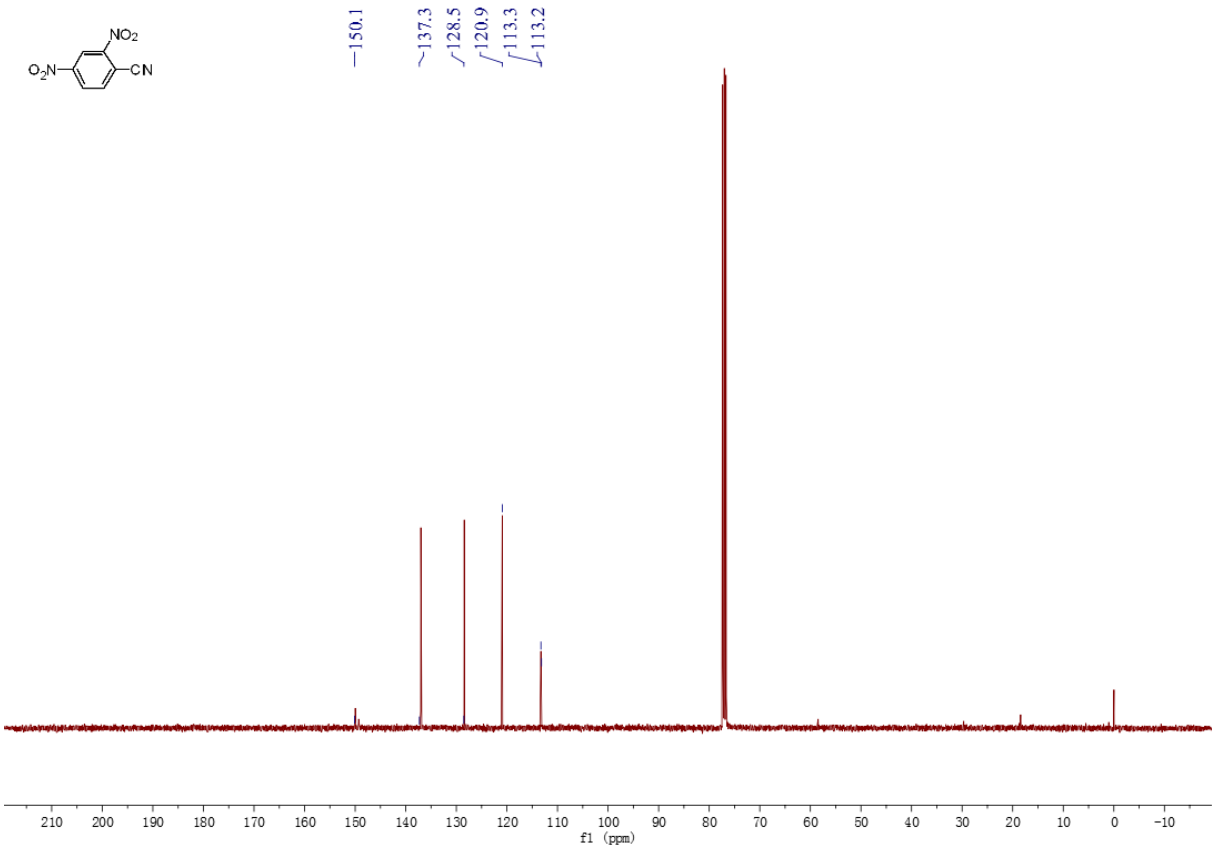
3-Nitrobenzonitrile (**3m**. ^{1}H NMR 400 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)



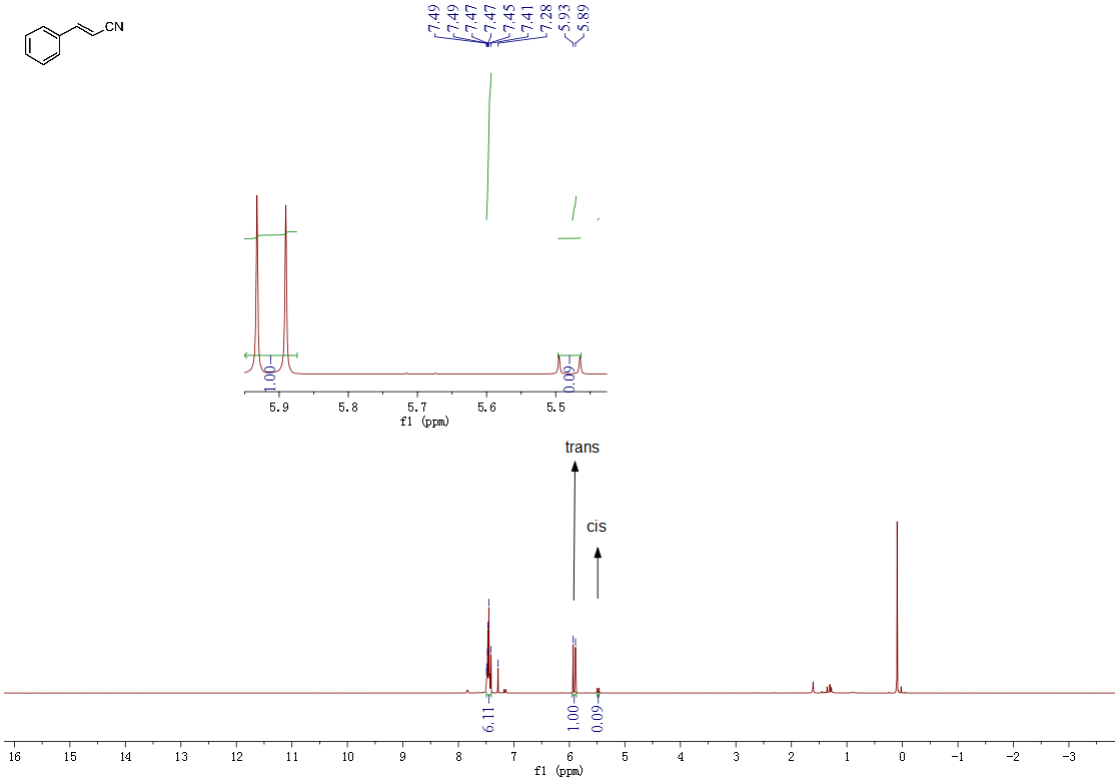


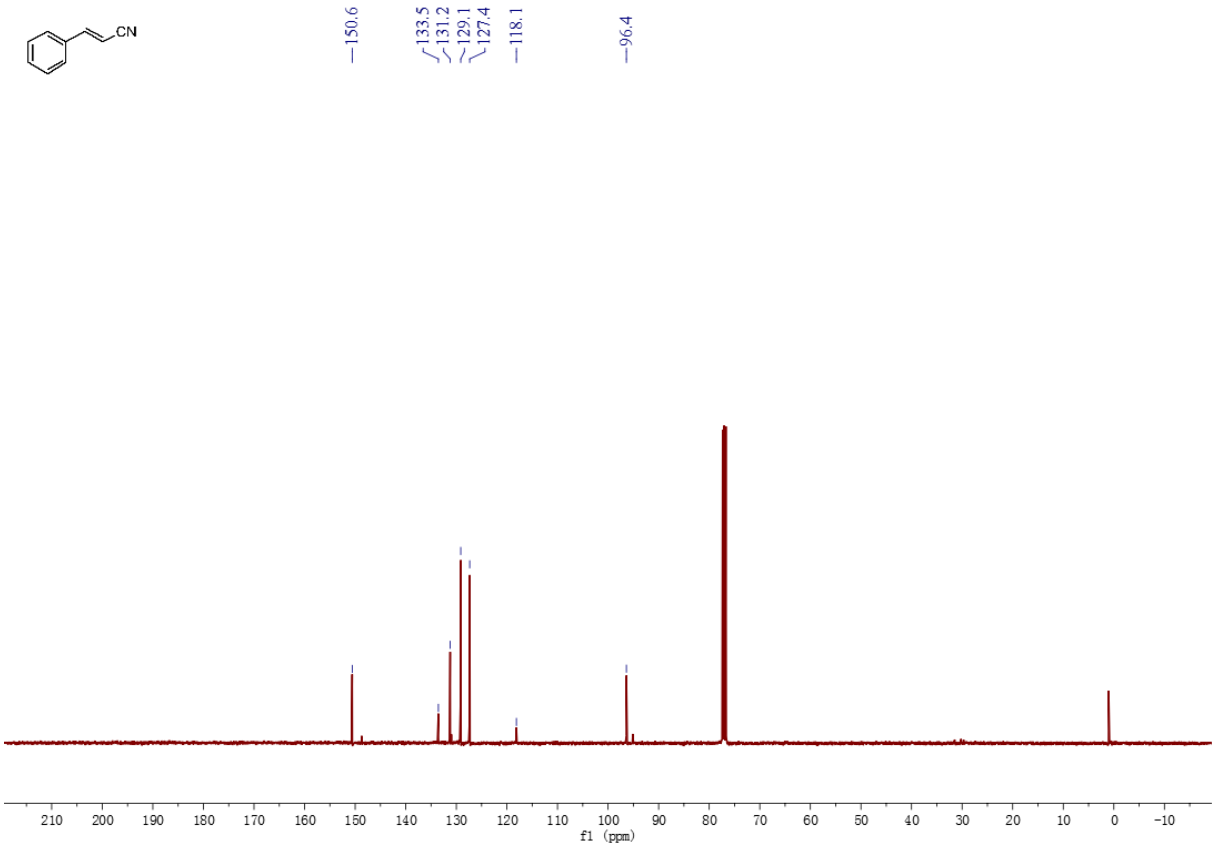
2,4-Dinitrobenzonitrile (**3n**. ^{1}H NMR 400 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)



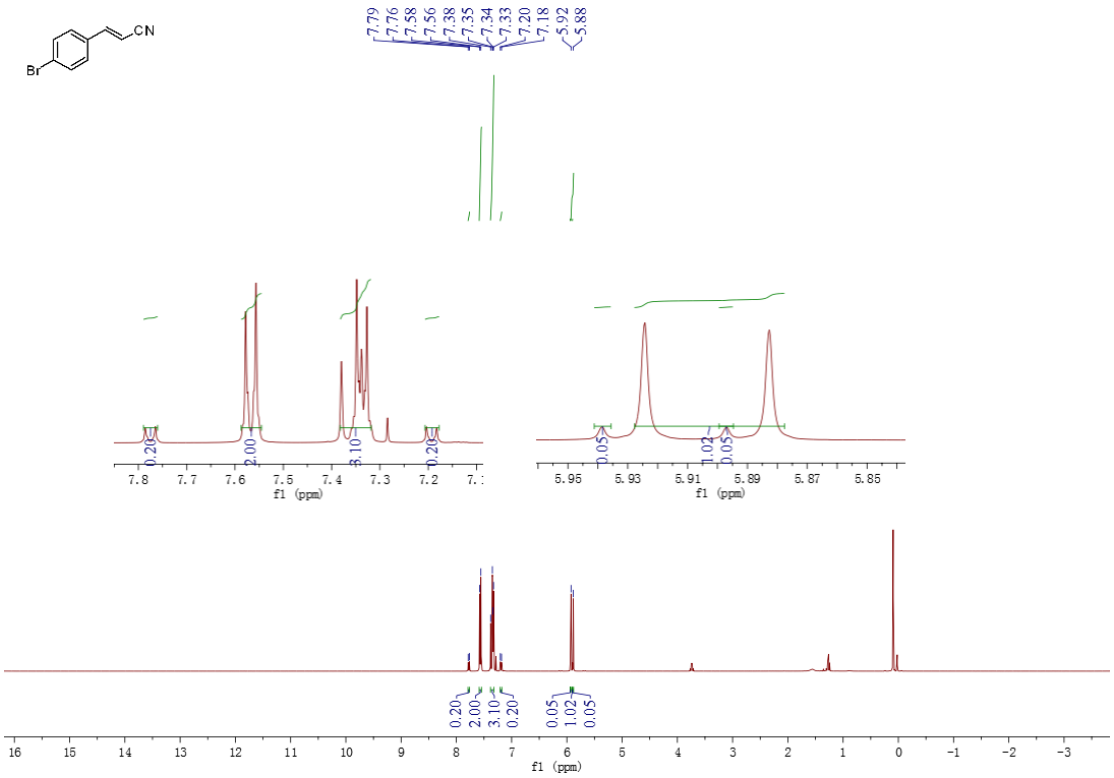


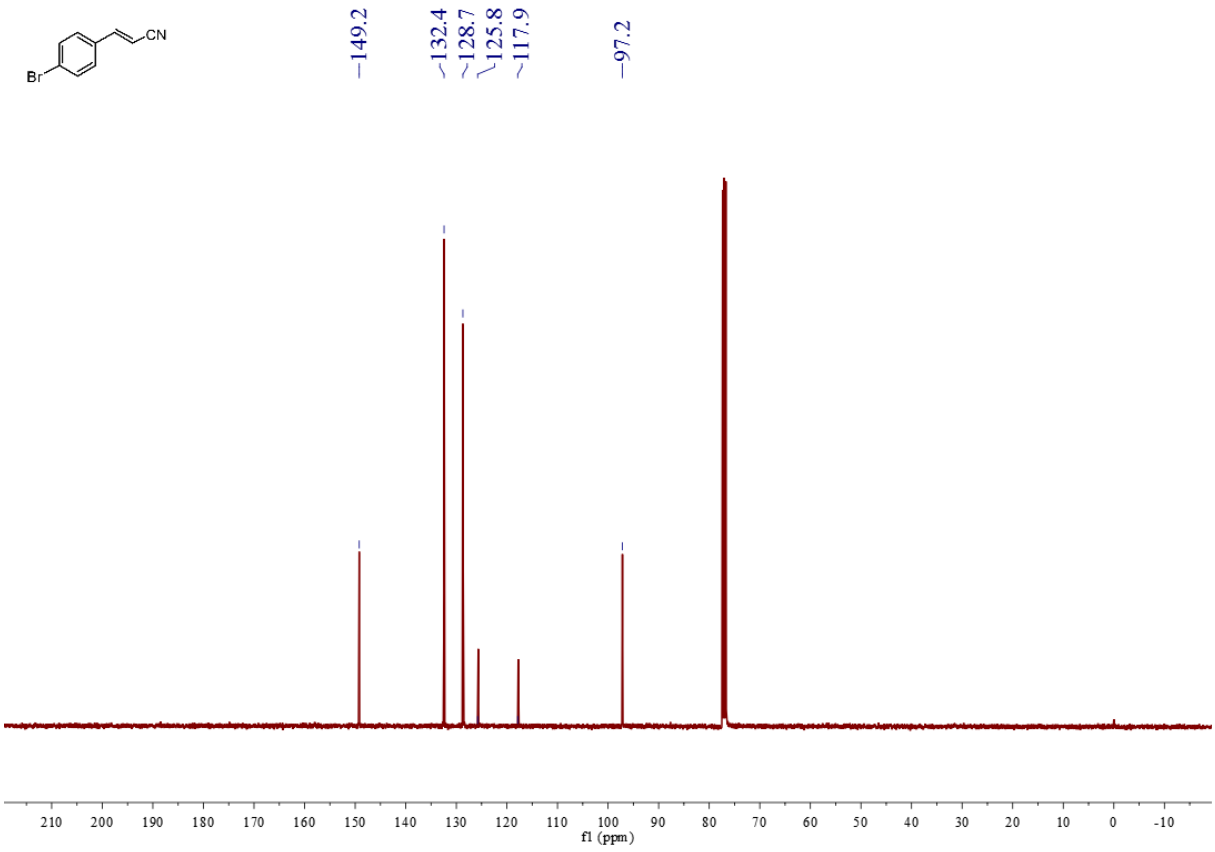
Cinnamonitrile (**4a**. ^{1}H NMR 400 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$) (trans/cis = 9:1)



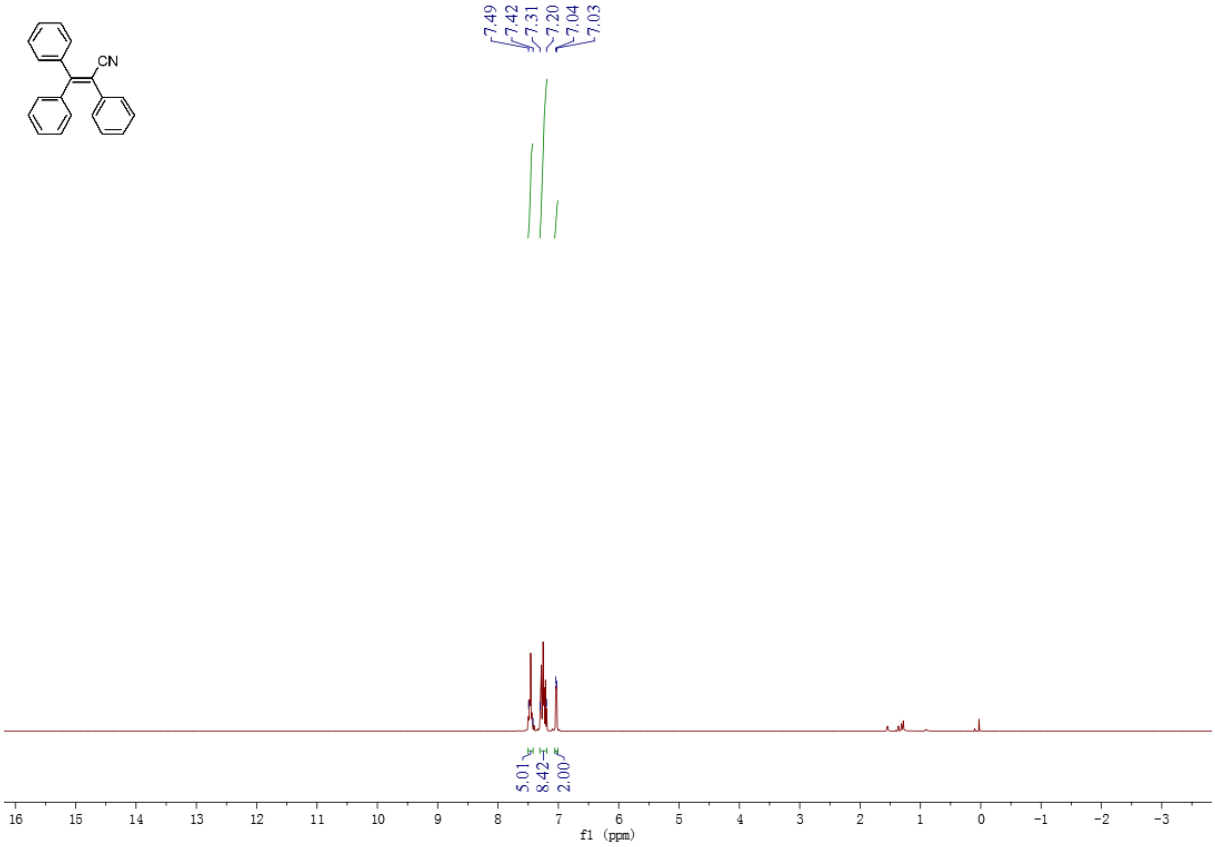


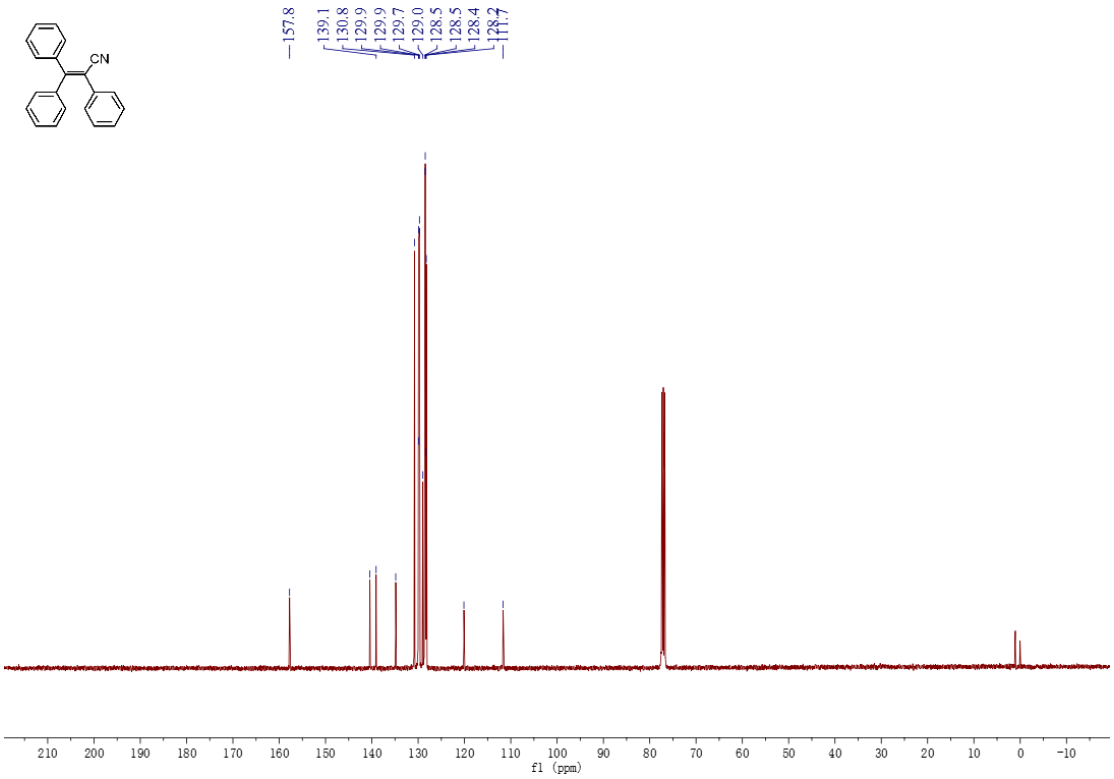
(*E*)-3-(4-bromophenyl)acrylonitrile (**4b**. ^{1}H NMR 400 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$) (contains minor amount of bis-cyanation side product in a ratio of *ca* 1:10 to **4b**)





2,3,3-Triphenylacrylonitrile (**4c**. ^{1}H NMR 400 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)





(*E*)-3-(4-methoxyphenyl)acrylonitrile (**4d**. ^{1}H NMR 400 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)