

Supporting Information

Tuning acid-base cooperativity to create bifunctional fiber catalysts for one-pot tandem reactions in water

Xian-Lei Shi^{a,b*}, Lijuan Jiang^a, Benyu Sun^a, Shuangshuang Liu^a, Mengmeng Du^a,
Qianqian Hu^a, Honghui Gong^a, Baozhong Liu^{a*}

^a *Synerigism Innovative Center of Coal Safety Production in Henan Province, Henan Polytechnic University, Jiaozuo, Henan 454003, P. R. China. E-mail: shixl@tju.edu.cn; Tel./fax: +86-0391-3986810*

^b *Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin University, No. 92, Weijin Road, Tianjin 300072, P. R. China*

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Experimental details

Materials

Commercially available PANF (93.0% acrylonitrile, 6.5% methyl acrylate, and 0.4-0.5% sodium styrene sulfonate) with a length of 10 cm and a diameter of $30 \pm 0.5 \mu\text{m}$ (from the Fushun Petrochemical Corporation of China) was used after dried (In order to avoid the possible impacts of water absorption on the subsequent reactions and the consequent possible sources for experimental errors, all the fiber samples before use were dried fully at $60 \text{ }^\circ\text{C}$ under vacuum in this study). All other chemicals used were analytical grade and employed without further purification. Water was deionized.

Apparatus and instruments

The mechanical properties of different fiber samples were tested with an electronic single fiber strength tester (Quanzhou Meibang Instrument Co., Ltd of China, model YG001E). Elemental analyses were performed on a thermo scientific flash 2000 auto-analyzer. Fourier transform infrared (FTIR) spectra were obtained with an AVATAR 360 FTIR spectrometer (Thermo Nicolet), KBr disc. A scanning electron microscope (Zeiss, merlin compact) was used to characterize the surface morphology of the fibers. The surface area and porosity of the fiber samples were tested on a Micromeritics-ASAP2420 specific surface area tester. The X-ray photoelectron spectroscopy (XPS) of the fiber samples was detected on a Thermo Fisher Scientific K-Alpha XPS system. The solid state ^{13}P NMR spectra measurements of the sample was conducted at 14.01 T using a JNM-ECZ600R spectrometer (JEOL RESONANCE Inc., Japan) operating at a ^1H resonance frequency of 599.7 MHz. ^1H NMR spectra were recorded on an AVANCE III (Bruker, 400 MHz) instrument using TMS as the internal standard. ^{13}C NMR spectra were recorded on an AVANCE III (Bruker, 101 MHz) instrument with complete proton decoupling.

Supplementary detection results

Table S1. Specific surface area and porosity of the PANF, PANF_{TETA} and PANF_{TETA-PA-C}.

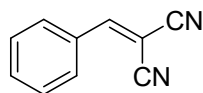
Entry	Fiber sample	S _{BET} (m ² g ⁻¹)	Average pore diameter (nm)
1	PANF	42	3.29
2	PANF _{TETA}	34	4.25
3	PANF _{TETA-PA-C}	31	4.71

Table S2. The elemental compositions of PANF_{TETA-PA-C} and PANF_{TETA-PA-C-1} determined from XPS test results.

Element	PANF _{TETA-PA-C} Atomic (%)	PANF _{TETA-PA-C-1} Atomic (%)
C	71.49	71.7
N	12.78	12.93
P	1.37	1.1
O	14.35	14.27

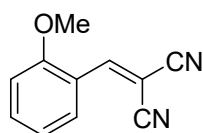
Characterization results of the synthesized compounds

Physical shape, melting point and ^1H NMR and ^{13}C NMR data



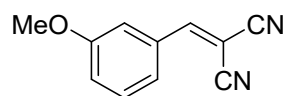
2-(Phenylmethylene)malononitrile. (3a)^[1,2,3]

White solid; m.p. = 79-81 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, $J = 7.7$ Hz, 2H), 7.79 (s, 1H), 7.64 (t, $J = 7.4$ Hz, 1H), 7.54 (t, $J = 7.6$ Hz, 2H); ^{13}C NMR (101MHz, CDCl_3) δ 160.1, 134.7, 130.9, 130.8, 129.7, 113.8, 112.6, 82.8.



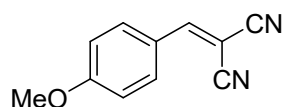
2-(2-Methoxyphenylmethylene)malononitrile. (3b)^[1,3]

Yellow solid; m.p. = 78-80 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.30 (s, 1H), 8.17 (d, $J = 7.9$ Hz, 1H), 7.59 (t, $J = 7.9$ Hz, 1H), 7.07 (t, $J = 7.7$ Hz, 1H), 7.00 (d, $J = 8.5$ Hz, 1H), 3.93 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 159.0, 154.5, 136.6, 128.9, 121.2, 120.2, 114.4, 113.1, 111.6, 81.3, 56.0.



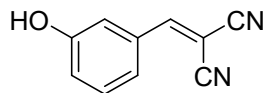
2-(3-Methoxyphenylmethylene)malononitrile. (3c)^[1,2]

Yellow solid; m.p. = 79-80 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.75 (s, 1H), 7.45-7.44 (m, 3H), 7.19-7.16 (m, 1H), 3.87 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 159.6, 132.1, 130.7, 123.7, 121.4, 114.1, 113.7, 112.7, 82.4, 55.5.



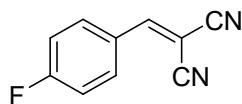
2-(4-Methoxyphenylmethylene)malononitrile. (3d) ^[1,2,3]

Yellow solid; m.p. = 111-112 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, *J* = 8.8 Hz, 2H), 7.66 (s, 1H), 7.02 (d, *J* = 8.9 Hz, 2H), 3.92 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 164.9, 159.0, 133.5, 124.0, 115.2, 114.5, 113.4, 78.4, 55.8.



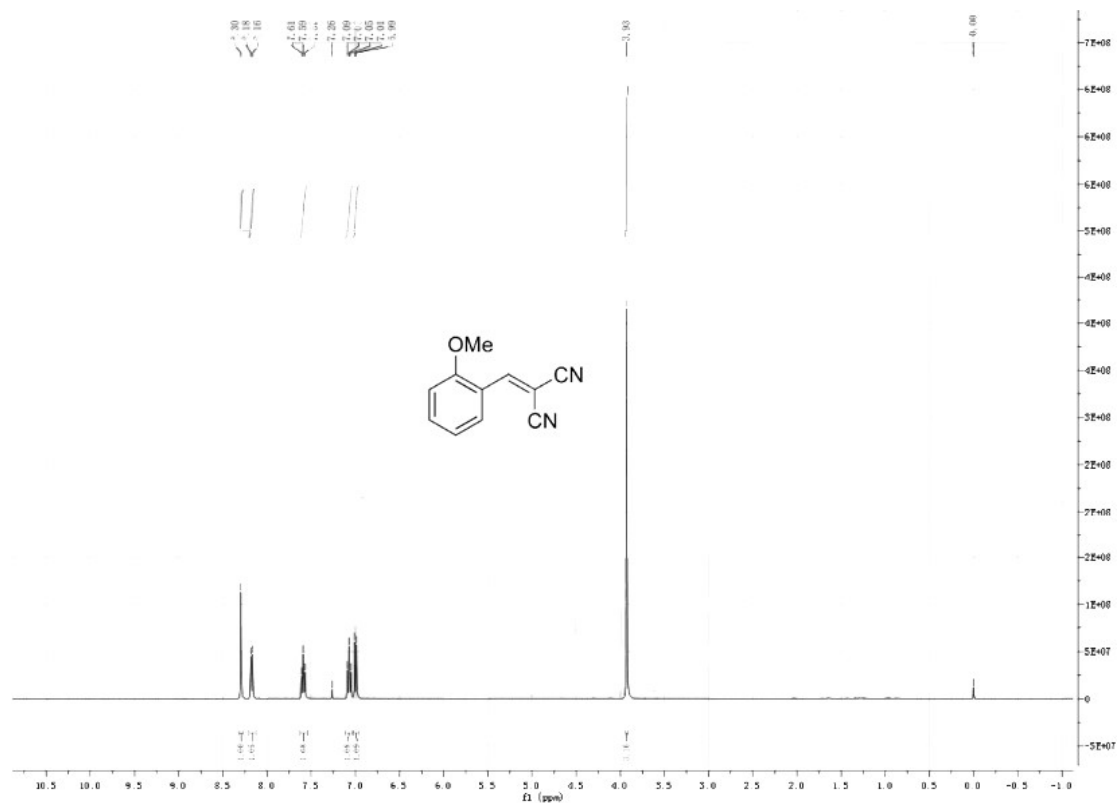
2-(3-Hydroxyphenylmethylene)malononitrile. (3e) ^[1,3]

Yellow solid; m.p. = 150-152 °C; ¹H NMR (400 MHz, DMSO-d₆) δ 10.13 (s, 1H), 8.44 (s, 1H), 7.39 (dd, *J* = 13.9, 7.6 Hz, 3H), 7.10 (d, *J* = 7.5 Hz, 1H); ¹³C NMR (101 MHz, DMSO-d₆) δ 162.1, 158.4, 132.9, 131.0, 122.5, 122.3, 116.6, 114.7, 113.6, 81.6.

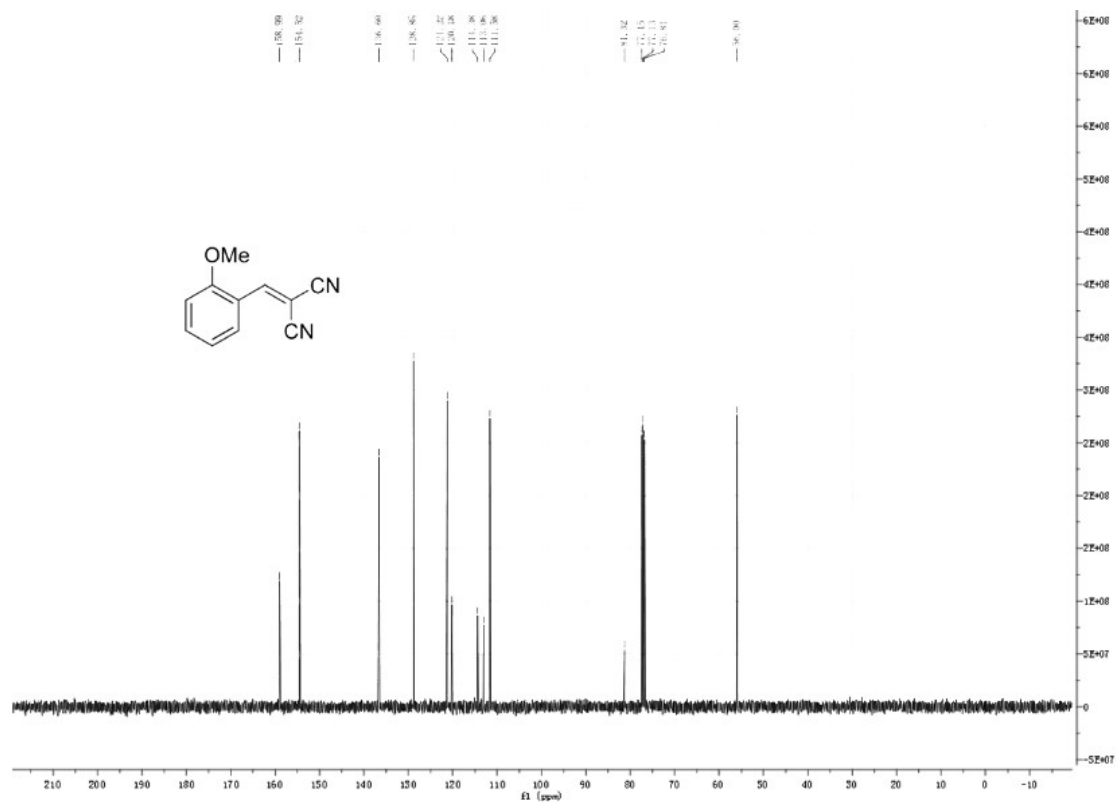


2-(4-Fluorophenylmethylene)malononitrile. (3f) ^[1,3]

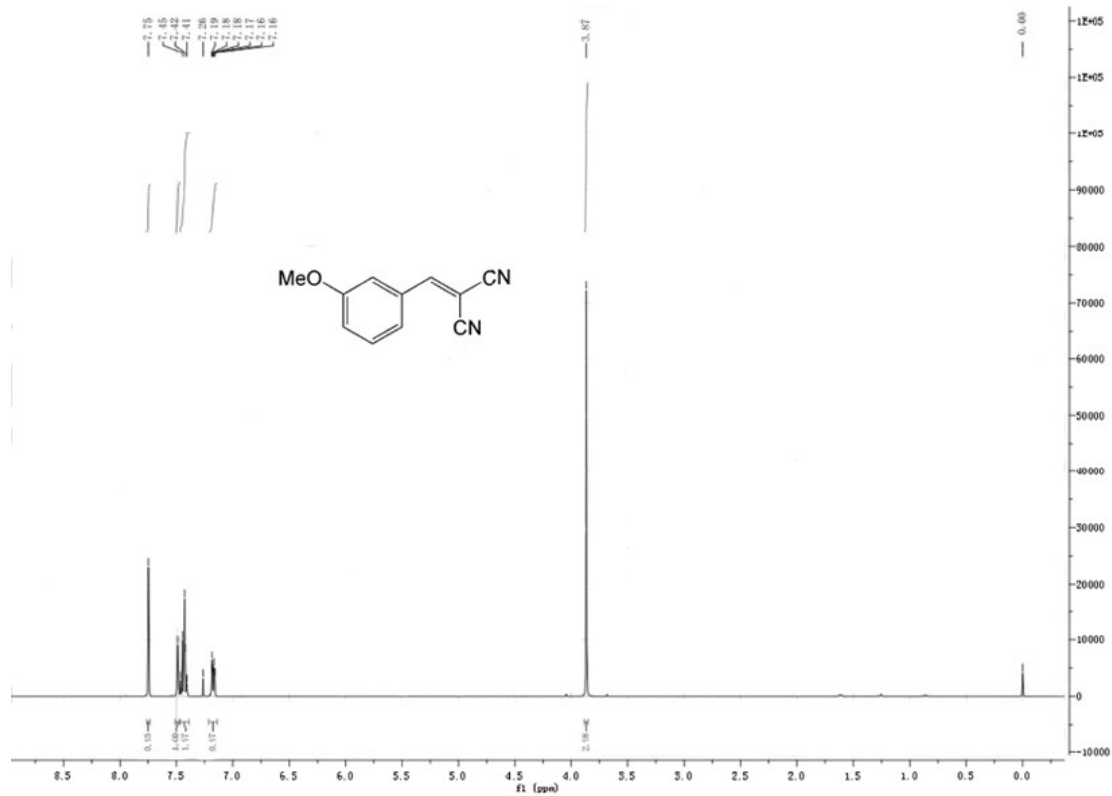
White solid; m.p. = 123-125 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.97 (dd, *J* = 8.7, 5.2 Hz, 2H), 7.77 (s, 1H), 7.25 (dd, *J* = 14.2, 5.8 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 164.8, 158.4, 133.5, 133.4, 127.4, 117.3, 117.1, 113.6, 112.6, 82.4.



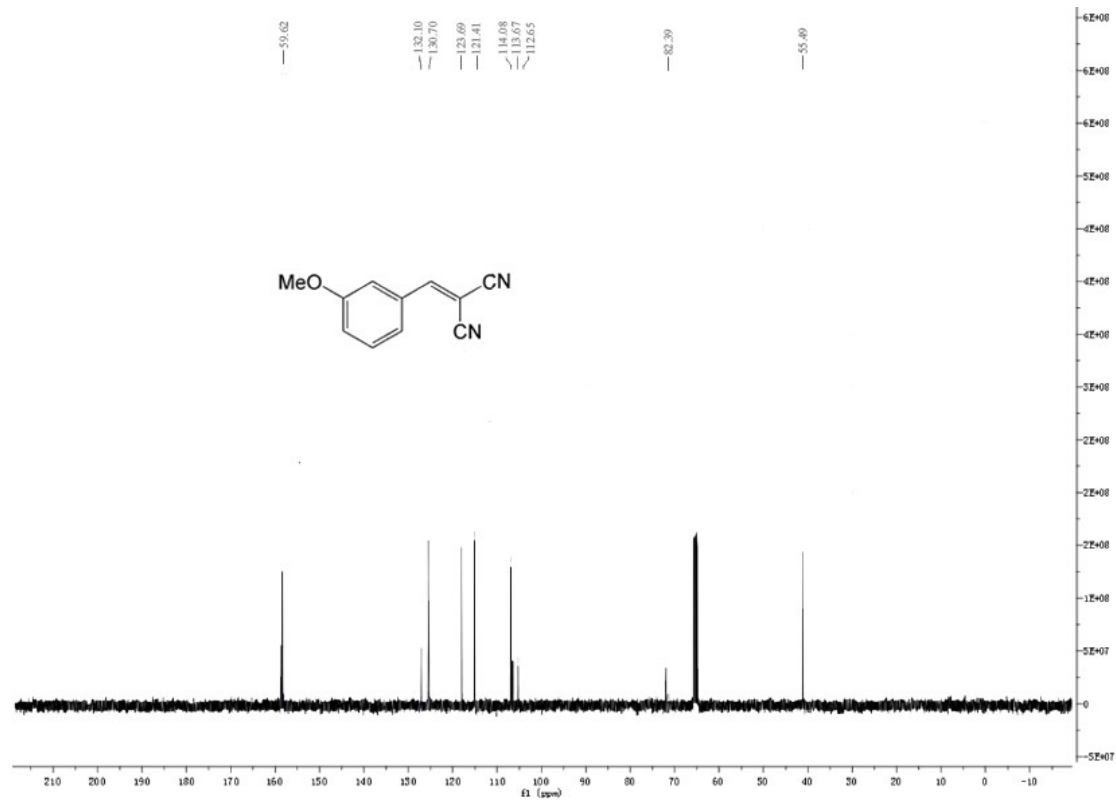
The ¹H NMR spectrum of 2-(2-methoxyphenylmethylene)malononitrile (3b).



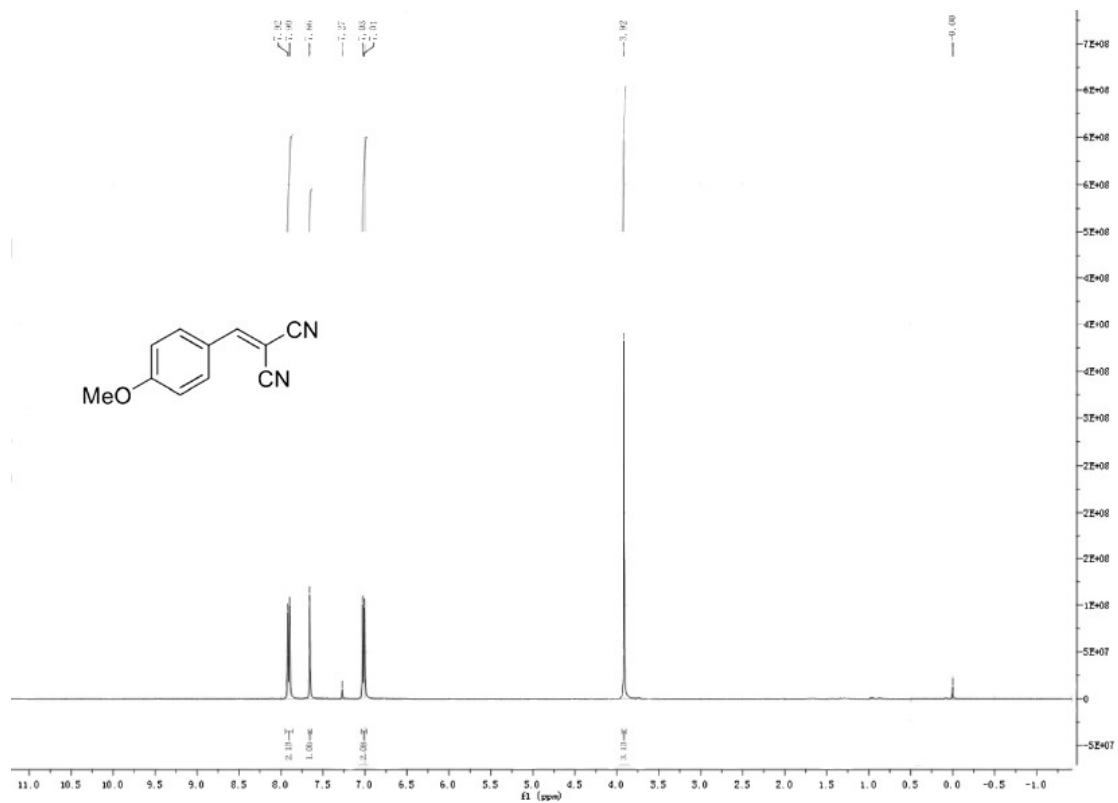
The ¹³C NMR spectrum of 2-(2-methoxyphenylmethylene)malononitrile (3b).



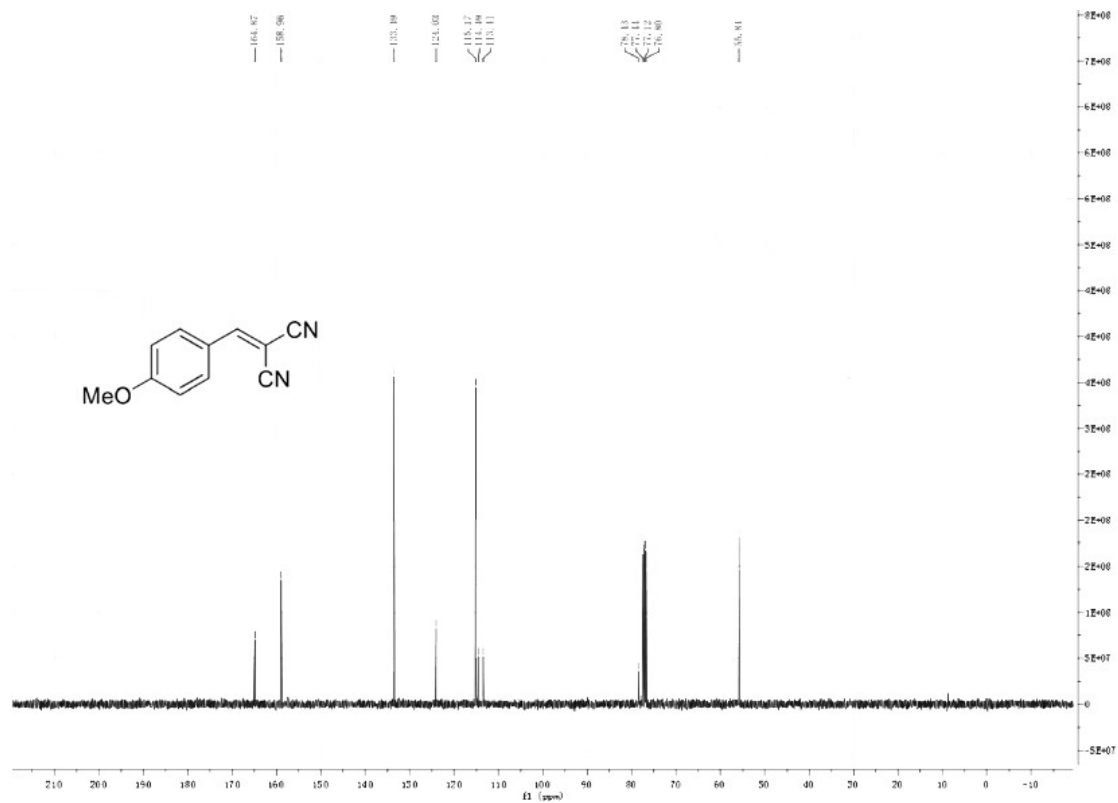
The ¹H NMR spectrum of 2-(3-methoxyphenylmethylene)malononitrile (3c).



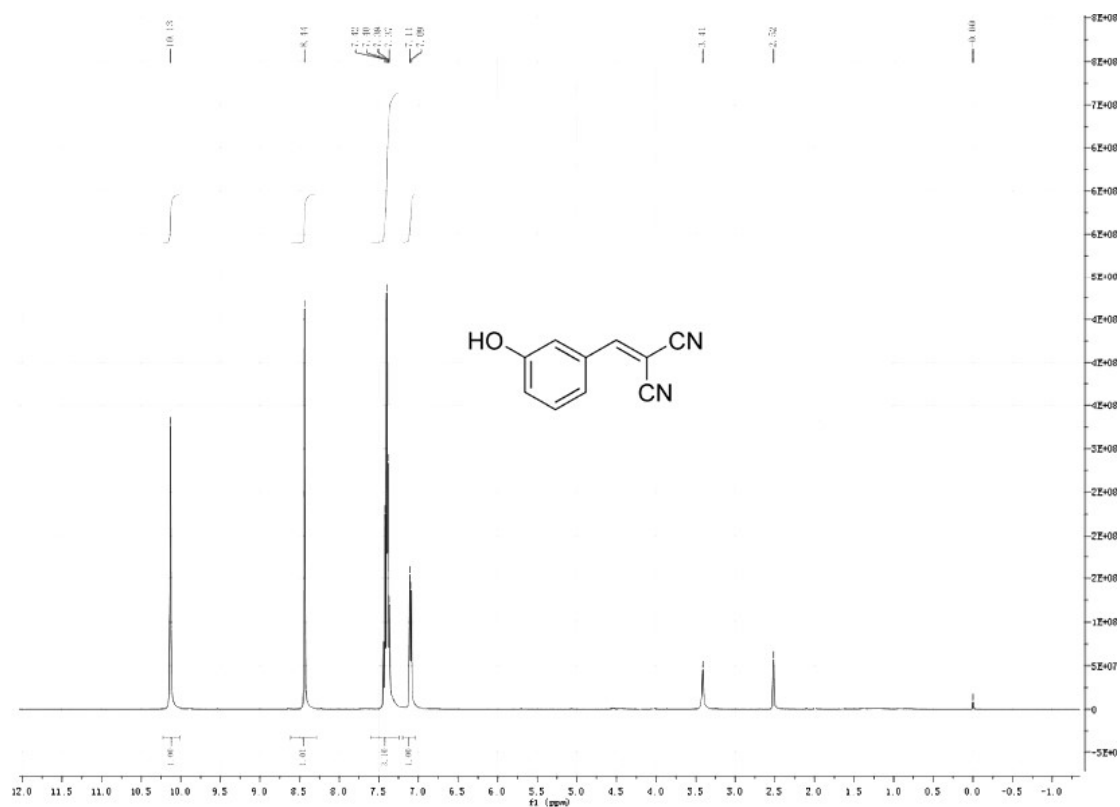
The ¹³C NMR spectrum of 2-(3-methoxyphenylmethylene)malononitrile (3c).



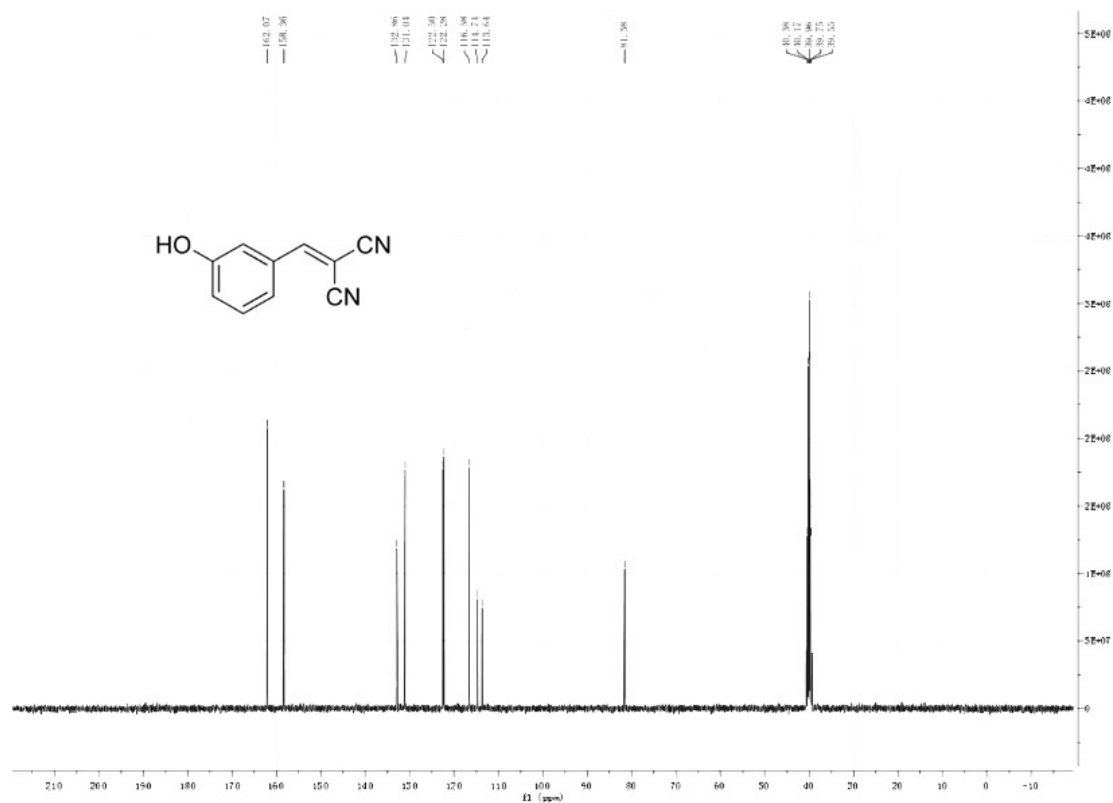
The ¹H NMR spectrum of 2-(4-methoxyphenylmethylene)malononitrile (3d).



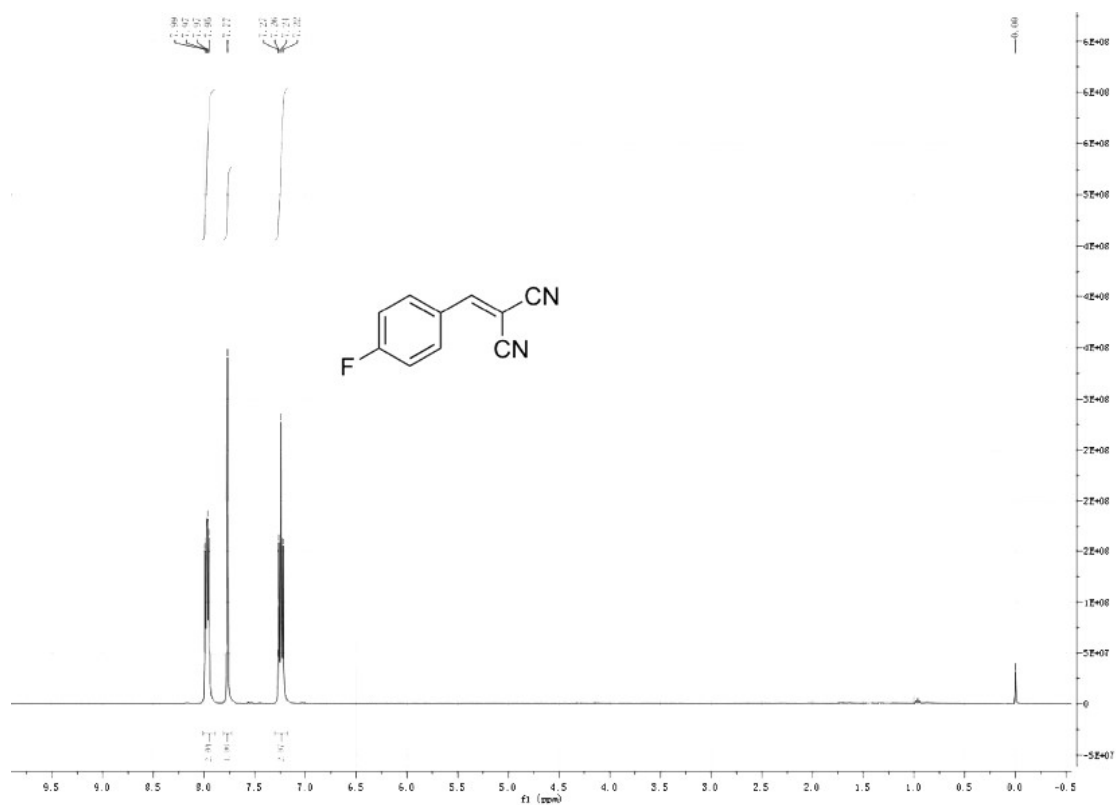
The ¹³C NMR spectrum of 2-(4-methoxyphenylmethylene)malononitrile (3d).



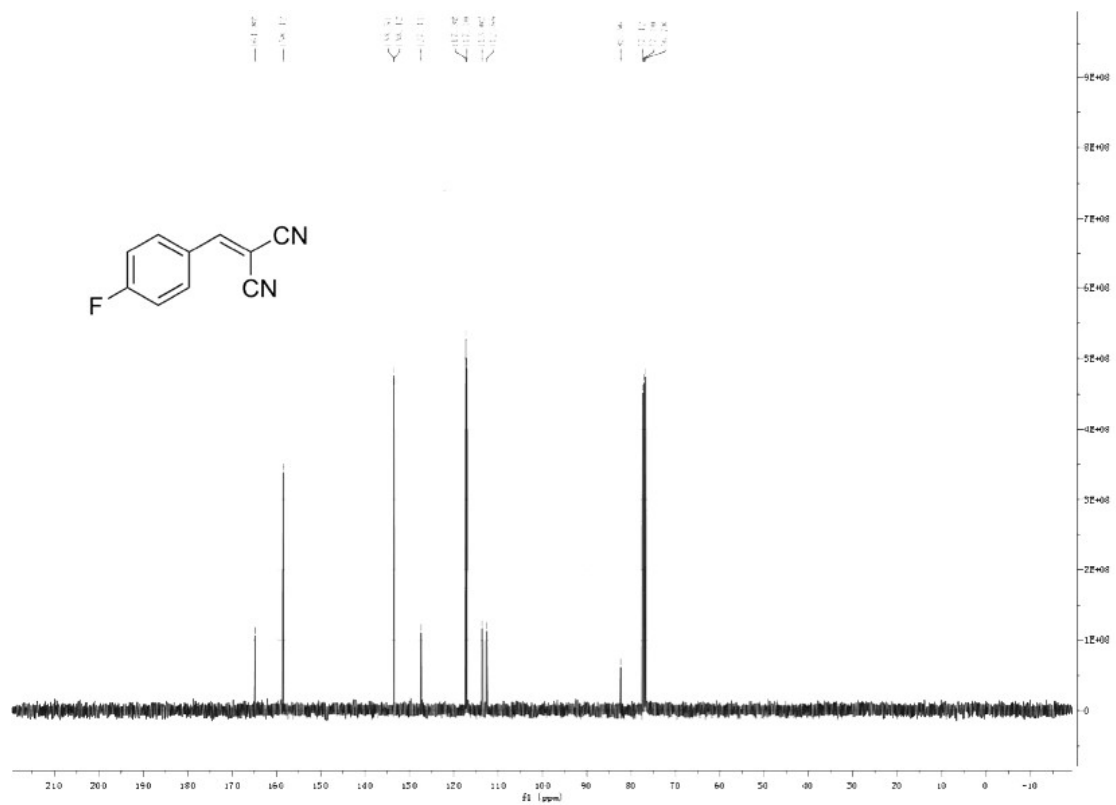
The ¹H NMR spectrum of 2-(3-hydroxyphenylmethylene)malononitrile (3e).



The ¹³C NMR spectrum of 2-(3-hydroxyphenylmethylene)malononitrile (3e).



The ^1H NMR spectrum of 2-(4-fluorophenylmethylene)malononitrile (3f).



The ^{13}C NMR spectrum of 2-(4-fluorophenylmethylene)malononitrile (3f).

References

- [1] G. Li, J. Xiao, W. Zhang, *Green. Chem.* **2011**, *13*, 1828-1836.
- [2] M. Tavakoliana, M. M. Najafpour, *New J. Chem.* **2019**, *43*, 16437-16440.
- [3] Q. Hu, X.-L. Shi, Y. Chen, X. Han, P. Duan, W. Zhang, *J. Ind. Eng. Chem.* **2017**, *54*, 75-81.