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Supporting Information

An efficient and recyclable acid-base bifunctional core-shell nano-catalyst for the one-pot deacetalization-Knoevenagel tandem reaction

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Table of Contents

1. Experimental Procedures

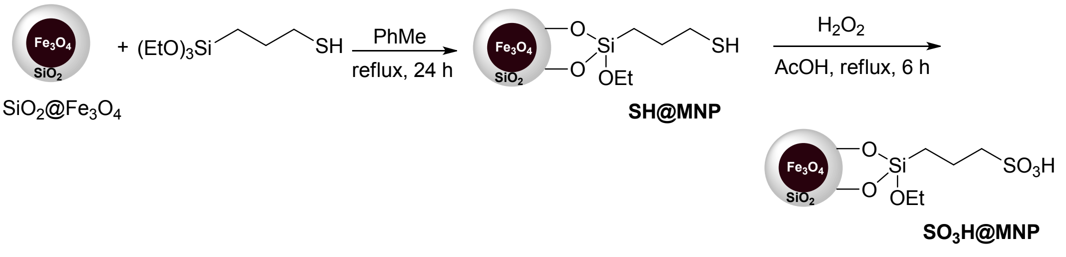
1.1 General information

The IR spectra were recorded on a Nicolet spectrometer (KBr). ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance-III DRX spectrometer operating at 500 MHz and 125 MHz respectively, using DMSO as solvent. X-ray diffraction (XRD) images were obtained from a Bruker XRD D8 Advance instrument with Cu Kα radiation (λ = 0.15418 nm). Transmission electron microscopy (TEM) images were obtained using a JEM-2100 instrument. The magnetization curve was obtained by a vibrating sample magnetometer (JDM-13T, China). Elemental analysis was performed with an Elementar Vario EL *β* recorder. X-ray photoelectron spectroscopy (XPS) spectra were obtained from an ESCALAB™ 250Xi instrument. All the solvents used were strictly dried according to standard operation and stored on 4 Å molecular sieves. All other chemicals (AR grade) were commercially available and used without further purification.

1.2 Synthesis of silica-coated Fe_3O_4 nanoparticles ($SiO_2@Fe_3O_4$)

Magnetite (Fe_3O_4) nanoparticles were prepared in a chemical co-precipitation step of ferric and ferrous ions in an alkaline solution. $FeCl_3·6H_2O$ (11.0 g) and $FeCl_2·4H_2O$ (4.0 g) were dissolved in 250 mL deionized water under nitrogen with vigorous stirring at 85 ℃. The pH value of the solution was adjusted to 9 by conc. $NH_3·H_2O$. After continuously stirring for 4 h, the magnetite precipitates were washed by amounts of deionized water to reach pH = 7. A black precipitate (Fe_3O_4) was collected with a permanent magnet under the reaction flask. Coating of a layer of silica on the surface of the nano-Fe_3O_4 was achieved by pre-mixing (ultrasonic) a dispersion of the above black precipitate (2.0 g) with ethanol (400 mL) for 30 min at room temperature. And conc. $NH_3·H_2O$ (12 mL) and TEOS (4.0 mL) were added successively. After stirring for 24 h, the black precipitate ($SiO_2@Fe_3O_4$) was collected using a permanent magnet, followed by washing with ethanol three times and drying in a vacuum. FT-IR (KBr, cm^{-1}): 3445, 1638, 1097, 580.

1.3 Synthesis of $SO_3H@MNP$



Scheme 1. Synthesis of $SO_3H@MNP$

0.2 g of SiO_2-coated Fe_3O_4 nanoparticles were dispersed in dry toluene (20 mL) by sonication for 0.5 h. (3-Mercaptopropyl)triethoxysilane (1.19g, 5 mmol) was then added, and the reaction mixture was refluxed for 24 h under nitrogen. After being cooled to ambient temperature, the acid-functionalized MNP was collected by a permanent magnet and washed thoroughly with toluene and acetone, and then dried under vacuum over-night.

The dried SH@MNP was dispersed in the mixed solution of acetic acid (15 mL) and hydrogen peroxide (10 mL, 30%), and the reaction mixture was refluxed for 6 h under nitrogen atmosphere. After being cooled to room temperature, the sulfonic acid supported MNP was collected by a permanent magnet and washed thoroughly with water and ethanol, and then dried under vacuum over-night.

1.4 Effect of water content on the SO_3H-AA@MNP catalyzed reaction

The reactions were carried out under optimized conditions mentioned in main paper except for using various content of water and the results were listed in Table S1.

Table S1 Effect of water content on the reaction

Entry	$n(H_2O):n(\text{acetal})$	yield (%)
1	0	52
2	0.5	63
3	1	71
4	1.5	69
5	2	38

Reaction conditions: Benzaldehyde dimethylacetal (2 mmol), malononitrile (2.1 mmol), toluene(20 mL), SO_3H-AA@MNP (20 mg), 40 min.

It can be seen from Table S1 that little water facilitates the reaction. The best result was obtained when one equivalent of water was used (Table S1, entry 3). More water decease the yield (Table S1, entry 3). When 2 equivalent of water was used, the yield is dramatically reduced to 38% (Table S1, entry 3).

2. TG curves of SO_3H-AA@MNP

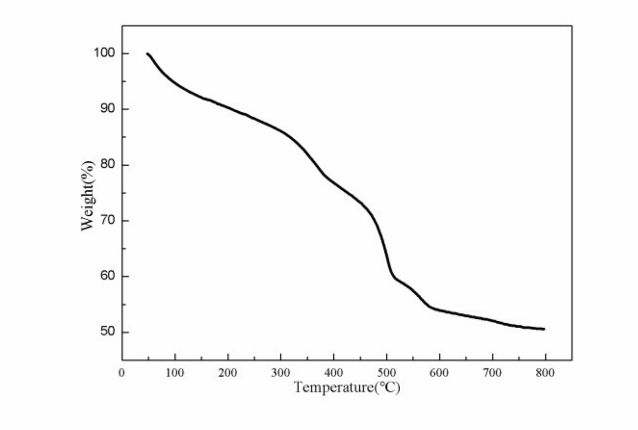
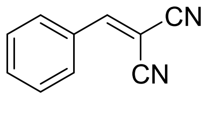
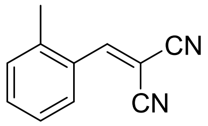


Figure 4. TG curve of SO_3H-AA@MNP

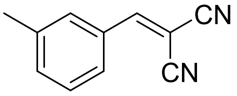
3. Spectroscopic Data of the Synthesized Compounds



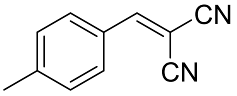
2-benzylidenemalononitrile (2a). ^{1}H NMR (500 MHz, DMSO) δ 8.56 (s, 1H), 7.96 (d, J = 7.5 Hz, 2H), 7.72 - 7.68 (m, 1H), 7.63 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (126 MHz, DMSO): 162.26, 135.07, 131.99, 131.20, 131.06, 130.22, 114.89, 113.90, 82.30. Elemental Analysis Calcd (%): C, 77.91; H, 3.92; N, 18.17; Found: C, 77.83; H, 3.96; N, 18.21.



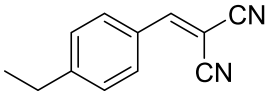
2-(2-methylbenzylidene)malononitrile (2b). ^{1}H NMR (500 MHz, DMSO) δ 8.73 (s, 1H), 7.92 (d, *J* = 7.7 Hz, 1H), 7.54 (m, 1H), 7.40 (m, 2H), 2.42 (s, 3H). ^{13}C NMR (126 MHz, DMSO): 161.51, 140.66, 134.23, 131.81, 131.21, 128.66, 127.21, 114.77, 113.82, 84.44, 19.96. Elemental Analysis Calcd (%): C, 78.55; H, 4.79; N, 16.66; Found: C, 78.47; H, 4.83; N, 16.70.



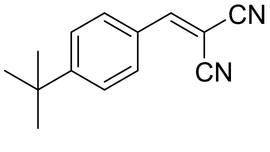
2-(3-methylbenzylidene)malononitrile (2c). ^{1}H NMR (500 MHz, DMSO) δ 8.48 (s, 1H), 7.78 (d, *J* = 1.3 Hz, 1H), 7.73 (s, 1H), 7.55 - 7.49 (m, 2H), 2.37 (s, 3H). ^{13}C NMR (126 MHz, DMSO): 162.25, 139.64, 135.82, 131.99, 131.70, 130.12, 128.27, 114.93, 113.92, 81.97, 21.48. Elemental Analysis Calcd (%): C, 78.55; H, 4.79; N, 16.66; Found: C, 78.58; H, 4.74; N, 16.68.



2-(4-methylbenzylidene)malononitrile (2d). ^{1}H NMR (500 MHz, DMSO) δ 8.46 (s, 1H), 7.86 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 2.41 (s, 3H).^{13}C NMR (126 MHz, DMSO): 161.95, 146.37, 131.39, 130.84, 129.44, 115.09, 114.12, 80.58, 22.16. Elemental Analysis Calcd (%): C, 78.55; H, 4.79; N, 16.66; Found: C, 78.66; H, 4.70; N, 16.64.

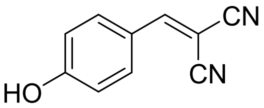


2-(4-ethylbenzylidene)malononitrile (2e). ^{1}H NMR (500 MHz, DMSO) δ 8.48 (s, 1H), 7.89 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 2.70 (q, *J* = 7.6 Hz, 2H), 1.21 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, DMSO): 161.99, 152.29, 131.52, 129.69, 115.09, 114.13, 80.66, 29.12, 15.61. Elemental Analysis Calcd (%): C, 79.10; H, 5.53; N, 15.37; Found: C, 79.18; H, 5.49; N, 15.33.

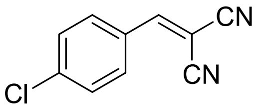


2-(4-(*tert*-butyl)benzylidene)malononitrile (2f). ^{1}H NMR (500 MHz, DMSO) δ 8.50 (s, 1H), 7.92 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 8.5 Hz, 2H), 1.31 (s, 9H). ^{13}C NMR (126 MHz, DMSO): 161.92, 158.85, 131.32, 129.47, 127.18, 115.09, 114.12, 80.82, 35.91, 31.29. Elemental Analysis

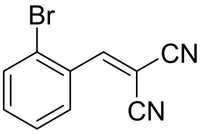
Calcd (%): C, 79.97; H, 6.71; N, 13.32; Found: C, 79.87; H, 6.77; N, 13.36.



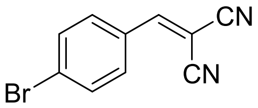
2-(4-hydroxybenzylidene)malononitrile (2g). ^{1}H NMR (500 MHz, DMSO) δ 11.08 (s, 1H), 8.30 (s, 1H), 7.89 (t, J = 5.7 Hz, 2H), 7.02 - 6.95 (m, 2H). ^{13}C NMR (126 MHz, DMSO): 164.60, 161.16, 134.57, 123.49, 117.31, 115.78, 114.86, 75.81. Elemental Analysis Calcd (%): C, 70.58; H, 3.55; N, 16.46; Found: C, 70.33; H, 3.44; N, 16.56.



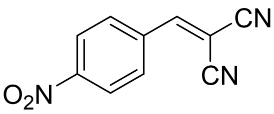
2-(4-chlorobenzylidene)malononitrile (2h). ^{1}H NMR (500 MHz, DMSO) δ 8.57 (s, 1H), 7.97 (d, J = 8.6 Hz, 2H), 7.73 (d, J = 8.6 Hz, 2H). ^{13}C NMR (126 MHz, DMSO): 160.79, 139.76, 132.83, 130.76, 130.41, 114.74, 113.69, 82.91. Elemental Analysis Calcd (%): C, 63.68; H, 2.67; N, 14.85; Found: C, 63.29; H, 2.86; N, 14.87.



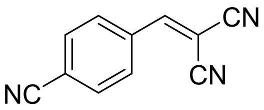
2-(2-bromobenzylidene)malononitrile (2i). ^{1}H NMR (500 MHz, DMSO) δ 8.61 (s, 1H), 7.99 (dd, J = 7.7, 1.4 Hz, 1H), 7.87 (dd, J = 7.9, 1.0 Hz, 1H), 7.64 (dd, J = 10.9, 4.1 Hz, 1H), 7.59 (dd, J = 7.8, 1.6 Hz, 1H). ^{13}C NMR (126 MHz, DMSO): 161.14, 135.44, 134.26, 132.20, 130.82, 129.17, 125.10, 114.07, 112.96, 87.45. Elemental Analysis Calcd (%): C, 51.53; H, 2.16; N, 12.02; Found: C, 51.21; H, 2.61; N, 11.78.



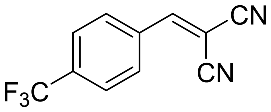
2-(4-bromobenzylidene)malononitrile (2j). ^{1}H NMR (500 MHz, DMSO) δ 8.53 (s, 1H), 7.93 - 7.78 (m, 4H). ^{13}C NMR (126 MHz, DMSO): 160.98, 133.38, 132.83, 131.08, 129.03, 114.77, 113.71, 83.01. Elemental Analysis Calcd (%): C, 51.53; H, 2.16; N, 12.02; Found: C, 51.28; H, 2.21; N, 11.85.



2-(4-nitrobenzylidene)malononitrile (2k). ^{1}H NMR (500 MHz, DMSO) δ 8.73 (s, 1H), 8.44 (d, J = 8.7 Hz, 2H), 8.14 (d, J = 8.7 Hz, 2H). ^{13}C NMR (126 MHz, DMSO): 160.00, 150.41, 137.37, 132.14, 125.07, 114.31, 113.21, 86.65. Elemental Analysis Calcd (%): C, 60.31; H, 2.53; N, 21.10; Found: C, 60.20; H, 2.82; N, 21.11.



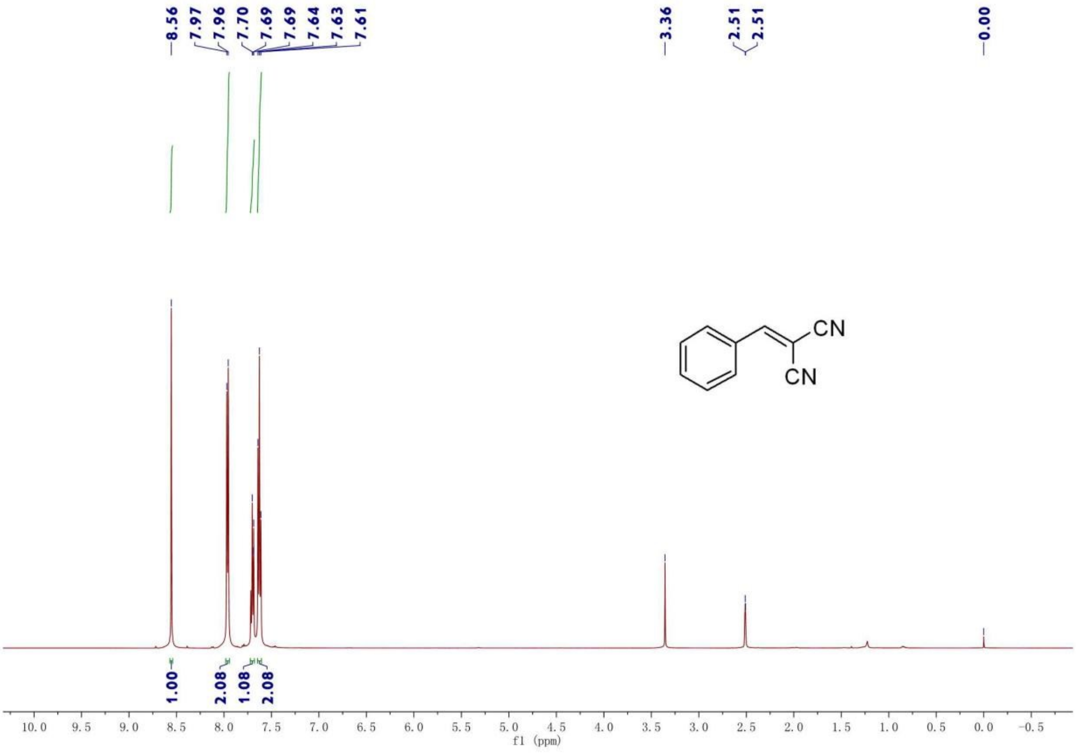
2-(4-cyanobenzylidene)malononitrile (2l). ^{1}H NMR (500 MHz, DMSO) δ 8.66 (s, 1H), 8.12 - 8.05 (m, 4H). ^{13}C NMR (126 MHz, DMSO): 160.36, 135.77, 133.87, 131.37, 118.62, 116.09, 114.36, 113.27, 86.05. Elemental Analysis Calcd (%): C, 73.74; H, 2.81; N, 23.45; Found: C, 73.94; H, 2.79; N, 23.27.



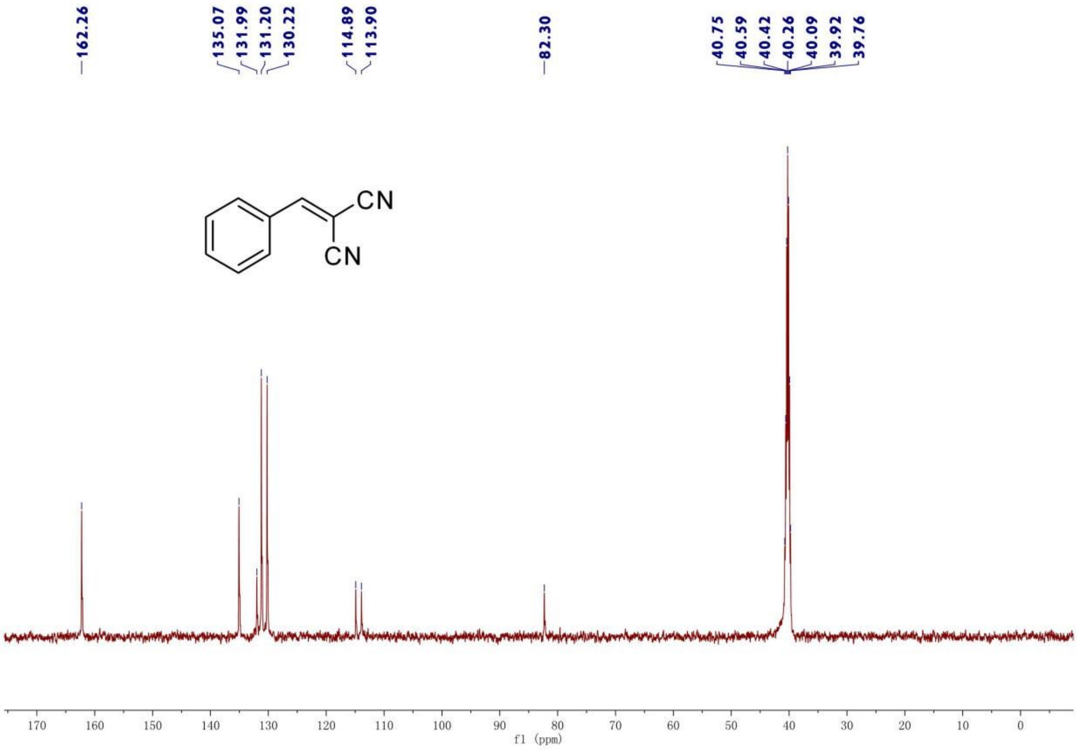
2-(4-(trifluoromethyl)benzylidene)malononitrile (2m). ^{1}H NMR (500 MHz, DMSO) δ 8.70 (s, 1H), 8.12 (d, J = 8.3 Hz, 2H), 8.01 (d, J = 8.4 Hz, 2H). ^{13}C NMR (126 MHz, DMSO): 160.72 (s), 135.51 (s), 133.47 (q, J = 32.5 Hz), 131.62 (s), 127.00 (s), 124.18 (d, J = 272.6 Hz), 114.40 (s), 113.33 (s), 85.64 (s). Elemental Analysis Calcd (%): C, 59.47; H, 2.27; N, 12.61; Found: C, 59.76; H, 2.04; N, 12.52.

3. ^{1}H-NMR and ^{13}C-NMR Spectra of Compounds

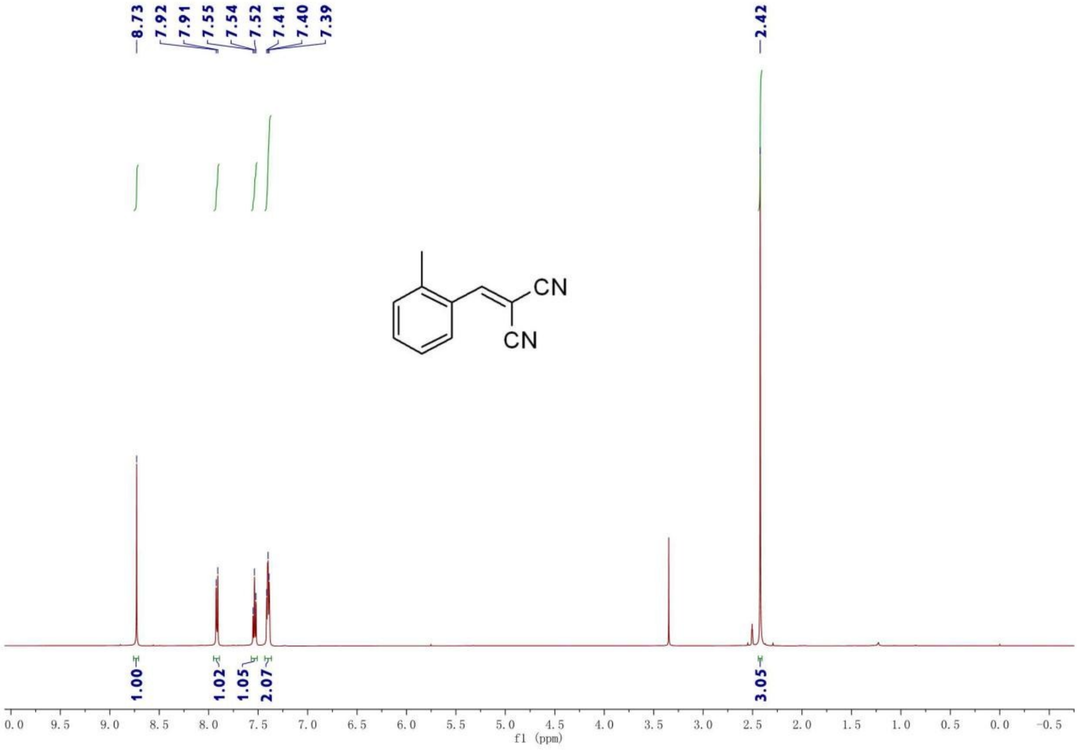
^{1}H NMR spectrum of the product of 2a (DMSO, 500 MHz)



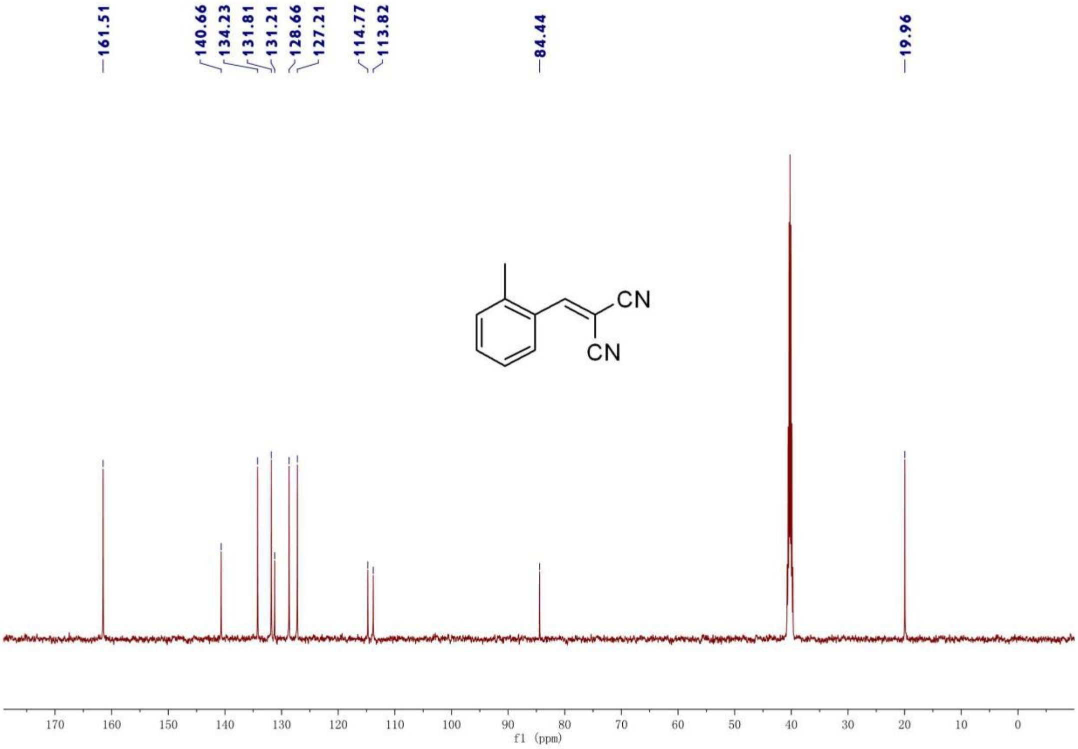
^{13}C NMR spectrum of the product of 2a (DMSO, 126 MHz)



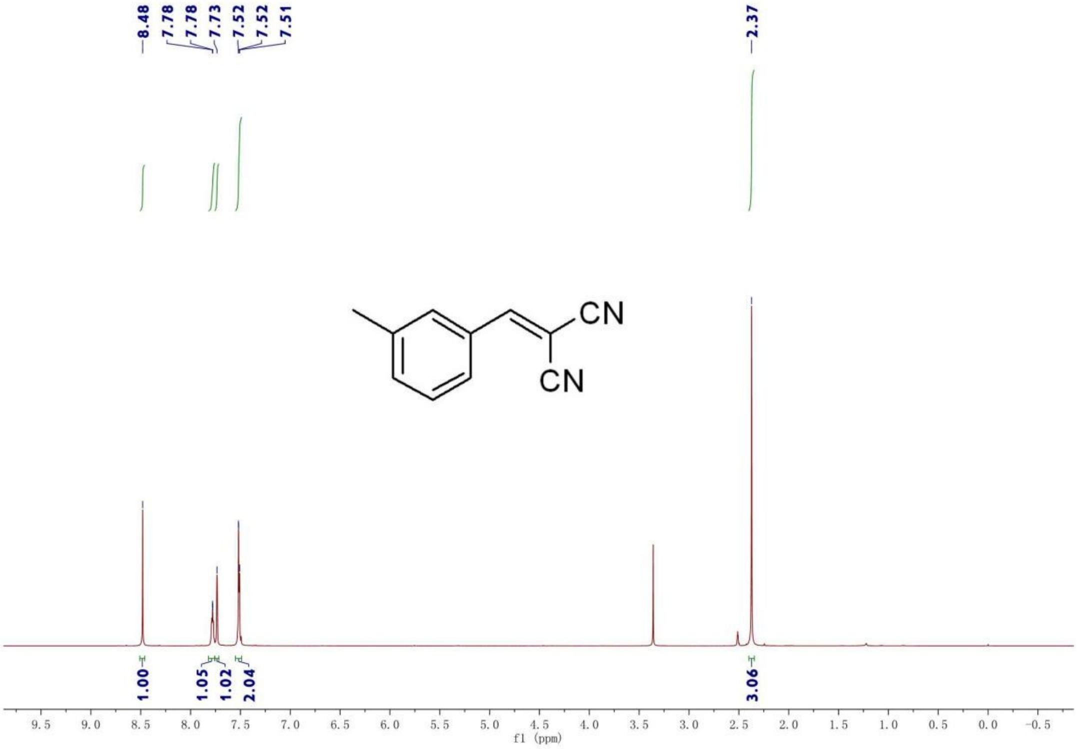
^{1}H NMR spectrum of the product of 2b (DMSO, 500 MHz)



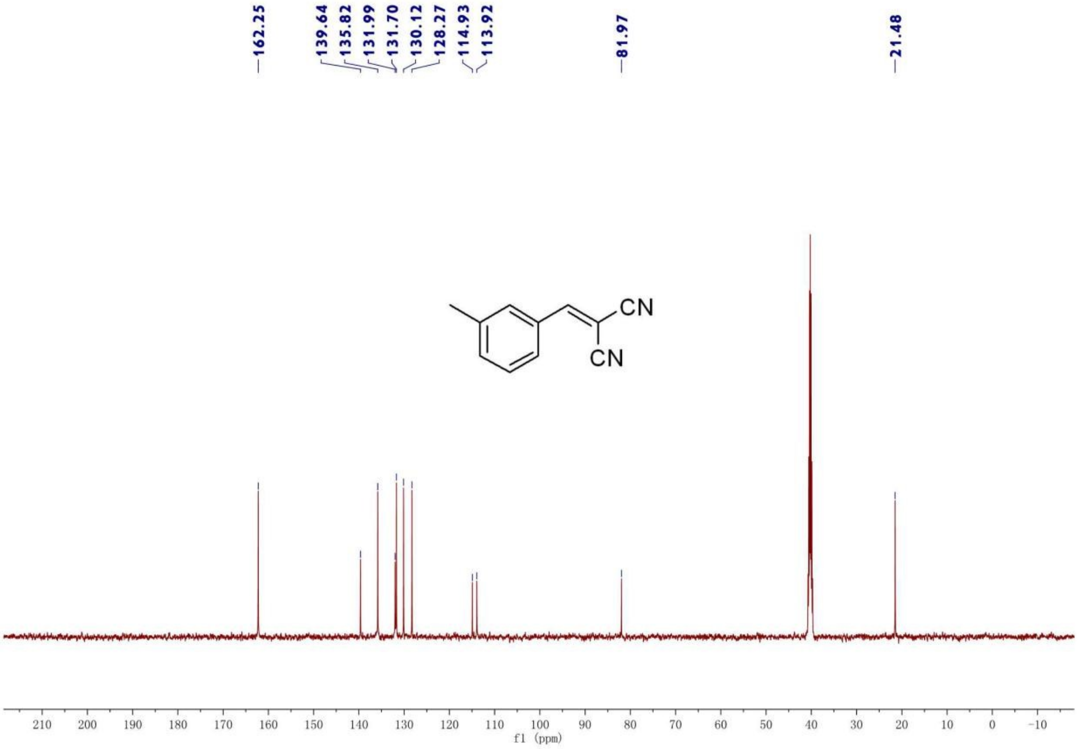
^{13}C NMR spectrum of the product of 2b (DMSO, 126 MHz)



^{1}H NMR spectrum of the product of 2c (DMSO, 500 MHz)



^{13}C NMR spectrum of the product of 2c (DMSO, 126 MHz)



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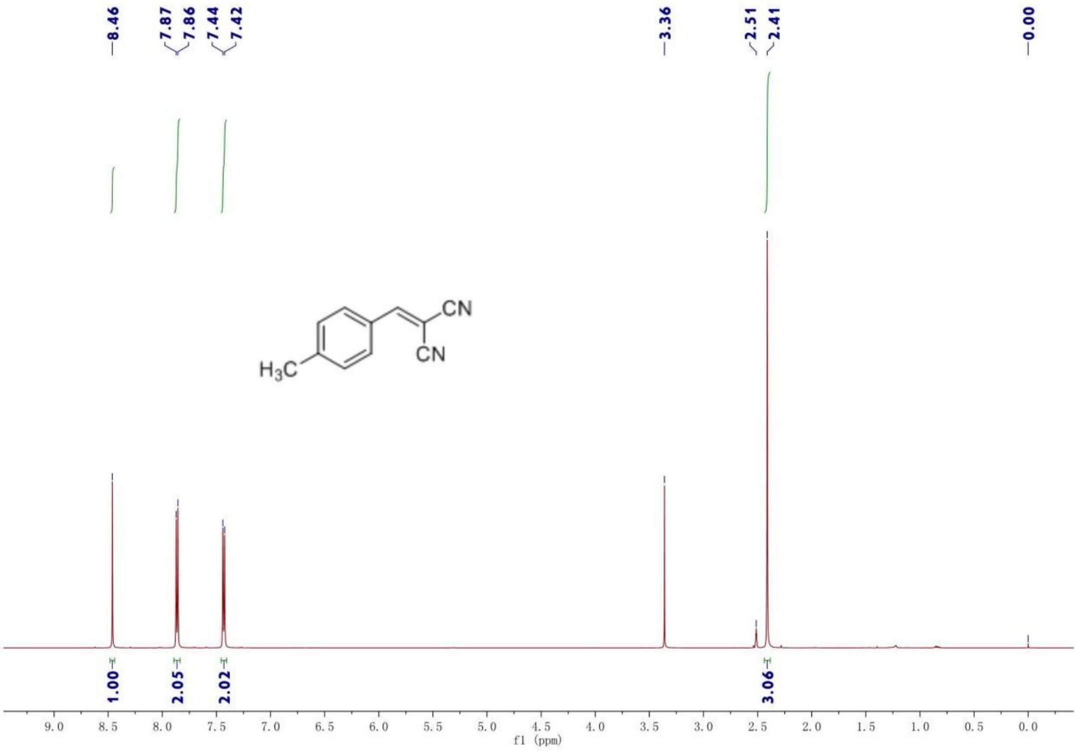

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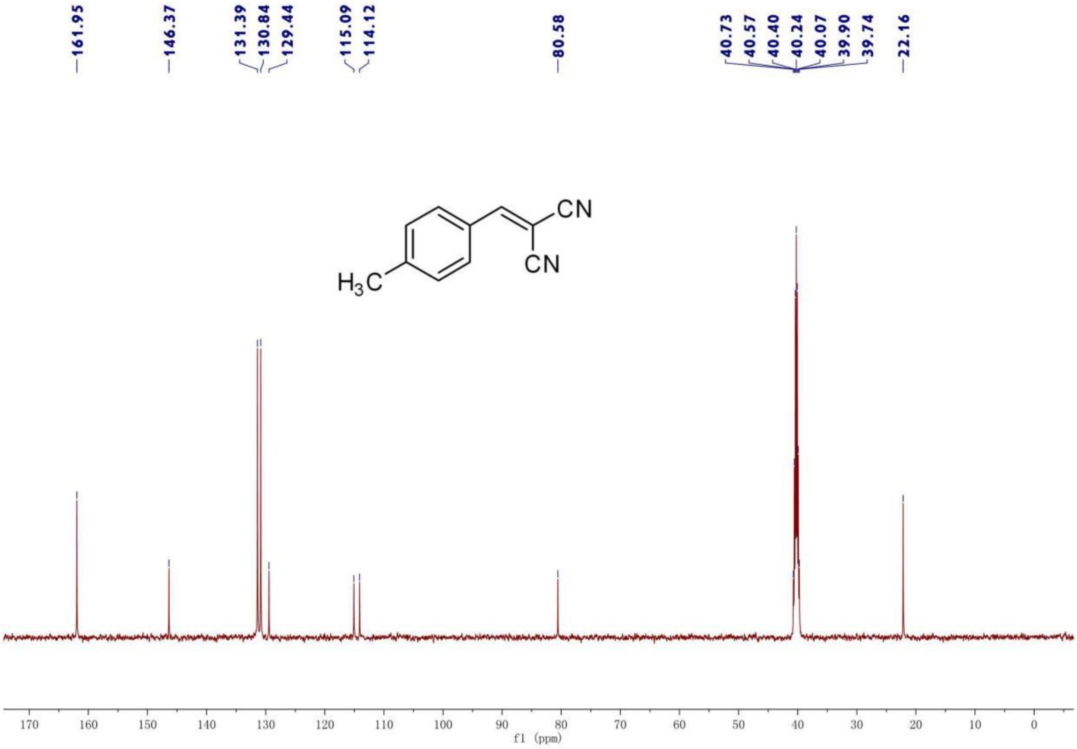
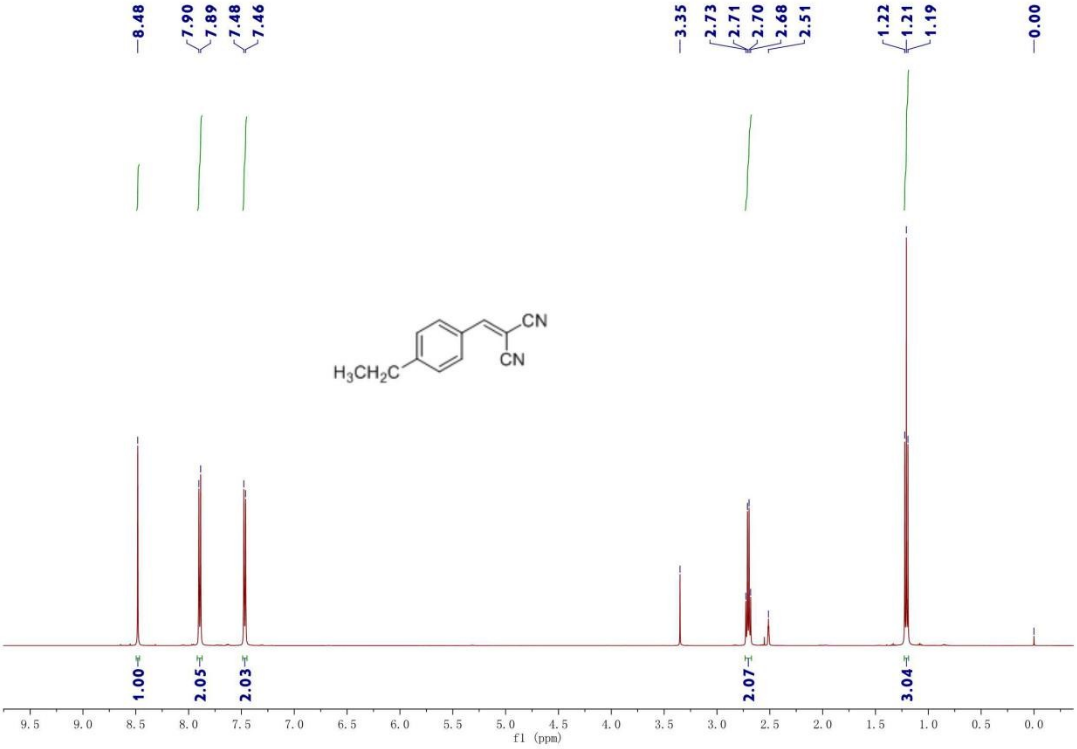
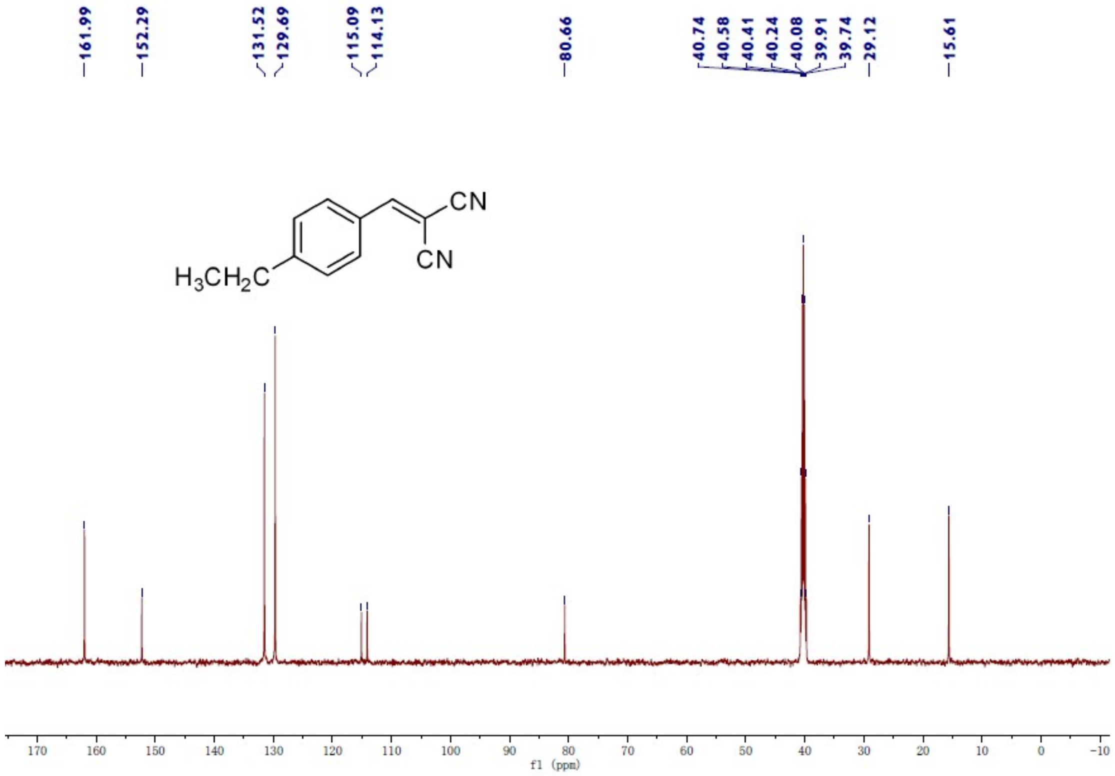


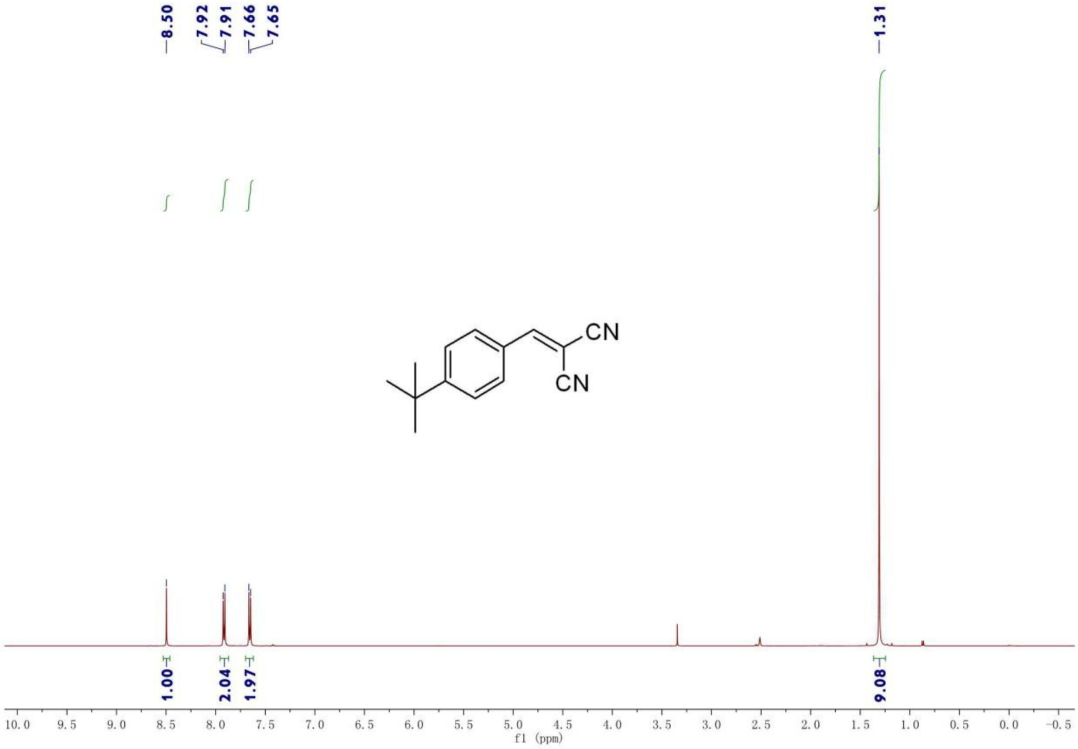
^{1}H NMR spectrum of the product of 2e (DMSO, 500 MHz)



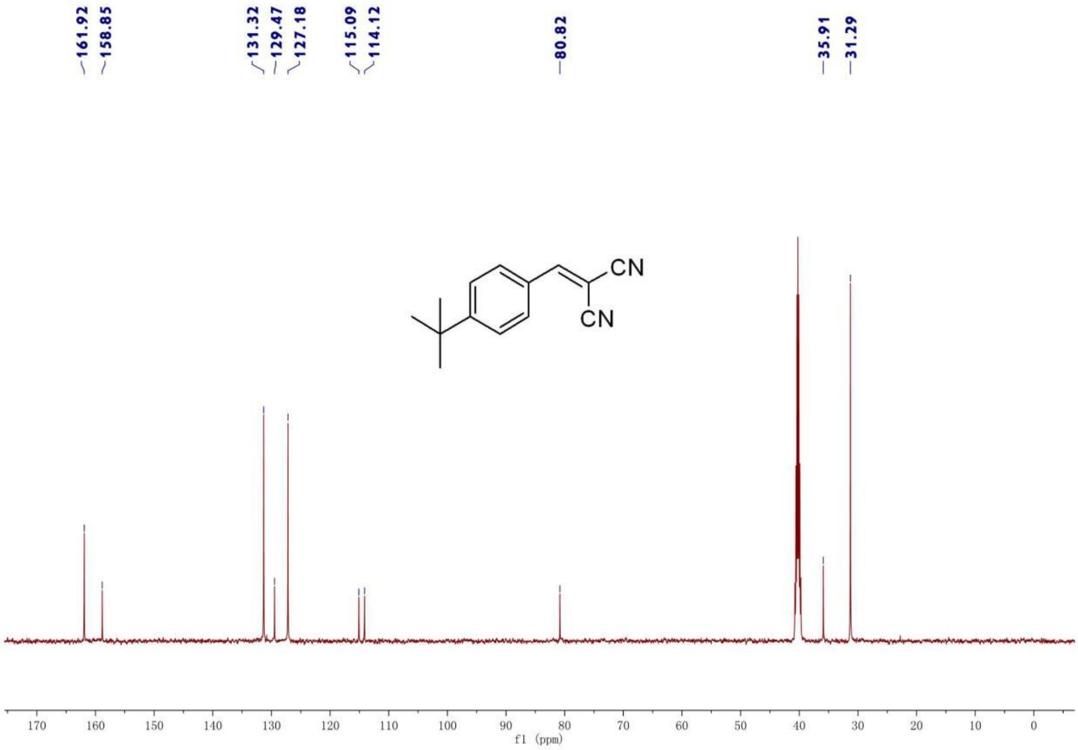
^{13}C NMR spectrum of the product of 2e (DMSO, 126 MHz)



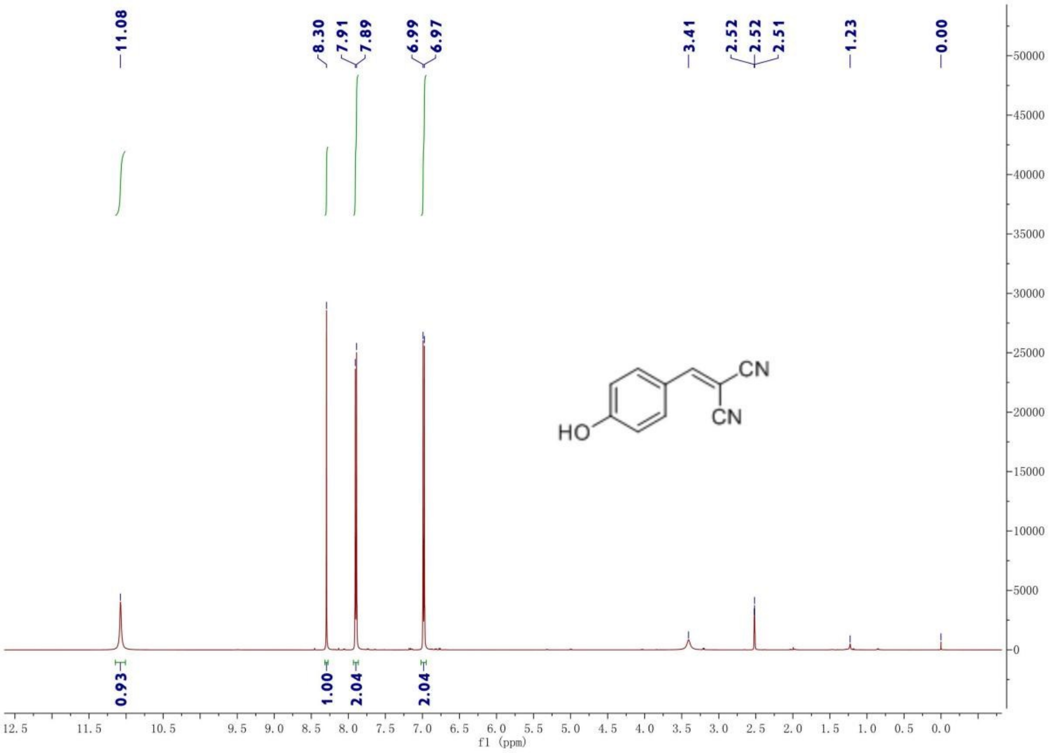
^1H NMR spectrum of the product of 2f (DMSO, 500 MHz)



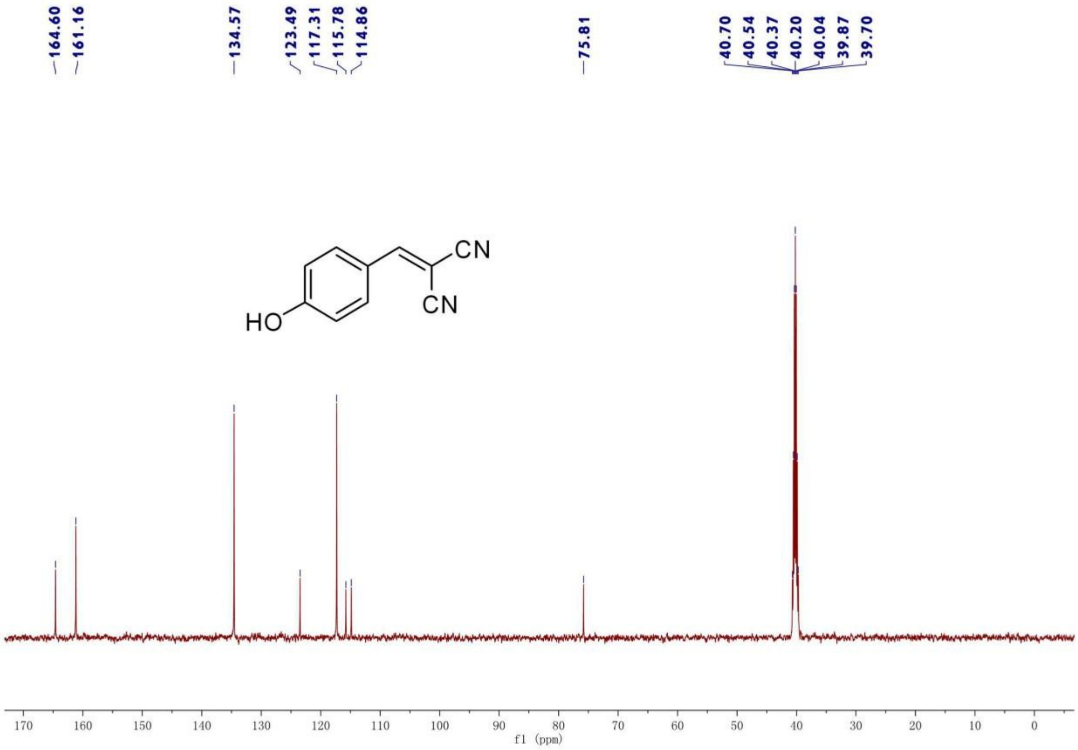
^{13}C NMR spectrum of the product of 2f (DMSO, 126 MHz)



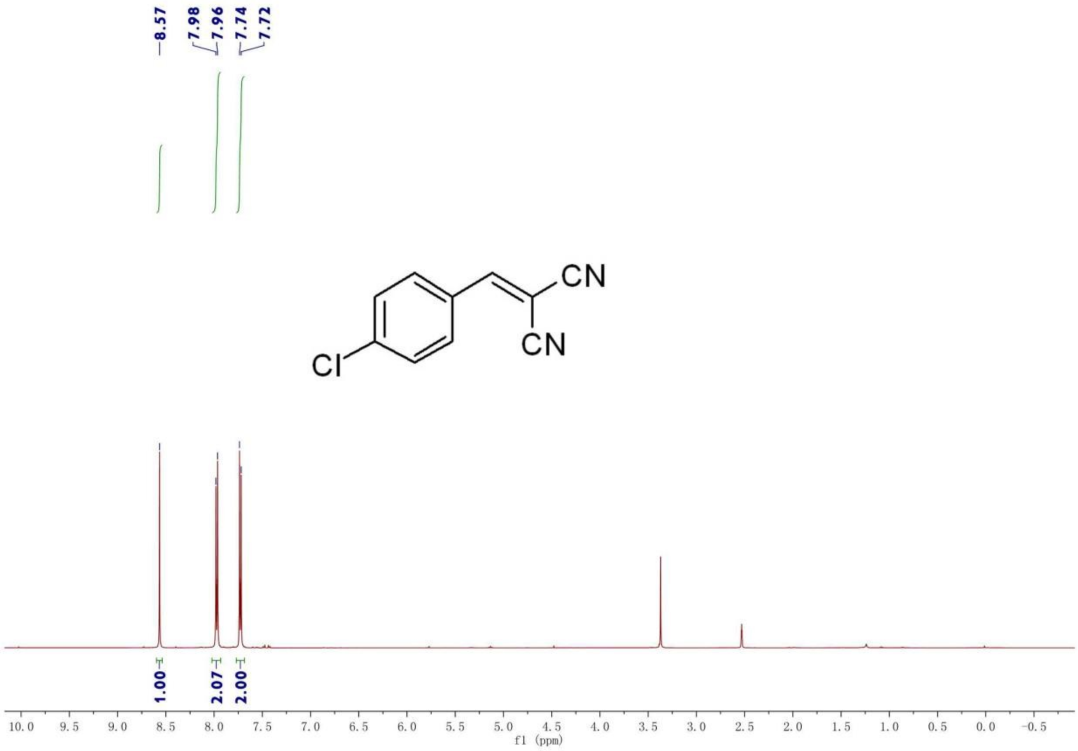
^{1}H NMR spectrum of the product of 2g (DMSO, 500 MHz)



^{13}C NMR spectrum of the product of 2g (DMSO, 126 MHz)



^{1}H NMR spectrum of the product of 2h (DMSO, 500 MHz)



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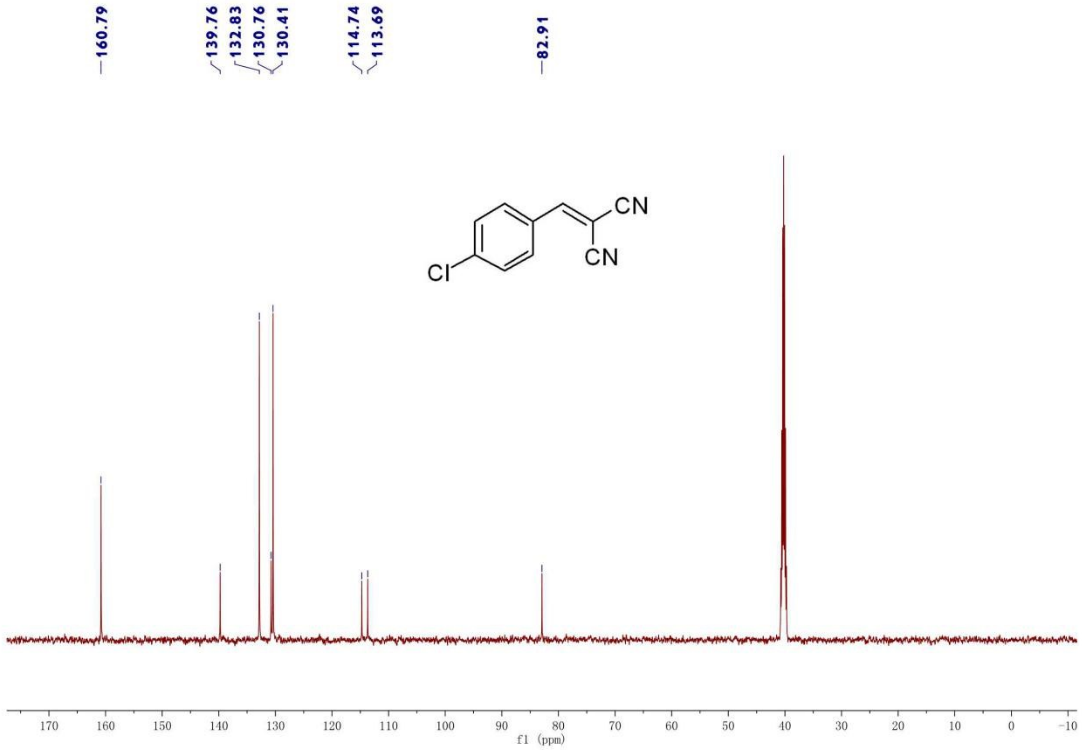
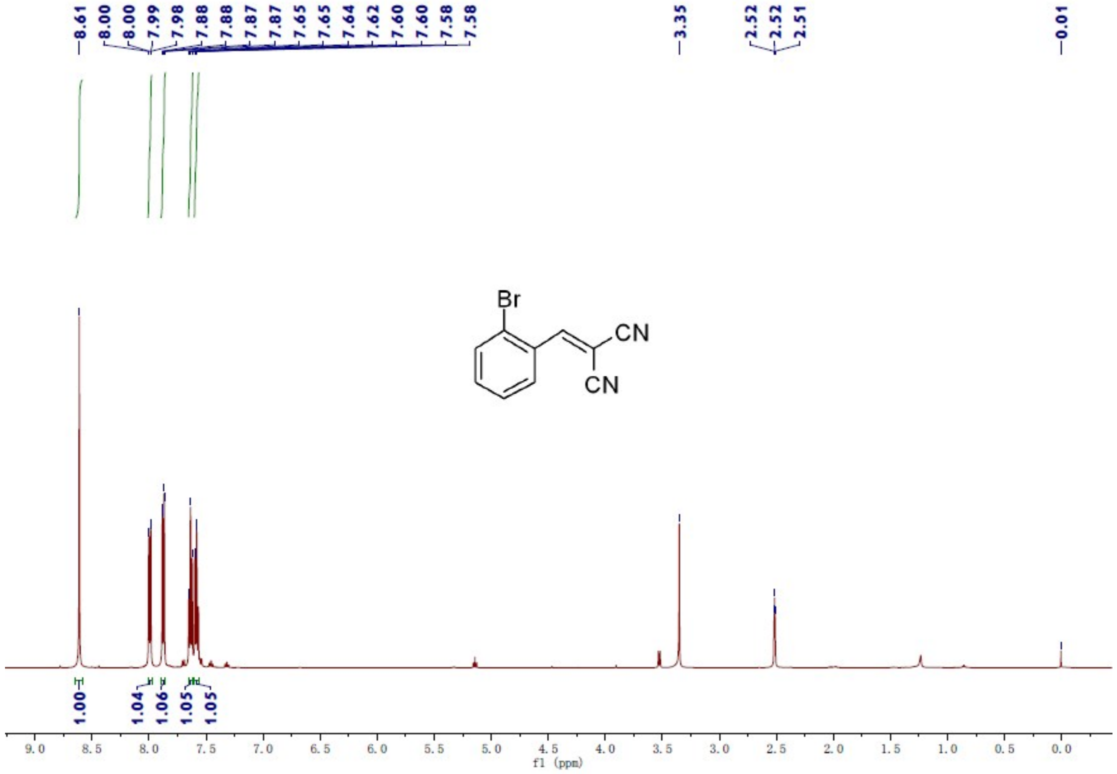
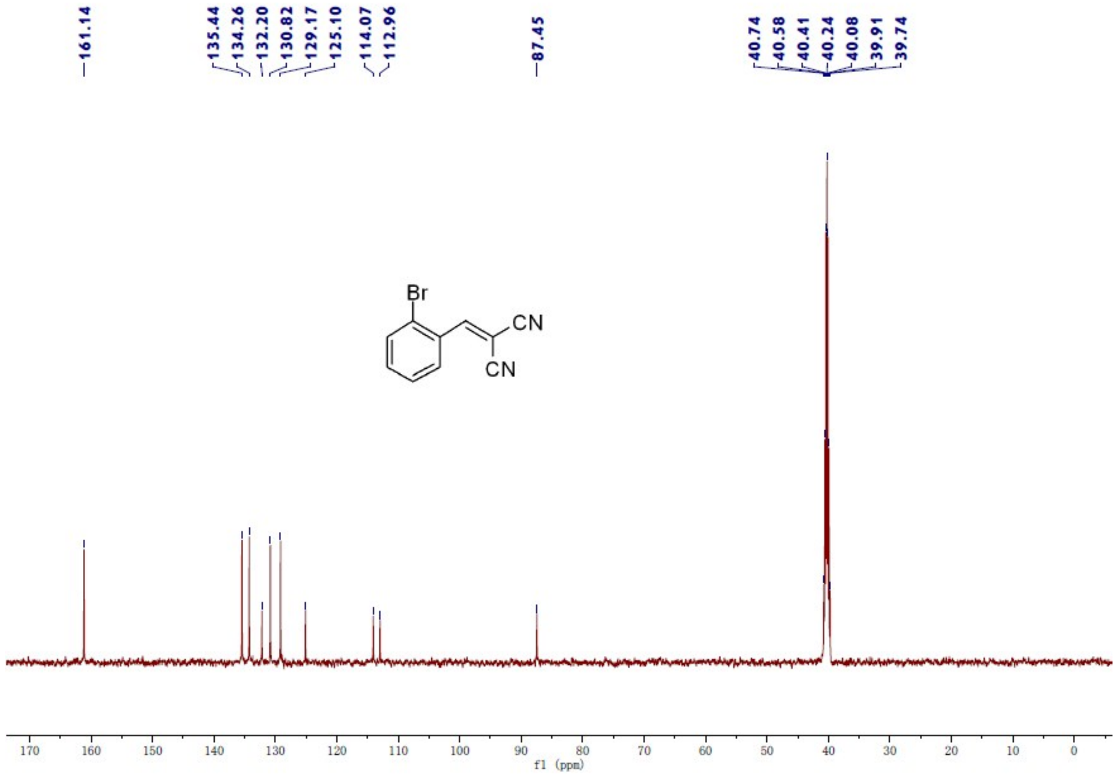


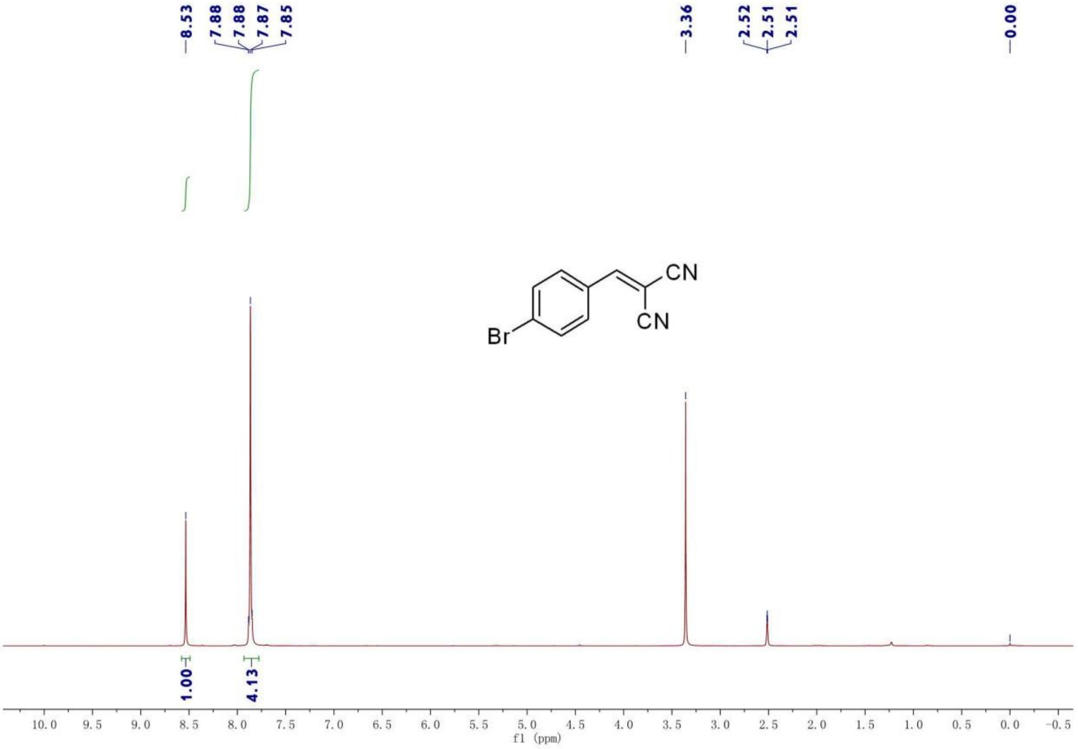
^{1}H NMR spectrum of the product of 2i (DMSO, 500 MHz)



^{13}C NMR spectrum of the product of 2i (DMSO, 126 MHz)



^{1}H NMR spectrum of the product of 2j (DMSO, 500 MHz)



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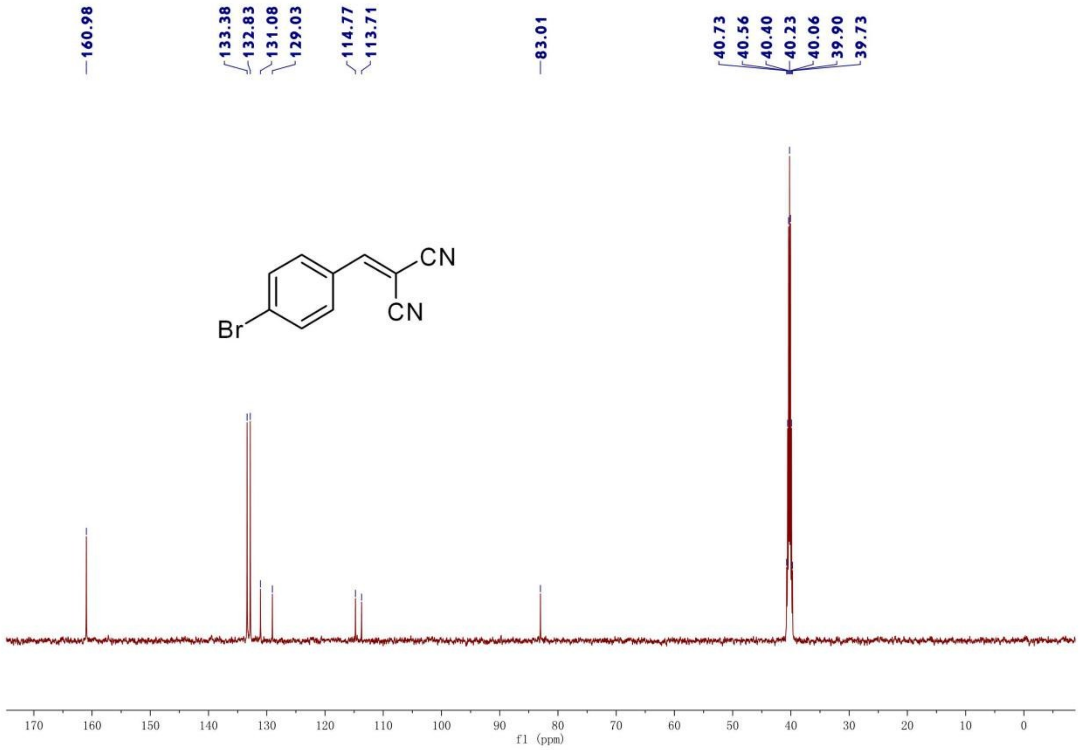
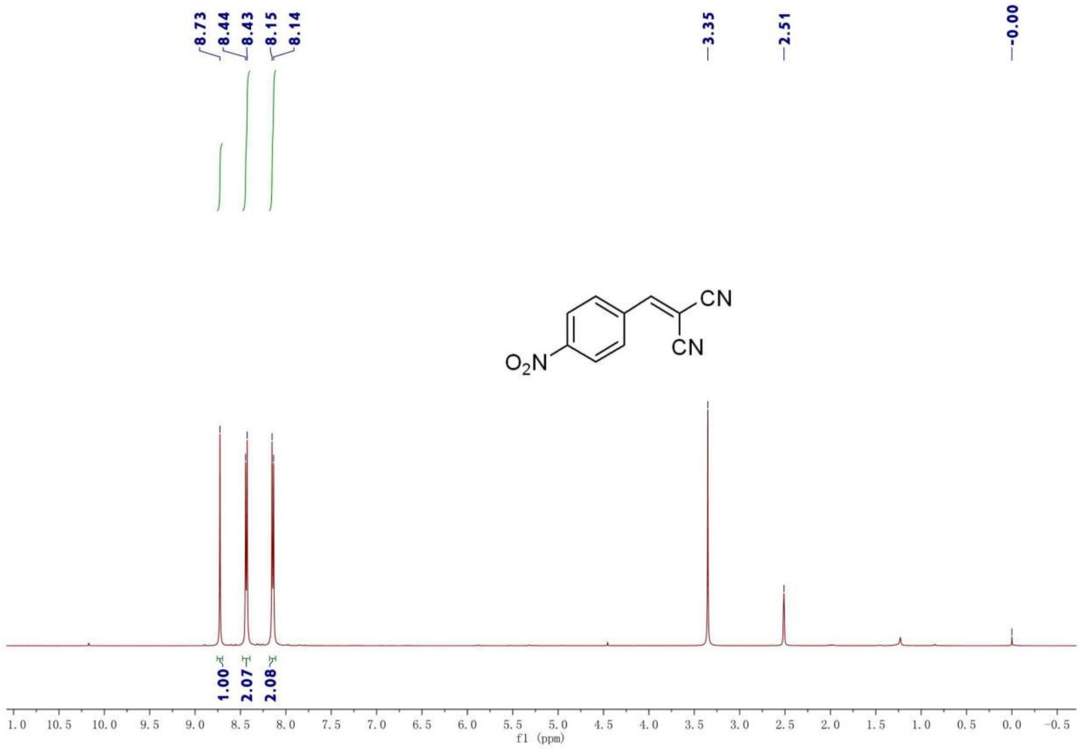
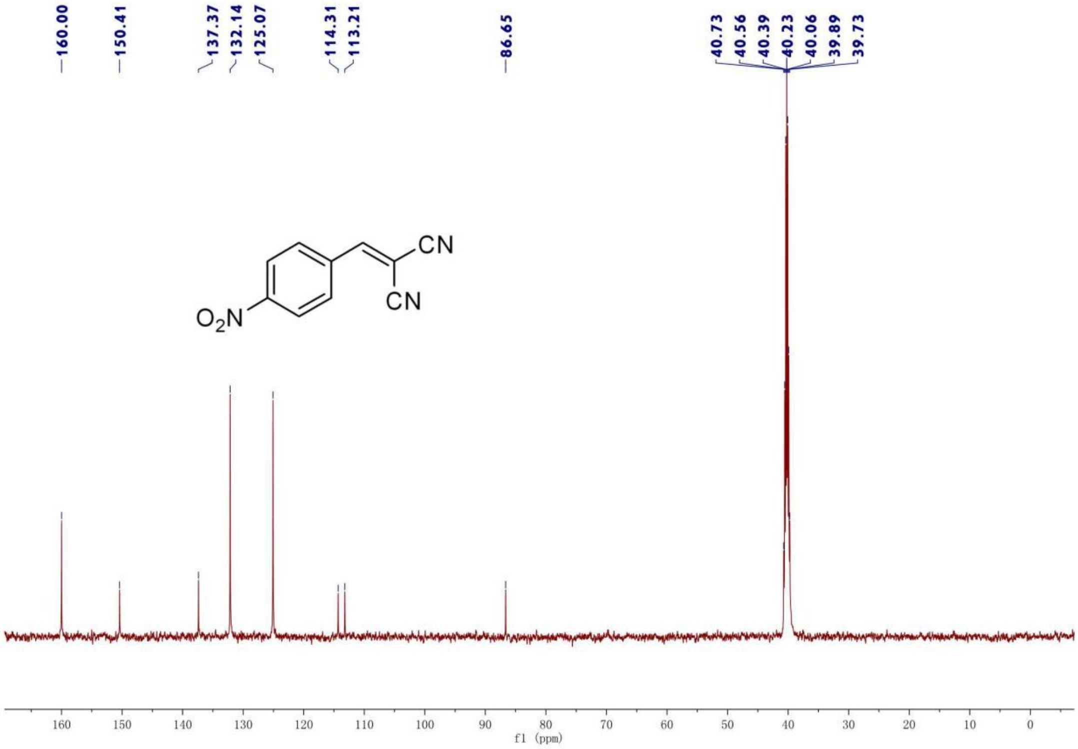


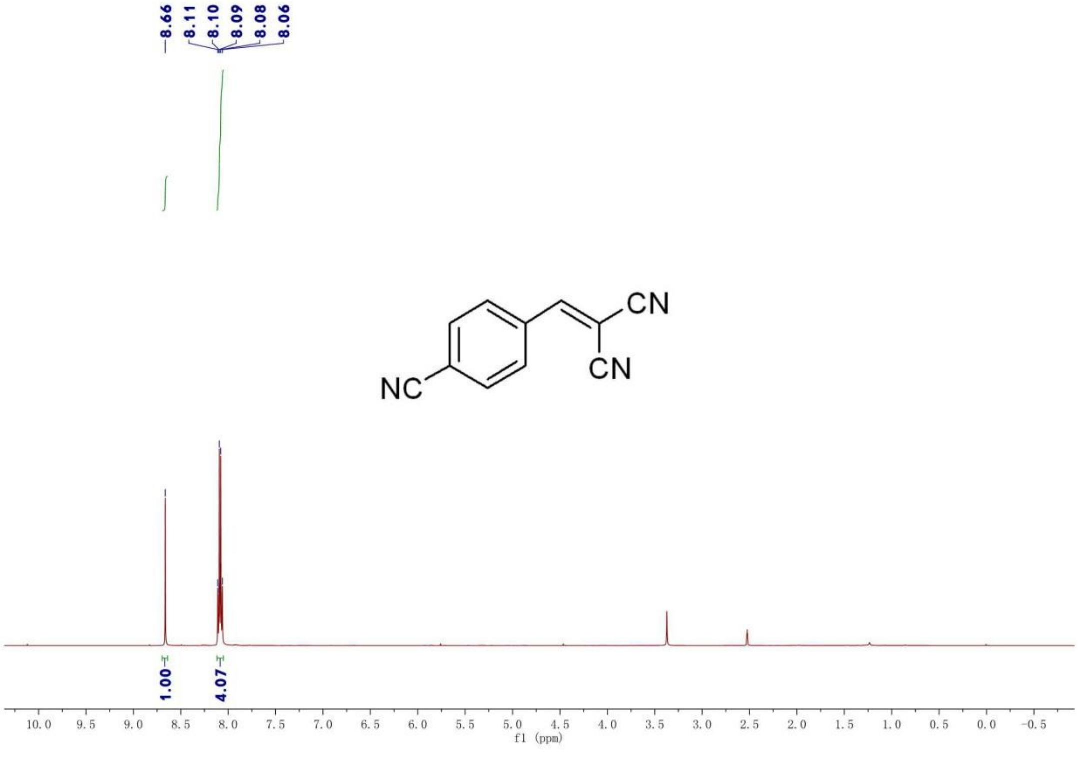
^{1}H NMR spectrum of the product of 2k (DMSO, 500 MHz)



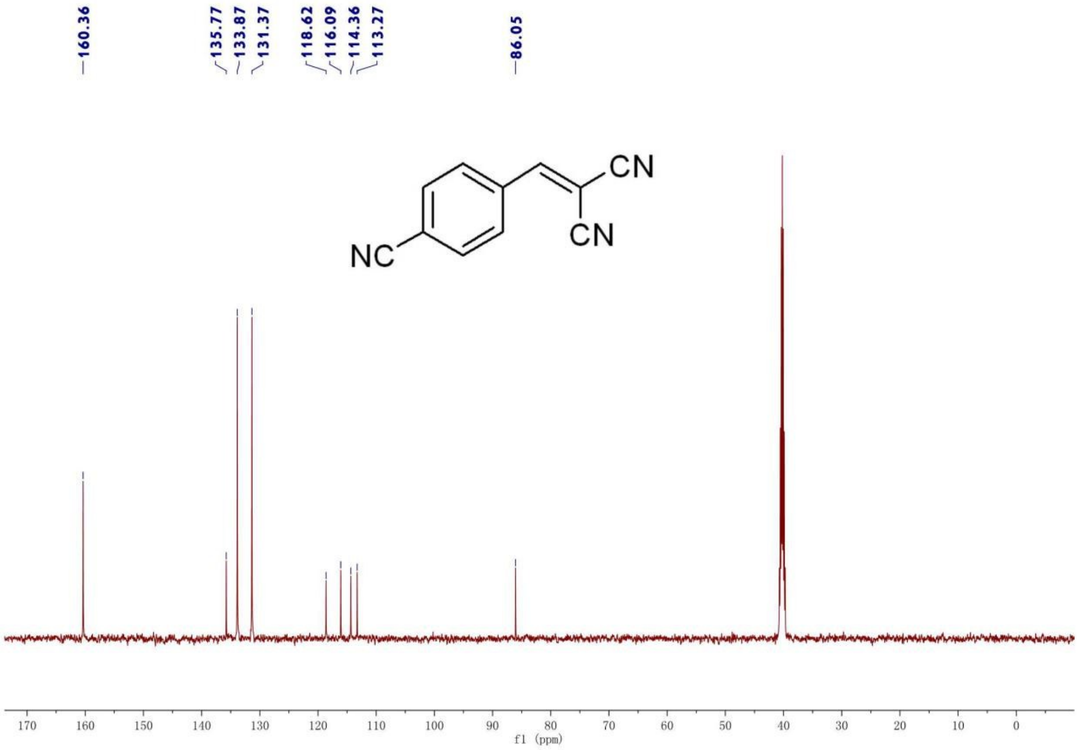
^{13}C NMR spectrum of the product of 2k (DMSO, 126 MHz)



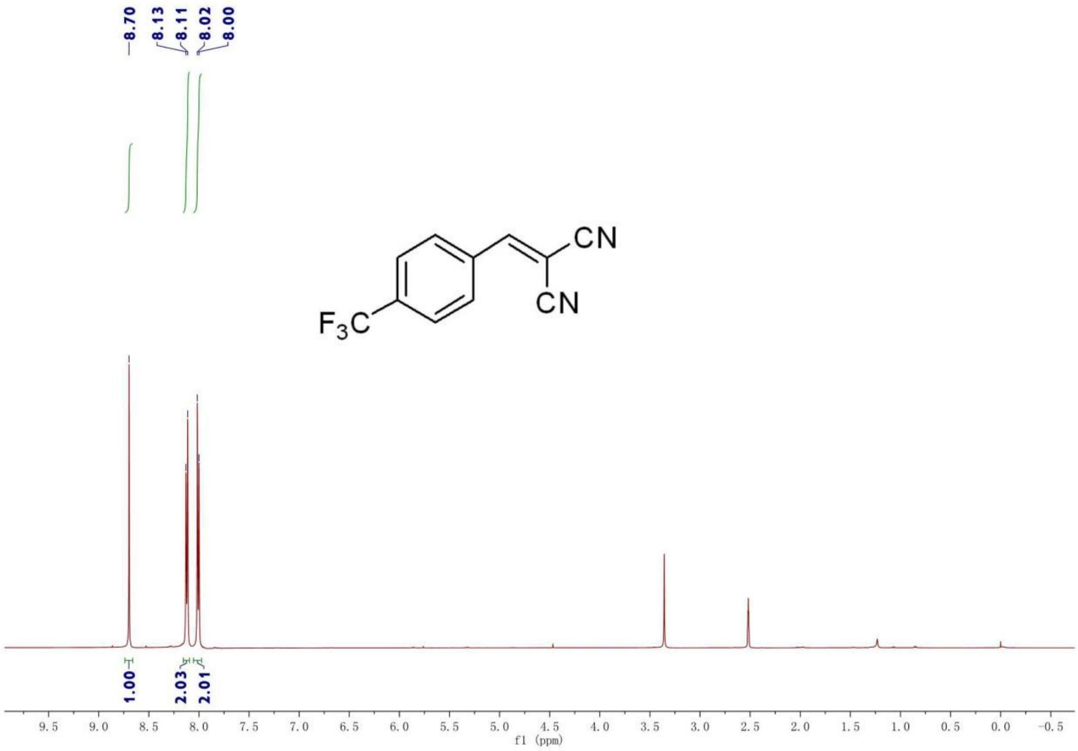
^{1}H NMR spectrum of the product of 2l (DMSO, 500 MHz)



^{13}C NMR spectrum of the product of 2l (DMSO, 126 MHz)



^{1}H NMR spectrum of the product of 2m (DMSO, 500 MHz)



^{13}C NMR spectrum of the product of 2m (DMSO, 126 MHz)