Supporting Information

Photosensitizing decatungstate-based MOF as heterogeneous photocatalyst for the selective C–H alkylation of aliphatic nitriles

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Section 1 Experimental Section

1. General methods and materials

All chemical materials were purchased from commercial sources and used without further purification. ^1H NMR was measured on a Varian INOVA-400 spectrometer with chemical shifts reported as ppm (in DMSO-d_6 or $CDCl_3$, TMS as internal standard). The elemental analyses (EA) of C, H and N were performed on a Vario EL III elemental analyzer. Inductively coupled plasma (ICP) analyses were performed on a NexION 300D spectrometer. The powder XRD diffractograms were obtained on a Riguku D/MAX-2400 X-ray diffractometer with Cu sealed tube (λ = 1.54178 Å). IR spectra were recorded as KBr pellets on a NEXUS instrument. Solid UV-vis absorption spectra were recorded on a U-4100 spectrometer. Solid fluorescent spectra were measured on a JASCO FP-6500 instrument. Thermogravimetric analyses (TGA) were carried out at a ramp rate of 5 $^{o}C \cdot min^{-1}$ in nitrogen flow with a SDTQ600 instrument. Products were purified by flash column chromatography on 200–300 mesh silica gel SiO_2.

Synthesis of DT–BPY: A mixture of $(TBA)_4[W_{10}O_{32}]$[S1] (66.4 mg, 0.02 mmol), 4,4′-bipyridine (31.2 mg, 0.20 mmol) and $Cu(ClO_4)_2 \cdot 6H_2O$ (37.1 mg, 0.10 mmol) in mixed water (3.0 mL) and acetonitrile (3.0 mL) was stirred and its pH value was adjusted to 2.3 with 1 $mol \cdot L^{-1}$ HCl. The resulting suspension was sealed in a 25 mL Teflon-lined reactor and kept at 140 ^{o}C for four days. After cooling the autoclave to room temperature, dark green block single crystals were separated, washed with water and air-dried. (Yield: *ca.* 51% based on $(TBA)_4[W_{10}O_{32}]$). EA and ICP calcd (%) for $C_{60}H_{54}N_{12}O_{35}Cl_2W_{10}Cu_4$: C 19.65, H 1.48, N 4.58, Cu 6.93, W 50.14; Found: C 19.76, H 1.61, N 4.44, Cu 6.82, W 50.01.

2. X-ray crystallography

Data of DT–**BPY** and **AN**@DT–**BPY** were collected on a Bruker Smart APEX CCD diffractometer with graphite-monochromated Mo-Kα (λ = 0.71073 Å) using the SMART and SAINT programs.[S2,S3] Routine Lorentz polarization and Multi-scan absorption correction were applied to intensity data. Their structures were determined and the heavy atoms were found by direct methods using the SHELXTL-97 program package.[S4] The remaining atoms were found from successive full-matrix least-squares refinements on F^2 and Fourier syntheses. Except some partly occupied solvent water molecules, the other non-hydrogen atoms were refined anisotropically. Hydrogen atoms within the ligand backbones were fixed geometrically at their positions and allowed to ride on the parent atoms. For the DT–**BPY** and **AN**@DT–**BPY** several bond distances constraints were used to help the refinement on the **BPY** moiety, and thermal parameters on adjacent oxygen atoms of the polyoxometalate anion were restrained to be similar.

Table S1 Crystallographic data structure refinement for DT–**BPY** and **AN**@DT–**BPY**.

	DT–**BPY**	**AN**@DT–**BPY**
Empirical formula	$C_{60}H_{54}N_{12}Cl_2O_{35}W_{10}Cu_4$	$C_{63}H_{53}N_{13}Cl_2O_{33}W_{10}Cu_4$
M, g·mol^{-1}	3666.71	3683.74
Crystal system	Monoclinic	Monoclinic
Space group	$C2/m$	$C2/m$
a, Å	20.0634(15)	20.0614(14)
b, Å	17.3159(12)	17.2660(13)
c, Å	15.642(2)	15.8142(18)
α, deg	90.00	90.00
β, deg	124.2110(10)	125.8820(10)
γ, deg	90.00	90.00
V, Å^3	4494.1(7)	4438.2(7)
Z	2	2
D_{calcd}, g·cm^{-3}	2.710	2.757
T, K	200(2)	200(2)
Refl. collected/unique	16005/5238, $R_{\mathrm{int}} = 0.0404$	12620/4044, $R_{\mathrm{int}} = 0.0285$
μ, mm^{-1}	13.804	13.977
GOOF	1.072	1.126
R_1^a ($I > 2\sigma(I)$)	0.0392	0.0343
wR_2^b ($I > 2\sigma(I)$)	0.1038	0.0955
R_1^a (all data)	0.0683	0.0471
wR_2^b (all data)	0.1125	0.1076
Diff peak and hole, e·Å^{-3}	2.911/–2.027	2.791/–1.835

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Section 2 Characterizations of Catalysts

Substrate Penetration: Before the adsorption of substrate, freash MOFs were briefly air-dried on a filter paper and used without further processing. Substrate penetration studies were carried out by soaking the MOFs in aliphatic nitrile or electron-deficient alkene for 36 h. After the soaked MOFs were rapidly washed with acetonitrile solution several times to remove the substrate molecules adsorbed on the external surfaces of the crystals.

Fig. S1 The IR spectra of isovaleronitrile (i), DT–**BPY** (ii), and solids of DT–**BPY** obtained after the absorption of isovaleronitrile (iii).

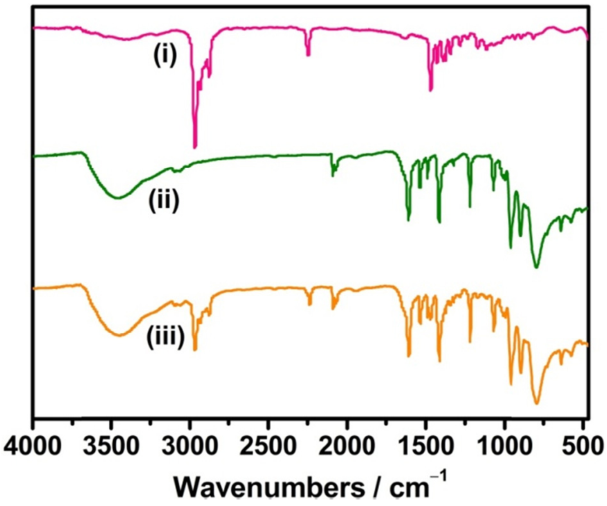
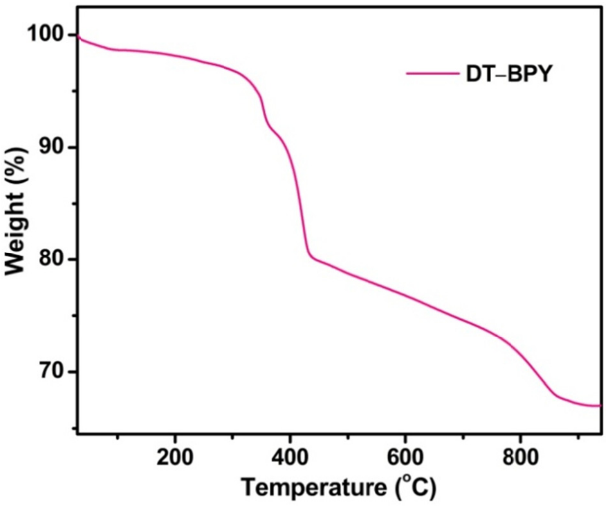


Fig. S2 TG curves of DT–**BPY** in the flowing nitrogen atmosphere.



Section 3 Catalysis Details

1. Typical Procedure for the Selective C–H Alkylation of Isovaleronitrile:

To aquartz glass tube equipped with a magnetic stirring bar was added isovaleronitrile (2.5 mmol), acrylonitrile (0.5 mmol), photocatalyst (1 mol %), TBA (4 mol %) and acetonitrile (1 mL). The reaction mixture was then degassed by three freeze-pump-thaw cycles. The reaction mixture was irradiated by a Xe lamp (500 W) at room temperaturefor 36 h. After the reaction, the resulting suspension was centrifuged, and the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexane/diethyl ether = 1/1).

Scheme S1 Proposed reaction mechanism for the DT–**BPY** photocatalyzed functionalization of unactivated C(sp^3)–H bonds.

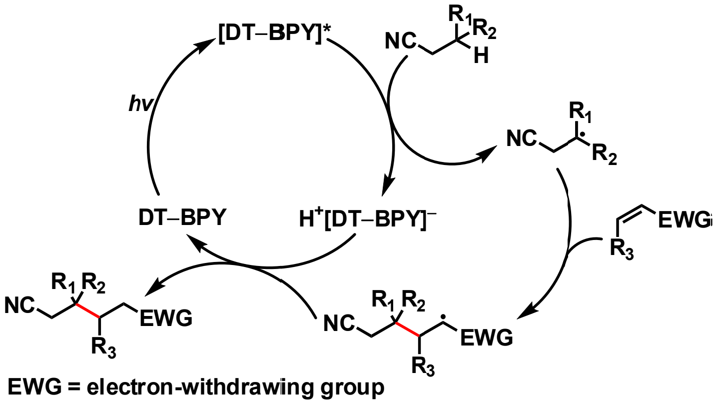
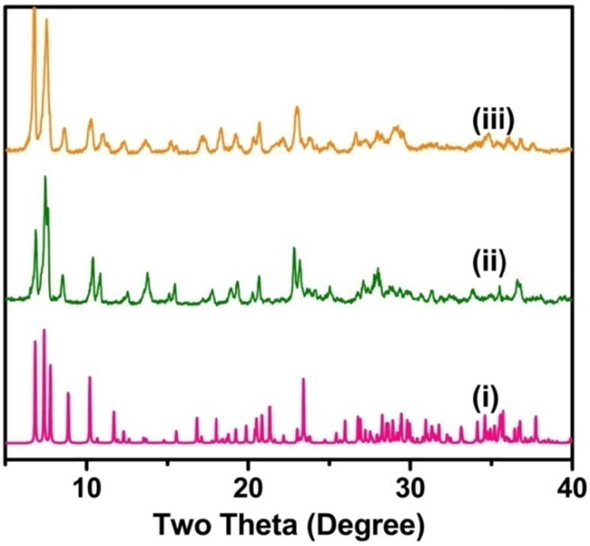


Fig. S3 Powder XRD pattern of DT–**BPY** showing the calculated pattern based on the single-crystal solutionand after three runs of the selective C–H alkylation [(i)-Simulated, (ii)-Experimental, (iii)-Recovery catalyst after three times runs].



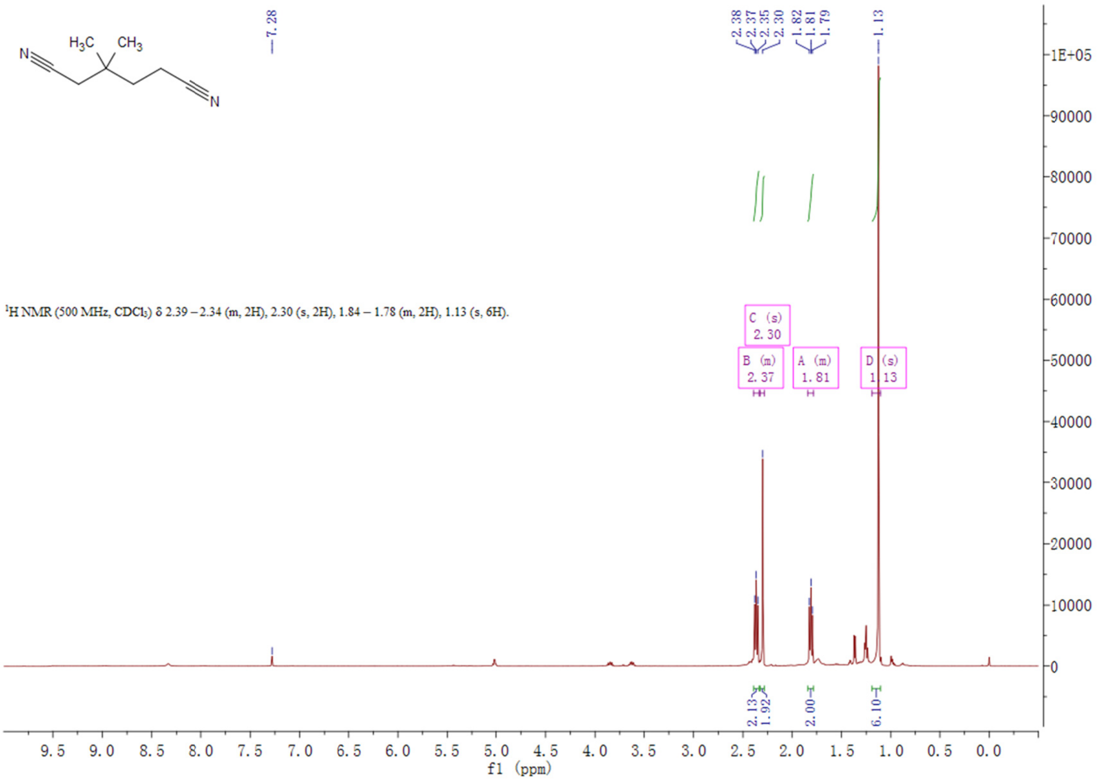
2. Study on the recyclability of DT–**BPY** as heterogeneous photocatalyst for the selective C–H alkylation of aliphatic nitriles in the optimum condition: isovaleronitrile (2.5 mmol), acrylonitrile (0.5 mmol), DT–**BPY** (1 mol %), TBA (4 mol %), acetonitrile (1 mL), 500 W Xe lamp, 36 h. Yields of product isolated after flash chromatography on SiO_2.

Entry	**Yield (%)**
Round 1	83
Round 2	81
Round 3	80

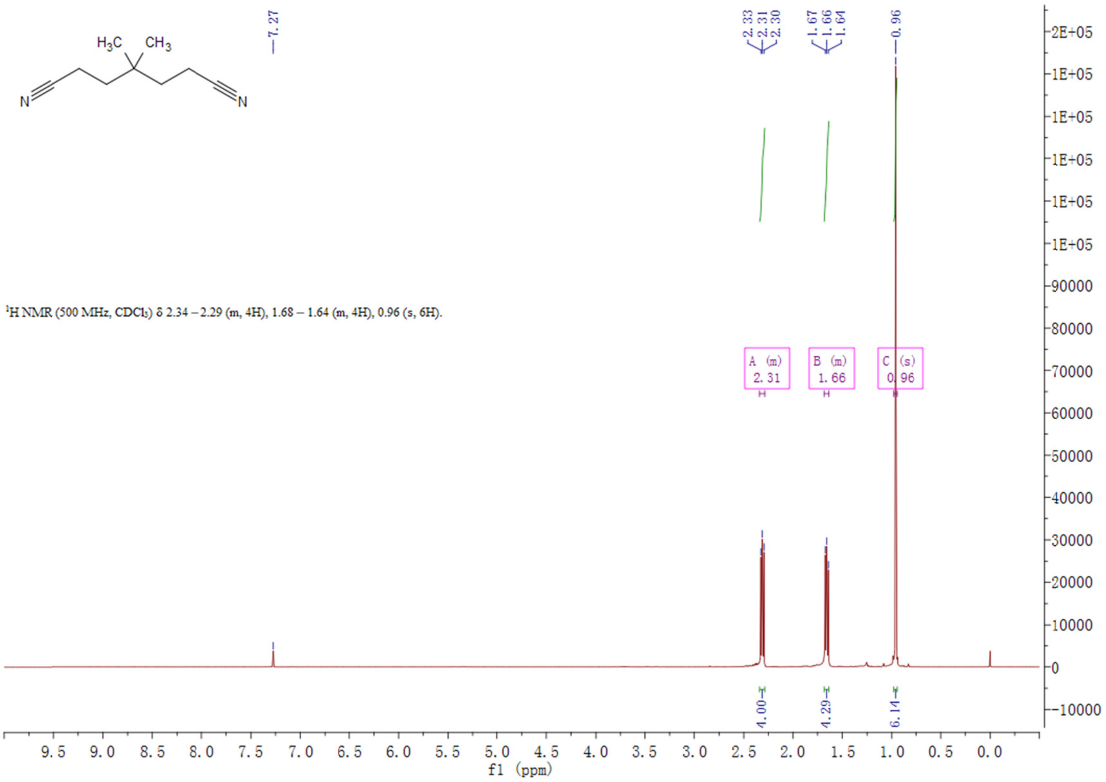
3. Study on the recyclability of DT–**BPY** as heterogeneous photocatalyst for the selective C–H alkylation of aliphatic nitriles in the optimum condition: isovaleronitrile (2.5 mmol), dimethyl maleate (0.5 mmol), DT–**BPY** (1 mol %), TBA (4 mol %), acetonitrile (1 mL), 500 W Xe lamp, 36 h. Yields of product isolated after flash chromatography on SiO_2.

Entry	**Yield (%)**
Round 1	84
Round 2	83
Round 3	83

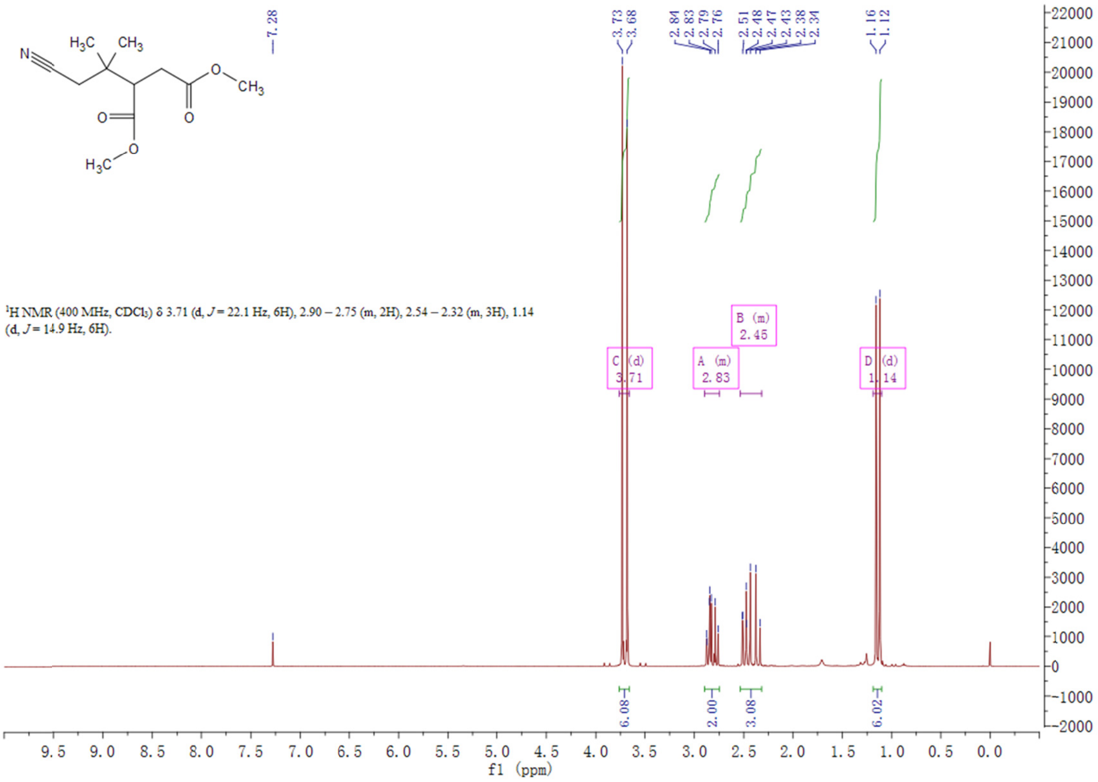
The ^{1}H NMR Spectra for the Catalytic Product:



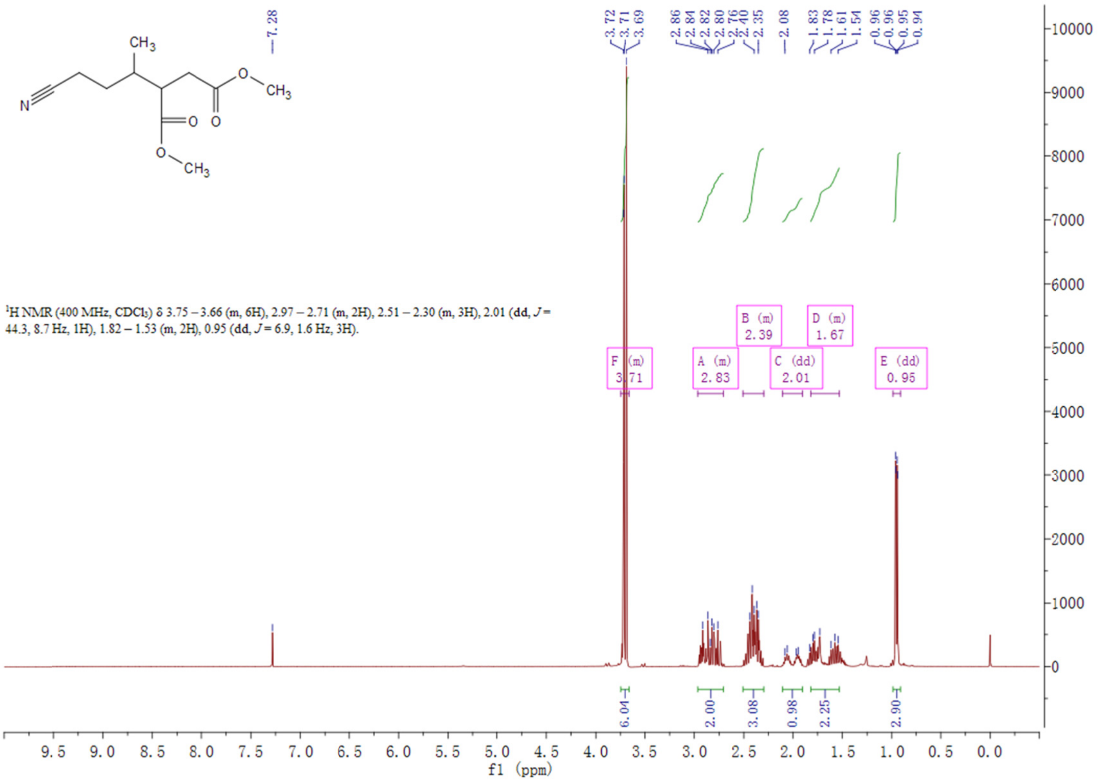
^{1}H NMR (500 MHz, $CDCl_3$) δ 2.39 – 2.34 (m, 2H), 2.30 (s, 2H), 1.84 – 1.78 (m, 2H), 1.13 (s, 6H).



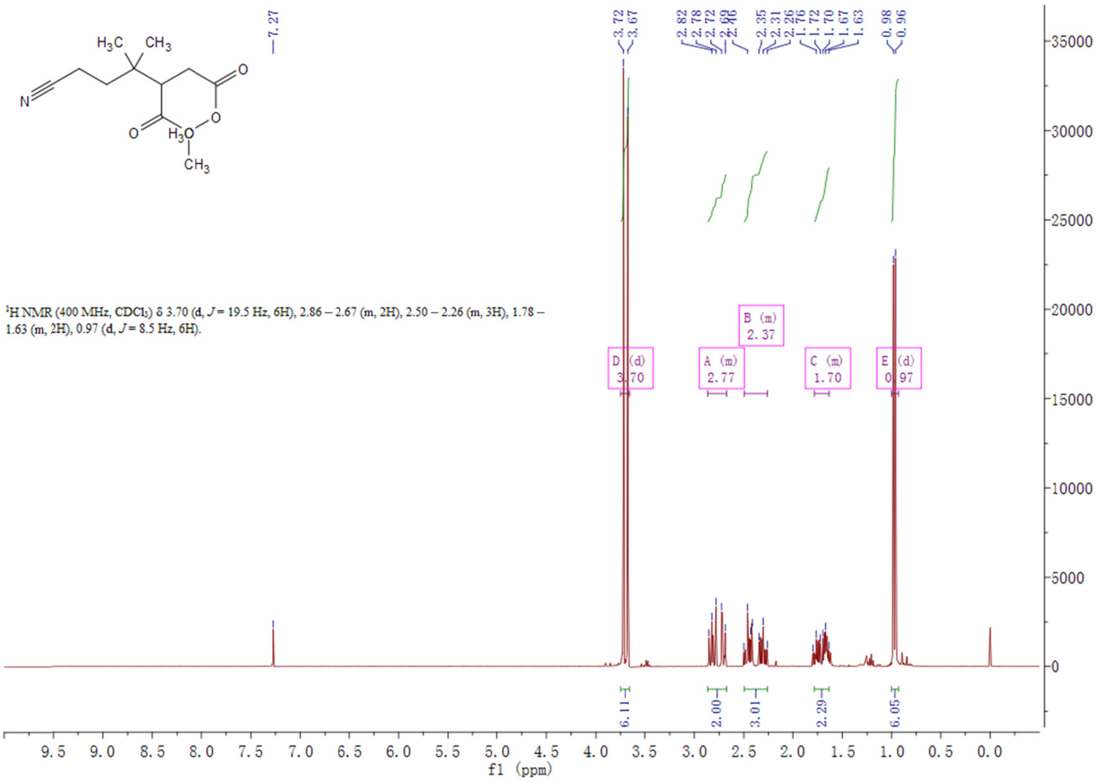
^{1}H NMR (500 MHz, $CDCl_3$) δ 2.34 – 2.29 (m, 4H), 1.68 – 1.64 (m, 4H), 0.96 (s, 6H).



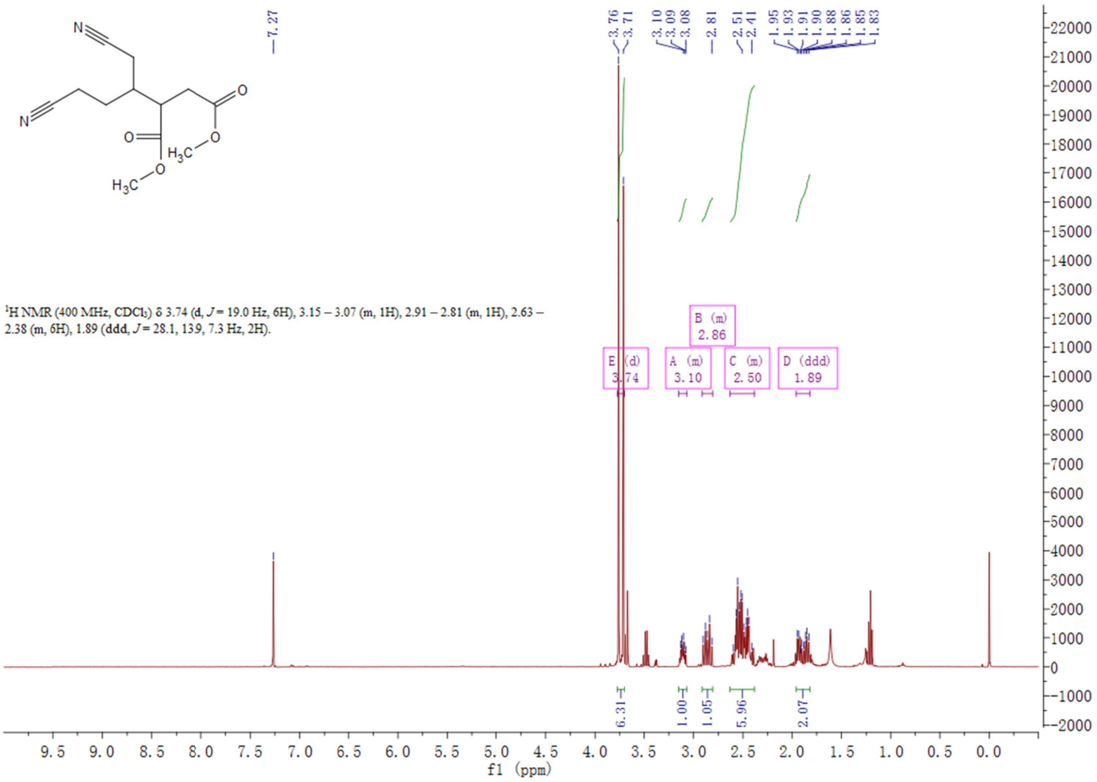
^{1}H NMR (400 MHz, CDCl$_3$) δ 3.71 (d, J = 22.1 Hz, 6H), 2.90 – 2.75 (m, 2H), 2.54 – 2.32 (m, 3H), 1.14 (d, J = 14.9 Hz, 6H).



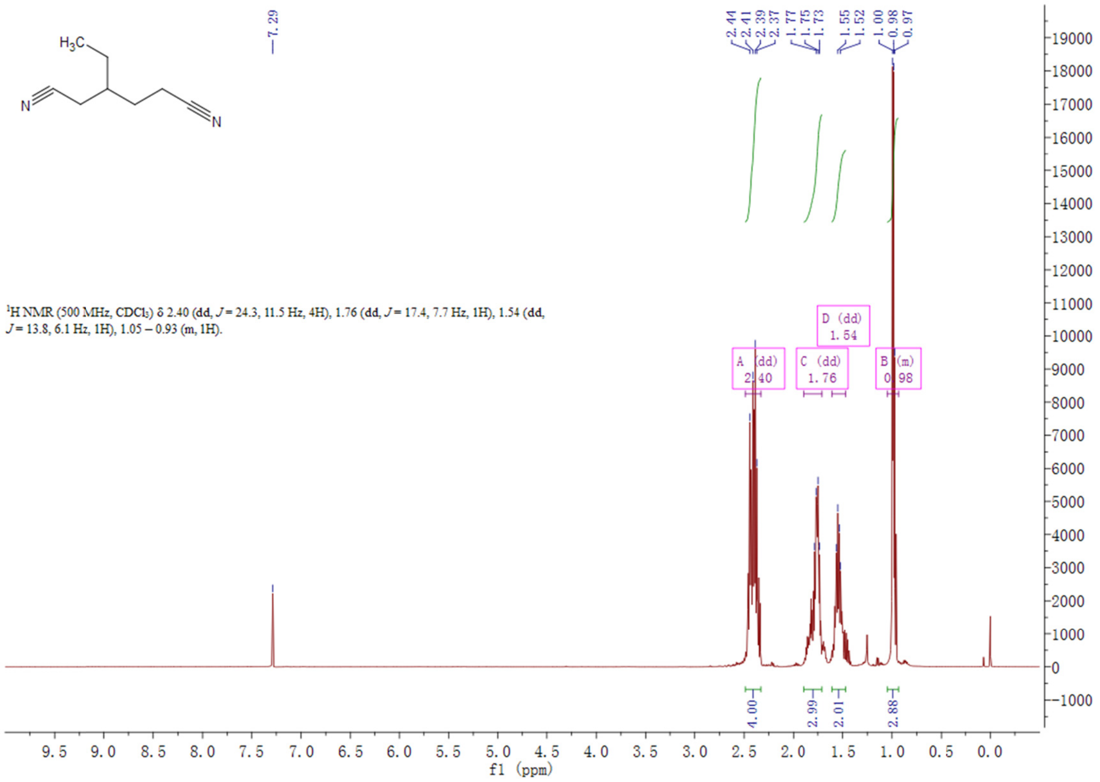
^{1}H NMR (400 MHz, CDCl$_3$) δ 3.75 – 3.66 (m, 6H), 2.97 – 2.71 (m, 2H), 2.51 – 2.30 (m, 3H), 2.01 (dd, J = 44.3, 8.7 Hz, 1H), 1.82 – 1.53 (m, 2H), 0.95 (dd, J = 6.9, 1.6 Hz, 3H).



^{1}H NMR (400 MHz, CDCl$_3$) δ 3.70 (d, *J* = 19.5 Hz, 6H), 2.86 – 2.67 (m, 2H), 2.50 – 2.26 (m, 3H), 1.78 – 1.63 (m, 2H), 0.97 (d, *J* = 8.5 Hz, 6H).



^{1}H NMR (400 MHz, CDCl$_3$) δ 3.74 (d, *J* = 19.0 Hz, 6H), 3.15 – 3.07 (m, 1H), 2.91 – 2.81 (m, 1H), 2.63 – 2.38 (m, 6H), 1.89 (ddd, *J* = 28.1, 13.9, 7.3 Hz, 2H).



^{1}H NMR (500 MHz, CDCl$_3$) δ 2.40 (dd, *J* = 24.3, 11.5 Hz, 4H), 1.76 (dd, *J* = 17.4, 7.7 Hz, 1H), 1.54 (dd, *J* = 13.8, 6.1 Hz, 1H), 1.05 – 0.93 (m, 1H).

Section 4 References

S1. Fournier, M.; Klemperer, W. G.; Silavwe, N. *Inorg. Synth.* **1990**, *27*, 81–83.

S2. SMART, *Data collection software (version 5.629)*; Bruker AXS Inc., Madison, WI, **2003**.

S3. SAINT, *Data reduction software (version 6.45)*; Bruker AXS Inc., Madison, WI, **2003**.

S4. Sheldrick, G. M. *SHELX-97, Program for crystal structure solution*; University of Göttingen: Göttingen, Germany, **1997**.