Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Facile synthesis of an organically- derivatized hexavanadate containing the remote amino group, $TBA_2[V_6O_{13}\{(OCH_2)_3CNH_2\}_2]$

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Supporting Information

Materials and general measurements

All the chemicals except dimethylacetamide were purchased and used without any further treatment. The dimethylacetamide was dried by refluxing in the presence of calcium hydride and distilled prior to use. IR spectra were obtained using a PerkinElmer FT-IR spectrometer. ^{1}H-NMR spectra were recorded using CD3CN/$CDCl_3$ as solvent with a JEOL JNM-EXC 400 spectrometer. ESI-MS spectra were recorded with a Thermo Q Exactive spectrometer in an acetonitrile solution (negative mode was used for compound **2** and **3**, positive mode for compound **1**). Elemental analysis was measured with Elementar Vario EL IIIelement analyzer.

Experimental details

Compound 1.

Compound **1** is synthesized according to the previously reported procedure.[1]

$C_{12}H_{17}NO_4$: Elemental analysis calcd (%) for $C_{12}H_{17}NO_4$: C 60.24, H 7.16, N 5.85; found: C 59.94, H 7.17, N 5.81; IR (KBr): ν= 3375 (w), 3287 (w), 2911 (w), 2872 (w), 1614 (m), 1586 (w), 1517 (m), 1448 (m), 1380 (w), 1303 (w), 1281 (w), 1249 (s), 1170 (m), 1051 (vs), 1029 (vs), 976 (s), 939 (m), 892 (w), 846 (m), 827 (m), 809 (m), 776 (w), 675 (w) cm^{-1}. ^1H NMR (400MHz, $CDCl_3$, standardized by TMS peak): *δ*= 2.30 (3H, br., NH, 2×OH), 3.59 and 3.71 (2H, AB syst., 2H-6, *J*=10.9 Hz), 3.68 and 3.81 (2H, AB syst., 2H-6', *J*=10.8 Hz), 3.61 and 3.89 (2H, AB syst., 2H-4, *J*=8.4 Hz), 3.81 (3H, s, OCH_3), 5.43 (1H, s, H-2), 6.90 (2H, d, 2H-ar, *J*=8.7 Hz), 7.41 (2H, d, 2H-ar, *J*=8.7 Hz). The peaks at 1.21 and 3.48 are attributed to ether used to wash NMR tube; ESI-MS: *m/z*(%): 262.10 (32.0) $[Na + \mathbf{1}]^+$, 240.12 (100) $[H + \mathbf{1}]^+$.

Compound 2.

A mixture of 0.844 g $TBA_3H_3V_{10}O_{28}$ (0.5 mmol) and 0.3589 g compound **1** (1.5 mmol) were added to 10 mL dried dimethylacetamide and the solution was heated for 72h at 80 °C. The reaction flask was covered with tin-foil to avoid direct illumination. After cooling down to room temperature, the insoluble solids were removed by the filtration. Slow diffusion of ether into filtrate over several days resulted in the formation of bulk red crystals of **2**. Yield: 26% (based on vanadium from $TBA_3H_3V_{10}O_{28}$).

$(BuN)_2[V_6O_{13}\{(OCH_2)_3CNC_8H_8O\}_2]$: Elemental analysis calcd (%) for $C_{56}H_{100}O_{21}N_4V_6$: C 45.72, H 6.85, N 3.81; found: C 45.17, H 6.85, N 3.94; IR (KBr): ν= 2960 (m), 2933 (m), 2874 (m), 1632 (w), 1603 (m), 1576 (w), 1512 (w), 1481 (w), 1379 (w), 1252 (m), 1165 (w), 1097 (m), 1050 (s), 949 (vs), 807 (s), 719 (s) cm^{-1}. ^1H NMR (400MHz, CD_3CN, standardized by solvent peak): *δ*= 0.97 (24H, t, TBA-H), 1.35-1.37 (16H, sextet, TBA-H), 1.62 (16H, quintet, TBA-H), 3.11 (16H, t, TBA-H), 3.81 (6H, s, OCH_3), 5.12 (12H, s, OCH_2), 6.94-6.96 (4H, d, benzene ring), 7.69-7.71 (4H, d, benzene ring), 8.46 (2H, s, NCH); ESI-MS: *m/z*(%): 986.79 (17.2) $[H + (\mathbf{2})]^-$, 492.90 (100.0) $[(\mathbf{2})]^{2-}$.

Crystal data for $(BuN)_2[V_6O_{13}\{(OCH_2)_3CNC_8H_8O\}_2]$: $C_{56}H_{100}O_{21}N_4V_6$, *Mr*=1471.04, crystal size 0.48×0.26×0.25 mm^3, monoclinic, space group *P2(1)/c*, a=11.598(2), b=19.518(4), c=15.301(3) Å, α=90.00, β=91.47(3), γ= 90.00°, V= 3462.5(12) $Å^3$, Z=2, ρ_{calcd}=1.411 g/cm^3, μ=0.847 mm^{-1}, *F*(000)= 1540. A total of 23314 reflections were collected, of which 6726 were unique (R_{int}=0.0308, theta and index (hkl)range measured: 2.86<θ<26.00, [-14,-24,-15]<[h,k,l]<[14,24,18]). The R_1 value was 0.0431 for 6302 independent reflections with $[I > 2\sigma(I)]$ and the wR_2 value was 0.1010 with $[I > 2\sigma(I)]$. The R_1 value was 0.0475 for all data and the wR_2 value was 0.1040 for all data. The goodness of fit on F^2 was 1.110. The data were collected at 153.15K on a Agilent Gemini E diffractometer with MoK_α monochromated radiation (λ=0.71073 Å). The structure was solved by direct methods using SHELXS-97 and refined using SHELXL-97.[2]

Compound 3.

The synthesis procedure is the same with compound **2** except for the following hydrolysis process. The filtrate of compound **2** was added into 100 mL ether under stirring. The generated precipitation was washed with ether and further dissolved in 15mL acetonitrile (insoluble solids were removed by filtration). The red precipitation formed after 0.3 mL concentrated hydrochloric acid was dropped into the solution. This red precipitation was added into 30mL of 1M HCl solution and stirred for 4 days. The resulting solids were obtained by the centrifugal separation and washed twice with acetonitrile. The dried solids were added to 10 mL of water and a few drops of ammonia water were added to obtain a clear solution (undissolved solids were removed by the filtration). The slow evaporation of clear solution gave rise to the formation of red crystals of compound **3**. Yield: 58% (based on vanadium from $TBA_3H_3V_{10}O_{28}$).

$[V_6O_{13}\{(OCH_2)_3CNH_3\}_2]\cdot 4H_2O$: Elemental analysis calcd (%) for $C_8H_{26}O_{23}N_2V_6$: C 11.66, H 3.18, N 3.40; found: C 11.80, H 3.33, N 3.51; IR (KBr): ν= 3034 (w), 1650 (w), 1549 (w), 1444 (w), 1108 (m), 1057 (s), 945 (vs), 814 (m), 791 (m), 712 (s) cm^{-1}. ^1H NMR (400MHz, DMSO-d6, standardized by solvent peak): δ = 4.99 (12H, s, OCH_2). ESI-MS: *m/z*(%): 750.71 (64.5) $[H+(\mathbf{3})]^-$, 374.85 (100.0) $[(\mathbf{3})]^{2-}$.

Crystal data for $[V_6O_{13}\{(OCH_2)_3CNH_3\}_2]\cdot 4H_2O$: $C_8H_{26}O_{23}N_2V_6$, *Mr*=823.95, crystal size 0.5×0.4×0.3 mm^3, monoclinic, space group *C2/m*, a=10.381(2), b=12.311(3), c=9.6175(19) Å, α=90.00, β=104.20(3), γ= 90.00°, V= 1191.6(4) Å^3, Z=2, ρ_{calcd}=2.296 g/cm^3, μ=2.366 mm^{-1}, *F*(000)= 820. A total of 5137 reflections were collected, of which 1230 were unique (R_{int}=0.0313, theta and index (hkl)range measured: 3.07<θ<26.00, [-12,-15,-11]<[h,k,l]<[12,15,11]). The R_1 value was 0.0281 for 1152 independent reflections with $[I>2\sigma(I)]$ and the wR_2 value was 0.0767 with $[I>2\sigma(I)]$. The R_1 value was 0.0297 for all data and the wR_2 value was 0.0776 for all data. The goodness of fit on F^2 was 1.128. The data were collected at 293K on a Rigaku R-Axis Spider diffractometer with MoK_α monochromated radiation (λ=0.71073 Å). The structure was solved by direct methods using SHELXS-97 and refined using SHELXL-97.[2]

Title compound $TBA_2[V_6O_{13}\{(OCH_2)_3CNH_2\}_2]$:

According to the previously reported work,[3] the dried solids obtained after the hydrolysis process above was suspended in 20mL of CH_3CN/DMF (2/1). To the suspension, 1.25 mL of 1.0 M tetrabutylammonium hydroxide in methanol was added. Insoluble substance was removed by the centrifugation. The diffusion of ether into the clean solution resulted in the formation of $TBA_2[V_6O_{13}\{(OCH_2)_3CNH_2\}_2]$. Yield: 53% (based on vanadium from $TBA_3H_3V_{10}O_{28}$).

Characterization and pictures

Table S1. Detailed information for hydrogen bond lengths (Angstroms) and angles (Degree).

D-H	d (D-H)	d (H..A)	<DHA	d (D..A)	A
O8-H8B	0.869	2.249	144.92	3.002	O7
O8-H8A	0.857	1.905	170.02	2.753	O2
N1-H2A	0.890	1.871	168.61	2.749	O8
N1-H2B	0.886	1.950	174.46	2.834	O6

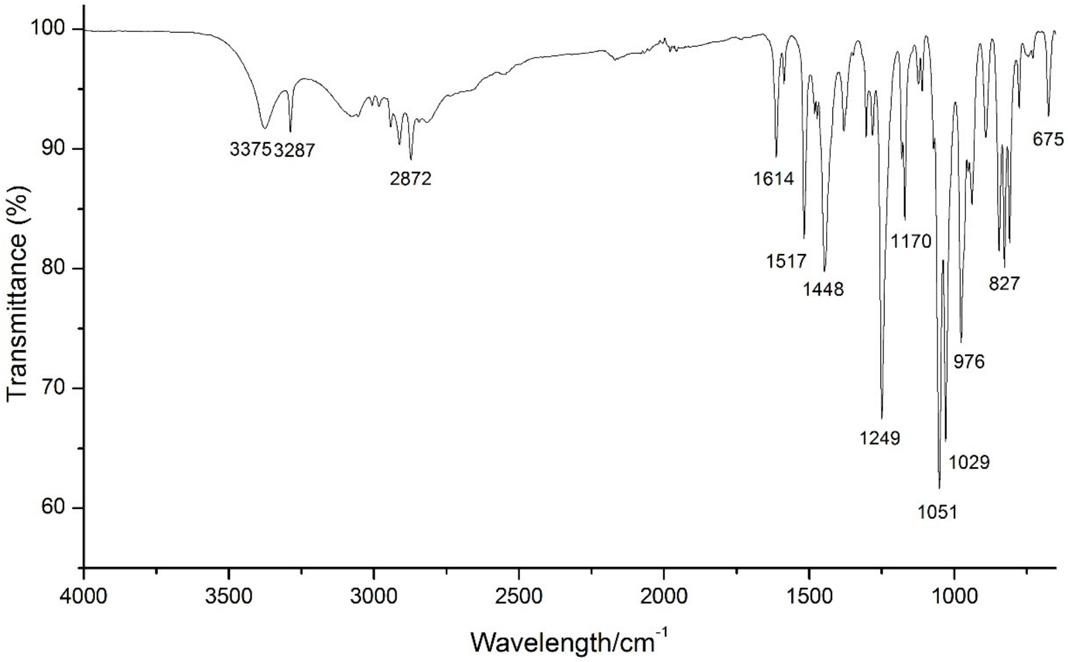

Figure S1. FT-IR spectrum measured for compound **1**.

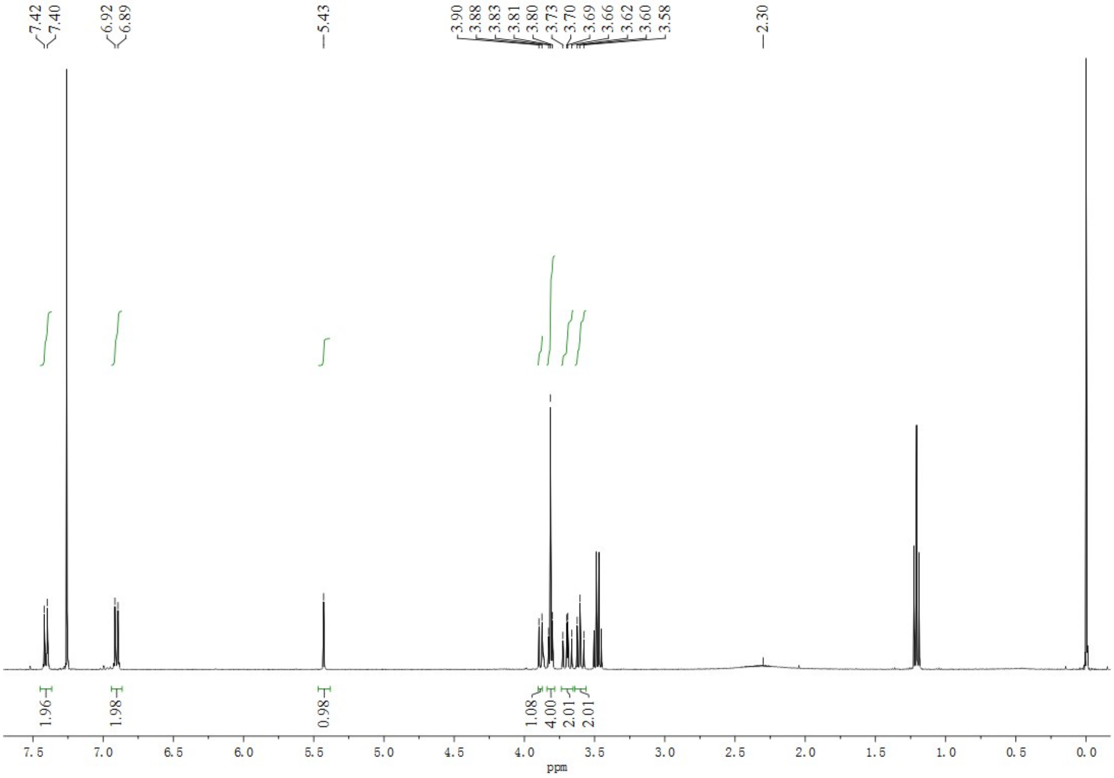

Figure S2. ^{1}H-NMR result of compound **1**.

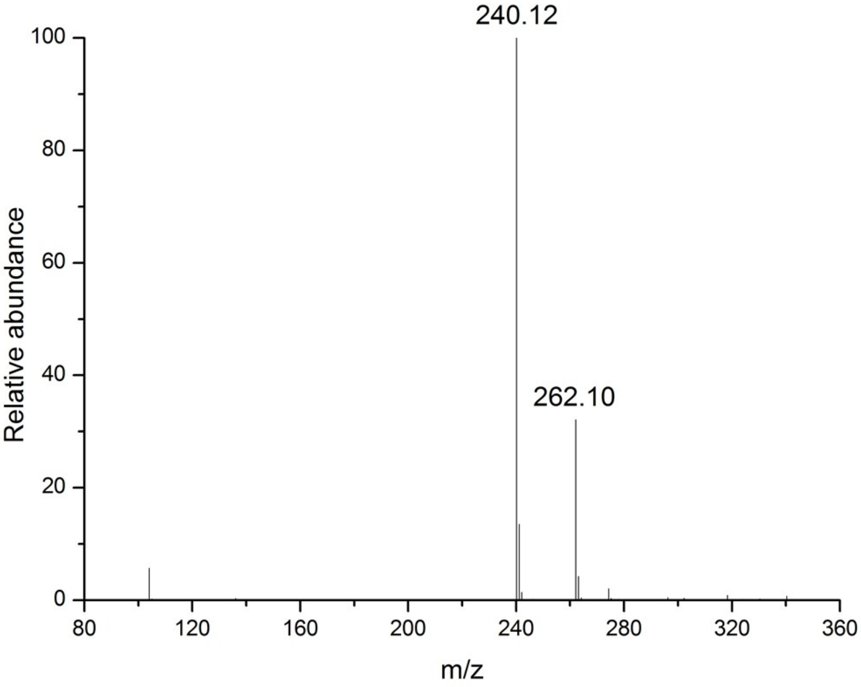

Figure S3. ESI-MS result of compound **1**.

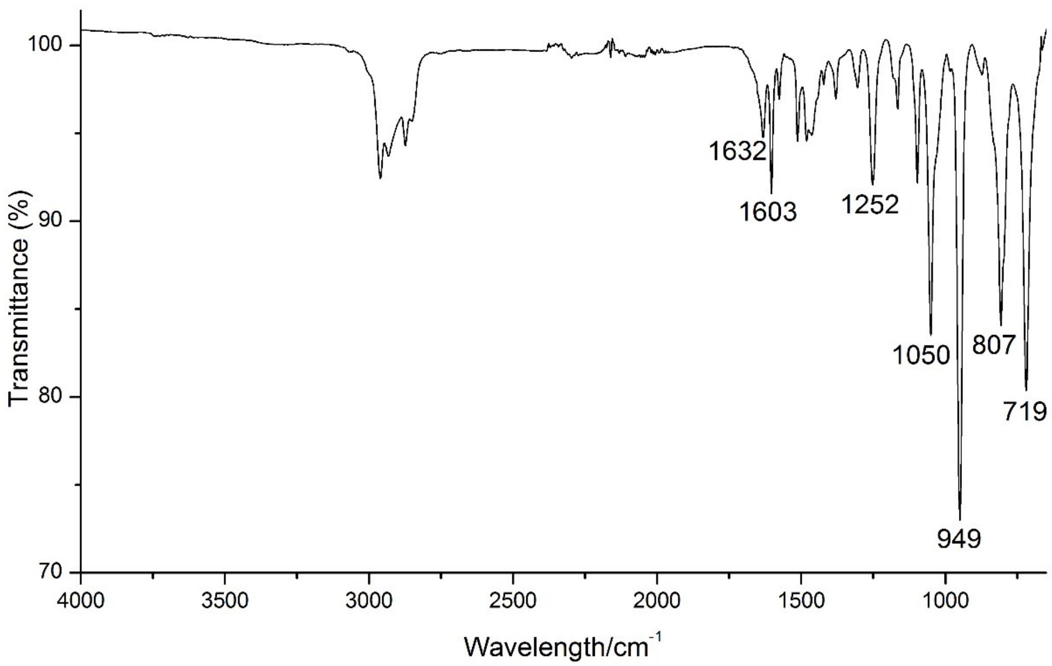

Figure S4. FT-IR spectrum measured for compound **2**.

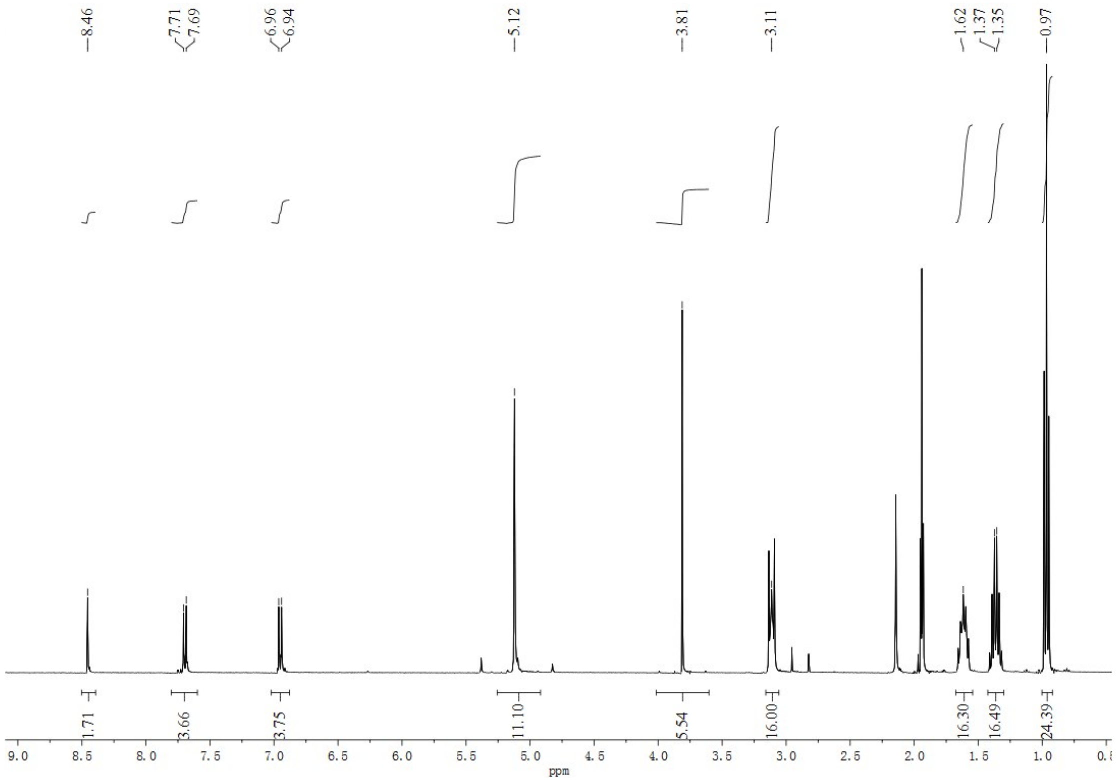

Figure S5. ^{1}H-NMR result of compound **2**.

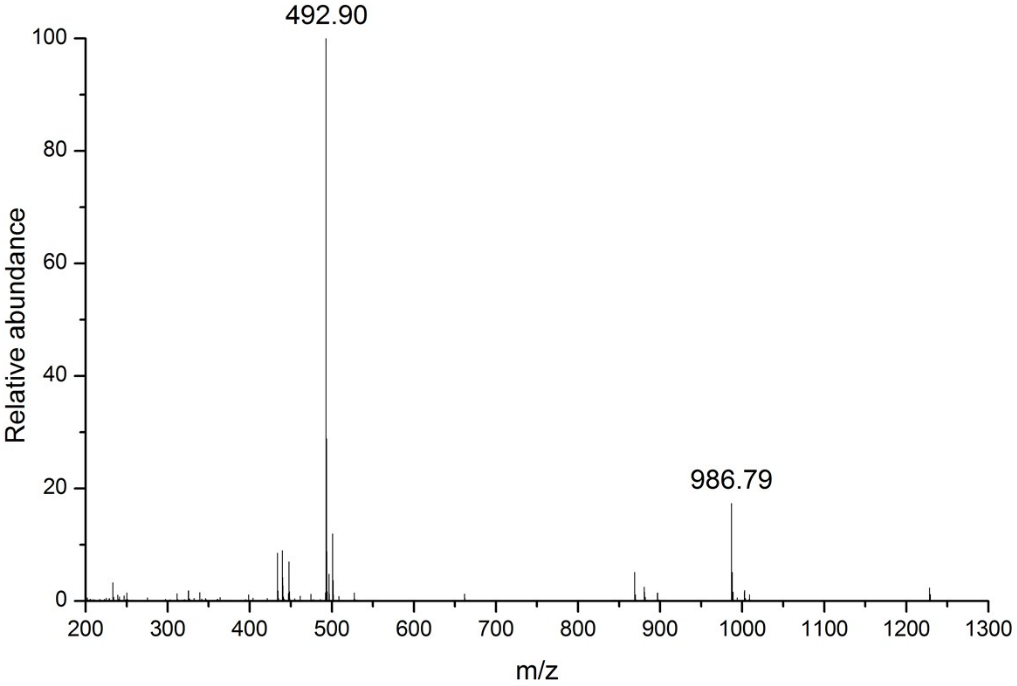

Figure S6. ESI-MS result of compound **2**.

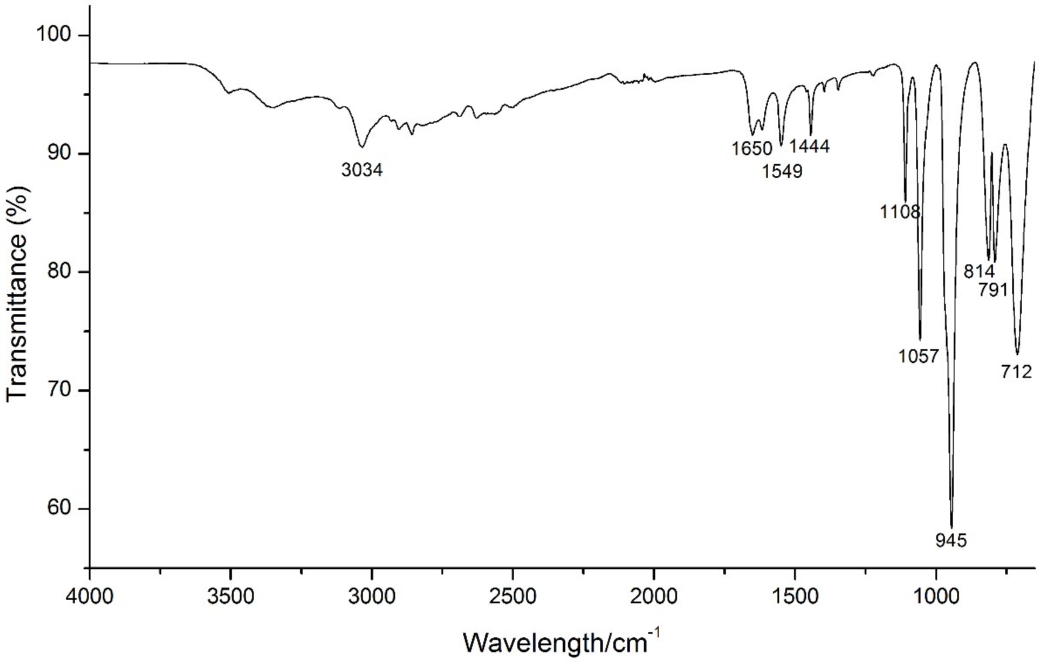

Figure S7. ^{1}H-NMR result of compound **3**.

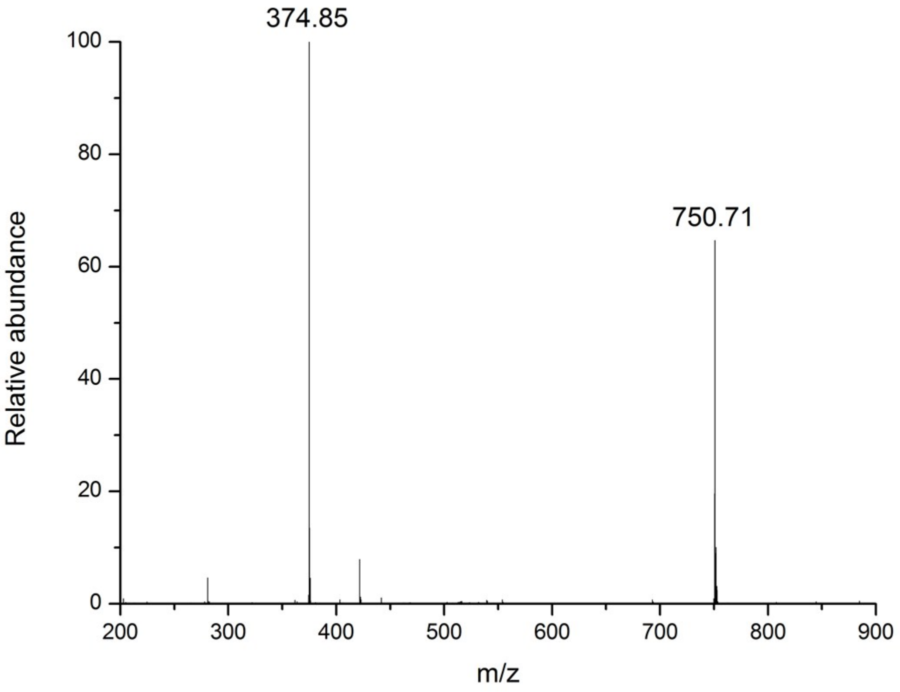

Figure S8. ESI-MS result of compound **3**.

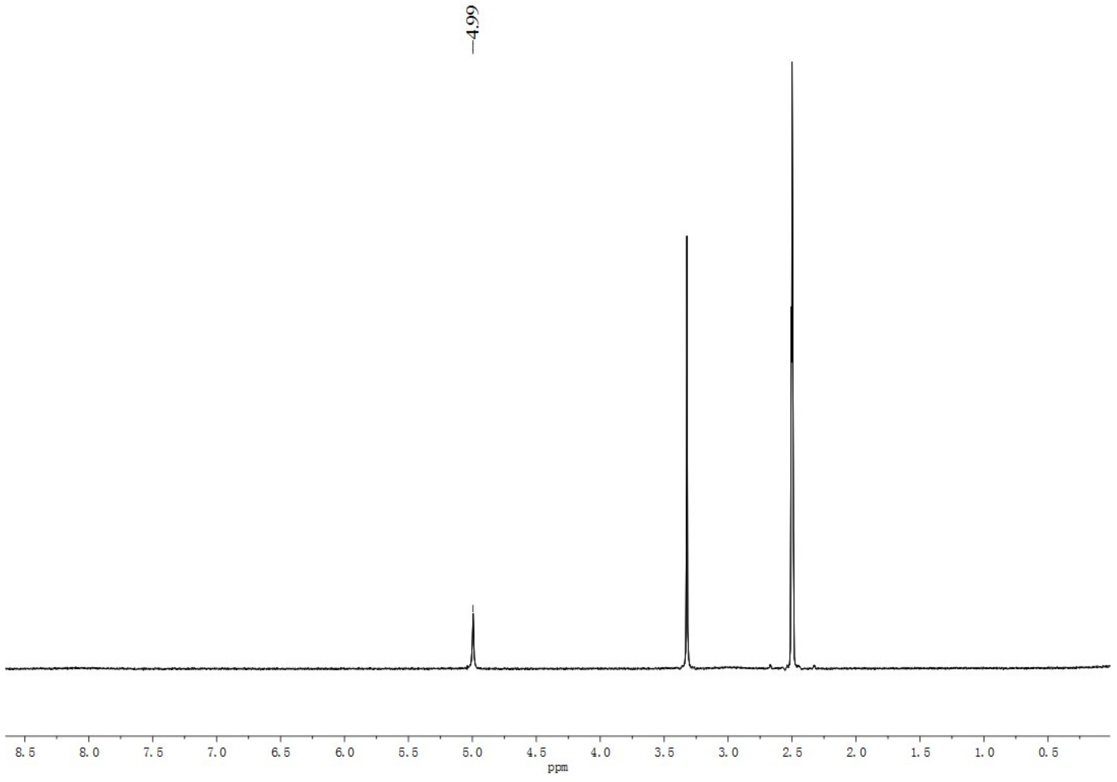

Figure S9. ^{1}H-NMR result of compound **3**.

References

(1) J. Sélambarom, S. Monge, F. Carré, J. P. Roque and A. A. Pavia, *Tetrahedron*, 2002, **58**, 9559.

(2) G. M. Sheldrick, SHELXTL v. 5.10, Structure Determination Software Suite, Bruker AXS, Madison, Wisconsin (USA), 1998.

(3) D. Li, J. Song, P.-C. Yin, S. Simotwo, A. J. Bassler, Y.-Y. Aung, J. E. Roberts, K. I. Hardcastle, C. L. Hill and T.-B. Liu, *J. Am. Chem. Soc.*, 2011, **133**, 14010