Supplementary information for

Supramolecular catalysis by an inside of a bowl-type dodecavanadate for cyanamide dimerization

Syadza Firdausiah, Hiroya Iwai and Yuji Kikukawa *
Department of Chemistry, Graduate School of Natural Science and Technology, Kanazawa University, Kakuma, Kanazawa 920-1192, Japan.
E-mail: kikukawa@se.kanazawa-u.ac.jp

Experimental Section

Instruments: NMR spectra were recorded with JEOL JNM-LA400 and Bruker Avance 400. IR spectra were measured on Jasco FT/IR-4200 using KBr method.

Reagents: Solvents, cyanamide (CA), and dicyandiamide (DCD) were commercially available and used as received unless otherwise specified. $[V_{12}O_{32}]^{4-}$ (**V12**) $\{n\mathrm{Bu_4N}\}_4[V_4O_{12}]$, $\{n\mathrm{Bu_4N}\}_3[H_3V_{10}O_{28}]$, $\{n\mathrm{Bu_4N}\}_4[HV_{12}O_{32}(Cl)]$, and $\{n\mathrm{Bu_4N}\}_5[V_{18}O_{46}(NO_3)]$ was prepared according to the literature.[22, S1-S4]

Synthesis of CA-incorporated V12 (V12(CA)). The single crystals suitable for X-ray crystal analysis were obtained as follows. 0.03 mmol of $\{^n\mathrm{Bu_4N}\}_4[V_{12}O_{32}]$ was dissolved in 0.9 mL of acetone. 0.2 M acetone solution of H_2NCN was prepared. 0.6 mL of 0.2 M acetone solution of H_2NCN was added to the **V12** solution. 0.05 mL of dimethyl sulfoxide was added. Slow addition of diethyl ether and the solution was kept at 0°C.

Synthesis of DCD-incorporated V12 (V12(DCD)). The single crystals suitable for X-ray crystal analysis were obtained as follows. 0.03 mmol of $\{^n\mathrm{Bu_4N}\}_4[V_{12}O_{32}]$ was dissolved in 0.9 mL of acetone. 2.5 M acetone solution of H_2NCN was prepared. 0.6 mL of 2.5 M acetone solution of H_2NCN was added to the **V12** solution. Slow addition of diethyl ether and the solution was kept at 0°C. The same single crystals were obtained even in the presence of 0.05 mL of dimethyl sulfoxide.

Titration experiment. Competitive inclusion of CA and DCD into **V12** was carried out in acetone to confirm the reason of the catalytic reaction plateau. The measurements were conducted in 20 mM of **V12** immediately after all compounds were mixed in NMR tube. For the evaluation of the affinity between **V12** and DCD, DMF was selected as a solvent according to the literature.[21] The series of V12 20 mM in DMF was prepared in the presence of DCD in the range of 0 – 400 mM (0, 1, 2, 5, 10, and 20 equiv.). Affinity between **V12** and a guest moiety depends on the solvent. Affinity of **V12** and CA/DCD in acetone is stronger than those in DMF. On the other hand, the solubilities of the guest-incorporated **V12** are too low to evaluate the affinity.

X-ray Crystallographic analysis: Single-crystal structural analysis was performed at 100 K with a XtaLAB Synergy-DW diffractometer with Cu-*K*α or Mo-*K*α radiation (λ = 1.54178 or 0.71073 Å,

respectively) and Hybrid Pixel Array Detector. The data reduction and absorption correction were completed using the CrysAlisPro program.[S5] The structural analyses were performed using Olex and winGX for Windows software.[S6,S7] All structures were solved by SHELXT (direct methods) and refined by SHELXL-2019/3.[S8] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms are positioned geometrically and refined using a riding model. Crystaline solvent in **V12**(DCD) was removed using the PLATON SQUEEZE tool.[S9]

Catalytic reaction: CA 1.5 mmol, catalyst 10 μmol, acetone 2 mL were put in the glass test tube with the screw cap. The solution was kept at 0 °C in the cool reactor (EYELA, PSL-1400) with ethanol as a cooling medium. The solution was stirred around 500 rpm with the Teflon-coated magnetic stir bar. DCD and **V12**(DCD) was precipitated during the reaction. After 7 days, the reaction mixture was allowed to room temperature, and acetonitrile 100 μL was added to remove the DCD from **V12**. Diethyl ether 8 mL was added to precipitate **V12**(AN). The filtrate was evaporated and the product was collected by crystallization in diethyl ether. Yields were determined by the weight of the products. The purity of the products was determined by ^{1}H NMR. In the case of $VO_{(acac)}$, yield was estimated by ^{1}H NMR because the catalyst could not be readily separated from the reaction mixture. TON and TOF values were calculated from the amount of DCD formed based on the corresponding yield.

Additional references:

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S2. V.W. Day, W.G. Klemperer, D.J. Maltbie, *J. Am. Chem. Soc*. 1987, **109**, 2991.

S3. Y. Inoue, Y. Kikukawa, S. Kuwajima, Y. Hayashi, *Dalton Trans*. 2016, **45**, 7563.

S4. I. Yoshida, R. Mitsuhashi, Y. Kikukawa, Y. Hayashi, *Inorganics*, 2024, **12**, 61.

S5. *Rigaku Oxford Diffraction CrysAlisPro Software System*; Rigaku Corporation: Wrocław, Poland, 2023.

S6. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Ouschmann, *J. Appl. Crystallogr.*2009, **32**, 339.

S7. L. J. Farrugia, *J. Appl. Crystallogr.*1999, **32**, 837.

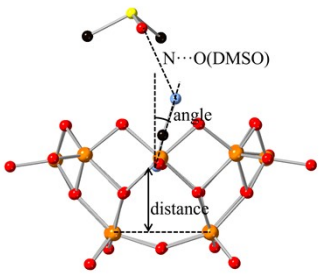
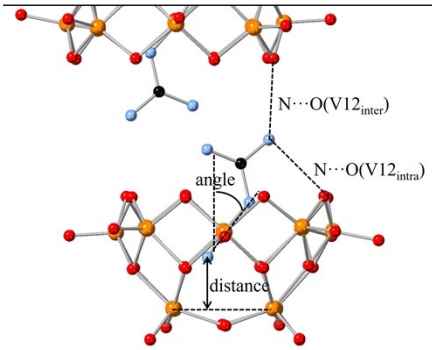
S8. G. M. Sheldrick, *Acta Crystallogr.* 2015, **C71**, 3.

S9. A. L. Spek, *Acta Crystallogr.* 2025, **C71**, 9.

Table S1. Crystallographic data for **V12**(CA) and **V12**(DCD).

	V12(CA)	**V12**(DCD)
formula	$C_{76}H_{176}N_6O_{37}S_4V_{12}$	$C_{66}H_{148}N_8O_{32}V_{12}$
fw	2505.74	2177.20
crystal system	tetragonal	monoclinic
space group	$P4_32_12$ (#96)	$P2_1/n$ (#14)
a (Å)	20.01620(10)	20.5157(4)
b (Å)	20.01620(10)	20.6039(4)
c (Å)	56.3966(4)	25.6521(5)
β (deg)	90	95.965(2)
V (Å^3)	22595.2(3)	10784.5(4)
Z	8	4
μ (mm^{-1})	9.245	1.055
R_1 ($I > 2\sigma(I)$)	0.0839	0.0897
wR_2	0.2316	0.3149

Table S2. Penetration of guest into the concave of **V12** and selected bond distances and angles

	V12(CA)	**V12**(DCD)
		
	penetration of guests	
distance[a]	2.38 Å	1.18 Å
angles[b]	15º	40º
	bond distances	
C≡N	1.108 Å	1.132 Å
C–N(H_2)	1.353 Å	
C–N(C(NH_2))		1.313 Å
N···O(DMSO)	2.772 Å	
N···O(**V12**$_{intra}$)		2.905 Å
N···O(**V12**$_{inter}$)		2.850 Å
N(≡C) ···V	3.290–3.902 Å (average 3.616 Å)	2.499–4.376 Å (average 3.577 Å)
	bond angles	
N≡C–N	171.2º	171.0º

[a]distances from the plane defined by the four bottom vanadium atoms. [b]angles of linear molecules from the pseudo-fourfold axis.

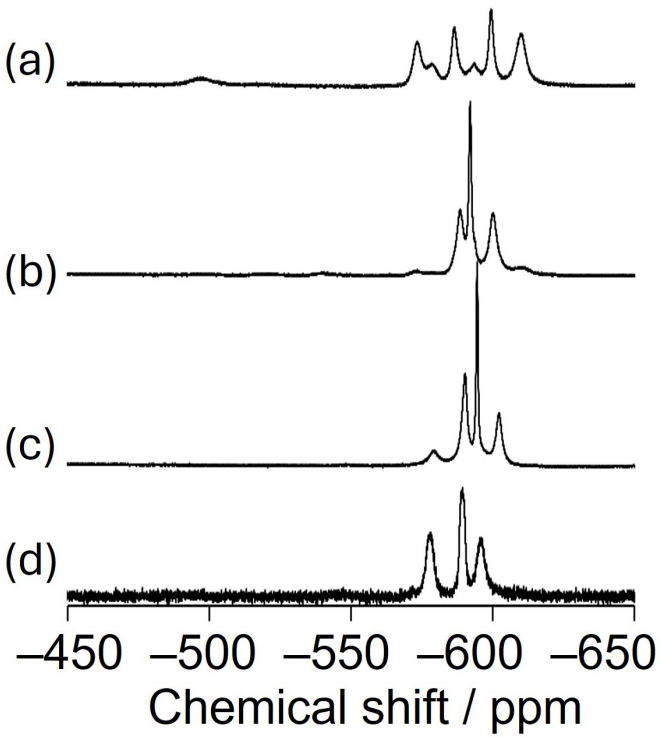


Figure S1. ^{51}V NMR spectra of acetone solution of (a) **V12**-free, (b) mixture of **V12**-free and 5 equiv. of CA (c) mixture of **V12**-free and 100 equiv. of CA, and (d) mixture of **V12**-free and 10 equiv. of DCD. In the spectrum (c), the ratio of **V12**(CA) to **V12**(DCD) was about 70:30.

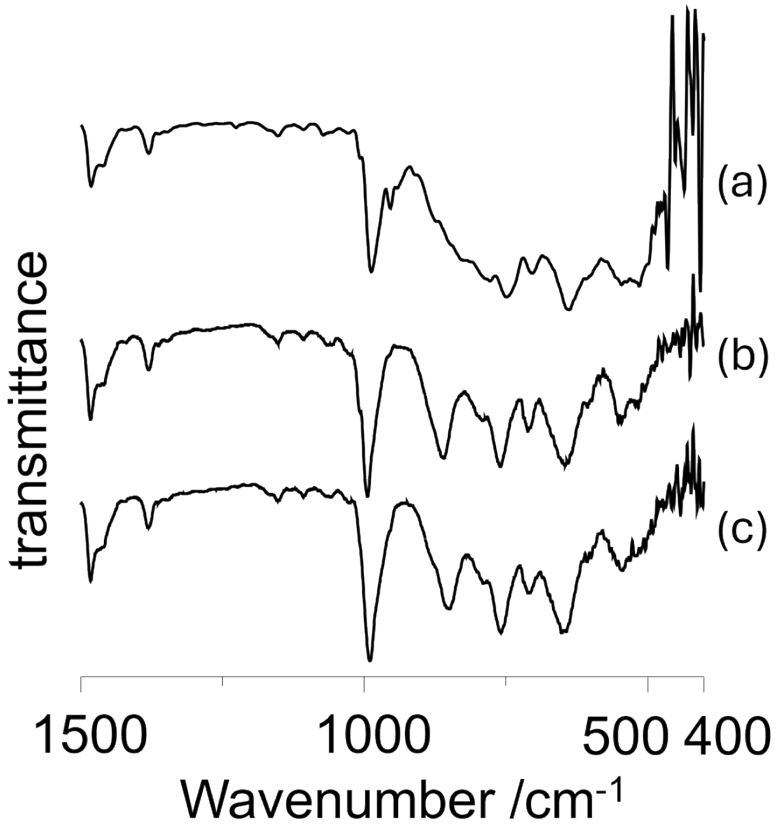


Figure S2. IR spectra of (a) **V12**-free, (b) **V12** obtained after the treatment with 5 equiv. of CA, (c) **V12** obtained after the treatment with 100 equiv. of CA.

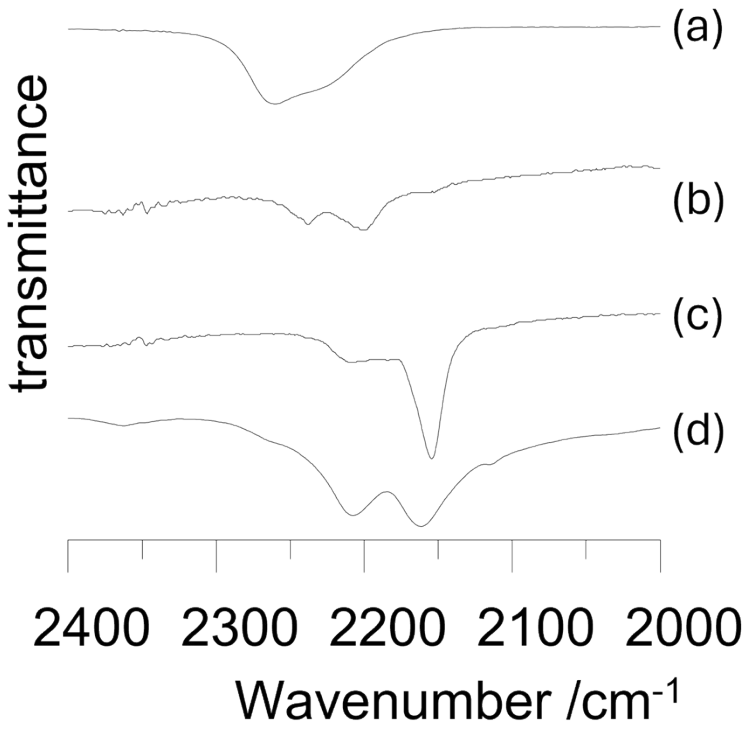


Figure S3. IR spectra of (a) CA, (b) **V12** obtained after the treatment with 5 equiv. of CA, (c) **V12** obtained after the treatment with 100 equiv. of CA and (d) DCD.

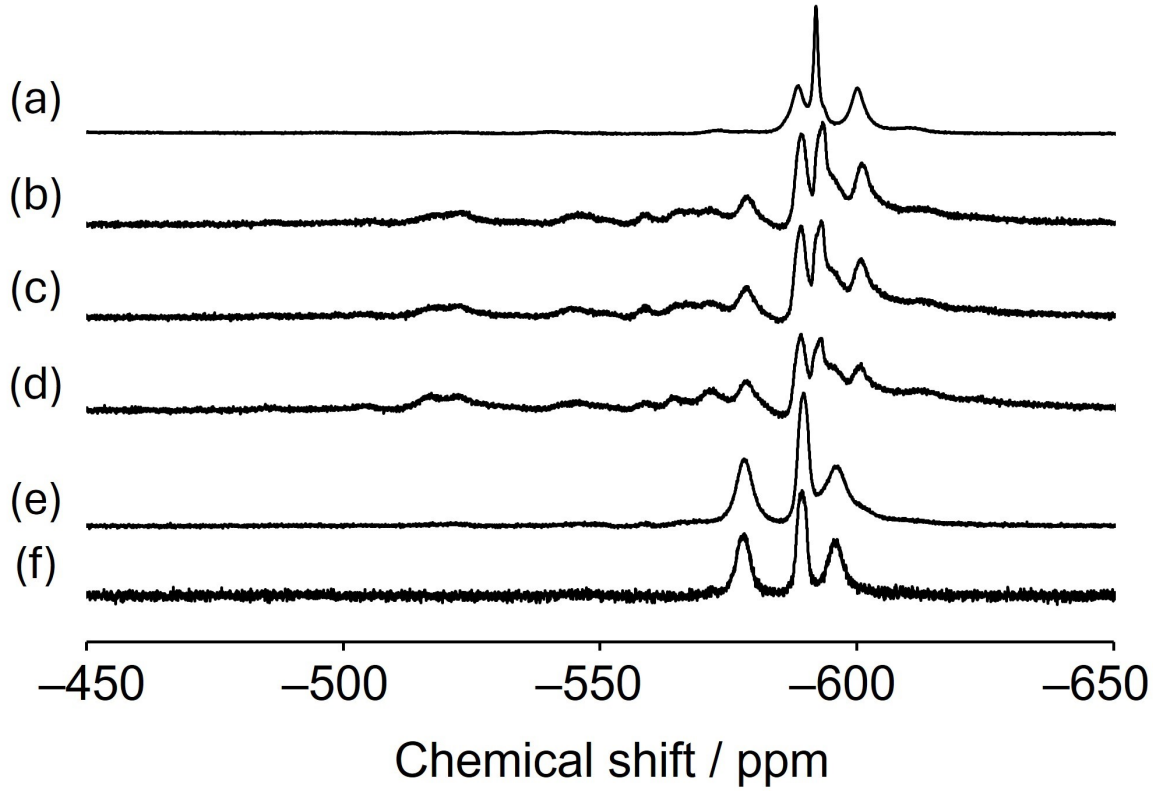


Figure S4. ^{51}V NMR spectra of acetone solution of **V12** in the presence of (a) 5 equiv. of CA (b) 146 equiv. of CA and 2 equiv. of DCD, (c) 100 equiv. of CA and 2 equiv. of DCD, and (d) 50 equiv. of CA and 50 equiv. of DCD and (f) 10 equiv. of DCD. The ratio of **V12**(CA) to **V12**(DCD) were around (b) 55:45, (c) 50:50, (d) 40:60.

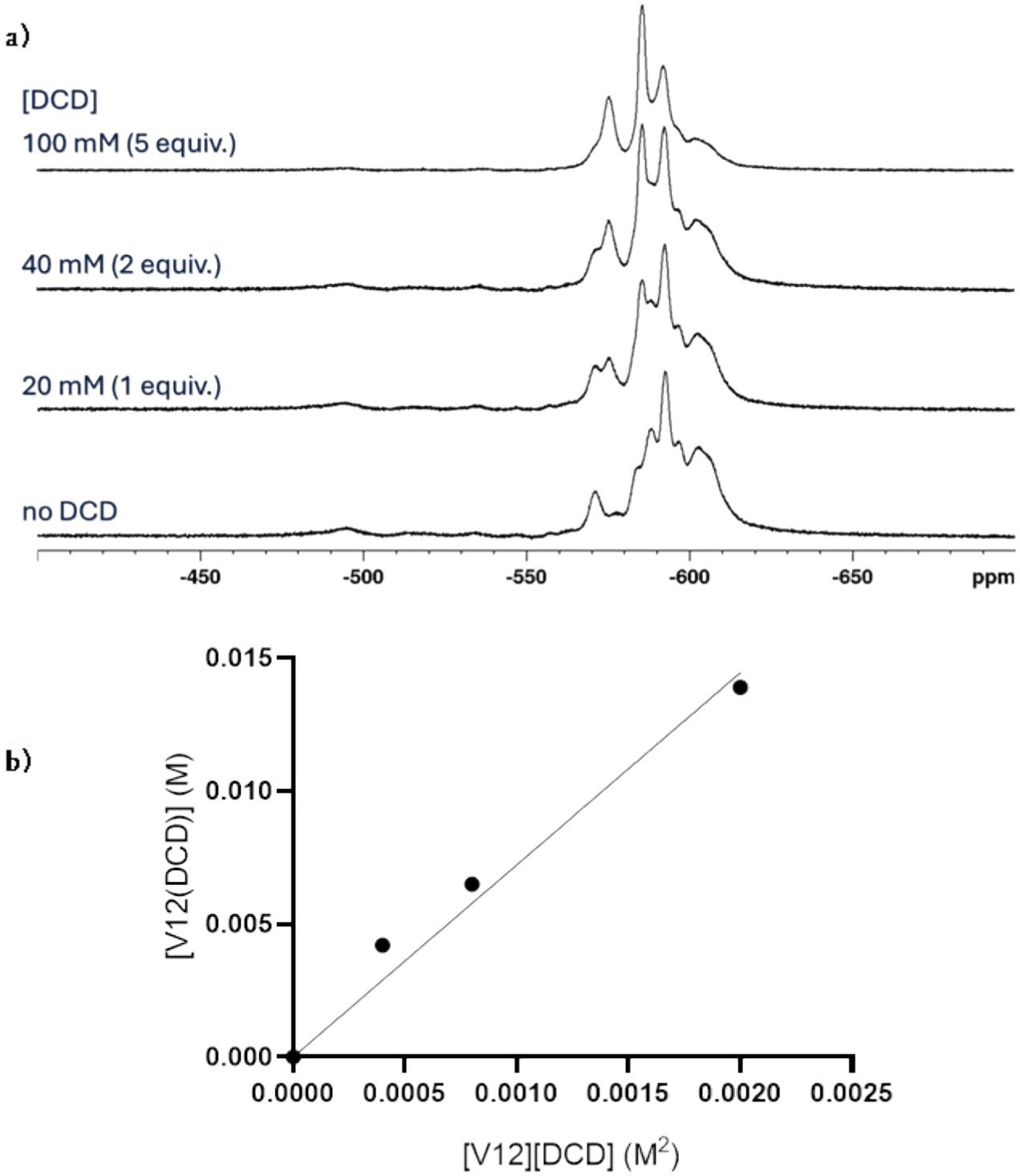


Figure S5. (a) ^{51}V NMR spectra of the titration experiment of **V12** 20 mM with DCD in DMF at 298 K, (b) linear regresion for the binding equation, K_a = 7.2 M^{-1}.

Table S3. Catalytic reaction using non bowl-shaped polyoxovanadates as controls[a]

Entry	Catalysts (μmol)	Yield (%)	TON
1	$\{^{n}Bu_4N\}_4[V_4O_{12}]$ □ (10 μmol)	n.d.	-
2	$\{^{n}Bu_4N\}_3[H_3V_{10}O_{28}]$ (10 μmol)	n.d.	-
3	$\{^{n}Bu_4N\}_4[HV_{12}O_{32}(Cl)]$ (10 μmol)	n.d.	-
4	$\{^{n}Bu_4N\}_5[V_{18}O_{46}(NO_3)]$ (10 μmol)	n.d.	-

[a] Reaction conditions: CA 1.5 mmol, catalyst, acetone 2 mL, 0ºC.

Table S4. Catalytic reaction using simple Lewis-acid as controls[a]

Entry	Catalyst (μmol)	Yield (%)	TON
1	$BF_3 \cdot OEt_2$ (10 μmol)	n.d.	-
2	$Sc(OTf)_3$ (10 μmol)	n.d.	-
3	$ZnBr_2$ (10 μmol)	n.d.	-
4	$BF_3 \cdot OEt_2$ (120 μmol)	2[b]	0.1
5	$Sc(OTf)_3$ (120 μmol)	3[b]	0.2
6	$ZnBr_2$ (120 μmol)	48[b]	3

[a] Reaction conditions: CA 1.5 mmol, catalyst, acetone 2 mL, 0ºC. [b] Yield was determined by ^{1}H NMR.

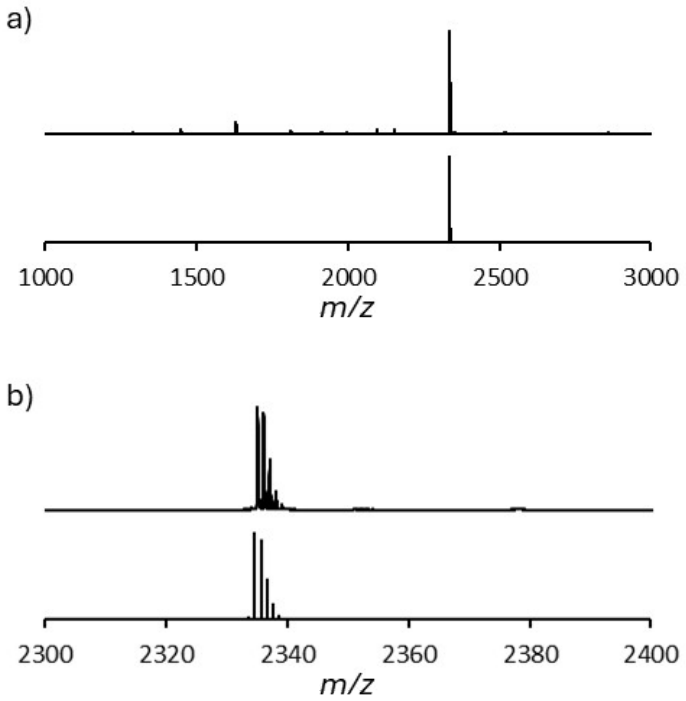


Figure S6. ESI-Mass spectrum of reaction mixture after 7 days of CA dimerization by **V12** in acetone at 0 ℃ (up) and predicted mass spectrum of V12 (bottom) in (a) wide and (b) narrow scales.

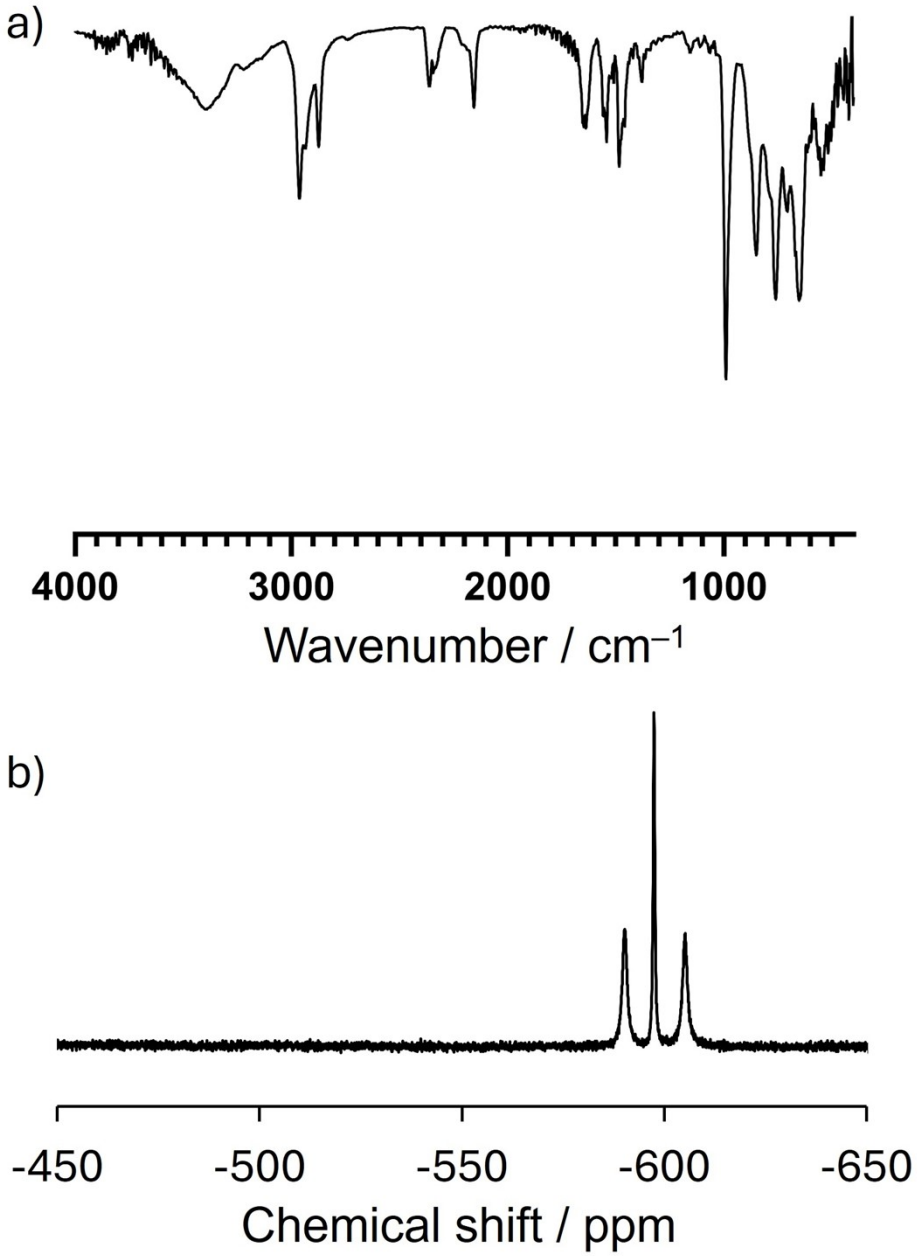


Figure S7. (a) IR spectrum and (b) ^{51}V NMR spectrum in acetonitrile of the catalyst collected after the catalytic reaction.

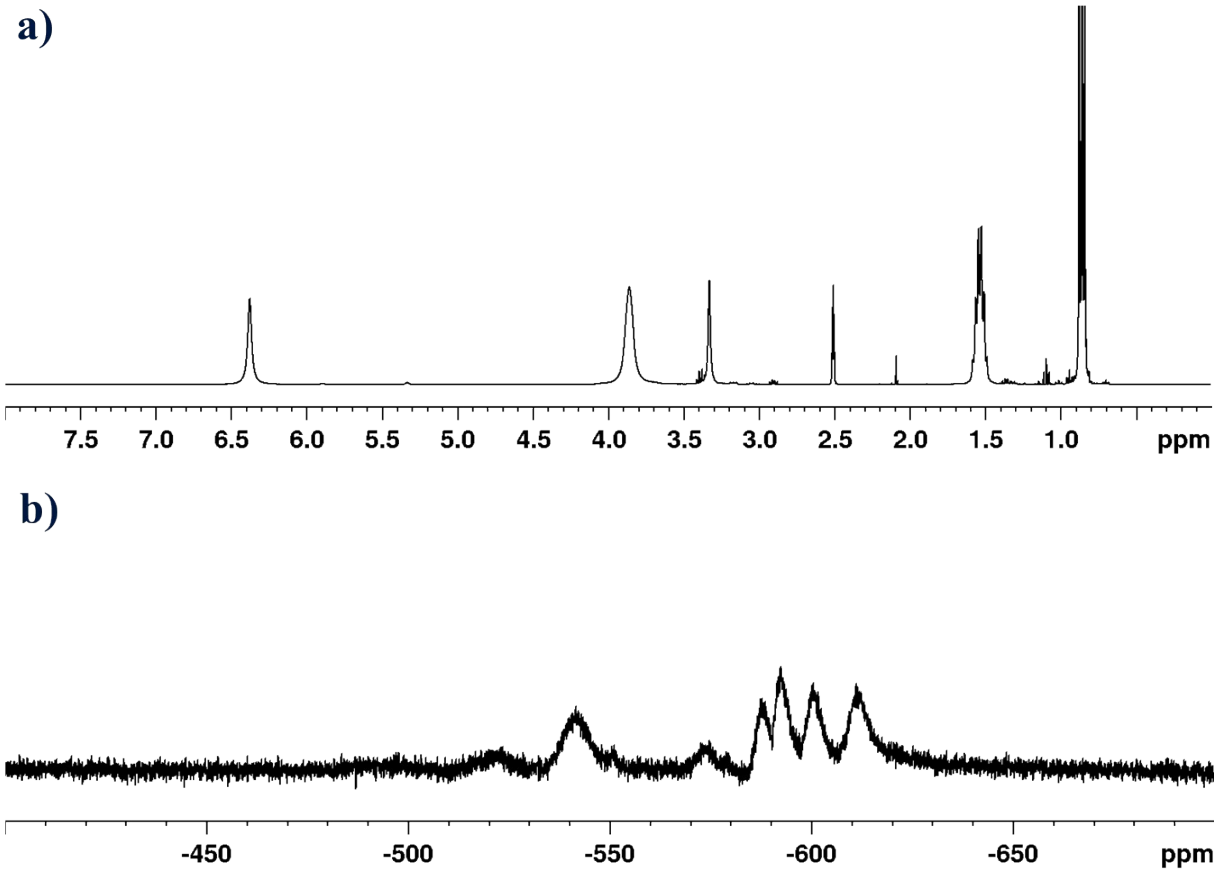


Figure S8. (a) ^{1}H NMR spectrum of the crude in DMSO-d_6 for the reaction of *n*-propylcyanamide with **V12** after 7 days (400 MHz, 298 K) and (b) ^{51}V NMR spectrum of the mixture of **V12** 5 mM and *n*-propylcyanamide 75 mM (15 equiv.) in acetone.