Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

A Micro-environment Tuning Approach for Enhancing the Catalytic Capabilities of lanthanide containing Polyoxometalate on cyanosilylation of ketones

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Table of Contents

1. Materials synthesis and characterization
2. Crystallographic data
3. Mass spectral data
4. Thermo Gravimetric Analyzer and differential scanning calorimetry analysis
5. Infrared spectra
6. UV-Vis spectra
7. Catalytic behavior
8. Powder X-ray diffraction data

1. Materials synthesis and characterization

Material synthesis

$K_8[\alpha\text{-}SiW_{11}O_{39}]\cdot 13H_2O$ was synthesized according to a previous study.[1]

Synthesis of compound 1

0.5 g $K_8SiW_{11}O_{39}$ and 0.2 g $(CH_3)_2NH\cdot HCl$ (DMA) were dissolved in 10 ml deionized water, and the pH value was adjusted to 2.5 with dilute HCl solution (1mol/L), and then 0.1 g 2-methylimidazole (2-MeIm) and 0.1g Nd $(NO_3)_3$ was added into the above mixture with continuous stirring, heated for 10 minutes, The solution was flittered off, block crystals of compounds 1 was appeared about two days of slow evaporation at room temperature. The crystal structure of compound 1 was identified by single crystal X-ray diffraction.

Synthesis of compound 2

0.1 g of the as prepared compound 1 was dissolved in 20 ml deionized water, then 5μl 1M dilute HCl and 1 g Tetrabutylammonium bromide (TBABr) were added to the above solution with continuous stirring, after filtration and washed three times with deionized water, white precipitate was collected and followed with vacuum drying at 50 ℃. The product was named compound 2 for brief.

Chemicals and measurements

All chemicals were purchased from commercial sources and used without further purification. The X-ray diffraction (XRD, Rigaku, Rint-2000) was employed to characterize the compound 1-2 using Cu-Ka in the range of 10-50° with the scanning rate of 10°/min. Gas chromatography (GC) analyses were performed by using a Nanjing

Kojie Analytical Instrument Company GC 5890N equipped with a capillary column PEG-20M (30 m, 0.32 mm), a FID detector and nitrogen as the gas carrier. GC-MS analyses were carried out by using a Hewlett-Packard HP 6890N Network GC system/5975 Mass Selective Detector equipped with an electron impact ionizer at 70 eV. Thermogravimetric analyses were performed with a NETZSCH STA 449C TGA instrument, inflowing Ar with a heating rate of 10 °C min^{-1}. UV/Vis absorption spectra were measured with a SHIMADZU UV2600 UV/Vis spectrophotometer. Fourier transform infrared spectroscopy of compound 1-2 and retrieved compound 2 were carried out (FT-IR, Nicolet 380, Thermo Nicolet Corporation) with KBr tablet. Diffraction data of was collected by a Bruker CCD diffractometer with monochromatized Mo-Kα radiation (λ= 0.71073 Å). The collected frames were processed with the software SAINT. The absorption correction was treated with SADABS. Structures were solved by direct methods and refined by full-matrix least-squares on F2 using the SHELXTL software package. ESI-MS spectra were obtained on a Bruker Bruker MicroTof Q II instrument. The morphological information was detected by field emission transmission electron microscope (FETEM, Titan, G2 60–300). The size distribution was detected by Malvern Zetasizer Nano. Agilent 5110 ICP-OES was used to analyse element distribution.

2. **Crystallographic data**

Tab. S1 Crystal data and structure refinement for compound 1

Identification code	1
Empirical formula	$NdSi_2W_{22}O_{88}C_{50}N_{25}H_{128}$
Deposition number	1975066
Formula weight	6732.5941
Temperature/K	296.15
Crystal system	triclinic
Space group	P-1
a/Å	13.4923(9)
b/Å	19.9659(14)
c/Å	24.4480(16)
α/°	102.869(4)
β/°	97.740(4)
γ/°	94.707(4)
Volume/Å3	6319.1(7)
Z	2
ρcalcg/cm3	3.577
μ/mm-1	20.465
F(000)	6118
Crystal size/mm3	0.15 × 0.15 × 0.1
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	2.388 to 52
Index ranges	--16≤h≤16, -24≤k≤ 24, -30≤l≤30
Reflections collected	93566
Independent reflections	24826[Rint =0.0373, Rsigma = 0.0360]
Data/restraints/parameters	24826/0/1626
Goodness-of-fit on F2	1.071
Final R indexes [I>=2σ(I)]	R1 = 0.0304, wR2 = 0.0618
Final R indexes [all data]	R1 =0.0434,wR2 =0.0661

Largest diff. peak/hole/e Å-3	1.82/-1.24

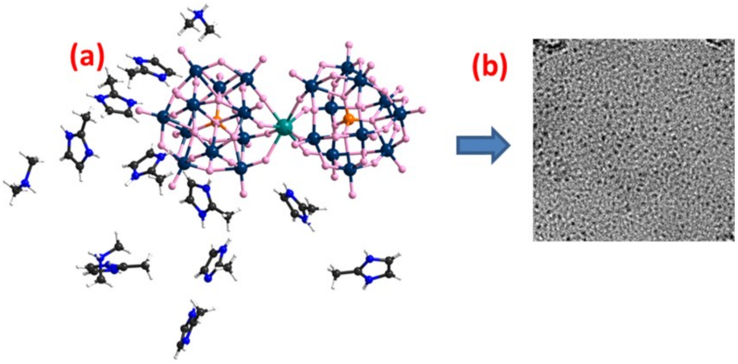


Fig. S1 (a) Crystal structure of compound 1, disordered waters and 2-Melm are omitted for brief, (b) Tem images of compound 1 dispersed H_2O.

3. Detailed assignment of mass spectral data for compound 1-2.

Fig. S2 MS spectra of compound 1-2

Tab. S2 detailed assignment of mass spectral data for compound 1-2

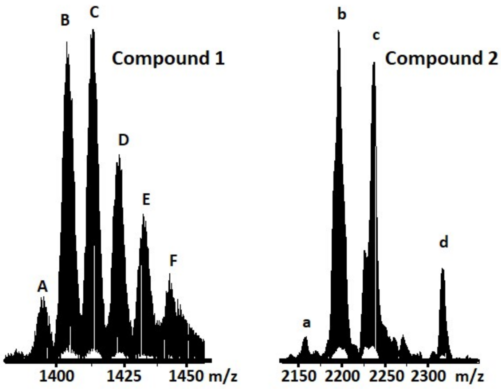


Fig. S2 MS spectra of compound 1 and TBA^+ substituted compound 2 were given in Fig.2

Tab. S2 detailed assignment of mass spectral data for compound 1 and compound 2

Entry	m/z(experiment)	Molecule formula	m/z(simulated)
A	1394.0389	$\{K(H_2O)_2H_8[Nd(SiW_{11}O_{39})_2]\}^{4-}$	1394.0187
B	1405.2310	$\{(DMA)K(H_2O)_2H_7[Nd(SiW_{11}O_{39})_2]\}^{4-}$	1405.2895
C	1414.2152	$\{(DMA)K(H_2O)_4H_7[Nd(SiW_{11}O_{39})_2]\}^{4-}$	1414.2971
D	1423.5060	$\{(2\text{-}Melm)K(H_2O)_4H_7[Nd(SiW_{11}O_{39})_2]\}^{4-}$	1423.5522

E	1432.5826	$\{(DMA)_2(2\text{-MeIm})K(H_2O)H_5[Nd(SiW_{11}O_{39})_2]\}^{4-}$	1432.5962
F	1441.8095	$\{(DMA)(2\text{-MeIm})_2K(H_2O)H_5[Nd(SiW_{11}O_{39})_2]\}^{4-}$	1441.8377
a	2156.2704	$\{(TBA)_4H_6[Nd(SiW_{11}O_{39})_2]\}^{3-}$	2156.2622
b	2197.3526	$\{(TBA)_4H_6[Nd(SiW_{11}O_{39})_2]\}^{3-}+CH_3CN$	2197.3141
c	2236.8025	$\{(TBA)_5H_5[Nd(SiW_{11}O_{39})_2]\}^{3-}$	2236.7476
d	2317.2350	$\{(TBA)_6H_4[Nd(SiW_{11}O_{39})_2]\}^{3-}$	2317.2331

4. **TGA and DSC analysis of compound 1-2.**

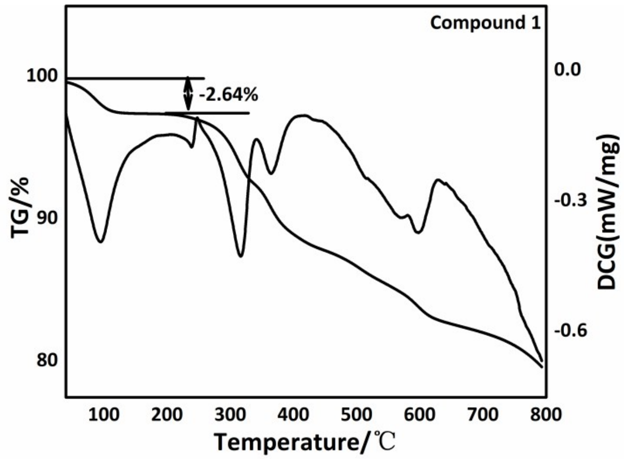


Fig. S3.1 TGA-DSC of compound 1

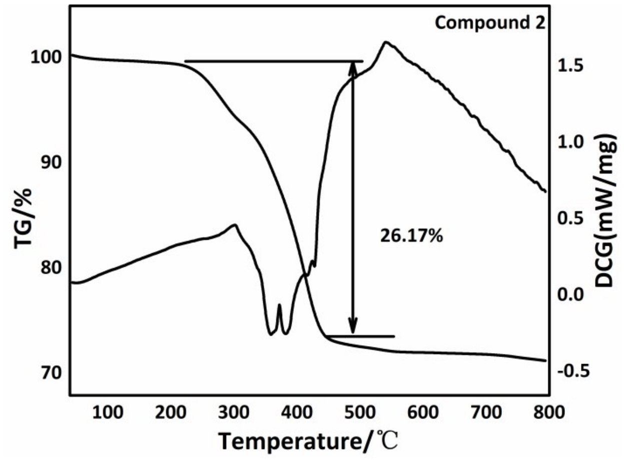


Fig. S3.2 TGA-DSC of compound 2

Tab.S3.1 detailed assignment of TGA-DSC data for compound 1

Entry	Weight loss of crystal water and bonding water (%)	
Compound 1	**experiment**	**2.23**

	calculated	**2.24**

Tab. S3.2 detailed assignment of TGA-DSC data for compound 2

Entry	Weight loss(experiment)	Weight loss(calculated)	Molecular weight
$(TBA)_8H_5[Nd(SiW_{11}O_{39})_2]$	**26.17%**	**26.06%**	**7435.7027**

Tab.S3.3 Theoretical and experimental C H N content of compound 2 (detected by inductively coupled plasma mass spectrum (ICP-OES)

Entry	$(TBA)_8H_5[Nd(SiW_{11}O_{39})_2]$
C (experimental)	**20.652%**
C (theoretical)	**20.673%**
N (experimental)	**1.506%**
N (theoretical)	**1.507%**
H(experimental)	**3.940%**
H (theoretical)	**3.958%**

5. **IR spectra for compound 1-2**

Fig. S4.1-Fig. S4.2 IR spectra of compound 1-2

Compound 1:$\{(DMA)_5(2\text{-}MeIm)_8[Nd(SiW_{11}O_{39})_2]\cdot(2\text{-}MeIm)_2(H_2O)_{10}\}$ 3469(br)-OH(stretching vibration) 3135(m) N-H 2996(m)-CH_3 2706(m) -CH_3 1621(vs) -C=N 14611(s) C-N 1003(s) W=Od 949(vs) Si-Oa 896(vs) W-Ob-W 766(s) W-Oc-W 712(s) W-Oc-W

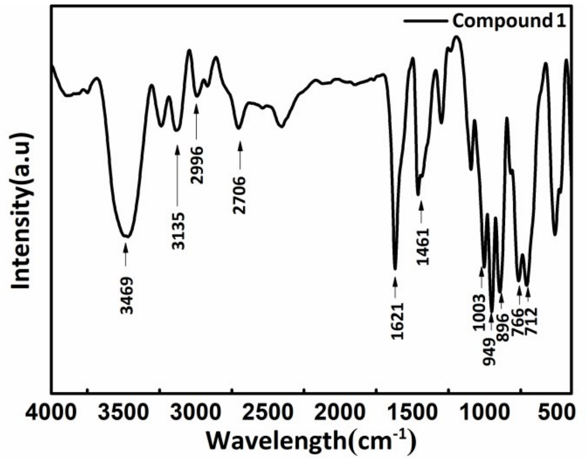


Fig. S4.1 IR spectra of compound 1

Compound 2: $(TBA)_8H_5[Nd(SiW_{11}O_{39})_2]$:3452(br)-OH(stretching vibration) 2962(s) -CH_3 2873(s)-CH_3 1627(s) H-O-H(bending vibration) 1484(s) C-N 1382(m) -CH_3 1004(m) W=Od 962(s) Si-Oa 908(vs) W-Ob-W 794(s) W-Oc-W 738(w) W-Oc-W

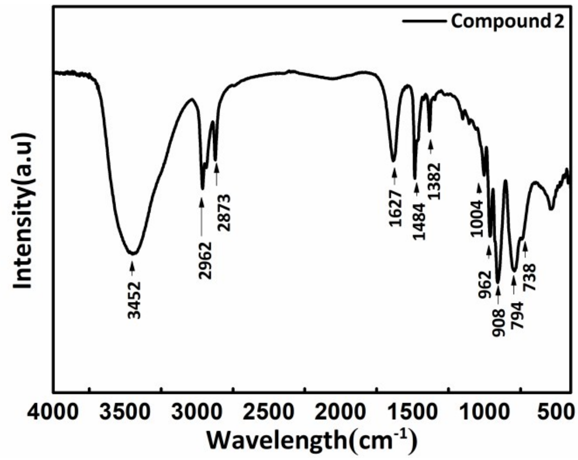


Fig. S4.2 IR spectra of compound 2

Retrived compound 2: $(TBA)_8H_5[Nd(SiW_{11}O_{39})_2]$:3469(br)-OH(stretching vibration) 2964(s) -CH_3 2877(s) -CH_3 1637(s)-OH(bending vibration) 1484(vs) C-N 1382(s) -CH_3 1005(s) W=Od 964(s) Si-Oa 904(vs) W-Ob-W 808(s) W-Oc-W 750(s) W-Oc-W

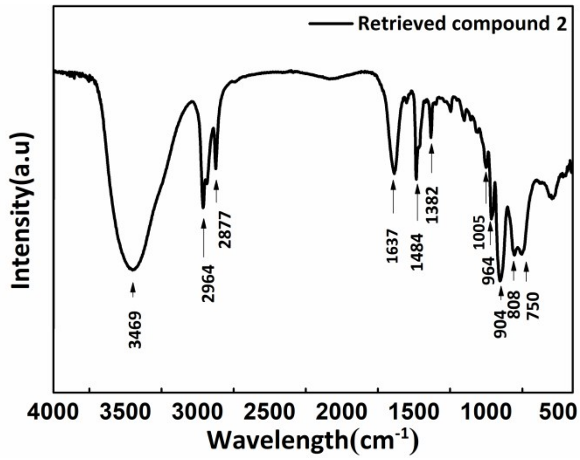


Fig.S4.3 IR spectra of compound 6 retrieved from catalytic experiment

6. **UV-Vis spectra of compound 1-2**

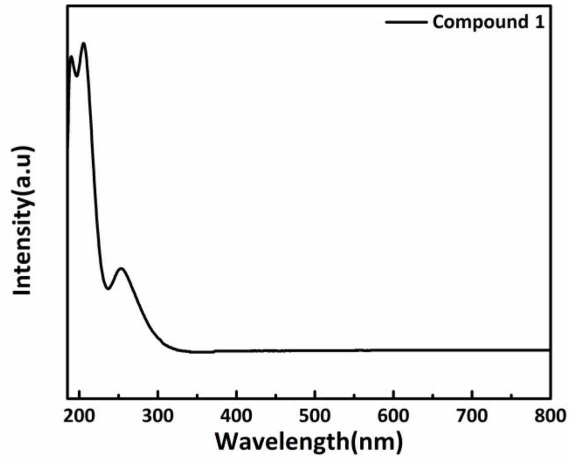


Fig.S5.1 UV-Vis spectra of compound 1

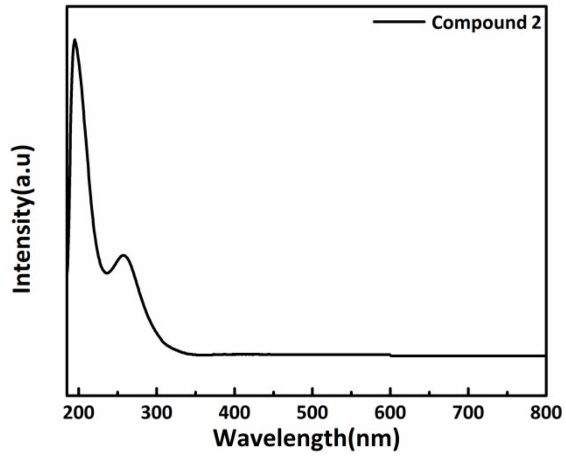


Fig.S5.2 UV-Vis spectra of compound 2

7. **Catalytic behavior**

For brief: equivalent molar ratio of electrolytes/catalyst (EMR)

Reaction model for the reactions in Tab. S4.1, Tab. S4.2, Tab. S4.3,

Tab. S4.1 Conversion rate of Cyanosilylation of cyclohexanone catalyzed by compound 2 with different type and amount of electrolytes (0≤ equivalent molar ratio of electrolyte/compound 2≤24).

EMR / Entry	0	4	8	12	16	20	24
TEA	83%	58%	65%	72%	55%	45%	41%
TPA		75%	79%	83%	75%	69%	58%
TMA		83%	89%	94%	92%	90%	89%
TBA		91%	94%	96%	95%	93%	87%

Reaction conditions: compound 2 (6mg, 0.064 mol%) and different amount of extra electrolytes, ketone (0.5 mmol), (TMS)CN (1.5 equiv with respect to ketone), Solvent free. Reaction temperature: 30 °C. Reaction time: 20 min

Tab. S4.2 Cyanosilylation of cyclohexanone catalyzed by compound 2 with different amount of NaCl and NaBr (0≤ equivalent molar ratio of salt/compound 2≤24)

EMR / Entry	0	4	8	12	16	20	24
NaCl	83%	83%	84%	83%	82%	83%	84%
NaBr	83%	82%	83%	83%	84%	83%	83%

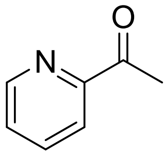
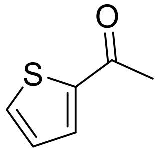
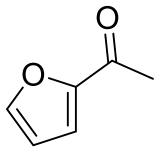
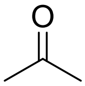
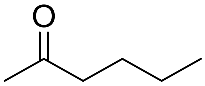
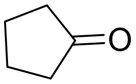
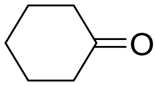
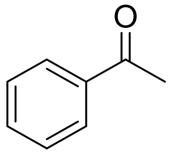
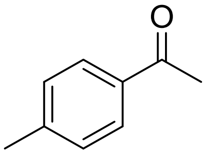
Reaction conditions: compound 2 (6mg, 0.064 mol%) and different amount of extra electrolytes, ketone (0.5 mmol), (TMS)CN (1.5 equiv with respect to ketone), Solvent free. Reaction temperature: 30 °C. Reaction time: 20 min.

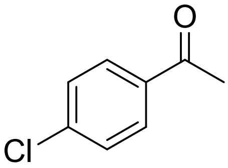
Tab. S4.3 Cyanosilylation of cyclohexanone catalyzed by compound 2 with different amount of NaOH (0≤molar ratio of alkali/protons of compound 2≤ 150)

EMR	0	37.5	65.6	96.8	121.8	150
Conversion rate	83	80%	74%	68%	55%	50%

Reaction conditions: compound 2 (6mg, 0.064 mol%) and different amount of extra electrolytes, ketone (0.5 mmol), (TMS)CN (1.5 equiv with respect to ketone), Solvent free. Reaction temperature: 30 °C. Reaction time: 20 min.

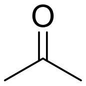
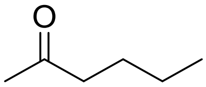
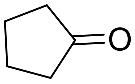
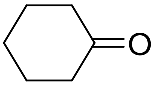
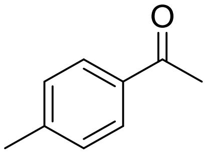
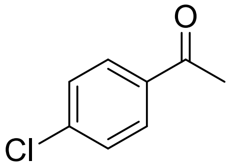
Tab. S4.4 Cyanosilylation reaction catalyzed by compound 2 among different Carbonyl Compounds

Compound	Time(min)	Conversion Rate (A)	TON	TOF	Time(min)	Conversion rate (B)	TON	TOF
	2	99+	347	10410	3.5	99+	1562	26777
	180	76	264	88	180	53	828	276
	180	87	302	100	180	56	875	292
	20	98	340	1020	30	96	1500	3000
	40	98	340	510	60	96	1500	1500
	30	96	333	666	60	95	1484	1484
	20	96	333	999	30	96	1500	3000
	60	98	340	340	180	88	1375	458
	180	99	343	114	180	75	1172	390

	30	98	340	680	180	94	1468	489

Reaction conditions: A: compound 2 (27mg，0.288mol%), ketone (0.5 mmol), (TMS)CN (1.5 equiv with respect to ketone), Solvent free. Reaction temperature: 30 °C, B: compound 2 (6mg, 0.064 mol%), ketone (0.5 mmol), (TMS)CN (1.5 equiv with respect to ketone), Solvent free. Reaction temperature:30 °C.

Tab. S4.5 Cyanosilylation reactions catalyzed by different catalyst among different Carbonyl Compounds

Compound	Time(min)	A	TON	TOF	B	TON	TOF	C	TON	TOF
	30	13	8.8	17.6	10	2564	5128	2	28	28
	60	4	2.7	2.7	4	1026	1026	1	14	14
	30	7	4.8	9.6	7	1795	3590	1	14	28
	30	11	7.5	15	25	6410	12820	3	42	84
	180	5	3.4	1.1	3	769	256	1	14	5
	180	19	12.9	4.3	9	2307	769	2	28	10

Reaction conditions: A, B and C are the conversion rate of cyanosilylation reaction catalyzed by different catalyst. A:TBABr (6mg,1.47mol%) B:compound 2 (6mg，0.0039 mol%), C:compound 1 (6mg,0.07mol%), ketone (0.5 mmol), (TMS)CN (1.5 equiv with respect to ketone), A,C employed solvent free method and B employed 1ml acetonitrile for solvent. Reaction temperature: 30 °C.

Tab. S4.6 Cyanisilylation reaction between cyclopentanone and TMSCN conducted by different catalyst

Entry	Cat(mol%)	Temp(℃)	Time(min)	Solvent	Yield(%)	ref
TBA-Nd-POM	0.064	30	30	None	96	This work
magnesium(I) complexes	0.10	30	480	C_6D_6	97	[2]

InPF-15	0.10	80	120	None	>99	3
Lanthanide Amido Complexes	0.10	30	120	None	98	4
PS-TPP	2.00	30	60	None	83	5
platinum(II) dicyanide	0.25	50	360	$CDCl_3$	98	6

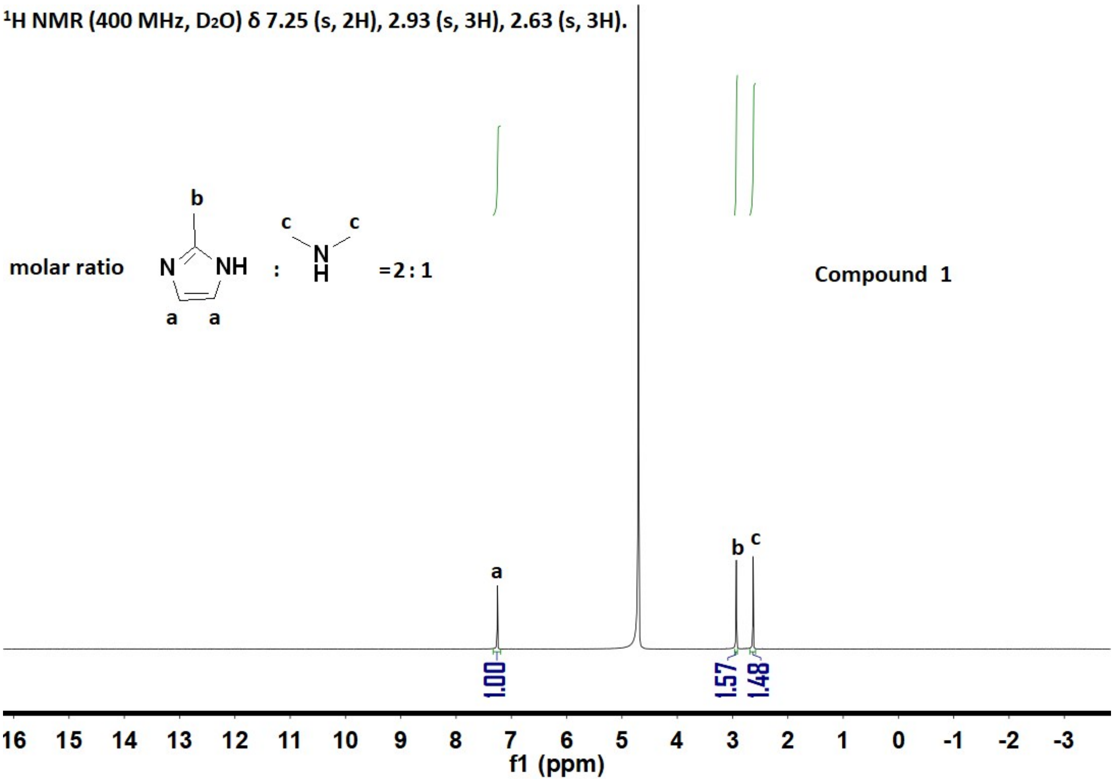


Fig. S6.1 ^{1}HNMR spectra of compound 1 (solvent D_2O)

^{1}H NMR (400 MHz, CD$_3$CN) δ 3.14 (t, 2H), 1.62 (dt, J = 16.1, 8.0 Hz, 2H), 1.37 (dq, J = 14.6, 7.3 Hz, 2H), 0.95 (t, J = 7.3 Hz, 3H).

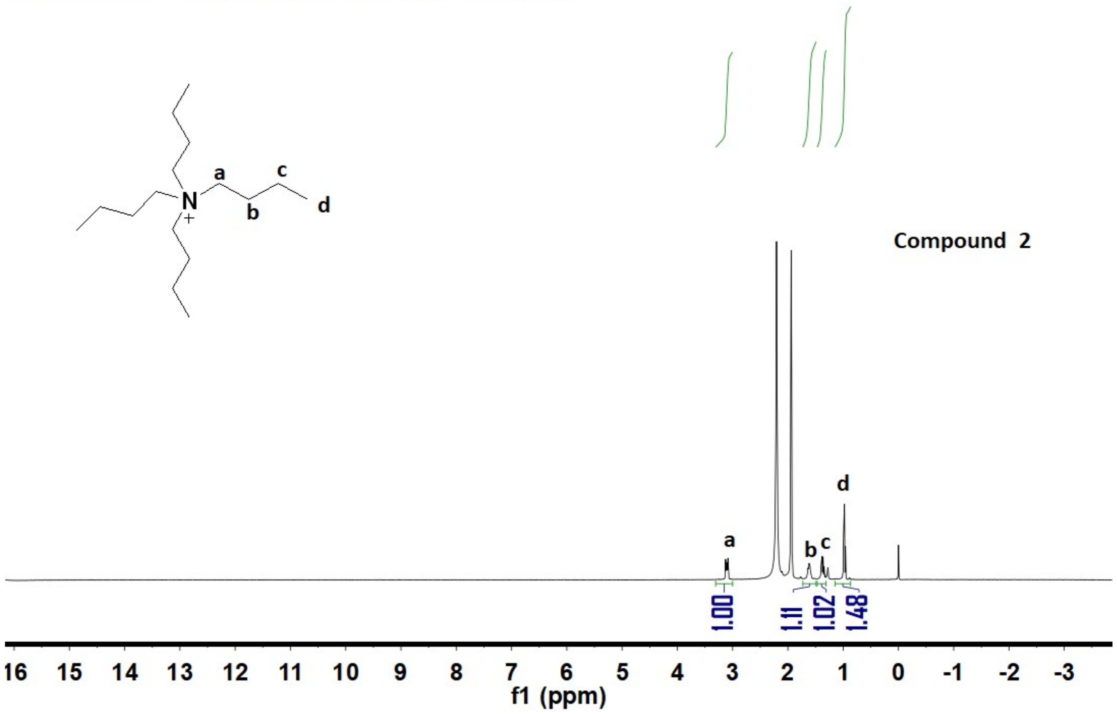


Fig. S6.2 ^{1}HNMR spectra of compound 2 (solvent CD$_3$CN)

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.65 (d, J = 2.4 Hz, 1H), 7.79 (dd, J = 10.8, 4.6 Hz, 1H), 7.62 (d, J = 7.9 Hz, 1H), 7.31 (t, J = 5.6 Hz, 1H), 1.94 (s, 3H), 0.26 (s, 9H).

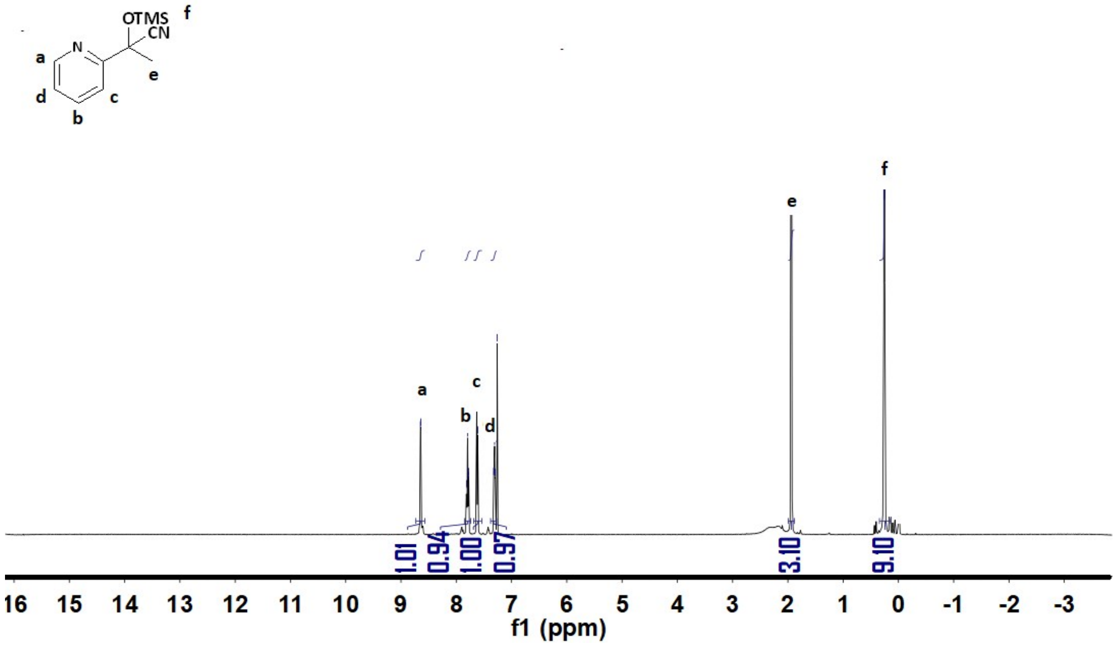


Fig. S6.3 ^{1}HNMR spectra of 1b catalyzed by compound 2

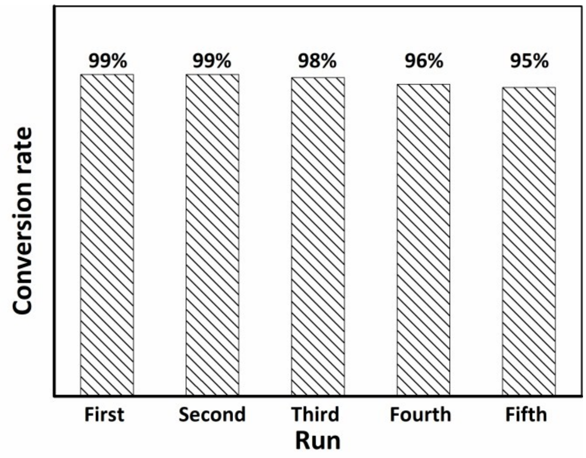


Fig. S7.1 cyanosilylation catalyzed by retrieved compound 2 for 5 runs

Reaction conditions: compound 2 (6mg, 0.064 mol%), ketone (0.5 mmol), (TMS)CN (1.5 equiv with respect to ketone), Solvent free. Reaction temperature: 30 °C. Reaction time: 30 min.

Reaction model:

8. **PXRD pattern for compound 1-2**

Fig. S8.1-Fig. S8.2 PXRD pattern of compound 1-2

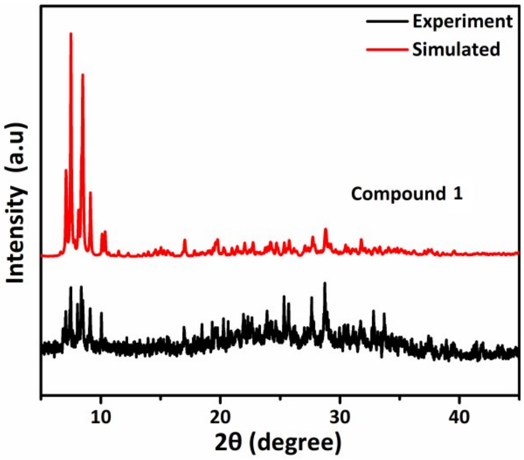


Fig. S8.1 PXRD pattern of dehydrated compound 1 and recycled compound 1 after catalysed experiment

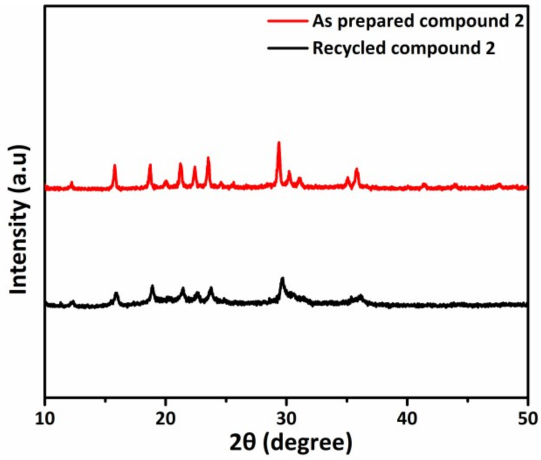


Fig. S8.2 PXRD pattern of dehydrated compound 2 and recycled compound 2 after catalysed experiment

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