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Supplementary Information for

Insight into the Catalytic Properties and Applications of Metal-Organic Frameworks in the Cyanosilylation of Aldehydes

Zhiguo Zhang, Jingwen Chen, Zongbi Bao, Ganggang Chang, Huabin Xing, Qilong Ren*

Key Laboratory of Biomass Chemical Engineering of Ministry of Education, College of Chemical and Biological Engineering, Zhejiang University, Zheda Road 38, Hangzhou 310027, China, e-mail: renql@zju.edu.cn

Table of Contents

S1. Materials and methods

Materials. All starting materials for the preparation of catalysts and those for the catalytic studies were used as purchased without further purification unless otherwise stated. All solvents, benzaldehyde, Hydrofluoric acid (37% in water), *o*-xylene were purchased from Sinopharm Chemical Reagent Co., Ltd. $Al(NO_3)_3{\cdot}9\ H_2O$, $Cr(NO_3)_3{\cdot}9\ H_2O$, $ZrCl_4$, trimethylsilyl cyanide (TMSCN), tridecane and other carbonyl compounds were purchased from Aladdin. Terephthalic acid (TPA) was purchased from Tokyo Chemical Industry Co., Ltd. VCl_3 was purchased from Alfa Aesar. Solvents used in the reaction were dried by standard methods and freshly distilled before use. The benzaldehyde was freshly distilled and then stored under nitrogen atmosphere. TMSCN was distilled as a colorless liquid at ambient pressure.

Methods. Nitrogen adsorption and desorption isotherms were measured on a micromeritics 3Flex instrument. The IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer in the range of 400-4000 cm^{-1} by using potassium bromide pellets. The powder X-ray diffraction (XRD) pattern of MIL-101 (Cr) was obtained on a SHIMADZU XRD-6000 diffractometer with Cu Kα radiation. Following conditions were used: 40 kV, 40 mA, scanning speed = 4 deg/min, increment = 0.02°.

The conversion of aldehyde was monitored by gas chromatograph (GC) at a given time intervals using SHIMADZU GC2010 Plus equipped with an FID detector and a non-polar DB-5HT column (5% phenyl-95% methyl polysiloxane, 30 m × 0.25 mm × 0.10 μm film thickness) from Agilent. All the products were confirmed by comparison with previously reported spectral data.

S2. Synthesis of MIL-47 (V), MIL-53 (Al), MIL-101 (Cr) and UiO-66 (Zr)

Synthesis of MIL-47 (V). MIL-47 (V) was synthesized according to the method reported in literature.[1] 4.88 g (31 mmol) of vanadium trichloride (VCl_3), 1.28 g (7.7 mmol) of terephthalic acid (TPA) and 60 mL of deionized water were added into a teflon-lined stainless steel autoclave. The reaction mixture was heated to 473 K and maintained with this temperature for 4 days under autogenous pressure. After cooling to room temperature, the light yellow solid was formed. Then the as-synthesized solid was calcinated in air at 573 K for 24 h to evacuate the terephthalic acid.

Synthesis of MIL-53 (Al). The MIL-53 (Al) was synthesized by a hydrothermal reaction.[2] 3.75 g (10 mmol) of aluminum nitrate nonahydrate ($Al(NO_3)_3{\cdot}\ 9\ H_2O$), 0.83 g (5 mmol) of terephthalic acid, and 14.4 mL of deionized water (molar composition was 1 Al:0.5 TPA:80 H_2O) were added consecutively into a teflon-lined stainless steel autoclave, and the reaction mixture was heated to 493 K and kept this temperature for 3 days under autogenous pressure. The resulted reaction mixture was washed with deionized water. Then the solid was purified upon heating in air at 603 K for 3 days to remove the unreacted and entrapped TPA molecules.

Synthesis of MIL-101 (Cr). MIL-101 (Cr) was synthesized and purified according to the method described in the literature.[3] A mixture of 8.00 g (10 mmol) of $Cr(NO_3)_3{\cdot}\ 9\ H_2O$, 3.28 g (20 mmol) of terephthalic acid, 300 μL of aqueous hydrofluoric acid (37% in water) and 140 mL of ultrapure water were introduced into a 250 mL teflon-lined stainless steel autoclave and sealed. Then heated up to 493 K and kept this temperature for 8 h. After natural cooling, a significant amount of recrystallized needle-shaped colorless terephthalic acid was present. To eliminate most of the carboxylic acid, the reaction mixture was filtered first using a stainless steel meshwork (diameter of 61 μm). The MIL-101 (Cr) suspension passed through the meshwork while the free acid retained on the meshwork. The filtrated MIL-101 (Cr) suspension was subsequently centrifuged at 3500 rpm for 10 min to collect the first precipitates of MIL-101 (Cr), and then centrifuged at 9000 rpm for 20 min to collect the second precipitates of MIL-101 (Cr). The second precipitates of MIL-101 (Cr) were washed with ultrapure water for several times, and dried at 423 K in an air oven for 12 h.

Synthesis of UiO-66 (Zr). According to the literature,[4] a typical route to get UiO-66 (Zr) is as follows: 0.233 g of $ZrCl_4$ (1.0 mmol) and 0.166 g of terephthalic acid (1.0 mmol) was dissolved in 10 mL of N,N'-dimethylformamide (DMF) (9.49 g, 135 mmol). Then mixed them evenly, sealed and placed in a pre-heated oven, and kept it at 120 °C for 24 h. The crystals were formed under static conditions. After cooling in air to room temperature, the resulting solid was filtered, washed with DMF and the exchanged with methanol. Finally, the solid was dried in vacuum at 423 K for 12 h.

S3. Characterization data for MIL-47 (V), MIL-53 (Al), MIL-101 (Cr) and UiO-66 (Zr).

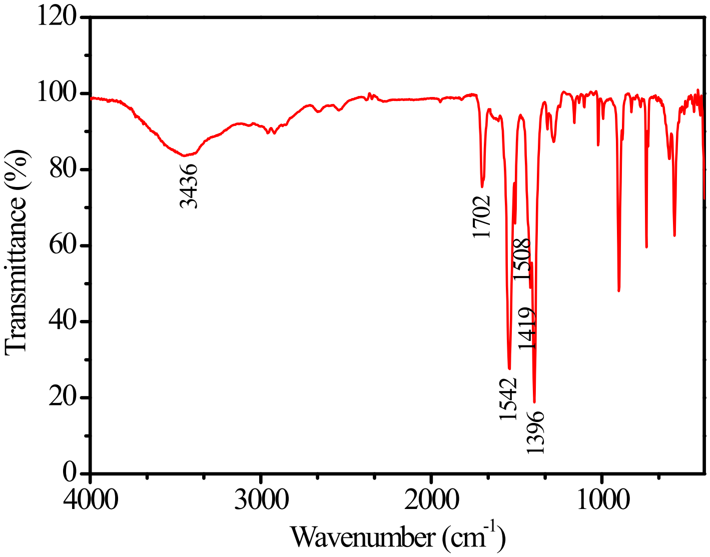


Fig. S1 FT-IR spectrum of MIL-47 (V). The two bands at 1542 and 1396 cm^{-1} can be assigned to the stretching vibration of $-CO_2$. Large bands around 3436 and 1702 cm^{-1} indicate the bending and stretching vibration of water molecules inside the pores of MIL-47 (V).

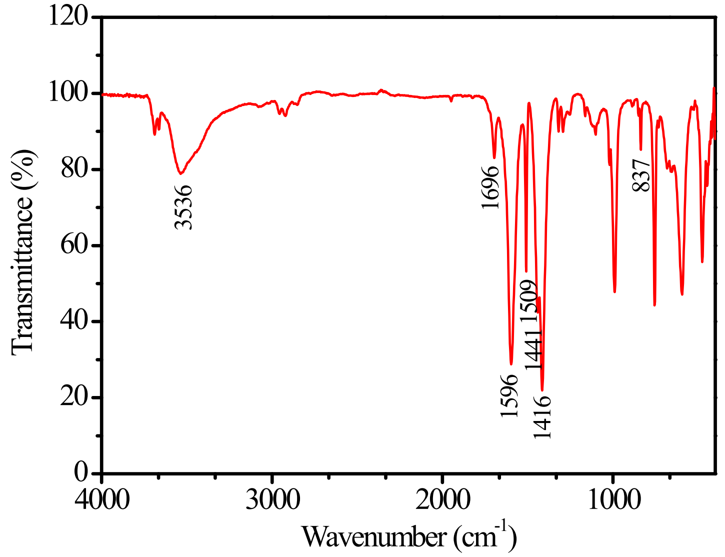


Fig. S2 FT-IR spectrum of MIL-53 (Al). Two absorption bands located at 1596 and 1509 cm^{-1} can be ascribed to $-CO_2$ asymmetric stretching, while the bands at 1441 and 1416 cm^{-1} can be assigned to $-CO_2$ symmetric stretching. The two bends around 1696 and 3536 cm^{-1} correspond to the bending and stretching modes of water that entrapped in the cavities of MIL-53 (Al).

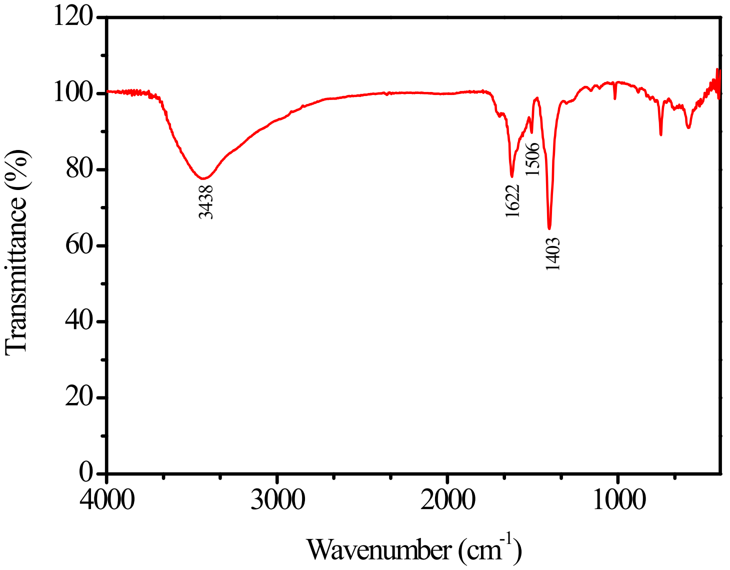


Fig. S3 FT-IR spectrum of MIL-101 (Cr). The two bands at 1506 and 1403 cm^{-1} can be assigned to the stretching vibration of $-CO_2$. Large bands around 3438 and 1622 cm^{-1} indicate the presence of water molecules within the cavities of MIL-101 (Cr).

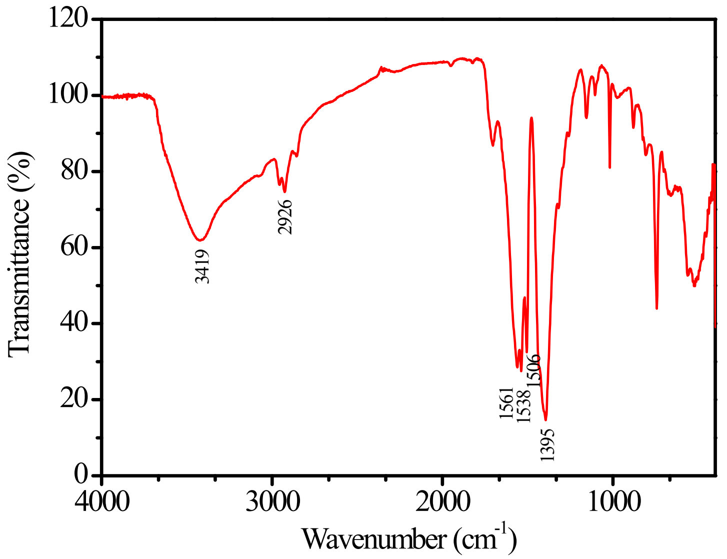


Fig. S4 FT-IR spectrum of UiO-66 (Zr). The intense doublet at 1561 and 1395 cm^{-1} can be assigned to the in- and out-of-plane stretching modes of the carboxylate group. The intense and broad band at 3419 cm^{-1} can be ascribed to the stretching vibration of physically absorbed water condensed inside the cavities. The week bands around 2926 cm^{-1} corresponds to the aromatic ν(C-H) modes of benzene ring.

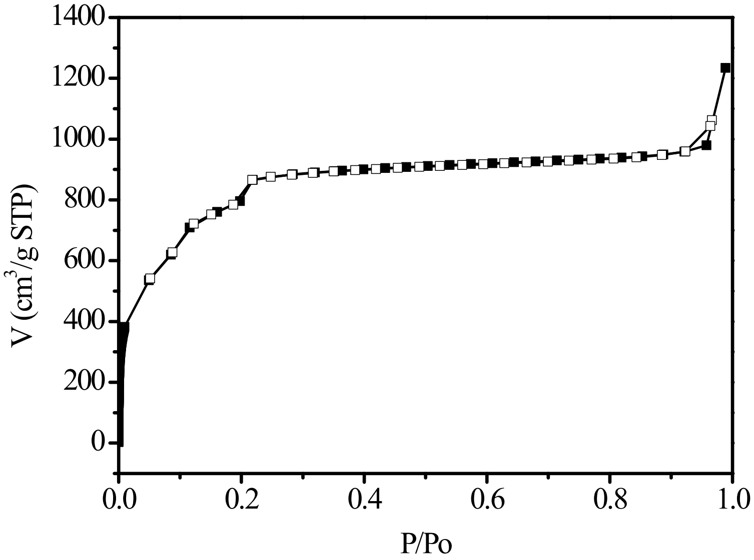


Fig. S5 Nitrogen adsorption isotherms of MIL-101 (Cr) (■), □ represents the desorption isotherm (BET surface area ～ 2903 m^2/g).

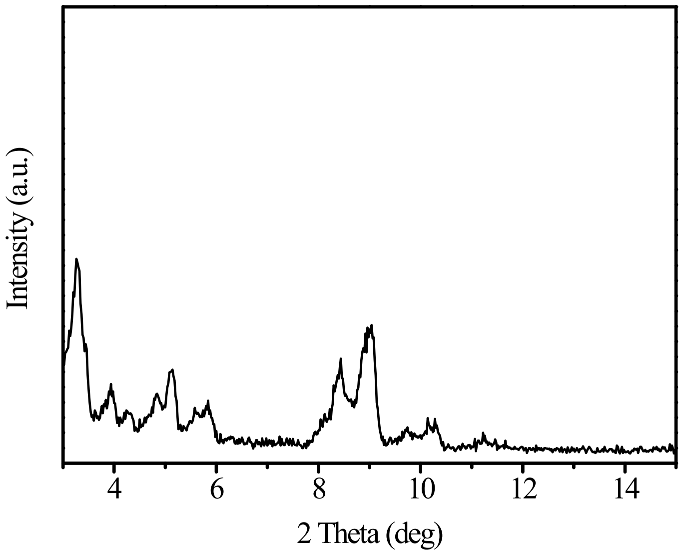


Fig. S6 The powder X-Ray diffraction pattern of MIL-101 (Cr).

S4. FT-IR spectra of benzaldehyde absorbed in the channels of MOFs

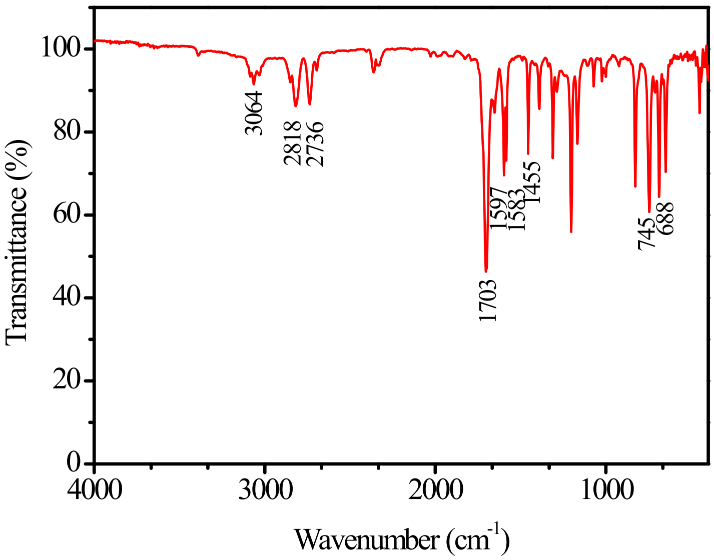


Fig. S7 FT-IR spectrum of benzaldehyde. The carbonyl stretching vibration frequency of benzaldehyde is 1703 cm^{-1}.

IR spectra of benzaldehyde-absorbed MOFs. The benzaldehyde-absorbed MOFs were prepared as follows: small amount (10-15 mg each) of activated MOF was weighed as quickly as possible to prevent the absorption of water molecules from the air. Then put it into a Schlenk flask, and heated in an oil bath at 120 °C under dynamic vacuum for 2 h. After the flask cooled to r.t., 0.05 mL of freshly distilled benzaldehyde was added into the bottom of the flask via a syringe. The dynamic vacuum was kept for 1 h. The benzaldehyde-absorbed MOF was taken out to make the KBr pellet for the determination of IR spectrum. The IR spectra are shown in Fig. S8-S11.

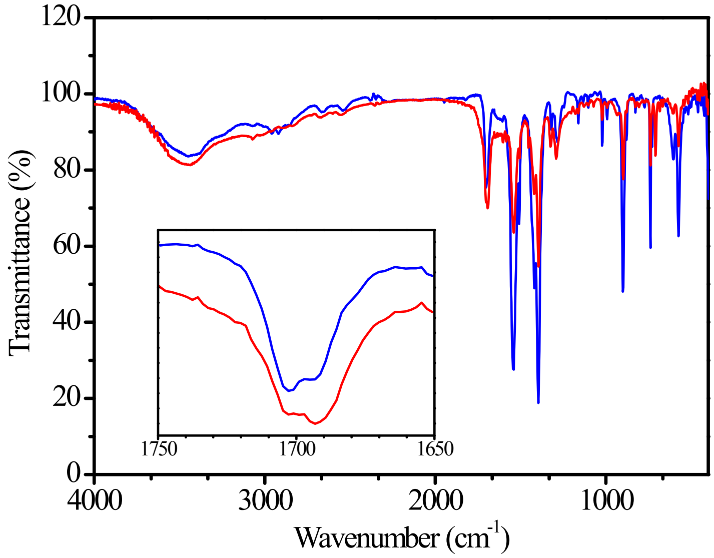


Fig. S8 FT-IR spectrum of MIL-47 (V) (blue) and benzaldehyde-absorbed MIL-47 (V) (red).

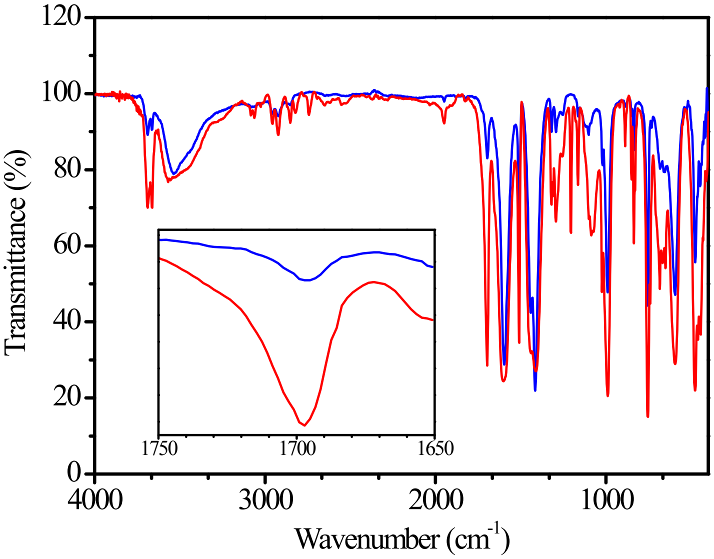


Fig. S9 FT-IR spectrum of MIL-53 (Al) (blue) and benzaldehyde-absorbed MIL-53 (Al) (red).

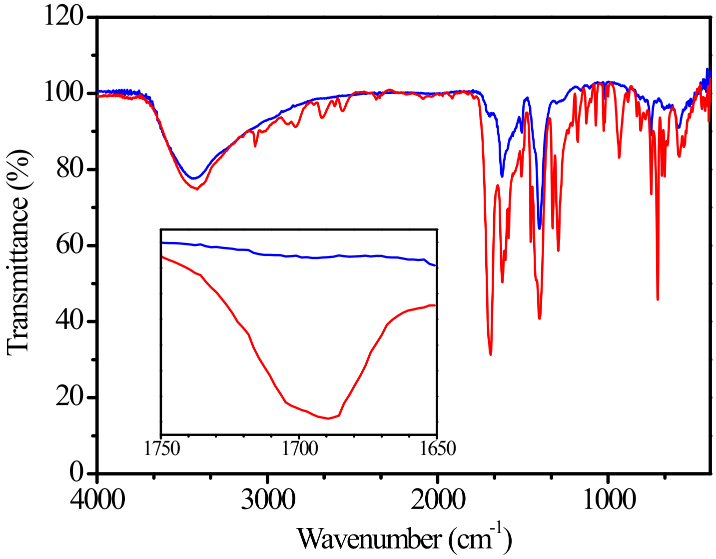


Fig. S10 FT-IR spectrum of MIL-101 (Cr) (blue) and benzaldehyde-absorbed MIL-101 (Cr) (red).

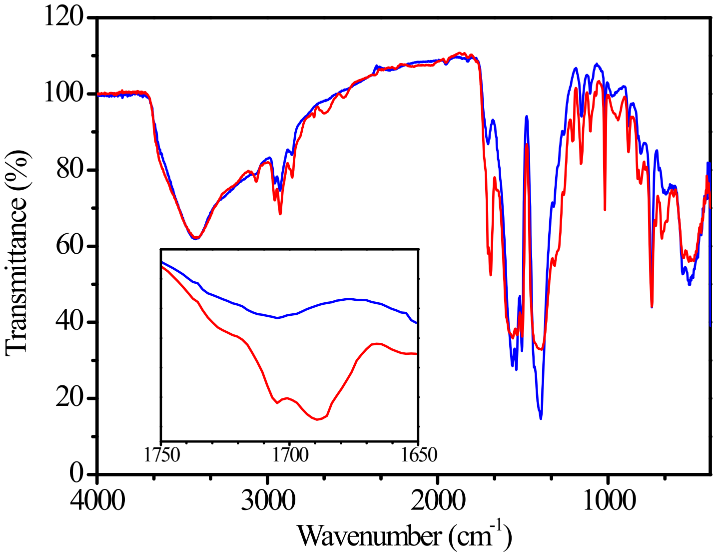


Fig. S11 FT-IR spectrum of UiO-66 (Zr) (blue) and benzaldehyde-absorbed UiO-66 (Zr) (red).

As MIL-101 (Cr) has an influence on the IR spectrum of benzaldehyde, we also detected the interaction between MIL-101 (Cr) and the other substrate.[5] In order to see whether MIL-101 (Cr) can activate TMSCN, we have determined the changes of the IR spectrum of TMSCN before and after being absorbed in MIL-101 (Cr).

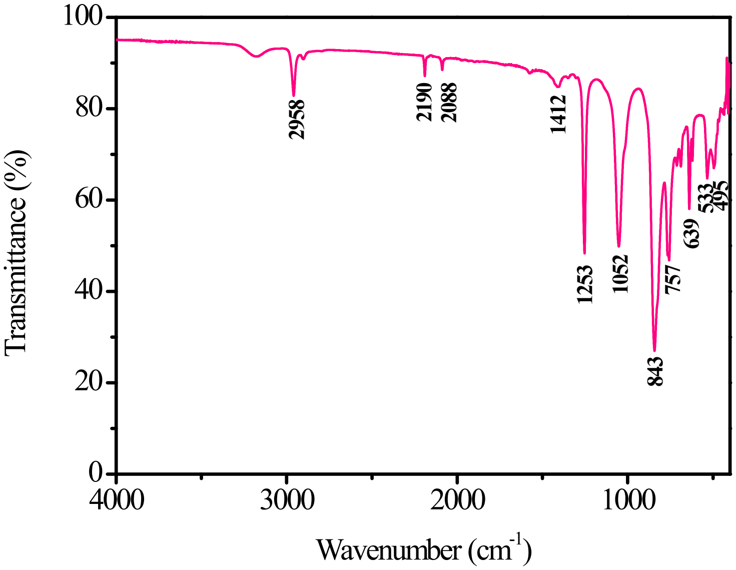


Fig. S12 FT-IR spectrum of TMSCN (ν: 2958 cm^{-1}, stretching vibration of –CH_3; 2190 cm^{-1}, stretching vibration of –CN; 2088 cm^{-1}, stretching vibration of –NC; 1253 cm^{-1} and 1052 cm^{-1}, bending vibration of –$Si(CH_3)_3$; 843 cm^{-1}, stretching vibration of Si-C).

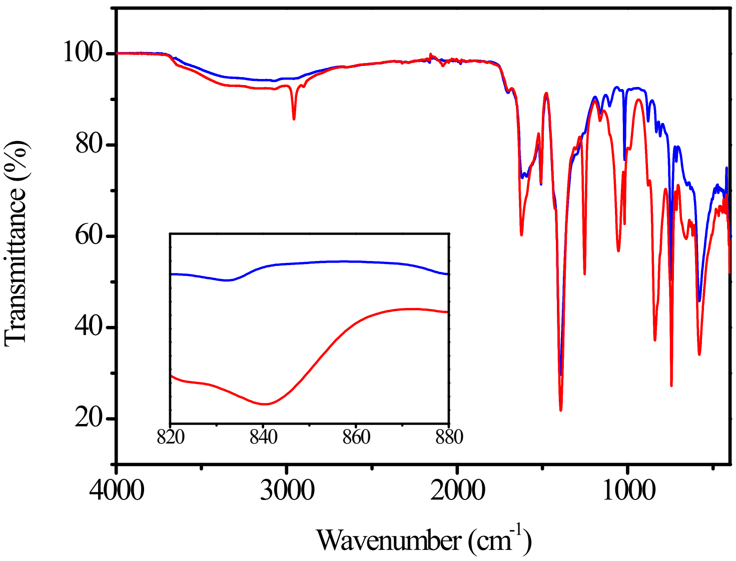
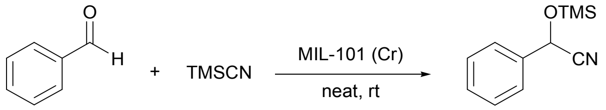


Fig. S13 FT-IR spectrum of MIL-101 (Cr) (blue) and TMSCN-absorbed MIL-101 (Cr) (red). ν (Si-C) in pure TMSCN is 843 cm^{-1}; ν (Si-C) in TMSCN-absorbed MIL-101 (Cr) is 840 cm^{-1}. MIL-101 (Cr) has a minor influence on the stretching vibration of Si-C (a low shift of 3 cm^{-1} was observed), which suggests a considerably weak interaction between TMSN and MIL-101 (Cr).

S5. Catalytic properties

The activation and catalytic amount of MOFs: All kinds of MOFs were treated at 150 °C for 12 h previously to get solvent free catalysts. The mol percent amount of catalyst was refers to the whole formula of MOFs. The amount of 1.0 mol% of catalysts in Table 1 is as follows: MIL-47 (V) (2.2 mg), MIL-53 (Al) (2.1 mg), MIL-101 (Cr) (7.2 mg) and UiO-66 (Zr) (12.1 mg). The amount of MIL-101 (Cr) in Fig. 2 is as follows: 1.00 mol% (7.2 mg), 0.55 mol% (4.0 mg), 0.30 mol% (2.2 mg), 0.25 mol% (1.8 mg) and 0.15 mol% (1.1 mg).

Table S1 The conversion of benzaldehyde catalyzed by different amount of MIL-101 (Cr).[a]



Entry	Catalyst loading (mol%)	t[b] (h)	Conv.[c] (%)	TOF[d] (h^{-1})
1	1.00	1.5	96	21
2	0.55	2.5	96	23
3	0.30	4.0	96	27
4	0.25	5.0	95	25
5	0.15	8.0	95	26

[a] Reaction conditions: aldehyde (1.0 mmol), TMSCN (1.2 mmol), and the catalyst, rt.
[b] The time when the reaction completed.
[c] The conversion of benzaldehyde is determined by GC analysis using tridecane as the internal standard.
[d] TOF = (yield)/((mol% of metal ions) × t).

When considering both high TOF, low catalyst loading and less reaction time, a 0.3 mol% of MIL-101 (Cr) was chosen for further study.

Comparison of the catalytic activity. In order to compare the catalytic activity of MIL-101 (Cr) with other reported MOFs, the results in literature are summarized in Table S2. Because the reaction conditions are different, it is inappropriate to compare the yields. Therefore, we calculated the TON and TOF values to compare their catalytic activity. It should be noted that MIL-101 (Cr) exhibited a higher activity under solvent free reaction condition, and lower amount of TMSCN was used in our reaction system. The mild reaction conditions are attractive to industry applications.

Table S2 Comparison of the cyanosilylation of benzaldehyde catalyzed by different MOFs.

Catalyst	Catalyst loading (mol%)	Molar ratio[a]	solvent	T (°C)	t (h)	Yield (%)	TON[b]	TOF[c] (h^{-1})	Ref
MIL-101 (Cr)	0.3	1:1.2	neat	r.t.	4	96	107	27	This work
$[Cd(bpy)_2(NO_3)_2]_\infty$	20	1:2	CH_2Cl_2	40	24	77	3.8	0.16	6
$[Sm(L\text{-}H_2)(L\text{-}H_3)]_\infty$	10	1:2	CH_2Cl_2	r.t.	16	69	6.9	0.43	7
$[Cu_3(BTC)_2]_\infty$	5	1:2	heptane	60	48	55	11	0.23	8
MIL-101 (Cr)	0.5	1:2	heptane	40	3	98	65	22	9
$[Mn_3((Mn_4Cl)_3(BTT)_8)_2]_\infty$	11	1:2	CH_2Cl_2	r.t.	9	98	8.9	1	10

Table S2 Continued.

Catalyst	Catalyst loading (mol%)	Molar ratio[a]	solvent	T (°C)	t (h)	Yield (%)	TON[b]	TOF[c] (h^{-1})	Ref
$Sc_2(C_4O_4)_3$	2	1:2	CH_2Cl_2	r.t.	12	90	45	3.75	11
$[Zn_2(ptaH)_2 \cdot 11H_2O]_n$	5[d]	1:2	CH_2Cl_2	0	2	32	6.4	3.2	12
Ce-MDIP1	2	1:2.4	CH_3CN	r.t.	11	100	50	4.5	13
$[Nd(btc)]_\infty$	4.5	1:2	CH_2Cl_2	r.t.	2	99	11	5.5	14
$[Zn_3(bpy)_{3.5}(\mu\text{-}O_2CH)_4(ClO_4)_2]_\infty$	13	1:2	CH_2Cl_2	r.t.	24	22	1.7	0.07	15
$[Fe_2Ag_2(pca)_4(pcaH)_4(ClO_4)_2]$	1.7	1:2	CH_2Cl_2	25	3	51	30	10	16
$[Cd(L)_2(ClO_4)_2]_\infty$[f]	5[d]	1:2	CH_2Cl_2	0	14	92	18	1.3	17
$[Pr(3,5\text{-}DSB)(H_2O)_5]_\infty$	1	1:1.5	neat	40	4	91	91	23	18
$[Gd_2(L)_3(dmf)_4] \cdot 4DMF \cdot 3H_2O$	10[d]	1:2	CH_2Cl_2	5	1	92	9.2	9.2	19
$[Nd(3,5\text{-}DSB)(Phen)]_\infty$	5	1:1.5	neat	50	2	95	19	9.5	20
$[Zn_3(TCPB)_2]_\infty$	2.5	1:2	Hexane	r.t.	13	100	40	3.1	21
Tb-PT	1	1:1.2	CH_2Cl_2	20	1.5	13	13	8.7	22
$[In_2(dpa)_3(1,10\text{-}phen)_2] \cdot H_2O$	2.5	1:1.5	neat	50	0.75	>99	20	26	23
$[Eu_2(MELL)(H_2O)_6]$	75[d]	1:2	toluene	r.t.	1	100	1.3	1.3	24
$[Sc_3(3,5\text{-}DSB)_2(\mu\text{-}O_2H_3)(\mu\text{-}OH)_2]$	5	1:1.5	neat	40	8	84	17	2.1	25
CoNiBpe	10	1:5	neat	50	16	77	7.7	0.5	26
$Tm(BDC)_{1.5}(DMF)(H_2O)$	2	-	neat	r.t.	5	57	28	5.6	27
La-BTTc	10	1:2	neat	r.t.	1	99	9.9	9.9	28
$C_{42}H_{57}CoN_6O_{30}Zn_3$	5	1:5	neat	r.t.	4	94	19	4.8	29
$[Zn_3(dpe)_4(\mu\text{-}OOCCH_3)_2]_4(dpe)(ClO_4)_2\}_n$	13	1:2	CH_2Cl_2	r.t.	24	18	1.4	0.06	30
RPF-20-Ln	2	1:1.5	neat	40	3	95	48	16	31
HKUST-1	10	1:2	CH_2Cl_2	40	70	80	8	0.1	32
UiO-66 (Zr)	10	1:2	CH_2Cl_2	40	20	99	9.9	0.5	32
MIL-101 (CR) (Cr)	1.5	1:2	Hexane	40	20	99	66	3.3	32
MIL-53 (AL) (Al)	10	1:2	Hexane	40	20	42	4.2	0.2	32
$[Cu_2(bpy)(H_2O)_{5.5}]_2[H_2W_{11}O_{38}]$	2	1:2.4	CH_3CN	r.t.	24	98	49	2	33
$Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(OH)_6(BTB)_2$	-	1:2	-	r.t.	24	100	-	-	34
CPO-27-Mn	10	1:2	CH_2Cl_2	reflux	1	100	10	10	35
Cu-DDQ[e]	2.5	1:2	neat	Ultrasound r.t.	1	95	38	38	36
(R)-**1**-Li[f]	0.5	1:1	toluene	-78	6	97	194	32	37
$[(Cu_4O_{0.27}Cl_{0.73})_3(H_{0.5}BTT)_8]_\infty$	1	1:2	neat	40	50	96	96	1.9	38
$[Me_2NH_2][Co_2(bptc)(\mu_3\text{-}OH)$	1	1:2	neat	r.t.	12	98	49	4	39

[a] PhCHO:TMSCN. [b] TON = (yield)/(mol% of metal ions). [c] TOF = TON/(t). [d] wt%. [e] H_2DDQ = N,N'-dibenzoic acid-2,3- diaminoquinoxaline. [f] **1** = $[Zn_4O(biphenol)_{3/2}] \cdot 16H_2O \cdot 4THF$.

Table S3 The conversion of benzaldehyde in three consecutive runs of MIL-101 (Cr) catalyzed cyanosilylation reaction.[a]

Entry	Reaction cycle	Conv. (%)[b]
1	First run	96
2	Second run	91
3	Third run	92
4	Fourth run	86

[a] Reaction conditions: benzaldehyde (1 mmol), TMSCN (1.2 mmol), MIL-101 (Cr) (0.3 mol%, 2.2 mg), and the reaction mixture was stirred vigorously at rt under solvent free conditions for 4 h. [b] The conversion was determined by GC analysis using tridecane as the internal standard.

S6. GC spectra for the determination of the conversions of aldehydes

1. For **Entry 1** of **Table 1**, the conversion of benzaldehyde catalyzed by 1.0 mol% of MIL-47 (V) was calculated as follows:

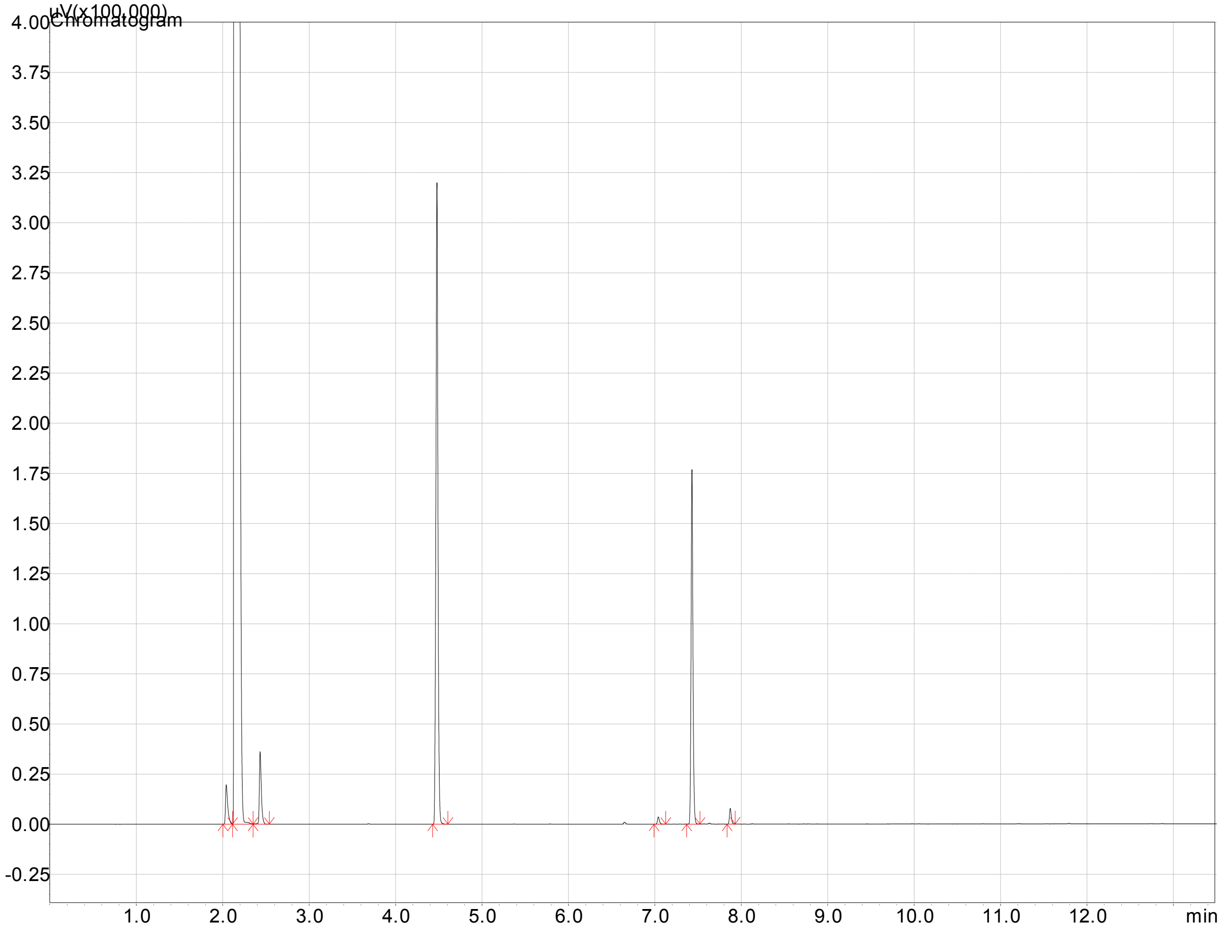


Fig. S14 GC spectrum of the control solution of the MIL-47 (V) catalyzed cyanosilylation reaction of benzaldehyde under solvent free conditions.

Table S4 The GC data of the control solution of the MIL-47 (V) catalyzed cyanosilylation reaction of benzaldehyde under solvent free conditions.

Peak#	Ret. Time	T. Plate	Initial Time	Final Time	Tailing F.	Area	Area%
1	2.042	33265.121	2.002	2.114	1.769	36041.9	0.1641
2	2.142	23609.942	2.114	2.352	2.230	21068737.2	95.9182
3	2.434	59247.633	2.352	2.539	1.512	58187.6	0.2649
4	4.479	183891.333	4.429	4.606	1.060	519472.0	2.3650

Table S4 Continued.

Peak#	Ret. Time	T. Plate	Initial Time	Final Time	Tailing F.	Area	Area%
5	7.040	501504.431	6.991	7.126	1.256	5578.6	0.0254
6	7.429	577215.835	7.369	7.523	1.158	265580.7	1.2091
7	7.873	645379.360	7.836	7.929	1.236	11716.3	0.0533

$t_{R(\text{benzaldehyde})} = 4.479$ min; $t_{R(\text{internal standard})} = 7.429$ min

$[\text{Area ration}]_{\text{control}} = [A_{\text{benzaldehyde}}/A_{(\text{intrnal standard})}]_{\text{control}} = (519472.0/265580.7) = 1.956$

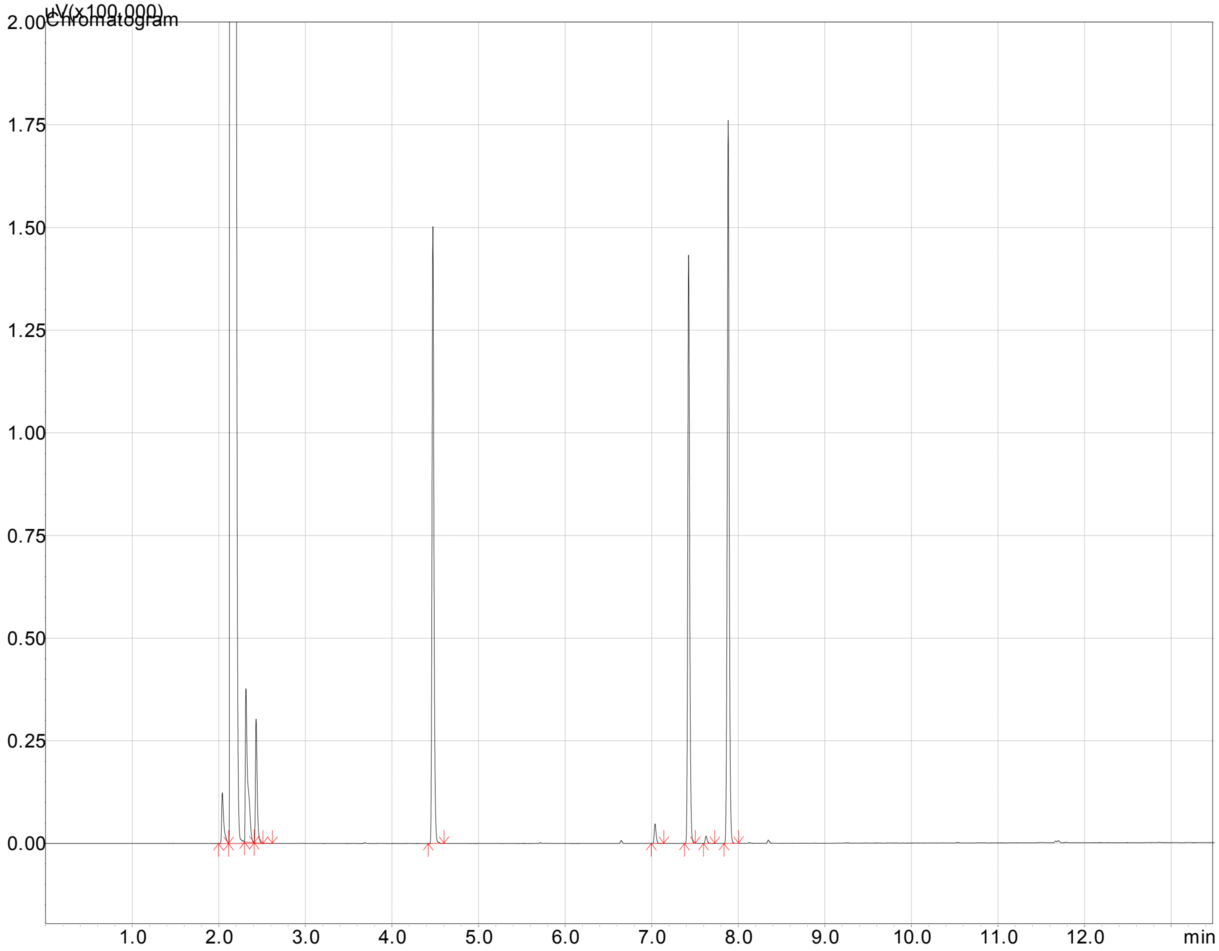


Fig. S15 GC spectrum of the reaction mixture of the MIL-47 (V) catalyzed cyanosilylation of benzaldehyde under solvent free conditions after 3 h.

Table S5 The GC data of the reaction mixture of the MIL-47 (V) catalyzed cyanosilylation of benzaldehyde under solvent free conditions after 3 h.

Peak#	Ret. Time	T. Plate	Initial Time	Final Time	Tailing F.	Area	Area%
1	2.042	42375.844	1.998	2.115	2.030	21321.5	0.0937
2	2.140	31170.752	2.115	2.619	2.249	21891652.7	96.2003
3	2.315	52179.199	2.297	2.409	2.751	72854.2	0.3201
4	2.432	73711.381	2.409	2.511	1.570	41806.3	0.1837
5	4.474	207474.122	4.420	4.602	1.211	229228.1	1.0073
6	7.040	511587.304	6.996	7.141	1.234	7282.8	0.0320
7	7.427	582793.066	7.379	7.505	1.172	215434.4	0.9467
8	7.629	592200.341	7.598	7.729	1.271	2755.8	0.0121
9	7.885	628967.494	7.836	8.004	1.066	273978.8	1.2040

$t_{R(benzaldehyde)}$ = 4.474 min; $t_{R(internal\ standard)}$ = 7.427 min; $t_{R(product)}$ = 7.885 min

$[\text{Area ration}]_{3\ h} = [A_{benzaldehyde}/A_{(intrnal\ standard)}]_{3\ h}$ = (229228.1/215434.4) = 1.064

The conversion of benzaldehyde is calculated as follows:

$$Conv.\% = \frac{[Area\ ratio]_{control} - [Area\ ratio]_{3\ h}}{[Area\ ratio]_{control}} \times 100\%$$

$$= \frac{1.956 - 1.064}{1.956} \times 100\% = 46\%$$

2. For **Entry 2** of **Table 1**, the conversion of benzaldehyde catalyzed by 1.0 mol% of MIL-53 (Al) was calculated as follows:

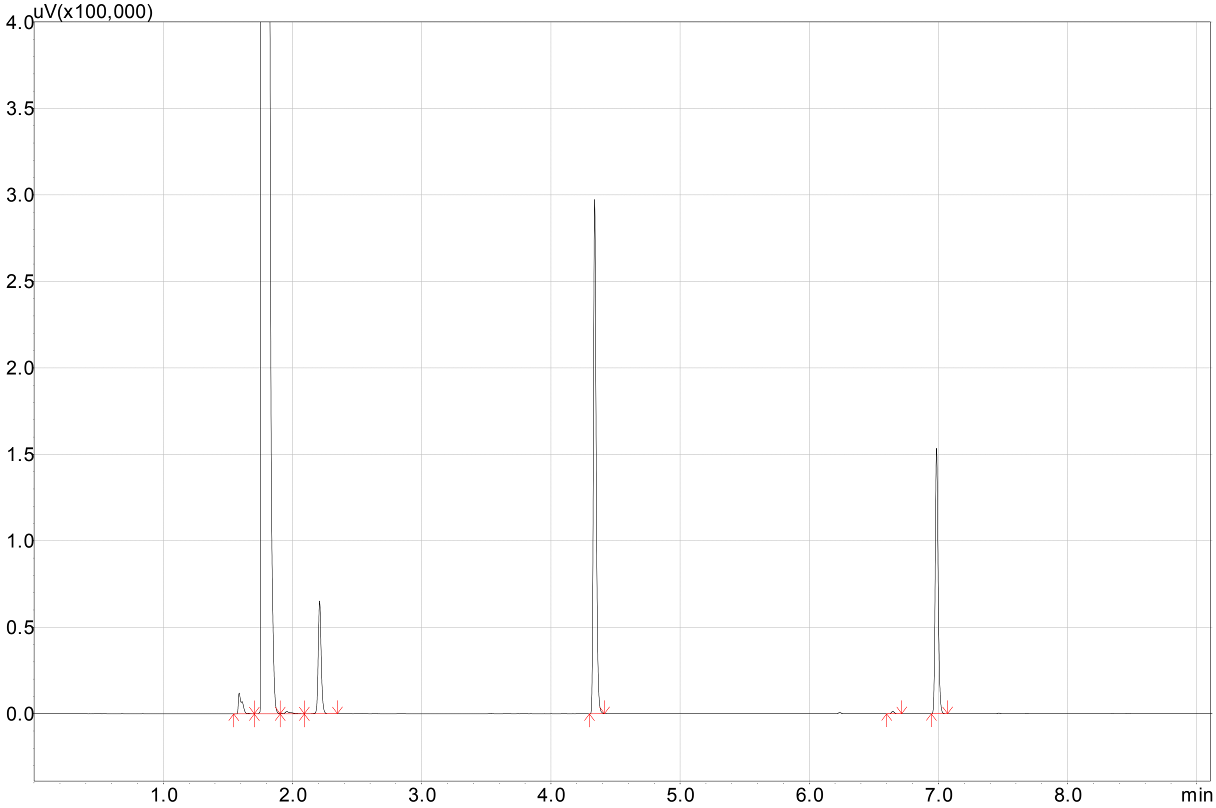


Fig. S16 GC spectrum of the control solution of the MIL-53 (Al) catalyzed cyanosilylation reaction of benzaldehyde under solvent free conditions.

Table S6 The GC data of the control solution of the MIL-53 (Al) catalyzed cyanosilylation reaction of benzaldehyde under solvent free conditions.

Peak#	Ret. Time	T. Plate	Initial Time	Final Time	Tailing F.	Area	Area%
1	1.588	10254.653	1.545	1.704	2.272	23810.2	0.1025
2	1.770	9750.885	1.704	1.904	1.977	22413426.1	96.4932
3	1.955	9283.439	1.904	2.091	--	5458.8	0.0235
4	2.210	46066.248	2.091	2.348	1.148	104931.1	0.4517
5	4.339	177829.422	4.298	4.415	1.236	439867.3	1.8937
6	6.646	407102.001	6.599	6.716	1.231	2242.2	0.0097
7	6.985	478556.234	6.944	7.070	1.188	238254.9	1.0257

$t_{R(benzaldehyde)}$ = 4.339 min; $t_{R(internal\ standard)}$ = 6.985 min

$[\text{Area ration}]_{control} = [A_{benzaldehyde}/A_{(intrnal\ standard)}]_{control}$ = (439867.3/238254.9) = 1.846

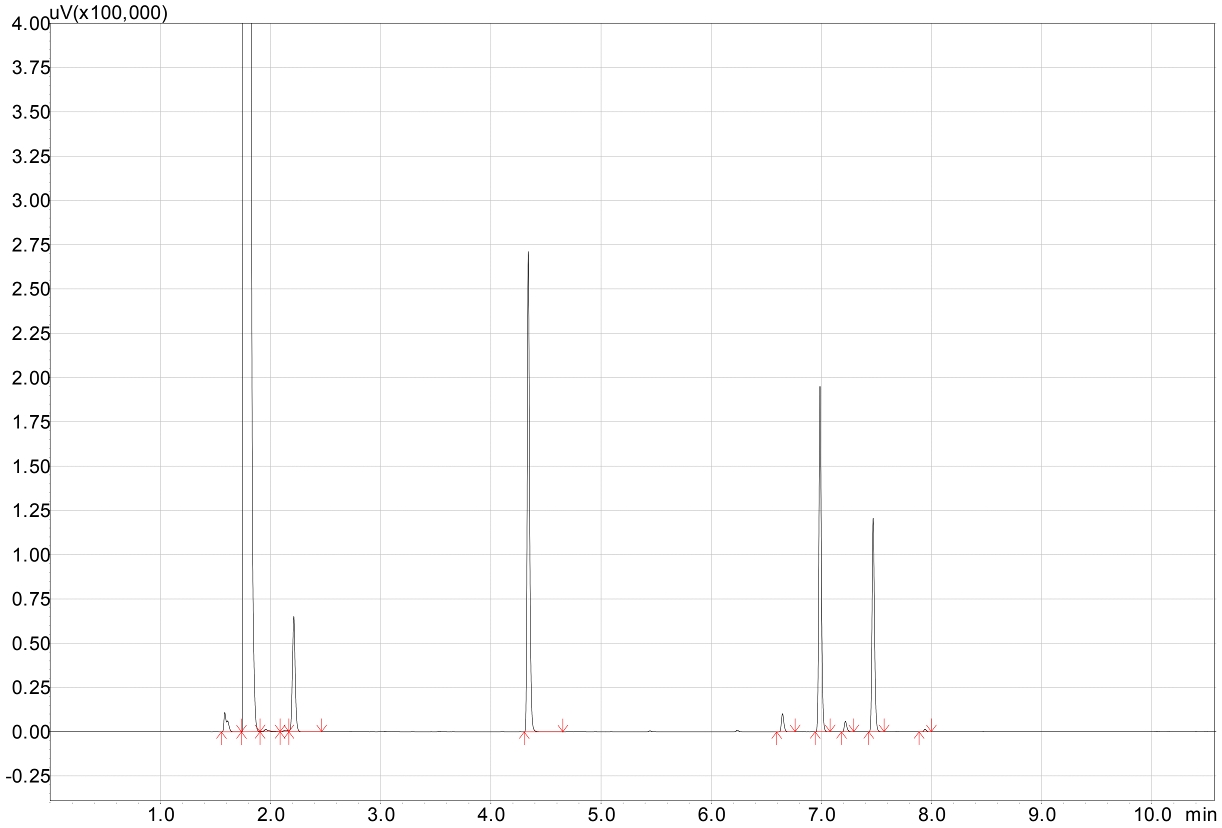


Fig. S17 GC spectrum of the reaction mixture of the MIL-53 (Al) catalyzed cyanosilylation of benzaldehyde under solvent free conditions after 3 h.

Table S7 The GC data of the reaction mixture of the MIL-53 (Al) catalyzed cyanosilylation of benzaldehyde under solvent free conditions after 3 h.

Peak#	Ret. Time	T. Plate	Initial Time	Final Time	Tailing F.	Area	Area%
1	1.585	8953.615	1.554	1.736	2.135	22961.1	0.0952
2	1.765	8697.655	1.736	1.904	2.225	23061234.7	95.5761
3	1.957	15005.454	1.904	2.086	--	5372.7	0.0223
4	2.142	--	2.086	2.166	--	2582.3	0.0107
5	2.211	36962.282	2.166	2.464	1.073	115555.0	0.4789
6	4.340	188406.398	4.303	4.653	1.233	405518.0	1.6806
7	6.647	414562.442	6.594	6.762	1.234	16421.1	0.0681
8	6.987	485656.718	6.944	7.080	1.176	299183.2	1.2399
9	7.218	484184.500	7.182	7.294	1.319	9672.6	0.0401
10	7.470	547334.944	7.430	7.570	1.191	187714.8	0.7780
11	7.941	575757.112	7.887	7.999	1.183	2445.8	0.0101

$t_{R(\text{benzaldehyde})}$ = 4.340 min; $t_{R(\text{internal standard})}$ = 6.987 min; $t_{R(\text{product})}$ = 7.470 min

[Area ration]$_{3\text{ h}}$ = [$A_{\text{benzaldehyde}}/A_{\text{(intrnal standard)}}$]$_{3\text{ h}}$ = (405518.0/299183.2) = 1.355

The conversion of benzaldehyde is calculated as follows:

$$Conv.\% = \frac{[Area\ ratio]_{control} - [Area\ ratio]_{3\ h}}{[Area\ ratio]_{control}} \times 100\%$$

$$= \frac{1.846 - 1.355}{1.846} \times 100\% = 26\%$$

3. For **Entry 3** of **Table 1**, the conversion of benzaldehyde catalyzed by 1.0 mol% of MIL-101 (Cr) was calculated as follows:

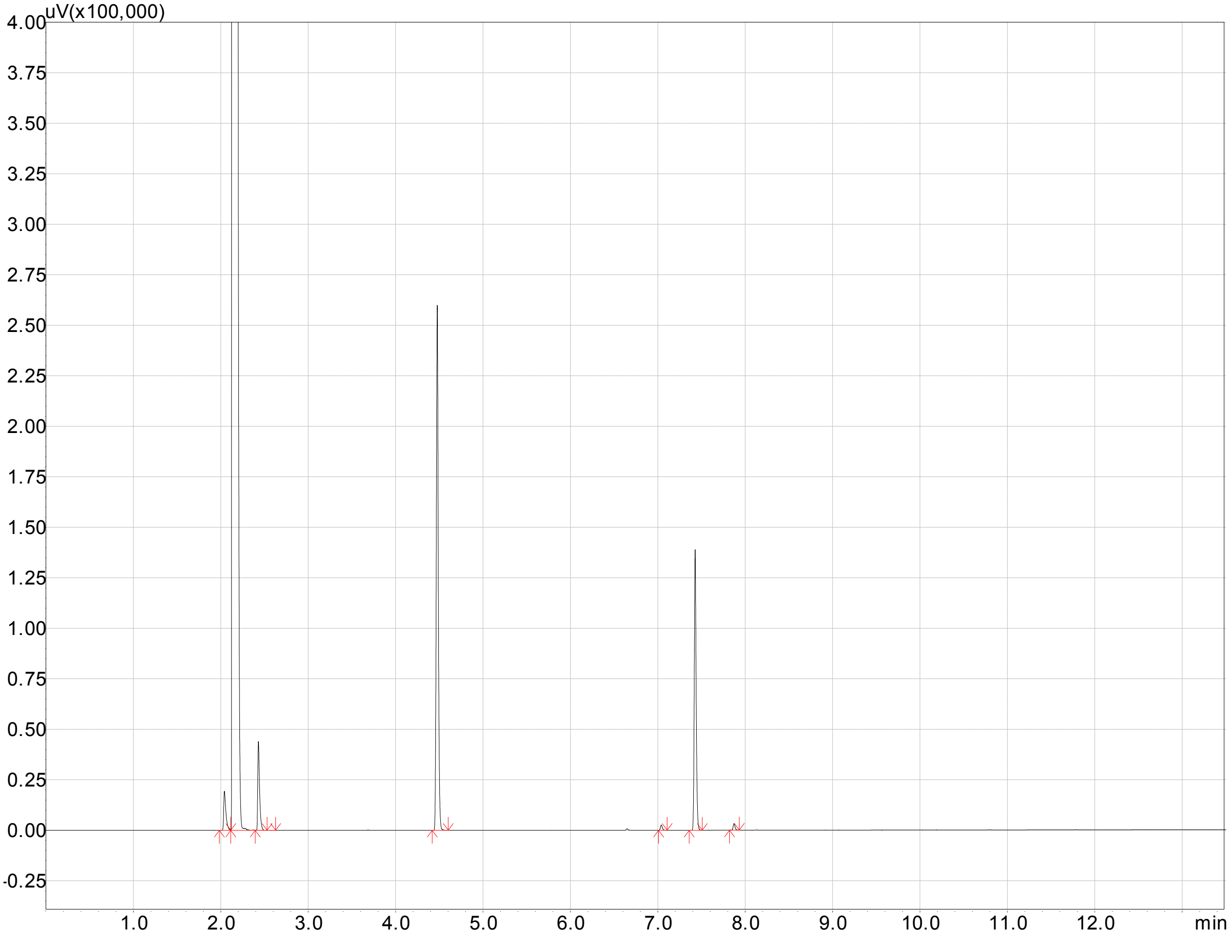


Fig. S18 GC spectrum of the control solution of the MIL-101 (Cr) catalyzed cyanosilylation reaction of benzaldehyde under solvent free conditions.

Table S8 The GC data of the control solution of the MIL-101 (Cr) catalyzed cyanosilylation reaction of benzaldehyde under solvent free conditions.

Peak#	Ret. Time	T. Plate	Initial Time	Final Time	Tailing F.	Area	Area%
1	2.042	35531.935	1.984	2.114	1.856	34501.0	0.1511
2	2.140	26170.886	2.114	2.627	2.328	22110745.1	96.8497
3	2.431	71050.694	2.394	2.530	1.698	63403.4	0.2777
4	4.477	197979.824	4.420	4.601	1.109	405044.7	1.7742
5	7.040	512370.287	7.010	7.107	1.214	3995.5	0.0175
6	7.428	598403.052	7.359	7.509	1.176	207327.4	0.9081
7	7.872	648035.440	7.822	7.934	1.263	4928.4	0.0216

$t_{R(\text{benzaldehyde})}$ = 4.477 min; $t_{R(\text{internal standard})}$ = 7.428 min
[Area ration]$_{\text{control}}$ = [$A_{\text{benzaldehyde}}$/$A_{(\text{intrnal standard})}$]$_{\text{control}}$ = (405044.7/207327.4) = 1.954

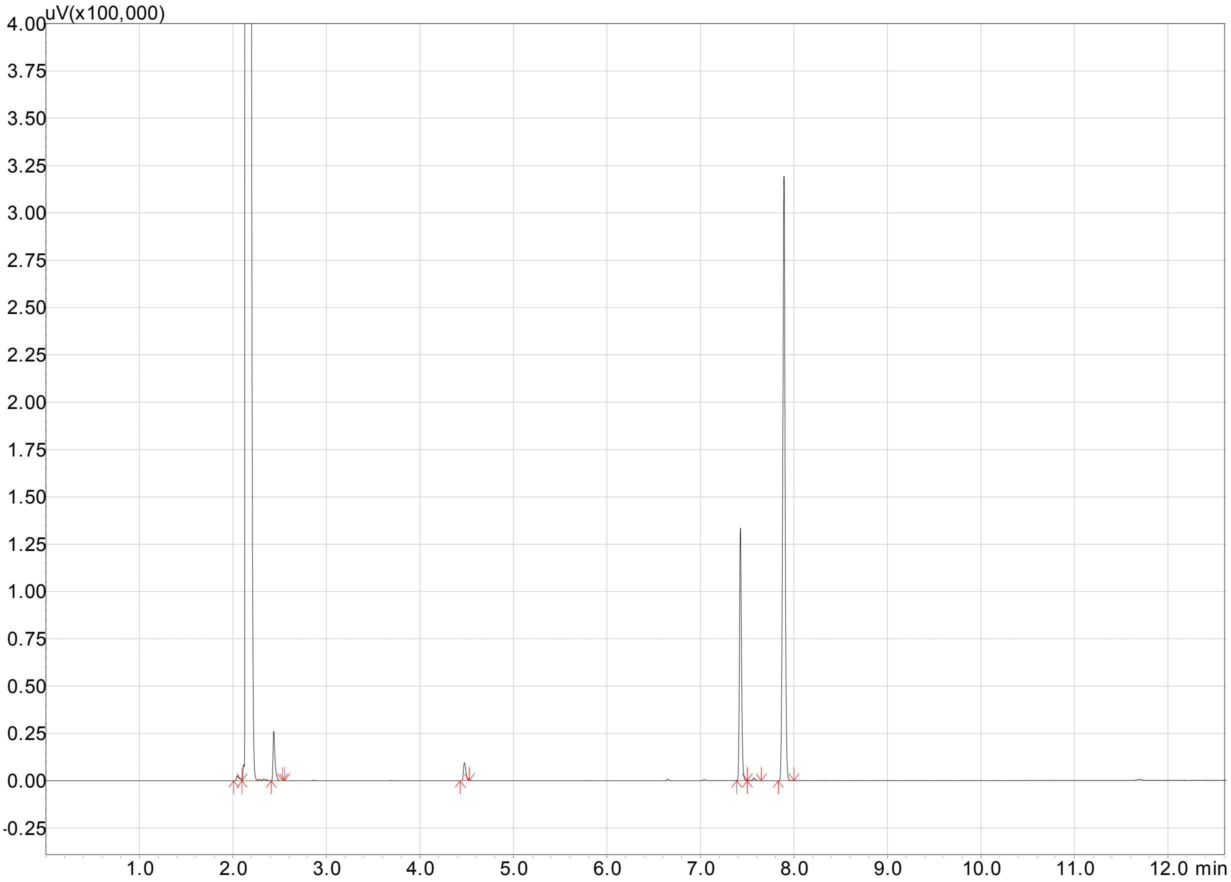


Fig. S19 GC spectrum of the reaction mixture of the MIL-101 (Cr) catalyzed cyanosilylation of benzaldehyde under solvent free conditions after 3 h.

Table S9 The GC data of the reaction mixture of the MIL-101 (Cr) catalyzed cyanosilylation of benzaldehyde under solvent free conditions after 3 h.

Peak#	Ret. Time	T. Plate	Initial Time	Final Time	Tailing F.	Area	Area%
1	2.045	23314.804	2.007	2.096	--	5745.0	0.0262
2	2.142	31181.422	2.096	2.553	2.179	21132375.7	96.2552
3	2.436	69078.202	2.409	2.530	1.685	38662.3	0.1761
4	4.476	131058.481	4.429	4.527	1.349	17021.7	0.0775
5	7.427	598295.637	7.388	7.500	1.181	198407.2	0.9037
6	7.571	498137.161	7.500	7.649	0.832	2213.7	0.0101
7	7.894	487865.817	7.831	7.999	0.958	560093.4	2.5512

$t_{R(\text{benzaldehyde})}$ = 4.476 min; $t_{R(\text{internal standard})}$ = 7.427 min; $t_{R(\text{product})}$ = 7.894 min

$[\text{Area ration}]_{3\text{ h}} = [A_{\text{benzaldehyde}}/A_{(\text{intrnal standard})}]_{3\text{ h}} = (17021.7/198407.2) = 0.086$

The conversion of benzaldehyde is calculated as follows:

$$Conv.\% = \frac{[Area\ ratio]_{control} - [Area\ ratio]_{3\ h}}{[Area\ ratio]_{control}} \times 100\%$$

$$= \frac{1.954 - 0.086}{1.954} \times 100\% = 96\%$$

4. For **Entry 4** of **Table 1**, the conversion of benzaldehyde catalyzed by 1.0 mol% of UiO-66 (Zr) was calculated as follows:

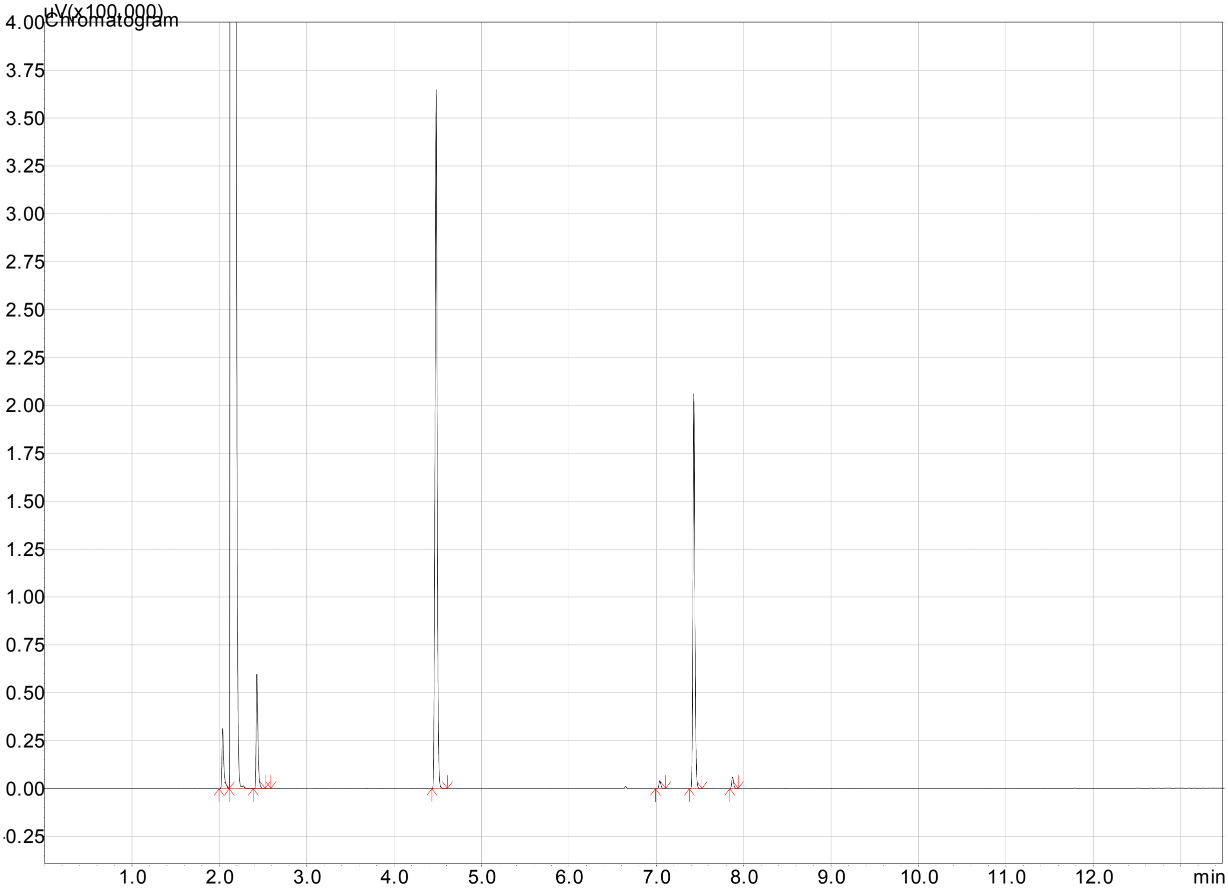


Fig. S20 GC spectrum of the control solution of the UiO-66 (Zr) catalyzed cyanosilylation reaction of benzaldehyde under solvent free conditions.

Table S10 The GC data of the control solution of the UiO-66 (Zr) catalyzed cyanosilylation reaction of benzaldehyde under solvent free conditions.

Peak#	Ret. Time	T. Plate	Initial Time	Final Time	Tailing F.	Area	Area%
1	2.039	56424.012	1.998	2.114	1.885	46391.4	0.2070
2	2.137	36289.605	2.114	2.590	2.212	21352316.4	95.2633
3	2.430	73737.013	2.390	2.525	1.498	83973.5	0.3746
4	4.482	172693.269	4.434	4.611	1.019	605235.6	2.7003
5	7.041	519892.265	6.991	7.108	1.218	6304.5	0.0281
6	7.430	564203.853	7.378	7.523	1.152	310881.5	1.3870
7	7.873	627120.789	7.840	7.938	1.247	8895.1	0.0397

$t_{R(\text{benzaldehyde})} = 4.482$ min; $t_{R(\text{internal standard})} = 7.430$ min

$[\text{Area ration}]_{\text{control}} = [A_{\text{benzaldehyde}}/A_{(\text{intrnal standard})}]_{\text{control}} = (605235.6/310881.5) = 1.947$

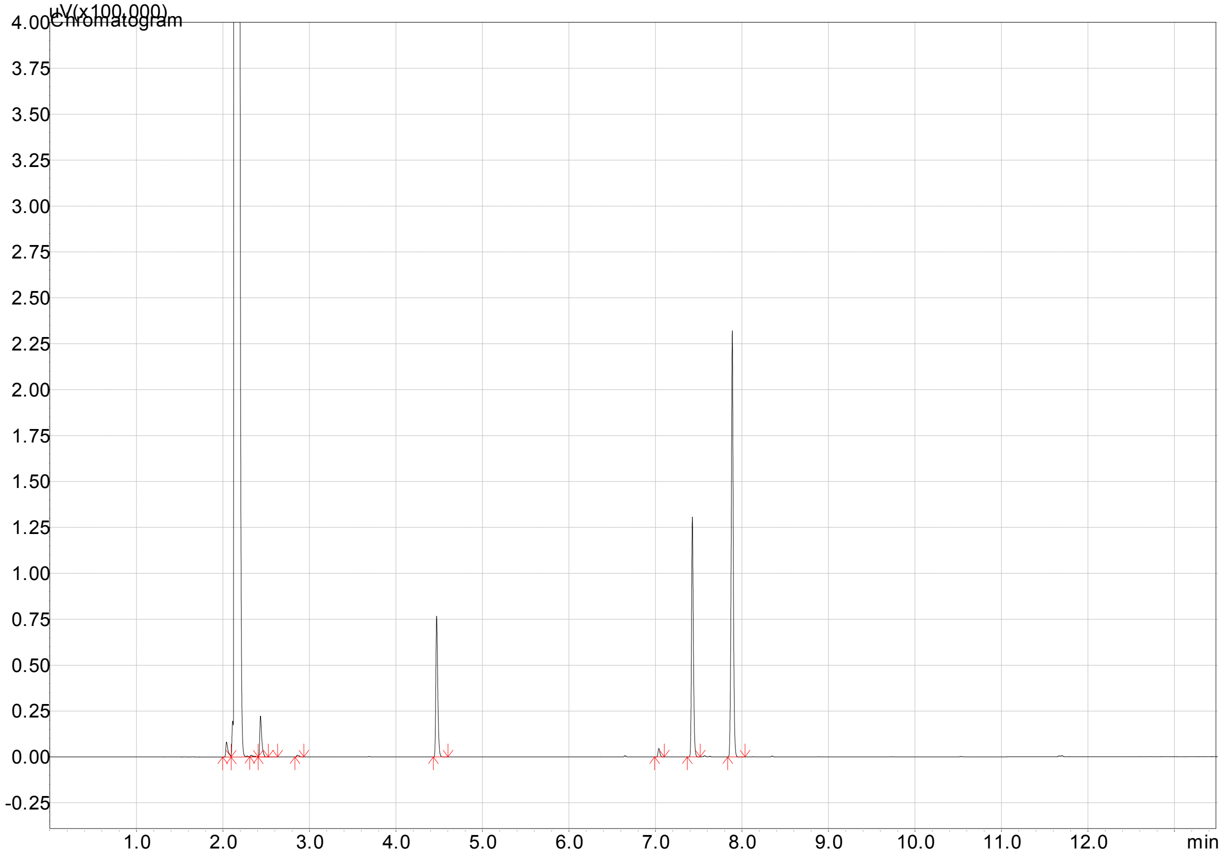


Fig. S21 GC spectrum of the reaction mixture of the UiO-66 (Zr) catalyzed cyanosilylation of benzaldehyde under solvent free conditions after 3 h.

Table S11 The GC data of the reaction mixture of the UiO-66 (Zr) catalyzed cyanosilylation of benzaldehyde under solvent free conditions after 3 h.

Peak#	Ret. Time	T. Plate	Initial Time	Final Time	Tailing F.	Area	Area%
1	2.042	36391.878	1.998	2.095	--	14988.0	0.0670
2	2.141	27781.184	2.095	2.632	2.214	21630056.1	96.6280
3	2.326	38910.452	2.310	2.408	2.694	1834.2	0.0082
4	2.435	62107.942	2.408	2.525	1.688	34707.9	0.1551
5	2.863	30520.861	2.833	2.936	1.688	2229.5	0.0100
6	4.471	189366.420	4.434	4.601	1.326	119791.8	0.5351
7	7.040	508660.394	6.991	7.103	1.239	7124.4	0.0318
8	7.427	601008.416	7.369	7.518	1.188	193938.4	0.8664
9	7.889	566644.563	7.835	8.036	1.009	380206.3	1.6985

$t_{R(\text{benzaldehyde})} = 4.471$ min; $t_{R(\text{internal standard})} = 7.427$ min; $t_{R(\text{product})} = 7.889$ min

$[\text{Area ration}]_{3\text{ h}} = [A_{\text{benzaldehyde}}/A_{(\text{intrnal standard})}]_{3\text{ h}} = (119791.8/193938.4) = 0.618$

The conversion of benzaldehyde is calculated as follows:

$$Conv.\% = \frac{[Area\ ratio]_{control} - [Area\ ratio]_{3\ h}}{[Area\ ratio]_{control}} \times 100\%$$

$$= \frac{1.947 - 0.618}{1.947} \times 100\% = 68\%$$

5. For **Entry 5** of **Table 1**, the conversion of benzaldehyde without catalyst was calculated as follows:

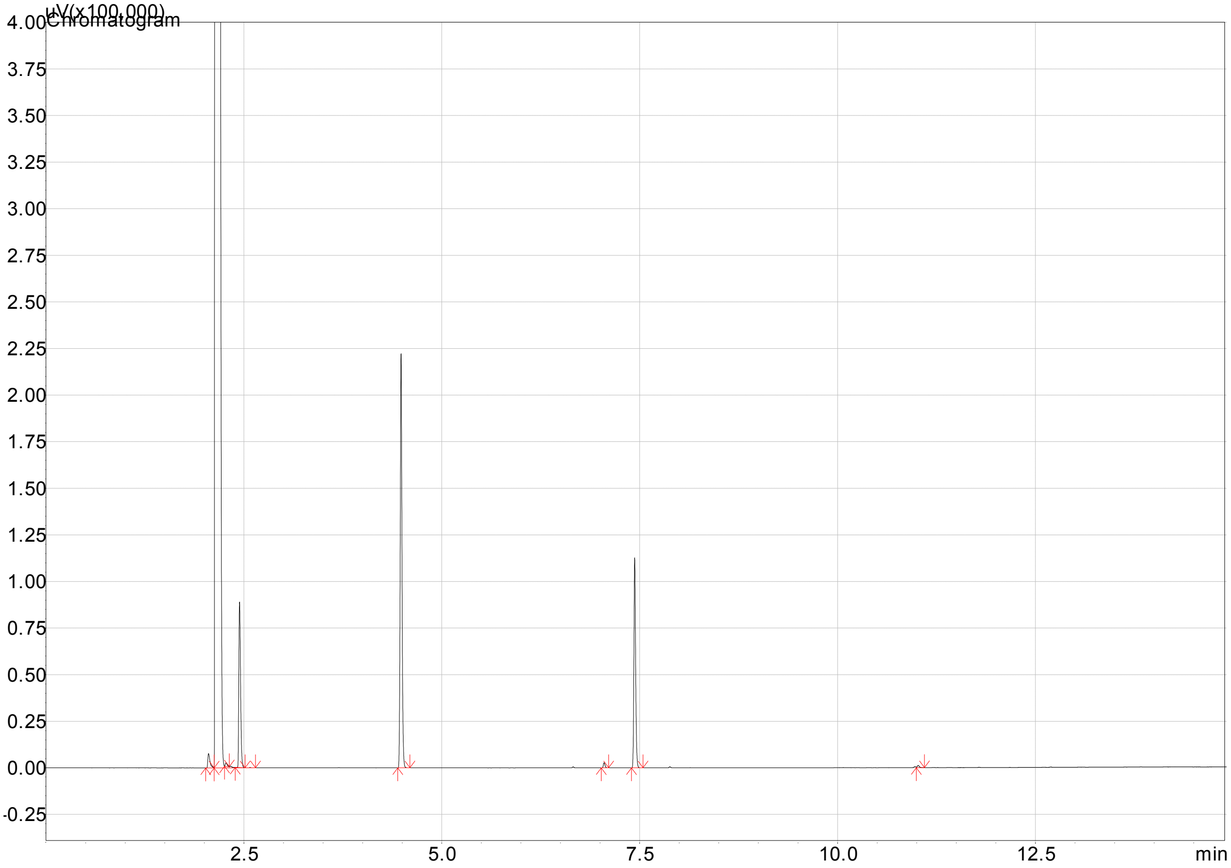


Fig. S22 GC spectrum of the control solution of the cyanosilylation reaction of benzaldehyde under solvent free conditions.

Table S12 The GC data of the control solution of the cyanosilylation reaction of benzaldehyde under solvent free conditions.

Peak#	Ret. Time	T. Plate	Initial Time	Final Time	Tailing F.	Area	Area%
1	2.054	30019.995	2.017	2.124	2.183	15000.2	0.0401
2	2.149	18130.549	2.124	2.647	1.824	36759553.8	98.2015
3	2.274	40949.826	2.255	2.315	1.559	2974.8	0.0079
4	2.445	57280.012	2.390	2.516	1.357	136031.2	0.3634
5	4.486	195986.303	4.443	4.597	1.112	343354.6	0.9173
6	7.051	519113.957	7.015	7.108	1.247	4211.2	0.0112
7	7.437	588629.209	7.397	7.542	1.179	169450.8	0.4527
8	11.019	856989.806	10.995	11.098	--	2208.6	0.0059

$t_{R(\text{benzaldehyde})} = 4.486$ min; $t_{R(\text{internal standard})} = 7.437$ min
$[\text{Area ration}]_{\text{control}} = [A_{\text{benzaldehyde}}/A_{(\text{intrnal standard})}]_{\text{control}} = (343354.6/169450.8) = 2.026$

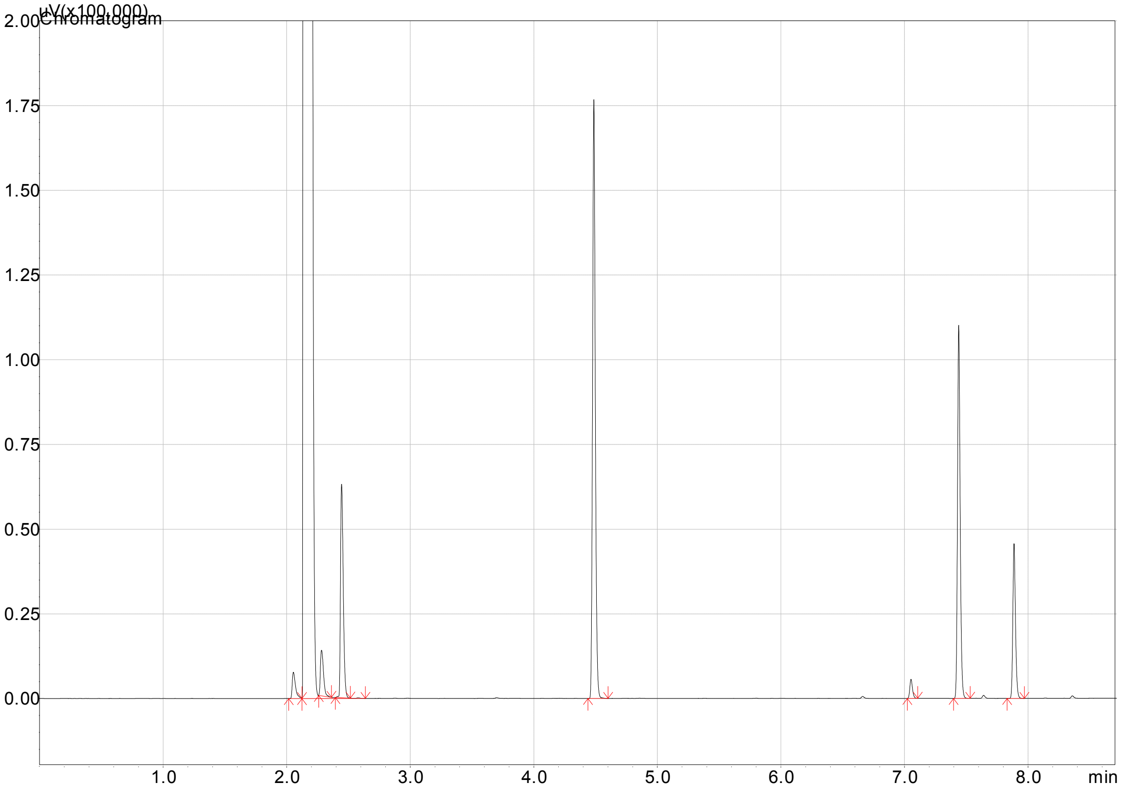


Fig. S23 GC spectrum of the reaction mixture of the cyanosilylation of benzaldehyde under solvent free conditions after 3 h.

Table S13 The GC data of the reaction mixture of the cyanosilylation of benzaldehyde under solvent free conditions after 3 h.

Peak#	Ret. Time	T. Plate	Initial Time	Final Time	Tailing F.	Area	Area%
1	2.054	31146.832	2.016	2.124	1.917	14403.2	0.0411
2	2.149	19484.317	2.124	2.637	1.919	34391534.0	98.1562
3	2.282	39440.255	2.259	2.362	1.462	23514.5	0.0671
4	2.445	56074.593	2.394	2.516	1.440	98202.9	0.2803
5	4.486	203347.795	4.438	4.602	1.156	270008.8	0.7706
6	7.053	509105.360	7.024	7.108	1.223	8483.5	0.0242
7	7.439	573748.473	7.397	7.532	1.195	164044.4	0.4682
8	7.887	661953.092	7.831	7.971	1.208	67360.9	0.1923

$t_{R(\text{benzaldehyde})} = 4.486$ min; $t_{R(\text{internal standard})} = 7.439$ min; $t_{R(\text{product})} = 7.887$ min

$[\text{Area ration}]_{3\text{ h}} = [A_{\text{benzaldehyde}}/A_{(\text{intrnal standard})}]_{3\text{ h}} = (270008.8/164044.4) = 1.646$

The conversion of benzaldehyde is calculated as follows:

$$Conv.\% = \frac{[Area\ ratio]_{control} - [Area\ ratio]_{3\ h}}{[Area\ ratio]_{control}} \times 100\%$$

$$= \frac{2.026 - 1.646}{2.026} \times 100\% = 19\%$$

6. For **Entry 1** of **Table 3**, the conversion of benzaldehyde under solvent free conditions catalyzed by 0.3 mol% of MIL-101 (Cr) was calculated as follows:

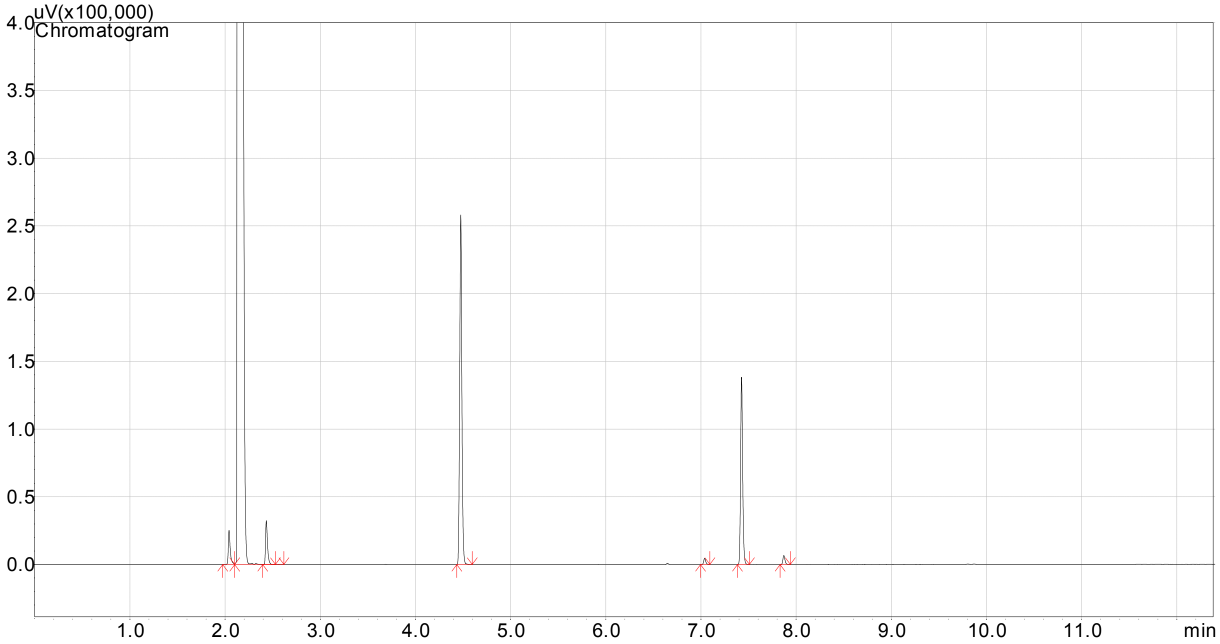


Fig. S24 GC spectrum of the control solution of 0.3 mol% of MIL-101 (Cr) catalyzed cyanosilylation reaction of benzaldehyde under solvent free conditions.

Table S14 The GC data of the control solution of 0.3 mol% of MIL-101 (Cr) catalyzed cyanosilylation reaction of benzaldehyde under solvent free conditions.

Peak#	Ret. Time	T. Plate	Initial Time	Final Time	Tailing F.	Area	Area%
1	2.042	57553.570	1.974	2.100	1.659	35925.8	0.1617
2	2.140	36906.933	2.100	2.618	2.060	21511024.3	96.8066
3	2.433	74155.669	2.394	2.530	1.493	45653.5	0.2055
4	4.476	187963.766	4.434	4.597	1.101	404555.2	1.8206
5	7.038	497609.662	6.996	7.094	1.244	6637.7	0.0299
6	7.426	582623.070	7.383	7.509	1.166	206826.0	0.9308
7	7.871	651574.000	7.831	7.938	1.238	9991.1	0.0450

$t_{R(\text{benzaldehyde})}$ = 4.476 min; $t_{R(\text{internal standard})}$ = 7.426 min

[Area ration]$_{\text{control}}$ = [$A_{\text{benzaldehyde}}$/$A_{\text{(intrnal standard)}}$]$_{\text{control}}$ = (404555.2/206826.0) = 1.956

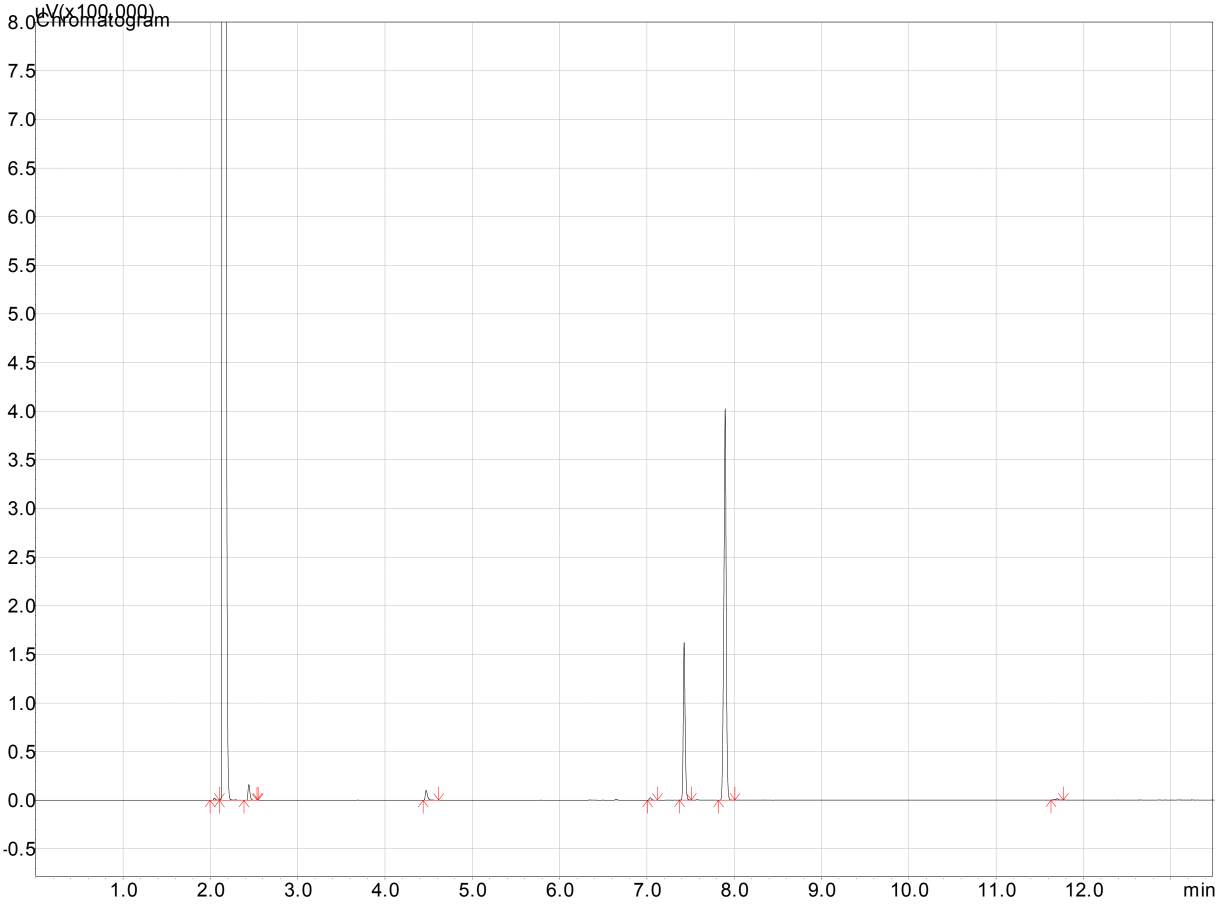


Fig. S25 GC spectrum of the reaction mixture of 0.3 mol% of MIL-101 (Cr) catalyzed cyanosilylation of benzaldehyde under solvent free conditions after 4 h.

Table S15 The GC data of the reaction mixture of 0.3 mol% of MIL-101 (Cr) catalyzed cyanosilylation of benzaldehyde under solvent free conditions after 4 h.

Peak#	Ret. Time	T. Plate	Initial Time	Final Time	Tailing F.	Area	Area%
1	2.046	44235.438	1.998	2.105	--	3582.7	0.0177
2	2.148	28660.182	2.105	2.548	1.603	19172748.0	94.8417
3	2.441	57648.392	2.385	2.534	1.328	24504.7	0.1212
4	4.473	169987.932	4.438	4.615	1.517	17580.6	0.0870
5	7.039	496399.782	7.010	7.122	1.237	3862.7	0.0191
6	7.427	604580.585	7.373	7.509	1.168	241047.8	1.1924
7	7.898	437600.921	7.822	8.008	0.920	748928.4	3.7047
8	11.699	1107348.844	11.630	11.770	0.846	3279.5	0.0162

$t_{R(\text{benzaldehyde})}$ = 4.473 min; $t_{R(\text{internal standard})}$ = 7.427 min; $t_{R(\text{product})}$ = 7.898 min

$[\text{Area ration}]_{4\text{ h}} = [A_{\text{benzaldehyde}}/A_{(\text{intrnal standard})}]_{4\text{ h}} = (17580.6/241047.8) = 0.073$

The conversion of benzaldehyde is calculated as follows:

$$Conv.\% = \frac{[Area\ ratio]_{control} - [Area\ ratio]_{4\ h}}{[Area\ ratio]_{control}} \times 100\%$$

$$= \frac{1.956 - 0.073}{1.956} \times 100\% = 96\%$$

7. For **Entry 2** of **Table 3**, the conversion of benzaldehyde in the cyanosilylation reaction in heptane catalyzed by 0.3 mol% of MIL-101 (Cr) was calculated as follows:

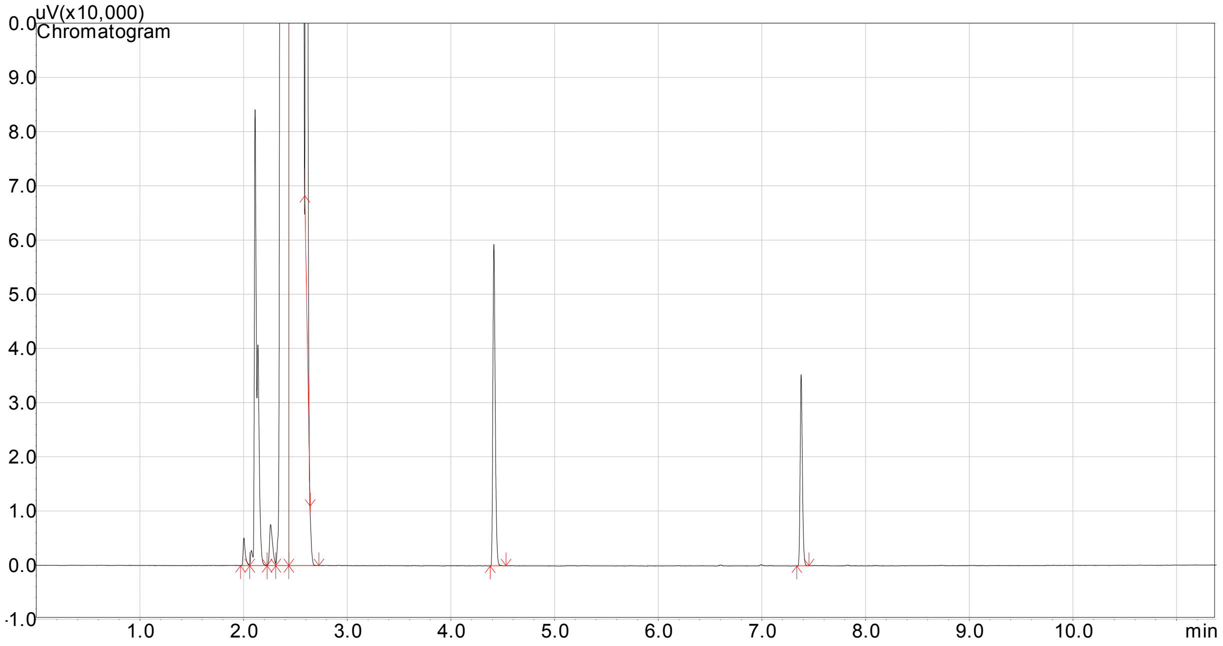


Fig. S26 The GC spectrum of the control solution of the cyanosilylation reaction of benzaldehyde in heptane.

Table S16 The GC data of the control solution of the cyanosilylation reaction of benzaldehyde in heptane.

Peak#	Ret. Time	T. Plate	Initial Time	Final Time	Tailing F.	Area	Area%
1	2.003	46754.277	1.970	2.059	1.781	7685.6	0.0059
2	2.111	59342.117	2.059	2.227	2.365	163986.9	0.1259
3	2.261	27283.800	2.227	2.311	--	15715.3	0.0121
4	2.385	8563.811	2.311	2.437	--	1530652.9	1.1756
5	2.535	12893.863	2.437	2.726	0.685	127917522.7	98.2449
6	2.604	125051.440	2.591	2.642	1.414	419979.6	0.3226
7	4.414	180103.386	4.378	4.532	1.297	94078.6	0.0723
8	7.379	555574.026	7.337	7.453	1.219	53025.8	0.0407

$t_{R(\text{benzaldehyde})}$ = 4.414 min; $t_{R(\text{internal standard})}$ = 7.379 min
[Area ration]$_{\text{control}}$ = [$A_{\text{benzaldehyde}}/A_{\text{(intrnal standard)}}$]$_{\text{control}}$ = (94078.6/53025.8) = 1.774

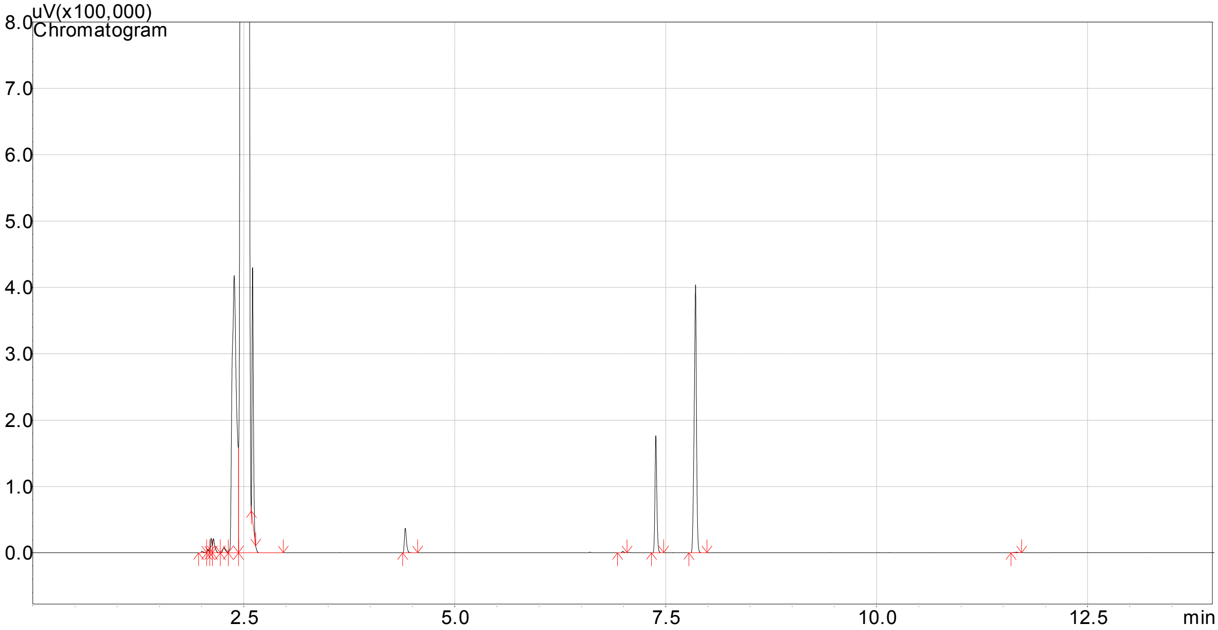


Fig. S27 The GC spectrum of the reaction mixture of the cyanosilylation of benzaldehyde in heptane after 4 h.

Table S17 The GC data of the reaction mixture of the cyanosilylation of benzaldehyde in heptane after 4 h.

Peak#	Ret. Time	T. Plate	Initial Time	Final Time	Tailing F.	Area	Area%
1	2.004	48757.465	1.965	2.058	--	4558.4	0.0036
2	2.076	38136.269	2.058	2.095	--	7668.8	0.0060
3	2.113	51892.300	2.095	2.128	--	26781.1	0.0210
4	2.141	36112.529	2.128	2.221	--	35706.2	0.0280
5	2.262	23426.519	2.221	2.315	--	16819.7	0.0132
6	2.386	8058.751	2.315	2.436	--	1514655.4	1.1896
7	2.534	13181.800	2.436	2.968	0.691	124216271.3	97.5570
8	2.604	122414.594	2.590	2.642	1.415	411233.1	0.3230
9	4.414	161293.941	4.382	4.559	1.360	63208.8	0.0496
10	6.992	480168.491	6.930	7.042	1.252	3346.8	0.0026
11	7.383	550732.924	7.332	7.476	1.155	265997.6	0.2089
12	7.853	416743.159	7.775	7.989	0.905	758511.6	0.5957
13	11.657	1058655.325	11.592	11.718	1.013	2129.8	0.0017

$t_{R(\text{benzaldehyde})} = 4.414$ min; $t_{R(\text{internal standard})} = 7.383$ min; $t_{R(\text{product})} = 7.853$ min

$[\text{Area ration}]_{4\text{ h}} = [A_{\text{benzaldehyde}}/A_{(\text{intrnal standard})}]_{4\text{ h}} = (63208.8/265997.6) = 0.238$

The conversion of benzaldehyde is calculated as follows:

$$Conv.\% = \frac{[Area\ ratio]_{control} - [Area\ ratio]_{4\ h}}{[Area\ ratio]_{control}} \times 100\%$$

$$= \frac{1.774 - 0.238}{1.774} \times 100\% = 87\%$$

8. For **Entry 3** of **Table 3**, the conversion of benzaldehyde in the cyanosilylation reaction in acetonitrile catalyzed by 0.3 mol% of MIL-101 (Cr) was calculated as follows:

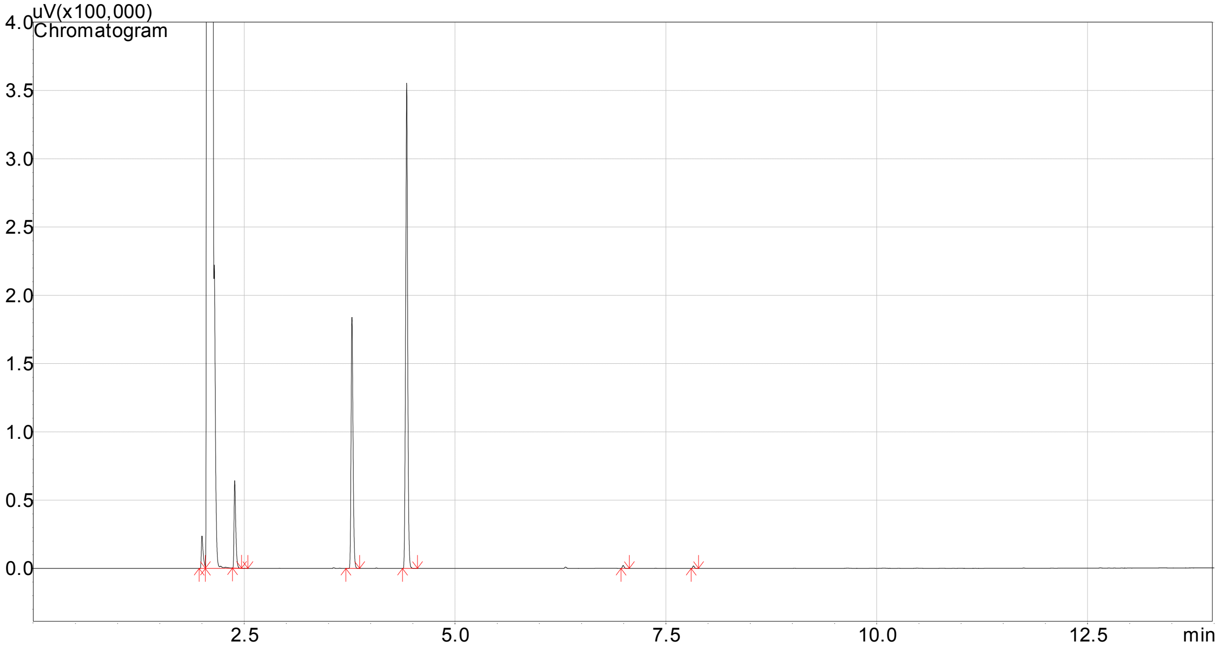


Fig. S28 The GC spectrum of the control solution of the cyanosilylation reaction of benzaldehyde in acetonitrile.

Table S18 The GC data of the control solution of the cyanosilylation reaction of benzaldehyde in acetonitrile.

Peak#	Ret. Time	T. Plate	Initial Time	Final Time	Tailing F.	Area	Area%
1	2.000	43781.595	1.965	2.040	--	36310.9	0.0476
2	2.095	21811.927	2.040	2.544	0.873	75226180.2	98.6671
3	2.388	70859.882	2.362	2.469	1.505	89846.6	0.1178
4	3.778	126349.867	3.706	3.869	1.225	298281.3	0.3912
5	4.427	174183.769	4.378	4.555	1.025	585673.8	0.7682
6	6.993	500525.776	6.968	7.066	1.232	3287.7	0.0043
7	7.827	628733.047	7.799	7.887	1.273	2815.5	0.0037

$t_{R(\text{benzaldehyde})} = 4.427$ min; $t_{R(\text{internal standard})} = 3.778$ min

$[\text{Area ration}]_{\text{control}} = [A_{\text{benzaldehyde}}/A_{(\text{intrnal standard})}]_{\text{control}} = (585673.8/298281.3) = 1.963$

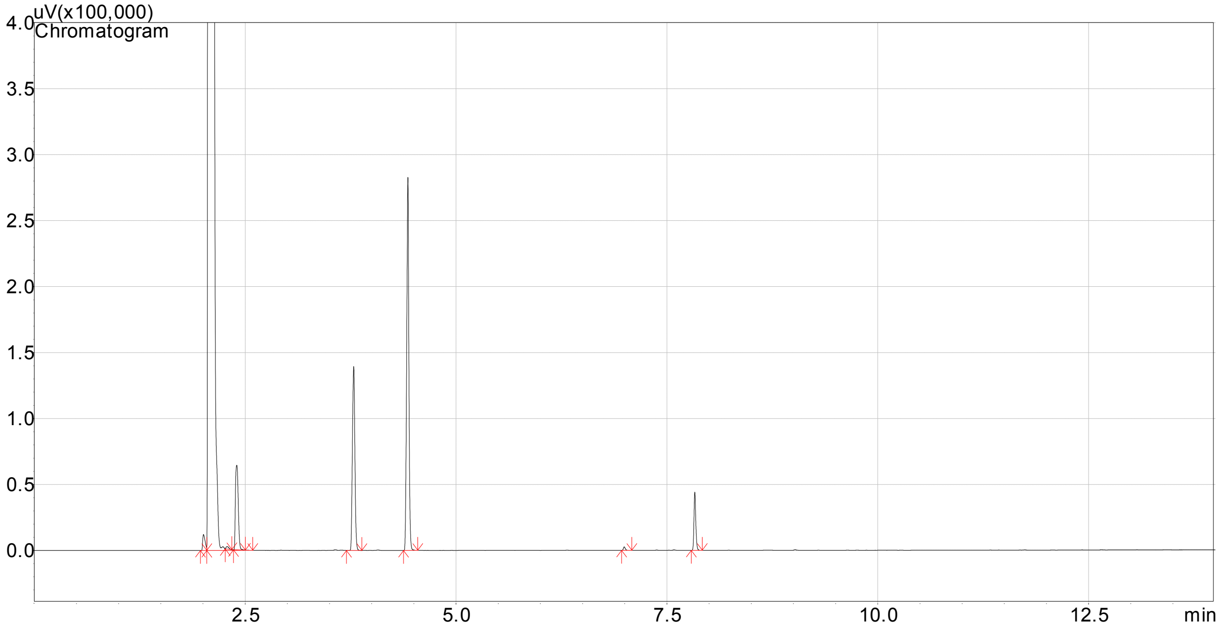


Fig. S29 The GC spectrum of the reaction mixture of the cyanosilylation of benzaldehyde in acetonitrile after 4 h.

Table S19 The GC data of the reaction mixture of the cyanosilylation of benzaldehyde in acetonitrile after 4 h.

Peak#	Ret. Time	T. Plate	Initial Time	Final Time	Tailing F.	Area	Area%
1	2.006	20372.621	1.970	2.044	--	24366.5	0.0317
2	2.096	18766.444	2.044	2.590	0.915	75720827.9	98.6501
3	2.287	20327.981	2.264	2.343	1.397	4034.0	0.0053
4	2.400	22725.921	2.361	2.502	1.261	149128.5	0.1943
5	3.787	76217.006	3.701	3.883	1.047	283014.0	0.3687
6	4.429	140435.940	4.378	4.545	0.991	505477.5	0.6585
7	6.994	507110.169	6.963	7.084	1.240	4011.2	0.0052
8	7.831	638460.249	7.789	7.920	1.203	66133.3	0.0862

$t_{R(\text{benzaldehyde})} = 4.429$ min; $t_{R(\text{internal standard})} = 3.787$ min; $t_{R(\text{product})} = 7.831$ min

$[\text{Area ration}]_{4\text{ h}} = [A_{\text{benzaldehyde}}/A_{(\text{intrnal standard})}]_{4\text{ h}} = (505477.5/283014.0) = 1.786$

The conversion of benzaldehyde is calculated as follows:

$$Conv.\% = \frac{[Area\ ratio]_{control} - [Area\ ratio]_{4\ h}}{[Area\ ratio]_{control}} \times 100\%$$

$$= \frac{1.963 - 1.786}{1.963} \times 100\% = 9\%$$

9. For **Entry 4** of **Table 3**, the conversion of benzaldehyde in the cyanosilylation reaction in dichloromethane catalyzed by 0.3 mol% of MIL-101 (Cr) was calculated as follows:

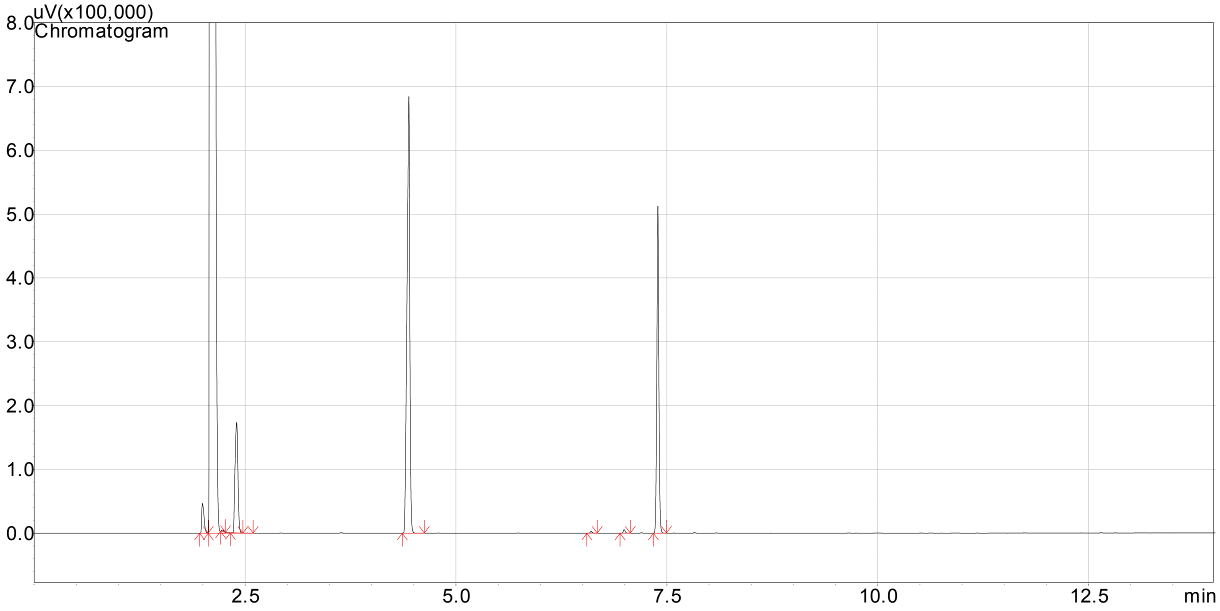


Fig. S30 The GC spectrum of the control solution of the cyanosilylation reaction of benzaldehyde in dichloromethane.

Table S20 The GC data of the control solution of the cyanosilylation reaction of benzaldehyde in dichloromethane.

Peak#	Ret. Time	T. Plate	Initial Time	Final Time	Tailing F.	Area	Area%
1	1.995	23089.434	1.960	2.063	1.691	89991.1	0.1656
2	2.098	11731.214	2.063	2.595	1.597	51439217.5	94.6548
3	2.232	37590.905	2.208	2.268	1.076	4235.7	0.0078
4	2.399	20595.451	2.324	2.474	1.021	409971.7	0.7544
5	4.441	85398.932	4.364	4.625	0.819	1555814.8	2.8629
6	6.602	433508.212	6.552	6.674	1.233	4169.4	0.0077
7	6.994	512236.074	6.944	7.066	1.255	8501.9	0.0156
8	7.394	506628.239	7.341	7.495	1.017	832097.6	1.5312

$t_{R(\text{benzaldehyde})} = 4.441$ min; $t_{R(\text{internal standard})} = 7.394$ min

$[\text{Area ration}]_{\text{control}} = [A_{\text{benzaldehyde}}/A_{(\text{intrnal standard})}]_{\text{control}} = (1555814.8/832097.6) = 1.870$

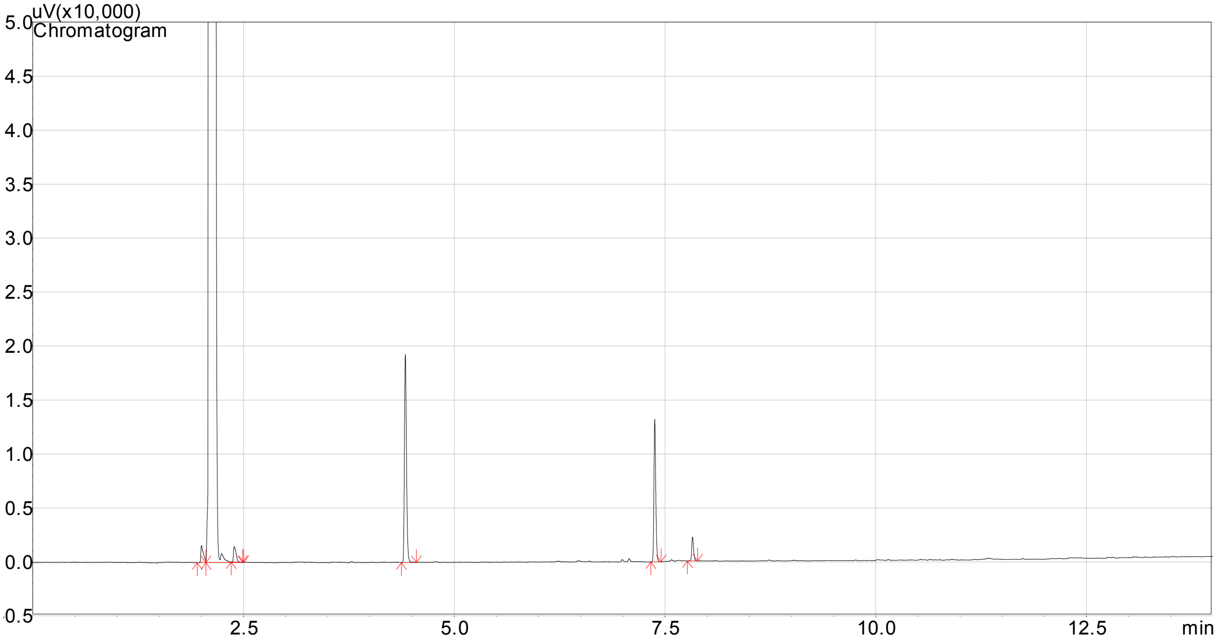


Fig. S31 The GC spectrum of the reaction mixture of the cyanosilylation of benzaldehyde in dichloromethane after 4 h.

Table S21 The GC data of the reaction mixture of the cyanosilylation of benzaldehyde in dichloromethane after 4 h.

Peak#	Ret. Time	T. Plate	Initial Time	Final Time	Tailing F.	Area	Area%
1	2.001	18443.130	1.951	2.054	--	3429.2	0.0088
2	2.097	10678.542	2.054	2.502	2.156	38853034.7	99.8390
3	2.389	24795.675	2.352	2.487	1.835	3109.4	0.0080
4	4.419	155427.522	4.373	4.550	1.255	32878.1	0.0845
5	7.378	561891.055	7.332	7.453	1.230	19827.7	0.0510
6	7.827	601647.008	7.766	7.887	1.228	3402.0	0.0087

$t_{R(\text{benzaldehyde})}$ = 4.419 min; $t_{R(\text{internal standard})}$ = 7.378 min; $t_{R(\text{product})}$ = 7.827 min

$[\text{Area ration}]_{4\text{ h}} = [A_{\text{benzaldehyde}}/A_{(\text{intrnal standard})}]_{4\text{ h}} = (32878.1/19827.7) = 1.658$

The conversion of benzaldehyde is calculated as follows:

$$Conv.\% = \frac{[Area\ ratio]_{control} - [Area\ ratio]_{4\ h}}{[Area\ ratio]_{control}} \times 100\%$$

$$= \frac{1.870 - 1.658}{1.870} \times 100\% = 11\%$$

10. For **Entry 5** of **Table 3**, the conversion of benzaldehyde in the cyanosilylation reaction in tetrahydrofuran catalyzed by 0.3 mol% of MIL-101 (Cr) was calculated as follows:

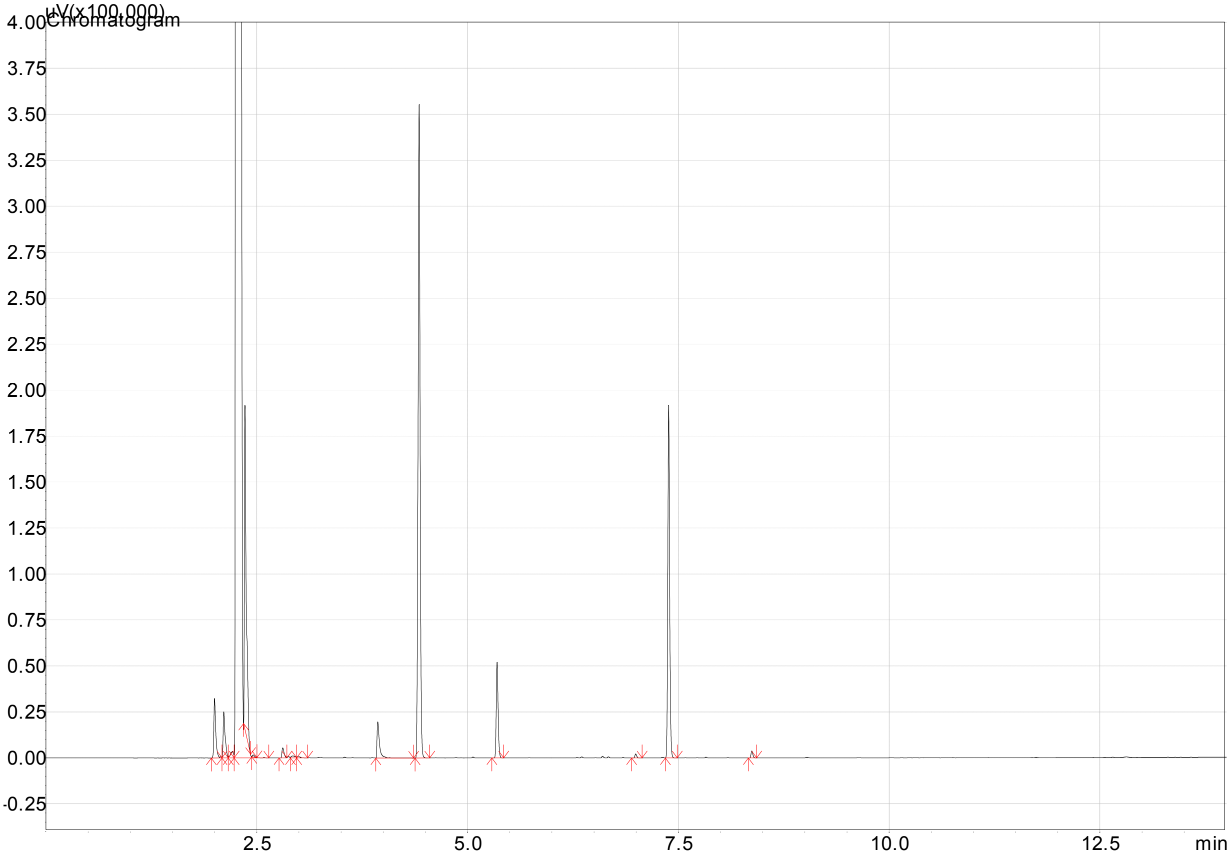


Fig. S32 The GC spectrum of the control solution of the cyanosilylation reaction of benzaldehyde in tetrahydrofuran.

Table S22 The GC data of the control solution of the cyanosilylation reaction of benzaldehyde in tetrahydrofuran.

Peak#	Ret. Time	T. Plate	Initial Time	Final Time	Tailing F.	Area	Area%
1	1.999	43551.344	1.960	2.087	1.629	51554.2	0.0464
2	2.109	44431.894	2.087	2.161	1.832	41830.7	0.0377
3	2.212	15158.738	2.161	2.231	--	9592.1	0.0086
4	2.275	45021.659	2.231	2.642	1.103	109657238.1	98.7505
5	2.360	77164.021	2.343	2.427	2.211	270092.5	0.2432
6	2.459	43235.203	2.441	2.502	1.421	1806.7	0.0016
7	2.808	60832.033	2.763	2.857	1.582	9821.1	0.0088
8	2.927	--	2.898	2.973	--	3911.4	0.0035
9	2.999	--	2.973	3.104	--	2371.8	0.0021
10	3.935	112764.386	3.911	4.359	2.438	39747.5	0.0358
11	4.426	173850.608	4.378	4.551	1.022	580683.5	0.5229
12	5.350	291701.402	5.288	5.428	1.198	79383.0	0.0715
13	6.994	523593.298	6.944	7.071	1.251	3398.7	0.0031
14	7.385	584661.002	7.346	7.486	1.143	287541.4	0.2589
15	8.371	734984.519	8.331	8.428	1.251	5782.6	0.0052

$t_{R(\text{benzaldehyde})} = 4.426$ min; $t_{R(\text{internal standard})} = 7.385$ min

$[\text{Area ration}]_{\text{control}} = [A_{\text{benzaldehyde}}/A_{(\text{intrnal standard})}]_{\text{control}} = (580683.5/287541.4) = 2.019$

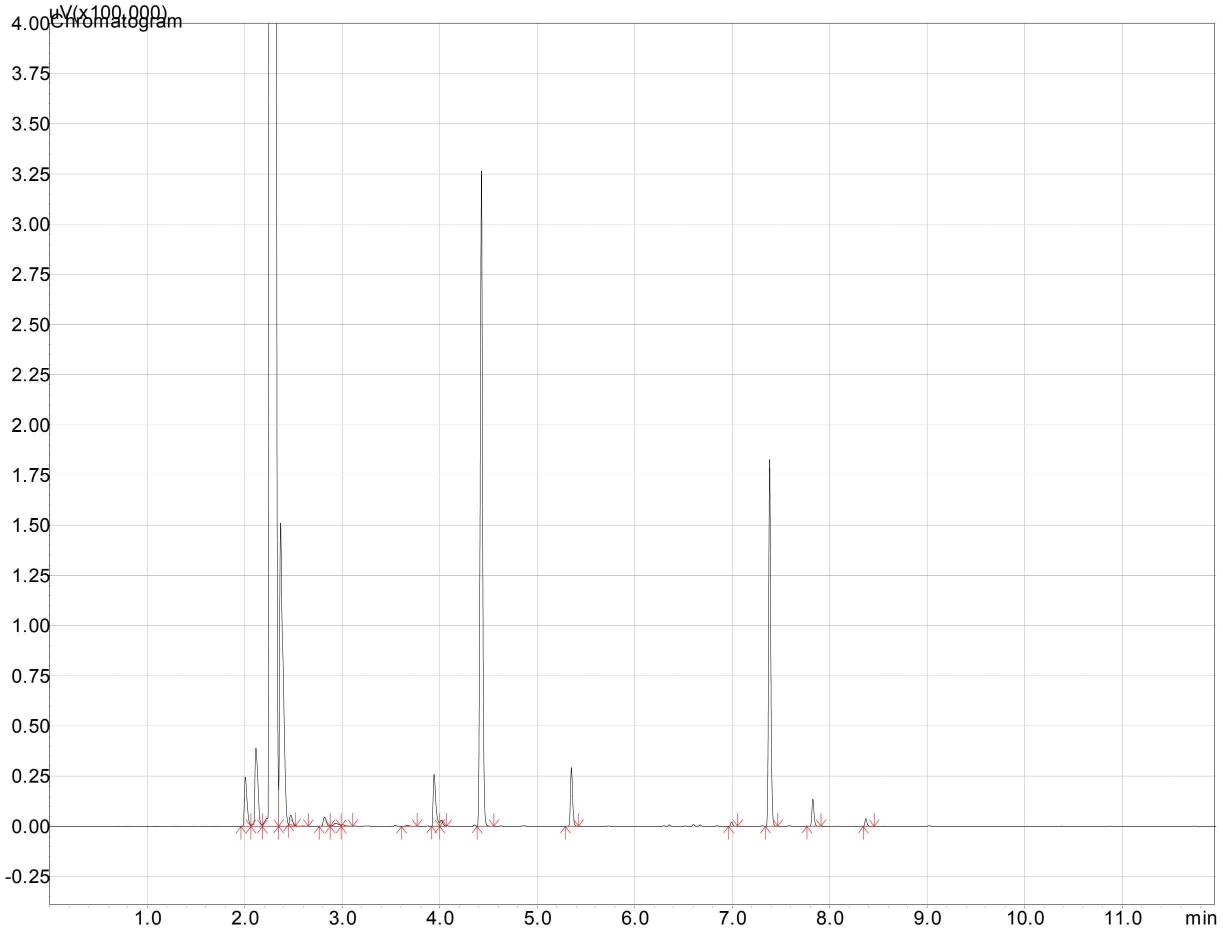


Fig. S33 The GC spectrum of the reaction mixture of the cyanosilylation of benzaldehyde in tetrahydrofuran after 4 h.

Table S23 The GC data of the reaction mixture of the cyanosilylation of benzaldehyde in tetrahydrofuran after 4 h.

Peak#	Ret. Time	T. Plate	Initial Time	Final Time	Tailing F.	Area	Area%
1	2.006	24906.709	1.961	2.063	1.645	47925.1	0.0414
2	2.115	20753.140	2.063	2.180	1.611	83957.4	0.0725
3	2.276	35754.351	2.180	2.348	1.167	114304626.0	98.7140
4	2.368	19476.474	2.348	2.651	--	366882.2	0.3168
5	2.471	34644.734	2.451	2.521	1.427	8770.8	0.0076
6	2.819	36551.256	2.763	2.875	1.345	10204.6	0.0088
7	2.933	--	2.875	2.987	--	6185.4	0.0053
8	3.006	--	2.987	3.109	--	2676.6	0.0023
9	3.668	52033.616	3.608	3.767	1.370	1860.9	0.0016
10	3.942	109572.107	3.916	4.000	--	49391.0	0.0427
11	4.015	--	4.000	4.070	--	6111.2	0.0053
12	4.428	162748.998	4.383	4.555	1.009	554641.2	0.4790
13	5.351	284380.085	5.288	5.423	1.218	45318.8	0.0391
14	6.994	497688.691	6.963	7.057	1.236	3407.5	0.0029
15	7.384	555567.313	7.341	7.467	1.151	275332.5	0.2378
16	7.827	614568.443	7.766	7.911	1.229	20634.4	0.0178
17	8.371	729576.031	8.345	8.457	1.244	5808.2	0.0050

$t_{\text{R(benzaldehyde)}} = 4.428$ min; $t_{\text{R(internal standard)}} = 7.384$ min; $t_{\text{R(product)}} = 7.827$ min

$[\text{Area ration}]_{4\text{ h}} = [A_{\text{benzaldehyde}}/A_{\text{(intrnal standard)}}]_{4\text{ h}} = (554641.2/275332.5) = 2.014$

The conversion of benzaldehyde is calculated as follows:

$$Conv.\% = \frac{[Area\ ratio]_{control} - [Area\ ratio]_{4\ h}}{[Area\ ratio]_{control}} \times 100\%$$
$$= \frac{2.019 - 2.014}{2.019} \times 100\% = 0.2\%$$

11. In Fig. 4, the conversion benzaldehyde in the cyanosilylation reaction catalyzed by 0.3 mol% of fresh MIL-101 (Cr) was the same as that of Table 3, Entry 1.
12. In Fig. 4, the conversion benzaldehyde in the 2nd run of the cyanosilylation reaction catalyzed by 0.3 mol% of recycled MIL-101 (Cr) was calculated as follows:

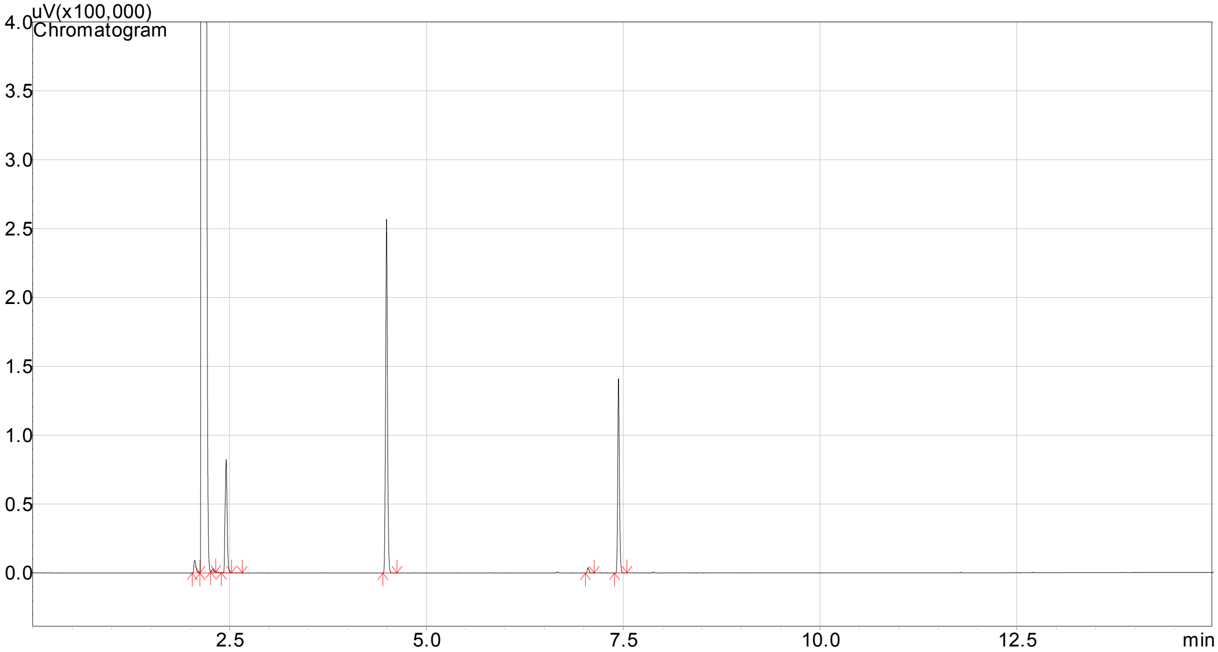


Fig. S34 The GC spectrum of the control solution of the cyanosilylation reaction of benzaldehyde in 2nd run.

Table S24 The GC data of the control solution of the cyanosilylation reaction of benzaldehyde in 2nd run.

Peak#	Ret. Time	T. Plate	Initial Time	Final Time	Tailing F.	Area	Area%
1	2.057	27680.778	2.026	2.124	1.856	18081.0	0.0457
2	2.155	15525.584	2.124	2.660	1.623	38749686.2	97.9499
3	2.287	49392.549	2.259	2.325	1.094	3288.4	0.0083
4	2.457	39898.643	2.394	2.525	1.090	145852.1	0.3687
5	4.494	172061.084	4.448	4.625	1.049	426479.2	1.0780
6	7.053	506941.031	7.019	7.131	1.237	6104.1	0.0154
7	7.440	575530.466	7.388	7.547	1.178	211233.4	0.5339

$t_{R(benzaldehyde)} = 4.494$ min; $t_{R(internal\ standard)} = 7.440$ min

$[\text{Area ration}]_{control} = [A_{benzaldehyde}/A_{(intrnal\ standard)}]_{control} = (426479.2/211233.4) = 2.019$

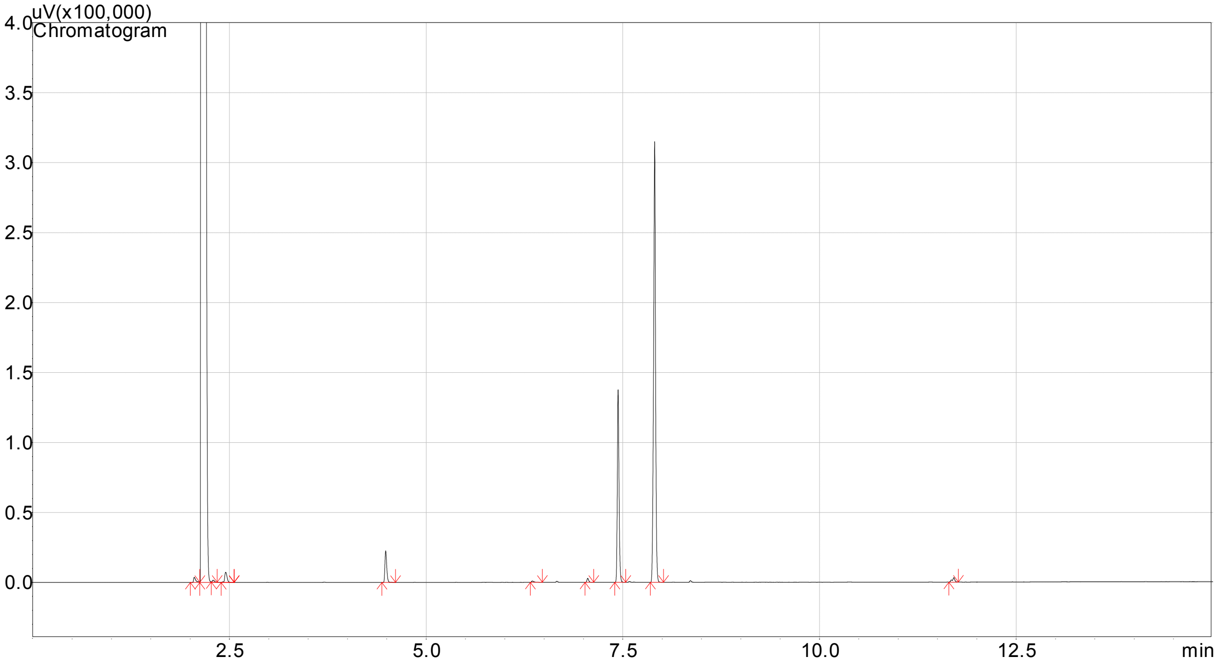


Fig. S35 The GC spectrum of the reaction mixture of the cyanosilylation of benzaldehyde in 2nd run after 4 h.

Table S25 The GC data of the reaction mixture of the cyanosilylation of benzaldehyde in 2nd run after 4 h.

Peak#	Ret. Time	T. Plate	Initial Time	Final Time	Tailing F.	Area	Area%
1	2.053	32683.571	2.002	2.124	--	7333.9	0.0192
2	2.154	17579.340	2.124	2.563	1.650	37275122.7	97.8311
3	2.294	33966.414	2.269	2.343	1.237	2340.0	0.0061
4	2.453	33134.214	2.394	2.558	1.005	15022.8	0.0394
5	4.486	176988.643	4.439	4.611	1.281	36824.1	0.0966
6	6.351	252760.421	6.324	6.478	2.383	2106.6	0.0055
7	7.054	507757.702	7.019	7.131	1.238	4343.4	0.0114
8	7.440	584824.464	7.397	7.537	1.180	205115.6	0.5383
9	7.905	504937.942	7.850	8.018	0.959	546044.3	1.4331
10	11.707	1211677.745	11.644	11.765	0.827	7240.9	0.0190

$t_{R(\text{benzaldehyde})}$ = 4.486 min; $t_{R(\text{internal standard})}$ = 7.440 min; $t_{R(\text{product})}$ = 7.905 min

$[\text{Area ration}]_{4\text{ h}} = [A_{\text{benzaldehyde}}/A_{(\text{intrnal standard})}]_{4\text{ h}} = (36824.1/205115.6) = 0.180$

The conversion of benzaldehyde is calculated as follows:

$$Conv.\% = \frac{[Area\ ratio]_{control} - [Area\ ratio]_{4\ h}}{[Area\ ratio]_{control}} \times 100\%$$

$$= \frac{2.019 - 0.180}{2.019} \times 100\% = 91\%$$

13. In Fig. 4, the conversion benzaldehyde in the 3rd run of the cyanosilylation reaction catalyzed by 0.3 mol% of recycled MIL-101 (Cr) was calculated as follows:

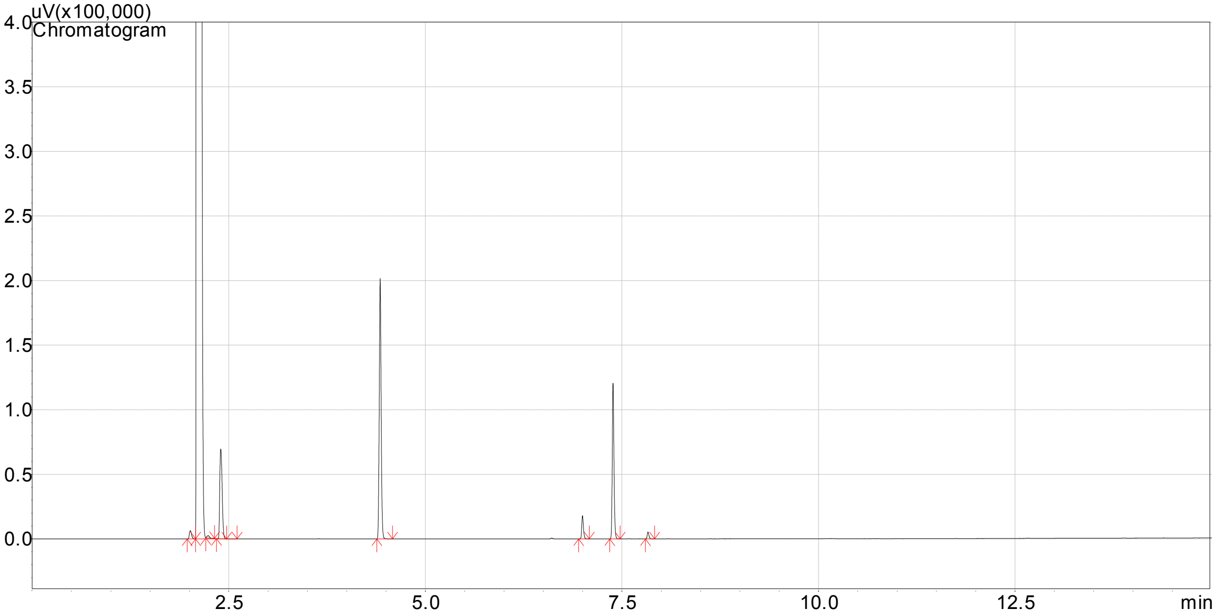


Fig. S36 The GC spectrum of the control solution of the cyanosilylation reaction of benzaldehyde in 3rd run.

Table S26 The GC data of the control solution of the cyanosilylation reaction of benzaldehyde in 3rd run.

Peak#	Ret. Time	T. Plate	Initial Time	Final Time	Tailing F.	Area	Area%
1	2.011	22855.924	1.970	2.077	1.392	12895.2	0.0316
2	2.104	16293.982	2.077	2.604	1.691	40057820.7	98.2575
3	2.238	23903.099	2.208	2.320	1.168	3955.3	0.0097
4	2.398	27455.371	2.343	2.474	1.313	145867.2	0.3578
5	4.426	167544.758	4.383	4.583	1.081	334003.0	0.8193
6	6.999	513727.682	6.949	7.085	1.226	27068.2	0.0664
7	7.387	590163.628	7.346	7.476	1.181	178457.5	0.4377
8	7.832	617027.122	7.798	7.915	1.257	8149.5	0.0200

$t_{R(\text{benzaldehyde})}$ = 4.426 min; $t_{R(\text{internal standard})}$ = 7.387 min

[Area ration]$_{\text{control}}$ = [A$_{\text{benzaldehyde}}$/A$_{\text{(intrnal standard)}}$]$_{\text{control}}$ = (334003.0/178457.5) = 1.872

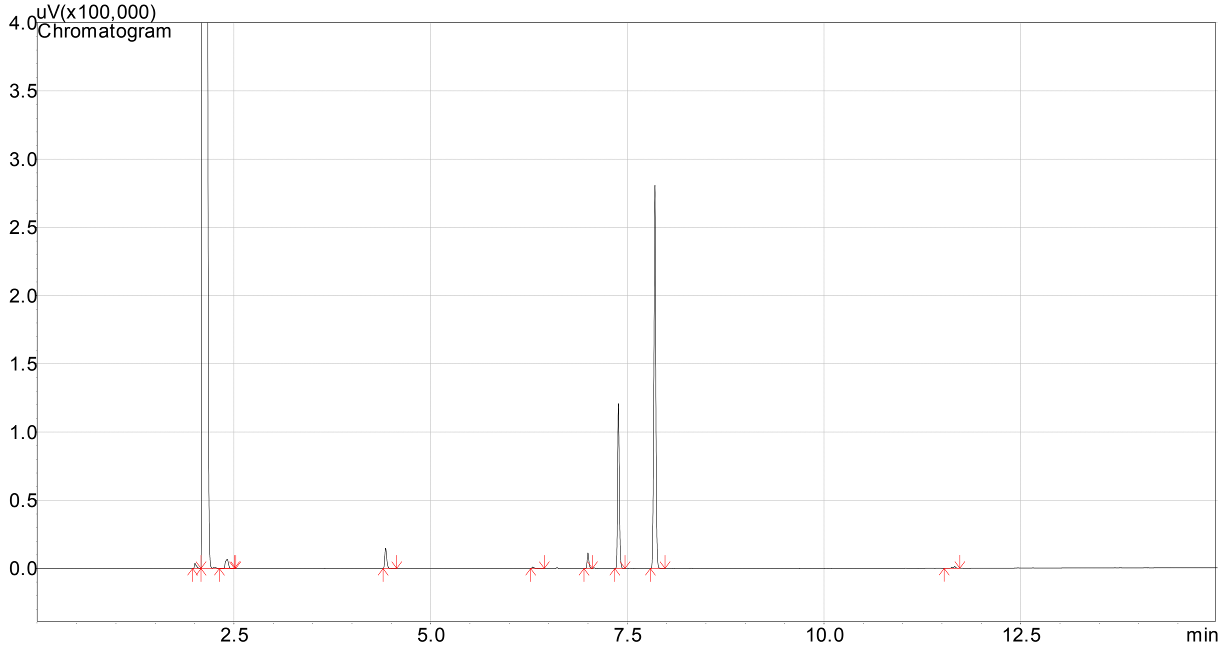


Fig. S37 The GC spectrum of the reaction mixture of the cyanosilylation of benzaldehyde in 3rd run after 4 h.

Table S27 The GC data of the reaction mixture of the cyanosilylation of benzaldehyde in 3rd run after 4 h.

Peak#	Ret. Time	T. Plate	Initial Time	Final Time	Tailing F.	Area	Area%
1	2.006	26872.003	1.974	2.082	2.243	7453.7	0.0183
2	2.107	9916.055	2.082	2.525	1.965	40010509.2	98.2071
3	2.414	16154.863	2.315	2.507	1.028	17910.7	0.0440
4	4.428	151456.275	4.396	4.569	1.307	26416.1	0.0648
5	6.299	262887.728	6.273	6.445	3.274	2727.0	0.0067
6	7.000	495043.416	6.949	7.056	1.233	17454.4	0.0428
7	7.387	575691.874	7.341	7.472	1.178	181178.3	0.4447
8	7.851	525187.513	7.794	7.981	0.974	474132.0	1.1638
9	11.662	1089254.708	11.527	11.728	0.844	3170.8	0.0078

$t_{R(\text{benzaldehyde})}$ = 4.428 min; $t_{R(\text{internal standard})}$ = 7.387 min; $t_{R(\text{product})}$ = 7.851 min

$[\text{Area ration}]_{4\text{ h}} = [A_{\text{benzaldehyde}}/A_{(\text{intrnal standard})}]_{4\text{ h}} = (26416.1/181178.3) = 0.146$

The conversion of benzaldehyde is calculated as follows:

$$Conv.\% = \frac{[Area\ ratio]_{control} - [Area\ ratio]_{4\ h}}{[Area\ ratio]_{control}} \times 100\%$$

$$= \frac{1.872 - 0.146}{1.872} \times 100\% = 92\%$$

14. In Fig. 4, the conversion benzaldehyde in the 4th run of the cyanosilylation reaction catalyzed by 0.3 mol% of recycled MIL-101 (Cr) was calculated as follows:

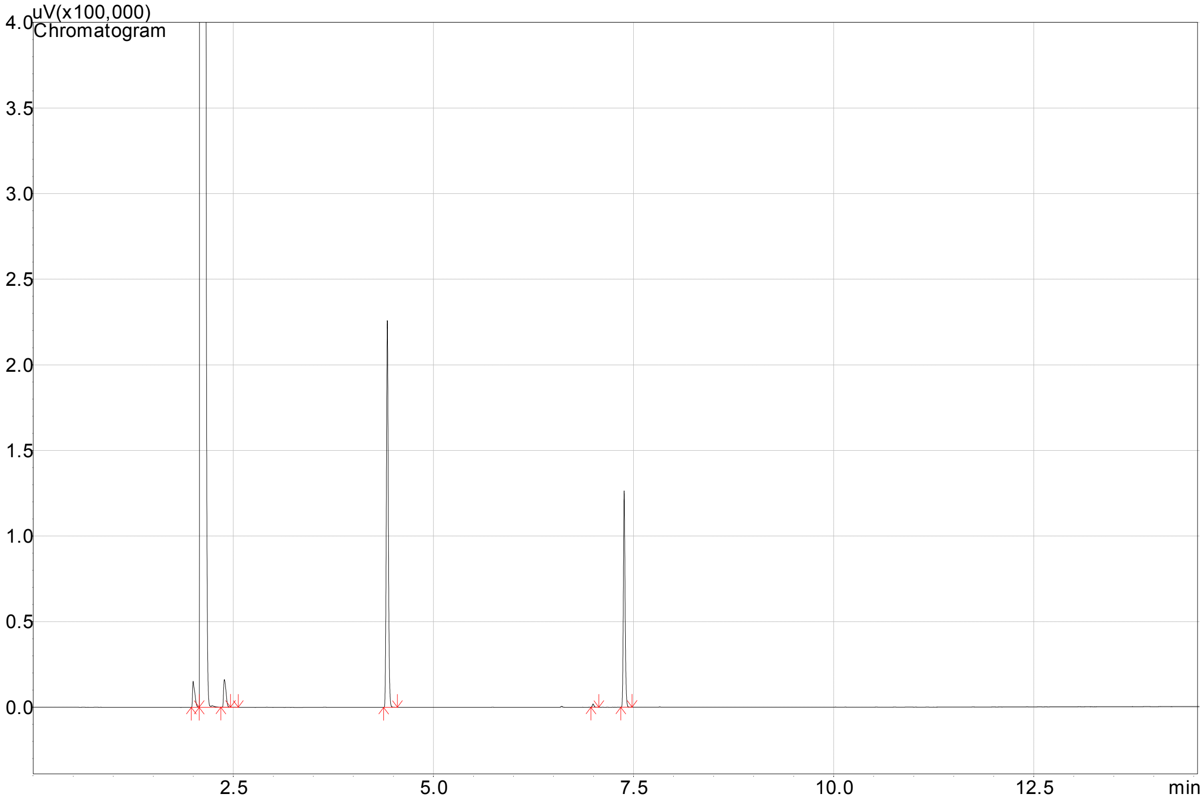


Fig. S38 The GC spectrum of the control solution of the cyanosilylation reaction of benzaldehyde in 4th run.

Table S28 The GC data of the control solution of the cyanosilylation reaction of benzaldehyde in 4th run.

Peak#	Ret. Time	T. Plate	Initial Time	Final Time	Tailing F.	Area	Area%
1	1.998	20775.165	1.974	2.072	2.015	30023.2	0.0757
2	2.096	10762.724	2.072	2.562	2.129	39027452.5	98.3885
3	2.389	26996.602	2.343	2.464	1.628	33938.7	0.0856
4	4.424	157356.489	4.378	4.550	1.062	383637.8	0.9672
5	6.994	502082.669	6.968	7.066	1.280	3027.3	0.0076
6	7.383	576630.634	7.341	7.481	1.179	188608.0	0.4755

$t_{R(\text{benzaldehyde})}$ = 4.424 min; $t_{R(\text{internal standard})}$ = 7.383 min
[Area ration]$_{\text{control}}$ = [A$_{\text{benzaldehyde}}$/A$_{\text{(intrnal standard)}}$]$_{\text{control}}$ = (383637.8/188608.0) = 2.034

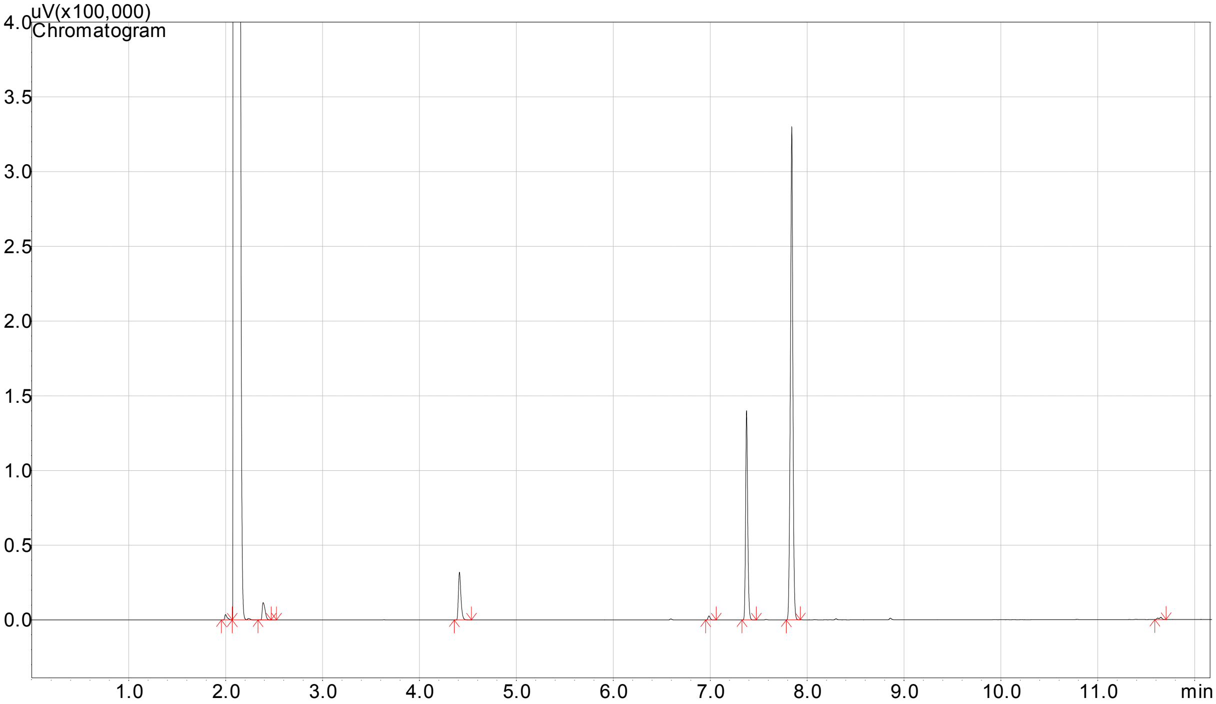


Fig. S39 The GC spectrum of the reaction mixture of the cyanosilylation of benzaldehyde in 4th run after 4 h.

Table S29 The GC data of the reaction mixture of the cyanosilylation of benzaldehyde in 4th run after 4 h.

Peak#	Ret. Time	T. Plate	Initial Time	Final Time	Tailing F.	Area	Area%
1	1.999	31593.083	1.956	2.068	2.231	6951.6	0.0175
2	2.096	13983.341	2.068	2.525	1.865	38755307.2	97.7601
3	2.388	28547.357	2.334	2.469	1.657	24578.6	0.0620
4	4.413	143349.933	4.359	4.537	1.379	58455.9	0.1475
5	6.987	467641.329	6.954	7.061	1.252	4218.5	0.0106
6	7.376	577218.070	7.327	7.477	1.166	209882.5	0.5294
7	7.842	478470.963	7.785	7.929	0.953	580107.9	1.4633
8	11.650	1056012.420	11.588	11.705	0.817	3784.8	0.0095

$t_{R(\text{benzaldehyde})}$ = 4.413 min; $t_{R(\text{internal standard})}$ = 7.376 min; $t_{R(\text{product})}$ = 7.842 min

$[\text{Area ration}]_{4\text{ h}} = [A_{\text{benzaldehyde}}/A_{(\text{intrnal standard})}]_{4\text{ h}} = (58455.9/209882.5) = 0.278$

The conversion of benzaldehyde is calculated as follows:

$$Conv.\% = \frac{[Area\ ratio]_{control} - [Area\ ratio]_{4\ h}}{[Area\ ratio]_{control}} \times 100\%$$

$$= \frac{2.034 - 0.278}{2.034} \times 100\% = 86\%$$

S7. ^{1}H NMR spectra for the determination of the yields of the cyanosilylation reaction

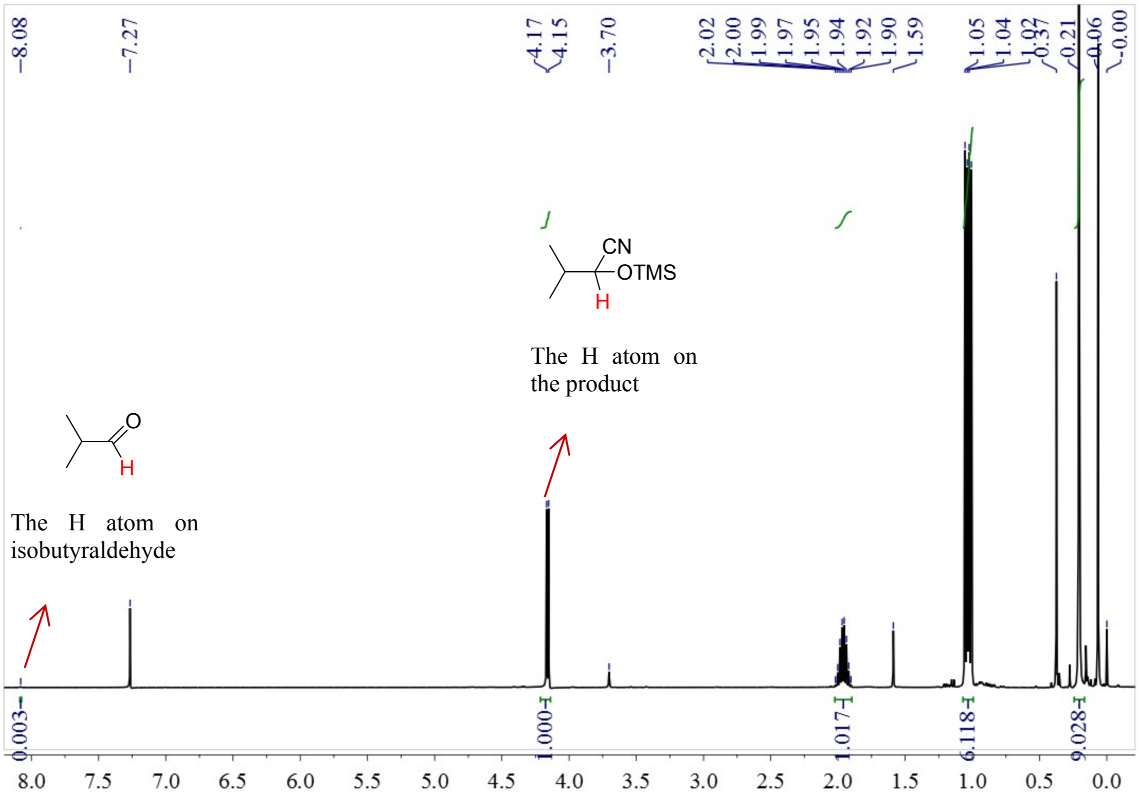


Fig. S40 The ^{1}H NMR spectra for the determination of the yields of the cyanosilylation reaction of isobutyraldehyde (Table 4, entry 1).

The yield of 3-methyl-2-trimethylsilyloxybutanenitrile is calculated as follows:

$$Yield\% = \frac{1}{1 + 0.003} \times 100\% \approx 100\%$$

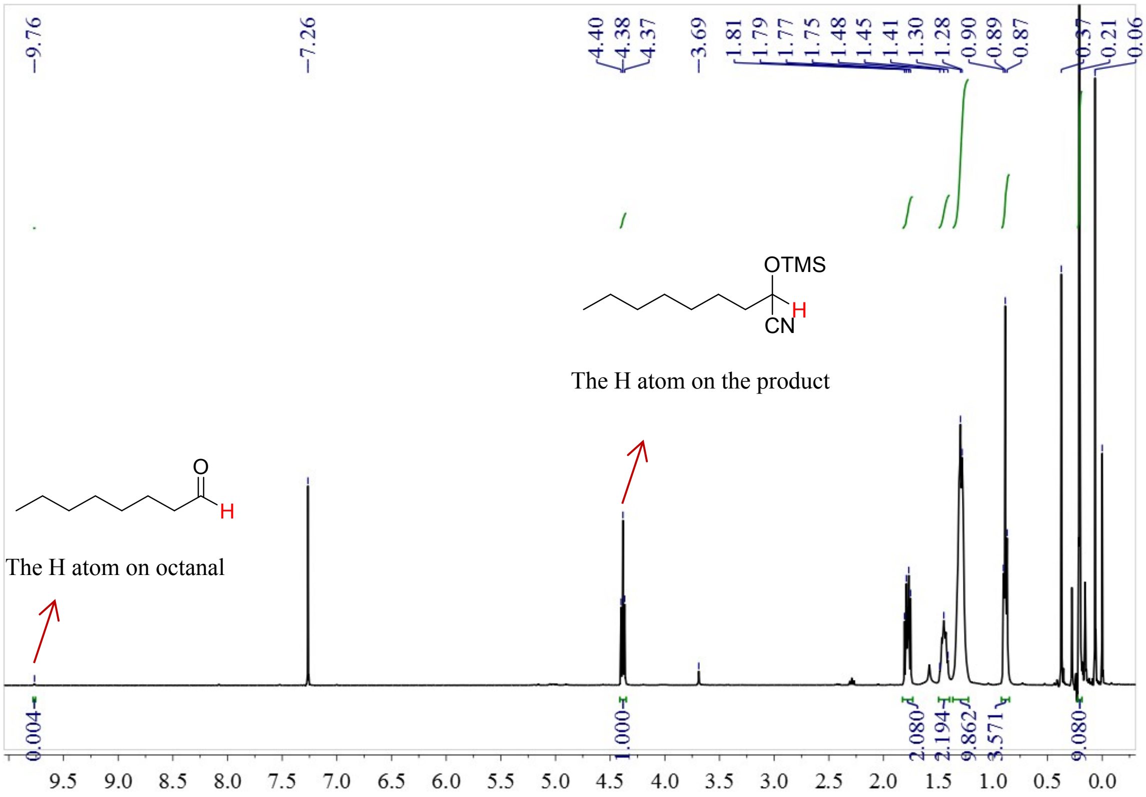


Fig. S41 The ^{1}H NMR spectra for the determination of the yields of the cyanosilylation reaction of octanal (Table 4, entry 2).

The yield of 2-trimethylsilyloxynonanenitrile is calculated as follows:

$$Yield\% = \frac{1}{1+0.004} \times 100\% \approx 100\%$$

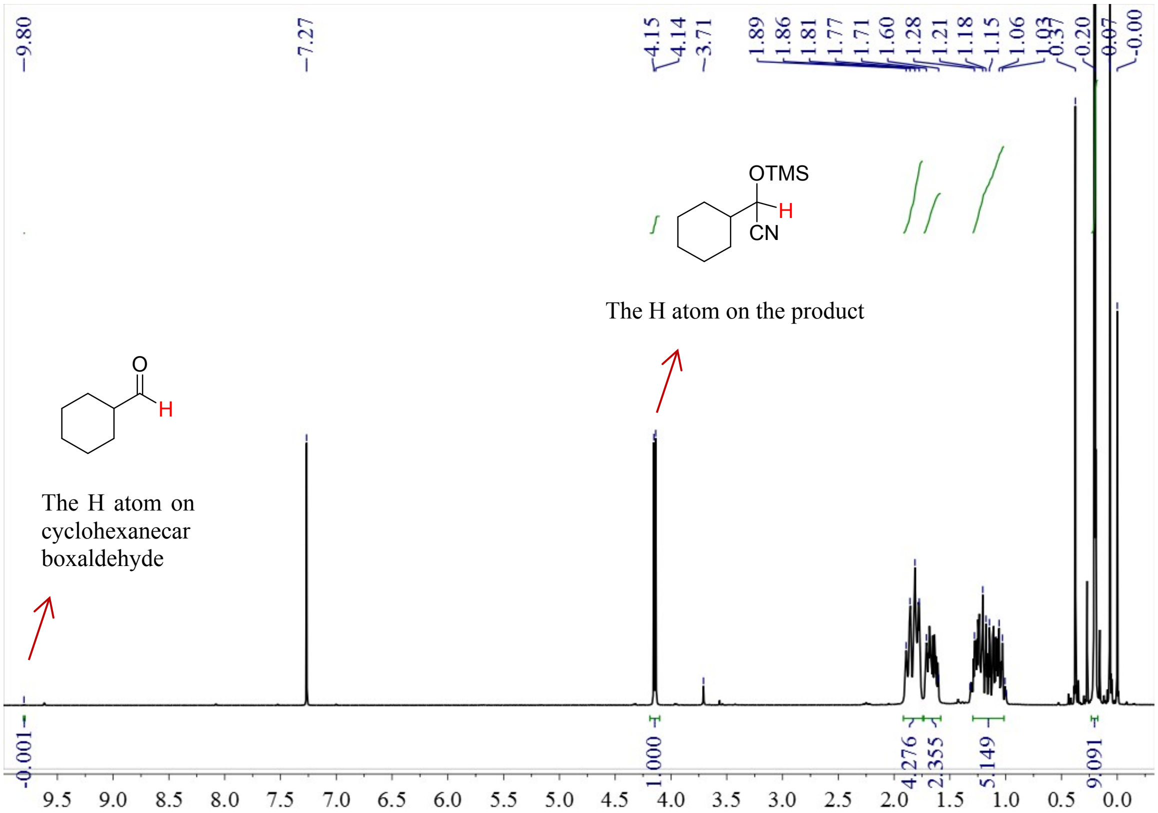


Fig. S42 The ^1H NMR spectra for the determination of the yields of the cyanosilylation reaction of cyclohexanecarboxaldehyde (Table 4, entry 3).

The yield of 2-cyclohexyl-2-trimethylsilyloxyacetonitrile is calculated as follows:

$$Yield\% = \frac{1}{1+0.001} \times 100\% \approx 100\%$$

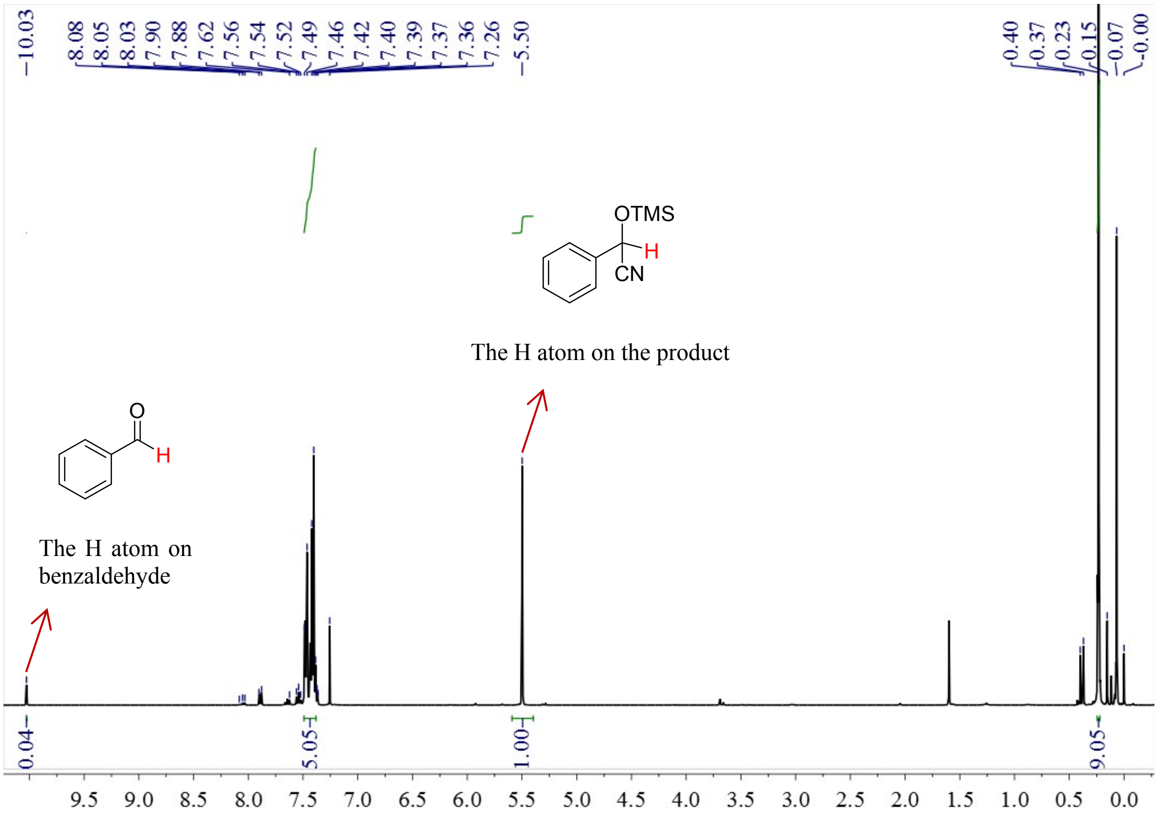
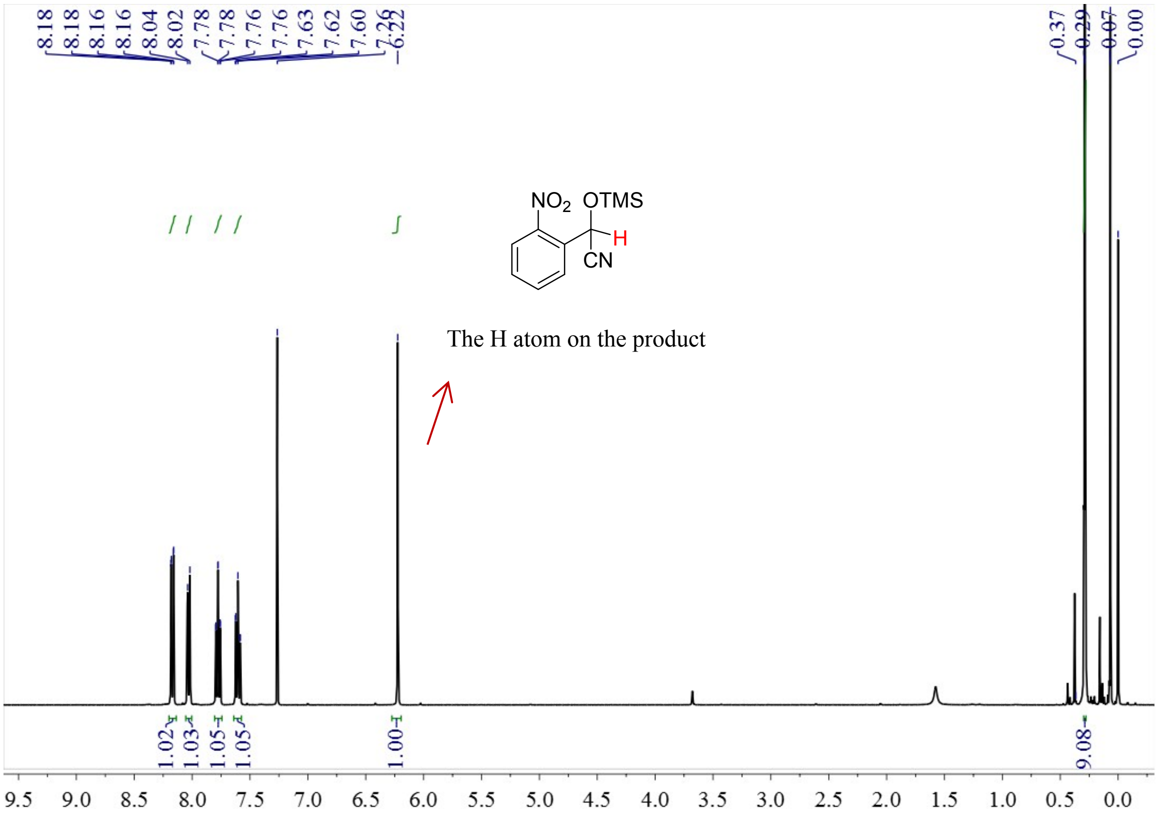


Fig. S43 The ^{1}H NMR spectra for the determination of the yields of the cyanosilylation reaction of benzaldehyde (Table 4, entry 4).

The yield of 2-phenyl-2-trimethylsilyloxyacetonitrile is calculated as follows:

$$Yield\% = \frac{1}{1 + 0.04} \times 100\% = 96\%$$



The H atom on the product

Fig. S44 The ^{1}H NMR spectra for the determination of the yields of the cyanosilylation reaction of 2-nitrobenzaldehyde (Table 4, entry 5).

There was no aldehyde detected on the ^{1}H NMR spectra of the reaction mixture, so the yield is 100%.

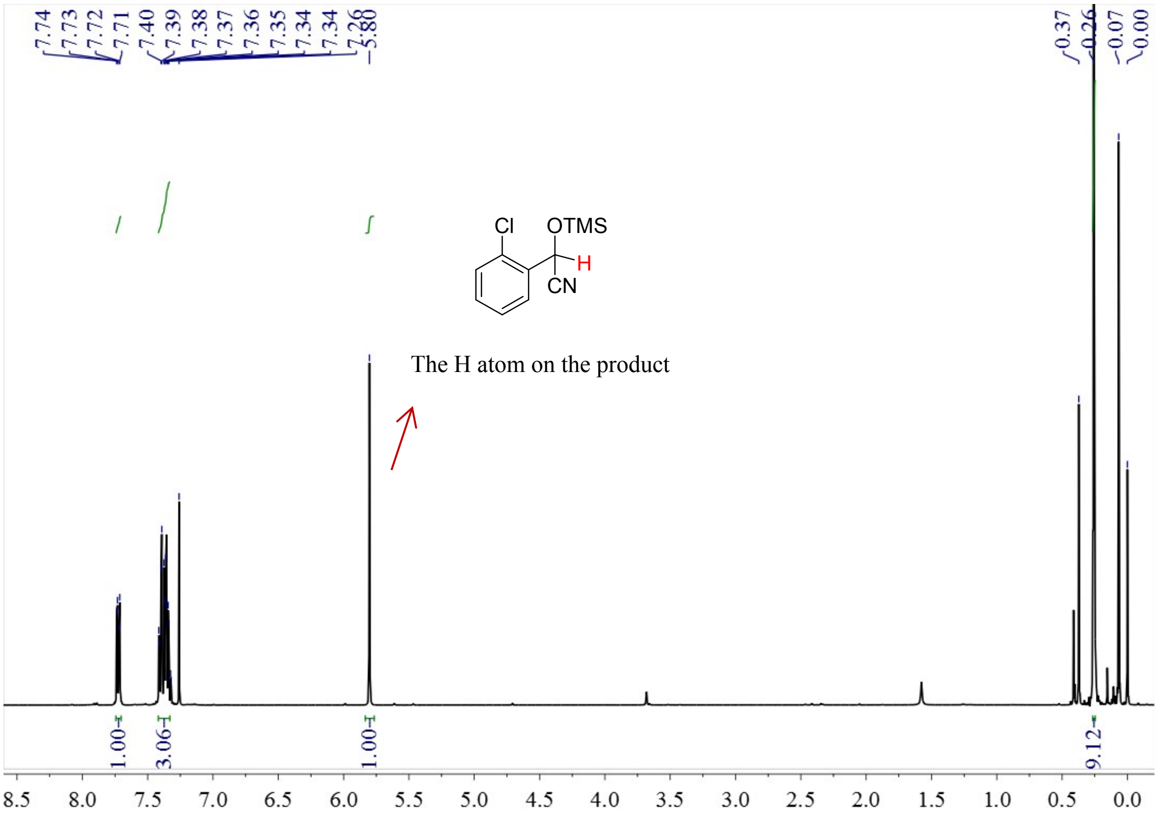


Fig. S45 The ^{1}H NMR spectra for the determination of the yields of the cyanosilylation reaction of 2-chlorobenzaldehyde (Table 4, entry 6).

There was no aldehyde detected on the ^{1}H NMR spectra of the reaction mixture, so the yield is 100%.

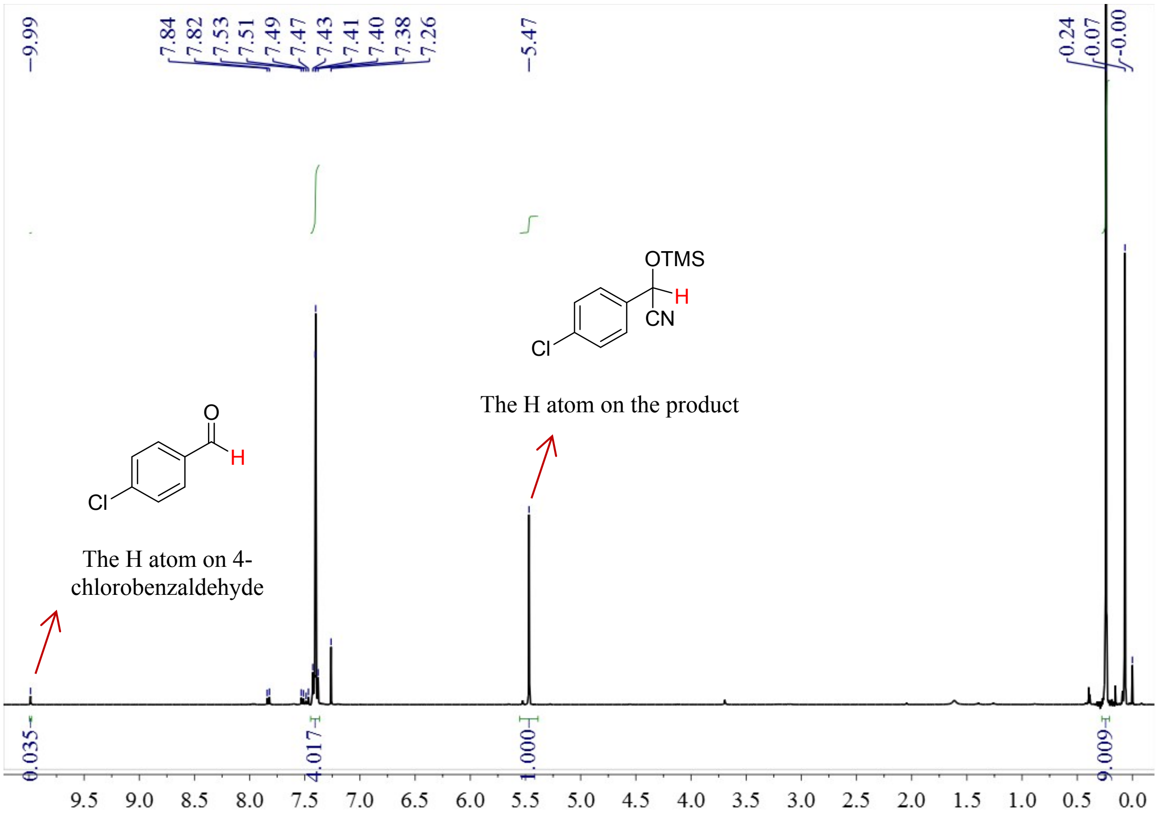
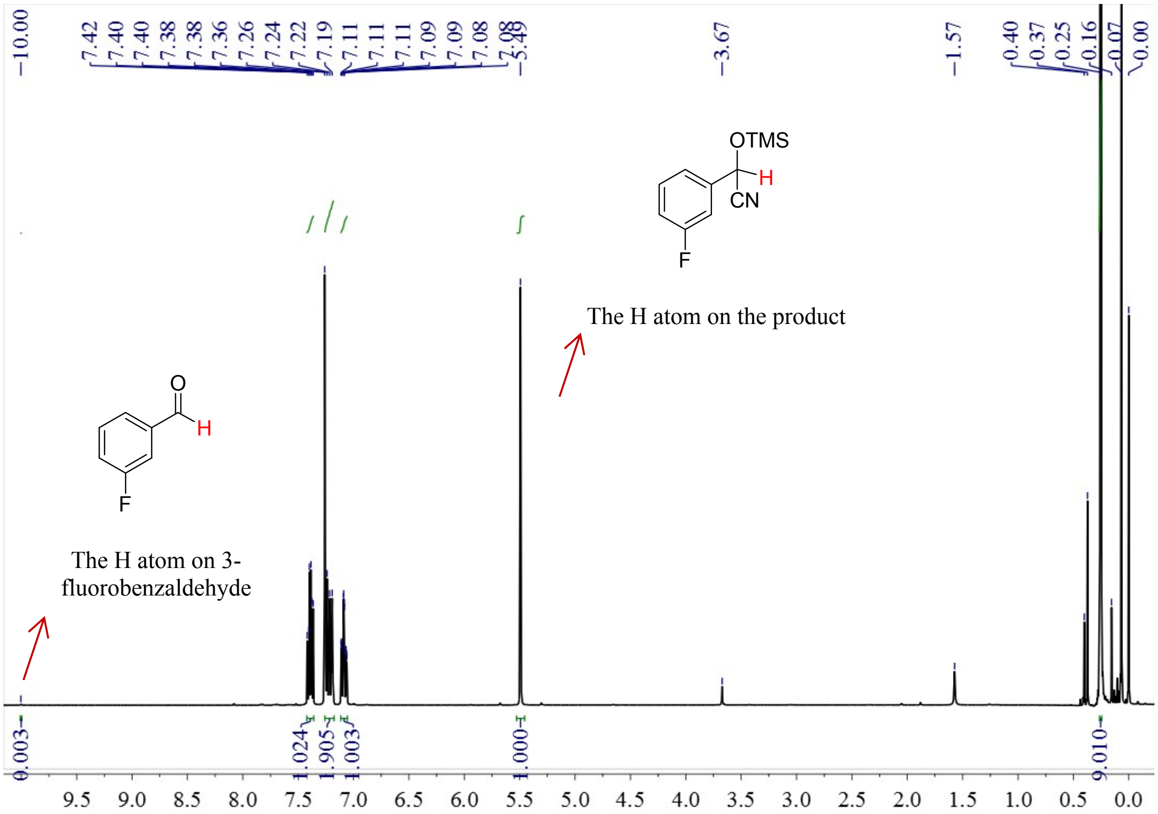


Fig. S46 The ^{1}H NMR spectra for the determination of the yields of the cyanosilylation reaction of 4-chlorobenzaldehyde (Table 4, entry 7).

The yield of 2-(4-chlorophenyl)-2-trimethylsilyloxyacetonitrile is calculated as follows:

$$Yield\% = \frac{1}{1 + 0.035} \times 100\% = 97\%$$



The H atom on the product

The H atom on 3-fluorobenzaldehyde

Fig. S47 The ^{1}H NMR spectra for the determination of the yields of the cyanosilylation reaction of 3-fluorobenzaldehyde (Table 4, entry 8).

The yield of 2-(3-fluorophenyl)-2-Trimethylsilyloxyacetonitrile is calculated as follows:

$$Yield\% = \frac{1}{1 + 0.003} \times 100\% \approx 100\%$$

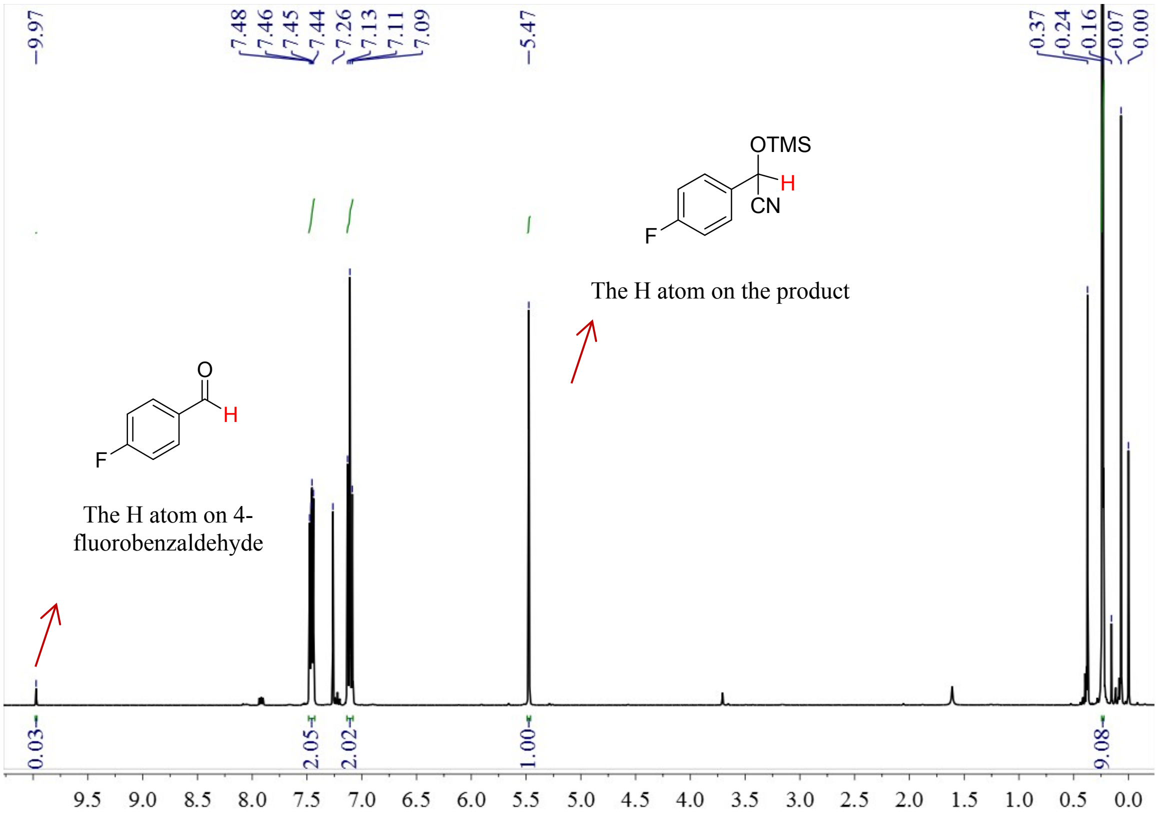


Fig. S48 The ^{1}H NMR spectra for the determination of the yields of the cyanosilylation reaction of 4-fluorobenzaldehyde (Table 4, entry 9).

The yield of 2-(4-fluorophenyl)-2-trimethylsilyloxyacetonitrile is calculated as follows:

$$Yield\% = \frac{1}{1 + 0.03} \times 100\% = 97\%$$

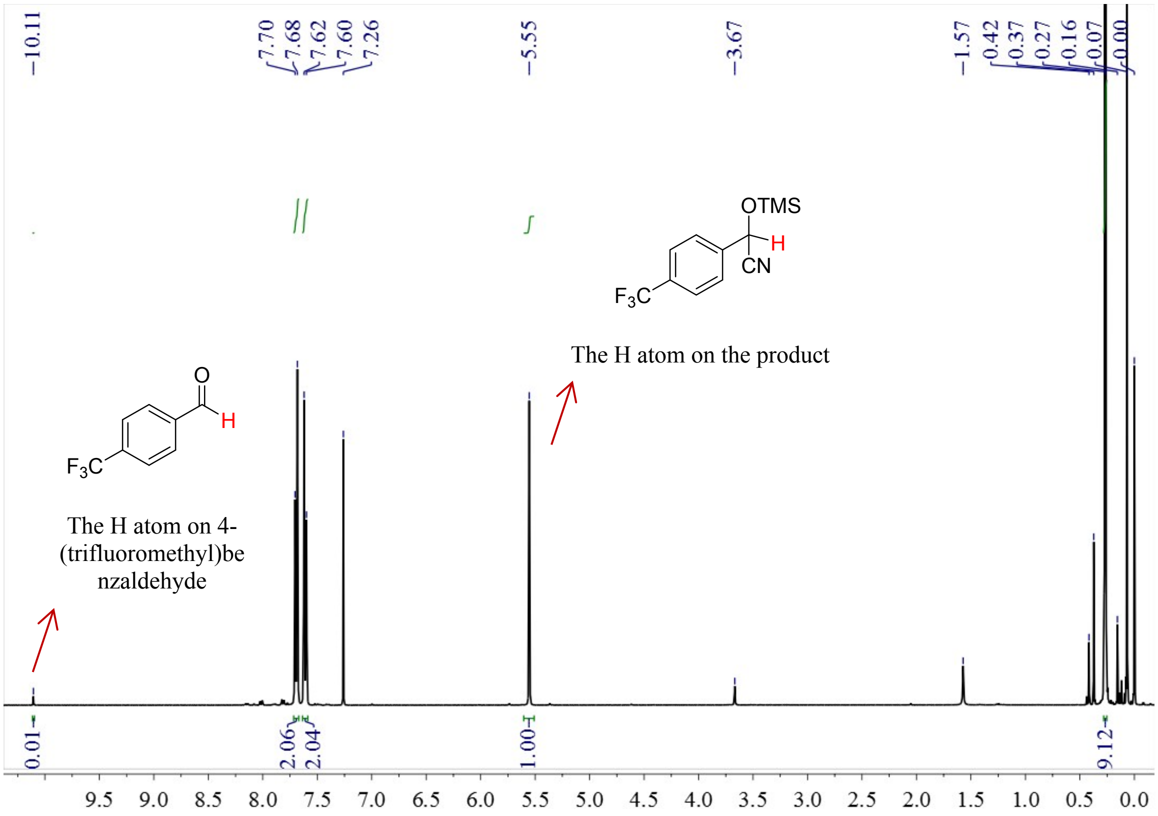


Fig. S49 The ^{1}H NMR spectra for the determination of the yields of the cyanosilylation reaction of 4-(trifluoromethyl)benzaldehyde (Table 4, entry 10).

The yield of 2-(4-trifluoromethylphenyl)-2-trimethylsilyloxyacetonitrile is calculated as follows:

$$Yield\% = \frac{1}{1 + 0.01} \times 100\% = 99\%$$

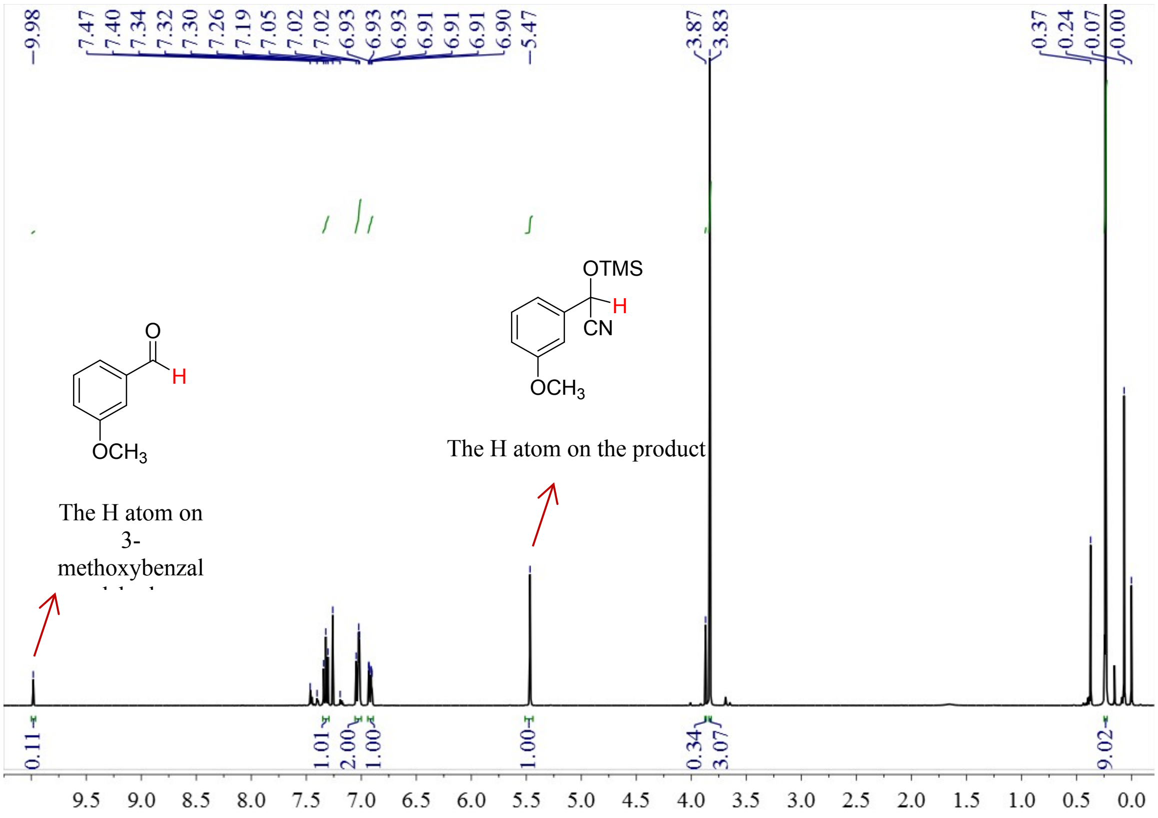


Fig. S50 The ^{1}H NMR spectra for the determination of the yields of the cyanosilylation reaction of 3-methoxybenzaldehyde (Table 4, entry 11).

The yield of 2-(3-methoxyphenyl)-2-trimethylsilyloxyacetonitrile is calculated as follows:

$$Yield\% = \frac{1}{1+0.11} \times 100\% = 90\%$$

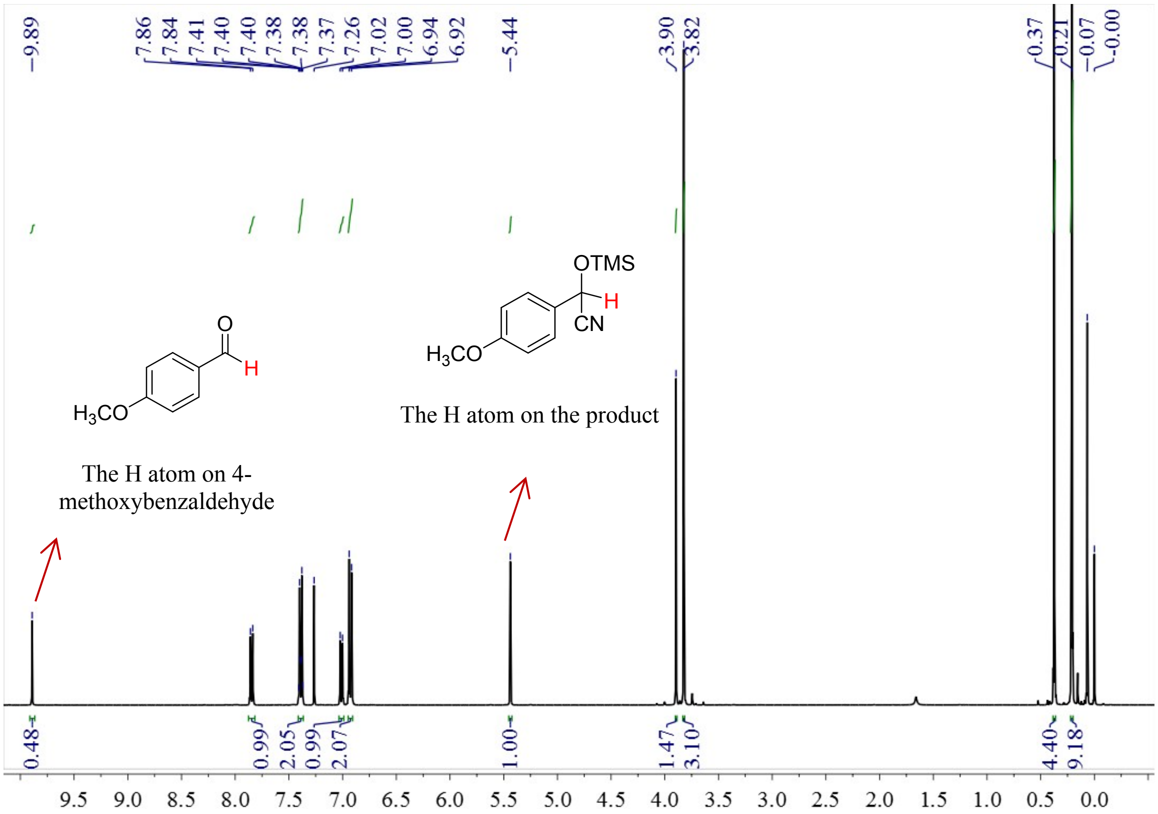


Fig. S51 The ^{1}H NMR spectra for the determination of the yields of the cyanosilylation reaction of 4-methoxybenzaldehyde (Table 4, entry 12).

The yield of 2-(4-methoxyphenyl)-2-trimethylsilyloxyacetonitrile is calculated as follows:

$$Yield\% = \frac{1}{1 + 0.48} \times 100\% = 68\%$$

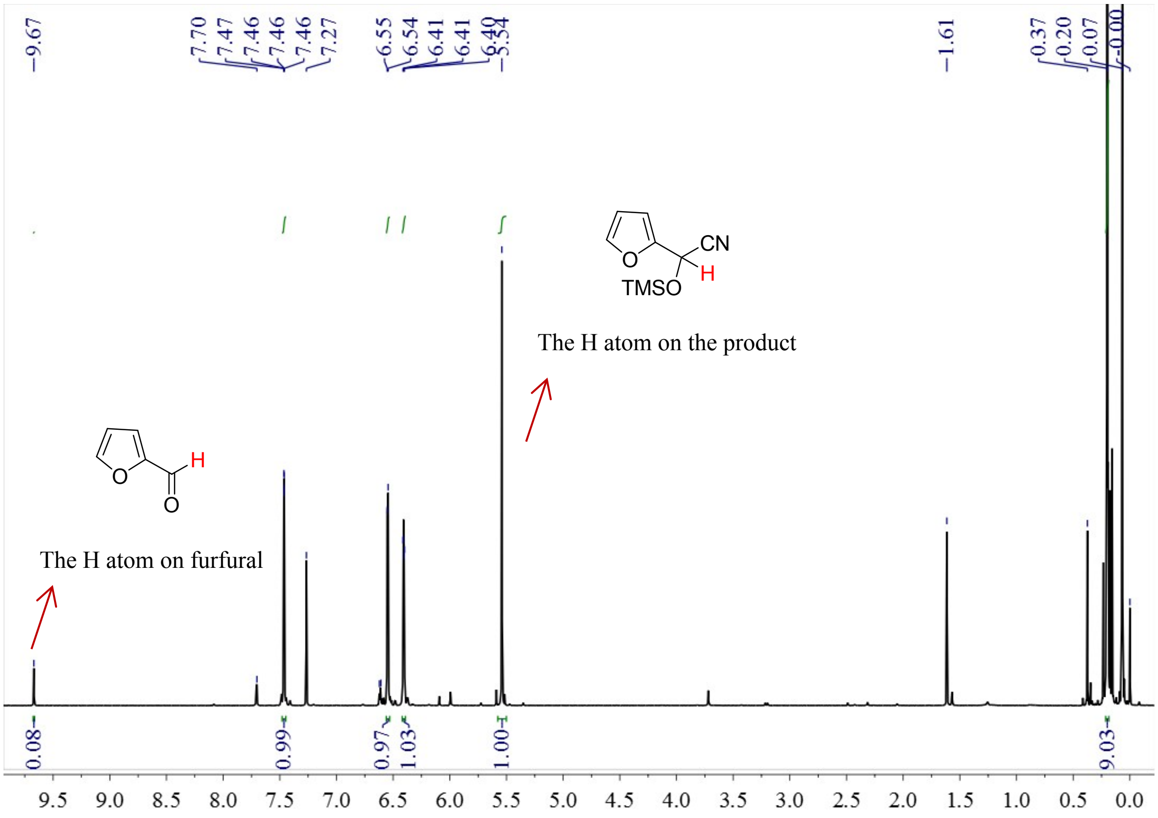


Fig. S52 The ^{1}H NMR spectra for the determination of the yields of the cyanosilylation reaction of furfural (Table 4, entry 13).

The yield of 2-furanyl-2-trimethylsilyloxyacetonitrile is calculated as follows:

$$Yield\% = \frac{1}{1+0.08} \times 100\% = 93\%$$

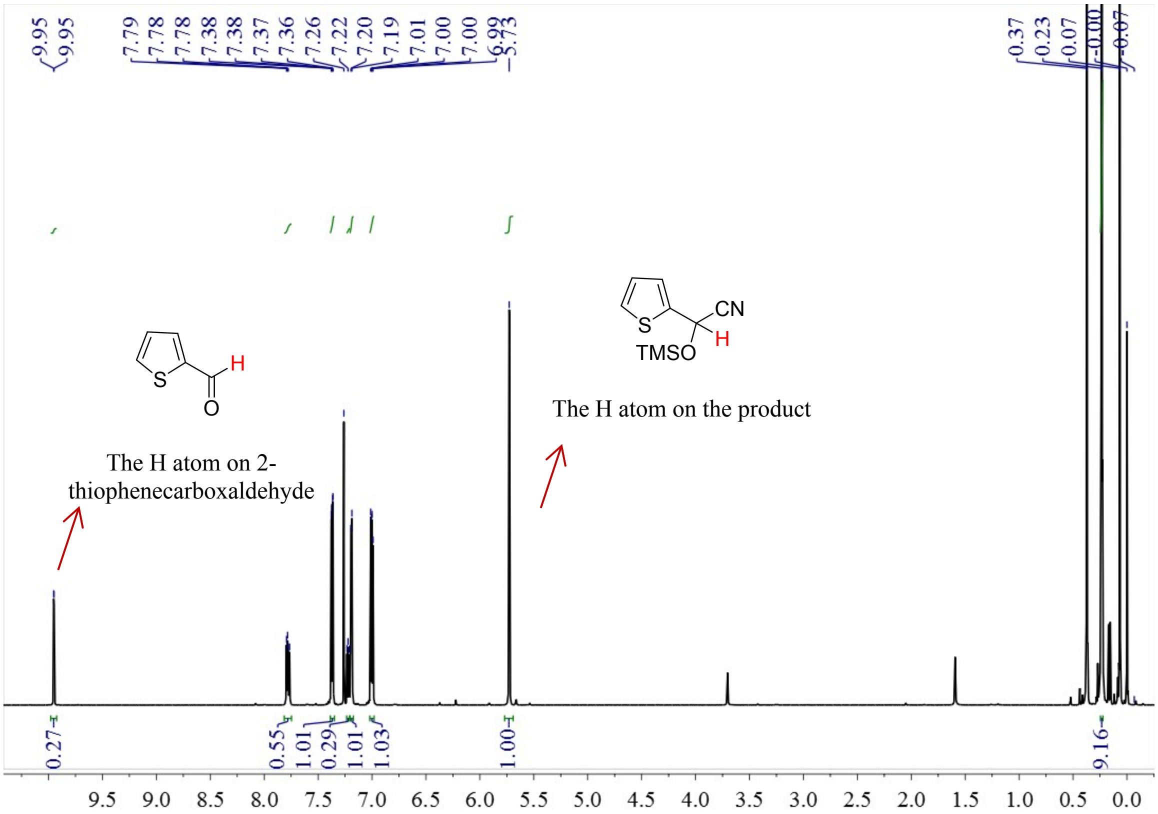


Fig. S53 The ^{1}H NMR spectra for the determination of the yields of the cyanosilylation reaction of 2-thiophenecarboxaldehyde (Table 4, entry 14).

The yield of 2-thienyl-2-trimethylsilyloxyacetonitrile is calculated as follows:

$$Yield\% = \frac{1}{1+0.27} \times 100\% = 79\%$$

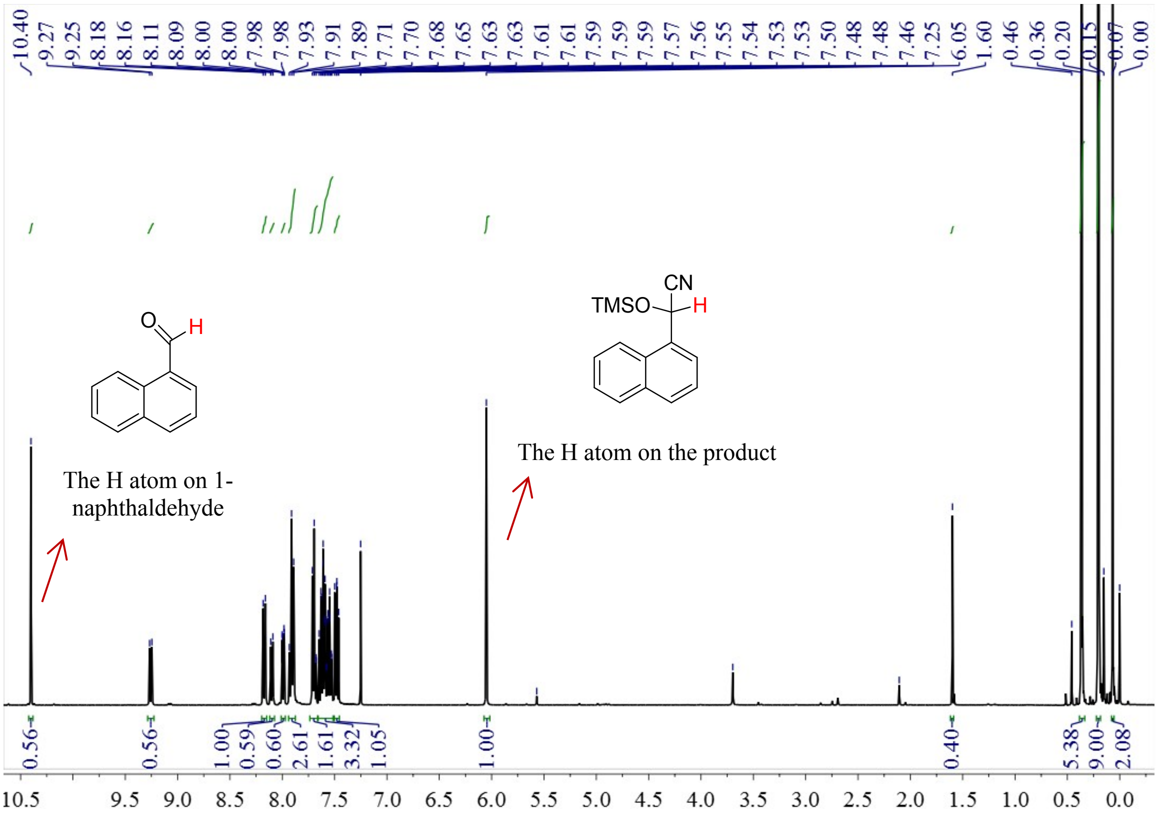


Fig. S54 The ^{1}H NMR spectra for the determination of the yields of the cyanosilylation reaction of 1-naphthaldehyde (Table 4, entry 15).

The yield of 2-naphthyl-2-trimethylsilyloxyacetonitrile is calculated as follows:

$$Yield\% = \frac{1}{1 + 0.56} \times 100\% = 64\%$$

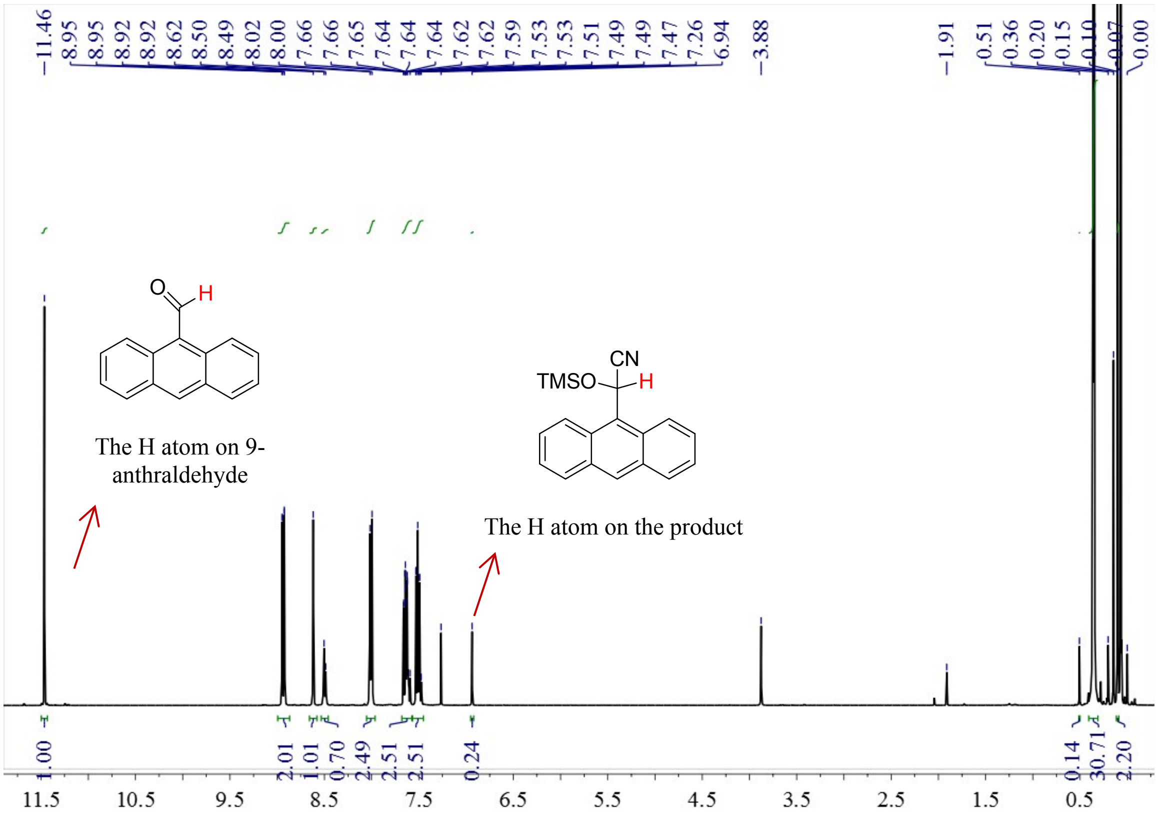


Fig. S55 The ^{1}H NMR spectra for the determination of the yields of the cyanosilylation reaction of 9-anthraldehyde (Table 4, entry 16).

The yield of 9-anthryl-2-trimethylsilyloxyacetonitrile is calculated as follows:

$$Yield\% = \frac{0.24}{1 + 0.24} \times 100\% = 19\%$$

S8. ^{1}H NMR spectral data of the product

3-methyl-2-trimethylsilyloxybutanenitrile (Table 4, Entry 1): ^{1}H NMR (400 MHz, CDCl$_3$): δ 4.16 (d, 1H, J = 5.9 Hz, CHCN), 2.02-1.90 (dq, 1H, J = 12.4, 6.7 Hz CH(CH$_3$)$_2$), 1.05-1.01 (dd, 6H, J = 12.4, 6.7 Hz, CH(CH$_3$)$_2$), 0.21 (s, 9H, Si(CH$_3$)$_3$).

2-trimethylsilyloxynonanenitrile (Table 4, Entry 2): ^{1}H NMR (400 MHz, CDCl$_3$): δ 4.38 (t, 1H, J = 6.6 Hz, CHCN), 1.81-1.75 (m, 2H, CH$_2$CHCN), 1.48-1.28 (m, 10H, (CH$_2$)$_5$CH$_3$), 0.89 (t, J = 6.9 Hz, 3H, CH$_2$CH$_3$), 0.21 (s, 9H, Si(CH$_3$)$_3$).

2-cyclohexyl-2-trimethylsilyloxyacetonitrile (Table 4, Entry 3): ^{1}H NMR (400 MHz, CDCl$_3$): δ 4.14 (d, 1H, J = 6.4 Hz, CHCN), 1.89-1.60 (m, 6H, protons of cyclohexyl), 1.32-0.99 (m, 5H, protons of cyclohexyl), 0.20 (s, 9H, Si(CH$_3$)$_3$).

2-phenyl-2-trimethylsilyloxyacetonitrile (Table 4, Entry 4): ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.49-7.39 (m, 5H, aromatics), 5.50 (s, 1H, CHCN), 0.23 (s, 9H, Si(CH$_3$)$_3$).

(2-nitrophenyl)trimethylsilyloxyacetonitrile (Table 4, Entry 5): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18-8.16 (d, 1 H, *J* = 8.2, 1.2 Hz, aromatic), 8.04-8.02 (d, 1 H, *J* = 8.2 Hz, aromatic), 7.80-7.76 (td, 1 H, *J* = 7.7, aromatic), 7.63-7.58 (t, 1 H, *J* = 7.7 Hz, aromatic), 6.22 (s, 1 H, CHCN), 0.29 (s, 9 H, $Si(CH_3)_3$).

2-(2-chlorophenyl)-2-trimethylsilyloxyacetonitrile (Table 4, Entry 6): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74-7.71 (m, 1H, aromatic), 7.41-7.32 (m, 3H, aromatics), 5.80 (s, 1H, CHCN), 0.26 (s, 9H, $Si(CH_3)_3$).

2-(4-chlorophenyl)-2-trimethylsilyloxyacetonitrile (Table 4, Entry 7): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.38 (m, 4H, aromatics), 5.47 (s, 1H, CHCN), 0.24 (s, 9H, $Si(CH_3)_3$).

2-(3-fluorophenyl)-2-Trimethylsilyloxyacetonitrile (Table 4, Entry 8): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.36 (td, 1H, *J* = 8.0, 5.7 Hz, aromatic), 7.24-7.19 (m, 2H, aromatics), 7.11-7.06 (tdd, 1H, *J* = 6.0, 2.6, 0.8 Hz, aromatic), 5.49 (s, 1H, CHCN), 0.25 (s, 9H, $Si(CH_3)_3$).

2-(4-fluorophenyl)-2-trimethylsilyloxyacetonitrile (Table 4, Entry 9): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (dd, *J* = 8.7, 5.2 Hz, 2H, aromatics), 7.11 (t, *J* = 8.7 Hz, 2H, aromatics), 5.47 (s, 1H, CHCN), 0.24 (s, 9H, $Si(CH_3)_3$).

2-(4-trifluoromethylphenyl)-2-trimethylsilyloxyacetonitrile (Table 4, Entry 10): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.2 Hz, 2H, aromatics), 7.61 (d, *J* = 8.2 Hz, 2H, aromatics), 5.55 (s, 1H, CHCN), 0.27 (s, 9H, $Si(CH_3)_3$).

2-(3-methoxyphenyl)-2-trimethylsilyloxyacetonitrile (Table 4, Entry 11): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (t, 1H, *J* = 7.9 Hz, aromatics), 7.05-7.02 (m, 2H, aromatics), 6.92 (dd, 1H, *J* = 8.2, 2.0 Hz aromatic), 5.47 (s, 1H, CHCN), 3.83 (s, 3H, CH_3O), 0.24 (s, 9H, $Si(CH_3)_3$).

2-(4-methoxyphenyl)-2-trimethylsilyloxyacetonitrile (Table 4, Entry 12): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, 2H, *J* = 8.8 Hz, aromatics), 6.93 (d, 2H, *J* = 8.8 Hz, aromatics), 5.44 (s, 1H, CHCN), 3.82 (s, 3H, CH_3O), 0.21 (s, 9H, $Si(CH_3)_3$).

2-furanyl-2-trimethylsilyloxyacetonitrile (Table 4, Entry 13): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (dd, 1H, *J* = 1.8, 0.7 Hz, OCH), 6.55 (d, 1H, *J* = 3.3 Hz, CCH), 6.40 (dd, 1H, *J* = 3.3, 1.8 Hz, CH), 5.54 (s, 1H, CHCN), 0.20 (s, 9H, $Si(CH_3)_3$).

2-thienyl-2-trimethylsilyloxyacetonitrile (Table 4, Entry 14): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.19 (d, *J* = 3.6 Hz, 1H), 7.00 (dd, *J* = 5.1, 3.6 Hz, 1H), 5.73 (s, 1H), 0.23 (s, 9H).

2-naphthyl-2-trimethylsilyloxyacetonitrile (Table 4, Entry 15): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, 1H, aromatic), 7.93-7.89 (t, 2H, aromatics), 7.71-7.67 (d, 1H, aromatic), 7.65-7.53 (m, 2H, aromatics), 7.48 (td, 1H, aromatic), 6.05 (s, 1H, CHCN), 0.20 (s, 9H, $Si(CH_3)_3$).

9-anthryl-2-trimethylsilyloxyacetonitrile (Table 4, Entry 16): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (d, 3H, aromatics), 8.01 (d, 2H, aromatics), 7.64 (ddd, 2H, *J* = 8.9, 6.7, 1.4 Hz, aromatics), 7.57-7.45 (m, 2H, *J* = 8.2, 6.7 Hz, aromatics), 6.94 (s, 1H, CHCN), 0.10 (s, 9H, $Si(CH_3)_3$).

S7. References

1 K. Barthelet, J. Marrot, D. Riou and G. Férey, *Angew. Chem., Int. Ed.*, 2002, **41**, 281.

2 T. Loiseau, C. Serre, C. Huguenard, G. Fink, F. Taulelle, M. Henry, T. Bataille and G. Férey, *Chem.—Eur. J.*, 2004, **10**, 1373.

3 (a) G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé and I. Margiolaki, *Science*, 2005, **309**, 2040; (b) K. Yang, Q. Sun, F. Xue and D. H. Lin, *J. Hazard. Mater.*, 2011, **195**, 124.
4 J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga and K. P. Lillerud, *J. Am. Chem. Soc.*, 2008, **130**, 13850.
5 L. M. Aguirre-Díaz, F. Gándara, M. Iglesias, N. Snejko, E. Gutiérrez-Puebla and M. Á. Monge, *J. Am. Chem. Soc.*, 2015, **137**, 6132.
6 M. Fujita, Y. J. Kwon, S. Washizu and K. Ogura, *J. Am. Chem. Soc.*, 1994, **116**, 1151.
7 O. R. Evans, H. L. Ngo and W. B. Lin, *J. Am. Chem. Soc.*, 2001, **123**, 10395.
8 K. Schlichte, T. Kratzke and S. Kaskel, *Microporous Mesoporous Mater.*, 2004, **73**, 81.
9 A. Henschel, K. Gedrich, R. Kraehnert and S. Kaskel, *Chem. Commun.*, 2008, 4192.
10 S. Horike, M. Dincă, K. Tamaki and J. R. Long, *J. Am. Chem. Soc.*, 2008, **130**, 5854.
11 F. Gándara, B. Gómez-Lor, M. Iglesias, N. Snejko, E. Gutiérrez-Puebla and A. Monge, *Chem. Commun.*, 2009, 2393.
12 S. Neogi, M. K. Sharma and P. K. Bharadwaj, *J. Mol. Catal. A: Chem.*, 2009, **299**, 1.
13 D. B. Dang, P. Y. Wu, C. He, Z. Xie and C. Y. Duan, *J. Am. Chem. Soc.*, 2010, **132**, 14321.
14 M. Gustafsson, A. Bartoszewicz, B. Martín-Matute, J. L. Sun, J. Grins, T. Zhao, Z. Y. Li, G. S. Zhu and X. D. Zou, *Chem. Mater.*, 2010, **22**, 3316.
15 P. Phuengphai, S. Youngme, P. Gamez and J. Reedijk, *Dalton Trans.*, 2010, **39**, 7936.
16 S. Nayak, K. Harms and S. Dehnen, *Inorg. Chem.*, 2011, **50**, 2714.
17 M. K. Sharma, P. P. Singh and P. K. Bharadwaj, *J. Mol. Catal. A: Chem.*, 2011, **342-343**, 6.
18 R. F. D'Vries, V. A. de la Peña-O'Shea, N. Snejko, M. Iglesias, E. Gutiérrez-Puebla and M. Á. Monge, *Cryst. Growth Des.*, 2012, **12**, 5535.
19 R. K. Das, A. Aijaz, M. K. Sharma, P. Lama and P. K. Bharadwaj, *Chem.—Eur. J.*, 2012, **18**, 6866.
20 R. F. D'Vries, M. Iglesias, N. Snejko, E. Gutiérrez-Puebla and M. A. Monge, *Inorg. Chem.*, 2012, **51**, 11349.
21 X. M. Lin, T. T. Li, Y. W. Wang, L. Zhang and C. Y. Su, *Chem.—Asian. J.*, 2012, **7**, 2796.
22 X. Wu, Z. H. Lin, C. He and C. Y. Duan, *New J. Chem.*, 2012, **36**, 161.
23 L. M. Aguirre-Díaz, M. Iglesias, N. Snejko, E. Gutiérrez-Puebla and M. Á. Monge, *CrystEngComm*, 2013, **15**, 9562.
24 P. K. Batista, D. J. M. Alves, M. O. Rodrigues, G. F. de Sá, S. A. Junior and J. A. Vale, *J. Mol. Catal. A: Chem.*, 2013, **379**, 68.
25 R. F. D'Vries, V. A. de la Peña-O'Shea, N. Snejko, M. Iglesias, E. Gutiérrez-Puebla and M. A. Monge, *J. Am. Chem. Soc.*, 2013, **135**, 5782.
26 R. Fernández de Luis, M. K. Urtiaga, J. L. Mesa, E. S. Larrea, M. Iglesias, T. Rojo and M. I. Arriortua, *Inorg. Chem.*, 2013, **52**, 2615.
27 H. Y. He, H. Q. Ma, D. Sun, L. L. Zhang, R. M. Wang and D. F. Sun, *Cryst. Growth Des.*, 2013, **13**, 3154.
28 T. Kajiwara, M. Higuchi, A. Yuasa, H. Higashimura and S. Kitagawa, *Chem. Commun.*, 2013, **49**, 10459.
29 G. Kumar and R. Gupta, *Inorg. Chem.*, 2013, **52**, 10773.
30 P. Phuengphai, S. Youngme, N. Chaichit and J. Reedijk, *Inorg. Chim. Acta*, 2013, **403**, 35.
31 R. F. D'Vries, N. Snejko, M. Iglesias, E. Gutiérrez-Puebla and M. A. Monge, *Cryst. Growth Des.*, 2014, **14**, 2516.
32 P. García-García, M. Müller and A. Corma, *Chem. Sci.*, 2014, **5**, 2979.
33 Q. X. Han, X. P. Sun, J. Li, P. T. Ma and J. Y. Niu, *Inorg. Chem.*, 2014, **53**, 6107.
34 R. M. Wang, Z. Y. Wang, Y. W. Xu, F. N. Dai, L. L. Zhang and D. F. Sun, *Inorg. Chem.*, 2014, **53**, 7086.
35 H. F. Yao, Y. Yang, H. Liu, F. G. Xi and E. Q. Gao, *J. Mol. Catal. A: Chem.*, 2014, **394**, 57.
36 Y. Zhu, Y. M. Wang, S. Y. Zhao, P. Liu, C. Wei, Y. L. Wu, C. K. Xia and J. M. Xie, *Inorg. Chem.*, 2014, **53**, 7692.
37 K. Mo, Y. H. Yang and Y. Cui, *J. Am. Chem. Soc.*, 2014, **136**, 1746.
38 L. J. Zhang, C. Y. Han, Q. Q. Dang, Y. H. Wang and X. M. Zhang, *RSC Adv.*, 2015, **5**, 24293.
39 X. Cui, M. C. Xu, L. J. Zhang, R. X. Yao and X. M. Zhang, *Dalton Trans.*, 2015, **44**, 12711-12716.