

Supporting Information

**Synthesis of Metallasiloxanes of Group 13-15 and Their
 Application in Catalysis**

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I. Crystal data and structure refinement for compounds 1–6 (Table S1.)

	1	2	3
formula	C ₄₀ H ₇₈ Bi ₂ N ₄ O ₄ Si ₄	C ₆₄ H ₁₁₈ N ₄ O ₈ Sb ₂ Si ₈	C ₄₈ H ₈₉ Ge ₂ N ₃ O ₆ Si ₆
formula weight	1209.38	1539.84	1117.94
crystal system	Triclinic	Triclinic	Hexagonal
space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> 6(3)
<i>a</i> /Å	9.819(2)	9.7585(7)	24.8315(3)
<i>b</i> /Å	11.045(3)	14.3218(9)	24.8315(3)
<i>c</i> /Å	13.189(3)	14.4294(9)	16.6832(3)
°/deg	111.32(2)	82.922(5)	90
°/deg	97.198(19)	86.529(5)	90
°/deg	101.63(2)	86.857(5)	120
<i>V</i> /Å ³	1273.9(5)	1995.3(2)	8908.7(2)
<i>Z</i>	1	1	6
$\rho_{\text{calcd}}/\text{g}\cdot\text{cm}^{-3}$	1.576	1.281	1.250
μ/mm^{-1}	7.030	0.845	1.177
<i>F</i> (000)	600	808	3564
crystal size/mm ³	0.20 × 0.10 × 0.05	0.30 × 0.15 × 0.12	0.38 × 0.35 × 0.25
θ range/deg	2.87–26.00	2.71–26.00	2.79–25.00
index ranges	–12 ≤ <i>h</i> ≤ 12 –13 ≤ <i>k</i> ≤ 13 –16 ≤ <i>l</i> ≤ 16	–12 ≤ <i>h</i> ≤ 11 –17 ≤ <i>k</i> ≤ 17 –17 ≤ <i>l</i> ≤ 17	–29 ≤ <i>h</i> ≤ 29 –29 ≤ <i>k</i> ≤ 29 –19 ≤ <i>l</i> ≤ 19
collected data	8581	14836	66089
unique data	4957 (<i>R</i> _{int} = 0.1256)	7821 (<i>R</i> _{int} = 0.0454)	10449 (<i>R</i> _{int} = 0.0482)
completeness to θ	99.1%	99.9%	99.8%
data/restraints/parameters	4957/187/284	7821/0/404	10449/150/547
GOF on <i>F</i> ²	0.956	1.009	1.215
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0800	<i>R</i> ₁ = 0.0430	<i>R</i> ₁ = 0.0705
sigma(<i>I</i>)	<i>wR</i> ₂ = 0.1335	<i>wR</i> ₂ = 0.0696	<i>wR</i> ₂ = 0.1702
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1278 <i>wR</i> ₂ = 0.1537	<i>R</i> ₁ = 0.0597 <i>wR</i> ₂ = 0.0760	<i>R</i> ₁ = 0.0935 <i>wR</i> ₂ = 0.1816
Largest diff peak/hole (e·Å ⁻³)	2.393/–1.479	0.531/–0.557	2.742/–4.661

	4	5·C₇H₈·0.5C₆H₁₄	6·0.75THF
formula	C ₄₂ H ₈₀ Al ₂ N ₂ O ₆ Si ₄	C ₇₀ H ₁₁₉ Bi ₄ N ₄ O ₁₂ Si ₈	C ₉₃ H ₁₇₆ Al ₆ N ₄ O _{18.75} Si ₈
formula weight	875.40	2269.33	2036.98
crystal system	Triclinic	Monoclinic	Orthorhombic
1space group	<i>P</i> -1	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> 2(1)2(1)2(1)
<i>a</i> /Å	10.273(2)	15.5155(5)	18.6059(5)
<i>b</i> /Å	11.090(2)	21.6905(6)	18.7005(5)
<i>c</i> /Å	12.605(3)	27.1120(7)	35.0951(11)
°deg	97.36(3)		
°deg	97.64(3)	92.249(3)	
°deg	114.32(3)		
<i>V</i> /Å ³	1270.1(4)	9117.2(5)	12211.0(6)
<i>Z</i>	1	4	4
$\rho_{\text{calcd}}/\text{g}\cdot\text{cm}^{-3}$	1.144	1.653	1.108
μ/mm^{-1}	0.194	7.854	0.187
<i>F</i> (000)	476	4428	4408
crystal size/mm ³	0.30 × 0.20 × 0.19	0.20 × 0.05 × 0.05	0.40 × 0.40 × 0.20
θ range/deg	3.04–26.00	2.71–26.00	2.70–26.00
index ranges	−12 ≤ <i>h</i> ≤ 12 −13 ≤ <i>k</i> ≤ 13 −14 ≤ <i>l</i> ≤ 15	−19 ≤ <i>h</i> ≤ 19 −26 ≤ <i>k</i> ≤ 26 −33 ≤ <i>l</i> ≤ 29	−22 ≤ <i>h</i> ≤ 22 −22 ≤ <i>k</i> ≤ 23 −43 ≤ <i>l</i> ≤ 40
collected data	10419	65416	90883
unique data	4893 (<i>R</i> _{int} = 0.1024)	17902 (<i>R</i> _{int} = 0.1286)	23933 (<i>R</i> _{int} = 0.0915)
completeness to θ	98.0%	99.9%	99.7%
data/restraints/parameters	4893/0/262	17902/391/900	23933/1246/1229
GOF on <i>F</i> ²	1.012	1.014	1.045
final <i>R</i> indices	<i>R</i> ₁ = 0.0725	<i>R</i> ₁ = 0.0664	<i>R</i> ₁ = 0.0793
[<i>I</i> > 2σ(<i>I</i>)]	<i>wR</i> ₂ = 0.1384	<i>wR</i> ₂ = 0.0958	<i>wR</i> ₂ = 0.1860
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1312 <i>wR</i> ₂ = 0.1565	<i>R</i> ₁ = 0.1181 <i>wR</i> ₂ = 0.1092	<i>R</i> ₁ = 0.1126 <i>wR</i> ₂ = 0.2045
Largest diff peak/hole (e·Å ⁻³)	0.347/−0.348	1.499/−1.129	0.838/−0.639

^a All data were collected at 173(2) K using Mo K α ($\lambda = 0.71073$ Å) radiation. $R_1 = \sum(|F_o| - |F_c|) / \sum|F_o|$, $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2 / \sum[w(F_o^2)^2]\}^{1/2}$, $GOF = \{\sum[w(F_o^2 - F_c^2)^2] / (N_o - N_p)\}^{1/2}$.

II. Crystal structures of compounds 2 and 4

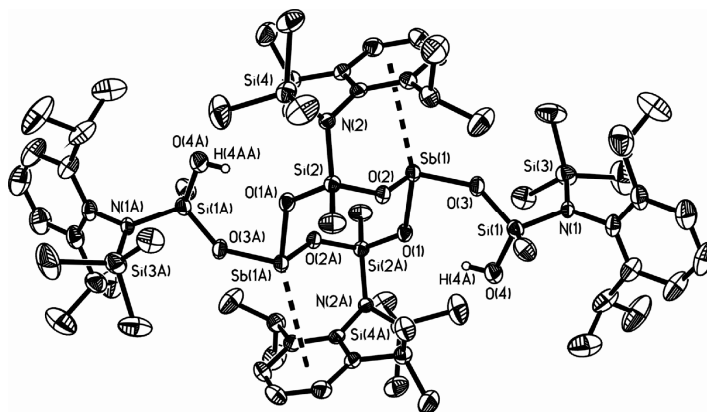


Figure S1. Thermal ellipsoid (50%) drawing of **2**. The H atoms are omitted for clarity except for the SiOH one. Sb...arene_{centroid}: 3.312 Å.

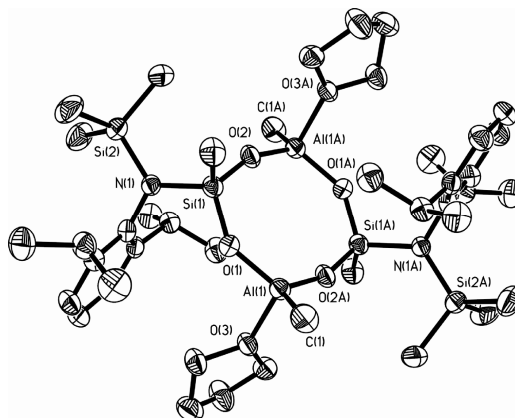


Figure S2. Thermal ellipsoid (50%) drawing of **4**. The H atoms are omitted for clarity.

III. Table S2. Summary of important core bond parameters for complexes 1–6

core	M–O (Å)	Si–O (Å)	O–M–O (°)	O–Si–O (°)
Si ₂ O ₄ Bi ₂ in 1	2.051(9)–2.075(9)	1.629(9)–1.650(10)	89.7(4)	112.6(6)
Si ₂ O ₄ Sb ₂ in 2	1.937(2)–1.973(2)	1.625(2)–1.643(2)	92.83(9)	108.22(12)
Si ₃ O ₆ Ge ₂ in 3	1.717(6)–1.738(7)	1.623(9)–1.641(8)	109.5(3)–110.5(4)	106.0(3)–107.2(5)
Si ₂ O ₄ Al ₂ in 4	1.711(3)–1.719(2)	1.605(2)–1.611(2)	116.31(13)	112.08(13)
Si ₄ O ₁₂ Bi ₄ in 5	2.014(7)–2.071(7)	1.598(7)–1.640(7)	89.8(3)–103.0(3)	108.1(4)–111.6(4)
Si ₃ O ₆ Al ₃ in 6	1.700(4)–1.731(4)	1.603(4)–1.621(4)	113.92(19)–114.7(2)	109.2(2)–110.9(2)

IV. Description of ring system of compounds 1-6

It can be seen that in the chair-like conformation of Si₂O₄Bi₂ in **1** and Si₂O₄Sb₂ in **2** the two metal centers are deviated from the Si₂O₄ plane by ± 1.2242 and ± 1.1881 Å, respectively. However, in **5** the conformation of Si₂O₄Bi₂ changes with respect to the slightly distorted Si₂O₄ plane ($\Delta_{\text{Si}_2\text{O}_4} = 0.1503$ Å) although its chair-like shape is retained. In **4** a flat chair-like conformation of Si₂O₄Al₂ is shown with the two metal centers away from the Si₂O₄ plane ($\Delta_{\text{Si}_2\text{O}_4} = 0.0505$ Å) by ± 0.3104 Å. But, when assembled into a bicyclic structure (in **6**), a boat-like conformation of the same ring is formed significantly different from that in **4**. A boat-like Si₂O₄Ge₂ conformation is also present in the bicyclic structure of **3**. Apparently, the Si₂O₄M₂ rings in **1–6** adopt different conformations owing to the different metals anchored. We pictured such rings in a lateral projecting view in Figure S3.

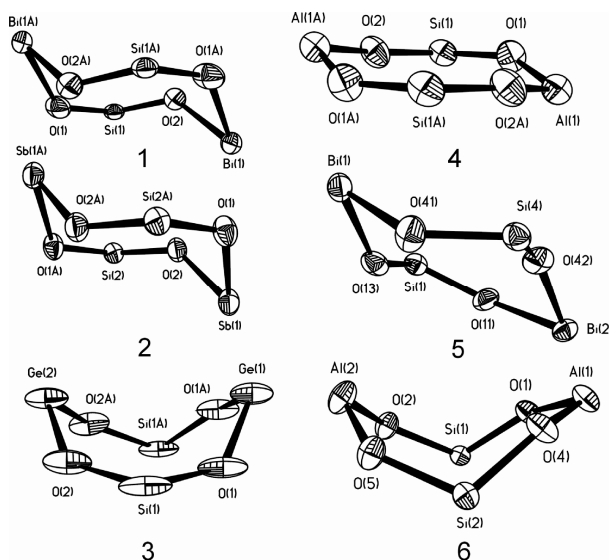


Figure S3. Lateral projecting view of the ring system of compounds 1-6

V. The completed results of compounds 1-6 as catalysts

Table S3. Addition reaction of TMSCN to benzaldehyde catalyzed by 1–6^a

Cat.	Reaction time	Yield ^b (%)
1	5 min	≥ 99
2	60 min	95
3	60 min	≥ 99
4	5 min	≥ 99
5	5 min	≥ 99
6	5 min	≥ 99

^a Benzaldehyde, 2 mmol; TMSCN, 3 mmol; catalyst, 0.02 mmol; at ambient temperature. ^b Yield was obtained according to Thin-Layer Chromatographic (TLC) and ¹H NMR spectral analysis.

The reaction of TMSCN with benzaldehyde was carried out in the presence of **1–6** (1 mol%, based on benzaldehyde) at ambient temperature in solvent-free condition. The results shown in Table S3 reveal that all the compounds **1–6** are catalytically active. The reactions approach completeness in 5 min to afford the product 2-trimethylsilyloxy-2-phenylacetonitrile when the bismuth(III) (**1**, **5**) and aluminum(III) (**4**, **6**) compounds are used as catalysts. However, the use of the antimony(III) (**2**) and germanium(IV) (**3**) compounds results in the respective yields of 95% and ≥ 99% of the product in 60 min. It has been reported that under similar conditions SbCl₃ catalyzed this reaction to afford the product in 30–90% yields within 30–240 min by loading amounts of 4.4–26 mol%. In the presence of organic solvent such as THF, ethyl acetate, ethanol, acetonitrile, dichloromethane, and *n*-hexane, lower yields of the product were achieved (0–50% yields, 15–300 min, 17 mol% loading).^{S1} The bismuth(III)

halide and aryl compounds are also reported to catalyze this reaction and yield of the product depends on the nature of substituent at the bismuth center.^{S2} In addition, the alumatranes ((AIL)₂ and (PhCHO)AIL (L = tris(2-oxy-3,5-dimethylbenzyl)amine) are also known to be catalytically active for this reaction but the reaction was slow even with a high loading.^{S3} However, **3** as a germanium(IV) compound is tested for the first time to show such catalytic property although heavier tin(IV) compounds such as SnCl₄ or R₂SnCl₂ (R = *n*Bu, Ph) are documented to exhibit good catalytic activities.^{S4} Comparatively, compounds **1–6** are effective catalysts for the addition reaction of TMSCN to benzaldehyde, of which the bismuth (**1** and **5**) and aluminum (**4** and **6**) compounds appear to be the best. Verkade et al. have well studied the catalytic properties of alumatranes by characterizing the possible interaction complexes on X-ray crystallography.^{S3a} Among **1** and **4–6**, compound **5** is homoleptic with a cage structure having the bismuth(III)⋯arene π -interactions which appears comparable to those of the alumatranes. This prompted us to select **5** as the catalyst for further investigations.

VI General procedures for the catalytic reactions of trimethylsilyl cyanide (TMSCN) with aldehyde or ketone.

Under N₂ atmosphere, a mixture of aldehyde or ketone (2 mmol), TMSCN (3mmol), and catalytic amount of the catalyst was stirred at room temperature. The reaction time was controlled within 5 min for quickly-done reactions or with a desired time to get satisfied result for relatively slow or slow reactions. The reaction progress was detected by combination of the Thin-Layer Chromatography (TLC) on 0.25 mm Merck silica gel sheets (60F-254) (4×2 cm²) equipped with UV light and the ¹H NMR spectral analysis. After workup, the mixture was allowed to directly pass through a silica-gel column using a mixture of petroleum ether and ethyl acetate (20:1) as an eluent. The eluents were collected and then evaporated to dryness to give the desired product that was studied by NMR (¹H, ¹³C, and ²⁹Si) and yield calculation.

C₆H₅CH(CN)OTMS. A colorless oil, 99% yield. ¹H NMR (500 MHz, CDCl₃, 298 K, ppm): δ 7.50–7.40 (m, 5 H, C₆H₅), 5.51 (s, 1 H, CH), 0.24 (s, 9 H, OSiMe₃). ¹³C NMR (125 MHz, CDCl₃, 298 K, ppm): δ 136.2, 129.2, 128.8, 126.2 (C₆H₅), 119.1 (CN), 63.5 (CH), –0.4 (OSiMe₃). ²⁹Si (99 MHz, CDCl₃, 298 K, ppm): δ 24.7 (OSiMe₃).

***o*-Br-C₆H₄CH(CN)OTMS.** A colorless oil, 89% yield. ¹H NMR (500 MHz, CDCl₃, 298 K, ppm): δ 7.74 (m, 1 H), 7.58 (m, 1 H), 7.42 (m, 1 H), 7.27 (m, 1 H) (C₆H₄), 5.78 (s, 1 H, CH), 0.27 (s, 9 H, OSiMe₃). ¹³C NMR (125 MHz, CDCl₃, 298 K, ppm): δ 135.4, 132.9, 130.8, 128.5, 128.1, 121.6 (C₆H₄), 118.2 (CN), 63.1 (CH), –0.4 (OSiMe₃). ²⁹Si (99 MHz, CDCl₃, 298 K, ppm): δ 25.7 (OSiMe₃).

***p*-MeO-C₆H₄CH(CN)OTMS.** A colorless oil, 99% yield. ¹H NMR (500 MHz, CDCl₃, 298 K, ppm): δ 7.39 (d, 2 H), 6.94 (d, 2 H) (C₆H₄), 5.44 (s, 1 H, CH), 3.83 (s, 3 H, OMe), 0.22 (s, 9 H, OSiMe₃). ¹³C NMR (125 MHz, CDCl₃, 298 K, ppm): δ 160.2, 128.4, 127.8, 114.2, 114.1 (C₆H₄), 119.2 (CN), 63.2 (CH), 55.1 (OMe), –0.4 (OSiMe₃). ²⁹Si (99 MHz, CDCl₃, 298 K,

ppm): δ 24.1 (OSiMe₃).

2-TMSO-C₆H₄CH(CN)OTMS. A colorless oil, 99% yield. ¹H NMR (500 MHz, CDCl₃, 298 K, ppm): δ 7.58–7.56 (m, 1 H), 7.28–7.25 (m, 1 H), 7.05–7.02 (m, 1 H), 6.86–6.84 (m, 1 H) (C₆H₄), 5.74 (m, 1 H, CH), 0.37 (s, 9 H, OSiMe₃ (ligated to aryl)), 0.24 (s, 9 H, OSiMe₃ (ligated to CH)). ¹³C NMR (125 MHz, CDCl₃, 298 K, ppm): δ 152.1, 130.1, 127.7, 126.9, 121.5, 118.1 (C₆H₄), 119.2 (CN), 58.5 (CH), 0.32 (OSiMe₃ (ligated to aryl)), –0.43 (OSiMe₃ (ligated to CH)). ²⁹Si (99 MHz, CDCl₃, 298 K, ppm): δ 24.1(OSiMe₃ (ligated to aryl), 21.6 (OSiMe₃ (ligated to CH))).

C₆H₅CH=CHCH(CN)OTMS. A colorless oil, 99% yield. ¹H NMR (500 MHz, CDCl₃, 298 K, ppm): δ 7.44–7.31 (m, 5 H, C₆H₅), 6.84 (d, 1 H, C₆H₅CH=CH), 6.22 (dd, 1 H, C₆H₅CH=CH), 5.14 (m, 1 H, CH), 0.29 (s, 9 H, OSiMe₃). ¹³C NMR (125 MHz, CDCl₃, 298 K, ppm): δ 135.0, 133.9, 128.7, 128.6, 126.9, 123.5 (C₆H₅CH=CH), 118.3 (CN), 62.2 (CH), –0.19 (OSiMe₃). ²⁹Si (99 MHz, CDCl₃, 298 K, ppm): δ 24.5 (OSiMe₃).

CH₃CH=CHCH(CN)OTMS. A colorless oil, 99% yield. ¹H NMR (500 MHz, CDCl₃, 298 K, ppm): δ 5.96 (m, 1 H, CH₃CH=CH), 5.55 (m, 1 H, CH₃CH=CH), 4.88 (m, 1 H, CH), 1.76 (m, 3 H, CH₃), 0.21 (s, 9 H, OSiMe₃). ¹³C NMR (125 MHz, CDCl₃, 298 K, ppm): δ 131.0 (CH₃CH=CH), 126.2 (CH₃CH=CH), 118.6 (CN), 62.0 (CH), 17.3 (CH₃), –0.3 (OSiMe₃). ²⁹Si (99 MHz, CDCl₃, 298 K, ppm): δ 23.9 (OSiMe₃).

CH₃CH₂CH(CN)OTMS. A colorless oil, 99% yield. ¹H NMR (500 MHz, CDCl₃, 298 K, ppm): δ 4.35 (t, 1 H, CH), 1.81 (m, 2 H, CH₂), 1.03 (t, 3 H, CH₃), 0.20 (s, 9 H, OSiMe₃). ¹³C NMR (125 MHz, CDCl₃, 298 K, ppm): δ 119.8 (CN), 62.6 (CH), 29.5 (CH₂), 8.8 (CH₃), –0.5 (OSiMe₃). ²⁹Si (99 MHz, CDCl₃, 298 K, ppm): δ 23.2 (OSiMe₃).

CH₃CH(Me)CH₂CH(CN)OTMS. A colorless oil, 99% yield. ¹H NMR (500 MHz, CDCl₃, 298 K, ppm): δ 4.42 (dd, 1 H, CH (ligated to OTMS)), 1.83 (m, 1 H, CH (ligated to Me)), 1.73 (m, 1 H), 1.63 (m, 1 H) (CH₂), 0.95 (d, 3 H), 0.93 (d, 3 H) (CH₃, Me), 0.20 (s, 9 H, OSiMe₃). ¹³C NMR (125 MHz, CDCl₃, 298 K, ppm): δ 120.2 (CN), 59.9 (CH (ligated to OTMS)), 44.9 (CH₂), 24.1, 22.4, 21.8 (CH (ligated to Me), CH₃), –0.5 (OSiMe₃). ²⁹Si (99 MHz, CDCl₃, 298 K, ppm): δ 23.1 (OSiMe₃).

CH₃(CH₂)₇CH₂CH(CN)OTMS. A colorless oil, 99% yield. ¹H NMR (500 MHz, CDCl₃, 298 K, ppm): δ 4.38 (t, 1 H, CH), 1.80–1.75 (m, 2 H, CH₃(CH₂)₇CH₂), 1.48–1.27 (m, 14 H, CH₃(CH₂)₇CH₂), 0.88 (t, 3 H, CH₃), 0.21 (s, 9 H, OSiMe₃). ¹³C NMR (125 MHz, CDCl₃, 298 K, ppm): δ 120.0 (CN), 61.4 (CH), 36.2, 31.8, 29.4, 29.3, 29.2, 28.9, 24.5, 22.6, 14.0 (CH₃(CH₂)₇CH₂), –0.5 (OSiMe₃). ²⁹Si (99 MHz, CDCl₃, 298 K, ppm): δ 24.7 (OSiMe₃).

Cl₃CCH(CN)OTMS. A colorless oil, 99% yield. ¹H NMR (500 MHz, CDCl₃, 298 K, ppm): δ 4.87 (s, 1 H, CH), 0.08 (s, 9 H, OSiMe₃). ¹³C NMR (125 MHz, CDCl₃, 298 K, ppm): δ 115.0 (CN), 96.6 (Cl₃C), 75.0 (CH), –0.5 (OSiMe₃). ²⁹Si (99 MHz, CDCl₃, 298 K, ppm): δ 24.4 (OSiMe₃).

2-C₄H₃S-CH(CN)OTMS. A colorless oil, 99% yield. ¹H NMR (500 MHz, CDCl₃, 298 K, ppm): δ 7.37 (d, 1 H), 7.20 (t, 1 H), 7.01 (m, 1 H) (C₄H₃S), 5.75 (s, 1 H, CH), 0.25 (s, 9 H, OSiMe₃). ¹³C NMR (125 MHz, CDCl₃, 298 K, ppm): δ 139.5, 127.1, 126.8, 126.2 (C₄H₃S), 118.2 (CN), 59.5 (CH), -0.4 (OSiMe₃). ²⁹Si (99 MHz, CDCl₃, 298 K, ppm): δ 25.3 (OSiMe₃).

2-C₄H₃O-CH(CN)OTMS. A colorless oil, 77% yield. ¹H NMR (500 MHz, CDCl₃, 298 K, ppm): δ 7.46 (m, 1 H), 6.54 (m, 1 H), 6.40 (m, 1 H) (C₄H₃O), 5.55 (s, 1 H, CH), 0.20 (s, 9 H, OSiMe₃). ¹³C NMR (125 MHz, CDCl₃, 298 K, ppm): δ 148.3, 143.8, 110.8, 109.7 (C₄H₃O), 117.1 (CN), 57.4 (CH), -0.4 (OSiMe₃). ²⁹Si (99 MHz, CDCl₃, 298 K, ppm): δ 25.0 (OSiMe₃).

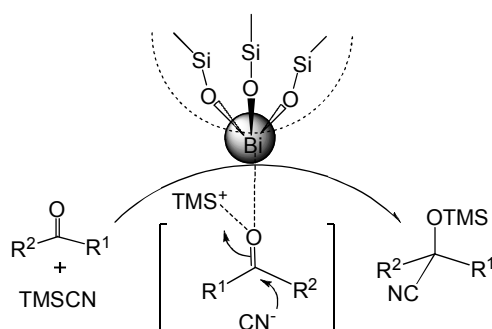
2-C₄H₃N(TMS)-CH(CN)OTMS. A colorless oil, 13% yield. ¹H NMR (500 MHz, CDCl₃, 298 K, ppm): δ 6.87–6.86 (m, 1 H), 6.56–6.55 (m, 1 H), 6.24–6.23 (m, 1 H) (C₄H₃N), 5.65 (s, 1 H, CH), 0.51 (s, 9 H, NSiMe₃), 0.20 (s, 9 H, OSiMe₃). ¹³C NMR (125 MHz, CDCl₃, 298 K, ppm): δ 131.4, 127.3, 114.2, 110.1 (C₄H₃N), 118.7 (CN), 58.3 (CH), 1.0 (NSiMe₃), -0.01 (OSiMe₃). ²⁹Si (99 MHz, CDCl₃, 298 K, ppm): δ 24.1 (NSiMe₃), 21.6 (OSiMe₃).

C₆H₅CMe(CN)OTMS. A colorless oil, 99% yield. ¹H NMR (500 MHz, CDCl₃, 298 K, ppm): δ 7.58–7.32 (m, 5 H, C₆H₅), 1.88 (s, 3 H, CMe), 0.20 (s, 9 H, OSiMe₃). ¹³C NMR (125 MHz, CDCl₃, 298 K, ppm): δ 142.0, 128.6, 124.6 (C₆H₅), 121.6 (CN), 71.6 (CMe), 33.5 (CMe), 1.0 (OSiMe₃). ²⁹Si (99 MHz, CDCl₃, 298 K, ppm): δ 20.4 (OSiMe₃).

4-MeO-C₆H₄CMe(CN)OTMS. A colorless oil, 68% yield. ¹H NMR (500 MHz, CDCl₃, 298 K, ppm): δ 7.47 (d, 2 H), 6.92 (d, 2 H) (C₆H₄), 3.83 (s, 3 H, OMe), 1.86 (s, 3 H, CMe), 0.17 (s, 9 H, OSiMe₃). ¹³C NMR (125 MHz, CDCl₃, 298 K, ppm): δ 159.8, 134.0, 126.0, 113.9 (C₆H₄), 121.7 (CN), 71.2 (CMe), 33.4 (OMe), 1.0 (OSiMe₃). ²⁹Si (99 MHz, CDCl₃, 298 K, ppm): δ 20.0 (OSiMe₃).

(CH₃CH₂)₂C(CN)OTMS. A colorless oil, 80% yield. ¹H NMR (500 MHz, CDCl₃, 298 K, ppm): δ 1.76 (td, 4 H, CH₃CH₂), 1.03 (t, 6 H, CH₃CH₂), 0.24 (s, 9 H, OSiMe₃). ¹³C NMR (125 MHz, CDCl₃, 298 K, ppm): δ 121.4 (CN), 74.3 (CCN), 33.5 (CH₃CH₂), 8.3 (CH₃CH₂), 1.2 (OSiMe₃). ²⁹Si (99 MHz, CDCl₃, 298 K, ppm): δ 17.5 (OSiMe₃).

VII. Proposed mechanism for the addition reaction of TMSCN to aldehyde or ketone to form cyanohydrin trimethylsilyl ethers catalyzed by 5. (Scheme S1)



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