ELECTRONIC SUPPORTING INFORMATION

Efficient synthesis of cyanohydrin trimethylsilyl ethers via 1,2-chemoselective cyanosilylation of carbonyls

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Experimental Section

Unless otherwise stated, all chemicals were purchased and used without any further purification. GC analyses were performed by using Hewlett-Packard HP 5890A equipped with a capillary column DB-35MS (30 m, 0.53 mm), a FID detector and helium as gas carrier. GC-EIMS 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.

All ¹H NMR and ¹³C NMR spectra were recorded at 200 MHz or 400 MHz, and at 50.3 or 100.6 MHz respectively, using a Bruker DRX-ADVANCE 200 MHz and a Bruker DRX-ADVANCE 400 MHz spectrometers. The deuterated solvent used was CDCl₃, and TMS was employed as internal standard. Chemical shifts were reported in ppm and coupling constants in hertz. Elemental analyses were realized by using a FISONS instrument EA 1108 CHN.

Triphenylphosphine on polystyrene (PS-TPP) (2% cross linking, 200-400 mesh) was purchased from Aldrich.

Compounds 2a¹, 2b², 2c³, 2d⁴, 2f⁵, 2g⁶, 4a⁴, 4b⁴, 4c⁷, 4d⁴, 4e⁸, 4f⁹, 4g¹⁰, 4h¹⁰, 4i¹¹, 4j¹¹, 4k¹², 4l⁶,

4m¹³ are known compounds. Compound **2e** is an unknown compound.

Characterization data and copies of the ¹H and ¹³C NMR spectra for compounds **2a-g** and **4a-m** are reported below.

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Batch procedure (20 mmol)

In a flask equipped with a magnetic stirrer PS-TPP (125 mg, 0.4 mmol, 3.2 mmol/g), acetophenone (**3a**) (d= 1.03, 2.3 mL, 2.4 g, 20 mmol), and TMSCN (d= 0.793, 2.75 mL, 2.18 g, 22 mmol) were consecutively added and the resulting mixture was left under stirring at 60 °C. After 3 hours the minimal amount of EtOAc to filter the catalyst was added (4 mL), then 4 x 1 mL of EtOAc were used to wash the catalyst from the remaining product (the effective presence of the product was checked after each addition of washing solvent). The organic layer was removed under vacuum and pure **4a** was obtained as an oil (99% yield, 4.33 g).

Cyclic-mode flow procedure (20 mmol)

Acetophenone (**3a**) (d = 1.03, 2.3 mL, 2.4 g, 20 mmol) and TMSCN (d= 0.793, 2.75 mL, 2.18 g, 22 mmol) were charged into a glass column functioning as reservoir and PS-TPP (0.4 mmol, 2 mol% measured on the ketone **3a**, 125 mg) was charged into a glass column (labelled as PS-TPP). The pump was set at 0.5 mL/min flow, and the reactor was heated to 60 °C. The reaction mixture was continuously pumped through the catalysts for 3 h untill complete conversion to **4a** was achieved. At this point the pump was left to run in order to recover the reaction mixture into the reservoir. Then EtOAc (2 x 1 mL) was introduced into the system and cyclically pumped (10 min) to wash the catalyst and then collected into the reservoir. After the evaporation of the solvent product **4a** was obtained pure in 99% yield and with a very low E-factor of 0.47 (see below for calculation).

Recycling catalyst procedure

The catalyst into the column coming from the EtOAc washing, was dried by flowing nitrogen and reused ten times following the cyclic-mode flow procedure.

Continuous flow procedure (200 mmol)

Acetophenone (**3a**) (d= 1.03, 23 mL, 24 g, 200 mmol) and TMSCN (d = 0.793, 27.5 mL, 21.8 g, 220 mmol) were charged into a flask while PS-TPP (125 mg, 0.4 mmol, 3.2 mmol/g) was dispersed in 45-60 mesh borosilicate spheres and charged into a glass column .

The reaction mixture was pumped at a 0.04 mL/min flow rate trough the catalyst at 60 °C for 20 h, and collected into a recovery flask. EtOAc (2.5 mL x 2) was then cyclically pumped through the catalyst, the system was washed and the product **4a** was recovered in 99% yield (oil, 43.3 g) and with a 0.16 E-factor value (see below for calculation).

Representative E-Factor calculation

-Batch (0.5 mmol): (Acetophenone (60 mg) + TMSCN (54 mg) + Washing EtO2 (710 mg) + PS-TPP (3 mg) – Product mass (106 mg)) / Product mass (106 mg) = 7

-Batch (20 mmol): (Acetophenone (2.4 g)+TMSCN (2.18 g)+Washing EtOAc (7.2 g) – Product mass (4.34 g)) / Product mass (4.34 g) = **1.7**

-Cyclic-mode flow reactor (20 mmol) (1st run):

(Acetophenone (2.4 g)+TMSCN (2.18 g)+Washing EtOAc (1.8 g) – Product mass (4.34 g)) / Product mass (4.34 g) = 0.47

- Continuous flow reactor (200 mmol):

(Acetophenone (24 g) + TMSCN (21.8 g) + Washing EtOAc (4.5 g) – Product mass (43.4 g)) / Product mass (43.4 g)= 0.16

S. A. Pourmousavi et al. Bulletin of the Korean Chemical Society (2011), 32(5), 1575-1578 To a stirred mixture of aldehyde (1 mmol) and TMSCN (1.5 mmol) was added SbCl3 (17 mol % for aldehydes and 26 mol % for ketones) at room temperature in a 10 mL round bottom flask. The reaction mixture was stirred continuously and progress of the reaction was followed by TLC using Cyclohexane/ Ethylacetate (9:1) as eluent. After completion of the reaction, the mixture was washed with n-hexane (3 × 5 mL) and filtered off. The combined organic layers were washed with distilled water (3 × 5 mL) and then dried over MgSO4 and evaporated under vacuum to give almost pure cyanosilylether. Further purification, if necessary, was preceded using preparative TLC by an appropriate solvent.

E-Factor: ((1 mmol acetophenone (120 mg) + 1.5 mmol TMSCN (149 mg) + 0.26 mmol SbCl3 (59 mg) + 15 ml hexane (9.8 g) + 15 ml water (15 g) – weight product (98% yield) (215 mg)) / weight product (98% yield) (215 mg)= **116**

Mohammad G. Dekamin et al. Applied Organometallic Chemistry (2010), 24(3), 229-235 TMSCN (1.2 mmol, 0.15 ml) was added to a mixture of 1.0 mmol of carbonyl compound and PBPDC (1, 0.02 mmol, 5.8 mg). The resulting mixture was stirred at room temperature for time indicated in Table 2. The reaction was monitored by TLC. After completion, the reaction mixture was quenched with water (1.0 ml) and the organic materials were extracted with EtOAc (2 × 1.5ml). The organic phase was washed with brine followed by water (1.5 ml) and dried over MgSO4. The solvent was evaporated under reduced pressure to afford the desired products which in some cases were essentially pure cyanohydrin TMS ethers. Further purification of the products could be performed by silica gel column chromatography (EtOAc–hexane, 1 : 10). The isolated yields were in good agreement with those obtained by GC analysis.

E-Factor: ((1 mmol acetophenone (120 mg) + 1.2 mmol TMSCN (119 mg) + 0.02 mmol PBPDC (5.8 mg) + 2.5 ml water (2.5 g) + 3 ml EtOAc (2.7 g) – weight product (62% yield) (136 mg)) / weight product (62% yield) (136 mg)= 39

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After standard cycles of evacuation and back-filling with dry and pure nitrogen, an oven-dried tube (Carousel ThermoFischer Scientific Omnistation) or a Schlenk tube equipped with a magnetic stirring bar was charged with the aldehyde or ketone (1.74 mmol, 1 eq.) trimethylsilylcyanide (280 μ L, 2.09 mmol, 1.2 eq.) and PNPCI catalyst. The tube was sealed under a positive pressure of nitrogen and stirred at room temperature for 1 to 8 hours. The crude product was purified by silica gel chromatography with heptanes/diethylether mixture.

E-Factor: ((1.74 mmol acetophenone (209 mg) + 2.1 mmol TMSCN (207 mg) + 0.017 mmol PNPCI (10 mg) – weight product (90% yield) (343 mg)) / weight product (90% yield) (343 mg) = 0.24

In the calculation is not reported the consumption of solvents for silica gel chromatography because not reported.





METHOD:

In a screw capped vial equipped with a magnetic stirrer PS-TPP (8 mg, 0.025 mmol, 3.2 mmol/g), (E)-non-3-en-2-one (**1b**) (0.087 mL, 0.5 mmol), and TMSCN (0.075 mL, 0.6 mmol) were consecutively added and the resulting mixture was left under stirring at 60 °C. After 4 hours Et_2O (1 mL) was added and the catalyst was filtered off and the solvent was removed under vacuum. In this way pure (E)-2-methyl-2-((trimethylsilyl)oxy)non-3-enenitrile (**2b**) was obtained as an oil (94% yield, 113 mg).

Mol Formula	C ₁₃ H ₂₅ NOSi	m.p.	Oil

Elemental Analysis: C, 65.21; H, 10.52; N, 5.85; found C, 65.31; H, 10.49; N, 5.80

	δ value	No. H	Mult.	j value/Hz
400 MHz	0.21	9	S	
	0.89	3	t	6.6
	1.24-1.46	6	т	
	1.63	3	S	
	2.04-2.10	2	т	
	5.45	1	d	15.4
	6.01	1	dt	15.4; 6.8

¹³C NMR (100.6 MHz, CDCl₃) δ: 1.3; 13.9; 22.3; 28.2; 30.8; 31.3; 31.6; 69.8; 120.9; 130.6; 132.7.

GC-EIMS (m/z, %): 239 (M⁺,1), 224 (57), 197 (38), 154 (36), 127 (51), 125 (47), 75 (100), 73 (58), 55 (30).





METHOD:

In a screw capped vial equipped with a magnetic stirrer PS-TPP (8 mg, 0.025 mmol, 3.2 mmol/g), (E)-chalcone (**1d**) (104 mg, 0.5 mmol), and TMSCN (0.075 mL, 0.6 mmol) were consecutively added and the resulting mixture was left under stirring at 60 °C. After 24 hours Et_2O (1 mL) was added and the catalyst was filtered off and the solvent was removed under vacuum. In this way pure (E)-2,4-diphenyl-2-((trimethylsilyl)oxy)but-3-enenitrile (**2d**) was obtained as an oil (97% yield, 150 mg).

Mol Formula	C ₁₉ H ₂₁ NOSi	m.p.	Oil		
Elemental Analysis: C, 74.22; H, 6.88; N, 4.56; found C, 74.30; H, 6.90; N, 4.50					

1.1.1.1.10	δ value	No. H	Mult.	j value/Hz	
400 MHz	0.24	9	S		
CDCI₃	6.19	1	d	15.8	
	7.00	1	d	15.8	
	7.28-7.42	8	т		
	7.56-7.58	2	т		
¹³ C NMR (100 140.4.	0.6 MHz, CDCl ₃)	δ : 1.4; 75	.1; 119.7; 125.5	; 127.1; 128.8; 128.9; 129.8; 131.0); 135.1;

GC-EIMS (m/z, %): 307 (M⁺, 81), 292 (57), 217 (65), 208 (85), 191 (48), 180 (45), 140 (100), 105 (48), 73 (77).



METHOD:

In a screw capped vial equipped with a magnetic stirrer PS-TPP (8 mg, 0.025 mmol, 3.2 mmol/g), (E)-3-(4'-chlorophenyl)-1-phenylprop-2-en-1-one (**1e**) (121 mg, 0.5 mmol), and TMSCN (0.075 mL, 0.6 mmol) were consecutively added and the resulting mixture was left under stirring at 60 °C. After 24 hours Et_2O (1 mL) was added and the catalyst was filtered off and the solvent was removed under vacuum. In this way pure (E)-4-(4'-chlorophenyl)-2-phenyl-2-((trimethylsilyl)oxy)but-3-enenitrile (**2e**) was obtained as an oil (90% yield, 153 mg).

Mol Formula	C ₁₉ H ₂₀ CINOSi	m.p.	Oil

Elemental Analysis: C, 66.74; H, 5.90; N, 4.10; found C, 66.78; H, 5.91; N, 4.13

	δ value	No. H	Mult.	j value/Hz	
400 MHz	0.23	9	S		
	6.16	1	d	15.8	
	6.94	1	d	15.8	
	7.29-7.43	7	т		
	7.55-7.57	2	т		

¹³C NMR (100.6 MHz, CDCl₃) δ : 1.3; 75.0; 119.5; 125.5; 128.3; 128.8; 128.9; 129.0; 129.5; 130.4; 133.6; 134.4; 140.1.

GC-EIMS (m/z, %): 343 (M⁺+2, 38), 341 (M⁺, 97), 326 (37), 252 (39), 242 (74), 225 (42), 216 (64), 214 (67), 207 (70), 179 (48), 140 (81), 105 (41), 73 (100).



METHOD:

In a screw capped vial equipped with a magnetic stirrer PS-TPP (0.008 mg, 0.025 mmol, 3.2 mmol/g), (E)-4-phenylbut-3-en-2-one (**1f**) (73 mg, 0.5 mmol), and TMSCN (0.094 mL, 0.75 mmol) were consecutively added and the resulting mixture was left under stirring at 60 °C. After 3 hours Et_2O (1 mL) was added and the catalyst was filtered off and the solvent was removed under vacuum. In this way pure (E)-2-methyl-4-phenyl-2-((trimethylsilyl)oxy)but-3-enenitrile (**2f**) was obtained as an oil (90% yield, 110 mg).

Mol Formula	C ₁₄ H ₁₉ NOSi	m.p.	Oil

Elemental Analysis: C, 68.52; H, 7.80; N, 5.71; found C, 68.60; H, 7.77; N, 5.68

	δ value	No. H	Mult.	j value/Hz
400 MHz	0.25	9	S	
	1.76	3	S	
	6.14	1	d	15.9
	6.89	1	d	15.9
	7.29-7.43	5	т	

¹³C NMR (100.6 MHz, CDCl₃) δ: 1.4; 30.9; 70.0; 120.7; 126.9; 128.6; 128.8; 129.6; 131.0; 135.1.

GC-EIMS (m/z, %): 245 (M⁺, 23), 230 (54), 202 (30), 156 (16), 131 (100), 129 (29), 128 (25), 103 (17), 77 (15), 75 (59), 73 (48).



METHOD:

In a screw capped vial equipped with a magnetic stirrer PS-TPP (8 mg, 0.025 mmol, 3.2 mmol/g), cinnamaldehyde (**1g**) (66 mg, 0.5 mmol), and TMSCN (0.075 mL, 0.6 mmol) were consecutively added and the resulting mixture was left under stirring at 30 °C. After 7 hours Et_2O (1 mL) was added and the catalyst was filtered off and the solvent was removed under vacuum. In this way pure (E)-4-phenyl-2-((trimethylsilyl)oxy)but-3-enenitrile (**2g**) was obtained as an oil (96% yield, 111 mg).

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Mol Formula	$C_{13}H_{17}NOSI$	m.p.	UI

Elemental Analysis: C, 67.49; H, 7.41; N, 6.05; found C, 67.55; H, 7.45; N, 6.	00
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	δ value	No. H	Mult.	j value/Hz
400 MHz	0.26	9	S	
CDCI ₃	5.12	1	d	5.9
	6.19	1	dd	15.8; 5.9
	6.81	1	d	15.8
	7.29-7.42	5	т	

¹³C NMR (100.6 MHz, CDCl₃) δ : 0.2; 62.1; 118.3; 123.5; 126.9; 128.7; 128.7; 133.8; 134.9.

GC-EIMS (m/z, %): 231 (M⁺, 36), 216 (46), 189 (35), 142 (36), 131 (27), 115 (100), 104 (98), 75 (28), 73 (70).



METHOD:

In a screw capped vial equipped with a magnetic stirrer PS-TPP (3 mg, 0.01 mmol, 3.2 mmol/g), acetophenone (**3a**) (0.058 mL, 0.5 mmol), and TMSCN (0.069 mL, 0.55 mmol) were consecutively added and the resulting mixture was left under stirring at 60 °C. After 3 hours Et_2O (1 mL) was added and the catalyst was filtered off and the solvent was removed under vacuum. In this way pure 2-phenyl-2-((trimethylsilyl)oxy)propanenitrile (**4a**) was obtained as an oil (97% yield, 106 mg).

Mol Formula	C ₁₂ H ₁₇ NOSi	m.p.	Oil

ental Analysis: C, 65.71; H, 7.81; N, 6.39; found C, 65.68; H, 7.85; N, 6.44
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	δ value	No. H	Mult.	j value/Hz
400 MHz	0.18	9	S	
	1.86	3	S	
	7.33-7.42	3	т	
	7.54-7.55	2	т	
¹³ C NMR (100.6	6 MHz, CDCl₃)	δ : 1.0; 33	.6; 71.6; 121.6; 1	24.6; 128.6, 142.0.
GC-EIMS (m/z,	%): 219 (M⁺, 1), 204 (84), 177 (100), 135	(22), 105 (62), 77 (26), 75 (66).



METHOD:

In a screw capped vial equipped with a magnetic stirrer PS-TPP (7.5 mg, 0.025 mmol, 3.2 mmol/g), 1-(p-tolyl)ethanone (**3b**) (0.067 mL, 0.5 mmol), and TMSCN (0.069 mL, 0.55 mmol) were consecutively added and the resulting mixture was left under stirring at 60 °C. After 7 hours Et_2O (1 mL) was added and the catalyst was filtered off and the solvent was removed under vacuum. In this way pure 2-(p-tolyl)-2-((trimethylsilyl)oxy)propanenitrile (**4b**) was obtained as an oil (96% yield, 112 mg).

Mol Formula	C ₁₃ H ₁₉ NOSi	m.p.	Oil

Elemental Analysis: C, 66.90; H, 8.21; N, 6.00; found C, 66.88; H, 8.26; N, 6.02

	δ value	No. H	Mult.	j value/Hz
400 MHz	0.16	9	S	
CDCI₃	1.84	3	S	
	2.36	3	S	
	7.18-7.20	2	т	
	7.41-7.43	2	т	
¹³ C NMR (100).6 MHz, CDCl ₃)	δ : 1.0; 20	.9; 33.4; 71.4; 12	21.6; 124.5; 129.2; 138.4; 139.0.

GC-EIMS (m/z, %): 233 (M⁺, 6), 218 (87), 191 (57), 119 (100), 91 (22), 75 (69).



METHOD:

In a screw capped vial equipped with a magnetic stirrer PS-TPP (3 mg, 0.01 mmol, 3.2 mmol/g), 1- (pyridin-2-yl)ethanone (**3c**) (0.056 mL, 0.5 mmol), and TMSCN (0.069 mL, 0.55 mmol) were consecutively added and the resulting mixture was left under stirring at 60 °C. After 2.5 hours Et_2O (1 mL) was added and the catalyst was filtered off and the solvent was removed under vacuum. In this way pure 2-(pyridin-2-yl)-2-((trimethylsilyl)oxy)propanenitrile (**4c**) was obtained as an oil (96% yield, 105 mg).

Mol Formula	$C_{11}H_{16}N_2OSi$	m.p.	Oil

Elemental Analysis: C, 59.96; H, 7.32; N, 12.71; found C, 60.02; H, 7.27; N, 12.65

	δ value	No. H	Mult.	j value/Hz
400 MHz	0.25	9	S	
	1.92	3	S	
	7.26-7.30	1	т	
	7.59-7.61	1	т	
	7.75-7.79	1	т	
	8.62-8.63	1	т	

¹³C NMR (100.6 MHz, CDCI₃) δ: 1.1; 31.2; 72.9; 119.0; 121.3; 123.4; 137.2; 149.0; 160.0.

GC-EIMS (m/z, %): 220 (M⁺, 3), 205 (100), 190 (22), 178 (61).



METHOD:

In a screw capped vial equipped with a magnetic stirrer PS-TPP (3 mg, 0.01 mmol, 3.2 mmol/g), benzophenone (**3d**) (91 mg, 0.5 mmol), and TMSCN (0.069 mL, 0.55 mmol) were consecutively added and the resulting mixture was left under stirring at 60 °C. After 1 hour Et_2O (1 mL) was added and the catalyst was filtered off and the solvent was removed under vacuum. In this way pure 2,2-diphenyl-2-((trimethylsilyl)oxy)acetonitrile (**4d**) was obtained as an oil (98% yield, 138 mg).

Mol Formula	Formula C ₁₇ H ₁₉ NOSi		m.p.	Oil					
Elemental Analysis: C, 72.55; H, 6.80; N, 4.98; found C, 72.60; H, 6.77; N, 4.95									
	δ value	No. H	Mult.	j value/Hz					
400 MHz	0.13	9	S						
	7.30-7.38	6	т						
	7.49-7.51	4	т						
¹³ C NMR (100.6 MHz, CDCI ₃) δ: 0.9; 76.3; 120.7; 125.9; 128.5; 128.6; 141.9.									
GC-EIMS (m/z, %): 205 (20), 190 (100), 116 (24), 105 (21), 84 (32).									



METHOD:

In a screw capped vial equipped with a magnetic stirrer PS-TPP (3 mg, 0.01 mmol, 3.2 mmol/g), 4methylpentan-2-one (**3e**) (0.062 mL, 0.5 mmol), and TMSCN (0.069 mL, 0.55 mmol) were consecutively added and the resulting mixture was left under stirring at 60 °C. After 8 hours Et_2O (1 mL) was added and the catalyst was filtered off and the solvent was removed under vacuum. In this way pure 2,4-dimethyl-2-((trimethylsilyl)oxy)pentanenitrile (**4e**) was obtained as an oil (72% yield, 72 mg).

Mol Formula	C ₁₀ H ₂₁ NOSi	m.p.	Oil

Elemental Analysis: C, 60.24; H, 10.62; N, 7.03; found C, 60.20; H, 10.70; N, 7.05

	δ value	No. H	Mult.	j value/Hz
400 MHz	0.24	9	S	
	1.01	6	dd	6.6; 4.2
	1.58-1.69	5	т	
	1.89-1.98	1	т	

¹³C NMR (100.6 MHz, CDCl₃) δ: 1.3; 23.7; 23.8; 24.9; 29.8; 51.4; 69.1; 122.6.

GC-EIMS (m/z, %): 184 (19), 157 (72), 142 (46), 115 (75), 100 (100), 75 (56), 73 (78), 45 (24).



METHOD:

In a screw capped vial equipped with a magnetic stirrer PS-TPP (3 mg, 0.01 mmol, 3.2 mmol/g), decan-2-one (**3f**) (78 mg, 0.5 mmol), and TMSCN (0.069 mL, 0.55 mmol) were consecutively added and the resulting mixture was left under stirring at 60 °C. After 4.5 hours Et_2O (1 mL) was added and the catalyst was filtered off and the solvent was removed under vacuum. In this way pure 2-methyl-2-((trimethylsilyl)oxy)decanenitrile (**4f**) was obtained as an oil (96% yield, 122 mg).

Mol Formula	C ₁₄ H ₂₉ NOSi	m.p.	Oil

Elemental Analysis: C, 65.82; H, 11.44; N, 5.48; found C, 65.88; H, 11.46; N, 5.44

δ value	No. H	Mult.	j value/Hz
0.23	9	S	
0.88	3	t	6.4
1.27-1.29	9	т	
1.39-1.60	6	т	
1.67-1.76	2	т	
	δ value 0.23 0.88 1.27-1.29 1.39-1.60 1.67-1.76	δ value No. H 0.23 9 0.88 3 1.27-1.29 9 1.39-1.60 6 1.67-1.76 2	δ value No. H Mult. 0.23 9 s 0.88 3 t 1.27-1.29 9 m 1.39-1.60 6 m 1.67-1.76 2 m

¹³C NMR (100.6 MHz, CDCl₃) δ: 1.2; 14.1; 22.6; 24.2; 28.8; 29.1; 29.3; 29.3; 31.8; 43.3; 69.6; 122.2.

GC-EIMS (m/z, %): 233 (6), 218 (84), 191 (53), 119 (100), 91 (22), 75 (71).



METHOD:

In a screw capped vial equipped with a magnetic stirrer PS-TPP (3 mg, 0.01 mmol, 3.2 mmol/g), cyclohexanecarbaldehyde (**3g**) (0.061 mL, 0.5 mmol), and TMSCN (0.069 mL, 0.55 mmol) were consecutively added and the resulting mixture was left under stirring at 30 °C. After 1 hour Et₂O (1 mL) was added and the catalyst was filtered off and the solvent was removed under vacuum. In this way pure 2-cyclohexyl-2-((trimethylsilyl)oxy)acetonitrile (**4g**) was obtained as an oil (83% yield, 88 mg).

Mol Formula	C ₁₁ H ₂₁ NOSi	m.p.	Oil

Elemental Analysis: C, 62.50; H, 10.01; N, 6.63; found C, 62.45; H, 10.07; N, 6.60

	δ value	No. H	Mult.	j value/Hz			
400 MHz	0.20	9	S				
CDCI ₃	1.00-1.32	5	т				
	1.60-1.71	2	т				
	1.77-1.89	4	т				
4.14 1 <i>d</i> 6.4							
¹³ C NMR (100.6 MHz, CDCl ₃) δ : -0.5; 25.5; 26.0; 27.8; 28.1; 28.8; 42.9; 66.4; 119.4.							

GC-EIMS (m/z, %): 211 (M⁺, 1), 169 (31), 129 (100), 75 (28), 73 (21).



METHOD:

In a screw capped vial equipped with a magnetic stirrer PS-TPP (3 mg, 0.01 mmol, 3.2 mmol/g), heptanal (**3h**) (0.067 mL, 0.5 mmol), and TMSCN (0.069 mL, 0.55 mmol) were consecutively added and the resulting mixture was left under stirring at 30 °C. After 1 hour Et₂O (1 mL) was added and the catalyst was filtered off and the solvent was removed under vacuum. In this way pure 2-((trimethylsilyl)oxy)octanenitrile (**4h**) was obtained as an oil (85% yield, 90 mg).

Mol Formula	C ₁₁ H ₂₃ NOSi	m.p.	Oil

Elemental Analysis: C, 61.91; H, 10.86; N, 6.56; found C, 61.99; H, 10.80; N, 6.60

	δ value	No. H	Mult.	j value/Hz
400 MHz	0.20	9	S	
CDCI₃	0.89	3	t	5.9
	1.25-1.36	6	т	
	1.40-1.48	2	т	
	1.75-1.81	2	т	
	4.38	1	t	6.6

¹³C NMR (100.6 MHz, CDCl₃) δ: -0.4; 14.0; 22.4; 24.5; 28.5; 31.5; 36.2; 61.4; 120.1.

GC-EIMS (m/z, %): 198 (38), 171 (100), 114 (20), 101 (29), 97 (23), 84 (21), 75 (58), 73 (50), 55 (81).



METHOD:

In a screw capped vial equipped with a magnetic stirrer PS-TPP (3 mg, 0.01 mmol, 3.2 mmol/g), 4nitrobenzaldehyde (**3i**) (75 mg, 0.5 mmol), and TMSCN (0.069 mL, 0.55 mmol) were consecutively added and the resulting mixture was left under stirring at 30 °C. After 1.5 hours Et_2O (1 mL) was added and the catalyst was filtered off and the solvent was removed under vacuum. In this way pure 2-(4'-nitrophenyl)-2-((trimethylsilyl)oxy)acetonitrile (**4i**) was obtained as an oil (95% yield, 119 mg).

Mol Formula	$C_{11}H_{14}N_2O_3Si$	m.p.	Oil		
Elemental Analysis: C, 52.78; H, 5.64; N, 11.19; found C, 52.86; H, 5.60; N, 11.24					

	δ value	No. H	Mult.	j value/Hz			
400 MHz	0.29	9	S				
	5.59	1	S				
7.66-7.68 2 <i>m</i>							
8.28-8.30 2 m							
¹³ C NMR (100.6 MHz, CDCI ₃) δ : 0.4; 62.6; 118.1; 124.1; 127.1; 142.8; 148.4.							
GC-EIMS (m/z,	%): 235 (100),	84 (63), 7	5 (10), 73 (13), 4	5 (10).			



METHOD:

In a screw capped vial equipped with a magnetic stirrer PS-TPP (3 mg, 0.01 mmol, 3.2 mmol/g), 3-chlorobenzaldehyde (**3j**) (0.057 mL, 0.5 mmol), and TMSCN (0.069 mL, 0.55 mmol) were consecutively added and the resulting mixture was left under stirring at 30 °C. After 3.5 hours Et_2O (1 mL) was added and the catalyst was filtered off and the solvent was removed under vacuum. In this way pure 2-(3'-chlorophenyl)-2-((trimethylsilyl)oxy)acetonitrile (**4j**) was obtained as an oil (96% yield, 115 mg).

Mol Formula	C ₁₁ H ₁₄ CINOSi	m.p.	Oil

Elemental Analysis: C, 55.10; H, 5.89; N, 5.84; found C, 55.15; H, 5.80; N, 5.88

	δ value	No. H	Mult.	j value/Hz		
400 MHz	0.25	9	S			
	5.47	1	S			
	7.36	3	т			
7.47 1 <i>m</i>						
¹³ C NMR (100	.6 MHz, CDCI ₃)	δ:- 0.3; 62	2.9; 118.7; 124.4;	126.4; 129.5; 130.2; 134.9; 138.2.		

GC-EIMS (m/z, %): 241 (M⁺+2, 3), 239 (M⁺, 9), 226 (39), 224 (100), 84 (54).



METHOD:

In a screw capped vial equipped with a magnetic stirrer PS-TPP (3 mg, 0.01 mmol, 3.2 mmol/g), 4chlorobenzaldehyde (**3k**) (70 mg, 0.5 mmol), and TMSCN (0.069 mL, 0.55 mmol) were consecutively added and the resulting mixture was left under stirring at 30 °C. After 3.5 hours Et_2O (1 mL) was added and the catalyst was filtered off and the solvent was removed under vacuum. In this way pure 2-(4'-chlorophenyl)-2-((trimethylsilyl)oxy)acetonitrile (**4k**) was obtained as an oil (95% yield, 114 mg).

Mol Formula	C ₁₁ H ₁₄ CINOSi	m.p.	Oil
Elemental Analysis:	C, 55.10; H, 5.89; N,	, 5.84; found	C, 55.08; H, 5.90; N, 5.91

	δ value	No. H	Mult.	j value/Hz
400 MHz	0.24	9	S	
	5.46	1	S	
	7.38-7.43	4	т	

¹³C NMR (100.6 MHz, CDCl₃) δ : -0.4; 62.9; 118.7; 127.6; 129.1; 134.8; 135.2.

GC-EIMS (m/z, %): 241 (M⁺+2, 4), 239 (M⁺, 12), 226 (38), 224 (100), 152 (11), 150 (34), 84 (42).



METHOD:

In a screw capped vial equipped with a magnetic stirrer PS-TPP (3 mg, 0.01 mmol, 3.2 mmol/g), 4cyanobenzaldehyde (**3I**) (65 mg, 0.5 mmol), and TMSCN (0.069 mL, 0.55 mmol) were consecutively added and the resulting mixture was left under stirring at 30 °C. After 2 hours Et_2O (1 mL) was added and the catalyst was filtered off and the solvent was removed under vacuum. In this way pure 2-(4'cyanophenyl)-2-((trimethylsilyl)oxy)acetonitrile (**4I**) was obtained as an oil (98% yield, 113 mg).

Mol Formula	$C_{12}H_{14}N_2OSi$	m.p.	Oil		
Iemental Analysis: C, 62.57; H, 6.13; N, 12.16; found C, 62.55; H, 6.08; N, 12.19					

	δ value	No. H	Mult.	j value/Hz		
400 MHz	0.27	9	S			
	5.54	1	S			
7.59-7.61 2 <i>m</i>						
7.72-7.74 2 m						
¹³ C NMR (100.6 MHz, CDCI ₃) δ : 0.4; 62.8; 113.2; 118.2; 118.1; 126.8; 132.7; 141.1.						
GC-EIMS (m/z	z, %): 230 (M ⁺ , 9), 215 (10	0), 114 (14), 84 (6	64), 45 (10).		



METHOD:

In a screw capped vial equipped with a magnetic stirrer PS-TPP (8 mg, 0.025 mmol, 3.2 mmol/g), 4methoxybenzaldehyde (**3m**) (0.061 mL, 0.5 mmol), and TMSCN (0.069 mL, 0.55 mmol) were consecutively added and the resulting mixture was left under stirring at 30 °C. After 7 hours Et_2O (1 mL) was added and the catalyst was filtered off and the solvent was removed under vacuum. In this way pure 2-(4'-methoxyphenyl)-2-((trimethylsilyl)oxy)acetonitrile (**4m**) was obtained as an oil (94% yield, 112 mg).

	Mol Formula	C ₁₂ H ₁₇ NO ₂ Si	m.p.	Oil
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Elemental Analysis: C, 61.24; H, 7.28; N, 5.95; found C, 61.30; H, 7.20; N, 5.93

¹ H NMR 400 MHz CDCI ₃	δ value	No. H	Mult.	j value/Hz
	0.21	9	S	
	3.82	3	S	
	5.44	1	S	
	6.92-6.94	2	т	
	7.38-7.40	2	т	

¹³C NMR (100.6 MHz, CDCl₃) δ: 0.3; 55.2; 63.2; 114.2; 119.3; 127.8; 128.4; 160.3.

GC-EIMS (m/z, %): 235 (M⁺, 31), 220 (48), 146 (100), 135 (15).









- 7.261





- 0.219



2-ethyl-2-((trimethylsilyl)oxy)but-3-enenitrile (2c)





(E)-2,4-diphneyl-2-((trimethylsilyl)oxy)but-3-enenitrile (2d)



0.243





ppm

mdd



77.443 77.125 76.807 74.976

T

(E)-4-(4'-chlorophenyl)-2-phenyl-2-((trimethylsilyl)oxy)but-3-enenitrile (2e)



1.283





















2-(pyridin-2-yl)-2-(trimethylsilyl)oxy)propanenitrile (4c)

























ESI 53







2-(4'-nitrophenyl)-2-(trimethylsilyl)oxy)acetonitrile (4i)



ESI 56

-0.360















