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Ytterbium Tricyanide: Preparation and Catalytic Activity for the Addition of Cyanotrimethylsilane to Carbonyl Compounds

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Ytterbium tricyanide was obtained quantitatively by the reaction of ytterbium tri-isopropoxide with cyanotrimethylsilane. The addition of cyanotrimethylsilane to various carbonyl compounds was catalyzed effectively by ytterbium tricyanide to proceed under mild conditions giving the adducts in high selectivities. 2-Methylcyclohexanone yielded the adduct in a highly diastereoselective manner and the reagent system also effectively gave the adducts from easily enolizable ketones as well as from acid-sensitive ones. α,β-Unsaturated ketones and aldehydes afforded 1,2-adducts exclusively.

Keywords: lanthanoid tricyanide; cyanohydrin; cyanotrimethylsilane

INTRODUCTION

Recently, organolanthanoids have attracted considerable attention in organic syntheses.[1,2] Various reagents have been produced and many useful reactions have been developed using lanthanoids as the key elements.[3] Although lanthanoid cyanides have been prepared,[4] chemical properties and synthetic utilities of these compounds have not been well investigated. In our previous communications, we have shown that ytterbium tricyanide **3** can be prepared by the reaction of tributylytterbium **1** with cyanotrimethylsilane **2** (Eqn [1]). Ytterbium tricyanide is an effective catalyst for regioselective reaction of cyanotrimethylsilane with oxiranes and aziridines.[5] The exchange reaction between ytterbium alkoxide and cyanotrimethylsilane affording ytterbium cyanide and alkoxytrimethylsilane was also disclosed (Eqn [2]).[6] These results suggested a novel access to lanthanoid tricyanides from the corresponding trialkoxides. This paper describes in detail the preparation of ytterbium tricyanide from easily accessible ytterbium tri-isopropoxide[7] and the catalytic application of the cyanides in organic synthesis.

$$\mathrm{YbCl_3} + 3\ n\text{-BuLi} \longrightarrow \underset{\mathbf{1}}{\left[n\text{-Bu}_3\mathrm{Yb}\right]} \xrightarrow[\mathbf{2}]{3\ \mathrm{Me_3SiCN}} \underset{\mathbf{3}}{\mathrm{Yb(CN)_3}} + 3\ \underset{\mathbf{4}}{n\text{-BuSiMe}_3} \qquad [1]$$

$$\mathrm{Yb(OR)L_2} + \mathrm{Me_3SiCN} \longrightarrow \mathrm{Yb(CN)L_2} + \mathrm{ROSiMe_3} \qquad [2]$$

RESULTS AND DISCUSSION

Preparation of ytterbium tricyanide

Reaction of ytterbium tri-isopropoxide **5** with 3 equiv. of cyanotrimethylsilane **2** proceeds smoothly to give ytterbium tricyanide **3** and isopropoxytrimethylsilane **6** quantitatively. As the reaction was carried out by the use of anhydrous reagents and in an argon atmosphere for 5 h pure ytterbium tricyanide was obtained as a white solid after removal of volatile isopropoxytrimethylsilane and excess cyanotrimethylsilane *in vacuo* (Eqn [3]).[8] The white solid was identified as ytterbium tricyanide by comparison of the IR spectrum with the reported one.[4a]

$$\underset{\mathbf{5}}{\mathrm{Yb(OCHMe_2)_3}} + 3\ \underset{\mathbf{2}}{\mathrm{Me_3SiCN}} \longrightarrow \underset{\mathbf{3}}{\mathrm{Yb(CN)_3}} + 3\ \underset{\mathbf{6}}{\mathrm{Me_2CHOSiMe_3}} \qquad [3]$$

This preparative procedure for lanthanoid tricyanide is superior to previous methods. Complete removal of lithium bromide from the ytterbium tricyanide obtained by the reaction of ytterbium tribromide with lithium cyanide was

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difficult.[4a] Ytterbium tricyanide obtained by our previous procedure also contained lithium chloride which was difficult to remove.[5] Compared with these previous procedures, the reaction described here yields pure ytterbium tricyanide quite easily.

Use of ytterbium tricyanide as a synthetic reagent

Cyanation of ketones

Ytterbium tricyanide has been reported to act both as a stoichiometric reagent and as a catalyst for the addition of cyanotrimethylsilane to oxiranes.[5] Similarly, ytterbium tricyanide works both as a stoichiometric reagent with ketones and as a catalyst for addition of cyanotrimethylsilane to ketones; stoichiometric reaction with 2-methylcyclohexanone in a molar ratio 1:3 gave a mixture of cyanohydrins in 42% yield and 40% de (Eqn [4]), whereas the catalytic reaction affords a mixture of the adduct in 87% yield and 86% diastereomeric excess (de) (Eqn [5]). In the stoichiometric reaction, the conversion of the ketone was 51% (1.5 mmol) but hydrolysis of the product upon the isolation of **9** caused the decreased yield. As ytterbium tricyanide was prepared from ytterbium tri-isopropoxide and cyanotrimethylsilane, the ytterbium tri-isopropoxide-catalyzed reaction was examined; the adduct was obtained in 88% yield and 84% de (Eqn [6]). As the ytterbium tricyanide-catalyzed reaction gives the product in the higher diastereomeric ratio, the addition of cyanotrimethylsilane to various carbonyl compounds under ytterbium tricyanide catalysis were examined.

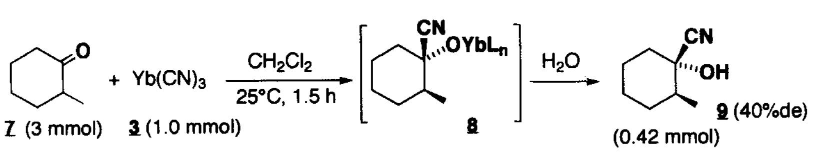
Ytterbium-catalyzed addition of cyanotrimethylsilane to carbonyl compounds

Ytterbium tricyanide-catalyzed reactions of ketones or aldehydes with cyanotrimethylsilane gave the corresponding adducts in excellent yields; results using other catalysts are also included in Table 1.[9–13] It is remarkable that ytterbium tricyanide-catalyzed reactions of substituted cyclohexanones with cyanotrimethylsilane proceed highly diastereoselectively (Table 1, entries 5–7).[14,15] 1,2-Asymmetric induction was observed;[10] the reactions with ketones possessing an α-substituent gave one diastereomer exclusively (Tables 1, entries 8, 9), and 2-acyl-1,3-oxathiane[16,17] afforded the adduct in the superior diastereoselectivity.

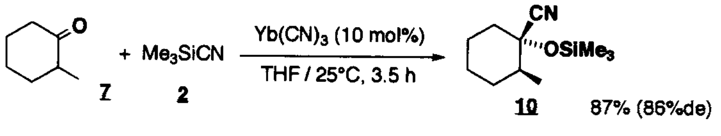
α,β-Unsaturated carbonyl compounds gave 1,2-adducts selectively and the results are shown in Table 2. All reactions afforded only 1,2-adducts. Reactions of hexahydronaphthalenone with cyanotrimethylsilane with ytterbium tricyanide catalyst both at room temperature and in refluxing THF gave only the 1,2-adduct **24**.[18]

When a mixture of cyclohexanone and 2,6-dimethylcyclohexanone was treated with cyanotrimethylsilane with a ytterbium tricyanide catalyst, the cyanated product of cyclohexanone was obtained in 68% yield and the unreacted 2,6-dimethylcyclohexanone was recovered quantitatively (Eqn [7]).

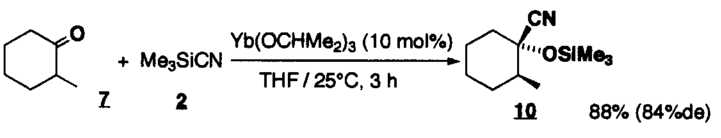
Treatment of easily enolizable or acid-sensitive substrates with the reagent gave the cyanated products in excellent yields without enolization or decomposition of the substrate.[12] Results with ytterbium tricyanide as well as with other catalysts are shown in Table 3.



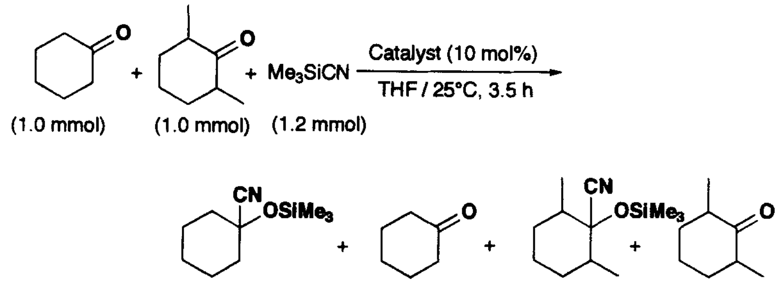
[4]



[5]



[6]



$Yb(CN)_3$	68%	32%	0%	100%
ZnI_2	85	15	32	67
KCN / 18-crown-6	74	26	15	85

[7]

In conclusion, ytterbium tricyanide, stable in air and even in a protic solvent such as ethanol,[4] was prepared efficiently from ytterbium tri-isopropoxide and cyanotrimethylsilane. It acts as a nucleophilic cyanation reagent, and catalyzes the addition of cyanotrimethylsilane to carbonyl compounds efficiently.

EXPERIMENTAL

General aspects

Distillation of the products was performed by the use of Kugelrohr (Büchi), and boiling points are indicated by air-bath temperature without correction. ^1H NMR and ^{13}C NMR spectra were taken on a Varian Gemini 300 spectrometer, $CDCl_3$ was used as solvent, and chemical shifts are given as δ with tetramethylsilane as an internal standard. IR spectra were determned on a Jasco IR-810 spectrometer. Gas–liquid-phase chromatography (GLPC) was performed with a Hitachi 163 gas chromatograph using a Silicon OV-1 capillary column. The analyses were carried out at the Elemental Analysis Center of Kyoto University. Tetrahydrofuran was distilled from benzophenone–sodium just before use. Dichloromethane was distilled from P_2O_5. Ytterbium chloride hexahydrate was purchased from Wako Chemical Industries.

Ytterbium(III) cyanide 3

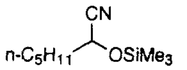
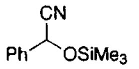
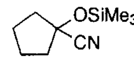
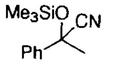
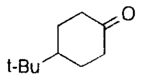
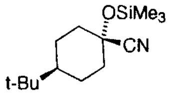
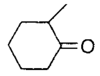
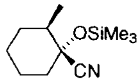
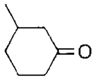
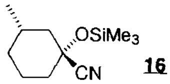
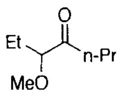
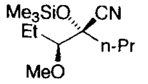
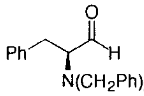
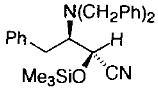
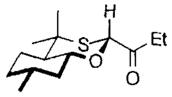
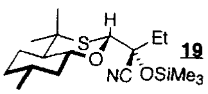
Ytterbium(III) tri-isopropoxide was prepared by the reported procedure[7] and can be purified by sublimation.[19] To a solution of ytterbium(III) tri-isopropoxide (1.8 g, 5.0 mmol) in dichloromethane (6.0 ml) was added cyanotrimethylsilane (1.6 g, 15.5 mmol) at 0 °C. The mixture was stirred for 1 h at 25 °C. The mixture was concentrated at reduced pressure, and the residue was dried *in vacuo*. Ytterbium tricyanide was obtained quantitatively as a white solid (1.28 g). IR (Nujol): ν 2214, 2104 cm^{-1}.[4a] GPLC analysis (Silicon OV-1, 25 m × 0.25 mm, 0.25 μm, 20 °C) of the reaction mixture using n-octane as an internal standard showed formation of isopropoxytrimethylsilane in 83% yield (12.5 mmol).

General procedure for the $Yb(CN)_3$-catalyzed cyanation of ketones with Me_3SiCN

4-T-Butyl-1-Cyano-1-trimethylsiloxycyclohexane 15

Cyanation of 4-t-butylcyclohexanone is representative. To a suspension of $Yb(CN)_3$ (0.1 mmol, 0.025 g) in THF (5.0 ml) was added a mixture of cyanotrimethylsilane (1.2 g, 1.2 mmol) and 4-t-butylcyclohexanone (0.15 g, 1.0 mmol) in THF (2.5 ml). The mixture was stirred for 2 h at 25 °C, and diluted with a mixture of hexane (10 ml) and ether (20 ml). The resulting mixture was filtered with a short Cerite column, and the filtrate was concentrated *in vacuo*. The crude product obtained was purified with alumina column chromatography. 4-t-Butyl-1-cyano-1-trimethylsiloxycyclohexane was obtained as a colorless oil in 88% yield (0.22 g). The ratio of diastereomers (94 : 6) was determined by GLPC analysis: Silicon OV-1, 25 m × 0.25 mm, 0.25 μm, 110 °C, T_r (major product: equatorial alcohol) = 12.72 min, T_r (axial alcohol) = 10.75 min. ^1H NMR ($CDCl_3$): δ 0.24 (s, 9H), 0.87 (s, 9H), 0.75–2.31 (m, 9H). ^{13}C NMR ($CDCl_3$): δ 1.5, 24.4, 27.5 (27.3 for minor product), 32.2, 39.8 (38.4), 46.6, 71.7, 121.6. IR (neat): 1254, 844 cm^{-1}. The compound

Table 1 Yb(CN)$_3$-catalyzed reactions of carbonyl compounds with Me$_3$SiCN

Entry	Substrate	Time (h)	Temp. (°C)	Product	Yield (%) (%de)[a]	ZnI$_2$[b]	Me$_3$SiOTf[c]	KCN/crown[d]
1	n-Hexanal	1	0	 **11**	94	94	60	98
2	PhCHO	1	0	 **12**	95	80	78	81
3	Cyclopentanone	1	0	 **13**	93	94	>99	99
4	Acetophenone	12	25	 **14**	>99	91	88	>99
5		2	0	 **15**	88(88)	97(80)	99(82)	99(56)
		3	−89[e]		>99(94)	—	—	—
6		3.5	0	 **10**	87(86)	94(32)	>99(31)	90(46)
		4	−89[e]		92(90)	—	—	—
7		2	0	 **16**	94(54)	94(2)	>99(4)	90(16)
		5	−89[e]		90(94)	—	—	—
8		5	0	 **17**	81(56)	82(64)	85(58)	80(10)
9		1	0	 **18**	91(44)	89(82)	99(82)	92(72)
10		1.5	0	 **19**	>99(70)	89(44)	74(44)	98(26)[f]
		2	−23		99(74)	—	—	—

[a] Isolated yields. [b] Ref. 9. [c] Ref. 11. [d] KCN, 18-crown-6: Ref. 12. [e] See Experimental section. [f] Major product is the diastereomer of the isomer shown in the Table.

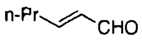
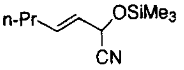
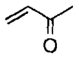
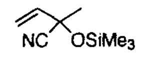
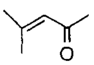
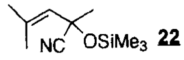
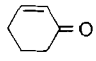
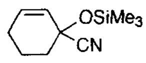
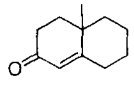
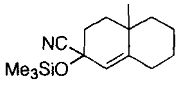
was identified with the authentic sample prepared by a reported procedure.[9]

As shown in Table 1, the reaction was also tried at a lower temperature. To a mixture of Yb(CN)$_3$ and ketone was added cyanotrimethylsilane at −89 °C, and the resulting mixture was stirred for 1 h at the same temperature. The reaction temperature was gradually raised to −10 °C for 3 h. The workup described above gave the product quantitatively with a higher diastereomeric ratio (97:3).

1-Cyano-2-methyl-1-trimethylsiloxycyclohexane 10

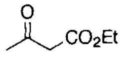
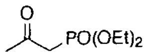
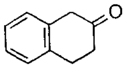
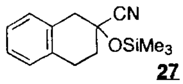
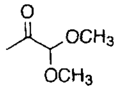
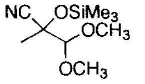
According to the procedure described above, the title compound was prepared from 2-methylcyclo-

Table 2 Yb(CN)$_3$-catalyzed reactions of α,β-unsaturated carbonyl compounds with Me$_3$SiCN

Entry	Substrate	Time (h)	Temp. (°C)	Product		Yield (%)[a,b]
1		0.5	25	25 	20	86
2		0.5	25	25 	21	68
3		1	25	25 	22	75
4		2	0	0 	23	96
5		1	0	0 	24	82

[a] Isolated yields. [b] No 1,4-adduct was detected.

Table 3 Yb(CN)$_3$-catalyzed reactions of easily enolizable and acid-sensitive ketones with Me$_3$SiCN

Entry	Substrate	Time (h)	Temp. (°C)	Product		Yield (%)[a]	ZnI$_2$[b]	Me$_3$SiOTf[c]	KCN/crown[d]
1		4	25		25	90	45[e]	42[e]	73
2		5.5	25		26	84	0	0	96
3		2	0		27	88	68	94	84
4		1	0		28	91	0	30	83

[a] Isolated yields. [b] Ref. 9. [c] Ref. 11. [d] Ref. 12. [e] Silyl enol ether was isolated in 50% yield (ZnI$_2$) and 48% yield (Ne$_3$SiOTf).

hexanone (0.12 g, 1.0 mmol) and isolated in 87% yield (0.18 g). The ratio of diastereomers (1*R**,2*R**/1*S**,2*R** = 93 : 7) was determined by GLPC analysis: Silicon OV-1, 25 m × 0.25 mm, 0.25 μm, 100 °C, T_r (major) = 4.92 min, T_r (minor) = 4.51 min. ^{1}H NMR (CDCl$_3$): δ 0.23 (s, 9H), 1.08 (d, J = 7.0 Hz, 3H), 0.82–2.27 (m, 9H). ^{13}C NMR (CDCl$_3$): δ 1.2, 16.2, 23.6, 24.7 (24.3 for minor product), 31.3, 39.5, 43.0, 75.8, 119.9. IR (Nujol): ν 1254, 844 cm^{-1}. The compound was identified with the authentic sample prepared by a reported procedure.[9]

1-Cyano-3-methyl-1-trimethylsiloxycyclohexane 16

According to the procedure described above, the title compound was prepared from 3-methylcyclohexanone (0.12 g, 1.0 mmol) and isolated in 94% yield (0.20 g) as a diastereomeric mixture. ^{1}H NMR (CDCl$_3$): δ 0.24 (s, 9H), 0.95 (d, J = 6.3 Hz, 3H), 0.70–2.21 (m, 9H). ^{13}C NMR (CDCl$_3$): δ 1.4, 21.6, 22.8, 30.0, 33.2, 39.2, 47.7, 71.4, 121.7. IR (Nujol): ν 1254, 1074, 845 cm^{-1}. The compound was identified with the authentic sample prepared by a reported procedure.[9]

The ratio of diastereomers could not be determined at this stage. The nitrile **16** was transformed into 1,3-dimethylcyclohexanol to determine the diastereomeric ratio. To a solution of **16** (0.17 g, 0.78 mmol) in hexane (2.0 ml) was added a hexane solution of di-isobutylaluminum hydride (1.0 M, 1.95 ml, 1.95 mmol) at −78 °C. The mixture was stirred for 1 h at the same temperature. A saturated aqueous solution of ammonium chloride (1.0 ml) was added dropwise, and the mixture was stirred for 5 min. The mixture obtained was dissolved in 10% aq. H_2SO_4 (5.0 ml) and extracted with ether. The combined ethereal solution was dried and concentrated. The obtained crude 3-methyl-1-hydroxycyclohexanecarbaldehyde (0.11 g) was used for further transformation without purification. Sodium borohydride (0.09 g, 2.34 mmol) was added to a solution of the crude aldehydes in ethanol (5 ml). Water (5 ml) was added to the mixture after 1 h, and the resulting mixture was extracted with ethyl acetate. The combined organic phases were dried and concentrated. To the obtained crude 1-hydroxymethyl-3-methylcyclohexanol (0.10 g) and methanesulfonyl chloride (0.18 g, 1.6 mmol) in dichloromethane (5.0 ml) was added triethylamine (0.16 g, 1.56 mmol) at 0 °C. The mixture was stirred for 4 h and poured into water. The whole was extracted with dichloromethane. The combined organic phases were washed with saturated $NaHCO_3$ and concentrated. The residue (0.15 g) was dissolved in THF (5.0 ml) and lithium aluminum hydride (0.09 g, 2.34 g) was added in one portion. The mixture was stirred for 2 h at 25 °C and poured into 1 M HCl. The resulting mixture was extracted with ether. The combined ethereal phases were dried and concentrated. A purification by silica gel column chromatography gave 1,3-dimethylcyclohexanol in 57% overall yield (57 mg). The ratio of diastereoisomers of 1,3-dimethylcyclohexanol (1*R**,3*S**/1*S**,3*S** = 77:23) was determined by GLPC analysis:[14] Silicon OV-1, 25 m × 0.25 mm, 0.25 μm, 100 °C, T_r (major) = 3.23 min, T_r (minor) = 2.87 min. The ratio represents the diastereomeric ratio of **16** (1*R**,3*S**/1*S**,3*S** = 77:23).

(*S*S*,3*S*)-2-Propyl-3-methoxy-2-trimethylsiloxypentanenitrile 17

According to the procedure described above, the title compound was prepared from 3-methoxy-4-heptanone (0.14 g, 1.0 mmol) and isolated in 81% yield (0.20 g). The isomeric ratio (2*S**,3*S**/2*R**,3*R** = 78:22) was determined by ^{1}H NMR analysis. B.p. 80 °C/8 Torr. ^{1}H NMR ($CDCl_3$): δ 0.24 (s, 9H), 0.96 (t, J = 6.8 Hz, 3H), 1.06 (t, J = 7.4 Hz, 3H), 1.23–2.00 (m, 6H), 3.12–3.32 (m, 1H), 3.54 (s, 2.34H), 3.58 (s, 0.66H). ^{13}C NMR ($CDCl_3$): δ 1.3, 8.2 (8.4), 14.2, 19.6 (19.7), 30.5 (29.3), 32.7 (32.2), 60.0 (61.2), 77.0 (76.7), 84.9 (85.5). IR (Nujol): ν 1254, 844 cm^{-1}. Analysis: found: C, 59.26, H, 10.61, N, 5.86. Calcd for $C_{12}H_{25}NO_2Si$: C, 59.21, H, 10.35, N, 5.86%.

(1*S*,3*S*,6*R*,9*R*)-3-(*R*-1-Cyano-1-trimethylsiloxypropyl)-5,5,9-trimethyl-2-oxa-4-thiabicyclo[4.4.0]decane 19

According to the procedure described above, the title compound was prepared from the corresponding ketone (Table 1, entry 10) (0.26 g, 1.0 mmol)[16,17] and isolated in 99% yield (0.38 g). The ratio of diastereomers was determined by ^{1}H NMR analysis. B.p. 150 °C/0.3 Torr. ^{1}H NMR ($CDCl_3$): δ 0.20 (s, 9H), 0.74–2.01 (m, 10H), 0.99 (t, J = 7.4 Hz, 3H), 1.22 (s, 3H), 1.34 (s, 3H), 3.39 (dt, J = 4.3 Hz, 10.4 Hz, 1H), 4.94 (s, 0.12H, for *S*-isomer), 4.96 (s, 0.88H, for *R*-isomer). ^{13}C NMR ($CDCl_3$): δ 1.6 (1.8), 8.1, 22.0 (22.1), 22.8, 24.3, 29.6, 31.4, 31.7, 34.5, 41.3, 43.4, 50.4, 76.7, 77.9, 82.8, (83.2), 119.6. IR (neat): ν 1252, 1093, 845 cm^{-1}. Analysis: found: C, 60.52, H, 9.43, N, 4.04. Calcd for $C_{18}H_{33}NO_2SSi$: C, 60.80, H, 9.35, N, 4.04%.

(*E*)-2-Trimethylsiloxy-3-heptenenitrile 20

According to the procedure described above, the title compound was prepared from (*E*)-2-hexenal (0.10 g, 1.0 mmol) and isolated in 86% yield (0.17 g). ^{1}H NMR ($CDCl_3$): δ 0.21 (s, 9H), 0.91 (t, J = 7.5 Hz, 3H), 1.43 (quint, J = 7.5 Hz, 2H), 2.07 (dt, J = 7.5 Hz, 7.0 Hz, 2H), 4.89 (q, J = 6.2 Hz, 1H), 5.53 (dd, J = 6.2 Hz, 1H), 5.94 (dt, J = 6.8 Hz, 15.0 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 0.28, 14.0, 22.1, 34.3, 62.7, 119.2, 125.4, 136.7. IR (Nujol): 2230, 1254, 1108 cm^{-1}. The compound was identified with the authentic sample prepared by a reported procedure.[19]

2-Methyl-2-Trimethylsiloxy-3-butenenitrile 21

According to the procedure described above, the title compound was prepared from methyl vinyl ketone (0.07 g, 1.0 mmol) and isolated in 68% yield (0.11 g). ^{1}H NMR ($CDCl_3$): δ 0.23 (s, 9H), 1.64 (s, 3H), 5.27 (d, J = 10.1 Hz, 1H), 5.58 (d, J = 17.1 Hz, 1H), 5.84 (dd, J = 10.1 Hz, 17.1 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 1.7, 30.8, 70.5, 116.3, 120.9, 139.1. IR (Nujol): ν 2246, 1255, 846 cm^{-1}. The compound was identified with the authentic sample prepared by a reported procedure.[9]

Ethyl 3-cyano-3-trimethylsiloxybutanoate 25

According to the procedure described above, the title compound was prepared from ethyl acetoacetate (0.13 g, 1.0 mmol) and isolated in 90%

yield (0.21 g). ^{1}H NMR ($CDCl_3$): δ 0.25 (s, 9H), 1.30 (t, $J = 7.1$ Hz, 3H), 1.72 (s, 3H), 2.77 (s, 2H), 4.21 (q, $J = 7.1$ Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 1.0, 14.0, 29.0, 47.3, 6.08, 66.5, 120.9, 167.8. IR (Nujol): ν 1743, 1256, 848 cm^{-1}. The compound was identified with the authentic sample prepared by a reported procedure.[12b]

Dimethyl 2-Cyano-2-trimethylsiloxypropylphosphate 26

According to the procedure described above, the title compound was prepared from dimethyl 2-oxopropylphosphate (0.17 g, 1.0 mmol) and isolated in 84% yield (0.22 g). ^{1}H NMR ($CDCl_3$): δ 0.28 (s, 9H), 1.80 (s, 3H), 2.37 (d, $J = 18$ Hz, 1H), 2.42 (s, 1H), 3.76 (d, $J = 2.2$ Hz, 3H), 3.82 (d, $J = 2.2$ Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 0.8, 29.5, 37.4, 40.3, 52.2, 65.7, 120.7. IR (neat): ν 1256, 1185, 1034, 847 cm^{-1}. The compounds are identified with the authentic sample prepared by a reported procedure.[12a]

2-Cyano-2-trimethylsiloxy-1,2,3,4-tetrahydronaphthalene 27

According to the procedure described above, the title compound was prepared from β-tetralone (0.15 g, 1.0 mmol) and isolated in 88% yield (0.22 g). ^{1}H NMR ($CDCl_3$): δ 0.25 (s, 9H), 2.04–2.43 (m, 2H), 3.02 (t, $J = 7.0$ Hz, 2H), 3.09 (d, $J = 16.5$ Hz, 1H), 3.31 (d, $J = 16.5$ Hz, 1H), 7.00–7.25 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 1.3, 26.1, 35.6, 42.9, 68.4, 121.5, 126.2, 126.7, 128.6, 129.1, 131.2, 133.8. IR (neat): ν 1254, 846, 748 cm^{-1}. The compound was identified with the authentic sample prepared by a reported procedure.[20]

3,3-Dimethoxy-2-methyl-2-trimethylsiloxypropanenitrile 28

According to the procedure described above, the title compound was prepared from pyruvic aldehyde dimethyl acetal (0.12 g, 1.0 mmol) and isolated in 91% yield (0.20 g). ^{1}H NMR ($CDCl_3$): δ 0.26 (s, 9H), 1.55 (s, 3H), 3.57 (s, 6H), 4.16 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 1.1, 23.7, 57.5, 57.7, 72.3, 107.5, 120.3. IR (neat): ν 1255, 1092 cm^{-1}. The compound was identified with the authentic sample prepared by a reported procedure.[12a]

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