SUPPORTING INFORMATION

for

Lithium Chloride: An Active and Simple Catalyst for Cyanosilylation of Aldehydes and Ketones

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CONTENTS

(A) Typical Procedure for Reaction of Benzaldehyde (100 mmol) with $(CH_3)_3SiCN$ catalyzed by LiCl Under Solvent-Free Conditions (S/C = 10 000)

Caution: $(CH_3)_3SiCN$ must be used in a well-ventilated hood due to its high toxicity.

A dry, 15-mL two-necked flask[1] connected with a rubber balloon filled with argon[2] was equipped with a Teflon-coated magnetic stirring bar and a serum-rubber cap. Solid LiCl (130.3 mg, 3.07 mmol)[3] and THF (10 mL)[4] were placed in this flask, and the mixture was sonicated for 10 min and used as a catalyst stock solution. Another 50-mL two-necked flask[1] connected with a rubber balloon filled with argon[2] was equipped with a Teflon-coated magnetic stirring bar and a serum-rubber cap. Benzaldehyde (**1a**) (10.76 g, 101.4 mmol)[5] and $(CH_3)_3SiCN$ (11.40 g, 114.9 mmol)[5] were introduced into the flask with glass syringes, and the mixture was stirred at 20 °C. To this mixture was added the catalyst solution (33 μL, 10.1 μmol) with a 50-μL micro-syringe at this temperature, and the reaction immediately started exothermically.[6] After stirring for 1 h, a distillation apparatus was connected to the reaction flask, and then the colorless reaction mixture was distilled to give 2-phenyl-2-trimethylsilyloxyacetonitrile (**2a**) (19.55 g, 94%), bp 92–94 °C/2.0 mmHg. The yield determined by GC analysis was 100%. GC (column, TC-5 (95% dimethylpolysiloxane–5% diphenylpolysiloxane), df = 1.5 μm, 0.53 mm i.d. x 15 m, GL-Science; carrier gas, nitrogen (10 kPa); column temp, 100 °C (1 min) then 10 °C/min to 150 °C (3 min); injection temp, 220 °C; detection temp, 200 °C; split ratio, 16:1), retention time (t_R) of **2a**, 6.90 min (100%): t_R of **1a**, 2.25 min (0%). ^1H NMR (270 MHz, $CDCl_3$) δ 0.23 (s, 9, $Si(CH_3)_3$), 5.50 (s, 1, CHCN), 7.37–7.50 (m, 5, aromatics). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ –0.3, 63.9, 119.2, 126.3, 128.9, 129.3, 136.2. HRMS m/z 205.0928 ([M^+]), calcd for $C_{11}H_{15}NOSi$: 205.0923.

Notes

(1) All apparatuses are dried in a 55 °C oven before use.

(2) Argon of 99.99% purity was used.

(3) LiCl (99% purity) purchased from Kanto Chemical Co. was used.

(4) Anhydrous THF (99.5% purity) was purchased from Kanto Chemical Co., and used without further purification.

(5) Benzaldehyde (98% purity, Wako Pure Chemical Co.) and $(CH_3)_3SiCN$ (97% purity, Wako Chemical Co.) were freshly distilled before use.

(6) The exothermic heat was not violate. The reaction temperature was spontaneously cooled down to ambient temperature.

(B) Procedure for Reaction of Benzaldehyde (678 mmol) with $(CH_3)_3SiCN$ catalyzed by LiCl Under Solvent-Free Conditions (S/C = 10 000)[1]

Caution: $(CH_3)_3SiCN$ must be used in a well-ventilated hood due to its high toxicity.

A dry, 200-mL two-necked flask connected with a rubber balloon filled with argon was equipped with a Teflon-coated magnetic stirring bar and a serum-rubber cap. Benzaldehyde (**1a**) (72.7 g, 678 mmol) and $(CH_3)_3SiCN$ (68.0 g, 685 mmol) were introduced into the flask with glass syringes, and the mixture was stirred at 20 °C. To this mixture was added solid LiCl (2.5 mg, 59 μmol) in one portion at this temperature, and the exothermic reaction immediately began. After stirring for 1 h, a distillation apparatus was connected to the reaction flask, and then the colorless reaction mixture was distilled to give 2-phenyl-2-trimethylsilyloxyacetonitrile (**2a**) (135.5 g, 97%), bp 92–94 °C/2.0 mmHg. The yield determined by GC analysis was 100%.

Notes

(1) See Notes of Part A.

(C) Reaction Conditions and Analytical Data of Products

Reaction of benzaldehyde (1a) and $(CH_3)_3SiCN$ (S/C = 100 000). See Part A and B for the reaction with an S/C of 10 000. Conditions (24 mM LiCl solution in THF (22 μL, 0.52 μmol), **1a** (5.28 g, 49.8 mmol), $(CH_3)_3SiCN$ (5.35 g, 54.0 mmol), 22 °C, 48 h). 2-phenyl-2-trimethylsilyloxyacetonitrile (**2a**) (99% GC yield). **Reaction of 1a (0.50 mmol) and $(CH_3)_3SiCN$ (S/C = 100).** Conditions (378 mM LiCl solution in THF (13 μL, 4.9 μmol), **1a** (53.5 mg, 0.50 mmol), $(CH_3)_3SiCN$ (160.6 mg, 1.62 mmol), 20 °C, 1 h). **2a** (100% GC yield). **Reaction of 1a and *t*-$C_4H_9(CH_3)_2SiCN$.** Conditions (60 mM LiCl solution in THF (17 μL, 1.0 μmol), **1a** (1.06 g, 10.0 mmol), *t*-$C_4H_9(CH_3)_3SiCN$ (1.50 g, 10.6 mmol), 22 °C, 5 h). 2-*tert*-butyldimethylsilyloxy-2-phenylacetonitrile (**3a**) (2.37 g, 96%). Bp 70 °C/0.35 mmHg (bulb-to-bulb). ^1H NMR (270 MHz, $CDCl_3$) δ 0.15 (s, 3, $SiCH_3$), 0.23

(s, 3, $SiCH_3$), 0.94 (s, 9, $SiC(CH_3)_3$), 5.52 (s, 1, CHCN), 7.38–7.46 (m, 5, aromatics). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ –5.2, –5.1, 18.1, 25.5, 64.0, 119.3, 126.0, 128.9, 129.2, 136.4. HRMS m/z 247.1400 ([M^+]), calcd for $C_{14}H_{21}NOSi$: 247.1392. **Reaction of 4-methylbenzaldehyde (1b) and $(CH_3)_3SiCN$.** Conditions (47 mM LiCl solution in THF (43 μL, 2.0 μmol), **1b** (1.20 g, 10.0 mmol), $(CH_3)_3SiCN$ (1.29 g, 12.9 mmol), 22 °C, 5 h). 2-(4-methylphenyl)-2-trimethylsilyloxyacetonitrile (**2b**) (2.15 g, 98%). Bp 60 °C/0.15 mmHg (bulb-to-bulb). ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.22 (s, 9, $Si(CH_3)_3$), 2.37 (s, 3, $CH_3C_6H_4$), 5.45 (s, 1, CHCN), 7.22 (d, 2, J = 8.3 Hz, aryl protons at C2 and C6 positions), 7.35 (d, 2, J = 8.3 Hz, aryl protons at C3 and C5 positions). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ –0.3, 21.2, 63.5, 119.3, 126.4, 129.6, 133.4, 139.3. HRMS m/z 219.1082 ([M^+]), calcd for $C_{12}H_{17}NOSi$: 219.1079. **Reaction of 2-chlorobenzaldehyde (1c) and $(CH_3)_3SiCN$.** Conditions (47 mM LiCl solution in THF (21 μL, 1.0 μmol), **1c** (1.42 g, 10.1 mmol), $(CH_3)_3SiCN$ (1.03 g, 10.4 mmol), 22 °C, 0.5 h). 2-(2-chlorophenyl)-2-trimethylsilyloxyacetonitrile (**2c**) (2.25 g, 93%). Bp 65 °C/0.15 mmHg (bulb-to-bulb). ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.26 (s, 9, $Si(CH_3)_3$), 5.80 (s, 1, CHCN), 7.35–7.43 (m, 3, aromatics), 7.71–7.74 (m, 1, aromatic). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ –0.3, 60.7, 118.3, 127.5, 128.3, 129.7, 130.6, 132.0, 133.8. HRMS m/z 239.0521 ([M^+]), calcd for $C_{11}H_{14}ClNOSi$: 239.0533. **Reaction of 1c and t-$C_4H_9(CH_3)_2SiCN$.** Conditions (41 mM LiCl solution in THF (25 μL, 1.0 μmol), **1c** (1.42 g, 10.1 mmol), t-$C_4H_9(CH_3)_3SiCN$ (1.45 g, 10.3 mmol), 22 °C, 1 h). 2-*tert*-butyldimethylsilyloxy-2-(2-chlorophenyl)acetonitrile (**3c**) (2.65 g, 93%). Bp 85 °C/0.15 mmHg (bulb-to-bulb). ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.16 (s, 3, $SiCH_3$), 0.26 (s, 3, $SiCH_3$), 0.94 (s, 9, $SiC(CH_3)_3$), 5.79 (s, 1, CHCN), 7.33–7.42 (m, 3, aromatics), 7.70–7.73 (m, 1, aromatic). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ –5.3, –5.2, 18.1, 25.5, 61.0, 118.2, 127.5, 128.0, 129.7, 130.5, 131.8, 134.0. HRMS m/z 304.0893 ([M + Na^+]), calcd for $C_{16}H_{19}ClNNaOSi$: 304.0895. **Reaction of 4-chlorobenzaldehyde (1d) and $(CH_3)_3SiCN$.** Conditions (42 mM LiCl solution in THF (19 μL, 1.0 μmol), **1d** (1.41 g, 9.98 mmol), $(CH_3)_3SiCN$ (1.04 g, 10.5

mmol), 22 °C, 0.6 h). 2-(4-chlorophenyl)-2-trimethylsilyloxyacetonitrile (**2d**) (2.31 g, 97%). Bp 80 °C/0.15 mmHg (bulb-to-bulb). ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.24 (s, 9, $Si(CH_3)_3$), 5.46 (s, 1, CHCN), 7.40 (s, 4, aromatics). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ –0.3, 62.9, 118.8, 127.7, 129.1, 134.8, 135.3. HRMS m/z 239.0528 ([M$^+$]), calcd for $C_{11}H_{14}ClNOSi$: 239.0533. **Reaction of 4-methoxybenzaldehyde (1e) and $(CH_3)_3SiCN$.** Conditions (50 mM LiCl solution in THF (40 μL, 2.0 μmol), **1e** (1.34 g, 9.84 mmol), $(CH_3)_3SiCN$ (1.24 g, 12.5 mmol), 22 °C, 6 h). 2-(4-methoxyphenyl)-2-trimethylsilyloxyacetonitrile (**2e**) (2.25 g, 97%). Bp 80 °C/0.20 mmHg (bulb-to-bulb). ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.21 (s, 9, $Si(CH_3)_3$), 3.82 (s, 3, CH_3O), 5.44 (s, 1, CHCN), 6.93 (d, 2, *J* = 8.9 Hz, aryl protons at C2 and C6 positions), 7.39 (d, 2, *J* = 8.9 Hz, aryl protons at C3 and C5 positions). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ –0.5, 55.1, 55.6, 63.1, 63.6, 114.0, 119.1, 127.7, 128.2, 160.1. HRMS m/z 235.1032 ([M$^+$]), calcd for $C_{12}H_{17}NO_2Si$: 235.1029. **Reaction of 4-trifluoromethylbenzaldehyde (1f) and $(CH_3)_3SiCN$.** Conditions (36 mM LiCl solution in THF (29 μL, 1.0 μmol), **1f** (1.80 g, 10.3 mmol), $(CH_3)_3SiCN$ (1.06 g, 10.7 mmol), 22 °C, 0.5 h). 2-(4-trifluoromethylphenyl)-2-trimethylsilyloxyacetonitrile (**2f**) (2.76 g, 98%). Bp 65 °C/0.15 mmHg (bulb-to-bulb). ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.27 (s, 9, $Si(CH_3)_3$), 0.23 (s, 3, $SiCH_3$), 5.55 (s, 1, CHCN), 7.61 (d, 2, *J* = 8.6 Hz, aryl protons at C2 and C6 positions), 7.70 (d, 2, *J* = 8.6 Hz, aryl protons at C3 and C5 positions). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ –0.4, 62.9, 118.5, 123.7 (q, $J_{C\text{-}F}$ = 272.1 Hz), 126.0 (q, $J_{C\text{-}F}$ = 3.3 Hz), 131.5 (q, $J_{C\text{-}F}$ = 33.1 Hz), 140.0. HRMS m/z 273.0795 ([M$^+$]), calcd for $C_{12}H_{14}$ F_3NOSi: 273.0797. **Reaction of 2-naphthalenecarbaldehyde (1g) and $(CH_3)_3SiCN$.** Conditions (57 mM LiCl solution in THF (17 μL, 1.0 μmol), **1g** (1.56 g, 10.0 mmol), $(CH_3)_3SiCN$ (1.03 g, 10.4 mmol), 22 °C, 0.4 h). 2-(2-naphthyl)-2-trimethylsilyloxyacetonitrile (**2g**) (2.45 g, 96%). Bp 90 °C/0.12 mmHg (bulb-to-bulb). ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.26 (s, 9, $Si(CH_3)_3$), 5.66 (s, 1, CHCN), 7.52–7.57 (m, 3, aromatics), 7.84–7.93 (m, 4, aromatics). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ –0.4, 63.7, 118.9, 123.4, 125.5, 126.5, 126.7, 127.6, 128.0, 128.9. 132.7, 133.29, 133.33. HRMS m/z 255.1067 ($[M^+]$), calcd for $C_{15}H_{17}NOSi$: 255.1079. **Reaction of cinnamaldehyde (1h) and $(CH_3)_3SiCN$.** Conditions (43 mM LiCl solution in THF (23 μL, 1.0 μmol), **1h** (1.29 g, 9.8 mmol), $(CH_3)_3SiCN$ (0.98 g, 9.9 mmol), 22 °C, 3 h). (*E*)-4-phenyl-2-trimethylsilyloxy-3-butenenitrile (**2h**) (1.99 g, 88%). Bp 80 °C/0.15 mmHg (bulb-to-bulb). ^1H NMR (270 MHz, $CDCl_3$) δ 0.26 (s, 9, $Si(CH_3)_3$), 5.12 (d, 1, *J* = 5.9 Hz, CHCN), 6.19 (dd, 1, *J* = 5.9 Hz and 15.8 Hz, $C_6H_5CH{=}C\mathit{H}$), 6.81 (d, 1, *J* = 15.8 Hz, $C_6H_5C\mathit{H}{=}CH$), 7.30–7.42 (m, 5, aromatics). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ –0.1, 62.3, 118.4, 123.5, 127.0, 128.7, 128.8, 134.0, 135.0. HRMS m/z 231.10829 ($[M^+]$), calcd for $C_{13}H_{17}NOSi$: 231.10793. **Reaction of 1h and *t*-$C_4H_9(CH_3)_2SiCN$.** Conditions (44 mM LiCl solution in THF (23 μL, 0.1 μmol), **1h** (1.33 g, 10.0 mmol), *t*-$C_4H_9(CH_3)_3SiCN$ (1.46 g, 10.3 mmol), 22 °C, 8 h). (*E*)-2-*tert*-butyldimethylsilyloxy-4-phenyl-3-butenenitrile (**3h**) (2.54 g, 93%). Bp 90 °C/0.14 mmHg (bulb-to-bulb). ^1H NMR (270 MHz, $CDCl_3$) δ 0.19 (s, 3, $SiCH_3$), 0.22 (s, 3, $SiCH_3$), 0.95 (s, 9, $SiC(CH_3)_3$), 5.14 (dd, 1, *J* = 1.3 Hz and 5.9 Hz, CHCN), 6.19 (dd, 1, *J* = 5.9 Hz and 15.8 Hz, $C_6H_5CH{=}C\mathit{H}$), 6.81 (d, 1, *J* = 15.8 Hz, $C_6H_5C\mathit{H}{=}CH$), 7.30–7.43 (m, 5, aromatics). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ –5.03, –4.98, 18.2, 25.2, 62.6, 118.4, 123.7, 126.9, 128.7, 133.6, 135.1. HRMS m/z 273.1544 ($[M^+]$), calcd for $C_{16}H_{23}NOSi$: 273.1549. **Reaction of (*E*)-2-octenal (1i) and $(CH_3)_3SiCN$.** Conditions (29 mM LiCl solution in THF (34 μL, 1.0 μmol), **1i** (1.25 g, 9.9 mmol), $(CH_3)_3SiCN$ (1.04 g, 10.5 mmol), 22 °C, 22 h). (*E*)-2-trimethylsilyloxy-3-nonenenitrile (**2h**) (2.18 g, 98%). Bp 55 °C/0.15 mmHg (bulb-to-bulb). ^1H NMR (270 MHz, $CDCl_3$) δ 0.21 (s, 9, $Si(CH_3)_3$), 0.89 (t, 3, *J* = 6.6 Hz, $CH_2C\mathit{H}_3$), 1.20–1.50 (m, 6, $(C\mathit{H}_2)_3CH_3$), 2.08 (dt, 2, *J* = 6.9 Hz and 6.9 Hz, $C\mathit{H}_2CH{=}CH$), 4.89 (d, 1, *J* = 6.3 Hz, CHCN), 5.53 (dd, 1, *J* = 6.3 Hz and 15.3 Hz, $CH_2CH{=}C\mathit{H}$), 5.96 (dt, 1, *J* = 15.3 Hz and 6.6 Hz, $CH_2C\mathit{H}{=}CH$). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ –0.2, 14.0, 22.4, 28.2, 31.3, 31.8, 62.3, 118.8, 124.8, 136.5. HRMS m/z 225.1545 ($[M^+]$), calcd for $C_{12}H_{23}NOSi$: 225.1549. **Reaction of octanal (1j) and $(CH_3)_3SiCN$.** Conditions (31 mM LiCl solution in THF (33 μL, 1.0 μmol), **1j** (1.27 g, 9.9 mmol), $(CH_3)_3SiCN$ (1.04 g, 10.4 mmol), 22 °C, 0.5 h). 2-

trimethylsilyloxynonanenitrile (**2j**) (2.14 g, 95%). Bp 50 °C/0.20 mmHg (bulb-to-bulb). ^{1}H NMR (270 MHz, CDCl$_3$) δ 0.21 (s, 9, Si(CH$_3$)$_3$), 0.89 (t, 3, *J* = 6.3 Hz, CH$_2$C*H*$_3$), 1.29–1.45 (m, 10, (C*H*$_2$)$_5$CH$_3$), 1.78 (m, 2, C*H*$_2$CHCN), 4.38 (t, 1, *J* = 6.6 Hz, CHCN). ^{13}C NMR (67.8 MHz, CDCl$_3$) δ –0.4, 14.1, 24.6, 28.9, 29.0, 31.7, 36.2, 61.5, 120.0. HRMS m/z 227.1693 ([M$^+$]), calcd for $C_{12}H_{25}NOSi$: 227.1705. **Reaction of cyclohexanecarbaldehyde (1k) and (CH$_3$)$_3$SiCN.** Conditions (44 mM LiCl solution in THF (23 μL, 1.0 μmol), **1k** (1.11 g, 9.8 mmol), (CH$_3$)$_3$SiCN (1.06 g, 10.6 mmol), 22 °C, 0.5 h). 2-cyclohexyl-2-trimethylsilyloxyacetonitrile (**2k**) (1.95 g, 94%). Bp 50 °C/0.20 mmHg (bulb-to-bulb). ^{1}H NMR (270 MHz, CDCl$_3$) δ 0.21 (s, 9, Si(CH$_3$)$_3$), 1.02–1.24 (m, 5, protons of cyclohexyl), 1.58–1.81 (m, 6, protons of cyclohexyl), 4.14 (d, 1, *J* = 6.6 Hz, CHCN). ^{13}C NMR (67.8 MHz, CDCl$_3$) δ –0.7, 25.3, 25.8, 27.7, 27.9, 42.7, 66.3, 119.2. HRMS m/z 211.1394 ([M$^+$]), calcd for $C_{11}H_{21}NOSi$: 211.1392. **Reaction of pivalaldehyde (1l) and (CH$_3$)$_3$SiCN.** Conditions (47 mM LiCl solution in THF (21 μL, 1.0 μmol), **1l** (0.85 g, 9.8 mmol), (CH$_3$)$_3$SiCN (1.05 g, 10.5 mmol), 22 °C, 0.17 h). 3,3-dimethyl-2-trimethylsilyloxybutanenitrile (**2l**) (1.78 g, 98%). Bp 90 °C/50 mmHg (bulb-to-bulb). ^{1}H NMR (270 MHz, CDCl$_3$) δ 0.21 (s, 9, Si(CH$_3$)$_3$), 1.01 (s, 9, C(CH$_3$)$_3$), 3.99 (s, 1, CHCN). ^{13}C NMR (67.8 MHz, CDCl$_3$) δ –0.5, 25.2, 36.1, 71.1, 119.6. HRMS m/z 185.1238 ([M$^+$]), calcd for $C_9H_{19}NOSi$: 185.1236. **Reaction of 1l and *t*-C$_4$H$_9$(CH$_3$)$_2$SiCN.** Conditions (42 mM LiCl solution in THF (24 μL, 1.0 μmol), **1l** (0.86 g, 9.9 mmol), *t*-C$_4$H$_9$(CH$_3$)$_3$SiCN (1.49 g, 10.5 mmol), 22 °C, 2 h). 2-*tert*-butyldimethylsilyloxy-3,3-dimethylbutanenitrile (**3l**) (2.02 g, 90%). Bp 100 °C/12 mmHg (bulb-to-bulb). ^{1}H NMR (270 MHz, CDCl$_3$) δ 0.13 (s, 3, SiCH$_3$), 0.21 (s, 3, SiCH$_3$), 0.93 (s, 9, SiC(CH$_3$)$_3$), 1.03 (s, 9, C(CH$_3$)$_3$), 4.01 (s, 1, CHCN). ^{13}C NMR (67.8 MHz, CDCl$_3$) δ –5.6, –5.3, 18.1, 25.0, 25.5, 36.1, 71.2, 119.3. HRMS m/z 227.1703 ([M$^+$]), calcd for $C_{12}H_{25}NOSi$: 227.1705. **Reaction of acetophenone (1m) and (CH$_3$)$_3$SiCN.** Conditions (0.21 M LiCl solution in THF (0.24 mL, 0.050 mmol), **1m** (0.61 g, 5.1 mmol), (CH$_3$)$_3$SiCN (0.67 g, 6.7 mmol), 20 °C, 3 h). 2-phenyl-2-trimethylsilyloxypropionitrile

(**2m**) (1.06 g, 96%). Bp 55 °C/0.45 mmHg (bulb-to-bulb). ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.16 (s, 9, $Si(CH_3)_3$), 1.86 (s, 3, CH_3CCN), 7.27–7.45 (m, 3, aromatics), 7.49–7.60 (m, 2, aromatics). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 1.1, 33.6, 71.6, 121.6, 124.6, 128.6, 141.9. HRMS m/z 219.1072 ([M$^+$]), calcd for $C_{12}H_{17}NOSi$: 219.1079. **Reaction of 5-nonanone (1n) and $(CH_3)_3SiCN$.** Conditions (0.20 M LiCl solution in THF (0.24 mL, 0.048 mmol), **1n** (0.60 g, 4.9 mmol), $(CH_3)_3SiCN$ (0.67 g, 6.7 mmol), 23 °C, 2.5 h). 2-*n*-butyl-2-trimethylsilyloxyhexanenitrile (**2n**) (1.09 g, 94%). Bp 100 °C/7 mmHg (bulb-to-bulb). ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.23 (s, 9, $Si(CH_3)_3$), 0.93 (t, 6, J = 6.9 Hz, $2CH_2CH_3$), 1.25–1.56 (m, 8, $2CH_2CH_2CH_3$), 1.71 (t, 4, J = 7.9 Hz, $2CH_2CCN$). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 1.3, 13.9, 22.6, 26.1, 40.7, 73.2, 121.8. HRMS m/z 241.1863 ([M$^+$]), calcd for $C_{13}H_{27}NOSi$: 241.1862.

(D) Kinetic Study of Cyanosilylation of *para*-Substituted Benzaldehydes

A series of kinetic experiments was conducted at 20–25 °C using an equimolar mixture of benzaldehyde and the *para*-substituted substrate. A dry, 15-mL two-necked flask connected with a rubber balloon filled with argon was equipped with a Teflon-coated magnetic stirring bar and a serum-rubber cap. Solid LiCl (12.5 mg, 295 μmol) and THF (10 mL) were placed in this flask, and the mixture was sonicated for 10 min and used as a catalyst stock solution. Another 15-mL two-necked flask connected with a rubber balloon filled with argon was equipped with a Teflon-coated magnetic stirring bar and a serum-rubber cap. Benzaldehyde (**1a**) (1.06 g, 10.0 mmol), *para*-substituted substrate (10.0 mmol), and $(CH_3)_3SiCN$ (1.03 g, 10.4 mmol) were introduced into the flask with glass syringes, and the mixture was stirred at 20–25 °C. To this mixture was added the catalyst solution (34 μL, 1.0 μmol) with a 50-μL micro-syringe. The reaction mixture was stirred, and small portions of the mixture were sampled after appropriate periods. Conversions were determined by ^{1}H NMR. The initial rates of reaction of the substituted benzaldehyde (v_X) and the parent aldehyde (v_H) were calculated from 3 or 4 experiment sets and were firstorder-plotted. Correlations between a substrate, $\log(v_X/v_H)$, and the σ_P value of the substituent are as follows: 4-methoxybenzaldehyde, –0.51, –0.28; 4-methylbenzaldehyde, –0.17, –0.14; benzaldehyde, 0, 0; 4-fluorobenzaldehyde, 0.06, 0.06; 4-chlorobenzaldehyde, 0.20, 0.22; 4-trifluoromethylbenzaldehyde, 0.62, 0.53; 4-cyanobenzaldehyde, 0.78, 0.71. The ρ value of the Hammett plot (Figure 1 in the main text) was determined to be +1.24.

(E) ^{13}C NMR Measurement of $(CH_3)_3SiCN$ with or without LiCl

^{13}C NMR spectra (67.8 MHz) were recorded on a JEOL JNM-EX270 spectrometer. All samples were measured in THF-d_8 solution at 20–25 °C. The chemical shifts are reported in parts-per-million (δ) relative to THF at 25.2 (α-CH_2). The obtained spectra are shown in the Figure S1.

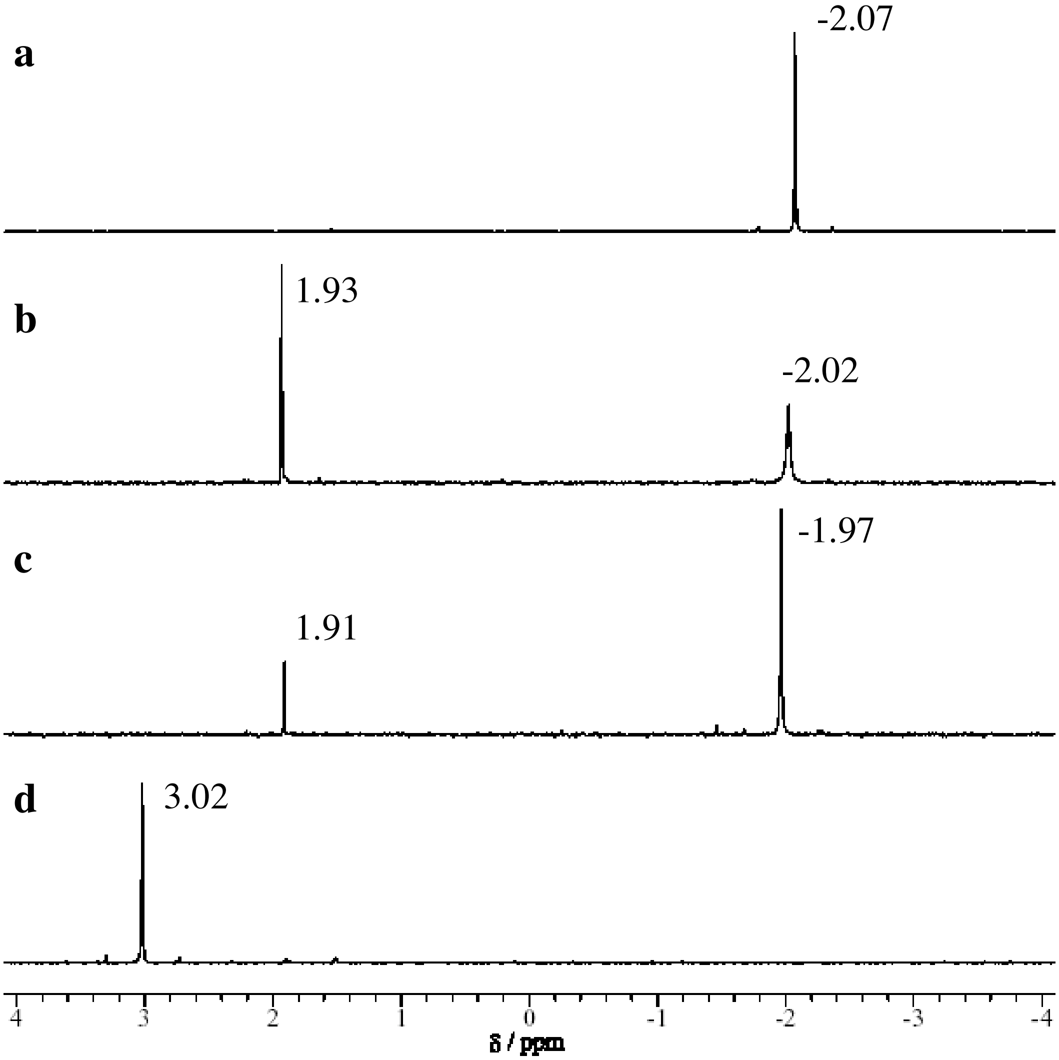

Figure S1. ^{13}C NMR spectra of the $(CH_3)_3Si$ region: (a) $(CH_3)_3SiCN$, (b) a 1:1 mixture of $(CH_3)_3SiCN$ and LiCl, (c) a 1.7:1:1 mixture of $(CH_3)_3SiCN$, 18-crown-6, and KCN, and (d) $(CH_3)_3SiCl$.