

## Supplementary Material

### Cyanosilylation of Aldehydes Catalyzed by Iron(III)-Arylhydrazone- $\beta$ -Diketone Complexes

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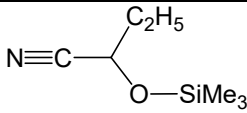
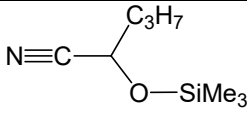
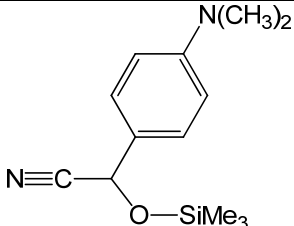
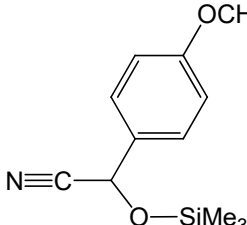
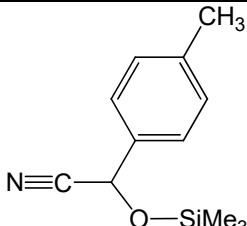
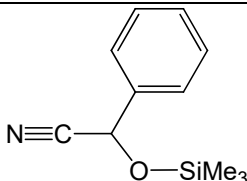
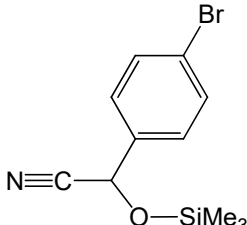
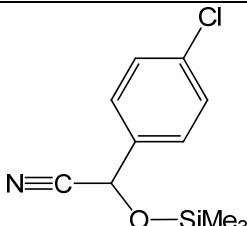
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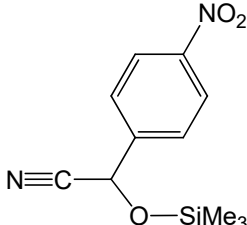
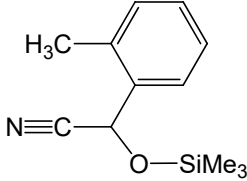
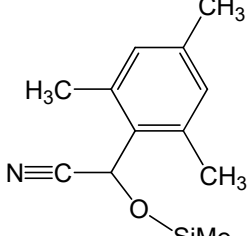
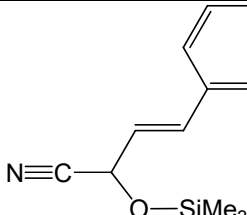
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**Table S1.** Analytical data of isolated products.

Products	Characterization	Ref.
	<b>2-((Trimethylsilyloxy)butanenitrile.</b> <sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> , ppm): δ 4.35 (t, 1H, CH), 1.81 (m, 2H, CH <sub>2</sub> ), 1.03 (t, 3H, CH <sub>3</sub> ), 0.20 (s, 9H, OSiMe <sub>3</sub> ). <sup>13</sup> C NMR (100 MHz, CDCl <sub>3</sub> ): δ 119.8 (CN), 62.6 (CH), 29.5 (CH <sub>2</sub> ), 8.8 (CH <sub>3</sub> ), -0.5 (OSiMe <sub>3</sub> ).	s1
	<b>2-(Trimethylsilyloxy)pentanenitrile.</b> <sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> ): δ 4.38 (t, <i>J</i> = 6.6 Hz, 1H), 1.75 (m, 2H), 0.94 (t, <i>J</i> = 7.3 Hz, 3H), 0.18 (s, 9H); <sup>13</sup> C NMR (100 MHz, CDCl <sub>3</sub> ): δ 120.5, 61.6, 38.6, 18.3, 13.8, 0.0.	s2
	<b>2-(4-(Dimethylamino)phenyl)-2-((trimethylsilyloxy)acetone nitrile</b> <sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> , ppm): δ 7.29–7.23 (m, 2H), 6.76–6.71 (m, 2H), 5.80 (s, 1H), 2.91 (s, 6H), 0.13 (s, 9H); <sup>13</sup> C NMR (100 MHz, CDCl <sub>3</sub> ): δ 150.9, 127.8, 123.7, 120.4, 112.1, 62.8, 40.0, -0.2.	s3
	<b>2-Trimethylsilyloxy-(4-methoxyphenyl)acetone nitrile.</b> <sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> , ppm): δ 0.21 (s, 9H, Si(CH <sub>3</sub> ) <sub>3</sub> ), 3.83 (s, 3H, OCH <sub>3</sub> ), 5.44 (1H, s, CHO), 6.93 (d, 2H, 3 <i>J</i> (H,H) = 8.5 Hz), 7.39 (d, 2H, 3 <i>J</i> (H,H) = 8.5 Hz); <sup>13</sup> C NMR (100 MHz, CDCl <sub>3</sub> ): δ -0.2 (Si(CH <sub>3</sub> ) <sub>3</sub> ), 55.3 (OCH <sub>3</sub> ), 63.3 (CHO), 114.3 (CAr), 119.3 (CN), 127.9 (CHAR), 128.5 (CHAR), 160.3 (CAr).	s4
	<b>2-Trimethylsilyloxy-(4-methylphenyl)acetone nitrile.</b> <sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> , ppm): δ 0.22 (s, 9H, Si(CH <sub>3</sub> ) <sub>3</sub> ), 2.37 (s, 3H, ArCH <sub>3</sub> ), 5.45 (1H, s, CHO), 7.22 (d, 2H, 3 <i>J</i> (H,H) = 7.9 Hz), 7.35 (d, 2H, 3 <i>J</i> (H,H) = 7.9 Hz); <sup>13</sup> C NMR (100 MHz, CDCl <sub>3</sub> ): δ -0.2 (Si(CH <sub>3</sub> ) <sub>3</sub> ), 21.2 (ArCH <sub>3</sub> ), 63.6 (CHO), 119.3 (CN), 126.4 (CHAR), 129.6 (CHAR), 133.4 (CAr), 139.4 (CAr).	s4
	<b>2-Phenyl-2-((trimethylsilyloxy)acetone nitrile.</b> <sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> , ppm): δ 7.49 - 7.39 (m, 5H), 5.50 (s, 1H), 0.24 (s, 3H); <sup>13</sup> C NMR (100 MHz, CDCl <sub>3</sub> ): δ 136.4, 129.5, 129.1, 126.5, 119.3, 63.8, -0.09.	s3
	<b>2-Trimethylsilyloxy-(4-bromophenyl)acetone nitrile.</b> <sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> , ppm): δ 0.24 (s, 9H, Si(CH <sub>3</sub> ) <sub>3</sub> ), 5.45 (s, 1H, CHO), 7.35 (d, 2H, 3 <i>J</i> (H,H) = 8.3 Hz), 7.55 (d, 2H, 3 <i>J</i> (H,H) = 8.3 Hz); <sup>13</sup> C NMR (100 MHz, CDCl <sub>3</sub> ): δ -0.3 (Si(CH <sub>3</sub> ) <sub>3</sub> ), 63.0 (CHO), 118.7 (CN), 123.5 (CHAR), 127.9 (CHAR), 132.1 (CAr), 135.3 (CAr).	s4
	<b>2-Trimethylsilyloxy-(4-chlorophenyl)acetone nitrile.</b> <sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> , ppm): δ 0.24 (s, 9H, Si(CH <sub>3</sub> ) <sub>3</sub> ), 5.46 (s, 1H, CHO), 7.3–7.5 (m, 4H, CHAR); <sup>13</sup> C NMR (100 MHz, CDCl <sub>3</sub> ): δ -0.2 (Si(CH <sub>3</sub> ) <sub>3</sub> ), 63.0 (CHO), 118.8 (CN), 127.7 (CHAR), 129.2 (CHAR), 134.8 (CAr), 135.3 (CAr).	s4

	<b>2-(4-nitrophenyl)-2-(trimethylsilyloxy)acetonitrile.</b> $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ , ppm): $\delta$ 8.38 (d, $J = 8.6$ Hz, 2H), 7.80 (d, $J = 8.3$ Hz, 2H), 5.75 (s, 1H), 0.38 (s, 9H); $^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ ): $\delta$ 149.08, 143.72, 127.75, 124.67, 118.88, 63.30, -0.12.	s5
	<b>2-Trimethylsilyloxy-2-(2-methylphenyl) acetonitrile.</b> $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ , ppm): $\delta$ 7.44-7.42 (m, 1H, ArH), 7.22-7.10 (m, 3H, ArH), 5.48 (s, 1H, CH), 2.34 (s, 3H, $\text{CH}_3$ ), 0.14 (s, 9H, $\text{CH}_3$ ); $^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ ): $\delta$ 135.9, 134.4, 131.3, 127.3, 126.7, 119.1, 62.3, 19.0, 0.	s6
	<b>2,4,6-Trimethyl-<math>\alpha</math>-[(trimethylsilyloxy)benzeneacetonitrile.</b> $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ , ppm): $\delta$ 0.18 (s, 9H, $\text{Si}(\text{CH}_3)_3$ ), 2.26 (s, 3H, $\text{CH}_3$ ), 2.46 (s, 6H, $\text{CH}_3$ ), 5.80 (s, 1H, $\text{CHOSi}(\text{CH}_3)_3$ ), 6.80 (s, 1H, Ph), 6.86 (s, 2H, Ph). $^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ ): $\delta$ -0.19 ( $\text{Si}(\text{CH}_3)_3$ ), 20.04 ( $\text{CH}_3$ ), 21.05 ( $\text{CH}_3$ ), 58.96 ( $\text{CHOSi}(\text{CH}_3)_3$ ), 119.32 (CN), 129.77 (CAr), 130.23 (CAr), 136.82 (CAr), 139.24 (CAr).	s7
	<b>(E)-4-phenyl-2-trimethylsilyloxy-3-butenenitrile.</b> $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ , ppm): $\delta$ 7.33-7.20 (m, 5H, ArH), 6.70 (dd, $J = 0.8$ and 15.6 Hz, 1H, CH), 6.08 (dd, $J = 6.0$ and 15.6 Hz, 1H, CH), 5.01 (dd, $J = 1.2$ and 6.0 Hz, 1H, CH), 0.15 (s, 9H, $\text{CH}_3$ ). $^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ ): $\delta$ 135.2, 134.0, 128.9, 128.8, 127.1, 123.7, 118.5, 62.3, 0.	s6

## Reference

- [s1] L. Yan, W. Jinjin, W. Yile, Zh. Hongping, S.P. Prinson, R.W. Herbert, Dalton Trans. 42 (2013) 13715.
- [s2] S. J. Jinhua, G. Fabrice, R.T. Jonathan, T. Zhulin, Y.K. Nathan, Ch.H. Senanayake, J. Org. Chem. 71 (2006) 1273.
- [s3] K. Johannes, T. Smeilus, O. Schackow, A. Giannis, Chem. Eur.J. 23 (2017) 5000.
- [s4] M. North, M. Omedes-Pujol, C. Williamson, Chem. Eur. J. 16 (2010) 11367.
- [s5] M. Liberman, L. Allegra, R.G. Bergman, T.D. Tilley, J. Am. Chem. Soc., 137 (2015) 5328.
- [s6] L. Chengwei, Ch. Qigan, X. Daqian, W. Shoufeng, X. Chungu, S. Wei, Eur. J. Org. Chem. (2011) 3407.
- [s7] Sh.K. Mahendra, S. Soumen, G. Mukherjee, G. Rajaraman, N. Selvarajan, Dalton Trans. 46 (2017) 7672.