

Electronic Supplementary Information (ESI) for

Rhodium acetate/base-catalyzed N-silylation of indole derivatives with hydrosilanes

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Experimental Details

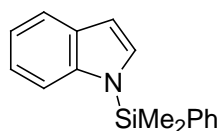
General: GC analyses were performed on Shimadzu GC-2014 with a FID detector equipped with a TC-1 or a TC-5 capillary column. Mass spectra were recorded on Shimadzu GCMS-QP2010 equipped with a TC-5HT or an InertCap 5MS/Sil capillary column. Liquid-state NMR spectra were recorded on a JEOL JNM-EX-270 (^1H , 270.0 MHz; ^{13}C , 67.80 MHz) or a JEOL ECA-500 (^1H , 500.0 MHz; ^{13}C , 124.50 MHz) spectrometer. CSI-MS spectra were measured with JEOL T 100-CS. $\text{Rh}_2(\text{OAc})_4$ was obtained from Aldrich (reagent grade) and used as received. Other metal salts and complexes were obtained from Wako Pure Chemical Industries, Kanto Chemical, TCI, or Aldrich (reagent grade) and used as received. TBA_2WO_4 was prepared according to the literature procedure^{S1} and handled in a glove box under Ar ($\text{O}_2 < 1.0$ ppm, $\text{H}_2\text{O} < 1.0$ ppm). Other bases were obtained from Kanto Chemical or TCI and used as received. Indoles, pyrrole, carbazole, and silanes were obtained from TCI and used as received. Acetonitrile was purified by The Ultimate Solvent System (Glass Contour Company).^{S2} Other solvents (dehydrated grade) were obtained from Wako Pure Chemical Industries, Kanto Chemical, or Aldrich and used in a glove box.

Typical procedure for N-silylation of indoles: The catalytic N-silylation of indoles with silanes was carried out in a Schlenk tube. In a glove box, TBA_2WO_4 (10 μmol) was dissolved in acetonitrile (2 mL). To a mixture of $\text{Rh}_2(\text{OAc})_4$ (5 μmol) and **1a** (0.5 mmol) were added the

acetonitrile solution of TBA_2WO_4 and **2a** (2.5 mmol) under a continuous Ar flow. The reaction mixture was stirred at 50 °C for 2 h, and the progress was monitored by GC (>99% yield). The reaction mixture of **3aa** was evaporated by a vacuum line, followed by the addition of hexane (2 mL) under a continuous Ar flow. The resulting yellow solution was subjected to flash column chromatography on silica gel using hexane to afford **3aa** as colorless oils in 79% yield.

Compound data

Compound **3aa** (Table 1, entry 1)



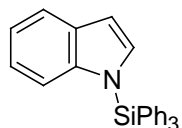
CAS Registry Number: 1343516-53-9; ^1H NMR (500.0 MHz, CDCl_3 , TMS): 0.770 (s, 6H), 6.61 (d, $J = 2.8$ Hz, 1H), 7.03–7.11 (m, 2H), 7.14 (d, $J = 2.8$ Hz, 1H), 7.25 (d, $J = 7.9$ Hz, 1H), 7.35 (t, $J = 7.4$ Hz, 2H), 7.40 (t, $J = 7.4$ Hz, 1H), 7.51 (d, $J = 6.2$ Hz, 2H), 7.63 (d, $J = 7.9$ Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (124.5 MHz, CDCl_3 , TMS): -1.06, 105.3, 113.7, 120.3, 121.1, 121.8, 128.6, 130.6, 130.8, 132.0, 134.1, 135.6, 140.7; MS (EI) m/z (%): 252 (24), 251 (100) [M^+], 250 (33), 236 (31), 136 (14), 135 (99), 117 (10), 107 (11), 105 (11).

Compound **3ab** (Table 1, entry 2)



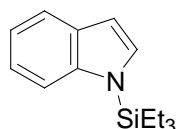
CAS Registry Number: 1343516-48-2; MS (EI) m/z (%): 314 (27), 313 (99) [M^+], 312 (22), 298 (10), 198 (17), 197 (100), 195 (12), 118 (12), 105 (14).

Compound **3ac** (Table 1, entry 3)



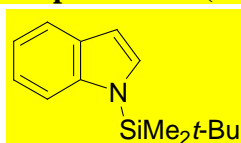
CAS Registry Number: 1256710-30-1; MS (EI) m/z (%): 376 (31), 375 (91) [M^+], 374 (15), 260 (24), 259 (100), 181 (22), 149 (18), 105 (12).

Compound 3ad (Table 1, entry 4)



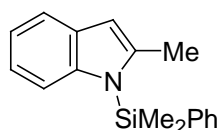
CAS Registry Number: 1343516-56-2; ^1H NMR (500.0 MHz, CDCl_3 , TMS): 0.964 (t, $J = 7.4$ Hz, 9H), 1.05 (q, $J = 7.9$ Hz, 6H), 6.60 (d, $J = 3.4$ Hz, 1H), 7.10–7.17 (m, 3H), 7.49 (d, $J = 7.9$ Hz, 1H), 7.64 (d, $J = 7.4$ Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (124.5 MHz, CDCl_3 , TMS): 4.59, 7.03, 104.9, 113.2, 120.2, 121.1, 121.7, 130.7, 131.8, 140.7; MS (EI) m/z (%): 232 (21), 231 (100) [M^+], 203 (25), 202 (76), 175 (17), 174 (91), 146 (57), 144 (12), 117 (13), 87 (27), 73 (10), 59 (17).

Compound 3ae (Table 1, entry 5)



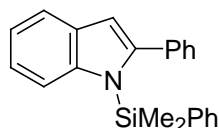
CAS Registry Number: 40899-73-8; MS (EI) m/z (%): 231 (36) [M^+], 176 (10), 175 (47), 174 (100).

Compound 3ba (Table 2, entry 2)



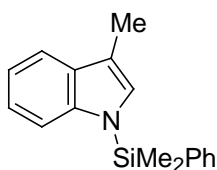
CAS Registry Number: 1343516-54-0; ^1H NMR (500.0 MHz, CDCl_3 , TMS): 0.835 (s, 6H), 2.33 (s, 3H), 6.34 (s, 1H), 6.96 (t, $J = 7.9$ Hz, 1H), 7.04 (t, $J = 7.4$ Hz, 1H), 7.25 (s, 1H), 7.33–7.42 (m, 3H), 7.47–7.50 (m, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (124.5 MHz, CDCl_3 , TMS): 1.71, 17.3, 106.3, 113.8, 119.7, 120.2, 120.8, 128.6, 130.3, 131.8, 133.8, 137.6, 142.0, 142.4; MS (EI) m/z (%): 266 (17), 265 (71) [M^+], 264 (10), 187 (20), 136 (14), 135 (100), 107 (10).

Compound 3ca (Table 2, entry 3)



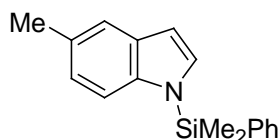
^1H NMR (500.0 MHz, CDCl_3 , TMS): 0.373 (s, 6H), 6.59 (s, 1H), 7.02 (t, $J = 7.6$ Hz, 1H), 7.11 (t, $J = 7.6$ Hz, 1H), 7.26–7.40 (m, 9H), 7.48 (d, $J = 6.8$ Hz, 2H), 7.61 (d, $J = 8.0$ Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (124.5 MHz, CDCl_3 , TMS): 1.25, 107.8, 115.0, 120.5, 120.7, 121.6, 128.2, 128.3, 128.5, 130.1, 130.2, 131.7, 133.7, 136.4, 137.9, 142.7, 146.5.

Compound 3da (Table 2, entry 4)



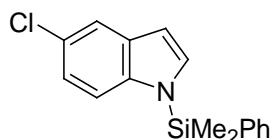
^1H NMR (500.0 MHz, CDCl_3 , TMS): 0.753 (s, 6H), 2.31 (s, 3H), 6.90 (s, 1H), 7.05 (t, $J = 7.4$ Hz, 1H), 7.10 (t, $J = 7.4$ Hz, 1H), 7.20 (d, $J = 7.9$ Hz, 1H), 7.35 (t, $J = 6.8$ Hz, 2H), 7.40 (t, $J = 6.8$ Hz, 1H), 7.52 (d, $J = 7.4$ Hz, 2H), 7.55 (d, $J = 7.4$ Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (124.5 MHz, CDCl_3 , TMS): -0.82, 10.0, 113.6, 114.2, 119.2, 119.8, 121.7, 128.0, 128.5, 130.5, 132.4, 134.2, 136.0, 141.1; MS (EI) m/z (%): 266 (25), 265 (100) [M^+], 264 (31), 250 (19), 136 (13), 135 (94), 107 (10).

Compound 3ea (Table 2, entry 5)



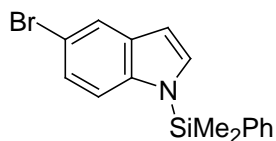
^1H NMR (500.0 MHz, CDCl_3 , TMS): 0.761 (s, 6H), 2.40 (s, 3H), 6.53 (d, $J = 3.4$ Hz, 1H), 6.88 (dd, $J = 1.4, 8.2$ Hz, 1H), 7.10–7.14 (m, 2H), 7.33–7.37 (m, 2H), 7.39–7.42 (m, 2H), 7.49 (dd, $J = 1.7, 7.9$ Hz, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (124.5 MHz, CDCl_3 , TMS): -1.07, 21.7, 104.9, 113.3, 120.8, 123.3, 128.5, 129.6, 130.6, 130.9, 132.3, 134.1, 135.8, 138.9; MS (EI) m/z (%): 266 (25), 265 (100) [M^+], 264 (31), 250 (36), 136 (11), 135 (79), 107 (10).

Compound 3fa (Table 2, entry 6)



^1H NMR (500.0 MHz, CDCl_3 , TMS): 0.779 (s, 6H), 6.55 (d, $J = 2.8$ Hz, 1H), 6.99 (dd, $J = 2.0, 8.8$ Hz, 1H), 7.11 (d, $J = 9.1$ Hz, 1H), 7.17 (d, $J = 3.4$ Hz, 1H), 7.38 (t, $J = 7.0$ Hz, 2H), 7.44 (t, $J = 7.4$ Hz, 1H), 7.50 (d, $J = 6.8$ Hz, 2H), 7.58 (d, $J = 2.3$ Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (124.5 MHz, CDCl_3 , TMS): -1.11, 105.0, 114.5, 120.5, 122.1, 126.1, 128.7, 130.8, 132.3, 133.1, 134.1, 135.2, 139.0.

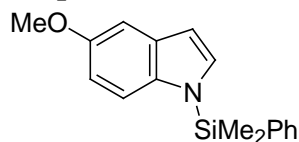
Compound 3ga (Table 2, entry 7)



^1H NMR (500.0 MHz, CDCl_3 , TMS): 0.773 (s, 6H), 6.55 (d, $J = 3.4$ Hz, 1H), 7.07 (d, $J = 9.1$ Hz, 1H), 7.12 (d, $J = 8.5$ Hz, 1H), 7.15 (d, $J = 3.4$ Hz, 1H), 7.37 (t, $J = 7.2$ Hz, 2H), 7.43 (t, $J = 7.4$ Hz, 1H), 7.49 (d, $J = 7.9$ Hz, 1H), 7.74 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (124.5 MHz, CDCl_3 ,

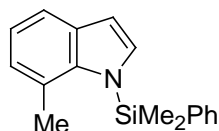
TMS): -1.12, 104.9, 113.8, 115.0, 123.6, 124.6, 128.7, 130.8, 132.1, 133.8, 134.1, 135.1, 139.3; MS (EI) m/z (%): 331 (39) [M^+], 330 (11), 329 (39) [M^+], 136 (14), 135 (100).

Compound 3ha (Table 2, entry 8)



^1H NMR (500.0 MHz, CDCl_3 , TMS): 0.756 (s, 6H), 3.80 (s, 3H), 6.54 (d, $J = 2.8$ Hz, 1H), 6.71 (dd, $J = 2.5, 8.8$ Hz, 1H), 7.09–7.12 (m, 3H), 7.35 (t, $J = 7.1$ Hz, 2H), 7.41 (tt, $J = 2.5, 7.4$ Hz, 1H), 7.50 (dd, $J = 1.1, 7.9$ Hz, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (124.5 MHz, CDCl_3 , TMS): -1.07, 56.0, 102.9, 105.2, 111.8, 114.2, 128.5, 130.6, 131.6, 132.5, 134.1, 135.6, 135.7, 154.6; MS (EI) m/z (%): 282 (24), 281 (100) [M^+], 266 (36), 136 (13), 135 (98), 107 (11).

Compound 3ia (Table 2, entry 9)



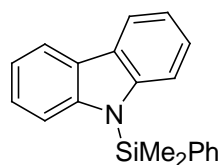
^1H NMR (500.0 MHz, CDCl_3 , TMS): 0.796 (s, 6H), 2.27 (s, 3H), 6.65 (d, $J = 2.9$ Hz, 1H), 6.86 (d, $J = 7.4$ Hz, 1H), 7.03 (t, $J = 7.4$ Hz, 1H), 7.30–7.33 (m, 3H), 7.36–7.41 (m, 3H), 7.50 (d, $J = 7.9$ Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (124.5 MHz, CDCl_3 , TMS): 2.38, 21.9, 105.7, 118.8, 120.9, 123.1, 124.9, 128.6, 130.2, 132.5, 133.2, 133.4, 138.6, 140.5.

Compound 5aa (Table 2, entry 10)



^1H NMR (500.0 MHz, CDCl_3 , TMS): 0.681 (s, 6H), 6.34 (s, 2H), 6.79 (s, 2H), 7.35–7.43 (m, 3H), 7.47 (d, $J = 6.8$ Hz, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (124.5 MHz, CDCl_3 , TMS): -1.37, 111.4, 124.0, 128.4, 130.6, 134.0, 135.9; MS (EI) m/z (%): 202 (19), 201 (99) [M^+], 200 (73), 187 (10), 186 (55), 184 (17), 136 (14), 135 (100), 107 (12), 105 (18), 93 (23).

Compound 7aa (Table 2, entry 11)



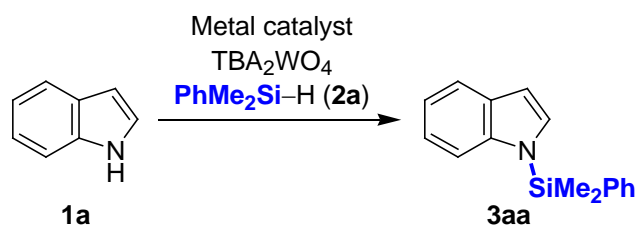
^1H NMR (500.0 MHz, CDCl_3 , TMS): 0.924 (s, 6H), 7.20–7.28 (m, 4H), 7.37 (t, $J = 7.4$ Hz, 4H), 7.43 (t, $J = 6.8$ Hz, 1H), 7.57 (d, $J = 7.3$ Hz, 2H), 8.07 (d, $J = 8.0$ Hz, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (124.5 MHz, CDCl_3 , TMS): 0.87, 113.9, 120.0, 120.3, 125.7, 126.7, 128.7, 130.5, 134.1,

136.9, 144.7; MS (EI) m/z (%): 302 (21), 301 (82) [M^+], 300 (12), 286 (18), 136 (14), 135 (100), 107 (10).

References

- S1 T. M. Che, V. W. Day, L. C. Francesconi, M. F. Fredrich, W. G. Klemperer and W. Shum, *Inorg. Chem.*, 1985, **24**, 4055.
- S2 A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, *Organometallics*, 1996, **15**, 1518.

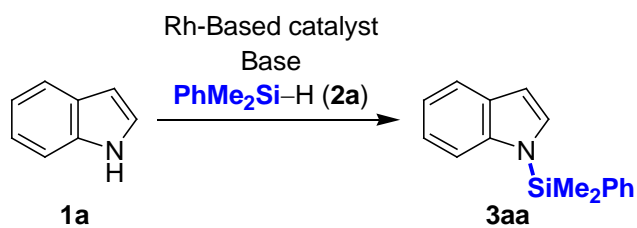
Table S1. N-Silylation of indole (**1a**) with dimethylphenylsilane (**2a**) using various metal catalysts^a



Entry	Catalyst	Conv. (%)	Yield (%)
1	Rh ₂ (OAc) ₄	>99	>99
2 ^b	Rh ₂ (OAc) ₄	83	83
3	Cu(OAc) ₂ ·H ₂ O	<1	nd
4	AgOAc	<1	nd
5	AuBr ₃	4	2
6	Pd(OAc) ₂	<1	nd
7	Co(OAc) ₂ ·4H ₂ O	<1	nd
8	Ni(OAc) ₂ ·4H ₂ O	<1	nd
9	Zn(OAc) ₂ ·2H ₂ O	1	nd
10	Ru(acac) ₃	<1	nd
11	[Ru₃(μ₃-O)(OAc)₆(H₂O)₃](OAc)	<1	nd
12	[RuCl ₂ (<i>p</i> -cymene)] ₂	1	<1
13	Pt(acac) ₂	<1	nd
14	Pt(OAc)₂·2AcOH	20	16
15	[IrCl ₂ Cp*] ₂	<1	nd
16	None	<1	nd

^a Reaction conditions: Metal catalyst (metal: 2 mol% with respect to **1a**), TBA₂WO₄ (2 mol% with respect to **1a**), **1a** (0.5 mmol), **2a** (2.5 mmol), CH₃CN (2 mL), Ar (1 atm), 50 °C, 2 h. Conversions and yields were based on **1a** and determined by GC analysis. nd = not detected. ^b **2a** (1.0 mmol).

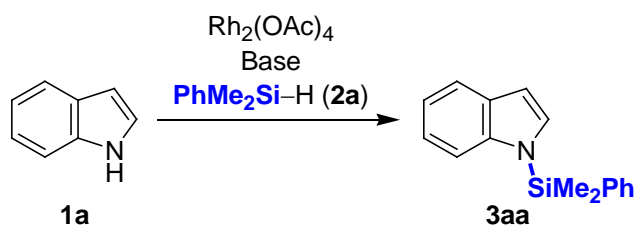
Table S2. N-Silylation of indole (**1a**) with dimethylphenylsilane (**2a**) using various Rh-based catalysts^a



Entry	Catalyst	Conv. (%)	Yield (%)
1	Rh ₂ (OAc) ₄	>99	>99
2	Rh₂(pfb)₄	25	24
3	RhCl ₃ · <i>n</i> H ₂ O	8	8
4	[RhCl ₂ Cp*] ₂	3	3
5	[Rh(cod)Cl] ₂	5	5
6	Rh(PPh ₃) ₃ Cl	10	10
7	[Rh(CO) ₂ Cl] ₂	1	1
8	Rh(OH) _{<i>x</i>} /TiO ₂	<1	nd

^a Reaction conditions: Rh-Based catalyst (Rh: 2 mol% with respect to **1a**), TBA₂WO₄ (2 mol% with respect to **1a**), **1a** (0.5 mmol), **2a** (2.5 mmol), CH₃CN (2 mL), Ar (1 atm), 50 °C, 2 h. Conversions and yields were based on **1a** and determined by GC analysis. nd = not detected.

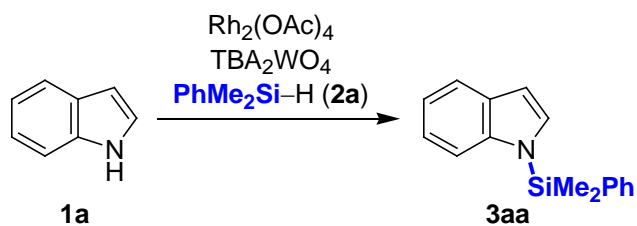
Table S3. N-Silylation of indole (**1a**) with dimethylphenylsilane (**2a**) using various bases^a



Entry	Base	Conv. (%)	Yield (%)
1	TBA ₂ WO ₄	>99	>99
2	KO ^t -Bu	71	69
3	K ₂ CO ₃	66	66
4	TBAOH	63	63
5	K ₃ PO ₄	34	33
6	Cs ₂ CO ₃	17	13
7	TBA ₄ [γ -SiW ₁₀ O ₃₄ (H ₂ O) ₂]	16	15
8	TBA ₄ [α -SiW ₁₂ O ₄₀]	3	nd
9	Et ₃ N	<1	nd
10	DBU	5	2
11	None	<1	nd

^a Reaction conditions: $\text{Rh}_2(\text{OAc})_4$ (1 mol% with respect to **1a**), base (2 mol% with respect to **1a**), **1a** (0.5 mmol), **2a** (2.5 mmol), CH₃CN (2 mL), Ar (1 atm), 50 °C, 2 h. Conversions and yields were based on **1a** and determined by GC analysis. nd = not detected.

Table S4. Effect of solvents on the N-silylation of indole (**1a**) with dimethylphenylsilane (**2a**)^a



Entry	Solvent	Conv. (%)	Yield (%)
1	Acetonitrile	>99	>99
2	Benzonitrile	82	82
3	DMSO	<1	<1
4	DMF	26	1
5	DCE	<1	<1
6	Acetone ^b	5	<1

^a Reaction conditions: $\text{Rh}_2(\text{OAc})_4$ (1 mol% with respect to **1a**), TBA_2WO_4 (2 mol% with respect to **1a**), **1a** (0.5 mmol), **2a** (2.5 mmol), solvent (2 mL), Ar (1 atm), 50 °C, 2 h. Conversions and yields were based on **1a** and determined by GC analysis. ^b The hydrosilylation of acetone proceeded.

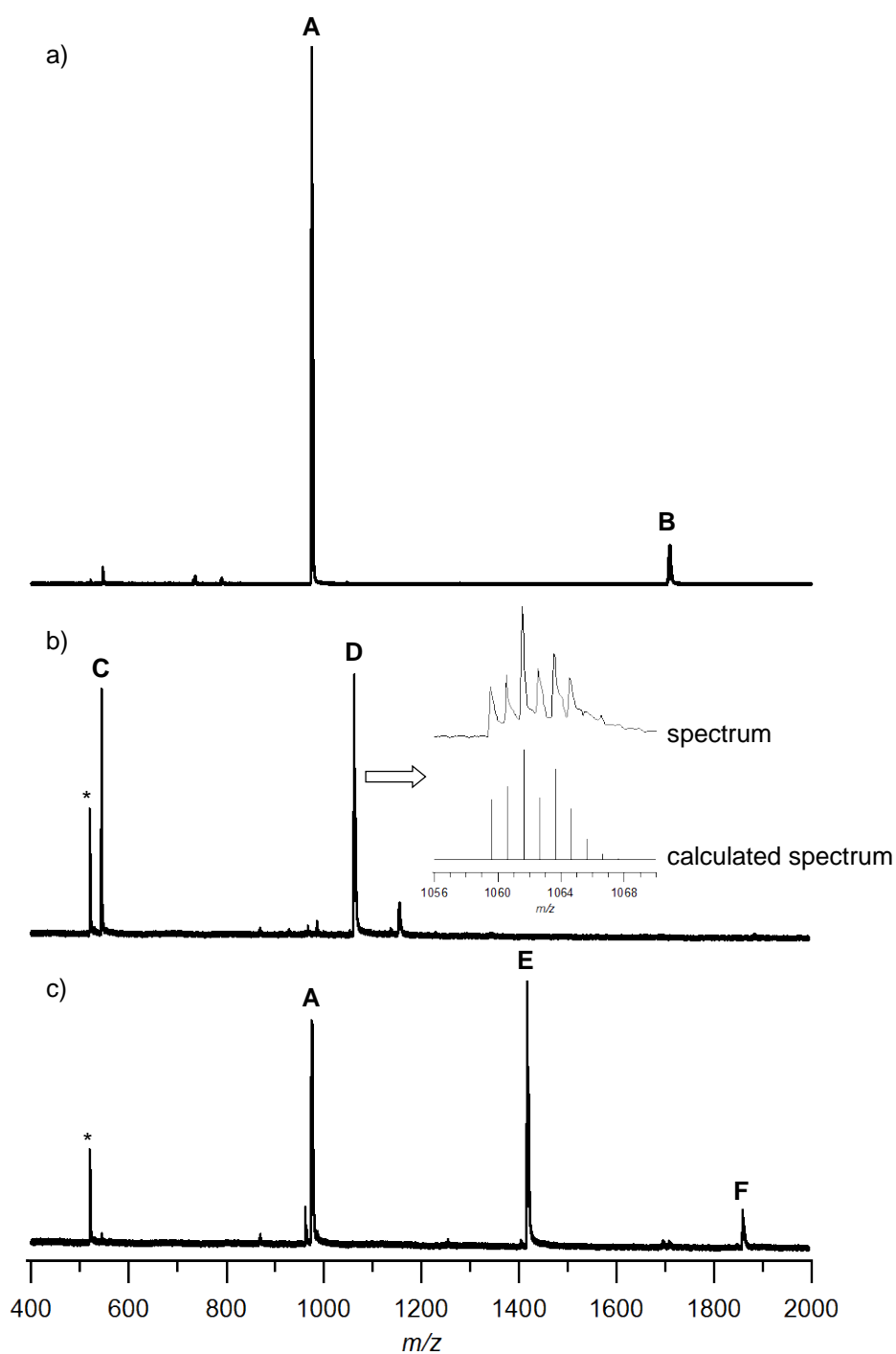


Fig. S1 Positive ion CSI-MS spectra of a) TBA_2WO_4 , b) $\text{Rh}_2(\text{OAc})_4$, TBA_2WO_4 , and **2a** ($\text{Rh}_2(\text{OAc})_4:\text{TBA}_2\text{WO}_4:\mathbf{2a} = 1:1:40$), and c) $\text{Rh}_2(\text{OAc})_4$ and TBA_2WO_4 ($\text{Rh}_2(\text{OAc})_4:\text{TBA}_2\text{WO}_4 = 1:1$) in acetonitrile. The signal sets **A**, **B**, **C**, **D**, **E**, and **F** are possibly assignable to $[\text{TBA}_3\text{WO}_4]^+$, $[\text{TBA}_5(\text{WO}_4)_2]^+$, $[\text{TBA}_2\text{OAc}]^+$, $[\text{TBA}_2(\text{PhMe}_2\text{Si})\text{WO}_4(\text{PhMe}_2\text{SiOAc})]^+$, $[\text{TBA}_3\text{WO}_4(\text{Rh}_2(\text{OAc})_4)]^+$, and $[\text{TBA}_3\text{WO}_4(\text{Rh}_2(\text{OAc})_4)_2]^+$, respectively. The asterisk is probably due to $\text{Rh}_2(\text{OAc})_4$ and/or the solvent. The lines in the inset are the calculated pattern for $[\text{TBA}_2(\text{PhMe}_2\text{Si})\text{WO}_4(\text{PhMe}_2\text{SiOAc})]^+$.

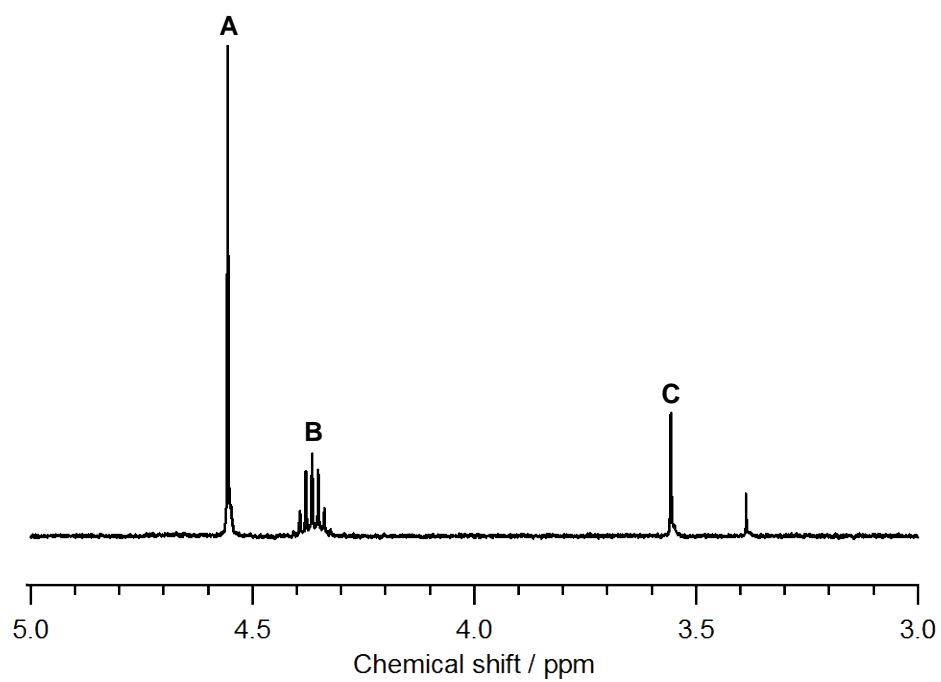


Fig. S2 ¹H NMR spectrum of Rh₂(OAc)₄ and **2a** in acetonitrile-*d*₃. The signals **A**, **B**, and **C** are possibly assignable to H₂, the SiH proton of **2a**, the OH proton of dimethylphenylsilanol, respectively. Conditions: Rh₂(OAc)₄ (25 mM), **2a** (10 mM).

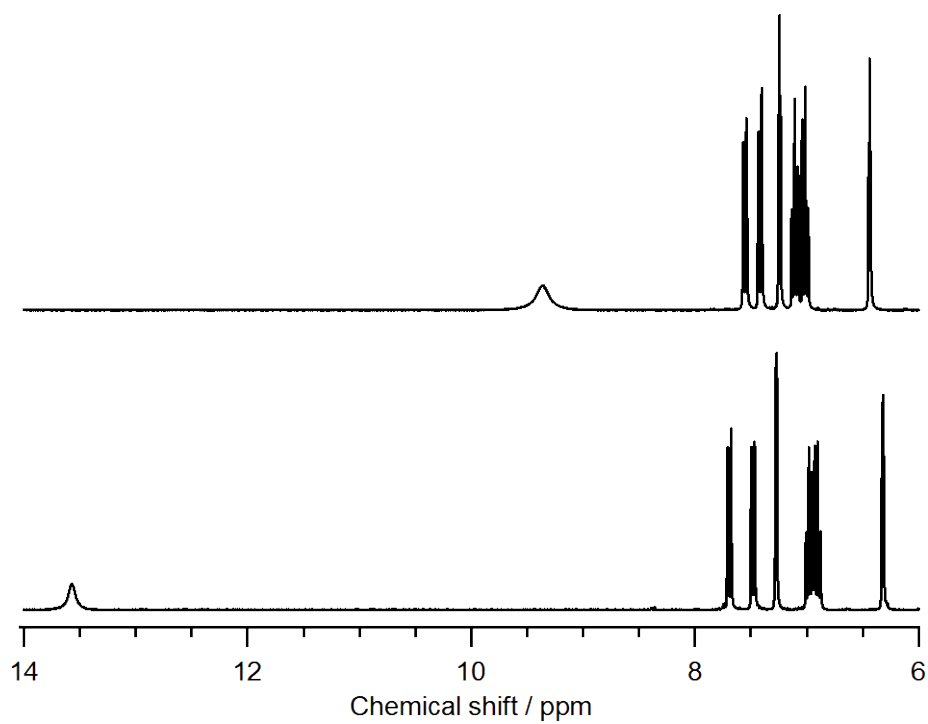
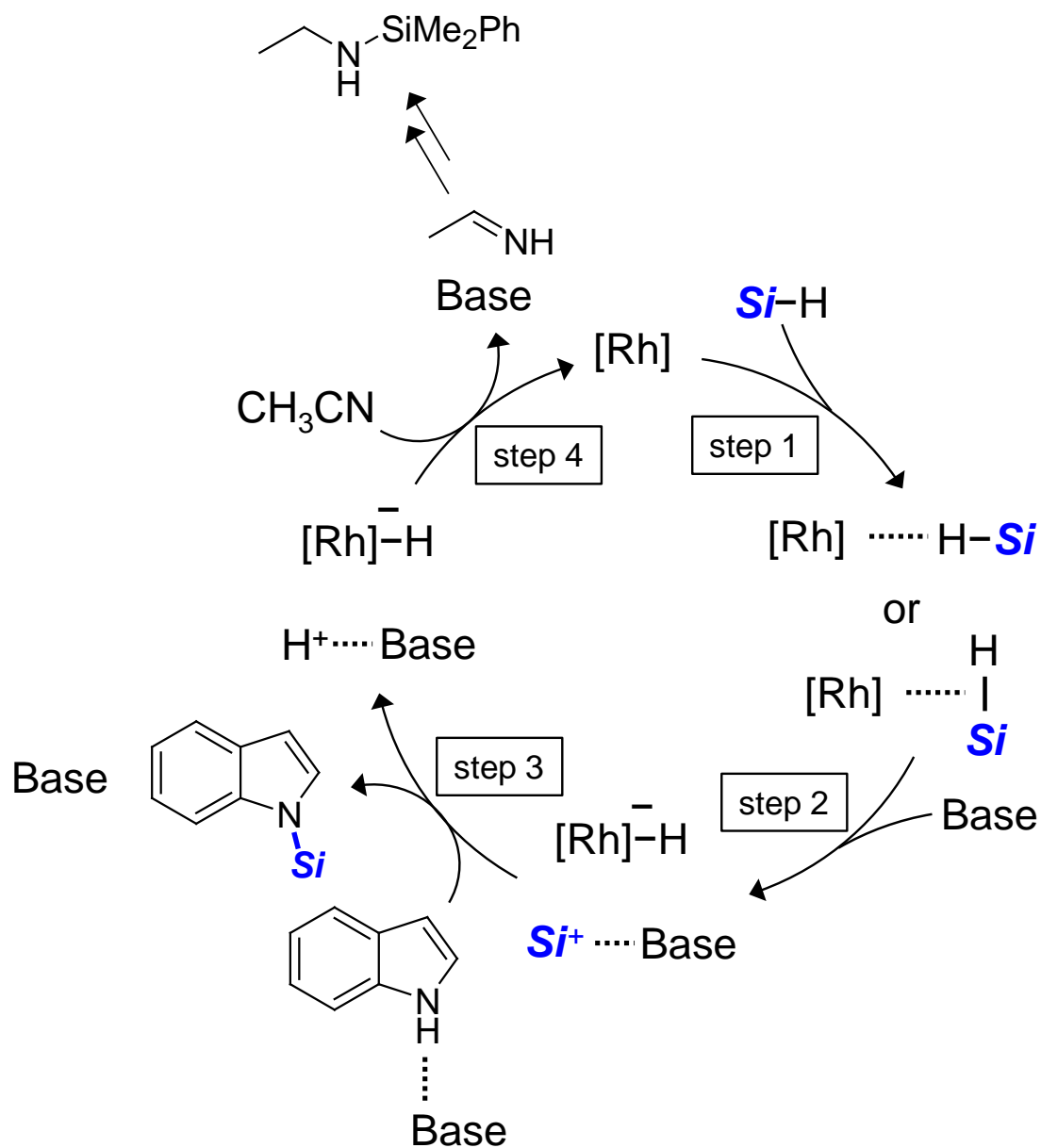


Fig. S3 ^1H NMR spectra of a) **1a** and b) **1a** and TBA_2WO_4 in acetonitrile- d_3 . Conditions: **1a** (50 mM), TBA_2WO_4 (50 mM), -20°C .



Scheme S1 Proposed catalytic cycle (Base = O-donor bases such as TBA_2WO_4 , $\text{KO}t\text{-Bu}$, K_2CO_3 , TBAOH , K_3PO_4 , and Cs_2CO_3).