

Regiocontrol in the Cobalt-Catalyzed Hydrosilylation of Alkynes

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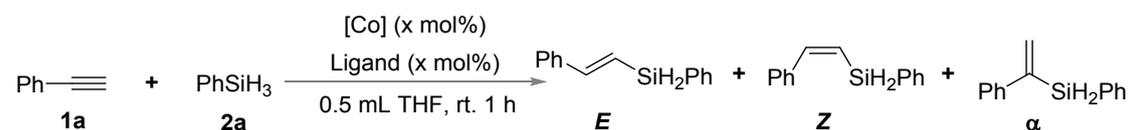
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1. General experimental methods.

Reagents were purchased from commercial suppliers and used without further purification. THF, toluene, and hexane, ethyl ether were used after distillation with the sodium. Dry acetonitrile and dichloromethane were purchased from Acros Organics. Column chromatograph was performed on 35-70 mesh silica gel (Acros Organics). ^1H , ^{13}C , spectra were recorded on a Bruker Avance 300 Kryo spectrometer using CDCl_3 as solvent. Chemical shifts are reported in ppm and referenced to residual solvent signal (CDCl_3 : ^1H NMR: δ 7.26 ppm, ^{13}C NMR: δ 77.0 ppm). High Resolution Mass Spectrometry (HRMS) were recorded on Finnigan MAT 900s. GC-yields was obtained using dodecane as internal standard with Gas chromatography with FID (GC-FID, HP6890 GC-System with injector 7683B and Agilent 7820A System, carried gas: H_2).

2. Method optimizations^[a]

Ligand Effect



entry	Cat. (x mol%)	Ligand	3a (%) ^[b]	<i>E/Z/</i> α
1	$\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.5)	dppe	72	87/0/13
2	$\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.5)	dppp	81	97/0/3
3	$\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.5)	dppb	95	98/0/2
4	$\text{Co}(\text{OAc})_2$ (0.5)	dppb	89	98/0/2
5	$\text{Co}(\text{acac})_2$ (0.5)	dppb	78	98/0/2
6	CoBr_2 (0.5)	dppb	ND	---
7	$\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.5)	dppf	92	97/0/3
8	$\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.5)	DPEphos	90	98/0/3
9	$\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.5)	Xantphos	81	87/2/11
10	$\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.5)	BINAP	<10	---
11	$\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.5)	TMEDA	ND	---
12	$\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.5)	bipy	75	10/0/90
13	$\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.5)	4-OMebipy	66	4/0/96
14	$\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.5)	4-Mebipy	70	5/0/95
15	$\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.5)	4-tBubipy	64	5/0/95
16	$\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.5)	2-Mebipy	50	20/0/80
17	$\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.5)	3-Mebipy	68	7/0/93
18	$\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.5)	phen	61	10/0/90
19	$\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.5)	tripy	ND	---
20	$\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.5)	L1	ND	---
21	$\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.5)	L2	ND	---
22	$\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.5)	L3	ND	---

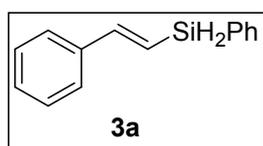
entry	Cat. (x mol%)	Ligand	5b (%) ^[b]	E/Z/ α
1	Co(OAc) ₂ •4H ₂ O (0.5)	dppb	78	90/0/10
2	Co(OAc) ₂ •4H ₂ O (0.5)	DPEphos	85	97/0/3
3	Co(OAc) ₂ •4H ₂ O (0.5)	dppf	86	93/0/7
4	Co(OAc) ₂ (0.5)	Xantphos	45 ^[c]	97/0/3

[a] Reaction conditions: **3b** (0.4 mmol), **2a** (0.48 mmol), Co(OAc)₂•4H₂O (1 mol%, 10 μ L MeOH), ligand (1 mol%) in 0.5 mL THF/MeCN = 4: 1. [b] GC yield using dodecane as internal standard.

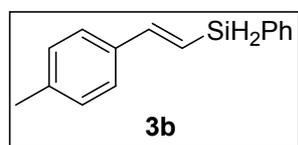
3. General Procedure and characterization data

Hydrosilylation of alkynes with Co-Phosphine ligands system.

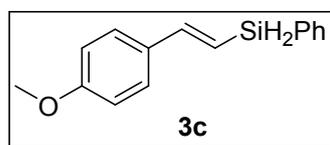
Co(OAc)₂•4H₂O (0.1 mg, 0.0004 mmol, 0.001 equiv, in 10 μ L MeOH), was added into 0.5 mL THF containing dppb (0.17 mg, 0.0004 mmol, 0.001 equiv). Alkyne (0.4 mmol, 1.0 equiv) was added into the system (Note: if it is solid, weigh it firstly), followed with PhSiH₃ (0.48 mmol, 1.2 equiv). The mixture was stirred at room temperature for 1 hours. The solvent was removed to leave a crude product, which was purified by column chromatography on silica gel to afford the product **3**. The similar procedure to afford the product **5** with 1mol% Co(OAc)₂•4H₂O with DPEphos or 0.1 mol% Co(OAc)₂•4H₂O with Xantphos and product **6** was obtained with 1mol% Co(OAc)₂•4H₂O with 4-Me^ebipy ligand.



The product **3a**^[1] was purified with silica gel chromatography (Pe) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.66-7.63 (m, 2H), 7.49-7.46 (m, 2H), 7.43-7.32 (m, 6H), 7.18 (d, J = 19.0 Hz, 1H), 6.53 (dt, J = 19.0, 3.3 Hz, 2H), 4.71 (d, J = 2.9 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 149.4, 137.8, 135.5, 131.7, 129.9, 128.70, 128.66, 128.2, 126.7, 119.4.

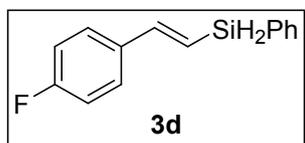


The product **3b** was purified with silica gel chromatography (Pe) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.66-7.63 (m, 2H), 7.44-7.37 (m, 5H), 7.18-7.12 (m, 3H), 7.18 (d, J = 19.0 Hz, 1H), 6.46 (dt, J = 19.0, 3.3 Hz, 2H), 4.71 (d, J = 3.2 Hz, 2H), 2.37 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 149.3, 138.7, 135.5, 135.1, 131.9, 129.8, 129.4, 128.1, 126.7, 117.8, 21.3; HRMS (EI) (m/z): [M]⁺ calcd for C₁₅H₁₆Si: 224.1016, found: 224.1016.

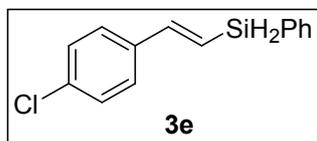


The product **3c** was purified with silica gel chromatography (Pe/EA = 50 : 1) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.64-7.61 (m, 2H), 7.42-7.38 (m, 5H), 7.11 (d, J = 19.0 Hz, 1H), 6.88 (d, J = 8.8, 2H), 6.33 (dt, J = 18.9, 3.3 Hz, 2H), 4.69 (d, J =

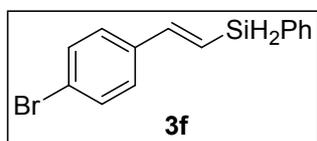
3.2 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 160.1, 148.8, 135.5, 132.0, 130.9, 129.8, 128.10, 128.06, 116.3, 113.4, 55.4; HRMS (EI) (m/z): $[\text{M}]^+$ calcd for $\text{C}_{15}\text{H}_{16}\text{OSi}$: 240.0965, found: 240.0962.



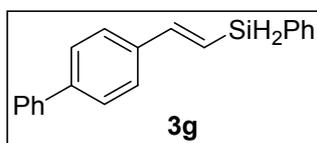
The product **3d** was purified with silica gel chromatography (Pe) as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 7.65-7.61 (m, 2H), 7.46-7.36 (m, 5H), 7.11 (d, $J = 19.0$ Hz, 1H), 7.04 (t, $J = 8.1$ Hz, 2H), 6.88 (d, $J = 8.8$, 2H), 6.42 (dt, $J = 18.9$, 3.3 Hz, 2H), 4.69 (d, $J = 3.2$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 163.0 (d, $J = 248.3$ Hz), 148.0, 135.5, 134.0 (d, $J = 3.3$ Hz), 131.6, 129.9, 128.4 (d, $J = 8.2$ Hz), 128.2, 119.2 (d, $J = 2.2$ Hz), 115.6 (d, $J = 21.7$ Hz); HRMS (EI) (m/z): $[\text{M}]^+$ calcd for $\text{C}_{14}\text{H}_{13}\text{FSi}$: 228.0765, found: 228.0767.



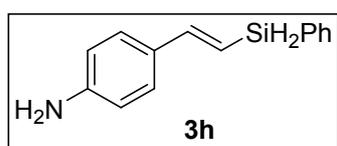
The product **3e** was purified with silica gel chromatography (Pe) as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 7.64-7.61 (m, 2H), 7.49-7.39 (m, 5H), 7.34-7.30 (m, 2H), 7.10 (d, $J = 19.0$ Hz, 1H), 6.49 (dt, $J = 19.0$, 3.2 Hz, 1H), 4.70 (d, $J = 3.2$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 147.8, 136.2, 135.5, 134.4, 131.4, 130.0, 128.8, 128.2, 127.9, 120.4; HRMS (EI) (m/z): $[\text{M}]^+$ calcd for $\text{C}_{14}\text{H}_{13}\text{ClSi}$: 244.0470, found: 244.0474.



The product **3f** was purified with silica gel chromatography (Pe) as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 7.64-7.61 (m, 2H), 7.44-7.37 (m, 5H), 7.32 (d, $J = 8.5$ Hz, 2H), 7.09 (d, $J = 19.0$ Hz, 1H), 6.51 (dt, $J = 19.0$, 3.2 Hz, 1H), 4.69 (d, $J = 3.2$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 147.8, 136.6, 135.5, 131.8, 131.3, 130.0, 128.2, 122.6, 120.6; HRMS (EI) (m/z): $[\text{M}]^+$ calcd for $\text{C}_{14}\text{H}_{13}\text{BrSi}$: 287.9964, found: 287.9957.

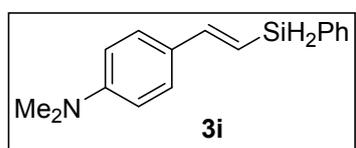


The product **3g** was purified with silica gel chromatography (Pe) as a white solid. ^1H NMR (300 MHz, CDCl_3) δ 7.66-7.52 (m, 8H), 7.47-7.35 (m, 6H), 7.20 (d, $J = 19.0$ Hz, 1H), 6.56 (dt, $J = 19.0$, 3.3 Hz, 1H), 4.72 (d, $J = 3.2$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 148.8, 141.4, 140.6, 136.8, 135.5, 131.7, 129.9, 128.8, 128.2, 127.5, 127.3, 127.2, 127.0, 119.5; HRMS (EI) (m/z): $[\text{M}]^+$ calcd for $\text{C}_{20}\text{H}_{18}\text{Si}$: 286.1172, found: 286.1170.

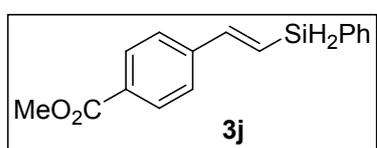


The product **3h** was purified with silica gel chromatography (Pe/EA = 5 : 1) as a pale yellow oil. ^1H NMR (300 MHz, CDCl_3) δ 7.64-7.61 (m, 2H), 7.41-7.38 (m, 3H), 7.29 (d, $J = 8.4$ Hz, 2H), 7.06 (d, $J = 18.9$ Hz, 1H), 6.65 (d, $J = 8.5$ Hz, 2H), 6.24 (dt, $J = 18.9$, 3.3 Hz, 1H), 4.63 (d, $J = 3.0$ Hz, 2H), 3.77 (brs, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 149.3,

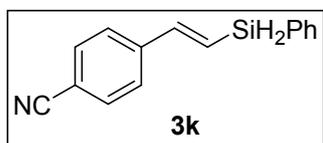
147.1, 135.5, 132.3, 129.7, 128.7, 128.1, 128.05, 114.9, 114.1; HRMS (EI) (m/z): $[M]^+$ calcd for $C_{14}H_{15}NSi$: 225.0968, found: 225.0962.



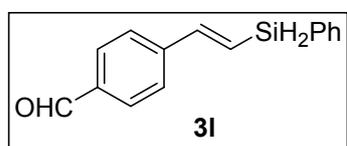
The product **3i** was purified with silica gel chromatography (Pe/EA = 30 : 1) as a pale yellow oil. 1H NMR (300 MHz, $CDCl_3$) δ 7.66-7.63 (m, 2H), 7.40-7.36 (m, 5H), 7.10 (d, $J = 18.9$ Hz, 1H), 6.69 (d, $J = 8.8$ Hz, 2H), 6.23 (dt, $J = 18.9, 3.3$ Hz, 1H), 4.70 (d, $J = 3.0$ Hz, 2H), 2.99 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.8, 149.5, 135.5, 132.6, 129.6, 128.0, 127.9, 126.4, 112.9, 112.1, 40.1; HRMS (EI) (m/z): $[M]^+$ calcd for $C_{16}H_{19}NSi$: 253.1281, found: 253.1285.



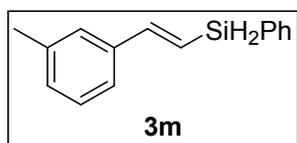
The product **3j** was purified with silica gel chromatography (Pe/EA = 30 : 1) as a colorless oil. 1H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, $J = 8.3$ Hz, 2H), 7.65-7.62 (m, 2H), 7.51 (d, $J = 8.4$ Hz, 2H), 7.45-7.38 (m, 3H), 7.18 (d, $J = 19.0$ Hz, 1H), 6.66 (dt, $J = 19.0, 3.2$ Hz, 1H), 4.71 (d, $J = 3.2$ Hz, 2H), 3.92 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 148.0, 141.9, 135.5, 131.1, 130.0, 129.98, 129.92, 128.2, 126.6, 123.1, 52.2; HRMS (EI) (m/z): $[M]^+$ calcd for $C_{16}H_{16}O_2Si$: 268.0914, found: 268.0890.



The product **3k** was purified with silica gel chromatography (Pe/EA = 30 : 1) as a colorless oil. 1H NMR (300 MHz, $CDCl_3$) δ 7.65-7.61 (m, 4H), 7.53 (d, $J = 8.4$ Hz, 2H), 7.45-7.43 (m, 3H), 7.14 (d, $J = 19.0$ Hz, 1H), 6.68 (dt, $J = 19.0, 3.2$ Hz, 1H), 4.71 (d, $J = 3.1$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.9, 141.7, 135.5, 132.4, 130.6, 130.1, 128.2, 127.1, 124.9, 118.8, 111.7; HRMS (EI) (m/z): $[M]^+$ calcd for $C_{15}H_{13}NSi$: 235.0812, found: 235.0813.

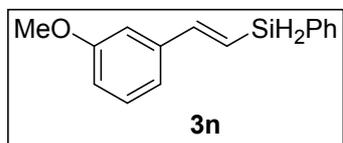


The product **3l** was purified with silica gel chromatography (Pe/EA = 30 : 1) as a colorless oil. 1H NMR (300 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.87 (d, $J = 8.3$ Hz, 2H), 7.65-7.59 (m, 4H), 7.45-7.39 (m, 3H), 7.19 (d, $J = 19.0$ Hz, 1H), 6.72 (dt, $J = 19.0, 3.2$ Hz, 1H), 4.72 (d, $J = 3.1$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.2, 147.7, 143.3, 136.1, 135.5, 130.9, 130.2, 130.1, 128.3, 127.2, 124.5; HRMS (EI) (m/z): $[M]^+$ calcd for $C_{15}H_{14}OSi$: 238.0808, found: 238.0803.

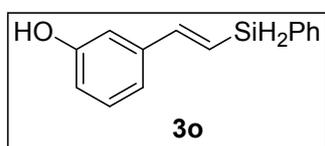


The product **3m** was purified with silica gel chromatography (Pe) as a colorless oil. 1H NMR (300 MHz, $CDCl_3$) δ 7.66-7.63 (m, 2H), 7.44-7.40 (m, 3H), 7.30-7.25 (m, 3H), 7.15 (d, $J = 19.0$ Hz, 1H), 6.51 (dt,

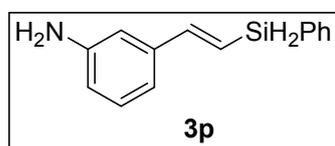
$J = 19.0, 3.3$ Hz, 1H), 4.71 (d, $J = 3.2$ Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 159.9, 149.2, 139.2, 135.3, 131.6, 129.9, 129.6, 128.2, 119.8, 119.5, 114.5, 111.7, 55.3; HRMS (EI) (m/z): $[\text{M}]^+$ calcd for $\text{C}_{15}\text{H}_{16}\text{Si}$: 224.1016, found: 224.1009.



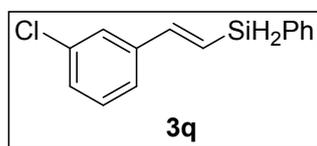
The product **3n** was purified with silica gel chromatography (Pe/EA = 50 : 1) as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 7.65-7.62 (m, 2H), 7.44-7.37 (m, 3H), 7.27 (t, $J = 7.9$ Hz, 1H), 7.14 (d, $J = 18.9$ Hz, 1H), 7.06 (d, $J = 7.6$ Hz, 1H), 7.01-7.00 (m, 1H), 6.87-6.84 (m, 1H), 6.51 (dt, $J = 18.9, 3.3$ Hz, 1H), 4.70 (d, $J = 3.2$ Hz, 2H), 2.83 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 149.5, 138.2, 137.7, 135.5, 131.8, 129.8, 129.5, 128.5, 128.1, 127.4, 123.9, 119.1, 21.4; HRMS (EI) (m/z): $[\text{M}]^+$ calcd for $\text{C}_{15}\text{H}_{16}\text{OSi}$: 240.0965, found: 240.0964.



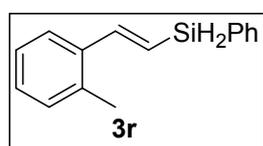
The product **3o** was purified with silica gel chromatography (Pe/EA = 10 : 1) as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 7.64-7.61 (m, 2H), 7.43-7.37 (m, 3H), 7.22 (t, $J = 7.8$ Hz, 1H), 7.10 (d, $J = 19.0$ Hz, 1H), 7.03 (d, $J = 7.7$ Hz, 1H), 7.95-7.93 (m, 1H), 6.79-6.76 (m, 1H), 6.49 (dt, $J = 18.9, 3.3$ Hz, 1H), 4.90 (brs, 1H), 4.69 (d, $J = 3.2$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 155.8, 148.8, 139.5, 135.5, 131.6, 129.88, 129.85, 128.2, 120.0, 119.6, 115.7, 113.1.; HRMS (EI) (m/z): $[\text{M}]^+$ calcd for $\text{C}_{14}\text{H}_{14}\text{OSi}$: 226.0808, found: 226.0812.



The product **3p** was purified with silica gel chromatography (Pe/EA = 5 : 1) as a pale yellow oil. ^1H NMR (300 MHz, CDCl_3) δ 7.66-7.62 (m, 2H), 7.43-7.40 (m, 3H), 7.16 (t, $J = 7.7$ Hz, 1H), 7.09 (d, $J = 19.3$ Hz, 1H), 6.89 (d, $J = 7.6$ Hz, 1H), 6.80-6.79 (m, 1H), 6.66-6.62 (m, 1H), 6.46 (dt, $J = 18.9, 3.3$ Hz, 1H), 4.70 (d, $J = 3.2$ Hz, 2H), 3.65 (brs, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 149.6, 146.7, 138.9, 135.5, 131.8, 129.8, 129.6, 128.1, 119.1, 117.5, 115.6, 113.1; HRMS (ESI) (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{16}\text{NSi}$: 226.1047, found: 226.1048.

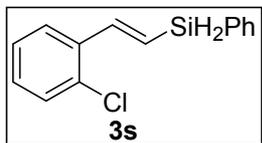


The product **3q** was purified with silica gel chromatography (Pe) as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 7.65-7.62 (m, 2H), 7.45-7.40 (m, 4H), 7.33-7.26 (m, 3H), 7.09 (d, $J = 19.0$ Hz, 1H), 6.54 (dt, $J = 18.9, 3.2$ Hz, 1H), 4.70 (d, $J = 3.2$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 147.7, 139.6, 135.5, 134.7, 131.2, 130.0, 129.9, 128.6, 128.2, 126.6, 124.9, 121.6; HRMS (EI) (m/z): $[\text{M}]^+$ calcd for $\text{C}_{14}\text{H}_{13}\text{ClSi}$: 244.0470, found: 244.0469.

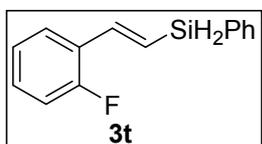


The product **3r** was purified with silica gel chromatography (Pe) as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 7.68-7.64 (m, 2H), 7.58-7.55 (m, 1H), 7.48-7.38 (m, 4H), 7.23-7.17 (m, 3H), 6.44 (dt, $J = 18.9, 3.3$ Hz,

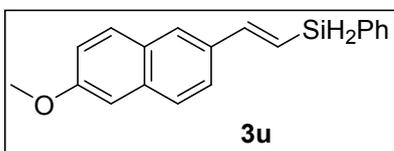
1H), 4.73 (d, $J = 2.8$ Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 147.3, 137.1, 135.7, 135.5, 131.8, 130.5, 129.9, 128.4, 128.2, 126.2, 125.6, 121.1, 19.7; HRMS (EI) (m/z): $[\text{M}]^+$ calcd for $\text{C}_{15}\text{H}_{16}\text{Si}$: 224.1016, found: 221.1016.



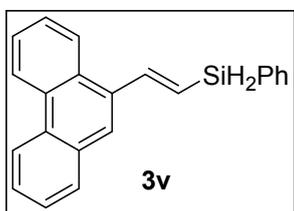
The product **3s** was purified with silica gel chromatography (Pe) as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 7.66-7.56 (m, overlap, 4H), 7.44-7.35 (m, 4H), 7.26-7.22 (m, 2H), 6.53 (dt, $J = 18.9, 3.3$ Hz, 1H), 4.73 (d, $J = 3.3$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 145.0, 135.8, 135.5, 133.4, 131.3, 129.9, 129.8, 129.5, 128.2, 126.94, 126.91, 123.2; HRMS (EI) (m/z): $[\text{M}]^+$ calcd for $\text{C}_{10}\text{H}_{13}\text{ClSi}$: 244.0470, found: 244.0460.



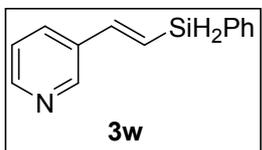
The product **3t** was purified with silica gel chromatography (Pe) as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 7.66-7.63 (m, 2H), 7.57 (td, $J = 7.7, 1.7$ Hz, 1H), 7.44-7.36 (m, 4H), 7.31-7.23 (m, 1H), 7.16-7.02 (m, 2H), 6.60 (dt, $J = 19.2, 3.3$ Hz, 1H), 4.72 (d, $J = 3.3$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 160.4 (d, $J = 250.7$ Hz), 141.1 (d, $J = 4.5$ Hz), 135.5, 131.4, 130.0, 129.9, 128.2, 127.2 (d, $J = 3.3$ Hz), 125.6 (d, $J = 11.6$ Hz), 124.2 (d, $J = 2.6$ Hz), 122.6 (d, $J = 3.8$ Hz), 115.6 (d, $J = 22.1$ Hz); HRMS (EI) (m/z): $[\text{M}]^+$ calcd for $\text{C}_{14}\text{H}_{13}\text{FSi}$: 228.0765, found: 228.0745.



The product **3u** was purified with silica gel chromatography (Pe/EA = 30 : 1) as a white solid. ^1H NMR (300 MHz, CDCl_3) δ 7.74-7.65 (m, 6H), 7.45-7.40 (m, 3H), 7.29 (d, $J = 19.2$ Hz, 1H), 7.17-7.13 (m, 2H), 6.57 (dt, $J = 18.9, 3.2$ Hz, 1H), 4.74 (d, $J = 3.1$ Hz, 2H), 3.93 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 158.1, 149.4, 135.6, 134.8, 133.2, 131.9, 129.9, 129.8, 128.9, 128.2, 127.2, 127.1, 123.9, 119.1, 118.3, 105.9, 55.4; HRMS (EI) (m/z): $[\text{M}]^+$ calcd for $\text{C}_{19}\text{H}_{18}\text{OSi}$: 290.1121, found: 290.1113.

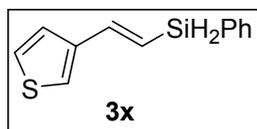


The product **3v** was purified with silica gel chromatography (Pe) as a white solid. ^1H NMR (300 MHz, CDCl_3) δ 8.73 (d, $J = 7.7$ Hz, 1H), 8.67 (d, $J = 8.0$ Hz, 1H), 8.19-8.16 (m, 1H), 7.99-7.89 (m, 3H), 7.74-7.59 (m, 6H), 7.46-7.42 (m, 3H), 6.70 (dt, $J = 18.6, 3.2$ Hz, 1H), 4.82 (d, $J = 2.6$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 147.3, 135.6, 135.1, 131.6, 130.5, 130.4, 130.2, 129.9, 128.9, 128.2, 126.88, 126.85, 126.8, 126.7, 125.2, 124.4, 124.1, 123.1, 122.6; HRMS (EI) (m/z): $[\text{M}]^+$ calcd for $\text{C}_{12}\text{H}_{18}\text{Si}$: 310.1172, found: 310.1167.

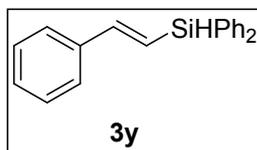


The product **3w** was purified with silica gel chromatography (Pe/EA = 5 : 1) as a pale yellow oil. ^1H NMR (300 MHz, CDCl_3) δ 8.66 (d, $J = 2.0$ Hz, 1H), 8.52 (dd, $J = 4.8, 1.5$ Hz, 1H), 8.78 (dt, $J = 8.0, 1.9$ Hz, 1H),

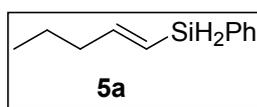
7.65-7.62 (m, 2H), 7.45-7.40 (m, 3H), 7.30-7.26 (m, 1H), 7.14 (d, $J = 19.0$ Hz, 1H), 6.62 (dt, $J = 19.0, 3.2$ Hz, 1H), 4.71 (d, $J = 3.2$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 143.0, 141.6, 135.5, 131.7, 129.9, 128.1, 126.2, 124.9, 123.9, 119.0; HRMS (EI) (m/z): $[\text{M}]^+$ calcd for $\text{C}_{13}\text{H}_{13}\text{NSi}$: 211.0812, found: 244.0799.



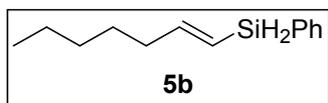
The product **3x** was purified with silica gel chromatography (Pe/EA = 30 : 1) as a pale yellow oil. ^1H NMR (300 MHz, CDCl_3) δ 7.65-7.62 (m, 2H), 7.42-7.39 (m, 3H), 7.30-7.26 (m, 3H), 7.15 (d, $J = 18.9$ Hz, 1H), 6.29 (dt, $J = 18.9, 3.3$ Hz, 1H), 4.68 (d, $J = 3.2$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 149.6, 148.8, 145.2, 135.5, 133.2, 133.0, 131.0, 130.1, 128.3, 123.6, 122.9; HRMS (EI) (m/z): $[\text{M}]^+$ calcd for $\text{C}_{12}\text{H}_{12}\text{SSi}$: 216.0424, found: 216.0427.



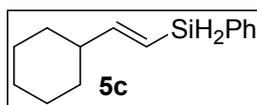
The product **3y**^[2] was purified with silica gel chromatography (Pe) as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 7.65-7.62 (m, 4H), 7.50-7.32 (m, 11H), 7.11 (d, $J = 19.0$ Hz, 1H), 6.73 (dt, $J = 19.0, 3.2$ Hz, 1H), 5.26 (d, $J = 3.2$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 149.1, 137.9, 135.6, 133.6, 129.8, 128.62, 128.1, 126.8, 121.5.



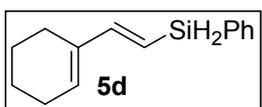
The product **5a** was purified with silica gel chromatography (Pe) as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 7.61-7.57 (m, 2H), 7.44-7.35 (m, 3H), 6.37 (dt, $J = 18.4, 6.3$ Hz, 1H), 5.78-5.69 (m, 1H), 4.55 (d, $J = 3.2$ Hz, 2H), 2.18 (q, $J = 7.1$ Hz, 2H), 1.47 (dd, $J = 14.8, 7.4$ Hz, 2H), 0.93 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 154.0, 135.4, 132.4, 129.6, 128.0, 120.1, 39.0, 21.6, 13.7; HRMS (EI) (m/z): $[\text{M}]^+$ calcd for $\text{C}_{11}\text{H}_{16}\text{Si}$: 176.1016, found: 176.1015.



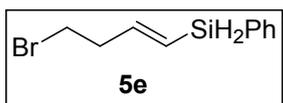
The product **5b** was purified with silica gel chromatography (Pe) as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 7.60-7.57 (m, 2H), 7.41-7.35 (m, 3H), 6.38 (dt, $J = 18.4, 6.3$ Hz, 1H), 5.77-5.69 (m, 1H), 4.54 (d, $J = 3.3$ Hz, 2H), 2.19 (q, $J = 6.7$ Hz, 2H), 1.46-1.42 (m, 2H), 1.33-1.29 (m, 4H), 0.90 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 154.3, 135.4, 132.4, 129.6, 128.0, 119.8, 36.9, 31.4, 28.1, 22.6, 14.1; HRMS (EI) (m/z): $[\text{M}]^+$ calcd for $\text{C}_{13}\text{H}_{20}\text{Si}$: 204.1329, found: 204.1311.



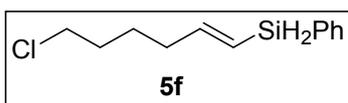
The product **5c** was purified with silica gel chromatography (Pe) as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 7.59-7.56 (m, 2H), 7.40-7.35 (m, 3H), 6.33 (dd, $J = 18.6, 6.0$ Hz, 1H), 5.72-5.63 (m, 1H), 4.54 (d, $J = 3.2$ Hz, 2H), 2.11-2.02 (m, 2H), 1.80-1.72 (m, 4H), 1.36-1.05 (m, 6H), 0.90 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 159.5, 135.4, 132.5, 129.6, 128.0, 116.7, 44.2, 32.1, 26.2, 26.0; HRMS (EI) (m/z): $[\text{M}]^+$ calcd for $\text{C}_{14}\text{H}_{20}\text{Si}$: 216.1329, found: 216.1327.



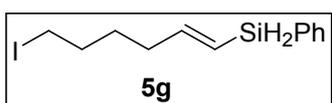
The product **5d** was purified with silica gel chromatography (Pe) as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 7.61-7.58 (m, 2H), 7.41-7.35 (m, 3H), 6.79 (d, $J = 18.8$ Hz, 1H), 5.88 (s, 1H), 5.73 (dt, $J = 18.8, 3.3$ Hz, 1H), 4.61 (d, $J = 3.2$ Hz, 2H), 2.19-2.16 (m, 4H), 1.71-1.59 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3) δ 153.1, 137.3, 135.4, 132.9, 132.4, 129.6, 128.0, 114.1, 26.0, 23.9, 22.5, 22.4; HRMS (EI) (m/z): $[\text{M}]^+$ calcd for $\text{C}_{14}\text{H}_{18}\text{OSi}$: 214.1172, found: 214.1168.



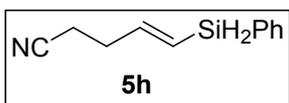
The product **5e** was purified with silica gel chromatography (Pe) as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 7.61-7.58 (m, 2H), 7.43-7.38 (m, 3H), 6.31 (dt, $J = 18.5, 6.2$ Hz, 1H), 5.93-5.84 (m, 1H), 4.56 (d, $J = 3.2$ Hz, 2H), 3.46 (t, $J = 7.0$ Hz, 2H), 2.76 (q, $J = 6.3$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 149.1, 135.4, 131.6, 129.8, 128.1, 124.1, 39.7, 31.1; HRMS (EI) (m/z): $[\text{M}]^+$ calcd for $\text{C}_{10}\text{H}_{13}\text{BrSi}$: 239.9964, found: 239.9937.



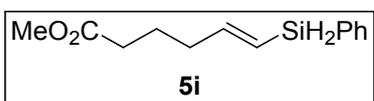
The product **5f** was purified with silica gel chromatography (Pe) as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 7.61-7.58 (m, 2H), 7.43-7.38 (m, 3H), 6.35 (dt, $J = 18.4, 6.2$ Hz, 1H), 5.81-5.72 (m, 1H), 4.54 (d, $J = 3.2$ Hz, 2H), 3.55 (t, $J = 6.6$ Hz, 2H), 2.23 (q, $J = 6.2$ Hz, 2H), 1.85-1.76 (m, 2H), 1.6-1.57 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 152.9, 135.4, 132.1, 129.7, 128.1, 120.9, 44.9, 36.0, 32.0, 25.6.; GC-MS (EI) (m/z): $[\text{M}]^+$ calcd for $\text{C}_{12}\text{H}_{17}\text{ClSi}$: 224.08, found: 224.07.



The product **5g** was purified with silica gel chromatography (Pe) as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 7.59-7.56 (m, 2H), 7.42-7.36 (m, 3H), 6.34 (dt, $J = 18.4, 6.3$ Hz, 1H), 5.81-5.71 (m, 1H), 4.45 (d, $J = 3.0$ Hz, 2H), 3.20 (t, $J = 6.9$ Hz, 2H), 2.22 (q, $J = 6.4$ Hz, 2H), 1.90-1.80 (m, 2H), 1.61-1.53 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 153.8, 135.4, 132.1, 129.7, 128.1, 121.0, 35.7, 32.9, 29.2, 6.8; HRMS (EI) (m/z): $[\text{M}]^+$ calcd for $\text{C}_{12}\text{H}_{17}\text{SiI}$: 316.0139, found: 316.0132.

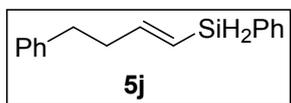


The product **5h** was purified with silica gel chromatography (Pe/EA = 10 : 1) as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 7.59-7.56 (m, 2H), 7.41-7.38 (m, 3H), 6.32 (dt, $J = 18.5, 5.6$ Hz, 1H), 5.97-5.88 (m, 1H), 4.56 (d, $J = 3.1$ Hz, 2H), 2.54-2.44 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3) δ 147.7, 135.4, 131.2, 129.9, 128.2, 124.4, 119.0, 31.9, 16.4; HRMS (ESI) (m/z): $[\text{M}+\text{NH}_4]^+$ calcd for $\text{C}_{11}\text{H}_{17}\text{N}_2\text{Si}$: 205.1156, found: 205.1157.

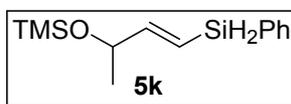


The product **5i** was purified with silica gel chromatography (Pe/EA = 50 : 1) as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 7.58-7.55 (m, 2H), 7.39-7.36 (m, 3H), 6.32 (dt, $J = 18.4, 6.3$

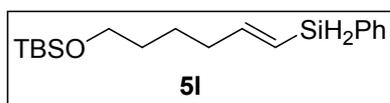
Hz, 1H), 5.81-5.72 (m, 1H), 4.53 (d, $J = 3.2$ Hz, 2H), 3.67 (s, 3H), 2.33 (d, $J = 7.5$ Hz, 2H), 2.23 (q, $J = 6.8$ Hz, 2H), 1.83-1.73 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 173.9, 152.4, 135.4, 132.1, 129.7, 128.0, 121.4, 51.6, 36.1, 33.4, 23.6; HRMS (ESI) (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{19}\text{O}_2\text{Si}$: 235.1149, found: 235.1150.



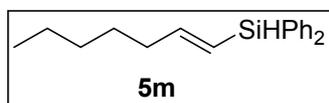
The product **5j** was purified with silica gel chromatography (Pe) as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 7.57-7.54 (m, 2H), 7.42-7.35 (m, 3H), 7.33-7.28 (m, 2H), 7.24-7.19 (m, 3H), 6.42 (dt, $J = 18.4$, 6.2 Hz, 1H), 5.82-5.74 (m, 1H), 4.55 (d, $J = 3.2$ Hz, 2H), 2.77 (d, $J = 7.8$ Hz, 2H), 2.53 (q, $J = 7.0$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 152.8, 141.6, 135.4, 132.2, 129.7, 128.5, 128.4, 128.0, 125.9, 120.9, 38.6, 34.9; HRMS (EI) (m/z): $[\text{M}]^+$ calcd for $\text{C}_{16}\text{H}_{18}\text{Si}$: 238.1172, found: 238.1173.



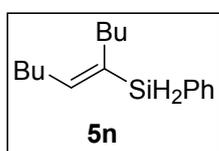
The product **5k** was purified with silica gel chromatography (Pe) as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 7.59-7.55 (m, 2H), 7.41-7.36 (m, 3H), 6.35 (dd, $J = 18.5$, 4.5 Hz, 1H), 5.95-5.87 (m, 1H), 4.56 (d, $J = 3.2$ Hz, 2H), 4.36-4.29 (m, 1H), 1.24 (d, $J = 6.5$ Hz, 3H), 0.13 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ 156.3, 135.4, 131.9, 129.7, 128.1, 117.6, 70.6, 23.8, 0.2; HRMS (ESI) (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{23}\text{OSi}_2$: 251.1282, found: 251.1280.



The product **5l** was purified with silica gel chromatography (Pe) as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 7.59-7.56 (m, 2H), 7.41-7.36 (m, 3H), 6.37 (dd, $J = 18.5$, 6.3 Hz, 1H), 5.95-5.87 (m, 1H), 4.53 (d, $J = 3.2$ Hz, 2H), 3.62 (t, $J = 6.4$ Hz, 2H), 2.25 (q, $J = 7.0$ Hz, 2H), 1.70-1.61 (m, 2H), 0.90 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 153.5, 135.4, 132.3, 129.6, 128.0, 120.3, 62.5, 33.2, 31.5, 26.0, 18.4, -5.3; HRMS (ESI) (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{31}\text{OSi}_2$: 307.1908, found: 307.1912.

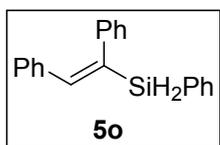


The product **5m** was purified with silica gel chromatography (Pe) as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 7.60-7.56 (m, 4H), 7.41-7.35 (m, 6H), 6.31 (dt, $J = 18.5$, 6.2 Hz, 1H), 5.97-5.89 (m, 1H), 5.09 (d, $J = 3.2$ Hz, 1H), 2.25 (q, $J = 6.9$ Hz, 2H), 1.49-1.40 (m, 2H), 1.33-1.27 (m, 4H), 0.90 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 154.1, 135.5, 134.3, 129.6, 128.0, 121.9, 37.0, 31.5, 28.1, 22.5, 14.1; HRMS (EI) (m/z): $[\text{M}]^+$ calcd for $\text{C}_{19}\text{H}_{24}\text{Si}$: 280.1642, found: 280.1637.

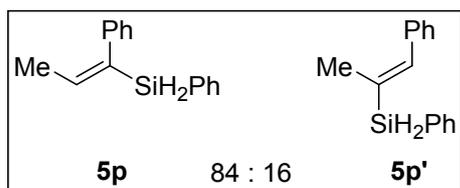


The product **5n** was purified with silica gel chromatography (Pe) as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 7.59-7.56 (m, 2H), 7.40-7.33 (m, 3H), 6.01 (t, $J = 6.9$ Hz, 1H), 4.53 (s, 2H), 2.20-2.12 (m, 4H), 1.39-1.26 (m, 8H), 0.91 (t, $J = 7.0$ Hz, 3H), 0.85 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (75

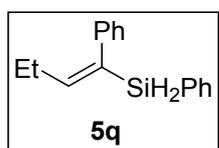
MHz, CDCl₃) δ 146.3, 135.6, 134.0, 132.8, 129.5, 127.9, 31.7, 31.5, 30.1, 28.6, 22.7, 22.5, 14.03, 13.97; HRMS (EI) (m/z): [M]⁺ calcd for C₁₆H₂₆Si: 246.1798, found: 246.1795.



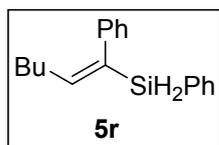
The product **5o**^[3] was purified with silica gel chromatography (Pe) as a white solid. ¹H NMR (300 MHz, CDCl₃) δ 7.61-7.58 (m, 2H), 7.43-7.35 (m, 3H), 7.28-7.22 (m, 3H), 7.15-7.02 (m, 8H), 4.81 (s, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 142.3, 141.4, 138.6, 136.9, 135.8, 131.4, 129.9, 129.6, 128.8, 128.1, 128.0, 127.8, 127.6, 126.4



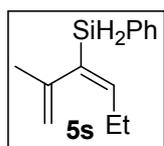
The product **5p** was purified with silica gel chromatography (Pe) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.66-7.63 (m, 0.44H), 7.55-7.52 (m, 2H), 7.40-7.28 (m, 6.64H), 7.22-7.16 (m, 1H), 7.09-7.06 (m, 2H), 6.37 (q, J = 6.7 Hz, 1H), 4.69 (s, 2H), 4.67 (s, 0.35H), 2.05 (d, J = 1.8 Hz, 0.6H), 1.73 (d, J = 6.7 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 141.6, 140.8, 137.3, 135.6, 131.9, 129.7, 129.0, 128.3, 128.2, 128.2, 128.1, 128.0, 127.1, 126.0, 17.5, 16.4; HRMS (EI) (m/z): [M]⁺ calcd for C₁₅H₁₆Si: 224.1016, found: 221.1012.



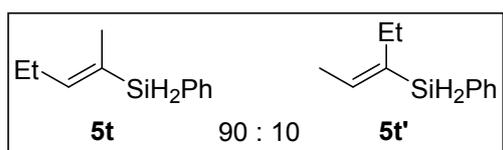
The product **5q** was purified with silica gel chromatography (Pe) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.55-7.51 (m, 2H), 7.39-7.26 (m, 5H), 7.21-7.15 (m, 1H), 7.06-7.04 (m, 2H), 6.26 (t, J = 7.1 Hz, 1H), 4.69 (s, 2H), 2.12 (p, J = 7.5 Hz, 2H), 0.98 (t, J = 7.5 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 149.0, 141.1, 135.6, 135.5, 132.0, 129.7, 128.2, 128.1, 128.0, 126.0, 23.7, 14.0; HRMS (EI) (m/z): [M]⁺ calcd for C₁₆H₁₈Si: 238.1172, found: 238.1173.



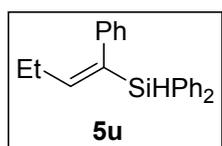
The product **5r** was purified with silica gel chromatography (Pe) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.54-7.51 (m, 2H), 7.39-7.26 (m, 5H), 7.21-7.16 (m, 1H), 7.06-7.03 (m, 2H), 6.27 (t, J = 7.1 Hz, 1H), 4.69 (s, 2H), 2.11 (q, J = 7.2 Hz, 2H), 1.37-1.23 (m, 4H), 0.84 (t, J = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 147.6, 141.1, 136.1, 135.6, 132.0, 129.7, 128.2, 128.1, 128.0, 125.9, 31.6, 30.1, 22.4, 13.9; HRMS (EI) (m/z): [M]⁺ calcd for C₁₈H₂₂OSi: 266.1485, found: 266.1483.



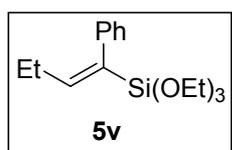
The product **5s** was purified with silica gel chromatography (Pe) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.60-7.57 (m, 2H), 7.40-7.35 (m, 3H), 5.96 (t, J = 7.1 Hz, 1H), 4.89-4.86 (m, 1H), 4.56 (s, 2H), 4.54-4.53 (m, 1H), 2.17 (p, J = 7.4 Hz, 2H), 1.76-1.75 (m, 3H), 0.99 (t, J = 7.5 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 147.0, 144.9, 137.6, 135.6, 132.3, 129.6, 127.9, 112.0, 23.9, 23.7, 14.2; HRMS (EI) (m/z): [M]⁺ calcd for C₁₃H₁₈Si: 202.1172, found: 202.1170.



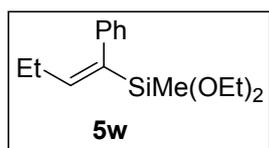
The product **5t** was purified with silica gel chromatography (Pe) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.60-7.56 (m, 2H), 7.41-7.37 (m, 3H), 6.07-6.02 (m, 1H), 4.54 (s, 0.17H), 4.52 (s, 1.74H), 2.17 (p, *J* = 7.4 Hz, 2H), 1.75-1.74 (m, 3H), 1.01 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 147.7, 135.5, 135.0, 132.3, 129.6, 128.0, 22.2, 15.4, 13.6; HRMS (EI) (*m/z*): [M]⁺ calcd for C₁₁H₁₆Si: 176.1016, found: 176.1016.



The product **5u**^[4] was purified with silica gel chromatography (Pe) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.55-7.52 (m, 4H), 7.41-7.32 (m, 6H), 7.26-7.21 (m, 2H), 7.18-7.12 (m, 1H), 7.02-6.99 (m, 2H), 6.21 (t, *J* = 7.1 Hz, 1H), 5.20 (s, 1H), 2.12 (p, *J* = 7.4 Hz, 2H), 0.97 (t, *J* = 6.9 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 149.5, 141.3, 137.2, 135.8, 133.6, 129.6, 128.4, 128.1, 127.9, 125.8, 23.7, 14.1.



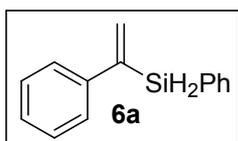
The product **5v** was purified with silica gel chromatography (Pe) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.32-7.27 (m, 2H), 7.21-7.12 (m, 3H), 6.38 (t, *J* = 7.1 Hz, 1H), 3.78 (q, *J* = 7.0 Hz, 6H), 2.09 (p, *J* = 7.5 Hz, 2H), 1.17 (t, *J* = 7.0 Hz, 9H), 0.97 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 149.1, 140.4, 134.6, 128.5, 127.9, 125.8, 58.7, 23.2, 18.1, 14.0; HRMS (ESI) (*m/z*): [M+H]⁺ calcd for C₁₆H₂₇O₃Si: 295.1724, found: 295.1730.



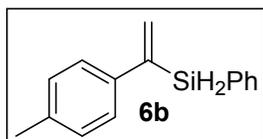
The product **5w** was purified with silica gel chromatography (Pe) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.32-7.27 (m, 2H), 7.21-7.15 (m, 1H), 7.09-7.06 (m, 2H), 6.27 (t, *J* = 7.1 Hz, 1H), 3.78 (dq, *J* = 7.0, 0.9 Hz, 4H), 2.14 (p, *J* = 7.5 Hz, 2H), 1.18 (t, *J* = 7.0 Hz, 6H), 0.96 (t, *J* = 7.5 Hz, 3H), 0.15 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 147.1, 140.9, 138.6, 128.3, 128.0, 125.6, 58.4, 23.16, 18.3, 14.0, -4.6; HRMS (ESI) (*m/z*): [M+H]⁺ calcd for C₁₅H₁₆Si: 265.1618, found: 265.1621.

Co(OAc)₂•4H₂O-⁴Me^bbipy catalysed Hydrosilylation

Co(OAc)₂•4H₂O (0.5 mg, 0.002 mmol, 0.005 equiv) and 4Me^bbipy (0.4 mg, 0.002 mmol, 0.005 equiv) were dissolved in 0.5 mL THF. Alkyne (0.4 mmol, 1.0 equiv) was added into the system (Note: if it is solid, weigh it firstly), followed with PhSiH₃ (0.48 mmol, 1.2 equiv). The mixture was stirred at room temperature for 3 hours. The solvent was removed to leave a crude product, which was purified by column chromatography on silica gel to afford the product **6**.

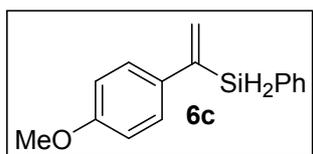


The product **6a** was purified with silica gel chromatography (Pe) as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 7.61 (dd, $J = 7.7, 1.7$ Hz, 2H), 7.42-7.27 (m, 8H), 6.26 (d, $J = 2.3$ Hz, 1H), 5.85 (d, $J = 2.3$ Hz, 1H), 4.86 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 144.2, 142.3, 135.6, 131.4, 131.2, 129.9, 128.5, 128.6, 127.3, 126.5; HRMS (EI) (m/z): $[\text{M}]^+$ calcd for $\text{C}_{14}\text{H}_{14}\text{Si}$: 210.0859, found: 210.0857.



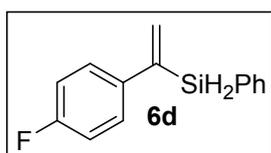
The product **6b** was purified with silica gel chromatography (Pe) as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 7.60 (dd, $J = 7.7, 1.7$ Hz, 2H), 7.41-7.35 (m, 3H), 7.29 (d, $J = 8.1$ Hz, 2H), 7.12 (d, $J = 7.9$ Hz, 2H), 6.23 (d, $J = 2.3$ Hz, 1H), 5.79 (d, $J = 2.3$ Hz, 1H), 4.83 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 143.7, 139.3, 137.1, 135.6, 131.3, 130.5, 129.9, 129.2, 128.1, 126.4, 21.1; HRMS (EI) (m/z): $[\text{M}]^+$ calcd for $\text{C}_{15}\text{H}_{16}\text{Si}$: 224.1016, found: 224.1010.

The product **6c** was purified with silica gel chromatography (Pe/EA = 50 : 1) as a colorless oil. ^1H



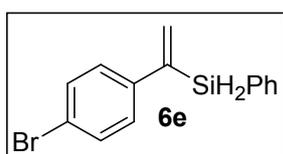
NMR (300 MHz, CDCl_3) δ 7.60 (dd, $J = 7.7, 1.7$ Hz, 2H), 7.39-7.32 (m, 5H), 6.85 (d, $J = 8.9$ Hz, 2H), 6.19 (d, $J = 2.3$ Hz, 1H), 5.75 (d, $J = 2.3$ Hz, 1H), 4.83 (s, 2H), 3.80 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 159.0, 143.1, 135.6, 134.6, 131.4, 129.9, 129.6, 128.1, 127.6, 113.9, 55.3; HRMS (EI) (m/z): $[\text{M}]^+$ calcd for $\text{C}_{15}\text{H}_{16}\text{OSi}$: 240.0965, found: 240.0963.

The product **6d** was purified with silica gel chromatography (Pe) as a colorless oil. ^1H NMR (300



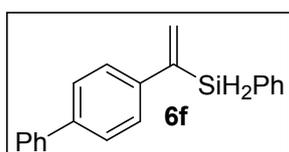
MHz, CDCl_3) δ 7.59 (dd, $J = 7.7, 1.6$ Hz, 2H), 7.42-7.31 (m, 5H), 7.03-7.69 (m, 2H), 6.19 (d, $J = 2.1$ Hz, 1H), 5.83 (d, $J = 2.2$ Hz, 1H), 4.83 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 162.2 (d, $J = 246.4$ Hz), 143.2, 138.3, 135.6, 131.3, 130.9, 130.0, 128.2, 128.1 (d, $J = 8.0$ Hz), 115.4 (d, $J = 21.4$ Hz); HRMS (EI) (m/z): $[\text{M}]^+$ calcd for $\text{C}_{14}\text{H}_{13}\text{FSi}$: 228.0765, found: 228.0763.

The product **6e** was purified with silica gel chromatography (Pe) as a colorless oil. ^1H NMR (300



MHz, CDCl_3) δ 7.58-7.55 (m, 2H), 7.45-7.36 (m, 5H), 7.24-7.21 (m, 2H), 6.21 (d, $J = 2.2$ Hz, 1H), 5.85 (d, $J = 2.2$ Hz, 1H), 4.81 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 143.3, 141.2, 135.6, 133.6, 131.9, 131.6, 130.1, 128.2, 128.1, 121.3; HRMS (EI) (m/z): $[\text{M}]^+$ calcd for $\text{C}_{14}\text{H}_{13}\text{BrSi}$: 287.9964, found: 287.9959.

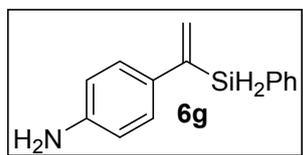
The product **6f** was purified with silica gel chromatography (Pe) as a white solid. ^1H NMR (300



MHz, CDCl_3) δ 7.61-7.57 (m, 3H), 7.55-7.53 (m, 2H), 7.51-7.50 (m,

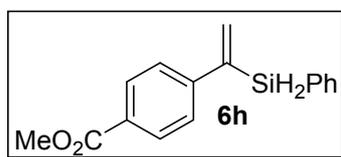
1H), 7.45-7.31 (m, 8H), 6.28 (d, $J = 2.3$ Hz, 1H), 5.84 (d, $J = 2.3$ Hz, 1H), 4.85 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 143.6, 141.2, 140.7, 140.2, 135.7, 131.3, 131.2, 130.0, 128.8, 128.2, 127.33, 127.26, 127.0, 126.9; HRMS (EI) (m/z): $[\text{M}]^+$ calcd for $\text{C}_{20}\text{H}_{18}\text{Si}$: 286.1172, found: 286.1170.

The product **6g** was purified with silica gel chromatography (Pe/EA = 5 : 1) as a pale yellow oil. ^1H



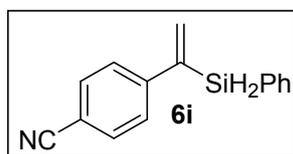
NMR (300 MHz, CDCl_3) δ 7.61-7.58 (m, 2H), 7.40-7.35 (m, 3H), 7.23 (d, $J = 8.6$ Hz, 2H), 6.62 (d, $J = 8.6$ Hz, 2H), 6.17 (d, $J = 2.3$ Hz, 1H), 5.68 (d, $J = 2.3$ Hz, 1H), 4.82 (s, 2H), 3.67 (brs, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 145.9, 143.0, 135.6, 132.4, 131.6, 129.8, 128.2, 128.1, 127.5, 115.1; HRMS (EI) (m/z): $[\text{M}]^+$ calcd for $\text{C}_{14}\text{H}_{15}\text{NSi}$: 225.0968, found: 225.0968.

The product **6h** was purified with silica gel chromatography (Pe/EA = 30 : 1) as a colorless oil. ^1H



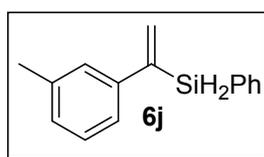
NMR (300 MHz, CDCl_3) δ 7.97 (d, $J = 8.6$ Hz, 2H), 7.57 (dd, $J = 7.8, 1.6$ Hz, 2H), 7.42-7.35 (m, 5H), 6.28 (d, $J = 2.3$ Hz, 1H), 5.92 (d, $J = 2.3$ Hz, 1H), 4.84 (s, 2H), 3.90 (brs, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 166.9, 147.1, 143.8, 135.6, 133.0, 130.6, 130.1, 129.9, 128.9, 128.2, 126.5, 52.1; HRMS (EI) (m/z): $[\text{M}]^+$ calcd for $\text{C}_{16}\text{H}_{16}\text{O}_2\text{Si}$: 268.0924, found: 268.0903.

The product **6i** was purified with silica gel chromatography (Pe/EA = 30 : 1) as a colorless oil. ^1H



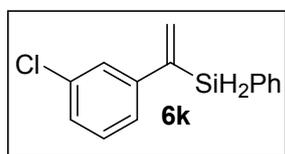
NMR (300 MHz, CDCl_3) δ 7.61-7.54 (m, 4H), 7.44-7.37 (m, 5H), 6.27 (d, $J = 2.0$ Hz, 1H), 5.96 (d, $J = 2.0$ Hz, 1H), 4.82 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 147.2, 143.5, 135.6, 134.0, 132.4, 130.3, 128.3, 127.2, 118.9, 110.8; HRMS (EI) (m/z): $[\text{M}]^+$ calcd for $\text{C}_{15}\text{H}_{13}\text{NSi}$: 235.0812, found: 235.0806.

The product **6j** was purified with silica gel chromatography (Pe) as a colorless oil. ^1H NMR (300



MHz, CDCl_3) δ 7.61 (dd, $J = 7.7, 1.8$ Hz, 2H), 7.42-7.35 (m, 3H), 7.21-7.19 (m, 3H), 7.10-7.06 (m, 1H), 6.24 (d, $J = 2.4$ Hz, 1H), 5.82 (d, $J = 2.4$ Hz, 1H), 4.84 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 144.2, 142.3, 138.1, 135.6, 131.3, 131.1, 129.9, 128.4, 128.1, 128.1, 127.1, 123.7, 21.5; HRMS (EI) (m/z): $[\text{M}]^+$ calcd for $\text{C}_{15}\text{H}_{16}\text{Si}$: 224.1016, found: 224.1019.

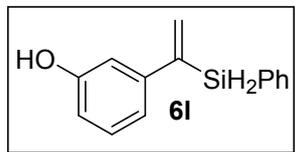
The product **6k** was purified with silica gel chromatography (Pe) as a colorless oil. ^1H NMR (300



MHz, CDCl_3) δ 7.59 (dd, $J = 7.7, 1.7$ Hz, 2H), 7.44-7.37 (m, 4H), 7.23 (d, $J = 7.7, 1.7$ Hz, 3H), 7.10-7.06 (m, 1H), 6.23 (d, $J = 2.1$ Hz, 1H), 5.87 (d, $J = 2.2$ Hz, 1H), 4.83 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ

144.2, 143.3, 135.6, 134.5, 132.5, 130.6, 130.1, 129.7, 128.3, 127.3, 126.5, 124.9; HRMS (EI) (m/z): $[M]^+$ calcd for $C_{14}H_{13}ClSi$: 244.0470, found: 224.0468.

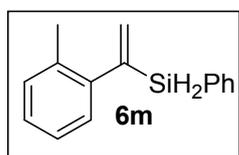
The product **6l** was purified with silica gel chromatography (Pe/EA = 10 : 1) as a colorless oil. 1H



NMR (300 MHz, $CDCl_3$) δ 7.59 (dd, $J = 7.7, 1.7$ Hz, 2H), 7.41-7.34 (m, 3H), 7.20-7.15 (m, 1H), 6.96-6.93 (m, 1H), 6.85-6.84 (m, 1H), 6.75-6.71 (m, 1H), 6.23 (d, $J = 2.3$ Hz, 1H), 5.83 (d, $J = 2.3$ Hz, 1H), 4.91 (s, 1H), 4.83 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.6, 144.1,

143.8, 135.6, 131.6, 131.1, 130.0, 129.8, 128.2, 119.3, 114.3, 113.3; HRMS (EI) (m/z): $[M]^+$ calcd for $C_{14}H_{14}OSi$: 226.0808, found: 226.0804.

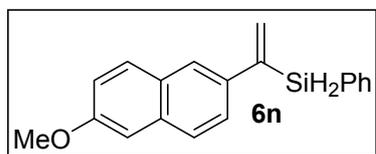
The product **6m** was purified with silica gel chromatography (Pe) as a colorless oil. 1H NMR (300



MHz, $CDCl_3$) δ 7.54 (dd, $J = 7.8, 1.6$ Hz, 2H), 7.41-7.35 (m, 3H), 7.17-7.10 (m, 3H), 6.99-6.96 (m, 1H), 5.92 (d, $J = 3.1$ Hz, 1H), 5.87 (d, $J = 3.0$ Hz, 1H), 4.70 (s, 2H), 2.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.5, 143.1, 135.6, 134.4, 133.0, 131.1, 130.1, 129.9, 128.0, 127.9, 126.6, 125.6, 20.3;

HRMS (EI) (m/z): $[M]^+$ calcd for $C_{15}H_{16}Si$: 224.1016, found: 224.1003.

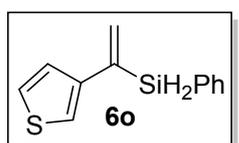
The product **6n** was purified with silica gel chromatography (Pe/EA = 30 : 1) as a white solid. 1H



NMR (300 MHz, $CDCl_3$) δ 7.74 (d, $J = 1.7$ Hz, 1H), 7.68 (d, $J = 8.4$ Hz, 2H), 7.74 (dd, $J = 7.7, 1.7$ Hz, 2H), 7.53 (dd, $J = 8.5, 1.9$ Hz, 1H), 7.40-7.33 (m, 3H), 7.14-7.10 (m, 2H), 6.35 (d, $J = 2.2$ Hz, 1H), 5.88 (d, $J = 2.2$ Hz, 1H), 4.91 (s, 2H), 3.92 (s,

3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.7, 143.8, 137.4, 135.6, 133.9, 131.3, 130.9, 129.9, 129.7, 128.9, 128.2, 12.0, 125.5, 125.0, 119.0, 105.6, 55.3; HRMS (EI) (m/z): $[M]^+$ calcd for $C_{19}H_{18}OSi$: 290.1121, found: 290.1117.

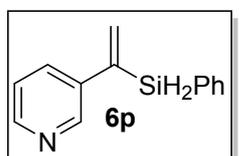
The product **6o** was purified with silica gel chromatography (Pe/EA = 30 : 1) as a pale yellow oil.



1H NMR (300 MHz, $CDCl_3$) δ 7.64-7.61 (m, 2H), 7.43-7.35 (m, 3H), 7.29-7.27 (m, 1H), 7.25-7.23 (m, 1H), 7.20-7.18 (m, 1H), 6.39 (d, $J = 2.3$ Hz, 1H), 5.78 (d, $J = 2.3$ Hz, 1H), 4.82 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.2, 137.6, 135.6, 131.0, 130.0, 129.7, 128.2, 125.7, 125.4, 121.8; HRMS (EI)

(m/z): $[M]^+$ calcd for $C_{12}H_{12}SSi$: 216.0424, found: 216.0432.

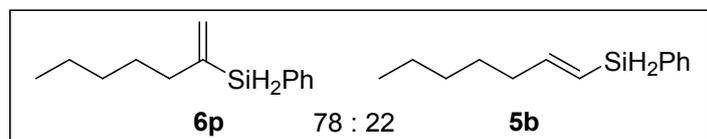
The product **6p** was purified with silica gel chromatography (Pe/EA = 5 : 1) as a pale yellow oil. 1H



NMR (300 MHz, $CDCl_3$) δ 8.6 (d, $J = 1.7$ Hz, 1H), 8.47 (dd, $J = 4.8, 1.6$ Hz, 1H), 7.64-7.56 (m, 3H), 7.42-7.33 (m, 3H), 7.23-7.19 (m, 1H), 6.26 (d, $J = 2.1$ Hz, 1H), 5.93 (d, $J = 2.1$ Hz, 1H), 4.83 (s, 2H); ^{13}C NMR (75 MHz,

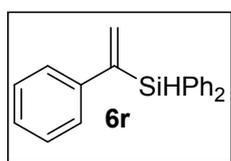
CDCl₃) δ 148.4, 147.7, 141.4, 138.0, 135.6, 133.7, 133.2, 130.24, 130.21, 128.3, 123.3; HRMS (EI) (m/z): [M]⁺ calcd for C₁₃H₁₃NSi: 211.0812, found: 211.0807.

The product **6q** was purified with silica gel chromatography (Pe) as a colorless oil. ¹H NMR (300



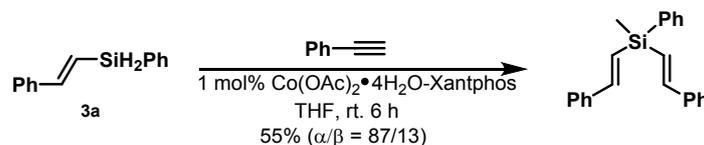
MHz, CDCl₃) δ 7.60-7.56 (m, 2H), 7.42-7.35 (m, 1H), 7.58-7.57 (m, 0.78H), 5.54 (d, J = 2.9 Hz, 0.78H), 4.54 (s, 1.56H), 2.23-2.14

(m, 2H), 1.48-1.37 (m, 2H), 1.29-1.20 (m, 4H), 0.91-0.84 (m, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 145.4, 135.6, 131.7, 129.7, 129.4, 128.0, 37.4, 31.5, 28.5, 22.5, 14.0; HRMS (EI) (m/z): [M]⁺ calcd for C₁₃H₂₀Si: 204.1329, found: 204.1323.

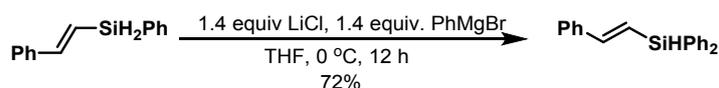


The product **6r**^[4] was purified with silica gel chromatography (Pe) as a white solid. ¹H NMR (300 MHz, CDCl₃) δ 7.59-7.56 (m, 4H), 7.42-7.34 (m, 8H), 7.30-7.19 (m, 3H), 6.30 (dd, J = 2.5, 1.0 Hz, 1H), 5.69 (d, J = 2.5 Hz, 1H), 5.40 (d, J = 0.7 Hz, 1H), 4.83 (s, 2H).

Transformations of vinylsilanes^[5, 6]

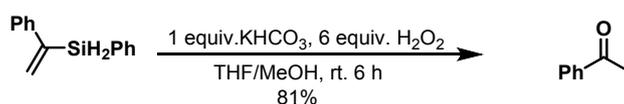


Co(OAc)₂•4H₂O (1.0 mg, 0.004 mmol, 0.01 equiv, in 10 μ L MeOH), was added into 0.5 mL THF containing Xantphos (2.3 mg, 0.004 mmol, 0.01 equiv). Phenylacetylene (0.4 mmol, 1.0 equiv) was added into the system, followed with **3a** (0.48 mmol, 1.2 equiv). The mixture was stirred at room temperature for 10 hours. The solvent was removed to leave a crude product, which was purified by column chromatography on silica gel to afford the desired product in 55% yield as a pale yellow oil. ¹H NMR (300 MHz, CDCl₃) δ 7.71-7.67 (m, 2H), 7.53-7.52 (m, 4H), 7.45-7.30 (m, 10H), 7.16 (d, J = 19.0 Hz, 2H), 6.67 (dd, J = 19.3, 3.1 Hz, 2H), 6.28 (d, J = 1.8 Hz, 0.14H), 5.83 (d, J = 2.5 Hz, 0.14H), 5.19 (d, J = 3.2 Hz, 0.13H), 5.06 (t, 4.83 (s, J = 3.7 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 148.7, 137.9, 135.3, 133.9, 129.7, 128.6, 128.6, 128.1, 126.7, 121.8.



The Phenylmagnesium Bromide (1.0 M in THF, 0.56 mL, 0.56 mmol) and (Z) silane (0.4 mmol) was added to a suspension of LiCl (23.8 mg) in THF (0.8 mL) under N₂. The reaction was stirred for 12 hours and quenched by adding saturated NH₄Cl solution (0.5 mL). The resulting solution was

extracted with Et₂O (2 x 10 mL) and dried over Na₂SO₄. The solvent was removed under reduced pressure and the crude product was purified with silica gel flash column chromatography with Pe as eluent to give **3y** a colourless oil in 72% yield. ¹H NMR (300 MHz, CDCl₃) δ 7.65-7.62 (m, 4H), 7.50-7.32 (m, 11H), 7.11 (d, *J* = 19.0 Hz, 1H), 6.73 (dt, *J* = 19.0, 3.2 Hz, 1H), 5.26 (d, *J* = 3.2 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 149.1, 137.9, 135.6, 133.6, 129.8, 128.64, 128.62, 128.1, 126.8, 121.5.

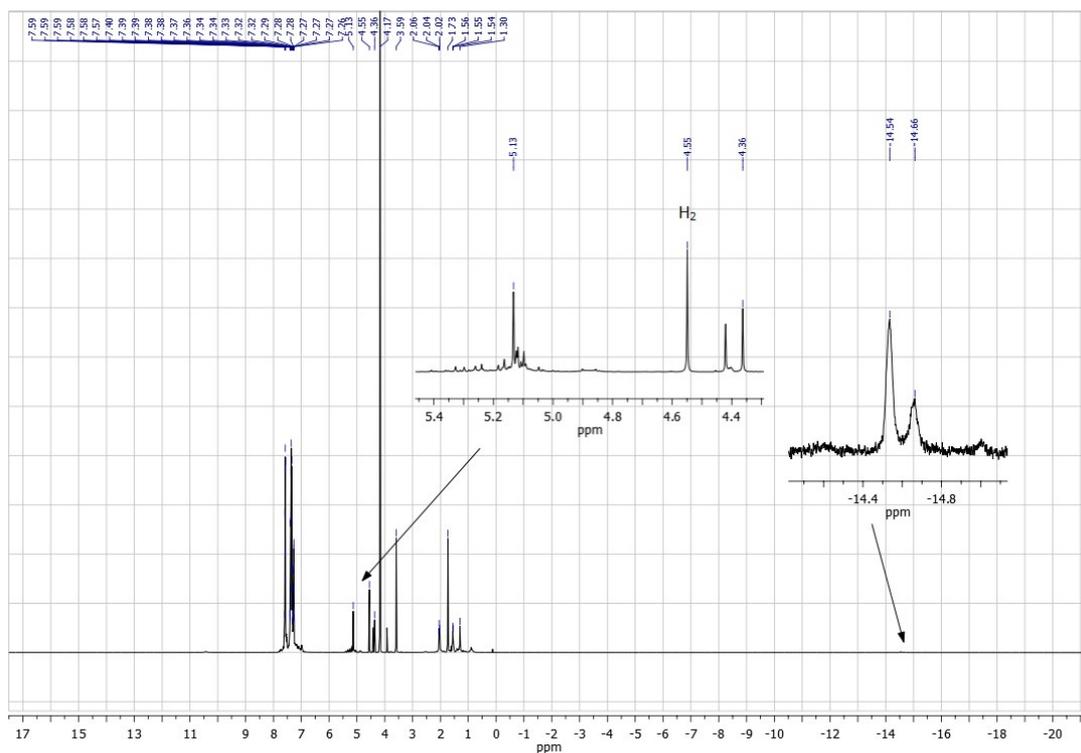


In a tube containing KHCO₃ (50 mg, 0.5 mmol) was added, THF (2.0 mL), MeOH (2.0 mL), **2** (0.5 mmol, 1.0 equiv.), then 30% H₂O₂ aq. (340 mg, 3.0 mmol). The resulting mixture was stirred at room temperature for 10 h before a saturated aqueous solution of Na₂S₂O₃ (5 mL) was added. The resulting solution was extracted with EtOAc and washed with brine (10 mL), dried over anhydrous Na₂SO₄. After filtration and evaporation of the solvent under vacuum, the residue was purified by flash column chromatography with Pe/EA (50/1) to give a colorless oil in 81% yield. ¹H NMR (300 MHz, CDCl₃) δ 7.98-7.95 (m, 2H), 7.60-7.54 (m, 1H), 7.49-7.44 (m, 2H), 2.61 (s, 3H).

4. NMR and kinetic studies

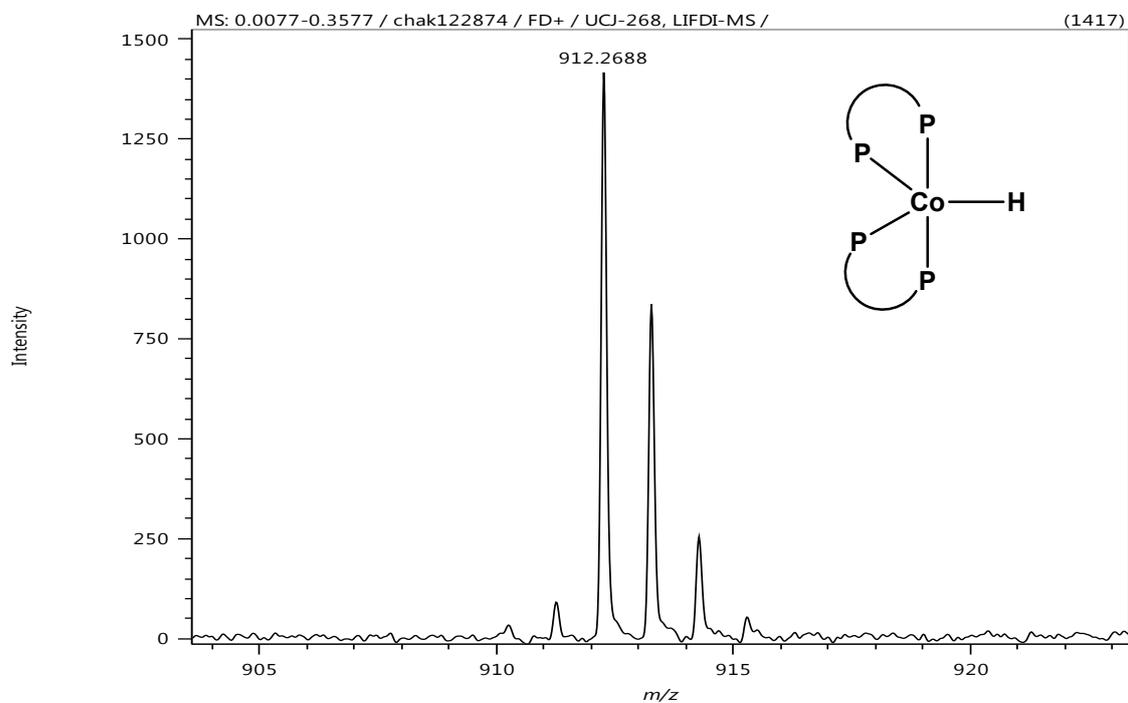
Reaction of Co(OAc)₂·4H₂O, dppb and PhSiH₃ (1:1:10):

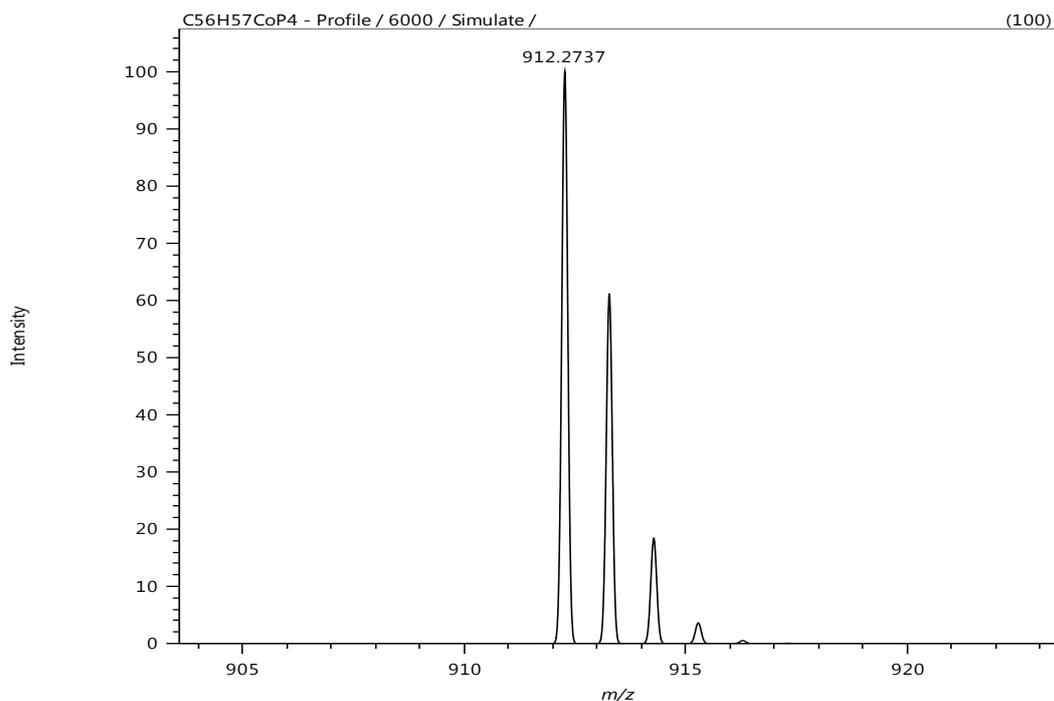
A mixture of Co(OAc)₂·4H₂O (5 mg, 0.2 mmol) and dppb (8.8 mg, 0.021 mmol) in 0.6 mL THF-d₈ was stirred for 20 minutes and then treated with PhSiH₃ (25 μL, 0.20 mmol). The reaction mixture was stirred for 1h and the obtained yellowish-orange mixture was filtered and subjected to NMR spectroscopy. The NMR sample was evaporated completely and the residue was re-dissolved in toluene and subjected to LIFDI-MS.



^1H NMR spectrum (in THF-d_8) of the reaction mixture of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, dppb and PhSiH_3 (1:1:10).

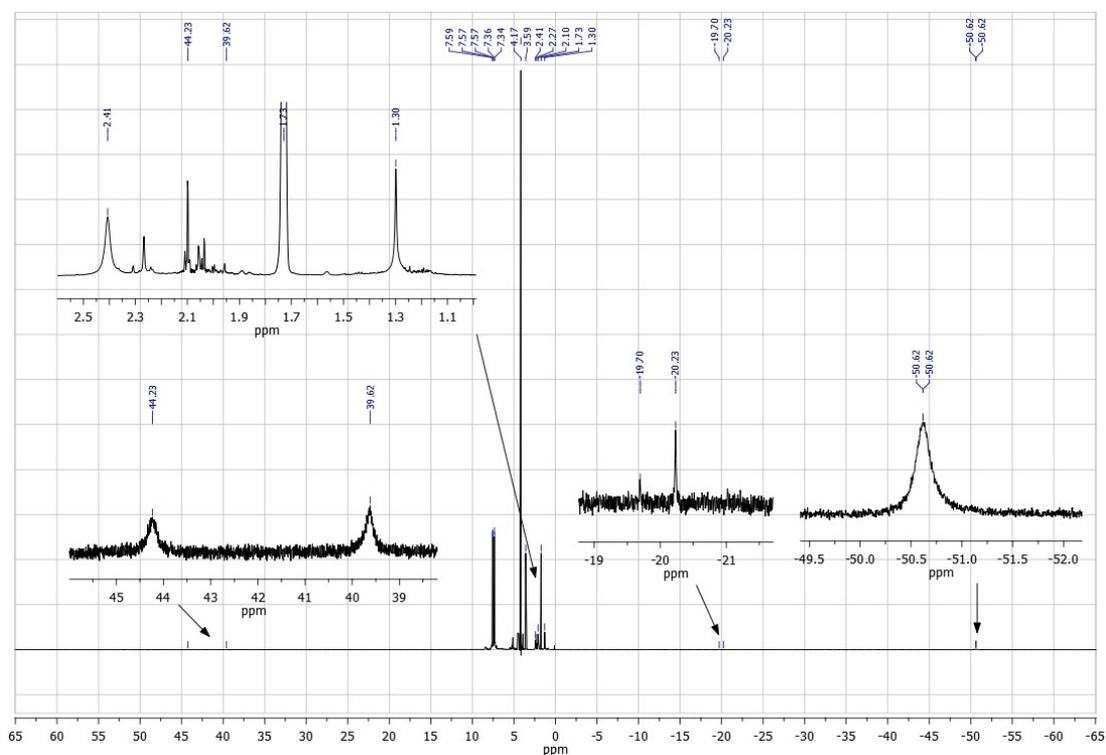
LIFDI-MS of the reaction mixture of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, dppb and PhSiH_3 (1:1:10) in toluene:





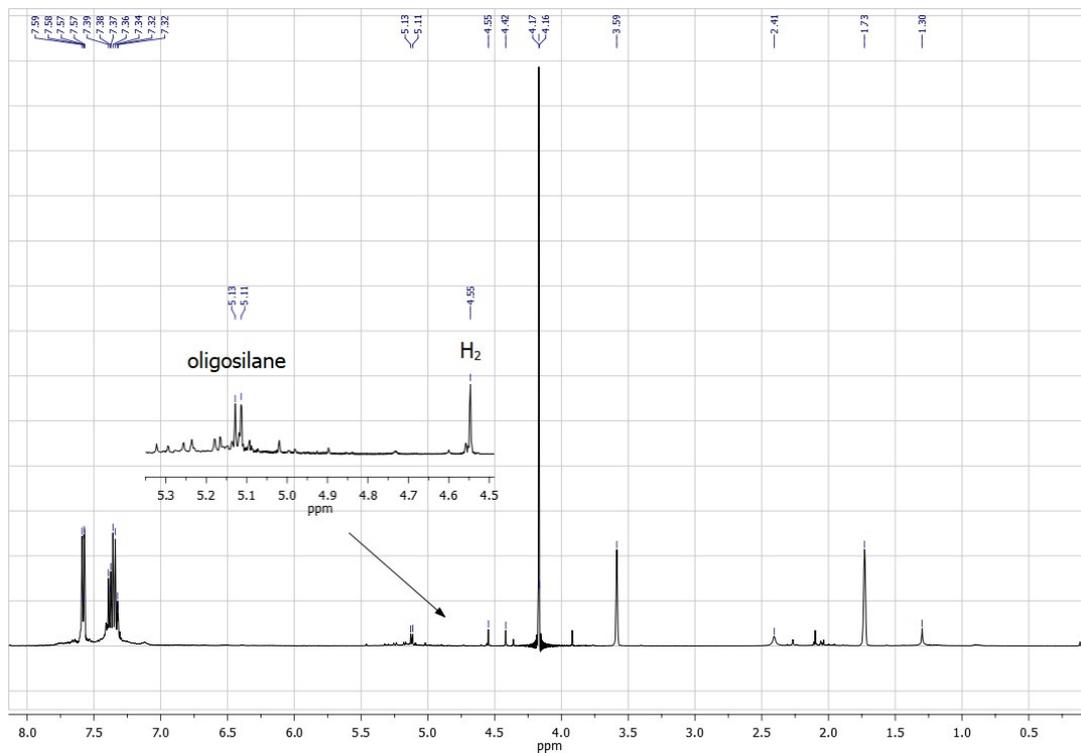
Reaction of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, 4-Mebipy** and PhSiH_3 (1:1:10):**

A mixture of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (5 mg, 0.2 mmol) and 4-Me**bipy** (3.8 mg, 0.021 mmol) in 0.6 mL THF- d_8 was stirred for 20 minutes and then treated with PhSiH_3 (25 μL , 0.20 mmol). The reaction mixture was stirred for 1h and the obtained black brown mixture



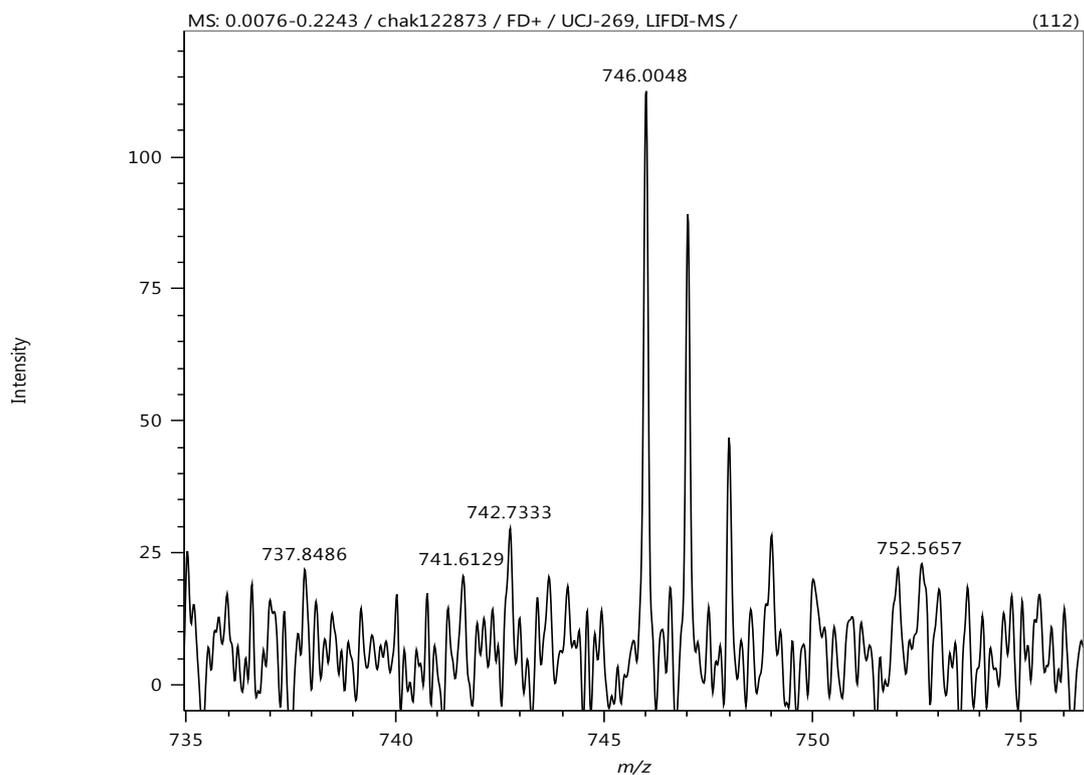
^1H NMR spectrum (in THF- d_8) of the reaction mixture of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, 4-Me**bipy** and PhSiH_3 (1:1:10).

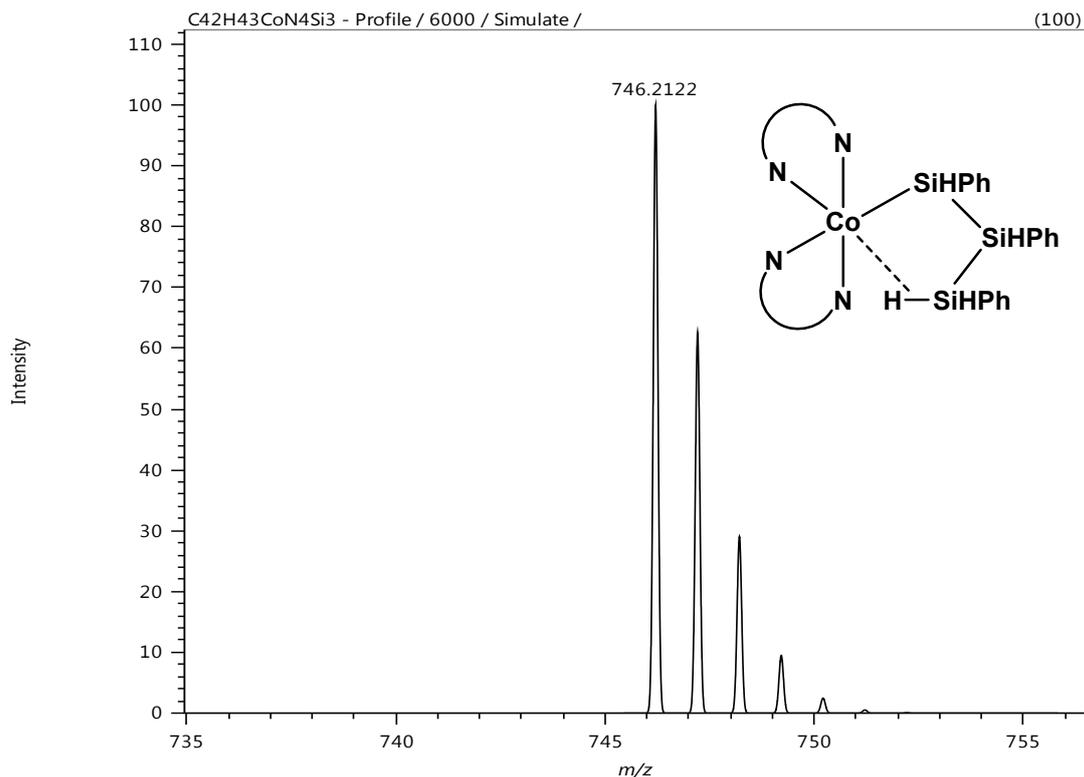
was filtered and subjected to NMR spectroscopy. The NMR sample was evaporated completely and the residue was re-dissolved in toluene and subjected to LIFDI-MS.



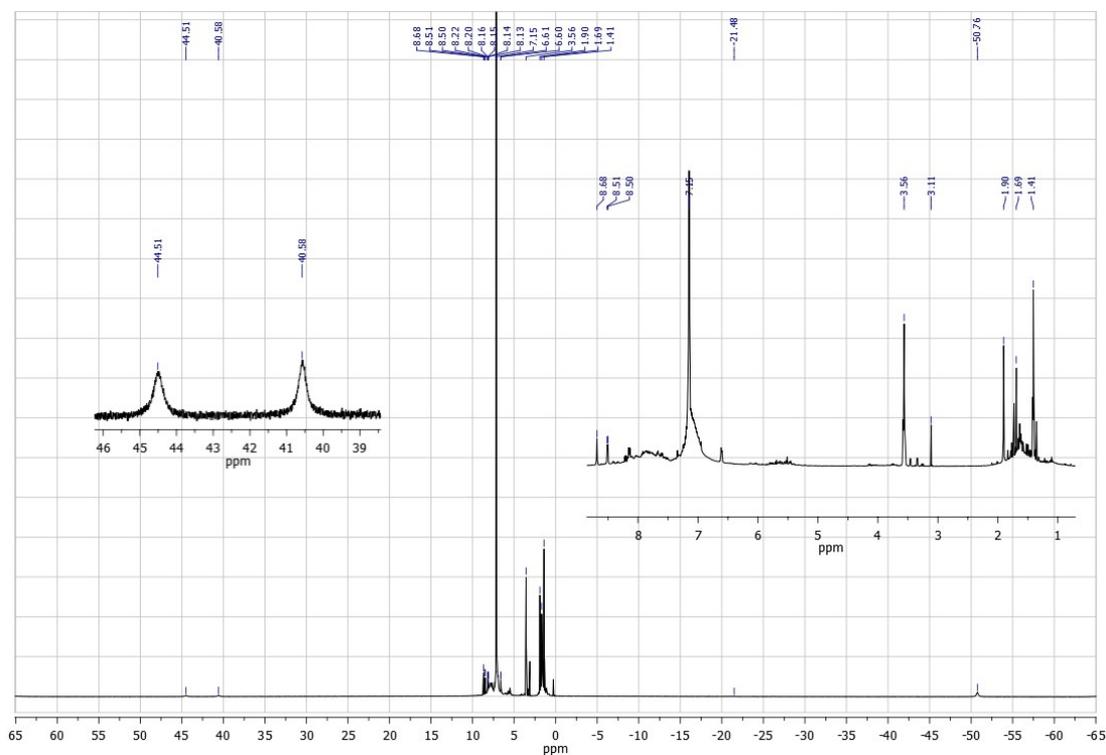
Expanded region (0.5 – 8 ppm) of the ^1H NMR spectrum (in THF-d_8) of the reaction mixture of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, $^4\text{-Me}$ bipy and PhSiH_3 (1:1:10).

LIFDI-MS of the reaction mixture of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, $^4\text{-Me}$ bipy and PhSiH_3 (1:1:10) in toluene:





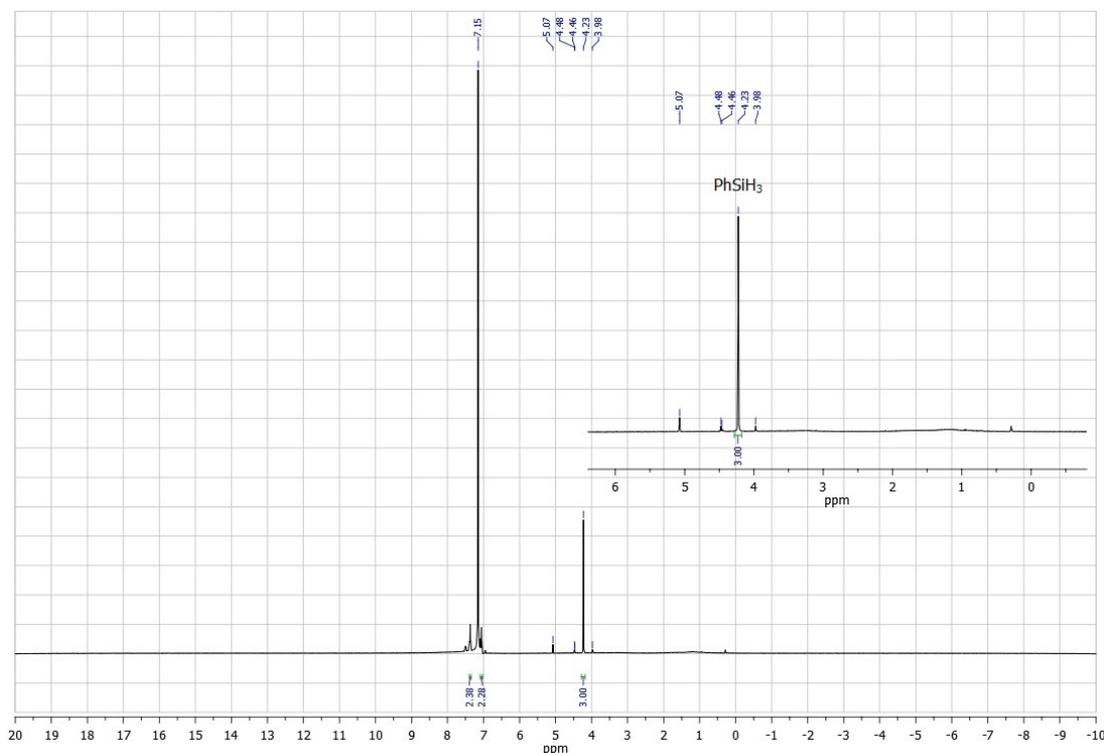
Reaction of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, $4\text{-Me}^e\text{bipy}$ and PhSiH_3 (1:1:5):



^1H NMR spectrum of the reaction mixture of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, $4\text{-Me}^e\text{bipy}$ and PhSiH_3 (1:1:5).

A mixture of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (5 mg, 0.2 mmol) and $4\text{-Me}^e\text{bipy}$ (3.8 mg, 0.021 mmol) in 0.6 mL C_6D_6 was stirred for 10 minutes and then treated with PhSiH_3 (12.5 μL , 0.20

mmol). The reaction mixture was stirred for 1h and the obtained black brown mixture was filtered and subjected to NMR spectroscopy. The NMR sample was treated with LiAlH_4 (2 mg, 0.053 mmol) and stirred overnight. Color of the solution changed to red then to dark purple and a NMR was recorded.

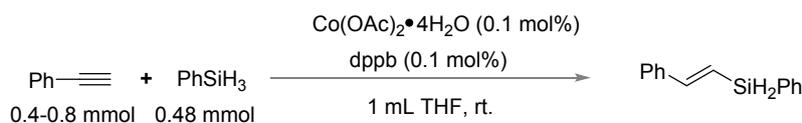


^1H NMR spectrum of the reaction mixture of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, $4\text{-Me}^e\text{bipy}$ and PhSiH_3 (1:1:5) upon treatment with LiAlH_4 .

Kinetic studies

General procedure to acquire kinetic data: In an Ar-filled glovebox, a 5 mL screw-capped vial was charged with $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (dissolved in 10 μL MeOH), ligand, phenylacetylene, dodecane (internal standard, 0.2 mmol), THF (1.0 mL) and a magnetic stirring bar. The timing was started upon addition of PhSiH_3 , and 1 μL of the solution was drawn at intervals and diluted immediately with ethyl acetate to quench the reaction. The yield of the product was measured based on GC analysis.

Figure S1. Kinetic profile with varying phenylacetylene concentrations



Phenylacetylene (mmol)	Rate (M/s)
0.4	3.31×10^{-3}
0.6	3.18×10^{-3}
0.8	3.04×10^{-3}

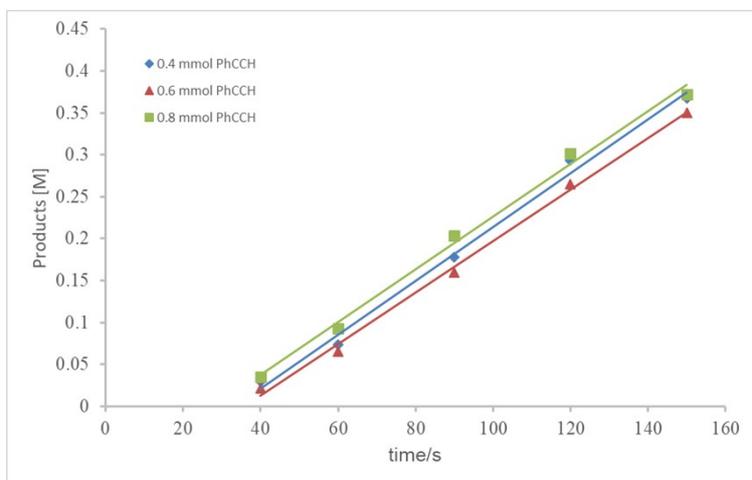
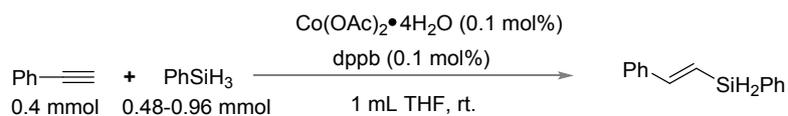


Figure S2. Kinetic profile with varying phenylsilane concentrations



PhSiH ₃ (mmol)	Rate (M/s)
0.48	3.21×10^{-3}
0.72	3.00×10^{-3}
0.96	3.09×10^{-3}

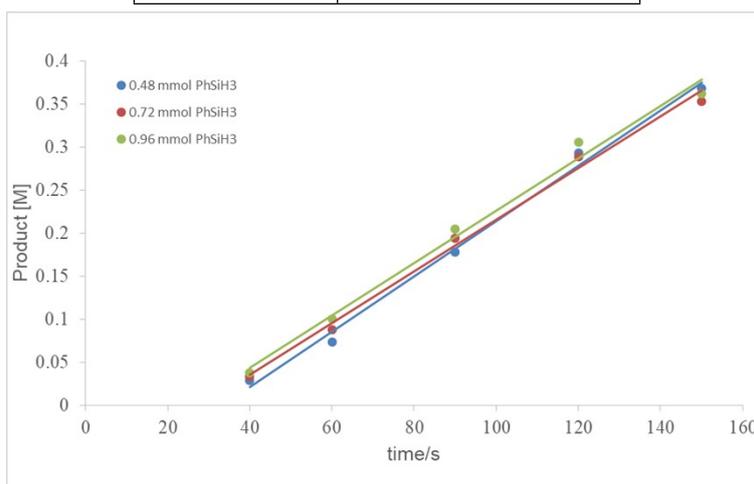
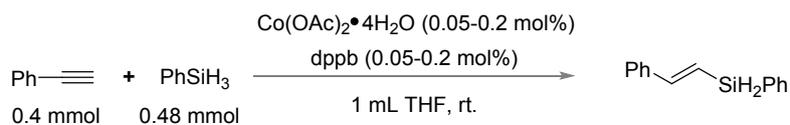


Figure S3. Kinetic profile with varying cobalt concentrations



Co(OAc) ₂ •4H ₂ O	Rate (M/s)
0.05 mol%	1.54 × 10 ⁻³
0.1 mol%	3.20 × 10 ⁻³
0.2 mol%	5.30 × 10 ⁻³

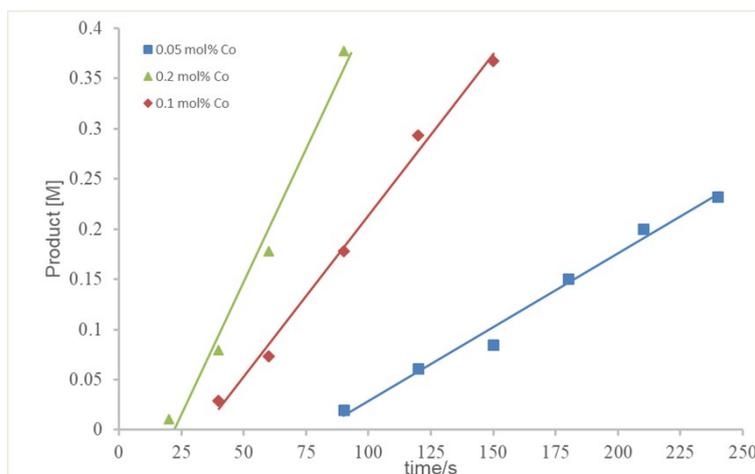
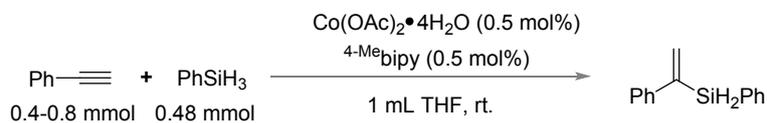


Figure S4. Kinetic profile with varying phenylacetylene concentrations



Phenylacetylene (mmol)	Rate (M/s)
0.4	7.90 × 10 ⁻⁴
0.6	8.37 × 10 ⁻⁴
0.8	7.38 × 10 ⁻⁴

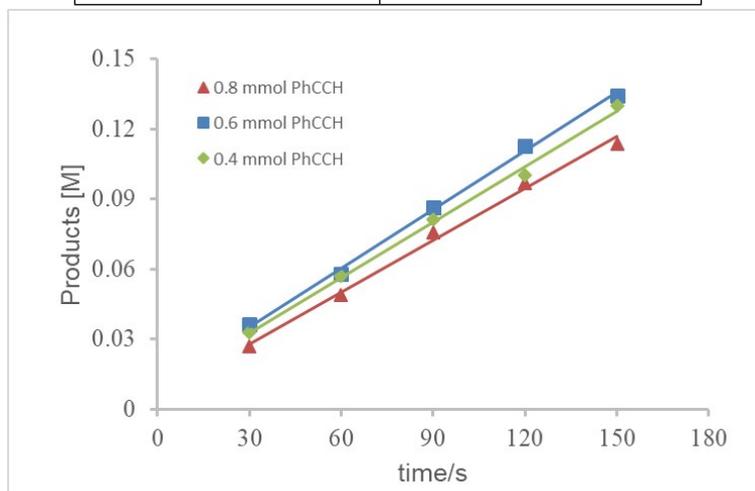


Figure S5. Kinetic profile with varying phenylsilane concentrations

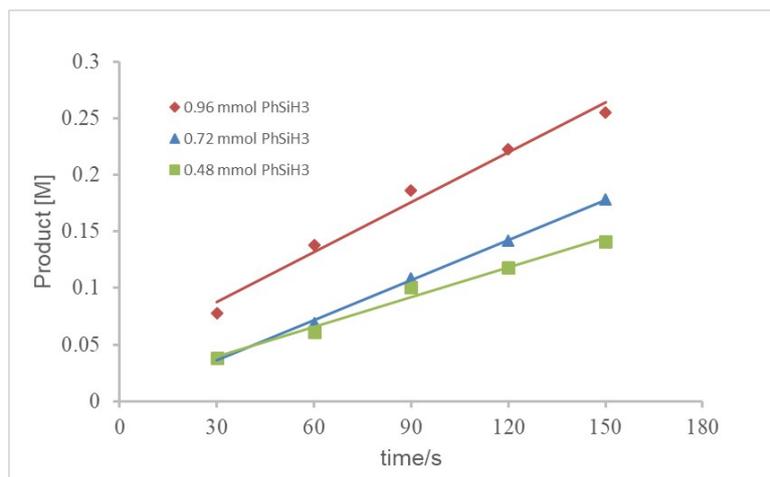
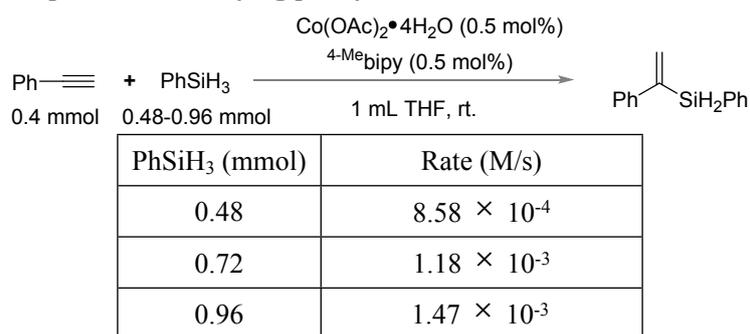
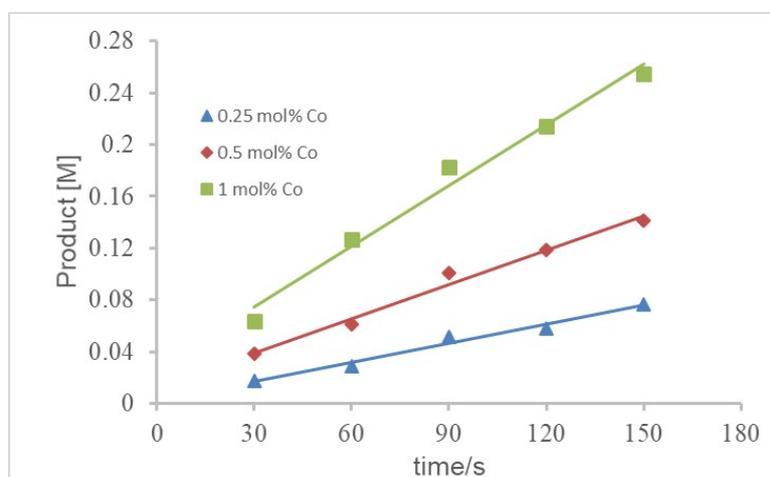
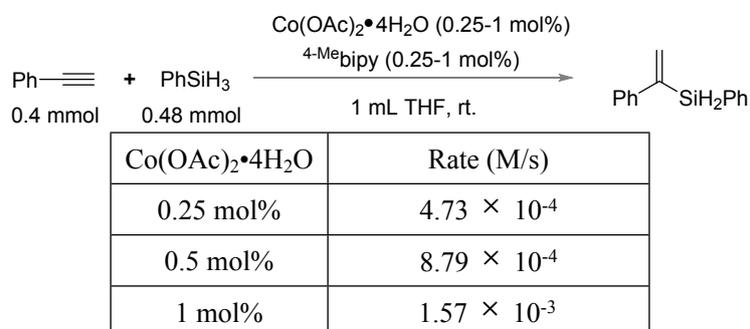


Figure S6. Kinetic profile with varying phenylsilane concentrations



5. Reference

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6. ^1H , ^{13}C NMR spectrum

