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Cobalt-Catalyzed Hydrosilylation/Cyclization of 1,6-Enynes

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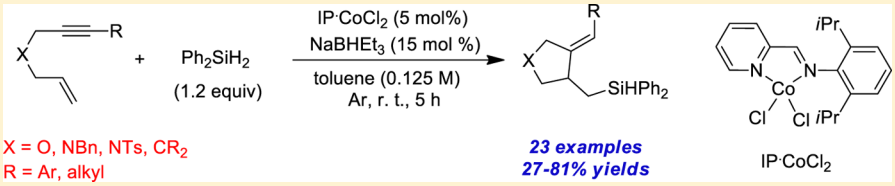
Supporting Information



ABSTRACT: An iminopyridine cobalt dichloride complex was synthesized and demonstrated as an effective precatalyst for hydrosilylation/cyclization of 1,6-enynes with silanes. Various functional groups such as amine, free aniline, ester, ether, cyano, halide, trifluoromethyl, and heterocycle were tolerated to afford a variety of silicon-containing compounds. The reaction could be scaled up to afford products on the gram scale which could undergo further derivatizations. A primary mechanism was proposed based on analysis of side products and a deuterated experiment.

INTRODUCTION

Cobalt is an earth-abundant, environment-friendly, and biocompatible metal and, therefore, plays an increasingly important role in organic synthesis. The development of various reactions based on cheap and easily obtained ligands is highly desirable. The simple iminopyridine ligand[1] has proven to show a unique noninnocent property through spectroscopic and structural characterizations by Wieghardt and co-workers; however, the utility of iminopyridine cobalt complex to catalyze organic transformations has not been previously reported.

Hydrosilylation/cyclization of 1,6-enynes is one of efficient and atom-economic methods[2] to construct silicon-containing five-membered carbocyclic and heterocyclic frameworks in which the new formed C−Si bond could potentially undergo further transformations.[3] In 1992, Ojima and co-workers first developed a highly efficient rhodium-catalyzed silylcarboncyclization of 1,6-enynes with methyldiphenylsilane under an atmosphere of carbon monoxide to afford vinyl silane product (type A) in quantitative yield.[4a] Other catalysts such as $Rh_4(CO)_{12}$,[4b] $Rh_2Co_2(CO)_{12}$,[4b] NHC−Rh complex,[4c] Rh−Co nanoparticle,[4d] and $Ni(cod)_2$[4e] were also used to promote hydrosilylation/cyclization of 1,6-enynes to form vinylsilane products, and further palladium-catalyzed cross-coupling reactions with aryl halides were demonstrated by Denmark.[5] Rhodium-catalyzed asymmetric hydrosilylation/cyclization of 1,6-enynes was successfully realized by Widenhoefer[6a] and Zhou[6b] by using chiral bisphosphine ligands. However, hydrosilylation/cyclization reactions of 1,6-enynes to form alkyl silane products were rare. Molander and co-workers reported an elegant yttrium complex-catalyzed cyclization/silylation of 1,6-enynes to afford alkyl silanes (type B); however, an air- and moisture-sensitive preprepared yttrium complex complicated the preparation and operation.[7] Yamamoto and co-workers reported a palladium-catalyzed reaction using $HSiCl_3$ as a silane source with only two examples presented.[8] In both types of reactions, the terminal aryl substituted alkynes are not well explored.

To the best of our knowledge, no example was described using base metals as sole catalysts to realize hydrosilylation/cyclization of 1,6-enynes. Herein, we describe an iminopyridine cobalt complex-catalyzed hydrosilylation/cyclization of 1,6-enynes with silanes to form alkyl silane (type B) products.

RESULTS AND DISCUSSION

According to the previously reported methods,[9] the iminopyridine cobalt complex could be obtained by simply mixing iminopyridine with a cobalt salt. The structure of the complex characterized by X-ray single crystal diffraction[10] is a dimer which is bench-stable (Scheme 1).

(3-(Allyloxy)prop-1-yn-1-yl)benzene **1a** was easily prepared as a model substrate to optimize the reaction conditions shown in Table 1. The reaction of **1a** with Ph_2SiH_2 (1.2 equiv) in the presence of the precatalyst IP·$CoCl_2$ (5 mol %) and $NaBHEt_3$ (15 mol %) as a reductant in toluene (0.5 M) at room temperature under an argon atmosphere for 5 h afforded the hydrosilylation/cyclization product **3a** in 71% yield (entry 1). Various solvents such as ether, THF, and dioxane were used instead of toluene; however, no further improvement was observed (entries 2−4). The reductant reagents ($LiBHEt_3$, $NaBH^sBu_3$, MeLi, MeMgBr, Et_2Zn) were also investigated to give **3a** in promising yields (entries 5−9). Decreasing the concentration to 0.125 M resulted in increasing the yields up to an 81% yield (entry 10). A slightly lower yield of **3a** was observed when 1 equiv of silane was used (entry 11, compared to entry 10). Additionally, the bi(imino)pyridine cobalt complex **I**[11] did not efficiently promote this transformation (entry 12). No desired products were afforded in the absence of

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Scheme 1. Hydrosilylation/Cyclization of 1,6-Enynes

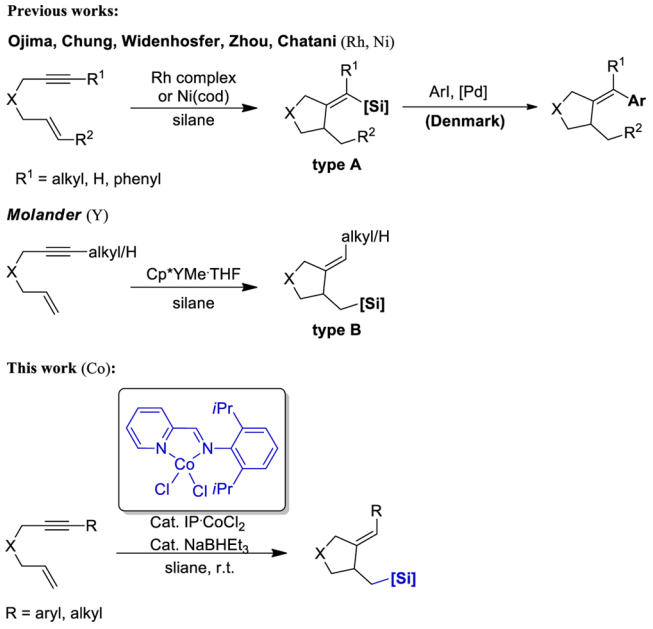
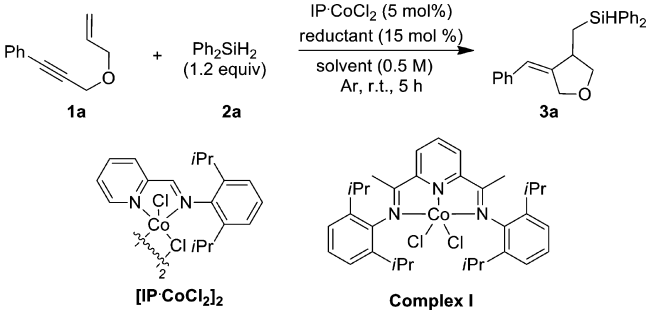


Table 1. Optimizations[a]



entry	reductant	solvent	yield[a] (%)
1	$NaBHEt_3$	toluene	71
2	$NaBHEt_3$	Et_2O	58
3	$NaBHEt_3$	THF	46
4	$NaBHEt_3$	dioxane	67
5	$LiBHEt_3$	toluene	71
6	$NaBH^sBu_3$	toluene	65
7	MeLi	toluene	71
8	MeMgBr	toluene	67
9	Et_2Zn	toluene	66
10[b]	$NaBHEt_3$	toluene	(81)
11[b,c]	$NaBHEt_3$	toluene	72
12[b,d]	$NaBHEt_3$	toluene	5
13[b]	–	toluene	0
14[b,e]	$NaBHEt_3$	toluene	0
15[b,f]	$NaBHEt_3$	toluene	0

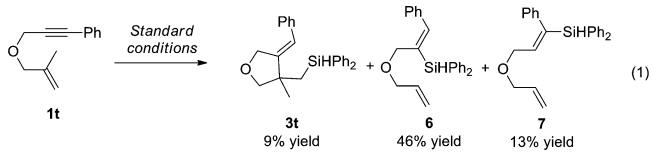
[a]Yields determined by ^1H NMR analysis using TMSPh as an internal standard. [b]Toluene (0.125 M). [c]1.0 equiv of Ph_2SiH_2. [d]Complex I instead of IP·$CoCl_2$. [e]No IP·$CoCl_2$. [f]No Ph_2SiH_2.

$NaBHEt_3$, IP·$CoCl_2$, or Ph_2SiH_2 (entries 13–15). Thus, we established the standard conditions as enyne (1 equiv), silane (1.2 equiv), IP·$CoCl_2$ (5 mol %), and $NaBHEt_3$ (15 mol %) in a solution of toluene (0.125 M) under argon at room temperature to explore the substrate scope.

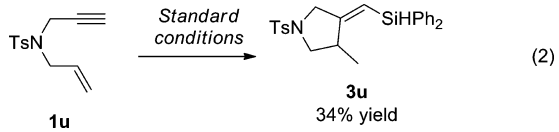
The scope of hydrosilylation/cyclization has been summarized in Table 2. Both electron-rich and electron-poor groups on the tethered nitrogen atom or carbon atom afforded the corresponding products **3b–d** in 65–78% yields. *Para*, *meta*-methoxy substitution gave **3e** and **3f** smoothly; interestingly, an *ortho*-methoxy group, which used to be regarded as a coordinating group to deactive catalysts, gave **3g** in a slightly better yield. Various functional groups such as phenyl, chloride, trifluoromethyl, cyano, ester, and free anline could be tolerated. Sterically bulky 3,5-dimethylphenyl and 1-naphthyl enynes could deliver hydrosilylation products in 60–71% yields. Heterocycles such as 2-thienyl, 2-indol were suitable. The reaction of alkyl alkyne could proceed smoothly to afford **3s** in 54% yield. Et_2SiH_2 was also a good silane source. Although low yields were observed, trisubstituted silanes could be silane sources.

The hydrosilylation/cyclization of **1c** could be scaled up to afford **3c** with 4.3695 g in 85% yield (Scheme 2). The synthetic utility of the organic silanes was also investgated. The silanol and alcohol could be obtained using the literature's oxidative conditions with 80% and 55% yields, respectively.[12]

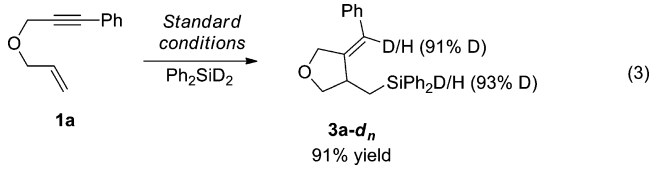
To evaluate the mechanism, the reaction of (3-((2-methylallyl)oxy)prop-1-yn-1-yl)benzene **1t** containing 1,1-disubstituted alkene was conducted to afford the cyclization product in only 9% yield as well as two regioisomers from alkyne hydrosilylation (eq 1).[13] This suggested that alkyne



insertion was the initial step. It was worth noting that the reaction of terminal alkyne **1u** gave the vinyl silane **3u**. The nature of this reversed selectivity was not clear (eq 2). The



reaction of **1a** with diphenyl(silane-d_2) **2a**-d_2 was conducted to give **3a** in 91% yield with 91% deuteration (eq 3). The traceless



amount of hydrogen should come from the reductant $NaBHEt_3$ which demonstrated that the initiated step to activate the precatalyst might generate the active cobalt hydride species.

Based on the above-mentioned experimental results and those in previously reported literatures,[7,8] a Chalk–Harrod mechanism[14] for hydrosilylation of alkenes was proposed (Scheme 3). The precatalyst dimer cobalt complex could be reduced by $NaBHEt_3$ to afford cobalt hydride species which might be an active intermediate. The insertion reaction of an alkyne to the cobalt–hydride bond afforded the vinyl cobalt species followed by insertion of an alkene to give the alkyl-cobalt species which could react with the silane to regenerate

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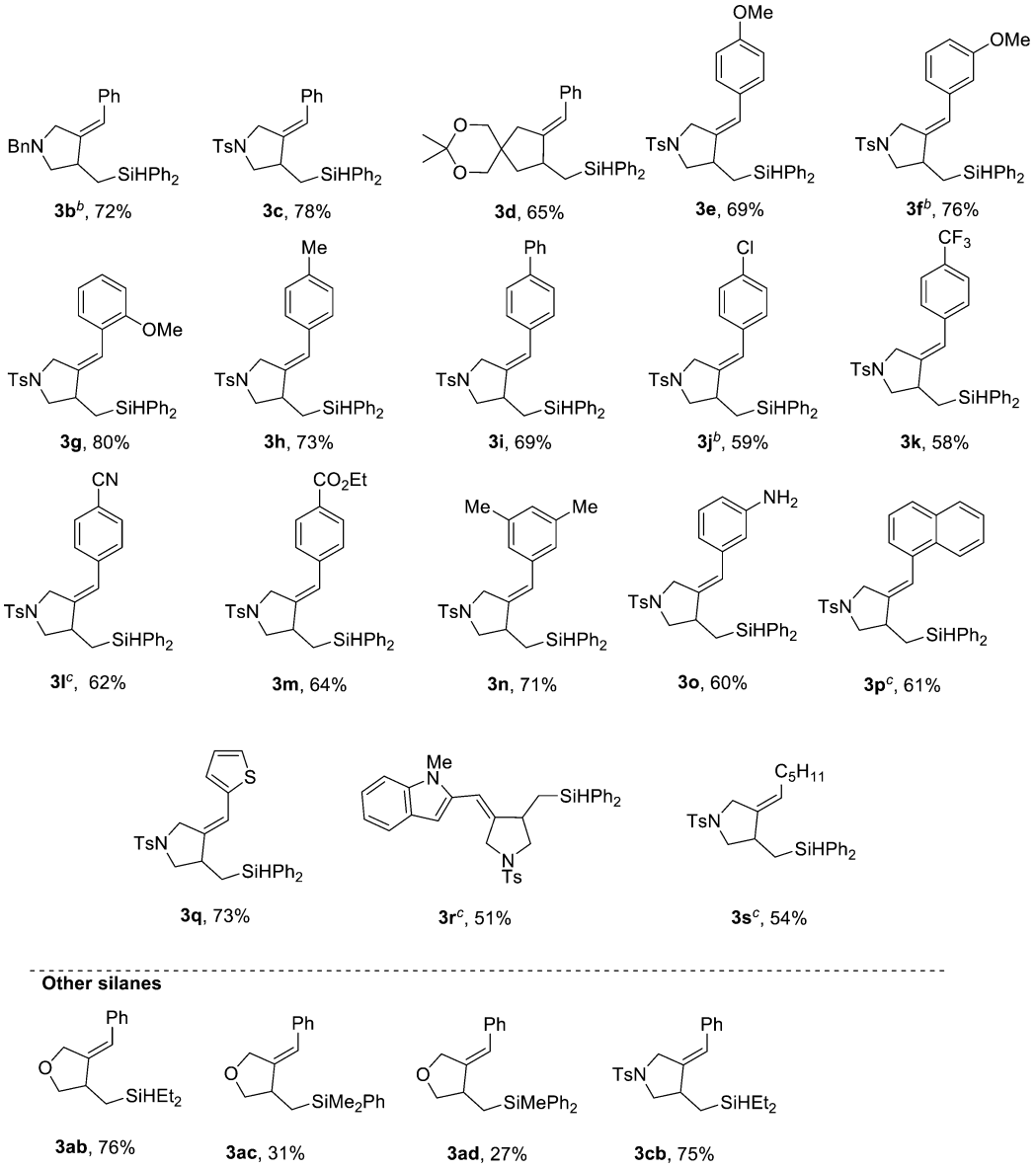
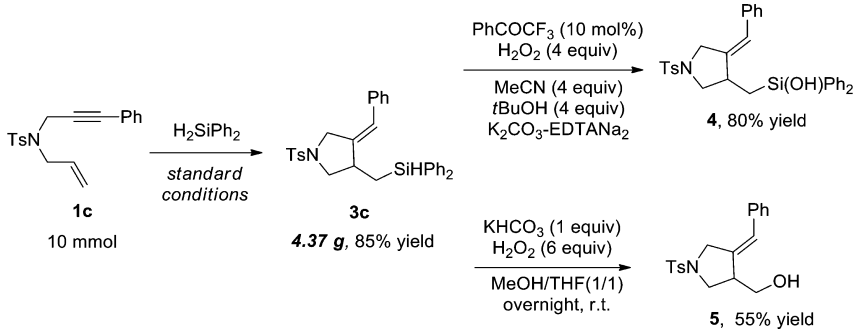
Table 2. Substrate Scope[a]



[a]Standard conditions: 1 mmol of **2**, 5 mol % of IP·$CoCl_2$, 15 mol % of $NaBHEt_3$, 1.2 mmol of Ph_2SiH_2 in toluene (0.5 M). [b]0.125 M. [c]10 mol % of IP·$CoCl_2$ and 30 mol % of $NaBHEt_3$.

Scheme 2. Gram-Scale Reaction and Further Derivatizations



the cobalt hydride species and afford the product. It should be noted that the configuration of alkenes is opposite to that in products obtained by silaboration/cross-coupling reactions of 1,6-enynes containing a terminal enyne with aryl halides.[15]

In summary, we described that a simple iminopyridine cobalt complex was an effective precatalyst for hydrosilylation/cyclization of 1,6-enynes with silanes. Various functional groups such as amine, free aniline, ester, ether, cyano, halide,

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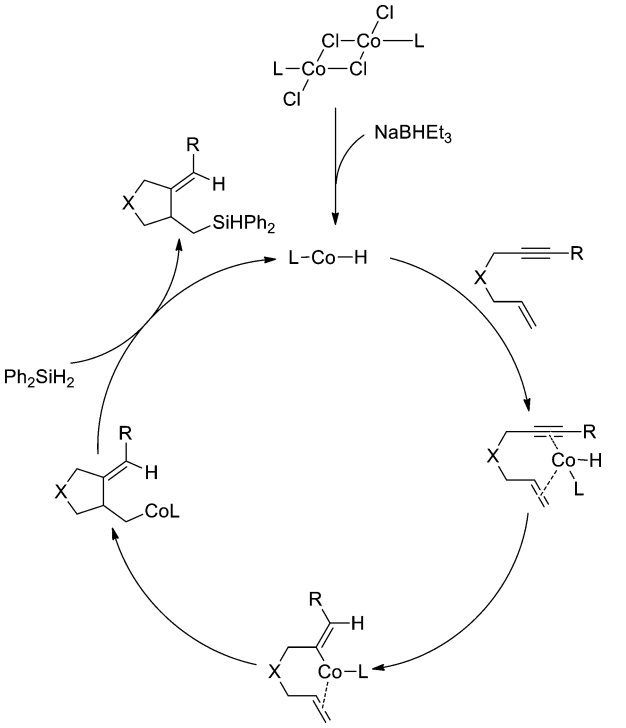
Scheme 3. Plausible Mechanism



trifluoromethyl, and heterocycle were tolerated to afford a variety of silicon-containing compounds. The reaction could be scaled up to afford products on the gram scale which could undergo further derivatizations. Further studies on asymmetric transformations are underway in our laboratory.

EXPERIMENTAL SECTION

General Information. Ether, tetrahydrofuran, 1,4-dioxane, and toluene were distilled from sodium benzophenone ketyl prior to use. All commercially available chemicals were used as received. NMR spectra were recorded on a 400 and 300 MHz instrument. ^{1}H NMR chemical shifts were referenced to the tetramethylsilane signal (0 ppm), ^{13}C NMR chemical shifts were referenced to the solvent resonance (77.00 ppm, $CDCl_3$), and ^{19}F NMR chemical shifts were referenced to the solvent resonance. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet, br = broad. IR spectra were recorded on an FTIR spectrometer with a diamond ATR accessory. High-resolution mass spectra (HRMS) were recorded on EI-TOF (electron ionization-time-of-flight). Substrates **1a–c**,[16] **1d**,[17] **1e–n**,[15] **1p–q**,[15] **1s**,[15] **1t**,[18] and **1u**[15] are known compounds and have been synthesized according to the reported methods.

Synthesis of IP·$CoCl_2$ Complex. According to a previously reported procedure,[19] a 100 mL Schlenk flask was charged with 1.0666 g (4.0 mmol) of (*E*)-2,6-diisopropyl-*N*-(pyridin-2-ylmethylene)aniline, 10 mL of THF, and 0.4948 g (3.8 mmol) of $CoCl_2$ in an argon atmosphere, then the mixture was stirred at room temperature for 5 h, and then 10 mL of ether were injected to precipitate the complex. The resulting mixture was filtered under air, washed with ether, and dried in vacuo to yield 1.2011 g (86% yield). **Complex I** was synthesized according to a previously reported procedure.[11]

*N-Allyl-N-(3-(3-aminophenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (**1o**).* To a solution of *N*-allyl-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (5.1692 g, 20.8 mmol, 1.04 equiv), 1-iodo-3-nitrobenzene (4.9876 g, 20 mmol, 1 equiv), $Pd(PPh_3)_2Cl_2$ (0.2764 g, 0.4 mmol, 2 mol %), and CuI (0.2196 g, 1.2 mmol, 6 mol %) in dry toluene (40 mL) under a nitrogen atmosphere was added NEt_3 (5.5 mL, 40 mmol, 2 equiv) at room temperature, followed by stirring overnight. The solvent was removed under vacuo, and the crude residue was purified by flash chromatography on silica gel to give *N*-allyl-4-methyl-*N*-(3-(3-nitrophenyl)prop-2-yn-1-yl)benzenesulfonamide (5.2647 g, 69%) as a yellow oil. *N*-Allyl-4-methyl-*N*-(3-(3-nitrophenyl)prop-2-yn-1-yl)benzenesulfonamide (1.1088 g, 3 mmol) treatment with zinc (21 equiv) and con. HCl (20 equiv) afforded **1o** (0.4971 g, 49%), with recrystallization in EtOH. IR (neat): 3469, 3379, 3056, 2915, 1598, 1491, 1445 cm^{-1}; ^{1}H NMR: (400.1 MHz, $CDCl_3$) δ 7.77 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 7.01 (dd, J = 8.0, 7.6 Hz, 1H), 6.60 (dd, J = 8.0, 2.4 Hz, 1H), 6.45 (d, J = 7.6 Hz, 1H), 6.42–6.39 (m, 1H), 5.84–5.73 (m, 1H), 5.36–5.28 (m, 1H), 5.28–5.23 (m, 1H), 4.28 (s, 2H), 3.87 (d, J = 6.8 Hz, 2H), 3.8–3.5 (br, 2H), 2.36 (s, 3H); ^{13}C NMR: (100.6 MHz, $CDCl_3$) δ 146.1, 143.4, 135.9, 132.0, 129.5, 129.0, 127.8, 122.9, 121.8, 119.9, 117.7, 115.3, 85.9, 80.9, 49.2, 36.7, 21.4; HRMS (EI) calculated for $[C_{19}H_{20}N_2O_2S]^+$ (M^+) requires m/z 340.1245, found m/z 340.1249.

*N-Allyl-4-methyl-N-(3-(1-methyl-1H-indol-2-yl)prop-2-yn-1-yl)-benzenesulfonamide (**1q**).* To a solution of *N*-allyl-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (5.0359 g, 20.25 mmol, 1.04 equiv), 2-iodo-1-methyl-1*H*-indole (4.7869 g, 19.5 mmol, 1 equiv),[20] $Pd(PPh_3)_2Cl_2$ (0.2864 g, 0.39 mmol, 2 mol %) and CuI (0.2402 g, 1.17 mmol, 6 mol %) in dry toluene (60 mL) under nitrogen atmosphere was added NEt_3 (5.4 mL, 39 mmol, 2 equiv) at room temperature and stirred for overnight. The solvent was removed under vacuo, and the crude residue was purified by flash chromatography on silica gel (PE/EA = 8/1) to give **1q** (5.3551 g, 76%)as a yellow solid. IR (neat): 3057, 2923, 1644, 1598, 1462, 1428 cm^{-1}; ^{1}H NMR: (400.1 MHz, $CDCl_3$) δ 7.77 (d, J = 7.6 Hz, 2H), 7.53 (d, J = 8.0 Hz, 1H), 7.28–7.22 (m, 4H), 7.13–7.07 (m, 1H), 6.47 (s, 1H), 5.87–5.75 (m, 1H), 5.37–5.31 (m, 1H), 5.31–5.26 (m, 1H), 4.40 (s, 2H), 3.92 (d, J = 6.4 Hz, 2H), 3.55 (s, 3H), 2.30 (s, 3H); ^{13}C NMR: (100.6 MHz, $CDCl_3$) δ 143.6, 136.9, 136.0, 132.0, 129.6, 127.7, 126.8, 123.2, 120.9, 120.8, 120.1, 120.0, 109.3, 107.7, 88.0, 77.5, 49.4, 36.9, 30.3, 21.4; HRMS (EI) calculated for $[C_{22}H_{22}N_2O_2S]^+$ (M^+) requires m/z 378.1402, found m/z 378.1408.

General Procedure for Hydrosilylation/Cyclization of 1,6-Enynes. To a 50 mL flame-dried Schlenk flask cooled under argon, IP·$CoCl_2$ (0.05 mmol) and toluene (8 mL) were added. The mixture was injected with $NaBHEt_3$ (1 M in THF) (0.15 mmol) dropwise and then stirred at room temperature for 3 min. Then silane **2** (1.2 mmol) and 1,6-enyne **1** (1.0 mmol) were added. The mixture was stir at room temperature for 5–24 h. The reaction was quenched by ether, concentrated, and then purified by flash column chromatography using PE/EtOAc as the eluent to give the corresponding hydrosilylation/cyclization product.

*(Z)-((4-Benzylidenetetrahydrofuran-3-yl)methyl)diphenylsilane (**3a**).* The reaction with (3-(allyloxy)prop-1-yn-1-yl)benzene **1a** (0.1712 g, 1.0 mmol), H_2SiPh_2 **2a** (223 μL, 1.2 mmol), IP·$CoCl_2$ (0.0198 g, 0.05 mmol), and $NaBHEt_3$ (150 μL, 0.15 mmol) in toluene (8 mL) for 5 h, using hexane/EtOAc (10/1) as eluent, afforded **3a** (0.2881 g, 81%) as a colorless oil; IR (neat): 3065, 2845, 2123, 1663, 1593, 1491, 1429 cm^{-1}; ^{1}H NMR: (300.1 MHz, $CDCl_3$) δ 7.63–7.56 (m, 4H), 7.45–7.29 (m, 8H), 7.23–8.16 (m, 1H), 7.09 (d, J = 7.5 Hz, 2H), 6.34 (d, J = 2.4 Hz, 1H), 4.96 (dd, J = 4.8, 3.3 Hz, 1H), 4.68–4.52 (m, 2H), 3.96 (dd, J = 8.4, 3.9 Hz, 1H), 3.40 (dd, J = 8.1, 7.8 Hz, 1H), 3.05–2.90 (m, 1H), 1.75–1.65 (ddd, J = 15.0, 1.8, 1.5 Hz, 1H), 1.40–1.28 (ddd, J = 15.0, 10.2, 3.3 Hz, 1H); ^{13}C NMR: (100.6 MHz, $CDCl_3$) δ 146.8, 137.2, 135.1, 135.0, 133.9, 133.7, 129.82, 129.81, 128.4, 128.2, 128.1, 127.9, 126.5, 120.3, 73.7, 70.0, 41.7, 15.4; HRMS (EI) calculated for $[C_{24}H_{24}OSi]^+$ (M^+) requires m/z 356.1596, found m/z 356.1599.

*(Z)-1-Benzyl-3-benzylidene-4-((diphenylsilyl)methyl)pyrrolidine (**3b**).* The reaction with *N*-benzyl-*N*-(3-phenylprop-2-yn-1-yl)prop-2-en-1-amine **1b** (0.2616 g, 1.0 mmol), H_2SiPh_2 **2a** (223 μL, 1.2 mmol), IP·$CoCl_2$ (0.0204 g, 0.05 mmol), and $NaBHEt_3$ (150 μL, 0.15 mmol) in toluene (8 mL) for 24 h, using hexane/EtOAc (30/1 to 20/1) as eluent, afforded **3b** (0.3195 g, 72%) as a white foam; IR (neat): 3063, 3024, 2786, 2112, 1662, 1596, 1492, 1429 cm^{-1}; ^{1}H NMR: (400.1 MHz, $CDCl_3$) δ 7.61–7.58 (m, 4H), 7.40–7.30 (m, 6H), 7.30–7.20 (m, 7H), 7.17–7.08 (m, 3H), 6.27 (d, J = 2.0 Hz, 1H), 4.95 (dd, J = 4.4, 3.2 Hz, 1H), 3.70–3.55 (m, 3H), 3.34–3.26 (m, 1H), 3.06–2.96

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(m, 1H), 2.92 (dd, J = 8.4, 7.2 Hz, 1H), 2.20 (dd, J = 8.4, 8.0 Hz, 1H), 1.71 (ddd, J = 14.8, 4.4, 4.4 Hz, 1H), 1.39 (ddd, J = 14.8. 10.0, 3.2 Hz, 1H); ^{13}C NMR: (100.6 MHz, $CDCl_3$) δ 148.0, 138.6, 137.9, 135.08, 135.06, 134.5, 134.2, 129.6, 129.5, 128.7, 128.3, 128.2, 128.04, 128.00, 127.9, 126.9, 126.1, 120.7, 60.8, 60.4, 57.9, 40.9, 17.2; HRMS (EI) calculated for $[C_{31}H_{31}NSi]^+$ (M^+) requires m/z 445.2226, found m/z 445.2221.

*(Z)-3-Benzylidene-4-((diphenylsilyl)methyl)-1-tosylpyrrolidine (**3c**).* The reaction with *N*-allyl-4-methyl-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide **1c** (0.3256 g, 1.0 mmol), H_2SiPh_2 **2a** (223 μL, 1.2 mmol), IP·$CoCl_2$ (0.0201 g, 0.05 mmol), and $NaBHEt_3$ (150 μL, 0.15 mmol) in toluene (2 mL) for 6 h, using hexane/EtOAc (10/1 to 5/1) as eluent, afforded **3c** (0.3984 g, 78%) as a white foam; IR (neat): 3067, 2877, 2123, 1662, 1597, 1471, 1402 cm^{-1}; ^{1}H NMR: (400.1 MHz, $CDCl_3$) δ 7.60 (d, J = 8.0 Hz, 2H), 7.56−7.53 (m, 4H), 7.44−7.34 (m, 6H), 7.33−7.67 (m, 2H), 7.24−7.19 (m, 3H), 7.05 (d, J = 7.6 Hz, 2H), 6.25 (d, J = 2.0 Hz, 1H), 4.93 (dd, J = 4.4, 3.2 Hz, 1H), 4.16 (dd, J = 15.2, 2.0 Hz, 1H), 4.03−3.96 (m, 1H), 3.48 (dd, J = 9.6, 6.8 Hz, 1H), 2.92−2.82 (m, 1H), 2.78 (dd, J = 9.2, 8.0 Hz, 1H), 2.35 (s, 3H), 1.58 (ddd, J = 14.8, 4.8, 4.8 Hz, 1H), 1.19 (ddd, J = 14.8, 9.6, 3.2 Hz, 1H); ^{13}C NMR: (100.6 MHz, $CDCl_3$) δ 143.5, 142.1, 136.3, 135.0, 133.5, 133.3, 132.8, 129.9, 129.7, 128.5, 128.2, 128.13, 128.07, 127.6, 127.0, 122.4, 53.7, 50.4, 40.9, 21.5, 15.8; HRMS (EI) calculated for $[C_{31}H_{31}NO_2SiS]^+$ (M^+) requires m/z 509.1845, found m/z 509.1849.

*(E)-((3-Benzylidene-8,8-dimethyl-7,9-dioxaspiro[4.5]decan-2-yl)-methyl)diphenylsilane (**3d**).* The reaction with 5-allyl-2,2-dimethyl-5-(3-phenylprop-2-yn-1-yl)-1,3-dioxane **1d** (0.2740 g, 1.0 mmol), H_2SiPh_2 **2a** (223 μL, 1.2 mmol), IP·$CoCl_2$ (0.0202 g, 0.05 mmol), and $NaBHEt_3$ (150 μL, 0.15 mmol) in toluene (2 mL) for 24 h, using hexane/EtOAc (30/1) as eluent, afforded **3d** (0.3005 g, 65%, 95% purity) as a colorless oil; IR (neat): 3066, 2839, 2123, 1606, 1511, 1462, 1429 cm^{-1}; ^{1}H NMR: (400.1 MHz, $CDCl_3$) δ 7.55−7.63 (m, 4H), 7.35−7.41 (m, 6H), 7.30 (d, J = 7.6 Hz, 2H), 7.25 (d, J = 7.6 Hz, 2H), 7.15−7.20 (m, 1H), 6.32 (d, J = 2.4 Hz, 1H), 4.98 (dd, J = 5.2, 2.8 Hz, 1H), 3.52−3.66 (m, 3H), 3.46 (d, J = 10.8 Hz, 1H), 2.68−2.84 (m, 2H), 2.38−2.46 (m, 1H), 2.01 (dd, J = 12.8, 7.6 Hz, 1H), 1.76 (ddd, J = 14.7, 4.8, 4.4 Hz, 1H), 1.40 (s, 3H), 1.38 (s, 3H), 1.26 (ddd, J = 14.8, 10.4, 2.8 Hz, 1H), 1.10 (dd, J = 12.8, 11.2 Hz, 1H); ^{13}C NMR: (100.6 MHz, $CDCl_3$) δ 148.9, 138.1, 135.14, 135.07, 134.5, 134.1, 129.7, 129.6, 128.3, 128.2, 128.1, 128.0, 126.0, 121.9, 97.9, 69.7, 68.1, 40.7, 40.2, 39.8, 38.7, 24.6, 22.9, 18.0; HRMS (EI) calculated for $[C_{30}H_{34}O_2Si]^+$ (M^+) requires m/z 454.2328, found m/z 454.2327.

*(Z)-3-((Diphenylsilyl)methyl)-4-(4-methoxybenzylidene)-1-tosyl-pyrrolidine (**3e**).* The reaction with *N*-allyl-*N*-(3-(4-methoxyphenyl)-prop-2-yn-1-yl)-4-methylbenzenesulfonamide **1e** (0.3591 g, 1.0 mmol), H_2SiPh_2 **2a** (223 μL, 1.2 mmol), IP·$CoCl_2$ (0.0206 g, 0.05 mmol), and $NaBHEt_3$ (150 μL, 0.15 mmol) in toluene (2 mL) for 24 h, using hexane/EtOAc (15/1) as eluent, afforded **3e** (0.3736 g, 69%) as a white foam; IR (neat): 3066, 2839, 2123, 1606, 1511, 1462, 1429 cm^{-1}; ^{1}H NMR: (400.1 MHz, $CDCl_3$) δ 7.61 (d, J = 8.0 Hz, 2H), 7.56−7.50 (m, 4H), 7.45−7.34 (m, 6H), 7.23 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 8.4 Hz, 2H), 6.85 (d, J = 8.4 Hz, 2H), 6.19 (d, J = 2.0 Hz, 1H), 4.92 (dd, J = 4.4, 3.2 Hz, 1H), 4.13 (dd, J = 14.8, 1.4 Hz, 1H), 4.00−3.94 (m, 1H), 3.80 (s, 3H), 3.47 (dd, J = 9.2, 6.8 Hz, 1H), 2.90−2.80 (m, 1H), 2.76 (dd, J = 8.8, 8.0 Hz, 1H), 2.37 (s, 3H), 1.57 (ddd, J = 14.8, 4.8, 4.8 Hz, 1H), 1.17 (ddd, J = 14.8, 9.6, 3.2 Hz, 1H); ^{13}C NMR: (100.6 MHz, $CDCl_3$) δ 158.5, 143.5, 139.8, 135.0, 133.6, 133.3, 132.9, 129.9, 129.6, 129.3, 129.1, 128.2, 128.1, 127.6, 121.8, 113.9, 55.2, 53.7, 50.3, 40.8, 21.5, 15.8; HRMS (EI) calculated for $[C_{32}H_{33}NO_3SiS]^+$ (M^+) requires m/z 539.1950, found m/z 539.1947.

*(Z)-3-((Diphenylsilyl)methyl)-4-(3-methoxybenzylidene)-1-tosyl-pyrrolidine (**3f**).* The reaction with *N*-allyl-*N*-(3-(3-methoxyphenyl)-prop-2-yn-1-yl)-4-methylbenzenesulfonamide **1f** (0.3567 g, 1.0 mmol), H_2SiPh_2 **2a** (223 μL, 1.2 mmol), IP·$CoCl_2$ (0.0201 g, 0.05 mmol), and $NaBHEt_3$ (150 μL, 0.15 mmol) in toluene (8 mL) for 24 h, using hexane/EtOAc (15/1 to 10/1) as eluent, afforded **3f** (0.4013 g, 76%) as a white foam; IR (neat): 3050, 2839, 2123, 1661, 1597, 1489, 1429 cm^{-1}; ^{1}H NMR: (400.1 MHz, $CDCl_3$) δ 7.60 (d, J = 8.4 Hz, 2H), 7.57−7.50 (m, 4H), 7.35−7.33 (m, 6H), 7.24−7.19 (m, 3H), 6.77 (dd, J = 8.4, 2.4 Hz, 1H), 6.66 (d, J = 7.6 Hz, 1H), 6.59 (s, 1H), 6.22 (d, J = 1.6 Hz, 1H), 4.93 (dd, J = 4.4, 3.2 Hz, 1H), 4.15 (dd, J = 11.2, 2.0 Hz, 1H), 4.02−3.94 (m, 1H), 3.77 (s, 3H), 3.48 (dd, J = 9.2, 6.8 Hz, 1H), 2.92−2.81 (m, 1H), 2.78 (dd, J = 8.8, 8.0 Hz, 1H), 2.36 (s, 3H), 1.58 (ddd, J = 14.8, 4.8, 4.4 Hz, 1H), 1.19 (ddd, J = 14.8, 10.0, 3.6 Hz, 1H); ^{13}C NMR: (100.6 MHz, $CDCl_3$) δ 159.6, 143.5, 142.5, 137.7, 135.0, 133.5, 133.2, 132.8, 129.89, 129.88, 129.7, 129.4, 128.2, 128.1, 127.6, 122.3, 120.5, 113.9, 112.3, 55.2, 53.6, 50.3, 40.9, 21.4, 15.7; HRMS (EI) calculated for $[C_{32}H_{33}NO_3SiS]^+$ (M^+) requires m/z 539.1950, found m/z 539.1953.

*(Z)-3-((Diphenylsilyl)methyl)-4-(2-methoxybenzylidene)-1-tosyl-pyrrolidine (**3g**).* The reaction with *N*-allyl-*N*-(3-(2-methoxyphenyl)-prop-2-yn-1-yl)-4-methylbenzenesulfonamide **1g** (0.3558 g, 1.0 mmol), H_2SiPh_2 **2a** (223 μL, 1.2 mmol), IP·$CoCl_2$ (0.0205 g, 0.05 mmol), and $NaBHEt_3$ (150 μL, 0.15 mmol) in toluene (2 mL) for 24 h, using hexane/EtOAc (15/1 to 10/1) as eluent, afforded **3g** (0.4344 g, 80%) as a white foam; IR (neat): 3066, 2840, 2124, 1597, 1489, 1463, 1431 cm^{-1}; ^{1}H NMR: (400.1 MHz, $CDCl_3$) δ 7.58 (d, J = 8.4 Hz, 2H), 7.56−7.52 (m, 4H), 7.45−7.34 (m, 6H), 7.25−7.18 (m, 3H), 6.95−6.88 (m, 2H), 6.84 (d, J = 8.0 Hz, 1H), 6.53 (d, J = 2.0 Hz, 1H), 4.93 (dd, J = 4.4, 3.2 Hz, 1H), 4.07 (dd, J = 14.8, 2.4 Hz, 1H), 3.98−3.89 (m, 1H), 3.79 (s, 3H), 3.48 (dd, J = 9.2, 6.8 Hz, 1H), 2.94−2.84 (m, 1H), 2.80 (dd, J = 9.2, 7.6 Hz, 1H), 2.38 (s, 3H), 1.60 (ddd, J = 14.8, 4.8, 4.8 Hz, 1H), 1.20 (ddd, J = 14.8, 9.6, 2.8 Hz, 1H); ^{13}C NMR: (100.6 MHz, $CDCl_3$) δ 156.5, 143.4, 142.0, 135.0, 133.6, 133.3, 133.0, 129.8, 129.6, 128.7, 128.5, 128.14, 128.08, 127.6, 125.2, 120.3, 117.1, 110.4, 55.3, 53.8, 50.2, 40.8, 21.4, 15.7; HRMS (EI) calculated for $[C_{32}H_{33}NO_3SiS]^+$ (M^+) requires m/z 539.1950, found m/z 539.1954.

*(Z)-3-((Diphenylsilyl)methyl)-4-(4-methylbenzylidene)-1-tosyl-pyrrolidine (**3h**).* The reaction with *N*-allyl-4-methyl-*N*-(3-(*p*-tolyl)-prop-2-yn-1-yl)benzenesulfonamide **1h** (0.3390 g, 1.0 mmol), H_2SiPh_2 **2a** (223 μL, 1.2 mmol), IP·$CoCl_2$ (0.0200 g, 0.05 mmol), and $NaBHEt_3$ (150 μL, 0.15 mmol) in toluene (2 mL) for 24 h, using hexane/EtOAc (10/1) as eluent, afforded **3h** (0.3810 g, 73%, 95% purity) as a white foam; IR (neat): 3048, 2863, 2124, 1596, 1512, 1429 cm^{-1}; ^{1}H NMR: (400.1 MHz, $CDCl_3$) δ 7.60 (d, J = 8.4 Hz, 2H), 7.56−7.51 (m, 4H), 7.45−7.33 (m, 6H), 7.23 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 6.96 (d, J = 8.0 Hz, 2H), 6.22 (d, J = 2.0 Hz, 1H), 4.92 (dd, J = 4.4, 3.2 Hz, 1H), 4.15 (dd, J = 14.8, 2.0 Hz, 1H), 4.01−3.94 (m, 1H), 3.47 (dd, J = 8.8, 6.8 Hz, 1H), 2.91−2.81 (m, 1H), 2.76 (dd, J = 9.2, 8.0 Hz, 1H), 2.37 (s, 3H), 2.33 (s, 3H), 1.58 (ddd, J = 15.2, 5.2, 4.8 Hz, 1H), 1.18 (ddd, J = 14.8, 10.0, 3.6 Hz, 1H); ^{13}C NMR: (100.6 MHz, $CDCl_3$) δ 143.5, 141.1, 136.8, 135.0, 133.6, 133.5, 133.3, 132.9, 129.89, 129.88, 129.7, 129.2, 128.2, 128.1, 128.0, 127.6, 122.3, 53.7, 50.4, 40.9, 21.5, 21.1, 15.8; HRMS (EI) calculated for $[C_{32}H_{33}NO_2SiS]^+$ (M^+) requires m/z 523.2001, found m/z 523.2003.

*(Z)-3-([1,1′-Biphenyl]-4-ylmethylene)-4-((diphenylsilyl)methyl)-1-tosylpyrrolidine (**3i**).* The reaction with *N*-(3-([1,1′-biphenyl]-4-yl)prop-2-yn-1-yl)-*N*-allyl-4-methylbenzenesulfonamide **1i** (0.4088 g, 1.0 mmol), H_2SiPh_2 **2a** (223 μL, 1.2 mmol), IP·$CoCl_2$ (0.0199 g, 0.05 mmol), and $NaBHEt_3$ (150 μL, 0.15 mmol) in toluene (2 mL) for 24 h, using hexane/EtOAc (8/1) as eluent, afforded **3i** (0.4103 g, 69%) as a white solid, mp 59−61 °C; IR (neat): 3063, 2874, 2124, 1660, 1597, 1518, 1452 cm^{-1}; ^{1}H NMR: (400.1 MHz, $CDCl_3$) δ 7.65−7.52 (m, 10H), 7.48−7.32 (m, 9H), 7.24 (d, J = 7.6 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 6.29 (d, J = 2.0 Hz, 1H), 4.94 (dd, J = 4.4, 3.6 Hz, 1H), 4.21 (dd, J = 14.8, 1.6 Hz, 1H), 4.07−4.00 (m, 1H), 3.50 (dd, J = 9.2, 7.2 Hz, 1H), 2.96−2.85 (m, 1H), 2.80 (dd, J = 9.2, 8.0 Hz, 1H), 2.38 (s, 3H), 1.61 (ddd, J = 14.8, 4.8, 4.8 Hz, 1H), 1.21 (ddd, J = 14.8, 10.0, 3.2 Hz, 1H); ^{13}C NMR: (100.6 MHz, $CDCl_3$) δ 143.5, 142.3, 140.4, 139.7, 135.3, 135.0, 133.6, 133.3, 132.9, 129.94, 129.93, 129.7, 128.8, 128.6, 128.23, 128.18, 127.6, 127.4, 127.1, 126.9, 122.1, 53.7, 50.5, 41.1, 21.5, 15.9; HRMS (EI) calculated for $[C_{37}H_{35}NO_2SiS]^+$ (M^+) requires m/z 585.2158, found m/z 585.2155.

*(Z)-3-(4-Chlorobenzylidene)-4-((diphenylsilyl)methyl)-1-tosyl-pyrrolidine (**3j**).* The reaction with *N*-allyl-*N*-(3-(4-chlorophenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide **1j** (0.3570 g, 1.0 mmol), H_2SiPh_2 **2a** (223 μL, 1.2 mmol), IP·$CoCl_2$ (0.0201 g, 0.05 mmol), and $NaBHEt_3$ (150 μL, 0.15 mmol) in toluene (8 mL) for 24 h, using hexane/EtOAc (15/1) as eluent, afforded **3j** (0.3204 g, 59%) as a

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white foam; IR (neat): 3066, 2878, 2124, 1662, 1595, 1491, 1428 cm^{-1}; ^1H NMR: (400.1 MHz, $CDCl_3$) δ 7.60 (d, J = 8.0 Hz, 2H), 7.56−7.49 (m, 4H), 7.45−7.33 (m, 6H), 7.30−7.22 (m, 4H), 6.96 (d, J = 8.4 Hz, 2H), 6.19 (s, 1H), 4.91 (dd, J = 4.0, 3.2 Hz, 1H), 4.10 (d, J = 14.8 Hz, 1H), 3.93 (d, J = 14.8 Hz, 1H), 3.48 (dd, J = 8.8, 7.2 Hz, 1H), 2.94−2.83 (m, 1H), 2.78 (dd, J = 9.2, 7.6 Hz, 1H), 2.38 (s, 3H), 1.57 (ddd, J = 14.8, 4.8, 4.8 Hz, 1H), 1.19 (ddd, J = 14.8, 9.6, 2.8 Hz, 1H); ^{13}C NMR: (100.6 MHz, $CDCl_3$) δ 143.6, 142.9, 135.0, 134.7, 133.5, 133.2, 132.8, 132.7, 129.9, 129.7, 129.3, 128.6, 128.2, 128.1, 127.6, 121.3, 53.6, 50.3, 41.0, 21.5, 15.8; HRMS (EI) calculated for $[C_{31}H_{30}NO_2SiSCl]^+$ (M^+) requires m/z 543.1455, found m/z 543.1458.

*(Z)-3-((Diphenylsilyl)methyl)-1-tosyl-4-(4-(trifluoromethyl)-benzylidene)pyrrolidine (**3k**).* The reaction with *N*-allyl-4-methyl-*N*-(3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-yl)benzenesulfonamide **1k** (0.3954 g, 1.0 mmol), H_2SiPh_2 **2a** (223 μL, 1.2 mmol), IP·$CoCl_2$ (0.0197 g, 0.05 mmol), and $NaBHEt_3$ (150 μL, 0.15 mmol) in toluene (2 mL) for 24 h, using hexane/EtOAc (20/1) as eluent, afforded **3k** (0.3393 g, 58%) as a white solid, 112−114 °C; IR (neat): 3013, 2879, 2124, 1663, 1615, 1470, 1427 cm^{-1}; ^1H NMR: (400.1 MHz, $CDCl_3$) δ 7.62 (d, J = 8.4 Hz, 2H), 7.57−5.51 (m, 6H), 7.44−7.33 (m, 6H), 7.23 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H), 6.28 (d, J = 1.6 Hz, 1H), 4.93 (dd, J = 4.4, 3.2 Hz, 1H), 4.14 (dd, J = 14.8, 2.0 Hz, 1H), 4.00−3.92 (m, 1H), 3.50 (dd, J = 9.2, 6.8 Hz, 1H), 2.97−2.86 (m, 1H), 2.81 (dd, J = 9.6, 8.0 Hz, 1H), 2.36 (s, 3H), 1.59 (ddd, J = 14.8, 4.8, 4.8 Hz, 1H), 1.22 (ddd, J = 14.8, 9.6, 3.2 Hz, 1H); ^{13}C NMR: (100.6 MHz, $CDCl_3$) δ 145.0, 143.6, 139.8 (q, J = 1.5 Hz), 134.92, 134.91, 133.3, 133.1, 132.7, 129.9, 129.7, 129.2, 128.7 (q, J = 32.4 Hz), 128.16, 128.17, 128.1, 127.5, 125.3 (q, J = 3.7 Hz), 122.7, 121.3, 53.5, 50.3, 41.1, 21.4, 15.8; ^{19}F NMR: (376.5 MHz, $CDCl_3$) δ −62.4; HRMS (EI) calculated for $[C_{32}H_{30}NO_2SiSF_3]^+$ (M^+) requires m/z 577.1719, found m/z 577.1723.

*(Z)-4-((4-((Diphenylsilyl)methyl)-1-tosylpyrrolidin-3-ylidene)-methyl)benzonitrile (**3l**).* The reaction with *N*-allyl-*N*-(3-(4-cyanophenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide **1l** (0.3526 g, 1.0 mmol), H_2SiPh_2 **2a** (223 μL, 1.2 mmol), IP·$CoCl_2$ (0.0408 g, 0.1 mmol), and $NaBHEt_3$ (300 μL, 0.3 mmol) in toluene (2 mL) for 24 h, using hexane/EtOAc (10/1 to 5/1) as eluent, afforded **3l** (0.3357 g, 62%, 95% purity) as a white foam; IR (neat): 3066, 2877, 2226, 2124, 1661, 1602, 1499, 1428 cm^{-1}; ^1H NMR: (400.1 MHz, $CDCl_3$) δ 7.62 (d, J = 8.0 Hz, 2H), 7.57 (d, J = 8.4 Hz, 2H), 7.55−7.50 (m, 4H), 7.45−7.33 (m, 6H), 7.25 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 6.26 (d, J = 2.0 Hz, 1H), 4.92 (dd, J = 4.4, 3.2 Hz, 1H), 4.12 (dd, J = 14.8, 2.0 Hz, 1H), 3.98−3.92 (m, 1H), 3.49 (dd, J = 9.2, 6.8 Hz, 1H), 2.98−2.87 (m, 1H), 2.82 (dd, J = 9.2, 7.6 Hz, 1H), 2.38 (s, 3H), 1.58 (ddd, J = 14.8, 5.2, 4.8 Hz, 1H), 1.22 (ddd, J = 14.8, 9.6, 3.2 Hz, 1H); ^{13}C NMR: (100.6 MHz, $CDCl_3$) δ 146.3, 143.7, 140.7, 134.87, 134.86, 133.2, 133.0, 132.5, 132.1, 129.9, 129.7, 128.4, 128.2, 128.1, 127.5, 121.2, 118.7, 110.2, 53.4, 50.3, 41.3, 21.4, 15.8; HRMS (EI) calculated for $[C_{32}H_{30}N_2O_2SiS]^+$ (M^+) requires m/z 534.1797, found m/z 534.1797.

*(Z)-Ethyl 4-((4-((diphenylsilyl)methyl)-1-tosylpyrrolidin-3-ylidene)methyl)benzoate (**3m**).* The reaction with ethyl 4-(3-(*N*-allyl-4-methylphenylsulfonamido)prop-1-yn-1-yl)benzoate **1m** (0.3968 g, 1.0 mmol), H_2SiPh_2 **2a** (223 μL, 1.2 mmol), IP·$CoCl_2$ (0.0207 g, 0.05 mmol), and $NaBHEt_3$ (150 μL, 0.15 mmol) in toluene (2 mL) for 24 h, using hexane/EtOAc (8/1 to 5/1) as eluent, afforded **3m** (0.3733 g, 64%) as a white foam; IR (neat): 3066, 2981, 2125, 1713, 1606, 1428 cm^{-1}; ^1H NMR: (400.1 MHz, $CDCl_3$) δ 7.99 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 8.4 Hz, 2H), 7.57−7.50 (m, 4H), 7.46−7.33 (m, 6H), 7.24 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 6.29 (d, J = 2.4 Hz, 1H), 4.93 (dd, J = 4.8, 3.2 Hz, 1H), 4.38 (q, J = 7.2 Hz, 2H), 4.15 (dd, J = 15.2, 2.0 Hz, 1H), 4.01−3.94 (m, 1H), 3.49 (dd, J = 13.2, 6.8 Hz, 1H), 2.97−2.86 (m, 1H), 2.80 (dd, J = 9.2, 7.6 Hz, 1H), 2.38 (s, 3H), 1.60 (ddd, J = 14.8, 4.8, 4.8 Hz, 1H), 1.40 (t, 3H), 1.22 (ddd, J = 14.8, 9.6, 3.2 Hz, 1H); ^{13}C NMR: (100.6 MHz, $CDCl_3$) δ 166.2, 144.9, 143.6, 140.6, 135.0, 133.4, 133.1, 132.7, 130.0, 129.9, 129.7, 128.8, 128.23, 128.17, 127.9, 127.6, 121.8, 61.0, 53.6, 50.4, 41.2, 21.5, 15.8, 14.3; HRMS (EI) calculated for $[C_{34}H_{35}NO_4SiS]^+$ (M^+) requires m/z 581.2056, found m/z 581.2060.

*(Z)-3-(3,5-Dimethylbenzylidene)-4-((diphenylsilyl)methyl)-1-tosyl-pyrrolidine (**3n**).* The reaction with *N*-allyl-*N*-(3-(3,5-dimethylphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide **1n** (0.3558 g, 1.0 mmol), H_2SiPh_2 **2a** (223 μL, 1.2 mmol), IP·$CoCl_2$ (0.0199 g, 0.05 mmol), and $NaBHEt_3$ (150 μL, 0.15 mmol) in toluene (2 mL) for 24 h, using hexane/EtOAc (15/1 to 10/1) as eluent, afforded **3n** (0.3861 g, 71%) as a white foam; IR (neat): 3047, 2921, 2854, 2124, 1599, 1467, 1429 cm^{-1}; ^1H NMR: (400.1 MHz, $CDCl_3$) δ 7.61 (d, J = 8.4 Hz, 2H), 7.56−7,51 (m, 4H), 7.46−7.34 (m, 6H), 7.23 (d, J = 8.0 Hz, 2H), 6.87 (s, 1H), 6.66 (s, 2H), 6.20 (d, J = 1.6 Hz, 1H), 4.91 (dd, J = 4.4, 3.2 Hz, 1H), 4.15 (dd, J = 14.8, 1.6 Hz, 1H), 4.20−3.96 (m, 1H), 3.47 (dd, J = 9.2, 6.8 Hz, 1H), 2.90−2.81 (m, 1H), 2.78 (dd, J = 8.8, 7.6 Hz, 1H), 2.38 (s, 3H), 2.30 (s, 6H), 1.57 (ddd, J = 14.8, 4.8, 4.8 Hz, 1H), 1.17 (ddd, J = 14.8, 9.2, 3.2 Hz, 1H); ^{13}C NMR: (100.6 MHz, $CDCl_3$) δ 143.5, 141.6, 137.9, 136.3, 135.0, 133.6, 133.4, 133.1, 129.9, 129.7, 128.8, 128.2, 128.1, 127.6, 125.9, 122.6, 53.7, 50.3, 40.9, 21.5, 21.3, 15.8; HRMS (EI) calculated for $[C_{33}H_{35}NO_2SiS]^+$ (M^+) requires m/z 537.2158, found m/z 537.2163.

*(Z)-3-((4-((Diphenylsilyl)methyl)-1-tosylpyrrolidin-3-ylidene)-methyl)aniline (**3o**).* The reaction with *N*-allyl-*N*-(3-(3-aminophenyl)-prop-2-yn-1-yl)-4-methylbenzenesulfonamide **1o** (0.3436 g, 1.0 mmol), H_2SiPh_2 **2a** (223 μL, 1.2 mmol), IP·$CoCl_2$ (0.0199 g, 0.05 mmol), and $NaBHEt_3$ (150 μL, 0.15 mmol) in toluene (8 mL) for 24 h, using hexane/EtOAc (3/1−2/1) as eluent, afforded **3o** (0.3163 g, 60%) as a yellow oil; IR (neat): 3463, 3376, 3051, 2923, 2123, 1599, 1492, 1455 cm^{-1}; ^1H NMR: (400.1 MHz, $CDCl_3$) δ 7.60 (d, J = 8.0 Hz, 2H), 7.56−7.50 (m, 4H), 7.45−7.33 (m, 6H), 7.23 (d, J = 8.0 Hz, 2H), 7.10 (dd, J = 8.0, 7.6 Hz, 1H), 6.55 (dd, J = 8.0, 2.4 Hz, 1H), 6.47 (d, J = 7.6 Hz, 1H), 6.38−6.34 (m, 1H), 6.16 (d, J = 2.0 Hz, 1H), 4.91 (dd, J = 4.4, 3.2 Hz, 1H), 4.15 (dd, J = 14.8, 2.0 Hz, 1H), 4.02−3.95 (m, 1H), 3.85−3.40 (br, 2H), 3.46 (dd, J = 9.2, 6.8 Hz, 1H), 2.90−2.79 (m, 1H), 2.76 (dd, J = 8.8, 8.0 Hz, 1H), 2.37 (s, 3H), 1.57 (ddd, J = 14.8, 4.8, 4.8 Hz, 1H), 1.17 (ddd, J = 14.8, 10.0, 3.2 Hz, 1H); ^{13}C NMR: (100.6 MHz, $CDCl_3$) δ 146.4, 143.5, 141.8, 137.4, 135.0, 133.6, 133.3, 132.9, 129.874, 129.866, 129.7, 129.4, 128.2, 128.1, 127.6, 122.6, 118.7, 114.5, 114.0, 53.6, 50.4, 40.9, 21.5, 15.7; HRMS (EI) calculated for $[C_{31}H_{32}N_2O_2SiS]^+$ (M^+) requires m/z 524.1954, found m/z 524.1956.

*(Z)-3-((Diphenylsilyl)methyl)-4-(naphthalen-1-ylmethylene)-1-tosylpyrrolidine (**3p**).* The reaction with *N*-allyl-4-methyl-*N*-(3-(naphthalen-1-yl)prop-2-yn-1-yl)benzenesulfonamide **1p** (0.3773 g, 1.0 mmol), H_2SiPh_2 **2a** (223 μL, 1.2 mmol), IP·$CoCl_2$ (0.0403 g, 0.1 mmol), and $NaBHEt_3$ (300 μL, 0.3 mmol) in toluene (2 mL) for 24 h, using hexane/EtOAc (8/1) as eluent, afforded **3p** (0.3066 g, 61%) as a white foam; IR (neat): 3063, 2878, 2124, 1594, 1429, 1397 cm^{-1}; ^1H NMR: (400.1 MHz, $CDCl_3$) δ 7.84 (dd, J = 7.6, 1.2 Hz, 1H), 7.77 (dd, J = 11.6, 8.4 Hz, 2H), 7.60−7.55 (m, 4H), 7.52 (d, J = 8.0 Hz, 2H), 7.50−7.35 (m, 9H), 7.15 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 7.2 Hz, 1H), 6.83 (d, J = 1.6 Hz, 1H), 4.99 (dd, J = 4.8, 3.2 Hz, 1H), 4.02 (dd, J = 15.2, 2.0 Hz, 1H), 3.89−3.81 (m, 1H), 3.57 (dd, J = 9.6, 7.2 Hz, 1H), 3.02−2.90 (m, 1H), 2.85 (dd, J = 9.2, 7.6 Hz, 1H), 2.34 (s, 3H), 1.71 (ddd, J = 14.8, 5.2, 4.8 Hz, 1H), 1.29 (ddd, J = 14.8, 9.6, 3.2 Hz, 1H); ^{13}C NMR: (100.6 MHz, $CDCl_3$) δ 144.3, 143.4, 135.04, 135.02, 133.53, 133.47, 133.4, 133.3, 133.0, 131.3, 130.0, 129.6, 128.5, 128.3, 128.2, 127.8, 127.5, 125.9, 125.84, 125.78, 125.3, 124.2, 119.9, 54.2, 50.1, 40.4, 21.4, 15.7; HRMS (EI) calculated for $[C_{35}H_{33}NO_2SiS]^+$ (M^+) requires m/z 559.2001, found m/z 559.1999.

*(Z)-3-((Diphenylsilyl)methyl)-4-(thiophen-2-ylmethylene)-1-tosyl-pyrrolidine (**3q**).* The reaction with *N*-allyl-4-methyl-*N*-(3-(thiophen-2-yl)prop-2-yn-1-yl)benzenesulfonamide **1q** (0.3333 g, 1.0 mmol), H_2SiPh_2 **2a** (223 μL, 1.2 mmol), IP·$CoCl_2$ (0.0201 g, 0.05 mmol), and $NaBHEt_3$ (150 μL, 0.15 mmol) in toluene (2 mL) for 24 h, using hexane/EtOAc (10/1 to 8/1) as eluent, afforded **3q** (0.3295 g, 73%) as a yellow oil; IR (neat): 3067, 2878, 2123, 1656, 1595, 1428, 1402 cm^{-1}; ^1H NMR: (400.1 MHz, $CDCl_3$) δ 7.63 (d, J = 8.4 Hz, 2H), 7.57−7.50 (m, 4H), 7.45−7.33 (m, 6H), 7.29−7.22 (m, 3H), 7.00 (dd, J = 5.2, 3.6 Hz, 1H), 6.81 (d, J = 3.6 Hz, 1H), 6.42 (d, J = 2.0 Hz, 1H), 4.92 (dd, J = 4.8, 3.6 Hz, 1H), 4.13 (d, J = 15.6 Hz, 1H), 3.97−3.90 (m, 1H), 3.51 (dd, J = 9.2, 7.2 Hz, 1H), 2.95−2.85 (m, 1H), 2.74 (dd, J = 8.8, 8.4 Hz, 1H), 2.38 (s, 3H), 1.58 (ddd, J = 14.8, 4.8, 4.8 Hz, 1H),

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1.17 (ddd, J = 14.8, 10.0, 3.2 Hz, 1H); ^{13}C NMR: (100.6 MHz, $CDCl_3$) δ 143.6, 140.7, 140.1, 135.0, 133.5, 133.2, 132.4, 129.94, 129.91, 129.7, 128.22, 128.15, 127.7, 127.4, 126.3, 125.6, 115.3, 54.2, 51.0, 40.5, 21.5, 15.7; HRMS (EI) calculated for $[C_{29}H_{29}NO_2SiS_2]^+$ (M^+) requires m/z 515.1409, found m/z 515.1402.

*(Z)-2-((4-((Diphenylsilyl)methyl)-1-tosylpyrrolidin-3-ylidene)-methyl)-1-methyl-1H-indole (**3r**).* The reaction with *N*-allyl-4-methyl-*N*-(3-(1-methyl-1*H*-indol-2-yl)prop-2-yn-1-yl)benzenesulfonamide **1r** (0.3790 g, 1.0 mmol), H_2SiPh_2 **2a** (223 μL, 1.2 mmol), IP·$CoCl_2$ (0.0394 g, 0.1 mmol), and $NaBHEt_3$ (300 μL, 0.3 mmol) in toluene (2 mL) for 24 h, using hexane/EtOAc (6/1) as eluent, afforded **3r** (0.2874 g, 51%) as a white solid, mp 146−148 °C; IR (neat): 3051, 2931, 2125, 1657, 1597, 1465, 1429 cm^{-1}; ^{1}H NMR: (400.1 MHz, $CDCl_3$) δ 7.66−7.58 (m, 3H), 7.58−7.52 (m, 4H), 7.47−7.35 (m, 6H), 7.28−7.17 (m, 4H), 7.13−7.07 (m, 1H), 6.30 (d, J = 2.4 Hz, 1H), 6.26 (s, 1H), 4.95 (dd, J = 4.4, 3.2 Hz, 1H), 4.20 (dd, J = 15.6, 1.4 Hz, 1H), 4.06−3.97 (m, 1H), 3.60 (s, 3H), 3.54 (dd, J = 9.2, 6.8 Hz, 1H), 3.04−2.92 (m, 1H), 2.80 (dd, J = 9.6, 8.4 Hz, 1H), 2.38 (s, 3H), 1.63 (ddd, J = 14.8, 5.2, 4.8 Hz, 1H), 1.25 (ddd, J = 14.8, 9.6, 3.6 Hz, 1H); ^{13}C NMR: (100.6 MHz, $CDCl_3$) δ 144.4, 143.5, 137.1, 135.3, 135.04, 135.03, 133.4, 133.2, 132.8, 130.0, 129.7, 128.3, 128.2, 127.8, 127.7, 122.1, 120.6, 119.8, 110.7, 109.0, 101.9, 54.1, 51.2, 40.9, 29.6, 21.5, 15.7; HRMS (EI) calculated for $[C_{34}H_{34}N_2O_2SiS]^+$ (M^+) requires m/z 562.2110, found m/z 562.2111.

*(Z)-3-((Diphenylsilyl)methyl)-4-hexylidene-1-tosylpyrrolidine (**3s**).* The reaction with *N*-allyl-4-methyl-*N*-(oct-2-yn-1-yl)benzenesulfonamide **1s** (0.3184 g, 1.0 mmol), H_2SiPh_2 **2a** (223 μL, 1.2 mmol), IP·$CoCl_2$ (0.0400 g, 0.1 mmol), and $NaBHEt_3$ (300 μL, 0.3 mmol) in toluene (2 mL) for 24 h, using hexane/EtOAc (30/1) as eluent, afforded **3s** (0.2728 g, 54%, 95% purity) as a yellow oil; IR (neat): 3065, 2956, 2926, 2858, 2123, 1596, 1461, 1430 cm^{-1}; ^{1}H NMR: (400.1 MHz, $CDCl_3$) δ 7.60 (d, J = 7.6 Hz, 2H), 7.54−7.48 (m, 4H), 7.42−7.32 (m, 6H), 7.26 (d, J = 8.4 Hz, 2H), 5.24−5.15 (m, 1H), 4.87 (dd, J = 8.4, 3.2 Hz, 1H), 3.82 (d, J = 13.6 Hz, 1H), 3.66 (d, J = 13.6 Hz, 1H), 3.50−3.41 (m, 1H), 2.72−2.60 (m, 2H), 2.40 (s, 3H), 1.81 (q, J = 6.8 Hz, 2H), 1.45 (ddd, J = 14.8, 4.4, 4.4 Hz, 1H), 1.30−1.15 (m, 6H), 1.03 (ddd, J = 14.8, 9.2, 3.2 Hz, 1H), 0.86 (t, J = 7.2 Hz, 3H); ^{13}C NMR: (100.6 MHz, $CDCl_3$) δ 143.4, 139.8, 135.6, 135.5, 135.0, 133.7, 133.5, 132.7, 129.79, 129.78, 129.6, 129.5, 128.11, 128.06, 127.7, 122.4, 54.9, 49.3, 38.9, 31.4, 29.1, 28.8, 22.4, 21.5, 15.4, 14.0; HRMS (EI) calculated for $[C_{30}H_{37}NO_2SiS]^+$ (M^+) requires m/z 503.2314, found m/z 503.2311.

*(Z)-((4-Benzylidenetetrahydrofuran-3-yl)methyl)diethylsilane (**3ab**).* The reaction with **1a** (0.1724 g, 1.0 mmol), H_2SiEt_2 **2b** (152 μL, 1.2 mmol), IP·$CoCl_2$ (0.0208 g, 0.05 mmol), and $NaBHEt_3$ (150 μL, 0.15 mmol) in toluene (2 mL) for 24 h, using hexane/EtOAc (30/1) as eluent, afforded **3ab** (0.1977 g, 76%) as a white foam; IR (neat): 3026, 2954, 2908, 2875, 2101, 1663, 1599, 1494, 1457 cm^{-1}; ^{1}H NMR: (400.1 MHz, $CDCl_3$) δ 7.36−7.30 (m, 2H), 7.21 (dd, J = 7.6, 7.2 Hz, 1H), 7.14 (d, J = 7.2 Hz, 2H), 6.34 (q, J = 2.4 Hz, 1H), 4.74−4.58 (m, 2H), 4.10 (dd, J = 8.0, 7.2 Hz, 1H), 3.80−3.73 (m, 1H), 3.40 (dd, J = 8.0, 8.0 Hz, 1H), 2.98−2.86 (m, 1H), 1.15 (ddd, J = 14.8, 4.4, 4.4 Hz, 1H), 1.02 (q, J = 6.8 Hz, 6H), 0.79 (ddd, J = 14.8, 10.0, 2.4 Hz, 1H), 0.66 (dq, J = 7.6, 2.4 Hz, 4H); ^{13}C NMR: (100.6 MHz, $CDCl_3$) δ 147.4, 137.4, 128.5, 127.9, 126.5, 119.9, 74.0, 70.0, 41.9, 13.5, 8.2, 8.1, 3.2, 3.0; HRMS (EI) calculated for $[C_{16}H_{24}OSi]^+$ (M^+) requires m/z 260.1596, found m/z 260.1590.

*(Z)-((4-Benzylidenetetrahydrofuran-3-yl)methyl)dimethyl-(phenyl)silane (**3ac**).* The reaction with **1a** (0.1727 g, 1.0 mmol), $HSiMe_2Ph$ **2c** (187 μL, 1.2 mmol), IP·$CoCl_2$ (0.0202 g, 0.05 mmol), and $NaBHEt_3$ (150 μL, 0.15 mmol) in toluene (2 mL) for 24 h, using hexane/EtOAc (80/1) as eluent, afforded **3ac** (0.0962 g, 31%) as a white foam; IR (neat): 3051, 2955, 2848, 1663, 1597, 1493, 1426 cm^{-1}; ^{1}H NMR: (400.1 MHz, $CDCl_3$) δ 7.56−7.50 (m, 2H), 7.39−7.34 (m, 3H), 7.34−7.28 (m, 2H), 7.21−7.16 (m, 1H), 7.09 (d, J = 7.2 Hz, 2H), 6.26 (q, J = 2.0 Hz, 1H), 4.64 (dd, J = 14.4, 1.6 Hz, 1H), 4.57−4.50 (m, 1H), 3.93 (dd, J = 8.0, 7.6 Hz, 1H), 3.21 (dd, J = 8.4, 8.0 Hz, 1H), 2.90−2.80 (m, 1H), 1.33 (dd, J = 14.8, 4.0 Hz, 1H), 0.92 (dd, J = 14.8, 10.4 Hz, 1H), 0.35 (d, J = 0.8 Hz, 6H); ^{13}C NMR: (100.6 MHz, $CDCl_3$) δ 147.4, 138.7, 137.3, 133.5, 129.1, 128.4, 127.90, 127.88, 126.4, 119.8, 73.9, 69.8, 41.5, 18.6, −2.3; HRMS (EI) calculated for $[C_{20}H_{24}OSi]^+$ (M^+) requires m/z 308.1596, found m/z 308.1591.

*(Z)-((4-Benzylidenetetrahydrofuran-3-yl)methyl)(methyl)-diphenylsilane (**3ad**).* The reaction with **1a** (0.1752 g, 1.0 mmol), $HSiMePh_2$ **2d** (235 μL, 1.2 mmol), IP·$CoCl_2$ (0.0203 g, 0.05 mmol), and $NaBHEt_3$ (150 μL, 0.15 mmol) in toluene (2 mL) for 24 h, using hexane/EtOAc (30/1) as eluent, afforded **3ad** (0.1023 g, 27%) as a white foam; IR (neat): 3065, 2959, 2846, 1661, 1595, 1491, 1427 cm^{-1}; ^{1}H NMR: (400.1 MHz, $CDCl_3$) δ 7.68−7.52 (m, 4H), 7.40−7.34 (m, 6H), 7.34−7.28 (m, 2H), 7.21−7.15 (m, 1H), 7.08 (d, J = 7.2 Hz, 2H), 6.29 (q, J = 2.0 Hz, 1H), 4.62 (dd, J = 14.0, 1.6 Hz, 1H), 4.57−4.50 (m, 1H), 3.80 (dd, J = 8.0, 6.8 Hz, 1H), 3.19 (dd, J = 8.4, 8.0 Hz, 1H), 2.99−2.88 (m, 1H), 1.65 (dd, J = 14.8, 3.6 Hz, 1H), 1.25 (dd, J = 14.8, 10.4 Hz, 1H), 0.63 (s, 3H); ^{13}C NMR: (100.6 MHz, $CDCl_3$) δ 147.3, 137.3, 136.7, 136.6, 134.37, 134.36, 129.40, 129.38, 128.4, 128.0, 127.95, 127.88, 126.4, 119.9, 73.9, 69.8, 41.4, 17.1, −3.7; HRMS (EI) calculated for $[C_{25}H_{26}OSi]^+$ (M^+) requires m/z 370.1753, found m/z 370.1751.

*(Z)-3-Benzylidene-4-((diethylsilyl)methyl)-1-tosylpyrrolidine (**3cb**).* The reaction with **1c** (0.3257 g, 1.0 mmol), **2b** (152 μL, 1.2 mmol), IP·$CoCl_2$ (0.0196 g, 0.05 mmol), and $NaBHEt_3$ (150 μL, 0.15 mmol) in toluene (2 mL) for 24 h, using hexane/EtOAc (18/1) as eluent, afforded **3cb** (0.3126 g, 75%) as a white foam; IR (neat): 2953, 2875, 2101, 1664, 1598, 1493, 1453 cm^{-1}; ^{1}H NMR: (400.1 MHz, $CDCl_3$) δ 7.72 (d, J = 8.4 Hz, 2H), 7.37−7.27 (m, 4H), 7.26−7.20 (m, 1H), 7.13 (d, J = 7.6 Hz, 2H), 6.27 (d, J = 2.0 Hz, 1H), 4.24 (dd, J = 14.8, 2.0 Hz, 1H), 4.08−4.01 (m, 1H), 3.76−3.70 (m, 1H), 3.59 (dd, J = 8.8, 6.4 Hz, 1H), 2.88−2.79 (m, 1H), 2.76 (dd, J = 8.8, 8.0 Hz, 1H), 2.40 (s, 3H), 1.08−0.94 (m, 7H), 0.70−0.57 (m, 5H); ^{13}C NMR: (100.6 MHz, $CDCl_3$) δ 143.6, 142.6, 136.5, 133.1, 129.7, 128.5, 128.1, 127.6, 126.9, 122.0, 53.7, 50.4, 41.2, 21.4, 13.8, 8.08, 8.06, 3.0, 2.9; HRMS (EI) calculated for $[C_{23}H_{31}NO_2SiS]^+$ (M^+) requires m/z 413.1845, found m/z 413.1849.

Gram-Scale Reaction. The reaction with **1c** (3.2666 g, 10 mmol), **2a** (2.3 mL, 12 mmol), IP·$CoCl_2$ (0.1995 g, 0.5 mmol), and $NaBHEt_3$ (1.5 mL, 1.5 mmol) in toluene (20 mL) for 24 h, using hexane/EtOAc (10/1 to 5/1) as eluent, afforded **3c** (4.3695 g, 85% yield) as a white foam.

*(Z)-((4-Benzylidene-1-tosylpyrrolidin-3-yl)methyl)diphenylsilanol (**4**).* Prepared according to a previously reported procedure,[12a] using 0.5040 g (1.0 mmol) of **3c**, 0.0204 g (0.1 mmol, 10 mol %) of $PhCOCF_3$, 0.2955 g (4 mmol) of *t*BuOH, 0.22 mL of MeCN, 0.5 mL (30% in H_2O) of H_2O_2, and 0.5 mL aqueous buffer solution (0.6 M K_2CO_3−4 × 10^{-5} M EDTA tetrasodium salt). The mixture was stirred at room temperature overnight, and the crude reaction mixture was then extracted with Et_2O (20 mL × 3). The combined organic layers were then dried over anhydrous Na_2SO_4, filtered, concentrated, and purified by flash column chromatography using PE/EtOAc = 4/1 as the eluent to give 0.4154 g (80% yield) of **4** as a white foam; IR (neat): 3492 (br), 3051, 2878, 1596, 1492, 1428 cm^{-1}; ^{1}H NMR: (400.1 MHz, $CDCl_3$) δ 7.63−7.56 (m, 6H), 7.46−7.35 (m, 6H), 7.35−7.28 (m, 2H), 7.26−7.18 (m, 3H), 7.04 (d, J = 7.6 Hz, 2H), 6.25 (d, J = 2.0 Hz, 1H), 4.05 (dd, J = 14.8, 2.0 Hz, 1H), 3.96−3.89 (m, 1H), 3.39 (dd, J = 9.2, 6.8 Hz, 1H), 2.99−2.90 (m, 1H), 2.86 (dd, J = 9.2, 7.2 Hz, 1H), 2.75 (br, 1H), 2.38 (s, 3H), 1.57 (dd, J = 14.8, 4.4 Hz, 1H), 1.24 (dd, J = 15.2, 9.6 Hz, 1H); ^{13}C NMR: (100.6 MHz, $CDCl_3$) δ 143.5, 142.6, 136.4, 135.8, 135.6, 134.04, 134.02, 132.8, 130.1, 129.7, 128.5, 128.1, 128.0, 127.7, 127.0, 122.3, 53.7, 50.3, 40.4, 21.5, 18.9; HRMS (EI) calculated for $[C_{31}H_{31}NO_3SSi]^+$ (M^+) requires m/z 525.1794, found m/z 525.1796.

*(Z)-(4-Benzylidene-1-tosylpyrrolidin-3-yl)methanol (**5**).* Prepared according to a previously reported procedure,[21] using 0.5051 g (1.0 mmol) of **3c**, 4 mL of MeOH, 4 mL of THF, 0.0998 g (1 mmol) of $KHCO_3$, and 0.6 mL (30%) of H_2O_2. The mixture was stirred at room temperature overnight, and the crude reaction mixture was then extracted with CH_2Cl_2 (20 mL × 3). The combined organic layers were then dried over anhydrous Na_2SO_4, filtered, concentrated, and purified by flash column chromatography using PE/EtOAc = 2:1 to 1:1 as the eluent to give 0.1858 g (55% yield) of **5** as a white solid; mp

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= 127−128 °C; IR (neat): 3515, 3056, 2870, 1598, 1493, 1449 cm^{-1}; ^1H NMR: (400.1 MHz, $CDCl_3$) δ 7.72 (d, J = 8.0 Hz, 2H), 7.37−7.29 (m, 4H), 7.27−7.21 (m, 1H), 7.13 (d, J = 8.0 Hz, 2H), 6.35 (d, J = 1.6 Hz, 1H), 4.24−4.17 (m, 1H), 4.00 (dd, J = 14.8, 2.4 Hz, 1H), 3.70−3.56 (m, 2H), 3.38 (dd, J = 10.0, 4.0 Hz, 1H), 3.27 (dd, J = 9.6, 6.8 Hz, 1H), 3.02−2.92 (m, 1H), 2.41 (s, 3H), 2.30−2.22 (br, 1H); ^{13}C NMR: (100.6 MHz, $CDCl_3$) δ 143.8, 136.9, 136.1, 132.4, 129.7, 128.5, 128.1, 127.7, 127.2, 124.6, 63.8, 50.7, 49.3, 47.4, 21.5; HRMS (EI) calculated for $[C_{19}H_{21}NO_3S]^+$ (M^+) requires m/z 343.1242, found m/z 343.1239.

Mechanistic Studies. The reaction with (3-((2-methylallyl)oxy)-prop-1-yn-1-yl)benzene **1t** (0.1828 g, 1.0 mmol), **2a** (223 μL, 1.2 mmol), IP·$CoCl_2$ (0.0205 g, 0.05 mmol), and $NaBHEt_3$ (150 μL, 0.15 mmol) in toluene (8 mL) for 5 h. The resulting solution was quenched by ether and filtered through a pad of silica gel, washing with ether (15 mL × 3). The solvents were removed under reduced pressure and afforded the crude product. Yields were determined by ^1H NMR analysis using 20 μL of TMSPh as an internal standard: product **3t** in 9% NMR yield, product **6** in 46% NMR yield, product **7** in 13% NMR yield.

Product ***3t***. Colorless oil; IR (neat): 3058, 2959, 2852, 2128, 1728, 1490, 1430 cm^{-1}; ^1H NMR: (400.1 MHz, $CDCl_3$) δ 7.58−7.50 (m, 4H), 7.37−7.26 (m, 8H), 7.22−7.15 (m, 1H), 6.98 (d, J = 7.2 Hz, 2H), 6.28−6.20 (m, 1H), 4.97 (dd, J = 4.0 Hz, 1H), 4.57 (dd, J = 14.4, 2.4 Hz, 1H), 4.49 (dd, J = 14.4, 2.4 Hz, 1H), 3.69 (d, J = 8.4 Hz, 1H), 3.48 (d, J = 8.4 Hz, 1H), 1.69 (dd, J = 14.8, 4.0 Hz, 1H), 1.54 (dd, J = 14.8, 4.0 Hz, 1H), 1.29 (s, 3H); ^{13}C NMR: (100.6 MHz, $CDCl_3$) δ 150.3, 137.2, 135.1, 135.03, 135.95, 134.8, 129.5, 129.4, 128.3, 128.99, 128.98, 128.95, 126.4, 119.2, 79.5, 70.6, 45.8, 26.2, 24.6; HRMS (EI) calculated for $[C_{25}H_{26}OSi]^+$ (M^+) requires m/z 370.1753, found m/z 370.1753.

Product ***6***. Colorless oil; IR (neat): 3063, 2931, 2857, 2127, 1731, 1583, 1428 cm^{-1}; ^1H NMR: (400.1 MHz, $CDCl_3$) δ 7.69−7.64 (m, 4H), 7.42−7.30 (m, 8H), 7.28−7.18 (m, 3H), 6.97 (s, 1H), 5.28 (s, 1H), 4.72 (d, J = 1.2 Hz, 2H), 4.40 (d, J = 1.6 Hz, 2H), 3.70 (s, 2H), 1.51 (s, 3H); ^{13}C NMR: (100.6 MHz, $CDCl_3$) δ 143.6, 142.0, 138.0, 137.3, 135.8, 134.1, 129.4, 129.0, 128.1, 127.8, 127.5, 111.9, 74.9, 70.2, 19.4; HRMS (EI) calculated for $[C_{25}H_{26}OSi]^+$ (M^+) requires m/z 370.1753, found m/z 370.1760.

Product ***7***. Colorless oil; IR (neat): 3064, 2925, 2857, 2127, 1728, 1597, 1433 cm^{-1}; ^1H NMR: (400.1 MHz, $CDCl_3$) δ 7.55−7.49 (m, 4H), 7.40−7.30 (m, 6H), 7.24−7.23 (m, 3H), 6.99−6.95 (m, 2H), 6.33 (t, J = 6.0 Hz, 1H), 5.22 (s, 1H), 4.88−4.80 (m, 2H), 4.00 (d, J = 6.0 Hz, 2H), 3.78 (s, 2H), 1.67 (s, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 143.4, 142.1, 141.0, 140.5, 135.8, 132.8, 129.8, 128.1, 128.0, 127.9, 126.3, 112.3, 74.4, 67.8, 19.5; HRMS (EI) calculated for $[C_{25}H_{26}OSi]^+$ (M^+) requires m/z 370.1753, found m/z 370.1753.

*(E)-3-((Diphenylsilyl)methylene)-4-methyl-1-tosylpyrrolidine (**3u**).* The reaction with *N*-allyl-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide **1u** (0.2442 g, 1.0 mmol), **2a** (223 μL, 1.2 mmol), IP·$CoCl_2$ (0.0199 g, 0.05 mmol), and $NaBHEt_3$ (150 μL, 0.15 mmol) in toluene (8 mL) was carried out for 24 h. The resulting solution was quenched by ether and filtered through a pad of silica gel, washing with ether (15 mL × 3). The solvents were removed under reduced pressure, affording the product **3u** (0.1438 g, 34%) as a white foam, using hexane/EtOAc (20/1−10/1) as eluent. IR (neat): 3066, 2969, 2867, 2127, 1633, 1597, 1452, 1429 cm^{-1}; ^1H NMR: (400.1 MHz, $CDCl_3$) δ 7.70 (d, J = 8.4 Hz, 2H), 7.47−7.53 (m, 4H), 7.30−7.42 (m, 8H), 5.66−5.72 (m, 1H), 5.17 (d, J = 6.0 Hz, 1H), 4.12 (d, J = 14.8 Hz, 1H), 3.69 (dd, J = 14.8, 1.6 Hz, 1H), 3.13−3.23 (m, 2H), 2.84−2.94 (m, 1H), 2.43 (s, 3H), 1.03 (d, J = 6.8 Hz, 3H); ^{13}C NMR: (100.6 MHz, $CDCl_3$) δ 162.6, 143.6, 135.2, 135.1, 133.6, 132.6, 129.8, 129.7, 128.1, 127.8, 113.9, 55.3, 54.0, 37.8, 21.5, 20.5; HRMS (EI) calculated for $[C_{25}H_{27}NO_2SiS]^+$ (M^+) requires m/z 433.1532, found m/z 433.1531.

Hydrosilylation/Cyclization of 1,6-Enynes with Ph_2SiD_2. The reaction with (3-(allyloxy)prop-1-yn-1-yl)benzene **1a** (0.1722 g, 1.0 mmol), Ph_2SiD_2 **2a-*d*$_2$**[12a] (0.2350 μL, 1.2 mmol, 99.5% D), IP·$CoCl_2$ (0.0195 g, 0.05 mmol), and $NaBHEt_3$ (150 μL, 0.15 mmol) in toluene (8 mL) for 5 h, using hexane/EtOAc (20/1) as eluent, afforded **3a-*d*$_n$** (0.3109 g, 91%) as a colorless oil. ^1H NMR: (300.1 MHz, $CDCl_3$) δ 7.63−7.56 (m, 4H), 7.45−7.29 (m, 8H), 7.23−8.16 (m, 1H), 7.09 (d, J = 7.5 Hz, 2H), 6.34 (d, J = 2.4 Hz, 0.09 H), 4.96 (dd, J = 4.8, 3.3 Hz, 0.07 H), 4.68−4.52 (m, 2H), 3.96 (dd, J = 8.4, 3.9 Hz, 1H), 3.40 (dd, J = 8.1, 7.8 Hz, 1H), 3.05−2.90 (m, 1H), 1.75−1.65 (ddd, J = 15.0, 1.8, 1.5 Hz, 1H), 1.40−1.28 (ddd, J = 15.0, 10.2, 3.3 Hz, 1H).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01555.

^1H NMR and ^{13}C NMR for all the products, and X-ray analysis of IP·$CoCl_2$ (PDF)

Crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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