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Unprecedented Cesium and Potassium Fluorides Catalyzed Trialkylsilylation and Tributylstannylation of Terminal Alkynes with Trifluoromethyl-Trialkylsilanes and -Tributylstannane

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Abstract—Cesium and potassium fluorides promoted trialkylsilylation and tributylstannylation of terminal alkynes with trifluoromethyl-trialkylsilanes and -tributylstannane were found to give 1-silyl- and 1-tributylatannyl-alkynes in high yield. The present reactions are applicable to 1-alkynes having a wide range of functional groups such as acetal, iodo, silyl, amino, amido and carbonyl (except for aldehyde) groups. © 2000 Elsevier Science Ltd. All rights reserved.

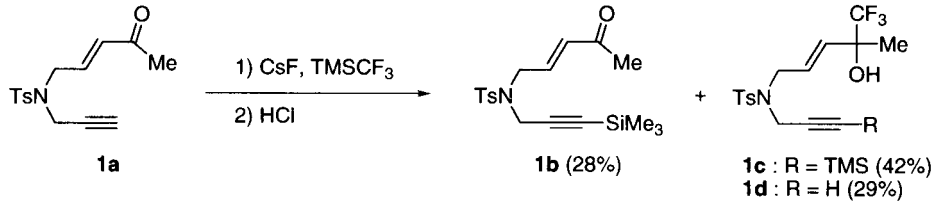
Introduction

Much attention has been focused on 1-silyl- and 1-stannyl-alkynes as versatile reagents for Lewis acid promoted alkynylation of various electrophiles,[1] substrates for alkynylation of organic halides or triflates,[2] and protecting groups for terminal alkynes.[3] For their synthesis, the direct trialkylsilylation or trialkylstannylation of terminal alkynes is a common method, which is performed by treatment with organometallic reagents such as BuLi,[4a,b] EtMgBr,[4c] Zn[4d,e] and Cu[4f] followed by the reaction with chloro-trialkylsilanes or -trialkylstannanes. Another approach toward trialkylsilylation is transition metal catalyzed reaction of terminal alkynes with hydrosilanes.[5] However, the former method requires stoichiometric amount of organometallic reagents for generation of acetylide and the latter reaction brings about hydrosilylation of alkynes as side-reaction.

During our studies[6] on Pauson–Khand reaction of fluorine-containing enynes, we found unexpected cesium fluoride (CsF) catalyzed trimethylsilylation of keto-1-alkyne (**1a**) with trifluoromethyltrimethylsilane ($TMSCF_3$)[7] to give 1-silylalkynes (**1b**, **c**) together with normal adduct (**1d**) (Scheme 1). This result indicated trifluoromethyltrialkylsilanes would serve as effective trialklylsilylating reagent for trialkylsilylation of 1-alkynes in the presence of appropriate catalyst. In a similar manner, trifluoromethyl-tributylstannane (Bu_3SnCF_3)[8]could be used for tributylstannylation of 1-alkyne (vide infra). Here, we describe unprecedented trialkylsilylation and tributylstannylation of 1-alkynes with trifluoromethyl-trialkylsilanes and -tributylstannane in the presence of CsF or potassium fluoride (KF).

Results and Discussion

First, in order to investigate effect of catalyst in the present reaction, various catalysts were examined (Scheme 2, Table 1).[9] Terminal alkyne (**2a**)[10] was chosen as a model compound. As shown in Table 1, the reaction without catalyst did not proceed at all. CsF in THF and KF in DMF were found to serve as effective catalyst in this system to give trimethylsilylacetylene (**2b**) in quantitative yield (entries 2, 5). These results suggested fluoride ion to play



1a → **1b** (28%) + **1c** : R = TMS (42%), **1d** : R = H (29%)

Scheme 1.

Keywords: 1-alkyne; trialkylsilylation; tributylstannylation; cesium fluoride; potassium fluoride.

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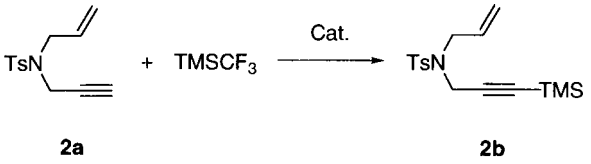


2a **2b**

Scheme 2.

Table 1. Effects of catalyst (unless otherwise noted, all reactions were carried out at rt using **2a** (1 equiv.), catalyst (0.16 equiv.), and $TMSCF_3$ (1.5 equiv.) under argon)

Entry	Catalyst	Solvent	Time (h)	Yield (%)[a]
1	None	THF	24	0
2	CsF	THF	0.5	100
3[b]	KF	THF	15	23 (76)
4[c]	KF	THF	24	28 (36)
5	KF	DMF	0.5	98
6	CsCl	THF	24	0
7	CsOH	THF	24	trace
8	TBAF	THF	24	0

[a] Isolated yield. Value in parenthesis was recovery of starting material.
[b] With 0.4 equiv. of KF.
[c] With 1 equiv. of KF.

an important role. Since the reaction with TBAF[11] did not proceed, the presence of a small amount of water was assumed to suppress the reaction. Because when CsF was not dried before using, incomplete reaction was observed sometimes.

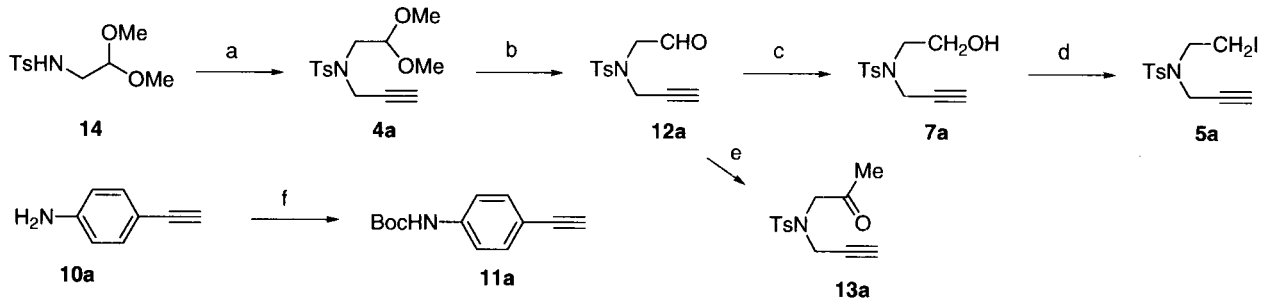
To apply the present reaction to other substrates, various 1-alkynes were synthesized as depicted in Scheme 3. Namely, propargylation of acetal tosylamide (**14**)[12] gave **4a**, acidic hydrolysis of which afforded an aldehyde (**12a**) in 93% yield. Reduction of **12a** with $NaBH_4$ furnished an alcohol (**7a**), which was converted to an iodide (**5a**) by standard way. Alternatively, methylation and oxidation of **12a** afforded methyl ketone (**13a**). A carbamate (**11a**) was obtained from 4-aminophenylacetylene (**10a**)[13] with Boc_2O in 89% yield.

After examination on amount of catalyst in the reaction, we found that the catalyst could be decreased to 2 mol%. Thus, the reaction (Method A; CsF in THF or Method B; KF in DMF) was carried out on various 1-alkynes with $TMSCF_3$ (1.2–4.8 equiv.) to give corresponding 1-trimethylsilyl-alkynes (Table 2). Trimethylsilylation of **2a**–**5a** smoothly proceeded, in which vinyl, acetal, and iodo groups remained intact (entries 1–8). The reaction of triphenylsilylacetylene (**6a**) took place successfully without desilylation (entries 9, 10). The reaction of alkynol (**7a**) using 1.2 equiv. of $TMSCF_3$ produced TMS ether (**7b**) predominately (entry 11), while that with 2.4 equiv. of $TMSCF_3$ gave bis(trimethylsilyl) compound (**7c**) quantitatively (entry 12). Diyne (**8a**) underwent bis(trimethylsilyl)silylation to furnish **8b** in quantitative yield (entries 14, 15). With 1-alkyne (**9a**) having an active methyne moiety, however, Method A interfered the reaction and Method B remarkably slowed the reaction (entries 16, 17). With amine (**10a**) and amide (**11a**), excess $TMSCF_3$ was needed and reaction time prolonged, although yields were still high (entries 18–21). Unfortunately, with aldehyde (**12a**), Method A could not avoid trifluoromethylation of carbonyl group (entry 22). However, Method B, furnished desired product (**12b**) along with trifluoromethylated product (**12d**) (entry 23).[14] In a similar manner, silylation of ketone (**13a**) by Method B gave 1-trimethylsilylalkyne (**13b**) and **13c**, respectively (entries 24). Also, silylation of **1a** by Method B proceeded successfully to give **1b** predominantly together with **1c** (entry 25). (Fig. 1)

Advantage of the present reaction is as follows: 1) A catalytic amount of promoter (CsF or KF): 2) Method A is simple work-up procedure (see Experimental): 3) the reaction is applicable to 1-alkynes bearing many functional groups such as acetal, iodo, silyl, amino, amido and carbonyl (except for aldehyde) groups.

Plausible reaction mechanism for trimethylsilylation of 1-alkynes is depicted in Fig. 2. Initially, reaction of $TMSCF_3$ with MF (M=Cs or K) generates pentacoordinated silicate species (**A**),[15] which reacted 1-alkynes to afford acetylide containing pentacoordinated silicate species (**B**). Then, **B** reacts with $TMSCF_3$ to furnish 1-trimethylsilyl-alkynes and **A**.

We additionally examined the reaction of **2a** with $TESCF_3$ and Bu_3SnCF_3 (Scheme 4, Table 3). In the case of triethylsilylation, long reaction time was required in both Method A and B (2 mol% of catalyst) (entries 1, 3). Increase of amount of CsF (10 mol%) markedly improved in both reaction time and yield (entry 2), although the reaction using KF was independent on the amount of the catalyst (entry 4). In a similar manner, tributylstannylation of **2a** was performed to furnish **2d** (entries 5, 6),



Scheme 3. (a) 3-bromopropyne, K_2CO_3, DMF, 100°C, 1.5 h, 97% (b) 3 M HCl, THF, Δ, 2 h 93% (c) $NaBH_4$, MeOH, 0°C, 0.5 h, 83% (d) I_2, imidazole, PPh_3, CH_2Cl_2, 0°C, 2 h, 93% (e) MeMgBr, THF, rt, 1 h; Dess–Martin periodinane, CH_2Cl_2, rt, 1 h, 75% (f) Boc_2O, THF, Δ, 3 h, 89%.

Table 2. Silylation of various 1-alkynes (all reactions were carried out at rt in THF (Method A) or DMF (Method B), unless otherwise noted)

Entry	Substrate	Method	$TMSCF_3$ (equiv.)	Time (h)	Product	Yield (%)[a]
1	**2a**	A	1.2	0.5	**2b**	100
2	**2a**	B	1.2	0.5	**2b**	99
3	**3a**	A	1.2	0.1	**3b**	100
4	**3a**	B	1.2	0.1	**3b**	100
5	**4a**	A	1.2	0.5	**4b**	100
6	**4a**	B	2.4	1.5	**4b**	99
7	**5a**	A	1.2	0.5	**5b**	100
8	**5a**	B	1.2	1.5	**5b**	98
9	**6a**	A	1.2	0.2	**6b**	100
10	**6a**	B	1.2	0.2	**6b**	100
11	**7a**	A	1.2	0.2	**7b**	100
12	**7a**	A	2.4	0.5	**7c**	100
13	**7a**	B	4.0	3	**7c**	100
14	**8a**	A	3.2	1.5	**8b**	100
15	**8a**	B	2.5	0.5	**8b**	100
16	**9a**	A	4.8	24	**9b**	–[b]
17	**9a**	B	3.6	24	**9b**	40 (14)
18	**10a**	A	2.4	1.5	**10b**	100
19	**10a**	B	3.0	18	**10b**	87
20	**11a**	A	3.0	18	**11b**	88 (8)
21	**11a**	B	3.0	18	**11b**	87 (11)
22	**12a**	A	2.7	6	**12c**+**12d**	33+37
23	**12a**	B	2.7	3	**12b**+**12d**	26+59
24[c]	**13a**	B	1.6	21	**13b**+**13c**	72+16
25[c]	**1a**	B	1.6	18	**1b**+**1c**	74+11

[a] Isolated yield. Value in parentheses was recovery of starting material.
[b] Complex mixture.
[c] The reaction was performed at 0°C.

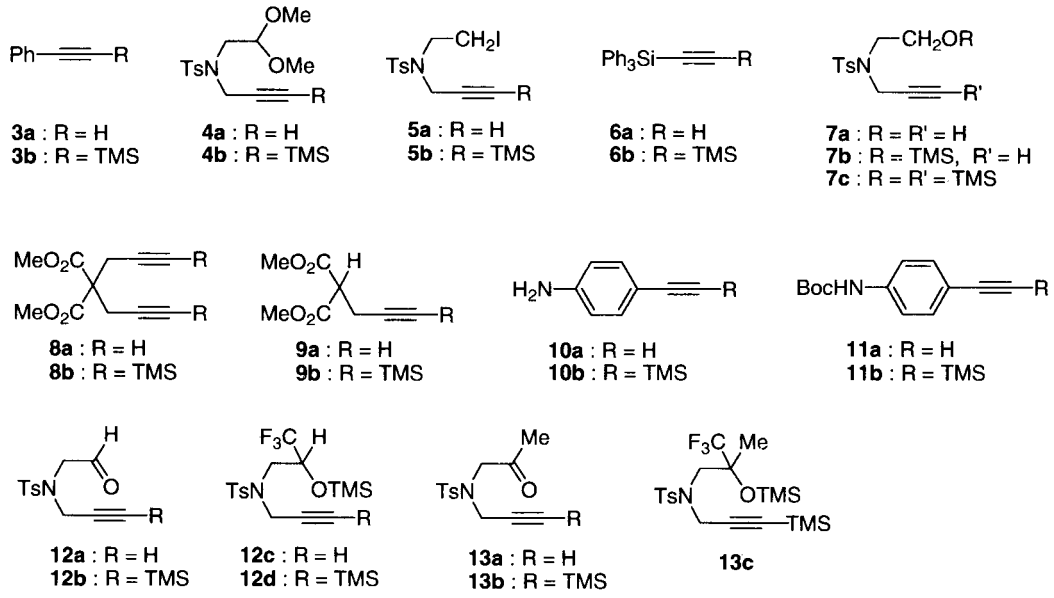


Figure 1.

Conclusion

In summary, we have demonstrated that trialkylsilylation and tributylstannylation of 1-alkynes with trifluoromethyltrialkylsilanes and -tributylstannane using a catalytic amount of CsF or KF proceeded in high yield. The present reactions are convenient and applicable to the 1-alkynes possessing a wide range of functional groups.

Experimental

General

^1H NMR spectra were taken with a JEOL EX-270 (270 MHz) spectrometer in $CDCl_3$ solution with tetramethylsilane as an internal standard. Mass spectra were measured on a Hitachi M-80 or a JEOL JMS D-300

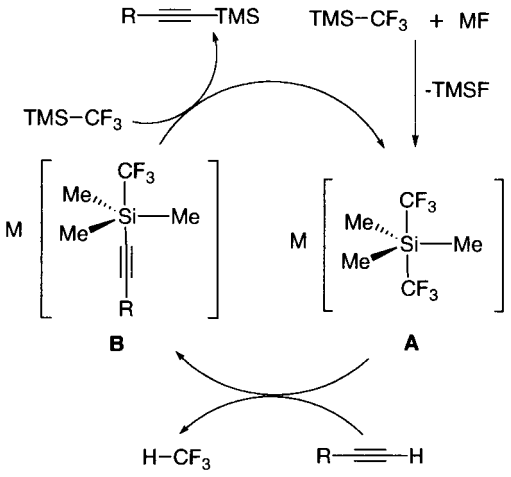
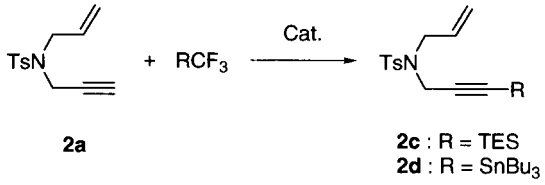


Figure 2.



Scheme 4.

Table 3. Triethylsilylation and tributylstannylation of **2a**

Entry	Cat.(mol%)	Reagent (equiv.)	Solvent	Time (h)	Yield (%)[a]
1	CsF (2)	$TESCF_3$ (2.5)	THF	72	42 (58)
2	CsF (10)	$TESCF_3$ (2.5)	THF	2.5	97
3	KF (2)	$TESCF_3$ (2.5)	DMF	24	89
4	KF (10)	$TESCF_3$ (2.5)	DMF	24	85
5	CsF (10)	Bu_3SnCF_3 (2.5)	THF	48	69 (20)
6	KF (2)	Bu_3SnCF_3 (2.0)	DMF	10	89

[a] Isolated yield. Value in parentheses was recovery of starting material.

spectrometer. Column chromatography was performed over silica gel (Merck Kiegelsel 60). CsF and KF were dried with heat gun in vacuo prior to use. THF was distilled from Na wire before use. DMF was stored over MS 4A. Starting materials (**3a**, **6a**) were purchased from Aldrich Co., and **2a**,[10] **8a**,[15] **9a**,[16] and **10a**[13] were synthesized according to reported procedure.

***N*-Dimethoxylethyl-*N*-(2-propynyl)tosylamide (4a).** A mixture of **14** (22.53 g, 87 mmol), 3-bromopropyne (12.42 g, 82 mmol), and K_2CO_3 (12.00 g, 61 mmol) in DMF (300 mL) was heated at 100°C for 1.5 h. After water was added to the mixture, the mixture was extracted with Et_2O. The organic extract was washed with water and brine, successively, dried, and evaporated under reduced pressure to give **4a** (25.01 g, 96.8%) as colorless crystals; mp 55–56°C; ^{1}H NMR δ 7.74, 7.29 (each 2H, d, J=8.3 Hz), 4.56 (1H, t, J=5.4 Hz), 4.26 (2H, d, J=2.3 Hz), 3.41 (6H, s), 3.27 (2H, d, J=5.4 Hz), 2.42 (3H, s), 2.00 (1H, t, J=2.3 Hz); MS m/z 297 (M^+); high-resolution mass m/z calcd for $C_{14}H_{19}NO_4S$ (M^+) 297.1035, found: 297.1033.

***N*-Iodoethyl-*N*-(2-propynyl)tosylamide (5a).** To a solution of **7a** (5.18 g, 20 mmol), PPh_3 (6.30 g, 24 mmol) and pyridine (2 mL) in CH_2Cl_2 (200 mL) was added at 0°C I_2 (6.10 g, 24 mmol) in one portion. After being stirred for 2 h, the reaction was quenched with 10% $Na_2S_2O_3$. The solvent was washed with 1 M HCl and brine, successively, dried, and evaporated under reduced pressure to give a residue, which was purified by column chromatography (AcOEt:hexane=1:3) to afford **5a** (6.88 g, 93.2%) as colorless crystals; mp 70–71°C; ^{1}H NMR δ 7.71, 7.29 (each 2H, d, J=8.3 Hz), 4.12 (1H, d, J=2.3 Hz), 3.52, 3.29 (each 2H, t, J=7.9 Hz), 2.41 (3H, s), 2.10 (1H, t, J=2.3 Hz); ^{13}C NMR δ 144.3, 135.7, 130.0, 129.7, 127.8, 77.0, 74.8, 49.7, 37.8, 21.9; MS m/z 362 (M^+); high-resolution mass m/z calcd for $C_{12}H_{14}INO_2S$ (M^+) 362.9790, found: 362.9790.

***N*-Hydroxyethyl-*N*-(2-propynyl)tosylamide (7a).** To a solution of **12a** (12.80 g, 50 mmol) in MeOH (250 mL) was added at 0°C $NaBH_4$ (0.95 g, 25 mmol) in one portion. After being stirred for 0.5 h, the reaction was quenched with water. The solvent was evaporated under reduced pressure to give a residue, which was taken up in $CHCl_3$. The organic extract was washed with brine, dried, and evaporated in vacuo to furnish **7a** (10.78 g, 83.2%) as colorless crystals; mp 67–68°C; ^{1}H NMR δ 7.75, 7.31 (each 2H, d, J=8.3 Hz), 4.42 (1H, d, J=2.3 Hz), 3.80, 3.36 (each 2H, t, J=5.3 Hz), 2.43 (3H, s), 2.09 (1H, t, J=2.3 Hz); ^{13}C NMR δ 144.32 135.7, 129.9, 128.0, 127.4, 77.2, 60.8, 49.2, 38.2, 21.8; MS m/z 253 (M^+); high-resolution mass m/z calcd for $C_{12}H_{15}NO_3S$ (M^+) 253.0773, found: 253.0770.

***N*-*tert*-Butoxycarbonyl-4-ethynylaniline (11a).** A mixture of **10a** (0.353 g, 3.0 mmol) and Boc_2O (2.006 g, 10.8 mmol) in THF (3 mL) was refluxed for 3 h. Then the solvent was removed in vacuo to give an oily residue, which was purified by column chromatography (AcOEt:hexane=1:15 then 1:5) to afford **11a** (0.581 g, 88.8%) as colorless crystals; mp 97°C; ^{1}H NMR δ 7.40, 7.31 (each 2H, d, J=8.3 Hz), 6.55 (1H, s), 3.01 (1H, s), 1.51 (9H, s); MS m/z 217 (M^+); high-resolution mass m/z calcd for $C_{13}H_{15}NO_2$ (M^+) 217.1103, found: 217.1100.

***N*-Formylmethyl-*N*-(2-propynyl)tosylamide (12a).** A mixture of **4a** (25.01 g, 84 mmol) and 3 M HCl (200 mL) in THF (250 mL) was refluxed for 2 h. Then the solvent was removed in vacuo. The mixture was extracted with Et_2O. The organic extract was washed with water and brine, successively, dried, and evaporated under reduced pressure to give an oily residue, which was purified by column chromatography (500 g, AcOEt:hexane=1:1) to afford **12a** (20.12 g, 93.0%) as colorless oil; ^{1}H NMR δ 9.66 (1H, t, J=1.3 Hz), 7.71, 7.33 (each 2H, d, J=8.3 Hz), 4.17 (1H, d, J=2.3 Hz), 3.96 (2H, d, J=1.3 Hz), 2.44 (3H, s), 2.17 (1H, t, J=2.3 Hz); MS m/z 251 (M^+); high-resolution mass m/z calcd for $C_{12}H_{13}NO_3S$ (M^+) 251.0616, found: 251.0622.

***N*-2-Oxopropyl-*N*-(2-propynyl)tosylamide (13a).** To a solution of **12a** (5.14 g, 20 mmol) in THF (80 mL) was added 40 mL of MeMgBr (1 M in THF, 40 mmol). After being stirred for 1 h, the reaction was quenched with 1 M HCl. The mixture was extracted with Et_2O. The organic extract was washed with water and brine, successively, dried, and evaporated under reduced pressure to give an

alcohol, which was treated with Dess–Martin periodinane (12.78 g, 30 mmol) in CH_2Cl_2 (200 mL) for 1 h. The mixture was washed with 10% $Na_2S_2O_3$ and brine, successively, dried, and evaporated under reduced pressure to give a residue, which was purified by column chromatography (AcOEt:hexane=1:2) to afford **13a** (4.08 g, 75.2%) as colorless crystals; mp 63°C; ^{1}H NMR δ 7.71, 7.31 (each 2H, d, J=8.3 Hz), 4.17 (1H, d, J=2.3 Hz), 4.03 (2H, s), 2.43, 2.22 (each 3H, s), 2.12 (1H, t, J=2.3 Hz); MS m/z 265 (M^+); high-resolution mass m/z calcd for $C_{13}H_{15}NO_3S$ (M^+) 265.0073, found: 265.0077.

General procedure for trimethylsilylation of 1-alkynes[17]

Method A. A mixture of acetylene (0.5 mmol), catalyst (0.01 mmol), and $TMSCF_3$ (0.6–2.4 mmol) in THF (2 mL) was stirred at rt. After the reaction was completed, the catalyst was filtered off by suction. The filtrate was evaporated under reduced pressure to give 1-silylacetylene in essentially pure form. For the reaction of **10a**–**13a**, purification was performed by column chromatography.

Method B. A mixture of acetylene (0.5 mmol), catalyst (0.01 mmol), and $TMSCF_3$ (0.6–2.0 mmol) in DMF (2 mL) was stirred at rt. After the reaction was completed, the reaction was quenched with water. The mixture was extracted with Et_2O. The organic extract was washed with water and brine, successively, dried ($MgSO_4$), and evaporated under reduced pressure to afford 1-silylacetylene in essentially pure form. For the reaction of **9a**–**13a**, purification was performed by column chromatography.

***N*-(4-Oxo-2-pentenyl)-*N*-[3-(trimethylsilyl)-2-propynyl]-tosylamide (1b).** Mp 93–94°C; ^{1}H NMR δ 7.76, 7.24 (each 2H, d, J=7.9 Hz), 6.59 (1H, dt, J=6, 15.8 Hz), 6.15 (1H, d, J=15.8 Hz), 4.03 (2H, s), 3.93(2H, d, J=6 Hz), 2.35, 2.17 (each 3H, s), −0.07 (9H, s); ^{13}C NMR δ 197.5, 143.6, 140.4, 132.8, 129.5, 127.5, 97.1, 91.4, 47.3, 37.6, 33.5, 26.9, 21.2, −0.7; IR 2929, 2864, 1705, 1624, 1448, 1412 cm^{-1}; MS m/z 363 (M^+); high-resolution mass m/z calcd for $C_{18}H_{25}NO_3SSi$ (M^+) 363.1324, found: 363.1320.

***N*-(2-Propenyl)-*N*-[3-(trimethylsilyl)-2-propynyl]tosylamide (2b).** Mp 60°C; ^{1}H NMR δ 7.72, 7.28 (each 2H, d, J=8.3 Hz), 5.68–5.83 (1H, m), 5.21–5.31 (2H, m), 4.09 (2H, s), 3.81 (2H, d, J=6.6 Hz), 2,41 (3H, s), −0.02 (9H, s); ^{13}C NMR δ 143.3, 136.1, 131.9, 129.5, 127.7, 119.8, 97.7, 90.9, 48.8, 37.6, 36.7, 21.5, −0.5; MS m/z 321 (M^+); high-resolution mass m/z calcd for $C_{16}H_{23}NO_2SSi$ (M^+) 321.1219 found: 321.1222.

Trimethylsilylphenylacetylene (3b). Oil; ^{1}H NMR δ 7.48–7.52 (2H, m), 7.29–7.33 (3H, m), 0.29 (9H, s); MS m/z 174 (M^+); high-resolution mass m/z calcd for $C_{11}H_{14}Si$ (M^+) 174.0865, found: 174.0865.

***N*-(3,3-Dimethoxyethyl)-*N*-[3-(trimethylsilyl)-2-propynyl]-tosylamide (4b).** Mp 86–87°C; ^{1}H NMR δ 7.66, 7.21 (each 2H, d, J=8.3 Hz), 4.49 (1H, t, J=5.6 Hz), 4.19 (2H, s), 3.33 (6H, s), 3.20 (2H, d, J=5.6 Hz), 2.33 (3H, s), −0.10 (9H, s); ^{13}C NMR δ 143.0, 135.8, 120.2, 127.6, 103.8, 98.2, 90.0, 54.1, 47.0, 38.6, 21.1, −0.8; MS m/z 383 (M^+); high-resolution mass m/z calcd for $C_{19}H_{29}O_4NSSi$ (M^+) 383.1592, found: 383.1587.

***N*-(2-Iodoethyl)-*N*-[3-(trimethylsilyl)-2-propynyl]tosylamide (5b).** Mp 87–88°C; ^{1}H NMR δ 7.78, 7.38 (each 2H, d, J=8.3 Hz), 4.20 (2H, s), 3.59, 3.57 (each 2H, t, J=7.8 Hz), 2.49 (3H, s), 0.10 (9H, s); ^{13}C NMR δ 143.4, 135.2, 129.4, 127.3, 97.5, 91.0, 48.9, 37.9, 21.2, 1.3, −0.7; MS m/z 435 (M^+); high-resolution mass m/z calcd for $C_{15}H_{22}O_2INSSi$ (M^+) 435.0177, found: 435.0185.

1-Trimethylsilyl-2-triphenylsilylacetylene (6b). Mp 67–68°C; ^{1}H NMR δ 7.80–7.92 (10H, m), 7.45–7.60 (15H, m), 0.45 (9H, s); ^{13}C NMR δ 135.5, 133.4, 128.8, 127.9, 119.5, 108.1, −0.2; MS m/z 356 (M^+); high-resolution mass m/z calcd for $C_{23}H_{24}Si_2$ (M^+) 356.1417, found: 356.1417

***N*-(2-Propynyl)-*N*-[2-(trimethylsilyloxy)ethyl]tosylamide (7b).** Oil; ^{1}H NMR δ 7.73, 7.28 (each 2H, d, J=8.3 Hz), 4.22 (2H, d, J=2.3 Hz), 3.78, 3.31 (each 2H, t, J=5.9 Hz), 2.41 (3H, s), 2.09 (2H, t, J=2.3 Hz), 0.11 (9H, s); ^{13}C NMR δ 143.3, 135.9, 129.3, 127.4, 73.8, 73.5, 61.8, 48.1, 38.0, 21.3, −0.8; MS m/z 325 (M^+); high-resolution mass m/z calcd for $C_{15}H_{23}O_3NSSi$ (M^+) 325.1163, found: 325.1168.

***N*-[2-(Trimethylsilyloxy)ethyl]-*N*-[3-(trimethylsilyl)-2-propynyl]tosylamide (7c).** Oil; ^{1}H NMR δ 7.67, 7.22 (each 2H, d, J=8.3 Hz), 4.17 (2H, s), 3.73, 2.44 (each 2H, t, J=6.1 Hz), 2.34 (3H, s), 0.06, −0.05 (each 9H, s); ^{13}C NMR δ 142.3, 136.0, 129.4, 127.7, 98.5, 90.2, 61.4, 48.0, 38.9, 21.2, 0.4, −0.8; MS m/z 397 (M^+); high-resolution mass m/z calcd for $C_{18}H_{31}O_3NSSi_2$ (M^+) 397.1560, found: 397.1563.

Dimethyl 2,2-Bis-[3-(trimethylsilyl)-2-propynyl]malonate (8b). Mp 50°C; ^{1}H NMR δ 3.70 (6H, s), 2.93 (4H, s), 0.08 (9H, s); ^{13}C NMR δ 168.5, 100.8, 87.8, 56.5, 52.4, 23.7, −0.4; MS m/z 352 (M^+); high-resolution mass m/z calcd for $C_{17}H_{28}O_4Si_2$ (M^+) 352.1521, found: 352.1526.

Dimethyl 2-[3-(trimethylsilyl)-2-propynyl]malonate (9b). Oil; ^{1}H NMR δ 3.73 (6H, s), 3.56 (1H, t, J=7.9 Hz), 2.76 (2H, d, J=7.9 Hz), 0.09 (9H, s); ^{13}C NMR δ 168.2, 102.0, 87.1, 52.6, 51.1, 18.8, −0.2; MS m/z 242 (M^+); high-resolution mass m/z calcd for $C_{11}H_{18}O_4Si$ (M^+) 242.0980, found: 242.0974.

4-(Trimethylsilylethynyl)aniline (10b). Mp 83–84°C; ^{1}H NMR δ 7.27, 6.55 (each 2H, d, J=8.6 Hz), 3.76 (2H, brs), 0.24 (9H, s); ^{13}C NMR δ 146.8, 133.1, 114.3, 111.9, 106.2, 91.3, 0.0; MS m/z 189 (M^+); high-resolution mass m/z calcd for $C_{11}H_{15}NSi$ (M^+) 189.0981, found: 189.0974.

***N*-*tert*-Butoxycarbonyl-4-(trimethylsilylethynyl)aniline (11b).** Mp 160–161°C; ^{1}H NMR δ 7.38, 7.30 (each 2H, d, J=8.6 Hz), 6.65 (1H, s), 1.50, 0.23 (each 9H, s); ^{13}C NMR δ 152.4, 138.7, 132.8, 117.8, 117.3, 105.1, 93.1, 80.8, 28.7, 0.0; MS m/z 289 (M^+); high-resolution mass m/z calcd for $C_{16}H_{23}O_2NSi$ (M^+) 289.1500, found: 289.1498.

***N*-(2-Oxoethyl)-*N*-[3-(trimethylsilyl)-2-propynyl]tosylamide (12b).** Oil; ^{1}H NMR δ 9.65 (1H, d, J=1 Hz),

7.69, 7.30 (each 2H, d, J=8.3 Hz), 4.17 (2H, s), 3.88 (2H, d, J=1 Hz), 2.41 (3H, s), 0.00 (9H, s); ^{13}C NMR δ 197.6, 144.2, 134.8, 128.8, 127.7, 97.1, 92.3, 50.9, 39.7, 21.5, −0.5; MS m/z 323 (M^+); high-resolution mass m/z calcd for $C_{15}H_{21}O_3NSSi$ (M^+) 323.1010, found: 323.1011.

***N*-[3,3,3-trifluoro-2-(trimethylsilyloxy)propyl]-*N*-(2-propynyl)tosylamide (12c).** Mp 88–89°C; ^{1}H NMR δ 7.73, 7.27 (each 2H, d, J=8.3 Hz), 4.20–4.40 (1H, m), 4.23 (2H, d, J=2.5 Hz), 3.30–3.50 (2H, m), 2.42 (3H, s), 2.11 (1H, t, J=2.5 Hz), 0.00 (9H, s); ^{13}C NMR δ 144.3, 134.7, 129.8, 127.8, 97.4, 91.9, 69.3 (q, J=30.6 Hz), 54.7, 46.7, 39.8, 21.5, −0.6; MS m/z 393 (M^+); high-resolution mass m/z calcd for $C_{16}H_{22}F_3O_3NSSi$ (M^+) 393.1041, found: 393.1042.

***N*-[3,3,3-trifluoro-2-(trimethylsilyloxy)propyl]-*N*-[3-(trimethylsilyl)-2-propynyl]tosylamide (12d).** Oil; ^{1}H NMR δ 7.71, 7.27 (each 2H, d, J=8.3 Hz), 4.35 (1H, d, J=18.7 Hz), 4.26–4.41 (1H, m), 4.04 (1H, d, J=18.7 Hz), 3.13–3.46 (2H, m), 2.39 (3H, s), −0.04, −0.05 (each 9H, s); MS m/z 465 (M^+); high-resolution mass m/z calcd for $C_{19}H_{30}F_3O_3NSSi_2$ (M^+) 465.1431, found: 465.1437.

***N*-(2-Oxopropyl)-*N*-[3-(trimethylsilyl)-2-propynyl]tosylamide (13b).** Mp 84–85°C; ^{1}H NMR δ 7.70, 7.30 (each 2H, d, J=8.3 Hz), 4.16 (2H, s), 3.97 (2H, s), 3.42(2H, s), 2.23 (3H, s), 0.01 (9H, s); ^{13}C NMR δ 203.3, 143.8, 135.0, 129.6, 127.5, 97.2, 91.7, 55.4, 38.9, 27.0, 21.4, −0.6; MS m/z 337 (M^+); high-resolution mass m/z calcd for $C_{16}H_{23}O_3NSSi$ (M^+) 337.1162, found: 337.1168.

***N*-[2-trifluoromethyl-2-(trimethylsilyloxy)propyl]-*N*-[3-(trimethylsilyl)-2-propynyl]tosylamide (13c).** Mp 60–61°C; ^{1}H NMR δ 7.75, 7.33 (each 2H, d, J=8.3 Hz), 4.45 (1H, d, J=18.7 Hz), 4.26 (1H, d, J=18.7 Hz), 3.52, 3.44 (each 1H, d, J=14.4 Hz), 2.46, 1.59 (each 3H, s), 0.22, 0.01 (each 9H, s); ^{13}C NMR δ 143.6, 136.0, 129.6, 127.9, 127.5, 97.8, 91.2, 77.0 (q, J=28.1 Hz), 50.3, 39.7, 21.5, 19.7, 1.8, −0.5; MS m/z 479 (M^+); high-resolution mass m/z calcd for $C_{20}H_{32}F_3O_3NSSi_2$ (M^+) 479.1591, found: 479.1594.

***N*-(2-Propenyl)-*N*-[3-(triethylsilyl)-2-propynyl]tosylamide (2c).** Oil; ^{1}H NMR δ 7.70, 7.25 (each 2H, d, J=8.2 Hz), 5.68–5.83 (1H, m), 5.19–5.29 (2H, m), 4.12 (2H, s), 3.82 (2H, d, J=6.3 Hz), 2.38 (3H, s), 0.82 (9H, t, J=7.8 Hz), 0.40 (6H, q, J=7.8 Hz); ^{13}C NMR δ 143.1, 135.9, 131.7, 129.3, 127.4, 120.0, 98.6, 88.1, 48.6, 36.5, 21.2, 7.0, 3.8; MS m/z 363 (M^+); high-resolution mass m/z calcd for $C_{19}H_{29}O_3NSi$ (M^+) 363.1692, found: 363.1688.

***N*-(2-Propenyl)-*N*-[3-(tributylstannanyl)-2-propynyl]-tosylamide (2d).** Mp 59–60°C; ^{1}H NMR δ 7.75, 7.27 (each 2H, d, J=8.5 Hz), 5.66–5.81 (1H, m), 5.21–5.31 (2H, m), 4.14 (2H, s), 3.84 (2H, d, J=6.6 Hz), 2,42 (3H, s), 1.16–1.64 (15H, m), 0.84–0.94 (12H, m); ^{13}C NMR δ 162.4, 143.6, 136.1, 131.9, 129.5, 127.8, 120.0, 73.7, 49.0, 35.8, 27.9, 27.2, 21.5, 16.7, 12.7; MS m/z 537 (M^+); high-resolution mass m/z calcd for $C_{25}H_{41}NO_2SSn$ (M^+) 537.1891, found: 537.1880.

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