JOC The Journal of Organic Chemistry

Article

pubs.acs.org/joc

Anti Carbocyanative Cyclization of Enynes under Nickel Catalysis

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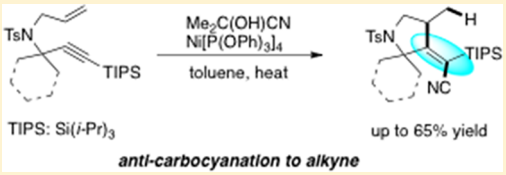
Supporting Information

ABSTRACT: *Anti* carbocyanative cyclization using 1,6-enynes under nickel catalysis is described. This reaction is triggered by hydronickelation to alkenes followed by carbometalation. Steric repulsion caused by the bulky substituents on alkynes promotes isomerization of the carbon−carbon double bond geometry in an organonickel intermediate to introduce both alkyl and cyano groups in an *anti* fashion.



INTRODUCTION

A cyano group is a synthetic equivalent of carbonyl and related functionalities, and its introduction into organic molecules, particularly by transition metal catalysis, has been a major challenge in synthetic organic chemistry. One of the most fundamental protocols for its introduction has been catalytic hydrocyanation to nonactivated carbon−carbon multiple bonds[1,2] using HCN with nickel catalysts[3] (Chart 1, eq 1). Since it was reported that C−CN bonds are easily cleaved[4] and suitable for cross coupling reactions,[5] carbocyanation through the cleavage of C−CN bonds by nickel complexes has been one of the most powerful tools for the introduction of a cyano functionality (eq 2).[6] The hydro- and carbometalation occur via migratory insertion so that the stereochemistry of the products is always controlled to be syn (eq 1 and 2). Another carbocyanation is Pd(II)-catalyzed 1,2-dicyanation through a unique nucleophilic cyanation (cyanopalladation) (eq 3).[7,8] This cyanation protocol has been quite useful for cyclizations[8a,9] and [4+2] cycloaddition.[10] Despite extensive investigations to identify cyanation protocols under transition metal catalysis, no examples that install both alkyl and cyano components in an *anti* fashion such as eq 4 have been reported to date. In this paper, we describe an alternative method for a regio- and stereoselective hydro- and carbometalation sequence that enables unprecedented *anti* carbocyanation through cyclization (eq 5).

RESULTS AND DISCUSSION

Initially, we chose enyne **1a** to study carbocyanative cyclization using acetone cyanohydrin (AC) as an inexpensive and easy-to-handle HCN source, in the presence of triphenylphosphite (1.2 equiv) and $Ni[P(OPh_3)]_4$ (10 mol %) at 150 °C (Table 1). The reaction proceeded to give a mixture of 5- and 6-*exo* products in respective yields of 32% and 3%. Careful investigation revealed that the side products were **4a** and **5a**, which could be obtained in 26% and 13% yields, respectively, by hydrocyanation of a C−C triple bond of **1a** (entry 1). Products such as **6a** were not observed at all. These results indicate that cyclization could be triggered by the hydronickelation of olefin, and its regioselectivity determines the ring size of the products. Hydronickelation of a C−C triple bond also occurred, but the resulting intermediate would be unsuitable for sequential carbometalative cyclization. This cyclization reaction was not affected by an external ligand (entry 2), and a higher loading of AC (20 equiv) improved the yields of **2a** (to 52%) and **3a** (to 24%) (entry 3). These results are summarized in Table 1.

To suppress the formation of simple hydrocyanation products **4a** and **5a**, bulkier TIPS and TBDPS groups were installed on C−C triple bonds (Table 2). As expected, their bulkiness prevented alkyne hydrocyanation and exclusive cyclization products were obtained with a remarkable improvement of the **2**/**3** ratio when **1b** was used (entry 1);however, both the yield and ratio decreased with **1c** (entry 2). These results suggest that a bulkier silyl group is more favored to reduce simple hydrocyanation that would give noncyclized products. The structures of the 5-*exo* products *Z*-**2b** and *E*-**2c** were confirmed by X-ray crystallographic analysis.[11]

The effect of the substituent at propargyl position was next examined, and this was shown to significantly influence the efficiency of cyclization. For example, **1d** was transformed exclusively to the corresponding 5-*exo* adduct **2d** in 32% yield (Table 3, entry 1). Its structure, including its stereochemistry, was established to be *E*-form by X-ray crystallographic analysis. This result indicates the C−C bonds that are newly created through carbocyanation are oriented in an *anti* fashion. To the best of our knowledge, this is the first example of *anti* carbocyanation to nonactivated C−C triple bonds. Because the addition of triphenylphosphite (1.2 equiv) slightly improved the yield of *E*-**2d** (entry 2), the survey was continued under these conditions. A reduced amount of AC (10 equiv) gave a lower conversion to **2d** and a significant amount of side products **7** through C−N bond cleavage (entry 3). The reaction was next investigated with a higher loading of AC (40 equiv), and *E*-**2d** was obtained in 65% yield as a sole product (entry 4). A methyl group at the allylic position (**1e**) reduced the efficiency of the cyclization, and *E*-**2e** was obtained in 37% yield (entry 5).

Received: February 20, 2013
Published: April 9, 2013

Chart 1

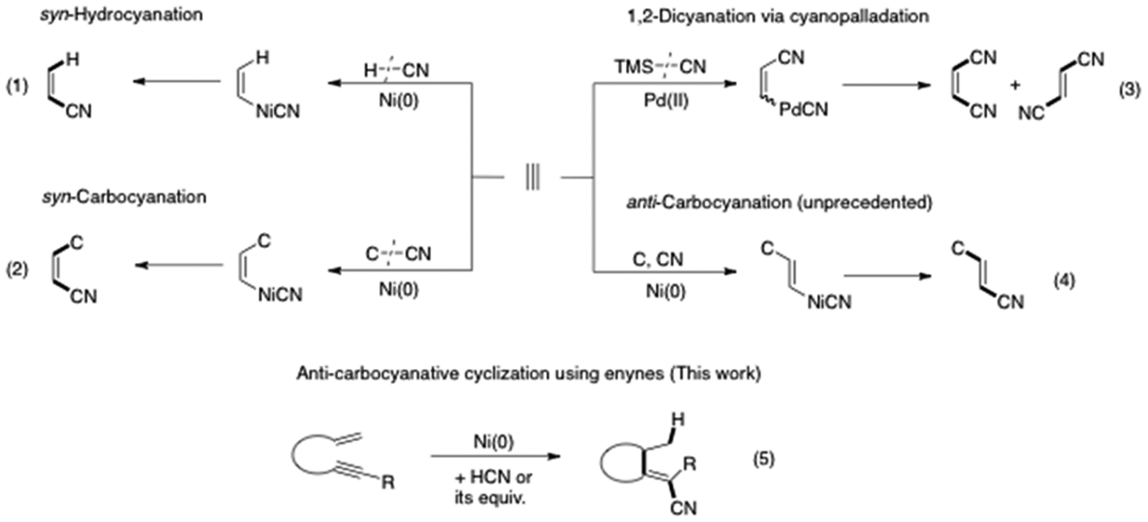
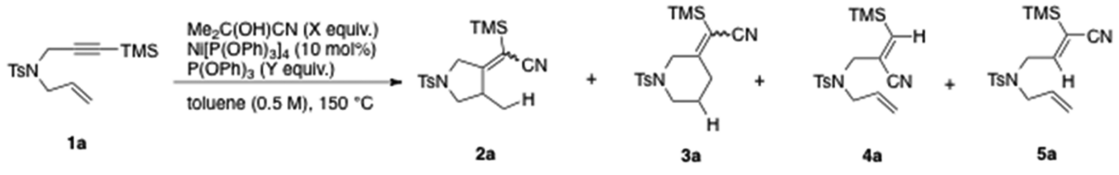
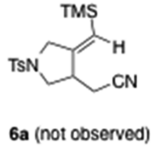


Table 1. Condition Survey Using 1a[a]

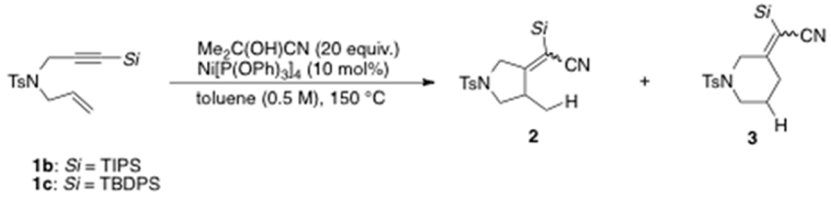


entry	X	Y	time (h)	2a (%)[a] (Z:E)	3a (%)[a] (Z:E)	4a (%)	5a (%)	recov. 1a (%)
1	5	1.2	11	32 (3:1)	3 (2:1)	26	13	26
2	5	0	7	27 (3.5:1)	12 (Z only)	13	3	33
3	20	0	3	52 (4.6:1)	24 (1.8:1)	9	3	-

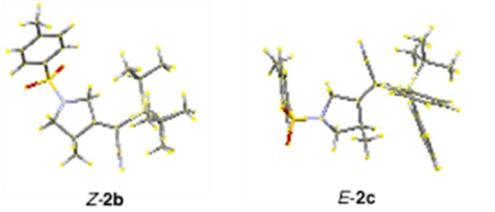


[a]Yields estimated by isolation of both stereoisomers.

Table 2. Substituent Effect



entry	substrate	time (h)	2 (%) (Z:E)	3 (%) (Z:E)
1	1b	4	2b: 60[a] (2:1)	3b: 11[b] (2.7:1)
2	1c	15	2c: 40[b] (1:1.2)	3c: 9[b] (2:1)



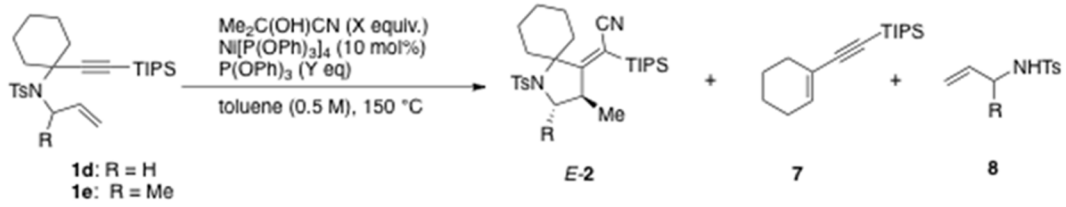
[a]Both isomers are isolated. [b]Inseparable stereoisomers.

To confirm the role of steric bulk around C−C triple bonds, **1f**, which has a TMS group instead, was examined next (Scheme 1). When the reaction was carried out for 15 h, major products were assigned to be *E*- and *Z*-**2f-H** along with a small amount of **2f**. A shorter reaction time was effective for reducing the above desilylated products to give an inseparable mixture of *E*- and *Z*-**2f** in 34% yield. This result suggests that both a bulky and stable functionality around the C−C triple bond is essential for *anti* carbocyanation.

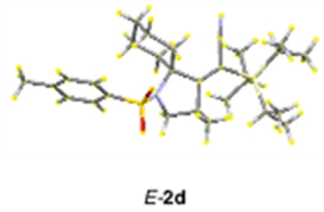
On the basis of these observations, a plausible catalytic pathway that reasonably explains the regio- and stereochemistry in the formation of **2** is shown in Scheme 2. The initial step is the formation of Ni(II) from AC or HCN and Ni(0) followed by regioselective hydronickelation to olefin. Bulky substituents around the C−C triple bonds would be key functionalities for

dx.doi.org/10.1021/jo400342y | J. Org. Chem. 2013, 78, 4366−4372

Table 3. Condition Survey Using TIPS Alkyne

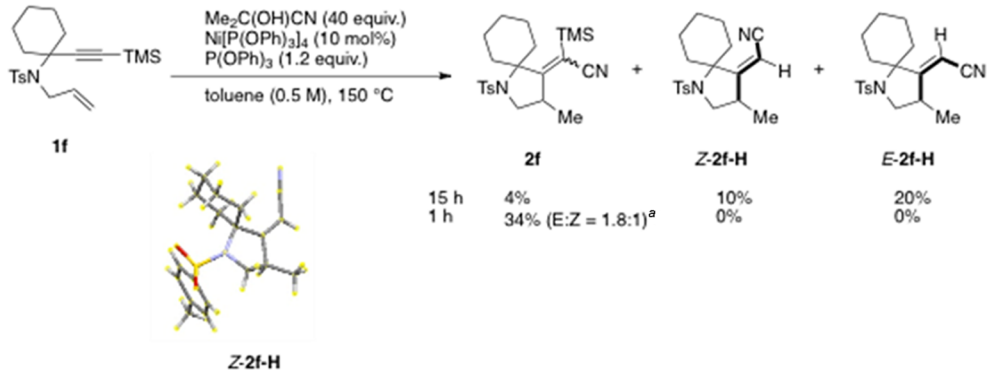


entry	1	X	Y	time (h)	*E*-**2** (%)[a]	**7** (%)[a]	**8** (%)[a]	recov. **1** (%)[a]
1	**1d**	20	0	23	**2d**: 32	trace	trace	36
2	**1d**	20	1.2	24	**2d**: 43	trace	4	30
3	**1d**	10	1.2	8	**2d**: 13	47	44	23
4	**1d**	40	1.2	24	**2d**: 65	trace	trace	13
5	**1e**	40	1.2	18	**2e**: 37	27	37	19



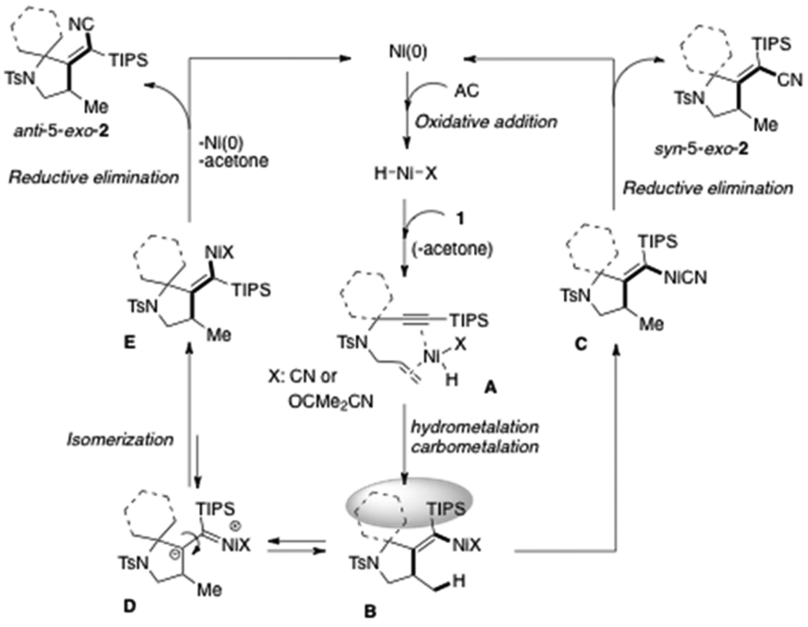
[a]Isolated yield.

Scheme 1. Reaction Using 1f



[a]Determined by NMR analysis.

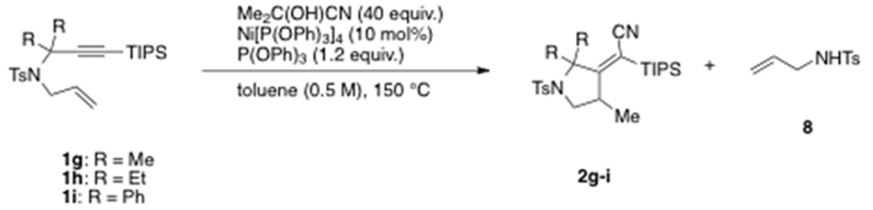
Scheme 2. Plausible Catalytic Pathway



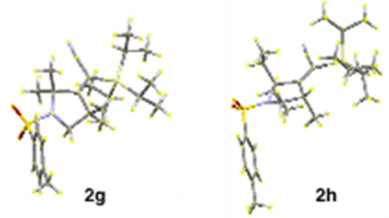
fixing both multiple C−C bonds as a bidentate ligand to the Ni center in **A** for smooth cyclization. This result suggests that the intermediate **A** would be a key structure for cyclization. Sequential 5-*exo* cyclization via carbometalation would give **B**, which is then converted to *syn*-5-*exo*-**2** through reductive elimination from **C**. When significant steric repulsion between

dx.doi.org/10.1021/jo400342y | J. Org. Chem. 2013, 78, 4366−4372

Table 4. Substrate Scope for *Anti* Carbocyanation

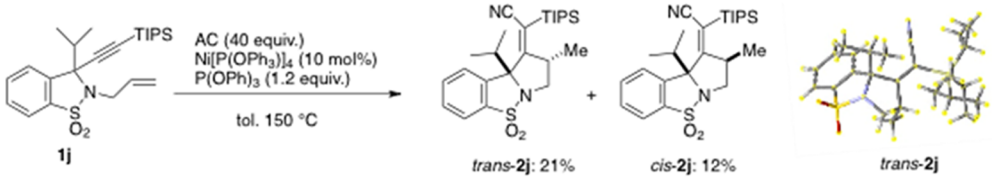


entry	substrate	time (h)	2 (%)[a]	others (%)[a]
1	**1g**	13	**2g**: 29	**8**: 10, **1g**: 38
2	**1h**	17	**2h**: 31	**1h**: 21
3	**1i**	19	**2i**: 7	**8**: 47, **1i**: 5



[a]Isolated yield.

Scheme 3. Reaction of 1j



Yields are estimated by NMR analysis.

two substituents is observed in **B**, isomerization would be promoted by the formation of a nickel−carbene intermediate[12] **D** and the resulting C−C σ-bond rotation would convert the double bond geometry to *E*-form, which gives *anti*-5-*exo*-**2** as an exclusive product. Isomerization of C−C double bonds in alkenyl metal species (Pd,[13a] Ir[13b]) is also strongly influenced by the steric bulk of the substituents.

The substrate scope is shown in Table 4. When **1g** and **1h** were subjected to the optimized conditions, *anti*-5-*exo*-**2g** and **2h** were obtained in respective yields of 29% and 31% without any other cyclized products (entries 1 and 2). In the case of **1i**, a C−N bond cleavage mainly occurred to give **8** in 47% yield, and **2i** was obtained in only 7% yield (entry 3).

In the case of saccharin derivative such as **1j**, the enyne moiety was also suitable for cyanative cyclization to give **2j** as a diastereomixture (Scheme 3). The major product was assigned to be *trans* on the basis of X-ray crystallography.

■ CONCLUSION

We have realized an unprecedented *anti* carbocyanation to nonactivated C−C triple bonds under nickel catalysis. Bulky substituents are essential for causing steric repulsion after cyclization, and this effect would control the geometry of the C−C double bond via a key nickel−carbene intermediate. These new results may contribute to the development of catalytic cyanation protocols, and their further application in organic synthesis for the preparation of useful molecules is currently underway.

■ EXPERIMENTAL SECTION

General Remarks. All reactions were performed with dry solvents, and reagents were purified by the usual methods. Reactions were monitored by thin-layer chromatography carried out on 0.25 mm. Column chromatography was performed with silica gel. IR spectra were recorded on a Fourier transform spectrophotometer. NMR spectra were recorded at 400 and 600 MHz for ^{1}H NMR and at 100 and 150 MHz for ^{13}C NMR, with calibration using residual undeuterated solvent as an internal reference. HRMS spectra were obtained using an ESI mass spectrometer.

Typical Procedure for Representative Cyanative Cyclization (synthesis of 2d). A solution of **1f** (72.0 mg, 0.15 mmol), $P(OPh)_3$ (55.4 mg, 0.18 mmol), $Ni[P(OPh)_3]_4$ (49.5 mg, 0.015 mmol, 10 mol %), and acetone cyanohydrin (0.55 mL, 6.0 mmol) in toluene (0.3 mL) was heated for 24 h at 150 °C under an argon atmosphere. The reaction was quenched by a mixture charged on a silica gel to be purified by column chromatography (hexane:AcOEt = 5:1). **2d** was obtained as a colorless solid (48.1 mg, 0.096 mmol, 65%, mp 151−152 °C).

(*Z*)-2-(4-Methyl-1-tosylpyrrolidin-3-ylidene)-2-(trimethylsilyl)acetonitrile (*Z*-2a). White solid (20.8 mg, 20%): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.70 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 4.12 (d, J = 16.8 Hz, 1H), 3.69 (d, J = 16.8 Hz, 1H), 3.23 (d, J = 9.0 Hz, 1H), 3.19−3.12 (m, 2H), 2.45 (s, 3H), 1.28 (d, J = 7.2 Hz, 3H), 0.25 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 175.2, 144.4, 131.8, 130.0, 127.9, 118.2, 107.0, 53.9, 51.8, 41.7, 21.7, 19.0, −1.3; IR (ATR) ν 2197, 1605, 1348, 1161 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{24}N_2NaO_2SSi$ $[M + Na]^+$ 371.1225, found 371.1228; mp 125−127 °C.

(*E*)-2-(4-Methyl-1-tosylpyrrolidin-3-ylidene)-2-(trimethylsilyl)acetonitrile (*E*-2a). Yellow oil (7.0 mg, 10%): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.72 (d, J = 7.8 Hz, 2H), 7.36 (d, J = 7.8 Hz, 2H), 4.35 (d, J = 17.4 Hz, 1H), 3.82 (d, J = 17.4 Hz, 1H), 3.40 (d, J = 9.6 Hz, 1H), 3.10 (dd, J = 5.4, 9.6 Hz, 1H), 2.93 (quin, J = 5.4 Hz, 1H), 2.45 (s, 3H), 1.21 (d, J = 5.4 Hz, 3H), 0.26 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 175.2, 144.2, 132.5, 130.0, 128.0, 118.2, 117.0, 55.1, 54.0, 38.3, 21.7, 20.8, −0.7; IR (ATR) ν 2962, 2159, 1452, 1348, 1160 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{24}N_2NaO_2SSi$ $[M + Na]^+$ 371.1225, found 371.1228.

(*Z*)-2-(1-Tosylpiperidin-3-ylidene)-2-(trimethylsilyl)-acetonitrile (*Z*-3a). Yellow oil (10.3 mg, 12%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.63 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 3.68 (s, 2H), 3.10 (dd, J = 5.6, 5.6 Hz, 2H), 2.56 (dd, J = 6.0, 6.0 Hz, 2H), 2.45

dx.doi.org/10.1021/jo400342y | J. Org. Chem. 2013, 78, 4366−4372

(s, 3H), 1.82 (tt, J = 5.6, 6.0 Hz, 2H), 0.36 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.3, 144.2, 132.6, 130.0, 128.0, 127.8, 119.0, 111.7, 50.5, 46.0, 34.0, 25.2, 21.6, −0.3; IR (ATR) ν 2957, 2181, 1598, 1443, 1348, 1161 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{24}N_2NaO_2SSi$ [M + Na]$^+$ 371.1225, found 371.1227.

(*E*)-2-(1-Tosylpiperidin-3-ylidene)-2-(trimethylsilyl)-acetonitrile (*E*-3a). White solid (6.1 mg, 7%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.71 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 3.97 (s, 2H), 3.26 (dd, J = 5.6, 6.0 Hz, 2H), 2.44 (s, 3H), 2.32 (dd, J = 6.4, 6.4 Hz, 2H), 1.75−1.69 (m, 2H), 0.23 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.1, 143.9, 134.0, 129.9, 127.9, 118.2, 110.8, 52.1, 45.7, 31.8, 24.8, 21.6, −0.5; IR (ATR) ν 2957, 2198, 1596, 1443, 1349, 1159 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{24}N_2NaO_2SSi$ [M + Na]$^+$ 371.1225, found 371.1227; mp 87−93 °C.

(*E*)-*N*-Allyl-*N*-(2-cyano-3-(trimethylsilyl)allyl)-4-methylbenzenesulfonamide (4a). Yellow oil (22.9 mg, 26%): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.76 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 6.66 (br, 1H), 5.78−5.72 (m, 1H), 5.23−5.20 (m, 2H), 4.04 (s, 2H), 3.90 (d, J = 7.2 Hz, 2H), 2.43 (s, 3H), 0.21 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 151.6, 142.7, 135.3, 131.3, 128.5, 126.4, 124.7, 118.8, 117.0, 49.7, 46.2, 20.4, −1.9; IR (ATR) ν 2203, 1589, 1161 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{24}N_2NaO_2SSi$ [M + Na]$^+$ 371.1225, found 371.1223.

(*Z*)-*N*-Allyl-*N*-(3-cyano-3-(trimethylsilyl)allyl)-4-methylbenzenesulfonamide (5a). Brown oil (11.6 mg, 13%): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.66 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 6.76 (t, J = 6.6 Hz, 1H), 5.66 (ddt, J = 6.0, 10.8, 17.4 Hz, 1H), 5.21 (d, J = 10.8 Hz, 1H), 5.17 (d, J = 17.4 Hz, 1H), 4.01 (d, J = 6.0 Hz, 2H), 3.79 (d, J = 6.6 Hz, 2H), 2.44 (s, 3H), 0.28 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 159.2, 150.5, 144.1, 136.8, 132.5, 127.2, 125.7, 119.9, 117.8, 50.7, 47.6, 21.7, −0.8; IR (ATR) ν 3065, 2203, 1488, 1161 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{24}N_2NaO_2SSi$ [M + Na]$^+$ 371.1225, found 371.1228.

(*Z*)-2-(4-Methyl-1-tosylpyrrolidin-3-ylidene)-2-(triisopropylsilyl)acetonitrile (*Z*-2b). White solid (40.8 mg, 40%): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.68 (d, J = 7.8 Hz, 2H), 7.34 (d, J = 7.8 Hz, 2H), 4.18 (dd, J = 0.8, 16.8 Hz, 1H), 3.70 (d, J = 16.8 Hz, 1H), 3.31−3.26 (m, 2H), 3.05 (dd, J = 7.2, 9.6 Hz, 1H), 2.43 (s, 3H), 1.30 (tt, J = 7.2, 7.8 Hz, 3H), 1.29 (d, J = 6.6 Hz, 3H), 1.08 (d, J = 7.8 Hz, 9H), 1.05 (d, J = 7.2 Hz, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 177.6, 144.4, 142.7, 129.9, 128.0, 119.2, 104.0, 53.7, 52.1, 42.5, 21.7, 19.5, 18.48, 18.42. 12.0; IR (ATR) ν 2213, 1647, 1597, 1349, 1160 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{37}N_2O_2SSi$ [M + H]$^+$ 433.2345, found 433.2353; mp 136−137 °C. CCDC no. 857691.

(*E*)-2-(4-Methyl-1-tosylpyrrolidin-3-ylidene)-2-(triisopropylsilyl)acetonitrile (*E*-2b). White solid (20.4 mg, 20%): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.73 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 4.38 (d, J = 16.2 Hz, 1H), 3.98 (d, J = 16.2 Hz, 1H), 3.45 (d, J = 10.2 Hz, 1H), 3.08 (dd, J = 6.6, 10.2 Hz, 1H), 2.88 (dd, J = 6.6, 6.6 Hz, 1H), 2.43 (s, 3H), 1.29 (q, J = 7.2 Hz, 3H), 1.18 (q, J = 6.6 Hz, 3H), 1.07 (d, J = 7.2 Hz, 18H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 176.6, 144.1, 132.9, 130.0, 128.0, 119.3, 103.7, 55.3, 53.7, 39.0, 21.7, 20.5, 18.7, 12.2; IR (ATR) ν 2188, 1636, 1558, 1339 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{36}N_2NaO_2SSi$ [M + Na]$^+$ 455.2164, found 455.2179; mp 84−91 °C.

(*Z*)-2-(1-Tosylpiperidin-3-ylidene)-2-(triisopropylsilyl)-acetonitrile (*Z*-3b). Colorless oil (7.8 mg, 9%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.60 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 3.58 (s, 2H), 3.04 (dd, J = 5.6, 5.6 Hz, 1H), 2.63 (dd, J = 6.4, 6,4 Hz, 2H), 2.44 (s, 3H), 1.84 (tt, J = 5.6, 6.4 Hz, 2H), 1.46 (q, J = 7.2 Hz, 3H), 1.14 (d, J = 7.2 Hz, 18H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.8, 144.3, 131.8, 130.0, 128.1, 119.9, 108.3, 51.5, 46.3, 34.3, 25.2, 21.7, 18.7, 12.7; IR (ATR) ν 1647, 1457, 1166 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{36}N_2NaO_2SSi$ [M + Na]$^+$ 455.2164, found 455.2168.

(*E*)-2-(1-Tosylpiperidin-3-ylidene)-2-(triisopropylsilyl)-acetonitrile (*E*-3b). Brown oil (2.7 mg, 3%): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.72 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 4.07 (s, 2H), 3.28 (dd, J = 6.0, 6.0 Hz, 1H), 2.41 (s, 3H), 2.33 (dd, J = 6.0, 6.0 Hz, 2H), 1.73 (tt, J = 6.0, 6.0 Hz, 2H), 1.34 (q, J = 7.2 Hz, 3H), 1.06 (d, J = 7.2 Hz, 18H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 166.9, 143.9, 134.1, 130.0, 127.8, 119.0, 107.2, 52.3, 45.6, 32.7, 24.9, 21.6, 18.7, 12.7; IR (ATR) ν 2238, 1461 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{36}N_2NaO_2SSi$ [M + Na]$^+$ 455.2164, found 455.2170.

(*Z*)-2-(*tert*-Butyldiphenylsilyl)-2-(4-methyl-1-tosylpyrrolidin-3-ylidene)acetonitrile (*Z*-2c). Yellow oil (30.0 mg, 20%): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.70−7.10 (m, 14H), 3.34−3.31 (m, 1H), 3.24 (d, J = 18 Hz, 1H), 3.17 (d, J = 9.6 Hz, 1H), 2.85 (dd, J = 9.6, 6.0 Hz, 1H), 2.68 (d, J = 18 Hz, 1H), 2.41 (s, 3H), 1.36 (d, J = 7.8 Hz, 3H), 1.13 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 182.0, 143.9, 135.89, 135.83, 131.3, 131.04, 130.97, 130.6, 130.4, 129.7, 128.6, 128.5, 127.9, 119.5, 101.6, 53.6, 52.6, 42.3, 28.2, 21.6, 19.2, 18.9; IR (ATR) ν 2923, 2853, 2200, 1669, 1577, 1464, 1351, 1161 cm^{-1}; HRMS (ESI) m/z calcd for $C_{30}H_{34}N_2NaO_2SSi$ [M + Na]$^+$ 537.2008, found 537.2027.

(*E*)-2-(*tert*-Butyldiphenylsilyl)-2-(4-methyl-1-tosylpyrrolidin-3-ylidene)acetonitrile (*E*-2c). White solid (24.8 mg, 20%): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.76−7.24 (m, 14H), 4.41 (d, J = 17.4 Hz, 1H), 4.09 (d, J = 17.4 Hz, 1H), 3.05 (d, J = 9.6 Hz, 1H), 2.80 (dd, J = 5.4, 9.6 Hz, 1H), 2.46 (s, 3H), 2.12−2.10 (m, 1H), 1.11 (s, 9H), 0.37 (d, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 181.1, 144.1, 135.8, 130.4, 130.0, 128.3, 128.3, 127.9, 119.6, 102.1, 55.0, 54.2, 38.4, 27.6, 27.0, 26.3, 21.7, 18.8; IR (ATR) ν 3047, 2240, 1541 cm^{-1}; HRMS (ESI) m/z calcd for $C_{30}H_{34}N_2NaO_2SSi$ [M + Na]$^+$ 537.2008, found 537.1997; mp 213−215 °C. CCDC no. 858856.

(*Z*)-2-(*tert*-Butyldiphenylsilyl)-2-(1-tosylpiperidin-3-ylidene)-acetonitrile (*Z*-3c). Yellow oil (6.5 mg, 6%): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.72 (d, J = 7.8 Hz, 2H), 7.54−7.32 (m, 8H), 7.10 (d, J = 8.4 Hz, 2H), 6.98 (d, J = 8.4 Hz, 2H), 2.97 (s, 2H), 2.87 (dd, J = 5.4, 5.4 Hz, 2H), 2.69 (dd, J = 6.0, 6.6 Hz, 2H), 2.36 (s, 3H), 1.85 (dddd, J = 5.4, 5.4, 6.0, 6.6 Hz, 2H), 1.20 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 170.2, 143.7, 135.9, 135.5, 132.2, 130.0, 129.4, 128.3, 127.8, 120.1, 106.5, 52.2, 45.6, 33.7, 27.4, 24.6, 21.6, 19.0; IR (ATR) ν 2857, 2197, 1684, 1558, 1507, 1458, 1353, 1166 cm^{-1}; HRMS (ESI) m/z calcd for $C_{30}H_{34}N_2NaO_2SSi$ [M + Na]$^+$ 537.2008, found 537.2008.

(*E*)-2-(*tert*-Butyldiphenylsilyl)-2-(1-tosylpiperidin-3-ylidene)-acetonitrile (*E*-3c). Yellow solid (3.6 mg, 3%): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.75 (d, J = 8.4 Hz, 2H), 7.62−7.38 (m, 4H), 7.40−7.34 (m, 6H), 4.14 (s, 2H), 3.10 (dd, J = 5.4, 6.0 Hz, 2H), 2.44 (s, 3H), 1.76 (dd, J = 6.0, 6.6 Hz, 2H), 1.13−1.10 (m, 11H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 170.8, 143.9, 135.8, 135.5, 132.3, 130.02, 129.96, 128.6, 128.5, 128.2, 128.0, 127.9, 119.4, 105.6, 52.0, 45.5, 33.2, 27.4, 26.9, 23.8, 21.7, 18.7; IR (ATR) ν 2931, 2859, 2202, 1577, 1428, 1352, 1165 cm^{-1}; HRMS (ESI) m/z calcd for $C_{30}H_{34}N_2NaO_2SSi$ [M + Na]$^+$ 537.2008, found 537.1997; mp 95−101 °C.

(*E*)-2-(3-Methyl-1-tosyl-1-azaspiro[4.5]decan-4-ylidene)-2-(triisopropylsilyl)acetonitrile (*E*-2d). White solid (48.1 mg, 65%): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.75 (d, J = 7.8 Hz, 2H), 7.28 (d, J = 7.8 Hz, 2H), 3.47 (d, J = 10.2 Hz, 1H), 3.32 (d, J = 4.8, 10.2 Hz, 1H), 2.79−2.75 (m, 1H), 2.65−2.59 (m, 1H), 2.41 (s, 3H), 2.38−2.20 (m, 2H), 1.90 (d, J = 14.4 Hz, 1H), 1.71−1.56 (m, 6H), 1.41−1.35 (m, 3H), 1.12 (d, J = 3.6 Hz, 9H), 1.11 (d, J = 3.6 Hz, 9H), 0.98 (d, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 190.5, 143.2, 139.2, 129.6, 127.2, 119.1, 100.8, 74.7, 53.8, 38.9, 34.7, 33.8, 22.4, 22.0, 21.7, 21.6, 20.2, 18.9, 12.7; IR (ATR) ν 2945, 2868, 2189, 1597, 1570, 1464, 1340, 1159 cm^{-1}; HRMS (ESI) m/z calcd for $C_{28}H_{45}N_2O_2SSi$ [M + H]$^+$ 501.2790, found 501.2963; mp 151−152 °C. CCDC no. 862635.

(*E*)-2-((2*R*,3*S*)-2,3-Dimethyl-1-tosyl-1-azaspiro[4.5]decan-4-ylidene)-2-(triisopropylsilyl)acetonitrile (*E*-2e). Brown oil (9.4 mg, 39%): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.79 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 3.84 (q, J = 7.2 Hz, 1H), 2.75 (dt, J = 4.8, 13.8 Hz, 1H), 2.58 (q, J = 7.2 Hz, 1H), 2.48−2.23 (m, 4H), 2.41 (s, 3H), 2.04−2.01 (m, 2H), 1.74−1.55 (m, 3H), 1.38 (tt, J = 7.2, 7.8 Hz, 3H), 1.28 (d, J = 7.2 Hz, 3H), 1.14 (d, J = 7.8 Hz, 9H), 1.12 (d, J = 7.2 Hz, 9H), 0.73 (d, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 190.8, 139.7, 129.6, 127.2, 120.8, 119.2, 102.6, 74.1, 63.6, 45.5, 39.7, 34.5, 23.0, 22.2, 22.0, 21.6, 21.5, 20.9, 19.02, 18.98, 12.6; IR (ATR) ν 2933, 2188, 1464, 1342, 1163 cm^{-1}; HRMS (ESI) m/z calcd for $C_{29}H_{46}N_2NaO_2SSi$ [M + Na]$^+$ 537.2946, found 537.2943.

2-(3-Methyl-1-tosyl-1-azaspiro[4.5]decan-4-ylidene)-2-(trimethylsilyl)acetonitrile (inseparable mixture of *E*- and *Z*-2f). White powder (22.2 mg, 1.8:1, 34%): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.74 (d, J = 7.2 Hz, 2H), 7.67 (d, J = 7.8 Hz, 2 × 0.69H),

dx.doi.org/10.1021/jo400342y | J. Org. Chem. 2013, 78, 4366−4372

7.28−7.25 (m, 2 + 2 × 0.69H), 3.95 (dd, J = 9.0, 13.8 Hz, 1 × 0.69H), 3.45 (dd, J = 5.4, 10.8 Hz, 1H), 3.39 (d, J = 10.8 Hz, 1H), 3.17 (d, J = 7.8, 13.8 Hz, 1 × 0.69H), 2.75−2.73 (m, 1H), 2.62−2.56 (m, 1 × 0.69H), 2.42 (s, 3 × 0.69H), 2.41 (s, 3H), 2.49−2.34 (m, 3H), 2.30−1.57 (m, 10H), 1.42−1.36 (m, 0.3H), 1.29−1.20 (m, 3.8H), 1.18 (d, J = 6.6 Hz, 3 × 0.69H), 0.97 (d, J = 7.2 Hz, 3H), 0.38 (s, 9 × 0.69H), 0.27 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 187.3, 186.4, 150.5, 144.2, 143.3, 138.9, 137.0, 129.9, 129.7, 129.6, 127.6, 127.4, 125.7, 120.2, 119.8, 118.1, 105.5, 104.0, 74.4, 73.8, 53.4, 52.5, 41.7, 41.2, 37.9, 34.8, 34.7, 34.24, 34.22, 33.2, 31.0, 29.7, 25.3, 25.0, 24.5, 23.2, 22.7, 22.5, 21.9, 21.8, 21.63, 21.57, 21.2, 20.8, 19.2, 2.2, −0.2; IR (ATR) ν 2931, 2189, 1453, 1340 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{32}N_2NaO_2SSi$ $[M + Na]^+$ 439.1851, found 439.1856; mp 112−116 °C.

(*Z*)-2-(3-Methyl-1-tosyl-1-azaspiro[4.5]decan-4-ylidene)-acetonitrile (*Z*-2f-H). White solid (8.4 mg, 10%): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.73 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 5.13 (d, J = 2.4 Hz, 1H), 3.79 (dd, J = 8.4, 12 Hz, 1H), 2.98 (dd, J = 9.6, 12 Hz, 1H), 2.72−2.66 (m, 1H), 2.42 (s, 3H), 2.35−2.26 (m, 2H), 2.14−2.05 (m, 2H), 1.86−1.80 (m, 2H), 1.72−1.65 (m, 3H), 1.53−1.46 (m, 1H), 1.03 (d, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 178.5, 143.6, 138.7, 129.8, 127.2, 115.7, 89.9, 73.4, 53.3, 39.0, 35.3, 33.1, 24.1, 22.1, 21.8, 21.6, 16.8; IR (ATR) ν 2924, 2854, 2217, 1451, 1325, 1156, 929 cm^{-1}; HRMS (ESI) m/z calcd for $C_{19}H_{24}N_2NaO_2S$ $[M + Na]^+$ 367.1456, found 367.1453; mp 140−145 °C. CCDC no. 911816.

(*E*)-2-(3-Methyl-1-tosyl-1-azaspiro[4.5]decan-4-ylidene)-acetonitrile (*E*-2f-H). Colorless oil (18.7 mg, 20%): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.72 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 5.62 (d, J = 1.8 Hz, 1H), 3.51 (dd, J = 7.2, 10.2 Hz, 1H), 3.13−3.09 (m, 2H), 2.77 (dt, J = 4.2, 13.2 Hz, 1H), 2.48 (dt, J = 4.8, 13.2 Hz, 1H), 2.41 (s, 3H), 1.83−1.69 (m, 6H), 1.52−1.38 (m, 2H), 1.19 (d, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 177.6, 143.5, 138.1, 129.7, 127.4, 116.0, 92.7, 70.7, 52.5, 38.3, 34.8, 33.7, 23.9, 22.3, 22.2, 21.6, 19.7; IR (ATR) ν 2930, 2874, 2219, 1455, 1330, 1155, 816 cm^{-1}; HRMS (ESI) m/z calcd for $C_{19}H_{24}N_2NaO_2S$ $[M + Na]^+$ 367.1456, found 367.1451.

(*E*)-2-(Triisopropylsilyl)-2-(2,2,4-trimethyl-1-tosylpyrrolidin-3-ylidene)acetonitrile (2g). White solid (27.9 mg, 29%): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.74 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 3.21−3.20 (m, 2H), 2.88−2.84 (m, 1H), 2.41 (s, 3H), 2.01 (m, 3H), 1.75 (m, 3H), 1.41−1.34 (m, 3H), 1.12−1.09 (m, 21H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 187.1, 143.4, 137.8, 129.7, 127.5, 119.1, 101.1, 70.6, 52.4, 38.9, 27.1, 24.0, 21.6, 21.4, 18.88, 18.85, 12.6; IR (ATR) ν 2948, 2868, 2192, 1580, 1463, 1333, 1158 cm^{-1}; HRMS (ESI) m/z calcd for $C_{25}H_{40}N_2NaO_2SSi$ $[M + Na]^+$ 483.2477, found 483.2466; mp 139−143 °C. CCDC no. 877975.

(*E*)-2-(2,2-Diethyl-4-methyl-1-tosylpyrrolidin-3-ylidene)-2-(triisopropylsilyl)acetonitrile (2h). White solid (30.5 mg, 31%): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.76 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 3.39 (dd, J = 9.6, 6.0 Hz, 1H), 3.27 (d, J = 9.6 Hz, 1H), 2.93−2.88 (m, 1H), 2.93−2.88 (m, 1H), 2.60−2.47 (m, 2H), 2.41 (s, 3H), 2.36−2.27 (m, 2H), 1.47−1.39 (m, 3H), 1.16 (d, J = 7.8 Hz, 9H), 1.14 (d, J = 7.2 Hz, 9H), 0.63 (t, J = 7.8 Hz, 3H), 0.62 (t, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 184.1, 143.4, 137.8, 129.7, 127.2, 118.9, 102.8, 80.9, 55.1, 37.6, 32.9, 30.7, 22.6, 21.6, 19.0, 18.7, 12.5, 10.6, 9.9; IR (ATR) ν 2944, 2868, 2189, 1597, 1462, 1335, 1160 cm^{-1}; HRMS (ESI) m/z calcd for $C_{27}H_{44}N_2NaO_2SSi$ $[M + Na]^+$ 511.2790, found 511.2789; mp 196−197 °C. CCDC no. 877574.

(*E*)-2-(4-Methyl-2,2-diphenyl-1-tosylpyrrolidin-3-ylidene)-2-(triisopropylsilyl)acetonitrile (2i) (obtained at 90% purity). Yellow oil (9.7 mg, 7%): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.49−7.06 (m, 14H), 4.13 (dd, J = 7.8, 9.0 Hz, 1H), 3.84 (d, J = 9.0 Hz, 1H), 3.17−3.15 (m, 1H), 2.36 (s, 3H), 1.32−0.91 (m, 24H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 169.3, 155.7, 147.3, 143.3, 141.8, 136.6, 134.2, 133.6, 131.2, 130.5, 130.0, 129.7, 129.4, 129.2, 129.1, 129.0, 128.7, 128.4, 128.20, 128.18, 127.9, 127.7, 127.5, 127.4, 127.3, 127.1, 127.0, 126.8, 126.7, 121.6, 120.8, 120.2, 118.1, 115.5, 115.4, 114.9, 114.7, 56.6, 23.9, 21.7, 19.1, 18.9, 18.8, 18.7, 17.8, 12.7, 12.4, 11.8, 11.5, 11.4; IR (ATR) ν 2942, 2890, 2865, 2172, 1597, 1491, 1447, 1343, 1160 cm^{-1}; HRMS (ESI) m/z calcd for $C_{35}H_{45}N_2O_2SSi$ $[M + H]^+$ 585.2971, found 585.2976.

(*E*)-2-((2*S*,9b*S*)-9b-Isopropyl-2-methyl-5,5-dioxido-2,3-dihydrobenzo[*d*]pyrrolo[1,2-*b*]isothiazol-1(9b*H*)-ylidene)-2-(triisopropylsilyl)acetonitrile (*trans*-2j). White solid (18.7 mg, 21%): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.31 (d, J = 8.4 Hz, 1H), 7.75 (d, J = 7.8 Hz, 1H), 7.57−7.54 (m, 2H), 4.04 (d, J = 12 Hz, 1H), 3.73−3.68 (m, 1H), 3.37 (dd, J = 12, 4.8 Hz, 1H), 3.00−2.95 (m, 1H), 1.47 (m, 3H), 1.19 (d, J = 7.2 Hz, 9H), 1.16 (d, J = 7.2 Hz, 9H), 0.85 (d, J = 7.2 Hz, 3H), 0.75 (d, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 181.8, 142.5, 135.0, 134.1, 130.0, 123.8, 121.9, 121.5, 104.8, 84.3, 52.8, 42.3, 35.9, 21.7, 19.1, 19.0, 17.5, 12.8; IR (ATR) ν 2947, 2869, 2190, 1573, 1466, 1387, 1169 cm^{-1}; HRMS (ESI) m/z calcd for $C_{25}H_{38}N_2NaO_2SSi$ $[M + Na]^+$ 481.2321, found 481.2314; mp 168−172 °C. CCDC no. 905347.

(*E*)-2-((9b*S*)-9b-Isopropyl-2-methyl-5,5-dioxido-2,3-dihydrobenzo[*d*]pyrrolo[1,2-*b*]isothiazol-1(9b*H*)-ylidene)-2-(triisopropylsilyl)acetonitrile (inseparable mixture of *trans*- and *cis*-2j, its ratio = 1/0.71): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.50 (d, J = 7.8 Hz, 1 × 0.71H), 8.31 (d, J = 8.4 Hz, 1H), 7.75 (d, J = 7.8 Hz, 1H), 7.73 (d, J = 7.8 Hz, 1 × 0.71H), 7.67−7.64 (m, 2 × 0.71H), 7.57−7.54 (m, 2H), 4.19 (dd, J = 9.6, 13.2 Hz, 1H), 4.04 (d, J = 12 Hz, 1H), 3.70 (tt, J = 6.0, 6.6 Hz, 1H), 3.44 (tt, J = 6.6, 6.6 Hz, 1H), 3.37 (dd, J = 12, 4.8 Hz, 1H), 3.26−3.21 (m, 1 × 0.71H), 3.00−2.93 (m, 1 + 1 × 0.71H), 1.49−1.40 (m, 3 + 3 × 0.71H), 1.29 (d, J = 6.6 Hz, 3 × 0.71H), 1.19 (d, J = 7.2 Hz, 9H), 1.16 (d, J = 7.2 Hz, 9H), 1.12 (d, J = 6.6 Hz, 3 + 3 × 0.71H), 1.08 (d, J = 7.8 Hz, 9 × 0.71H), 1.05 (d, J = 7.8 Hz, 9 × 0.71H), 0.90 (d, J = 6.6 Hz, 3 × 0.71H), 0.85 (d, J = 7.2 Hz, 3H), 0.75 (d, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 182.9, 181.9, 142.5, 139.5, 134.8, 134.2, 133.8, 133.7, 130.3, 130.1, 126.7, 123.7, 121.9, 121.8, 121.5, 121.4, 107.6, 104.7, 86.9, 84.3, 52.8, 51.6, 42.3, 40.7, 35.9, 35.3, 21.9, 21.5, 19.6, 19.3, 19.11, 19.06, 19.0, 18.9, 18.6, 17.6, 17.5; IR (ATR) ν 2946, 2868, 2191, 1582, 1312, 1178 cm^{-1}; HRMS (ESI) m/z calcd for $C_{25}H_{38}N_2NaO_2SSi$ $[M + Na]^+$ 481.2321, found 481.2314.

***N*-Allyl-*N*-(3-(*tert*-butyldiphenylsilyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1c).** Yellow oil: ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.71−7.67 (m, 3H), 7.57−7.55 (m, 3H), 7.42−7.36 (m, 3H), 7.34−7.32 (m, 3H), 6.96 (d, J = 8.4 Hz, 2H), 5.79 (ddt, J = 6.6, 10.8, 17.4 Hz, 1H), 5.28 (dd, J = 1.2, 17.4 Hz, 1H), 5.25 (dd, J = 1.2, 10.8 Hz, 1H), 4.32 (s, 2H), 3.90 (d, J = 6.6 Hz, 2H), 2.10 (s, 3H), 0.94 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 143.6, 135.5, 134.9, 133.6, 132.9, 132.1, 129.8, 129.7, 127.8, 120.2, 102.2, 86.5, 49.1, 37.0, 27.0, 21.4, 18.4; IR (ATR) ν 2931, 2185, 1507, 1473, 1429, 1351, 1164 cm^{-1}; HRMS (ESI) m/z calcd for $C_{29}H_{33}NNaO_2SSi$ $[M + Na]^+$ 510.1899, found 510.1887.

***N*-Allyl-4-methyl-*N*-(1-((triisopropylsilyl)ethynyl)cyclohexyl)-benzenesulfonamide (1d).** Yellow oil: ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.71 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.4 Hz, 6.05 (ddt, J = 6.0, 10.2, 17.4 Hz, 1H), 5.25 (d, J = 17.4 Hz, 1H), 5.12 (dt, J = 1.2, 10.2 Hz, 1H), 4.22 (dd, J = 1.2, 6.0 Hz, 2H), 2.38 (s, 3H), 2.04−1.95 (m, 4H), 1.64−1.55 (m, 5H), 1.04−0.90 (m, 21H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 142.7, 140.1, 137.6, 129.5, 127.3, 116.5, 107.2, 88.2, 63.6, 50.9, 37.9, 24.9, 23.8, 21.5, 18.7, 11.3; IR (ATR) ν 2933, 2860, 2170, 1445, 1330, 1157, 863 cm^{-1}; HRMS (ESI) m/z calcd for $C_{27}H_{43}NNaO_2SSi$ $[M + Na]^+$ 496.2682, found 496.2669.

***N*-(But-3-en-2-yl)-4-methyl-*N*-(1-((triisopropylsilyl)ethynyl)-cyclohexyl)benzenesulfonamide (1e).** Colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.76 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 6.44 (ddd, J = 6.8, 10.8, 17.6 Hz, 1H), 5.17 (d, J = 17.6 Hz, 1H), 5.10 (d, J = 10.8 Hz, 1H), 4.75 (dq, J = 6.8, 6.8 Hz, 1H), 2.39 (s, 3H), 2.12−1.95 (m, 4H), 1.73 (d, J = 6.8 Hz, 3H), 1.62−1.55 (m, 4H), 1.07 (br, 21H); IR (ATR) ν 2938, 2863, 2170, 1599, 1462, 1326, 1154 cm^{-1}; HRMS (ESI) m/z calcd for $C_{28}H_{45}NNaO_2SSi$ $[M + Na]^+$ 510.2838, found 510.2831.

***N*-Allyl-4-methyl-*N*-(1-((trimethylsilyl)ethynyl)cyclohexyl)-benzenesulfonamide (1f).** Colorless oil: ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.72 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.4 Hz, 2H), 6.02 (ddt, J = 4.8, 10.8, 17.4 Hz, 1H), 5.26 (dd, J = 1.2, 17.4 Hz, 1H), 5.14 (dd, J = 1.2, 10.8 Hz, 1H), 4.15 (d, J = 4.8 Hz, 2H), 2.39 (s, 3H), 2.03−1.92 (m, 4H), 1.64−1.50 (m, 5H), 1.14−1.10 (m, 1H), 0.07 (s, 9H); ^{13}C

dx.doi.org/10.1021/jo400342y | J. Org. Chem. 2013, 78, 4366−4372

NMR ($CDCl_3$, 150 MHz) δ 142.8, 139.8, 137.4, 129.4, 127.5, 116.6, 105.3, 91.8, 63.1, 50.6, 37.8, 37.8, 24.9, 23.8, 21.6, −0.1; IR (ATR) ν 2933, 2860, 1599, 1445, 1330, 1157, 863 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{31}NNaO_2SSi$ $[M + Na]^+$ 412.1742, found 412.1737.

***N*-Allyl-4-methyl-*N*-(2-methyl-4-(triisopropylsilyl)but-3-yn-2-yl)benzenesulfonamide (1g).** Orange oil: ^1H NMR ($CDCl_3$, 400 MHz) δ 7.73 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H), 6.09−6.02 (m, 1H), 5.27 (dd, J = 1.6, 17.2 Hz, 1H), 5.15 (dd, J = 1.6, 10 Hz, 1H), 4.22 (d, J = 5.6 Hz, 2H), 2.40 (s, 3H), 1.69 (s, 6H), 1.06−0.96 (m, 21H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.8, 139.9, 129.5, 127.2, 116.9, 110.1, 84.5, 57.6, 51.2, 31.1, 21.5, 18.6, 11.2; IR (ATR) ν 2942, 2891, 2864, 2164, 1599, 1462, 1384, 1332, 1153, 880 cm^{-1}; HRMS (ESI) m/z calcd for $C_{24}H_{39}NNaO_2SSi$ $[M + Na]^+$ 456.2369, found 456.2380.

***N*-Allyl-*N*-(3-ethyl-1-(triisopropylsilyl)pent-1-yn-3-yl)-4-methylbenzenesulfonamide (1h).** Yellow solid: ^1H NMR ($CDCl_3$, 600 MHz) δ 7.76 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H), 5.94−5.84 (m, 1H), 5.05 (d, J = 17.4 Hz, 1H), 4.99 (d, J = 10.2 Hz, 1H), 4.18 (d, J = 6.0 Hz, 2H), 2.41 (s, 3H), 2.31−2.74 (m, 2H), 1.95−1.92 (m, 2H), 1.09−1.04 (m, 21H), 1.00 (t, J = 7.2 Hz, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 147.8, 139.4, 129.2, 127.7, 116.4, 107.3, 83.8, 69.3, 67.3, 51.7, 33.6, 21.4, 18.6, 11.2, 9.8; IR (ATR) ν 2941, 2865, 2174, 1599, 1461, 1350, 1159, 883 cm^{-1}; HRMS (ESI) m/z calcd for $C_{26}H_{43}NNaO_2SSi$ $[M + Na]^+$ 484.2682, found 484.2688; mp 47−50 °C.

***N*-Allyl-*N*-(1,1-diphenyl-3-(triisopropylsilyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1i).** Yellow oil: ^1H NMR ($CDCl_3$, 600 MHz) δ 7.52−7.49 (m, 4H), 7.24−7.22 (m, 2H), 7.18−7.15 (m, 6H), 7.05−7.03 (m, 2H), 6.15−6.09 (m, 1H), 5.12−5.07 (m, 1H), 4.24 (d, J = 5.4 Hz, 2H), 2.36 (s, 3H), 1.10−1.06 (m, 21H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 143.3, 141.0, 139.7, 135.8, 129.7, 128.9, 127.7, 127.5, 127.4, 117.9, 108.7, 90.0, 71.7, 52.7, 21.5, 18.7, 11.5; IR (ATR) ν 2890, 2160, 1598, 1491, 1448, 1338, 1158, 882 cm^{-1}; HRMS (ESI) m/z calcd for $C_{34}H_{43}NNaO_2SSi$ $[M + Na]^+$ 580.2681, found 580.2668.

2-Allyl-3-isopropyl-3-((triisopropylsilyl)ethynyl)-2,3-dihydrobenzo[*d*]isothiazole 1,1-dioxide (1j): ^1H NMR ($CDCl_3$, 400 MHz) δ 7.78 (d, J = 7.6 Hz, 1H), 7.63−7.59 (m, 1H), 7.55−7.50 (m, 2H), 6.12−6.03 (m, 1H), 5.44 (d, J = 17.2 Hz, 1H), 5.26 (d, J = 10 Hz, 1H), 4.21 (dd, J = 6.4, 16.4 Hz, 1H), 4.04 (dd, J = 6.4, 16.4 Hz, 1H), 2.35 (tt, J = 6.8, 6.8 Hz, 1H), 1.04−1.02 (m, 21H), 0.99 (d, J = 6.8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.4, 134.2, 134.1, 132.9, 129.7, 124.5, 121.4, 118.5, 103.7, 90.6, 69.4, 46.1, 39.6, 18.8, 17.5, 17.4, 11.2; IR (ATR) ν 2943, 2864, 1463, 1387, 1160, 998, 930 cm^{-1}; HRMS (ESI) m/z calcd for $C_{24}H_{37}NNaO_2SSi$ $[M + Na]^+$ 454.2212, found 454.2206; mp 68−71 °C.

(Cyclohex-1-en-1-ylethynyl)triisopropylsilane (7). Colorless oil: ^1H NMR ($CDCl_3$, 600 MHz) δ 6.15 (m, 1H), 2.14−2.07 (m, 4H), 1.63−1.55 (m, 4H), 1.08−1.04 (m, 21H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 135.5, 121.2, 109.4, 87.0, 29.8, 25.7, 22.3, 21.6, 18.7, 11.4; IR (ATR) ν 2144, 1677, 1462 cm^{-1}; LRMS (EI) m/z 226 (M^+), 233 ($M^+ - Me_2 - H$), 219 ($M^+ - iPr$), 191, 88, 70, 61; HRMS (ESI) m/z calcd for $C_{17}H_{30}NaSi$ $[M + Na]^+$ 285.2015, found 285.2017.

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^1H and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge financial support from a Grant-in-Aid for Scientific Research(C) from JSPS KAKEHNHI (21590003), helpful discussion in "Workshop on Chirality in Chiba University (WCCU)", and kind support for X-ray crystallographic analysis by Mr. Masaki Hoshi (Chiba University).

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(11) For *Z*-**2b** (CCDC no. 857691), *E*-**2c** (858856), *E*-**2d** (862635), *E*-**2f-H** (911816), **2g** (877975), **2h** (877574), and *trans*-**2j** (905347), these data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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