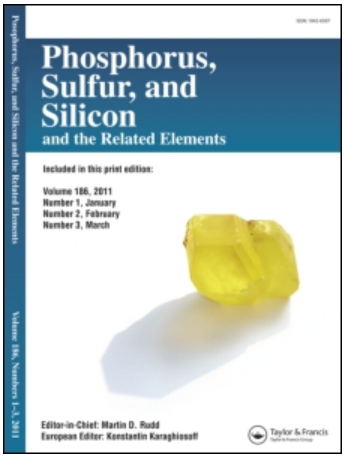

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Syntheses and Stability of Alkynyl *S,N*-Acetals Derived from 2-Propynals

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Syntheses and Stability of Alkynyl *S,N*-Acetals Derived from 2-Propynals

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Two types of synthetic methods for S, N-acetals derived from 2-propynals were described. Thioformamides, lithium acetylides, and alkylating agents were the key substrates. In the first method, methylation of thioformamides with MeOTf followed by reacting with lithium acetylides led to the title compounds. As an alternative method, the direct addition of lithium acetylides to thioformamides gave lithium thiolates, which was then alkylated. With these two methods, a wide range of derivatives including bis-S, N-acetals were provided, and their stability was influenced by the substituents at the alkynyl carbon atom. The introduction of silyl group enhanced the stability effectively.

Keywords Alkynyl *S, N*-acetals; alkynylation; thioiminium salts

INTRODUCTION

Alkynyl *S, S*-acetals derived from 2-propynals are important synthetic units leading to a wide variety of alkynes and allenes.[1] Similarly, *N,N*-acetals derived from 2-propynals have been prepared[2] and used as key precursors leading to propargylamines.[3] In contrast, only one article has described acyclic alkynyl *S, N*-acetals[4] to the best of our knowledge before our studies,[5] although cyclic derivatives are synthesized.[6] For example, the addition of lithium phenylacetylide to 3-methylbenzothiazolium iodide gives 2-alkynylbenzothiazole

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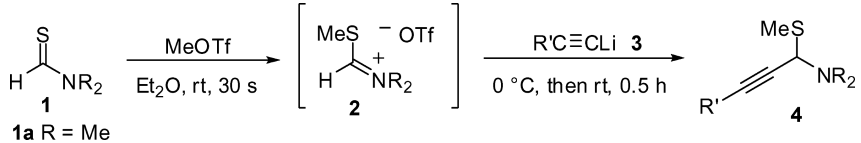
derivative where the sulfur and nitrogen atoms are within a five-membered ring.[6b]

During the course of our studies on the reactivity of thioamides,[7] alkynylation of the thioiminium salts **2** derived from the thioformamides **1** with lithium acetylides **3** was found to give the alkynyl *S, N*-acetals **4** with high efficiency (Scheme 1).[5] We report herein the detail of two types of synthetic methods leading to alkynyl *S, N*-acetals and their stability.



1 **2** **4**

1a R = Me

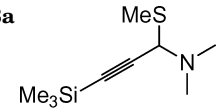
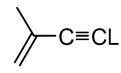
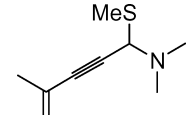
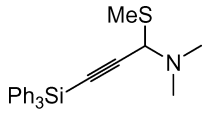
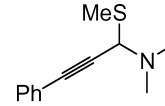
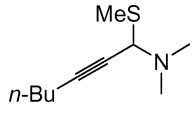
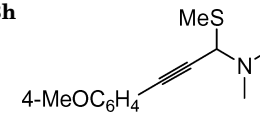
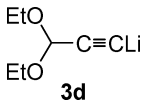
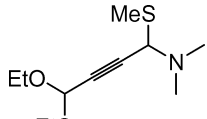
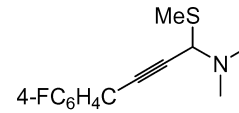
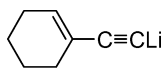
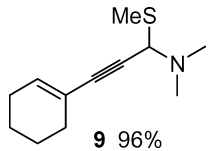
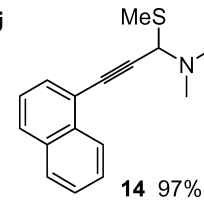
SCHEME 1

RESULTS AND DISCUSSION

The reaction of thioiminium salt **2a** generated in situ from thioformamide **1a** and methyl triflate (MeOTf) with lithium acetylide **3a** gave alkynyl *S, N*-acetal **5** in 92% yield (Table I). Thus, the reactions of in situ generated thioiminium salt **2a** with various lithium acetylides were carried out. In almost all cases, the *S, N*-acetals were obtained in moderate to high yields without any purification. Aliphatic lithium acetylide **3c** with an acetal skeleton **3d** were used, and the corresponding *S, N*-acetals **7** and **8** were obtained. The use of **3e** and **3f** derived from enynes also gave *S, N*-acetals **9** and **10** in high yields. When aromatic lithium acetylides were used in this reaction, the yields of the products were not greatly affected by the electron-donating and -withdrawing groups on the aryl groups (Table I). The reaction with **3j** derived from 1-naphthylacetylene[8] proceeded smoothly to give the desired product **14** in 97% yield.

Then, the reactions of thioformamides **1** with various substituents at the nitrogen atom with MeOTf and lithium acetylides **3** were examined, and a wide range of thioiminium salts participated in the reaction (Table II). *N,N*-Diethyl thioformamide (**1b**),[9] *N,N*-diphenyl thioformamide (**1c**), and *N,N*-dibenzyl thioformamide (**1d**) worked well as a starting thioamide affording the acetals **15**, **16**, and **17**. Similarly, the use of thioformamides having two different substituents on the nitrogen atom gave the desired acetals **18** and **19**. 4-Morpholinecarbothioaldehyde (**1g**)[10] was also applied to this reaction, and the corresponding *S, N*-acetal **20** was formed. *S, N*-Acetals with

TABLE I Synthesis of *S, N*-Acetals by the Reaction of Thioiminium Salts with Lithium Acetylides[a]

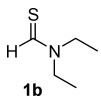
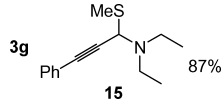
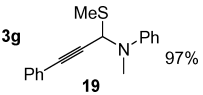
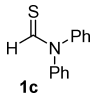
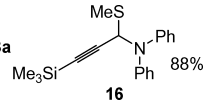
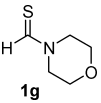
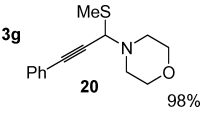
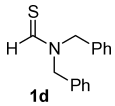
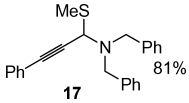
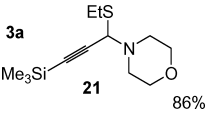
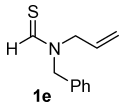
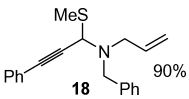
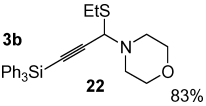
RC≡CLi **3**	*S,N*–acetal yield[b]	RC≡CLi **3**	*S,N*-acetal yield[b]
$ME_3SiC{\equiv}CLi$ **3a**	 **5** 92%	 **3f**	 **10** 89%
$Ph_3SiC{\equiv}CLi$ **3b**	 **6** 88%	PhC≡CLi **3g**	 **11** 98%
n-BuC≡CLi **3c**	 **7** 90%	4-$MeOC_6H_4C{\equiv}CLi$ **3h**	 **12** 90%
 **3d**	 **8** 88%	4-$FC_6H_4C{\equiv}CLi$ **3i**	 **13** 83%
 **3e**	 **9** 96%	1-naphthylC≡CLi **3j**	 **14** 97%

[a]The reaction was carried out as follows unless otherwise noted: Thioformamide **1a** (1.0 mmol) was treated with methyl triflate (1.0 mmol) in Et_2O (2 mL) at 0°C for 30s. Then, to the reaction mixture was added an Et_2O solution of the lithium acetylides **3** (1.5 mmol) at 0°C, and the mixture was stirred at room temperature for 0.5 h. [b]Crude yield. [c]Lithium acetylide **3l** (1.2 mmol) was used.

ethylthio group **21** and **23** were readily synthesized by using EtOTf instead of MeOTf (Table II).

The synthesis of the alkynyl *S, N*-acetals was carried out by the alternative method shown in Scheme 2 and Table III. The addition of methyl iodide (**23a**) to lithium thiolate derived from thioformamide **1a** and lithium acetylide **3a** led to *S, N*-acetal **5** in 87% yield. Several types

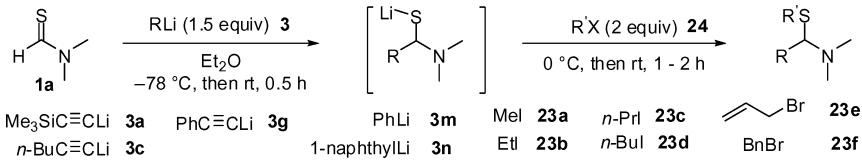
TABLE II Synthesis of *S,N*-Acetals by the Reaction of Thioiminium Salts with Lithium Acetylides[a]

thiloformamide **1**	**3**	*S,N*-acetal yield[b]	thioformamide **1**	**3**	*S,N*−acetal yield[b]
 **1b**	**3g**	 **15** 87%	 **1f**	**3g**	 **19** 97%
 **1c**	**3a**	 **16** 88%	 **1g**	**3g**	 **20** 98%
 **1d**	**3g**	 **17** 81%	**1g**	**3a**	 **21** 86%
 **1e**	**3g**	 **18** 90%	**1g**[cd]	**3b**	 **22** 83%

[a]The reaction was carried out as follows unless otherwise noted: Thioformamide **1** (1.0 mmol) was treated with methyl triflate (1.0 mmol) in Et_2O (2 mL) at 0°C for 30s. Then, to the reaction mixture was added an Et_2O solution of the lithium acetylides **3** (1.5 mmol) at 0°C, and the mixture was stirred at room temperature for 0.5 h. [b]Crude yield. [c]EtOTf was used. [d]Lithium acetylide **3b** (1.2 mmol) was used.

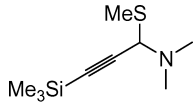
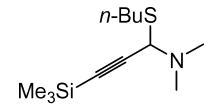
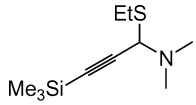
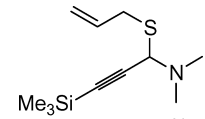
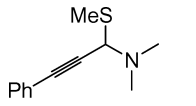
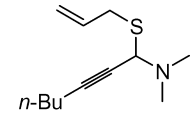
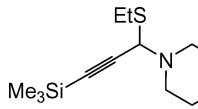
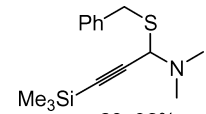
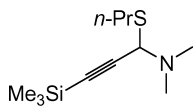
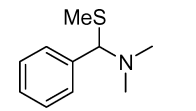
of lithium acetylides **3** and alkyl halides **23** were applied to the present reaction. Ethyl iodide (**23b**), *n*-propyl iodide (**23c**), and *n*-butyl iodide (**23d**) could be used as alkylating agents to give the corresponding *S,N*-acetals **24**, **25**, and **26** in moderate yields.

The reaction of lithium thiolates formed in situ from lithium acetylides **3a** and **3c** with allyl bromide (**23e**) proceeded smoothly under the identical conditions leading to *S,N*-acetals **27** and **28**. Handling of these products should be carried out in a well-ventilated hood since they stink more heavily than any other *S,N*-acetals. The reaction of



SCHEME 2

TABLE III Synthesis of *S*, *N*-Acetals by the Reaction of Lithium Thiolates with Alkyl Haldiles[a]

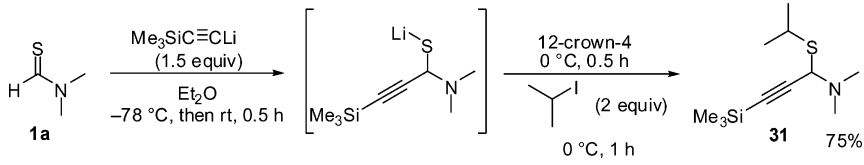
substrate	S,N-acetal yield[b]	substrate	*S*, *N*-acetal yield[b]
1a[c] **3a**[c] **23a**[c]	 **5** 87%	**1a** **3a** **23d**	 **26** 70%
1a **3a** **23b**	 **24** 69%	**1a** **3a** **23e**	 **27** 85%
1a[c] **3g**[c] **23a**[c]	 **11** 53%	**1a** **3c** **23e**	 **28** 95%
1g[d] **3a**[d] **23b**[d]	 **22** 84%	**1a**[f] **3a**[f] **23f**[f]	 **29** 92%
1g[e] **3a**[e] **23c**[e]	 **25** 57%	**1a**[g] **3m**[g] **23a**[g]	 **30** 86%

[a]The reaction was carried out as follows unless otherwise noted: Thioformamide **1a** (1.0 mmol) was treated with lithium acetylides **3** (1.5 mmol) in Et_2O (2 mL) at −78°C and the mixture was stirred at room temperature for 0.5 h. Then, to the reaction mixture was added alkyl halides **5** (2 mmol) at 0°C, and the mixture was stirred at room temperature for 2 h. [b]Crude yield. [c]The reaction mixture was stirred for 1 h. [d]Thioformyl morpholine **1g** was used. [e]The reaction mixture was stirred for 1.5 h. [f] BnBr (1 equiv) was added to lithium thiolate, and then the mixture was stirred at room temperature for 4 h. [g]The reaction mixture was stirred for 0.5 h.

thioformamide possessing morpholyl group **1g** and lithium acetylide **3a** also formed the corresponding lithium thiolate. Then, the ethylation of the lithium thiolate gave *S*, *N*-acetal **22** in 84% yield. The use of exactly 1 equiv of benzyl bromide (**23f**) was necessary for the synthesis of *S*, *N*-acetal **29**. The use of excess **23f** resulted in the further benzylation

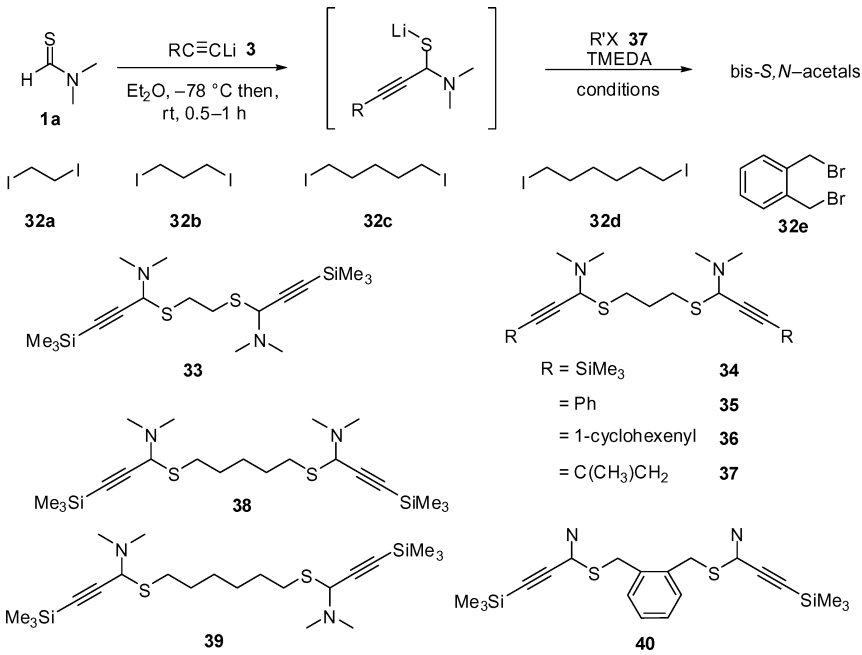
of **29**. Instead of lithium acetylides, phenyllithium (**3m**) was used for the synthesis of phenyl *S,N*–acetal,[11] which could not be obtained by the method via the thioiminium salt shown in Scheme 1. The reaction of **1a**, **3m**, and **23a** gave **30** with the contamination of a small amount of benzaldehyde. The purification of **30** was not successful. A similar reaction with 1-naphthyllithium did not give the desired products, but the complex mixture was formed. These indicated that aromatic *S,N*-acetals were less stable than alkynyl *S,N*-acetals. In other words, the alkynyl group played important roles to enhance the stability of *S,N*-acetals.

The introduction of the *sec*-alkyl group to the sulfur atom of *S,N*-acetals was carried out (Scheme 3). To an Et_2O solution of lithium thiolate generated in situ from thioformamide **1a** and **3a**, 12-crown-4-ether at 0°C was added, and this was stirred at this temperature for 30 min. To the reaction mixture was added isopropyl iodide at 0°C, and this was stirred at the same temperature for 1 h. After workup, the desired alkynyl *S,N*–acetal **31** was obtained in 75% yield. When no additive was present, **31** was not formed. The use of TMEDA as the additive gave **31** rather in lower yield (46%).



SCHEME 3

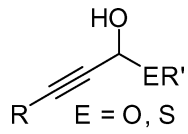
Finally, bis-*S,N*-acetals linked through alkyl groups were synthesized (Scheme 4). The reaction of lithium thiolate derived from **1** and **3a** with 1,2-diiodoethane (**32a**) was carried out. To obtain the desired product **33**, the various combinations of the molar ratio of **1a**, **3a**, and **32a** were tested, but they usually gave a complex mixture. This may be partly because of the instability of **33** and/or an initially formed intermediate. 1,3-Diiodopropane (**32b**) was then used. The reaction mixture (**1a**:**3a**:**9b**:TMEDA = 3:4.5:1:5) was stirred for 4 h, and the desired bis-*S,N*-acetal **34** with two *S,N*-acetal groups in one molecule was obtained quantitatively. A similar reaction of lithium thiolate derived from lithium phenylacetylide (**3g**) and thioformamide **1a** gave the desired bis-*S,N*-acetal **35** in a mixture with other unidentified products. The reaction of lithium thiolates bearing ethynylcyclohexen-1-yl and 3-methylbut-3-en-1-ynyl groups with 1,3-diiodopropane (**32b**) worked in



SCHEME 4

a similar way to give corresponding bis-*S*, *N*-acetals **36** and **37**. On the basis of NMR spectra of the crude samples, they contained several types of unidentified compounds. The further purification of the crude samples resulted in the decomposition of **36** and **37**. Therefore, the stability of these bis-*S*, *N*-acetals depends on the substituents at the alkynyl carbon atom, and TMS group has contributed to the enhancement of the stability of the products. A similar effect of silyl group has been observed for the synthesis of alkynyl hemithioacetals. The addition of alcohols and ethanethiol to the formyl group of 3-(trimethylsilyl)-2-propynal gives hemithioacetals **41** (Figure 1) in high yields.[12]

The reaction of **1a** with lithium (trimethylsilyl)acetylide (**3a**) followed by the addition of 1,5-diiodopentane (**32c**) or 1,6-diiodohexane (**32d**) gave the corresponding product **38** or **39** quantitatively. In addition, the α,α' -dibromo-*o*-xylene (**32e**) was also used to lead to the corresponding bis-*S*, *N*-acetal **40** in high yield. The purification of bis-*S*, *N*-acetals shown in Scheme 4 by column chromatography on silica gel and alumina resulted in the partial decomposition of the products, but those derived from **3a** showed purity higher than 90%.



41

FIGURE 1 Hemiacetals and hemithioacetals.

In summary, two types of synthetic protocols leading to alkynyl *S*, *N*-acetals have been demonstrated. The reaction of thioiminium salts derived from thioformamides and MeOTf with lithium acetylides gives the desired acetals. Alternatively, the direct addition of lithium acetylides to thioformamides generates lithium thiolates followed by the addition of alkyl halides to lead to alkynyl *S*, *N*-acetals. The versatility of these starting materials allows the construction of diverse sets of alkynyl *S*, *N*-acetals. To improve the yields of the products, the use of 12-crown-4 ether and TMEDA is effective. These methods also lead to bis-*S*, *N*-acetals. The stability of alkynyl *S*, *N*-acetals is enhanced by the introduction of silyl groups to the alkynyl carbon atoms.

EXPERIMENTAL

Melting points were measured by a Yanagimoto micro melting point apparatus (uncorrected). IR spectra were obtained on a JASCO FT/IR 410 spectrophotometer. ^{1}H (399.7 MHz), ^{13}C (100.4 MHz), and ^{19}F (376.0 MHz) NMR spectra were measured on a JEOL α-400 spectrometer. The ^{1}H and ^{13}C chemical shifts are reported in δ values with reference to Me_4Si and $CDCl_3$ as internal standards, respectively. The ^{19}F chemical shifts are expressed in δ values deshielded with respect to CF_3COOH as an external standard. All spectra were acquired in the proton-decoupled mode. Mass (MS) and high-resolution mass spectra (HRMS) were measured on a SHIMAZU GCMS QP 1000, a JEOL GC-mate II mass spectrometer, or a JEOL JMS-700 spectrometer. Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University. All the manipulations were carried out under Ar atmosphere.

Synthesis of Alkynyl *S,N*-Acetals via Thioiminium Salts: General Procedure

To a dried Et_2O solution of thioformamide **1** methyl triflate (1 equiv.) was added at room temperature, and the mixture was stirred for

30 sec at this temperature. To the reaction mixture an Et_2O solution of lithium acetylide **3** (1.5 equiv.) prepared from acetylene and BuLi (1.6 M hexane solution) at 0°C was added, and this was stirred for 0.5 h at room temperature. The resulting mixture was poured into a saturated aqueous solution of $NaHCO_3$, and extracted with Et_2O. The organic layer was dried over $MgSO_4$ and concentrated in vacuo to give *S, N*-acetal in purity higher than 95%.

N,N-Dimethyl-1-(methylthio)-3-(trimethylsilyl)-2-propyn-1-amine (5)

Red oil; IR (neat) 2958, 2860, 2825, 2783, 2163, 1489, 1251 cm^{-1}; ^1H NMR ($CDCl_3$)$\delta = 0.20$ (s, 9H, $SiMe_3$), 2.22 (s, 3H, SMe), 2.35 (s, 6H, NMe_2), 4.70 (s, 1H, CH); ^{13}C NMR ($CDCl_3$)$\delta = -0.07$ $SiMe_3$), 14.9 (SMe), 40.6 (NMe_2), 64.3 (CH), 92.2, 99.5 (C≡C); MS (EI) *m/z* 201 (M^+); Anal. Calcd. for $C_9H_{19}NSSi$: C, 53.67; H, 9.51. Found: C, 53.93; H, 9.37%.

N,N-Dimethyl-1-(methylthio)-3-(triphenylsilyl)-2-propyn-1-amine (6)

Orange oil; IR (neat) 2958, 2860, 2825, 2782, 2162, 1508, 1046 cm^{-1}; ^1H NMR ($CDCl_3$)$\delta = 2.23$ (s, 3H, SMe), 2.41 (s, 6H, NMe_2), 4.81 (s, 1H, CH), 7.23–7.63 (m, 9H, Ar), 7.64-7.70 (m, 6H, Ar); ^{13}C NMR ($CDCl_3$)$\delta = 15.0$ (SMe), 40.9 (NMe_2), 64.4 (CH), 87.4, 104.5 (C≡C), 127.9, 129.9, 133.3, 135.5 (Ar); MS (EI) *m/z* 388 (M^+).

N,N-Dimethyl-1-(methylthio)-2-heptyn-1-amine (7)

Dark brown oil; IR (neat) 3389, 2957, 2934, 2861, 2824, 2780, 2233, 1655, 1631, 1574, 1456, 1343, 1279, 1214, 1158, 1095, 1021, 960, 820, 724, 688, 661 cm^{-1}; ^1H NMR ($CDCl_3$)$\delta = 0..84$ (t, $J = 7.3$ Hz, 3H, CH_3), 1.35 (m, 2H, CH_2), 1.44, (m, 2H, CH_2), 2.09 (s, 3H, SCH_3), 2.21 (dt, $J = 2.0$, 6.8 Hz, 2H, CH_2), 2.28 (s, 6H, $N(CH_3)_2$), 4.61 (t, $J = 2.0$ Hz, 1H, CH); ^{13}C NMR ($CDCl_3$)$\delta = 13.7$ (CH_3), 15.1 (SCH_3), 18.6, 22.1, 30.9 (CH_2), 40.7 ($N(CH_3)_2$), 64.3 (CH), 74.8, 88.1 (C≡C); MS (EI) *m/z* 185 (M^+); HRMS (EI) calcd. for $C_{10}H_{19}NS$ (M^+) 185.1238, found 185.1264.

N,N-Dimethyl-1-(methylthio)-4,4-diethoxy-2-butyn-1-amine (8)

Dark brown oil; IR (neat) 3410, 2977, 2931, 2884, 2827, 2783, 2362, 2238, 1660, 1583, 1561, 1454, 1390, 1355, 1329, 1279, 1213, 1130, 1053,

1013, 824 cm^{-1}; ^1H NMR ($CDCl_3$)$\delta = 1.18$ (t, $J = 7.1$ Hz, 6H, CH_3), 2.17 (s, 3H, SCH_3), 2.32, (s, 6H, $N(CH_3)_2$), 3.55 (dq, $J = 2.4$, 7.3 Hz, 2H, CH_2), 3.68 (dq, $J = 2.4$, 7.8 Hz, 2H, CH_2), 4.65 (d, $J = 1.5$ Hz, 1H, CH), 5.31 (d, $J = 1.5$ Hz, 1H, OCH); ^{13}C NMR ($CDCl_3$)δ 15.1 (SCH_3), 40.7 ($N(CH_3)_2$), 60.9 (CH_3), 63.7 (CH_2), 73.4 (CH), 80.1, 82.7 (C≡C), 91.3 (OCH); MS (EI) *m/z* 231 (M^+); HRMS (EI) calcd. for $C_{11}H_{21}NO_2S$ (M^+) 231.1293, found 231.1296.

N,N-Dimethyl-1-(methylthio)-3-(cyclohex-1-yl)-2-propyn-1-amine (9)

Red oil; IR (neat) 3395, 3024, 2933, 2857, 2827, 2778, 2361, 2178, 1661, 1435, 1343, 1259, 1217, 1158, 1135, 1047, 1016, 917, 840, 823, 800, 665, 634, 618 cm^{-1}; ^1H NMR ($CDCl_3$)$\delta = 1.60$ (m, 4H, CH_2), 2.12 (m, 4H, CH_2), 2.22 (s, 3H, SCH_3), 2.37(s, 6H, $N(CH_3)_2$), 4.80 (s, 1H, CH), 6.14 (m, 1H, C=C<u>H</u>CH_2); ^{13}C NMR ($CDCl_3$)$\delta = 14.1$ (SCH_3), 21.4, 22.2, 25.6, 29.3 (CH_2), 40.6 ($N(CH_3)_2$), 64.6 (CH), 74.3, 89.4 (C≡C), 120.0 (<u>C</u>=CH), 135.4 (C=<u>C</u>H); MS (EI) *m/z* 209 (M^+); HRMS (EI) calcd. for $C_{12}H_{19}NS$ (M^+) 209.1238, found 209.1259.

*N,N,*4-Trimethyl-1-(methylthio)-4-penten-2-yn-1-amine (10)

Red oil; IR (neat) 3304, 3096, 2975 ,2945, 2920, 2860, 2825, 2781, 2372, 2219, 2104, 1803, 1614, 1453, 1373, 1342, 1289, 1212, 1159, 1094, 1046, 1016, 963, 899, 824 cm^{-1}; ^1H NMR ($CDCl_3$)$\delta = 1.84$ (s, 3H, CH_3), 2.16 (s, 3H, SCH_3), 2.30 (s, 6H, $N(CH_3)_2$), 4.72 (s, 1H, CH), 5.18 (s, 1H, C=CH_2), 5.25 (s, 1H, C=CH_2); ^{13}C NMR ($CDCl_3$)$\delta = 14.7$ (SCH_3), 23.3 (CH_3), 40.4 ($N(CH_3)_2$), 64.1 (CH), 82.8, 88.4 (C≡C), 122.1 (<u>C</u>H_2 =C), 125.9 (CH_2=<u>C</u>); MS (EI) *m/z* 169 (M^+); HRMS (EI) calcd. for $C_9H_{15}NS$ (M^+) 169.2871, found 169.0910.

N,N-Dimethyl-1-(methylthio)-3-phenyl-2-propyn-1-amine (11)

Dark red oil; IR (neat) 2943, 2860, 2825, 2781, 2189, 1489, 1028 cm^{-1}; ^1H NMR ($CDCl_3$)$\delta = 2.31$ (s, 3H, SMe), 2.42 (s, 6H, NMe_2), 4.90 (s, 1H, CH), 7.25–7.34 (m, 3H, Ar), 7.42–7.50 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$)δ = 15.0 (SMe), 40.7 (NMe_2), 64.5 (CH), 84.0, 87.4 (C≡C), 128.2, 128.4, 131.8, 132.0 (Ar); MS (EI) *m/z* 205 (M^+).

N,N-Dimethyl-1-(methylthio)-3-(4-methoxyphenyl)-2-propyn-1-amine (12)

Brown oil: IR (neat) 3285, 2940, 2836, 2780, 2219, 2180, 1656, 1605, 1569, 1509, 1455, 1291, 1249, 1173, 1106, 1031, 832, 803 cm^{-1}; ^1H NMR ($CDCl_3$)δ = 2.10 (s, 3H, SCH_3), 2.43 (s, 6H, $N(CH_3)_2$), 3.8 (s, 3H, OCH_3), 4.90 (s, 1H, CH), 6.83 (d, J = 8.8 Hz, 2H, Ar), 7.39 (d, J = 8.8 Hz, 2H, Ar); ^{13}C NMR ($CDCl_3$)δ = 14.9 (SCH_3), 40.7 ($N(CH_3)_2$), 55.3 (OCH_3), 64.7 (CH), 75.8, 82.6, 87.4 (C), 113.9, 133.2, 159.7 (Ar); MS (EI) m/z 236 (M^+); HRMS (EI) calcd. for $C_{13}H_{17}NOS$ (M^+) 235.1031, found 235.1039.

N,N-Dimethyl-1-(methylthio)-3-(4-fluorophenyl)-2-propyn-1-amine (13)

Brown oil: IR (neat) 3404, 3048, 2943, 2859, 5824, 2778, 2226, 1894, 1660, 1600, 1561, 1506, 1469, 1453, 1437, 1226, 1156, 1042, 1015, 836 cm^{-1}; ^1H NMR ($CDCl_3$)δ = 2.20 (s, 3H, SCH_3), 2.35 (s, 6H, $N(CH_3)_2$), 4.80 (s, 1H, CH), 6.90–6.95 (m, 2H, Ar), 7.34–7.41 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$)δ = 15.0 (SCH_3), 40.7 ($N(CH_3)_2$), 64.5 (CH), 83.8, 86.3 (C≡C), 115.5, 118.5 (Ar), 133.9 (Ar, $^2J_{CF}$ = 37.1 Hz), 162.6 (Ar, $^1J_{CF}$ = 249.6 Hz); MS (EI) m/z 224 (M^++ 1), 176 (M^+ – SCH_3), 133 (M^+ – SCH_3 – $N(CH_3)_2$); HRMS (EI) calcd. for $C_{12}H_{14}FNS$ (M^+) 223.0831, found 223.0822.

N,N-Dimethyl-1-(methylthio)-3-(1-naphthyl)-2-propyn-1-amine (14)

Red oil: IR (neat) 3294, 3057, 2942, 2858, 2824, 2779, 2361, 1937, 1662, 1586, 1507, 1452, 1395, 1335, 1260, 1210, 1157, 1094, 1026, 799, 773 cm^{-1}; ^1H NMR ($CDCl_3$)δ = 2.44 (s, 3H, SCH_3), 2.51 (s, 6H, $N(CH_3)_2$), 5.04 (s, 1H, CH), 7.39–7.43 (1H, Ar), 7.49–7.59 (2H, Ar), 7.69–7.71 (1H, Ar), 7.83 (t, J = 7.6 Hz, 2H, Ar), 8.32 (d, J = 7.8 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$)δ = 15.1 (SCH_3), 40.9 ($N(CH_3)_2$), 64.8 (CH), 85.5, 89.0 (C≡C), 120.2, 125.2, 126.1, 126.4, 126.9, 128.3, 128.9, 130.8, 133.1, 133.3 (Ar); MS (EI) m/z 208 (M^+ – SCH_3); HRMS (EI) calcd. for $C_{16}H_{17}NS$ (M^+) 255.1082, (M^+ – SCH_3) 208.1126, found 208.1090.

N,N-Diethyl-1-(methylthio)-3-phenyl-2-propyn-1-amine (15)

Dark brown oil; IR (neat) 3399, 3061, 2970, 2918, 2826, 2341, 1664, 1598, 1490, 1442, 1383, 1258, 1194, 1157, 1115, 1069, 756, 690 cm^{-1}; ^1H NMR ($CDCl_3$)δ = 1.05 (t, J = 7.1 Hz, 6H, CH_3), 2.18 (s, 3H, SCH_3),

2.66 (dq, $J = 13.7$, 6.7 Hz, 2H, CH_2) 2.76 (dq, $J = 13.7$, 6.7 Hz, 2H, CH_2), 5.0 (s, 1H, CH) 7.18-7.23 (m, 3H, Ar), 7.36–7.39 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$)$\delta = 13.6$ (CH_3), 14.6 (SCH_3), 44.3 (CH_2), 60.9 (CH), 85.4, 86.4(C≡C), 122.7, 128.2, 128.3, 131.7 (Ar); MS (EI) *m/z* 234 (M^+); HRMS calcd. for $C_{14}H_{19}NS$ (M^+) 233.1238, found 233.1254.

N,N-Diphenyl-1-(methylthio)-3-(trimethylsilyl)-2-propyn-1-amine (16)

Dark brown oil; IR (neat) 3395, 3060, 3036, 2959, 2917, 2173, 1945, 1691, 1591, 1495, 1450, 1412, 1357, 1250, 1184, 1097, 1074, 1030, 1014, 846, 750, 697, 671 cm^{-1}; ^{1}H NMR ($CDCl_3$)$\delta = 0.11$ (s, 9H, $Si(CH_3)_3$), 2.12 (s, 3H, SCH_3), 5.89 (s, 1H, CH), 7.02–7.07 (m, 2H, Ar), 7.10–7.13 (m, 4H, Ar), 7.25–7.29 (m, 4H, Ar); ^{13}C NMR ($CDCl_3$)$\delta = -0.35$ ($Si(CH_3)_3$) 14.7 (SCH_3), 57.6 (CH), 93.7, 99.9 (C≡C), 123.1, 123.5, 128.9, 145.8 (NPh_2); MS (EI) *m/z* 325 (M^+); HRMS (EI) calcd. for $C_{19}H_{23}NSSi$ (M^+) 325.1321, found 325.1313.

N,N-Di(phenylmethyl)-1-(methylthio)-3-phenyl-2-propyn-1-amine (17)

Dark brown oil; IR (neat) 3435, 3084, 3061, 3027, 2977, 2918, 2835, 2340, 1951, 1879, 1809, 1677 1600, 1542, 1492, 1454, 1443, 1363, 1258, 1205, 1156, 1119, 1071, 1028, 957, 913, 859, 823, 780, 755, 698, 670, 609, 528, 485, cm^{-1}; ^{1}H NMR ($CDCl_3$)$\delta = 2.20$ (s, 3H, SCH_3), 3.78 (d, $J = 13.7$ Hz, 2H, CH_2Ph), 3.94 (d, $J = 13.7$ Hz, 2H, CH_2Ph), 4.86 (s, 1H, CH), 7.24–7.27 (m, 2H, Ar), 7.31–7.33 (m, 7H, Ar), 7.39–7.40 (m, 4H, Ar), 7.46–7.49 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$)$\delta = 14.5$ (SCH_3), 54.0 (CH_2Ph), 59.2 (CH), 84.4, 87.2 (C≡C), 122.6, 127.2, 128.3, 128.4, 128.5, 129.0, 131.9, 138.9 (Ar; The signals due to several aromatic carbon atoms were overlapped.); MS (EI) *m/z* 358 (M^+); HRMS (EI) calcd. for $C_{24}H_{23}NS$ (M^+) 357.1551, found 357.1543.

N-(2-Propenyl)-*N*-phenylmethyl-1-(methylthio)-3-phenyl-2-propyn-1-amine (18)

Dark brown oil; IR (neat) 3399, 3061, 3028, 2919, 2833, 2362, 1952, 1874, 1674, 1640, 1598, 1491, 1442, 1416, 1365, 1259, 1205, 1116, 1071, 1027, 994, 920, 756, 691 cm^{-1}; ^{1}H NMR ($CDCl_3$)$\delta = 2.22$ (s, 3H, SCH_3), 3.29 (dd, $J = 5.4$, 14.2 Hz, 1H, $C\underline{H}_2CH{=}CH_2$), 3.44 (dd, $J = 6.4$, 14.2 Hz, 1H, $C\underline{H}_2CH{=}CH_2$), 3.84 (m, 2H, CH_2Ph), 4.97 (s, 1H, CH), 5.17 (d, $J = 10.2$ Hz, 1H, $CH_2CH{=}C\underline{H}_2$), 5.28 (d, $J = 17.1$ Hz,

1H, $CH_2CH{=}C\underline{H}_2$), 5.86 (m, 1H, $CH_2C\underline{H}{=}CH_2$), 7.20–7.49 (m, 10H, Ar); ^{13}C NMR ($CDCl_3$)δ = 14.4 (SCH_3), 53.0 (NCH_2), 53.9 (NCH_2), 59.5 (CH), 84.5, 87.0 (C≡C), 118.0 (CH=$\underline{C}H_2$), 122.6, 127.1, 128.2, 128.3, 129.0, 131.8, 132.1 (Ar), 135.8 ($\underline{C}H{=}CH_2$), (Ar); MS (EI) *m/z* 307 (M^+); HRMS (EI) calcd. for $C_{20}H_{21}NS$ (M^+) 307.4524, found 307.1411.

N-Methy-*N*-phenyl-1-(methylthio)-3-phenyl-2-propyn-1-amine (19)

Orange solid; mp 75.8–78.0 (dec.); IR (KBr) 3422, 3060, 2987, 2912, 2817, 2592, 2372, 2222, 1964, 1895, 1822, 1770, 1685, 1595, 1505, 1489, 1472, 1454, 1440, 1424, 1364, 1350, 1304, 1289, 1265, 1224, 1184, 1098, 1070, 1032, 992, 965, 921, 762, 749, 691, 616, 762, 749, 691, 616, 533, 517, 503 cm^{-1}; ^{1}H NMR ($CDCl_3$)δ = 2.16 (s, 3H, SCH_3), 3.08 (s, 3H, CH_3), 5.98 (s, 1H, CH), 6.83–6.87 (m, 1H, Ar), 6.96–6.98 (m, 2H, Ar), 7.25–7.30 (m, 5H, Ar), 7.43–7.45 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$)δ = 14.7 (SCH_3), 33.3 (CH_3), 59.0 (CH), 84.2, 87.2(C≡C), 115.5, 119.4, 122.2, 128.3, 128.6, 129.2, 131.8, 148.5 (Ar); MS (EI) *m/z* 267 (M^+), HRMS (EI) calcd for $C_{17}H_{17}NS$ (M^+); found 267.1067. Anal. Calcd. for $C_{17}H_{17}NS$: C, 76.36; H, 6.41; N, 5.24, Found C, 76.66; H, 6.54; N, 5.24%.

N-(1-Methylthio-3-phenyl-2-propyn-1-yl)morpholine (20)

Dark brown oil; IR (neat) 3395, 3055, 2958, 2917, 2854, 2825, 2758, 2688, 2223, 1970, 1712, 1656, 1598, 1490, 1443, 1341, 1325, 1291, 1258, 1116, 1071, 1030, 999, 980, 861 757, 691, 563 cm^{-1}; ^{1}H NMR ($CDCl_3$)δ = 2.27 (s, 3H, SCH_3), 2.79 (m, 4H, CH_2), 3.76 (t, J = 4.9 Hz, 4H, CH_2), 4.83 (s, 1H, CH), 7.44–7.47 (m, 2H, Ar) 7.25–7.33 (m, 3H, Ar); ^{13}C NMR ($CDCl_3$)δ = 14.7 (SCH_3), 49.0 (CH_2NCH_2), 63.5 (CH), 66.8 (CH_2OCH_2), 83.3, 88.0 (C≡C), 128.3, 128.6, 131.4, 131.8 (Ar); MS (EI) *m/z* 247 (M^+); HRMS (EI) calcd. for $C_{14}H_{17}NOS$ (M^+) 247.1031, found 247.1015.

N-[1-Ethylthio-3-(trimethylsilyl)-2-propyn-1-yl]morpholine (21)

Orange oil: IR (neat) 3423, 2961, 2927, 2898, 2855, 2827, 2758, 2683, 2360, 2246, 2165, 1974, 1664, 1612, 1452, 1322, 1292, 1251, 1201, 1118, 1070, 1057, 1008, 989, 845, 789, 761, 734 cm^{-1}; ^{1}H NMR ($CDCl_3$)δ = 0.14 (s, 9H, $Si(CH_3)_3$), 1.24 (t, J = 7.6 Hz, 3H, CH_3), 2.65 (m, 6H, CH_2), 3.69 (t, J = 4.4 Hz, 4H, CH_2), 4.65 (s, 1H, CH); ^{13}C NMR ($CDCl_3$)δ = –0.06 ($Si(CH_3)_3$), 15.0, 25.5 (SCH_2CH_3), 48.8 (CH_2NCH_2), 62.0 (CH), 66.8 (CH_2OCH_2), 92.6, 99.0 (C≡C); MS (EI) *m/z* 196 ($M^+ - SCH_2CH_3$);

HRMS (EI) calcd. for $C_{10}H_{18}NOSSi$ ($M^+ - CH_2CH_3$) 228.0878, found 228.0883.

N-[1-Ethylthio-3-(triphenylsilyl)-2-propyn-1-yl]morpholine (22)

Pale yellow oil: IR (neat) 3399, 3068, 2961, 2925, 2854, 2165, 2027, 1956, 1884, 1822, 1588, 1485, 1451, 1429, 1376, 1321, 1291, 1252, 1189, 1115, 989, 709, 699, 507 cm^{-1}; ^1H NMR ($CDCl_3$)$\delta = 1.14$ (t, $J = 7.3$ Hz, 3H, CH_3), 2.57–2.67 (m, 6H, CH_2), 3.63 (t, $J = 4.6$ Hz, 4H, CH_2), 4.72 (s, 1H, CH), 7.24–7.33 (m, 10H, Ar), 7.53–7.57 (m, 5H, Ar); ^{13}C NMR ($CDCl_3$)$\delta = 14.9$, 25.5 (SCH_2CH_3), 49.1 (CH_2NCH_2), 62.1 (CH), 66.9 (CH_2OCH_2), 87.8, 104.3 (C≡C), 128.1, 130.1, 133.3, 135.6 (Ar).

Synthesis of Alkynyl *S,N*-Acetals via Lithium Thiolates: General Procedure

To a dried Et_2O solution of lithium acetylide **3** (1.5 equiv.), thioformamide **1** was added at −78°C, and this was stirred at room temperature for 0.5 h. To the reaction mixture, alkyl halides (2 equiv.) at 0°C was added, and this was stirred at room temperature for 2 h. The resulting mixture was poured into a saturated aqueous solution of $NaHCO_3$, and extracted with Et_2O. The organic layer was dried over $MgSO_4$ and concentrated in vacuo to give *S,N*-acetals in purity higher than 90%.

N,N-Dimethyl-1-(ethylthio)-3-(trimethylsilyl)-2-propyn-1-amine (24)

Brown oil: IR (neat) 3399, 2959, 2861, 2824, 2782, 2163, 1665, 1452, 1445, 1251, 1208, 1158, 1075, 1045, 1018, 988, 843, 760, 699 cm^{-1}; ^1H NMR ($CDCl_3$)$\delta = 0.15$ (s, 9H, $Si(CH_3)_3$), 1.24 (t, $J = 7.5$ Hz, 3H, CH_3), 2.31 (s, 6H, $N(CH_3)_2$), 2.66 (q, $J = 7.5$ Hz, 2H, CH_2), 4.73 (s, 1H, CH); ^{13}C NMR ($CDCl_3$)$\delta = 0.13$ ($Si(CH_3)_3$), 15.2 (CH_3), 25.7 (CH_2), 40.5 ($N(CH_3)_2$), 63.2 (CH), 91.8, 100.0 (C≡C); MS (EI) m/z 154 ($M^+ - SCH_2CH_3$).

N,N-Dimethyl-1-(propylthio)-3-(trimethylsilyl)-2-propyn-1-amine (25)

Brown oil: IR (neat) 2959, 2861, 2825, 2782, 2341, 2163, 1625, 1454, 1407, 1250, 1073, 1046, 1021, 988, 843, 760, 515, 413 cm^{-1}; ^1H NMR ($CDCl_3$)$\delta = 0.15$ (s, 9H, $Si(CH_3)_3$), 0.96 (t, $J = 7.4$ Hz, 3H, CH_3), 1.60 (sext, $J = 7.4$ Hz, 2H, $C\underline{H}_2CH_3$), 2.31 (s, 6H, $N(CH_3)_2$), 2.63 (t, $J = 7.4$

Hz, 2H, SCH_2), 4.71 (s, 1H, CH); ^{13}C NMR ($CDCl_3$)$\delta = -0.06$ ($Si(CH_3)_3$), 13.6, 23.5, 33.7 ($CH_2CH_2CH_3$), 40.7 ($N(CH_3)_2$), 63.4 (CH), 91.7, 100.2 (C≡C).

N,N-Dimethyl-1-(butylthio)-3-(trimethylsilyl)-2-propyn-1-amine (26)

Brown oil: IR (neat) 3407, 2957, 2861, 2782, 2163, 1740, 1625, 1453, 1250, 1074, 1022, 843, 760, 698 cm^{-1}; ^1H NMR ($CDCl_3$)$\delta = 0.16$ (s, 9H, $Si(CH_3)_3$), 0.88 (t, $J = 7.3$ Hz, 3H, CH_3), 1.38 (sext, $J = 7.3$ Hz, 2H, $C\underline{H}_2CH_3$), 1.56 (quint, $J = 7.3$ Hz, 2H, $C\underline{H}_2CH_2CH_3$), 2.31 (s, 6H, $N(CH_3)_2$), 2.64 (dt, $J = 2.7$, 7.3 Hz, 2H, SCH_2),4.70 (s, 1H, CH); ^{13}C NMR ($CDCl_3$)$\delta = -0.06$ ($Si(CH_3)_3$), 13.7, 22.1, 31.4, 32.2 ($CH_2CH_2CH_2CH_3$), 40.6 ($N(CH_3)_2$), 63.5 (CH), 91.7, 100.2 (C≡C); MS (EI) m/z 212 ($M^+ - CH_2CH_3$).

N,N-Dimethyl-1-(2-propenylthio)-3-(trimethylsilyl)-2-propyn-1-amine (27)

Brown oil: IR (neat) 3387, 3071, 2958, 2860, 2824, 2782, 2341, 2163, 1636, 1456, 1338, 1251, 1076, 1026, 989, 844, 760 cm^{-1}; ^1H NMR ($CDCl_3$)$\delta = 0.12$ (s, 9H, $Si(CH_3)_3$), 2.23 (s, 6H, $N(CH_3)_2$), 3.22 (m, 2H, SCH_2), 4.60 (s, 1H, CH), 5.07 (m, 2H, $CHC\underline{H}_2$), 5.77 (ddt, $J = 17.1$, 9.8, 7.1 Hz, 1H, $C\underline{H}CH_2$); ^{13}C NMR ($CDCl_3$)$\delta = -0.04$ ($Si(CH_3)_3$), 34.1 (SCH_2), 40.5 ($N(CH_3)_2$), 62.1 (CH), 92.0, 99.9 (C≡C), 117.1 ($CH\underline{C}H_2$), 134.2 ($\underline{C}HCH_2$).

N,N-Dimethyl-1-(2-propenylthio)-2-heptyn-1-amine (28)

Orange oil: IR (neat) 3855, 3823, 3737, 3651, 3366, 3081, 2957, 2934, 2861, 2823, 2780, 2342, 2233, 1832, 1663, 1634, 1577, 1456, 1431, 1400, 1379, 1340, 1217, 1158, 1096, 1046, 1009, 989, 916 cm^{-1}; ^1H NMR ($CDCl_3$)$\delta = 0.86$ (t, $J = 7.3$ Hz, 3H, CH_3), 1.42 (m, 4H, CH_2CH_2), 2.21 (dt, $J = 2.1$, 7.1 Hz, 2H, CH_2), 2.28 (s, 6H, $N(CH_3)_2$), 3.22 (m, 2H, SCH_2), 4.59 (t, $J = 2.0$ Hz, 1H, CH), 5.05 (m, 2H, $CHC\underline{H}_2$), 5.78 (ddt, $J = 17.3$, 9.5, 7.1 Hz, 1H, $C\underline{H}CH_2$); ^{13}C NMR ($CDCl_3$)$\delta = 13.5$ (CH_3), 18.4, 21.9, 30.7 (CH_2) 34.1 (SCH_2), 40.4 ($N(CH_3)_2$), 62.0 (CH), 75.0, 87.9 (C≡C), 116.9 ($CH\underline{C}H_2$), 134.3 ($\underline{C}HCH_2$); MS (EI) m/z 169 ($M^+ - CH_2CHCH_2$).

N,N-Dimethyl-1-(phenylmethylthio)-3-(trimethylsilyl)-2-propyn-1-amine (29)

Orange oil: IR (neat) 3412, 3061, 3029, 2953, 2782, 2163, 1947, 1870, 1624, 1495, 1454, 1407, 1250, 1070, 1029, 844, 762, 699 cm^{-1}; ^1H NMR ($CDCl_3$)δ = 0.19 (s, 9H, $Si(CH_3)_3$), 2.32 (s, 6H, $N(CH_3)_3$), 3.81 (d, J = 13.2 Hz, 1H, $C\underline{H}_2Ph$), 3.90 (d, J = 13.2 Hz, 1H, $C\underline{H}_2Ph$), 4.56 (s, 1H, CH), 7.22–7.34 (m, 5H, Ar); ^{13}C NMR ($CDCl_3$)δ = –0.05 ($Si(CH_3)_3$), 35.3 (CH_2Ph), 40.5 ($N(CH_3)_2$), 62.4 (CH), 92.3, 99.7 (C≡C), 126.9, 128.2, 129.0, 138.4 (Ar); MS (EI) *m/z* 154 (M^+ – SCH_2Ph); HRMS (EI) calcd. for $C_{15}H_{23}NSSi$ (M^++ 1) 278.1320, found 278.1414.

N,N-Dimethyl-1-(1-methylethylthio)-3-(trimethylsilyl)-2-propyn-1-amine (31)

The thioformamide (0.085 mL, 1 mmol), a dried Et_2O solution (4 mL) of alkynyllithium (1.5 mmol) at −78°C was added, and this was stirred at room temperature for 1 h. To the reaction mixture was added 12-crown-4-ether (0.243 mL, 1.5 mmol) at 0°C, and this was stirred at this temperature for 0.5 h. Then, isopropyl iodide (0.2 mL, 2 mmol) was added at 0°C, and this mixture was stirred at this temperature for 1 h. The resulting mixture was poured into a saturated aqueous solution of $NaHCO_3$, and extracted with Et_2O. The organic layer was dried over $MgSO_4$ and concentrated in vacuo to give **31** (0.171 g, 75%) in purity higher than 90% as a brown oil: IR (neat) 3415, 2957, 2864, 2783, 2162, 1626, 1451, 1407, 1383, 1365, 1247, 1096, 1049, 1023, 842, 759 cm^{-1}; ^1H NMR ($CDCl_3$)δ = 0.17 (s, 9H, $Si(CH_3)_3$), 1.28 (d, J = 6.8 Hz, 3H, $CHC\underline{H}_3$), 1.32 (d, J = 6.8 Hz, 3H, $CHC\underline{H}_3$), 2.34 (s, 6H, $N(CH_3)_3$), 3.08 (septet, J = 6.8 Hz, 1H, $C\underline{H}(CH_3)_2$), 4.73 (s, 1H, CHC≡C); ^{13}C NMR ($CDCl_3$)δ = –0.05 ($Si(CH_3)_3$), 23.9 (CH_3) 35.2 ($\underline{C}H(CH_3)_2$), 40.5 ($N(CH_3)_2$), 62.2 ($\underline{C}HC{\equiv}C$), 91.4, 100.4 (C≡C); MS (EI) *m/z* 154 (M^+ – $SCH(CH_3)_2$); HRMS (EI) calcd. for $C_{11}H_{23}NSSi$ (M^++ 1) 230.1320, found 230.1415(M^++ 1).

3,9-Bis(dimethylamino)-1,11-bis(trimethylsilyl)-4,8-dithiaundeca-1,10-diyne (34)

The thioformamide (0.128 mL, 0.5 mmol) was added an Et_2O solution (5 mL) of alkynyllithium (2.25 mmol) at −78°C, and this was stirred at room temperature for 0.5 h. To the reaction mixture, 1,3-diiodopropane (0.057 mL, 0.5 mmol) and TMEDA (0.37 mL, 2.5 mmol) at 0°C was added, and this was stirred at room temperature for 4 h. The resulting mixture was poured into a saturated aqueous solution of $NaHCO_3$,

and extracted with Et_2O. The organic layer was dried over $MgSO_4$ and concentrated in vacuo to give **34** (0.267 g, quant.) in purity higher than 90% as a brown oil: IR (neat) 2956, 2860, 2824, 2782, 2362, 2162, 1717, 1625, 1453, 1338, 1250, 1209, 1159, 1076, 1046, 1025, 988, 844 cm^{-1}; ^1H NMR ($CDCl_3$)$\delta = 0.15$ (s, 18H, $Si(CH_3)_3$), 1.89 (quint, $J = 7.2$ Hz, 2H, CH_2), 2.31 (s, 12H, $N(CH_3)_2$), 2.75 (t, $J = 7.2$ Hz, 4H, CH_2), 4.71 (s, 2H, CH); ^{13}C NMR ($CDCl_3$)$\delta = -0.09$ ($Si(CH_3)_3$), 30.2, 30.3, 30.5 (CH_2), 40.5 ($N(CH_3)_2$), 63.5 (CH), 91.9, 99.9 (C≡C); MS (EI) m/z 414 (M^+).

3,11-Bis(dimethylamino)-1,13-bis(trimethylsilyl)-4,10-dithiatrideca-1,12-diyne (38)

The thioformamide (0.77 mL, 3 mmol) was added a dried Et_2O solution (20 mL) of alkynyllithium (10.8 mmol) at −78°C, and this was stirred at room temperature for 0.5 h. To the reaction mixture, 1,3-diiodopropane (0.45 mL, 3 mmol) and TMEDA (2.2 mL, 15 mmol) at 0°C was added, and this was stirred at room temperature for 4 h. The resulting mixture was poured into a saturated aqueous solution of $NaHCO_3$, and extracted with Et_2O. The organic layer was dried over $MgSO_4$ and concentrated in vacuo to give **38** (1.852 g, quant.) in purity higher than 80% as a brown oil: IR (neat) 2954, 2859, 2824, 2781, 2360, 2162, 1627, 1454, 1337, 1250, 1208, 1158, 1075, 1046, 1021, 988, 844 cm^{-1}; ^1H NMR ($CDCl_3$)$\delta = 0.14$ (s, 18H, $Si(CH_3)_3$), 0.78–0.92 (bm, 2H, CH_2), 2.14–2.24 (bm, 4H, CH_2), 2.29 (s, 12H, $N(CH_3)_2$), 2.61–2.64 (bm, 4H, CH_2), 4.68 (s, 2H, CH); ^{13}C NMR ($CDCl_3$)$\delta = -0.09$ ($Si(CH_3)_3$), 28.3, 29.6, 31.4 (CH_2), 40.5 ($N(CH_3)_2$), 63.4 (CH), 91.8, 100.0 (C≡C); MS (EI) m/z 411 ($M^+ - 2CH_3 - 1$).

3,12-Bis(dimethylamino)-1,14-bis(trimethylsilyl)-4,11-dithiatetradeca-1,13-diyne (39)

The thioformamide (0.77 mL, 9 mmol), a dried Et_2O solution (20 mL) of alkynyllithium (10.8 mmol) at −78°C was added, and this was stirred at room temperature for 0.5 h. To the reaction mixture was added 1,6-diiodohexane (0.49 mL, 3 mmol) and TMEDA (2.2 mL, 15 mmol) at 0°C, and this was stirred at room temperature for 4 h. The resulting mixture was poured into a saturated aqueous solution of $NaHCO_3$, and extracted with Et_2O. The organic layer was dried over $MgSO_4$ and concentrated in vacuo to give **39** (1.811 g, quant.) in purity higher than 90% as a brown oil: IR (neat) 2952, 2858, 2824, 2781, 2162, 1717, 1664, 1453, 1335, 1250, 1208, 1075, 1046, 1023, 988, 844, 760, 698 cm^{-1}; ^1H NMR ($CDCl_3$)$\delta = 0.13$ (s, 18H, $Si(CH_3)_3$), 1.36 (bm, 4H, CH_2), 1.56 (bm,

4H, CH_2), 2.29 (s, 12H, $N(CH_3)_2$), 2.62 (bt, $J = 7.0$ Hz, 4H, CH_2), 4.68 (s, 2H, CH); ^{13}C NMR ($CDCl_3$)δ –0.07 ($Si(CH_3)_3$), 28.6, 29.9, 31.5 (CH_2), 40.5 ($N(CH_3)_2$), 63.4 (CH), 91.7, 100.1 (C≡C); MS (EI) *m/z* 456 (M^+), 302 (M^+ –$CHN(CH_3)_2C{\equiv}CSiMe_3$); HRMS (EI) calcd. for $C_{14}H_{28}N_1S_2Si_1$ (M^+ – $CHN(CH_3)_2C{\equiv}CSiMe_3$) 302.1435, found 302.1427.

1,2-Bis[3-(dimethylamino)-5-(trimethylsilyl)-2-thiapent-4-yn-1-yl]benzene (40)

The thioformamide (0.26 mL, 3 mmol) was added a dried Et_2O solution (10 mL) of alkynyllithium (3.9 mmol) at −78°C, and this was stirred at room temperature for 0.5 h. To the reaction mixture, α, α' -dibromo-*o*-xylene (0.264 g, 1 mmol) and TMEDA (0.74 mL, 5 mmol) at 0°C was added, and this was stirred at room temperature for 4 h. The resulting mixture was poured into a saturated aqueous solution of $NaHCO_3$ and extracted with Et_2O. The organic layer was dried over $MgSO_4$ and concentrated in vacuo to give **40** (0.528 g, quant.) in purity higher than 90% as a brown oil: IR (neat) 2951, 2898, 2859, 2824, 2781, 2360, 2342, 2160, 1625, 1453, 1416, 1339, 1249, 1205, 1158, 1076, 1045, 1025, 986, 844, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$)$\delta = 0.12$ (s, 18H, $Si(CH_3)_3$), 2.27 (s, 12H, $N(CH_3)_2$), 3.96 (dq, J = 2.3, 13.3 Hz, 4H, CH_2), 4.51 (d, $J = 3.6$ Hz, 2H, CH), 7.10–7.12 (m, 2H, Ar), 7.19–7.21 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$)$\delta = 0.02$ ($Si(CH_3)_3$), 32.58, 32.63 (CH_2), 40.48, 40.50 ($N(CH_3)_2$), 62.64, 62.75 (CH), 92.38, 92.42, 99.56, 99.65 (C≡C), 127.31, 130.68, 130.71, 136.59 (Ar); MS (EI) *m/z* 430 (M^+ – $N(CH_3)_2$–1); HRMS (EI) calcd. for $C_{23}H_{37}N_2S_2Si_2$ (M^+ – CH_3) 461.1937, found 461.1924.

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