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# Brønsted acid-promoted cyclizations of siloxy alkynes with unactivated arenes, alkenes, and alkynes

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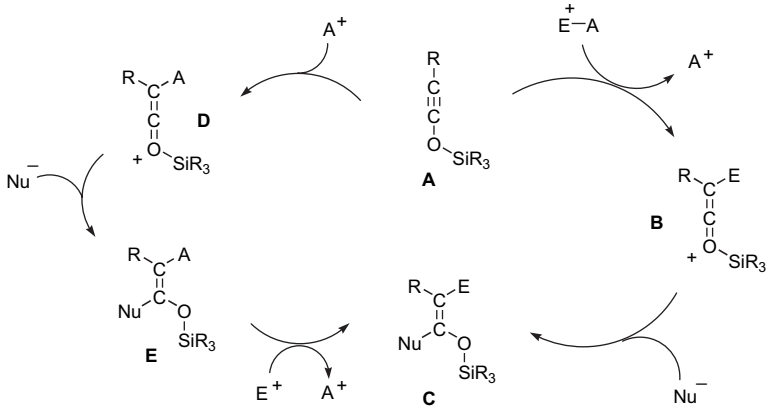
**Abstract**—In this article, we describe the development of a general concept for the development of new carbon–carbon bond-forming processes, which is based on Brønsted acid-mediated activation of a siloxy alkyne, followed by efficient interception of the resulting highly reactive ketenium ion by unactivated arenes, alkenes or alkynes. We found that trifluoromethane sulfonimide ($HNTf_2$) proved to be a superior promoter of these reactions compared to a range of other Brønsted acids. This finding could be attributed to a high acidity of $HNTf_2$ in aprotic organic solvents combined with a low nucleophilicity of the $NTf_2^-$ anion. Depending on the nature of the nucleophile, the carbocyclizations proceeded either via *6-endo-dig* or *5-endo-dig* manifolds. In the case of 1-siloxy-1,5-diynes, the cyclizations occurred with a concomitant halide abstraction or arylation.


## 1. Introduction

Invention of efficient reactions that enable formation of new carbon–carbon bonds is of central significance in organic synthesis. Our laboratory has been engaged in a comprehensive investigation of fundamental reactivity of siloxy alkynes as a prelude to the development of a series of new carbon–carbon bond-forming processes.[1] While enol silanes have been extensively employed in organic synthesis,[2] siloxy alkynes have only been utilized in a very few transformations prior to our work,[3] including Arens olefination[4] and Danheiser benzannulation.[5] We felt that siloxy alkynes had a significantly greater potential for the development of an arsenal of new reactions of broad applicability. We anticipated that such processes could be enabled by two alternative modes of activation depicted in Scheme 1. The first pathway is based on the LUMO-lowering activation of an electrophile, which is expected to react with electron-rich alkyne **A**; subsequent trapping of the ketenium intermediate **B** would give the expected product **C**. Alternatively, direct activation of the alkyne **A** by either a soft or hard π-acid would generate a highly reactive intermediate **D**, which would be expected to react with appropriate nucleophiles and electrophiles to give **C**. It is important to note that siloxy




**Scheme 1**. General strategy for siloxy alkyne activation.

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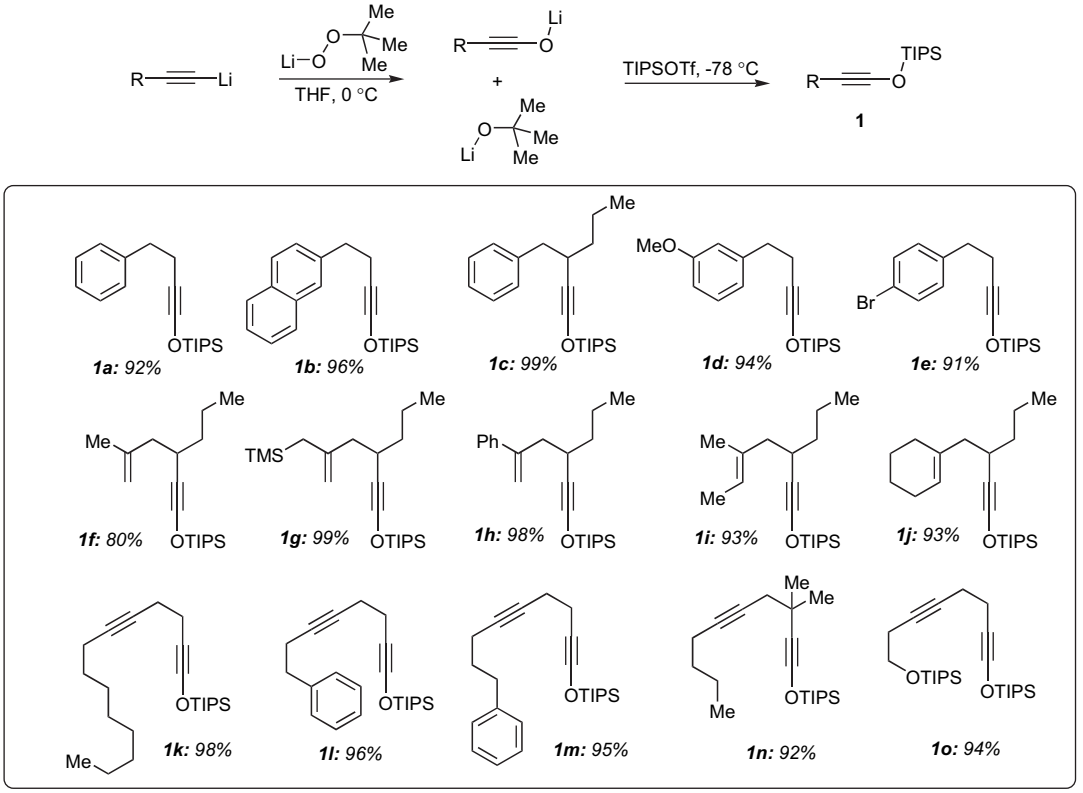
alkynes would offer a unique platform for the generation of highly reactive ketenium ions **B** an **D**, which cannot be obtained from the corresponding ketenes.[6] Due to the high reactivity of ketenium ions, we anticipated that a broad range of nucleophiles and electrophiles could be potentially employed. The challenge was to ensure that these highly reactive intermediates would undergo productive bond-forming transformations. In this account, we describe the full details of our investigation that resulted in the successful development of a series of new Brønsted acid-promoted carbocyclizations of siloxy alkynes with unactivated arenes, alkenes, and alkynes.

## 2. Siloxy alkynes: preparation

The general approach for the preparation of siloxy alkynes relies on O-silylation of the corresponding ynolate anion. Bulky silyl groups, i.e., TBS or TIPS, must be employed to ensure sufficient hydrolytic stability of the resulting ynol silanes. Several methods for the generation of ynolate anions have been developed.[7] During our studies, we found that the protocol reported by Julia in 1993[8] represents a simple, versatile, and highly efficient approach to a range of structurally diverse siloxy alkynes. The Julia method entails the generation of the acetylide anion from the corresponding terminal alkyne, followed by the addition of lithium *tert*-butyl hydroperoxide,[9] at 0 °C which promotes facile oxidation of the lithium acetylide to give lithium ynolate and lithium *tert*-butoxide (Scheme 2). While silyl chloride was employed in the original Julia's report to furnish the corresponding siloxy alkyne in 60% yield, we found that the use of triisopropylsilyl trifluoromethanesulfonate (TISPOTf) resulted in formation of the desired siloxy alkynes in excellent isolated yields. This modification also enables the use of only 1 equiv of the silylating agent to enable selective silylation of the ynolate anion in the presence of a bulkier lithium *tert*-butoxide. The Julia protocol was employed for the preparation of a series of 1-siloxy-1-alkynes **1**, which were required for this study (Scheme 2). We found that the Kowalski protocol[7d] was better suited for the preparation of siloxy alkynes **1n**. While siloxy alkynes are stable toward bulb-to-bulb distillation, in many instances, the products were obtained in a sufficiently pure form for the use in the next transformation directly.

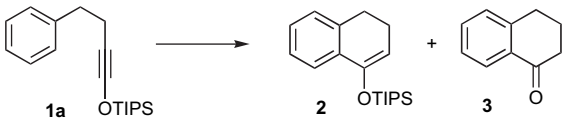
## 3. Development of arene–siloxyalkyne carbocyclizations

Our investigation of the cyclization of 4-phenyl-1-siloxy-1-butyne (**1a**, Scheme 3) began with an examination of a range of metal salts known to promote alkyne carbocyclizations, including $PtCl_2$, $GaCl_3$, $HfCl_4$, and $Hg(OTf)_2$.[10] Unfortunately, formation of the desired cyclization product **2** was not observed under a range of reaction conditions examined. Prompted by our recently developed [2+2] cycloadditions of siloxy alkynes, we decided to examine several silver-based catalysts. Indeed, we found that treatment of alkyne **1a** with $AgNTf_2$ (20 mol %) resulted in the formation of silyl enol ether **2** in 65% isolated yield (Scheme 3). Interestingly, the use of AgOTf gave rise to the isolation of tetralone **3** as a sole reaction product, albeit in a low yield. This dramatic difference in the outcome of these two experiments indicated that the nature of silver counterion played a dominant role in controlling the efficiency and the outcome of the reaction. In order to probe the role of silver in the process, we subjected




**Scheme 2**. Preparation of siloxy alkynes.

alkyne **1a** to $HNTf_2$ (10 mol %), which resulted in a facile cyclization to give the same product **2** that was observed using $AgNTf_2$. A series of additional studies indicated that $HNTf_2$, which is produced following the rearomatization event, was most likely the active catalyst when $AgNTf_2$ was employed initially for cyclization of **1a**. Interestingly, the efficiency of the reaction diminished significantly when TfOH was employed favoring the formation of tetralone **3**. Thus, the optimized conditions for the cyclizations of **1a** entailed the use of 10 mol % of $HNTf_2$ at ambient temperature to give silyl enol ether **2** in 86% isolated yield.[11]

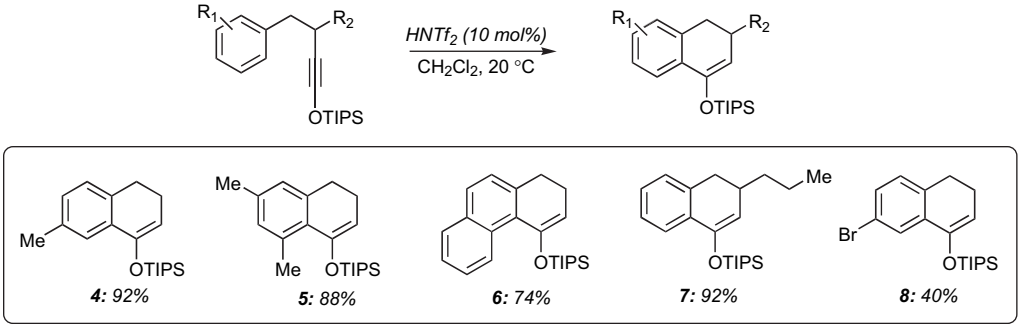



| | | |
|---|---|---|
| *$AgNTf_2$ (20 mol%)* | 65% | none |
| *AgOTf (20 mol%)* | none | 15% |
| *$HNTf_2$ (10 mol%)* | 86% | none |
| *HOTf (20 mol%)* | none | 25% |

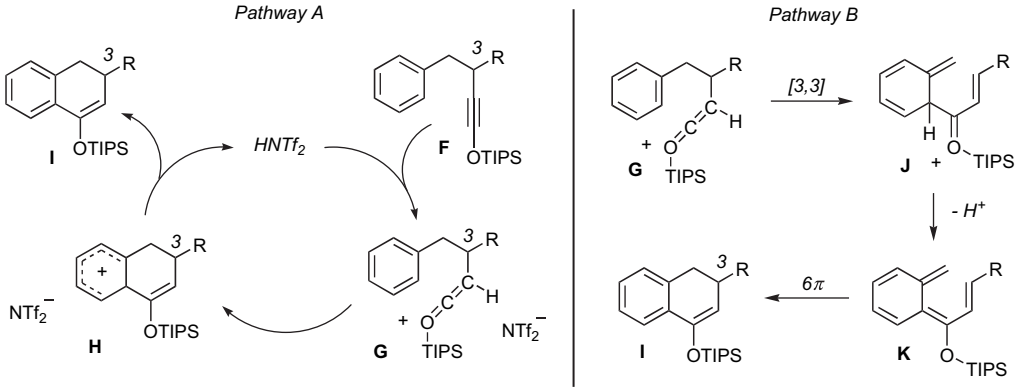
**Scheme 3**. Effect of silver salts and Brønsted acids on carbocyclization of alkyne **1a**.

Having established an effective reaction protocol, we examined the scope of arene substitution in this process. We found that di- and tri-alkyl substituted benzenes efficiently participated in the cyclization to give the expected silyl enol ethers **4** and **5**, respectively (Scheme 4). Furthermore, 2-naphthyl-1-siloxy-1-butyne afforded tricyclic enol silane **6** in 74% yield. Alkyl substitution at the 3-position of the alkyne was well tolerated as demonstrated by efficient assembly of silyl enol ether **7**. Importantly, the chirality of this product was fully preserved when the starting silyl enol ether was prepared in highly enantiomerically enriched form via semi-preparative HPLC using a chiral stationary phase. In addition to expanding the scope of the process, this experiment provided an important mechanistic probe (vide infra). It is highly noteworthy that successful participation of a range of unactivated arenes in the carbocyclization with siloxy alkynes distinguishes this process uniquely from the metal-mediated carbocyclizations of alkynes that generally require electron-rich arenes or alkenes.[10] Indeed, as expected, introduction of electron-donating substitution into the arene moiety resulted in a facile cyclization to give silyl enol ether as a 72:25 mixture of *para/ortho* cyclized products in combined yield of 84% (not shown). Bromine substitution was also tolerated. However, the product **8** was obtained in lower yield, presumably due to the electron-withdrawing effect of the halogen atom.

Based on the results obtained in the studies described above, we propose that the cyclization reaction proceeds via a mechanism depicted in Scheme 5A. The catalytic process begins with the protonation of siloxy alkyne **F** by $HNTf_2$ to give highly reactive ketenium ion **G**, which is poised for intramolecular interception by the arene to give σ-complex **H**. Elimination of the proton regenerates the Brønsted acid catalysts and affords the observed enol silane **I**. We believe that the low nucleophilicity of the $NTf_2^-$ anion is crucial for enabling the formation and effective interception of highly reactive ketenium ion **G**. An alternative mechanism shown in Scheme 5B involving a [3,3]-sigmatropic rearrangement of ketenium ion **G**, followed by 6π-electron cyclization of intermediate **K** would result in racemization of stereogenic




**Scheme 4**. Scope of arene–siloxyalkyne carbocyclizations catalyzed by $HNTf_2$.

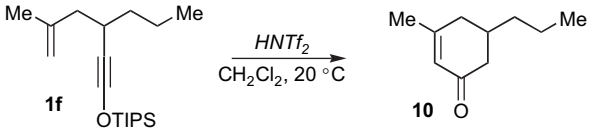



**Scheme 5**. Mechanism of the arene–siloxyalkyne carbocyclization.

center at the C(3) position of **I** (see Scheme 4), which was not observed.

## 4. Development of 1-siloxy-1,5-enyne carbocyclizations

We next examined the possibility of achieving the 6-*endo-dig* carbocyclization of the 1-siloxy-1,5-enyne **1f** to give cyclohexenone **10** (Scheme 6) or the corresponding silyl enol ether (not shown). Since $HNTf_2$ proved effective in catalyzing the corresponding arene alkyne cyclizations, our study began by treatment of enyne **1f** with 10 mol % of this Brønsted acid (Scheme 6). Indeed, the desired enone **10** was produced, albeit in low isolated yield. Further studies depicted in Scheme 6 demonstrated that $HNTf_2$ could indeed promote the efficient conversion of enyne **1f** to enone **10**. However, the stoichiometric amount of acid was required to accomplish this transformation; enone **10** was obtained in 74% isolated yield employing 120 mol % of $HNTf_2$.



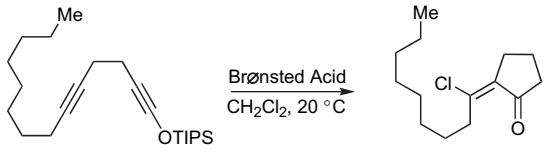

| $HNTf_2$ | Yield, % |
|---|---|
| 10 mol% | 20 |
| 50 mol% | 50 |
| 120 mol% | 74 |

**Scheme 6**. Development of $HNTf_2$-promoted 1-siloxy-5,1-enyne cyclization.

Investigation of the scope of $HNTf_2$-promoted siloxy enyne cyclization is summarized in Scheme 7. Cyclization of phenyl-substituted enyne proceeded efficiently to give phenyl cyclohexanone **11** in 80% yield. Similarly, treatment of enyne containing an allyl silane functionality ($R_1$=$CH_2TMS$) resulted in facile formation of enone **10** with a concomitant loss of trimethyl silyl group. During these studies, we found that an alternative protocol, which entailed the use of 1–4 equiv of MsOH in $CH_2Cl_2$ proved more effective for a series of other enones shown in Scheme 7, which corresponded to the cyclizations of either trisubstituted or monosubstituted alkenes. Indeed, under these conditions, enones **12** and **13** were obtained in good to excellent yields, further expanding the scope of this process. Our efforts to identify a catalytic protocol to effect these siloxy enyne cyclizations have been thus far unsuccessful. The challenge entails the ability to regenerate the active Brønsted acid catalyst upon loss of the proton following the initial carbon–carbon bond-forming event.

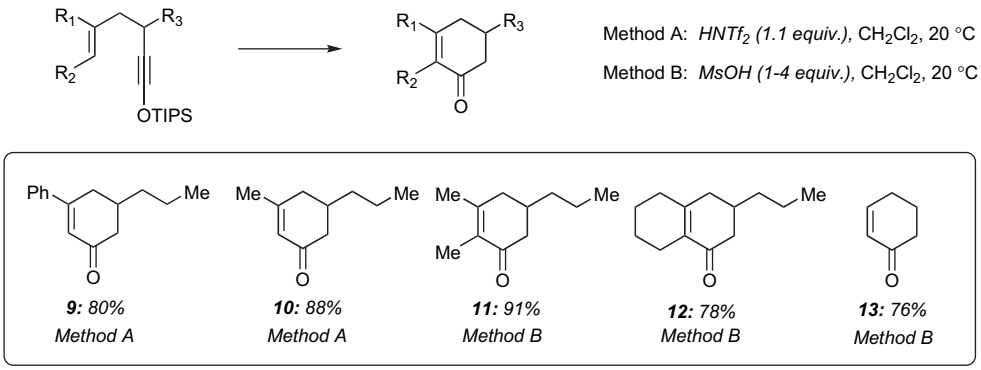
## 5. Development of 1-siloxy-1,5-diyne carbocyclizations

Having established that $HNTf_2$ was capable of efficient activation of siloxy alkynes toward intramolecular trapping by unactivated arenes and alkenes, we next examined the application of this concept to the carbocyclization of 1-siloxy-1,5-diynes. It was our expectation that Brønsted acid would promote chemoselective activation of the more electron-rich siloxy alkyne, which should enable the carbocyclization via an intramolecular attack by the other alkyne fragment. 1-Siloxy-1,5-diyne **1k** (Scheme 8) was prepared according to the Julia protocol described above. Treatment of 1-siloxy-1,5-diyne **1k** with $HNTf_2$ (110 mol %) in $CH_2Cl_2$ resulted in an efficient transformation of **1k** to a new product, which was isolated in 70% yield. Analysis of the reaction by GC–MS indicated incorporation of the chlorine atom into the reaction product. Based on the combination of COSY, NOESY, and HMBC experiments, the structure of the reaction product was assigned as enone **14**, which was generated as a single alkene isomer. This assignment was further confirmed by the synthesis of **14** using an independent method.[12] Interestingly, the outcome of the carbocyclization of 1-siloxy-1,5-diyne **1k** was significantly different from that observed in our prior studies of cyclizations of siloxy alkynes with arenes and alkenes. Not only the diyne carbocyclization favored the 5-*endo-dig* pathway, but also the




| | |
|---|---|
| $HNTf_2$ (1.1 equiv) | 70% |
| $HBF_4$ (1.1 equiv) | 32% |
| TfOH (1.1 equiv) | 22% |
| TFA (1.1 equiv) | 20% |
| TsOH (1.1 equiv) | <5% |

**Scheme 8**. Development of $HNTf_2$-promoted 1-siloxy-1,5-diyne cyclization.



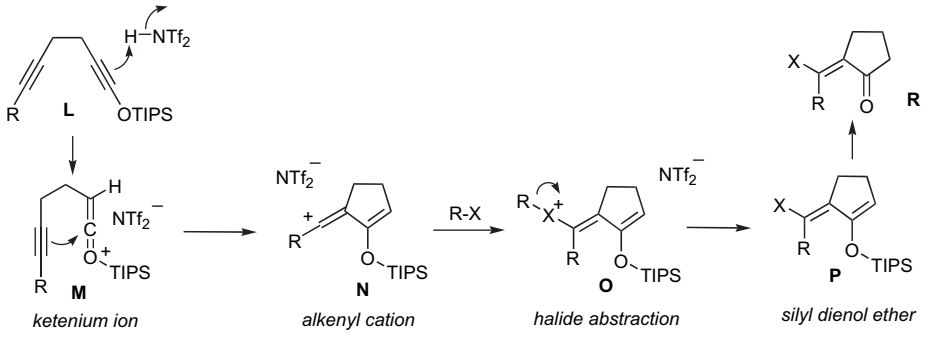

**Scheme 7**. Scope of $HNTf_2$-promoted 1-siloxy-5,1-enyne cyclization.

process proceeded with a concomitant incorporation of the chloride originating exclusively from $CH_2Cl_2$. Subsequent studies revealed that $HNTf_2$ proved superior to any of the other Brønsted acids examined (Scheme 8). While $HBF_4$, TfOH, and TFA were able to promote the reaction, the efficiency of the process deteriorated significantly (32%, 22%, and 20% yields, respectively). Interestingly, the use of either CSA or anhydrous HCl resulted in the formation of uncyclized products resulting from the hydrolysis of siloxyalkyne to the corresponding silyl ester and acid chloride, respectively.

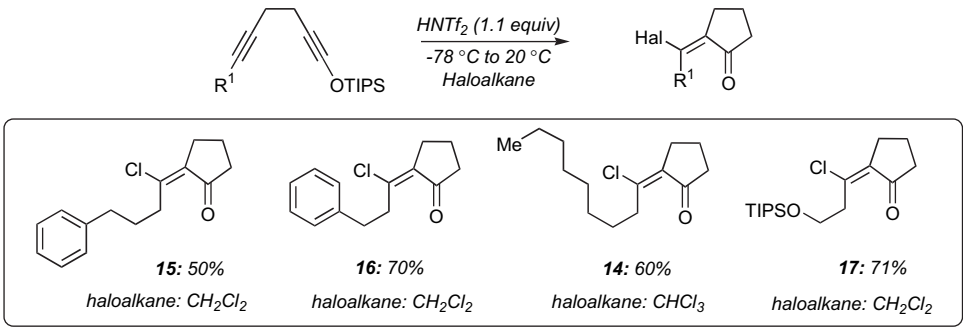
We propose that carbocyclization of 1-siloxy-1,5-diynes proceeds according to the reaction mechanism depicted in Scheme 9. Initial protonation occurs chemoselectively at the more electron-rich siloxy alkyne to give an intermediate ketenium ion **M**. This highly reactive cation is poised for *5-endo-dig* intramolecular interception by the proximate alkyne to give alkenyl cation **N**, which in turn abstracts a chloride ion from $CH_2Cl_2$ presumably via the intermediacy of halonium ion **O**. The final step entails the protodesilylation of enol silane **P** to give enone **R**. The silyl enol ether can be detected and isolated as the major product by conducting the reaction in the presence of substoichiometric amount (20–30 mol %) of $HNTf_2$ or by subjecting a diyne **L** to 110 mol % of $HNTf_2$, followed by treatment of the crude reaction mixture with $Et_3N$. Importantly, halide abstraction by structurally different alkenyl cations finds two precedents in the literature,[13] which provides further support for our mechanistic analysis. Furthermore, subsequent GC–MS analysis of the cyclization, which was performed in the presence of MeOH, revealed the formation of $XCH_2OMe$ providing another evidence of the generation of $XCH_2^+$ cations in the reaction mixture.

Our initial investigation of the scope of this process is depicted in Scheme 10. We found that a range of diyne substitution was well tolerated in the reaction. Subjection of phenyl-substituted diynes to the general reaction protocol (1.1 equiv $HNTf_2$, $CH_2Cl_2$, 20 °C) efficiently afforded the expected enones **15** and **16**. Interestingly, the chloride abstraction was favored over the possible intra- or intermolecular arylation of the intermediate alkenyl cation. We found that the replacement of $CH_2Cl_2$ with $CHCl_3$ as a reaction medium was also effective in producing enone **14**. Furthermore, TIPS-protected primary alcohol in enone **17** was retained under the standard cyclization conditions, demonstrating that the reaction protocol was fully compatible with the use of silyl protecting group despite the presence of a strong Brønsted acid.

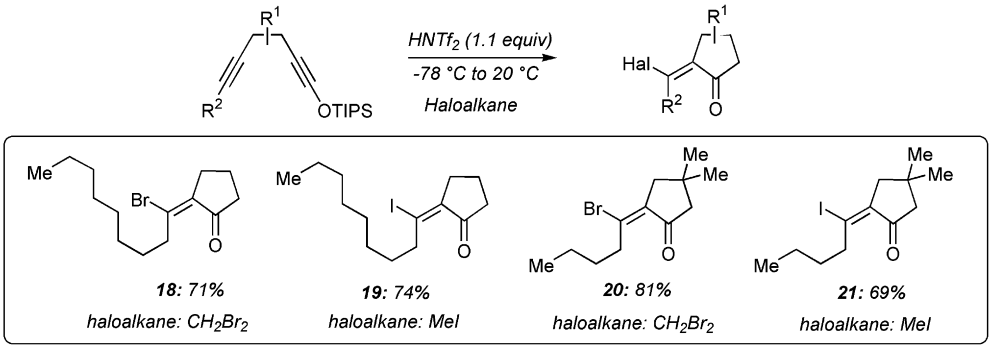
Having observed efficient chloride abstraction in the cyclizations described above, we decided to examine next the possibility of incorporation of other halides into the enone products. Subjection of diyne **1k** to $HNTf_2$ (1.1 equiv) in $CH_2Br_2$ afforded β-bromo enone **18** in 71% yield (Scheme 11) as a single alkene isomer. The use of MeI as a reaction solvent resulted in efficient formation of the expected iodoenone **19**. Subjection of 3,3-dimethyl siloxy diyne to $HNTf_2$ in either $CH_2Br_2$ or MeI afforded the corresponding enones **20** and **21**, indicating that the increased steric congestion proximate to the siloxy alkyne moiety did not lower the reaction efficiency. It is noteworthy that excellent diastereoselectivity of the present method combined with the ability to access a range of β-halo enones compares this approach favorably to other known methods for the preparation of this class of compounds. At present, however, this concept could not be extended to cyclizations of homologous 1-siloxy-1,6-enynes.




**Scheme 9**. Mechanism of the siloxy diyne carbocyclization.

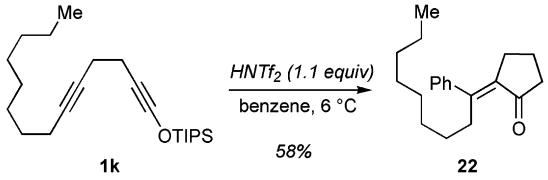



**Scheme 10**. Scope of siloxy diyne cyclization using $CH_2Cl_2$ and $CHCl_3$.




**Scheme 11**. Scope of siloxy diyne cyclization using $CH_2Br_2$ and MeI.

During these studies, we also discovered that generation of alkenyl cations could enable carbon–carbon bond-forming event via an intermolecular arylation. Indeed, treatment of diyne **1k** with $HNTf_2$ in benzene afforded tetrasubstituted enone **22** (Scheme 12), which was generated as a single detectable alkene isomer. The alkene geometry is controlled, presumably, via a less sterically hindered approach of the nucleophile *syn* to the methylene moiety of the alkenyl cation (Scheme 9).




**Scheme 12**. $HNTf_2$-promoted 1-siloxy-1,5-diyne cyclization–arylation.

## 6. Concluding remarks

We have presented a broadly useful concept for Brønsted acid-based activation of siloxy alkynes that enabled the development of a series of new carbocyclization reactions via the intermediacy of highly reactive ketenium ions. We found that trifluoromethane sulfonimide $HNTf_2$ proved to be superior reaction promoter compared to a range of other Brønsted acids.[14] This finding could be attributed to a high acidity of $HNTf_2$ in aprotic organic solvents combined with a low nucleophilicity of the $NTf_2^-$ anion. Depending on the nature of the nucleophile, the carbocyclizations proceeded either via *6-endo-dig* or *5-endo-dig* manifolds. In the case of 1-siloxy-1,5-diynes, the cyclizations occurred with a concomitant halide abstraction or arylation.

## 7. Experimental

### 7.1. General

Ethyl acetate (ACS grade), hexanes (ACS grade), and diethyl ether (ACS grade) were purchased from Fisher Scientific and used without further purification. Anhydrous dichloromethane (HPLC grade) was purified by distillation over calcium hydride. Anhydrous tetrahydrofuran was freshly distilled from sodium–benzophenone. Triisopropylsilyl trifluoromethanesulfonate (TIPSOTf) was distilled under reduced pressure over calcium hydride. Commercially available reagents were used without further purification. Reactions were monitored by thin layer chromatography (TLC) using Whatman precoated silica gel plates. Flash column chromatography was performed over silacycle silica gel (230–400 mesh). $^1$H NMR and $^{13}$C NMR spectra were recorded on Bruker DRX-400 or DMX-500 spectrometers using residue solvent peaks as internal standards. Infrared spectra were recorded with a Nicolet FTIR spectrometer and are reported in reciprocal centimeter ($cm^{-1}$). Mass spectra were recorded with a Varian Saturn 2000 GC–MS using EI method or an Agilent 1100 LCMS using APCI or ES methods. Preparation of terminal alkynes was described in detail in our previous reports.[1d,f]

### 7.2. Procedure for the preparation of siloxy alkynes

Anhydrous *tert*-butyl hydroperoxide (TBHP) was prepared following a detailed literature procedure.[9] *Caution: solutions of oxidants and oxidizable substrates are potentially hazardous and possibly subject to violent decomposition by adventitious catalysts*. Safety considerations related to handling solutions of TBHP have been previously discussed. See Ref. 9 and further references cited therein. A solution of alkyne (2 mmol) in THF (10 mL) was treated at −78 °C with freshly prepared 1.0 M solution of LiHMDS in THF (2.4 mL). At the same time, a solution of lithium *tert*-butyl peroxide was generated by treating a solution of anhydrous *tert*-butyl hydrogen peroxide (3.7 M in toluene, 2.4 mmol, 0.65 mL) in THF (10 mL) with 1.0 M LiHMDS (2.6 mL) at −78 °C. Lithium *tert*-butyl peroxide solution was transferred to the alkynyl lithium solution via cannula and the resulting mixture was allowed to warm to 0 °C over 0.5 h, stirred at the same temperature for 2 h and cooled to −78 °C before triisopropylsilyl trifluoromethanesulfonate (2.6 mmol, 0.7 mL) was added dropwise. The reaction mixture was allowed to warm to 0 °C, stirred for 0.5 h and diluted with hexanes (50 mL). The resulting solution was washed with saturated aqueous $NaHCO_3$ (40 mL), $H_2O$ (40 mL), and brine (30 mL), then dried ($MgSO_4$), filtered, and concentrated. The residue was subjected to purification via bulb-to-bulb distillation.

**7.2.1. Siloxy alkyne 1a.** $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.27 (dd, 2H, $J$=7.1, 8.1 Hz), 7.21 (d, 2H, $J$=8.1 Hz), 7.18 (t, 1H, $J$=7.1 Hz), 2.75 (t, 2H, $J$=7.5 Hz), 2.39 (t, 2H, $J$=7.5 Hz), 1.21 (h, 3H, $J$=7.3 Hz), 1.09 (d, 18H, $J$=7.3 Hz);

$^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 141.5, 128.4, 128.2, 125.9, 87.2, 36.4, 29.9, 19.3, 17.3, 11.8; IR (neat, $cm^{-1}$) 3296, 2945, 2868, 2279, 1603, 1454; MS (APCI) calculated for $[C_{19}H_{31}OSi]^+$: 303.21; found: 303.1.

**7.2.2. Siloxy alkyne 1b.** $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.82–7.72 (m, 3H), 7.66 (s, 1H), 7.47–7.41 (m, 2H), 7.37 (d, 1H, $J$=8.5 Hz), 2.93 (t, 2H, $J$=7.5 Hz), 2.51 (t, 2H, $J$=7.5 Hz), 1.15 (h, 3H, $J$=7.5 Hz), 1.04 (d, 18H, $J$=7.5 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 138.9, 133.5, 132.1, 127.7, 127.5, 127.4, 127.2, 126.6, 125.1, 87.4, 36.4, 29.8, 19.2, 18.0, 17.3, 11.7; IR (neat, $cm^{-1}$) 2945, 2867, 2278, 1463; MS (APCI) calculated for $[C_{23}H_{33}OSi]^+$: 353.23; found: 353.2.

**7.2.3. Siloxy alkyne 1c.** $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.31–7.17 (m, 5H), 2.69 (d, 2H, $J$=7.0 Hz), 2.56 (m, 1H), 1.57 (m, 1H), 1.44–1.30 (m, 3H), 1.20 (h, 3H, $J$=7.5 Hz), 1.09 (d, 18H, $J$=7.5 Hz), 0.89 (t, 3H, $J$= 7.0 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 140.7, 129.2, 127.9, 125.7, 88.5, 42.8, 37.8, 33.5, 32.2, 20.5, 17.3, 13.9, 11.7; IR (neat, $cm^{-1}$) 3063, 3027, 2946, 2868, 2273, 2077, 1604, 1464; MS (APCI) calculated for $[C_{22}H_{37}OSi]^+$: 345.26; found: 345.2.

**7.2.4. Siloxy alkyne 1d.** $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.19 (t, 1H, $J$=8.0 Hz), 6.80 (d, 1H, $J$=8.0 Hz), 6.76 (s, 1H), 6.74 (d, 1H, $J$=8.0 Hz), 3.80 (s, 3H), 2.74 (t, 2H, $J$=7.5 Hz), 2.39 (t, 2H, $J$=7.5 Hz), 1.19 (h, 3H, $J$=7.5 Hz), 1.09 (d, 18H, $J$=7.5 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 159.5, 143.1, 129.1, 120.8, 114.2, 111.2, 87.2, 55.1, 36.5, 29.9, 19.2, 17.3, 11.7; IR (neat, $cm^{-1}$) 2946, 2868, 2279, 1602, 1585, 1490; MS (APCI) calculated for $[C_{20}H_{33}O_2Si]^+$: 333.22; found: 333.2.

**7.2.5. Siloxy alkyne 1e.** $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.38 (d, 2H, $J$=8.5 Hz), 7.08 (d, 2H, $J$=8.5 Hz), 2.69 (t, 2H, $J$=7.5 Hz), 2.37 (t, 2H, $J$= 7.5 Hz), 1.17 (h, 3H, $J$=7.0 Hz), 1.06 (d, 18H, $J$=7.0 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 140.4, 131.2, 130.3, 119.7, 87.5, 35.6, 29.4, 19.1, 17.3, 11.7; IR (neat, $cm^{-1}$) 2945, 2867, 2279, 1592, 1488, 1463; MS (APCI) calculated for $[C_{19}H_{30}BrOSi]^+$: 381.12; found: 381.1.

**7.2.6. Siloxy alkyne 1f.** $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 4.74 (s, 1H), 4.71 (s, 1H), 2.43 (m, 1H), 2.13–2.05 (m, 2H), 1.71 (s, 3H), 1.54 (m, 1H), 1.42–1.31 (m, 3H), 1.25 (h, 3H, $J$=7.5 Hz), 1.11 (d, 18H, $J$=7.5 Hz), 0.89 (t, 3H, $J$= 7.2 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 144.1, 111.6, 88.0, 44.9, 38.0, 33.6, 28.5, 22.2, 20.5, 17.4, 13.9, 11.8; IR (neat, $cm^{-1}$) 2947, 2869, 2274, 2078, 1649, 1464; MS (APCI) calculated for $[C_{19}H_{37}OSi]^+$: 309.26; found: 309.2.

**7.2.7. Siloxy alkyne 1g.** $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 4.64 (s, 1H), 4.56 (s, 1H), 2.42 (m, 1H), 2.08 (dd, 1H, $J$=8.5, 14.5 Hz), 1.58–1.48 (m, 2H), 1.42–1.32 (m, 2H), 1.24 (h, 3H, $J$=7.5 Hz), 1.12 (d, 18H, $J$=7.5 Hz), 1.07 (m, 2H), 0.87 (t, 3H, $J$=7.0 Hz), 0.01 (s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 145.6, 108.8, 88.0, 45.3, 38.0, 33.9, 28.7, 26.5, 20.5, 17.4, 14.0, 11.8, −1.3; IR (neat, $cm^{-1}$) 3073, 2955, 2869, 2274, 2078, 1632, 1464; MS (APCI) calculated for $[C_{22}H_{45}OSi_2]^+$: 381.30; found: 381.2.

**7.2.8. Siloxy alkyne 1h.** $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.38 (d, 2H, $J$=7.5 Hz), 7.31 (dd, 2H, $J$=6.0, 7.5 Hz), 7.25 (t, 1H, $J$=6.0 Hz), 5.29 (d, 1H, $J$=1.5 Hz), 5.12 (d, 1H, $J$=1.5 Hz), 2.63 (dd, 1H, $J$=7.0, 9.0 Hz), 2.57 (dd, 1H, $J$=6.5, 9.0 Hz), 2.35 (m, 1H), 1.53 (m, 1H), 1.43–1.23 (m, 6H), 1.12 (d, 18H, $J$=7.5 Hz), 0.85 (t, 3H, $J$=7.0 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 146.7, 141.2, 128.2, 127.2, 126.3, 114.0, 88.2, 42.6, 37.9, 33.6, 28.8, 20.4, 17.4, 14.0, 11.8; IR (neat, $cm^{-1}$) 3082, 2947, 2868, 2273, 2076, 1628, 1464, 1385; MS (APCI) calculated for $[C_{24}H_{39}OSi]^+$: 371.28; found: 371.2.

**7.2.9. Siloxy alkyne 1i.** $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 5.23 (q, 1H, $J$=5.5 Hz), 2.40 (m, 1H), 2.04 (m, 2H), 1.58–1.51 (m, 7H), 1.36–1.32 (m, 3H), 1.28–1.21 (m, 3H), 1.11 (d, 18H, $J$=7.5 Hz), 0.88 (t, 3H, $J$=7.5 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 134.1, 120.0, 88.0, 46.8, 38.0, 33.9, 28.6, 20.5, 17.3, 15.4, 14.0, 13.3, 11.8; IR (neat, $cm^{-1}$) 2947, 2869, 2273, 2077, 1602, 1464; MS (APCI) calculated for $[C_{20}H_{39}OSi]^+$: 323.28; found: 323.2.

**7.2.10. Siloxy alkyne 1j.** $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 5.42 (s, 1H), 2.38 (m, 1H), 2.05–1.83 (m, 6H), 1.60–1.50 (m, 5H), 1.41–1.37 (m, 2H), 1.23 (h, 3H, $J$=7.5 Hz), 1.11 (d, 18H, $J$=7.5 Hz), 0.88 (t, 3H, $J$=7.2 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 136.0, 122.5, 87.8, 45.3, 38.1, 33.9, 28.3, 28.1, 25.3, 23.0, 22.5, 20.5, 17.4, 14.0, 11.7; IR (neat, $cm^{-1}$) 2929, 2868, 2273, 1607, 1464; MS (APCI) calculated for $[C_{22}H_{40}OSi]^+$: 349.29; found: 349.5.

**7.2.11. Siloxy alkyne 1k.** $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 2.30–2.24 (m, 4H), 2.14–2.11 (m, 2H), 1.51–1.44 (m, 2H), 1.34–1.22 (m, 13H), 1.13–1.12 (d, 18H, $J$=7.5 Hz), 0.88 (t, 3H, $J$=6.8 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 87.3, 80.7, 79.2, 31.9, 29.5, 29.2, 29.1, 29.1, 28.9, 22.7, 20.4, 18.7, 18.2, 17.3, 14.1, 11.8; IR (neat, $cm^{-1}$) 2928, 2868, 2361, 2281; MS (APCI) calculated for $[C_{23}H_{43}OSi]^+$: 363.31; found: 363.3.

**7.2.12. Siloxy alkyne 1l.** $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.33–7.29 (m, 2H), 7.24–7.21 (m, 3H), 2.82 (t, 2H, $J$=7.5 Hz), 2.46–2.42 (m, 2H), 2.31–2.26 (m, 4H), 1.32–1.24 (m, 3H), 1.15 (d, 18H, $J$=4.0 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 141.0, 128.4, 128.3, 126.1, 87.4, 80.1, 80.0, 35.5, 29.4, 21.0, 20.3, 18.1, 17.3, 11.8; IR (neat, $cm^{-1}$) 3028, 2945, 2868, 2280, 1604; MS (APCI) calculated for $[C_{23}H_{35}OSi]^+$: 355.25; found: 355.2.

**7.2.13. Siloxy alkyne 1m.** $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.32–7.27 (m, 2H), 7.23–7.19 (m, 3H), 2.74 (t, 2H, $J$=7.8 Hz), 2.35–2.29 (m, 4H), 2.20–2.17 (m, 2H), 1.85–1.79 (m, 2H), 1.34–1.25 (m, 3H), 1.15 (d, 18H, $J$=7.5 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 141.8, 128.5, 128.2, 125.7, 87.4, 80.2, 79.9, 34.8, 30.6, 29.4, 20.4, 18.2, 18.0, 17.3, 11.8; IR (neat, $cm^{-1}$) 2945, 2868, 2280, 1604, 1463; MS (APCI) calculated for $[C_{24}H_{37}OSi]^+$: 369.26; found: 369.2.

**7.2.14. Siloxy alkyne 1n.** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 2.25 (t, 2H, $J$=2.4 Hz), 2.18–2.13 (m, 2H), 1.51–1.36 (m, 4H), 1.30–1.22 (m, 3H), 1.20 (s, 6H), 1.12 (d, 18H, $J$=7.1 Hz), 0.90 (t, 3H, $J$=7.2 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 87.2, 81.9, 77.6, 37.8, 34.5, 31.2, 30.1, 29.2, 21.9, 18.5, 17.3, 13.6, 11.8; IR (neat, $cm^{-1}$) 2961, 2869,

2361, 2277; MS (APCI) calculated for $[C_{21}H_{39}OSi]^+$: 335.28; found: 335.2.

**7.2.15. Siloxy alkyne 1o.** $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 3.76 (t, 2H, $J$=7.5 Hz), 2.41–2.37 (m, 2H), 2.29–2.23 (m, 4H), 1.30–1.22 (m, 3H), 1.13 (d, 18H, $J$=7.5 Hz), 1.10–1.05 (m, 21H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 87.4, 80.5, 77.4, 62.6, 29.4, 23.2, 20.4, 18.0, 17.9, 17.3, 12.0, 11.8; IR (neat, cm$^{-1}$) 2867, 2728, 2281, 1623, 1464; MS (APCI) calculated for $[C_{26}H_{51}O_2Si_2]^+$: 451.34; found: 451.2.

### 7.3. Procedure for aryl siloxy alkyne cyclizations catalyzed by $HNTf_2$

Under $N_2$ atmosphere, a flame-dried Airfree® flask was charged with $CH_2Cl_2$ (25 mL) and siloxy alkyne (0.31 mmol). The solution was treated with $HNTf_2$ in $CH_2Cl_2$ (0.153 M, 0.2 mL, 0.1 equiv) dropwise as an orange color developed. After stirring at room temperature for 1 h, the reaction mixture was treated with diisopropylethylamine (0.1 mL) and stirred further for 0.5 h. The resulting solution was then diluted with hexanes (20 mL), washed with HCl (1 M, 10 mL), saturated aqueous $NaHCO_3$ (10 mL), $H_2O$ (10 mL), and brine (10 mL), then dried ($MgSO_4$), filtered, and concentrated. The residue was purified by silica gel flash chromatography to afford the silyl enol ether.

**7.3.1. Silyl enol ether 2.** $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.55 (d, 1H, $J$=7.5 Hz), 7.20 (t, 1H, $J$=7.5 Hz), 7.15 (t, 1H, $J$=7.5 Hz), 7.10 (d, 1H, $J$=7.5 Hz), 5.17 (t, 1H, $J$=5.0 Hz), 2.75 (t, 2H, $J$=8.0 Hz), 2.30 (dt, 2H, $J$=5.0, 8.0 Hz), 1.29 (h, 3H, $J$=6.5 Hz), 1.13 (d, 18H, $J$=6.5 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 148.5, 137.1, 133.7, 127.1, 126.9, 126.1, 122.0, 103.8, 28.2, 22.2, 18.1, 12.8; IR (neat, cm$^{-1}$) 2943, 2890, 2866, 1638, 1464; MS (APCI) calculated for $[C_{19}H_{31}OSi]^+$: 303.21; found: 303.2.

**7.3.2. Silyl enol ether 4.** $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.38 (s, 1H), 7.01 (d, 1H, $J$=7.5 Hz), 6.97 (d, 1H, $J$=7.5 Hz), 5.16 (t, 1H, $J$=5.0 Hz), 2.71 (t, 2H, $J$=7.5 Hz), 2.33 (s, 3H), 2.28 (dt, 2H, $J$=5.0, 7.5 Hz), 1.30 (h, 3H, $J$=7.5 Hz), 1.24 (d, 18H, $J$=7.5 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 148.4, 135.4, 134.1, 133.5, 127.6, 126.7, 122.7, 103.7, 27.7, 22.3, 21.3, 18.1, 12.8; IR (neat, cm$^{-1}$) 3043, 2944, 2866, 1638, 1609, 1463; MS (APCI) calculated for $[C_{20}H_{33}OSi]^+$: 317.23; found: 317.2.

**7.3.3. Silyl enol ether 5.** $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 6.81 (s, 2H), 5.18 (t, 1H, $J$=5.0 Hz), 2.61 (t, 2H, $J$=7.5 Hz), 2.51 (3, 3H), 2.26 (s, 3H), 2.12 (dt, 2H, $J$=5.0, 7.5 Hz), 1.28 (h, 3H, $J$=7.5 Hz), 1.11 (d, 18H, $J$=7.5 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 151.1, 139.2, 136.2, 134.0, 131.0, 129.7, 125.6, 104.7, 30.3, 22.7, 22.4, 20.9, 18.1, 13.0; IR (neat, cm$^{-1}$) 2944, 2867, 1629, 1463; MS (APCI) calculated for $[C_{21}H_{35}OSi]^+$: 331.25; found: 331.2

**7.3.4. Silyl enol ether 6.** $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.96 (d, 1H, $J$=8.0 Hz), 7.82–7.67 (m, 2H), 7.67 (d, 1H, $J$=8.2 Hz), 7.50–7.35 (m, 2H), 7.31 (d, 1H, $J$=8.2 Hz), 5.46 (t, 1H, $J$=5.0 Hz), 2.82 (t, 1H, $J$=7.0 Hz), 2.32 (dt, 1H, $J$=5.0, 7.0 Hz), 1.30 (h, 3H, $J$=7.5 Hz), 1.10 (d, 18H, $J$=7.5 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 151.3, 136.9, 133.5, 129.62, 129.59, 128.0, 127.62, 127.59, 126.0, 125.0, 1254.5, 106.5, 30.5, 21.9, 18.0, 12.8; IR (neat, cm$^{-1}$) 3051, 2944, 2866, 1630, 1463; MS (APCI) calculated for $[C_{23}H_{33}OSi]^+$: 353.23; found: 353.2.

**7.3.5. Silyl enol ether 7.** $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.53 (d, 1H, $J$=7.5 Hz), 7.20 (t, 1H, $J$=7.5 Hz), 7.15 (t, 1H, $J$=7.5 Hz), 7.10 (d, 1H, $J$=7.5 Hz), 5.10 (d, 1H, $J$=4.0 Hz), 2.83 (dd, 1H, $J$=6.0, 10.0 Hz), 2.55 (dd, 1H, $J$=5.0, 10.0 Hz), 2.47 (m, 1H), 1.38–1.35 (m, 4H), 1.29 (h, 3H, $J$=7.5 Hz), 1.13 (d, 18H, $J$=7.5 Hz), 0.90 (m, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 147.8, 136.4, 133.5, 127.2, 127.1, 126.0, 121.8, 109.1, 37.4, 34.4, 33.0, 20.1, 18.1, 14.2, 12.8; IR (neat, cm$^{-1}$) 3062, 2945, 2867, 2077, 1635, 1464; MS (APCI) calculated for $[C_{22}H_{37}OSi]^+$: 345.26; found: 345.2.

**7.3.6. Silyl enol ether 8.** $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.65 (d, 1H, $J$=2.0 Hz), 7.26 (dd, 1H, $J$=2.0, 7.5 Hz), 6.97 (d, 1H, $J$=7.5 Hz), 5.21 (t, 1H, $J$=4.5 Hz), 2.69 (t, 2H, $J$=8.0 Hz), 2.29 (dt, 2H, $J$=4.5, 8.0 Hz), 1.29 (h, 3H, $J$=7.5 Hz), 1.13 (d, 18H, $J$=7.5 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 147.5, 135.8, 135.7, 129.8, 128.5, 125.1, 120.0, 104.9, 27.6, 22.0, 18.1, 12.8; IR (neat, cm$^{-1}$) 3062, 2944, 2890, 2866, 1636, 1591, 1477; MS (APCI) calculated for $[C_{19}H_{30}BrOSi]^+$: 381.12; found: 381.2.

### 7.4. Procedure for $HNTf_2$-promoted 1-siloxy-5,1-enyne cyclization

Under $N_2$ atmosphere, a flame-dried Airfree® flask was charged with $CH_2Cl_2$ (2 mL) and $HNTf_2$ (0.16 M in $CH_2Cl_2$, 0.16 mmol, 1 mL). Siloxy enyne (0.13 mmol) was added dropwise to the solution and the resulting mixture was stirred for 1 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (10 mL), extracted with hexanes (3×10 mL). The combined organic layers were washed with $H_2O$ (10 mL) and brine (10 mL), dried ($MgSO_4$) and concentrated. The residue was purified by silica gel column chromatography to afford the desired enone.

**7.4.1. Enone 9.** $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.54 (m, 2H), 7.42–7.39 (m, 3H), 6.40 (d, 1H, $J$=2.5 Hz), 2.87 (dd, 1H, $J$=4.0, 18.0 Hz), 2.59 (d, 1H, $J$=4.0 Hz), 2.45 (dd, 1H, $J$=5.0, 18.0 Hz), 2.20 (m, 1H), 2.16 (dd, 1H, $J$=12.5, 14.0 Hz), 1.49–1.39 (m, 4H), 0.94 (t, 3H, $J$=7.0 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 200.2, 159.1, 138.8, 129.9, 128.7, 126.1, 125.2, 43.6, 38.0, 34.9, 34.8, 19.7, 14.1; IR (neat, cm$^{-1}$) 2957, 2927, 2871, 1663, 1606, 1447; MS (EI) calculated for $[C_{15}H_{18}]^+$: 214.14; found: 214.

**7.4.2. Enone 10.** $^1$H and $^{13}$C NMR spectra of compound **10** are in agreement with those described in the literature.

### 7.5. Procedure for MsOH-promoted 1-siloxy-5,1-enyne cyclization

Under $N_2$ atmosphere, a flame-dried Airfree® flask was charged with $CH_2Cl_2$ (2 mL) and MsOH (0.046 g, 0.48 mmol). Siloxy enyne (0.12 mmol) was added dropwise to the solution and the resulting mixture was stirred for 1 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (10 mL), extracted with hexanes (3×10 mL).

The combined organic layers were washed with $H_2O$ (10 mL) and brine (10 mL), dried ($MgSO_4$) and concentrated. The residue was purified by silica gel column chromatography to afford the desired enone.

**7.5.1. Enone 11.** $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 2.47 (dd, 1H, $J$=10.0, 24.0 Hz), 2.31 (d, 1H, $J$=17.5 Hz), 2.08–1.94 (m, 3H), 1.89 (s, 3H), 1.73 (s, 3H), 1.35–1.26 (m, 4H), 0.87 (t, 3H, $J$=7.0 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 199.6, 154.4, 130.8, 43.9, 39.5, 38.1, 34.1, 21.5, 19.6, 14.1, 10.7; IR (neat, cm$^{-1}$) 2958, 2925, 2872, 1667, 1636, 1465, 1380; MS (EI) calculated for $C_{16}H_{18}O$: 166.14; found: 166.

**7.5.2. Enone 12.** $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 2.49 (m, 1H), 2.30–1.90 (m, 8H), 1.72–1.65 (m, 2H), 1.57–1.45 (m, 2H), 1.35–1.28 (m, 4H), 0.90 (t, 3H, $J$=7.0 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 199.6, 156.3, 132.0, 44.2, 38.1, 34.3, 31.8, 22.1, 22.0, 19.6, 17.7, 14.1, 12.2; IR (neat, cm$^{-1}$) 2928, 2869, 1665, 1636, 1457, 1436; MS (EI) calculated for $C_{13}H_{20}O$: 192.15; found: 192.

### 7.6. Procedure for $HNTf_2$-promoted cyclizations of 1-siloxy-1,5-diynes

An oven-dried Airfree® flask was filled with nitrogen, charged with a solution of $HNTf_2$ (77.3 mg, 0.28 mmol) in $CH_2Cl_2$ (or $CHCl_3$ 10 mL; or $CH_2Br_2$ 10 mL; or MeI 5 mL; or PhH 10 mL), and cooled to −78 °C (−60 °C in $CHCl_3$; −50 °C in $CH_2Br_2$; −60 °C in MeI; 6 °C in PhH). This solution was slowly treated with siloxy diyne (0.25 mmol) dissolved in the same solvent (5 mL) causing a red color to develop immediately. After stirring at low temperature for 10 min, the reaction mixture was allowed to warm to room temperature and diluted with $CH_2Cl_2$ (30 mL; or hexanes for PhH case), washed with saturated aqueous $NaHCO_3$ (15 mL), $H_2O$ (15 mL), and brine (15 mL), then dried over anhydrous $Na_2SO_4$ and concentrated. The crude product was purified by silica gel column chromatography.

**7.6.1. Enone 14.** $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 3.02 (t, 2H, $J$=7.5 Hz), 2.78 (t, 2H, $J$=7.4 Hz), 2.43 (t, 2H, $J$=7.9 Hz), 1.93–1.87 (m, 2H), 1.60–1.54 (m, 2H), 1.34–1.26 (m, 10H), 0.88 (t, 3H, $J$=7.0 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 204.2, 150.7, 133.0, 41.4, 34.9, 31.8, 31.6, 29.3, 29.2, 28.8, 28.0, 22.6, 18.8, 14.1; IR (neat, cm$^{-1}$) 2927, 2855, 1718, 1621; MS (APCI) calculated for $[C_{14}H_{24}ClO]^+$: 243.15; found: 243.1.

**7.6.2. Enone 15.** $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.21–7.17 (m, 2H), 7.12–7.08 (m, 3H), 3.02 (t, 2H, $J$=7.3 Hz), 2.69 (t, 2H, $J$=7.5 Hz), 2.57 (t, 2H, $J$=7.8 Hz), 2.34 (t, 2H, $J$=7.8 Hz), 1.86–1.78 (m, 4H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 204.1, 149.8, 141.8, 133.4, 128.3, 128.2, 125.8, 41.3, 35.0, 34.6, 31.5, 29.6, 18.7; IR (neat, cm$^{-1}$) 3026, 2938, 1717, 1617; MS (APCI) calculated for $[C_{15}H_{18}ClO]^+$: 249.11; found: 249.1.

**7.6.3. Enone 16.** $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.22–7.16 (m, 4H), 7.12–7.10 (m, 1H), 3.25 (t, 2H, $J$=8.0 Hz), 2.80 (t, 2H, $J$=8.0 Hz), 2.68 (t, 2H, $J$=7.3 Hz), 2.29 (t, 2H, $J$=7.8 Hz), 1.81–1.75 (m, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 204.0, 148.6, 140.3, 133.7, 128.6, 128.2, 126.1, 41.1, 36.8, 34.2, 31.5, 18.7; IR (neat, cm$^{-1}$) 3028, 2929, 1716, 1621; MS (APCI) calculated for $[C_{14}H_{16}ClO]^+$: 235.09; found: 235.1.

**7.6.4. Enone 17.** $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 3.91 (t, 2H, $J$=6.5 Hz), 3.30 (t, 2H, $J$=6.5 Hz), 2.78 (t, 2H, $J$=7.3 Hz), 2.42 (t, 2H, $J$=8.0 Hz), 1.93–1.87 (m, 2H), 1.16–1.00 (m, 21H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 203.9, 146.6, 134.7, 61.2, 41.2, 38.4, 31.6, 18.7, 17.9, 11.9; IR (neat, cm$^{-1}$) 2943, 2866, 1719, 1627, 1464, 1383; MS (APCI) calculated for $[C_{17}H_{32}ClO_2Si]^+$: 331.19; found: 331.1.

**7.6.5. Enone 18.** $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 3.18 (t, 2H, $J$=7.5 Hz), 2.76 (t, 2H, $J$=7.4 Hz), 2.47 (t, 2H, $J$=7.9 Hz), 1.93–1.87 (m, 2H), 1.60–1.54 (m, 2H), 1.31–1.28 (m, 10H), 0.88 (t, 3H, $J$=6.9 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 202.9, 145.9, 135.9, 41.8, 37.2, 34.7, 31.8, 29.3, 29.2, 28.9, 28.7, 22.6, 18.7, 14.1; IR (neat, cm$^{-1}$) 2927, 2855, 1718, 1616; MS (APCI) calculated for $[C_{14}H_{24}BrO]^+$: 287.10; found: 287.0.

**7.6.6. Enone 19.** $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 3.28 (t, 2H, $J$=7.5 Hz), 2.71 (t, 2H, $J$=7.4 Hz), 2.52 (t, 2H, $J$=7.9 Hz), 1.92–1.86 (m, 2H), 1.56–1.50 (m, 2H), 1.31–1.28 (m, 10H), 0.88 (t, 3H, $J$=7.0 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 200.4, 141.7, 129.5, 42.5, 41.0, 40.3, 31.8, 30.3, 29.4, 29.2, 28.4, 22.6, 18.8, 14.1; IR (neat, cm$^{-1}$) 2925, 2854, 1716, 1603; MS (APCI) calculated for $[C_{14}H_{24}IO]^+$: 335.09; found: 335.0.

**7.6.7. Enone 20.** $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 3.19 (t, 2H, $J$=7.5 Hz), 2.56 (s, 2H), 2.30 (s, 2H), 1.59–1.53 (m, 2H), 1.38–1.30 (m, 2H), 1.10 (s, 6H), 0.92 (t, 3H, $J$=7.3 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 202.3, 145.9, 136.7, 56.3, 49.2, 37.0, 32.6, 31.0, 28.5, 21.7, 13.9; IR (neat, cm$^{-1}$) 2956, 2930, 2869, 1720, 1619, 1464; MS (APCI) calculated for $[C_{12}H_{20}BrO]^+$: 259.07; found: 259.0.

**7.6.8. Enone 21.** $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 3.29 (t, 2H, $J$=7.3 Hz), 2.52 (s, 2H), 2.38 (s, 2H), 1.55–1.49 (m, 2H), 1.38–1.31 (m, 2H), 1.10 (s, 6H), 0.92 (t, 3H, $J$=7.3 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 199.8, 142.6, 129.6, 57.0, 54.8, 40.9, 32.7, 32.4, 28.4, 21.5, 13.9; IR (neat, cm$^{-1}$) 2955, 2928, 2869, 1718, 1606, 1464; MS (APCI) calculated for $[C_{12}H_{20}IO]^+$: 307.06; found: 307.0.

**7.6.9. Enone 22.** $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.38–7.35 (m, 2H), 7.32–7.31 (m, 1H), 7.20–7.19 (m, 2H), 3.02 (t, 2H, $J$=7.0 Hz), 2.50 (t, 2H, $J$=7.0 Hz), 2.36 (t, 2H, $J$=7.8 Hz), 1.81–1.75 (m, 2H), 1.30–1.21 (m, 12H), 0.85 (t, 3H, $J$=7.0 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 208.3, 153.1, 142.4, 132.2, 128.1, 127.6, 127.4, 40.6, 32.5, 31.8, 31.6, 28.6, 29.4, 29.2, 28.7, 22.6, 20.3, 14.1; IR (neat, cm$^{-1}$) 3057, 3020, 2956, 2926, 2855, 1732, 1706, 1616; MS (APCI) calculated for $[C_{20}H_{29}O]^+$: 285.22; found: 285.2.

## Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2006.06.037.

## References and notes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