Tetrahedron 69 (2013) 9105–9110

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Regio- and stereoselectivity in the concatenated enyne cross metathesis–metallotropic [1,3]-shift of terminal 1,3-diyne

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ARTICLE INFO

Article history:
Received 21 May 2013
Received in revised form 10 August 2013
Accepted 13 August 2013
Available online 20 August 2013

This article is dedicated to Professor Paul A. Wender on the occasion of his receiving the 2012 Tetrahedron Prize for Creativity in Organic Chemistry

Keywords:
Enyne metathesis
Metallotropic shift
1,3-Diyne

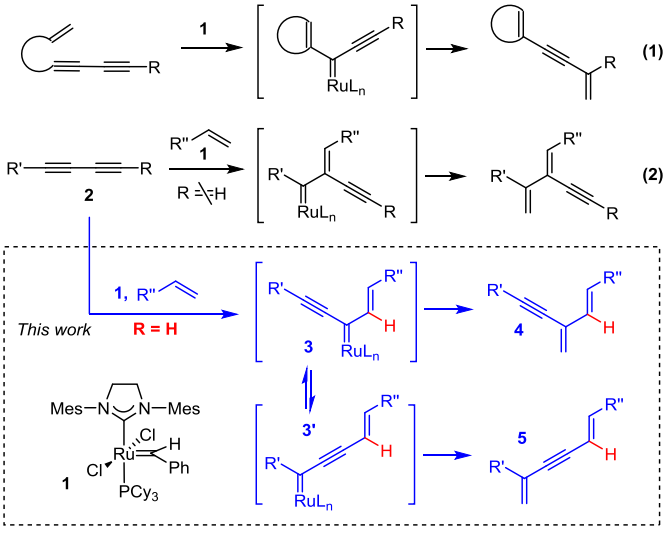
ABSTRACT

Enyne cross metathesis of terminal 1,3-diynes with various alkenes afforded two products of distinctive connectivity, as the result of a uniform mode of initiation but different modes of termination events with or without metallotropic [1,3]-shift. Steric and electronic factors of the substituents on the 1,3-diynes play an important role in controlling the metallotropic [1,3]-shift of the propagating alkylidene intermediates and their regioselective trapping to the final products.

1. Introduction

Enyne metathesis is a powerful synthetic tool to create 1,3-dienes from alkynes and alkenes in an atom economical manner.[1] While enyne ring-closing metathesis has been applied to the synthesis of various natural products and complex molecular frameworks,[2] the analogous intermolecular processes are employed to a significantly lesser extent probably due to the lack of chemo- and stereoselectivity as well as lower substrate generality.[3–5] Thus the development of new enyne cross metathesis that can not only expand the substrate scope but also generate synthetically versatile building blocks is highly desirable.

We previously reported ring-closing and cross metathesis of various 1,3-diyne substrates[6,7] catalyzed by ruthenium alkylidene complex **1**[8] (Scheme 1). In general, metallotropic [1,3]-shift was ensued upon ring-closure of an alkylidene onto a 1,3-diyne moiety (Eq. 1),[9,10] whereas only cross metathesis without metallotropic shift was observed in the cross metathesis of internal 1,3-diynes and alkenes (Eq. 2).[6a] The lack of the metallotropic shift event in



Scheme 1. Enyne metathesis and metallotropic [1,3]-shift.

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http://dx.doi.org/10.1016/j.tet.2013.08.024

the latter case is the consequence of generating the propagating alkylidene at the homopropargylic carbon rather than propargylic carbon center. These differences clearly indicate that the inherently favored regioselectivity of forming alkylidene carbene at the homopropargylic carbon is switched over in the ring-closing metathesis due to the constraint imposed by the tether to form the kinetically favorable alkylidene carbene at the propargylic carbon, which then undergoes metallotropic [1,3]-shift driven by steric pressure around the propargylic carbon center or by thermodynamic preference to form more fully conjugated end products.[11] In conjunction with these observations, we envision that the cross metathesis of terminal 1,3-diyne **2** (R=H), where the regiochemistry of the initiation would also be reversed from that of internal diynes such that intermediate **3** should be formed. This reversed regiochemical preference is the consequence of the thermodynamic preference of forming disubstituted alkylidene rather than the mono-substituted one. Once formed, alkylidene **3** will be in equilibrium with a new alkylidene species **3′** via the metallotropic [1,3]-shift, the respective termination of which would ultimately generate structurally distinctive 2-alkynyl-1,3-diene **4** and 1,5-diene-3-yne **5**. We anticipated that the steric and electronic factors of the substituent R would affect the metallotropic [1,3]-shift,[12] which in turn would influence the preference of the final trapping process. Herein we report a tandem enyne cross metathesis–metallotripic [1,3]-shift process of terminal 1,3-diynes and its regio- and stereoselectivity profiles.

2. Result and discussion

First, the effect of the substituents on the diynes were examined with terminal diyne[13] substrates **6a**–**h** and triyne substrate **6i** with allyl acetate as the alkene counterpart (Table 1). The product distribution from these reactions is consistent with the combined effect of both steric and electronic factors. The diyne substrate **6a** containing triisopropylsilyl group did not undergo metallotropic [1,3]-shift, affording 2-alkynyl-3,4-diene **7a** as a single regio- and stereoisomer (entry 1). Considering relatively low *E*/*Z*-selectivity in enyne cross metathesis, the formation of single stereoisomer of **7a** is noteworthy.[14]

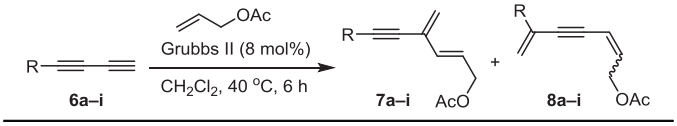
While the substrate **6b** possessing secondary alkyl group afforded a 1:1 mixture of **7b** and **8b** (entry 2), primary alkyl group substituted 1,3-diyne **6c** afforded a mixture of **7c** and **8c** with a 1:1.5 ratio (entry 3). Interestingly, the products **7a**–**c** formed without metallotropic [1,3]-shift are all *E*-isomers, whereas products **8a**–**c** that were generated via metallotropic [1,3]-shift are mixtures of *E* and *Z* isomers with varying ratios.

Next we examined substrates containing oxygen functionality at the α-, β-, and γ-carbon from the alkyne as a directing element for metallotropic [1,3]-shift. 1,3-Diynes **6d** and **6e** containing the oxygen substituent remote from the alkyne moiety, provided product distributions similar to those of simple alkyl group substituted 1,3-diynes (entries 4 and 5). Running the metathesis under the ethylene atmosphere[15] did not improve the *E*-selectivity for **8d**.[16] While the silyloxy substituent at the homopropargylic carbon in **6f** did not affect either the metallotropic [1,3]-shift or the *E*/*Z*-selectivity (entry 6), the corresponding free hydroxyl group in **6g** significantly increased the metallotropic [1,3]-shift process to give a 1:4 mixture of **7g** and **8g** (entry 7). Previously we reported that the conjugated triyne substrate containing oxygen-based substituent at the propargylic carbon undergoes facile metallotropic shift after ring-closing enyne metathesis.[12a] Similarly, the oxygen substituent at the propargylic carbon in **6h** promoted metallotropic [1,3]-shift effectively, providing single regioisomer **8h** as a mixture of *E*/*Z*-isomers (entry 8).[12] Terminal triyne **6i** provided similar reactivity with slightly diminished yield compared to substrate **6d**.

Next we explored the effect of protecting groups on the propargylic hydroxyl group employing 1°, 2°, 3° propargylic alcohols and their protected derivatives (Table 2).

The CM of 1,3-diyne substrate **6j** containing 1° propargylic hydroxyl group provided only **8j** in 69% yield (entry 1), but that of its

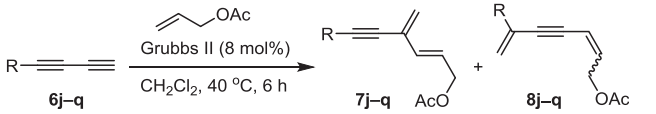
Table 1
Reaction scope for enyne metathesis and metallotropic [1,3]-shift



Entry		Substrate	7:8 (*E*/*Z* of 8)[a]	Yield %[b]
1	**6a**	*i*-Pr$_3$Si	1:0	47[c]
2	**6b**		1:1 (1:4)	73
3	**6c**		1:1.5 (1:2)	79
4[d]	**6d**	TBSO	1:1.3 (1:2.3)	80
5[e]	**6e**	HO	1:1.6 (1:1.3)	67
6	**6f**	TBSO	1:1.5 (1:2)	81
7[e]	**6g**	HO	1:4 (1:3)	73
8	**6h**	TBSO	0:1 (1.2:1)	77
9[f]	**6I**	OTBS	1:1.4 (1:2.4)	41

[a] Ratio was determined by ^{1}H NMR (See Supplementary data).
[b] Combined yields of a mixture of three isomers after column chromatography.
[c] 40% of **6a** was recovered.
[d] Introduction of 20 psi of ethylene gives similar ratio and yield.
[e] 5% of HOAc was added into the reaction.[17]
[f] R=TBSO(CH$_2$)$_3$C≡C.

Table 2
Propargylic hydroxyl group-directed enyne metathesis and metallotropic [1,3]-shift



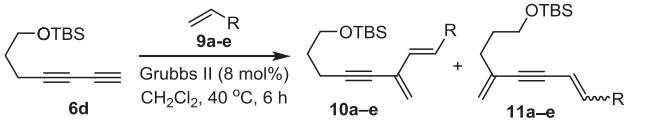
Entry		1,3-Diyne	7:8 (*E*/*Z* of 8)	Yield %[a]
1[b]	**6j**	HO	0:1 (1:0.8)	69
2	**6k**	BnO	1:10 (1:0.9)	84
3[b]	**6l**	HO	0:1 (1:0.9)	71
4	**6m**	TMSO	0:1 (1:0.9)	75
5	**6n**	TBSO	1:1.7 (1:2)	79
6	**6o**	BnO	1:1.3 (1:2)	74
7	**6p**	HO	1:5.5 (1:1.7)	42
8	**6q**	HO	0:1 (1:4)	69

[a] Combined yields of a mixture of three isomers after column chromatography.
[b] 5% of HOAc was added into the reaction.[17]

benzyl ether derivative **6k** generated a 1:10 mixture of **7k** and **8k** (entry 2). 1,3-Diyne substrates containing 2° hydroxyl group and its trimethylsilyl ether derivative afforded metallotropic [1,3]-shifted products **8l** and **8m** as a mixture of *E*/*Z*-isomers (entries 3 and 4). On the other hand, the corresponding *t*-butyldimethylsilyl and benzyl protected substrates **6n** and **6o** afforded a 1:1.7 and 1:1.3 mixture of **7n**/**8n** and **7o**/**8o**, respectively (entries 5 and 6). Substrates containing 3° hydroxyl group favor metallotropic [1,3]-shift, providing high selectivity (entries 7 and 8).

Having identified the heteroatom effect on 1,3-diynes that affects metallotropic [1,3]-shift, we also examined the effect of heteroatom substituent at the allylic carbon of the alkene counterpart (Table 3). Metathesis reaction of 1,3-diyne **6d** with tolyl and pivaloyl-protected allylic alcohol derivatives **9a**, **9b** showed almost the same product distribution as that with allyl acetate, affording **10a**, **11a**, and **10b**, **11b** in a 1:1.5 and 1:1.3 ratio, respectively (entries 1 and 2). However, the yields with allyl pivalate (39%) and allyl tolyl ether (56%) are much lower compared to that with allyl acetate (80%). Surprisingly, the reaction with allyl alcohol **9c** gave only a trace amount of cross metathesis product and 1,3-diyne substrate **6c** was recovered (entry 3).[14] Allyl trimethylsilane **9d** promoted slightly favorable metallotropic [1,3]-shift, providing **10d** and **11d** in a 1:2.6 ratio in 76% yield (entry 4), whereas with ethylene **9e** completely suppressed the metallotropic [1,3]-shift, affording only **10e** but in low conversion (entry 5).

Table 3
Cross metathesis with alkenes with different allylic substituents

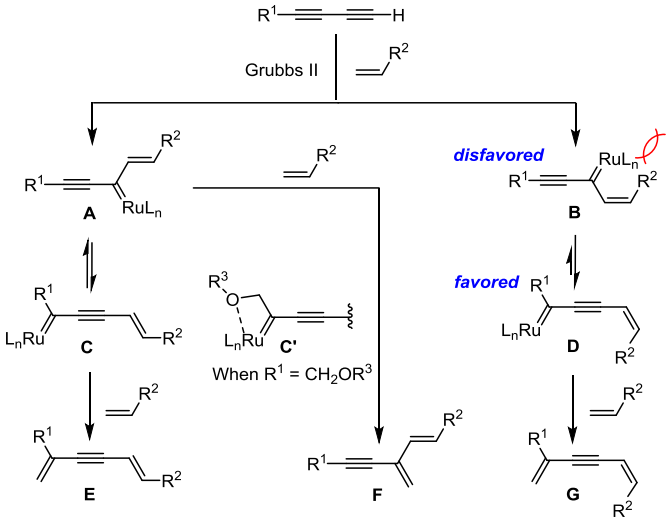


Entry	R in alkene		**10**:**11** (*E*/*Z* of **11**)	Yield %
1	CH_2OTol	**9a**	1:1.5 (1:2)	56[a]
2	CH_2OPiv	**9b**	1:1.3 (1:2.3)	39[a]
3	CH_2OH	**9c**	N/A	0
4	CH_2SiMe_3	**9d**	1:2.6 (1:2)	76[b]
5	H	**9e**	1:0	29[c]

[a] Yield was determined by ^1H NMR with internal standard after short column purification.
[b] Isolated yield.
[c] 20 psi of ethylene was introduced and 60% of **6e** was recovered.

Overall, it was found that the substituent pattern on diyne significantly affects the regioselectivity of the metallotropic [1,3]-shift, whereas the influence of substituent on alkene is marginal. Specifically, the introduction of silyl group on terminal diyne ensures the formation of *E*-2-alkynyl-3,4-diene. While the oxygen substituent remote from alkyne does not exert a noticeable influence on metallotropic shift behavior, propargylic hydroxyl group markedly facilitates metallotropic shift. The choice of protecting group of propargylic hydroxyl group in substrate design is also critical to obtain a single regioisomer.

A reasonable explanation for the product distribution with and without metallotropic [1,3]-shift is depicted in Scheme 2. Cross metathesis of a 1,3-diyne with an alkene initiated by ruthenium alkylidene would lead to two *E*/*Z*-isomeric new ruthenium alkylidene intermediates **A** and **B**. While **A** equilibrates with **C** via metallotropic [1,3]-shift, its termination provides **F**, whereas termination of **C** leads to **E**. When R^1 possesses oxygen-based substituent at the propargylic carbon center, [1,3]-shift is facilitated most likely because of the favorable chelation event between the oxygen and the ruthenium center. If R^1 is sterically hindered, **A** is more favorable than **C** and also its termination should be faster



Scheme 2. Rational for the observed product distribution.

than that of **C**. For alkylidene intermediate **B** carrying *Z*-alkene substituent, unfavorable steric interaction between the substituent R^2 and the sterically bulky ruthenium center promotes its metallotropic [1,3]-shift to another alkylidene **D**. Selective termination from **D** generates final product **G** containing a *Z*-alkene moiety.

3. Conclusion

In summary, we have investigated a concatenated enyne cross metathesis–metallotropic [1,3]-shift employing terminal 1,3-diynes and alkenes, and for the first time, metallotropic [1,3]-shift was promoted by cross metathesis. The regioselectivity of the initial propagating alkylidene formation could be reversed relative to the corresponding internal 1,3-diynes so that metallotropic [1,3]-shift behavior could be examined. As opposed to the invariably favorable metallotropic [1,3]-shift observed in the ring-closing metathesis of 1,3-diynes containing tethered alkene, the extent of metallotropic [1,3]-shift is significantly affected by steric and electronic effects of the substituent on propargylic carbon of 1,3-diynes. This unprecedented enyne cross metathesis of 1,3-diynes involving the predictable behavior of metallotropic [1,3]-shift of the intermediate propagating alkylidene species would provide guidance in the design of more efficient substrates for tandem enyne cross metathesis and metallotropic [1,3]-shift.

4. Experimental section

4.1. General

Compounds were purchased from Aldrich unless otherwise noted. CH_2Cl_2 were purified based on standard procedures. Flash chromatography was performed using silica gel 60 Å (32–63 mesh) purchased from Sorbent Technologies. Analytical thin layer chromatography (TLC) was performed on 0.25 mm E. Merck pre-coated silica gel 60 (particle size 0.040–0.063 mm). ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AV-500 MHz or Varian Mercury 300 MHz spectrometer. Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), qn (quintet), m (multiplet), and br (broad). Coupling constants, *J*, are reported in Hertz. Electron impact (EI) mass spectra were obtained using a Micromass AutoSpecTM at the Mass Spectrometry Laboratory in the University of Illinois at Urbana-Champaign.

4.2. General procedure for cross enyne metathesis

In a flame dried Schlenk tube, 1,3-diyne (1 equiv), allyl acetate (5 equiv), and Grubbs second-generation catalyst (8 mol %) were dissolved in anhydrous CH_2Cl_2. The reaction mixture was degassed under vacuum and re-filled with nitrogen gas. The tube was then stirred in an oil bath at 40 °C for 6 h (Warning: reaction might be explosive due to the internal pressure build up in the sealed tube). After 6 h, the tube was opened to the air at room temperature and the solvent was removed by the rotary aspirator. The organic product was isolated by column chromatography on silica gel (EtOAc/hexane) to afford the cross metathesis product.

*4.2.1. (E)-4-Methylene-6-(triisopropylsilyl)hex-2-en-5-ynyl acetate (**7a**).* Yellow oil, ^{1}H NMR (501 MHz, $CDCl_3$) δ 6.27 (d, J=15.4 Hz, 1H), 6.20 (td, J=5.8, 15.3 Hz, 1H), 5.56 (s, 1H), 5.44 (s, 1H), 4.66 (d, J=5.7 Hz, 2H), 2.08 (s, 3H), 1.01 (s, 21H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.7, 132.7, 129.0, 127.6, 124.9, 64.7, 64.4, 64.1, 20.6, 18.7, 11.3; HRMS (EI) calcd for $C_{18}H_{30}O_2Si$ $[M]^+$: 306.2015, found 306.2022.

*4.2.2. (E)-6-Cyclohexyl-4-methylenehex-2-en-5-ynyl acetate (**7b**) and 6-cyclohexylhepta-2,6-dien-4-ynyl acetate (**8b**+**8b′**).* Pale yellow oil, ^{1}H NMR (501 MHz, $CDCl_3$) **7b**+**8b**+**8b′**: δ 6.27 (**7b**, d, J=15.4 Hz, 1H), 6.17–6.10 (**8b**+**8b′**, m, 2H), 5.97 (**7b**, td, J=6.6, 10.9 Hz, 1H), 5.87 (**8b**, d, J=16.0 Hz, 1H), 5.78 (**8b′**, d, J=10.8 Hz, 1H), 5.43 (**7b**, s, 1H), 5.35 (**7b**, s, 1H), 5.29 (**8b′**, s, 1H), 5.27 (**8b**, s, 1H), 5.25 (**8b′**, s, 1H), 5.23 (**8b**, s, 1H), 4.83 (**8b′**, d, J=6.6 Hz, 2H), 4.64 (**7b**, d, J=6.1 Hz, 2H), 4.60 (**8b**, d, J=6.1 Hz, 2H), 2.53 (**7b**, m, 1H), 2.08 (**7b**, s, 3H), 2.08–2.02 (**8b**+**8b′**, m, 2H), 2.06 (**8b**+**8b′**, s, 6H), 1.51–1.09 (**7b**+**8b**+**8b′**, m, 30H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.67, 170.63, 170.5, 137.2, 135.7, 135.4, 133.5, 129.1, 126.8, 122.2, 119.7, 119.4, 113.7, 113.1, 97.0, 96.2, 94.7, 76.8, 64.1, 64.0, 62.3, 44.8, 32.6, 31.9, 29.5, 26.2, 25.9, 25.8, 24.9, 20.9, 20.8; HRMS (EI) calcd for $C_{15}H_{20}O_2$ $[M]^+$: 232.1463, found 232.1470.

*4.2.3. (E)-4-Methylenedec-2-en-5-ynyl acetate (**7c**) and 6-methylenedec-2-en-4-ynyl acetate (**8c**+**8c′**).* Colorless oil, ^{1}H NMR (501 MHz, $CDCl_3$) δ 6.24 (**7c**, d, J=15.3 Hz, 1H), 6.15–6.08 (**8c**+**8c′**, m, 2H), 5.84 (**8c**, d, J=15.9 Hz, 1H), 5.76 (**8c′**, d, J=10.8 Hz, 1H), 5.41 (**7c**, s, 1H), 5.32 (**7c**, s, 1H), 5.30 (**8c′**, s, 1H), 5.28 (**8c′**, s, 1H), 5.22 (**8c′**, s, 1H), 5.20 (**8c**, s, 1H), 4.80 (**8c′**, dd, J=1.3, 6.6 Hz, 2H), 4.62 (**7c**, d, J=6.1 Hz, 2H), 4.58 (**8c**, dd, J=1.4, 6.1 Hz, 2H), 2.33 (**7c**, t, J=7.1 Hz, 2H), 2.17–2.10 (**8c**+**8c′**, m, 4H), 2.05 (**7c**, s, 3H), 2.03 (**8c**+**8c′**, s, 6H), 1.56–1.24 (**7c**+**8c**+**8c′**, m, 18H), 0.92–0.84 (**7c**+**8c**+**8c′**, m, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.52, 170.47, 170.3, 144.5, 141.7, 135.8, 135.5, 133.4, 131.5, 126.9, 126.5, 123.1, 121.4, 121.2, 113.5, 112.8, 96.6, 96.1, 93.4, 62.8, 91.4, 86.3, 84.0, 76.9, 64.0, 63.9, 62.2, 36.7, 36.69, 36.65, 30.7, 30.2, 21.9, 20.8, 20.7, 18.8, 13.7, 13.5; HRMS (EI) calcd for $C_{14}H_{20}O_2$ $[M]^+$: 220.1463, found 220.1474.

*4.2.4. (E)-9-(tert-Butyldimethylsilyloxy)-4-methylenenon-2-en-5-ynyl acetate (**7d**) and 9-(tert-butyldimethylsilyloxy)-6-methylenenon-2-en-4-ynyl acetate (**8d**+**8d′**).* Colorless oil, ^{1}H NMR (501 MHz, $CDCl_3$) **7d**: δ 6.28 (d, J=15.3 Hz, 1H), 6.15 (td, J=6.1, 15.2 Hz, 1H), 5.45 (s, 1H), 5.37 (s, 1H), 4.65 (d, J=6.1 Hz, 2H), 3.72 (t, J=6.1 Hz, 1H), 2.46 (t, J=7.1 Hz, 1H), 2.09 (s, 3H), 1.78 (m, 2H), 0.90 (s, 9H), 0.06 (s, 6H), **8d**+**8d′**: δ 6.15 (**8d**, td, J=6.1, 15.9 Hz, 1H), 5.98 (**8d′**, td, J=6.6, 10.8 Hz, 1H), 5.87 (**8d**, d, J=15.8 Hz, 1H), 5.79 (**8d′**, d, J=10.8 Hz, 1H), 5.36 (**8d′**, s, 1H), 5.33 (**8d**, s, 1H), 5.29 (**8d′**, s, 1H), 5.27 (**8d**, s, 1H), 4.83 (**8d′**, dd, J=1.2, 6.6 Hz, 2H), 4.61 (**8d**, dd, J=1.4, 6.1 Hz, 2H), 3.66–3.59 (m, 4H), 2.29–2.21 (m, 4H), 2.08 (s, 6H), 1.79–1.70 (m, 4H), 0.89 (s, 18H), 0.05 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.68, 170.64, 170.5, 144.7, 141.8, 136.0, 135.7, 134.2, 133.4, 131.1, 131.0, 129.1, 128.6, 128.0, 126.9, 126.6, 125.5, 123.4, 123.2, 121.9, 121.7, 113.5, 112.9, 96.5, 93.6, 92.4, 91.3, 86.5, 84.2, 65.0, 64.9, 63.9, 62.2, 62.1, 62.0, 61.6, 33.4, 31.7, 31.1, 30.3, 29.7, 25.9, 20.89, 20.82, 20.79, 18.3, 15.7, −5.3, −5.4; HRMS (EI) calcd for $C_{18}H_{31}O_3Si$ $[M+H]^+$: 323.2043, found 323.2061.

*4.2.5. (E)-9-Hydroxy-4-methylenenon-2-en-5-ynyl acetate (**7e**) and 9-hydroxy-6-methylenenon-2-en-4-ynyl acetate (**8e**+**8e′**).* Pale yellow oil, ^{1}H NMR (501 MHz, $CDCl_3$) **7e**: δ 6.25 (d, J=15.4 Hz, 1H), 5.97 (td, J=6.6, 10.8 Hz, 1H), 5.42 (s, 1H), 5.35 (s, 1H), 4.62 (d, J=6.1 Hz, 2H), 3.74 (t, J=6.1 Hz, 2H), 2.46 (t, J=7.0 Hz, 2H), 2.06 (s, 3H), 1.79 (m, 2H); **8e**+**8e′**: 6.14–6.09 (m, 2H), 5.84 (**8e**, d, J=15.9 Hz, 1H), 5.77 (**8e′**, d, J=10.8 Hz, 1H), 5.34 (**8e′**, s, 1H), 5.32 (**8e**, s, 1H), 5.28 (**8e′**, s, 1H), 5.26 (**8e**, s, 1H), 4.81 (**8e′**, dd, J=1.1, 6.6 Hz, 2H), 4.58 (**8e**, dd, J=1.3, 6.0 Hz, 2H), 3.67–3.61 (m, 4H), 2.28–2.22 (m, 4H), 2.05 (s, 6H), 1.82–1.71 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 170.8, 170.5, 144.8, 142.1, 136.1, 135.6, 133.4, 130.8, 128.9, 126.9, 123.6, 122.1, 121.9, 113.4, 112.9, 96.2, 93.3, 91.9, 91.0, 86.7, 84.4, 77.4, 64.1, 63.9, 62.2, 61.8, 61.7, 61.5, 33.3, 31.3, 31.1, 31.0, 20.8, 20.7, 15.7; HRMS (EI) calcd for $C_{12}H_{16}O_3$ $[M]^+$: 208.1099, found 208.1105.

*4.2.6. (E)-8-(tert-Butyldimethylsilyloxy)-4-methyleneoct-2-en-5-ynyl acetate (**7f**) and 8-(tert-butyldimethylsilyloxy)-6-methylene-oct-2-en-4-ynyl acetate (**8f**+**8f′**).* Colorless oil, ^{1}H NMR (501 MHz, $CDCl_3$) **7f**: δ 6.26 (d, J=15.4 Hz, 1H), 5.98 (td, J=6.6, 10.9 Hz, 1H), 5.45 (s, 1H), 5.37 (s, 1H), 4.64 (d, J=6.0 Hz, 2H), 3.77 (m, 2H), 2.57 (d, J=7.0 Hz, 2H), 2.07 (s, 3H), 0.89 (s, 9H), 0.07 (s, 6H), **8f**+**8f′**: 6.19–6.09 (m, 2H), 5.85 (**8f**, d, J=15.9 Hz, 1H), 5.78 (**8f′**, d, J=10.8 Hz, 1H), 5.41 (**8f′**, s, 1H), 5.38 (**8f**, s, 1H), 5.32 (**8f′**, s, 1H), 5.29 (**8f**, s, 1H), 4.81 (**8f′**, dd, J=1.3, 6.6 Hz, 2H), 4.61 (**8f**, dd, J=1.4, 6.1 Hz, 2H), 3.79–3.73 (m, 4H), 2.41–2.34 (m, 4H), 2.07 (**8f**, s, 3H), 2.06 (**8f′**, s, 3H), 0.88 (**8f**, s, 9H), 0.87 (**8f′**, s, 9H), 0.05 (**8f**, s, 6H), 0.04 (**8f′**, s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.66, 170.64, 136.0, 135.7, 133.2, 128.9, 128.2, 128.1, 127.1, 123.60, 123.59, 123.4, 113.5, 112.9, 96.3, 91.2, 89.7, 86.5, 84.2, 78.0, 64.1, 63.9, 62.2, 61.8, 61.6, 61.5, 40.60, 40.56, 30.3, 25.88, 25.84, 23.7, 20.9, 20.8, 18.3, −5.3; HRMS (EI) calcd for $C_{17}H_{28}O_3Si$ $[M]^+$: 308.1808, found 308.1793.

*4.2.7. (E)-8-Hydroxy-4-methyleneoct-2-en-5-ynyl acetate (**7g**) and 8-hydroxy-6-methyleneoct-2-en-4-ynyl acetate (**8g**+**8g′**).* Pale yellow oil, ^{1}H NMR (501 MHz, $CDCl_3$) δ 6.27 (**7g**, d, J=15.4 Hz, 1H), 6.20–6.10 (**7g**+**8g**, m, 2H), 5.84 (**8g**, d, J=15.9 Hz, 1H), 5.79 (**8g′**, d, J=10.8 Hz, 1H), 5.48 (**7g**, s, 1H), 5.47 (**8g′**, s, 1H), 5.45 (**8g**, s, 1H), 5.40 (**7g**, s, 1H), 5.38 (**8g′**, s, 1H), 5.36 (**8g**, s, 1H), 4.82 (**8g′**, dd, J=0.9, 6.7 Hz, 1H), 4.64 (**7g**, d, J=6.1 Hz, 1H), 4.61 (**8g**, dd, J=1.2, 6.0 Hz, 1H), 2.66–2.62 (**8g**+**8g′**, m, 4H), 2.57 (**7g**, t, J=6.2 Hz, 2H), 2.46–2.40 (**7g**+**8g**+**8g′**, m, 6H), 2.08 (**7g**, s, 3H), 2.07 (**8g**+**8g′**, s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8, 170.7, 167.2, 142.6, 136.6, 136.1, 133.1, 128.6, 127.8, 127.1, 124.2, 124.1, 124.0, 113.1, 112.8, 110.8, 95.6, 93.0, 84.8, 78.8, 75.3, 64.1, 62.2, 61.1, 60.9, 60.7, 60.6, 40.3, 30.3, 24.0, 23.6, 20.8; HRMS (EI) calcd for $C_{11}H_{14}O_3$ $[M]^+$: 194.0943, found 194.0928.

*4.2.8. 6-((tert-Butyldimethylsilyloxy)methyl)hepta-2,6-dien-4-ynyl acetate (**8h**+**8h′**).* Pale yellow oil, ^{1}H NMR (501 MHz, $CDCl_3$) δ 6.16 (**8h**, td, J=6.0, 15.9 Hz, 1H), 5.99 (**8h′**, td, J=6.6, 10.9 Hz, 1H), 5.85 (**8h**, d, J=15.9 Hz, 1H), 5.78 (**8h′**, d, J=10.9 Hz, 1H), 5.62 (**8h′**, dd, J=1.9, 3.8 Hz, 1H), 5.60 (**8h**, dd, J=1.8, 3.7 Hz, 1H), 5.48 (**8h′**, dd, J=1.8, 3.5 Hz, 1H), 5.45 (**8h**, dd, J=1.7, 3.4 Hz, 1H), 4.82 (**8h′**, dd, J=1.4, 6.6 Hz, 2H), 4.61 (**8h**, dd, J=1.5, 6.0 Hz, 2H), 4.16 (**8h′**, t, J=1.8, 2H), 4.14 (**8h**, t, J=1.7 Hz, 2H), 2.07 (**8h**+**8h′**, s, 6H), 0.90 (**8h**+**8h′**, s, 18H), 0.08 (**8h**+**8h′**, s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.7, 170.4, 136.4, 136.0, 130.70, 130.66, 119.99, 119.74, 113.3, 112.6, 94.0, 88.9, 87.6, 85.3, 64.9, 64.8, 63.9, 62.3, 25.8, 20.8, 18.4, −5.4; HRMS (EI) calcd for $C_{16}H_{25}O_3Si$ $[M-H]^+$: 293.1573, found 293.1582.

*4.2.9. (E)-11-(tert-Butyldimethylsilyloxy)-4-methyleneundeca-2-en-5,7-diynyl acetate (**7i**) and 11-(tert-butyldimethylsilyloxy)-8-methyleneundeca-2-en-4,6-diynyl acetate (**8i**+**8i′**).* Pale yellow oil, ^{1}H NMR (501 MHz, $CDCl_3$) **7i**: δ 6.26 (d, J=15.4 Hz, 1H), 6.16 (m, 1H),

5.62 (s, 1H), 5.53 (s, 1H), 4.65 (d, *J*=5.9 Hz, 2H), 3.69 (t, *J*=5.9 Hz, 2H), 2.43 (t, *J*=7.1 Hz, 2H), 2.09 (s, 3H), 1.72 (m, 2H), 0.89 (s, 9H), 0.06 (s, 6H); **8i**+**8i′**: 6.29 (**8i**, td, *J*=5.8, 15.9 Hz, 1H), 6.14 (**8i′**, td, *J*=6.5, 11.0 Hz, 1H), 5.82 (**8i**, td, *J*=1.6, 15.9 Hz, 1H), 5.77 (**8i′**, td, *J*=1.5, 11.0 Hz, 1H), 5.50 (**8i′**, s, 1H), 5.49 (**8i**, s, 1H), 5.42 (**8i′**, d, *J*=1.5 Hz, 1H), 5.40 (**8i**, d, *J*=1.6 Hz, 1H), 4.84 (**8i′**, dd, *J*=1.5, 6.5 Hz, 2H), 4.63 (**8i**, dd, *J*=1.6, 5.8 Hz, 2H), 3.62 (**8i′**, t, *J*=6.2 Hz, 2H), 3.61 (**8i**, t, *J*=6.2 Hz, 2H), 2.25 (m, 2H), 2.08 (s, 3H), 1.74 (m, 2H), 0.89 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.6, 170.4, 139.8, 139.6, 134.2, 132.2, 130.2, 128.6, 128.1, 127.8, 126.6, 126.4, 125.2, 125.0, 124.8, 123.2, 112.0, 111.6, 84.7, 83.8, 82.4, 80.1, 78.7, 76.3, 75.2, 73.4, 73.2, 71.3, 65.1, 64.8, 63.9, 63.6, 62.4, 61.9, 61.3, 33.1, 33.0, 31.2, 31.1, 26.1, 25.9, 20.9, 20.8, 18.3, 16.2, 16.0, −5.3, −5.5; HRMS (EI) calcd for $C_{20}H_{30}O_3Si$ $[M]^+$: 346.1964, found 346.1969.

*4.2.10. 6-(Hydroxymethyl)hepta-2,6-dien-4-ynyl acetate (**8j**+**8j′**).* Colorless oil, ^{1}H NMR (501 MHz, $CDCl_3$) **8j**: δ 6.19 (td, *J*=6.0, 15.9 Hz, 1H), 5.87 (d, *J*=15.9 Hz, 1H), 5.56 (s, 1H), 5.49 (s, 1H), 4.62 (d, *J*=5.3 Hz, 2H), 4.15 (d, *J*=6.1 Hz, 2H), 2.08 (s, 3H), 1.76 (t, *J*=6.3 Hz, 1H); **8j′**: 6.03 (td, *J*=6.7, 10.9 Hz, 1H), 5.81 (d, *J*=10.9 Hz, 1H), 5.57 (s, 1H), 5.51 (s, 1H), 4.84 (d, *J*=6.7 Hz, 2H), 4.18 (d, *J*=6.3 Hz, 2H), 2.08 (s, 3H), 2.01 (t, *J*=6.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8, 170.5, 136.9, 136.3, 131.0, 121.1, 120.9, 113.0, 112.8, 93.7, 88.5, 88.3, 86.0, 65.32, 65.26, 63.9, 62.1, 20.88, 20.81; HRMS (EI) calcd for $C_{10}H_{11}O_3$ $[M-H]^+$: 179.0708, found 179.0717.

*4.2.11. (E)-7-(Benzyloxy)-4-methylenehept-2-en-5-ynyl acetate (**7k**) and 6-(benzyloxymethyl)hepta-2,6-dien-4-ynyl acetate (**8k**+**8k′**).* Yellow oil, ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.40–7.23 (**7k**+**8k**+**8k′**, m, 15H), 6.30 (**7k**, d, *J*=15.4 Hz, 1H), 6.23–6.15 (**7k**+**8k**, m, 2H), 6.02 (**8k′**, td, *J*=6.6, 11.0 Hz, 1H), 5.88 (**8k**, d, *J*=15.9 Hz, 1H), 5.80 (**8k′**, d, *J*=10.9 Hz, 1H), 5.64–5.58 (m, 6H), 4.84 (**8k′**, d, *J*=6.6 Hz, 1H), 4.67 (**7k**, d, *J*=5.9 Hz, 1H), 4.62 (**8k**, d, *J*=6.0 Hz, 1H), 4.57 (**7k**+**8k**+**8k′**, s, 6H), 4.06 (**7k**+**8k**+**8k′**, s, 6H), 2.09 (**7k**, s, 3H), 2.08 (**8k**, s, 3H), 2.07 (**8k′**, s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.6, 170.5, 170.4, 137.9, 136.6, 136.3, 132.5, 128.3, 128.23, 128.18, 128.0, 127.64, 127.61, 127.5, 124.8, 122.5, 122.3, 113.1, 112.5, 94.2, 89.1, 87.6, 85.3, 72.13, 72.08, 71.6, 63.9, 63.8, 62.2, 57.6, 20.8, 20.75, 20.71; HRMS (EI) calcd for $C_{17}H_{17}O_3$ $[M-H]^+$: 269.1178, found 269.1168.

*4.2.12. 7-Hydroxy-6-methyleneoct-2-en-4-ynyl acetate (**8l**+**8l′**).* Colorless oil, ^{1}H NMR (501 MHz, $CDCl_3$) **8l**: δ 6.16 (td, *J*=6.0, 15.8 Hz, 1H), 5.85 (d, *J*=15.9 Hz, 1H), 5.50 (s, 1H), 5.39 (s, 1H), 4.59 (d, *J*=6.0 Hz, 2H), 4.29 (m, 1H), 2.26 (br, 1H), 2.05 (s, 3H), 1.33 (d, *J*=6.5 Hz, 3H); **8l′**: 5.99 (td, *J*=6.7, 10.9 Hz, 1H), 5.77 (d, *J*=10.8 Hz, 1H), 5.52 (s, 1H), 5.41 (s, 1H), 4.81 (d, *J*=6.7 Hz, 2H), 4.28 (m, 1H), 2.43 (br, 1H), 2.04 (s, 3H), 1.35 (d, *J*=6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 170.6, 142.9, 136.4, 136.1, 135.8, 120.4, 120.1, 113.2, 112.9, 93.6, 92.5, 88.8, 88.4, 86.5, 70.3, 63.9, 62.2, 22.54, 22.51, 20.86, 20.8; HRMS (EI) calcd for $C_{11}H_{14}O_3$ $[M]^+$: 194.0943, found 194.0962.

*4.2.13. 6-Methylene-7-(trimethylsilyloxy)oct-2-en-4-ynyl acetate (**8m**+**8m′**).* Pale yellow oil, ^{1}H NMR (501 MHz, $CDCl_3$) δ 6.17 (**8m**, td, *J*=6.0, 15.8 Hz, 1H), 6.00 (**8m′**, td, *J*=6.6, 10.8 Hz, 1H), 5.88 (**8m**, d, *J*=15.8 Hz, 1H), 5.81 (**8m′**, d, *J*=10.8 Hz, 1H), 5.57 (**8m′**, s, 1H), 5.55 (**8m**, s, 1H), 5.42 (**8m′**, s, 1H), 5.39 (**8m**, s, 1H), 4.84 (**8m′**, d, *J*=6.6 Hz, 2H), 4.62 (**8m**, d, *J*=6.0 Hz, 2H), 4.32–4.24 (**8m**+**8m′**, m, 2H), 2.07 (**8m**+**8m′**, s, 6H), 1.35–1.30 (**8m**+**8m′**, s, 6H), 0.13 (**8m**+**8m′**, s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8, 170.5, 136.2, 135.9, 135.8, 128.6, 128.1, 126.6, 120.0, 119.8, 113.5, 112.9, 94.5, 89.4, 88.3, 86.0, 70.4, 63.1, 62.3, 23.8, 23.7, 20.9, 0.01; HRMS (EI) calcd for $C_{14}H_{21}O_3Si$ $[M-H]^+$: 266.1330, found 266.1337.

*4.2.14. (E)-7-(tert-Butyldimethylsilyloxy)-4-methyleneoct-2-en-5-ynyl acetate (**7n**) and 7-(tert-butyldimethylsilyloxy)-6-methyleneoct-2-en-4-ynyl acetate (**8n**+**8n′**).* Colorless oil, ^{1}H NMR (501 MHz, $CDCl_3$) δ 6.26 (**7n**, d, *J*=15.4 Hz, 1H), 6.14 (**8n**+**8n′**, m, 2H), 5.98 (**7n**, td, *J*=6.6, 10.9 Hz, 1H), 5.87 (**8n**, d, *J*=15.9 Hz, 1H), 5.79 (**8n′**, d, *J*=10.8 Hz, 1H), 5.58 (**8n**, s, 1H), 5.57 (**8n′**, s, 1H), 5.47 (**8n**, s, 1H), 5.40 (**7n**, s, 2H), 5.38 (**8n′**, s, 1H), 4.83 (**8n′**, d, *J*=6.8 Hz, 1H), 4.68 (**7n**, dd, *J*=6.5, 13.2 Hz, 1H), 4.64 (**7n**, d, *J*=6.0 Hz, 2H), 4.61 (**8n**, d, *J*=7.5 Hz, 2H), 4.31–4.24 (**8n**+**8n′**, m, 4H), 2.07 (s, 3H), 2.06 (s, 6H), 1.46 (d, *J*=6.5 Hz, 3H), 1.32 (d, *J*=6.5 Hz, 3H), 1.30 (d, *J*=6.7 Hz, 3H), 0.90 (s, 9H), 0.89 (s, 18H), 0.12 (d, *J*=4.6 Hz, 6H), 0.06 (d, *J*=6.3 Hz, 6H), 0.05 (d, *J*=5.2 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.65, 170.56, 136.1, 135.8, 132.7, 128.5, 127.3, 124.0, 119.7, 119.4, 113.5, 112.8, 94.6, 94.3, 89.5, 85.9, 79.8, 70.6, 70.5, 63.97, 63.91, 62.3, 59.3, 30.3, 25.8, 25.4, 23.9, 20.8, 18.2, −4.6, −4.9, −5.0; HRMS (CI) calcd for $C_{16}H_{25}O_3Si$ $[M-CH_3]^+$: 293.1573, found 293.1568.

*4.2.15. (E)-7-(Benzyloxy)-4-methyleneoct-2-en-5-ynyl acetate (**7o**) and 7-(benzyloxy)-6-methyleneoct-2-en-4-ynyl acetate (**8o**+**8o′**).* Yellow oil, ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.43–7.24 (**7o**+**8o**+**8o′**, m, 15H), 6.31 (**7o**, d, *J*=15.4 Hz, 1H), 6.24–6.14 (**7o**+**8o**, m, 2H), 6.03 (**8o′**, td, *J*=6.6, 10.9 Hz, 1H), 5.59–5.46 (**7o**+**8o**+**8o′**, m, 6H), 4.87 (**8o′**, d, *J*=6.3 Hz, 2H), 4.82 (**8o**, d, *J*=6.3 Hz, 2H), 4.68 (**7o**, d, *J*=6.3 Hz, 2H), 4.65–4.59 (**7o**+**8o**+**8o′**, m, 4H), 4.41 (**7o**, dd, *J*=6.6, 13.3 Hz, 2H), 4.39–4.33 (**7o**+**8o**+**8o′**, m, 3H), 4.03–3.95 (**8o**+**8o′**, m, 2H), 2.09 (**7o**, s, 3H), 2.086 (**8o**, s, 3H), 2.076 (**8o′**, s, 3H), 1.55 (**7o**, d, *J*=6.6 Hz, 3H), 1.42–1.38 (**8o**+**8o′**, m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.6, 170.5, 170.3, 138.3, 137.9, 136.5, 136.2, 133.34, 133.29, 132.7, 128.32, 128.27, 128.2, 127.9, 127.7, 127.43, 127.36, 124.6, 122.2, 122.0, 113.3, 112.7, 93.7, 91.5, 88.6, 88.4, 86.1, 81.7, 77.2, 70.6, 70.2, 64.8, 63.9, 63.8, 62.2, 22.1, 21.0, 20.83, 20.78; HRMS (EI) calcd for $C_{18}H_{19}O_3$ $[M-H]^+$: 283.1334, found 283.1351.

*4.2.16. (E)-7-Hydroxy-7-methyl-4-methyleneoct-2-en-5-ynyl acetate (**7p**) and 7-hydroxy-7-methyl-6-methyleneoct-2-en-4-ynyl acetate (**8p**+**8p′**).* Yellow oil, ^{1}H NMR (501 MHz, $CDCl_3$) δ 6.27 (**7p**, d, *J*=6.6 Hz, 1H), 6.21–6.07 (**7p**+**8p**, m, 2H), 6.01 (**8p′**, td, *J*=6.7, 10.8 Hz, 1H), 5.89 (**8p**, d, *J*=15.9 Hz, 1H), 5.82 (**8p′**, d, *J*=10.8 Hz, 1H), 5.62 (**8p′**, *J*=1.2 Hz, 1H), 5.60 (**8p**, *J*=1.2 Hz, 1H), 5.50 (**7p**, s, 1H), 5.43 (**8p′**, d, *J*=0.8 Hz, 1H), 5.41 (**8p**, d, *J*=1.0 Hz, 1H), 5.40 (**7p**, s, 1H), 4.83 (**8p′**, dd, *J*=1.5, 6.0 Hz, 2H), 4.65 (**7p**, d, *J*=6.1 Hz, 2H), 4.62 (**8p**, dd, *J*=1.5, 6.0 Hz, 2H), 2.09 (**7p**, s, 3H), 2.08 (**8p**, s, 3H), 2.07 (**8p′**, s, 3H), 1.58 (**7p**, s, 6H), 1.44 (**8p′**, s, 6H), 1.42 (**8p**, s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.7, 170.6, 170.5, 145.6, 142.7, 139.4, 136.4, 136.0, 132.8, 129.3, 128.2, 127.2, 125.5, 124.5, 119.1, 118.8, 113.3, 113.0, 94.4, 92.6, 89.2, 88.7, 86.5, 72.7, 72.6, 64.0, 63.9, 62.1, 31.5, 31.4, 30.9, 30.3, 29.1, 20.94, 20.87; HRMS (EI) calcd for $C_{12}H_{16}O_3$ $[M]^+$: 208.1100, found 208.1088.

*4.2.17. 6-(1-Hydroxycyclohexyl)hepta-2,6-dien-4-ynyl acetate (**8q**+**8q′**).* Yellow oil, ^{1}H NMR (501 MHz, $CDCl_3$) **8q**: δ 6.18 (td, *J*=6.1, 15.9 Hz, 1H), 5.90 (d, *J*=6.1, 15.9 Hz, 1H), 5.63 (s, 1H), 5.45 (s, 1H), 4.62 (d, *J*=4.8 Hz, 2H), 2.08 (s, 3H), 1.86–1.75 (m, 4H), 1.71–1.49 (m, 6H); **8q′**: δ 6.02 (td, *J*=6.7, 10.8 Hz, 1H), 5.83 (d, *J*=10.8 Hz, 1H), 5.65 (s, 1H), 5.47 (s, 1H), 4.84 (d, *J*=6.7 Hz, 2H), 2.08 (s, 3H), 1.86–1.75 (m, 4H), 1.71–1.49 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.7, 145.6, 140.0, 136.3, 135.8, 125.5, 119.7, 119.5, 113.4, 113.1, 95.2, 94.7, 89.5, 86.4, 63.9, 62.2, 39.9, 36.3, 30.3, 29.7, 25.3, 25.1, 23.3, 21.8, 20.9, 20.5; HRMS (EI) calcd for $C_{15}H_{20}O_3$ $[M]^+$: 248.1413, found 248.1418.

*4.2.18. (E)-tert-Butyldimethyl(6-methylene-9-(p-tolyloxy)non-7-en-4-ynyloxy)silane (**10a**) and tert-butyldimethyl(4-methylene-9-(p-tolyloxy)non-7-en-5-ynyloxy)silane (**11a**+**11a′**).* Pale yellow oil, ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.14–7.08 (**10a**+**11a**+**11a′**, m, 6H), 6.88–6.82 (**10a**+**11a**+**11a′**, m, 6H), 6.40 (**10a**, d, *J*=15.5 Hz, 1H), 6.36–6.27 (**10a**+**11a**, m, 2H), 6.15 (**11a′**, td, *J*=6.2, 11.0 Hz, 1H), 5.99 (**11a**, d, *J*=15.9 Hz, 1H), 5.84 (**11a′**, d, *J*=10.9 Hz, 1H), 5.47 (**10a**, s, 1H), 5.41 (**11a′**, s, 1H), 5.39 (**10a**, s, 1H), 5.37 (**11a**, s, 1H), 5.33 (**11a′**, s, 1H), 5.31 (**11a**, s, 1H), 4.83 (**11a′**, dd, *J*=1.6, 6.2 Hz, 2H), 4.62 (**11a**, d,

J=4.9 Hz, 2H), 4.59 (**11a**, dd, *J*=1.8, 5.3 Hz, 2H), 3.76 (**11a′**, t, *J*=6.0 Hz, 2H), 3.71 (**11a**, t, *J*=5.9 Hz, 2H), 3.66 (**10a**, t, *J*=6.3 Hz, 2H), 2.50 (**11a′**, t, *J*=7.1 Hz, 2H), 2.39 (**11a**, t, *J*=7.0 Hz, 2H), 2.32 (**10a**+**11a**+**11a′**, s, 9H), 2.32–2.29 (**10a**, m, 2H), 1.86–1.72 (**10a**+**11a**+**11a′**, m, 6H), 0.99–0.90 (**10a**+**11a**+**11a′**, m, 27H), 0.14–0.04 (**10a**+**11a**+**11a′**, m, 18H); HRMS (EI) calcd for $C_{23}H_{34}O_4SSi$ $[M]^+$: 434.1947, found 434.1955.

*4.2.19. (E)-9-(tert-Butyldimethylsilyloxy)-4-methylenenon-2-en-5-ynyl pivalate (**10b**) and 9-(tert-butyldimethylsilyloxy)-6-methylenenon-2-en-4-ynyl pivalate (**11b**+**11b′**).* Yellow oil, ^1H NMR (501 MHz, $CDCl_3$) δ 6.25 (**11b**, d, *J*=15.3 Hz, 2H), 6.18–6.09 (**10b**+**11b**, m, 2H), 5.96 (**11b′**, td, *J*=6.5, 11.1 Hz, 1H), 5.84 (**11b**, d, *J*=15.9, 1H), 5.76 (**11b′**, d, *J*=10.8 Hz, 1H), 5.42 (**10b**, s, 1H), 5.35 (**10b**, s, 1H), 5.34 (**11b′**, s, 1H), 5.32 (**11b**, s, 1H), 5.27 (**11b′**, s, 1H), 5.25 (**11b**, s, 1H), 4.80 (**11b′**, d, *J*=6.5 Hz, 1H), 4.63 (**10b**, d, *J*=5.8 Hz, 1H), 4.59 (**11b**, d, *J*=5.8 Hz, 1H), 3.73–3.60 (**10b**+**11b**+**11b′**, m, 6H), 2.48–2.60 (**10b**+**11b**+**11b′**, m, 6H), 1.80–1.69 (**10b**+**11b**+**11b′**, m, 6H), 1.29 (**10b**+**11b**+**11b′**, s, 9H), 1.21 (**10b**+**11b**+**11b′**, s, 9H), 1.20 (**10b**+**11b**+**11b′**, s, 9H), 0.88 (**10b**+**11b**+**11b′**, s, 27H), 0.05–0.03 (**10b**+**11b**+**11b′**, m, 18H); HRMS (EI) calcd for $C_{21}H_{36}O_3Si$ $[M]^+$: 364.2434, found 364.2629.

*4.2.20. (E)-tert-Butyldimethyl(6-methylene-9-(trimethylsilyl)-non-7-en-4-ynyloxy)silane (**10d**) and tert-butyldimethyl(4-methylene-9-(trimethylsilyl)non-7-en-5-ynyloxy)silane (**11d**+**11d′**).* Colorless oil, ^1H NMR (501 MHz, $CDCl_3$) δ 6.20–6.06 (**10d**+**11d**, m, 2H), 5.97 (**11d′**, dd, *J*=8.8, 19.3 Hz, 1H), 5.45 (**11d′**, d, *J*=10.6 Hz, 1H), 5.42 (**11d**, *J*=15.7 Hz, 1H), 5.27 (**11d′**, s, 1H), 5.263 (**10d**, s, 1H), 5.261 (**11d**, s, 1H), 5.20 (**11d′**, s, 1H), 5.18 (**11d**, s, 1H), 5.14 (**10d**, s, 1H), 3.73 (**10d**, t, *J*=6.1 Hz, 2H), 3.63 (**11d**+**11d′**, t, *J*=6.3 Hz, 4H), 2.45 (**10d**, t, *J*=7.0 Hz, 2H), 2.27–2.20 (**11d**+**11d′**, m, 4H), 1.85 (**11d′**, d, *J*=8.8 Hz, 2H), 1.81–1.72 (**10d**+**11d**+**11d′**, m, 6H), 1.61 (**11d**, d, *J*=8.3 Hz, 1H), 1.58 (**10d**, d, *J*=8.4 Hz, 1H), 0.90 (**10d**+**11d**+**11d′**, s, 37H), 0.07–0.01 (**10d**+**11d**+**11d′**, m, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.1, 141.1, 131.9, 131.73, 131.67, 130.3, 128.5, 120.1, 118.5, 107.4, 106.2, 93.8, 91.3, 89.0, 87.4, 87.0, 78.2, 62.3, 62.2, 61.6, 33.73, 33.68, 31.9, 31.3, 26.0, 24.9, 23.30, 22.96, 18.3, 15.7, −1.62, −1.88, −1.91, −5.31; HRMS (EI) calcd for $C_{19}H_{36}OSi_2$ $[M]^+$: 336.2305, found 336.2298.

*4.2.21. tert-Butyldimethyl(6-methyleneoct-7-en-4-ynyloxy)-silane (**10e**).* Yellow oil, ^1H NMR (501 MHz, $CDCl_3$) δ 6.35 (dd, *J*=10.1, 17.0 Hz, 1H), 5.62 (d, *J*=17.0 Hz, 1H), 5.44 (s, 1H), 5.35 (s, 1H), 5.22 (d, *J*=10.1 Hz, 1H), 3.68 (t, *J*=5.9 Hz, 2H), 2.46 (t, *J*=7.1 Hz, 2H), 1.73 (m, 2H), 0.90 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.2, 136.6, 122.7, 117.4, 64.4, 61.6, 61.3, 31.8, 25.9, 1.02, −5.33; HRMS (EI) calcd for $C_{15}H_{26}OSi$ $[M]^+$: 250.1753, found 250.1757.

Acknowledgements

We are grateful to the University of Illinois at Chicago for the financial support.

Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2013.08.024.

References and notes

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