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Synthetic Studies on and Mechanistic Insight into $[W(CO)_5(L)]$-Catalyzed Stereoselective Construction of Functionalized Bicyclo[5.3.0]decane Frameworks

Yuji Onizawa, Masahiro Hara, Takuya Hashimoto, Hiroyuki Kusama, and Nobuharu Iwasawa*[a]

Abstract: Stereoselective preparation of a variety of synthetically useful functionalized bicyclo[5.3.0]decane derivatives was achieved by tandem cyclization of 3-siloxy-1,3,9-triene-7-yne derivatives based on the electrophilic activation of alkynes catalyzed by $[W(CO)_5(L)]$. The reaction proceeded smoothly under photoirradiation, and various substrates were cyclized to give the corresponding bicyclic compounds with up to four chiral centers stereospecifically. Reactions of siloxydienes with a silyl substituent as an equivalent of a hydroxyl group also proceeded with wide generality to afford silyl-substituted bicyclo[5.3.0]decanes, which were highly useful as synthetic intermediates. Stereochemical studies concerning the silyl enol ether moiety suggested that two types of reaction pathway for the formation of seven-membered rings were present. The reaction of (*Z*)-enol silyl ethers proceeded through Cope rearrangement of *cis*-divinylcyclopropane intermediates, and that of (*E*)-enol silyl ethers by 1,4-addition of the dienyl tungsten species at the position δ to the metal atom. In the reactions of siloxydiene derivatives with silyl substituents, all possible diastereomers could be synthesized stereoselectively by changing the geometry of the silyl enol ether and enyne moieties.

Keywords: cyclization · enynes · polycycles · synthetic methods · tungsten

Introduction

Several thousand sesquiterpenes have been isolated from natural sources, and about 1000 of them have a bicyclo[5.3.0]decane framework, most of which have important biological activity.[1] Therefore, development of novel methodologies for efficient and stereoselective synthesis of bicyclo[5.3.0]decane derivatives is of great importance in synthetic chemistry.

Many methods have already been reported for the synthesis of the bicyclo[5.3.0]decane framework,[2,3] but efficient methods from easily available starting materials are quite limited. An example is Rh-catalyzed intramolecular [5+2] cycloaddition reactions of alkynyl, alkenyl, and allenyl vinylcyclopropanes to give bicyclo[5.3.0]decanes, developed by Wender et al.,[4] while Trost et al. reported the same type of reaction using Ru catalysts under milder conditions.[5] Wender et al. further applied this reaction to the total synthesis of natural products such as aphanamol[4c] and dictamnol,[4d] but it still remains difficult to stereoselectively introduce desired substituents into the bicyclo[5.3.0]decane core at chosen positions.

We recently reported rhenium(I)-catalyzed tandem cyclization of 3-siloxy-1,3-diene-7-ynes **1** to give bicyclo[3.3.0]octane derivatives **2** based on the geminal carbo-functionalization strategy (Scheme 1).[6] Thus, treatment of acetylenic dienol silyl ethers **1** with rhenium carbonyl complexes gave zwitterionic intermediates **B** by 5-*endo* nucleophilic cyclization of the enol silyl ether part to electrophilically activated η^2-alkyne complexes **A**. The resulting alkenyl rhenium moiety performed an intramolecular attack on the α,β-unsaturated silyloxonium moiety at the position β to the metal atom to generate bicyclic unstabilized carbene complexes **C**. Finally, the unstabilized carbene complexes underwent 1,2-hydrogen migration to give bicyclo[3.3.0]octane derivatives **2** with regeneration of the reactive metal species. This reaction enables successive for-

[a] Dr. Y. Onizawa, M. Hara, T. Hashimoto, Dr. H. Kusama, Prof. Dr. N. Iwasawa
Department of Chemistry, Tokyo Institute of Technology
2-12-1-E1-2 O-okayama, Meguro-ku, Tokyo 152-8551 (Japan)
Fax: (+81) 3-5734-2931
E-mail: niwasawa@chem.titech.ac.jp

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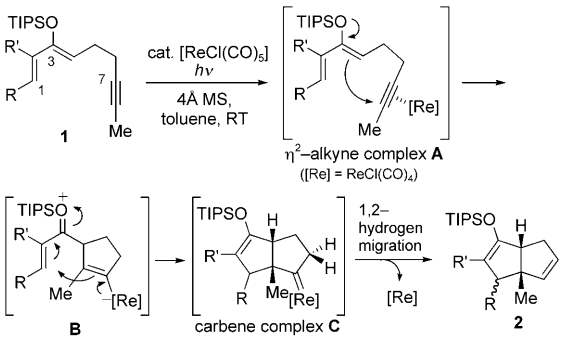
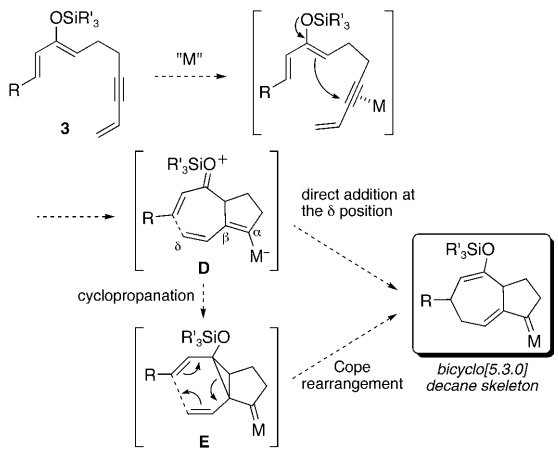


Scheme 1. Re^{I}-catalyzed tandem cyclization of 3-siloxy-1,3-diene-7-ynes. MS = molecular sieves, TIPS = iPr$_3$Si.

mation of two carbon–carbon bonds on the same alkyne carbon atom and provides synthetically useful bicyclic compounds from easily available acyclic substrates in a single operation.

During this study, we thought of applying this tandem cyclization protocol to vinylogous substrates (Scheme 2). We expected that treatment of 3-siloxy-1,3,9-triene-7-ynes **3** with an appropriate electrophilic metal reagent would give zwitterionic intermediates **D** with a dienyl metal moiety by a similar 5-*endo* cyclization. Addition to the α,β-unsaturated silyloxonium moiety at the position β to the metal atom would give similar bicyclo[3.3.0]octane derivatives with a vinyl substituent, but we expected it might be possible to obtain synthetically useful bicyclo[5.3.0]decane derivatives by addition of the dienyl metal moiety at the position δ to the metal atom.[7] Alternatively, the alkenyl metallic species might add directly to the silyloxonium carbon atom at the position β to the metal atom to afford divinylcyclopropane intermediates **E**, which would undergo Cope rearrangement to give the same bicyclo[5.3.0]decanes smoothly.[8,9] Realization of such reactions would open up a new avenue to efficient and stereoselective preparation of highly useful bicyclo[5.3.0]decane derivatives from simple acyclic precursors.

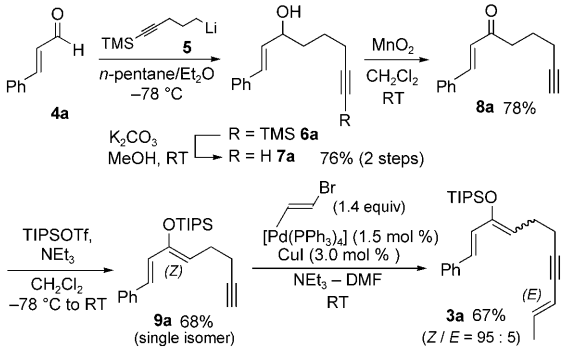


Scheme 2. Possible reaction pathways, including seven-membered ring formation in tandem cyclization of 3-siloxy-1,3,9-triene-7-yne derivatives.

Based on the above considerations, we examined various aspects of the reactions of 3-siloxy-1,3,9-triene-7-ynes for the stereoselective construction of bicyclo[5.3.0]decane framework.[10] Herein, we report a full account of this work, including the scope, synthetic application, and mechanistic aspects of this reaction.

Results and Discussion

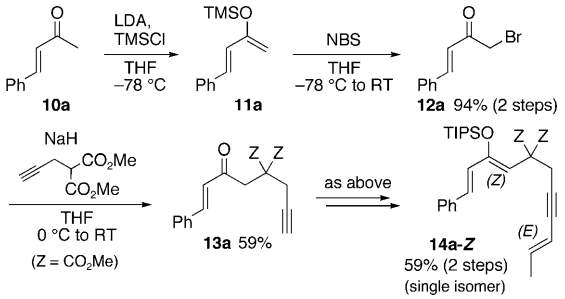
Development of tungsten-catalyzed stereoselective construction of bicyclo[5.3.0]decane frameworks from 3-siloxy-1,3,9-triene-7-yne derivatives: Preparation of 3-siloxy-1,3,9-triene-7-yne (**3a**) is shown in Scheme 3. Addition reaction of alkyl lithium **5** with cinnamaldehyde **4a** gave allylic alcohol **6a**. Then, removal of the TMS protecting group at the alkyne terminus followed by oxidation of the allylic alcohol moiety provided enone **8a**, which was treated with TIPSOTf in the presence of NEt_3 to afford siloxydiene **9a** with a (*Z*)-enol silyl ether moiety as a single geometrical isomer. Finally, the enyne was successfully prepared by Sonogashira coupling of terminal alkyne **9a** with (*E*)-1-bromoprop-1-ene to give siloxydiene **3a** as a mixture of geometrical isomers (*Z*/*E* = 95:5). A small amount of (*E*)-enol silyl ether was produced by isomerization during purification by column chromatography on silica gel.



Scheme 3. Preparation of **3a**. TMS = $SiMe_3$.

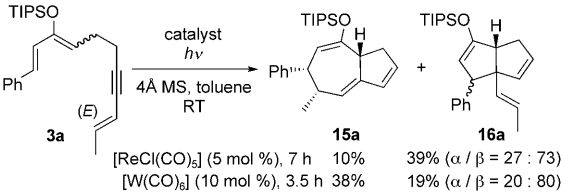
Dimethyl malonate derivative **14a-*Z*** was prepared as shown in Scheme 4. Benzalacetone (**10a**) was converted to α-bromo ketone **12a** by bromination of silyl enol ether **11a**. Then, alkylation of dimethyl prop-2-ynylmalonate with α-bromo ketone **12a** gave alkenyl ketone **13a**, which was converted to enyne **14a-*Z*** with a siloxydiene moiety as a single geometrical isomer by the same procedure as that described above. A variety of substrates could be prepared by employing α,β-unsaturated ketones as starting materials and alkenyl halides as coupling partners of the final step.

According to the previously established protocol for the [$ReCl(CO)_4$(L)]-catalyzed geminal carbo-functionalization of 3-siloxy-1,3-diene-7-ynes for the preparation of bicyclo-



Scheme 4. Preparation of **14a-*Z***. LDA = lithium diisopropylamide, NBS = *N*-bromosuccinimide.

[3.3.0]octane derivatives,[6a] we first examined the reaction of enyne **3a** with $[ReCl(CO)_5]$ (5 mol%) under photoirradiation (super-high-pressure Hg lamp) in toluene in the presence of 4 Å molecular sieves (Scheme 5). The starting



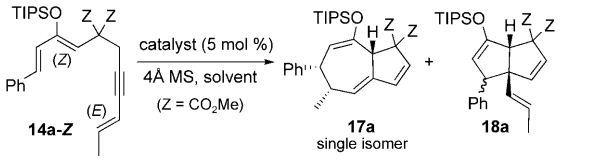
Scheme 5. Initial studies on tandem cyclization of **3a**.

material was consumed within 7 h, but the desired bicyclo[5.3.0]decane derivative **15a** was obtained only in 10% yield, and the major product was bicyclo[3.3.0]octane derivative **16a** (39% yield). We next examined the same reaction employing $[W(CO)_6]$ (10 mol%) under the same reaction conditions and found that the desired bicyclo[5.3.0]decane derivative **15a** was obtained as a major product (38% yield) accompanied by the bicyclo[3.3.0]octane derivative **16a** (19% yield).

Next, enyne **14a-*Z*** with a geminal diester moiety in the tether (C_5 position) was employed (Table 1). While the rhenium catalyst showed low catalytic activity (Table 1, entry 1), the tungsten-catalyzed reaction proceeded smoothly to give the desired bicyclo[5.3.0]decane derivative **17a** in 66% yield (bicyclo[3.3.0]octane derivative **18a**: 3%; Table 1, entry 5). The product **17a** was obtained as a single diastereomer and the structure was confirmed by X-ray analysis.

Since stereoselective construction of the bicyclo[5.3.0]decane derivative was achieved as expected, we next examined several other typical electrophilic transition-metal catalysts for this reaction (Table 1). Whereas Pt^{II} and cationic Au^{I} catalysts[11] showed low catalytic activity (Table 1, entries 2 and 4), neutral Au^{I} complex showed moderate activity in toluene at 70°C (Table 1, entry 3). Among the catalysts examined, $[W(CO)_5(L)]$ was found to be the most suitable catalyst for this reaction. Although the reaction with preformed $[W(CO)_5(thf)]$ (10 mol%) without photoirradiation

Table 1. Screening of catalysts and optimization of reaction conditions.



Entry	Conditions	Additive	*t* [h]	Yield [%] **17a**	**18a**
1	$[ReCl(CO)_5]$/toluene, *hν*, RT	–	34	4	–
2	$PtCl_2$/toluene, 70°C	–	17	12	–
3	AuCl/toluene, 70°C	–	3	54	–
4	$[(Ph_3P)Au]SbF_6/ClCH_2CH_2Cl$, 70°C	–	6	0	–
5	$[W(CO)_6]$/toluene, *hν*, RT	–	2	66	3
6[a]	$[W(CO)_5(thf)]$/THF, 60°C	–	13	78	–
7	$[W(CO)_6]$/THF, *hν*, RT	–	38	40	–
8	$[W(CO)_6]$/toluene, *hν*, RT	NEt_3[b]	2	83	4

[a] 10 mol% of $[W(CO)_5(thf)]$ was used. [b] 10 mol%.

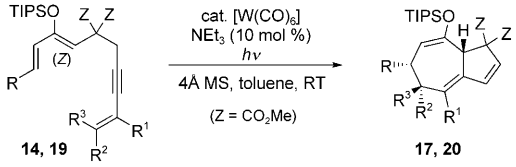
did not proceed to an appreciable degree at room temperature, heating the reaction mixture to 60°C promoted the reaction in good yield (Table 1, entry 6). Thus, photoirradiation is not indispensable for the present reaction. When the reaction was carried out in toluene under photoirradiation, as little as 5 mol% of $[W(CO)_6]$ was sufficient to complete the reaction within 2 h at room temperature (Table 1, entry 5). In addition, by carrying out the same reaction in the presence of NEt_3 (10 mol%), the formation of small amounts of unidentified compounds was suppressed and the yield of **17a** was further improved to 83% (Table 1, entry 8). In these cases, a small amount (3–4% yield) of bicyclo[3.3.0]octane derivative **18a** was obtained, the formation of which is thought to be due to the reaction of the corresponding (*E*)-enol silyl ether isomer produced by photoisomerization (see below).

Having established that $[W(CO)_5(L)]$ efficiently catalyzes formation of seven-membered rings, we examined the reaction with several kinds of substrates bearing a (*Z*)-enol silyl ether moiety (Table 2). Vinylic, mono-substituted, and disubstituted enynes were cyclized to afford the corresponding bicyclo[5.3.0]decane derivative in good yield as a single stereoisomer (Table 2, entries 1–3 and 6). Furthermore, enynes with an acetal (Table 2, entry 4) and an ester (Table 2, entry 5) moiety and of alkyl-substituted dienes (Table 2, entries 7 and 8) also underwent seven-membered ring formation smoothly in good yield with only a catalytic amount of $[W(CO)_6]$. In these reactions, only a trace of bicyclo[3.3.0]octane derivatives was produced.

Furthermore, the reaction of dienol silyl ethers with a cyclohexenyl group at the alkyne terminus or as part of the diene moiety with a catalytic amount of $[W(CO)_6]$ also proceeded to give synthetically useful tricyclic compounds with a 6–7–5 ring system in good yields stereoselectively (Scheme 6).

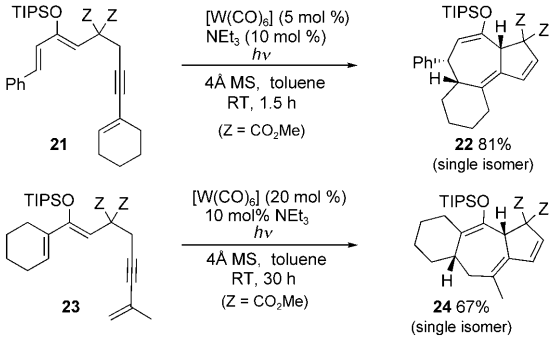
Comparison of the reactions of (*E*)-propenyl derivative **14a-*Z*** and (*Z*)-propenyl derivative **14g** clearly indicates stereospecificity of seven-membered ring formation. The reaction of (*E*)-propenyl derivative **14a-*Z*** afforded the desired

Table 2. Generality of bicyclo[5.3.0]decane syntheses from enynes **14**, **19**.



Entry	R	(R^1, R^2, R^3)	$[W(CO)_6]$ [mol %]	*t* [h]	Yield [%]
1[a]	Ph	(**14b**)	10	3	63 (**17b**)
2		(**14c-*Z***)	5	2	79 (**17c**)
3		(**14d**)	5	3	78 (**17d**)
4[a]		(**14e**) $(MeO)_2CH$ ($E/Z = 6:1$)	5	3.5	71 (**17e**)
5[a]		EtO_2C (**14f**)	20	5	57 (**17f**)
6		(**14g**)	5	3	80 (**17g**)
7	*i*Pr	(**19a**)	5	2	83 (**20a**)
8		(**19b**)	10	1.5	61 (**20b**)

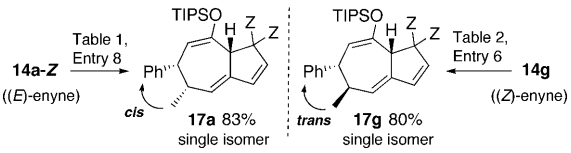
[a] In the absence of NEt_3. [b] **17e** was obtained as a 6:1 mixture of diastereomers.



Scheme 6. Synthesis of tricyclic compounds.

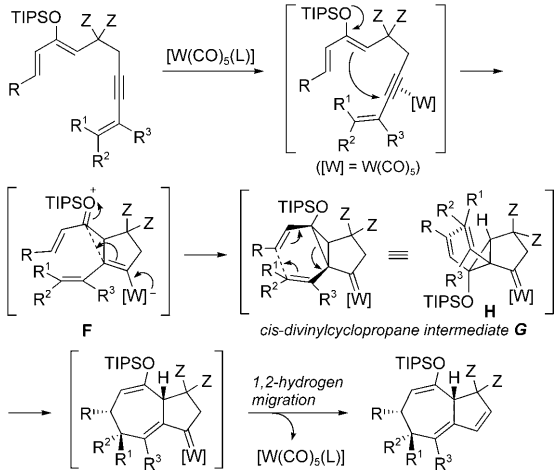
bicyclic compound **17a** as a single diastereomer, the relative stereochemistry of which was *cis* between the phenyl and methyl groups. On the contrary, that of the product **17g** derived from (*Z*)-propenyl derivative **14g** was *trans* (Scheme 7).

This stereoselectivity can be explained by the following *cis*-divinylcyclopropane rearrangement pathway, the proposal of which is based on the fact that the reaction proceeded much faster than the previous bicyclo[3.3.0]octane synthesis.



Scheme 7. Stereospecificity of seven-membered ring formation.

Thus, *cis*-divinylcyclopropane intermediates **G** would be generated by direct and rapid addition of the alkenyl tungsten moiety to the silyloxonium carbon in zwitterionic intermediate **F**, which was produced by 5-*endo* nucleophilic cyclization of the (*Z*)-enol silyl ether part to the electrophilically activated η^2-alkyne complexes. Then, this *cis*-divinylcyclopropane intermediates undergo Cope rearrangement via conformation **H**[12] in a stereospecific manner to give bicyclo[5.3.0]decane derivatives (Scheme 8).



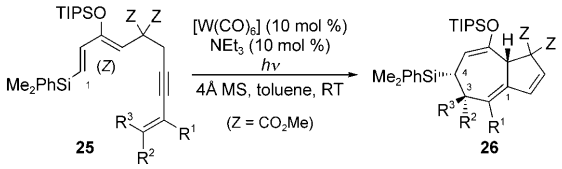
Scheme 8. Plausible mechanism and stereochemical aspect of the tandem cyclization.

The different catalytic activities of several electrophilic metal reagents, in particular, the reason why $[W(CO)_5(L)]$ showed higher activity, could be explained as follows based on the assumption that formation of the divinylcyclopropane intermediate is a crucial step in this reaction. Thus, in zwitterionic intermediate **F**, the nucleophilicity of the alkenyl metal species would be dependent on the nature of the metal. While highly electrophilic metals such as Pt^{II} or cationic Au^{I} showed almost no nucleophilicity as alkenyl metal compounds, $[W(CO)_5(L)]$ showed the highest nucleophilicity because this alkenyl tungsten is zero valent and therefore anionic. Thus, $[W(CO)_5(L)]$ was the most suitable catalyst for this reaction (see Table 1).

Synthesis of functionalized bicyclo[5.3.0]decane frameworks: Among many natural products containing the bicyclo[5.3.0]decane skeleton, those with oxygen functionality at the 4-position are common.[13] With the purpose of expanding the synthetic utility of the present reaction, we next examined the possibility of introducing an alkoxy substituent at the diene terminus; however, elimination of the oxygen group after tandem cyclization predominated. We then examined the use of an arylsilyl group at the diene terminus as an equivalent of oxygen functionality.[14] When the reaction of 3-siloxy-1,3,9-triene-7-ynes **25**, with a Me_2PhSi group at the 1-position, was carried out under the same reaction conditions as for Ph-substituted dienes, the expected

silyl-substituted bicyclo[5.3.0]decane derivatives **26** were obtained in moderate to excellent yield with perfect stereoselectivity (Table 3, entries 1 and 2). Again, the reaction proceeded stereospecifically concerning the geometry of the enyne moiety (Table 3, entries 3 and 4). Furthermore, highly functionalized bicyclo[5.3.0]decanes with a TMS or an ethoxycarbonyl group could also be synthesized stereoselectively by this reaction (Table 3, entries 5 and 6).[15]

Table 3. Generality of Me_2PhSi-substituted bicyclo[5.3.0]decane synthesis.

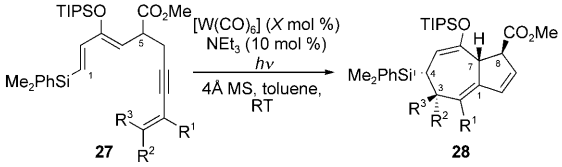


Entry	R^1	R^2	R^3		t [h]	Yield [%]
1	H	H	H	**25a-*Z***	1	54 (**26a-α**)
2	Me	H	H	**25b-*Z***	0.5	93 (**26b**)
3	H	Me	H	**25c-*Z***	0.5	90 (**26c-α**)
4	H	H	Me	**25d-*Z***	0.5	94 (**26d-α**)
5	H	Me_3Si	H	**25e**	2	54 (**26e**)
6[a]	H	H	EtO_2C	**25f**	0.5	66 (**26f**)

[a] The reaction was performed with 40 mol% of $[W(CO)_6]$ in the absence of NEt_3.

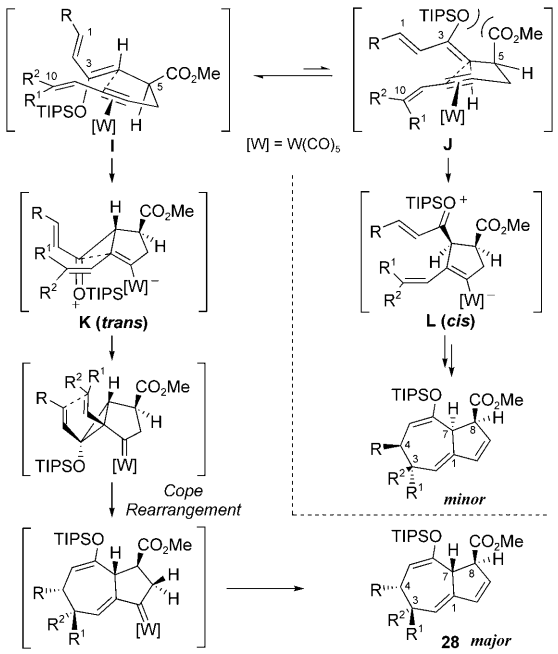
Next, we examined the reaction of substrates **27** with a monoester substituent at the C_5 position[16] to determine the effect of substitution at this position on the efficiency and the stereoselectivity of the reaction (Table 4). When the reaction of isopropenyl derivative **27a** was carried out with $[W(CO)_6]$ (20 mol%) and NEt_3 (10 mol%) under photoirradiation, silyl-substituted bicyclo[5.3.0]decane derivative **28a** with three stereogenic centers at the 4-, 7-, and 8-positions was obtained in 88% yield as a single diastereomer (Table 4, entry 1). This result shows that almost complete asymmetric induction by the C^5 chirality on the substrate was achieved. The asymmetric induction can be explained as follows: in the π-alkyne complexes, conformer **I** is expected to be more favorable than **J** due to the 1,3-allylic strain between C^3 and C^5 (Scheme 9, C^5: H vs. CO_2Me). The more favorable conformer **I** cyclizes to afford zwitterionic intermediate **K-*trans***, which further undergoes cyclopropane formation and Cope rearrangement stereospecifically to give bicyclo[5.3.0]decane derivative **28** in a highly stereocontrolled manner (Scheme 9). The reactions of *E* and *Z* propenyl derivatives **27b** and **27c** also proceeded with high diastereoselectivity (10:1 to 20:1)[17] to give bicyclo[5.3.0]decane derivatives **28b** and **28c** with four stereogenic centers at the 3-, 4-, 7-, and 8-positions in good yield, respectively (Table 4, entries 2 and 3).

Table 4. Stereoselective reaction of mono-ester substituted substrates **27**.



Entry	R^1	R^2	R^3		X [mol%]	t [h]	Yield [%]
1	Me	H	H	**27a**	20	4	88 (**28a**)
2	H	Me	H	**27b**	5	4	87 (**28b**)[a]
3	H	H	Me	**27c**	5	10	72 (**28c**)[b]

[a] 10:1 mixture of diastereomers. [b] 20:1 mixture of diastereomers.

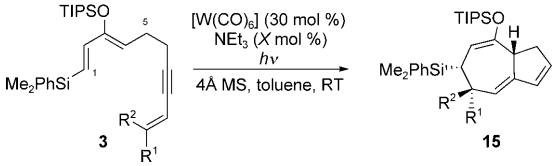


Scheme 9. Schematic representation on the origin of the stereoselectivity in the reactions of mono-ester substrates **27**.

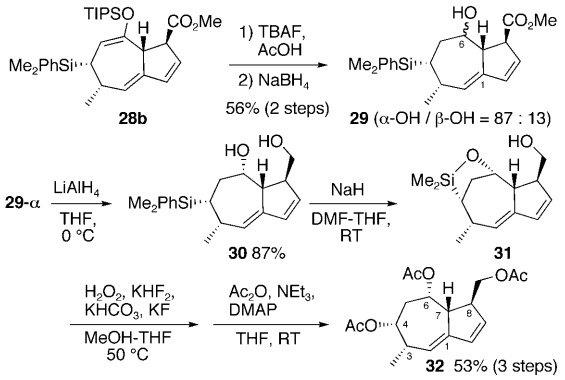
Interestingly, the reaction of silyl-substituted dienes (**3b**, **3c**) with no substituent on the tether also gave the desired seven-membered ring products (**15b**, **15c**) in good yield (Table 5). These results are noteworthy because the reaction of phenyl-substituted diene **3a** gave a mixture of bicyclo[5.3.0]decane derivative **15a** (38% yield) and bicyclo[3.3.0]octane derivative **16a** (19% yield) in moderate yield (see Scheme 5).

The Me_2PhSi substituent was successfully converted to a hydroxyl group by Fleming–Tamao oxidation (Scheme 10).

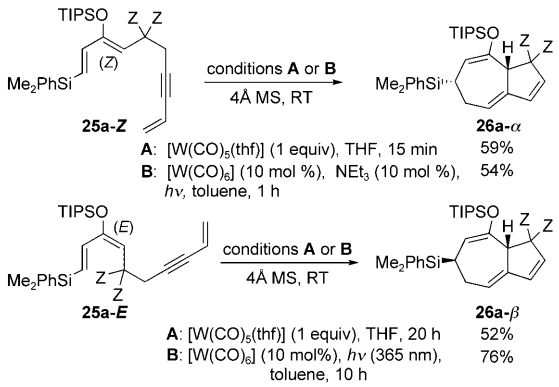
Table 5. Reactions of substrates having no substituent at the 5-position.



Entry	R^1	R^2		X [mol%]	t [h]	Yield [%]
1	Me	H	**3b**	0	2	67 (**15b**)
2	H	Me	**3c**	10	10	70 (**15c**)



Scheme 10. Conversion of Me_2PhSi to a hydroxyl group. TBAF = tetra-*n*-butylammonium fluoride.



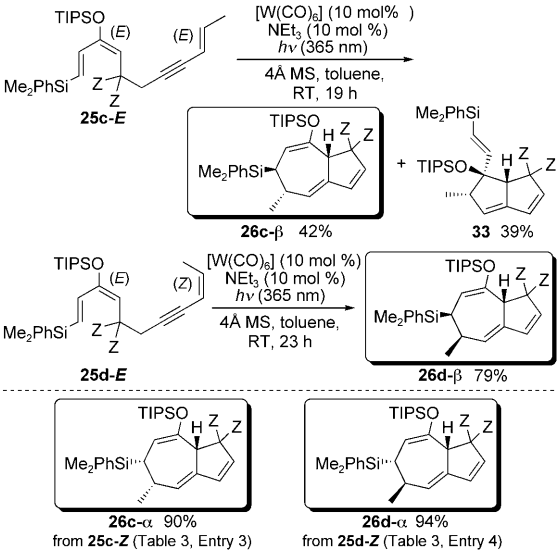
Scheme 11. Comparison of the reactions of *Z* and *E* isomers.

Treatment of **28b** with TBAF/AcOH in THF gave a ketone by hydrolysis of the silyl enol ether moiety. Then, stereoselective reduction of the ketone by $NaBH_4$ followed by reduction of the ester group with $LiAlH_4$ gave diol **30**. The resulting γ-hydroxy phenyl silane moiety could be converted to cyclic alkoxy silane **31** under mild conditions[18] by nucleophilic addition of the alkoxide anion to the phenyl silane moiety followed by protonation of the Si–Ph bond. The reaction of alkoxy silane **31** under standard Fleming–Tamao oxidation conditions successfully afforded desired oxygen-functionalized bicyclo[5.3.0]decane **32** with five stereogenic centers.

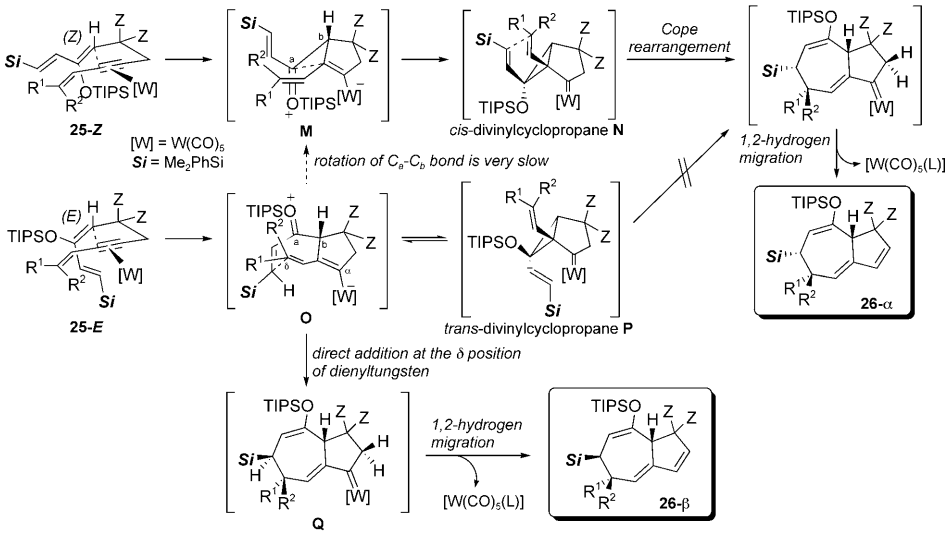
Mechanistic study and further synthetic utility: To expand the generality of the reaction and to obtain information on the mechanism of this reaction, we further examined the reaction of the geometrical isomers concerning the silyl enol ether moiety. All substrates employed so far were *Z* isomers prepared from the corresponding ketones by using TIPSOTf and NEt_3. The corresponding *E* isomers were prepared by photoisomerization of *Z* isomers with a super-high-pressure Hg lamp (>300 nm). Treatment of *Z* isomers in toluene under photoirradiation gave a mixture of *E* and *Z* isomers (*E*/*Z* = 4:1 to 6:1), which could be easily separated by column chromatography on silica gel to give pure *E* isomers.[19] To compare the reactivity of these two isomers, we first examined the reaction with preformed $[W(CO)_5(thf)]$ to avoid photoisomerization of the silyl enol ether moiety during the reaction (Scheme 11, conditions **A**). Thus, treatment of *Z* derivative **25a-*Z*** with a stoichiometric amount of preformed $[W(CO)_5(thf)]$ at room temperature for 15 min afforded the same bicyclo[5.3.0]decane derivative **26a-α** as obtained under photoirradiation without problems. On the other hand, the same reaction employing *E* derivative **25a-*E*** required a much longer reaction time (20 h), and silyl-substituted bicyclo[5.3.0]decane derivative **26a-β**, a diastereomer of the product **26a-α**, was obtained in good yield as a single diastereomer. Furthermore, we found that when the photoirradiation wavelength was limited to 365 nm, no scrambling of the products occurred under catalytic photoirradiation conditions (conditions **B**).[20] Thus, the reaction was found to be stereospecific concerning the geometry of the silyl enol ether moiety.

This stereospecificity is also apparent in the following reaction of *E* and *Z* propenyl derivatives **25c-*E*** and **25d-*E*** with an (*E*)-enol silyl ether moiety. In this case, the reaction was stereospecific concerning both the geometry of the silyl enol ether moiety and of the enyne moiety although the yield of **26c-β** obtained from (*E*)-propenyl derivative **25c-*E*** was moderate due to formation of another bicyclo-[3.3.0]octane derivative, namely, **33**. Thus, it is possible to prepare all four possible diastereomers stereoselectively by changing the geometry of the silyl enol ether and enyne moieties (Scheme 12).

As already mentioned, *Z* derivative **25-*Z*** could give bicyclo[5.3.0]decane derivative **26-α** through Cope rearrangement of *cis*-divinylcyclopropane intermediate **N**. On the other hand, in the case of *E* derivative **25-*E***, *trans*-divinylcyclopropane intermediate **P** would be formed initially in a similar manner but can not undergo Cope rearrangement (Scheme 13). It is expected that this *trans*-divinylcyclo-



Scheme 12. Stereoselective synthesis of the four possible diastereomers.



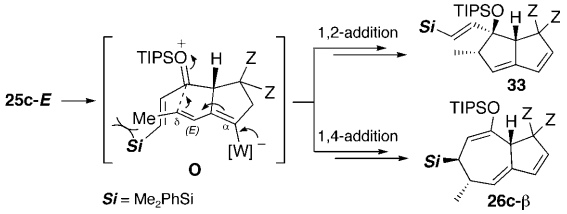
Scheme 13. Proposed mechanisms for tandem cyclization of 3-siloxy-1,3,9-triene-7-yne derivatives bearing (*Z*)- and (*E*)-enol silyl ethers.

Although a similar tandem cyclization pathway is possible for the (*Z*)-enol silyl ether derivative, we believe the reaction of the *Z* isomer proceeds through the divinylcyclopropane intermediate based on the following results:

The first is the reaction in the presence of methanol. Treatment of **25a-*Z*** with preformed $[W(CO)_5(thf)]$ in the presence of MeOH afforded bicyclo[5.3.0]decane derivative **26a-α** in 66% without formation of monocyclic product. On the other hand, when the reaction of the corresponding *E* isomer **25a-*E*** was carried out under the same conditions, monocyclic ketone **34**, the protonated product of the zwitterionic intermediate produced by the first cyclization, was obtained in 41% yield accompanied by bicyclo[5.3.0]decane derivative **26a-β** (Scheme 15). These results support that seven-membered ring formation from (*Z*)-enol silyl ether proceeds in a concerted manner (Cope rearrangement of *cis*-divinylcyclopropane), and that from its *E* counterpart in a stepwise manner (direct addition to unsaturated silyloxonium moiety at the δ position of the zwitterionic intermediate).

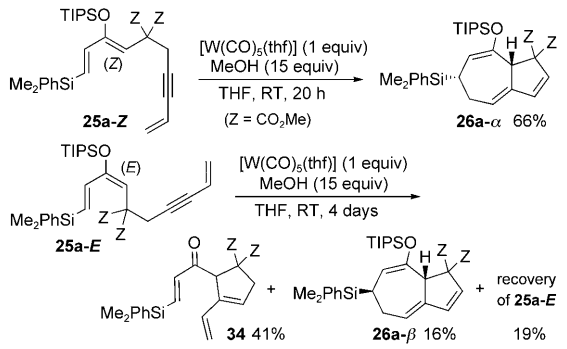
propane intermediate **P** would be in equilibrium with zwitterionic intermediate **O** by an aldol/retro-aldol-type process. In zwitterionic intermediate **O**, the rotational barrier around the C_a–C_b bond is thought to be very high due to the steric hindrance between the TIPSO group and the neighboring alkenyl group or geminal diester moiety, and this intermediate **O** is thought to be difficult to be converted to the conformational isomer **M** by rotation about the C_a–C_b bond. Thus, intermediate **O** slowly undergoes addition of the dienyl tungsten compound to the α,β-unsaturated silyloxonium moiety at the δ position to the metal atom preferentially to give carbene complex intermediate **Q** with a bicyclo[5.3.0]decane skeleton, which undergoes 1,2-hydrogen migration to afford the product **26-β** with regeneration of the catalyst. As already mentioned, in the zwitterionic intermediate **O**, the conformation of the alkenyl substituent and the unsaturated silyloxonium moiety is strictly fixed due to steric hindrance, and thus the second cyclization proceeded from this conformation with perfect selectivity to afford bicyclo[5.3.0]decane derivatives **26-β** stereoselectively and stereospecifically.

Furthermore, formation of a considerable amount of bicyclo[3.3.0]octane derivative **33** from (*E*)-propenyl derivative **25c-*E*** (R^1 = Me, R^2 = H) could be explained as follows: in zwitterionic intermediate **O**, attack of the dienyl tungsten moiety on the α,β-unsaturated silyloxonium moiety (1,4-addition) at the position δ to the metal atom is unfavorable due to steric repulsion between silyl substituent and (*E*)-propenyl group. Thus, intermediate **O** undergoes addition to the silyloxonium moiety directly (1,2-addition) at the position δ to the metal atom to give bicyclo[3.3.0]octane derivative **33** (Scheme 14). This repulsion would be reduced when *Z* propenyl derivative **25d-*E*** (R^1 = H, R^2 = Me) is employed, and only bicyclo[5.3.0]decane derivative **26d-β** is obtained in this case.



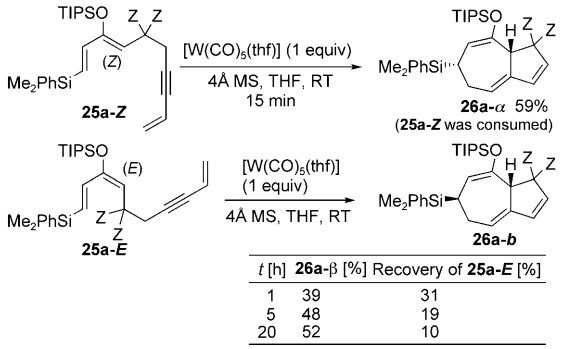
Scheme 14. 1,2-Addition versus 1,4-addition of intermediate **O**.

The second is the difference in reaction rate between *Z* and *E* isomers. The reaction of *Z* isomer **25a-*Z*** with an



Scheme 15. Reactions in the presence of methanol.

equimolar amount of preformed $[W(CO)_5(thf)]$ in THF was complete within 15 min, whereas that of *E* derivative **25a-*E*** was not complete even after 20 h of stirring (Scheme 16).

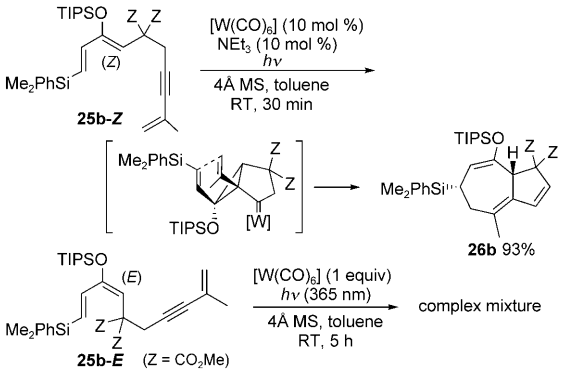


t [h]	**26a**-β [%]	Recovery of **25a-*E*** [%]
1	39	31
5	48	19
20	52	10

Scheme 16. Difference in reaction rate between **25a-*Z*** and **25a-*E***.

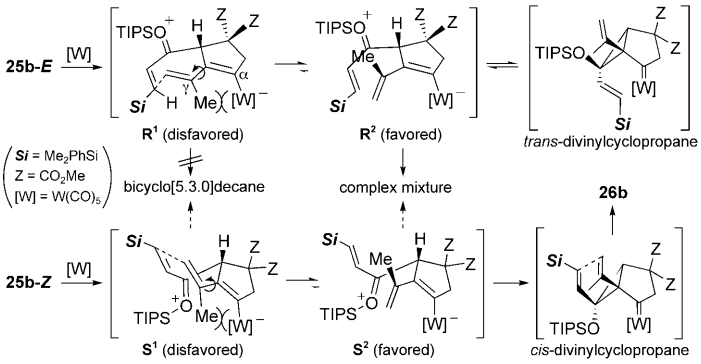
This large difference in reaction rate between the two isomers also supports that these two reactions proceeded in a different manner.

The third is the difference in reactivity between (*Z*)- and (*E*)-enol silyl ethers observed with isopropenyl derivatives **25b**. Whereas the reaction of (*Z*)-enol silyl ether proceeded smoothly to give desired bicyclo[5.3.0]decane **26b** in excellent yield, that of (*E*)-enol silyl ether was complicated and proceeded without bicyclo[5.3.0]decane formation (Scheme 17).



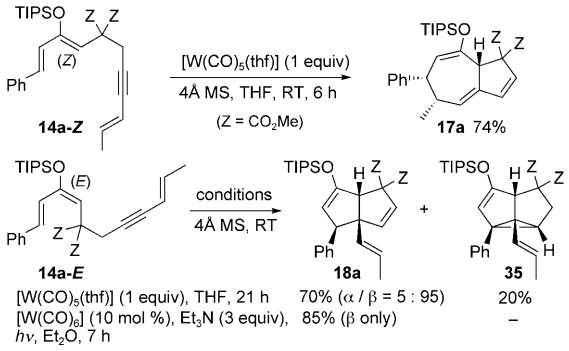
Scheme 17. Difference in reactivity between isopropenyl derivatives **25b-*Z*** and **25b-*E***.

Probably, zwitterionic intermediate **R** generated by cyclization of (*E*)-enol silyl ether only undergoes the second cyclization step (seven-membered ring formation) with difficulty because the propenyl group cannot conjugate with the alkenyl tungsten moiety due to steric repulsion between the methyl group at the γ position to the metal atom and the tungsten pentacarbonyl moiety. The same situation must exist in zwitterionic intermediate **S** generated from the *Z* isomer, and if the reaction of the *Z* isomer proceeds through this intermediate, then the reaction should become sluggish in a similar manner to that of the *E* isomer, which in fact was not the case (Scheme 18).



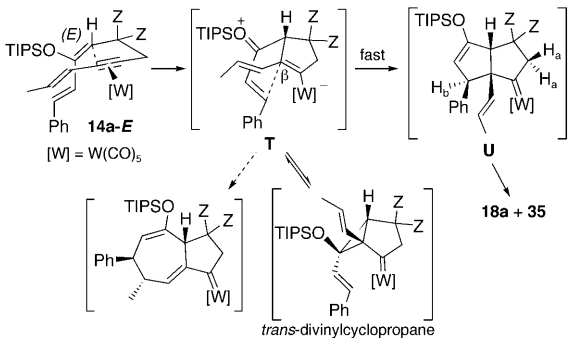
Scheme 18. Possible reaction pathways in the reactions of isopropenyl derivatives **25b**.

Finally, another intriguing result was obtained when we examined the reaction of the *E* isomer of phenyl-substituted diene. In contrast to the reaction of *Z* derivative **14a-*Z***, which gave the same bicyclo[5.3.0]decane derivative **17a** as before without problem with a stoichiometric amount of preformed $[W(CO)_5(thf)]$ (6 h), the same reaction employing the *E* derivative **14a-*E*** required a longer reaction time (21 h) and gave bicyclo[3.3.0]octane derivative **18a** as a major product (70%) accompanied by tricyclic compound **35** (20%) without formation of bicyclo[5.3.0]decane derivative **17a**. Furthermore, by carrying out the reaction in diethyl ether under photoirradiation in the presence of triethylamine, formation of **35** was completely suppressed and **18a** was obtained in good yield catalytically (Scheme 19).



Scheme 19. Reactions of phenyl-substituted dienes **14a**.

The differences in reactivity between Ph- and Si-substituted dienes could be explained as follows (Scheme 20): As a Ph substituent is less bulky than a $PhMe_2Si$ group, attack of the alkenyl tungsten group on the α,β-unsaturated silyloxonium moiety at the β position to the metal atom (kinetically favored five-membered ring formation) is possible in the reaction of the Ph-substituted compound to give carbene complex intermediate **U** with a bicyclo[3.3.0]octane skeleton,



Scheme 20. Reaction course of *E* isomer of phenyl-substituted diene **14a-*E***.

from which 1,2-hydrogen migration of H_a or insertion into the neighboring benzylic C–H_b bond occurred to afford bicyclic and tricyclic products **18a** and **35**. By carrying out the reaction in the presence of Et_3N, deprotonation of carbene complex intermediate **U** is promoted to give **18a** selectively.[21] Based on the above-mentioned experimental results, we believe that there are two distinct reaction pathways depending on the geometry of the silyl enol ether moiety in this unique cyclization reaction.

Conclusion

We have developed [$W(CO)_5$(L)]-catalyzed stereoselective construction of the bicyclo[5.3.0]decane framework from simple enynes with a siloxydiene moiety. A variety of functionalized bicyclo[5.3.0]decanes can be prepared in a stereoselective and stereospecific manner. Furthermore, all diastereomers could be synthesized stereoselectively simply by changing the geometry of the silyl enol ether moiety and the enyne moiety by using silyl-substituted dienes as the substrate. Through stereochemical analyses, it was shown that two mechanisms of seven-membered ring formation exist: 1) Cope rearrangement of the *cis*-divinylcyclopropane intermediate generated from (*Z*)-enol silyl ether, and 2) addition to α,β-unsaturated silyloxonium moiety at the δ position of the dienyltungsten moiety in the zwitterionic intermediate from (*E*)-enol silyl ether. This reaction would provide a powerful method for the synthesis of natural products with a bicyclo[5.3.0]decane framework.

Experimental Section

General: General procedures and spectral data of the cyclization precursors (**3**, **14**, **19**, **21**, **23**, **25**, **27**), stereochemical assignment of the tandem cyclization products (**15**, **17**, **20**, **22**, **24**, **26**, **28**), and experimental procedures for Scheme 10 are described in the Supporting Information.

Tandem cyclization of trienynes bearing a (*Z*)-enol silyl ether moiety: A typical procedure for the cyclization of enynes is described for the reaction of **14a-*Z*** as a substrate: **14a-*Z*** (64 mg, 0.125 mmol) and NEt_3 (1.8 μL, 0.013 mmol, 10 mol%) in degassed toluene (1.3 mL) were added to a mixture of [$W(CO)_6$] (2.3 mg, 0.0065 mmol, 5 mol%) and activated 4 Å MS After the mixture was photoirradiated (250 W super-high-pressure Hg lamp) for 2 h at room temperature, the suspension was filtered, and then the solvent was removed under reduced pressure to give crude product, which was purified by PTLC (10% ethyl acetate in hexane) to give 53 mg of **17a** (0.104 mmol, 83%).

Compound 17a: White crystal (m.p. 111–112 °C); IR (KBr): $\tilde{\nu}$ = 2953, 2866, 1751, 1732, 1656, 1451, 1264 cm^{-1}; ^1H NMR (400 MHz in $CDCl_3$): δ = 1.01 (d, J = 7.2 Hz, 3H), 1.07–1.11 (m, 18H), 1.17–1.26 (m, 3H), 3.00–3.08 (m, 1H), 3.42–3.47 (m, 1H), 3.70 (s, 3H), 3.81 (s, 3H), 4.86 (brs, 1H), 5.09 (dd, J = 8.0, 2.0 Hz, 1H), 5.12 (dd, J = 3.2, 2.4 Hz, 1H), 6.05 (d, J = 5.4 Hz, 1H), 6.20 (d, J = 5.4 Hz, 1H), 7.19–7.28 (m, 3H), 7.34 (d, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz in $CDCl_3$): δ = 13.3, 18.2, 20.1, 36.5, 49.7, 51.7, 52.3, 52.7, 70.7, 111.3, 126.1, 127.1, 128.3, 130.3, 132.4, 136.9, 141.3, 143.9, 149.2, 169.1, 170.3; elemental analysis (%) calcd for $C_{30}H_{42}O_5Si$: C 70.55, H 8.29; found: C 70.36, H 8.54.

Compound 17b: White solid (m.p. 92–96 °C); IR (KBr): $\tilde{\nu}$ = 2945, 2867, 1743, 1654, 1432, 1198 cm^{-1}; ^1H NMR (500 MHz in $CDCl_3$): δ = 1.10 (d, J = 7.5 Hz, 18H), 1.16–1.25 (m, 3H), 2.41 (dt, J = 14.8, 7.0 Hz, 1H), 2.74–2.80 (m, 1H), 3.73 (s, 3H), 3.76–3.80 (m, 1H), 3.81 (s, 3H), 4.84–4.87 (m, 1H), 5.04 (dd, J = 7.5, 2.0 Hz, 1H), 5.49–5.52 (m, 1H), 6.02 (d, J = 5.5 Hz, 1H), 6.18 (d, J = 5.5 Hz, 1H), 7.19 (t, J = 7.5 Hz, 1H), 7.26–7.30 (m, 2H), 7.34 (d, J = 7.5 Hz, 2H); ^{13}C NMR (125 MHz in $CDCl_3$): δ = 13.2, 18.1, 18.2, 34.0, 42.6, 51.3, 52.3, 52.7, 70.3, 109.8, 121.9, 126.0, 127.9, 128.4, 131.9, 137.2, 144.9, 145.6, 150.3, 169.3, 170.4; elemental analysis (%) calcd for $C_{29}H_{40}O_5Si$: C 70.12, H 8.12; found: C 69.85, H 8.41

Compound 17c: White solid; IR (KBr): $\tilde{\nu}$ = 2951, 2866, 1739, 1656, 1462, 1195 cm^{-1}; ^1H NMR (500 MHz in $CDCl_3$): δ = 1.08–1.11 (m, 18H), 1.17–1.26 (m, 3H), 1.25 (d, J = 2.0 Hz, 3H), 2.18 (dd, J = 13.8, 6.2 Hz, 1H), 2.93 (brd, J = 13.8 Hz, 1H), 3.74 (s, 3H), 3.77–3.80 (m, 1H), 3.80 (s, 3H), 4.84 (brs, 1H), 5.01 (dd, J = 7.4, 1.7 Hz, 1H), 5.98 (d, J = 5.7 Hz, 1H), 6.42 (d, J = 5.7 Hz, 1H), 7.19 (t, J = 7.3 Hz, 1H), 7.25–7.30 (m, 2H), 7.36 (d, J = 7.3 Hz, 2H); ^{13}C NMR (125 MHz in $CDCl_3$): δ = 13.3, 18.1, 18.2, 22.5, 41.3, 42.4, 51.3, 52.3, 52.7, 70.2, 109.2, 125.9, 127.8, 128.5, 129.5, 130.4, 133.8, 138.2, 143.9, 151.2, 169.5, 170.7; elemental analysis (%) calcd for $C_{30}H_{42}O_5Si$: C 70.55, H 8.29; found: C 70.34, H 8.29

Compound 17d: White solid (m.p. 104–105 °C); IR (KBr): $\tilde{\nu}$ = 2950, 2867, 1747, 1655, 1467, 1209 cm^{-1}; ^1H NMR (500 MHz, 330 K in $CDCl_3$) δ = 0.94 (s, 3H), 1.06–1.10 (m, 18H), 1.17–1.26 (m, 3H), 1.28 (s, 3H), 3.25–3.29 (m, 1H), 3.66 (s, 3H), 3.81 (s, 3H), 4.78–4.81 (m, 1H), 4.99 (dd, J = 7.7, 2.3 Hz, 1H), 5.40 (d, J = 3.0 Hz, 1H), 6.03 (d, J = 5.5 Hz, 1H), 6.20 (d, J = 5.5 Hz, 1H), 7.15–7.25 (m, 3H), 7.35 (d, J = 7.0 Hz, 2H); ^{13}C NMR (125 MHz, 330 K in $CDCl_3$) δ = 13.2, 18.1, 18.2, 28.1, 29.8, 37.3, 51.9, 52.1, 52.5, 55.2, 70.7, 109.6, 126.1, 127.3, 130.2, 131.9, 133.0, 138.4, 142.8, 143.4, 148.0, 169.1, 170.4; elemental analysis (%) calcd for $C_{31}H_{44}O_5Si$: C 70.95, H 8.45; found: C 70.69, H 8.34

Compound 17e-*cis*: White crystal (m.p. 129–131 °C); IR (KBr): $\tilde{\nu}$ = 2949, 2868, 1748, 1654, 1459, 1197 cm^{-1}; ^1H NMR (400 MHz in $CDCl_3$): δ = 1.06–1.11 (m, 18H), 1.17–1.26 (m, 3H), 3.20–3.27 (m, 1H), 3.27 (s, 3H), 3.39 (s, 3H), 3.70 (s, 3H), 3.78–3.83 (m, 1H), 3.81 (s, 3H), 4.12 (d, J = 9.6 Hz, 1H), 4.88 (brs, 1H), 5.10 (dd, J = 8.2, 2.2 Hz, 1H), 5.23 (dd, J = 5.8, 3.0 Hz, 1H), 6.08 (d, J = 5.6 Hz, 1H), 6.24 (d, J = 5.6 Hz, 1H), 7.18–7.29 (m, 3H), 7.39 (d, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz in $CDCl_3$): δ = 13.3, 18.2, 18.3, 43.46, 43.53, 50.9, 51.6, 52.3, 52.8, 53.1, 70.9, 103.6, 111.3, 121.8, 126.3, 127.4, 130.4, 132.8, 136.7, 140.9, 145.1, 149.4, 169.0, 170.1; elemental analysis (%) calcd for $C_{32}H_{46}O_7Si$: C 67.34, H 8.12; found: C 67.47, H 8.41

Compound 17e-*trans*: White solid (m.p. 133–135 °C); IR (KBr): $\tilde{\nu}$ = 2922, 2866, 1742, 1656, 1459, 1200 cm^{-1}; ^1H NMR (500 MHz in $CDCl_3$): δ = 1.07–1.12 (m, 18H), 1.19–1.26 (m, 3H), 2.70 (td, J = 8.5, 4.2 Hz, 1H), 3.29 (s, 3H), 3.43 (s, 3H), 3.74 (s, 3H), 3.80 (s, 3H), 3.83–3.87 (m, 1H), 4.71 (d, J = 8.5 Hz, 1H), 4.74.79 (m, 1H), 4.90 (dd, J = 7.7, 2.1 Hz, 1H), 5.52 (dd, J = 8.5, 3.0 Hz, 1H), 6.02 (d, J = 5.5 Hz, 1H), 6.20 (d, J = 5.5 Hz, 1H), 7.17–7.21 (m, 1H), 7.25–7.29 (m, 2H), 7.40 (d, J = 7.2 Hz, 2H); ^{13}C NMR (125 MHz in $CDCl_3$): δ = 13.1, 18.16, 18.20, 43.5, 47.0, 52.2, 52.4, 52.7, 53.1, 53.9, 70.8, 103.6, 107.4, 121.1, 126.0, 127.9, 129.0, 132.2, 138.2, 144.7, 145.5, 149.2, 169.2, 170.3; elemental analysis (%) calcd for $C_{32}H_{46}O_7Si$: C 67.34, H 8.12; found: C 67.11, H 8.20

Compound 17f: Colorless oil; IR (neat): $\tilde{\nu}$ = 2949, 2868, 1745, 1656, 1464, 1264, 1168 cm^{-1}; ^1H NMR (400 MHz in C_6D_6) δ = 0.99 (t, J = 7.2 Hz, 3H), 1.13–1.31 (m, 21H), 3.42 (s, 3H), 3.41–3.46 (m, 1H), 3.53 (s, 3H), 3.98 (dq, J = 11.0, 7.2 Hz, 1H), 4.07 (dq, J = 11.0, 7.2 Hz, 1H), 4.44–4.49 (m, 1H), 5.06 (dd, J = 7.6, 1.9 Hz, 1H), 5.21–5.23 (m, 1H), 5.32 (dd, J = 8.0, 2.9 Hz, 1H), 5.92 (d, J = 5.5 Hz, 1H), 6.12 (d, J = 5.5 Hz, 1H), 7.02–7.08 (m, 1H), 7.15–7.22 (m, 2H), 7.50–7.52 (m, 2H); ^{13}C NMR (100 MHz in $CDCl_3$): δ = 13.1, 14.1, 18.0, 18.1, 45.2, 50.2, 51.8, 52.4, 52.7, 61.0, 70.3, 106.7, 118.3, 126.4, 128.0, 128.8, 133.5, 137.5, 143.6, 147.8, 150.4, 169.2, 170.0, 171.7; elemental analysis (%) calcd for $C_{32}H_{44}O_7Si$: C 67.57, H 7.80; found: C 67.69, H 8.04

Compound 17g: White solid (m.p. 85–87 °C); IR (KBr): $\tilde{\nu}$ = 2951, 2867, 1745, 1655, 1451, 1204 cm^{-1}; ^1H NMR (500 MHz in $CDCl_3$): δ = 1.07–1.10 (m, 18H), 1.17–1.26 (m, 3H), 1.21 (d, J = 7.1 Hz, 3H), 2.54–2.61 (m, 1H), 3.50–3.54 (m, 1H), 3.73 (s, 3H), 3.80 (s, 3H), 4.80–4.83 (m, 1H), 4.88 (dd, J = 5.2, 2.1 Hz, 1H), 5.59 (dd, J = 7.4, 2.9 Hz, 1H), 6.01 (d, J = 5.4 Hz, 1H), 6.16 (d, J = 5.4 Hz, 1H), 7.16–7.21 (m, 1H), 7.25–7.29 (m, 2H), 7.34 (d, J = 7.1 Hz, 2H); ^{13}C NMR (100 MHz in $CDCl_3$): δ = 13.3, 18.08, 18.10, 19.1, 38.5, 49.5, 51.4, 52.3, 52.7, 70.3, 107.2, 125.9, 127.1, 127.9, 128.6, 131.5, 138.0, 144.0, 145.8, 149.7, 169.3, 170.5; elemental analysis (%) calcd for $C_{30}H_{42}O_5Si$: C 70.55, H 8.29; found: C 70.30, H 8.21

Compound 20a: Pale yellow oil; IR (neat): $\tilde{\nu}$ = 2952, 2869, 1746, 1651, 1464, 1434, 1261 cm^{-1}; ^1H NMR (500 MHz, 330 K in $CDCl_3$): δ = 0.94 (d, J = 6.7 Hz, 3H), 0.95 (d, J = 6.7 Hz, 3H), 0.99 (d, J = 7.0 Hz, 3H), 1.09–1.13 (m, 18H), 1.20–1.28 (m, 3H), 1.63–1.70 (m, 1H), 2.17–2.22 (m, 1H), 2.58–2.65 (m, 1H), 3.63 (s, 3H), 3.76 (s, 3H), 4.60–4.63 (m, 1H), 4.66 (brs, 1H), 5.61 (dd, J = 7.0, 2.8 Hz, 1H), 5.97 (d, J = 5.5 Hz, 1H), 6.16 (d, J = 5.5 Hz, 1H); ^{13}C NMR (125 MHz, 330 K in $CDCl_3$): δ = 13.2, 16.1, 18.1, 21.5, 21.9, 30.4, 33.6, 46.9, 50.9, 52.1, 52.4, 69.0, 107.2, 130.2, 131.3, 137.9, 142.7, 150.5, 169.6, 170.5; elemental analysis (%) calcd for $C_{27}H_{44}O_5Si$: C 68.02, H 9.30; found: C 67.80, H 9.51

Compound 20b: Pale yellow oil; IR (neat): $\tilde{\nu}$ = 2951, 2868, 1742, 1643, 1464, 1262 cm^{-1}; ^1H NMR (500 MHz in $CDCl_3$): δ = 0.93 (d, J = 6.7 Hz, 3H), 0.95 (d, J = 6.7 Hz, 3H), 1.03–1.08 (m, 18H), 1.14–1.21 (m, 3H), 1.57–1.63 (m, 1H), 1.78 (s, 3H), 1.94 (dd, J = 16.5, 9.6 Hz, 1H), 2.23–2.30 (m, 1H), 2.45 (d, J = 16.5 Hz,1H), 3.65 (s, 3H), 3.74 (s, 3H), 4.67 (d, J = 7.4 Hz, 1H), 4.77 (brs, 1H), 5.99 (d, J = 5.7 Hz, 1H), 6.50 (d, J = 5.7 Hz, 1H); ^{13}C NMR (125 MHz in $CDCl_3$): δ = 13.1, 17.9, 18.1, 20.7, 21.3, 22.5, 32.4, 37.1, 42.0, 49.9, 52.1, 52.8, 68.4, 106.8, 129.2, 130.2, 133.8, 138.2, 151.2, 169.4, 170.8; elemental analysis (%) calcd for $C_{27}H_{44}O_5Si$: C 68.02, H 9.30; found: C 68.07, H 9.50.

Compound 22: White crystal (m.p. 161–164 °C); IR (KBr): $\tilde{\nu}$ = 2934, 2864, 1737, 1655, 1459, 1210 cm^{-1}; ^1H NMR (500 MHz, 330 K in $CDCl_3$) δ = 1.09–1.13 (m, 18H), 1.20–1.40 (m, 5H), 1.44–1.54 (m, 2H), 1.56–1.65 (m, 2H), 1.71–1.80 (m, 1H), 2.01–2.08 (m, 1H), 2.68–2.73 (m, 1H), 3.69 (s, 3H), 3.79 (s, 3H), 3.79–3.84 (m, 1H), 4.95 (brs, 1H), 5.09 (dd, J = 8.0, 2.1 Hz, 1H), 6.03 (d, J = 5.8 Hz, 1H), 6.55 (d, J = 5.8 Hz, 1H), 7.18–7.22 (m, 1H), 7.25–7.29 (m, 2H), 7.33–7.36 (m, 2H); ^{13}C NMR (125 MHz, 330 K in $CDCl_3$) δ = 13.2, 18.22, 18.23, 23.5, 24.6, 27.5, 30.1, 45.6, 47.0, 51.2, 52.1, 52.5, 69.5, 107.8, 126.1, 127.7, 129.4, 130.6, 133.7, 136.4, 136.6, 142.6, 151.2, 169.5, 170.7; elemental analysis (%) calcd for $C_{33}H_{46}O_5Si$: C 71.96, H 8.42; found: C 72.19, H 8.66.

Compound 24: White solid; IR (KBr): $\tilde{\nu}$ = 2926, 2866, 1743, 1646, 1434, 1260 cm^{-1}; ^1H NMR (500 MHz in $CDCl_3$): δ = 1.10–1.13 (m, 18H), 1.20–1.32 (m, 4H), 1.39–1.80 (m, 7H), 1.83 (dd, J = 13.8, 5.1 Hz, 1H), 1.85 (d, J = 2.2 Hz, 3H), 2.18–2.23 (m, 1H), 2.66 (brd, J = 12.1 Hz, 1H), 2.79 (d, J = 13.5 Hz, 1H), 3.64 (s, 3H), 3.78 (s, 3H), 4.92 (brs, 1H), 5.83 (d, J = 5.7 Hz, 1H), 6.49 (d, J = 5.7 Hz, 1H); ^{13}C NMR (125 MHz, 350 K in [D_6]benzene): δ = 14.2, 18.5, 18.9, 22.7, 27.3, 28.5, 32.4, 33.6, 39.4, 43.5, 51.5, 52.1, 53.5, 72.2, 124.5, 129.9, 131.1, 133.7, 138.9, 142.2, 169.1, 171.2; elemental analysis (%) calcd for $C_{28}H_{44}O_5Si$: C 68.81, H 9.07; found: C 68.60, H 8.78.

Compound 26a-α: Pale yellow oil; IR (neat): $\tilde{\nu}$ = 2949, 2867, 1744, 1645, 1464, 1433, 1248 cm^{-1}; ^1H NMR (400 MHz [D_6]benzene): δ = = 0.34 (s, 3H), 0.35 (s, 3H), 1.16–1.28 (m, 21H), 1.86–1.92 (m, 1H), 2.00–2.08 (m, 1H), 2.46–2.54 (m, 1H), 3.45 (s, 6H), 4.99 (dd, J = 7.8, 1.7 Hz, 1H), 5.05–5.08 (m, 1H), 5.57–5.61 (m, 1H), 5.96 (d, J = 5.6 Hz, 1H), 6.08 (d, J = 5.6 Hz, 1H), 7.20–7.27 (m, 3H), 7.48–7.51 (m, 2H); ^{13}C NMR (100 MHz in CD_2Cl_2) δ = −3.5, −3.2, 13.5, 18.27, 18.32, 26.6, 27.9, 51.4, 52.4, 52.8, 70.5, 108.2, 124.6, 128.0, 129.2, 132.2, 134.1, 137.4, 139.1, 145.9, 148.2, 169.7, 170.9; elemental analysis (%) calcd for $C_{31}H_{46}O_5Si_2$: C 67.10, H 8.36; found: C 66.99, H 8.48.

Compound 26b: Pale yellow solid; IR (KBr): $\tilde{\nu}$ = 2949, 2866, 1740, 1432, 1249 cm^{-1}; ^1H NMR (500 MHz in $CDCl_3$): δ = 0.29 (s, 3H), 0.35 (s, 3H), 0.99–1.03 (m, 18H), 1.04–1.11 (m, 3H), 1.71 (s, 3H), 1.98 (dd, J = 14.8, 7.1 Hz, 1H), 2.02–2.07 (m, 1H), 2.69 (brd, J = 14.8 Hz, 1H), 3.67 (s, 3H), 3.75 (s, 3H), 4.76 (brd, J = 7.5 Hz, 1H), 4.91 (brs, 1H), 5.97 (d, J = 5.7 Hz, 1H), 6.44 (d, J = 5.7 Hz, 1H), 7.32–7.36 (m, 3H), 7.52–7.54 (m, 2H); ^{13}C NMR (125 MHz in $CDCl_3$): δ = −4.2, −3.6, 13.1, 18.0, 18.1, 22.3, 25.6, 34.6, 50.6, 52.1, 52.7, 69.4, 106.3, 127.7, 128.9, 130.4, 130.6, 133.77, 133.80, 138.5, 138.6, 149.1, 169.5, 170.9. HRMS (EI^+) calcd for $C_{32}H_{48}O_5Si_2$: 568.3040; found: 568.3053

Compound 26c-α: Pale yellow solid; IR (KBr): $\tilde{\nu}$ = 2946, 2865, 1748, 1727, 1431, 1267, 1175 cm^{-1}; ^1H NMR (500 MHz, 363 K in [D_8]toluene) δ = 0.38 (s, 3H), 0.39 (s, 3H), 0.95 (d, J = 7.2 Hz, 3H), 1.13–1.16 (m, 18H), 1.20–1.27 (m, 3H), 2.04 (dt, J = 8.2, 3.0 Hz, 1H), 2.95–2.98 (m, 1H), 3.49 (s, 3H), 3.52 (s, 3H), 4.89–4.91 (m, 1H), 5.01 (dd, J = 8.2, 2.2 Hz, 1H), 5.41 (dd, J = 6.3, 3.0 Hz, 1H), 5.94 (d, J = 5.6 Hz, 1H), 5.97 (d, J = 5.6 Hz, 1H), 7.16–7.21 (m, 3H), 7.49–7.51 (m, 2H); ^{13}C NMR (125 MHz, 363 K in [D_8]toluene) δ = −1.4, −1.0, 13.9, 18.6, 18.7, 21.6, 35.2, 35.7, 51.7, 52.0, 52.5, 71.1, 109.8, 128.2, 129.1, 131.7, 132.9, 134.4, 137.3, 140.5, 143.9, 148.7, 169.3, 170.7. HRMS (EI^+) Calcd for $C_{32}H_{48}O_5Si_2$: 568.3040; found: 568.3026

Compound 26d-α: Pale yellow oil; IR (neat): $\tilde{\nu}$ = 2952, 2868, 1745, 1434, 1251 cm^{-1}; ^1H NMR (400 MHz in CD_2Cl_2) δ = 0.29 (s, 3H), 0.31 (s, 3H), 1.02–1.18 (m, 21H), 1.21(d, J=6.8 Hz, 3H), 1.76–1.84 (m, 1H), 2.38–2.48 (m, 1H), 3.65 (s, 3H), 3.74 (s, 3H), 4.76 (d, J = 8.0 Hz 1H), 4.74–4.78 (m, 1H), 5.30–5.32 (m, 1H), 5.90–5.98 (m, 2H), 6.17 (d, J = 5.2 Hz, 1H), 7.30–7.38 (m, 3H), 7.48–7.55 (m, 2H); ^{13}C NMR (100 MHz in CD_2Cl_2): δ = −3.6, −3.1, 13.3, 18.06, 18.09, 19.7, 31.2, 34.7, 52.1, 52.2, 52.5, 71.0, 106.2, 127.6, 128.4, 128.7, 131.7, 133.7, 137.8, 139.1, 143.98, 144.04, 169.2, 170.5; HRMS (EI^+) calcd for $C_{32}H_{48}O_5Si_2$: 568.3040; found: 568.3054

Compound 26e: Pale yellow oil; IR (neat): $\tilde{\nu}$ = 2951, 2868, 1744, 1631, 1464, 1252 cm^{-1}; two conformers of **26e** interconvert very slowly on the NMR timescale, and sharp signals in the ^1H NMR for both conformers are noted in a ratio of 60:40 at room temperature; ^1H NMR (500 MHz in CD_2Cl_2): major conformer: δ = 0.04 (s, 9H), 0.36 (s, 6H), 1.01–1.22 (m, 21H), 1.88–1.91 (m, 1H), 2.72–2.75 (m, 1H), 3.56 (s, 3H), 3.72 (s, 3H), 4.92–4.96 (m, 2H), 5.82 (d, J = 5.5 Hz, 1H), 5.88–5.91 (m, 1H), 6.17 (d, J = 5.5 Hz, 1H), 7.30–7.36 (m, 3H), 7.50–7.53 (m, 2H); minor conformer: δ = −0.15 (s, 9H), 0.27 (s, 3H), 0.36 (s, 3H), 1.01–1.22 (m, 21H), 2.14 (ddd, J = 8.2, 3.9, 1.8 Hz, 1H), 2.37 (d, J = 8.2 Hz, 1H), 3.64 (s, 3H), 3.74 (s, 3H), 4.85–4.88 (m, 1H), 5.10 (dd, J = 8.2, 2.0 Hz, 1H), 5.76 (dd, J = 8.2, 2.9 Hz, 1H), 5.99 (d, J = 5.5 Hz, 1H), 6.22 (d, J = 5.5 Hz, 1H), 7.30–7.36 (m, 3H), 7.50–7.53 (m, 2H); ^{13}C NMR (125 MHz in CD_2Cl_2): δ = −3.4, −2.9, −2.5, −1.8, −1.2, −0.2, 12.6, 12.9, 17.57, 17.62, 17.65, 17.69, 25.6, 29.5, 30.7, 31.4, 51.3, 51.4, 51.7, 51.8, 51.9, 52.1, 68.2, 70.3, 103.3, 115.6, 125.9, 127.3, 127.4, 128.3, 128.4, 128.6, 130.9, 132.3, 133.6, 133.8, 136.1, 138.6, 138.7, 138.9, 139.9, 145.2, 147.0, 153.8, 169.1, 169.5, 170.2, 170.4; elemental analysis (%) calcd for $C_{34}H_{54}O_5Si_3$: C 65.13, H 8.68; found: C 64.92, H 8.85.

Compound 26f: Pale yellow oil; IR (neat): $\tilde{\nu}$ = 2950, 2867, 1743, 1651, 1433, 1257 cm^{-1}; ^1H NMR (400 MHz in CD_2Cl_2) δ = 0.33 (s, 3H), 0.36 (s, 3H), 0.92–1.15 (m, 21H), 1.20 (t, J = 7.2 Hz, 3H), 2.45–2.51 (m, 1H), 3.08 (dd, J = 9.0, 3.4 Hz, 1H), 3.65 (s, 3H), 3.73(s, 3H), 4.02 (dq, J = 10.8, 7.2 Hz, 1H), 4.12 (dq, J = 10.8, 7.2 Hz, 1H), 4.73–4.79 (m, 2H), 5.76 (dd, J = 9.0, 3.0 Hz, 1H), 6.06 (d, J = 5.6 Hz, 1H), 6.26 (d, J = 5.6, 1H), 7.33–7.39 (m, 3H), 7.52–7.57 (m, 2H); ^{13}C NMR (100 MHz in CD_2Cl_2) δ = −3.4, −2.8, 13.5, 14.3, 18.4, 31.3, 43.4, 52.4, 52.7, 52.8, 61.1, 71.0, 106.0, 120.3, 128.1, 129.4, 134.0, 134.1, 137.4, 138.4, 145.8, 148.5, 169.3, 170.5, 173.2; HRMS (EI^+) calcd for $C_{32}H_{48}O_5Si_2$: 626.3095; found: 626.3069

Compound 28a: Pale yellow oil; IR (neat): $\tilde{\nu}$ = 2947, 2866, 1741, 1643, 1464, 1249, 1176 cm^{-1}; ^1H NMR (400 MHz in CD_2Cl_2) δ = 0.29 (s, 3H), 0.31 (s, 3H), 0.99–1.19 (m, 21H), 1.68 (brs, 3H), 1.97 (dd, J = 16.8, 11.0 Hz, 1H), 2.13–2.20 (m, 1H), 2.40 (d, J = 16.8 Hz, 1H), 3.67 (s, 3H), 4.23–4.28 (m, 1H), 4.55–4.60 (m, 1H), 4.77 (dd, J = 7.2, 2.0 Hz, 1H), 5.83

(dd, $J=5.6$, 3.0 Hz, 1H), 6.35 (dd, $J=5.6$, 2.6 Hz, 1H), 7.33–7.36 (m, 3H), 7.51–7.55 (m, 2H); ^{13}C NMR (125 MHz in $CDCl_3$): $\delta=-4.5$, −4.4, 12.7, 17.9, 18.0, 21.9, 22.5, 34.1, 45.3, 51.9, 52.6, 103.3, 127.6, 128.6, 128.9, 129.6, 131.9, 133.9, 138.0, 138.5, 152.9, 174.5; elemental analysis (%) calcd for $C_{30}H_{46}O_3Si_2$: C 70.53, H 9.08; found: C 70.32, H 9.34

Compound 28b: Compound **28b** and the other diastereomer were obtained as an inseparable mixture in a ratio of 10:1. Pale yellow oil; IR (neat): $\tilde{\nu}$ = 2949, 2867, 1744, 1637, 1463, 1255 cm^{-1}; ^{1}H NMR (500 MHz, 350 K in [D$_6$]benzene): major isomer: $\delta=0.320$ (s, 3H), 0.322 (s, 3H), 0.98 (d, $J=7.1$ Hz, 3H), 1.09–1.11 (m, 18H), 1.13–1.20 (m, 3H), 2.32–2.36 (m, 1H), 2.67–2.74 (m, 1H), 3.43 (s, 3H), 4.41–4.43 (m, 1H), 4.88–4.90 (m, 1H), 4.94 (dd, $J=8.0$, 2.2 Hz, 1H), 5.37 (dd, $J=5.6$, 2.6 Hz, 1H), 5.86–5.88 (m, 2H), 7.17–7.23 (m, 3H), 7.48–7.51 (m, 2H); ^{13}C NMR (125 MHz, 350 K in [D$_8$]dioxane): major isomer: $\delta=-2.6$, −2.5, 13.4, 18.19, 18.21, 19.8, 30.7, 34.1, 46.4, 51.5, 54.0, 103.7, 128.2, 129.3, 130.3, 131.4, 134.5, 135.7, 139.7, 144.8, 173.7 (1C missing); elemental analysis (%) calcd for $C_{30}H_{46}O_3Si_2$: C 70.53, H 9.08; found: C 70.75, H 9.29

Compound 28c: Compound **28c** and the other diastereomer were obtained as an inseparable mixture in a ratio of 20:1. Pale yellow oil; IR (neat): $\tilde{\nu}$ = 2950, 2867, 1746, 1650, 1463, 1248, 1163 cm^{-1}; ^{1}H NMR (400 MHz in $CDCl_3$): major isomer: $\delta=0.23$ (s, 3H), 0.24 (s, 3H), 1.01–1.08 (m, 21H), 1.20 (d, $J=7.1$ Hz, 3H), 1.76–1.81 (m, 1H), 2.34–2.43 (m, 1H), 3.70 (s, 3H), 3.89–3.91 (m, 1H), 4.36–4.40 (m, 1H), 4.70 (dd, $J=8.1$, 1.7 Hz, 1H), 5.73–5.77 (m, 2H), 6.01 (dd, $J=5.4$, 2.7 Hz, 1H), 7.29–7.35 (m, 3H), 7.46–7.53 (m, 2H); ^{13}C NMR (100 MHz in $CDCl_3$): major isomer: $\delta=-3.5$, −3.3, 13.0, 18.0, 19.6, 31.8, 33.4, 47.9, 51.8, 56.1, 103.4, 127.0, 127.6, 128.7, 130.8, 133.8, 136.5, 139.0, 145.0, 146.6, 174.0; elemental analysis (%) calcd for $C_{30}H_{46}O_3Si_2$: C 70.53, H 9.08; found: C 70.78, H 9.38.

Compound 15a: Compounds **15a**, **16a-α**, and **16a-β** were obtained as an inseparable mixture in a ratio of 67:8:25. Pale yellow oil; IR (neat): $\tilde{\nu}$ = 2944, 2867, 1646, 1463, 1333, 1202 cm^{-1}; elemental analysis (%) calcd for $C_{26}H_{38}OSi$: C 79.12, H 9.70; found: C 78.89, H 9.82. **15a**: ^{1}H NMR (500 MHz, 350 K in CD_3CN) $\delta=0.93$ (d, $J=7.1$ Hz, 3H), 1.11–1.13 (m, 18H), 1.22–1.30 (m, 3H), 2.75 (dd, $J=18.5$, 9.0 Hz, 1H), 2.86–2.92 (m, 1H), 3.03–3.09 (m, 1H), 3.75–3.79 (m, 1H), 4.10–4.14 (m, 1H), 5.09 (dd, $J=7.1$, 2.2 Hz, 1H), 5.17–5.20 (m, 1H), 6.01–6.05 (m, 2H), 7.16–7.20 (m, 1H), 7.24–7.28 (m, 4H); ^{13}C NMR (125 MHz, 350 K in CD_3CN): $\delta=14.2$, 18.8, 18.9, 37.7, 38.1, 44.7, 49.0, 109.3, 126.5, 127.4, 129.0, 130.8, 134.7, 136.0, 144.0, 148.7, 154.2.

Compound 15b: Pale yellow oil; IR (neat): $\tilde{\nu}$ = 2945, 2866, 1634, 1463, 1427, 1255 cm^{-1}; ^{1}H NMR (500 MHz, 330 K in $CDCl_3$) $\delta=0.34$ (s, 3H), 0.37 (s, 3H), 1.00 (d, $J=7.2$ Hz, 3H), 1.09–1.12 (m, 18H), 1.13–1.21 (m, 3H), 2.19–2.21 (m, 1H), 2.66 (dd, $J=17.8$, 9.0 Hz, 1H), 2.73–2.80 (m, 1H), 2.90–2.96 (m, 1H), 4.06–4.12 (m, 1H), 4.88 (dd, $J=8.1$, 2.0 Hz, 1H), 5.41 (dd, $J=5.4$, 3.1 Hz, 1H), 5.92–5.95 (m, 1H), 5.96–5.98 (m, 1H), 7.33–7.35 (m, 3H), 7.53–7.56 (m, 2H); ^{13}C NMR (125 MHz, 330 K in $CDCl_3$) $\delta=-2.5$, −2.3, 12.9, 18.1, 20.3, 31.4, 34.0, 36.4, 43.6, 104.4, 127.6, 127.7, 128.7, 133.87, 133.94, 134.1, 139.7, 146.0, 153.4; elemental analysis (%) calcd for $C_{28}H_{44}OSi_2$: C 74.27, H 9.79; found: C 74.04, H 10.03

Compound 15c: Pale yellow oil; IR (neat): $\tilde{\nu}$ = 2945, 2866, 1662, 1464, 1248, 1171 cm^{-1}; ^{1}H NMR (400 MHz in $CDCl_3$): $\delta=0.22$ (s, 3H), 0.24, (s, 3H), 1.04–1.13 (m, 21H), 1.16 (d, $J=7.1$ Hz, 3H), 1.71–1.76 (m, 1H), 2.33–2.42 (m, 1H), 2.58–2.66 (m, 1H), 2.74–2.82 (m, 1H), 3.72–3.78 (m, 1H), 4.73 (dd, $J=8.2$, 1.7 Hz, 1H), 5.70 (dd, $J=8.2$, 3.1 Hz, 1H), 5.88–5.93 (m, 1H), 5.96–6.00 (m, 1H), 7.30–7.33 (m, 3H), 7.47–7.52 (m, 2H); ^{13}C NMR (100 MHz in $CDCl_3$): $\delta=-3.6$, −3.2, 12.8, 18.2, 19.7, 31.7, 33.8, 39.1, 46.1, 103.3, 124.5, 127.5, 128.6, 133.7, 133.8, 135.1, 139.4, 146.5, 147.6; elemental analysis (%) calcd for $C_{28}H_{44}OSi_2$: C 74.27, H 9.79; found: C 74.03, H 9.80

Tandem cyclization of trienynes bearing (*E*)-enol silyl ether moiety: A typical procedure for the cyclization of enynes is described for **25a-*E*** as substrate: **25a-*E*** (25 mg, 0.045 mmol) in degassed toluene (0.7 mL) was added to a mixture of [W(CO)$_6$] (1.6 mg, 0.0045 mmol, 10 mol%) and activated 4 Å molecular sieves. After the mixture was photoirradiated (250 W super-high-pressure Hg lamp through 365 nm bandpass filter) for 10 h at room temperature, the suspension was filtered and then the solvent was removed under reduced pressure to give the crude product, which was purified by PTLC (7% ethyl acetate in hexane) to give 19 mg of **26a-β** (0.034 mmol, 76%).

Compound 26a-β: Pale yellow oil; IR (neat): $\tilde{\nu}$ = 2950, 2867, 1744, 1642, 1433, 1251, 1203 cm^{-1}; ^{1}H NMR (400 MHz in $CDCl_3$): $\delta=0.27$ (s, 3H), 0.29 (s, 3H), 0.96–1.13 (m, 21H), 1.96–2.02 (m, 1H), 2.15–2.21 (m, 1H), 2.25–2.33 (m, 1H), 3.61 (s, 3H), 3.75 (s, 3H), 4.68 (brs, 1H), 4.82–4.85 (m, 1H), 5.89 (d, $J=5.6$ Hz, 1H), 6.01–6.04 (m, 1H), 6.24 (d, $J=5.6$ Hz, 1H), 7.32–7.35 (m, 3H), 7.47–7.50 (m, 2H); ^{13}C NMR (100 MHz in $CDCl_3$): $\delta=-5.3$, −4.4, 13.3, 18.0, 25.6, 27.4, 52.1, 52.6, 52.7, 70.5, 108.4, 126.7, 127.8, 129.1, 131.7, 134.0, 137.50, 137.55, 144.1, 148.1, 169.2, 170.4; elemental analysis (%) calcd for $C_{31}H_{46}O_5Si_2$: C 67.10, H 8.36; found: C 66.86, H 8.46

Compound 26c-β: White solid (m.p. 70–75 °C); IR (KBr): $\tilde{\nu}$ = 2952, 2865, 1740, 1725, 1638, 1429, 1246 cm$^{<M->1}$; ^{1}H NMR (500 MHz in $CDCl_3$): $\delta=0.36$ (s, 6H), 1.01–1.10 (m, 21H), 1.14 (d, $J=6.9$ Hz, 3H), 1.78 (dd, $J=8.3$, 4.7 Hz, 1H), 2.58–2.62 (m, 1H), 3.59 (s, 3H), 3.74 (s, 3H), 4.39 (brs, 1H), 4.84 (dd, $J=8.3$, 2.3 Hz, 1H), 5.70 (dd, $J=6.5$, 2.9 Hz, 1H), 5.84 (d, $J=5.5$ Hz, 1H), 6.18 (d, $J=5.5$ Hz, 1H), 7.30–7.32 (m, 3H), 7.50–7.52 (m, 2H); ^{13}C NMR (125 MHz in $CDCl_3$): $\delta=-3.1$, −2.1, 13.1, 18.0, 18.1, 23.9, 32.1, 32.9, 52.1, 52.4, 52.9, 68.6, 103.3, 127.6, 128.8, 129.9, 130.9, 133.8, 138.5, 139.3, 140.8, 149.1, 169.1, 170.1; elemental analysis (%) calcd for $C_{32}H_{48}O_5Si_2$: C 67.56, H 8.50; found: C 67.30, H 8.72

Compound 33: Colorless oil; IR (neat): $\tilde{\nu}$ = 2952, 2867, 1737, 1615, 1431, 1254 cm^{-1}; ^{1}H NMR (500 MHz in $CDCl_3$): $\delta=0.28$ (s, 3H), 0.36 (s, 3H), 0.84 (d, $J=7.2$ Hz, 3H), 1.10–1.17 (m, 18H), 1.21–1.28 (m, 3H), 3.29 (s, 3H), 3.36–3.40 (m, 1H), 3.70 (s, 3H), 4.52 (t, $J=2.8$ Hz, 1H), 5.24–5.26 (m, 1H), 5.88 (d, $J=18.6$ Hz, 1H), 6.11 (d, $J=5.5$ Hz, 1H), 6.20 (d, $J=18.6$ Hz, 1H), 6.37 (d, $J=5.5$ Hz, 1H), 7.29–7.32 (m, 3H), 7.50–7.53 (m, 2H); ^{13}C NMR (125 MHz in $CDCl_3$): $\delta=-2.8$, −2.0, 13.6, 14.2, 18.4, 18.6, 51.6, 52.9, 55.0, 61.3, 64.2, 93.0, 121.8, 126.6, 127.6, 128.7, 129.6, 133.7, 138.6, 139.4, 145.2, 149.5, 169.5, 170.5; elemental analysis (%) calcd for $C_{32}H_{48}O_5Si_2$: C 67.56, H 8.50; found: C 67.34, H 8.73

Compound 26d-β: Pale yellow oil; IR (neat): $\tilde{\nu}$ = 2950, 2867, 1747, 1649, 1432, 1250 cm^{-1}; ^{1}H NMR (500 MHz in $CDCl_3$): $\delta=0.31$ (s, 3H), 0.32 (s, 3H), 1.01–1.08 (m, 18H), 1.09 (d, $J=7.2$ Hz, 3H), 1.10–1.15 (m, 3H), 2.26–2.29 (m, 1H), 2.48–2.53 (m, 1H), 3.58 (s, 3H), 3.76 (s, 3H), 4.54–4.57 (m, 1H), 4.74 (dd, $J=3.5$, 1.4 Hz, 1H), 5.84 (d, $J=5.5$ Hz, 1H), 6.15 (dd, $J=8.7$, 3.1 Hz, 1H), 6.23 (d, $J=5.5$ Hz, 1H), 7.32–7.40 (m, 3H), 7.49–7.52 (m, 2H); ^{13}C NMR (125 MHz in $CDCl_3$): $\delta=-3.62$, −3.55, 13.3, 15.8, 18.00, 18.04, 30.0, 31.5, 52.0, 52.5, 53.9, 70.2, 103.9, 127.7, 129.0, 131.1, 133.4, 133.9, 138.0, 138.9, 141.4, 147.8, 169.1, 170.3; elemental analysis (%) calcd for $C_{32}H_{48}O_5Si_2$: C 67.56, H 8.50; found: C 67.32, H 8.70

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