Catalytic Ring Closing Metathesis of Dienynes: Construction of Fused Bicyclic [*n.m.*0] Rings

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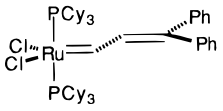
Ruthenium carbene **1** ($Cl_2(PCy_3)_2Ru{=}CHCH{=}CPh_2$) mediates the efficient and selective conversion of acyclic dienynes to fused bicyclic [*n.m*.0] rings containing five-, six-, and seven-membered rings. Studies with various X-substituted acetylenes (X = H, alkyls, Ph, CO_2Me, $SnBu_3$, TMS, Cl, Br, I) suggest that the dienyne metathesis is sensitive not only to these substituents but also to the catalysts employed. Among the various metal alkylidenes examined, only the ruthenium catalyst **1** exhibited metathesis activity for a range of substrates. These observations further expand the scope of catalytic RCM for the construction of complex organic compounds.

Introduction

Fused bicyclic [*n.m*.0] structural frameworks represent an important substructure in many natural products, and the efficient synthesis of functionalized fused bicyclic rings remains an important goal.[1] Strategies and methods that accomplish the rapid construction of functionalized fused bicyclic rings from simple precursors are therefore desired. We recently reported a short and highly convergent metathesis-based strategy for the construction of functionalized fused bicyclic rings.[2] The key step of the approach involves the ruthenium carbene **1** catalyzed double ring-closing metathesis (RCM) of dienynes.[3]



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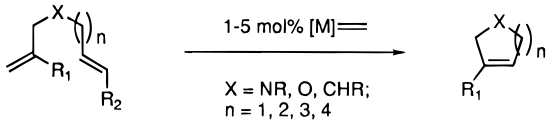
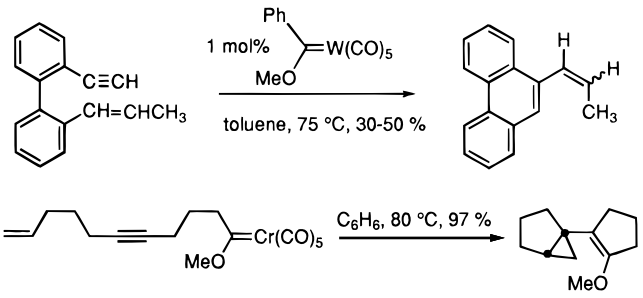
Previous reports have established that metal alkylidene-mediated catalytic RCM of dienes is a general approach to the construction of carbocycles and heterocyles (Scheme 1).[4] To investigate the scope of this reaction, a metathesis-based strategy for double ring (or multiple) cyclization of a single substrate to give a fused bicyclic [*n.m*.0] ring was explored.

Scheme 1. Catalytic Ring Closing Metathesis (RCM) of Dienes



Scheme 2. Metal Carbene Mediated Ene−Yne Metathesis



Several researchers have established that intramolecular ene−yne metathesis can be used to construct ring structures. Katz and Sivavec first reported that pentacarbonyltungsten carbene catalyzes intramolecular *ene−yne* metathesis (single ring closure) to generate substituted 1-vinylcycloolefins (Scheme 2).[5] Subsequently, other researchers have studied the *ene−yne−ene* transformation (bis-ring annulation) with electrophilic (Fischer) carbenes and rhodium-catalyzed decomposition of α-diazo ketones to generate compounds containing two rings linked with a single bond. With the Fischer carbenes, pre-formed and stoichiometric carbenes were required, and the second ring closure led to cyclopropanes through the reductive elimination of the intermediate metallacyclobutane.[6] With the rhodium-catalyzed decomposition of α-diazo ketones, a complex product distribution arising from several competing processes was observed.[7]

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(1) See, for instance: *Natural Products Chemistry*; Nakanishi, K., Ed.; Academic Press: New York, 1974; Vols. 1−3.

(2) Preliminary work was reported in a communication. Kim, S. H.; Bowden, N.; Grubbs, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 10801.

(3) For the preparation and characterization of catalyst **1**: (a) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1992**, *114*, 3974. (b) Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 9858.

(4) Previous reports on RCM from this laboratory: (a) Fu, G. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 5426. (b) Fu, G. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 7324. (c) Fu, G. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 3800. (d) Fu, G. C.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 9856. (e) Fujimura, O.; Fu, G. C.; Grubbs, R. H. *J. Org. Chem.* **1994**, *59*, 4029. (f) Miller, S. J.; Kim, S. H.; Chen, Z.; Grubbs, R. H. *J. Am. Chem. Soc.* **1995**, 117, 2108. (g) Miller, S. J.; Grubbs, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 5855−5856. (h) Grubbs, R. H.; Miller, S. J.; Fu, G. C. *Acc. Chem. Res.* **1995**, *28*, 446−452. For recent applications of RCM to natural product synthesis: (i) Martin, S. F.; Liao, Y.; Rein, T. *Tetrahedron Lett.* **1994**, *35*, 691. (j) Borer, B. C.; Deerenberg, S.; Bieraugel, H.; Pandit, U. K. *Tetrahedron Lett.* **1994**, *35*, 3191. (k) Wagman, A. S.; Martin, S. F. *Tetrahedron Lett.* **1995**, *36*, 1169. (l) Houri, A. F.; Xu, Z.; Logan, D. A.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1995**, *117*, 2943. For a review on applications of olefin metathesis in organic synthesis: Grubbs, R. H.; Pine, S. H. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: New York, 1991; Vol. 5, Chapter 9.3.

(5) Katz, T. J.; Sivavec, T. M. *J. Am. Chem. Soc.* **1985**, *107*, 737.

(6) (a) Korkowski, P. F.; Hoye, T. R.; Rydberg, D. B. *J. Am. Chem. Soc.* **1988**, *110*, 2676. (b) Harvey, D. F.; Brown, M. F. *J. Org. Chem.* **1992**, *57*, 5559. For a review on the chemistry of Fischer carbenes with ene-yne substrates see: Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: New York, 1991; Vol. 5, Chapter 9.2.

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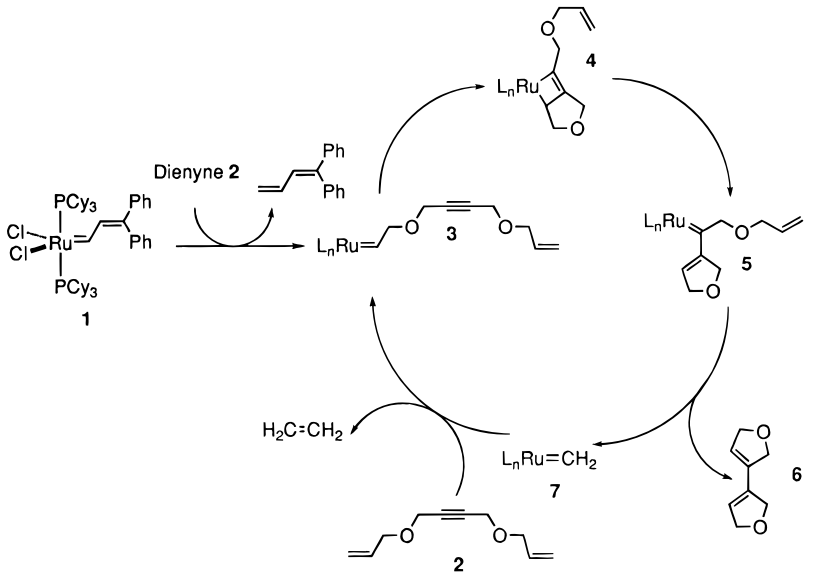
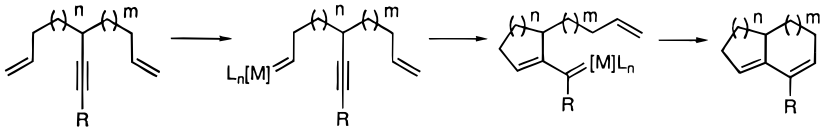
Scheme 3. Ruthenium Carbene 1 Catalyzed Dienyne Metathesis



Scheme 4. Construction of Fused Bicyclic [*n.m*.0] Rings via Dienyne Metathesis



These studies demonstrated that the course of ene−yne metathesis is dependent on the metal complex employed. Furthermore, these synthetic methods are somewhat limited due to the lack of substrate flexibility,[8] several unpredictable competing pathways,[9] modest yields, and stoichiometry of reaction.[10] Nevertheless, an important principle was demonstrated: the acetylene acts as an olefin metathesis relay. Thus, the *ene−yne* metathesis generates the first ring in addition to the regenerated carbene which undergoes *diene RCM* to generate a second ring. This property of dienyne cyclization was utilized for a new metathesis-based strategy for the construction of fused bicyclic [*n.m*.0] rings (*vide infra*).

Results and Discussion

Initial Model Studies. Earlier studies from our group and others have established that the ruthenium carbene **1** is a efficient catalyst for diene RCM.[4d,f] Thus, our first objective was to determine the reactivity of ruthenium carbene **1** (and other RCM catalysts) toward the ene−yne metathesis.

From the readily prepared compound **2**[11] under standard diene RCM conditions (3 mol % **1**, C_6H_6, rt, 4 h), product **6** was obtained in 90% yield. No other side products were detected. The steps leading from dienyne **2** to product **6** are shown in Scheme 3. The first step involves intermolecular acyclic metathesis to generate intermediate **3**, which undergoes intramolecular ene−yne metathesis to give the first ring plus the regenerated carbene **5**. A second diene RCM produced the second ring and the regenerated catalyst **7**.[12] During this process, two rings are generated, and the resulting rings contain olefins that may be further functionalized.

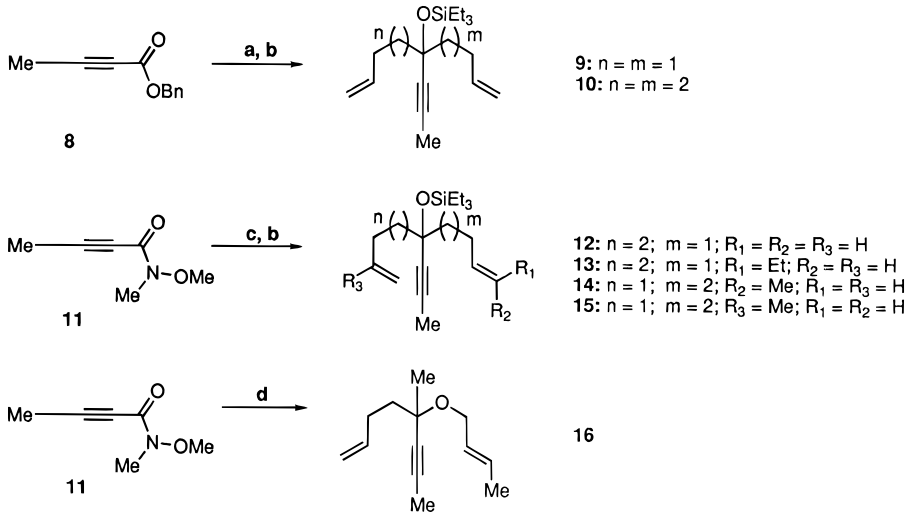
Construction of Fused [*n.m*.0] Rings. The strategy to generate the fused bicyclic [*n.m*.0] framework (the smallest unit of fused polycyclic structure) is shown in Scheme 4. The key feature is the location of the acetylene group in a *branched* position between the two olefins. The ene−yne metathesis generates the first ring plus the regenerated carbene, which undergoes a second diene RCM to produce the fused [*n.m*.0] bicyclic ring. These studies indicate that the strategy is general and allows for the efficient and rapid construction of a variety of fused bicyclic rings. Futhermore, they suggest that the rurthenium carbene **1** is the catalyst of choice. Among the metal alkylidenes examined, only the ruthenium complex catalyzed dienyne cyclization for a range of substrates.

A rapid route to a variety of starting dienynes was established to explore the scope of this reaction. The synthesis of branched dienynes **9**−**16** is shown in Scheme 5. The symmetrical dienynes were synthesized by double Grignard addition to the benzyl ester **8**. The unsymetrical dienynes were prepared by the sequential Grignard addition to the *N*-methoxy-*N*-methylamide **11**. The resulting alcohols were protected as their triethylsilyl ethers.[13]

All reactions were initially monitored by ^{1}H NMR spectroscopy.[14] Both the starting vinylcarbene and propagating methylidene α proton resonances are observed downfield in the range 19−20 ppm. As dienyne metathesis proceeds, the vinyl carbene doublet disappears as

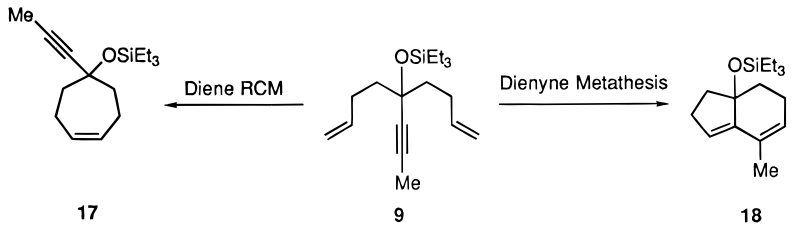
(7) Hoye, T. R.; Dinsmore, C. J. *J. Am. Chem. Soc.* **1991**, *113*, 4343.
(8) Some substrates possess specific structural requirements such as pre-formed carbenes and specific α-diazocarbonyl compounds.
(9) For instance, the rhodium-catalyzed reaction showed a complex product distribution arising from several competing processes (ref 7).
(10) The dienyne cyclization shown in Scheme 2 required a stoichiometric amount of pre-formed Fischer carbene (ref 6a).
(11) Dienyne **2** was synthesized from 2-butyne-1,4-diol: NaH, CH_2=$CHCH_2Br$, DMF.
(12) The possibility that the first step involves an alkyne metathesis followed by two diene RCM steps cannot be ruled out. However, later experiments favor the proposed mechanism (see text).
(13) Dienyne RCM proceeds at a somewhat slower rate with the free alcohols.
(14) NMR reactions were conducted in 0.2−0.3 mmol scale at 0.01−0.07 M substrate concentration.

Scheme 5. Synthesis of Starting Dienynes[a]



[a] Key: (a) $MgBr(CH_2)_nCH_2CH{=}CH_2$, THF; (b) Et_3SiOTf, TEA, CH_2Cl_2; (c) stepwise addition of Grignard reagents, $MgBrR_3$, THF and $MgBrR_1R_2$, THF; (d) $MgBr(CH_2)_2CH{=}CH_2$; MgBrMe; NaH, crotyl bromide, DMF.

Scheme 6. Competing Pathways: Diene RCM and Dienyne Metathesis



the methylidene singlet emerges. Each catalytic cycle produces one molecule of ethylene which appears as a sharp singlet at 5.35 ppm. Additionally, the characteristic signal pattern for a terminal olefin disappears as the reaction progresses.

The first substrate to be examined was dienyne **9**, which shares a close structural similarity with dienyne **2**. The acetylene was disubstituted, and the length of the diene tether was the same. One important difference was the possibility of a competing diene RCM to give cycloheptene (Scheme 6). This possible side reaction was absent in the linear dienyne **2** since diene RCM would have involved the unfavorable formation of a 10-membered ring (Scheme 4). When dienyne **9** was treated with 3 mol % ruthenium carbene **1** in CH_2Cl_2, the fused bicyclo[4.3.0] ring **18** was isolated in 95% yield along with trace amount (<3%) of cycloheptene **17** arising from competing RCM of dienes. Thus, the dienyne metathesis is largely favored over competing diene RCM. The reaction can be carried out in variety of solvents and temperatures (Table 1). For instance, the same substrate cyclized (quantitative yield, ^1H NMR scale) in 2 h in benzene at 65 °C with only 1 mol % catalyst. As shown in entry 3 (Table 1), increasing each olefinic tether by one methylene unit yielded the bicyclo[5.4.0] ring **19** in 88% yield. As expected, no product arising from competing diene RCM was detected.

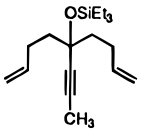
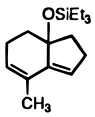
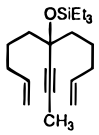
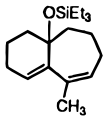
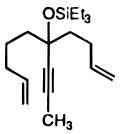
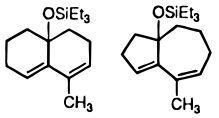
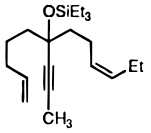
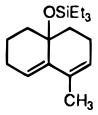
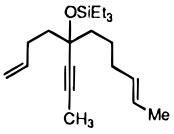
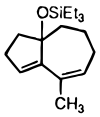
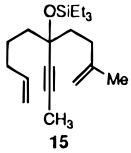
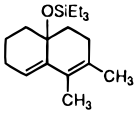
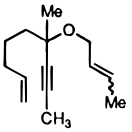
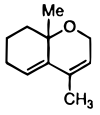
When the unsymmetrical dienyne **12** was treated with the ruthenium catalyst (entry 3, Table 1) two bicyclic compounds, [4.4.0] and [5.3.0], were isolated in equal amounts. The steps leading to these products are shown in Scheme 7. Presumably, the 1:1 product ratio arises from the unselective (statistical) initial acyclic metathesis ($k_1 \approx k_2$).

Earlier work from these laboratories on diene RCM suggested a straightforward solution for control of the products.[4b] These studies have shown that the site of initial acyclic metathesis (regiochemical control) could be achieved by different substitution on the olefins. Monosubstituted olefins undergo intermolecular acyclic metathesis faster than disubstituted olefins. This fact suggested a simple variable for regiochemical control of the initial acyclic metathesis, the committed step in the formation of the bicyclic compound.

The sterically-biased dienyne **13** produced bicyclo[4.4.0] adduct **20** in 83% yield (entry 4, Table 1). Furthermore, the corresponding bicyclic[5.3.0] ring **21** was isolated as the sole product when the substitution of the olefin was reversed (entry 5, Table 1). Not only do these observations greatly expand the scope of this methodology, they also provide further evidence for the proposed mechanism. The dienyne **15** with internally substituted olefin also displayed high regioselectivity, leading to the formation of tetrasubstituted bicyclo[4.4.0] compound **22** (entry 6, Table 1). It also represented the first example where a sterically congested tetrasubstituted olefin was constructed using the ruthenium catalyst. Finally, the presence of a heteroatom within the diene tether did not alter the expected outcome (entry 7, Table 1); a single bicyclic product **23** was obtained. No complications arose from possible chelation involving the ether moeity.

Effect of Acetylene Substituent. In the proposed mechanism for dienyne RCM, the acetylenic substituent is transformed into a vinylic substituent (Scheme 8). These vinylic substituents of the product might be further functionalized by any of a number of available techniques. Several different substrates with varying acetylenic substituents X were synthesized and subjected to dienyne metathesis. Concurrently, the comparative reactivity of **1** with other well-defined metal alkylidenes was examined.[15]

Table 1. Catalytic RCM of Dieneynes

Entry	Substrate	Product	Conditions (Yield)
1	 **9**	 **18**	3 mol% **1**, 8 h, 25 °C, 95%, CH_2Cl_2 (0.06 M)
2	 **10**	 **19**	6 mol% **1**, 8 h, 65 °C, 88 %, C_6H_6 (0.06 M)
3	 **12**	 **20** **21**	3 mol% **1**, 15 h, 65 °C, 86 %, C_6H_6 (0.02 M), 1:1 of [4.4.0] and [3.5.0]
4	 **13**	 **20**	3 mol% **1**, 6 h, 65 °C, 83 %, C_6H_6 (0.03 M)
5	 **14**	 **21**	15 mol% **1**, 1.5 h, 100 °C, 78 %, toluene (0.01 M)
6	 **15**	 **22**	15 mol% **1**, 12 h, 65 ° C, 89 %, C_6H_6 (0.05 M)
7	 **16**	 **23**	3 mol% **1**, 6 h, 65 ° C, 88 %, C_6H_6 (0.05 M)

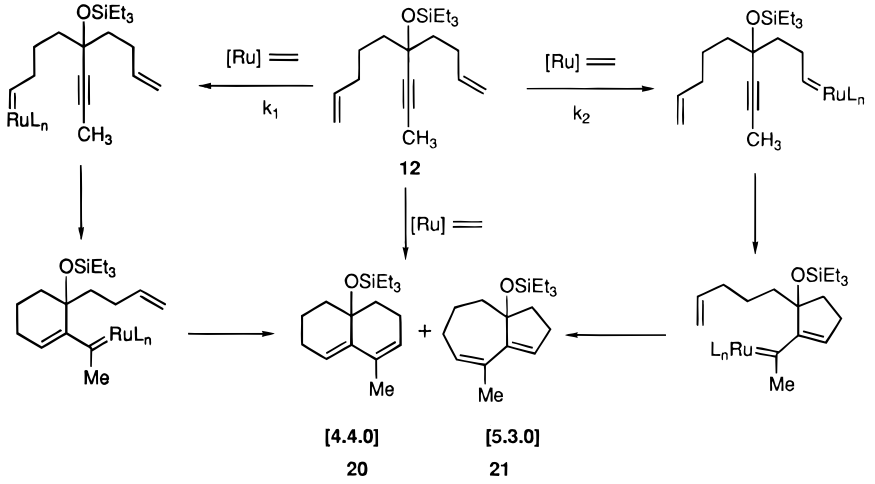
The substituted dienynes **24**−**33** were readily prepared from 1,8-nonadien-5-one (Scheme 9). The appropriate acetylide anions were added to the ketone, and the resultant alcohols were protected as the triethylsilyl ethers. For those substrates not accessible by acetylide addition, the terminal acetylenedienyne **24** was deprotonated with *n*-BuLi and quenched with the appropriate electrophile. The iodo- and bromoalkyne substrates were synthesized by the method of Hofmeister.[16] Compounds **24**−**33** were isolated as clear, colorless oils, and all were stable at ambient temperature.

Results of the RCM reactions of ruthenium alkylidene **1** with compounds **24**−**33** are summarized in Table 2.[17] The ruthenium catalyst **1** showed broad activity with

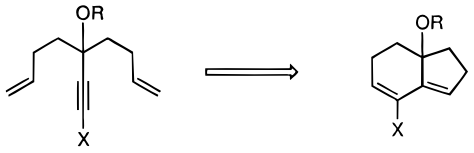
(15) (WAr)($CHCMe_3$)($OCMe(CF_3)_2$)$_2$ (Ar = 2,6-(i-Pr)$_2C_6H_3$) (**34**): (a) Schrock, R. R.; DePue, R. T.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1423. (b) Schrock, R. R.; DePue, R. T.; Feldman, J.; Yap, K. B.; Yang, D. C.; Davis, W. M.; Park, L.; DiMare, M.; Schofield, M.; Anhaus, J.; Walborsky, E.; Evitt, E.; Kruger, C.; Betz, P. *Organometallics* **1990**, *9*, 2262. (c) Mo(NAr)-($CHCMe_2Ph$)($OCMe(CF_3)_2$)$_2$ (Ar = 2,6-(i-Pr)$_2C_6H_3$) (**35**): Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875. (d) Bazan, G. C.; Oskam, J. H.; Cho, H.-N.; Park, L. Y.; Schrock, R. R. *J. Am. Chem. Soc.* **1991**, *113*, 6899. Both the tungsten **34** and molybdenum **35** alkylidenes have been successfully employed for diene RCM (ref 4 and Grubbs, R. H., unpublished results).

(16) Hofmeister, H.; Annen, K.; Laurent, H.; Wiechert, R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 727−729.

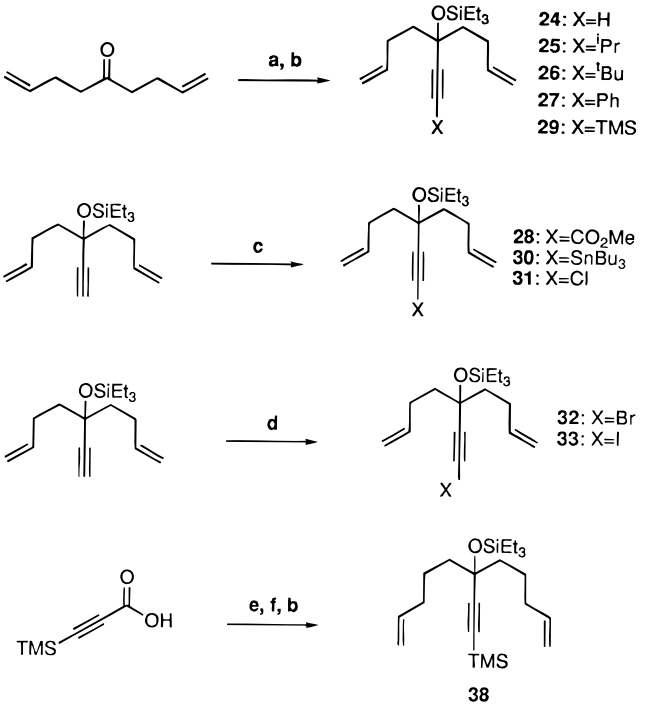
Scheme 7. Formation of Different Bicyclic Products with Unsymmetrical Dienynes



Scheme 8. Metathesis of Substituted Dienynes



Scheme 9. Synthesis of Substituted Acetylenes[a]

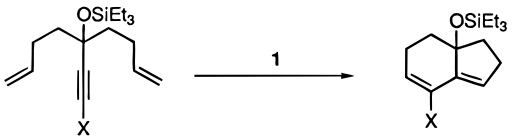


[a] Key: (a) XCCH, BuLi, THF; (b) Et_3SiOTf, NEt_3, CH_2Cl_2; (c) BuLi, [$ClCO_2Me$, $ClSnBu_3$, NCS], THF; (d) [NBS, NIS], $AgNO_3$ (cat.), acetone; (e) DBU, BnBr, MeCN; (f) $MgBrCH_2CH_2CH_2CH{=}CH_2$, THF.

various substituents, and without exception, it favored the dienyne metathesis over the competing diene RCM. With alkyl substitution, steric effects were important and reaction rates followed the expected trend (X = H > Me > *i*-Pr ≈ Ph). With the bulky *tert*-butyl substituent the dienyne cyclization was not observed. The ester substituted dienyne **28** cyclized cleanly and with rates similar

(17) Reactions were conducted at 0.05−0.1 M concentration in C_6D_6 with 3−5 mol % catalyst.

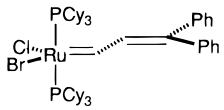
Table 2. Metathesis of Substituted Dienynes Using Ruthenium Catalyst 1



entry	acetylene substituent X		yield (%), conditions
1	H	24	**39**, >98, 15 min, rt
2	Me	**9**	**18**, 95, 8 h, rt
3	^{i}Pr	**25**	**40**, 78, 4 h, 60 °C
4	^{t}Bu	**26**	NR
5	Ph	**27**	**41**, 96, 3 h, 60 °C
6	CO_2Me	**28**	**42**, 82, 4 h, 60 °C
7	TMS	**29**	NR
8	$SnBu_3$	**30**	NR
9	Cl	**31**	NR
10	Br	**32**	NR
11	I	**33**	NR

to the isopropyl-substituted substrate **25** (entry 6, Table 2). Substrates containing heteroatoms directly attached to the acetylene were not cyclized by **1**.

The bromo- and iodoalkyne dienyne substrates did not cyclize under standard RCM conditions with any of the catalysts listed.[18] However, reaction with a stoichiometric amount of ruthenium carbene **1** resulted in a halide exchange reaction. After 2 h at 60 °C, a significant amount of both 1,1-diphenylbutadiene and a new vinyl carbene species are observed in the ^{1}H NMR spectrum of the reaction mixture. The α proton resonance of the new carbene species is upfield and the *β* proton is downfield compared to the starting carbene. These two signals coincide with the resonances of an intermediate observed in the reaction of **1** with 20 equiv of LiBr in benzene to produce the dibromo analogue of **1**[19] and are consistent with the mixed halide vinyl carbene species **45**.

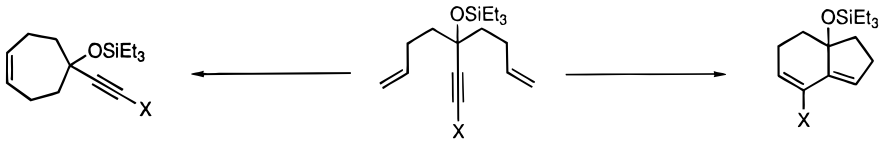


45

(18) Catalyst **1** fails to metathesize vinyl halide species as well. Kim, S.-H.; Grubbs, R. H. Unpublished results.

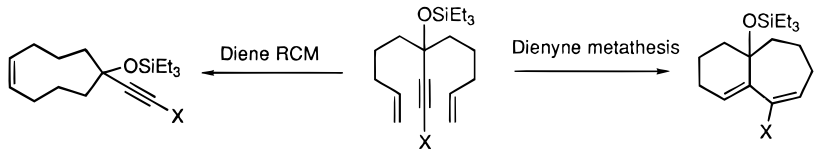
(19) Dias, E. L.; Grubbs, R. H. Unpublished results.

Table 3. Metathesis of Substituted Dienynes Using Tungsten Catalyst 34 and Molybdenum Catalyst 35



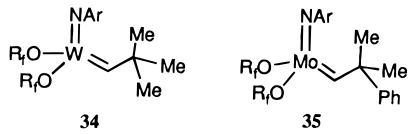
entry	acetylene substituent X		catalyst **34**	catalyst **35**
1	H	24	**39**, >98%, 20 min, rt	**39**, 97%, 20 min, rt
2	Me	**9**	cycloheptene and [4.3.0] (1:4)	NR
3	^{i}Pr	**25**	cycloheptene	NR
4	^{t}Bu	**26**	cycloheptene	NR
5	Ph	**27**	NR	NR
6	CO_2Me	**28**	**44**, cycloheptene	NR
7	TMS	**29**	cycloheptene	NR
8	$SnBu_3$	**30**	NR	NR
9	Cl	**31**	NR	NR
10	Br	**32**	NR	NR
11	I	**33**	NR	NR

Scheme 10. Metathesis of TMS-Substituted Dienyne with Tungsten Catalyst 34



38: X = TMS
10: X = Me

The reactions of tungsten catalyst **34** and molybdenum catalyst **35** are summarized in Table 3. Some general trends for all three catalysts were observed.[20]



34 **35**

The substrates with non-carbon substituents (X = TMS, Cl, Br, I, and $SnBu_3$, compounds **29**−**33**) failed to produce the bicyclic [4.3.0] compound with all three catalysts. Another important trend is that the outcome of a reaction is largely determined by the catalyst employed. Unlike catalyst **1** (entries 7 and 8, Table 3), competing diene RCM to cycloheptene was observed with the tungsten catalyst **34**. Among the catalysts, the molybdenum catalyst **35** is the least productive one; it produced a bicyclic product only with the unsubstituted acetylene (X = H, compound **24**, entry 1, Table 2). With the other substrates (entries 2−11), only the unreacted starting material was recovered in reaction with the molybdenum catalyst. Taken together, these results strongly suggest that the ruthenium alkylidene **1** is the catalyst of choice for a range of substituted dienynes.

The tungsten catalyst **34** cleanly converted the unsubstituted acetylene (X = H, entry 1, Table 2) to the bicyclic product. However, with several substrates containing a variety of acetylenic substitution (^{i}Pr, ^{t}Bu, phenyl, TMS, $SnBu_3$), diene RCM is favored over ene−yne−ene metathesis, yielding the cycloheptene instead of the bicyclic compound. The methyl-substituted dienyne **9** yields a mixture (95:3) of the cycloheptene and the bicyclic product. A homologous methyl-substituted dienyne substrate **10** is cyclized to the bicyclic [5.4.0] ring **19** (Scheme 10), and no cyclononene product is observed. The homologous TMS substituted dienyne **38** gave no observable product, and only the unreacted starting dienyne was recovered. The reactions of **10** and **38**, in which diene RCM was expected to be highly unfavorable since it would involve the formation of a nine-membered ring, indicated that the TMS group effectively shuts down olefin−acetylene metathesis, leaving diene RCM as the only available pathway. However, the RCM reaction of substrate **9** reflects competitive rates of the two processes. In any case, it is evident that the product distribution is critically dependent on the steric bulk of the acetylenic substituents when using tungsten catalyst **34**.

Conclusion

We have presented metathesis-based methodology for the construction of fused bicyclic [*n.m*.0] rings, an important structural framework in a variety of natural products. The ruthenium carbene **1** catalyzes the conversion of acyclic dienynes to fused bicyclic rings containing five-, six-, and seven-membered rings. The key step in the strategy involves the metal alkylidene catalyzed ene−yne−ene metathesis. During this process, two rings are formed in a single catalytic step. The acetylene plays a critical strategic role by relaying one RCM to another. Studies with different substituents on the acetylene and other well-defined alkylidenes have revealed important reactivity patterns. Product distribution is largely catalyst dependent. Among the well-defined catalysts examined, only the ruthenuim alkylidene **1** exhibited dienyne metathesis for a variety of substituents in good yields. These properties of the catalyst and the dienyne reaction significantly expand the scope of catalytic RCM for the construction of complex organic compounds.

(20) The dienyne **9** was treated with other metal alkylidenes. With Basset's tungsten catalyst,[16a] the reaction failed to go to completion and only 30% of the bicyclo[4.3.0] compound **18** was observed. With Tebbe reagent,[16b] only unreacted starting material was recovered. (a) Couturier, J.-M.; Pailet, C.; Leconte, M.; Basset, J.-M.; Weiss, K. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 628. (b) Tebbe, F. N.; Parshall, G. W.; Overall, D. W. *J. Am. Chem. Soc.* **1979**, *101*, 5074.

Experimental Section

General Methods. High resolution mass spectra were obtained from the Southern California Mass Spectrometry Facility (University of California, Riverside). Analytical thin-layer chromatography (TLC) was performed using silica gel 60 F254 precoated plates (0.25 mm thickness) with a fluorescent indicator. Flash column chromatography was performed using silica gel 60 (230−400 mesh) from EM Science.[21] Catalysts **1**, **34**, and **35** were prepared according to published procedures.[3,15] All reactions were carried out under an argon atmosphere with dry, degassed solvents under anhydrous conditions.

2-Butyne-1,4-diol Diallyl Ether (2). NaH (92 mg, 3.9 mmol) was added to a solution of 2-butyne-1,4-diol (200 mg, 1.75 mmol) in 50 mL of DMF at room temperature. $ICH_2CH{=}CH_2$ (650 mg, 3.9 mmol) was added, and the resulting suspension was stirred for 2 h. The reaction was quenched with H_2O (50 mL), extracted with hexanes (3 × 50 mL), dried over $MgSO_4$, concentrated, and purified by flash chromatography to give 250 mg (74%) of **2** as colorless oil: ^{1}H NMR (C_6D_6, 300 MHz) δ 5.21 (dq, J = 17.1, 1.8 Hz, 1H), 4.99 (dq, J = 10.5, 1.5 Hz, 1H), 5.73 (m, 1H), 3.87 (dt, J = 5.4, 1.5 Hz, 2H), 3.94 (s, 2H); ^{13}C NMR (C_6D_6, 75 MHz) δ 117.9, 133.9, 82.3, 70.6, 57.4; IR (neat, cm^{-1}) 3081, 2924, 2854, 1250; HRMS calcd for $C_{10}H_{14}O_2$ (M^+) 166.0994, found 166.0989.

1-(4-Oxa-1-cyclopentenyl)-4-oxacyclopentene (6). Ruthenium catalyst **1** (30 mg, 0.032 mmol) was added to a solution of dienyne **2** (190 mg, 1.14 mmol) in 35 mL of C_6H_6. The resulting light brown solution was maintained at room temperature for 4 h. The solution was quenched by opening to air, concentrated under reduced pressure, and purified by flash chromatography to give **6**, which was isolated as a colorless oil (140 mg, 90% yield): ^{1}H NMR (C_6D_6, 300 MHz) δ 4.92 (br s, 1H), 4.61 (m, 2H), 4.47 (m, 2H); ^{13}C NMR (C_6D_6, 75 MHz) δ 132.0, 123.2, 76.2, 75.0; IR (neat, cm^{-1}) 2922, 2867, 1743, 1459; HRMS calcd for $C_8H_{10}O_2$ (M^+) 138.0681, found 138.0680.

A Representative Procedure for the Synthesis of Symmetrical Dienynes: 5-(1-Propynyl)-5-[(triethylsilyl)oxy]-1,8-nonadiene (9). $BrCH_2CH_2CH{=}CH_2$ (5.8 g, 43 mmol) in 10 mL of THF was added dropwise over a period of 20 min to a suspension of Mg (1.4 g, 57.4 mmol) in 100 mL of THF at room temperature. The suspension was then stirred at room temperature for an additional 40 min. The reaction mixture was then transferred via cannula to $MeCCCO_2Bn$ **8** (2.5 g, 14.3 mmol) in 50 mL of THF at 0 °C. After 15 min, saturated NH_4Cl was added (200 mL) and the aqueous layer was extracted with Et_2O (2 × 100 mL). The combined organic layers were washed with saturated NaCl (2 × 100 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude reaction mixture was dried with benzene azeotrope (2 × 5 mL) and taken to the next step without further purification.

$Et_3SiOSO_2CF_3$ (3.25 mL, 14.3 mmol) was added to crude alcohol and NEt_3 (4.0 mL, 28.7 mmol) in 50 mL of CH_2Cl_2 at 0 °C. After 30 min, the reaction was quenched over saturated $NaHCO_3$ (100 mL), extracted with CH_2Cl_2 (2 × 50 mL), dried over Na_2SO_4, concentrated, and purified by flash chromatography (petroleum ether) to give 1.9 g (45%, two steps) of **9** as a colorless oil: ^{1}H NMR (C_6D_6, 300 MHz) δ 5.89−5.76 (m, 2H), 5.10−4.94 (m, 4H), 2.35−2.30 (m, 4H), 1.83−1.77 (m, 4H), 1.43 (s, 3H), 1.07 (t, J = 7.5 Hz, 9H), 0.78 (q, J = 7.8 Hz, 6H); ^{13}C NMR (C_6D_6, 75 MHz) δ 138.9, 114.5, 83.1, 81.1, 72.1, 42.5, 29.4, 7.5, 6.7, 3.1; IR (neat, cm^{-1}) 2952, 2918, 2876, 2247, 1426, 1239; HRMS calcd for $C_{18}H_{33}OSi$ (MH^+) 293.2302, found 293.2301.

6-(1-Propynyl)-6-[(triethylsilyl)oxy]-1,10-undecadiene (10) was isolated in 62% yield (two steps) as a colorless oil: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.89−5.75 (m, 2H), 4.99−4.92 (m, 4H), 2.09−2.01 (m, 4H), 1.82 (s, 3H), 1.55 (m, 8H), 0.96 (t, J = 7.6 Hz, 9H), 0.66 (q, J = 7.7 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 138.9, 114.3, 83.2, 80.2, 71.9, 42.3, 33.9, 23.6, 7.1, 6.2, 3.5; IR (neat, cm^{-1}) 3077, 2950, 2918, 2876, 2244, 1415, 1238; HRMS calcd for $C_{20}H_{37}OSi$ (MH^+) 321.2615, found 321.2614.

A Representative Procedure for the Synthesis of Unsymmetrical Dienynes: 5-(1-Propynyl)-5-[(triethylsilyl)oxy]-1,9-decadiene (12). $BrCH_2CH_2CH{=}CH_2$ (1.6 mL, 15.7 mmol) in 5 mL of THF was added dropwise over a period of 30 min to a suspension of Mg (575 mg, 23.6 mmol) in 10 mL of THF at room temperature. The suspension was then stirred at room temperature for an additional 30 min. The reaction mixture was then transferred via cannula to $MeCCCON(OMe)Me$ (**11**) (1.0 g, 7.9 mmol) in 10 mL of THF at −78 °C. After 60 min, saturated NH_4Cl was added (100 mL), and the aqueous layer was extracted with Et_2O (2 × 50 mL). The combined organic layers were washed with saturated NaCl (2 × 100 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude ketone was taken to the next step without further purification.

$BrCH_2CH_2CH_2CH{=}CH_2$ (1.9 mL, 15.7 mmol) in 5 mL of THF was added dropwise over a period of 30 min to a suspension of Mg (575 mg, 23.6 mmol) in 10 mL of THF at room temperature. The suspension was then stirred at room temperature for an additional 30 min. The reaction mixture was then transferred via cannula to the crude ketone in 10 mL of THF at −78 °C. After 60 min, saturated NH_4Cl was added (100 mL), and the aqueous layer was extracted with Et_2O (2 × 50 mL). The combined organic layers were washed with saturated NaCl (2 × 100 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude alcohol was dried with benzene azeotrope (2 × 5 mL) and taken to the next step without further purification.

$Et_3SiOSO_2CF_3$ (1.75 mL, 7.86 mmol) was added to the crude alcohol and NEt_3 (2.2 mL, 15.7 mmol) in 10 mL of CH_2Cl_2 at 0 °C. After 30 min, the reaction was quenched over saturated $NaHCO_3$ (50 mL) and extracted with CH_2Cl_2 (2 × 50 mL), dried over Na_2SO_4, concentrated, and purified by flash chromatography (petroleum ether) to give 900 mg (38%, three steps) of **12** as colorless oil: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.89−5.78 (m, 2H), 5.06−4.91 (m, 4H), 2.23−2.13 (m, 2H), 2.09−2.02 (m, 2H), 1.82 (s, 3H), 1.69−1.47 (m, 6H), 0.97 (t, J = 7.8 Hz, 9H), 0.66 (q, J = 7.8 Hz, 6H); ^{13}C NMR (C_6D_6, 75 MHz) δ 138.89, 138.94, 114.4, 113.5, 82.9, 80.4, 71.8, 42.3, 41.8, 33.9, 28.8, 23.6, 7.1, 6.2, 3.5; IR (neat, cm^{-1}) 3078, 2952, 2918, 2876, 2244, 1416, 1238; HRMS calcd for $C_{19}H_{35}OSi$ (MH^+) 307.2458, found 307.2457.

***(Z)*-5-(1-Propynyl)-5-[(triethylsilyl)oxy]-1,9-undecadiene (13)** was isolated in 31% yield (three steps) as a colorless, clear oil: ^{1}H NMR (C_6D_6, 300 MHz) δ 5.93−5.80 (m, 1H), 5.50−5.36 (m, 2H), 5.13−4.96 (m, 2H), 2.45−2.35 (m, 2H), 2.06−1.98 (m, 2H), 1.88−1.82 (m, 2H), 1.80−1.62 (m, 4H), 1.58 (d, J = 4.7 Hz, 3H), 1.44 (s, 3H), 1.11 (q, J = 7.5 Hz, 6H), 0.82 (t, J = 7.5 Hz, 9H); ^{13}C NMR (C_6D_6, 75 MHz) δ 139.0, 131.6, 125.2, 114.4, 83.5, 80.9, 72.4, 42.9, 42.5, 33.2, 29.4, 24.8, 18.1, 7.5, 6.7, 3.1; IR (neat, cm^{-1}) 2951, 2876, 2244, 1415, 1238; HRMS calcd for $C_{20}H_{37}OSi$ (MH^+) 321.2615, found 321.2614.

***(E)*-6-(1-Propynyl)-6-[(triethylsilyl)oxy]-1,9-dodecadiene (14)** was isolated in 15% yield (three steps) as a colorless, clear oil: ^{1}H NMR (C_6D_6, 300 MHz) δ 5.86−5.72 (m, 1H), 5.53−5.40 (m, 2H), 5.07−4.94 (m, 2H), 2.45−2.35 (m, 2H), 2.17−2.06 (m, 2H), 2.04−1.97 (m, 2H), 1.85−1.60 (m, 6H), 1.45 (s, 3H), 1.11 (t, J = 7.8 Hz, 9H), 0.94 (t, J = 7.5 Hz, 6H); ^{13}C NMR (C_6D_6, 75 MHz) δ 138.9, 131.9, 129.2, 114.8, 83.5, 80.9, 72.5, 43.4, 42.8, 34.3, 24.2, 22.9, 20.9, 14.5, 7.5, 6.7, 3.2; IR (neat, cm^{-1}) 3006, 2953, 2876, 2243, 1415, 1238; HRMS calcd for $C_{21}H_{39}OSi$ (MH^+) 335.2772, found 335.2770.

2-Methyl-5-(1-propynyl)-5-(triethylsiloxy)-1,9-decadiene (15) was isolated in 21% yield (three steps) as a colorless, clear oil: ^{1}H NMR (C_6D_6, 300 MHz) δ 5.86−5.73 (m, 1H), 5.10−4.95 (m, 2H), 4.88 (m, 1H), 4.81 (m, 1H), 2.42−2.34 (m, 2H), 2.07−1.92 (m, 4H), 1.80−1.62 (m, 7H), 1.44 (s, 3H), 1.12 (t, J = 7.5 Hz, 9H), 0.83 (q, J = 7.5 Hz, 6H); ^{13}C NMR (C_6D_6, 75 MHz) δ 146.0, 138.9, 114.8, 110.0, 83.5, 80.9, 72.4, 42.8, 41.6, 34.3, 33.1, 24.2, 22.9, 7.5, 6.7, 3.1; IR (neat, cm^{-1}) 3076, 2952, 2876, 2917, 2242, 1415, 1238; HRMS calcd for $C_{20}H_{37}OSi$ (MH^+) 321.2615, found 321.2614.

6-Methyl-6-(1-propynyl)-7-oxa-1,9-undecadiene (16). Two sequential Grignard reactions ($MgBrCH_2CH_2CH_2CH{=}CH_2$ and MgBrMe) gave a 60% yield (two steps) of crude alcohol. Alkylation of crude tertiary alcohol: NaH (95%, 130 mg, 5.3 mmol) was added to the crude tertiary alcohol (540 mg, 3.5

(21) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

mmol) in 5 mL of DMF. After 15 min, excess $ClCH_2$-CH=CHMe (3.4 mL, 35 mmol) was added and the resulting mixture was heated to 80 °C for 6 h. The reaction was quenched with saturated NH_4Cl (50 mL), extracted with hexanes, dried over Na_2SO_4, concentrated, and purified by flash chromatography (5% diethyl ether/petroleum ether) to give 340 mg (47%) of **16** as colorless oil: ^{1}H NMR (C_6D_6, 300 MHz, *ca.* 4:1 mixture of *Z*:*E* isomers) δ 5.85−5.60 and 5.55−5.42 (m, 3H), 5.05−4.92 (m, 2H), 4.40−4.08 (m, 2H), 2.05−1.95 (m, 2H), 1.86−1.60 (m, 4H), 1.55−1.53 (m, 3H), 1.49 (s, 3H), 1.42 (d, J = 2.4 Hz, 3H); ^{13}C NMR (C_6D_6, 75 MHz) δ 139.0, 129.5, 129.0, 127.0, 125.9, 114.7, 81.5, 80.9, 80.8, 73.4, 73.3, 64.9, 60.0, 42.1, 42.0, 34.3, 26.9, 24.1, 17.8, 13.3, 3.2; IR (neat, cm^{-1}) 2978, 2944, 2929, 2858, 2242, 1441, 1248; HRMS calcd for $C_{11}H_{17}O$ (MH^+) 207.1750, found 207.1749.

A Representative Procedure for Catalytic Dienyne Metathesis: 2-Methyl-6-[(triethylsilyl)oxy]bicyclo[4.4.0]-deca-2,10-diene (20). Ruthenium catalyst **1** (FW 925.1, 0.03 equiv, 5.6 mg) in C_6H_6 (1.0 mL) was added through a cannula to a solution of dienyne **13** (FW 334.6, 1.0 equiv, 0.2 mmol, 67 mg, entry 4) in C_6H_6 (5.7 mL, 0.03 M). The resulting light brown solution was placed in a 65 °C oil bath. After 6.5 h, the starting material was completely converted to a compound with a R_f = 0.4 (petroleum ether) on TLC. The solution was concentrated under reduced pressure and purified by flash chromatography. The fused bicyclo[4.4.0] ring **20** was isolated as a colorless, volatile oil (46 mg, 83% yield): ^{1}H NMR (C_6D_6, 300 MHz) δ 5.54−5.47 (br m, 2H), 2.55−2.40 (br m, 1H), 2.12−2.02 (br m, 1H), 1.97−1.77 (m, 4H), 1.76−1.72 (br m, 3H), 1.75−1.3 (m, 4H), 1.03 (t, J = 7.8 Hz, 9H), 0.65 (q, J = 7.8 Hz, 6H); ^{13}C NMR (C_6D_6, 75 MHz) δ 138.7, 131.0, 125.5, 123.1, 70.0, 38.9, 38.2, 26.5, 22.8, 20.2, 18.2, 7.7, 7.0; IR (neat, cm^{-1}) 2937, 2875, 1440, 1237; HRMS calcd for $C_{17}H_{30}OSi$ (M^+) 278.2067, found 278.2066.

2-Methyl-6-[(triethylsilyl)oxy]bicyclo[4.3.0]nona-2,9-diene (18): ^{1}H NMR (C_6D_6, 300 MHz) δ 5.47 (d, J = 3.9 Hz, 1H), 5.42 (br s, 1H), 2.65−2.47 (br m, 2H), 2.18−1.87 (m, 4H), 1.78 (q, J = 1.1 Hz), 1.71 (ddt, J = 8.6, 8.6, 13.6 Hz, 1H), 1.47−1.35 (m, 1H), 1.01 (t, J = 8.1 Hz, 9H), 0.59 (q, J = 8.1 Hz, 6H); ^{13}C NMR (C_6D_6, 75 MHz) δ 145.6, 128.7, 126.7, 124.3, 83.3, 39.6, 37.5, 30.1, 24.2, 19.3, 7.5, 6.5; IR (neat, cm^{-1}) 2935, 2876, 1455, 1237; HRMS calcd for $C_{16}H_{28}OSi$ (M^+) 264.1910, found 264.1909.

2-Methyl-7-[(triethylsilyl)oxy]bicyclo[5.4.0]undeca-2,-11-diene (19): ^{1}H NMR (C_6D_6, 300 MHz) δ 5.59 (dt, J = 5.4, 1.3 Hz, 1H), 5.48 (t, J = 3.8 Hz, 1H), 2.3−2.17 (br m, 1H), 2.13−1.96 (br m, 1H), 1.94 (q, J = 1.5 Hz, 3H), 1.92−1.68 (m, 6H), 1.65−1.45 (m, 4H), 1.06 (t, J = 7.8 Hz, 9H), 0.64 (q, J = 7.8 Hz); ^{13}C NMR (C_6D_6, 75 MHz) δ 145.1, 135.1, 125.9, 124.3, 76.3, 43.7, 40.4, 29.2, 26.3, 25.7, 23.6, 20.7, 7.6, 7.4; IR (neat, cm^{-1}) 2937, 2834, 1456, 1238; HRMS calcd for $C_{18}H_{32}OSi$ (M^+) 292.2224, found 292.2222.

2-Methyl-7-[(triethylsilyl)oxy]bicyclo[5.3.0]deca-2,11-diene (21): ^{1}H NMR (C_6D_6, 300 MHz) δ 5.58 (t, J = 5 Hz, 1H), 5.5 (t, J = 2.5 Hz, 1H), 2.47−2.26 (m, 2H), 2.17−1.92 (m, 4H), 1.9 (d, J = 1.2 Hz, 3H), 1.87−1.8 (m, 2H), 1.66−1.45 (m, 4H), 1.04 (t, J = 8 Hz, 9H), 0.64 (q, J = 8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 150.0, 130.3, 128.2, 127.9, 87.2, 42.4, 41.9, 29.3, 29.2, 24.8, 22.5, 7.2, 6.3; IR (neat, cm^{-1}) 2951, 2875, 1455, 1237; HRMS calcd for $C_{17}H_{31}OSi$ (MH^+) 279.2145, found 279.2144. **21** is a somewhat unstable compound when concentrated; the sample contains a small amount (<3%) of unidentified decomposition substance.

2,3-Dimethyl-6-[(triethylsilyl)oxy]bicyclo[4.4.0]deca-2,-10-diene (22): ^{1}H NMR (C_6D_6, 300 MHz, sample contains a small amount (<3%) of unknown decomposition product) δ 5.54−5.51 (br m, 1H), 2.56−2.4 (br m, 1H), 2.2−1.95 (br m, 1H), 1.94−1.76 (m, 4H), 1.68 (br s, 3H), 1.72 (br s, 3H), 1.55−1.32 (m, 4H), 1.03 (t, J = 7.9 Hz, 9H), 0.63 (q, J = 7.7 Hz, 6H); ^{13}C NMR (C_6D_6, 75 MHz) δ 139.4, 130.2, 124.6, 121.3, 69.9, 39.4, 38.2, 29.5, 26.7, 20.5, 18.1, 14.6, 7.7, 6.9; IR (neat, cm^{-1}) 2936, 2829, 1455, 1237; HRMS calcd for $C_{18}H_{33}OSi$ (MH^+) 293.2302, found 293.2301.

2,6-Dimethyl-5-oxabicyclo[4.4.0]deca-2,10-diene (23): ^{1}H NMR (C_6D_6, 300 MHz, somewhat unstable compound when concentrated) δ 5.39 (m, 1H), 5.21 (br s, 1H), 5.37 (br d, J = 17 Hz, 1H), 4.04 (br d, J = 17 Hz, 1H), 1.97−1.89 (m, 2H), 1.87−1.76 (m, 1H), 1.69 (br s, 3H), 1.58−1.47 (m, 2H), 1.27 (d, J = 0.5 Hz, 3H); ^{13}C NMR (C_6D_6, 75 MHz) δ 138.3, 129.0, 122.4, 120.0, 71.1, 60.8, 36.9, 25.8, 21.9, 20.2, 18.9; IR (neat, cm^{-1}) 2971, 2938, 2830, 1452, 1391, 1366; HRMS calcd for $C_{11}H_{16}O$ (M^+) 164.1202, found 164.1201.

5-Ethynyl-5-[(triethylsilyl)oxy]-1,8-nonadiene (24). To a stirred solution of the dienyne alcohol (0.95 g, 5.8 mmol) and anhydrous NEt_3 (1.9 mL, 13 mmol) in CH_2Cl_2 (60 mL) at 0 °C was added Et_3SiOTf (1.1 mL, 5.8 mmol). The addition was followed by TLC. When finished by TLC, the reaction mixture was quenched with 60 mL of saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2 (3 × 50 mL). Purification by chromatography (petroleum ether elution) yielded the product as a clear, colorless oil: 1.25 g, 78%; ^{1}H NMR (C_6D_6, 300 MHz) δ 5.84−5.74 (m, 2H), 5.09−4.94 (m, 4H), 2.34−2.27 (m, 4H), 1.97 (s, 1H), 1.82−1.76 (m, 4H), 1.05 (t, J = 7.8 Hz, 9H), 0.78 (q, J = 7.6 Hz, 6H); ^{13}C NMR (C_6D_6, 75 MHz) δ 138.5, 114.6, 87.2, 73.7, 71.9, 42.1, 29.1, 7.4, 6.6; IR (neat, cm^{-1}) 3307, 3079, 2953, 2914, 2109; HRMS calcd for $C_{17}H_{31}OSi$ (MH^+) 279.2136, found 279.2144.

6-[(Triethylsilyl)oxy]bicyclo[4.3.0]nona-2,9-diene (39): ^{1}H NMR (C_6D_6, 300 MHz) δ 6.20 (dd, J = 9.9, 2.4 Hz, 1 H), 5.73−5.68 (m, 1H), 5.35 (d, J = 0.9 Hz, 1H), 2.59−2.47 (m, 2H), 2.12−1.86 (m, 4H), 1.70−1.35 (m, 2H), 1.02 (t, J = 7.9 Hz, 9H), 0.62 (q, J = 7.8 Hz, 6H); ^{13}C NMR (C_6D_6, 75 MHz) δ 143.2, 129.8, 125.6, 122.7, 82.5, 38.9, 36.9, 29.9, 23.7, 7.2, 6.2; IR (neat, cm^{-1}) 3030, 2953, 2875; HRMS calcd for $C_{15}H_{26}OSi$ (M^+) 250.1746, found 250.1743.

1,8-Nonadien-5-one. In a dry 500 mL round-bottom flask were placed Mg (40−80 mesh powder, 3.6 g, 147 mmol), I_2 (10 mg), and THF (200 mL). To this mixture was added 4-bromo-1-butene (15 mL, 147 mmol) in anhydrous THF (50 mL) dropwise over 15 min and stirred for an additional 30 min. The Grignard reagent was transferred to an addition funnel connected to a 1000 mL round-bottom flask containing *N*-methoxy-*N*-methyl-4-pentenamide[22] in THF (500 mL) at −10 °C. The Grignard reagent was added dropwise to a solution of the Weinreb amide in THF over 20 min. After addition was complete, the reaction was stirred until complete by TLC (ca. 45 min). The reaction was quenched with NH_4Cl (saturated aqueous, 200 mL) and extracted with Et_2O (3 × 200 mL). The organics were combined, dried over Na_2SO_4, and concentrated under vacuum to yield a yellow oil. This oil was purified by flash chromatography (10% EtOAc in petroleum ether elution) to yield the desired product: 9.4 g, 76%; ^{1}H NMR (C_6D_6, 300 MHz) δ 5.74−5.61 (m, 2H), 4.97−4.88 (m, 4H), 2.22−2.15 (m, 4H), 1.98−1.94 (m, 4H); ^{13}C NMR (C_6D_6, 75 MHz) δ 206.8, 137.7, 115.0, 41.7, 28.0; IR (neat, cm^{-1}) 3080, 2979, 1715.

A Representative Procedure for the Synthesis of Dienynes via Acetylide Addition to Ketone: 5-[(Trimethylsilyl)ethynyl]-5-[(triethylsilyl)oxy]-1,8-nonadiene (29). To a solution of (trimethylsilyl)acetylene (0.25 mL, 1.8 mmol) in THF (10 mL) at −78 °C was added BuLi (1.1 mL, 1.6 M in hexanes, 1.8 mmol) and the resulting mixture stirred for 10 min. The deprotonated acetylene was then added via cannula to a stirring solution of 1,8-nonadien-5-one (202 mg, 1.46 mmol) in THF (10 mL) over 3 min. The reaction was stirred at −78 °C until complete by TLC (about 30 min). The reaction was quenched with NH_4Cl (saturated aqueous, 20 mL) and extracted with EtOAc (3 × 10 mL). The organic fractions were combined, dried over Na_2SO_4, and concentrated under vacuum to yield a brown oil. The oil was dissolved in 10 mL of CH_2Cl_2, and NEt_3 (1.0 mL, 3.0 mmol) was added to the solution. The solution was cooled to 0 °C, and Et_3SiOTf (0.55 mL) was added until the reaction was complete by TLC (petroleum ether elution). The reaction mixture was quenched with $NaHCO_3$ (aqueous, 20 mL) and extracted with Et_2O (3 × 10 mL). The organics were combined, dried over Na_2SO_4, and concentrated under vacuum to yield a yellow oil. This oil was purified by silica gel chromatography (10% EtOAc in petroleum ether elution) to yield the product as a clear, colorless oil: 330 mg, 96%; ^{1}H NMR (C_6D_6, 300 MHz) δ 5.87−5.78 (m, 2H), 5.10−4.94 (m, 4H), 2.39−2.33 (m, 4H), 1.87−1.81 (m, 4H), 1.09 (t, J = 7.8 Hz, 9H), 0.84 (q, J = 7.8 Hz, 6H), 0.15 (s, 9H); ^{13}C NMR

(22) Nahm, S.; Weinreb, S. M. *Tetrahedron Lett.* **1981**, *22*, 3815−3818.

(C_6D_6, 75 MHz) δ 138.7, 114.6, 110.0, 89.7, 72.4, 42.2, 29.3, 7.4, 6.7, −0.2; IR (neat, cm^{-1}) 3079, 2954, 2914, 2164; HRMS calcd for $C_{20}H_{39}OSi_2$ (MH^+) 351.2529, found 351.2539.

5-[(Triethylsilyl)oxy]-5-[(trimethylsilyl)ethynyl]cycloheptene (44): ^1H NMR (C_6D_6, 300 MHz) δ 5.76−5.73 (m, 2H), 2.22−1.84 (m, 8H), 1.12 (t, J = 7.8 Hz, 9H), 0.84 (q, J = 7.8 Hz, 6H), 0.16 (s, 9H); ^{13}C NMR (C_6D_6, 75 MHz) δ 132.2, 111.0, 89.5, 73.8, 42.3, 23.3, 7.5, 7.4, −0.2; IR (neat, cm^{-1}) 3022, 2954, 2162; HRMS calcd for $C_{18}H_{34}OSi_2$ (M^+) 322.2139, found 322.2148.

5-(Phenylethynyl)-5-[(triethylsilyl)oxy]-1,8-nonadiene (27): ^1H NMR (C_6D_6, 300 MHz) δ 7.41−7.38 (m, 2H), 6.97−6.95 (m, 3H), 5.88−5.82 (m, 2H), 5.13−4.98 (m, 4H), 2.45−2.41 (m, 4H0, 1.97−1.91 (m, 4H), 1.08 (t, J = 7.8 Hz, 9H), 0.85 (q, J = 7.8 Hz, 6H); ^{13}C NMR (C_6D_6, 75 MHz) δ 138.7, 131.7, 128.6, 128.4, 123.4, 114.7, 93.2, 85.8, 72.5, 42.2, 29.4, 7.4, 6.7; IR (neat, cm^{-1}) 3079, 3034, 2952, 2913, 2226; HRMS calcd for $C_{23}H_{34}OSi$ (M^+) 354.2370, found 354.2359.

2-Phenyl-6-[(triethylsilyl)oxy]bicyclo[4.3.0]nona-1,9-diene (41): ^1H NMR (C_6D_6, 300 MHz) δ 7.47−7.12 (m, 5H), 5.81−5.79 (m, 1H), 5.63 (s, 1H), 2.16−2.00(m, 4H), 1.80−1.69 (m, 2H), 1.52−1.44 (m, 2H), 1.04 (t, J = 7.9 Hz, 9H), 0.66 (q, J = 7.7 Hz, 6H); ^{13}C NMR (C_6D_6, 75 MHz) δ 143.6, 141.7, 135.7, 128.8, 128.5, 128.4, 127.3, 127.2, 85.6, 39.3, 37.4, 30.1, 24.7, 7.6, 6.6; IR (neat, cm^{-1}) 3078, 3055, 3022, 2952; HRMS calcd for $C_{21}H_{31}OSi$ (MH^+) 327.2137, found 327.2153.

5-(3-Methyl-1-butynyl)-5-[(triethylsilyl)oxy]nona-1,8-diene (25): ^1H NMR (C_6D_6, 300 MHz) δ 5.92−5.78 (m, 2H), 5.12−4.95 (m, 4H), 2.39−2.32 (m, 5H), 1.86−1.80 (m, 4H), 1.09 (t, J = 7.9 Hz, 9H), 1.01 (d, J = 6.8 Hz, 6H), 0.82 (q, J = 7.7 Hz, 6H); ^{13}C NMR (C_6D_6, 75 MHz) δ 138.8, 114.5, 90.9, 83.3, 72.1, 42.6, 29.4, 23.0, 20.7, 7.6, 6.6; IR (neat, cm^{-1}) 3078, 2952, 2235: HRMS calcd for $C_{20}H_{37}OSi$ (MH^+) 321.2605, found 321.2622.

2-(2-Propyl)-6-[(triethylsilyl)oxy]bicyclo[4.3.0]nona--1,9-diene (40): ^1H NMR (C_6D_6, 300 MHz) δ 5.56 (d, J = 5.1 Hz, 1H), 5.49 (s, 1H), 2.60−2.49 (m, 2H), 2.18−1.96 (m, 3H), 1.75−1.65 (m, 2H), 1.46−1.36 (m, 2H), 1.13 (d, J = 3.0 Hz, 3H), 1.11 (d, J = 2.7 Hz, 3H), 1.02 (t, J = 8.0 Hz, 9H), 0.61 (q, J = 8.0 Hz, 6H); ^{13}C NMR (C_6D_6) δ 144.5, 139.3, 123.4, 122.5, 83.9, 39.4, 37.4, 30.4, 30.2, 24.2, 23.0, 22.1, 7.4, 6.7; IR (neat, cm^{-1}) 3044, 2957, 2929; HRMS calcd for $C_{18}H_{34}OSi$ (MH^+) 293.2293, found 293.2300.

5-(*tert*-Butylethynyl)-5-[(triethylysilyl)oxy]nona-1,8-diene (26): ^1H NMR (C_6D_6, 300 MHz) δ 5.91−5.82 (m, 2H), 5.14−4.96 (m, 4H), 2.41−2.33 (m, 4H), 1.87−1.81 (m, 4H), 1.13 (s, 9H), 1.10 (t, J = 7.8 Hz, 9H), 0.83 (q, J = 7.8 Hz, 6H); ^{13}C NMR (C_6D_6, 75 MHz) δ 139.0, 114.5, 93.6, 82.6, 72.0, 42.7, 30.9, 29.5, 27.5, 7.5, 6.7; IR (neat, cm^{-1}) 3078, 2951, 2239; HRMS calcd for $C_{21}H_{39}OSi$ (MH^+) 335.2760, found 335.2770.

5-(*tert*-Butylethynyl)-5-[(triethylsilyl)oxy]cycloheptene (43): ^1H NMR (C_6D_6, 300 MHz) δ 5.81−5.78 (m, 2H), 2.22−2.00 (m, 4H), 1.90−1.82 (m, 4H), 1.13 (t, J = 7.8 Hz, 9H), 1.15 (s, 9H), 0.84 (q, J = 7.8 Hz, 6H); ^{13}C NMR (C_6D_6, 75 MHz) δ 132.3, 94.2, 83.4, 73.7, 42.8, 31.0, 27.5, 23.5, 7.5, 6.8; IR (neat, cm^{-1}) 3021, 2951, 2237; HRMS calcd for $C_{19}H_{34}OSi$ (M^+) 306.2370, found 306.2379.

A Representative Procedure for Synthesis of Substituted Acetylenes via Deprotonation of Substrate 24: 5-(Carbomethoxyethynyl)-5-[(triethylysilyl)oxy]nona-1,8-diene (28). To a stirring solution of **24** (316 mg, 1.13 mmol) in 8 mL of THF at −78 °C was added BuLi (2.5 M in hexanes, 0.50 mL, 1.2 mmol, 1.1 equiv) and the resulting mixture allowed to stir for 3 min. The acetylide was transferred via cannula to a stirring solution of $ClCO_2Me$ (119 mg, 1.26 mmol, 1.1 equiv) in 12 mL of THF. The reaction was slowly warmed to ambient temperature. When TLC showed complete conversion, the reaction was quenched by addition of 25 mL of saturated aqueous NH_4Cl. The aqueous solution was extracted with EtOAc (3 × 25 mL) and purified by silica gel chromatography (10% Et_2O in petroleum ether elution) to yield the product as a clear, colorless oil: 351 mg, 92%; ^1H NMR (C_6D_6, 300 MHz) δ 5.72−5.67 (m, 2H), 5.03−4.92 (m, 4H), 3.21 (s, 3H), 2.26−2.20 (m, 4H), 1.03 (t, J = 7.8 Hz, 9H), 0.77 (q, J = 7.8 Hz, 6H); ^{13}C NMR (C_6D_6, 75 MHz) δ 153.6, 138.0, 115.0, 90.3, 77.8, 72.0, 52.1, 41.5, 28.8, 7.3, 6.5; IR (neat, cm^{-1}) 3079, 2954, 2914, 2232, 1827, 1721; HRMS calcd for $C_{19}H_{33}O_3Si$ (MH^+) 337.2190, found 337.2199.

2-(Carbomethoxy)-6-[(triethylsilyl)oxy]bicyclo[4.3.0]nona-1,9-diene (42) was isolated as an orange oil that was somewhat unstable at ambient temperature: ^1H NMR (C_6D_6, 300 MHz) δ 6.96 (m, 1H), 6.66 (m, 1H), 3.41 (s, 3H), 2.61−2.46 (m, 2H), 2.19−2.10 (m, 1H), 2.02−1.87 (m, 3H), 1.80−1.58 (m, 1H), 1.39−1.09 (m, 1H), 0.97 (t, J = 7.9 Hz, 9H), 0.58 (q, J = 7.8 Hz, 6H); ^{13}C NMR (C_6D_6) δ 166.3, 140.6, 138.7, 131.8, 130.1, 83.9, 51.0, 38.4, 36.6, 30.7, 24.8, 7.4, 6.5; IR (neat, cm^{-1}) 3044, 2951, 2934, 1721, 1255; HRMS calcd for $C_{17}H_{29}O_3Si$ (MH^+) 309.1886, found 309.1895.

5-(Chloroethynyl)-5-[(triethylsilyl)oxy]nona-1,8-diene (31): ^1H NMR (C_6D_6, 300 MHz) δ 5.82−5.70 (m, 2H), 5.05−4.93 (m, 4H), 2.27−2.18 (m, 4H), 1.76−1.70 (m, 4H), 1.03 (t, J = 8.0 Hz, 9H), 0.73 (q, J = 7.8 Hz, 6H); ^{13}C NMR (C_6D_6, 75 MHz) δ 138.3, 114.7, 73.2, 72.5, 63.8, 42.0, 29.0, 7.3, 6.5; IR (neat, cm^{-1}) 3080, 2954, 2914, 2223; HRMS calcd for $C_{17}H_{30}ClOSi$ (MH^+) 313.1754, found 313.1762.

A Representative Procedure for the Synthesis of Bromo- or Iodoacetylenic Dienynes: 5-(Bromoethynyl)-5-[(triethylsilyl)oxy]nona-1,8-diene (32). The terminal acetylene substrate **24** (306 mg, 1.10 mmol) was dissolved in acetone (8 mL). To this solution was added NBS (231 mg, 1.30 mmol) followed by $AgNO_3$ (42 mg, 0.25 mmol). After being stirred for 25 min, the reaction was complete as judged by TLC and was quenched by pouring it into 10 mL of ice−water. The aqueous solution was extracted with EtOAc (5 × 15 mL) and purified by silica gel chromatography to yield the product as a clear oil: 383 mg, 97%; ^1H NMR (C_6D_6, 300 MHz) δ 5.79−5.70 (m, 2H), 5.04−4.92 (m, 4H), 2.27−2.21 (m, 4H), 1.77−1.71 (m, 4H), 1.03 (t, J = 7.8 Hz, 9H), 0.74 (q, J = 7.8 Hz, 6H); ^{13}C NMR (C_6D_6, 75 MHz) δ 138.4, 114.7, 83.9, 73.1, 45.7, 42.0, 29.0, 7.4, 6.5; IR (neat, cm^{-1}) 3078, 2955, 2931, 2140; HRMS calcd for $C_{17}H_{30}BrOSi$ (MH^+) 357.1235, found 357.1249.

5-(Iodoethynyl)-5-[(triethylsilyl)oxy]nona-1,8-diene (33): ^1H NMR (C_6D_6, 300 MHz) δ 5.81−5.68 (m, 2H), 5.05−4.92 (m, 4H), 2.30−2.21 (m, 4H), 1.78−1.72 (m, 4H), 1.04 (t, J = 8.0 Hz, 9H), 0.75 (t, J = 7.6 Hz, 6H); ^{13}C NMR (C_6D_6, 75 MHz) δ 138.4, 114.7, 102.9, 98.2, 73.7, 42.2, 29.1, 7.4, 6.5; IR (neat, cm^{-1}) 3078, 2952, 2913, 2176; HRMS calcd for $C_{17}H_{30}IOSi$ (MH^+) 405.1111, found 405.1127.

6-[(Triethylsilyl)oxy]-6-[(trimethylsilyl)ethynyl]-1,10-undecadiene (38): ^1H NMR (C_6D_6, 300 MHz) δ 5.86−5.72 (m, 2H), 5.08−4.95 (m, 4H), 2.04−1.98 (m, 4H), 1.80−1.68 (m, 8H), 1.13 (t, J = 7.8 Hz, 9H), 0.87 (q, J = 7.9 Hz, 6H), 0.16 (s, 9H); ^{13}C NMR (C_6D_6, 75 MHz) δ 138.8, 114.8, 110.7, 89.2, 72.7, 42.1, 34.1, 23.8, 7.4, 6.6, −0.5; IR (neat, cm^{-1}) 3075, 2953, 2924, 2280, 2163; HRMS calcd for $C_{22}H_{43}OSi$ (MH^+) 379.2852, found 379.2830.

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