Ruthenium-Catalyzed Polycyclization Reactions

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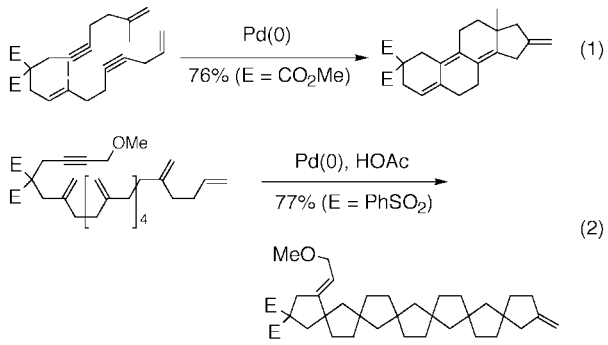
The application of ruthenium alkylidenes such as **1** to the catalysis of polycyclization reactions is reported. Several acyclic precursors have been synthesized and reacted with **1**. These precursors vary in topology and contain acetylenic and/or cycloolefinic metathesis relays. The cyclization reactions proceed in moderate to good yields to produce polycyclic polyenes when the precursors are subjected to catalytic amounts of **1**. In general, precursors bearing *n* relay units generate polycycles containing (*n* + 1) rings.

Introduction

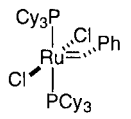
Cascade reactions have proven effective in the assembly of complex polycyclic systems from simple acyclic precursors.[1] These cascade cyclizations are characterized by the formation of a reactive intermediate that undergoes a series ring-forming steps before termination. Examples have been reported for cationic,[2] anionic,[3] radical,[4] and transition-metal-mediated cascade processes.[1] The application of homogeneous transition metal catalysts to cascade cyclizations of polyenes and polyynes appears very promising for the synthesis of polycyclic structures. For example, the groups of Negishi (eq 1)[5] and Trost (eq 2)[6] have utilized cyclic carbopalladation cascades in the one-step, catalytic assembly of systems containing up to seven rings (Scheme 1). Despite tremendous progress in this area, the development of efficient methods for the construction of polycyclic systems remains an important goal of synthetic chemistry.

Previous reports from this laboratory[7] demonstrate the possibility of extending catalytic diene ring-closing metathesis[8] (RCM, eq 3) to the formation of polycyclic structures by a cascade of ring-opening olefin metathesis or carbene−acetylene metathesis reactions.[9] For example, when a precursor diene containing an acetylene

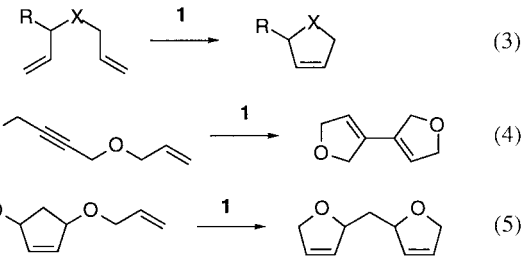
Scheme 1



or a cyclolefin is exposed to ruthenium alkylidene **1**,[10] bicyclics are produced (eqs 4 and 5). Extending this reaction to analogous precursors bearing two or more of these olefin metathesis relays should lead to the production of polycyclic molecules. Herein we report the synthesis of such precursors and their cascade cyclization reactions catalyzed by **1**.



1



Results and Discussion

Precursor Synthesis. Several dienes containing two or more olefin metathesis relay units were prepared in order to study the possibility of ruthenium-catalyzed

(1) (a) Teitze, L. F. *Chem. Rev.* **1996**, *96*, 115−136. (b) Hudlicky, T. *Chem. Rev.* **1996**, *96*, 3−30. (c) Ho, T.-L. *Tandem Reactions in Organic Synthesis*; Wiley-Interscience: New York, 1992. (d) Bunce, R. A. *Tetrahedron* **1995**, *51*, 13103−13159.

(2) Johnson, W. S.; Wiedhaup, K.; Brady, S. F.; Olson, G. L. *J. Am. Chem. Soc.* **1974**, *96*, 3979−3984.

(3) Ihara, M.; Makita, K.; Tokunaga, Y.; Fukumoto, K. *J. Org. Chem.* **1994**, *59*, 6008.

(4) Takahashi, T.; Katouda, W.; Sakamoto, Y.; Tomida, S.; Yamada, H. *Tetrahedron Lett.* **1995**, *36*, 2273.

(5) (a) Zhang, Y.; Wu, G.; Agnel, G.; Negishi, E. *J. Am. Chem. Soc.* **1990**, *112*, 8590. (b) Negishi, E. *Pure Appl. Chem.* **1992**, *64*, 323−334.

(6) Trost, B. M.; Shi, Y. *J. Am. Chem. Soc.* **1993**, *115*, 9421−9438.

(7) (a) Kim, S.-H.; Bowden, N. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 10801. (b) Kim, S.-H.; Zuercher, W. J.; Bowden, N. B.; Grubbs, R. H. *J. Org. Chem.* **1996**, *61*, 1073−1081. (c) Zuercher, W. J.; Hashimoto, M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 6634−6640.

(8) Recent examples of RCM of α,ω-dienes: (a) Grubbs, R. H.; Chang, S. B. *Tetrahedron* **1997**, *38*, 4757−4760 and references therein. (b) General RCM: Grubbs, R. H.; Miller, S. J.; Fu, G. C. *Acc. Chem. Res.* **1995**, *28*, 446−452 and references therein. General olefin metathesis: Ivin, K. J.; Mol, J. C. *Olefin Metathesis and Metathesis Polymerization*; Academic: San Diego, 1997.

(9) A cascade of diene RCM reactions was employed in the quantitative RCM of poly(1,2-butadiene) to produce a cyclopentene-based polymer. Coates, G. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 230−231.

(10) (a) Synthesis: Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100−110. (b) Mechanism and activity: Dias, E. L.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 3887−3897.

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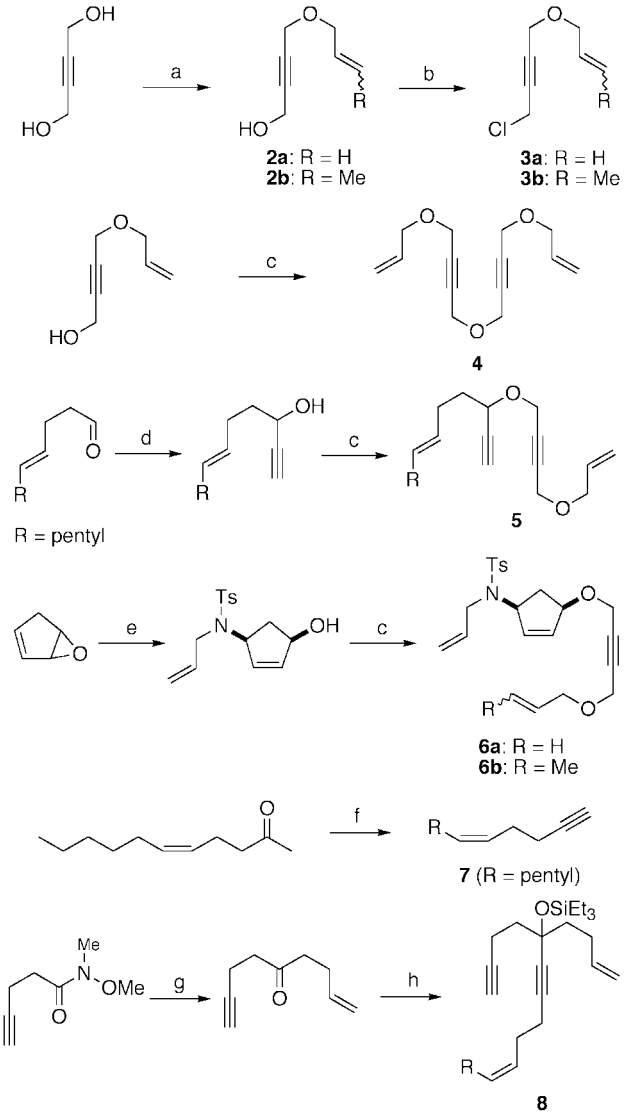
Scheme 2[a]



[a] Key: (a) NaH allyl or crotyl bromide, DMF, 70%; (b) TsCl, NEt_3, DMAP, CH_2Cl_2; (c) NaH, DMF, **3a**, 60−82%; (d) (i) TMSC-CH, BuLi, THF, (ii) K_2CO_3, MeOH, 86%; (e) allyl-NHTs, Pd_2dba_3·$CHCl_3$, dppe, BSA, THF, %; (f) 3-butenylMgBr, THF, 89%; (g) Ph_3PCH_2Br, *t*-BuOK, THF, 70%; (h) (i) BuLi, THF then **14**, (ii) Et_3SiOTf, NEt_3, CH_2Cl_2, two steps, 60%.

polycyclizations (Scheme 2). The linear precursor **4** was prepared by alkylation of the anion of 2-butyne-1,4-diol monoallyl ether **2a** with propargyl chloride **3a**.[11] For the preparation of **5**, lithium (trimethylsilyl)acetylide was added to *trans*-4-decenal; after desilylation, O-alkylation with **3a** produced **5**. Palladium-catalyzed ring opening[6] of cyclopentadiene monoepoxide with *N*-allyl-*p*-toluenesulfonamide and O-alkylation of the resulting amino alcohol with propargyl chlorides **3a** and **3b** produced **6a** and **6b**, respectively. The branched precursor **8** was formed via sequential addition of 3-butenylmagnesium bromide and the lithium anion of **7** to the Weinreb amide[12] of 4-pentynoic acid[13] followed by silylation with TESOTf. Enyne **7** was prepared via Corey−Fuchs reaction of *cis*-4-decenal.[14]

The synthesis of dienetriyne **14** (Scheme 3) began with silylation of 4-pentyn-1-ol with TBSCl. Deprotonation of *O*-silyl derivative **9** and BF_3·OEt_3-promoted ring-opening of oxetane afforded the monoprotected acetylenic diol **10**. Oxidation and Wittig olefination of the resultant aldehyde produced *O*-silyl enyne **11**. Desilylation and oxidation with Jones reagent produced the carboxylic acid **12**. Conversion of **12** to the Weinreb amide **13** was accomplished via the acid chloride. Sequential addition of 3-butenylmagnesium bromide and the lithium monoanion of 1,5-hexadiyne produced the tertiary alcohol, which was protected with TBSOTf to afford dienetriyne **14**.

Four N-protected polyamines (**26**−**29**) bearing one to four cycloolefinic relay linkages, respectively, were prepared to study the possibility of a cascade ring-opening/ring-closing metathesis in such systems. The strategy for the synthesis of **26**−**29** (Scheme 4) was comprised by four reactions: (a) palladium-catalyzed ring opening[6] of cyclopentadiene monoepoxide; (b) treatment of the resulting amino alcohol with methyl chloroformate to form an amino carbonate; and (c) or (d) palladium-catalyzed amination[6,15] reactions with either sodium *p*-toluenesulfonamide or *N*-allyl-*p*-toluenesulfonamide. Steps a−c were repeated one to four times, respectively, and terminated with step d, which yielded the desired protected polyamines **26**−**29**. The N-protected polyamine **37** was prepared by the above-outlined procedure to study the effect of olefin substitution on the yield of the metathesis reaction. Because palladium-catalyzed ring-opening of cyclopentadiene monoxide is stereoselective and yields only the syn isomer, the total number of stereoisomers in **26**−**29** and **37** was equal to the number of relay linkages *n*.

To explore the possibility of utilizing cyclohexenes as relays for polyamines in ring-opening/ring-closing metathesis reactions, **30** was prepared by palladium-catalyzed 1,4-diacetoxylation[16] of 1,3-cyclohexadiene followed by palladium-catalyzed amination of the resulting diacetate.

Polycyclization Reactions. Treatment of the acyclic precursors containing acetylenic relay units with a catalytic amount of **1** at ambient or slightly elevated temperatures results in the formation of fused and nonfused carbo- and heterocyclic products in moderate to good yields (Table 1).[17] The products contain conjugated triene and tetraene systems.

In general, fused polycyclics are formed in higher yield than nonfused ring systems (i.e., **17** and **18** vs **15**). In the intermediate case where the product contains both types of ring linkages, **16**, yields are also high. However, it is not known whether this originates from the thermodynamic stability of product due to increased conjugation (**17** and **18** are conformationally rigid while **15** is not), a kinetic factor of conformational origin, or some other effect.

The mechanism of the polycyclizations involves the initial formation of a ruthenium alkylidene that under-

(11) Propargyl chloride **3**, rather than the tosylate, was isolated from the reaction of **2** with tosyl chloride.

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

(13) Trost, B. M.; Shi, Y. *J. Am. Chem. Soc.* **1993**, *115*, 9421−9438.

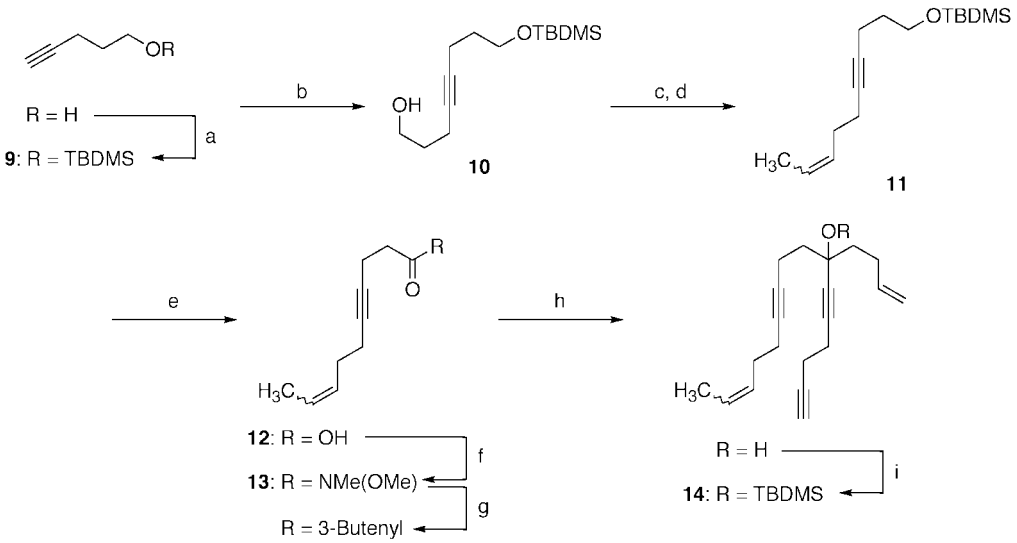
(14) (a) Matsumoto, M.; Kuroda, K. *Tetrahedron Lett.* **1980**, *21*, 4021−4024. (b) Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, *13*, 3679.

(15) Bäckvall, J.-E.; Byström, S. E.; Aslanian, R. *Tetrahedron Lett.* **1985**, *26*, 1749−1752.

(16) Bäckvall, J.-E.; Byström, S. E.; Nordberg, R. E. *J. Org. Chem.* **1984**, *49*, 4619.

(17) Compounds **4** and **5** have been protected as trialkylsilyl ethers. Cyclization proceeds without this protection, but the reaction rate is slowed dramatically, possibly due to intramolecular chelation.

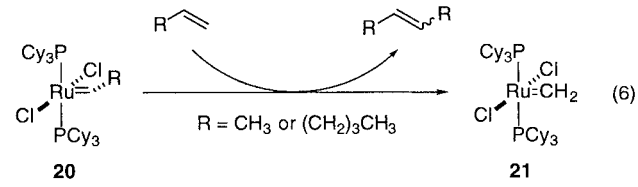
Scheme 3[a]



[a] Key: (a) TBDMSCl, NEt_3, CH_2Cl_2, 98%; (b) BuLi, THF then oxetane, $BF_3{\cdot}OEt_2$, 84%; (c) PDC, CH_2Cl_2; (d) BuLi, Ph_3PEtBr, THF, 64% from **10**; (e) CrO_3, H_2SO_4, *i*-PrOH, 83%; (f) $(COCl)_2$, CH_2Cl_2 then $H_2NMe(OMe)Cl$, NEt_3, 72%; (g) 3-butenylMgBr, THF, 86%; (h) 1,5-hexadiyne, 1.0 equiv of BuLi, THF, 48%; (i) TBDMSOTf, NEt_3, CH_2Cl_2, 96%.

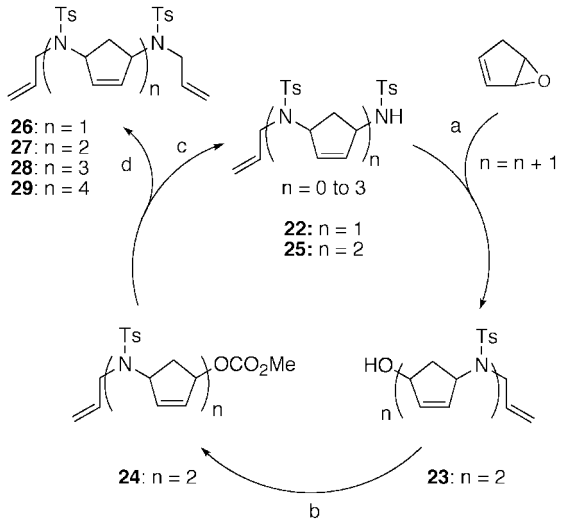
goes a series of intramolecular metatheses with the relay units prior to termination by a final ring closure. For example, the conversion of **8** to **17** (Scheme 5) presumably begins with metathesis of **1** with the monosubstituted olefin of **8**.[18] The newly formed carbene subsequently undergoes two intramolecular carbene−acetylene metatheses[19] involving the respective metallacyclobutene intermediates. The cyclization is completed by intramolecular metathesis of the vinylcarbene with the disubstituted olefin to yield product **17** and propagating alkylidene **20**.

The initiation and subsequent reactions of **1** are followed by observing the ^1H NMR signal of the α-proton of the ruthenium alkylidene. As the benzylidene (singlet 20.02 ppm in CD_2Cl_2) is consumed, a signal for the propagating alkylidene **20** appears. In the reactions of **5**, **8**, and **14**, this species is expected to be ethylidene or *n*-pentylidene and is observed initially as a multiplet (ethylidene: quartet at 19.26 ppm in CD_2Cl_2; *n*-pentylidene: triplet at 19.24 ppm). However, as the reaction progresses, a singlet corresponding to the ruthenium methylidene **21** (18.94 ppm in CD_2Cl_2) grows as the alkylidene signal decays. Additionally, the formation of ethylene (singlet, 5.35 ppm in CD_2Cl_2) and either 2-butene or 5-decene is observed in the reaction mixture. These observations indicate a secondary metathesis with the α-olefin byproduct of the cyclization reaction (eq 6) and are consistent with the reported reactivity of **1** with α-olefins.[10a]



Despite initial observation of low yields and competing side reactions, cycloolefins as well as acetylenes are effective relays in these polycyclization reactions. When precursor **6a** is exposed to 4 mol % **1**, tricycle **19** is recovered in only 40% yield. The mass balance is found in an uncharacterized side product that appears to be oligomerized starting material. This type of side reaction

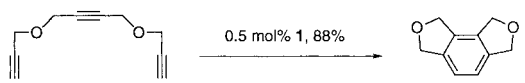
Scheme 4[a]



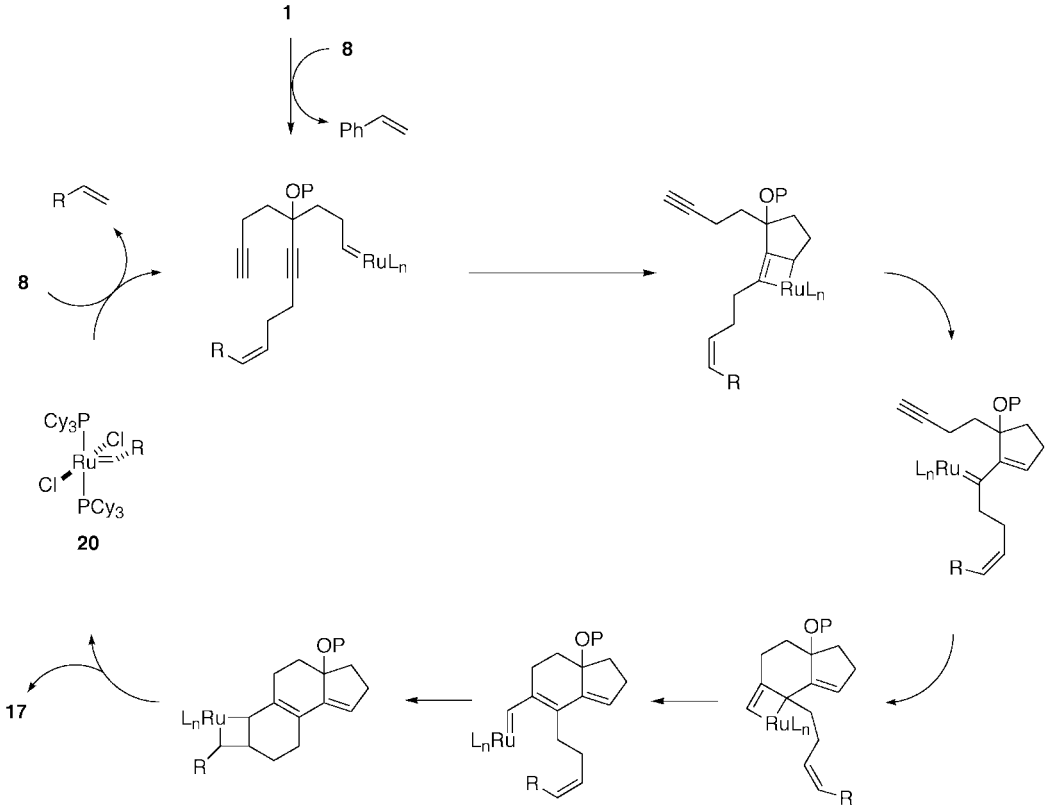
[a] Key: (a) $Pd_2dba_3{\cdot}CHCl_3$, dppe, BSA, THF, 40−100%; (b) CH_3OCOCl, C_5H_5N, CH_2Cl_2, 80−100%; (c) Ts-NHNa, $Pd(PPh_3)_4$, dppe, THF, 60−80%; (d) allyl-NHTs, $Pd_2dba_3{\cdot}CHCl_3$, PPh_3, BSA, THF, 40−88% or allyl-NTsNa, $Pd(PPh_3)_4$, dppe, THF, 72%.

(18) The extra substituent on the disubstituted olefin is employed to increase the relative rate of metathesis at the monosubstituted "productive" olefin. When the reaction is conducted with an acyclic precursor containing two monosubstituted olefins, product formation is observed at a slower rate and to a lesser extent.

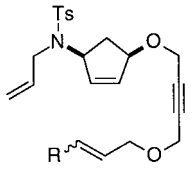
(19) A related process involving carbene−acetylene metathesis, enyne metathesis ring-closure, has been reported utilizing tungsten and ruthenium carbene complexes. (a) Katz, T. J.; Sivavec, T. M. *J. Am. Chem. Soc.* **1985**, *107*, 737. (b) Kinoshita, A.; Mori, M. *Synlett* **1994**, 1020. (c) Kinoshita, A.; Mori, M. *J. Org. Chem.* **1996**, *61*, 8356. Similarly, carbene−acetylene metathesis allows for the recently reported rearrangement−cyclization of triynes to produce aromatics, an example of which is shown. (d) Peters, J. U.; Blechert, S. *Chem. Commun.* **1997**, 1983.



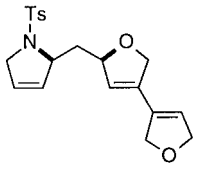
Scheme 5



has been observed previously in cycloolefins metathesis relay reactions, and the problem was ameliorated through alkyl substitution of one of the acyclic olefins of **6a**, thereby slowing the relative rate of the competing side reaction.[7c] This strategy works in the present study as well: when **6b** is exposed to 4 mol % **1**, cyclization proceeds cleanly to a single product, and the tricycle **19** is isolated in 76% yield.

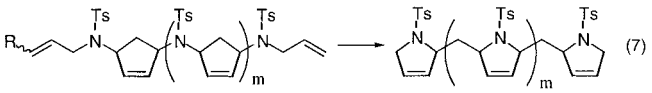


6a: R = H
6b: R = Me



19

Multiple cycloolefinic relays can be used to promote cascades of ring-opening/ring-closing metathesis reactions. Treatment of N-protected polyamines **26**−**29**, bearing one to four cycloolefinic relays, respectively, with catalytic amounts of **1** at ambient or slightly elevated temperatures results in the formation of *N*-protected polycyclic amines **31**−**34** in moderate to good yields (eq 7; Table 2). Similarly, N-protected polyamine **37**, bearing one terminal and one methyl-substituted olefin, is converted to N-protected polycyclic amine **31** in good yield.[20]

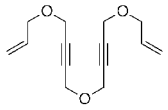
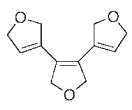
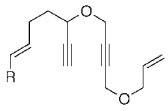
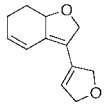
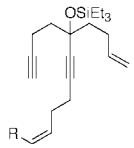
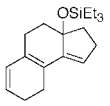
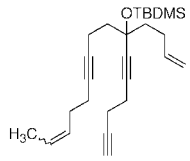
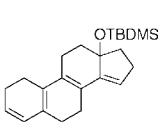


(7)

R = H **26**: m = 0; **27**: m = 1; **28**: m = 2; **29**: m = 3
R = Me **37**: m = 0

31: m = 0; **32**: m = 1; **33**: m = 2; **34**: m = 3
31: m = 0

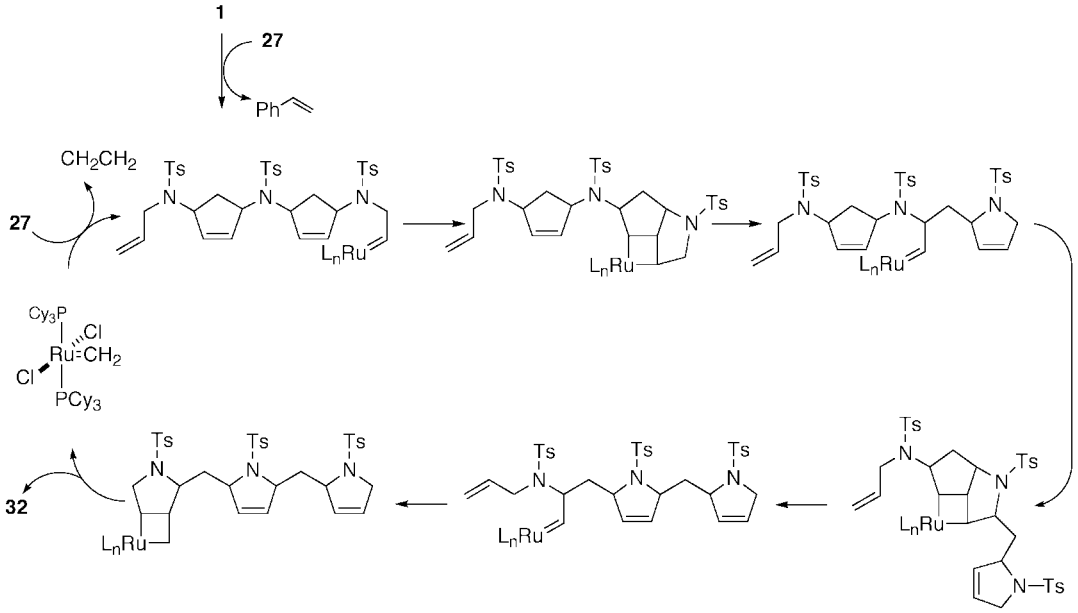
Table 1. Results of Ring-Opening−Ring-Closing Metathesis Reactions

Entry	Precursor	Product	Yield and Conditions
1	 **4**	 **15**	8 mol% **1**, 0.1 M (C_6H_6), 45°C, 4h, 60%
2	 **5** (R = pentyl)	 **16**	5 mol% **1**, 0.05 M (C_6H_6), 40°C, 5h, 79%
3	 **8** (R = pentyl)	 **17**	4 mol% **1**, 0.05 M (C_6H_6), 45°C, 4h, 84%
4	 **14**	 **18**	4 mol% **1**, 0.05 M (C_6H_6), rt, 4h, 70%

The mechanism of these polycyclizations is thought to be similar to the previously described mechanism for the

(20) Although olefin substitution results only in a 4% increase in yield of **31** (Table 2, entries 1 and 2), the workup is greatly simplified due to the absence of difficult to separate impurities.

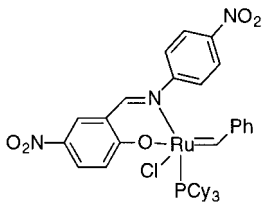
Scheme 6



polycyclization of polyenes bearing acetylenic relays (Scheme 5) and involves an initial formation of a ruthenium alkylidene that undergoes a series of intramolecular metatheses with the cyclopentene relay units prior to termination by a final ring closure. For example, the conversion of **27** to **32** (Scheme 6) presumably begins with metathesis of **1** with the monosubstituted olefin of **27**. The newly formed carbene subsequently undergoes two intramolecular ring-opening/ring-closing metathesis reactions, involving the respective metallacyclobutene intermediates. The cyclization is completed by metathesis of the ruthenium carbene with the monosubstituted olefin to yield product **32** and a propagating methylidene.

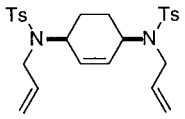
The polycyclization reactions of polyamines containing one to two cyclopentene metathesis relays proceed in good yields (Table 2). However, an increasing number of cyclopentene relays allows for a greater variety of intermolecular side reactions and the yields drop off sharply under the same conditions (Table 2, entry 3). This problem is effectively solved by decreasing reaction concentration and temperature (Table 2, entry 4); this decreases the relative rate of intermolecular side reactions with respect to intramolecular metathesis cyclizations and lowers the rate of catalyst decomposition.

Ruthenium alkylidenes with salen ligands such as **35** have exhibited greater stability than **1** in the RCM of diallyl malonates.[21] Although the cyclizations catalyzed by **35** are generally slower, increased yields of an additional 8−10% for the more challenging substrates (Table 2, entries 5 and 7) are observed.

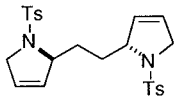


35

In addition to cyclopentenes, cyclohexenes are also effective as metathesis relays in the polycyclizations of N-protected polyamines. At 45 °C, **30** is converted to **36** in 66% yield in a 0.05 M benzene solution.



30



36

It is anticipated that treatment of acyclic N-protected polyamines bearing multiple cyclohexene relays with olefin metathesis catalysts will lead to polycyclic N-protected amines.

Table 2. Results of Ruthenium-Catalyzed Polycyclizations of Acyclic Polyamines (Eq 7) upon Treatment with 5 mol % Catalyst

entry	precursor	catalyst	time (h)	solvent	concn (M)	*T* (°C)	yield (%)
1	26	**1**	1	C_6H_6	0.05	rt	76
2	37	**1**	4	C_6H_6	0.05	rt	80
3	27	**1**	3	C_6H_6	0.05	45	70
4	28	**1**	8	C_6H_6	0.06	45	20
5	28	**1**	8	CH_2Cl_2	0.003	rt	50
6	28	**35**	24	CH_2Cl_2	0.003	40	60
7	29	**1**	48	CH_2Cl_2	0.003	rt	51
8	29	**35**	48	CH_2Cl_2	0.003	40	59

Conclusions

We have presented an efficient, catalytic method for the production of polycyclic molecules from acyclic precursors. The reaction proceeds through a cascade of metathesis steps with either acetylenic or cycloalkenyl relay units. A variety of structural types are accessible depending on the topology of the precursor and relay unit employed. The use of more and varied metathesis relays as well as the further functionalization of the resulting cyclolefin systems are currently under investigation.

Experimental Section

General Methods. High-resolution mass spectra were provided by the Southern California Mass Spectrometry Facility (University of California at Riverside). Analytical thin-

(21) Chang, S.; Jones, L., II; Wang, C.; Henling, L. M.; Grubbs, R. H.; *Organometallics* **1997**, submitted for publication.

layer chromatography (TLC) was performed using silica gel 60 F254 precoated plates (0.25 mm thickness) with a fluorescent indicator. Visualization was accomplished with one or more of the following: UV light, $KMnO_4$, phosphomolybdic acid (PMA), cerric ammonium nitrate (CAN), or *p*-anisaldehyde solution followed by heating. Flash chromatography was performed using silica gel 60 (230−400 mesh) from EM Science.[22]

All reactions were carried out under an inert atmosphere in oven-dried glassware unless otherwise specified. Catalyst **1** was prepared according to published procedure and is commercially available.[10a] Catalyst **35** was prepared according to the published procedure and was generously provided by Dr. Sukbok Chang.[21] Solvents were purified by passage through a column containing A-5 alumina (all solvents) followed by a column containing Q-5 reactant (nonethereal solvents). Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves (Linde). Allyl bromide was purchased from ARCOS. All other reagents were purchased from the Aldrich Chemical Co. Cyclopentadiene monoepoxide was prepared following the published procedure.[23]

4,9,16-Trioxa-1,16-heptadecadiene-6,11-diyne (4): ^{1}H NMR (C_6D_6, 300 MHz) δ 5.74−5.63 (m, 1H), 5.18−5.10 (m, 1H), 4.96−4.91 (m, 1H), 4.04 (t, J = 1.8 Hz, 2H), 3.86 (t, J = 1.8 Hz, 2H), 3.81−3.78 (m, 2H); ^{13}C NMR (C_6D_6, 100 MHz) δ 134.7, 116.8, 83.1, 81.6, 70.0, 56.8, 56.1; IR (neat, cm^{-1}) 3080, 3015, 2982, 2943, 2854, 1074; HRMS calcd for $C_{14}H_{18}O_3$ (MNH_4^+) 252.1600, found 252.1599.

(*E*)-10-Ethynyl-4,9-dioxa-1,13-nonadecadien-6-yne (5): ^{1}H NMR (C_6D_6, 300 MHz) δ 5.96−5.83 (m, 1H), 5.48−5.19 (m, 4H), 4.31 (m, 3H), 4.19 (t, J = 1.2 Hz, 2H), 4.05 (dt, J = 5.8, 1.3 Hz, 2H) 2.45 (d, J = 2.1 Hz, 1H), 2.15 (q, J = 7.2 Hz, 2H), 1.96 (q, J = 6.6 Hz, 2H), 1.84 (m, 2H), 1.35−1.23 (m, 6H), 0.87 (t, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 133.9, 131.6, 128.5, 117.9, 82.3, 82.0, 81.9, 74.4, 70.6, 67.4, 57.4, 56.0, 35.2, 32.5, 31.3, 29.2, 28.1, 22.5, 14.1; IR (neat, cm^{-1}) 3304, 3080, 3017, 2954, 2925, 2854, 2112, 1071; HRMS calcd for $C_{19}H_{27}O_2$ ([M − H]$^+$) 287.2011, found 287.1999.

Compound 6a: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.70 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 5.99−5.76 (m, 3H), 5.62−5.59 (m, 1H), 5.32−5.07 (m, 4H), 4.97−4.93 (m, 1H), 4.46−4.42 (m, 1H), 4.15−4.12 (m, 4H), 4.03−4.00 (m, 2H), 3.72−3.54 (m, 2H), 2.43 (dt, J = 14.7, 8.0 Hz, 1H), 2.41 (s, 3H), 1.38 (dt, J = 14.4, 4.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.2, 137.3, 135.9, 134.3, 134.2, 133.8, 129.6, 127.2, 117, 9, 116.9, 82.2, 80.9, 70.6, 61.7, 57.3, 56.6, 45.6, 34.9, 21.5; IR (neat, cm^{-1}) 3078, 3020, 2980, 2922, 2854, 1645, 1088; HRMS calcd for $C_{22}H_{31}N_2O_4S$ (MNH_4^+) 419.2004, found 419.2004.

Compound 6b trans isomer (major): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.70 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 5.97 (dt, J = 5.5, 2.2 Hz, 1H), 5.87−5.50 (m, 3H), 5.22−5.07 (m, 4H), 4.96−4.93 (m, 1H), 4.46−4.43 (m, 1H), 4.16−4.07 (m, 4H), 3.95−3.93 (m, 2H), 3.73−3.56 (m, 2H), 2.40 (s, 3H), 1.71−1.64 (m, 3H), 1.42−1.36 (dt, J = 14.3, 4.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.3, 137.6, 136.1, 134.5, 134.3, 130.7, 129.7, 127.3, 126.8, 117.1, 82.2, 81.0, 70.5, 65.0, 61.9, 57.1, 56.7, 45.7, 35.2, 21.6, 17.8; IR (neat, cm^{-1}) 2939, 2854, 2359, 1340, 1160, 1091; HRMS calcd for $C_{23}H_{30}NO_4S$ (MH$^+$) 416.1912, found 416.1905.

(*Z*)-5-(3-Butynyl)-5-[(triethylsilyl)oxy]-1,10-hexadecadien-6-yne (8): ^{1}H NMR (C_6D_6, 300 MHz) δ 5.85−5.72 (m, 1H), 5.54−5.38 (m, 2H), 5.06 (dd, J = 17.1, 1.6 Hz, 1H), 4.96 (dd, J = 10.0, 0.7 Hz, 1H), 2.54−2.47 (m, 2H), 2.30−2.23 (m, 2H), 2.15−1.93 (m, 8H), 1.79−1.72 (m, 3H), 1.29−1.23 (m, 6H), 1.04 (t, J = 7.9 Hz, 9H), 0.89 (t, J = 6.9, 3H), 0.76 (q, J = 7.9 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 138.56, 131.43, 127.65, 114.27, 85.50, 84.85, 82.67, 71.15, 67.79, 42.01, 41.56, 31.50, 29.31, 28.80, 27.28, 26.40, 22.56, 19.14, 14.08, 13.90, 7.09, 6.11; IR (neat, cm^{-1}) 3313, 3078, 3007, 2956, 2875, 2236, 2121, 1642, 1090; HRMS calcd for $C_{26}H_{45}OSi$ (MH$^+$) 401.3240, found 401.3247.

Compound 14: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.89−5.76 (m, 1H), 5.55−5.40 (m, 2H), 5.01 (dd, J = 17.2, 1.8 Hz, 1H), 4.93 (dd, J = 10.0, 1.8 Hz, 1H), 2.45−2.14 (m, 12H), 2.01 (t, J = 2.4 Hz, 1H), 1.84−1.77 (m, 3H), 1.69−1.61 (m, 4H), 0.85 (s, 9H), 0.14 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 138.7, 129.8, 129.0, 125.9, 125.0, 114.2, 83.9, 83.8, 82.6, 80.3, 79.5, 71.4, 69.4, 42.4, 42.2, 32.3, 28.8, 26.7, 25.8, 19.0, 18.8, 18.6, 18.2, 14.2, 12.8, −2.9; IR (neat, cm^{-1}) 3311, 3078, 3015, 2928, 2856, 2236, 2122, 1641, 1254, 1090; HRMS calcd for $C_{26}H_{40}OSi$ (MH$^+$) 397.2927, found 397.2912.

3,4-Bis(2,5-dihydrofuran-3-yl)-2,5-dihydrofuran (15): ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 5.78 (s, 2H), 4.74 (s, 4H), 4.65 (s, 8H); ^{13}C NMR (CD_2Cl_2, 100 MHz) δ 132.2 (s), 128.1 (s), 125.9 (d, J = 179 Hz), 78.2 (t, J = 147 Hz), 75.6 (t, J = 147 Hz), 75.5 (t, J = 147 Hz); IR (neat, cm^{-1}) 3076, 2846, 1078, 1064; HRMS calcd for $C_{12}H_{14}O_3$ (M$^+$) 206.0943, found 206.0937.

3-(2,5-Dihydrofuran-3-yl)-1,6,7,8-tetrahydrobenzofuran (16). To a stirring solution of **5** (305 mg, 1.1 mmol) in benzene (20 mL, 0.05 M) was added **1** (36 mg, 44 μmol, 0.04 equiv). The reaction was stirred at 45 °C until complete consumption of the starting material was observed by TLC (product R_f = 0.2; 10% EtOAc in hexanes), about 4 h. The solvent was removed under reduced pressure, and the remaining colored oil was purified by flash chromatography (10% EtOAc in hexanes) to yield the product **17** as a clear, light yellow oil (158 mg, 79%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.18 (dt, J = 9.9, 2.0 Hz, 1H), 6.00−5.90 (m, 1H), 5.64 (t, J = 2.0 Hz), 4.68−4.28 (m, 2H), 4.78−4.67 (m, 5H), 2.32−2.18 (m, 3H), 1.70−1.59 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 134.2, 133.6, 132.5, 123.0, 121.0, 120.2, 84.3, 75.3, 75.2, 75.1, 29.9, 25.1; IR (neat, cm^{-1}) 3033, 2942, 2840, 1099, 1086; HRMS calcd for $C_{12}H_{14}O_2$ (M$^+$) 190.0994, found 190.0985.

10-[(Triethylsilyl)oxy]tricyclo[8.3.0.0^{1,10}]trideca-1(13),-2(7),5-triene (17). To a stirring solution of **1** (9.9 mg, 12 μmol, 0.04 equiv) in benzene (10 mL, 0.05 M) was added **8** (199 mg, 0.50 mmol). The reaction was stirred at 45 °C until complete consumption of starting material was observed by TLC (product R_f = 0.3; 2% Et_2O in hexanes), about 4 h. The solvent was removed under reduced pressure, and the remaining dark oil was purified by flash chromatography (2% Et_2O in hexanes) to yield the product **17** as a clear, light yellow oil (126 mg, 84%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.84−5.82 (m, 2H), 5.60 (s, 1H), 2.68−2.51 (m, 4H), 2.39−1.78 (m, 6H), 1.57−1.45 (m, 2H), 0.88 (t, J = 7.9 Hz, 9H), 0.49 (q, J = 7.9, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.10, 130.32, 128.54, 126.45, 123.58, 123.48, 82.94, 39.44, 37.05, 30.33, 27.03, 23.10, 22.99, 7.18, 6.06; IR (neat, cm^{-1}) 3028, 2953, 2875, 1622, 1080; HRMS calcd for $C_{19}H_{30}OSi$ (M$^+$) 302.2066, found 302.2051.

Compound (18): To a stirring solution of **14** (42 mg, 0.1 mmol) in C_6H_6 (2 mL, 0.05 M) was added **1** (3.5 mg, 4 μmol, 0.04 equiv). After the mixture was stirred for 4 h at room temperature, **14** was not detectable by TLC (product R_f = 0.5; 1% NEt_3 in hexanes), and the reaction mixture was purified by flash chromatography (1% NEt_3 in hexanes elution). The product **18** was isolated as a viscous, light yellow oil: 26 mg, 70%; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.95−5.91 (m, 1H), 5.75−5.69 (m, 1H), 5.46 (s, 1H), 2.64−2.53 (m, 2H), 2.40−2.34 (m, 2H), 2.21−2.02 (m, 4H), 1.82−1.71 (m, 1H), 1.52−1.42 (m, 1H), 0.99 (s, 9H), 0.09 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (C_6D_6, 100 MHz) δ 145.0, 132.6, 128.5, 125.3, 124.3, 124.0, 82.9, 46.8, 39.7, 37.1, 30.6, 27.7, 26.2, 25.9, 24.1, 23.8, 18.7, 14.2, 12.5, −2.7, −3.1; IR (neat, cm^{-1}) 3037, 2954, 2929, 2855, 1634, 1472, 1252, 1076.

Compound 19: ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 7.66 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 5.73−5.57 (m, 4H), 5.03−4.93 (m, 1H), 4.82−4.67 (m, 6H), 4.52−4.46 (m, 1H), 4.16−4.01 (m, 2H), 2.41 (s, 3H), 2.21−2.13 (m, 1H), 2.00−1.90 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.7, 132.2, 132.0, 130.1, 129.8, 127.4, 126.4, 124.2, 123.4, 84.0, 76.2, 75.0, 74.5, 64.7, 55.5, 42.3, 21.2; IR (neat, cm^{-1}) 2847, 1597, 1470, 1162, 1088; HRMS calcd for $C_{20}H_{24}NO_4S$ (MH$^+$) 374.1426, found 374.1423.

(22) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
(23) Korach, M.; Nielsen, D. R.; Rideout, W. H. *J. Am. Chem. Soc.* **1960**, *82*, 4328.

General Procedure for the Formation of Aminocyclopentenyl Alcohols (Scheme 4a). To a stirring solution of palladium dibenzylidene acetone adduct (21 mg, 0.02 mmol, 0.02 equiv) in THF (1 mL, 0.02 M) was added (diphenylphosphino)ethane (32 mg, 0.08 mmol, 0.08 equiv). The resulting deep violet mixture was stirred for several minutes at room temperature until its color changed to yellow. To this reaction mixture was added **22** (447 mg, 1.0 mmol, 1 equiv) in THF (1 mL, 1 M). The resulting mixture was cooled to 0 °C and treated with *N*,*O*-bis(trimethylsilyl)acetamide (305 mg, 1.5 mmol, 1.5 equiv). The reaction mixture was allowed to stir for 20 min, after which time cyclopentadiene monoxide (123 mg, 1.5 mmol, 1.5 equiv) was added dropwise over a period of 1 h. The temperature was kept at 0 °C for an additional hour, after which it was allowed to warm to room temperature and stirred overnight. The solvent was removed under reduced pressure. The remaining, dark brown residue was redissolved in Et_2O (10 mL) and hydrolyzed with 4 N aqueous HCl (5 mL) until complete disappearance of the initial reaction product, TMS-protected alcohol, was observed by TLC ($R_f = 0.6$, 30% EtOAc in hexanes). The organic phase was separated, and the aqueous phase was extracted twice with Et_2O (10 mL). The organic phases were combined and dried over $MgSO_4$, and the solvent was removed under reduced pressure. The free alcohol **23** (400 mg, 76%) was isolated by flash chromatography as a clear colorless oil.

General Procedure for the Formation of Aminocyclopentenyl Carbonates (Scheme 4b). To a stirring solution of **23** (11.0 g, 37.5 mmol) in CH_2Cl_2 (300 mL, 0.125 M) were slowly added at 0 °C methyl chloroformate (17.8 g, 188 mmol, 5 equiv) and pyridine (5.93 g, 75 mmol, 2 equiv). The reaction mixture was stirred at room temperature until complete consumption of starting material was observed by TLC (product $R_f = 0.4$, 30% EtOAc in hexanes). The reaction mixture was washed twice with water (100 mL), dried over $MgSO_4$, and filtered, and the solvent was removed under reduced pressure. Flash chromatography afforded **24** as a yellow oil (13.4 g, 100%).

General Procedure for the Formation of Aminocyclopentenyl *p*-Toluenesulfonamides (Scheme 4c). To a stirring solution of **24** (8.5 g, 24.4 mmol, 1.0 equiv) in THF (120 mL, 0.2M) were added sodium *p*-toluenesulfonamide (4.17 g, 24.4 mmol, 1 equiv), $Pd(PPh_3)_4$ (2.26 g, 1.95 mmol, 0.08 equiv), and (diphenylphosphino)ethane (777 mg, 1.95 mmol, 0.08 equiv). The resulting reaction mixture was stirred overnight. The solvent was removed under reduced pressure, and the remaining dark residue was purified by flash chromatography to afford **25**, as a yellow solid (8.6 g, 79%).

General Procedure for the Formation of Aminocyclopentenyl *N*-Allyl-*p*-toluenesulfonamides (Scheme 4d). To a stirring solution of palladium dibenzylidene acetone adduct (43 mg, 42 μmol, 0.08 equiv) in THF (2 mL, 0.02 M) was added triphenylphosphine (27 mg, 104 μmol, 0.2 equiv). The resulting yellow-brown mixture was stirred at room temperature for 20 min. To this reaction mixture was added *N*-allyl-*p*-toluenesulfonamide (115 mg, 546 μmol, 1.05 equiv). The resulting mixture was cooled to 0 °C and treated with *N*,*O*-bis(trimethylsilyl)acetamide (212 mg, 1.04 mmol, 2 equiv) for 20 min, after which time **24** (300 mg, 520 μmol, 1.0 equiv) in THF (2.5 mL, 0.21 M) was added dropwise over a period of 1 h. The temperature was kept at 0 °C for an additional hour, after which the reaction mixture was allowed to warm to room temperature and stirred overnight. The solvent was removed under reduced pressure. Compound **27** (300 mg, 80%) was isolated by flash chromatography as a yellow solid.

Typical Procedure for the Metathesis Reaction of 26 (Eq 7). To a stirring solution of **26** (200 mg, 0.41 mol) in benzene (8 mL, 0.05M) was added **1** (17 mg, 21 μm, 0.05 equiv). The reaction mixture was stirred at 45 °C for 1 h, at which time complete consumption of the starting material was observed by TLC (product $R_f = 0.3$; 30% EtOAc in hexanes). The solvent was removed under reduced pressure. The remaining dark oil was redissolved in 1 mL of benzene and treated with concentrated H_2SO_4 (1 mL) and 0.1 mL of H_2O (0.1 mL) until TLC of the organic phase indicates disappearance of the product. The reaction mixture was diluted with H_2O (10 mL) and benzene (10 mL), cooled to 0 °C, and carefully made basic with KOH. The liquid phases were separated, and the aqueous phase was extracted twice with CH_2Cl_2 (10 mL). All organic phases were combined, dried over $MgSO_4$, and filtered, and the solvent was removed under reduced pressure. The resulting oil was purified by flash chromatography (20% EtOAc in hexanes) to yield **31** as a white solid (135 mg, 72%).

Typical Procedure for the Metathesis Reaction of 37 (Eq 7). To a stirring solution of **37** (500 mg, 1.0 mmol) in C_6H_6 (20 mL, 0.05 M) was added **1** (41 mg, 0.05 mmol, 0.05 equiv). The reaction mixture was stirred at rt for 4 h, at which time complete consumption of the starting material was observed by TLC. The reaction mixture was purified by flash chromatography (20% EtOAc in hexanes) to yield **31** as a white solid (365 mg, 80%).

General Procedure for the Metathesis Reactions of 27−29 (Eq 7). To a stirring solution of **29** (45 mg, 38 μmol) in CH_2Cl_2 (12.5 mL, 0.003 M) was added **35** (1.7 mg, 1.89 μmol, 0.05 equiv). The reaction mixture was stirred at 40 °C for 24 h, at which time complete consumption of the starting material was observed by TLC (product $R_f = 0.4$; 40% EtOAc in hexanes). The solvent was removed under reduced pressure. The remaining residue was purified by flash chromatography (20% EtOAc in hexanes) to yield **34** as a white solid (26 mg, 59%).

Compound 26: ^{1}H NMR (C_6D_6, 300 MHz) δ 7.65 (d, J = 8.2 Hz, 4H), 6.74 (d, J = 8.2 Hz, 4H), 5.80−5.67 (m, 2H), 5.19 (s, 2H), 5.10 (dd, J = 17.2, 1.4 Hz, 2H), 4.84 (dd, J = 10.2, 1.4 Hz, 2H), 4.78 (app t, J = 8.1 Hz, 2H), 3.56−3.52 (m, 4H), 2.19 (app dt, J = 13.4, 8.1 Hz, 1H), 1.88 (s, 6H), 1.44 (app dt, J = 13.4, 8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.5, 137.6, 135.8, 133.9, 129.8, 127.2, 117.1, 61.6, 46.6, 34.4, 21.5; IR (neat, cm^{-1}) 2921, 1598, 1335, 1158, 1091; HRMS calcd for $C_{25}H_{31}N_2O_4S_2$ (MH^+) 487.1725, found 487.1730.

Compound 27, two isomers: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.71−7.55 (m, 6H), 7.33−7.22 (m, 6H), 5.92−5.74 (m, 2H), 5.63−5.44 (m, 4H), 5.24−5.03 (m, 4H), 4.87−4.74 (m, 2H), 4.38−4.22 (m, 2H), 3.90−3.66 (m, 4H), 2.41−2.31 (m, 11H), 1.88−1.73 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.5, 143.4, 138.9, 137.7, 136.2, 134.6, 134.1, 133.1, 132.7, 129.8, 129.8, 127.2, 127.2, 127.1, 117.0, 116.9, 61.9, 61.8, 60.9, 60.7, 46.6, 46.6, 36.5, 36.1, 21.5; IR (neat, cm^{-1}) 3065, 2954, 1598, 1340, 1158, 1091; HRMS calcd for $C_{37}H_{43}N_3O_6S_3Na$ (MNa^+) 744.2212, found 744.2245.

Compound 28, three isomers: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.67−7.56 (m, 8H), 7.36−7.18 (m, 8H), 5.89−5.74 (m, 2H), 5.72−5.60 (m, 2H), 5.58−5.48 (m, 2H), 5.45−5.38 (m, 2H), 5.23−5.00 (m, 4H) 4.88−4.76 (m, 2H), 4.47−4.31 (m, 4H), 3.89−3.71 (m, 4H), 2.55−2.34 (m, 15H), 2.00−1.83 (m, 3H); IR (neat, cm^{-1}) 2923, 1597, 1331, 1155, 1085; HRMS calcd for $C_{49}H_{56}N_4O_8S_4Na$ (MNa^+) 979.2879, found 979.2915.

Compound 29, four isomers: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.68−7.58 (m, 10H), 7.31−7.23 (m, 10H), 5.92−5.53 (m, 8H), 5.45−5.40 (m, 2H), 5.25−5.04 (m, 4H), 4.88−4.78 (m, 2H), 4.51−4.37 (m, 6H), 3.90−3.72 (m, 4H), 2.58−2.43 (m, 19H), 2.12−1.84 (m, 4H); IR (neat, cm^{-1}) 3063, 2955, 1598, 1332, 1157, 1092; LRMS calcd for $C_{61}H_{70}N_5O_{10}S_5$ (MH^+) 1192, found 1192.

Compound 30: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.66 (d, J = 8.1 Hz, 4H), 7.26 (d, J = 8.1, 4H), 5.85−5.72 (m, 2H), 5.35 (s, 2H), 5.20−5.06 (m, 4H), 4.29 (s, 2H), 3.90−3.83 (dd, J = 16.9, 5.4 Hz, 2H), 3.69−3.61 (dd, J = 16.9, 5.8 Hz, 2H), 2.40 (s, 6H), 1.73−1.71 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.3, 138.1, 136.0, 131.9, 129.8, 127.1, 116.9, 52.3, 47.5, 25.8, 21.5; IR (neat, cm^{-1}) 3028, 2923, 1598, 1337, 1163, 1090; HRMS calcd for $C_{26}H_{33}N_2O_4S_2$ (MH^+) 501.1882, found 501.1889.

Compound 31: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.70 (d, J = 8.3 Hz, 4H), 7.31 (d, J = 8.3 Hz, 4H), 5.86−5.81 (m, 2H), 5.64−5.61 (m, 2H), 4.61−4.54 (m, 2H), 4.19−4.04 (m, 4H), 2.47−2.40 (m, 7H), 2.17−2.07 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.6, 134.3, 130.5, 129.8, 127.6, 24.6, 64.7, 55.4, 42.6, 21.5; IR (neat, cm^{-1}) 3066, 2918, 2861, 1596, 1340, 1163, 1095; HRMS calcd for $C_{23}H_{27}N_2O_4S_2$ (MH^+) 459.1412, found 459.1404.

Compound 32, two isomers: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.70−7.65 (m, 6H), 7.29−7.27 (m, 6H), 6.09 (s, 2H), 5.62−5.56 (m, 4H), 4.72 (d, J = 8.8 Hz, 2H), 4.56−4.48 (m, 2H), 4.14−4.02 (m, 4H), 2.69−2.64 (m, 2H), 2.40−2.37 (m, 9H), 1.95−1.88 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.7, 142.9, 139.4, 134.4, 130.5, 129.8, 129.7, 129.6, 127.6, 126.8, 125.0, 65.0, 64.7, 55.4, 40.1, 21.6, 21.5; IR (neat, cm^{-1}) 2923, 1597, 1340, 1161, 1093; HRMS calcd for $C_{35}H_{40}N_3O_6S_3$ (MH^+) 694.2079, found 694.2068.

Compound 33, three isomers: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.73−7.64 (m, 8H), 7.30−7.26 (m, 8H), 6.15−6.03 (m, 2H), 5.84−5.71 (m, 2H), 5.62−5.57 (m, 4H), 4.82−4.37 (m, 6H), 4.17−4.04 (m, 4H), 2.95−2.91, 2.72−2.54 (m, 3H), 2.44−2.28 (m, 12H), 2.11−1.85 (m, 3H); IR (neat, cm^{-1}) 3066, 2923, 2869, 1598, 1339, 1162, 1099; HRMS calcd for $C_{47}H_{53}N_4O_8S_4$ (MH^+) 929.2746, found 929.2747.

Compound 34, four isomers: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.77−7.62 (m, 10H), 7.34−7.26 (m, 10H), 6.18−6.12 (m, 2H), 5.92−5.55 (m, 8H), 4.85−4.36 (m, 8H), 4.17−4.03 (m, 4H), 2.96−2.92, 2.71−2.51, 2.40−2.63 (m, 19H), 2.12−1.81 (m, 4H); IR (neat, cm^{-1}) 2922, 1598, 1338, 1162, 1092; HRMS calcd for $C_{59}H_{66}N_5O_{10}S_5$ (MH^+) 1164.3413, found 1164.3467.

Compound 36: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.69 (d, J = 8.3 Hz, 4H), 7.29 (d, J = 8.3, 4H), 5.63−5.54 (m, 4H), 4.54 (s, 2H), 4.18−4.03 (m, 4H), 2.40 (s, 6H), 1.83−1.82 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.4, 134.7, 129.8, 129.7, 127.5, 125.0, 67.1, 56.0, 30.0, 21.5; IR (neat, cm^{-1}) 2911, 2859, 1592, 1330, 1157, 1089, 1047; HRMS calcd for $C_{24}H_{29}N_2O_4S_2$ (MH^+) 473.1569, found 473.1570.

Compound 37, trans isomer (major): ^{1}H NMR (C_6D_6, 300 MHz) δ 7.62 (app t, J = 6.6 Hz, 4H), 7.26 (d, J = 6.6 Hz, 2H), 7.24 (d, J = 6.6 Hz, 2H), 5.78−5.71 (m, 1H), 5.52−5.28 (m, 4H), 5.14−5.04 (m, 2H), 4.76−4.72 (m, 1H), 3.70−3.51 (m, 4H), 2.39 (s, 3H), 2.38 (s, 3H), 2.29 (dt, J = 10.0, 6.2 Hz, 1H), 1.57 (dd, J = 4.9, 1.1 Hz, 3H), 1.46 (dt, J = 10.0, 6.2, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.5, 143.3, 137.8, 137.5, 135.8, 134.2, 133.5, 129.8, 129.7, 128.5, 128.4, 127.2, 127.1, 117.1, 61.5, 61.5, 46.5,46.4, 34.5, 21.6, 21.5, 17.6; IR (neat, cm^{-1}) 2922, 1594, 1440, 1379, 1331, 1156, 1085; HRMS calcd for $C_{26}H_{36}N_3O_4S_2$ (MNH_4^+) 518.7145, found 518.7145.

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Supporting Information Available: ^{1}H NMR of all new compounds prepared in this study (20 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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