Steric effects in the thermal C^2-C^6 diradical cyclization of enyne-allenes

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This manuscript is dedicated to Professor Waldemar Adam on the occasion of his 70th birthday for his inspiring research in chemistry

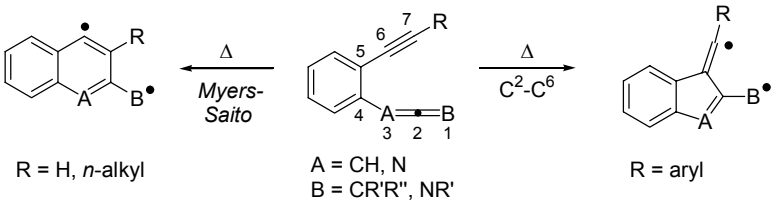
Abstract
The thermal reaction of enyne-allenes **1** carrying bulky substituents (*tert*-butyl, trimethylsilyl, triisopropylsilyl) at the acetylene terminus uniquely leads to C^2-C^6 cyclization products in high yields independent of other structural motifs at the enyne-allene (*e.g.* benzannulation, substituents at allene). The thermal cyclization can also be set up in a continous process, the latter protocol explored with a Cellular Process Chemistry (CPC) reactor. Bulky groups (*e.g.* *t*Bu, TMS, TIPS) at the alkyne terminus stabilize the enyne-allene against cyclization, while the exchange of a hydrogen by a methyl group at the inner locus of the allene unit destabilizes the enyne-allene. DFT calculations at B3LYP/6-311G** level suggest that the observed acceleration is mostly brought about by increasing the equilibrium amount of the reactive *s-cis* conformer.

Keywords: Enyne-allenes, diradical, cyclization, sterics

Introduction

Cycloaromatizations of enediynes[1,2] (*Bergman* cyclization) and enyne-allenes[3,4] (*Myers-Saito* cyclization) have aroused large interest over the last two decades because the intermediate diradicals constitute key intermediates in the *mode of action* of natural enediyne antitumor antibiotics.[5,6] However, while the above cyclizations furnish aromatic diradicals *via* in-plane aromatic transition states[7,8] the C^2-C^6 cyclization of enyne-allenes,[9-12] sometimes denoted as *Schmittel* cyclization,[13-20] leads to a fulvene diradical intermediate (Scheme 1). Our initial studies showed that the proper choice of aryl substituents at the alkyne terminus allowed steering of the

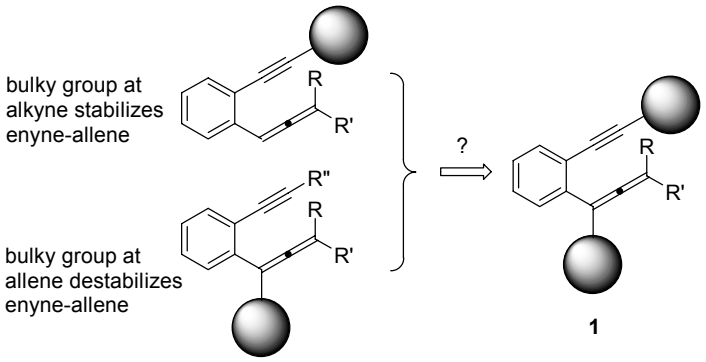
regioselectivity of thermal enyne-allene diradical cyclizations away from the *Myers-Saito* towards the C^2-C^6 pathway.[9-12] Analogous regiocontrol of the thermal diradical cyclizations of enyne-carbodiimids[21-23] and enyne-ketenimines[24,25] was realized only little later.



Scheme 1. The *Myers-Saito* and C^2-C^6 cyclizations as competing pathways.

Compared to other thermal diradical cycloaromatizations, the C^2–C^6 cyclization proceeds in rather high yields, which can be ascribed to very efficient intramolecular follow-up reactions of the intermediate benzofulvene diradical[9-12] either to formal ene or formal Diels–Alder type products. In some cases, the mechanism of the C^2–C^6 cyclization may even shift from a stepwise to a concerted protocol.[26] Clearly, the trapping of the benzofulvene diradical by external reagents remains synthetically rather unsatisfying.[12] As the C^2-C^6 cyclization has recently moved into the focus of DNA cleavage[27,28] and synthetic studies (*e.g.* towards kinamycins,[29] neocryptolepines[30] and complex hydrocarbon frameworks[19,31-33]), it seemed to be important to study more closely factors that allow to steer the regioselectivity of the thermal diradical cyclization.

Over the last few years theoretical investigations[8,12,14,16-18,34] have largely contributed to our understanding of the switch from the *Myers-Saito* to the C^2–C^6 cyclization and of the character of the fulvene diradical intermediate. Substituent effects (aryl substituents at the acetylene,[12] ring size and ring strain,[14,35-37] benzannulation,[16] oxy-anion substitution[15,17]) on the kinetics and the thermodynamics and character of the diradical have been elucidated. In contrast, steric effects exerted by bulky substituents at the alkyne terminus or at the allene have received less attention although the first experimental observations go back several years.[27] A recent study on oxyanion-accelerated cyclization of *tert*-butyl and silyl substituted enyne-allenes[15] unfortunately is less informative in this respect because the cyclization does not involve diradical but closed–shell zwitterionic intermediates.[17] Stimulated by our earlier results[27a] and a recent theoretical investigation by Engels *et al.*[38] we have prepared a series of enyne-allenes to probe the effect of steric bulk on the regioselectivity of cyclization.

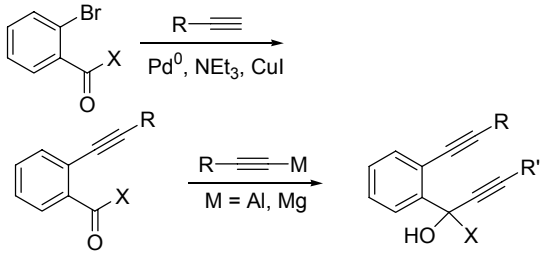


Scheme 2. Steric effects in enyne-allenes on the thermal stability of enyne-allenes.

Herein, we would like to detail our findings that bulky substituents at the alkyne terminus and at the inner allene locus[9] can be used to change dramatically the temperature for diradical cyclization. Whereas bulky groups at the alkyne terminus thermally stabilize the enyne-allene, the simple exchange of a H for a methyl group at the inner locus of the allene unit leads to de-stabilization. In addition, we also wanted to check which one of these two counter-running effects would dominate in controlling the thermal stability of enyne-allenes.

Results

Synthesis of enyne-allenes. So called „masked" enyne-allenes, in which the ene substructure is part of an aromatic system,[39] were readily available in a three or four step synthesis. For example Sonogashira couplings with *o*-bromobenzaldehyde or *o*-bromoacetophenone[40] afforded compounds **2-5** that were further reacted with an additional acetylide, either *n*BuC≡CMgBr or $(PhC{\equiv}C)_2AlH_2Na$,[41] to furnish the resultant propargyl alcohols **6a-h**.

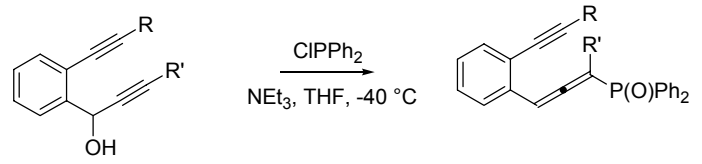


2: R = $SiMe_3$, X = H (87%)
3: R = *t*Bu, X = H (84%)
4: R = Si(*i*Pr)$_3$, X = H (95%)
5: R = Si(*i*Pr)$_3$, X = Me (64%)

6a: R = $SiMe_3$, R' = *n*Bu, X = H (98%)
6b: R = *t*Bu, R' = *n*Bu, X = H (83%)
6c: R = *t*Bu, R' = Ph, X = H (67%)
6e: R = Si(*i*Pr)$_3$, R' = *n*Bu, X = H (99%)
6f: R = Si(*i*Pr)$_3$, R' = Ph, X = H (97%)
6g: R = Si(*i*Pr)$_3$, R' = *n*Bu, X = Me (86%)
6h: R = Si(*i*Pr)$_3$, R' = Ph, X = Me (73%)

Scheme 3. Preparation of propargyl alcohols **6a-h.**

Propargyl alcohols **6a-c** were treated with $ClPPh_2$ to provide the diphenylphosphine oxide substituted enyne-allenes **1a-c** after a 2,3-sigmatropic rearrangement.

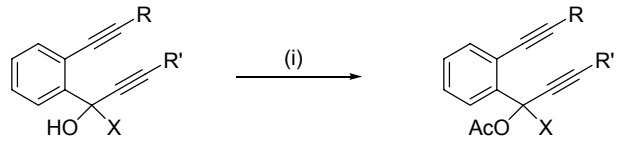


6a: R = $SiMe_3$, R' = *n*Bu
6b: R = *t*Bu, R' = *n*Bu
6c: R = *t*Bu, R' = Ph

1a: R = $SiMe_3$, R' = *n*Bu (85%)
1b: R = *t*Bu, R' = *n*Bu (80%)
1c: R = *t*Bu, R' = Ph (42%)

Scheme 4. Rearrangement of propargyl alcohols with $ClPPh_2$ to yield enyne-allenes **1a-c**.

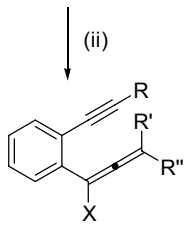
Enyne-allenes **1d-i** were obtained in a different manner. Propargyl alcohols **6b,e-h** were first treated with acetic anhydride in presence of DMAP and NEt_3 to furnish the propargyl acetates **7d-h** that were subsequently reacted with arylzinc or alkylzinc chloride in the presence of palladium(0)[27b,42] to yield enyne-allenes **1d-i** in moderate yields.



6b: R = *t*Bu, R' = *n*Bu, X = H

6e: R = Si(*i*Pr)$_3$, R' = *n*Bu, X = H
6f: R = Si(*i*Pr)$_3$, R' = Ph, X = H
6g: R = Si(*i*Pr)$_3$, R' = *n*Bu, X = Me
6h: R = Si(*i*Pr)$_3$, R' = Ph, X = Me

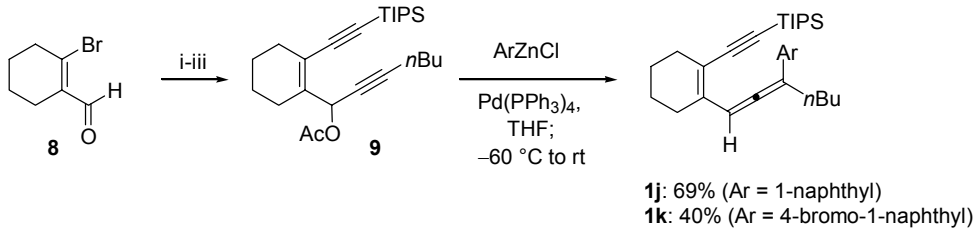
7d: R = *t*Bu, R' = nBu, X = H (97%)
7e: R = Si(*i*Pr)$_3$, R' = *n*Bu, X = H (69%)
7f: R = Si(*i*Pr)$_3$, R' = Ph, X = H (70%)
7g: R = Si(*i*Pr)$_3$, R' = *n*Bu, X = Me (71%)
7h: R = Si(*i*Pr)$_3$, R' = Ph, X = Me (65%)



1d: R = *t*Bu, R' = *n*Bu, R'' = *p*An, X = H (45%)
1e: R = Si(*i*Pr)$_3$, R' = *n*Bu, R'' = Ph, X = H (70%)
1e´: R = Si(*i*Pr)$_3$, R' = *n*Bu, R'' = pAn, X = H (93%) [26b]
1f: R = Si(*i*Pr)$_3$, R' = Ph, R'' = Ph, X = H, (67%)
[**1g**: R = Si(*i*Pr)$_3$, R' = *n*Bu, R'' = *n*Bu, X = Me
1h: R = Si(*i*Pr)$_3$, R' = *n*Bu, R'' = Ph, X = Me
1i: R = Si(*i*Pr)$_3$, R' = Ph, R'' = Ph, X = Me]

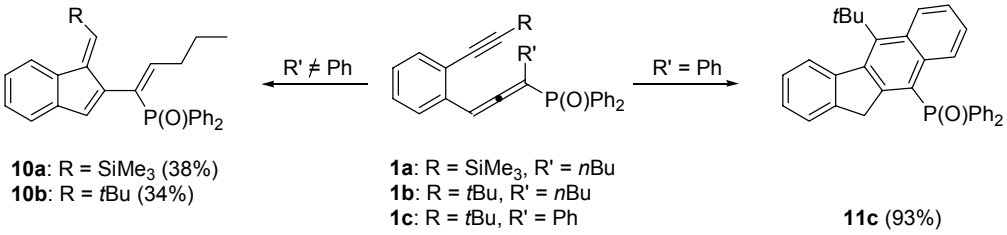
Scheme 5. Synthesis of enyne-allenes **1d-i.** (i) Ac_2O; DMAP, NEt_3; (ii) R″-MgBr, $ZnCl_2$, THF, –40 °C, $Pd(PPh_3)_4$

Cyclohexene derived enyne-allenes **1j,k** were prepared starting from **8** *via* propargyl acetate **9**. As for **1d-i**, the last step involved a palladium catalyzed addition of arylchlorozincate to the propargyl acetate **9**.



Scheme 6. Synthesis of enyne-allenes **1j,k** (i). TIPS-C≡CH, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, 94%. (ii). *n*Bu-C≡CH/EtMgBr, THF, 78%. (iii). Ac_2O, DMAP, Et_3N, 80%.

Thermolysis of enyne-allenes. When enyne-allenes **1a-f** were heated in toluene for several hours in presence of an excess of 1,4-cyclohexadiene (1,4-CHD) only C^2-C^6 cyclization, but no *Myers–Saito* products were observed. From enyne-allenes **1a** (50 eqs. of 1,4-CHD, 90 °C, 20 h) and **1b** (50 eqs. of 1,4-CHD, 90-95 °C, 48 h) the formal ene products **10a,b** (38% and 34%, respectively) were received whereas thermolysis of **1c** (20 eqs. of 1,4-CHD, 110 °C, 30 h) resulted in 93% of the formal Diels-Alder product **11c** (Scheme 7).



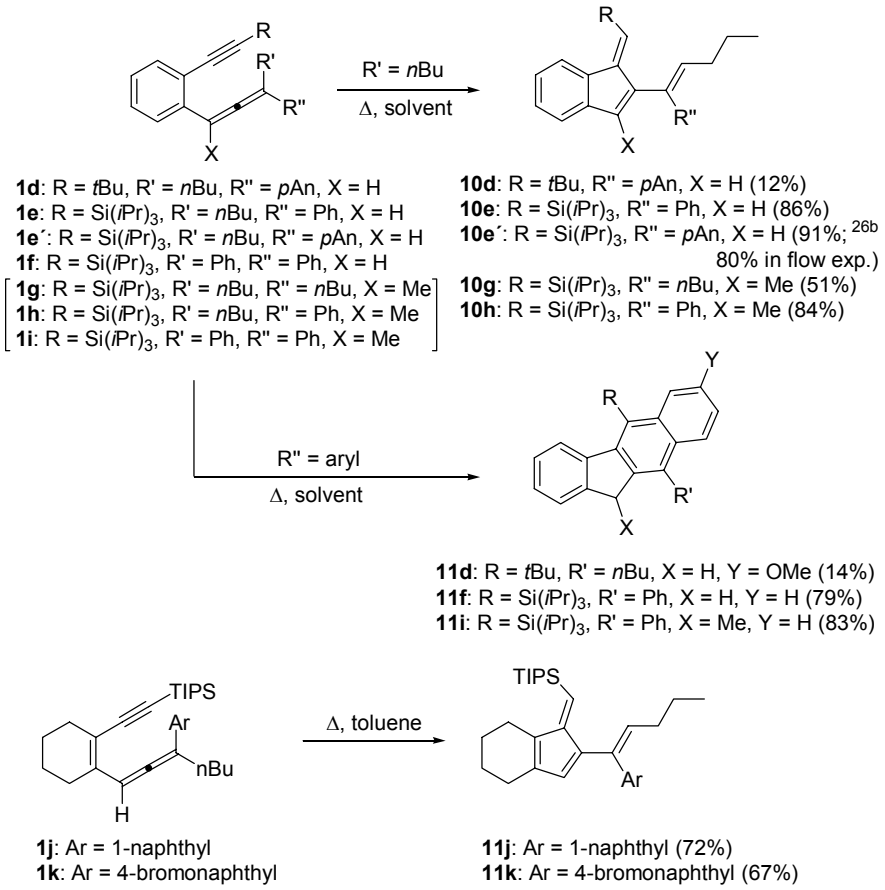
10a: R = $SiMe_3$ (38%)
10b: R = *t*Bu (34%)

1a: R = $SiMe_3$, R' = *n*Bu
1b: R = *t*Bu, R' = *n*Bu
1c: R = *t*Bu, R' = Ph

11c (93%)

Scheme 7. Thermolysis of enyne-allenes **1a-c**.

Thermolysis of enyne-allene **1d** (20 eqs. of 1,4-CHD, 110 °C, 48 h) led to the two products **10d** (12%) and **11d** (14%), both of which are again derived from a C^2-C^6 cyclization.



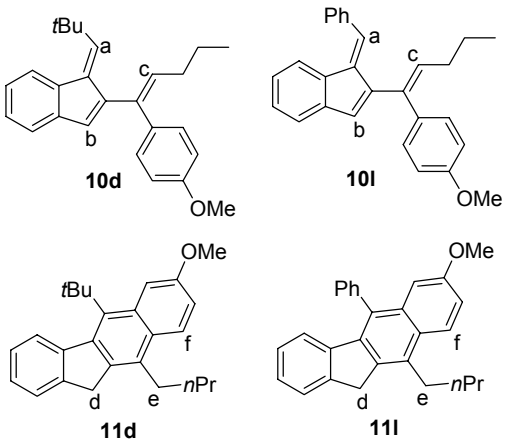
Scheme 8. Thermolysis of enyne-allenes **1d-k**.

In contrast, the thermolysis of enyne-allenes **1e-f** in presence of 20 eqs. of 1,4-CHD in toluene (**1e**: 110 °C, 4 h, 86%; **1e´:** 110 °C, 14 h, 91%;[26b] **1f**: 80 °C, 4 h, 79%) produced only one C^2–C^6 cyclization product. Due to a methyl group at the inner locus of the allene, **1g-i** were not stable at room temperature. It was, however, possible to isolate their cyclization products **10g,h** and **11i**. Cyclohex-enyne-allenes **1j,k** were isolated and subjected to thermolysis at reflux temperature in toluene (48 h) affording only formal ene-products **11j,k**, while no formal Diels–Alder products were detected.

The implementation of the enyne-allene thermolysis into a continuous process was investigated by using a CPC systems (Cellular Process Chemistry Systems) microreactor.[43,44] The high yield thermal conversion of enyne-allene **1e´** to **10e´** was chosen as a test case for a flow reactor process. Due to the slow reaction of **1e´** at 95 °C, significantly higher temperature had to be realized in the CPC microreactor as the dwell time in the mixing chamber of the microreactor at a flow rate of 0.4 mL min^{-1} does only allow for a reaction time of a few minutes. By using xylene at a high flow rate and high temperature (5 mL min^{-1}, 145 °C) full conversion of **1e´** to **10e´** could be effected in the CPC system. The yield was quantitative as judged from the

^{1}H NMR analysis of the crude material after removal of the solvent. However, for analytically pure compound, traces of the solvent had to be removed by chromatography finally furnishing **10e´** in 80% yield.

The structures of the isolated cyclization products were assigned on the basis of H,H and C,H COSY techniques, combined with mass spectroscopy. Thermolysis of enyne-allene **1d** afforded a mixture of products **10d** and **11d**, which could not be separated using various chromatographic techniques (column chromatography, MPLC and HPLC). Fortunately, characterization of the structures was nevertheless possible by assigning the individual signals in the mixture in comparison with those of the known cyclization products **10l** and **11l**[45] (scheme 9, table 1) using ^{1}H NMR and high resolution mass spectroscopy.



Scheme 9. Comparison of unknown and well characterized cyclization[45] products.

Table 1. ^{1}H NMR data for unknown (**10d, 11d**) and known (**10l, 11l**) products

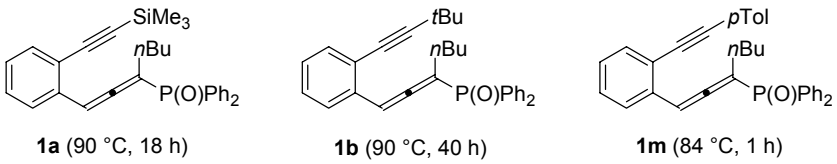
Protons	**10d** (new)	**10l** (ref.[45])	Proton	**11d** (new)	**11l** (ref. [45])
a	6.68, s, 1H	6.23, s, 1H	d	4.08, s, 2H	3.88, s, 2H
b	7.03, s, 1H	6.47, s, 1H	e	3.21, t, 2H	2.95, t, 2H
c	6.23, t, 1H	6.09, t, 1H	f	8.00, d, 1H	7.98, d, 1H

Discussion

While the factors controlling the regioselectivity of monoradical cyclizations are rather well understood,[46] the role of substituents on the regioselectivity of diradical cyclizations is still a widely unexplored area. Ten years ago we disclosed that aryl substitution at the alkyne terminus does change the course of the thermal enyne-allene diradical ring closure from the *Myers-Saito* (C^2-C^7) to the C^2–C^6 cyclization mode. In our first interpretation,[9] this switch was ascribed to the possibility that the aryl group at the alkyne may stabilize the incipient vinyl radical center,[47] and

as a consequence the TS of the C^2–C^6 cyclization was expected to fall beneath that of the *Myers-Saito* cycloaromatization. However, later calculations by Engels[34] and Schreiner[14] clearly indicated that the TS of the C^2–C^6 cyclization has no unpaired spin. Hence, substituent effects that lead to the stabilization of monoradicals may not be applicable for the TS of biradical cyclizations. An additional motif for a switch from the *Myers–Saito* to the C^2–C^6 cyclization may arise from steric effects exerted by the substituents at the alkyne and allene termini, as they must experience a repulsive interaction as *ortho*-substituents (R---B in scheme 1) in the TS of the *Myers–Saito* process, resulting in a tangible destabilization of the TS. Indeed, enyne-allenes **1a-k**, all of them characterized by bulky groups at the alkyne terminus, exhibited exclusively C^2–C^6 cyclization upon heating, although the substituents at the allene terminus were varied in some manner (aryl, alkyl, $P(O)Ph_2$). The role of benzannulation in promoting the C^2-C^6 cyclization as against the *Myers–Saito* process became not visible as both benzannulated and cyclohex-enyne-allenes, *i.e*. **1e,e'** *vs*. **1j,k**, underwent clean cyclization towards the fulvene intermediate.

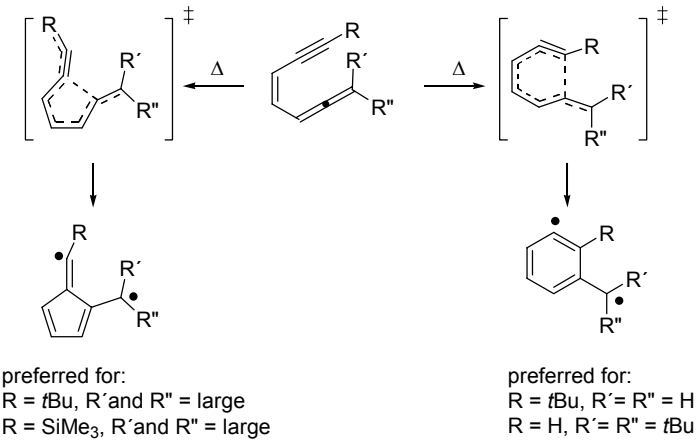
Steric bulk at the alkyne terminus. Enyne-allenes **1a-d**, being characterized by bulky *t*Bu and $SiMe_3$ groups at the alkyne terminus, cyclize at notably higher temperatures (**1a**: 90 °C, 14 h; **1b**: 90 °C, 40 h) than the phenyl analogues (*e.g*. **1m:** 84 °C, $t_{1/2}$ = 1 h)[9] in agreement with recent calculations.[38] This provides the following order of reactivity: *t*Bu < $SiMe_3$ < *p*Tol.



1a (90 °C, 18 h) **1b** (90 °C, 40 h) **1m** (84 °C, 1 h)

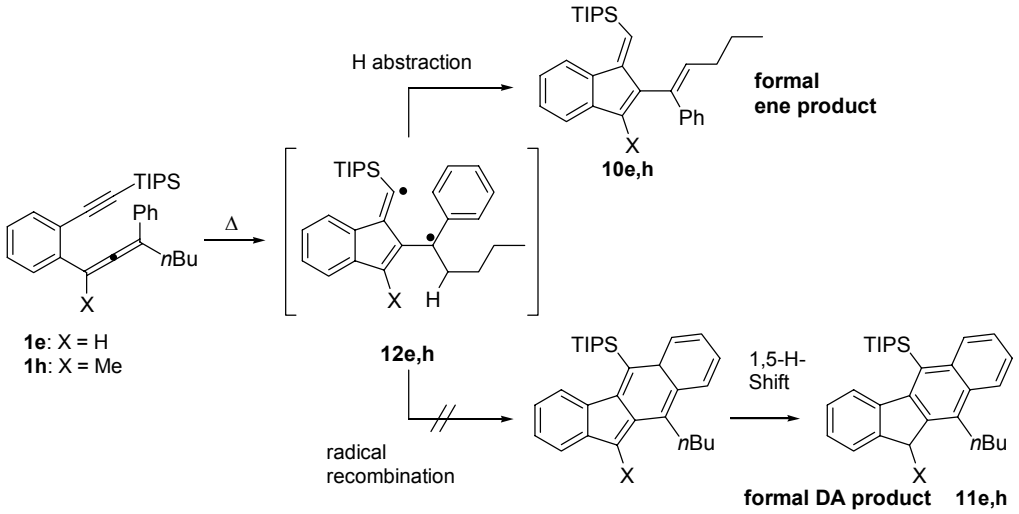
Scheme 10. Thermolysis conditions for different enyne-allenes.

Formation of products **10** and **11** demonstrates that the switch from the *Myers-Saito* cyclization to the C^2–C^6 cyclization cannot only be brought about by aryl substituents but systematically by sterically demanding groups at the alkyne terminus.[27a] This outcome is surprising at first in light of calculations by Engels *et al.*,[38] since they predict a lower activation barrier for the *Myers-Saito* pathway in case of *tert*-butyl substituents at the alkyne terminus. Moreover, Wang *et al*.[48] clearly demonstrated that bulky substituents at the allene terminus still allow for a cyclization along the *Myers-Saito* pathway. Apparently, a switch towards the C^2–C^6 cyclization *requires enough steric bulk at both the alkyne and allene terminus* in order to sufficiently increase the *ortho*-repulsion in the *Myers-Saito* transition state, a result that is summarized in scheme 11.



Scheme 11

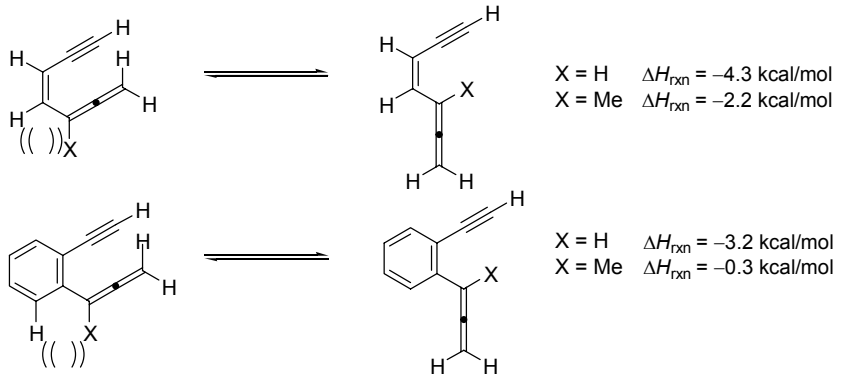
It is instructive to look at the cyclization of enyne-allene **1d** with a *tert*-butyl group at the alkyne, as both formal ene and formal Diels-Alder products are formed. The concurrent formation of **10d** and **11d** suggests a common intermediate for both processes. Interestingly, this contrasts to the exclusive formation of formal ene-products **10e,h** found in the thermolysis of enyne-allenes **1e,h**, having a similar terminal substitution at the allene as **1d** and a TIPS group at the alkyne terminus. Due to intermolecular kinetic isotope effects observed in the thermolysis of enyne-allene **1e'**,[26b] it is reasonable to assume a stepwise process for **1e**. Hence, to rationalize the exclusiveness of the formal ene reaction pathway in presence of the bulky TIPS group, it is illustrative to have a look at the full mechanistic scheme. Once diradical **12e,h** is formed, two reaction channels open up: either a radical recombination (ring closure reaction with subsequent rearomatization to the formal *Diels-Alder* product **11e,h**) or a hydrogen abstraction to the formal ene-product **10e,h** may take place. Since both steps should be irreversible, one has to assume that steric demands brought about by the groups at the alkyne and allene termini lead to a strong kinetic bias towards the hydrogen transfer reaction.



Scheme 12

Steric bulk at the inner allene locus. While the energetic situation of the C^2-C^6 TS itself will clearly be influenced by steric and electronic effects conveyed by the adjacent groups, the activation energy should also be biased by ground state effects, as one has additionally to consider the equilibrium between the *s-cis* and *s-trans* conformers (Scheme 13).

As noted in the experimental section, enyne-allenes **1g-i** are not stable at room temperature and undergo thermal C^2-C^6 cyclization to products **10g,h** and **11i**. It is interesting to compare the former to the structurally similar, but isolable enyne-allenes **1e,f** whose stability was investigated by DSC measurements. Exothermic peaks corresponding to the cyclization process were observed only far above room temp. (**1e**: 116 °C; **1f**: 80 °C), in agreement with thermolysis conditions to form products **10e** and **11f.** Obviously, replacing a hydrogen by a methyl group at the inner allene locus leads to a dramatic thermal destabilization of enyne-allenes.



Scheme 13. Equilibrium between *s-cis* and *s-trans* conformers (DFT calculation, see text).

DFT calculations on the ground state equilibrium (Scheme 13) using B3LYP/6-311G** suggest that by changing X = H to Me the *s-cis* conformer will be present in a much higher equilibrium concentration. If one considers that the *s-cis* conformer will additionally be activated by back-strain effects, then the fast reaction of enyne-allenes **1g-i** becomes readily understandable.

Another comment is warranted on the initial concept presented in scheme 1. Apparently, the stabilizing effect of the TIPS group on the kinetics of enyne-allenes **1g-i** is overruled by the much more pronounced thermal destabilization of enyne-allenes caused by Me substitution at the inner allene locus.

In summary, the thermal cyclization of enyne-allenes **1** carrying bulky substituents (*tert*-butyl, trimethylsilyl, triisopropylsilyl) at the acetylene terminus uniquely follows the C^2-C^6 cyclization pathway independent of other structural motifs at the remainder of the enyne-allene (*e.g.* benzannulation, substituents at allene). The alternative *Myers-Saito* pathway is not available due to severe *ortho*-repulsion in the transition state. Bulky groups at the alkyne terminus thermally stabilize the enyne-allene, while the exchange of a hydrogen by a methyl group at the inner locus

of the allene unit severely destabilizes the enyne-allene due to increased amounts of the reactive *cis*-conformer present in the equilibrium mixture.

Experimental Section

General Procedures. ^{1}H and ^{13}C NMR were recorded on Bruker AC200, AC250 and Avance 400 spectrometers with $CDCl_3$, C_6D_6, CD_3CN, CD_3OD or DMSO-d_6 as solvent. IR spectra were recorded on Perkin-Elmer 1605 FT-IR and 1750 FT-IR spectrometers. For DSC analysis DuPont 9000 and Perkin-Elmer DSC7 spectrometers were used with scan rates of 10 °C/min. TLC analysis was performed on Merck silica gel 60 F_{254} plates and for chromatographic separations silica gel 60 (0.0063-0.0200 mm, Fa. Merck) was used. The continuous process was established using a CYTOS® microreactor from Cellular Process Chemistry Systems,[43] Germany.
The *s-cis* and *s-trans* conformers were optimized on the B3LYP/6-311G** level of theory using Gaussian 98.[49]
Enyne-allene 1a. A mixture of **6a** (1.42 g, 5.00 mmol) and NEt_3 (680 µL, 5.43 mmol) in THF (10 mL) was cooled to –65 °C and treated with chlorodiphenylphosphine (950 µL, 5.12 mmol). The suspension was allowed to warm to –40 °C while stirring was continued for 1.5 h. After the reaction had been quenched by addition of water (30 mL) the organic layer was separated and the aqueous layer extracted with Et_2O (3 x 50 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated. Purification of the residue by column chromatography (Et_2O, R_f = 0.53) afforded **1a** (1.99 g, 85%) as a yellow oil. IR (neat): $\tilde{\nu}$ = 3057, 2958, 2930, 2871, 2154 (C≡C), 1932 (C=C=C), 1592, 1484, 1438, 1250, 1196, 1069, 1028, 998, 865, 843, 758, 696, 647 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.31 (s, 9H, $SiMe_3$), 0.91 (t, ^{3}J = 7.2 Hz, 3H), 1.23-1.32 (m, 2H), 1.58-1.72 (m, 2H), 2.48 (m, 2H), 6.72 (td, ^{4}J (H,P) = 11.0 Hz, ^{5}J (H,H) = 3.2 Hz, 1H), 7.12-7.28 (m, 2H), 7.32-7.58 (m, 8H), 7.73- 7.87 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = –0.1 ($SiMe_3$), 13.7, 22.3, 27.8 (d, J_P = 7 Hz), 30.5 (d, J_P = 6 Hz), 95.5 (d, J_P = 14 Hz), 102.6, 103.1 (d, J_P = 97 Hz), 104.0, 126.5 (d, J_P = 40 Hz), 128.1 (d, J_P = 12 Hz), 128.1, 128.3, 128.5, 131.3 (d, J_P = 8 Hz), 131.5, 131.6, 131.8, 132.5, 209.7; HRMS ($C_{30}H_{33}OPSi$): calcd 468.2038, found 468.2042.
Enyne-allene 1b. As described above for the synthesis of **1a**, a mixture of **6b** (1.34 g, 5.00 mmol) and NEt_3 (750 µL, 5.43 mmol) was treated with chlorodiphenylphosphine (1.13 g, 5.12 mmol). The remaining residue was purified by column chromatography (Et_2O, R_f = 0.56) to furnish **1b** (1.82 g, 80%) as a yellow oil. IR (neat): $\tilde{\nu}$ = 3056, 2966, 2868, 2234 (C≡C), 1931 (C=C=C), 1592, 1485, 1438, 1362, 1296, 1197, 1118, 1069, 918, 826, 755, 696 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.84 (t, ^{3}J = 9.0 Hz, 3H), 1.28 (s, 9H, CH_3), 1.36 (m, 2H), 1.55 (m, 2H), 2.39 (m, 2H), 6.62 (dt, ^{4}J (H,P) = 14.0 Hz, ^{5}J (H,H) = 4.0 Hz, 1H), 7.02-7.14 (m, 3H), 7.19-7.49 (m, 7H), 7.58-7.74 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.7, 22.3, 27.7 (d, J_P = 6 Hz), 28.1, 30.5 (d, J_P = 5 Hz), 30.9, 70.5, 95.5 (d, J_P = 14 Hz), 102.8 (d, J_P = 97 Hz), 103.6, 121.8, 126.5 (d, J_P = 40 Hz), 127.5, 128.2 (d, 12 Hz), 131.3 (d, J_P = 3 Hz), 131.6, 131.7, 132.1, 132.4,

132.9, 209.7 (d, J_P = 6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ = 29.16 (s); $C_{31}H_{33}OP$ (452.6) calcd C 82.27, H 7.35, found C 81.83, H 7.07.

Enyne-allene 1c. As described above for the synthesis of **1a**, a mixture of **6c** (615 mg, 2.13 mmol) and NEt_3 (350 μL, 2.53 mmol) was treated with chlorodiphenylphosphine (528 mg, 2.39 mmol). The remaining residue was purified by column chromatography (ethyl acetate/*n*-pentane 1:1, R_f = 0.48) to afford **1c** (423 mg, 42%) as yellow crystals. M.p. 114 °C (decomp.); IR (CCl_4): $\tilde{\nu}$ = 3061, 3026, 2971, 2867, 2236 (C≡C), 1924 (C=C=C), 1595, 1535, 1494, 1438, 1362, 1296, 1200, 1119, 1030, 919 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.29 (s, 9H, CH_3), 6.80 (d, ^4J (H,P) = 10.7 Hz, 1H), 7.08-7.16 (m, 2H), 7.24-7.38 (m, 10H), 7.44 (ddd, ^3J = 6.1 Hz, ^3J = 5.8 Hz, ^4J = 1.5 Hz, 1H), 7.66-7.69 (m, 2H), 7.73-7.81 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 28.1, 30.9, 96.6, 96.8, 101.5, 103.9, 126.1, 127.3, 127.6, 127.9, 128.2 (d, J_P = 11 Hz), 128.2, 128.7, 131.5, 131.6 (d, J_P = 6 Hz), 131.7, 131.8, 131.9, 131.9, 132.2, 213.5; HRMS ($C_{33}H_{29}OP$): calcd 472.1956, found 472.1969.

Enyne-allene 1d. The Grignard reagent was prepared from a mixture of magnesium (156 mg, 6.40 mmol) and 4-bromoanisole (1.19 g, 6.40 mmol) in THF (10 mL). The solution was refluxed for 30 min and cooled then to room temperature. To the Grignard reagent was added a $ZnCl_2$ solution in THF, which was prepared by dissolving the glassy residue of molten zinc(II)chloride (866 mg, 6.40 mmol) in THF (5 mL). After stirring again for 30 min the solution was cooled down to –40 °C and both tetrakis(triphenylphosphano)palladium(0)[50] (164 mg, 80.0 μmol) and **7d** (400 mg, 1.28 mmol) were added. After further 16 h stirring at ambient temperature the yellow mixture was quenched with saturated aqueous NH_4Cl. The organic layer was separated and the aqueous layer extracted with *n*-pentane (2 x 15 mL). The combined organic layers were washed with water (5 x 20 mL) and dried (K_2CO_3), filtered and concentrated. Purification of the crude product by fractionated crystallization (*n*-pentane) and column chromatography (*n*-hexane:Et_2O = 8:1) afforded **1d** (540 mg, 45%) as yellow oil. IR (film): $\tilde{\nu}$ = 3063, 2959, 2836, 2233 (C≡C), 1929 (C=C=C), 1602, 1511, 1487, 822, 756 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.00 (t, ^3J = 7.2 Hz, 3H), 1.44 (s, 9H, 3x CH_3), 1.49-1.74 (m, 4H), 2.61 (td, ^3J = 8.4 Hz, ^5J = 3.0 Hz, 2H, =C-CH_2), 3.84 (s, 3H), 6.93 (d, ^3J = 8.9 Hz, 2H), 6.97 (d, ^5J = 3.0 Hz, 1H), 7.00-7.15 (m, 2H), 7.27-7.26 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.6, 24.3, 29.9, 31.4, 31.7, 32.8, 56.9, 78.9, 97.6, 105.2, 111.0, 115.6, 123.5, 127.7, 128.0, 128.9, 129.3, 130.0, 134.1, 137.6, 160.4, 208.4; HRMS ($C_{26}H_{30}O$): calcd 358.2297, found 358.2302.

Enyne-allene 1e. Under nitrogen, magnesium (49.8 mg, 2.05 mmol) and bromobenzene (323 mg, 2.05 mmol) in THF (5 mL) were brought to reaction. After stirring for 30 min at 60 °C the mixture was allowed to cool down to room temperature and a solution of 1 M zinc(II)chloride in Et_2O (2.06 mL, 2.06 mmol) was added. After additional stirring for 10 min at room temperature the mixture was cooled down to –60 °C and firstly $Pd(PPh_3)_4$[50] (59.4 mg, 51.4 μmol) in THF (2 mL) and secondly **7e** (216 mg, 520 μmol) in THF (2 mL) were added. The reaction mixture was stirred for 16 h at room temperature and then hydrolyzed with aqueous saturated NH_4Cl (30 mL). The aqueous layer was extracted with *n*-pentane (3 × 25 mL) and the combined extracts were washed with water (3 × 25 mL), dried (K_2CO_3) and evaporated under

reduced pressure to leave a red oil, which was purified by column chromatography on silica using *n*-hexane as the eluent to furnish **1e** (156 mg, 70%) as a bright yellow oil; IR (neat): $\tilde{\nu}$ = 3059, 2956, 2151 (C≡C) and 1932 (C=C=C) cm^{-1}; ^1H NMR (200 MHz; $CDCl_3$): δ = 0.98 (t, *J* = 7.1 Hz, 3H, CH_2CH_3), 1.23 (bs, 21H, 3 × $CH(CH_3)_2$), 1.45-1.71 (m, 4H, $CH_2CH_2CH_2CH_3$), 2.59 (td, *J* = 7.2, *J* = 2.9, 2H, C=C=CCH_2CH_2), 7.13-7.43 (m, 4H, Ar*H* + C=C=C*H*), 7.50-7.65 (m, 6H, ArH); ^{13}C (50 MHz; $CDCl_3$): δ = 11.5, 14.1, 18.9, 22.8, 29.9, 30.2, 95.9, 96.2, 105.3, 110.0, 121.6, 126.2, 126.7, 127.3, 127.4, 128.7, 128.9, 133.2, 136.8, 141.4, 207.6; MS(EI): 428 (M^+, 9%), 385 (M^+-15, 9%), 157 ($Si(C_3H_7)_3$, 100). HRMS ($C_{30}H_{40}Si$): calcd 428.2899, found 428.2898.

Enyne-allene 1f. As described for the synthesis of **1e**, magnesium (49.8 mg, 2.05 mmol) and bromobenzene (314 mg, 2.00 mmol) in THF (5 mL) were reacted with a 1 M zinc(II) chloride solution in Et_2O (2.00 mL, 2.00 mmol), $Pd(PPh_3)_4$ (60 mg, 51 μmol) and **7f** (300 mg, 698 μmol). After work up the mixture was purified by column chromatography on silica using *n*-hexane as the eluent (R_f = 0.6). **1f** (209 mg, 67%) was received as a yellow oil; IR (neat): $\tilde{\nu}$ = 3059, 2941, 2152 (C≡C), 1929 (C=C=C); ^1H NMR (200 MHz; $CDCl_3$) δ = 1.11 (bs, 21H, 3 × $CH(CH_3)_2$), 6.89 (s, 1 H, CH), 7.23-7.42 (m, 10H, ArH), 7.53 (dd, ^3J = 6.9 Hz, ^4J = 1.5 Hz, 4H, ArH); ^{13}C (50 MHz; $CDCl_3$) δ = 12.4, 19.8, 96.9, 97.0, 105.9, 114.8, 122.7, 127.3, 128.2, 128.3, 128.7, 129.8, 134.2, 136.7, 137.0, 142.2, 210.2; HRMS ($C_{32}H_{36}Si$): calcd 448.2586, found 448.2588.

Enyne-allene 1j. To 1-bromonaphthalene (199 mg, 960 μmol) in 9 mL of dry diethyl ether, cooled to 0 °C in an ice bath, *n*BuLi (2.5 M) (420 μL, 1.05 mmol) was added dropwise. After stirring for 4 h, this reaction mixture added dropwise to a 1 M $ZnCl_2$ solution (130 mg in a 0.95 mL of diethyl ether) and stirred for 30 min at room temperature. Upon cooling this reaction mixture to −60 °C, $Pd(PPh_3)_4$ (27.0 mg, 23.0 μmol) in dry THF (2 mL) was added dropwise. Finally, after stirring for 30 min at the same temperature, propargyl acetate **9** (100 mg, 0.24 mmol) in dry THF (3 mL) was added dropwise. After stirring for 16 h at room temperature reaction mixture was quenched with aqueous saturated ammonium chloride solution. The aqueous layer was washed with pentane (2 x 25 mL). The combined organic layers were dried over sodium sulfate and evaporated under reduced pressure. After purification by column chromatography (silica gel, *n*-pentane, R_f = 0.76) compound **1j** (80 mg, 69%) was isolated as colorless oil; IR (neat): $\tilde{\nu}$ = 3020 (s), 2943 (s), 2865 (s), 2131 (m, C≡C), 1937 (w, C=C=C) cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ = 0.91 (t, ^3J = 7.2 Hz, 3H), 1.11 (s, 21H), 1.36-1.45 (m, 2H), 1.49-1.71 (m, 6H), 2.19-2.33 (m, 4H), 2.46-2.57 (m, 2H), 6.85 (t, ^5J = 2.9 Hz, 1H, -CH=), 7.39-7.53 (m, 4H), 7.77 (d, ^3J = 7.8 Hz, 1H, ArH), 7.83-7.88 (m, 1H, ArH), 8.13-8.17 (m, 1H, ArH); ^{13}C NMR (100 MHz; $CDCl_3$) δ = 11.3, 14.0, 18.7, 22.2, 22.4, 22.5, 26.7, 30.3, 30.7, 34.8, 94.9, 96.2, 107.2, 107.4, 117.2, 125.4, 125.5, 125.6, 125.8, 127.4, 128.3, 131.3, 133.9, 136.5, 139.0, 205.2; HRMS ($C_{34}H_{46}Si$): calcd 482.3369, found 482.3369.

Enyne-allene 1k. To a solution of 1,4-dibromonaphthalene (634 mg, 2.21 mmol) in dry diethyl ether (13 mL), cooled to 0 °C by an ice bath, *n*BuLi (2.5 M) (0.89 ml, 2.23 mmol) was added dropwise. After stirring for 4 h, the received reaction mixture was added dropwise to 1 M $ZnCl_2$ solution (302 mg in 2.21 mL of diethyl ether) and stirred for 30 min at room temperature. After cooling the reaction mixture to −60 °C, $Pd(PPh_3)_4$ (64.0 mg, 55.3 μmol) in dry THF (6 mL) was

added dropwise, and after stirring for 30 min at the same temperature propargyl acetate **9** (238 mg, 550 μmol) in dry THF (5 mL) was added dropwise. After stirring for 16 h at room temperature the reaction mixture was quenched with aqueous saturated ammonium chloride solution. The aqueous layer was washed with pentane (2 x 50 mL). The combined organic layer was dried over sodium sulfate and evaporated under reduced pressure. After purification by column chromatography (silica gel, *n*-pentane, R_f = 0.57) compound **1k** (118 mg, 40%) was isolated as colorless oil; IR (neat): $\tilde{\nu}$ = 2942 (s, C-H), 2131 (w, C≡C), 1937 (w, C=C=C) cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) δ = 0.91 (t, ^3J = 7.3 Hz, 3H, CH_3), 1.11 (s, 21H, C*H*(CH_3)$_2$), 1.35-1.45 (m, 2H), 1.47-1.57 (m, 2H), 1.57-1.70 (m, 4H), 2.10-2.35 (m, 4H), 2.41- 2.55 (m, 2H), 6.85 (t, ^5J = 2.9 Hz, 1H, -CH=), 7.26 (d, ^3J = 7.8 Hz, 1H, ArH), 7.52-7.63 (m, 2H), 7.75 (d, ^3J = 7.8 Hz, 1H, ArH), 8.15 (dd, ^3J = 8.0 Hz, ^4J = 1.2 Hz, 1H), 8.27 (dd, ^3J = 8.0 Hz, ^4J = 1.2 Hz, 1H, ArH); ^{13}C NMR (100 MHz; $CDCl_3$) δ = 11.3, 14.0, 18.7, 22.2, 22.4, 22.5, 26.7, 30.3, 30.7, 34.8, 95.1, 96.4, 106.9, 107.1, 117.6, 121.9, 125.9, 126.2, 126.6, 127.1, 127.6, 129.5, 132.2, 132.5, 136.8, 138.5, 205.2; HRMS ($C_{34}H_{45}BrSi$): calcd 560.2474, found 560.2474.

Thermolysis of enyne-allenes 1. All enyne-allenes were thermolyzed in toluene or mesitylene with various equivalents of the hydrogen donor, 1,4-cyclohexadiene added (for solvent, duration, temperature, and yield see table 4). After several hours the solvent was removed under reduced pressure and the mixture was purified by column chromatography if necessary.

Table 4. Thermolysis conditions

Enyne-allene	Conditions	Product
1a	50 eq. of 1,4-CHD, toluene, 90 °C, 20 h	**10a** (38%)
1b	50 eq. of 1,4-CHD, toluene, 90-95 °C, 2 d	**10b** (34%)
1c	20 eq. of 1,4-CHD, toluene, reflux, 30 h	**11c** (93%)
1d	20 eq. of 1,4-CHD, toluene, reflux, 48 h	**10d** (12%), **11d** (14%)
1e	chlorobenzene, 120 °C, 16 h	**10e** (86%)
1f	toluene, 110 °C, 16 h	**11f** (79%)
1g	room temperature	**10g** (51%)
1h	room temperature	**10h** (84%)
1i	room temperature	**11i** (83%)
1j	toluene, reflux, 48 h	**11j** (72%)
1k	toluene, reflux, 48 h	**11k** (67%)

Compound 10a. IR (neat): $\tilde{\nu}$ = 3056, 2956, 2907, 2880, 1652, 1623, 1590, 1453, 1436, 1249, 1189, 1101, 998, 958, 863, 755, 696 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.11 (s, 9H), 0.88 (t, ^3J = 7.4 Hz, 3H), 1.48 (tq, ^3J = 7.4 Hz, ^3J = 7.4 Hz, 2H), 2.06 (m, 2H), 5.83 (s, 1H), 6.34 (d, ^4J (H,P) = 3.2 Hz, 1H), 7.03-7.15 (m, 3H), 7.18-7.23 (m, 2H), 7.28-7.48 (br. m, 6H), 7.53-7.74 (br. m, 4H); ^{13}C NMR (63 MHz, $CDCl_3$): δ = -0.6, 13.9, 21.9, 32.8 (d, J_P = 13 Hz), 120.7, 123.1,

124.9, 127.8, 127.9, 131.7, 132.1, 132.1, 132.3, 135.3, 136.1, 137.7, 137.8, 143.2, 151.1 (d, J_P = 6 Hz), 153.1; $C_{30}H_{33}OPSi$ (486.6): calcd C 76.89, H 7.10, found C 77.28, H 7.05.

Compound 10b. IR (neat): $\tilde{\nu}$ = 3054, 2958, 2907, 1650, 1623, 1591, 1453, 1236, 1191, 1095, 998, 861, 755 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 0.86 (t, ^3J = 7.3 Hz, 3H), 1.04 (s, 9H), 1.38-1.57 (m, 2H), 2.01 (m, 2H), 5.83 (s, 1H), 6.20 (d, ^4J (H,P) = 3.1 Hz, 1H), 7.13-7.16 (m, 3H), 7.27-7.31 (m, 2H), 7.39-7.54 (m, 6H), 7.65-7.75 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.0, 22.0, 29.9, 32.4, 32.9, 120.8, 122.4, 126.3, 127.0, 128.0, 128.5, 129.4, 131.6, 131.9, 132.5, 132.9, 136.1, 143.9, 146.1, 150.1, 151.4; $C_{31}H_{33}OP$ (452.6): calcd C 82.27, H 7.35, found C 81.96, H 7.03.

Compound 11c. IR (neat): $\tilde{\nu}$ = 3054, 2965, 1819, 2869, 1590, 1560, 1464, 1436, 1400, 1368, 1306, 1283, 1189, 1116, 949, 907, 834, 759, 722, 696 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 1.84 (s, 9H, CH_3), 3.98 (s, 2H, CH_2), 7.12 (m, 1H), 7.16-7.23 (m, 2H), 7.28-7.36 (m, 3H), 7.44-7.57 (m, 5H), 7.68-7.78 (m, 4H), 8.00 (m, 2H), 8.40 (d, 1H, ^3J = 8.9 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 32.8, 38.0, 39.1, 122.7, 124.3, 124.5, 125.5, 126.7, 126.8, 126.9, 127.9, 128.7 (d, J_P = 12 Hz), 131.8 (d, J_P = 10 Hz), 131.8, 133.1, 133.3, 133.6, 134.0 (d, J_P = 8 Hz), 135.7, 141.4, 143.9, 148.6, 151.0; $C_{33}H_{29}OP$ (472.6): calcd C 83.87, H 6.19, found C 84.32, H 6.44.

Compound 10d. The mixture of **10d** and **11d** could not be separated. But some ^1H NMR signals are indicative for the Diels–Alder follow up product. And it was also possible to verify the structure *via* a mass spectrum which shows that the fragmentation peaks of the mixture correspond to the fragmentation of known ene products. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.26 (s, 9H, *t*Bu), 3.70 (s, 3H, OMe), 6.09 (t, ^3J (H, H) = 7.9 Hz, 2H), 6.23 (s, 1H), 6.47 (s, 1H).

Compound 11d. The mixture of **10d** and **11d** could not be separated. While some ^1H NMR signals are indicative of the ene product **10d**. In addition, it was also possible to verify the structure of **11d** *via* the mass spectrum showing the typical fragmentation peaks as those of known Diels–Alder products. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.76 (s, 9H, *t*Bu), 3.21 (t, ^3J (H, H) = 7.9 Hz, 2H), 3.88 (s, 3H, OMe), 4.08 (s, 2H), 7.98 (d, ^3J (H, H) = 8.4 Hz, 1H).

Compound 10e. 1e (110 mg, 257 μmol) was dissolved in chlorobenzene (80 mL) and stirred for 16 h at 120 °C. After cooling down the yellow solution was evaporated and the remaining yellow oil purified by column chromatography on silica with *n*-hexane to furnish the cyclization product **10e** as a yellow oil (95.0 mg, 86%); IR (neat): $\tilde{\nu}$ = 3056 (Ar*H*), 2941 (C-H), 1596 (C=C), 1492 (C=C), 1459 (C=C) cm^{-1}; ^1H NMR (200 MHz; $CDCl_3$) δ = 0.90 (t, ^3J = 7.1 Hz, 3H, CH_2CH_3), 1.00 (d, 18H, ^3J = 7.1 Hz, 3 × $CH(CH_3)_2$), 1.27-1.53 (m, 5H, $CH_2CH_2CH_3$, 3 × $CH(CH_3)_2$), 2.16 (dt, ^3J = 7.3 Hz, ^3J = 7.1 Hz, 2H, $CHCH_2CH_2$), 6.25 (s, 1H, CH), 6.31 (t, ^3J = 7.3 Hz, 1H, $CHCH_2CH_2$), 6.72 (s, 1H, CH), 7.14-7.28 (m, 6H, ArH), 7.34-7.39 (m, 2H, ArH), 7.79 (dd, ^3J = 7.4 Hz, ^4J = 0.7 Hz, 1H, ArH); ^1H NMR (50 MHz; $CDCl_3$): δ = 12.9, 13.8, 18.9, 22.9, 32.3, 120.4, 124.6, 125.1, 125.5, 125.8, 126.2, 126.3, 126.6, 127.7, 128.0, 128.2, 130.4, 132.4, 132.6, 132.9; MS (EI): *m/z* = 428 (M^+, 1%), 413 (M^+-15, 12%), 385 (M^+-43, 31%), 308 (M^+-120, 98%); HRMS ($C_{30}H_{40}Si$): calcd 428.2899, found 428.2906.

Compound 11f. 1f (49.8 mg, 111 μmol) was dissolved in toluene (50 mL) and stirred for 16 h at 110 °C. After cooling, the removal of the solvent resulted in a brown oil that was purified by

column chromatography on silica with *n*-hexane as eluent to leave **11f** (R_f = 0.8) as yellow oil (39 mg, 79%); IR (neat): $\tilde{\nu}$ = 3057 (Ar*H*), 2925 (C-H), 2854, 1601, 1515, 1487 cm^{-1}; ^{1}H NMR (200 MHz; $CDCl_3$): δ = 0.95 (d, ^3J = 7.6 Hz, 18H, 3 × CH(CH_3)$_2$), 1.83 (septet, ^3J = 7.6 Hz, 3H, 3 × C*H*(CH$_3$)$_2$), 3.98 (s, 2H, CH_2), 7.15-7.30 (m, 8H, ArH), 7.39-7.47 (m, 4H, ArH), 8.04 (d, ^3J = 8.1 Hz, 1H, ArH); ^{13}C NMR (50 MHz; $CDCl_3$) δ = 12.5, 21.4, 42.1, 117.6, 120.5, 124.2, 125.3, 125.4, 124.2, 125.3, 125.9, 127.1, 127.8, 128.0, 128.7, 129.0, 131.0, 132.3, 133.5, 135.9, 138.7, 144.5, 149.9; HRMS ($C_{32}H_{36}Si$): calcd 448.2586, found 448.2586.

Compound 10g. As described for **1e**, a mixture of magnesium (75.0 mg, 3.09 mmol) and 1-bromobutane (420 mg, 3.06 mmol) in THF (5 mL) was brought to reaction with a 1 M zinc(II)chloride solution in Et_2O (3.08 mL, 3.08 mmol), $Pd(PPh_3)_4$ (90.0 mg, 77.9 μmol) and **7g** (216 mg, 510 μmol). After work up, purification by column chromatography on silica using cyclohexane as the eluent (R_f = 0.9) furnished the cyclization product **10g** (110 mg, 51%) as a yellow oil; IR (neat): $\tilde{\nu}$ = 2956, 2865, 1602, 1558, 1457 cm^{-1}; ^{1}H NMR (200 MHz; $CDCl_3$) δ = 0.81 (t, ^3J = 7.3 Hz, 6H, 2 × CH_2CH_3), 1.10 (d, ^3J = 7.3 Hz, 18H, 3 × CH(CH_3)$_2$), 1.23-1.40 (m, 9H, 3 × CH_2, 3 × C*H*(CH$_3$)$_2$), 1.76 (t, ^3J = 7.1 Hz, 2H, CH_2), 2.02 (s, 3H, CH_3), 2.15-2.24 (s, 2H, CH_2), 5.67 (t, ^3J = 7.3 Hz, 1H, CH), 6.18 (s, 1H, CH), 7.13 (dt, ^3J = 7.3, ^4J = 1.5 Hz, 1H, ArH), 7.20-7.28 (m, 2H, ArH), 7.65 (d, ^3J = 7.3 Hz, 1H, ArH); ^{13}C NMR (50 MHz; $CDCl_3$): δ = 11.3, 13.1, 13.9, 14.0, 19.2, 22.8, 31.0, 31.6, 117.5, 117.9, 121.6, 124.3, 127.3, 127.7, 130.5, 134.9, 136.1, 140.9, 145.9, 155.5; HRMS ($C_{29}H_{46}Si$): calcd 422.3369, found 422.3372.

Compound 10h. As described for **1e**, a mixture of magnesium (50.0 mg, 2.06 mmol) and bromobenzene (323 mg, 2.06 mmol) in THF (5 mL) was reacted with a 1 M zinc(II)chloride solution in Et_2O (2.06 mL, 2.06 mmol), $Pd(PPh_3)_4$ (60.0 mg, 51.4 μmol) and **7g** (216 mg, 510 μmol). After work up, purification by column chromatography on silica with *n*-pentane as eluent resulted in the cyclization product **10h** (191 mg, 84%) as a yellow oil; IR (neat): $\tilde{\nu}$ = 3058, 2941, 1597, 1568, 1482 cm^{-1}; ^{1}H NMR (250 MHz; $CDCl_3$) δ = 0.89 (t, ^3J = 7.2 Hz, 3H, CH_2CH_3), 1.04 (d, ^3J = 7.2 Hz, 18H, 3 × CH(CH_3)$_2$), 1.29-1.53 (m, 5H, CH_2CH_2CH$_3$, 3 × C*H*(CH$_3$)$_2$), 2.05 (s, 3H, CH_3), 2.08 (dt, ^3J = 7.3 and 7.2 Hz, 2H, CH_2CH$_2$CH$_3$), 6.12 (s, 1H, C*H*), 6.38 (t, ^3J = 7.3 Hz, 1H, C*H*CH$_2$), 7.06-7.25 (m, 8H, ArH), 7.60 (d, ^3J = 7.3 Hz, 1H, ArH); ^{13}C NMR (50 MHz; $CDCl_3$) δ = 11.8, 13.4, 14.3, 19.4, 23.0, 32.6, 118.7, 122.1, 125.1, 126.6, 126.9, 128.2, 128.5, 129.4, 133.2, 135.2, 136.6, 137.8, 139.7, 142.5, 146.0, 155.7; HRMS ($C_{31}H_{42}Si$): calcd 442.3056, found 442.3058.

Compound 11i. As described for **1e**, a mixture of magnesium (50.0 mg, 2.00 mmol) and bromobenzene (314 mg, 2.00 mmol) in THF (5 mL) was brought to reaction with a 1 M zinc(II)chloride solution in Et_2O (2.00 mL, 2.00 mmol), $Pd(PPh_3)_4$ (60.0 mg, 52.0 μmol) and **7h** (100 mg, 225 μmol). After work up, purification by column chromatography on silica as *n*-pentane as eluent (R_f = 0.8) afforded the cyclization product **11i** (86.2 mg, 83%) as a yellow oil; IR (neat): $\tilde{\nu}$ = 3058, 2924, 1598, 1491, 1463 cm^{-1}; ^{1}H NMR (250 MHz; $CDCl_3$) δ = 0.77 (bs, 21H, 3 × C*H*(CH_3)$_2$), 0.95 (d, ^3J = 7.3 Hz, 3H, CH_3), 4.01 (q, ^3J = 7.3 Hz, 1H, CH), 7.21-7.53 (m, 9H, ArH), 7.56 (d, ^3J = 8.5 Hz, 1H, ArH), 7.82-7.90 (m, 3H, ArH); ^{13}C NMR (50 MHz; $CDCl_3$) δ = 11.5, 18.6, 19.5, 42.6, 118.0, 120.9, 124.6, 125.8, 126.4, 127.6, 127.7, 127.8, 128.3,

128.6, 129.2, 129.4, 129.9, 131.4, 132.7, 133.9, 136.4, 139.2, 144.9, 150.3; HRMS ($C_{33}H_{38}Si$): calcd 462.2742, found 462.2737.

Compound 11j. In 50 mL of dry toluene, 29.0 mg (0.06 mmol) of enyne-allene **1j** was refluxed for 48 h, and then toluene was removed under reduced pressure. After purification by preparative tlc (aluminium sheet, silica gel $60F_{254}$, *n*-pentane, R_f = 0.77) compound **11j** (21 mg, 72%) was isolated as an orange oil. IR (neat): $\tilde{\nu}$ = 2943 (m), 2865 (m), 2253 (m), 1464 (m) cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ = 0.97 (t+d, ^3J = 7 Hz, 18H + 3H, 3 × $(CH_3)_2$, CH_3), 1.09-1.22 (m, 3H), 1.51 (sextet, ^3J = 7.3 Hz, 2H, CH_2-C*H*$_2$-CH_3), 1.70 (t, ^3J = 2.7 Hz, 4H, CH_2), 2.25-2.41 (m, 6H), 5.91 (t, ^3J = 7.2 Hz, 1H, =C*H*-CH_2), 6.00 (s, 1H, =C*H*-TIPS), 6.42 (s, 1H), 7.31-7.44 (m, 4H), 7.69 (d, *J* = 8.0 Hz, 1H, ArH), 7.80 (dd, ^3J = 7.8 Hz, ^4J = 1.5 Hz, 1H, ArH), 8.28 (dd, ^3J = 8.0, ^4J = 1.0 Hz, 1H, ArH); ^{13}C NMR (100 MHz; $CDCl_3$) δ = 13.2, 13.9, 19.0, 22.6, 23.2, 23.3, 23.7, 25.1, 32.8, 125.2, 125.4, 126.3, 126.4, 126.7, 127.6, 128.1, 131.1, 131.6, 133.5, 134.0, 134.4, 135.9, 137.9, 143.1, 143.6, 160.0; HRMS ($C_{34}H_{46}Si$): calcd 482.337, found 482.337.

Compound 11k. In 50 mL of dry toluene, 43.0 mg (76.0 μmol) of enyne-allene **1k** was refluxed for 48 h. After removal of toluene under reduced pressure and purification by preparative tlc (aluminum sheet, silica gel 60 F_{254}, *n*-pentane, R_f = 0.57) compound **11k** (29 mg, 67%) was isolated as an orange oil. IR (neat): $\tilde{\nu}$ = 2943 (m), 2866 (m), 1580 (w), 1464 (m) cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ = 0.95 (t+d, ^3J = 7 Hz, 18H + 3H, 3 × $(CH_3)_2$, CH_3), 1.07-1.20 (m, 3H), 1.51 (sextet, ^3J = 7.3 Hz, 2H, CH_2-C*H*$_2$-CH_3), 1.69 (t, ^3J = 2.7 Hz, 4H), 2.25-2.39 (m, 6H), 5.89 (t, ^3J = 7.2 Hz, 1H, =C*H*-CH_2), 5.99 (s, 1H, =C*H*-TIPS), 6.36 (s, 1H), 7.17 (d, ^3J = 7.6 Hz, 1H, ArH), 7.39-7.44 (m, 1H, ArH), 7.50-7.55 (m, 1H, ArH), 7.68 (d, ^3J = 7.5 Hz, 1H, ArH), 8.22 (dd, ^3J = 8.4 Hz, ^4J = 0.6 Hz, 1H, ArH), 8.28 (dd, ^3J = 8.4 Hz, ^4J = 0.6 Hz, 1H, ArH); ^{13}C NMR (100 MHz; $CDCl_3$) δ = 13.2, 13.9, 19.0, 22.6, 23.2, 23.3, 23.6, 25.1, 32.9, 121.2, 126.2, 126.7, 127.0, 127.3, 127.9, 129.3, 131.5, 132.2, 132.9, 133.7, 133.8, 136.4, 137.4, 143.3, 143.5, 159.9; HRMS ($C_{34}H_{45}{}^{81}BrSi$): calcd 562.246, found 562.244.

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