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Thermal C^2-C^6 Cyclization of Enyne−Allenes. Experimental Evidence for a Stepwise Mechanism and for an Unusual Thermal Silyl Shift

Michael Schmittel,*[,†] Atul A. Mahajan,[†] Götz Bucher,*[,‡] and Jan W. Bats[§]

Organische Chemie I, FB 8 (Chemie-Biologie), Universität Siegen, Adolf-Reichwein-Str., D-57068 Siegen, Germany, Lehrstuhl für Organische Chemie II, Ruhr-Universität Bochum, Universitätsstr. 150, D-44801 Bochum, Germany, and Institut für Organische Chemie und Chemische Biologie, Johann Wolfgang Goethe-Universität, Marie-Curie-Strasse 11, D 60439 Frankfurt am Main, Germany

schmittel@chemie.uni-siegen.de

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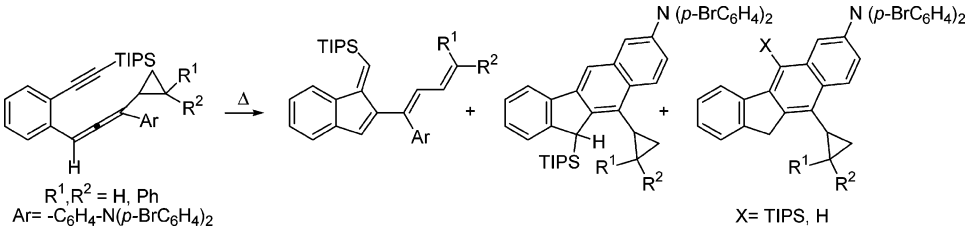

Enyne−allenes **4a**−**c** bearing various cyclopropyl systems as radical clock reporter groups at the allene terminus have been synthesized and subjected to thermal C^2-C^6 cyclization. The ratio of ene versus formal Diels−Alder products could be rationalized on the basis of steric effects. Only the thermolysis of **4c**, equipped with the fast diphenylcyclopropylcarbinyl radical clock, afforded a 1,3-butadienyl benzofulvene clearly formed via cyclopropyl ring opening. This finding provides unambiguous evidence for a stepwise mechanism of the C^2-C^6 cyclization making it possible to suggest a lifetime for the intermediate diradical of $>1 \times 10^{-10}$ s (at 170 °C). An interesting corollary was the isolation of an unexpected silyl shift product in the thermolysis of all three enyne−allenes that allows explanation of the loss of the TIPS group in some of the Diels−Alder products. For a full understanding of the mechanism, silyl and hydrogen shift processes were interrogated using DFT.

Introduction

The thermal cyclization of enediynes (Bergman)[1] and enyne−allenes (Myers-Saito, C^2-C^7)[2] has aroused great interest over the past two decades, because their diradical intermediates play a key role in the action of natural enediyne antitumor antibiotics.[3] Interestingly, the C^2-C^7 (Myers-Saito) cyclization has to compete against another thermal reaction mode of enyne−allenes, the C^2-C^6 cyclization (Scheme 1), as disclosed in 1995.[4] In the ensuing years, the thermal C^2-C^6 cyclization has been extensively studied mechanistically[5] and theoretically,[6] exhibiting an attractive potential for the synthesis of complex carbocycles[7] and for DNA cleavage.[8]

The cyclopropylcarbinyl ring opening has been widely used in mechanistic investigations as a "radical clock" to report about the intermediacy of short-lived radicals and diradicals.[9] More-

† Universität Siegen.
‡ Ruhr-Universität Bochum.
§ Johann Wolfgang Goethe-Universität.

(1) (a) Bergman, R. G.; Jones, R. R. *J. Am. Chem. Soc.* **1972**, *94*, 660−661. (b) Bergman, R. G. *Acc. Chem. Res.* **1973**, *6*, 25−31.

(2) (a) Myers, A. G.; Kuo, E. Y.; Finney, N. S. *J. Am. Chem. Soc.* **1989**, *111*, 8057−8059. (b) Nagata, R.; Yamanaka, H.; Okazaki, E.; Saito, I. *Tetrahedron Lett.* **1989**, *30*, 4995−4998.

(3) (a) Nicolaou, K. C.; Dai, W.-M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1387−1416. (b) Borders, D. B.; Doyle, T. W. *Enediyne Antibiotics as Antitumor Agents*; Marcel Dekker: New York, 1995.

(4) Schmittel, M.; Strittmatter, M.; Kiau, S. *Tetrahedron Lett.* **1995**, *36*, 4975−4978.

(5) (a) Schmittel, M.; Strittmatter, M.; Kiau, S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1843−1845. (b) Schmittel, M.; Strittmatter, M.; Vollmann, K.; Kiau, S. *Tetrahedron Lett.* **1996**, *37*, 999−1002. (c) Schmittel, M.; Steffen, J. P.; Auer, D.; Maywald, M. *Tetrahedron Lett.* **1997**, *38*, 6177−6180. (d) Schmittel, M.; Keller, M.; Kiau, S.; Strittmatter, M. *Chem. Eur. J.* **1997**, *3*, 807−816. (e) Engels, B.; Lennartz, C.; Hanrath, M.; Schmittel, M.; Strittmatter, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 1960−1963. (f) Schmittel, M.; Strittmatter, M. *Tetrahedron* **1998**, *54*, 13751−13760. (g) Li, H. B.; Zhang, H. R.; Petersen, J. L.; Wang, K. K. *J. Org. Chem.* **2001**, *66*, 6662−6668. (h) Schmittel, M.; Steffen, J. P.; Maywald, M.; Engels, B.; Helten, H.; Musch, P. *J. Chem. Soc., Perkin Trans.* **2001**, *2*, 1331−1339. (i) Yang, Y. H.; Petersen, J. L.; Wang, K. K. *J. Org. Chem.* **2003**, *68*, 5832−5837. (j) Yang, Y. H.; Petersen, J. L.; Wang, K. K. *J. Org. Chem.* **2003**, *68*, 8545−8549.

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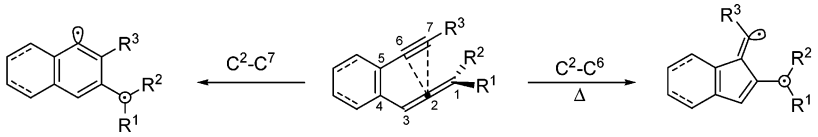
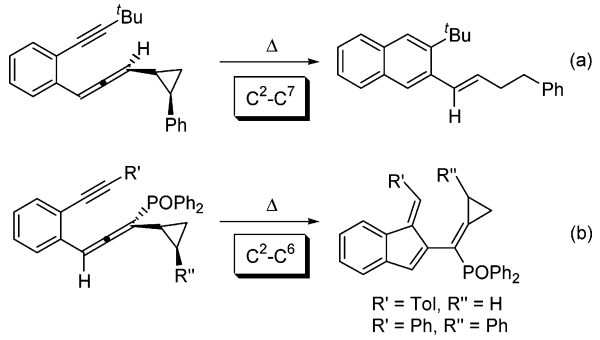
SCHEME 1. Thermal Myers−Saito (C^2-C^7) and C^2-C^6 Cyclizations of Enyne−Allenes



SCHEME 2. Radical Clock Reporter Groups in Thermal Cyclizations of Enyne−Allenes as Employed by (a) Finn et al.[11] and (b) Schmittel et al.[5a,d]



over, radical clocks have been exploited to differentiate between stepwise versus concerted mechanisms in various reaction scenarios, such as for example in the ene reaction.[10] In the context of the Myers-Saito cyclization (Scheme 2a), Dopico and Finn studied the thermolysis of enyne−allenes carrying either a cyclopropyl or a 2-phenylcyclopropyl group at the allene terminus. Their results clearly suggested that the cyclopropylcarbinyl ring opening strongly depends on the reaction condition; in the presence of 1,4-cyclohexadiene (1,4-CHD) the reaction proceeded via a diradical intermediate, whereas in the presence of methanol the reaction advanced via a zwitterionic intermediate.[11]

First investigations on the cyclopropylcarbinyl ring opening in the thermal C^2-C^6 cyclization of enyne−allenes (Scheme 2b) demonstrated that the substituted and unsubstituted cyclopropylcarbinyl radical clock remained intact, leading to the assumption that the rate constant for hydrogen transfer on the stage of the postulated diradical has to be much faster than 10^6 s^{-1}.[5a,d] An equally intact cyclopropyl ring in the C^2-C^6 products was found by Lipton et al. after an oxyanion-accelerated cyclization of cyclopropyl-substituted enyne−allenes.[12] Both studies seem at first to argue against diradical intermediates in the C^2-C^6 cyclization, but a stringent interpretation of the data suggests that a short-lived diradical intermediate cannot be discounted. Recently, kinetic isotope effects have revealed further insight into the mechanism of the C^2-C^6 cyclization. Results by Singleton et al.[13] suggested that for a selected example there is one common transition state for the stepwise and concerted C^2-C^6 cyclization. In contrast, the results of Schmittel et al.[14] could rather be reconciled with a stepwise diradical mechanism, leading either to ene or formal Diels−Alder products.

The rising dispute about the mechanism of the C^2-C^6 cyclization asked for further experimental interrogation of the putative diradical intermediate. As a consequence, we have designed enyne−allenes **4a−c** carrying various cyclopropyl substrates at the allene terminus, including the ultrafast diphenylcyclopropylcarbinyl radical clock. Herein, we report on the thermal C^2-C^6 cyclization of these enyne−allenes and their ring-closed and ring-opened products. Moreover, the formation of an unexpected silyl shift product was identified by X-ray, and its formation was investigated computationally.

Results

Synthesis. The required enyne−allenes **4a−c** were prepared according to our established protocol (Scheme 3), starting with the Sonogashira cross coupling of triisopropylsilyl acetylene with 2-iodobenzaldehyde furnishing compound **1** in quantitative yield.[15] Addition of BrMgC≡C−R (R = cyclopropyl, phenylcyclopropyl,[16] diphenylcyclopropyl[17]) afforded propargyl alcohols **2a−c** in good yield[18] (the ^{1}H NMR of compound **2c** showed two isomers, which were used in the next step without any further separation). Compounds **2a−c** were treated with Ac_2O and 4-(*N*,*N*-dimethylamino)-pyridine (DMAP) in triethylamine/DCM at room temperature, furnishing propargyl acetates **3a−c**

(6) (a) Engels, B.; Hanrath, M. *J. Am. Chem. Soc.* **1998**, *120*, 6356−6361. (b) Schreiner, P. R.; Prall, M. *J. Am. Chem. Soc.* **1999**, *121*, 8615−8627. (c) Cramer, C. J.; Kormos, B. L.; Seierstad, M.; Sherer, E. C.; Winget, P. *Org. Lett.* **2001**, *3*, 1881−1884. (d) de Visser, S. P.; Filatov, M.; Shaik, S. *Phys. Chem. Chem. Phys.* **2001**, *3*, 1242−1245. (e) Stahl, F.; Moran, D.; Schleyer, P. V.; Prall, M.; Schreiner, P. R. *J. Org. Chem.* **2002**, *67*, 1453−1461. (f) Schreiner, P. R.; Navarro-Vazquez, A.; Prall, M. *Acc. Chem. Res.* **2005**, *38*, 29−37.

(7) (a) Zhang, H.-R.; Wang, K. K. *J. Org. Chem.* **1999**, *64*, 7996−7999. (b) Wang, K. K.; Zhang, H.-R.; Petersen, J. L. *J. Org. Chem.* **1999**, *64*, 1650−1656. (c) Li, H. B.; Zhang, H. R.; Petersen, J. L.; Wang, K. K. *J. Org. Chem.* **2001**, *66*, 6662−6668. (d) Li, H. B.; Petersen, J. L.; Wang, K. K. *J. Org. Chem.* **2001**, *66*, 7804−7810. (e) Yang, Y. H.; Petersen, J. L.; Wang, K. K. *J. Org. Chem.* **2003**, *68*, 8545−8549. (f) Dai, W. X.; Petersen, J. L.; Wang, K. K. *J. Org. Chem.* **2005**, *70*, 6647−6652.

(8) (a) Schmittel, M.; Kiau, S.; Siebert, T.; Strittmatter, M. *Tetrahedron Lett.* **1996**, *37*, 7691−7694. (b) Schmittel, M.; Maywald, M.; Strittmatter, M. *Synlett* **1997**, 165−166.

(9) (a) Ingold, K. U.; Griller, D. *Acc. Chem. Res.* **1980**, *13*, 317−323. (b) Engel, P. S.; Keys, D. E. *J. Am. Chem. Soc.* **1982**, *104*, 6860−6861. (c) Campredon, M.; Kanabus-Kaminska, J. M.; Griller, D. *J. Org. Chem.* **1988**, *53*, 5393−5396. (d) Castellino, A. J.; Bruice, T. C. *J. Am. Chem. Soc.* **1988**, *110*, 1313−1315. (e) Newcomb, M.; Manek, M. B.; Glenn, A. G. *J. Am. Chem. Soc.* **1991,** *113*, 949−958. (f) Adam, W.; Heil, M. *J. Am. Chem. Soc.* **1991**, *113*, 1730−1736. (g) Adam, W.; Finzel, R. *J. Am. Chem. Soc.* **1992**, *114*, 4563−4568. (h) Newcomb, M. *Tetrahedron* **1993**, *49*, 1151−1176. (i) Engel, P. S.; Wu, A. *J. Org. Chem.* **1994**, *59*, 3969−3974. (j) Caldwell, R. A.; Zhou, L. *J. Am. Chem. Soc.* **1994**, *116*, 2271−2275. (k) Engel, P. S.; Lowe, K. L. *Tetrahedron Lett.* **1994**, *35*, 2267−2270. (l) Tanko, J. M.; Blackert, J. F. *J. Chem. Soc., Perkin Trans. 2* **1996**, 1775−1779. (m) Cooksy, A. L.; King, H. K.; Richardson, W. H. *J. Org. Chem.* **2003**, *68*, 9441−9492.

(10) Roubelakis, M. M.; Vougioukalakis, G. C.; Angelis, Y. S.; Orfanopoulos, M. *Org. Lett.* **2006**, *8*, 39−42.

(11) Dopico, P. G.; Finn, M. G. *Tetrahedron* **1999**, *55*, 29−62.

(12) Brunette, S. R.; Lipton, M. A. *J. Org. Chem.* **2000**, *65*, 5114−5119.

(13) Bekele, T.; Christian, C. F.; Lipton, M. A.; Singleton, D. A. *J. Am. Chem. Soc.* **2005**, *127*, 9216−9223.

(14) Schmittel, M.; Vavilala, C. *J. Org. Chem.* **2005**, *70*, 4865−4868.

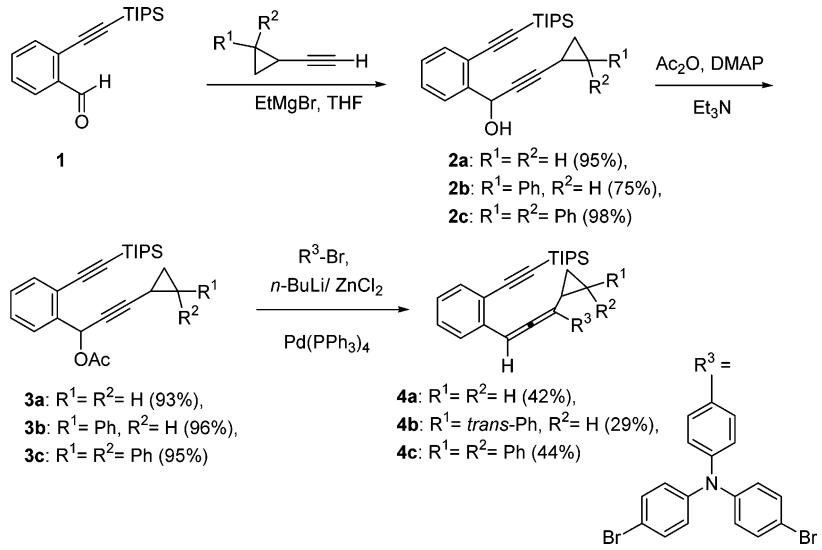
(15) Kevin, R. R.; Larock, R. C. *J. Org. Chem.* **2002**, *67*, 86−94.

(16) The synthesis of *trans*-(2-ethynylcyclopropyl)benzene is described in Supporting Information.

(17) Bettinetti, G. F.; Desimoni, G.; Gruenanger, P. *Gazz. Chim. Ital.* **1964**, *94*, 91−108. For the modified synthesis of (2-ethynyl-1-phenylcyclopropyl)benzene and its molecular structure, as derived from X-ray diffraction analysis, please see Supporting Information.

(18) Schmittel, M.; Strittmatter, M.; Schenk, W. A.; Hagel, M. *Z. Naturforsch., B: Chem. Sci.* **1998**, *53*, 1015−1020.

SCHEME 3. Synthesis of Enyne−Allenes 4a−c



in high yield.[19] Enyne−allenes **4a**−**c** were finally received through a Pd-promoted reaction of R^3-ZnCl with **3a**−**c** at −60 °C in moderate yield.[20]

Thermal Cyclization. Upon thermolysis of enyne−allene **4a** in toluene at 110 °C (reflux temperature) in the presence of an excess of 1,4-CHD, the ene product **5a** and the formal Diels−Alder products **6a**, **6a′**, and **6a″** (with TIPS and without TIPS group) were isolated (Scheme 4, Table 1). Most notable was the formation of the silyl migration product **6a** in 13% yield.

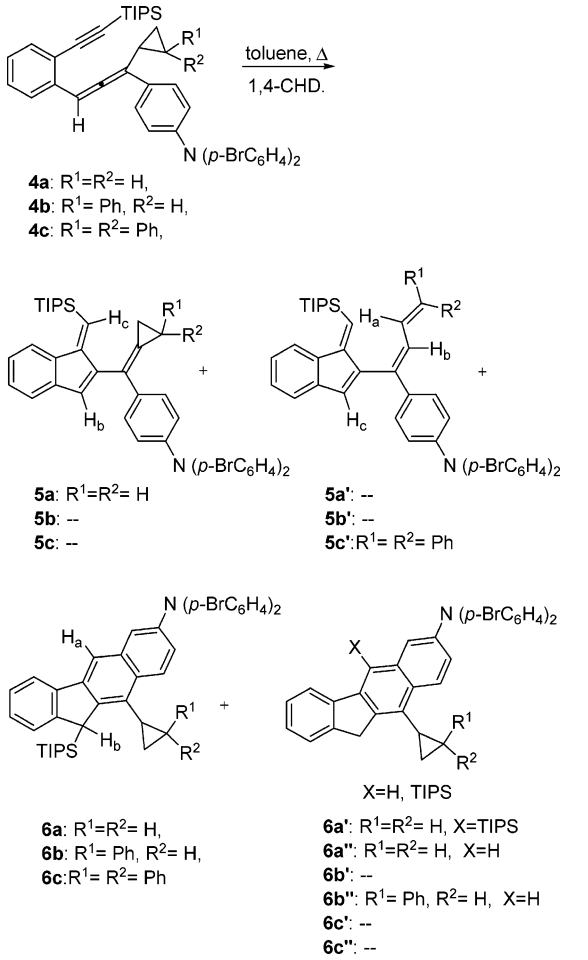
The structures of the ene and the formal Diels−Alder products were assigned on the basis of ^{1}H, ^{13}C, ^{1}H,^{1}H-COSY, and HRMS. The ^{1}H NMR of the silyl migration product **6a** showed a characteristic singlet for proton H_b at 4.76 and another one for H_a at 7.91 ppm. Moreover, the structure of compound **6a** was assigned on the basis of ^{1}H,^{1}H-COSY NMR.

In contrast, thermolysis of enyne−allene **4b** in toluene/1,4-CHD (100 equiv) at 110 °C afforded the silyl migration product **6b** (two isomers) and the formal Diels−Alder product **6b″** (without TIPS group). No formal ene product was observed. The two isomers of compound **6b** showed characteristic singlets in the ^{1}H NMR for proton H_b at 4.69 and 4.78 ppm and for H_a at 7.92 and 7.94 ppm, respectively. The desilylated product **6b″** exhibited a characteristic signal at 4.16 ppm for the -CH_2- unit of the fulvene ring.

When enyne−allene **4c** was heated at 170 °C in a sealed tube in the presence of an excess of 1,4-CHD (100-fold excess) in toluene, the cyclopropyl ring-opened product **5c′** (32%) and silyl shift compound **6c** (25%) yield were isolated. A control experiment in toluene-d_8 did not exhibit deuterium incorporation into **5c′**, suggesting an intramolecular hydrogen transfer.

The structure of ene product **5c′** was assigned on the basis of ^{1}H, ^{13}C, ^{1}H,^{1}H-COSY, HSQC, and HRMS. The ^{1}H NMR of compound **5c′** showed a characteristic doublet with a coupling constant of 11.5 Hz for the two olefinic protons H_a and H_b, suggesting that both protons are *anti* to each other. Product **6c** (a formal Diels−Alder) showed a characteristic singlet at δ = 4.87 for proton H_b and δ = 7.79 for proton H_a. Moreover, the structure of **6c** was established by X-ray structure analysis,

SCHEME 4. Thermal Cyclization of Enyne−Allenes 4a−c



providing unambiguous proof for the silyl group migration (for the X-ray crystal structure see Supporting Information).

Discussion

Radical Clock Experiments. The only reported example of a radical clock experiment in the thermal C^2-C^6 cyclization of enyne−allenes (Scheme 2b) did not exhibit cyclopropyl ring

(19) Borzilleri, R. M.; Weinreb, S. M.; Parvez, M. *J. Am. Chem. Soc.* **1994**, *116*, 9789−9790.

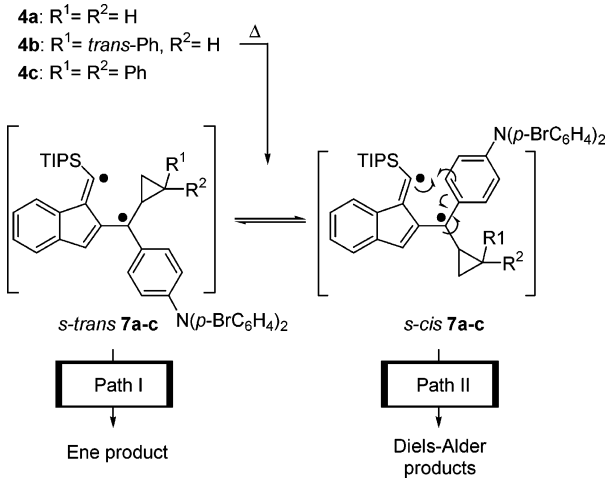
(20) Elsevier, C. J.; Stehouwer, P. M.; Westmijze, H.; Vermeer, P. *J. Org. Chem.* **1983**, *48*, 1103−1105.

TABLE 1. Yields of the Thermal C^2-C^6 Cyclization of 4a−c[a]

			% yield			
entry	compound	reaction condition	ene product **5**/**5′**	DA (with TIPS) **6′**	DA (without TIPS) **6″**	silyl migration product **6** (%)
1	**4a**	110 °C; 14 h	25 (**5a**)	7	20	13
2	**4b**	110 °C; 14 h			15	32
3	**4c**	170 °C; 7 h	32 (**5c′**)			25

[a] In the presence of excess of 1,4-CHD (100 equiv). DA: formal Diels−Alder product.

SCHEME 5. Visualization of the Two Competing Pathways in the Diradical Cyclization of Enyne−Allenes



opening.[5a,d] At that time, in 1996, a stepwise mechanism was derived from the finding that the two diastereomeric enyne−allenes did not convert stereospecifically to the ene product. As the 1996 experiment used an enyne−allene with a cyclopropylcarbinyl reporter group and a phosphine oxide at the allene terminus, we now decided to interrogate the thermal cyclization of enyne−allenes carrying an aryl group at the terminal allene center, as this should emphasize the radical character in the diradical. Triplet and open shell singlet diradicals should be perfectly poised for cyclopropyl ring opening at rates similar to those of monoradicals. Fortunately, rate constants for radical clock reactions in monoradicals are well gauged or can be rather reliably approximated. Computations by Engels,[6a] Schreiner,[6b] and Shaik[6d] et al. advise that the C^2-C^6 diradical has a triplet ground state. Whether this state is involved in the thermal reaction remains unclear, since the thermal reaction conditions should first lead to an open shell singlet diradical from which follow-up ene and formal Diels−Alder products should originate with a low barrier in competition to the radical clock opening.

As described above, thermolysis of enyne−allene **4a** afforded ene and formal Diels−Alder products without ring opening. A look at the proposed stepwise mechanism (Scheme 5) suggests that some appreciable part of diradical **7a** is available in the *s-cis* conformation as the formal Diels−Alder products can only be derived therefrom. In contrast, for the intramolecular hydrogen transfer the benzofulvene diradical **7a** has to adopt the *s-trans* conformation. The ratio of ene versus Diels−Alder products is 5:8. Since interconversion of *s-cis* and *s-trans* **7a** must involve rotation about a C−C bond with partial double bond character, it is not clear whether rotation can compete with the fast and irreversible follow-up reactions leading to the observed products. Clearly, as both reactions prevail in the competition with the radical clock process, they must be much faster than the cyclopropyl ring opening for the α,α-diphenyl-cyclopropylcarbinyl system ($k = 1.1 \times 10^3$ s^{-1} at 20 °C, ca. 2.2×10^5 s^{-1} at 110 °C).[21−23]

In the thermolysis of enyne−allene **4b**, only Diels−Alder products **6b**, **6b″** and no ene product were isolated. As the remote attachment of a phenyl group at the cyclopropyl ring should not influence the electronic situation in the diradical **7b**, the failure to observe any ene product suggests that *s-trans* **7b** is sterically not available, most likely due a repulsive interaction between the phenylcyclopropane and the bulky TIPS group at the alkyne. Exclusive formation of formal Diels−Alder products thus proposes that the diradical intermediate *s-cis* **7b** undergoes radical combination to **6b**,**6b″** faster than cyclopropyl ring opening. As ring opening in *s-cis* **7b** is best mimicked by the opening of the α,α-diphenyl-(2-phenylcyclopropyl)carbinyl radical with an activation energy $E_a = 8.5$ kcal mol,$^{-1}$[1,24] one has to postulate a barrier for the radical combination in **7b** of less than 8 kcal mol^{-1}.

The diphenylcyclopropylcarbinyl group with a rate constant for ring opening of $k = 5.0 \times 10^{11}$ s^{-1} at 25 °C[25a] has been widely used as a ultrafast "radical clock" to trap short-lived radical intermediates.[25] As formation of **6b,6b″** in the thermolysis of **4b** has shown that steric bulk caused by the phenyl group at the cyclopropyl ring will lead preferentially to the *s-cis* diradical, we expected the diphenylcyclopropyl unit in **4c** to entail an even higher population of the *s-cis* diradical **7c**. As a consequence, its ring opening cannot be impeded by the sterically demanding TIPS group. Indeed, with **4c** we were able to see, aside of the Diels−Alder product **6c**, the first radical clock ring opening as indicated by the formation of butadienyl benzofulvene **5c′**. A control experiment in toluene-d_8 verified that **5c′** was exclusively formed by an intramolecular hydrogen transfer, rejecting any mechanistic hypothesis in which the regular ene product **5c** could have served as precursor to **5c′**. Hence, transformation from **4c** to **5c′** should involve ring

(21) Beckwith, A. L. J.; Bowry, V. W. *J. Am. Chem. Soc.* **1994**, *116*, 2710−2716.

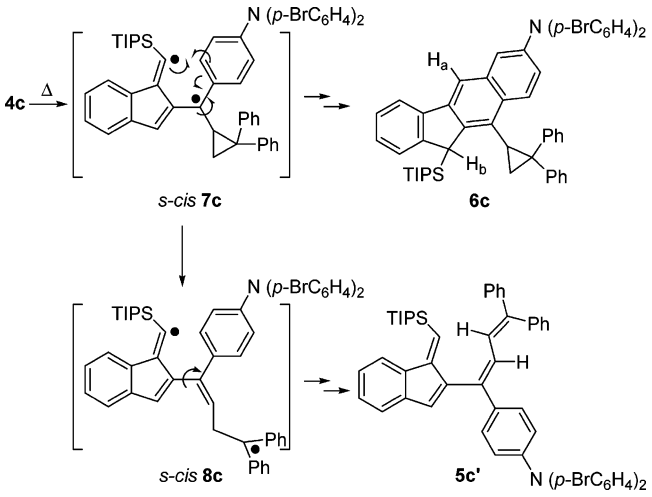
(22) Hollis, R.; Hughes, L.; Bowry, V. W.; Ingold, K. U. *J. Org. Chem* **1992**, *57*, 4284−4287.

(23) For calculations of cyclopropyl ring-opening rate constants at other temperatures, we use the pre-exponential factor $10^{12.85}$ s^{-1} as in ref 22.

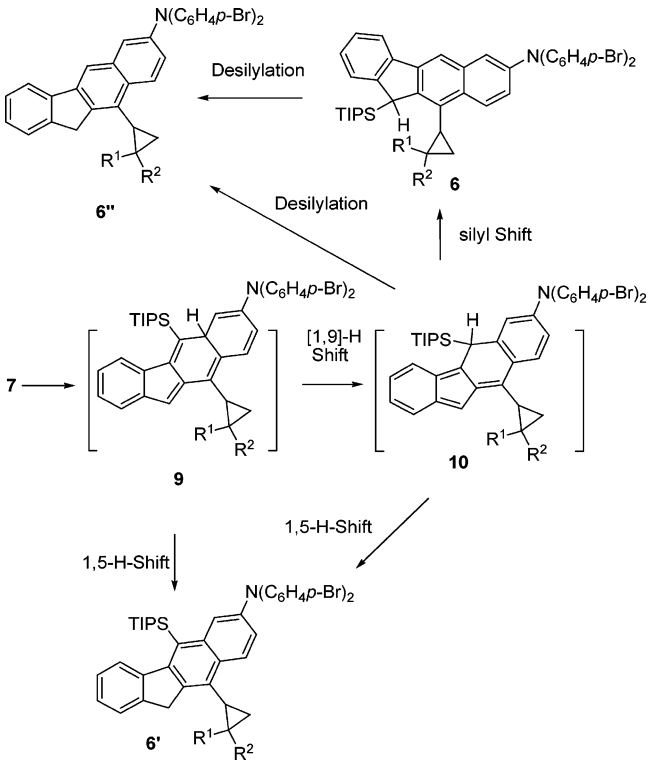
(24) We assume a rate constant of k (20 °C) $= 3.1 \times 10^6$ s^{-1} for the ring opening of the α,α-diphenyl-(2-phenylcyclopropyl)carbinyl radical. At first, the accelerating effect of a 2-phenyl group on the ring opening (2788 x) was evaluated from the comparison of the α-phenyl(cyclopropyl)carbinyl and the cyclopropylcarbinyl radical opening (see refs 22 and 25). This effect was translated onto the ring opening of α,α-diphenyl-(cyclopropyl)carbinyl radical ($k = 1.1 \times 10^3$ s^{-1} at 20 °C).

(25) (a) Newcomb, M.; Johnson, C. C.; Manek, M. B.; Varik, T. R. *J. Am. Chem. Soc.* **1992**, *114*, 10915−10921. (b) Newcomb, M.; Tanaka, N.; Bouvier, A.; Tronche, C.; Horner, J. H.; Musa, O. M.; Martinez, F. N. *J. Am. Chem. Soc.* **1996**, *118*, 8505−8506. (c) Newcomb, M.; Choi, S.-Y.; Horner, J. H. *J. Org. Chem.* **1999**, *64*, 1225−1231. (d) Newcomb, M.; Daublain, P.; Horner, J. H. *J. Org. Chem.* **2002**, *67*, 8669−8671.

SCHEME 6. Thermal Cyclization of Enyne−Allene 4c



SCHEME 7



opening[26] of the intermediate *s-cis* **7c** to *s-cis* **8c** (Scheme 6), followed by rotation to *s-trans* **8c** and an intramolecular hydrogen transfer via a seven-membered transition state. The rate constant of the 2,2-diphenylcyclopropyl methyl radical ring opening in diradical **7c** has become competitive to the rate constant for radical combination in *s-cis* **7c** to **6c**. Unfortunately, on the basis of known data an estimate of the rate constant for opening of the α,α-diphenyl-(2,2-diphenylcyclopropyl)carbinyl radical is imprecise, but it may be approximated with the rate constant of the α-phenyl-(2-phenylcyclopropyl)carbinyl radical ($k_{40°C} = 3.6 \times 10^8$ s^{-1}).[22] Thus, the activation energy for the ring opening of *s-cis* **7c** to *s-cis* **8c** may be estimated to 6 kcal mol^{-1},[22] providing us with a rate constant of $k_{170°C} = 7 \times 10^9$ s^{-1}.

In concluding this part of the discussion, it seems reasonable to state that with the rising number of phenyl groups (from **4a** to **4c**) there is an concomitant increase in the steric repulsion between the cyclopropyl unit and the TIPS group. Hence, in the thermolysis of **4a−c** an augmenting amount of the *s-cis* diradical **7** is formed as an intermediate, which does not allow any more for the stepwise ene reaction to occur with **4b,c**. On the other side, the *s-cis* conformation allows for both the formal Diels−Alder reaction and for the sterically unimpeded ring opening of the cyclopropylcarbinyl reporter group. Only in **4c** the ring opening, however, can compete. This allows us to roughly predict a barrier for the radical combination reaction in **4c**.

Silyl Shift. A further matter of the present work was to understand the multistep process leading to the formal Diels−Alder products. As mentioned above, the *s-cis* diradical **7** suffers radical combination to the unstable Diels−Alder product **9**. In order to account for the isolated products **6**, **6′**, and **6″**, at some stage a partial desilylation process must have occurred after formation of **9**. A clear hint to explain the formation of the desilylated product **6″** came from the isolation and identification of **6**, which was observed in the thermal cyclization of all enyne−allenes **4**. Compound **6** is a good candidate to lose a TIPS group in a very mild hydrolysis reaction.

Similar to **6**, the benzylic silane **10** should also be apt to lose its silyl substituent. However, due its thermodynamic instability, **10** is expected to undergo a variety of hydrogen or silyl shifts, and hence may only be a short-lived intermediate. Thus in summary, **6a−c** seem more to be more promising candidates for TIPS loss. To investigate this matter, we have performed a detailed density functional theory study of the potential reaction pathways leading to the observed products. To reduce the costs in CPU time, a simplified model system was investigated, in which any (phenyl)cyclopropyl substituent was replaced by a methyl group and bromine atoms at the diphenylamine moiety were omitted. In the calculated reaction sequence the starting molecule **9** is thus represented by **X1** and **10** is represented by the two conformers **X5** ⇌ **Y1**.

We selected the standard B3LYP/6-31G(d) method for the investigation of the hydrogen and silyl shifts. In order to test its adequacy, the 1,5-H shift in *s-trans-cis*-1,3-pentadiene was initially studied as a benchmark test. The best estimate for the activation enthalpy of this reaction had been reported as $\Delta H^{\ddagger} = 38.4$ kcal mol^{-1} by Lynch and Truhlar.[27] Employing B3LYP/6-31G(d) we obtained $\Delta H^{\ddagger} = 36.6$ kcal mol^{-1}, which is in reasonable agreement with the above value. We conclude that the B3LYP hybrid density functional[28] is likely to be suitable for the system investigated. In constructing the PES connecting **X1** with **X9** and **Y7**, we have limited our investigations to H and TIPS shifts occurring around the perimeters of the inner two rings of the benzofluorene ring system.[29]

Figure 1 gives a summary of the results of our calculations. Initially, **X1** faces a choice between two orbital-symmetry

(26) (a) Shimizu, N.; Nishida, S. *J. Chem. Soc., Chem. Commun.* **1972**, 389−390. (b) Rudolph, A.; Weedon, A. *Can. J. Chem.* **1990**, *68*, 1590−1596. (c) Adam, W.; Curci, R.; D'Accolti, L.; Dinoi, A.; Fusco, C.; Gasparrini, F.; Kluge, R.; Paredes, R.; Schulz, M.; Smerz, A. K.; Veloza, L. A.; Weinkotz, S.; Winde, R. *Chem. Eur. J.* **1997**, *3*, 105−109.

(27) Lynch, B. J.; Truhlar, D. G. *J. Phys. Chem. A* **2001**, *105*, 2936−2941.

(28) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

(29) This limitation appears justified, as a 1,9-H-shift to position 4 in the benzofluorene framework (a H-shift to the right hand side from **X1** as depicted in Figure 4) results in a thermodynamically very unfavorable quinoidal product.

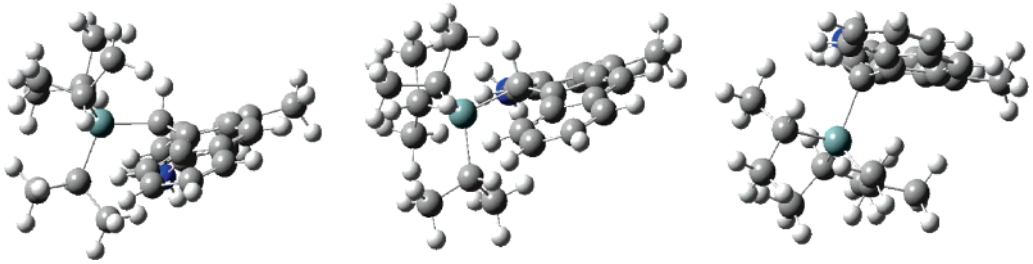


FIGURE 1. Structures of **X5** (left), the transition state connecting **X5** and **Y1** (middle), and **Y1** (right), as calculated at the B3LYP/6-31G(d) level of theory. The diphenylamino group present in the molecules was replaced by a simple amino group for the sake of clarity.

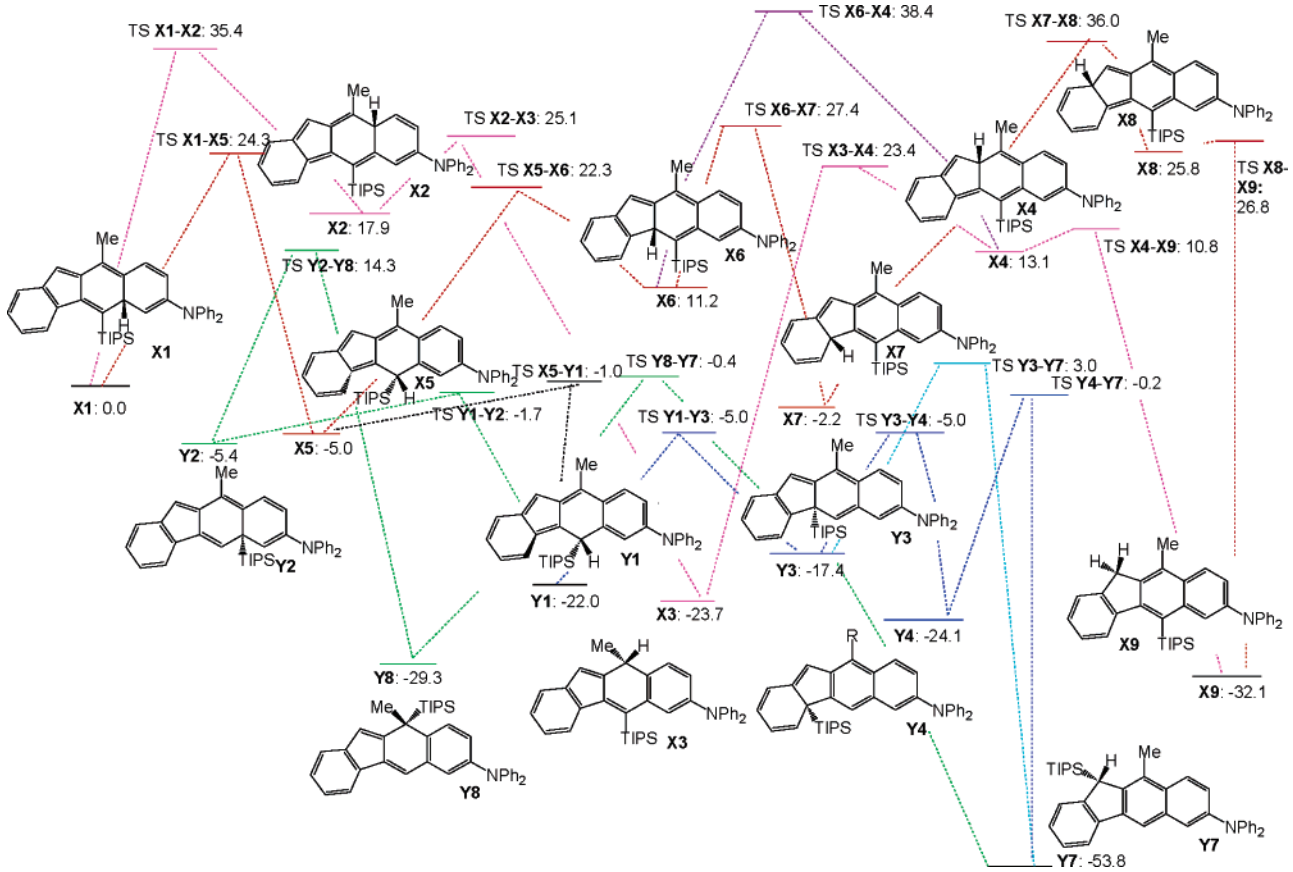


FIGURE 2. Calculated reaction pathways leading from **X1** to **X9** and **Y7**. Color encoding has been used to facilitate visualization of individual reaction pathways. "Warm" colors (red, magenta, dark violet) indicate reaction pathways involving hydrogen shift, whereas "cold" colors (dark blue, light blue, green) indicate a reaction pathway involving a triisopropylsilyl shift. The color black is used for the starting point **X1**, the end points **X9** and **Y7**, and for **Y1**. The energies given are in kcal mol^{-1} relative to **X1** = 0.

allowed 1,9-hydrogen shifts yielding **X2** and **X5**. Of the two reactions, the one yielding **X5** is predicted to be kinetically favored by a wide margin. From **X2**, on the other hand, the thermodynamically very favorable product **X3** may become accessible with a small barrier. **X5** represents 3-diphenylamino-11-methyl-5-triisopropylsilyl-5*H*-benzofluorene in the higher energy conformation, with the TIPS group being located equatorially and the hydrogen atom 5-H located in axial position, as required for further hydrogen shifts. In the second, much more favorable conformer **Y1** the bulky TIPS substituent has moved to the axial position. The $\Delta H^{\ddagger} = -17.0$ kcal mol^{-1} for **X5** → **Y1** is most likely due to a very unfavorable *peri*-interaction with the hydrogen atom located in position 6 leading to a destabilization of **X5**. The barrier for conversion of **X5** to **Y1** is predicted to be small (4.0 kcal mol^{-1}), suggesting that **X5** will be rapidly converted to **Y1** (Figure 2). Obviously, the axial TIPS substituent is ideally positioned for further TIPS-shifts that may ultimately lead to the formation to **Y7**, corresponding to product **6** in the experiment. Conversion of **X5** into **Y1** is analogous to the movement of a hinge connecting the reaction pathways involving hydrogen transfer and those involving silyl transfer. In the transition state linking **X5** and **Y1**, the vibrational mode with the imaginary force constant corresponds to a rotation around the C5−Si bond coupled to an out-of-plane movement of the C6−C7−C8−C9 ring fragment. This movement can be compared to the interaction of a balance spring (C6−C7−C8−C9 ring fragment) and a tooth-wheel (TIPS group) in a clockwork.

From **Y1**, the reaction may again bifurcate. The kinetically preferred pathway (dark blue) runs via the TIPS-benzofluorene

Y3 and via the TIPS-benzofluorene **Y4** to the final product **Y7**. We note that 3-diphenylamino-11-methyl-9b-triisopropylsilyl-9b*H*-benzofluorene (**Y6**, see Supporting Information), which is expected to be found along the reaction coordinate connecting **Y4** and **Y7**, in our hands was a minimum structure only in preoptimizations performed at the RHF/STO-3G level of theory. It could no longer be located if density functional theory (B3LYP/6-31G(d) or BHandHLYP/6-31G(d)) was used. Similarly, 3-diphenylamino-11-methyl-10b-triisopropylsilyl-10b*H*-benzofluorene (**Y5**, see Supporting Information) between **Y3** and **Y7** (reaction pathway indicated by light blue color) and 3-diphenylamino-11-methyl-11b-triisopropylsilyl-11b*H*-benzofluorene (**Y9**, see Supporting Information) between **Y2** and **Y8** (reaction pathway indicated by green color) could not be located at the B3LYP/6-31G(d) level of theory. This finding does not rule out that these structures could be true minima. However, it appears highly unlikely that these molecules, even if they existed, would be protected by significant barriers against decay by TIPS shift. The barriers for the TIPS shifts are generally predicted to be smaller than the barriers for the hydrogen shift reactions. This observation is consistent with our failure to isolate any of the **Y** compounds except the final product **Y7**.

Formation of **X5** from **X1** ("red" pathway) is predicted to be kinetically favored over formation of **X2**/**X3** ("magenta" pathway) by such a wide margin ($\Delta\Delta H^{\ddagger} = 10.1$ kcal mol^{-1}) that essentially only the red pathway should be followed. As a result of the low barrier for conversion of **X5** into **Y1**, all **X5** formed in the course of the reaction is likely to convert to **Y1**, which will eventually rearrange to final product **Y7**.

Our calculations on the facile thermal silyl shifts in the model system thus suggest that only products should be formed that have undergone TIPS shifts. This is in agreement with the experimental results obtained with **4b** and **4c** but contrasts with the behavior of **4a**, where small amounts of the Diels−Alder product with the TIPS substituent still in its original place were also formed. The reason for this discrepancy is unclear at present.

Conclusions

In the present investigation we describe the first successful trapping of a thermally generated C^2-C^6 diradical intermediate using an ultrafast radical clock. Therefore, the present results furnish direct evidence for a stepwise mechanism in the C^2-C^6 cyclization of enyne−allenes. In several cases, the C^2-C^6 cyclization of enyne−allenes to formal Diels−Alder products is accompanied by a loss of the TIPS group. Through a combination of experimental and computational studies it is suggested that a facile silyl shift followed by a desilylation is operative.

Experimental Section

Bis(4-bromophenyl)-(4-{1-cyclopropyl-3-[(2-triisopropylsilanylethynyl)phenyl]-propa-1,2-dienyl}phenyl)amine (4a). In 50 mL of dry diethyl ether tris(4-bromophenyl)-amine (1.46 g, 3.02 mmol) was cooled to 0 °C in an ice bath. *n*-BuLi (2.5 M) (1.21 mL, 3.02 mmol) was added dropwise and stirred. After 4 h this reaction mixture was added dropwise to a 1 M $ZnCl_2$ solution (412 mg in 3.02 mL of diethyl ether) and stirred for 60 min at room temperature. Now the reaction mixture was cooled to −60 °C, and $Pd(PPh_3)_4$ (87.0 mg, 750 μmol) in dry THF (5 mL) was added dropwise. After stirring for 30 min at the same temperature, propargyl acetate **3a** (300 mg, 730 μmol) in dry THF (10 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 diethyl ether (2 × 50 mL). The combined organic layers were dried over sodium sulfate and evaporated under reduced pressure. After purification by column chromatography (neutral alumina, *n*-pentane) compound **4a** was isolated as light yellow oil. $R_f = 0.5$. Yield: 236 mg, 42%. IR (film) $\tilde{\nu}$: 3068 (w), 2942 (s, C−H), 2864 (s), 2151 (s, C≡C), 1928 (m, C═C═C), 1580 (s), 1505 (s), 1482 (m), 1313 (s), 1285 (s), 1178 (m), 1118 (m), 1072 (m), 1008 (m), 821 (s), 665 (m) cm^{-1}. ^{1}H NMR (400 MHz, acetone-d_6): δ 0.51−0.55 (m, 1H), 0.59−0.63 (m, 1H), 0.92−0.97 (m, 2H), 1.18 (s, 21H), 1.73−1.80 (m, 1H), 7.01 (d, $J = 8.9$ Hz, 4H), 7.08 (d, $J = 8.7$ Hz, 2H), 7.21 (d, $J = 2.5$ Hz, 1H), 7.24 (td, $J = 7.5$, 1.3 Hz, 1H), 7.33 (td, $J = 7.6$, 1.2 Hz, 1H), 7.39 (d, $J = 7.2$ Hz, 1H), 7.44 (d, $J = 8.8$ Hz, 4H), 7.52 (dd, $J = 7.6$, 0.9 Hz, 1H), 7.57 (d, $J = 8.5$ Hz, 2H). ^{13}C NMR (100 MHz, acetone-d_6): 7.2, 7.9, 11.6, 12.0, 19.0, 96.3, 97.6, 106.0, 116.0, 122.1, 125.4, 126.5, 126.7, 128.0, 128.4, 129.9, 132.1, 133.3, 133.8, 134.3, 134.5, 147.0, 147.4, 207.4 ppm. HRMS: calcd for $C_{41}H_{43}{}^{79}Br_2NSi$ 735.153, found 735.152.

Bis(4-bromophenyl)-(4-{1-(2-(*trans*-phenylcyclopropyl)-3-[(2-triisopropylsilanylethynyl)-phenyl]-propa-1,2-dienyl}-phenyl)-amine (4b). Procedure as for **4a**. Yield: 165 mg, 29%. IR (film) $\tilde{\nu}$: 3065 (w), 2942 (s, C−H), 2864 (s), 2153 (s, C≡C), 1929 (m, C═C═C), 1747 (s), 1581 (s), 1505 (s), 1486 (s), 1370 (m), 1313 (s), 1285 (s), 1235 (s), 1179 (m), 1118 (m), 1073 (m), 1009 (m), 822 (s), 665 (m) cm^{-1}. ^{1}H NMR (400 MHz, acetone-d_6) two isomers: δ 1.17−1.20 (m, 21H), 1.26−1.34 (m, 1H), 1.36−1.42 (m, 1H), 2.01−2.06 (m, 1H), 2.16−2.21 (m, 1H), 6.97 (d, $J = 8.8$ Hz, 4H), 7.01 (d, $J = 8.7$ Hz, 2H), 7.16−7.22 (m, 3H, Ar-H), 7.25−7.38 (m, 5H), 7.42 (d, $J = 8.8$ Hz, 4H), 7.46 (d, $J = 8.4$ Hz, 2H), 7.45−7.56 (m, 2H, Ar-H). ^{13}C NMR (100 MHz, acetone-d_6) two isomers : 12.0, 16.6, 17.1, 19.1, 23.6, 24.0, 26.9, 27.5, 96.4, 96.5, 98.1 (2C), 106.0 (2C), 113.3, 113.4, 116.1, 122.2, 124.6, 124.8, 124.9, 125.2, 125.3, 125.5, 125.6, 125.9, 126.4, 126.5 (3C), 126.6, 126.7, 127.0, 128.1, 128.3, 128.4, 129.3, 130.0 (2C), 130.4, 131.6, 131.8, 133.0, 133.2, 133.8, 136.5, 136.8, 142.9, 147.1 (2C), 147.3, 207.4, 207.5 ppm. HRMS: calcd for $C_{47}H_{47}{}^{79}Br_2NSi$ 811.184, found 811.183.

Bis(4-bromophenyl)-(4-{1-(2,2-diphenylcyclopropyl)-3-[(2-triisopropylsilanylethynyl)-phenyl]-propa-1,2-dienyl}-phenyl)-amine (4c). Procedure as for **4a**. Yield: 219 mg, 44%. IR (film) $\tilde{\nu}$: 3031 (w), 2942 (s, C−H), 2864 (s), 2151 (m, C≡C), 1929 (w, C═C═C), 1581 (m), 1505 (s), 1486 (s), 1313 (s), 1285 (s), 1235 (s), 1179 (m), 1073 (m), 1008 (m), 882 (m), 822 (m), 757 (m), 701 (m), 677 (m) cm^{-1}. ^{1}H NMR (400 MHz, acetone-d_6) two isomers: δ 1.16 (s, 42H), 1.62−1.67 (m, 2H), 1.71−1.74 (m, 1H), 1.82 (t, $J = 5.5$ Hz, 1H), 2.58−2.64 (m, 1H), 2.69 (t, $J = 6.7$ Hz, 1H), 5.66 (s, 1H), 5.68 (s, 1H), 6.83 (t, $J = 7.6$ Hz, 1H), 6.94−7.08 (m, 15H), 7.18−7.33 (m, 22H), 7.38−7.49 (m, 14H). ^{13}C NMR (100 MHz, acetone-d_6) two isomers: 11.1, 18.2 (2C), 19.8, 20.0, 26.2, 28.0, 38.7, 39.3, 95.2, 95.3, 96.6, 96.8, 105.0, 105.1, 109.5, 109.6, 115.2 (2C), 120.8. 120.9, 123.6 (2C), 123.7 (2C), 124.1 (2C), 124.6 (2C), 125.1, 125.2, 125.6 (2C), 125.7, 125.8, 126.1, 126.2, 126.4, 126.7, 126.8, 127.0, 127.2, 127.3, 127.4, 127.7, 128.3, 128.4, 128.9, 129.0, 129.5, 130.4, 131.1, 131.5, 131.6, 132.1 (2C), 132.3 (2C), 132.4, 132.9, 135.0, 135.8, 140.3, 141.2, 145.9 (2C), 146.0 (2C), 146.3, 207.6, 208.1 ppm. HRMS: calcd for $C_{53}H_{51}{}^{81}Br^{79}$-BrNSi 889.215, found 889.215.

Standard Protocol for Thermolysis. Enyne−allenes **4a−c** were dissolved in dry toluene in the presence of 1,4-CHD (100 equiv) and heated at 110 (reflux temperature) or 170 °C (sealed tube) for 7−14 h. After removal of toluene under reduced pressure and purification by chromatography (aluminum sheet, silica gel $60F_{254}$, *n*-hexane) products were isolated as a yellow oil/solid.

Bis(4-bromophenyl)-[4-(cyclopropylidene-{1-[(triisopropylsilanyl)-methylene]-1*H*-inden-2-yl}-methyl)-phenyl]-amine (5a). Yield: 5.0 mg, 25%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.00 (d, $J = 7.4$ Hz, 18H), 1.21−1.25 (m, 2H), 1.32 (septet, $J = 7.5$ Hz, 3H),

1.56−1.61 (m, 2H), 6.20 (s, 1H), 6.81 (s, 1H), 6.92 (d, J = 8.8 Hz, 4H), 6.95 (d, J = 8.6 Hz, 2H), 7.12−7.18 (m, 1H), 7.22−7.25 (m, 2H), 7.31 (d, J = 8.8 Hz, 4H), 7.43 (d, J = 8.5 Hz, 2H), 7.65 (d, J = 7.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 2.2, 5.5, 12.9, 19.1, 115.3, 120.5, 122.1, 124.1, 124.5, 124.7, 125.2, 125.3, 125.6, 128.1, 130.6, 132.2, 132.5, 136.2, 136.8, 144.0, 144.3, 145.2, 146.4, 155.1 ppm. HRMS: calcd for $C_{41}H_{43}{}^{81}Br^{79}BrNSi$ 737.152, found 737.151.

Bis(4-bromophenyl)-(10-cyclopropyl-11-triisopropylsilanyl-11*H*-benzo[*b*]fluoren-7-yl)-amine (6a). Yield: 2.6 mg, 13%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.38−0.44 (m, 1H), 0.74−0.79 (m, 1H), 0.83 (d, J = 7.5 Hz, 9H), 0.85 (d, J = 7.5 Hz, 9H), 1.18−1.23 (m, 5H), 2.26−2.38 (m, 1H), 4.76 (s, 1H), 7.03 (d, J = 8.8 Hz, 4H), 7.23 (dd, J = 9.1, 2.4 Hz, 1H), 7.28−7.32 (m, 2H), 7.37 (d, J = 8.8 Hz, 4H), 7.48 (d, J = 2.3 Hz, 1H), 7.54 (d, J = 7.2 Hz, 1H), 7.82 (d, J = 6.7 Hz, 1H), 7.91 (s, 1H), 8.40 (d, J = 9.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 8.9, 10.3, 12.1, 12.9, 18.5, 18.7, 29.7, 38.5, 115.4, 116.1, 120.5, 121.7, 122.9, 124.1, 125.3, 125.5, 126.6, 126.8, 132.3 (2C), 132.7, 133.4, 139.9, 140.4, 143.0, 145.4, 146.6, 147.2 ppm. HRMS: calcd for $C_{41}H_{43}{}^{81}Br^{79}BrNSi$ 737.152, found 737.152

Bis(4-bromophenyl)-(10-cyclopropyl-5-triisopropylsilanyl-11*H*-benzo[*b*]fluoren-7-yl)-amine (6a′). Yield: 1.5 mg, 7%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.83−0.88 (m, 2H), 1.11 (d, J = 7.4 Hz, 18H), 1.20−1.23 (m, 2H), 1.46 (septet, J = 7.4 Hz, 3H), 2.15−2.21 (m, 1H), 4.16 (s, 2H), 7.02 (d, J = 8.8 Hz, 4H), 7.23 (dd, J = 9.1, 2.3 Hz, 1H), 7.37 (d, J = 8.8 Hz, 4H), 7.47 (d, J = 7.4 Hz, 1H), 7.51 (d, J = 2.3 Hz, 1H), 7.58 (d, J = 7.5 Hz, 1H), 7.92 (s, 1H), 7.96 (s, 1H), 8.46 (d, J = 9.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 7.2, 10.9, 11.3, 18.6, 29.7, 36.2, 115.5, 116.0, 119.5, 121.9, 123.0, 124.3, 125.6, 126.7, 127.1, 130.1, 132.3, 133.0, 133.4, 134.6, 140.1, 140.6, 141.0, 143.7, 144.4, 146.6 ppm. HRMS: calcd for $C_{41}H_{43}{}^{79}Br_2NSi$ 735.153, found 735.152.

Bis(4-bromophenyl)-(10-cyclopropyl-11*H*-benzo[*b*]fluoren-7-yl)-amine (6a″). Yield: 3.1 mg, 20%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86−0.90 (m, 2H), 1.19−1.23 (m, 2H), 2.16−2.23 (m, 1H), 4.16 (s, 2H), 7.02 (d, J = 8.8 Hz, 4H), 7.23 (dd, J = 9.1, 2.3 Hz, 1H), 7.34 (m, 2H, Ar-H), 7.37 (d, J = 8.8 Hz, 4H, Ar-H), 7.51 (d, J = 2.1 Hz, 1H), 7.58 (d, J = 7.1 Hz, 1H), 7.83 (d, J = 6.8 Hz, 1H), 7.90 (s, 1H), 8.47 (d, J = 9.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 7.2, 11.3, 29.7, 36.2, 115.5, 116.3, 120.5, 122.1, 123.3, 125.1, 125.5, 126.7, 126.8, 127.6, 130.2, 132.3, 133.4, 134.6, 140.7, 140.8, 140.9, 143.8, 143.9, 146.6 ppm. HRMS: calcd for $C_{32}H_{23}{}^{79}Br_2N$ 579.020, found 579.019.

Bis(4-bromophenyl)-[10-(2-phenylcyclopropyl)-11-triisopropylsilanyl-11*H*-benzo[*b*]fluoren-7-yl]-amine (6b). Yield: 8.6 mg, 32%. IR (film) $\tilde{\nu}$: 2865 (s, C−H), 1580 (m, C═C), 1485 (s), 1282 (m), 1072 (m), 883 (m), 821 (m), 755 (m), 698 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) two isomers: δ 0.54 (d, J = 7.5 Hz, 9H), 0.66 (d, J = 7.5 Hz, 9H), 0.89 (2 × d, J = 7.6 Hz, 18H + 3H), 0.98−1.07 (m, 3H), 1.46−1.50 (m, 2H), 1.66−1.73 (m, 2H), 1.86−1.91 (m, 1H), 2.03−2.07 (m, 1H), 2.57−2.63 (m, 1H), 2.65−2.71 (m, 1H), 4.69 (s, 1H), 4.78 (s, 1H), 6.77 (d, J = 8.9 Hz, 1H), 7.02 (d, J = 8.8 Hz, 4H), 7.05 (d, J = 8.8 Hz, 4H), 7.15 (dd, J = 9.1, 2.4 Hz, 1H), 7.19−7.24 (m, 5H), 7.33−7.41 (m, 17H), 7.48−7.57 (m, 4H), 7.85 (d, J = 7.2 Hz, 2H), 7.92 (s, 1H), 7.94 (s, 1H), 8.04 (d, J = 9.1 Hz, 1H), 8.40 (d, J = 9.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) two isomers: δ 11.5, 12.1, 18.3, 18.5, 18.6, 18.7, 24.9, 26.6, 26.7, 28.1, 38.4, 40.3, 115.5 (2C), 116.2, 116.3, 120.6, 120.7, 121.5, 121.8, 123.0, 123.1, 124.0, 124.1, 124.9, 125.2, 125.4, 125.6 (2C), 125.8, 125.9, 126.6, 126.7, 126.8, 127.1, 128.5, 128.7, 129.7, 130.4, 131.9, 132.1, 132.4 (2C), 133.5, 133.6, 139.7, 139.8, 140.0, 140.4, 140.5, 142.8, 143.0, 143.2, 143.9, 144.9, 146.1, 146.6 (2C), 147.0, 147.3 ppm. HRMS: calcd for $C_{47}H_{47}{}^{81}Br^{79}BrN$ 813.183, found 813.182.

Bis(4-bromophenyl)-[10-(2-phenylcyclopropyl)-11*H*-benzo[*b*]fluoren-7-yl]-amine (6b″). Yield: 3.3 mg, 15%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.59−1.62 (m, 1H), 1.66−1.70 (m, 1H), 2.25−2.32 (m, 1H), 2.50−2.57 (m, 1H), 4.16 (s, 2H), 7.01 (d, J = 8.8 Hz, 4H), 7.20 (dd, J = 9.1, 2.3 Hz, 1H), 7.30−7.41 (m, 11H), 7.52 (d, J = 2.4 Hz, 1H), 7.58 (d, J = 7.2 Hz, 1H), 7.84 (d, J = 6.9 Hz, 1H), 7.92 (s, 1H), 8.26 (d, J = 9.1 Hz, 1H). HRMS: calcd for $C_{38}H_{27}{}^{79}Br_2N$ 655.051, found 655.050.

Bis(4-bromophenyl)-[4-((*E*)-4,4-diphenyl-1-{1-[1-trimethylsilanyl-meth-(*E*)-ylidene]-1*H*-inden-2-yl}-buta-1,3-dienyl)-phenyl]-amine (5c′). Yield: 12 mg, 32%. IR (film) $\tilde{\nu}$: 3051 (m), 2942 (s, C−H), 2865 (s), 1582 (m), 1486 (s), 1312 (s), 1265 (s), 1178 (w), 1072 (m), 1008 (m), 882 (m), 823 (s), 740 (s), 702 (s) cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ 1.03 (d, J = 7.4 Hz, 18H), 1.32 (septet, J = 7.5 Hz, 3H), 6.52 (d, J = 8.8 Hz, 4H), 6.60 (d, J = 8.7 Hz, 2H), 6.69 (s, 1H), 6.83 (s, 1H), 6.90−6.93 (m, 3H), 7.10 (d, J = 8.8 Hz, 4H), 7.12−7.16 (m, 3H), 7.16−7.24 (m, 8H), 7.30 (d, J = 11.5 Hz, 1H), 7.37 (d, J = 6.9 Hz, 2H), 7.94 (dd, J = 5.4, 2.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.9, 19.1, 115.6, 120.9, 122.2, 123.7, 125.0, 125.5, 126.4, 127.3, 127.4, 127.6, 127.7, 127.9, 128.1, 128.2, 130.7, 132.3, 132.7, 133.5, 136.2, 137.2, 137.7, 139.9, 142.3, 142.7, 143.3, 143.9, 145.9, 146.2, 155.4 ppm. HRMS: calcd for $C_{33}H_{27}{}^{81}Br^{79}BrN$ 889.215, found 889.215.

Bis(4-bromophenyl)-[10-(2,2-diphenylcyclopropyl)-11-triisopropylsilanyl-11*H*-benzo[*b*]fluoren-7-yl]-amine (6c). Yield: 9.3 mg, 25%. IR (film) $\tilde{\nu}$: 3053 (m), 2978 (s, C−H), 2872 (s), 2306 (w), 1488 (m), 1446 (m), 1384 (m), 1266 (s), 1152 (m), 1114 (m), 1076 (m), 896 (m), 740 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.82 (d, J = 7.4 Hz, 9H), 0.86 (d, J = 7.5 Hz, 9H), 1.25 (septet, J = 7.5 Hz, 3H), 1.90 (dd, J = 8.9, 4.9 Hz, 1H), 2.19 (dd, J = 6.2, 5.2 Hz, 1H), 3.63 (t, J = 7.7 Hz, 1H), 4.87 (s, 1H), 6.28 (d, J = 7.4 Hz, 2H), 6.58 (t, J = 7.7 Hz, 2H), 6.71 (t, J = 7.2 Hz, 1H), 6.83 (d, J = 8.9 Hz, 4H), 6.93 (dd, J = 9.0, 2.3 Hz, 1H), 7.23 (d, J = 2.2 Hz, 1H), 7.29−7.35 (m, 2H), 7.32 (d, J = 8.8 Hz, 4H), 7.43 (t, J = 7.6 Hz, 2H), 7.61 (d, J = 7.9 Hz, 3H), 7.79 (s, 1H), 7.84 (dd, J = 6.8, 1.4 Hz, 1H), 8.18 (d, J = 9.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.1, 18.6 (CH_3 (CH) Si), 18.7 (CH_3 (CH) Si), 24.5, 29.0, 38.0, 38.9, 115.0, 116.3, 120.5, 121.9, 122.9, 124.1, 124.6, 125.0, 125.4, 126.2, 126.5, 126.6, 127.4, 127.8, 128.7, 129.3, 130.6, 131.9, 132.1, 132.7, 139.9, 140.2, 140.7, 142.6, 146.1, 146.6, 146.7, 146.8 ppm. HRMS: calcd for $C_{33}H_{27}{}^{81}Br^{79}BrN$ 889.215, found 889.215.

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Supporting Information Available: Experimental procedures for compound **2a,c**−**3a,c**, ^{1}H, ^{13}C spectra for all compounds, ORTEP drawings of compound (2-ethynyl-1-phenylcyclopropyl)-benzene (**17**), and crystallographic data for the X-ray diffraction analyses of **6c** and **17** in CIF format. Details of the computation. This material is available free of charge via the Internet at http://pubs.acs.org.

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