Classical Versus Nonstatistical Behavior in the C^2–C^6/Ene Cyclization of Enyne–Allenes: Intramolecular Kinetic Isotope Effects and Radical Clock Reactions

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Dedicated to Professor Rolf Huisgen on the occasion of his 90th birthday

Abstract: The effects of aryl groups on the mechanism of the C^2–C^6/ene cyclization of enyne–allenes were studied by means of radical clock openings and intramolecular kinetic isotope effects. Upon attachment of a single aryl group at either the alkyne or the allene terminus, the thermal reaction proceeds by a stepwise mechanism that shows significant nonstatistical dynamic effects. Despite this, we were able to intercept the intermediate diradical intramolecularly by using the ultrafast diphenylcyclopropyl radical clock reaction. When aryl groups were present at both the alkyne and allene termini, the intramolecular kinetic isotope effects were consistent with a classical stepwise mechanism. The present study thus demonstrates the shift in reaction mechanism from a nonstatistical stepwise mechanism to a classical stepwise behavior, depending on the substituents.

Key words: ene reactions, allenes, alkynes, radical reactions, ring closure, kinetic isotope effects

A major concern in chemistry is the elucidation of the precise mechanism for a given chemical reaction. Two main categories of mechanism are addressed within classical physical organic chemistry: concerted and stepwise. By using experimental techniques such as kinetic isotope effect (KIE) studies, trapping experiments, stereospecific labeling, and spectroscopic observations,[1] in conjunction with theoretical studies, many mechanisms have been classified as either concerted or stepwise. Even two decades ago, however, Carpenter emphasized that the complexity of a reaction mechanism may depend on the significance and contribution of nonstatistical dynamic effects.[2] In particular, when molecules with a large excess of kinetic energy pass through an intermediate that lies in a shallow energy well, they may fail to undergo vibrational energy redistribution and may proceed along a vibrational mode that is mainly determined in the preceding transition state to form products directly. In such cases, the overall reaction mechanism will appear to be a concerted process in terms of the nature of its products and stereoselectivity, despite the existence of an intermediate on the potential-energy surface.[3] Several reactions involving diradical intermediates show this type of behavior.

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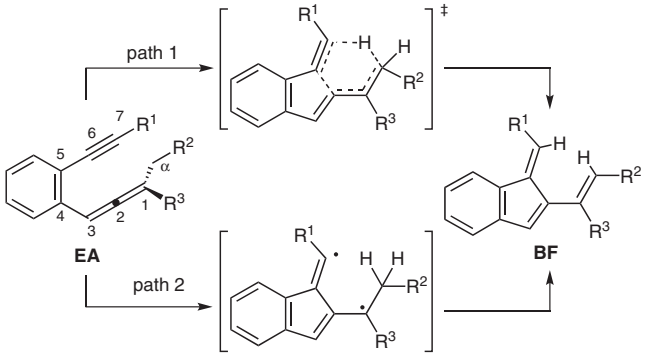
The thermal C^2–C^6 cyclization of enyne–allenes,[4] a regiovariant of the well-known Myers–Saito cyclization,[5] has been extensively studied both mechanistically[6] and theoretically,[7] because of its importance in the synthesis of complex carbocycles[8] and in DNA cleavage.[9] On the basis of the trapping of an intermediate with cyclohexa-1,4-diene,[6e] the observation of DNA double-strand cleavage,[9] and computational studies,[6e] we proposed a diradical mechanism for the C^2–C^6 cyclization similar to that of the Myers-Saito cyclization. In one variant of the thermal C^2–C^6 cyclization of enyne–allenes, a formal ene reaction was observed upon incorporation of an alkyl group at the allene terminus (Scheme 1). In such cases, the intermediate C^2–C^6 diradical abstracts a C_α hydrogen to give a formal ene product.



Scheme 1 Possible reaction mechanisms for the thermal C^2–C^6/ene cyclization of enyne–allenes (**EA**); concerted route (path 1) versus stepwise route (path 2).

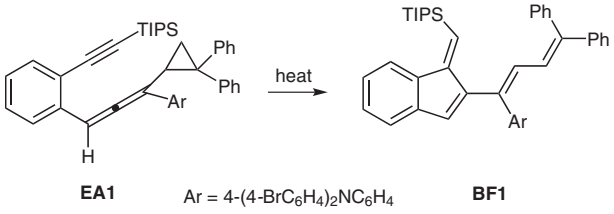
Depending on the substituents at the alkyne and allene termini, the mechanistic course of the C^2–C^6/ene cyclization may change, and different products will be formed. On the basis of calculations at the (U)B3LYP/6-31G(d) level, Engels[10] predicted that the attachment of a phenyl group to the alkyne (C7) terminus results in a stepwise reaction mechanism, whereas a concerted process is more favored when a hydrogen or a *tert*-butyl group is present. Recent results have led to a broader generalization: an aryl group (or any other radical-stabilizing group) at either the allene or alkyne terminus should steer the reaction toward a stepwise mechanism involving a diradical intermediate. Convincing support for this mechanism has only been

established for aryl substitution at the allene terminus (with a triisopropylsilyl group at the alkyne locus and a 4-methoxyphenyl group at the allene terminus) in an intermolecular KIE study.[11]

However, the mechanistic situation is much more complex than merely a dichotomy between a concerted and a stepwise reaction. The C^2–C^6/ene cyclization of an enyne–allene lacking any radical-stabilizing substituents was examined by Singleton and Lipton through studies on the intermolecular KIE, as well as by theoretical and dynamic calculations of trajectories.[12] The observed KIE of 1.43 agreed well with the theoretically predicted value of 1.54 for a concerted ene process. For the parent enyne–allene **EA** (R^1 = Me; R^2 = R^3 = H), which lacks benzannulation, the authors could locate only one transition state at the (U)B3LYP/6-31G(d,p) level that corresponded to the concerted process. In dynamic trajectory simulations starting from this transition state, many of the trajectories led to the diradical intermediate (28 out of 101), while the remainder took the concerted route. As a consequence, Singleton and Lipton postulated that both the stepwise and concerted ene reaction of enyne–allenes proceed via a single transition state, and that dynamic effects at a post-transition-state valley–ridge inflection point decide whether concerted or stepwise trajectories are adopted.

This theoretical study received strong experimental conformation from our recent studies on the KIEs in the C^2–C^6/ene cyclization of various enyne–allenes substituted at the alkyne terminus with *tert*-butyl, trimethylsilyl, or triisopropylsilyl groups and at the allene terminus with 4-methoxyphenyl or trimethylsilyl groups,[13] as the observed inter- and intramolecular KIEs clearly deviated from the statistical ratios. When a radical-stabilizing substituent, such as 4-methoxyphenyl, was present at the allene terminus, the stepwise mechanism was more pronounced than the concerted one. In the absence of a radical-stabilizing group, however, the concerted mechanism was more favored. The results from the kinetic isotope study were also consistent with recent radical clock experiments.[14] In the case of allene **EA1** (Scheme 2), which has an aryl group at the allene terminus, trapping of the diradical intermediate was readily accomplished by using an ultrafast diphenylcyclopropyl radical clock, whereas slower radical clocks, e.g. cyclopropyl or phenylcyclopropyl groups, did not permit trapping of the diradical intermediate.[14]

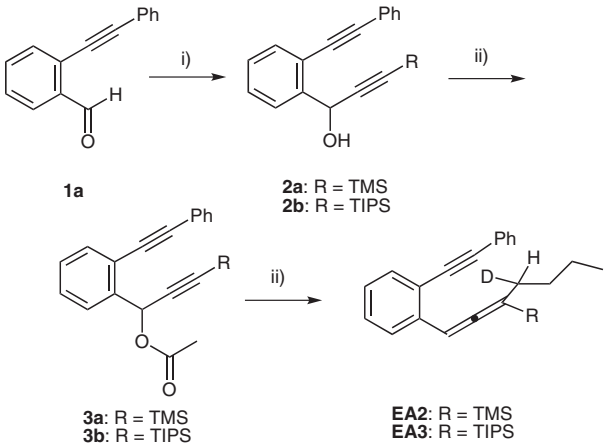
The results of all mechanistic studies conducted until now reveal a complex picture for the C^2–C^6/ene cyclization, pointing to a common transition state[12,13] for both stepwise and concerted processes, and showing important contributions from nonstatistical dynamic effects. Further changes in the substituents at key positions of the enyne–allene should lead to formal ene reactions in which dynamic or classic mechanistic scenarios would operate. In an attempt to understand these substituent effects more thoroughly, we examined the effects of the presence of aryl substituents at the alkyne terminus and at both the alkyne and allene loci. The results of intramolecular KIE studies and of radical-trapping experiments presented herein show that the choice of an appropriate substituent triggers either classical or dynamic behavior of enyne–allenes in thermal cyclization reactions.



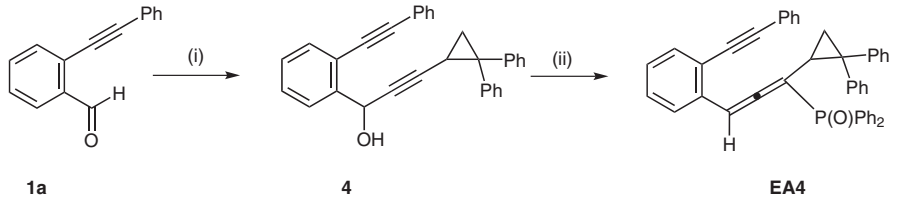
Scheme 2 Thermal ring opening of the allene **EA1**[14]

For our studies on benzannulated enyne–allenes with a phenyl group at the alkyne terminus, we chose the allenes **EA2–4**, which carry bulky, non-radical-stabilizing groups (such as trimethylsilyl, triisopropylsilyl, or diphenylphosphoryl) at the allene terminus and a 1-deuteriobut-1-yl or a diphenylcyclopropyl group for mechanistic inspection. To study the effects of radical-stabilizing groups at both the allene and alkyne termini, we selected the enyne–allenes **EA5–7**, which have a phenyl or a 4-tolyl group at the alkyne locus and a mesityl or a 3-tolyl group at the allene terminus. Again, a 1-deuteriobut-1-yl group was chosen for evaluation of the intramolecular KIE.

The synthesis of **EA2** and **EA3** began with Sonogashira cross-coupling of 2-iodobenzaldehyde with phenylacetylene to give the aldehyde **1a**.[15] Addition of a Grignard reagent RC≡CMgBr (R = TMS, TIPS) (Scheme 3) gave the corresponding propargylic alcohols **2a** and **2b**.[16] Subsequent reaction with acetic anhydride at room temperature in the presence of 4-(*N*,*N*-dimethylamino)pyridine (DMAP) gave the corresponding propargyl acetate **3a** or **3b**.[17] Enyne–allenes **EA2** and **EA3** were finally obtained by means of the copper(I) iodide/lithium bromide-promoted reaction[18] of bromo(butyl)magnesium-d_1 with **3a** or **3b** at 0 °C. ^{1}H and ^{13}C NMR and IR spectroscopy and high-resolution MS confirmed the structural assignment of **EA2** and **EA3**.



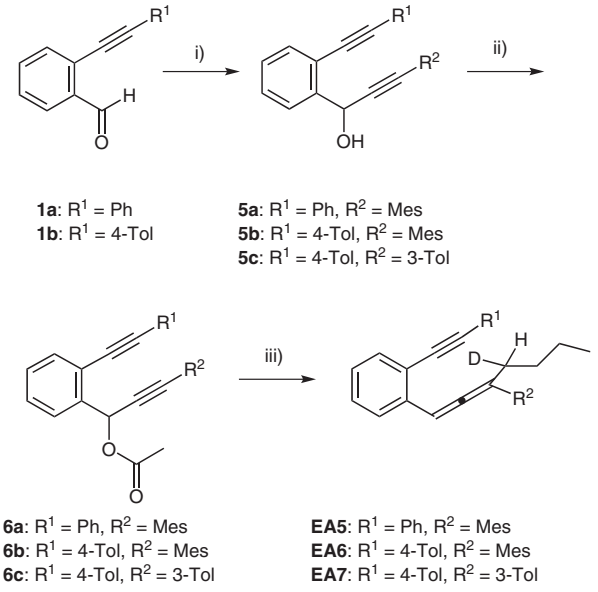
Scheme 3 Synthesis of enyne–allenes **EA2** and **EA3**. *Reagents and conditions:* (i) EtMgBr, HC≡CR, THF, r.t., 8 h, **2a**: 88%, **2b**: 92%; (ii) Ac_2O, DMAP, Et_3N, r.t., 1 h, **3a**: 91%, **3b**: 80%; (iii) PrCHDMgBr, CuI/LiBr, 0 °C, 2 h, **EA2**: 74%, **EA3**: 47%.



Scheme 4 Synthesis of **EA4**. *Reagents and conditions:* (i) EtMgBr, 1,1′-(2-ethynylcyclopropane-1,1-diyl)dibenzene, THF, r.t., 8 h, **4**: 89%; (ii) $ClPPh_2$, Et_3N, THF, –40 °C to r.t., 3 h, **EA4**: 47%.

EA4 was obtained in three steps from **1a**. Addition of the Grignard reagent prepared by the reaction of bromo(ethyl)magnesium with 1,1′-(2-ethynylcyclopropane-1,1-diyl)dibenzene and subsequent reaction with chloro(diphenyl)phosphine[6d] gave the required enyne–allene **EA4** in 47% yield (Scheme 4).

Enyne–allenes **EA5–7** were synthesized analogously to **EA2** and **EA3** by the copper(I) iodide/lithium bromide protocol (Scheme 5).



Scheme 5 Synthesis of enyne–allenes **EA5–7.** *Reagents and conditions:* (i) EtMgBr, HC≡CR², THF, 8 h, **5a**: 83%, **5b**: 79%, **5c**: 79%; (ii) Ac_2O, DMAP, Et_3N, 1 h, **6a**: 85%, **6b**: 80%, **6c**: 84%; (iii) PrCHDMgBr, CuI/LiBr, 0 °C, 2 h, **EA5**: 68%, **EA6**: 57%, **EA7**: 57%.

Thermolysis of enyne–allenes **EA2** and **EA3** in toluene furnished the formal ene products **BF2** and **BF3**, respectively, in good yields.

The intramolecular KIE (Table 1) was determined from the relative integration of the olefinic hydrogens H^A and H^B of **BF** in the ^1H NMR (400 MHz) spectrum (Scheme 6). Two to four independent experiments were performed to establish the values from the KIEs (this number is reported as *n* in Tables 1– 3).

Table 1 Experimental Intramolecular KIEs in the Thermal C²–C⁶/ene Cyclization of **EA2** and **EA3**

Compound	Temp (°C)	Intramolecular KIE (*n*)
EA2	100	1.002 ± 0.001 (3)
EA3	100	1.003 ± 0.001 (3)

Furthermore, the intramolecular KIE for **EA2** was found to be near unity over a wide range of temperatures (Table 2).

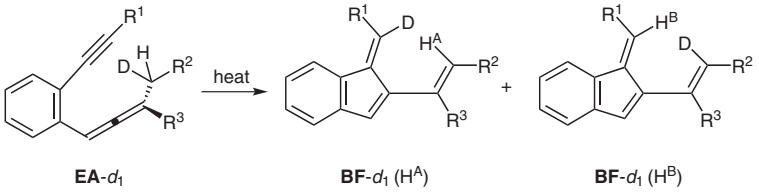
Table 2 Temperature Effects on the Intramolecular KIE for the Thermal Ene Reaction of **EA2**

Entry	Temp (°C)	Intramolecular KIE (*n*)
1	80	1.002 ± 0.001 (2)
2	100	1.002 ± 0.001 (3)
3	120	1.003 ± 0.001 (2)
4	150	1.002 ± 0.001 (2)

For **EA5**, **EA6**, and **EA7**, the observed intramolecular KIEs are shown in Table 3. Those of **EA5** and **EA7** were measured at various temperatures and showed the typical trend of lower KIEs at higher temperatures.

Thermal cyclization of **EA4** in toluene at 110 °C gave the cyclopropyl ring-opened product **BF4** in 40% yield (Scheme 7).

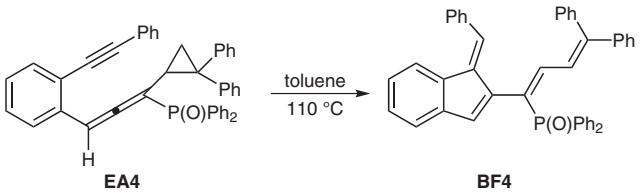
The structure of **BF4** was assigned on the basis of ^1H and ^{13}C NMR spectroscopy and high-resolution mass spectroscopy, and established unambiguously by means of X-ray crystal structure analysis (Figure 1).



Scheme 6 Measurement of the intramolecular KIE from the product ratio **BF**-d_1 (H^A)/**BF**-d_1 (H^B)

Table 3 Observed Intramolecular KIEs for **EA5–7**

Compound	Temp (°C)	Intramolecular KIE (*n*)
EA5	60	1.739 ± 0.004 (2)
EA5	80	1.551 ± 0.003 (4)
EA6	80	1.543 ± 0.003 (2)
EA7	50	1.581 ± 0.004 (4)
EA7	60	1.339 ± 0.006 (4)



EA4 **BF4**

Scheme 7 Thermolysis of **EA4**

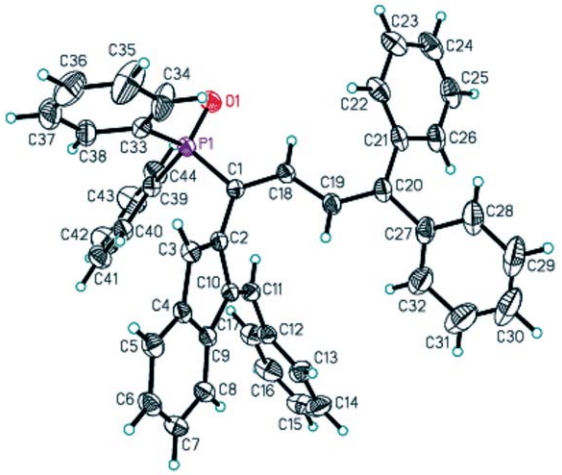


Figure 1 Crystal structure of **BF4**

The indene group is approximately planar, and the mean deviation of the C atoms from the best plane is 0.012 Å. The angle between the plane of the indene group and the plane of the phenyl ring (labeled C12 through C17) is 61.7°. The P–O bond is coplanar with the C1–C18 double bond [torsion angle O1–P1–C1–C18 = 0.6(1)°], resulting in a short intramolecular contact distance of 2.47 Å between O1 and H18A. There is a short intramolecular C–H···π contact between the C11–H11A bond and atom C1 (distance H11A···C1 = 2.59 Å). Very similar intramolecular contacts are found in a related compound.[6d] The C1–C18 and C19–C20 double bonds are coplanar [torsion angle C1–C18–C19–C20 = 178.8(1)°]. The angle between the planes of the phenyl groups attached to phosphorous atom P1 is 58.1°. The angles between the plane of the C19–C20 double bond and the planes of the phenyl groups attached to C20 are 44.0 and 50.1°, respectively, and the angle between the planes of these phenyl groups is 76.7°. The crystal packing shows two short intermolecular C–H···O contacts with H···O distances of 2.44 and 2.48 Å, and a weak intermolecular C-H···π-phenyl interaction.

The structures of all the model compounds used in the study are summarized in Figure 2.

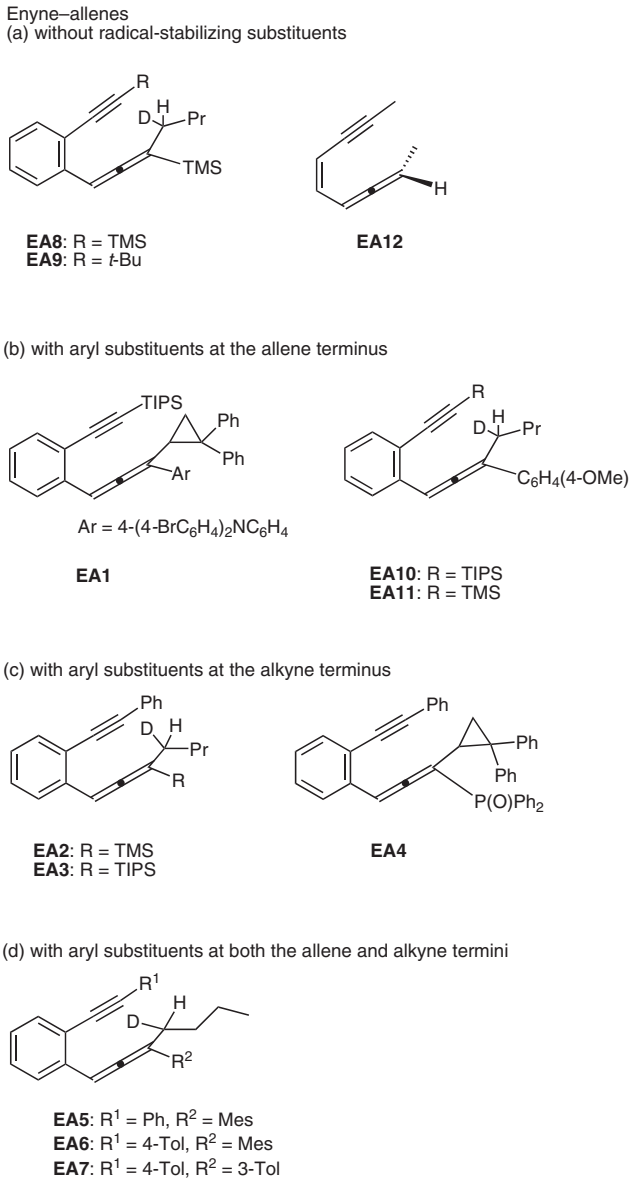


Figure 2 A full list of model compounds

The present results complement data obtained with enyne–allenes **EA8–EA11**, which have been presented in a short communication,[13] and now provide a fully consistent picture regarding the mode of the C^2–C^6/ene reaction. For a comprehensive analysis, we differentiate between four different groups of compounds: (a) enyne–allenes without radical-stabilizing substituents; (b) enyne–allenes with aryl groups at the alkyne unit; (c) enyne–allenes with aryl groups at the allene terminus; and (d) enyne–allenes with aryl groups at both the allene and alkyne termini. In Table 4, collected data from the present study and an earlier study[13] are presented in full, allowing us to address all the cases (a)–(d) systematically.

Table 4 Summary of KIEs and Other Properties of **EA1–12**

Category	Compound	Intermolecular KIE (d_0/d_2)	Intramolecular KIE (d_1)	Remarks	Prevailing character of mechanism
(a) No radical-stabilizing substituent	**EA8**	1.60[a]	1.352[a]	KIE temp. dependent	concerted
	EA12	1.61[a,b]	1.57[a,c]		concerted
	EA9	1.24[a]	1.286[a]		boundary
	EA1			ring opens[e,f]	stepwise + dynamic
(b) Aryl substituent at the allene terminus	**EA10**	1.17[d]	1.003[a]		stepwise + dynamic
	EA11	1.08[a]	1.001[a]	KIE temp. independent	stepwise + dynamic
	EA2		1.002[g]	KIE temp. independent	stepwise + dynamic
(c) Aryl substituent at alkyne terminus	**EA3**		1.003[g]		stepwise + dynamic
	EA4			ring opens[f,g]	stepwise + dynamic
	EA5		1.55[g]	KIE temp. dependent	stepwise + dynamic
(d) Aryl groups at both the allene and alkyne loci	**EA6**		1.54[g]		stepwise + dynamic
	EA7		1.34[g]	KIE temp. dependent	stepwise + dynamic

[a] Ref. 13.
[b] k_{CH3}/k_{CD3}.
[c] k_{CH3}/k_{CH2D}.
[d] Ref. 11.
[e] Ref. 14.
[f] Diphenylcyclopropyl ring opens in the thermolysis.
[g] This work.

With regard to group (a) enyne–allenes without any radical stabilizing substituents, **EA8** and **EA9**, as described in a previous communication,[13] are typical of enyne–allenes that lack any radical-stabilizing subunit. Their experimental intra- and intermolecular KIEs in the C²–C⁶/ene reaction are significantly greater than one. In addition, the observed intramolecular KIEs deviate from the corresponding intermolecular KIEs more than can be explained in terms of secondary isotope effects. We interpreted[13] the difference between inter- and intramolecular KIEs as representing a mixing of stepwise and concerted trajectories, with contributions from the former predominating.

The intra- and intermolecular KIEs for **EA10** and **EA11**, each of which has an aryl group at the allene terminus, have previously been studied as representatives of group (b).[13] For both systems, the observed values of the intermolecular KIEs are close to one, but not within the expected range for a classical interpretation of a stepwise process (i.e., 1.00–1.05).[19] Extensive computational results for the parent system **EA12**[12,13] led us to assume that there is a single transition state for both the concerted and stepwise processes for both **EA10** and **EA11**. Indeed, the somewhat elevated intermolecular KIEs of 1.08–1.17 suggest that the transition states for **EA10** and **EA11** involve contributions from both the concerted (roughly 10–20%) and stepwise (80–90%) mechanisms.

Importantly, the observed values of the intramolecular KIEs for **EA10** and **EA11** were both one, and they were constant over a wide range of temperatures (80–150 °C for **EA10**).[13] The near-unity intramolecular KIE and its temperature independence can only be explained reasonably in terms of Carpenter's dynamic model.[2] Carpenter argued that, in cases such as this, an intermediate will not explore the local minimum through statistical kinetic behavior. Instead, the intermediate is formed with such an excess of kinetic energy that it overcomes the barrier for the second step in a nonstatistical dynamic mode to collapse directly to the product.[3] This assumption is substantiated by the low computed value of the barrier for hydrogen transfer from C1 to C7 of 1.8 kcal mol^{-1}, and a value of the energy difference between the preceding transition state **TS1** and the diradical of about 18 kcal mol^{-1}.[13] These reaction features provide the impetus for conservation-of-momentum, nonstatistical, dynamic behavior in the conversion of the diradical into the ene products. As a result, in experiments we detected a complete lack of discrimination between hydrogen and deuterium in the intramolecular abstraction process. To provide a rational explanation of why the intramolecular KIE is greater than 1.005, the trajectories must be exclusively stepwise, because the mixing in of even small amounts of concerted trajectories would raise the value of the KIE significantly above one.

For group (c), as judged by the experimental KIEs and radical clock reactivity, the presence of an aryl group at the alkyne terminus appears to have the same effect as one at the allene terminus. For example, for enyne–allenes

EA2 and **EA3**, the observed values of the intramolecular KIEs were very close to one (**EA2**: 1.002; **EA3**: 1.003) and, in the case of **EA2**, the KIE was constant over a wide range of temperatures (80–150 °C). The C^2–C^6/ene reaction of enyne–allenes belonging to group (c) therefore proceeds by a stepwise mechanism; this hypothesis is supported by the radical clock results for **EA4**. In the case of this compound, which is substituted with an aryl group at the alkyne terminus, we were able to trap the diradical intermediate intramolecularly through the ultrafast diphenylcyclopropyl radical clock reaction. As the intramolecular trapping did not work with the slower phenylcyclopropyl clock (as in the case of **EA4′**),[6a] hydrogen transfer in the C^2–C^6/ene mode of **EA4′** must be faster than the ring-opening reaction (Scheme 8).

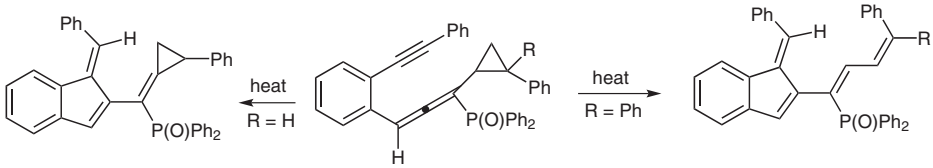
For the model system **EA12**, the barrier to hydrogen transfer in the diradical to give the ene product was computed to be ~2 kcal mol^{-1}, which has to be compared with the higher barrier for phenylcyclopropyl ring opening of ~6 kcal mol^{-1}.[6a] In contrast, the barrier for diphenylcyclopropyl ring opening of about 1–3 kcal mol^{-1} allows this reaction to compete with hydrogen transfer.[20] Thus, the experimental results for **EA4** and **EA4′** are well in line with the computed barriers. Interestingly, we were able to trap the diradical by using the diphenylcyclopropyl unit even though there is no isotopic discrimination in **EA2** and **EA3**, as can be seen from the corresponding intramolecular KIEs. How is it possible to rationalize the competition between ring opening and hydrogen transfer, when the latter is classified as a nonstatistical dynamic process? One possible explanation is that the C–C bond cleavage of the cyclopropyl ring occurs as a nonstatistical dynamic process that is promoted by conformational bias in the diradical intermediate. The adoption of an appropriate conformation to allow opening of the diphenylcyclopropyl ring prevents the nonstatistical dynamic hydrogen transfer. On the basis of these considerations, we suggest that radical clocks do not necessarily probe intermediate radical species, but that they might also be subject to nonstatistical dynamic processes.

The group (d) enyne–allenes **EA5**, **EA6**, and **EA7**, which have aryl groups at both alkyne and allene termini showed intramolecular KIEs that clearly deviated from unity (Tables 3 and 4). Both, the size of the intramolecular KIEs and their notable temperature dependence point to classical behavior of the diradicals in the hydrogen-abstraction step. It appears, therefore, that thermolysis of **EA5**–**7** leads to diradicals that vibrationally equilibrate at their local minima, in agreement with conventional view that radical-stabilizing (aryl) groups at both the alkyne and allene termini markedly stabilize the resulting diradical, leading to a higher barrier for any subsequent reactions. As a result of intramolecular redistribution of the vibrational energy in the diradical, its subsequent reactions will be subject to classical statistical kinetics, leading to discrimination between the abstraction of hydrogen and that of deuterium.

The C^2–C^6/ene reaction of enyne–allenes emerges as a unique case of mechanistic diversity, at the borderline between nonstatistical dynamic and classical behavior (Table 4).

Depending on the substituent pattern at the enyne–allene, various reaction scenarios may apply, as judged purely on experimental criteria. For enyne–allenes with no radical-stabilizing substituents [group (a)], a mechanism seems to apply that is mainly described as concerted; however, the discrepancy between the inter- and intramolecular KIEs at a given temperature indicates that a sizeable proportion (~20%) of the trajectories pass through the diradical intermediate.[13] For enyne–allenes with one radical-stabilizing substituent at either the allene terminus or the alkyne terminus [groups (b) and (c)], the mechanism is clearly stepwise, as judged by the values of the intramolecular KIEs, which are near unity. Both, the values of the intramolecular KIEs and their temperature independence clearly show that the subsequent hydrogen abstraction in the intermediate diradical is controlled by nonstatistical dynamics. Indirectly, the radical clock ring openings for enyne–allenes in groups (b) and (c) suggest that such processes may also be subject to dynamic effects. Finally, for enyne–allenes with radical-stabilizing substituents at both the allene and alkyne termini [group (d)], the mechanism is clearly stepwise and follows predominantly a classical statistical basis, as shown by the value and the temperature dependence of the intramolecular KIEs.

The present study clearly showed that reactions such as the thermal C^2–C^6/ene reaction of enyne–allenes cannot be fully understood on the basis of conventional statistical approaches to reaction mechanisms. Instead, the C^2–C^6/ene process has an intricate mechanism that lies at the intersection between concerted and stepwise processes and at the border between nonstatistical dynamics and classic statistical kinetic behavior. An interesting corollary of the present study is that radical clock openings can compete with nonstatistical dynamic hydrogen-abstraction pro-



EA4 (R = Ph)
EA4' (R = H)

Scheme 8 The faster diphenylcyclopropyl radical clock opens, whereas the phenylcyclopropyl radical clock remains closed in the thermal reaction of enyne–allenes

cesses. Although additional theoretical studies are required, this finding may point to the occurrence of nonstatistical dynamic radical clock ring openings.

NMR spectra were recorded on a Bruker AC 400 spectrometer. Chemical shift values are reported in δ (ppm) versus TMS. IR spectra were recorded on a Perkin-Elmer 1750 FT-IR spectrometer. Anhyd THF and Et_2O were distilled over Na/benzophenone. CH_2Cl_2 and Et_3N were freshly distilled from CaH under N_2. Anhyd toluene was distilled from K. Commercial reagents were used as received. Analytical TLC was carried out on Merck silica gel 60 F_{254} plates. Column chromatography was performed on Merck silica gel 63–200 μm. All solvents for column chromatography were distilled before use. 2-(2-Phenylethynyl)benzaldehyde (**1a**),[15] 2-[2-(4-tolyl)ethynyl]benzaldehyde (**1b**),[6d] 3-mesityl-1-{2-[(4-tolyl)ethynyl]phenyl}prop-2-yn-1-ol (**5b**),[21] and 1,1′-(2-ethynylcyclopropane-1,1-diyl)dibenzene[14] were synthesized by using procedures described in the literature.

1-[2-(Phenylethynyl)phenyl]-3-(trimethylsilyl)prop-2-yn-1-ol (2a);[22] Typical Procedure

A soln of EtMgBr prepared from EtBr (1.32 g, 12.1 mmol) and Mg turnings (294 mg, 12.1 mmol) in anhyd THF (5 mL) was refluxed for 30 min and then cooled to r.t. A soln of TMSCCH (1.19 g, 12.1 mmol) in anhyd THF (5 mL) was added, and the mixture was stirred at r.t. for 4 h. A soln of aldehyde **1a** (1.00 g, 4.85 mmol) in anhyd THF (5 mL) was added and the mixture was again stirred for 4 h at r.t. The reaction was quenched with sat. aq NH_4Cl, and the aqueous layer was extracted with Et_2O (2 × 25 mL). The combined organic layers were dried (Na_2SO_4) and concentrated under reduced pressure, and the residue was purified by column chromatography [silica gel, hexane–Et_2O (95:5)] to give a colorless oil; yield: 1.30 g (88%); R_f = 0.52.

IR (film): 3540 (m), 2960 (s), 2898 (m), 2172 (m), 1611 (s), 1493 (s), 1250 (s), 1186 (m), 1037 (s), 984 (s), 868 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.21 (s, 9 H), 2.85 (d, *J* = 5.9 Hz, 1 H), 5.96 (d, *J* = 5.9 Hz, 1 H), 7.33 (td, *J* = 7.5, 1.3 Hz, 1 H), 7.36–7.42 (m, 4 H), 7.36–7.42 (m, 3 H), 7.75 (d, *J* = 7.3 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.25, 63.6, 86.5, 91.3, 94.9, 104.3, 121.4, 122.7, 126.6, 128.2, 128.3, 128.5, 128.8, 131.5, 132.3, 141.9.

HRMS (EI): *m/z* calcd for $C_{20}H_{20}OSi$: 304.128; found: 304.128.

1-[2-(Phenylethynyl)phenyl]-3-(triisopropylsilyl)prop-2-yn-1-ol (2b)

Yield: 92%.

IR (film): 3541 (m), 2960 (s), 2898 (m), 2173 (m), 1611 (s), 1493 (s), 1251 (s), 1189 (m), 1037 (s), 983 (s), 868 (s), 757 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.06 (s, 21 H), 2.61 (d, *J* = 5.1 Hz, 1 H), 5.98 (d, *J* = 5.1 Hz, 1 H), 7.32–7.39 (m, 5 H), 7.54–7.57 (m, 3 H), 7.75 (d, *J* = 7.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.1, 18.6, 63.7, 86.6, 88.0, 94.8, 106.3, 121.6, 122.8, 126.7, 128.2, 128.3, 128.6, 128.8, 131.6, 132.4, 142.2.

HRMS (EI): *m/z* calcd for $C_{26}H_{32}OSi$: 388.222; found: 388.222.

1-[2-(Phenylethynyl)phenyl]-3-(trimethylsilyl)prop-2-yn-1-yl Acetate (3a); Typical Procedure

A soln of propargyl alcohol **2a** (500 mg, 1.64 mmol), DMAP (182 mg, 1.80 mmol), and Et_3N (183 mg, 1.80 mmol) in anhyd CH_2Cl_2 (25 mL) was stirred at r.t. while soln Ac_2O (219 mg, 1.80 mmol) was added dropwise. The mixture was stirred for 1 h at r.t., and then the reaction was quenched with sat aq $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2 (2 × 25 mL). The combined organic layers were washed with H_2O and brine, then dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by column chromatography [silica gel, hexane–Et_2O (98:2)] to give a colorless oil; yield: 518 mg (91%); R_f = 0.51.

IR (film): 2945 (s), 2866 (s), 2230 (w), 2159 (m), 1741 (s), 1494 (s), 1464 (m), 1370 (s), 1238 (s), 1227 (s), 1042 (m), 957 (s), 920 (w), 883 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.23 (s, 9 H), 2.10 (s, 3 H), 7.01 (s, 1 H), 7.33–7.39 (m, 5 H), 7.58–7.61 (m, 3 H), 7.75 (d, *J* = 7.5 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.30, 20.8, 64.2, 86.1, 92.6, 95.0, 100.8, 122.7, 122.8, 127.9, 128.3, 128.5 (2C), 128.8, 131.6, 132.2, 137.8, 169.4.

HRMS (EI): *m/z* calcd for $C_{22}H_{22}O_2Si$: 346.139; found: 346.139.

1-[2-(Phenylethynyl)phenyl]-3-(triisopropylsilyl)prop-2-yn-1-yl Acetate (3b)

Yield: 80%.

IR (film): 2943 (s), 2866 (s), 2230 (w), 2157 (w), 1745 (s), 1494 (s), 1463 (m), 1368 (s), 1239 (s), 1227 (s), 1042 (m), 956 (s), 920 (w), 882 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.09 (s, 21 H), 2.07 (s, 3 H), 6.97 (s, 1 H), 7.34–7.42 (m, 5 H), 7.56 (m, 3 H), 7.88 (d, *J* = 7.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.1, 18.5, 20.8, 64.5, 86.1, 89.4, 94.9, 102.9, 122.8, 123.0, 128.1, 128.3, 128.5, 128.5, 128.8, 131.7, 132.2, 137.9, 169.5.

HRMS (EI): *m/z* calcd for $C_{28}H_{34}O_2Si$: 430.233; found: 430.230.

{1-(1-Deuteriobutyl)-3-[2-(phenylethynyl)phenyl]propa-1,2-dien-1-yl}(trimethyl)silane (EA2)

A soln of PrCHDMgBr, prepared from Mg (41.0 mg, 1.73 mmol) and PrCHDBr (241 mg, 1.73 mmol)[23] in anhyd THF (10 mL), was added to a well-stirred mixture of LiBr (298 mg, 3.46 mmol) and CuI (330 mg, 1.73 mmol) in THF at 0 °C, and the soln was stirred for 15 min before a soln of propargyl acetate **3a** (200 mg, 578 μmol) in anhyd THF (5 mL) was added dropwise at 0 °C. The mixture was stirred for 2 h and then the reaction was quenched with sat. aq NH_4Cl. The aqueous layer was extracted with Et_2O (2 × 25 mL), and the combined organic layers were dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, pentane) to give a colorless oil; yield: 148 mg (74%); R_f = 0.67.

IR (film): 3500 (m), 2954 (s), 1917 (w), 1598 (m), 1493 (s), 1443 (m), 1249 (m), 839 (m), 754 (s) cm^{-1}.

^1H NMR (400 MHz, toluene-d_8): δ = 0.10 (s, 9 H), 0.83 (t, *J* = 7.4 Hz, 3 H), 1.30 (sext, *J* = 7.4 Hz, 2 H), 1.40–1.49 (m, 2 H), 1.98–2.01 (br m, 1 H), 6.49 (d, *J* = 3.0 Hz, 1 H), 7.16 (td, *J* = 7.4, 1.3 Hz, 1 H), 7.31 (td, *J* = 7.4, 1.3 Hz, 1 H), 7.38–7.44 (m, 3 H), 7.48 (dd, *J* = 8.0, 0.8 Hz, 1 H), 7.55 (dd, *J* = 7.7, 1.1 Hz, 1 H), 7.62–7.66 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = –1.29, 13.9, 22.6, 28.8 (CHD), 31.4, 87.9, 88.0, 93.8, 101.0, 119.8, 123.5, 125.2, 125.3, 128.1, 128.3, 128.4, 131.5, 132.3, 138.1, 205.6.

HRMS (EI): *m/z* calcd for $C_{24}H_{27}DSi$: 345.202; found: 345.202.

{1-(1-Deuteriobutyl)-3-[2-(phenylethynyl)phenyl]propa-1,2-dien-1-yl}(triisopropyl)silane (EA3)

Yield: 47%.

IR (film): 3478 (w), 2942 (s), 2865 (m), 1915 (w), 1599 (m), 1493 (s), 1462 (m), 1382 (m), 1017 (w), 883 (m), 754 (s) cm^{-1}.

^{1}H NMR (400 MHz, toluene-d_8): δ = 0.87 (t, *J* = 7.4 Hz, 3 H), 1.06–1.20 (br m, 21 H), 1.36 (sext, *J* = 7.4 Hz, 2 H), 1.58–1.72 (m, 2 H), 2.06–2.15 (br m, 1 H), 6.85 (dd, *J* = 7.6, 1.1 Hz, 1 H), 6.95–7.02 (m, 4 H), 7.08 (td, *J* = 7.6, 1.1 Hz, 1 H), 7.40–7-44 (m, 2 H), 7.46 (dd, *J* = 7.8, 0.9 Hz, 1 H), 7.69 (bd, *J* = 7.8 Hz, 1 H).

^{13}C NMR (100 MHz, toluene-d_8): δ = 11.9, 14.1, 19.0, 23.1, 29.9, 31.5 (CHD), 88.6, 89.4, 94.6, 97.4, 120.8, 124.0, 125.9, 126.1, 128.2, 128.5, 128.6, 131.8, 132.9, 138.4, 207.6.

HRMS (EI): *m/z* calcd for $C_{30}H_{39}DSi$: 429.296; found: 429.296.

[1-(1-Benzylidene-1*H*-inden-2-yl)-2-deuteriopent-1-en-1-yl](trimethyl)silane and (1-{1-[Deuterio(phenyl)methylene]-1*H*-inden-2-yl}pent-1-en-1-yl)(trimethyl)silane (BF2; Mixture of Isotopomers)

A soln of allene **EA2** (50.0 mg, 144 μmol) in anhyd toluene (20 mL) was degassed then heated at 100 °C for 12 h. The solvent was removed under reduced pressure, and the residue was purified by TLC (silica gel 60 F_{254}, pentane) to give a pale yellow oil; yield: 42 mg (84%); R_f = 0.59.

IR (film): 2943 (s), 2867 (m), 1606 (m), 1599 (s), 1542 (m), 1462 (m), 1381 (m), 1252 (s), 1097 (m), 1072 (m), 1017 (m), 919 (s), 883 (m), 756 (s) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.13 (s, 9 H), 0.89 (t, *J* = 7.3 Hz, 3 H), 1.42 (sext, *J* = 7.3 Hz, 2 H), 2.02–2.06 (m, 2 H), 6.15 (t, *J* = 6.7 Hz, 0.5 H), 6.35 (s, 1 H), 6.90 (t, *J* = 7.4 Hz, 1 H), 7.00 (s, 0.5 H), 7.14–7.19 (m, 2 H), 7.34–7.45 (m, 4 H), 7.51–7.53 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = –1.45, 13.9, 22.6, 33.3, 119.8, 122.9, 123.8, 126.3, 126.4, 127.8, 128.0, 128.0, 129.1, 129.1, 133.2, 134.2, 137.0, 137.1, 138.0, 138.2, 140.8, 140.9, 144.4, 144.8, 144.9.

HRMS (EI): *m/z* calcd for $C_{24}H_{27}DSi$: 345.202; found: 345.202.

[1-(1-Benzylidene-1*H*-inden-2-yl)-2-deuteriopent-1-en-1-yl](triisopropyl)silane and (1-{1-[Deuterio(phenyl)methylene]-1*H*-inden-2-yl}pent-1-en-1-yl)(triisopropyl)silane (BF3; Mixture of Isotopomers)

A soln of allene **EA3** (20 mg, 46 μmol) in anhyd toluene (15 mL) was heated at 100 °C for 12 h. The solvent was removed under reduced pressure and the residue was purified TLC (silica gel 60 F_{254}, pentane) to give a pale yellow oil; yield: 17 mg (85%), R_f = 0.59.

IR (film): 2945 (s), 2866 (m), 1606 (m), 1599 (m), 1542 (m), 1463 (m), 1381 (m), 1096 (m), 909 (s), 883 (m) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 7.4 Hz, 3 H), 1.09–1.15 (m, 18 H), 1.24–1.31 (m, 3 H), 1.40–1.50 (m, 2 H), 2.04–2.15 (m, 2 H), 6.19 (t, *J* = 6.9 Hz, 0.5 H), 6.39 (s, 1 H), 6.89 (t, *J* = 7.1 Hz, 1 H), 7.14–7.19 (m, 1 H), 7.28 (s, 0.5 H), 7.39 (t, *J* = 7.1 Hz, 2 H), 7.45 (t, *J* = 7.5 Hz, 3 H), 7.50–7.52 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.4, 13.8, 18.7, 19.0, 22.6, 33.5, 33.6, 119.8, 123.0, 123.8, 126.4, 126.5, 127.8, 128.0, 128.0, 128.4, 129.1, 129.1, 131.4, 132.9, 133.1, 133.3, 134.1, 137.1, 137.2, 140.9, 141.0, 144.7, 145.5, 147.6.

HRMS (EI): *m/z* calcd for $C_{30}H_{39}DSi$: 429.296; found: 429.296.

3-(2,2-Diphenylcyclopropyl)-1-[2-(2-phenylethynyl)phenyl]prop-2-yn-1-ol (4; Two Diastereomers)

Procedure as described for the synthesis of **2a**; yield: 89%.

IR (film): 3565 (m, OH), 3059 (s), 2987 (s), 2237 (s), 1600(m), 1494 (s), 1446 (m), 1378 (w), 1311 (w), 1270 (m), 1124 (w), 1024 (m), 988 (m), 896 (m), 866 (m) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.62–1.67 (m, 1 H), 1.73 (t, *J* = 5.2 Hz, 0.4 H), 1.80 (t, *J* = 5.2 Hz, 0.6 H), 2.25–2.31 (m, 2 H), 5.81 (s, 1 H), 7.04 (d, *J* = 7.5 Hz, 0.4 H), 7.12 (d, *J* = 7.5 Hz, 0.6 H), 7.16–7.30 (m, 10 H), 7.36–7.45 (m, 5 H), 7.48–7.54 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.8, 15.9, 23.0, 23.1, 37.9, 38.0, 63.1, 63.2, 80.4, 80.5, 86.6, 86.7, 87.3, 87.4, 94.4, 94.5, 121.2, 121.3, 126.4, 126.5, 126.7, 126.7, 126.7, 127.2, 127.4, 127.8, 127.9, 128.0, 128.1, 128.1, 128.4, 128.4, 128.4, 128.5, 128.8, 130.1, 130.2, 131.5, 132.1, 132.1, 140.8, 140.8, 142.2, 142.3, 144.6, 144.6.

HRMS (EI): *m/z* calcd for $C_{32}H_{24}O$: 424.183; found: 424.181.

({1-(2,2-Diphenylcyclopropyl)-3-[2-(phenylethynyl)phenyl]propa-1,2-dien-1-yl}(diphenyl)phosphine Oxide (EA4)

A soln of Ph_2PCl (114 mg, 566 μmol) in anhyd THF (5 mL) was added dropwise during 15 min to a vigorously stirred soln of propargyl alcohol **4** (200 mg, 471 μmol) and Et_3N (57 mg, 566 μmol) in THF (10 mL) cooled to –40 °C. The suspension was stirred at –40 °C for another 60 min then allowed to warm slowly to r.t. (2 h). H_2O (20 mL) and EtOAc (20 mL) were added, the organic layer was separated, and the aqueous layer was extracted with EtOAc (2 × 25 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated in vacuo to give a residue that was purified by chromatography [silica gel, hexane–EtOAc (3:2)]; yield: 134 mg (47%); R_f = 0.57.

IR (film): 3054 (w), 2987 (s), 2853 (s), 2184 (w), 1936 (m), 1599 (w), 1494 (m), 1429 (s), 1186 (s), 1119 (s), 895 (s), 755 (s), 722 (s), 694 (s) cm^{-1}.

^{1}H NMR (400 MHz, acetone-d_6): δ = 1.63–1.68 (m, 0.45 H), 1.70–1.74 (m, 1 H), 1.83 (t, *J* = 5.6 Hz, 0.55 H), 2.38–2.45 (m, 0.45 H), 2.46–2.55 (m, 0.55 H), 5.40 (d, *J* = 7.6 Hz, 0.45 H), 5.94 (d, *J* = 10.4 Hz, 0.55 H), 6.87 (td, *J* = 7.7, 1.3 Hz, 0.45 H), 7.06 (dd, *J* = 10.8, 2.3 Hz, 0.55 H), 7.12–7.44 (m, 10 H), 7.47–7.74 (m, 15 H), 7.88–7.90 (m, 1 H), 8.03 (ddd, *J* = 12.0, 7.6, 1.6 Hz, 1 H), 8.12 (ddd, *J* = 12.0, 7.6, 1.6 Hz, 1 H).

^{13}C NMR (100 MHz, acetone-d_6): δ = 17.5, 17.5, 19.8, 19.8, 23.2, 23.4, 24.7, 24.8, 40.7, 40.3, 86.6, 86.7, 93.9, 94.1, 95.5, 95.6, 95.8, 95.9, 102.5, 102.8, 103.5, 103.7, 120.1, 120.2, 120.4, 120.4, 122.6, 122.7, 126.0, 126.1, 126.2, 126.4, 126.5, 126.7, 126.7, 126.8, 127.3, 127.6, 127.7, 127.8, 127.9, 128.0, 128.0, 128.4, 128.4, 128.4, 128.5, 128.5, 128.6, 131.2, 131.2, 131.3, 131.3, 131.3, 131.4, 131.5, 131.5, 131.6, 131.8, 131.8, 131.9, 131.9, 132.0, 132.1, 132.2, 132.4, 133.1, 133.1, 133.3, 133.4, 133.9, 133.9, 140.4, 141.7, 146.1, 146.8, 208.6, 208.6 (diastereomers and rotamers).

HRMS (EI): *m/z* calcd for $C_{44}H_{33}OP$: 608.227; found: 608.227.

{(1*Z*)-1-[(1*E*)-1-Benzylidene-1*H*-inden-2-yl]-4,4-diphenylbuta-1,3-dien-1-yl}(diphenyl)phosphine Oxide (BF4)

Allene **EA4** (40 mg, 66 μmol) was dissolved in anhyd toluene (50 mL) and heated at 110 °C for 14 h. The toluene was then removed under reduced pressure, and the residue was purified by TLC [silica gel 60 F_{254}, hexane–EtOAc (3:2)] to give a pale yellow amorphous solid; yield: 16 mg (40%); R_f = 0.34.

IR (film): 2959 (s), 2928 (m), 1621 (m), 1509 (w), 1437 (s), 1198 (m), 1139 (m), 1021 (m), 910 (s) cm^{-1}.

^{1}H NMR (400 MHz, toluene-d_8): δ = 6.70 (td, *J* = 7.1, 1.9 Hz, 2 H), 6.86–6.93 (m, 7 H), 7.01–7.08 (m, 4 H), 7.16–7.20 (m, 4 H), 7.23 (d, *J* = 1.6 Hz, 1 H), 7.28–7.34 (m, 3 H), 7.41 (s, 2 H), 7.48 (d, *J* = 7.6 Hz, 2 H), 7.56 (d, *J* = 11.5 Hz, 1 H), 7.61 (d, *J* = 11.5 Hz, 1 H), 7.85 (dd, *J* = 10.8, 7.6 Hz, 6 H).

^{13}C NMR (100 MHz, toluene-d_8): δ = 121.4, 123.6, 124.6, 124.8, 125.5, 128.3, 128.4, 128.5, 128.5, 128.6, 129.4, 129.5, 129.7, 129.7, 130.8, 131.3, 131.3, 132.4, 132.5, 133.7, 133.8, 134.8, 135.4, 137.2, 137.6, 137.7, 138.0, 138.0, 139.0, 141.2, 141.2, 142.1, 142.9, 143.0, 143.9, 144.0, 150.0.

HRMS (EI): *m/z* calcd for $C_{44}H_{33}OP$: 608.227; found: 608.227.

3-Mesityl-1-[2-(phenylethynyl)phenyl]prop-2-yn-1-ol (5a)

Procedure as described for the synthesis of **2a**; yield: 83%.

IR (film): 3419 (m), 3061 (s), 2977 (s), 2856 (s), 2221 (s), 1610 (m), 1494 (s), 1446 (m), 1377 (w), 1311 (w), 1241 (m), 1186 (m), 1027 (s), 968 (m), 853 (m) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.27 (s, 3 H), 2.38 (s, 6 H), 2.79 (d, *J* = 5.0 Hz, 1 H), 6.26 (d, *J* = 5.0 Hz, 1 H), 6.84 (s, 2 H), 7.32–7.37 (m, 4 H), 7.41 (td, *J* = 7.5, 1.2 Hz, 1 H), 7.55–7.58 (m, 2 H), 7.59 (dd, *J* = 7.6, 1.2 Hz, 1 H), 7.84 (d, *J* = 7.6 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0, 21.3, 64.0, 84.5, 86.7, 94.9, 95.8, 119.2, 121.4, 122.8, 126.7, 127.5, 128.2, 128.4, 128.6, 128.9, 131.6, 132.5, 137.9, 140.4, 142.8.

HRMS (EI): *m/z* calcd for $C_{26}H_{22}O$: 350.167; found: 350.167.

3-(3-Tolyl)-1-{2-[(4-tolyl)ethynyl]phenyl}prop-2-yn-1-ol (5c)
Procedure as described for the synthesis of **2a**; yield: 79%.

IR (film): 3439 (m), 3030 (s), 2923 (s), 2856 (s), 2215 (s), 1598 (m), 1510 (s), 1484 (s), 1449 (m), 1381 (w), 1241 (m), 1182 (m), 1093 (m), 1032 (s), 972 (s), 882 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.31 (s, 3 H), 2.39 (s, 3 H), 2.95 (d, *J* = 5.9 Hz, 1 H), 6.18 (d, *J* = 5.9 Hz, 1 H), 7.13–7.22 (m, 4 H), 7.27–7.30 (m, 2 H), 7.34 (td, *J* = 7.5, 1.3 Hz, 1 H), 7.41 (td, *J* = 7.5, 1.3 Hz, 1 H), 7.50 (d, *J* = 8.1 Hz, 1 H), 7.59 (dd, *J* = 7.6, 1.2 Hz, 1 H), 7.81 (dd, *J* = 7.6, 1.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.1, 21.5, 63.8, 86.0, 86.6, 87.9, 95.3, 119.7, 121.6, 122.3, 126.7, 128.1, 128.2, 128.7, 129.1, 129.3, 131.4, 132.3, 137.8, 138.8, 142.2.

HRMS (EI): *m/z* calcd for $C_{25}H_{20}O$: 336.151; found: 336.150.

3-Mesityl-1-[2-(phenylethynyl)phenyl]prop-2-yn-1-yl Acetate (6a)
Procedure as described for the synthesis of **3a**; yield: 85%.

IR (film): 2977 (s), 2856 (m), 2223 (w), 1739 (s), 1609 (m), 1494 (s), 1370 (m), 1336 (w), 1265 (s), 1214 (s), 1014 (s), 909 (s), 855 (m) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.99 (s, 3 H), 2.14 (s, 3 H), 2.29 (s, 6 H), 6.72 (s, 2 H), 7.13 (s, 1 H), 7.20–7.31 (m, 5 H), 7.43–7.48 (m, 3 H), 7.83 (d, *J* = 7.4 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0, 21.3, 28.8, 64.9, 85.5, 86.2, 92.6, 95.0, 118.9, 122.8, 122.8, 125.4, 127.5, 128.1, 128.4, 128.5, 128.8, 131.7, 132.3, 138.2, 138.4, 140.6, 169.7.

HRMS (EI): *m/z* calcd for $C_{28}H_{24}O_2$: 392.178; found: 392.178.

3-Mesityl-1-{2-[(4-tolyl)ethynyl]phenyl}prop-2-yn-1-yl Acetate (6b)
Procedure as described for the synthesis of **3a**, starting from **5b**;[21] yield: 80%.

IR (film): 2917 (s), 2851 (m), 2222 (w), 1740 (s), 1610 (m), 1494 (s), 1369 (m), 1336 (w), 1277 (s), 1214 (s), 1013 (s), 954 (s), 911 (s), 855 (m) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.11 (s, 3 H), 2.27 (s, 3 H), 2.38 (s, 3 H), 2.41 (s, 6 H), 6.86 (s, 2 H), 7.17 (d, *J* = 8.0 Hz, 2 H), 7.23 (s, 1 H), 7.38 (td, *J* = 7.4, 2.0 Hz, 1 H), 7.42 (td, *J* = 7.4, 2.0 Hz, 1 H), 7.47 (d, *J* = 8.0 Hz, 2 H), 7.59 (dd, *J* = 7.4, 2.0 Hz, 1 H), 7.95 (dd, *J* = 7.4, 2.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0, 21.3, 21.5, 65.0, 85.5, 85.6, 92.6, 95.3, 119.0, 119.8, 123.1, 127.6, 128.1, 128.3, 128.8, 129.1, 131.6, 132.3, 138.2, 138.3, 138.7, 140.7, 169.7.

HRMS (EI): *m/z* calcd for $C_{29}H_{26}O_2$: 406.193; found: 406.194.

3-(3-Tolyl)-1-{2-[(4-tolyl)ethynyl]phenyl}prop-2-yn-1-yl Acetate (6c)
Procedure as described for the synthesis of **3a**; yield: 84%.

IR (film): 3027 (s), 2870 (m), 2221 (w), 1741 (s), 1610 (m), 1510 (m), 1483 (s), 1369 (m), 1310 (s), 1214 (s), 1117 (s), 1013 (s), 954 (s), 875 (m) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.98 (s, 3 H), 2.18 (s, 3 H), 2.24 (s, 3 H), 7.01–7.09 (m, 5 H), 7.17–7.28 (m, 4 H), 7.36 (d, *J* = 8.0 Hz, 2 H), 7.46 (dd, *J* = 7.2, 1.6 Hz, 1 H), 7.77 (dd, *J* = 7.6, 1.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.9, 21.1, 21.5, 64.5, 84.8, 85.6, 87.4, 95.3, 119.7, 121.9, 123.0, 128.0, 128.1, 128.3, 128.8, 129.0, 129.1, 129.6, 131.6, 132.2, 132.5, 137.9, 138.0, 138.7, 169.6.

HRMS (EI): *m/z* calcd for $C_{27}H_{22}O_2$: 378.162; found: 378.162.

2-{1-(1-Deuteriobutyl)-3-[2-(phenylethynyl)phenyl]propa-1,2-dien-1-yl}-1,3,5-trimethylbenzene (EA5)
Procedure as described for the synthesis of **EA2**; yield: 68%.

IR (film): 2956 (s), 2860 (m), 2151 (w), 1943 (m), 1607 (m), 1510 (s), 1444 (m), 1376 (m), 1311 (s), 1247 (s), 1213 (m), 1037 (m), 946 (s), 849 (s) cm^{-1}.

^1H NMR (400 MHz, benzene-d_6): δ = 0.83 (t, *J* = 7.4 Hz, 3 H), 1.31 (sext, *J* = 7.4 Hz, 2 H), 1.58–1.65 (m, 2 H), 2.15 (s, 3 H), 2.25–2.31 (br m, 1 H), 2.34 (s, 6 H), 6.79 (s, 2 H), 6.87 (td, *J* = 7.6, 1.2 Hz, 1 H), 6.94–6.98 (m, 3 H), 7.08 (td, *J* = 7.6, 1.2 Hz, 1 H), 7.32 (d, *J* = 3.5 Hz, 1 H), 7.42–7.44 (m, 2 H), 7.52 (dd, *J* = 7.8, 1.1 Hz, 1 H), 7.83 (br d, *J* = 7.8 Hz, 1 H).

^{13}C NMR (100 MHz, benzene-d_6): δ = 14.1, 20.6, 21.0, 23.0, 30.1, 33.7 (CHD), 88.4, 93.4, 94.7, 108.6, 121.7, 123.8, 126.7, 127.1, 128.4, 128.5, 128.7, 128.9, 131.9, 133.0, 134.6, 135.6, 136.4, 137.6, 203.9.

HRMS (EI): *m/z* calcd for $C_{30}H_{29}D$: 391.241; found: 391.241.

2-(1-(1-Deuteriobutyl)-3-{2-[(4-tolyl)ethynyl]phenyl}propa-1,2-dien-1-yl)-1,3,5-trimethylbenzene (EA6)
Procedure as described for the synthesis of **EA2**; yield: 57%.

IR (film): 2956 (s), 2859 (m), 2152 (w), 1943 (m), 1607 (m), 1511 (s), 1444 (m), 1375 (m), 1311 (s), 1247 (s), 1213 (m), 1117 (m), 1037 (m), 946 (s), 850 (s) cm^{-1}.

^1H NMR (400 MHz, toluene-d_8): δ = 0.85 (t, *J* = 7.4 Hz, 3 H), 1.32 (sext, *J* = 7.4 Hz, 2 H), 1.57–1.64 (m, 2 H), 2.01 (s, 3 H), 2.15 (s, 3 H), 2.23–2.29 (br m, 1 H), 2.36 (s, 6 H), 6.75 (s, 2 H), 6.79 (d, *J* = 8.0 Hz, 2 H), 6.87 (td, *J* = 7.6, 1.2 Hz, 1 H), 7.07 (td, *J* = 7.6, 1.2 Hz, 1 H), 7.24 (d, *J* = 3.5 Hz, 1 H), 7.36 (d, *J* = 8.0 Hz, 2 H), 7.48 (dd, *J* = 7.8, 1.1 Hz, 1 H), 7.77 (br d, *J* = 7.8 Hz, 1 H).

^{13}C NMR (100 MHz, toluene-d_8): δ = 14.1, 19.8, 20.9, 21.2, 23.1, 30.2, 33.7 (CHD), 87.8, 93.5, 94.9, 108.5, 120.9, 121.9, 126.6, 127.0, 128.4, 128.9, 129.1, 129.3, 131.8, 133.0, 134.6, 135.5, 136.3, 138.3, 203.8.

HRMS (EI): *m/z* calcd for $C_{31}H_{31}D$: 405.257; found: 405.257.

1-[4-Deuterio-3-(3-tolyl)hepta-1,2-dien-1-yl]-2-[(4-tolyl)ethynyl]benzene (EA7)
Procedure as described for the synthesis of **EA2**, yield 57%.

IR (film): 2985 (s), 2864 (m), 2153 (w), 1942 (m), 1607 (m), 1511 (s), 1484 (m), 1450 (s), 1422 (m), 1338 (s), 1311 (s), 1272 (s), 1213 (m), 1141 (m), 1032 (s), 956 (s), 910 (s) cm^{-1}.

^1H NMR (400 MHz, Et_2O-d_{10}): δ = 0.94 (t, *J* = 7.2 Hz, 3 H), 1.48 (sext, *J* = 7.2 Hz, 2 H), 1.56–1.70 (m, 2 H), 2.30 (s, 3 H), 2.32 (s, 3 H), 2.48–2.62 (br m, 1 H), 7.00 (d, *J* = 7.5 Hz, 1 H), 7.11–7.27 (m, 7 H), 7.30 (s, 1 H), 7.42 (d, *J* = 8.7 Hz, 2 H), 7.50 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (100 MHz, Et_2O-d_{10}): δ = 13.2, 20.5, 20.6, 22.4, 29.4 (CHD), 29.9, 86.6, 94.1, 95.6, 109.8, 120.4, 121.4, 123.0, 125.9, 126.2, 126.5, 127.5, 127.9, 128.0, 128.7, 131.1, 132.2, 135.7, 135.8, 137.4, 137.8, 207.2.

HRMS (EI): *m/z* calcd for $C_{29}H_{27}D$: 377.225; found: 377.225.

Crystal data for BF4

$C_{44}H_{33}OP$, $M = 608.67$, triclinic, $a = 11.568(2)$, $b = 11.872(2)$, $c = 14.540(2)$ Å, $\alpha = 84.532(13)°$, $\beta = 68.391(12)°$, $\gamma = 66.780(11)°$, $V = 1703.3(5)$ Å^3, $T = 163(2)$ K, space group $P\bar{1}$ (Nr. 2), $Z = 2$, $\rho_{calcd} = 1.187$ g cm^{-3}, $\mu = 0.114$ mm^{-1}, reflections collected: 28184, independent: 9486, $R_1 = 0.0475$, $wR_2 = 0.1246$ [$I > 2\sigma(I)$], GOF = 1.032. Data were recorded with a Siemens SMART 1K CCD diffractometer with Mo-K_α radiation at 163 K. Structure determination by direct methods.[24] H atoms were positioned geometrically and were constrained. Final $R(F) = 0.048$ for 7513 reflections with $F^2 > 2(F^2)$ and $R(F) = 0.063$ for all 9486 reflections. The full crystallographic data for compound **BF4** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 773136; copies can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(1223)336033 or email: deposit@ccdc.cam.ac.uk].

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