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Cyclization of Carbonyl Substituted Enyne-Allenes: C^2-C^6-Cyclization Induced by Heat or by Addition of Samarium(II) Iodide, Samarium(III) Chloride, or Boron Trifluoride[1]

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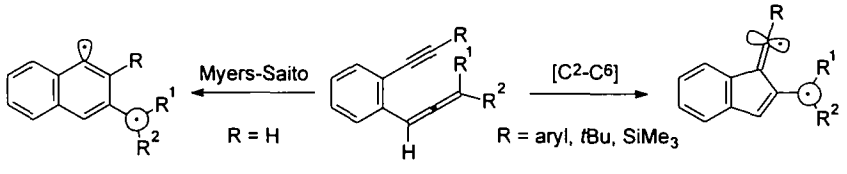
Abstract : Under a variety of conditions the reaction of enyne-allenes with carbonyl substituents at the allene and phenyl or *t*-butyl groups at the alkyne terminus afforded products *via* the new C^2-C^6-cyclization. Products of the Myers-Saito-cyclization were not detected.

Keywords: Allene, Cyclization, Fulvenes, Samarium and compounds

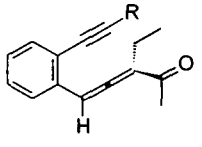
Introduction

Due to their importance as model compounds for the natural antitumor antibiotic neocarzinostatin,[2] the cyclization of enyne-allenes by the Myers-Saito-[3,4] and by the C^2-C^6-cyclization[5] to afford reactive biradicals has been extensively investigated.

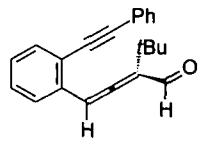


Scheme 1.

So far, several different methods have been described to induce cyclization in enyne-allenes besides simple thermal heating, *i.e.* cyclizations were initiated by light,[6] by oxidation with SeO_2,[7] and by addition of acid[8] or base.[9] Interestingly, no report in the literature has so far dealt with using electron transfer activation[10] to trigger the cyclization. As a consequence, we wanted to study whether SmI_2[11] could be used to accelerate the cyclization of the



1a R = Ph
1b R = *t*Bu



1c

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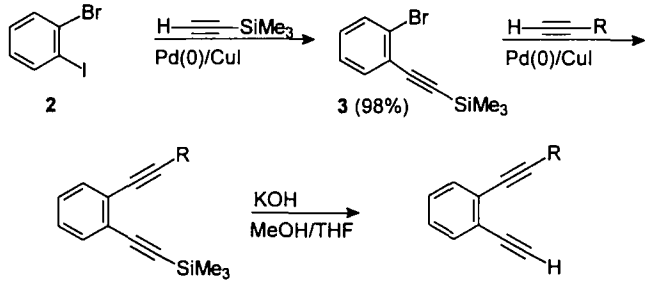
carbonyl substituted enyne-allenes **1** in analogy to samarium(II) iodide induced intramolecular ketyl-olefin coupling reactions.[12]

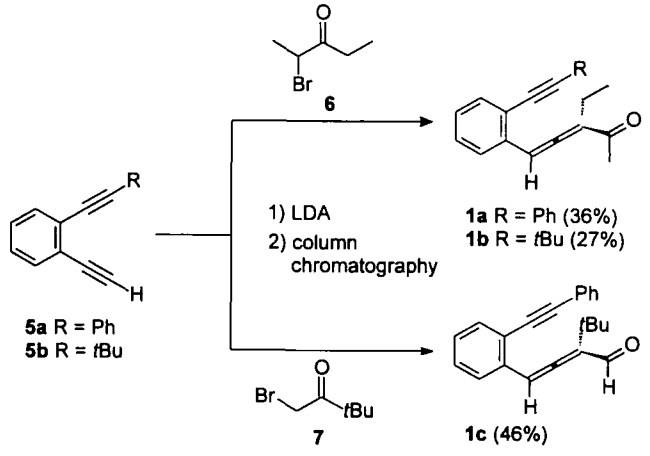
Results and Discussion

For the preparation of the α-carbonyl substituted enyne-allenes **1a-c** we established a new four step synthesis.[13] First, Pd-catalyzed alkynylation of 1-bromo-2-iodobenzene (**2**) with trimethylsilylacetylene (1 h, rt) furnished the alkynyl bromobenzene **3** in almost quantitative yield. In contrast, the second alkynylation only worked under much more drastic reaction conditions (at 80 °C for several days) in much lower yields. The reaction of enediynes **4a,b** with KOH finally afforded compounds **5a,b** in excellent yield.



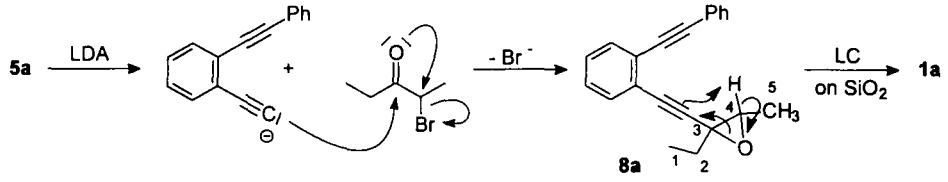
Scheme 2.

To obtain the desired enyne-allenes **1a,b** enediynes **5a,b** were first deprotonated with LDA and then treated with α-bromoketone **6**. After aqueous workup and column chromatography the α-carbonyl substituted enyne-allenes **1a** and **1b** were isolated in 36% and 27% yield, respectively. Analogously, the reaction of **5a** with **7** afforded after column chromatography the enyne-allene **1c** (46%).



Scheme 3.

The formation of enyne-allenes **1a-c** can only be understood assuming a migration of the carbonyl group. Accordingly, a plausible mechanism would involve attack of the acetylide at the carbonyl group followed by ring closure to furnish an intermediate oxirane. Indeed, ^{1}H NMR investigations on the crude product in the reaction **5a** + **6** revealed a set of signals the chemical shift and multiplicity thereof would strongly support the intermediate formation of oxirane **8a**. During column chromatography on silica gel the set of signals belonging to **8a** disappeared and that of **1a** emerged.

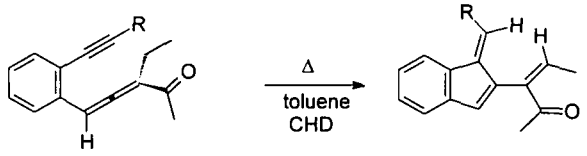


Scheme 4. Mechanism proposed for the formation of enyne-allene **1a**.

Table 1. Spectroscopic data of the oxirane **8a**.

	1-H	2-H	4-H	5-H
δ [ppm]	1.12	1.66	3.34	1.29
m; ^3J(H,H) [Hz]	t; 7.4	q; 7.4	q; 5.5	d; 5.5

In order to investigate their thermal behavior, enyne-allenes **1a-c** were heated with excess of CHD (1,4-cyclohexadiene) as a hydrogen donor in toluene for several hours. After 20 h at 80 °C enyne-allene **1a** afforded the benzofulvene **9a** (60%) as the only isolable product. Analogously, after thermolysis of **1b** in toluene (80 °C, 40 h) the benzofulvene **9b** could be isolated in 16% yield besides 34% of unchanged **1b**. In principle, both benzofulvenes are ene reaction products formed either in a concerted or stepwise process.[5a]

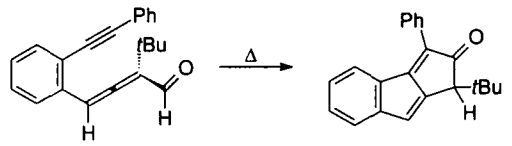


1a R = Ph
1b R = *t*Bu

9a R = Ph (60%)
9b R = *t*Bu (16%)

Scheme 5.

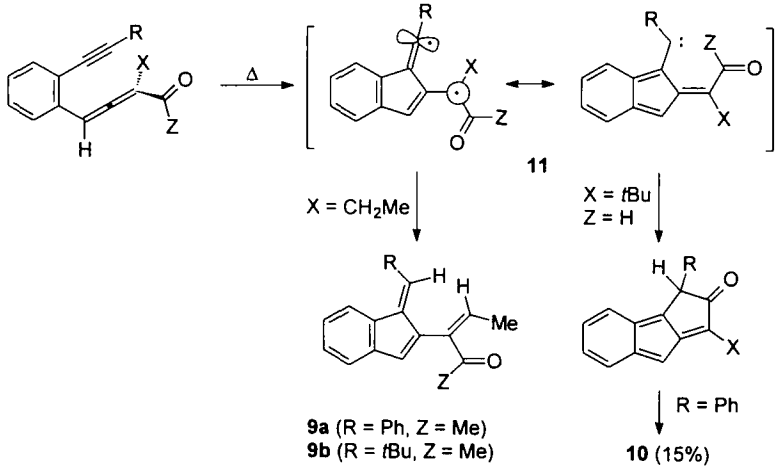
Due to the substitution pattern the ene reaction pathway is impossible for enyne-allene **1c**. Heating of compound **1c** in toluene (90 °C, 20 h) afforded a ketone (15%) which, on the basis of the available spectroscopic data, could be tentatively identified as the 1,2-dihydrocyclopent[*a*]inden-2-one **10**.



1c **10** (15%)

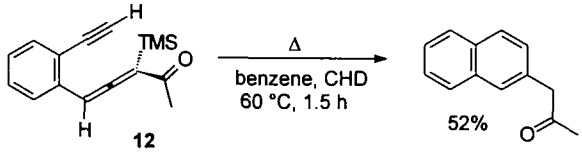
Scheme 6.

Although the yield in the last reaction is rather low the structural resemblance of **10** and **9a,b** suggests to assume a similar initial step for the thermal cyclizations since the substituent modifications at the allene terminus in **1a-1c** are not that large. Indeed, formation of products **9** and **10** can readily be explained assuming a C^2-C^6 biradical cyclization in **1a-1c** in analogy to our earlier findings on other enyne-allenes.[5b] In the cyclization of **1a,b** [1,5]-hydrogen transfer takes place on the stage of **11** (biradical) to furnish **9a,b**, whereas in absence of appropriate hydrogen atoms **11** may act as a carbene by a C-H insertion reaction.



Scheme 7. Postulated mechanism for the formation of enyne-allenes **1a-1c**.

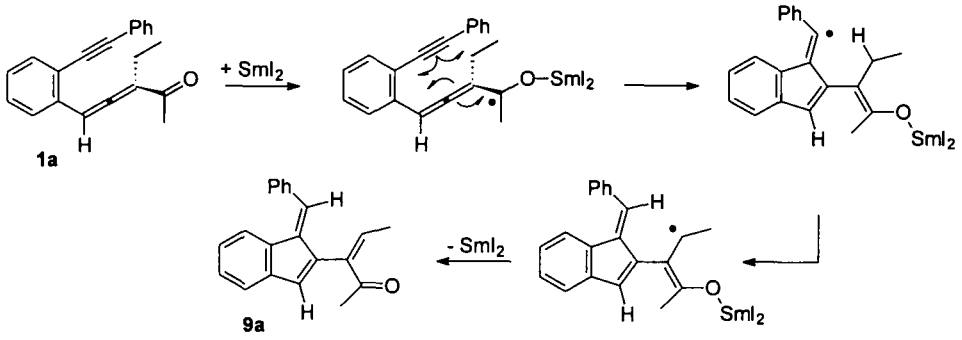
When comparing the results of the thermal cyclization of **1a-c** with that of other α-carbonyl substituted enyne-allenes[13] it is interesting to note that exclusive C^2-C^6-cyclization is operative in presence of the phenyl or *t*-butyl groups at the alkyne terminus. With a terminal acetylene as in enyne-allene **12**, however, again the C^2-C^7-cyclization pathway (Myers-Saito) is realized.[13a]



12

Scheme 8. Thermal cyclization of enyne-allene **12**.[13a]

With the carbonyl substituted enyne-allenes **1a-1c** at hand the question surfaced whether a cyclization could equally be effected by electron transfer reduction using SmI_2. To our surprise treatment of enyne-allene **1a** with 2.2 eqs of SmI_2 afforded after one hour at room temperature the benzofulvene **9a** in 38% yield as the only isolable product (table 2, entry 2). No product witnessing reduction of the carbonyl group could be found despite an extensive search. To explain this unexpected outcome the following mechanism seemed to be conceivable: In a first step a ketyl radical is formed *via* an inner-sphere electron transfer in analogy to many examples in the literature.[12] The ketyl radical then undergoes a 5-*exo*-*dig*-cyclization that is followed by a [1,5]-hydrogen transfer to yield an enone complexed to SmI_2. After release of SmI_2 benzofulvene **9a** is then formed in the final step.



Scheme 9. Possible mechanism for the SmI_2 initiated formation of **9a**

If the mechanism in scheme 9 were operative the cyclization should be catalytic in SmI_2. However, when carrying out the reaction in presence of 50 mol% of SmI_2 the benzofulvene **9a** was only obtained in about 30% yield whereas about 40% of the enyne-allene **1a** could be recovered. This reaction outcome was independent of the reaction time (15 min or 4 d).

Table 2. Reactions of enyne-allene **1a**

entry	reaction conditions	**1a** (%)	**9a** (%)
1	20 eqs. of 1,4-CHD, toluene, 80 °C, 20 h	-	60
2	2.2 eqs. of SmI_2, THF, rt, 1 h	-	38
3	0.5 eqs. of SmI_2, THF, rt, 15 min	43	29
4	0.5 eqs. of SmI_2, THF, rt, 4 d	38	31
5	0.15 eqs. of $SmCl_3$, THF, rt, 5 min	-	67
6	0.1 eqs. of CF_3COOH, THF, rt, 4d	35	13
7	0.1 eqs. of $BF_3{\cdot}Et_2O$, THF, rt, 20 h	-	32
8	THF, rt, 4d	82	-

In addition, we tested whether the above cyclization could be initiated through Lewis acids, in particular by Sm(III)-species[14] that should be formed from Sm(II) after oxidation. When **1a** was treated with 15 mol% of $SmCl_3$ a smooth reaction occurred furnishing benzofulvene **9a** (67%) after 5 min at room temperature. The analogous cyclization could be triggered using other Lewis acids, such as $BF_3{\cdot}Et_2O$ (table, entry 7), and trifluoroacetic acid as a protic acid (entry 6), although in comparison the yields were disappointing despite longer reaction times. Nevertheless, various acids can apparently promote the C^2-C^6-cyclization of carbonyl substituted enyne-allenes, most likely by attack at the carbonyl oxygen.

The above findings make it difficult to come up with a reasonable mechanism for the SmI_2-induced cyclization. While we cannot rigorously exclude that **9a** is formed by a Sm(III)-catalyzed mechanism when reacting **1a** with SmI_2 (entries 2-4, table 2) we would expect to find 1). reduction products, and 2). a time dependence of the formation of **9a**. Both are not the case. Cyclic voltammetry studies have provided now interesting information about compounds **1a** and **9a**. Accordingly, **1a** was irreversibly reduced at -2.17 V_{NHE} in THF, while **9a** exhibited a *reversible* wave at -1.52 V_{NHE} (both at $v = 100$ $mV^{-1}s^{-1}$). Hence, at present we tentatively suggest that the mechanism provided in scheme 9 is operative. Because of the high persistency of $\mathbf{9a}^{\bullet -}$ SmI_2 may be complexed to **9a** without a net reduction result. Upon work-up the $\mathbf{9a}{\cdot}SmI_2$ complex is cleaved.

In conclusion, we have described herein the preparation of enyne-allenes **1a-c** that carry a carbonyl functionality at the allene terminus. Their thermal cyclization leads to benzofulvenes in contrast to that of the related enyne-allene **12** with a hydrogen at the alkyne terminus. In addition, formation of benzofulvenes can be induced by SmI_2 and by addition of both Lewis as well as Brønsted acids.

Experimental

General techniques: All reactions were carried out under N_2 using freshly distilled, anhydrous solvents, unless noted otherwise. Tetrahydrofuran (THF), diethyl ether (Et_2O) were distilled from sodium/benzophenone, while triethylamine (NEt_3) was distilled from calcium hydride. All reactions were followed by thin-layer chromatography on Merck silica gel plates (60F-254). For column chromatography Merck silica gel (particle size 0.063-0.200 mm) was used. Unless noted otherwise, all yields correspond to analytically pure isolated material. *o*-Phenylethinylbenzaldehyde was prepared according to reference.[5b]

^1H and ^{13}C NMR spectra were recorded on Bruker AC-200 or AM-250 instruments and calibrated with tetramethylsilane as an internal reference (TMS, $\delta = 0.0$ ppm). The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; q_i, quintet; m, multiplet. IR spectra were recorded on a Perkin-Elmer 1605 series FT-IR-spectrometer. High resolution mass spectra (HRMS) were recorded on a Finnigan MAT-90 mass spectrometer under EI (70 eV) conditions.

1-Bromo-2-(trimethylsilylethynyl)-benzene (3): A solution of 1-bromo-2-iodobenzene (**2**) (4.00 g, 14.1 mmol) and trimethylsilylacetylene (1.53 g, 15.6 mmol) in NEt_3 (100 mL) was treated with

dichlorobis(triphenylphosphine)palladium(II) (144 mg, 204 μmol) and copper(I)iodide (65.4 mg, 342 μmol). After the reaction mixture had been stirred at room temperature for 1 h, saturated aqueous NH_4Cl (80 mL) was added. The organic layer was then separated and the aqueous layer extracted with CH_2Cl_2 (4 x 50 ml). The combined layers were dried ($MgSO_4$), filtered, and concentrated to obtain 3.62 g (14.0 mmol, 98%) of **3** which could be used without further purification. IR (neat): $\tilde{\nu}$ = 3067, 2959, 2898, 2163 (C≡C), 1466, 1433, 1250, 1220, 1120, 1046, 1028, 945, 865, 843, 754 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 0.29 (s, 9H, $SiMe_3$), 7.15 (ddd, ^3J(H, H) = 7.6 Hz, ^3J(H, H) = 7.6 Hz, ^4J(H, H) = 1.5 Hz, 1H), 7.24 (ddd, ^3J(H, H) = 7.6 Hz, ^3J(H, H) = 7.6 Hz, ^4J(H, H) = 1.5 Hz, 1H), 7.49 (dd, ^3J(H, H) = 7.6 Hz, ^4J(H, H) = 1.5 Hz, 1H), 7.57 (dd, ^3J(H, H) = 7.6 Hz, ^4J(H, H) = 1.5 Hz, 1H); ^{13}C NMR in accordance with the literature.[15]

1-(Phenylethynyl)-2-(trimethylsilylethynyl)-benzene (4a): To a mixture of **3** (2.59 g, 10.0 mmol), dichlorobis(triphenylphosphine)palladium(II) (98.3 mg, 140 μmol), and copper(I)iodide (46.5 mg, 244 μmol) in NEt_3 (80 mL) a solution of phenylacetylene (1.74 g, 17.0 mmol) in NEt_3 (10 mL) was added during 6 h using a syringe pump. After the reaction mixture had been stirred at 80 °C for 3 d, saturated aqueous NH_4Cl (50 mL) was added. The organic layer was then separated and the aqueous layer extracted with CH_2Cl_2 (3 x 60 ml). The combined layers were dried ($MgSO_4$), filtered, and concentrated. Purification of the residue by column chromatography (petroleum ether 30-50, R_f = 0.48) afforded **4a** (2.22 g, 81,0 mmol, 81%) as a yellow oil. IR (neat): $\tilde{\nu}$ = 3059, 2959, 2897, 2219 (C≡C), 2158 (C≡C), 1598, 1573, 1494, 1472, 1443, 1250, 1210, 1094, 871, 846, 755, 690, 644 cm 1; ^1H NMR (250 MHz, $CDCl_3$): δ = 0.28 (s, 9H, $SiMe_3$), 7.23-7.28 (m, 2H), 7.33-7.36 (m, 3H), 7.49 (m, 4H); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 0.0 ($SiMe_3$), 88.6, 93.4, 98.6, 103.5, 123.2, 125.6, 126.0, 127.8, 128.1, 128.3, 128.4, 131.6, 131.9, 132.2. In accordance with the literature.[16]

1-(3,3-Dimethylbutynyl)-2-(trimethylsilylethynyl)-benzene (4b): As described above for the synthesis of **4a**, **3** (1.30 g, 5,00 mmol), dichloro-bis(triphenylphosphine)palladium(II) (49.2 mg, 70 μmol), copper(I)iodide (24.0 mg, 120 μmol) in NEt_3 (40 mL) were brought to reaction at 60 °C with a solution of 3,3-dimethylbutyne (821 mg, 10.0 mmol) in NEt_3 (2 mL). The crude product was purified by column chromatography (petroleum ether 30-70, R_f = 0.42) to furnish **4b** (482 mg, 1.89 mmol, 38%) as a pale yellow oil. IR (neat): $\tilde{\nu}$ = 3060, 2967, 2899, 2868, 2239 (C≡C), 2159 (C≡C), 1473, 1441, 1362, 1298, 1250, 1201, 1100, 1037, 864, 843, 758, 697 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 0.30 (s, 9H, $SiMe_3$), 1.37 (s, 9H), 7.18-7.23 (m, 2H), 7.41 (m, 1H), 7.46 (m, 1H); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 0.1 ($SiMe_3$), 28.2, 31.0, 77.8, 97.5, 102.7, 103.7, 125.3, 127.0, 128.03, 128.4, 131.7, 132.3; $C_{17}H_{22}Si$ (254.5): calcd C 80.25, H 8.72; found C 80.55, H 8.64.

2-(Phenylethynyl)-phenylacetylene (5a): A solution of **4a** (1.11 g, 4.04 mmol) in a mixture of ethanol (20 mL) and THF (15 mL) was treated with aqueous 1 N KOH (24 mL). After the reaction mixture had been stirred at room temperature for 1.5 h, water (20 mL) was added and the reaction mixture treated with aqueous 1 N HCl until a pH = 7 was adjusted. The organic layer was then separated and the aqueous layer extracted with CH_2Cl_2 (3 x 70 ml). The combined layers were dried ($MgSO_4$), filtered, and concentrated to afford **5a** (752 mg, 3.72 mmol, 92%) as pale yellow oil that could be used without further purification. IR (neat): $\tilde{\nu}$ = 3287 (≡C-H), 3060, 2975, 2873, 2218 (C≡C), 2107 (C≡C), 1599, 1572, 1494, 1442, 1091, 1068, 1026, 915, 755, 690 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 3.37 (s, 1H), 7.27-7.37 (m, 5H), 7.52-7.60 (m, 4H). In accordance with the literature.[16]

2-(3,3-Dimethylbutynyl)-phenylacetylene (5b): As described above for the synthesis of **5a**, a solution of **4b** (417 mg, 1.85 mmol) in a mixture of methanol (12 mL) and THF (3 mL) was treated with aqueous KOH (2 pellets in 2 mL water) to afford **4b** (336 mg, 1.84 mmol, 99%) as a yellow oil that could be used without further purification. IR (neat): $\tilde{\nu}$ =3298 (≡C-H), 3058, 2968, 2927, 2866, 2239 (C≡C), 2107 (C≡CH), 1472, 1438, 1362, 1297, 1261, 1120, 808, 758, 695 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 1.36 (s, 9H), 3.26 (s, 1H), 7.18-7.23 (m, 2H), 7.39 (m, 1H), 7.48 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 29.6, 30.9, 70.6, 75.2, 86.8, 95.1, 127.5, 128.4, 128.6, 132.0, 132.2, 133.3; HRMS calcd for $C_{14}H_{13}$ (M^+-H): 181.1017, found 181.1011.

3-Ethynyl-5-(2-phenylethynylphenyl)-penta-3,4-dien-2-one (1a): A mixture of LDA (3.00 mmol) and HMPA (493 mg, 2.75 mmol) in THF (20 mL) was treated at −80 °C with a solution of **5a** (506 mg, 2.50 mmol) in 2 ml of THF. After the mixture had been stirred at −80 °C for 40 min a solution of 2-bromo-3-pentanone (**6**) (621 mg, 3.75 mmol) in THF (4 mL) was added dropwise. After 30 min the reaction mixture was allowed to warm to room temperature and quenched with water (20 mL). The organic layer was then separated and the aqueous layer extracted with Et_2O (3 x 50 ml). The combined layers were dried ($MgSO_4$), filtered, and concentrated. Purification of the residue by column chromatography ($CHCl_3$/*n*-pentane, 3:2, R_f = 0.42) afforded **1a** (259 mg, 906 μmol, 36%). IR (neat): $\tilde{\nu}$ = 3060, 3021, 2967, 2931, 2874, 2214 (C≡C), 1933 (C=C=C), 1681 (C=O), 1589, 1494, 1444, 1357, 1236, 915, 823, 754, 690 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 1.06 (t, ^3J(H, H) = 7.4 Hz, 3H), 2.31-2.42 (m, 2H), 2.33 (s, 3H), 7.25-7.31 (m, 3H), 7.36-7.39 (m, 5H), 7.55 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 12.3, 20.3, 27.4, 87.1, 94.2, 97.4, 114.8, 121.6, 126.4, 127.5, 128.4, 128.6, 128.7, 129.3, 131.5, 132.7, 133.6, 197.8, 215.4; CV: E_{pa} (THF) = −2.17 V_{NHE}; HRMS calcd for $C_{21}H_{18}O$ (M^+): 286.1358, found 286.1353.

5-[2-(3,3-Dimethylbutynyl)phenyl)]-3-ethyl-penta-3,4-dien-2-one (1b): As described above for the synthesis of **1a**, LDA (3.00 mmol), HMPA (493 mg, 2.75 mmol), **5b** (320 mg, 1.76 mmol) and 2-bromo-3-pentanone (**6**) (497 mg, 3.00 mmol) were brought to reaction. Purification of the residue by column chromatography ($CHCl_3$/*n*-pentane, 1:1, R_f = 0.48) afforded **1b** (128 mg, 480 μmol, 27%) as a yellow oil. IR (neat): $\tilde{\nu}$ = 3060, 2966, 2861, 2253 (C≡C), 1932 (C=C=C), 1682 (C=O), 1597, 1487, 1443, 1360, 1296, 1235, 1205, 1092, 913, 829, 755, 691 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 1.08 (t, ^3J(H, H) = 7.5 Hz, 3H), 1.38 (s, 9H, CH_3), 2.33 (s, 3H), 2.31-2.44 (m, 2H), 7.13-7.18 (m, 2H), 7.17 (s, 1H), 7.34-7.46 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 12.4, 20.4, 26.9, 28.2, 31.0, 97.4, 97.5, 104.2, 114.8, 122.4, 126.2, 127.4, 127.9, 132.6, 133.3, 198.0, 215.3; HRMS calcd for $C_{19}H_{22}O$ (M^+): 266.1671, found 266.1679.

4,4-Dimethyl-3-formyl-1-(2-phenylethynylphenyl)-penta-1,2-diene (1c): As described above for the synthesis of **1a**, LDA (2.71 mmol), HMPA (408 mg, 2.71 mmol), **5a** (480 mg, 2.37 mmol) and 2-bromo-3,3-dimethyl-butan-2-one (**7**) (662 mg, 3.70 mmol) were brought to reaction. Purification of the residue by column chromatography (CH_2Cl_2/cyclohexane, 1:1, R_f = 0.44) afforded **1c** (330 mg, 1.10 mmol, 46%) as orange crystals. M.p. 76 °C (decomposition); IR (KBr): $\tilde{\nu}$ = 3060, 2965, 2214 (C≡C), 1920 (C=C=C), 1688 (C=O), 1590, 1494, 1476, 1442, 1295, 1227, 1050, 996, 924, 757, 691 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 1.28 (s, 9H), 7.23-7.30 (m, 3H), 7.34-7.40 (m, 4H), 7.54-7.59 (m, 3H), 9.62 (s, 1H); ^{13}C NMR (50 MHz,

$CDCl_3$): δ = 29.1, 33.7, 87.1, 94.0, 94.9, 98.0, 122.9, 124.1, 126.5, 127.8, 128.5, 128.7, 128.8, 131.6, 132.8, 133.3, 190.8, 221.1; HRMS calcd for $C_{22}H_{20}O$ (M^+): 300.1514, found 300.1510.

Thermolysis of 1a: A mixture of **1a** (69.0 mg, 241 μmol) and 1,4-cyclohexadiene (386 mg, 4.82 mmol) in toluene (100 mL) was heated to 80 °C for 20 h. After evaporation of the solvent the crude residue was purified by column chromatography ($CHCl_3$, R_f = 0.33) to furnish 1-phenyl-3-(pent-3-en-2-on-3-yl)-benzofulvene (**9a**) (41.2 mg, 60%) as a yellow oil. IR (neat): $\tilde{\nu}$ = 3058, 2970, 2932, 1672 (C=O), 1623, 1599, 1492, 1444, 1386, 1353, 1253, 1232, 1195, 1072, 1026, 876, 759, 725, 698 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 1.85 (d, ^3J(H, H) = 7.0 Hz, 3H), 2.33 (s, 3H), 6.70 (s, 1H), 6.93 (s, 1H), 7.02 (ddd, ^3J(H, H) = 7.4 Hz, ^3J(H, H) = 7.4 Hz, ^4J(H, H) = 1.5 Hz, 1H), 7.18 (q, ^3J(H, H) = 7.0 Hz, 1H), 7.21 (ddd, ^3J(H, H) = 7.4 Hz, ^3J(H, H) = 7.4 Hz, ^4J(H, H) = 0.9 Hz, 1H), 7.28 (m, 1H), 7.40-7.46 (m, 3H), 7.52-7.56 (m, 3H); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 16.1, 27.9, 120.9, 123.2, 125.1, 128.1, 128.4, 129.3, 129.3, 131.5, 133.0, 134.2, 136.3, 137.8, 138.5, 140.4, 141.3, 143.6, 198.9; CV: $E_{1/2}$ (THF) = −1.52 V_{FcNHE}; MS-EI (70 eV): m/z (%) = 286 (57) [M^+], 271 (11) [M^+-CH_3], 243 (100) [M^+-$COCH_3$]; HRMS calcd for $C_{21}H_{18}O$ (M^+): 286.1358, found 286.1362.

Thermolysis of 1b: A mixture of **1b** (78.0 mg, 292 μmol) and 1,4-cyclohexadiene (939 mg, 11.7 mmol) in toluene (200 mL) was heated to 80 °C for 40 h. After evaporation of the solvent the crude residue was purified by column chromatography (cyclohexane/$CHCl_3$, R_f = 0.21) to furnish 1-*tert.*-butyl-3-(pent-3-en-2-on-3-yl)-benzofulvene (**9b**) (11 mg, 16%) as a yellow oil. IR (neat): $\tilde{\nu}$ = 3055, 2978, 2932, 1672 (C=O), 1623, 1599, 1492, 1444, 1352, 1255, 1232, 1195, 1026, 878, 756, 698 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 1.40 (s, 9H), 1.73 (d, ^3J(H, H) = 7.0 Hz, 3H), 2.21 (s, 3H), 6.10 (s, 1H), 6.58 (s, 1H), 7.12 (q, ^3J(H, H) = 7.0 Hz, 1H), 7.20 (m, 3H), 7.92 (m, 1H); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 16.3, 28.3, 30.7 33.9, 121.3, 124.9, 126.9, 127.8, 129.2, 129.9, 133.2, 138.3, 140.1, 141.6, 145.1, 149.1, 197.6; HRMS calcd for $C_{19}H_{22}O$ (M^+): 266.1671, found 266.1677.

Thermolysis of 1c: A mixture of **1c** (148 mg, 493 μmol) and 1,4-cyclohexadiene (790 mg, 9.85 mmol) in toluene (150 mL) was heated to 90 °C for 20 h. After evaporation of the solvent the crude residue was purified by column chromatography (cyclohexane/CH_2Cl_2, R_f = 0.46) to furnish **10** (22.2 mg, 15%) as yellow oil. IR (CCl_4): $\tilde{\nu}$ = 3058, 2960, 2869, 2168, 1712 (C=O), 1603, 1551, 1447, 1365, 1322, 1263, 908 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 1.12 (s, 9H), 3.09 (s, 1H), 6.55 (s, 1H), 7.04 (ddd, ^3J(H, H) = 7.3 Hz, ^3J(H, H) = 7.3 Hz, ^4J(H, H) = 1.5 Hz, 1H), 7.22 (m, 1H), 7.31 (ddd, ^3J(H, H) = 7.3 Hz, ^3J(H, H) = 7.3 Hz, ^4J(H, H) = 1.5 Hz, 1H), 7.47 (m, 3H), 7.72 (m, 3H); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 28.0, 35.0, 55.7, 121.5, 123.3, 124.7, 125.2, 128.5, 129.3, 129.7, 130.2, 130.9, 131.6, 206.8.

Reaction of 1a with SmI_2: a) with 2.2 eq. of SmI_2: A 0.1 M samariumdiiodide-THF-solution (8.0 mL) was treated with HMPA (1.10 g, 6.14 mmol). After the deep purple reaction mixture had been stirred for 15 min at room temperature, a solution of **1a** (100 mg, 349 μmol) and *tert.*-butanol in toluene (10 mL) was added. The reaction mixture was immediately quenched with water (20 mL). The organic layer was the separated and the aqueous layer extracted with CH_2Cl_2 (3 x 50 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated. Purification of the residue by column chromatography ($CHCl_3$) afforded **9a** (37.6 mg, 38%) as the only isolable product.

Reaction of 1a with other reagents: As described in table 2 **1a** was treated with various reagents under different reaction conditions.

Cyclic voltammetry. In a glove box tetra(*n*-butyl)ammoniumhexafluorophosphate (232 mg, 600 µmol) and the electroactive species (6 µmol) were placed into a thoroughly dried CV cell. At a high purity argon line THF (6.0 mL) was added through a gastight syringe. Then a platinum disc working electrode (⌀ = 1 mm), a platinum wire counter electrode, and a silver wire as pseudo reference electrode were placed into the solution. The cyclic voltammograms were recorded at various scan rates using different starting and switching potentials. For determination of the oxidation potentials, ferrocene ($E_{1/2}$ = + 0.63 V vs. NHE) was added as the internal standard. Cyclic voltammograms were recorded using a Princeton Applied Research Model 362 potentiostat with a Philips model PM 8271 XYt-recorder for scan rates < 1 V s^{-1}.

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