The Aminium Salt and Photoinduced Electron Transfer Initiated Diels–Alder Cycloaddition of Electron-Rich Allenes: Evidence for a Stepwise Mechanism and the Importance of Steric and Electronic Effects for the Reactivity of Distonic Radical Cation Intermediates**

Michael Schmittel,* Clemens Wöhrle, and Ingo Bohn

Dedicated to Prof. Dr. S. Hünig on the occasion of his 75th birthday

Abstract: Several novel electron-rich arylallenes have been synthesized, characterized, and used as dienophiles in the radical-cation-catalyzed cycloaddition with 1,2,3,4,5-pentamethylcyclopentadiene, which affords, in most cases, the Diels–Alder products in 5 min at 0 °C with a high peri-, chemo-, facial, and stereoselectivity. In line with oxidation-potential considerations it is concluded that the electron-transfer-induced reaction proceeds along a [3+2] pathway by cycloaddition of the diene radical cation to a neutral allene with a rather short chain length. The low cycloaddition yields from some of the allenes are interpreted as evidence for a stepwise mechanism involving distonic radical cations as key intermediates. We discuss the tendency of the distonic radical cations to undergo ring closure to the Diels–Alder-product radical cations in terms of enthalpy considerations, which, we suggest, offer a novel criterion for the design of stepwise radical cation reactions.

Keywords
allenes · cycloadditions · Diels–Alder reactions · mechanistic studies · radical cations

Introduction

In recent years, the radical-cation-catalyzed Diels–Alder (DA) reaction[1–3] has become a prominent example for the potential of electron-transfer (ET) activation, in part owing to the striking rate accelerations as encountered in the Diels–Alder cyclodimerization of cyclohexadiene,[4,5] and also for the potential to trigger transformations that have not been realized by any other method. Reactions such as Diels–Alder cycloadditions with ketenes[6] and indoles[7] as dienophiles, of vinylindoles[8] to carbazoles and pyrido[1,2a]indoles have impressively underlined the increasing utility of this methodology.

Despite these and many other successful examples, the mechanistic complexity of such a reaction mode is far from being well understood. In early years most authors on radical-cation-catalyzed cycloadditions supported the [4+1] pathway as an exclusive and concerted although nonsynchronous pathway.[2] While orbital symmetry considerations classify the [4+1] mode as formally allowed,[9] more recent investigations have indicated that the formally symmetry-forbidden [3+2] mechanism is certainly a viable low-energy alternative.[6,10,11] However, increasing evidence has been presented to show that such a [3+2] reaction mechanism is best described as nonconcerted with a distonic 1,6 radical cation as a crucial intermediate.[12]

We have very recently reported on the first examples of a radical-cation-catalyzed cycloaddition of allenes,[12] a reaction that proceeded at 0 °C in 5 min with an astounding degree of peri-, chemo-, facial, and stereoselectivity when 1,2,3,4,5-pentamethylcyclopentadiene was used. From the results of various mechanistic tests it was inferred that the reaction proceeded along a [3+2] pathway with a rather short chain length by cycloaddition of the diene radical cation to a neutral allene. Unfortunately, with an ethoxycarbonyl group at the remote end of the allene functionality the cycloaddition constituted only a minor reaction path. In addition, only a very narrow range of dienes seemed to be tolerated. To understand the mechanism and the limitations of this radical-cation-initiated cycloaddition we started the present investigation to examine the compatibility of a large variety of substituents in radical-cation-catalyzed processes. Our experimental results have led to the formulation of a novel criterion enabling the prediction of the tendency of intermediate distonic radical cations to undergo ring closure to the Diels–Alder products.

Results

For a complete overview we have included some of the results of earlier investigations[12] with allenes **1a–c** and **1n,o**.

[*] Prof. Dr. M. Schmittel, Dr. C. Wöhrle, Dipl.-Chem. I. Bohn
Institut für Organische Chemie, Universität Würzburg
Am Hubland, D-97074 Würzburg (Germany)
Fax: Int. code +(931)888-4606
e-mail: mjls@chemie.uni-wuerzburg.de

[**] Radical-Cation-Catalyzed Reactions, Part 8. Part 7: see ref. [1].

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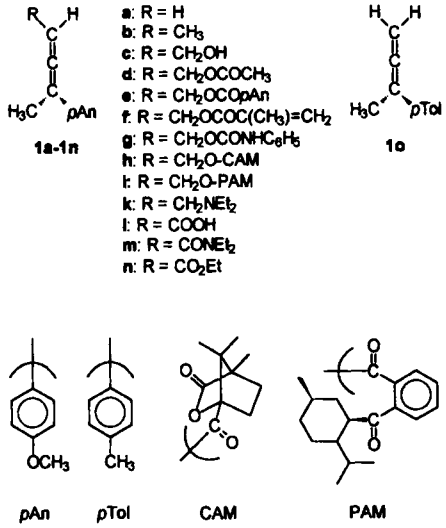
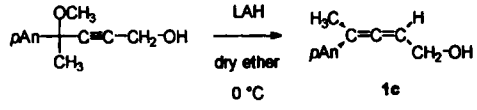
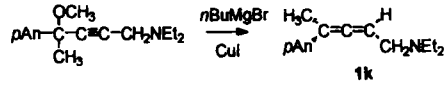


Synthesis of allenes: The synthesis of allenes **1a–c** and **1n,o** has been described earlier,[12b] but since the reported preparation of **1c** proved to be unsatisfactory for larger amounts, we have used an alternative 4-step approach relying on the LAH-induced rearrangement of 4-methoxy-4-(4-methoxyphenyl)pent-2-yn-1-ol (Scheme 1) in analogy to Olsson and Claesson's work.[13]



Scheme 1.

With allene **1c** to hand in larger quantities, the allene esters **1d–i** could be prepared relatively easily by reaction with the corresponding acid chlorides. The amino-substituted allene **1k** was prepared from the BuMgBr/CuI-induced rearrangement of *N,N*-diethyl-4-methoxy-4-(4-methoxyphenyl)pent-2-yn-1-amine (Scheme 2, 37% yield after chromatography). The acceptor-



Scheme 2.

substituted allenes **1m** and **1n**[12b] were obtained from Horner–Wadsworth–Emmons reactions of (4-methoxyphenyl)-methylketene[6] with diethyl (diethylcarbamoylmethyl)phosphonate and diethyl (ethoxycarbonylmethyl)phosphonate, respectively, the latter allene providing the allenic acid **1l** after ester hydrolysis.

The structural identity of all allenes was deduced from their spectral data, some of which are listed in Table 1. Characteristically, for all allenes $\tilde{\nu}$(C=C=C) showed up between 1937 and 1955 cm^{-1}, and the ^{13}C NMR resonances of the central carbon of the allene moiety between δ = 202 and 215.

Cyclic voltammetry investigations of allenes 1a–o: In order to understand the relevance of the difference in oxidation potential between diene **2** and the various allenes, we determined the oxidation potentials of **1a–n** (except for **1i**[14]) by cyclic voltammetry vs. Fc.[15] Unfortunately, all allenes exhibited only irreversible oxidation waves at all scan rates applied in acetonitrile or methylene chloride, so we can only report on the anodic peak potentials. Even when we investigated the allenes by fast-scan cyclic voltammetry with scan rates up to 50000 Vs^{-1} only irreversible signals were obtained.

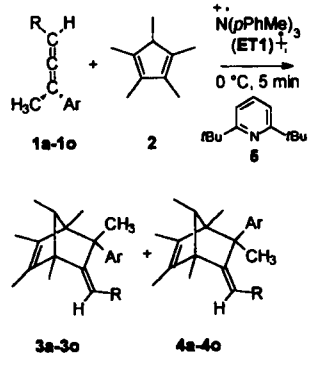
Table 1. Characteristic spectroscopic data of allenes **1**.

Allene	E_{pa} (V vs. Fc)	$\tilde{\nu}$(C=C=C) (cm^{-1})	^1H NMR (δ) C=C=C-*H*	^{13}C NMR (δ) C=*C*=C
1a [a]	0.94	1937	4.99	n.d. [b]
1b [a]	0.93	1955	5.38	204.51
1c [a]	0.95	1955	5.67	202.50
1d	0.92	1945	5.58	204.03
1e	0.92	1950	5.68	205.24
1f	0.95	1949	5.56	205.10
1g	0.89	1945	5.65	205.07
1h	0.93	1950	5.61	205.47
1i	n.d. [b]	1954	5.62	205.44
1k	0.67	1948	5.43	204.64
1l	1.08	1941	5.88	215.49
1m	0.98	1950	6.14	209.83
1n [a]	1.11	1943	5.85	214.02
1o [a]	1.23	1930	5.23	n.d. [b]

[a] Taken from ref. [12b]. [b] Not determined.

The oxidation potentials of products **3** and **4** have not been measured, except for that of **3h**, **4h** (E_{pa} = 1.02 V vs. Fc). It is expected that E_{pa} is 1.02±0.10 V for all Diels–Alder products **3,4a–n**, since the main electrophore remains unchanged (the anisyl group).

Synthesis of norbornenes 3, 4: While norbornenes **3a–h**, **4a–h** and **3n,o**, **4n,o** have been prepared through the radical-cation-catalyzed cycloaddition of **1** to **2** (Scheme 3),[16] some of them (**3d–h**, **4d–h**) were more conveniently isolated from the reaction of **3c**, **4c** with the corresponding acid chlorides (except **3g**, **4g**). In contrast, norbornenes **3l**, **4l** were formed in the radical cation reaction to an extent so small as to preclude simple isolation. Because of their great structural similarity with **3a–h**, **4a–h**, they could nevertheless be unambiguously assigned in the crude reaction mixture, as shown by the data in Tables 2 and 3.



Scheme 3.

The structures and the stereochemical relationships of all norbornenes were readily identified from the isomer mixtures by comparison of their ^1H and ^{13}C NMR resonances with those of norbornenes **3b**, **4b** (see Tables 2 and 3). The structures of the *endo*-norbornene **3b** and of the corresponding *exo*-isomer **4b** have been unambiguously determined by X-ray analysis[17] and extensive NOE investigations,[12b] thus providing a reliable reference. No diastereoselectivity was observed in the cycloaddition leading to norbornenes **3h** and **4h**. The ratio of the diastereomers (1:1) could readily be determined based on different ^1H NMR resonances for the 13-H and the methoxy group for the two *endo*- and the two *exo*-diastereomers. However, no full assignment of the diastereomers was undertaken. Characteristically, all norbornenes exhibited strong signals for a retro-DA cleavage in the mass spectra.

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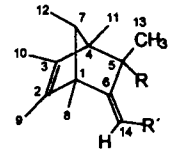
Table 2. Characteristic ^{1}H NMR shifts of some selected cycloadducts **3,4** (solvent $CDCl_3$, all shifts δ vs. TMS).

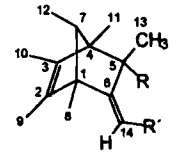


3,4

Cyclo-adduct	δ(7-H)		δ(10-H)		δ(12-H)		δ(13-H)		δ(14-H)	
3,4	**3**	**4**	**3**	**4**	**3**	**4**	**3**	**4**	**3**	**4**
a [a]	1.91	1.81	0.55	1.55	0.68	0.57	1.48	1.27	4.64, 4.94	4.64, 4.98
b [a]	1.87	1.78	0.57	1.48	0.68	0.54	1.53	1.35	5.22	5.28
c [a]	1.94	1.86	0.60	1.50	0.70	0.60	1.54	1.36	5.38	5.44
d	1.96	1.86	0.59	1.50	0.69	0.58	1.36	1.36	5.31	5.37
e	1.91	1.82	0.54	1.50	0.62	0.52	1.54	1.34	5.36	5.36
f	1.96	1.85	0.60	1.50	0.70	0.57	1.55	1.37	5.35	5.41
g	1.96	1.88	0.59	1.51	0.70	0.59	1.56	1.37	5.36	5.40
h	1.85–2.03 [b]	1.85–2.03 [b]	0.60	1.48	0.69	0.59	1.54	1.37	5.33	5.40
l	2.01	2.01	0.63	1.48	0.70	0.61	1.68	1.50	5.77	5.83
n [a]	2.03	1.99	0.64	1.50	0.72	0.62	1.70	1.52	5.75	5.83
o [a]	1.94	1.85	0.55	1.50	0.69	0.58	1.50	1.30	4.66, 4.96	4.66, 4.99

[a] ^{1}H NMR data taken from ref. [12b]. [b] Coincides with other signals.

Table 3. Some characteristic ^{13}C NMR shifts of cycloadducts **3b–h** and **3n,o** (solvent $CDCl_3$, all shifts δ vs. TMS).



3,4

Cyclo-adduct	δ(C-1, C-4)	δ(C-2, C-3)	δ(C-5)	δ(C-6)	δ(C-7)	δ(C-14)
3b [a]	57.92, 60.10	136.50, 137.81	53.14	153.44	56.90	111.14
3c [a]	58.12, 60.24	137.58, 138.08	53.79	156.60	57.26	116.11
3d	58.46, 60.36	137.54, 138.00	53.96	157.60	55.22	111.42
3e	58.50, 60.38	137.98	55.21	157.56	55.49	129.84
3f	58.39, 60.28	137.52, 137.92	53.91	157.48	55.14	129.73
3g	58.50, 60.38	137.63, 138.07	54.02	157.61	55.21	129.77
3h	58.46, 60.30	137.39, 138.13	53.96	157.55	55.12	110.50
3n [a]	60.49, 60.58	138.11, 140.71	56.26	166.00	55.19	109.63
3o [a]	58.26, 59.69	134.54, 137.79	54.93	164.02	57.77	101.97

[a] ^{13}C NMR data taken from ref. [12b].

The aminium salt initiated cycloaddition of allenes 1a–o (except 1i[14]) to 2:[18] Based on our previous experience[12] we used aminium salt **ET1**$^{\bullet+}$ ($E_{1/2}$ = 0.37 V) as the sole one-electron oxidant for the radical-cation-initiated cycloadditions since its redox potential compared favorably with that of diene **2** (E_{pa} = 0.54 V). In all cases studied a ratio of **1**:**2**:**ET1**$^{\bullet+}$ = 5:1:1 provided the best cycloaddition yields if di-*tert*-2,6-butylpyridine (**5**) was present.[12b] If the base was omitted the yields of cycloadducts were reduced and higher amounts of polymers were formed, except in the cycloaddition of **2** to allenes **1f, g, l,** and **n**, which exhibited an inverse behavior (Table 4). If yields of **3, 4** turned out to be low, in most cases—unless noted otherwise—intractable oligomeric products were formed.

The photoinduced electron transfer (PET) initiated cycloaddition of allenes 1a,c with 2: Several different sensitizers and various concentrations and conditions to initiate the cycloaddition have been tested. In the PET reaction of **1a** and **2** with **ET2** or **ET3** and the pyrylium salts **ET4** and **ET5** no DA adducts were afforded. DA cycloadducts could only be obtained in the presence of biphenyl (**ET6**) as a cosensitizer in conjunction with **ET2** and **ET3**, when the latter two were used in rather high amounts. In general, **ET2** proved to be superior to **ET3**, and these reactions are listed in Table 5.

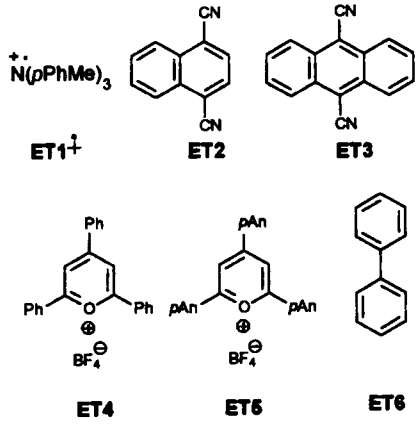


Table 4. Yields [a] for the aminium salt initiated cycloaddition of **1a–o** and **2** to give cycloadducts **3a–o, 4a–o** (ratio **1**:**2**:**ET1** = 5:1:1, base **5**).

Allene	Base 5	Yields 3,4 (%) (*endo*:*exo*)	Allene	Base 5	Yields 3,4 (%) (*endo*:*exo*)
1a [b]	+	80 (5.2:1)	**1h**	+	39 (8.8:1)
	–	37 (5.2:1)		–	28 (6:1)
1b [b]	+	72 (7:1)	**1i**	not det. [f]	not det. [f]
	–	52 (4.8:1)		not det. [f]	not det. [f]
1c [b]	+	81 (5.2:1)	**1k**	+	– [g]
	–	– [c]		not det.	not det.
1d	+	46 (4.8:1)	**1l**	+	4 [b]
	–	– [c]		–	10 [b]
1e	+	51 (4.1:1)	**1m**	+	– [i]
	–	25 (4.0:1) [d]		–	– [i]
1f	+	8 (4.3:1) [e]	**1n** [b]	+	5 (4:1) [k]
	–	27 (4.4:1) [e]		–	11 (10:1) [k]
1g	+	21 (4.3:1) [d]	**1o** [b]	+	60 (4:1)
	–	25 (4.3:1) [d]		–	7 (6:1) [k]

[a] Determined by ^{1}H NMR with acetophenone as internal standard. [b] Taken from ref. [12b]. [c] By-products, probably formed by acid catalysis. [d] Polymeric compounds detected, probably formed by oxidation of an intermediate similar to **9f**. [e] Polymeric compounds detected, probably formed by oxidation of **9f**. [f] Not determined because of a high degree of decomposition of the parent allene **1i**. [g] Allene **1k** was re-isolated. [h] *Endo* and *exo* product, no more allene **1l** was detected. [i] Raw mixture contained only the educts (besides **ET1**). [k] Further products detected, see ref. [12b].

Discussion

While the present results demonstrate the potential of electron transfer under mild conditions successfully initiating Diels–Alder reactions with electron-rich allenes as dienophiles in the presence of various functional groups (**1a–h**), it has become obvious that some substituents (**1k–n**) are poor choices for a radical cation reaction (see Table 4). Hence, in the following we will elaborate on some of our novel findings in order to provide a more detailed and comprehensive understanding of radical cation catalysis.

Table 5. PET-induced reactions (ratio 1:2 = 5:1, 0.2 M $LiClO_4$ [a], solvent acetonitrile [b]).

Allene	mol% ET6 [c]	mol% ET2 [c]	Yields 3	Yields 4	Irradiation time
1a	–	–	–	–	5 d
1a	500	–	3	2	2 d
1a	200	20	traces	traces	5 d
1a	500	20	5	2	5 d
1a	500	20	9	4	5 d
1a	500	20	10	6	2 d
1a [d]	500	20	10	6	2 d
1a	500	60	14	11	2 d
1a	500	60	14	14	5 d
1c [d]	500	20	13	3	2 d
1c [d]	500	20	17	3	3 d

[a] Addition of lithium perchlorate reduces electron back-transfer in the $[ET2^{\bullet-}\cdot 2^{\bullet+}]$ contact ion pair ("salt effect") by formation of $[ET2^{\bullet-}\cdot Li^{+}]$. [b] Polar solvents are known to ease separation of contact ion pairs. [c] Related to 2. [d] 250 mol% Sodium bicarbonate (related to 2) was added.

PET-induced cycloaddition of 1a,c and 2: The photoinduced cycloaddition was probed for allenes **1a** and **1c** with several different acceptors. An analysis of the driving force for the initial ET step by the Rehm–Weller equation[19] indicated that both allenes and diene should efficiently quench the excited acceptors. Indeed, in the UV spectrum of **2**/**ET2** a weak charge transfer absorption at $\lambda_{max} = 367$ nm ($\varepsilon = 10$) could be detected, suggesting that exciting **ET2** should result in formation of $[ET2^{\bullet-}\cdot 2^{\bullet+}]$, but no reaction was observed when **ET2**–**ET5** were used. However, the cycloaddition was initiated with **ET2** in the presence of biphenyl (**ET6**) as a cosensitizer. This may be indicative of a fast electron back-transfer from $[ET2^{\bullet-}\cdot 2^{\bullet+}]$ to regenerate the reactants or alternatively of a rather slow reaction of $2^{\bullet+}$ with allenes **1a,c**. In the presence of large amounts of **ET6** (200–500 mol%) the excited acceptor **ET2*** is now predominantly quenched to generate the ion pair $[ET2^{\bullet-}\cdot ET6^{\bullet+}]$, which separates by diffusion to provide a high yield of free ions.[20] Importantly, with **ET2**/**ET6** the DA cycloadducts **3**, **4** were formed in up to 28% yield[21] with yields increasing the higher the amount of **ET2**. This dependence on the amount of oxidant likewise showed up when chemical oxidation was used.[12b] A decisive disadvantage of the PET-induced reaction, however, is the fact that long irradiation times were needed (up to 5 d) that are not compatible with photochemical and thermal stabilities of allenes **1**. Thus, thermal oxidation has proven far superior to PET initiation.

The mechanism: In our earlier publications[12] we excluded an acid-catalyzed pathway to the Diels–Alder cycloadducts and proposed a radical-cation chain process with a rather short chain length. This suggestion is indeed now being confirmed by the results from PET initiation, although the yields of **3**, **4** were rather moderate regardless of which PET system was used. Nevertheless, formation of the Diels–Alder products in the PET format points unambiguously to radical cations as reactive species and rigorously excludes reactant/aminium salt complexes as reaction intermediates. The role of the base is to trap the acid liberated from the acidic radical cations and to avoid acid-catalyzed processes.[12]

The question of a [3+2] or a [4+1] mechanism [Equations (i)–(iii) and (iv)–(vi), respectively; DA = Diels–Alder product] for radical-cation-catalyzed cycloadditions has initiated a lively controversy over the last decade. A [4+1] mechanism has been favored for years, since in contrast to the [3+2] variant it is formally symmetry-allowed[22] and in essence all of the earlier radical-cation DA cross-reactions involved readily oxidizable dienophiles.[2,23,24] Recent work from several groups,[6,10,11] however, has disclosed that the [3+2] pathway is a viable mechanistic choice, if the diene prefers the *s-cis* conformation as does **2**. Since a comparison of the anodic peak potentials of allenes **1a–o** (see Table 1) with that of diene **2** ($E_{pa} = 0.54$ V) reveals the diene as the component with the lowest oxidation potential and since DA product yields could be improved in all successful cases when the allene was present in a fivefold excess over the diene[12b] we propose a clear preference for the [3+2] pathway.

[3+2] mechanism:

$$\text{diene} - e^{-} \rightarrow \text{diene}^{\bullet+} \quad \text{(i)}$$

$$\text{diene}^{\bullet+} + \text{allene} \rightarrow DA^{\bullet+} \quad \text{(ii)}$$

$$DA^{\bullet+} + \text{diene (or } NR_3) \rightarrow DA + \text{diene}^{\bullet+} \text{ (or } NR_3^{\bullet+}) \quad \text{(iii)}$$

[4+1] mechanism:

$$\text{allene} - e^{-} \rightarrow \text{allene}^{\bullet+} \quad \text{(iv)}$$

$$\text{allene}^{\bullet+} + \text{diene} \rightarrow DA^{\bullet+} \quad \text{(v)}$$

$$DA^{\bullet+} + \text{allene (or } NR_3) \rightarrow DA + \text{allene}^{\bullet+} \text{ (or } NR_3^{\bullet+}) \quad \text{(vi)}$$

Cycloaddition at the radical cation stage: The above mechanistic discrimination between [4+1] and [3+2] mechanisms does not necessarily have any bearing on whether the cycloaddition occurs in a concerted or stepwise mode. Unfortunately, no stereochemical markers are available in the present cycloaddition that could testify concerning the intermediacy of a distonic radical cation. Nevertheless, several results that are discussed in detail below provide strong evidence for a stepwise mechanism.

Cycloaddition with allenes 1a–1n: The various allenes used in the aminium salt initiated cycloaddition may be roughly grouped into three categories: a) allenes with two or three electron-rich substituents, such as **1a–h**, which permit DA cycloaddition in yields up to 81%; b) allenes with one electron-withdrawing substituent at the remote end of the allene electrophore, such as **1l–n**, which undergo only very moderate DA cycloaddition; and c) the allene **1k** with an amino group at the remote end that is reluctant to undergo DA reaction at all. Intriguingly, the successful cycloadditions of **1e** and **1g** demonstrate that even redox-sensitive functionalities such as a *p*-methoxybenzoyl and a carbamate group are tolerated in the radical cation format. Unfortunately, no diastereoselectivity was evinced in the cycloaddition of **1h** with **2**, because the camphanoyl group is too remote from the allene double bond. While allene **1i** certainly should be more promising in this respect it proved to be too unstable for the cycloaddition format.[14]

Electronic and steric substituent effects: The failure of allene **1k** to react in the radical-cation DA reaction is most easily explained by taking a closer look at its oxidation potential. Since $E_{pa}(\mathbf{1k}) = 0.67$ V is considerably lower than the E_{pa} values of all other allenes, the amino group constitutes the electrophore with the highest HOMO energy and likewise the highest nucleophilicity. Although in the aminium salt initiated cycloaddition of **1k** and diene **2** the latter is still the most readily oxidizable component, the resulting $2^{\bullet+}$ should be attacked by the amino group of **1k** rather than by the allene bond system.

In contrast, the situation with allenes **1l–m** is more complicated and needs some detailed discussion. Although only a very small yield of 4–5% DA products is recorded for allenes **1l,n** and **2**, we have to remember that in the absence of base **5** the yields are more than doubled. As steric interactions of the sub-

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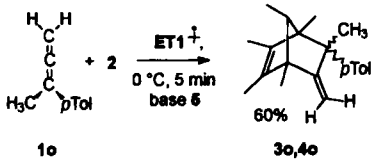
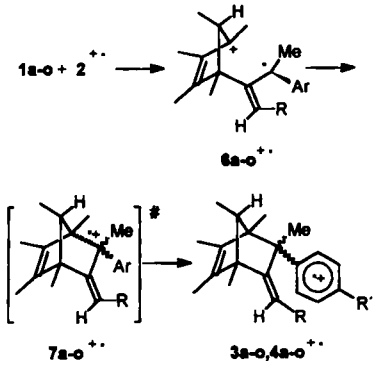
stituent R should exert only a small effect on the cycloaddition (see **1d** vs. **1h**), the low yield is certainly attributable to electronic effects caused by the electron-withdrawing substituents. However, it should be pointed out that oxidation potential differences of the two reactants, $\Delta E_{pa} = E_{pa}(\mathbf{1l}\text{ or }\mathbf{1n}) - E_{pa}(\mathbf{2}) = 0.54$ or 0.57 V, respectively (an argument quite often cited in the recent literature[10]), cannot account for this drop in yield, since with 1-tolyl-1-methylallene (**1o**) a satisfactory yield of 60% was obtained[12b] although $\Delta E_{pa} = E_{pa}(\mathbf{1o}) - E_{pa}(\mathbf{2}) = 0.69$ V (Scheme 4). However, electronic effects exerted by R = COOH and COOEt should only play a minor role in a *concerted* pathway, since the C–C bonds develop almost perpendicular to the *exo*-methylene group. The observed low yields from **1l** and **1n** provide strong evidence for a *stepwise* mechanism of the cycloaddition, which would allow the various functionalities R at the far end of the *exo*-methylene group to exert some influence at the stage of a distonic radical cation $\mathbf{6}^{\bullet+}$. The reaction course in Scheme 5 is thus conceived. In the initial step of the radical cation cycloaddition $\mathbf{2}^{\bullet+}$ is attacked by the allene **1**, presumably the faster the smaller $\Delta E_{pa} = E_{pa}(\mathbf{1}) - E_{pa}(\mathbf{2})$, in line with FMO considerations.[10] At this point in the discussion, we cannot exclude the possibility of a concerted reaction for the electron-rich allenes **1a–h**, but the cycloaddition should proceed in a stepwise manner for allenes with electron-withdrawing substituents R as in **1l–n**. This mechanistic hypothesis necessarily leads to the formulation of the distonic radical cations $\mathbf{6}^{\bullet+}$, which ought to develop a two-center–one-electron bond in the transition state $[\mathbf{7}^{\bullet+}]^{\ddagger}$[25] before giving rise to **3**, $\mathbf{4}^{\bullet+}$. In the product radical cations the charge and spin is expected to be localized on the aromatic ring and not in the newly established carbon–carbon bond.[26]

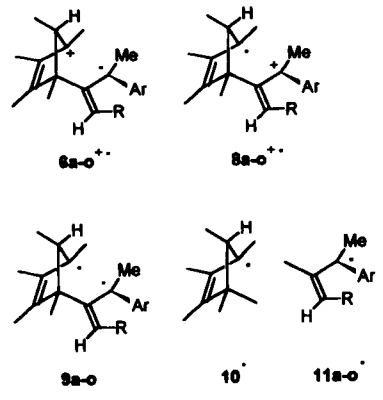


Scheme 4.



Scheme 5.

Mechanistic details of the stepwise cycloaddition: But what is the kinetic barrier to C–C bond formation when such an open radical cation converts to **3**, $\mathbf{4}^{\bullet+}$ via transition state $[\mathbf{7}^{\bullet+}]^{\ddagger}$? Simple ionization potential considerations indicate a distinct difference for the distonic radical cations $\mathbf{6l–n}^{\bullet+}$ as opposed to $\mathbf{6a–h}^{\bullet+}$. Indeed, when we look at the open distonic radical cations, there are two options for the charge distribution (Scheme 6). Interestingly, for all substituents Ar and R studied so far there is a clear preference for the charge distribution as in $\mathbf{6}^{\bullet+}$. However, while for systems **a–h** the enthalpy difference $\Delta H_f^\circ(\mathbf{8}^{\bullet+}) - \Delta H_f^\circ(\mathbf{6}^{\bullet+})$[27] is of the order of 0.37 – 0.45 eV,[28] it is substantially increased to 0.71 – 0.89 eV for systems containing electron-withdrawing groups as in **l–n**. It seems quite likely on the basis of simple FMO considerations that formation of **3**, $\mathbf{4}^{\bullet+}$ via transition state $[\mathbf{7}^{\bullet+}]^{\ddagger}$ should depend to some extent on $\Delta H_f^\circ(\mathbf{8}^{\bullet+}) - \Delta H_f^\circ(\mathbf{6}^{\bullet+})$, as the positive charge has to develop into the carbon–carbon bond between the two centers and needs stabilization from both fragments. But what would one expect if this ring closure reaction is slow? Obviously another typical reaction of radical cations, rapid C–H deprotonation, which could be responsible for excessive depletion of oxidant[12b] and thus for a short chain length, should start to divert the reaction course from the cycloaddition pathway. Such behavior is indeed observed with **1l,n** and **2**, since here, quite in contrast to most other systems, the cycloaddition yields can be increased through removal of base **5**, thus avoiding excessive deprotonation of intermediate radical cations. With **1m** the situation is even more disastrous than for **1l,n** as the $CONEt_2$ functionality may act as an internal base that diverts $\mathbf{6m}^{\bullet+}$ to deprotonation, independent of whether base **5** is added or not.

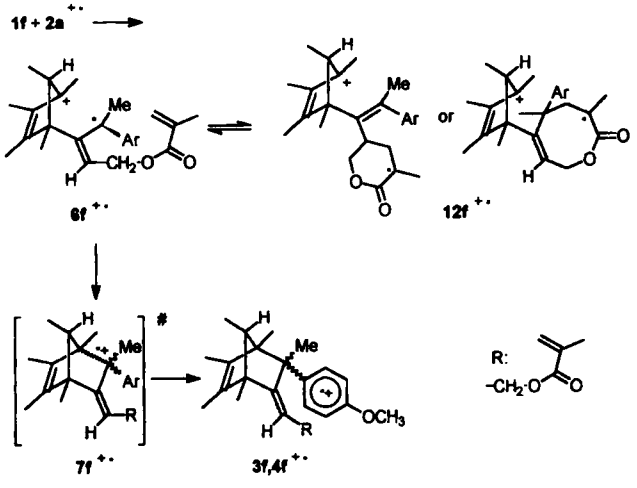


Scheme 6. Two charge distributions in the open distonic radical cations are conceivable: $\mathbf{6a–o}^{\bullet+}$ or $\mathbf{8a–o}^{\bullet+}$. Ionization potentials of the two radical sites in the biradical **9a–o** were approximated from the ionization potentials of radicals **10**$^{\bullet}$ and **11a–o**$^{\bullet}$ as representative fragments of **9a–o** [27].

For allenes **1a–h** an almost constant anodic peak potential between 0.89–0.95 V is registered, indicating that variations in the substituents in other locations on the molecule do not exert any significant effect on the HOMO energy of the allene. Accordingly, one would naively expect the cycloaddition with $\mathbf{2}^{\bullet+}$ to be equally facile for all the allenes. Nevertheless, we observe distinct differences in the DA cycloaddition yields in the presence of base **5**. For instance, while the switch from R = H to CH_3 and CH_2OH (**1a–c**) does not greatly affect the yields of between 72 and 81%, simple esterification to $CH_2OC(O)CH_3$ and $CH_2OC(O)C_6H_4OCH_3$ (**1d,e**) reduces the cycloaddition yield to about 50%. As oxidation potential differences in allenes **1** are certainly negligible this trend seems to be brought about by the increased steric requirements of the latter two remote substituents R, the more so since with R = CH_2O–CAM (**1h**), an even more sterically demanding group, the yield is further reduced (38%).

However, with **1f** the situation is much more complicated; yields are rather low (8%) but certainly not because of steric bulk. For a deeper insight, we have to take into consideration the surprising fact that the DA yield is significantly increased (27%) upon removal of base **5**, as with **1l,n**. While this behavior cannot be understood on the basis of a concerted cycloaddition mechanism, again the stepwise mode offers a straightforward explanation. One may readily conceive a distonic radical cation $\mathbf{6f}^{\bullet+}$, which should ring-close as rapidly as $\mathbf{6a–e}^{\bullet+}$ to **3**, $\mathbf{4f}^{\bullet+}$ (based on $\Delta H_f^\circ(\mathbf{8}^{\bullet+}) - \Delta H_f^\circ(\mathbf{6}^{\bullet+})$ considerations). However, in contrast to those it may be diverted in an intramolecular and reversible radical addition reaction[29] furnishing either a 6- or 8-membered lactone $\mathbf{12f}^{\bullet+}$ (Scheme 7). Since this new distonic radical cation is very difficult to oxidize at the α-carbonyl radical center[30] it may either deprotonate in the presence of base, revert to $\mathbf{6f}^{\bullet+}$, undergo hydrogen abstraction or initiate an oligomerization process. Noticeably, the yield from **1f** is increased in the absence of base **5**, indicating the presence of a base-sensitive intermediate that can revert to the cycloaddition route.

Since **1f** is electronically related to **1a–e, g–h**, the stepwise mechanism should apply to all electron-rich allenes presented in



Scheme 7.

this study as well. In retrospect, the charge distribution in $6^{\bullet+}$ is equally well supported by the observation of an efficient cycloaddition with allene **1c**. The corresponding distonic radical cation would be expected to divert rapidly from the cycloaddition route through dihydrofuran formation if the charge distribution was inverted as in $8c^{\bullet+}$. But why is the yield increased for most systems in the presence of base **5**, but not for **1f, l, n**? If ring closure to **3**, $4^{\bullet+}$ is rapid enough, any added base should not divert $6^{\bullet+}$ from the cycloaddition route, but rather should exert beneficial effects. Since, in the reactions examined, protons are inevitably liberated from such acidic species as radical cations,[31] it is always important to minimize acid-induced side reactions, which can be largely suppressed in the presence of **5**.[12]

Details of the PET reaction: Having shed some light on the mechanism of the radical cation cycloaddition initiated with $ET1^{\bullet+}$, it is worth reexamining the reaction under PET conditions where much lower yields have been obtained. As outlined above, formation of a two-center–one-electron bond in the transition state $[7^{\bullet+}]^*$ seems to be one of the pivotal steps in the cycloaddition, but the electron-transfer reduction of $3^{\bullet+}$, $4^{\bullet+}$ is similarly important.[6b] While for the thermal reaction this is most easily accomplished with tri-*p*-tolylamine as reducing agent rather than with **2**,[6b] no good reductant other than $ET2^{\bullet-}$ is available for the PET reaction. However, $ET2^{\bullet-}$ is only present in minute concentrations; thus a lower yield in the PET reaction may be at least partly due to inefficient reduction of **3**, $4^{\bullet+}$. Such a reduction pathway explains rather easily why cycloaddition could only be accomplished with **ET2** and **ET3**, as in contrast the pyrylium radicals **ET4**$^{\bullet}$ and **ET5**$^{\bullet}$ are much weaker reductants than $ET2^{\bullet-}$ and $ET3^{\bullet-}$.[32]

Another severe disadvantage of the PET format is the long irradiation time, which permits unintended oxidation of norbornene **3, 4**. According to the Rehm–Weller equation[19] oxidation of **3, 4** by **ET2**$^{\bullet}$ or $ET6^{\bullet+}$ is possible. A surprising and mechanistically important feature of the PET reaction of **1a,c** with **2** is the much lower *endo*/*exo* selectivity observed (**3**:**4**) compared with that in the thermal oxidation. Indeed, in the PET reaction another pathway to **3, 4** is conceivable through one-electron reduction of $6^{\bullet+}$ by $ET2^{\bullet-}$ generating biradical **9** [Equation (vii)]. While the redox properties of radicals preclude reduction of the radical site of $6^{\bullet+}$ to an anion by **ET2** ($E^{ox}_{1/2}$ = −1.67 V vs. Fc[15,19b]),[33] the corresponding cationic site[34] ought to be readily reduced. Again, as above, $ET2^{\bullet-}$ should be much more effective as reductant than all other PET systems used, which explains in retrospect the failure of the PET reaction with **ET4** and **ET5**.

$$6^{\bullet+} + ET2^{\bullet-} \rightarrow 9 + ET2 \rightarrow 3, 4 + ET2 \qquad \text{(vii)}$$

While generation of **3, 4** from **9** could constitute an interesting alternative, in particular for systems **l–n**, first exploratory investigations of the PET cycloaddition of **1m** and **ET2**/**ET6** proved to be unsuccessful.

Conclusion

The present study provides indirect but conclusive evidence from several experiments for a stepwise cycloaddition of allenes **1a–n** and diene **2** by a [3+2] mechanism. Since the [3+2] mechanism is formally symmetry-forbidden, it should be interesting to see whether in general the [3+2] pathway constitutes a stepwise reaction, as opposed to the [4+1] alternative. The latter variant is formally symmetry-allowed and evidence has been provided to indicate that it proceeds in a concerted manner.[2] In addition, we have presented a novel and helpful criterion, the $\Delta H_f^{\circ}(8^{\bullet+}) - \Delta H_f^{\circ}(6^{\bullet+})$ enthalpy difference,[35] that we suppose to play an essential role in the bond formation of the distonic radical cations $6^{\bullet+}$ to **3**, $4^{\bullet+}$.

Experimental Procedures

General methods and materials: For apparatus used in this work, see refs. [6b] and [12b]. $CDCl_3$ was the solvent of choice for all NMR experiments (RT) unless noted otherwise. Cyclic voltammetry experiments were performed in homemade cells consisting of a disk working electrode, an auxiliary electrode (platinum wire) and a reference electrode (silver wire). For standard voltammetric experiments a platinum working electrode (diameter = 1 mm) was immersed in a 10^{-3} M solution of the substrate in acetonitrile or dichloromethane containing tetra-*n*-butylammonium hexafluorophosphate (0.1 M). The voltage sweep was controlled by a Princeton Applied Research 362 potentiostat. All potentials are referenced to the ferrocene/ferrocenium couple [15]. The diene **2** and 2,6-di-*tert*-butylpyridine (**5**) were reagent-grade materials, freshly distilled before use. The one-electron oxidants: $ET1^{\bullet+}$ was synthesized from commercially available tris(4-methylphenyl)amine (Kodak) and nitrosonium hexafluoroantimonate (Ozark Mahoning) in acetonitrile. **ET2**, **ET4**, and **ET5** were synthesized according to refs. [36] and [19c], respectively. **ET3** and **ET6** were of commercial grade.

Preparation of allenes: The allenes known in the literature, 2-(4-methoxyphenyl)-2,3-butadiene (**1a**) and ethyl 4-(4-methoxyphenyl)-penta-2,3-dienoate (**1n**), were prepared according to ref. [12b].

Three-step preparation of allene 1c by LAH reduction of 4-methoxy-4-(4-methoxyphenyl)pent-2-yn-1-ol:

a) Synthesis of 3-methoxy-3-(4-methoxyphenyl)but-1-yne: To a solution of butyllithium (9.60 mL, 24.0 mmol, 2.5 M in *n*-hexane) in dry tetrahydrofuran (20 mL) and dry *n*-hexane (10 mL) at −25 °C was added dropwise a solution of 2-(4-methoxyphenyl)-but-3-yn-2-ol [37] (3.72 g, 22.1 mmol) in dry tetrahydrofuran (5 mL) over 5 min. Dry dimethylsulfoxide was added at once to the clear yellow solution, whereupon a white solid started to precipitate. After stirring for 5 min at 25 °C, iodomethane (4.77 g, 33.6 mmol) was added and the precipitate disappeared. Once more the mixture was stirred for 1 h at 10 °C and 1 h at 50 °C before hydrolysis with a saturated NaCl solution and extraction (three times) with diethyl ether. The combined organic layers were washed with aqueous NaCl and dried ($MgSO_4$), and the solvent was removed. The clear yellow liquid was distilled at 0.4 Torr and 83–86 °C to afford 2.7 g (64%) of 3-methoxy-3-(4-methoxyphenyl)but-1-yne. IR (CCl_4): $\tilde{\nu}$ = 3280 (s, acetylene H); 3045 (w, aryl H), 2990, 2935, 2900 (s, C–H), 2820 (m, OCH_3), 2110 (w, C≡C), 1602, 1580, 1510 (s, arom. C–C), 1455 (s, C–H), 1365 (m, CH_3), 1305 (s), 1254, 1173, 1090, 1045, 1030 (s, C–O), 860 (m), 828 (s) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 1.74 (s, 3H), 2.72 (s, 1H), 3.20 (s, 3H), 3.84 (s, 3H), 6.92 (m, 2H), 7.54 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 32.46, 52.34, 55.35, 75.29, 76.03, 84.03, 113.66, 127.35, 134.27, 159.35; MS (70 eV, EI) *m*/*z* (%): 190 (11) [M^+], 176 (12), 175 (100), 160 (13), 159 (66), 135 (5), 128 (5), 127 (6), 116 (10), 115 (19), 89 (11); HRMS calcd. for $C_{12}H_{14}O_2$: 190.0994, found: 190.1001.

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b) 4-methoxy-4-(4-methoxyphenyl)pent-2-yn-1-ol: A Grignard reagent was synthesized from a mixture of magnesium (2.75 g, 113 mmol) and 1-bromoethane (12.3 g, 113 mmol) under nitrogen in dry tetrahydrofuran (30 mL). 3-methoxy-3-(4-methoxyphenyl)but-1-yne (20.7 g, 109 mmol) was added dropwise over 15 min at 0 °C. The mixture was allowed to warm to room temperature and a formaldehyde stream (generated by heating 3.70 g paraformaldehyde to 180–200 °C) was carefully conducted onto the surface of the solution. After stirring for 2.5 h the reaction mixture was hydrolyzed with saturated ammonium chloride (100 mL) and extracted three times with diethyl ether (100 mL). The combined organic layers were washed with water and saturated NaCl. The solvent was removed, and the crude orange oil was dried (Na_2SO_4) and chromatographed over silica gel (cyclohexane/ethyl acetate = 3/1, R_f = 0.17) to afford 16.7 g (69%) of 4-methoxy-4-(4-methoxyphenyl)-pent-2-yn-1-ol. IR (CCl_4): $\tilde{\nu}$ = 3420–3360 (s br, OH), 3030 (w, aryl H), 2980, 2925 (s, C–H), 2820 (m, OCH_3), 1600 (s, arom. C–C), 1578 (m, arom. C–C), 1504 (vs, arom. C–C), 1455, 1435 (m, C–H), 1405 (m), 1362 (m, CH_3), 1295, 1235 (s, OH), 1170, 1086, 1025 (s, C–O), 990 (m), 855 (m), 825 (s) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 1.72 (s, 3H), 2.32 (br s, 1H; OH), 3.19 (s, 3H), 3.84 (s, 3H), 4.44 (s, 2H), 6.90 (m, 2H), 7.51 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 32.32, 51.15, 52.30, 55.34, 76.12, 85.64, 85.81, 113.64, 127.36, 134.41, 159.28; MS (70 eV, EI) *m/z* (%): 220 (8) [M^+], 206 (13), 205 (100), 190 (5), 189 (35), 174 (8), 161 (9), 159 (8), 151 (18), 146 (8), 145 (14), 135 (7), 131 (8), 128 (7), 127 (6), 121 (8), 115 (11); HRMS calcd. for $C_{13}H_{16}O_3$: 220.1099, found: 220.1104.

c) 4-(4-methoxyphenyl)-2,3-pentadienol (**1c**): To a suspension of LAH (0.88 g, 23.0 mmol) in dry diethyl ether (100 mL) at 0 °C was added a solution of 4-methoxy-4-(4-methoxyphenyl)pent-2-yn-1-ol (5.11 g, 23.0 mmol) in dry ethyl ether (20 mL) dropwise over 15 min. After stirring for 1 h the reaction mixture was hydrolyzed with water, extracted three times with dichloromethane (50 mL), washed with water and saturated NaCl, and dried (Na_2SO_4). After the solvent had been removed, the crude yellow solid was chromatographed over silica gel (trichloromethane/ethyl acetate = 20/1, R_f = 0.35) to afford 2.2 g (50%) of **1c**. IR (CCl_4): $\tilde{\nu}$ = 3638, 3605 (w, OH), 2961, 2943 (s, C–H), 2838 (m, OCH_3), 1955 (w, allene C=C=C), 1608, 1508 (m, arom. C–C), 1463, 1445 (m, C–H), 1398 (w), 1374 (m, CH_3), 1296, 1239 (s, O–H), 1179, 1039 (vs, C–O) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 2.13 (d, ^5J(H,H) = 3.0 Hz, 3H), 3.84 (s, 3H), 4.21 (d, ^3J(H,H) = 6.0 Hz, 1H), 4.23 (d, ^3J(H,H) = 6.0 Hz, 1H), 5.67 (ddq, ^3J_d(H,H) = 6.0 Hz, ^3J_d(H,H) = 6.0 Hz, ^5J_s(H,H) = 3.0 Hz, 1H), 6.89 (m, 2H), 7.35 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.32, 55.34, 60.83, 93.87, 103.24, 113.95, 126.95, 128.93, 158.83, 202.54; MS (70 eV, EI) *m/z* (%): 191 (5), 190 (32) [M^+], 161 (8), 160 (18), 159 (100), 158 (10), 147 (25), 145 (6), 144 (11), 129 (6), 128 (16), 127 (15), 116 (21), 115 (35); E_{pa} = 0.95 V; HRMS calcd. for $C_{12}H_{14}O_2$: 190.0994, found: 190.1001.

Preparation of allene 1d: A solution of **1c** (800 mg, 4.21 mmol), 4-*N*,*N*-dimethylaminopyridine (40.0 mg, 0.32 mmol) in dry pyridine (4.0 mL) and dry acetic anhydride (4.0 mL) was stirred under nitrogen for 1 h at RT. The reaction mixture was poured onto ice and extracted with dichloromethane (three times). The combined organic layers were extracted with water, saturated sodium bicarbonate, and then water again. After drying ($MgSO_4$), the solvent was removed. The crude mixture was chromatographed over silica gel (cyclohexane/ethyl acetate = 1/1, R_f = 0.88) to afford 400 mg (41%) of **1d**. IR (CCl_4): $\tilde{\nu}$ = 3640 (w), 2980, 2940, 2895 (m, C–H), 2826 (m, OCH_3), 2040 (w), 1945 (w, allene C=C=C), 1735 (vs, C=O), 1600 (s, arom. C–C), 1573 (m, arom. C–C), 1505 (s, arom. C–C), 1453, 1435 (m, C–H), 1395 (w), 1365 (s, CH_3), 1290 (m, C–O), 1240, 1220, 1173, 1023 (s, C–O), 955 (m), 828 (s) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 2.10 (s, 3H), 2.11 (d, ^5J(H,H) = 3.0 Hz, 3H), 3.82 (s, 3H), 4.66 (d, ^3J(H,H) = 6.0 Hz, 1H), 4.68 (d, ^3J(H,H) = 6.0 Hz, 1H), 5.58 (ddq, ^3J_d(H,H) = 6.0 Hz, ^3J_d(H,H) = 6.0 Hz, ^5J_s(H,H) = 3.0 Hz, 1H), 6.90 (m, 2H), 7.33 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.99, 19.93, 54.29, 61.54, 87.94, 101.38, 112.87, 126.00, 128.70, 157.84, 169.73, 204.03; MS (70 eV, EI) *m/z* (%): 232 (11) [M^+], 231 (2), 191 (5), 190 (62), 189 (20), 175 (63), 174 (16), 173 (15), 172 (10), 161 (7), 160 (16), 159 (39), 158 (18), 157 (22), 147 (9), 146 (5), 145 (5), 144 (7), 129 (15), 128 (20), 128 (16), 127 (15), 116 (14), 115 (29), 43 (100); E_{pa} = 0.91 V; HRMS calcd. for $C_{14}H_{16}O_3$: 232.1099, found: 232.1096.

Preparation of allene 1e: A solution of **1c** (250.1 mg, 1.332 mmol) and freshly distilled 4-methoxybenzoyl chloride (270.6 mg, 1.586 mmol) in dry pyridine (25 mL) was stirred under nitrogen for 1 d at RT. Trichloromethane (15 mL) was added and the solution was washed with 1N aqueous sodium hydroxide and saturated NaCl solution (twice). After drying (Na_2SO_4), the solvent was removed and the crude oil was chromatographed over silica gel (diethyl ether, R_f = 0.80) to furnish 195.7 mg (46%) of **1e**. IR (CCl_4): $\tilde{\nu}$ = 3000, 2975, 2920 (m, C–H), 2830 (m, OCH_3), 1950 (vw, allene C=C=C), 1705 (s, C=O), 1600 (s, arom. C–C), 1575 (w, arom. C–C), 1505 (s, arom. C–C), 1455, 1435, 1415 (m, C–H), 1310, 1265, 1250, 1175, 1160, 1095, 1030, 1005 (C–O), 840 (w), 830 (w), 780 (s), 755 (s) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 2.09 (d, ^5J(H,H) = 2.5 Hz, 3H), 3.81 (s, 3H), 3.86 (s, 3H), 4.86 (d, ^3J(H,H) = 7.0 Hz, 2H), 5.68 (m, 1H), 6.88 (d, ^3J(H,H) = 7.0 Hz, 2H), 6.92 (d, ^3J(H,H) = 7.0 Hz, 2H), 7.33 (d, ^3J(H,H) = 7.0 Hz, 2H), 8.01 (d, ^3J(H,H) = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.08, 55.37, 55.43, 62.79, 89.23, 102.48, 113.67, 113.92, 122.83, 127.10, 128.73, 131.73, 158.88, 163.45, 166.17, 205.24; MS (70 eV, EI) *m/z* (%): 324 (9) [M^+], 172 (8), 159 (7), 157 (11), 136 (34), 135 (100), 129 (7), 128 (8), 115 (12), 107 (25), 92 (20), 78 (6), 77 (49), 69 (5), 65 (7), 64 (15), 63 (13), 57 (11), 55 (10), 53 (5), 51 (12), 50 (7), 44 (7), 43 (28), 41 (10), 39 (15), 38 (8); E_{pa} = 0.92 V; HRMS calcd for $C_{20}H_{20}O_4$: 324.1361, found: 324.1365.

Preparation of allene 1f: A solution of **1c** (154.0 mg, 0.184 mmol) and freshly distilled 2-methacryloyl chloride (127.6 mg, 1.221 mmol) in dry pyridine (10 mL) was stirred under nitrogen for 30 min at RT. Trichloromethane (5 mL) was added and the solution was washed with saturated sodium bicarbonate and water (five times). After drying (Na_2SO_4), the solvent was removed to afford 150 mg (72%) of **1f** sufficiently pure (>95%) for further use. IR (CCl_4): $\tilde{\nu}$ = 2960 (m, C–H), 2930 (m, C–H), 2840 (w, OCH_3), 1949 (vw, allene C=C=C), 1720 (s, C=O), 1605 (m, arom. C–C), 1510 (m, arom. C–C), 1455 (m, C–H), 1400 (w, C–H), 1372 (w, CH_3), 1295 (m, C–O–C), 1235 (m, C–O–C), 1155 (s, C–O–C), 1035 (s, C–O–C), 905 (m) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 1.94 (t, ^5J(H,H) = 1.5 Hz, 3H), 2.07 (d, ^5J(H,H) = 2.5 Hz, 3H), 3.79 (s, 3H), 4.72 (d, ^3J(H,H) = 7.0 Hz, 2H), 5.56 (m, 1H), 5.60 (m, 1H), 6.11 (m, 1H), 6.86 (d, ^3J(H,H) = 7.0 Hz, 2H), 7.31 (d, ^3J(H,H) = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.05, 18.36, 55.38, 62.66, 89.07, 102.57, 113.92, 125.60, 127.09, 128.69, 136.45, 158.89, 167.24, 205.10; MS (70 eV, EI) *m/z* (%): 258 (7) [M^+], 219 (22), 205 (5), 190 (5), 189 (29), 175 (11), 173 (5), 172 (7), 161 (9), 159 (13), 157 (5), 151 (21), 150 (25), 136 (9), 135 (100), 133 (7), 128 (6), 127 (8), 115 (9), 107 (8), 92 (18), 91 (6), 77 (23), 69 (57), 64 (7), 63 (10), 57 (5), 55 (7), 43 (15), 41 (20), 39 (9); E_{pa} = 0.95 V; HRMS calcd. for $C_{16}H_{18}O_3$: 258.1256, found: 258.1253.

Preparation of allene 1g: A solution of **1c** (48.0 mg, 0.254 mmol) and freshly distilled phenylisocyanate (45.3 mg, 0.381 mmol) in dry pyridine (5 mL) was stirred under nitrogen for 2 h at RT. Trichloromethane (3 mL) was added and the solution was washed with saturated sodium bicarbonate and water. After drying (Na_2SO_4), the solvent was removed and the crude product was chromatographed over silica gel (trichloromethane, R_f = 0.60) to afford 99 mg (24%) of **1g**. IR (CCl_4): $\tilde{\nu}$ = 3440 (s, N–H), 3060, 3030 (w, aryl H), 2990 (w, C–H), 2950, 2900 (m, C–H), 2828 (m, OCH_3), 1945 (vw, allene C=C=C), 1735 (s, C=O), 1593 (m, arom. C–C), 1500 (m, arom. C–C), 1460 (w, C–H), 1433 (s, C–H), 1393 (vw, C–H), 1368 (w, C–H), 1305, 1190, 1172 1079 (m-s, C–N and C–O–C), 1032, 1022 (s, C–O), 972 (m), 905 (w), 685 (w) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 2.01 (d, ^5J(H,H) = 2.5 Hz, 3H), 3.73 (s, 3H), 4.66 (d, ^3J(H,H) = 7.0 Hz, 2H), 5.65 (m, 1H), 6.79 (d, ^3J(H,H) = 7.0 Hz, 2H), 6.99 (m, 1H), 7.21–7.27 (m, 6H; 7-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.06, 55.34, 63.25, 89.26, 102.56, 113.94, 118.89, 123.51, 127.89, 129.06, 137.91, 158.88, 205.07; MS (70 eV, EI) *m/z* (%): 309 (9) [M^+], 191 (14), 190 (100), 189 (14), 176 (9), 175 (71), 174 (7), 173 (16), 172 (15), 161 (4), 160 (8), 159 (29), 158 (13), 157 (11), 147 (7), 143 (5), 141 (5), 135 (7), 133 (9), 129 (8), 128 (9), 119 (6), 115 (15), 93 (8), 92 (6), 91 (7), 77 (15), 65 (10), 57 (8), 55 (6), 51 (6), 43 (6), 41 (5), 39 (7); E_{pa} = 0.89 V; HRMS calcd. for $C_{19}H_{19}O_3N$: 309.1365, found: 309.1357.

Preparation of allene 1h: To a solution of **1c** (1.30 g, 6.84 mmol), 4-*N*,*N*-dimethylaminopyridine (0.23 g, 1.84 mmol) in dry pyridine (60 mL) was added (−)-camphanoyl chloride (2.22 g, 10.3 mmol). The reaction mixture was stirred at RT for 3 h, poured onto ice and extracted (three times) with dichloromethane (50 mL). The combined organic layers were washed with water, sodium bicarbonate, and water. After drying ($MgSO_4$), the solvent was removed and the crude mixture was chromatographed over silica gel (dichloromethane/ethyl acetate = 20/1, R_f = 0.48) to afford 2.0 g (79%) of **1h** [38]. IR (CCl_4): $\tilde{\nu}$ = 3575 (w), 2960, 2925 (s, C–H), 2830 (m, OCH_3), 2255 (w), 1950 (w, allene C=C=C), 1785 (vs, C=O), 1745, 1725 (s, C=O), 1603 (s, arom. C–C), 1577 (m, arom. C–C), 1507 (s, arom. C–C), 1455, 1440 (m, C–H), 1392 (m), 1370 (m, CH_3), 1303 (s, C–O), 1250 (br s, C–O), 1170, 1160, 1095, 1055, 1025 (s, C–O), 988, 955, 928 (m), 830 (s) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 0.96 (2 s, 6H), 1.03 (s, 3H), 1.04 (s, 3H), 1.11 (s, 6H), 1.63–1.74 (m, 2H), 1.84–2.09 (m, 4H), 2.09 (d, ^5J(H,H) = 2.0 Hz), 2.30–2.49 (m, 2H), 3.82 (s, 6H), 4.81 (d, ^3J(H,H) = 7.5 Hz), 5.61 (m, 2H), 6.89 (m, 4H), 7.31 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.72, 16.70, 16.74, 17.01, 29.01, 30.67, 30.71, 54.19, 54.83, 55.36, 63.40, 63.44, 88.43, 88.45, 91.15, 102.97, 103.03, 113.94, 127.12, 128.25, 128.45, 158.99, 167.20, 178.06, 205.39, 205.47; MS (70 eV, EI) *m/z* (%): 370 (10) [M^+], 315 (3), 193 (3), 191 (4), 190 (15), 189 (100), 188 (6), 175 (4), 174 (3), 173 (13), 172 (14), 161 (11), 159 (12), 158 (8), 157 (7), 147 (6), 143 (4), 133 (12), 129 (7), 128 (8), 115 (16), 113 (9), 97 (15), 83 (63); E_{pa} = 0.93 V; HRMS calcd. for $C_{22}H_{26}O_5$: 370.1780, found: 370.1782.

Preparation of allene 1i: To a solution of mono-(10*R*,11*S*,14*R*)-menthylphthalic acid (127 mg, 417 μmol), **1c** (95.0 mg, 500 μmol), and 4-*N*,*N*-dimethylaminopyridine (5.10 mg, 42.0 μmol) in 10 mL dry dichloromethane was added *N*,*N*-dicyclohexylcarbodiimide (94.4 mg, 458 μmol). The reaction mixture was stirred at 0 °C for 5 min and at RT for 3 h. *N*,*N*-dicyclohexylcarbodiimide was filtered off and the solution was washed with saturated sodium bicarbonate solution and water. After drying ($MgSO_4$), the solvent was removed and the yellow oil was chromatographed over silica gel (dichloromethane, R_f = 0.55) to afford 125 mg (62%) of **1i**. IR (CCl_4): $\tilde{\nu}$ = 3060 (w, aryl H), 2949 (s, C–H), 2865 (m, OCH_3), 1954 (m, allene C=C=C), 1729 (vs, C=O), 1609, 1519 (w, arom. C–C), 1450 (m, C–H), 1380 (w, CH_3), 1269 (br vs, C–O), 1189, 1129, 1078, 1049 (s, C–O), 870 (m) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 0.72–0.92 (m, 2H), 0.76 (d, ^3J(H,H) = 7.5 Hz, 6H), 0.86 (m, 12H), 0.96–1.13 (m, 4H), 1.35–1.50 (m, 4H), 1.60–1.70 (m, 4H), 1.83–1.90 (m, 2H), 2.03 (d, ^5J(H,H) = 2.0 Hz, 3H), 2.04 (d, ^5J(H,H) = 2.0 Hz, 3H), 2.10–2.20 (m, 2H), 3.76 (s, 6H), 4.75–4.94 (m, 6H), 5.62 (m, 2H), 6.79 (m, 2H), 6.80 (m, 2H), 7.30 (m, 4H), 7.48 (m, 4H), 7.60 (m, 2H), 7.69 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.09, 17.11, 16.38, 20.92, 22.10, 23.52, 26.33, 31.53, 34.38,

40.71, 47.29, 55.39, 63.75, 75.80, 88.88, 102.53, 113.97, 127.18, 128.59, 128.62, 128.88, 128.95, 130.87, 130.98, 132.47, 132.53, 158.94, 166.83, 107.58, 205.44; MS (isobutane, CI) *m/z* (%): 478 (11), 477 (39) [$M^+ + 1$], 476 (9) [M^+], 460 (7), 459 (24), 458 (5), 340 (7), 339 (21), 321 (11), 305 (10), 231 (6), 229 (6), 211 (7), 192 (6), 191 (31), 175 (15), 174 (22), 173 (100), 172 (20), 167 (27); HRMS calcd. for $C_{30}H_{36}O_5$: 476.2563, found: 476.2571.

Preparation of allene 1k: From a mixture of magnesium (1.69 g, 69.5 mmol) and 1-bromobutane (8.95 g, 64.3 mmol) in dry tetrahydrofuran (30 mL) the Grignard reagent was obtained. After cooling to −5 °C, copper(I) iodide (1.33 g, 7.30 mmol) was added and the reaction mixture was stirred for 5 min. The green solution and *N,N*-diethyl-4-methoxy-4-(4-methoxyphenyl)pent-2-yn-1-amine (3.87 g, 14.0 mmol) in dry tetrahydrofuran (10 mL) were stirred for 3 h at 0 °C. After it had been poured into 10% aqueous ammonia, the mixture was extracted with diethyl ether (three times) and the combined organic layers were washed with concentrated ammonia and twice with water. After drying (Na_2SO_4), the solvent was removed and the viscous orange liquid was chromatographed over silica gel (ethyl acetate, $R_f = 0.07$) to afford 1.3 g (37%) of **1k**. IR (CCl_4): $\tilde{\nu}$ = 2965, 2930 (s, C–H), 2865, 2830 (m, OCH_3), 2800 (m), 1948 (m, allene C=C=C), 1610, 1582 (m, arom. C–C), 1518 (vs, arom. C–C), 1470, 1460, 1445 (m, C–H), 1388, 1376 (m, CH_3), 1355, 1328 (w), 1312, 1298 (m), 1250, 1185, 1120, 1045 (s), 865 (s) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 1.10 (t, $^3J(H,H)$ = 7.5 Hz, 6H), 2.10 (d, $^5J(H,H)$ = 2.0 Hz, 3H), 2.62 (q, $^3J(H,H)$ = 7.5 Hz, 4H), 3.30 (d, $^3J(H,H)$ = 7.5 Hz, 2H), 3.81 (s, 3H), 5.43 (m, 1H), 6.88 (m, 2H), 7.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.15, 17.32, 46.74, 51.83, 55.31, 88.70, 99.68, 113.81, 126.82, 129.61, 158.51, 204.64; MS (70 eV, EI): *m/z* (%): 245 (4) [M^+], 175 (9), 174 (59), 173 (5), 160 (2), 159 (17), 158 (5), 144 (3), 143 (5), 141 (3), 135 (3), 133 (4), 129 (4), 128 (6), 115 (16), 108 (7), 87 (45), 86 (100); E_{pa} = 0.67 V; HRMS calcd. for $C_{16}H_{23}NO$: 245.1780, found: 245.1774.

Preparation of allene 1l: Crude allene **1n** (11.0 g), prepared according to ref. [12b], was dissolved in ethanol (60 mL) and heated to reflux in the presence of aqueous sodium hydroxide (7.20 g, 175 mmol in 150 mL of water) for 2.5 h. After cooling to RT the orange reaction mixture was extracted twice with trichloromethane. The pH of the aqueous layer was adjusted to 6–7 with a mixture of concentrated sulfuric acid/water (10/1) and extracted with diethyl ether (three times). After the combined organic layers had been dried ($MgSO_4$), the solvent was removed to afford 1.05 g of pure **1l**. IR (CCl_4): $\tilde{\nu}$ = 3100–2900 (br m, OH), 3010 (w, aryl H), 2960 (m, C–H), 2838 (m, OCH_3), 1941 (m, allene C=C=C), 1723 (vs, C=O), 1635 (m), 1604, 1510 (s, arom. C–C), 1468, 1440, 1403 (m, C–H), 1293 (m, C–O), 1252, 1220, 1178, 1027 (s, C–O), 830 (s) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 2.20 (d, $^5J(H,H)$ = 2.5 Hz, 3H), 3.82 (s, 3H), 5.88 (q, $^5J(H,H)$ = 2.5 Hz, 1H), 6.90 (m, 2H), 7.32 (m, 2H) cm^{-1}; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.24, 55.36, 89.06, 105.61, 114.19, 127.53, 128.62, 159.60, 170.48, 215.49; MS (70 eV, EI): *m/z* (%): 205 (14), 204 (100) [M^+], 189 (27), 188 (6), 186 (8), 180 (6), 161 (42), 160 (9), 159 (69), 135 (27), 133 (10), 128 (6), 127 (5), 116 (7), 115 (14); E_{pa} = 1.08 V; HRMS calcd. for $C_{12}H_{13}O_3$: 204.0786, found: 204.0793.

Preparation of allene 1m: A solution of sodium hydride (4.20 g, 177 mmol) in dry tetrahydrofuran (400 mL) under nitrogen at 0 °C was mixed dropwise with diethyl (diethylcarbamoylmethyl)phosphonate (23.8 g, 95.0 mmol). When no more gas evolved, the mixture was stirred for 1 h at RT and the remaining traces of sodium hydride were filtered off under nitrogen. The filtrate was refluxed for 5 min and a solution of (4-methoxyphenyl)methylketene (16.3 g, 101 mmol) in dry dimethoxyethylene (50 mL) was added rapidly. After refluxing for 30 min the reaction mixture was poured into 5% aqueous potassium bicarbonate solution. The aqueous layer was extracted with diethyl ether (three times), the combined organic layers were dried ($MgSO_4$) and the solvent was removed. The crude product (26 g) was chromatographed twice over silica gel (cyclohexane/ethyl acetate = 1/3, $R_f = 0.60$) to afford 3.8 g (15%) of **1m**. IR (CCl_4): $\tilde{\nu}$ = 2976, 2935 (s, C–H), 2840 (w, OCH_3), 1950 (m, allene C=C=C), 1740 (w), 1636 (vs, C=O), 1620, 1520 (m, arom. C–C), 1468, 1440 (s, C–H), 1390, 1373 (m, CH_3), 1320, 1308, 1285 (m), 1253 (s), 1190, 1145, 1050 (s, C–O) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 1.16 (br t, $^3J(H,H)$ = 7.0 Hz, 6H), 2.16 (d, $^5J(H,H)$ = 2.5 Hz, 3H), 3.43 (br q, $^3J(H,H)$ = 7.0 Hz, 4H), 3.81 (s, 3H), 6.14 (q, $^5J(H,H)$ = 2.5 Hz, 1H), 6.90 (m, 2H), 7.35 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.03, 14.57, 16.56, 40.87, 42.91, 55.32, 90.00, 103.79, 114.02, 127.31, 127.44, 159.19, 164.47, 209.83; MS (70 eV, EI): *m/z* (%): 260 (9), 259 (51) [M^+], 244 (6), 235 (9), 230 (6), 189 (8), 188 (56), 175 (13), 162 (9), 160 (7), 159 (33), 145 (7), 136 (9), 135 (88), 134 (8), 116 (6), 115 (13), 101 (7), 100 (100); E_{pa} = 0.97 V; HRMS calcd. for $C_{16}H_{21}NO_2$: 259.1572, found: 259.1577.

General procedure for radical-cation-initiated reactions: All reactions were carried out under highly purified argon by standard Schlenk techniques. In a typical run, 100 mol% of the one-electron oxidant **ET1**$^{\cdot+}$ dissolved in acetonitrile (0.4 mL) were added over 2 min to a solution of allene **1**, diene **2**, and base **5** in acetonitrile (0.4 mL) at 0 °C. Usually a molar ratio of the reactants **1**:**2**:**ET1**$^{\cdot+}$:**5** = 5:1:1:1.05 was used. In the beginning, the deep blue color of the aminium salt solution instantaneously disappeared but reappeared after a third of the one-electron oxidant was added. After addition the reaction mixture was stirred for 5 min at 0 °C and quenched with 2 N methanolic sodium methanolate, neutralized with saturated sodium bicarbonate and extracted (three times) with dichloromethane. After drying (Na_2SO_4), the solvent and all volatile components were removed. The crude reaction mixtures were analyzed by ^1H NMR spectroscopy and GC-MS. To determine the yields an internal NMR standard (acetophenone) was added.

Norbornenes: For identification the novel norbornenes **3d–3h**, **4d–4h** were independently synthesized starting from norbornene **3c**,**4c** by the appropriate derivatization procedure [39]. After work-up the crude products were first purified by chromatography over silica gel and then by HPLC (Merck LiChrosorb Si 60/7 μm, diameter 25 mm). The pure norbornenes were characterized by IR, ^1H NMR, ^{13}C NMR, MS, HRMS, and E_{pa}.

Preparation of norbornenes 3c, 4c [12b]: To a solution of **1c** (305 mg, 1.60 mmol), **2** (72.8 mg, 0.535 mmol), and **5** (86.0 mg, 0.450 mmol) in acetonitrile (5 mL) under argon at 0 °C was added a solution of **ET1**$^{\cdot+}$ (224 mg, 0.428 mmol) in acetonitrile (5 mL) over 20 min. After stirring for 45 min at 0 °C the reaction mixture was quenched with 2 N methanolic sodium methanolate, neutralized with an excess of saturated sodium bicarbonate, and extracted with dichloromethane (three times). After the combined organic layers had been dried ($MgSO_4$), the solvent was removed. The green oil was distilled by means of a Kugelrohr apparatus (0.1 Torr, 65 °C, 1.5 h) and chromatographed over silica gel (cyclohexane/ethyl acetate = 2/1, $R_f = 0.49$) to afford 142 mg (81%) of **3c**, **4c** (*endo*/*exo* = 5/1).

Preparation of norbornenes 3d, 4d: In the presence of a catalytic amount of 4-*N,N*-dimethylaminopyridine a solution of **3c**, **4c** (40.0 mg, 0.123 mmol) and acetic anhydride (20.0 mg, 0.233 mmol) in dry pyridine (5 mL) was stirred for 2 h at RT under nitrogen. The reaction mixture was poured onto ice and extracted with dichloromethane, and the combined organic layers were washed with water, saturated sodium bicarbonate solution, and water again. After drying ($MgSO_4$), the solvent was removed and the crude yellow oil (40 mg, 85% purity) was chromatographed over HPLC (*n*-hexane/dichloromethane = 1/9, flow = 6.0 mL/min, t_R = 15 min and 17 min) to afford 9.0 mg (20%) of pure **3d**, **4d** (*endo*/*exo* = 5/1).

Data for **3d**: ^1H NMR (250 MHz, $CDCl_3$): δ = 0.59 (q, $^5J(H,H)$ < 1.0 Hz, 3H), 0.69 (d, $^3J(H,H)$ = 7.5 Hz, 3H), 0.96 (s, 3H), 1.13 (s, 3H), 1.47 (q, $^5J(H,H)$ < 1.0 Hz, 3H), 1.54 (s, 3H), 1.96 (q, $^3J(H,H)$ = 7.5 Hz, 1H), 2.01 (s, 3H), 3.78 (s, 3H), 4.21 (d, $^3J(H,H)$ = 7.0 Hz, 1H), 4.23 (d, $^3J(H,H)$ = 7.0 Hz, 1H), 5.31 (t, $^3J(H,H)$ = 7.0 Hz, 1H), 6.57–6.85 (m, 4H; coalescence); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 8.67, 9.55, 9.68, 11.50, 12.48, 21.16, 22.84, 53.96, 55.22, 57.17, 58.46, 60.36, 62.91, 111.42, 112–113 (coalescence), 127–130 (coalescence), 129.77, 137.54, 138.00, 157.60, 158.75, 171.04.

Data for **4d**: ^1H NMR (250 MHz, $CDCl_3$): δ = 0.58 (d, $^3J(H,H)$ = 7.5 Hz, 3H), 0.70 (s, 3H), 1.13 (s, 3H), 1.36 (s, 3H), 1.50 (q, $^5J(H,H)$ < 1.0 Hz, 3H), 1.65 (q, $^5J(H,H)$ < 1.0 Hz, 3H), 1.86 (q, $^3J(H,H)$ = 7.5 Hz, 1H), 2.00 (s, 3H), 3.79 (s, 3H), 4.16 (d, $^3J(H,H)$ = 7.0 Hz, 1H), 4.28 (d, $^3J(H,H)$ = 7.0 Hz, 1H), 5.37 (t, $^3J(H,H)$ = 7.0 Hz, 1H), 6.79 (m, 2H), 7.21 (m, 2H).

Data for **3d**, **4d**: IR (CCl_4): $\tilde{\nu}$ = 2937 (s, C–H), 2902 (vs, C–H), 2837 (s, OCH_3), 1734 (s, C=O), 1606, 1507 (w, arom. C–C), 1454 (m, C–H), 1378 (m, CH_3), 1294 (m, C–O), 1230 (s, C–O), 1183 (m, C–O), 1097 (br s, C–O), 1022 (br s) cm^{-1}; MS (70 eV, EI) *m/z* (%): 369 (5) [$M^+ + 1$], 368 (15) [M^+], 308 (6), 288 (7), 287 (19), 286 (6), 207 (4), 137 (8), 136 (100), 135 (20), 134 (6), 128 (4), 121 (22); HRMS calcd. for $C_{24}H_{32}O_3$: 368.2351, found: 368.2359.

Preparation of norbornenes 3e, 4e: A solution of **3c**, **4c** (37.5 mg, 0.115 mmol) and 4-methoxybenzoyl chloride (29.5 mg, 0.173 mmol) in dry pyridine (10 mL) was stirred for 6.5 h at RT under nitrogen. After addition of trichloromethane (20 mL) the reaction mixture was washed with saturated sodium bicarbonate and water. After drying (Na_2SO_4), the solvent was removed and the crude pale brown solid was chromatographed over silica gel (cyclohexane/ethyl acetate = 1/1, $R_f = 0.88$) and HPLC (*n*-hexane/dichloromethane = 1/3, flow = 6 mL min^{-1}, t_R = 107 min) to afford 6 mg (11%) of pure **3e**, **4e** (*endo*/*exo* = 4/1).

Data for **3e**: ^1H NMR (250 MHz, $CDCl_3$): δ = 0.54 (q, $^5J(H,H)$ = 1.0 Hz, 3H), 0.62 (d, $^3J(H,H)$ = 7.5 Hz, 3H), 0.91 (s, 3H), 1.09 (s, 3H), 1.44 (q, $^5J(H,H)$ = 1.0 Hz, 3H), 1.54 (s, 3H), 1.91 (q, $^3J(H,H)$ = 7.5 Hz, 1H), 3.69 (s, 3H), 3.79 (s, 3H), 4.36 (m, 2H), 5.36 (t, $^3J(H,H)$ = 8.0 Hz, 1H), 6.50–6.77 (m, 4H; coalescence), 6.84 (m, 2H), 7.90 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 8.69, 9.57, 9.71, 11.53, 12.53, 22.97, 55.21, 55.49, 56.04, 57.16, 58.50, 60.38, 62.99, 111.64, 112.32, 112.64, 113.58, 123.27, 129.84, 131.67, 137.64, 137.98, 157.56, 158.85, 163.28, 166.34.

Data for **4e**: ^1H NMR (250 MHz, $CDCl_3$): δ = 0.52 (d, $^3J(H,H)$ = 7.5 Hz, 3H), 0.66 (s, 3H), 1.10 (s, 3H), 1.34 (s, 3H), 1.50 (q, $^5J(H,H)$ = 1.0 Hz, 3H), 1.59 (q, $^5J(H,H)$ = 1.0 Hz, 3H), 1.82 (q, $^3J(H,H)$ = 7.5 Hz, 1H), 3.71 (s, 3H), 3.79 (s, 3H), 4.36 (m, 2H), 5.36 (t, $^3J(H,H)$ = 8.0 Hz, 1H), 6.80 (m, 2H), 6.84 (m, 2H), 7.20 (m, 2H), 7.90 (m, 2H).

Data for **3e**, **4e**: IR (CCl_4): $\tilde{\nu}$ = 2975, 2920 (s, C–H), 2850 (m, OCH_3), 1710 (s, C=O), 1600 (m, arom. C–C), 1505, 1455 (m, arom. C–C), 1372 (m, C–H), 1242 (s, C–O), 1180 (w, C–O), 1162 (m, C–O), 1095, 1032 (s, C–O) cm^{-1}; MS (70 eV, EI) *m/z* (%): 460 (< 1) [M^+], 137 (16), 136 (100), 135 (26), 121 (26), 105 (6), 57 (6), 55 (5), 43 (8), 41 (5); MS (isobutane, CI) *m/z* (%): 461 (< 1) [$M^+ + 1$], 311 (6), 310 (17), 309 (100), 308 (9), 295 (9), 154 (9), 153 (79), 152 (10), 137 (8), 136 (5), 135 (6), 123 (6), 71 (6); HRMS calcd. for $C_{30}H_{36}O_4$: 460.2614, found: 460.2626.

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Preparation of norbornenes 3f, 4f: A solution of **3c, 4c** (35.6 mg, 0.109 mmol) and 2-methacryloyl chloride (17.2 mg, 0.164 mmol) in dry pyridine (10 mL) was stirred for 1 h at RT under nitrogen. Trichloromethane (20 mL) was added and the reaction mixture was washed with saturated sodium bicarbonate and water. After drying (Na_2SO_4), the solvent was removed and the crude brown oil was chromatographed over HPLC (*n*-hexane/dichloromethane = 1/3, flow = 6 mL min^{-1}, t_R = 37 min) to afford 7 mg (16%) of pure **3f, 4f** (*endo/exo* = 4/1).

Data for **3f**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.60 (q, ^5J(H,H) = 1.0 Hz, 3H), 0.70 (d, ^3J(H,H) = 7.5 Hz, 3H), 0.96 (s, 3H), 1.14 (s, 3H), 1.48 (q, ^5J(H,H) = 1.0 Hz, 3H), 1.55 (s, 3H), 1.90 (s, 3H), 1.96 (q, ^3J(H,H) = 7.5 Hz, 1H), 3.77 (s, 3H), 4.37 (m, 2H), 5.35 (t, ^3J(H,H) = 8.0 Hz), 5.51 (s, 1H), 6.06 (s, 1H), 6.53–6.86 (m, 4H; coalescence); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 8.59, 9.45, 9.61, 11.44, 12.42, 18.34, 22.85, 53.91, 55.14, 57.05, 58.39, 60.28, 62.89, 111.36, 112–113 (coalescence), 124.96, 127–130 (coalescence), 129.73, 136.69, 137.52, 137.92, 157.48, 158.78, 167.38.

Data for **4f**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.57 (d, ^3J(H,H) = 7.5 Hz, 3H), 0.70 (s, 3H), 1.14 (s, 3H), 1.37 (s, 3H), 1.50 (q, ^5J(H,H) = 1.0 Hz, 3H), 1.63 (q, ^5J(H,H) = 1.0 Hz, 3H), 1.85 (q, ^3J(H,H) = 7.5 Hz, 1H), 1.90 (s, 3H), 3.79 (s, 3H), 4.37 (m, 2H), 5.41 (t, ^3J(H,H) = 8.0 Hz, 1H), 5.51 (s, 1H), 6.06 (s, 1H), 6.76 (m, 2H), 7.21 (m, 2H).

Data for **3f, 4f**: IR (CCl_4): $\tilde{\nu}$ = 2965 (s, C–H), 2935 (m, C–H), 2877 (w, OCH_3), 1712 (s, C=O), 1662 (m, arom. C–C), 1627 (s, arom. C–C), 1507 (w, arom. C–C), 1451, 1438 (w, C–H), 1373 (m, C–H), 1292 (s, C–O–C), 1155, 1120, 1034 (s, C–O), 662 (m) cm^{-1}; MS (70 eV, EI) *m/z* (%): 395 (4), 394 (14) [M^+], 189 (7), 137 (43), 136 (100), 135 (11), 122 (5), 121 (46), 119 (5), 105 (10), 93 (5), 91 (6), 69 (13), 41 (18); HRMS calcd. for $C_{26}H_{34}O_3$: 394.2508, found: 394.2501.

Preparation of norbornenes 3g, 4g: A solution of **3c, 4c** (52.8 mg, 0.162 mmol) and phenylisocyanate (28.9 mg, 0.243 mmol) in dry pyridine (10 mL) was stirred for 12 h at RT under nitrogen. Trichloromethane (20 mL) was added and the reaction mixture was washed with saturated sodium bicarbonate solution and water. After drying (Na_2SO_4), the solvent was removed and the crude nearly colorless oil was chromatographed over HPLC (*n*-hexane/dichloromethane = 1/4, flow = 6 mL min^{-1}, t_R = 35 min and 44 min) to afford 15 mg (31%) of pure **3g, 4g** (*endo/exo* = 4/1).

Data for **3g**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.59 (q, ^5J(H,H) = 1.0 Hz, 3H), 0.70 (d, ^3J(H,H) = 7.5 Hz, 3H), 0.95 (s, 3H), 1.14 (s, 3H), 1.48 (q, ^5J(H,H) = 1.0 Hz, 3H), 1.56 (s, 3H), 1.96 (q, ^3J(H,H) = 7.5 Hz, 1H), 3.76 (s, 3H), 4.41 (m, 2H), 5.36 (t, ^3J(H,H) = 8.0 Hz, 1H), 6.59–6.79 (m, 4H; coalescence), 7.04 (m, 1H), 7.31 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 8.67, 9.55, 9.70, 11.53, 12.51, 22.94, 54.02, 55.21, 57.21, 58.50, 60.38, 63.57, 111.49, 112.6 (coalescence), 118.62, 123.31, 129.08, 129.77, 130.7 (coalescence), 137.63, 138.07, 138.15, 157.61, 159.05.

Data for **4g**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.59 (d, ^3J(H,H) = 7.5 Hz, 3H), 0.71 (s, 3H), 1.14 (s, 3H), 1.37 (s, 3H), 1.51 (q, ^5J(H,H) = 1.0 Hz, 3H), 1.64 (q, ^5J(H,H) = 1.0 Hz, 3H), 1.88 (q, ^3J(H,H) = 7.5 Hz, 1H), 3.79 (s, 3H), 4.41 (m, 2H), 5.40 (t, ^3J(H,H) = 8.0 Hz, 1H), 6.79 (m, 2H), 7.04 (m, 1H), 7.31 (m, 5H).

Data for **3g,4g**: IR (CCl_4): $\tilde{\nu}$ = 3442 (m, N–H), 3061, 3032 (w, arom. C–H), 2960, 2913, 2902 (s, C–H), 2870 (w, OCH_3), 1730 (s, C=O), 1593 (w, arom. C–C), 1500 (m, arom. C–C), 1435 (s, C–H), 1375 (m, C–H), 1321 (w), 1308, 1292 (m), 1192, 1178 (s), 1150 (m), 1078 (m), 1040, 1026 (m, C–N, C–O–C, C–O), 907 (m) cm^{-1}; MS (70 eV, EI) *m/z* (%): 445 (10) [M^+], 190 (6), 137 (33), 136 (100), 135 (11), 121 (34), 119 (6), 105 (7), 91 (5); HRMS calcd. for $C_{29}H_{35}O_3N$: 445.2617, found: 445.2608.

Preparation of norbornenes 3h,4h: A solution of **3c,4c** (50.0 mg, 0.153 mmol), (–)-camphanoyl chloride (49.8 mg, 0.230 mmol) and 4-*N*,*N*-dimethylpyridine in catalytic amounts in dry pyridine (7 mL) was stirred under nitrogen for 1 h at RT. The reaction mixture was poured onto ice and extracted with dichloromethane, and the combined organic layers were washed with saturated sodium bicarbonate and water (twice). After drying ($MgSO_4$), the solvent was removed and the crude yellow oil was chromatographed over HPLC (*n*-hexane/ethyl acetate = 87/13, flow = 9 mL min^{-1}, t_R = 20 min) to afford 35 mg (45%) of pure **3h, 4h** (*endo/exo* = 5/1). Data for **3h**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.60 (q, ^5J(H,H) < 1.0 Hz, 6H), 0.69 (d, ^3J(H,H) = 7.5 Hz, 6H), 0.93 (2 s, 6H), 0.95 (s, 6H), 1.02 (s, 6H), 1.10 (s, 6H), 1.13 (s, 6H), 1.48 (q, ^5J(H,H) < 1.0 Hz, 6H), 1.54 (2 s, 6H), 1.64–1.70 (m, 2H), 1.85–2.03 (m, 6H), 2.33–2.41 (m, 2H), 3.76 (2 s, 6H), 4.35–4.58 (m, 4H), 5.33 (t, ^3J(H,H) = 7.5 Hz, 2H), 6.40–6.80 (m, 8H; coalescense); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 8.57, 9.46, 9.57, 9.71, 11.46, 12.41, 16.70, 16.74, 16.78, 22.98, 23.01, 29.02, 30.54, 53.96, 54.12, 54.76, 55.12, 57.10, 58.46, 60.30, 63.86, 91.14, 110.45, 110.50, 112 (coalescense), 113 (coalescense), 127–128 (coalescense), 129–130 (coalescense), 129.63, 137.39, 138.13, 157.55, 159.75, 159.89, 167.32, 178.27.

Data for **4h**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.59 (d, ^3J(H,H) = 7.5 Hz, 6H), 0.70 (s, 6H), 0.90 (2 s, 6H), 1.01 (s, 6H), 1.10 (s, 6H), 1.14 (s, 6H), 1.37 (2 s, 6H), 1.48 (q, ^5J(H,H) < 1.0 Hz, 6H), 1.64 (q, ^5J(H,H) < 1.0 Hz, 6H), 1.64–1.70 (m, 2H), 1.85–2.03 (m, 6H), 2.33–2.41 (m, 2H), 3.78 (2 s, 6H), 4.35–4.58 (m, 4H), 5.40 (t, ^3J(H,H) = 7.5 Hz, 2H), 6.78 (2 m, 4H), 7.20 (2 m, 4H).

Data for **3h, 4h**: IR (CCl_4): $\tilde{\nu}$ = 2969, 2942 cm^{-1} (s, C–H), 2882 (m, OCH_3), 1802 (vs, C=O), 1733 (s, C=O), 1514 (w, arom. C–C), 1446 (m, C–H), 1382 (m, CH_3), 1348 (w), 1316, 1299 (m), 1259 (brs, C–O), 1185, 1169, 1102, 1062, 1042 (s, C–O), 713 (s); MS (70 eV, EI) *m/z* (%): 506 (1) [M^+], 315 (2), 314 (9), 312 (1), 296 (2), 277 (1), 252 (2), 189 (2), 173 (1), 167 (2), 159 (1), 149 (6), 147 (1), 146 (1), 137 (16), 136 (100), 135 (5), 121 (23), 115 (6); HRMS calcd. for $C_{32}H_{45}O_5$: 506.3032, found: 506.3033.

General procedure for photoinduced electron transfer reactions: As in the chemical one-electron oxidations an allene/diene ratio = 5/1 was used. A Pyrex tube was loaded with allene, biphenyl (**ET2**), lithium perchlorate (0.2 M) and sodium carbonate (if used) under nitrogen and evacuated for 45 min. Solvent and diene (**2**) were added and the tube was closed. The reaction mixture was stirred and irradiated at λ = 350 nm (fluorescence filter, Gräntzel) in a Gräntzel apparatus (1000 W, Gräntzel, air-cooled). The norbornenes **3,4** were characterized by ^{1}H NMR spectroscopy, GC, and GC-MS. Yields were measured against an internal standard (acetophenone). A control experiment revealed that in the absence of a PET initiator, both allene and diene were recovered unchanged after 5 d.

PET-induced cycloaddition of 1a with 2: Allene **1a** (82.5 mg, 515 μmol) and **2** (14.0 mg, 103 μmol) were dissolved in acetonitrile (5.15 mL) and irradiated for 5 d. No cycloadducts **3a, 4a** could be detected.

Allene **1a** (68.6 mg, 428 μmol), **2** (11.7 mg, 85.7 μmol), **ET6** (66.0 mg, 428 μmol), and lithium perchlorate (91.2 mg, 857 μmol) were dissolved in acetonitrile (4.28 mL) and irradiated for 2 d. 3% **3a** and 2% **4a** were detected.

Allene **1a** (135 mg, 841 μmol), **2** (22.9 mg, 168 μmol), **ET6** (51.8 mg, 336 μmol), **ET2** (5.99 mg, 33.6 μmol), and lithium perchlorate (21.8 mg, 200 μmol) were dissolved in acetonitrile (1.0 mL) and irradiated for 2 d. Traces of **3a** and **4a** were detected.

Allene **1a** (94.6 mg, 591 μmol), **2** (16.1 mg, 118 μmol), **ET6** (91.1 mg, 591 μmol), **ET2** (4.21 mg, 23.7 μmol) and lithium perchlorate (12.8 mg, 120 μmol) were dissolved in acetonitrile (0.60 mL) and irradiated for 5 d. 5% **3a** and 2% **4a** were detected.

Allene **1a** (78.6 mg, 491 μmol), **2** (13.4 mg, 98.2 μmol), **ET6** (75.6 mg, 491 μmol), **ET2** (3.50 mg, 19.6 μmol) and lithium perchlorate (104 mg, 982 μmol) were dissolved in acetonitrile (4.91 mL) and irradiated for 5 d. 9% **3a** and 4% **4a** were detected.

Allene **1a** (96.2 mg, 601 μmol), **2** (16.4 mg, 120 μmol), **ET6** (92.6 mg, 601 μmol), **ET2** (4.28 mg, 24.1 μmol) and lithium perchlorate (128 mg, 1.20 mmol) were dissolved in acetonitrile (6.01 mL) and irradiated for 2 d. 10% **3a** and 6% **4a** were detected.

Allene **1a** (83.0 mg, 519 μmol), **2** (14.1 mg, 104 μmol), **ET6** (79.9 mg, 519 μmol), **ET2** (3.69 mg, 20.8 μmol), lithium perchlorate (110 mg, 1.04 mmol), and sodium carbonate (27.6 mg, 260 μmol) were dissolved in acetonitrile (5.19 mL) and irradiated for 2 d. 10% **3a** and 6% **4a** were detected.

Allene **1a** (109 mg, 680 μmol), **2** (18.5 mg, 136 μmol), **ET6** (105 mg, 680 μmol), **ET2** (14.5 mg, 81.6 μmol), and lithium perchlorate (145 mg, 1.36 mmol) were dissolved in acetonitrile (6.80 mL) and irradiated for 2 d. 14% **3a** and 11% **4a** were detected.

Allene **1a** (98.7 mg, 617 μmol), **2** (16.8 mg, 123 μmol), **ET6** (95.0 mg, 617 μmol), **ET2** (13.2 mg, 74.0 μmol) and lithium perchlorate (131 mg, 1.23 mmol) were dissolved in acetonitrile (6.20 mL) and irradiated for 5 d. 14% **3a** and 14% **4a** were detected.

PET-induced cycloaddition of 1c with 2: Allene **1c** (55.0 mg, 290 μmol), **2** (7.89 mg, 57.9 μmol), **ET6** (44.6 mg, 290 μmol), **ET2** (2.06 mg, 11.6 μmol), lithium perchlorate (61.6 mg, 579 μmol), and sodium bicarbonate (15.4 mg, 145 μmol) were dissolved in acetonitrile (2.89 mL) and irradiated for 2 d. 13% **3c** and 3% **4c** were detected.

Allene **1c** (50.1 mg, 264 μmol), **2** (7.18 mg, 52.7 μmol), **ET6** (40.6 mg, 264 μmol), **ET2** (1.88 mg, 10.5 μmol), lithium perchlorate (56.1 mg, 527 μmol), and sodium bicarbonate (14.3 mg, 135 μmol) were dissolved in acetonitrile (2.64 mL) and irradiated for 3 d. 17% **3c** and 3% **4c** were detected.

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