Electrocyclization Reactions of 1-Aza- and 1-Oxapentadienyl and -heptatrienyl Cations: Synthesis of Pyrrole and Furan Derivatives

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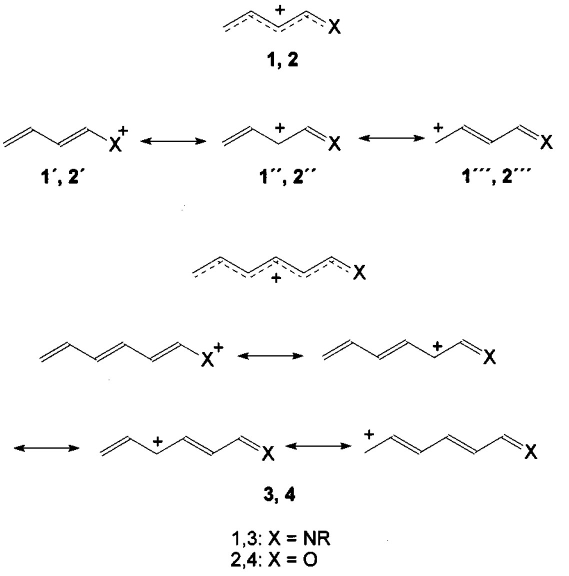
Dedicated to Prof. Dr. H. J. Schäfer on the occasion of his 65th birthday

Keywords: Cations / Density functional calculations / Electrocyclic reactions / Nitrogen heterocycles / Oxygen heterocycles

Quantum chemical DFT calculations (B3LYP/6–31+G*) have been used to gain insight into the conformational and energy properties of the 1-aza- and 1-oxapentadienyl and -heptatrienyl cations **1**, **2**, **3**, and **4**. The calculated thermodynamic and kinetic data of the ring-closure reactions giving the cyclic products **5**–**14** are reported and discussed with respect to the experimental results. Experimentally, synthetic routes to the α,β-unsaturated carbonyl compounds **24** and **27**, each with a leaving group in the γ-position, have been developed. These compounds have been investigated with respect to their ability to undergo 1,5-electrocyclization reactions to yield 2,5-disubstituted furans **28** upon heating in the presence of acid, presumably through the intermediate formation of the 1-oxapentadienyl cations **2**. From the corresponding imine **29a** the pyrrole **30d** was obtained after treatment with tetrakis(triphenylphosphane)palladium. In the presence of benzylamine and the Pd^0 catalyst, the corresponding pyrroles **30a**–**c** were formed from **24** and **27**. The homologous α,β,γ,δ-unsaturated carbonyl compounds **31** afforded 2-vinyl-substituted furans **32** upon heating with acid, and the 2-vinyl-substituted pyrroles **34** on treatment with benzylamine and the Pd catalyst. No seven-membered heterocyclic rings were formed. Surprisingly, the α,β-unsaturated carbonyl compounds with two phenyl substituents at the γ-position also provided pyrrole derivatives **40** through a formal dimerization.

Introduction

Like 1-aza- and 1-oxaallyl cations,[1,2] 1-azapentadienyl and 1-oxapentadienyl cations (**1** and **2**) are destabilized conjugated cations.[3] Both systems are more electrophilic than the pentadienyl cation itself, due to the electronegative heteroatom at the 1-position. The mesomeric structures **1′**, **2′**, **1′′**, and **2′′** indicate their reactivity either as nitrenium/oxenium species with six-electron configurations on the nitrogen/oxygen atom, or as allyl cations with electron-withdrawing imino/carbonyl functions (Scheme 1). In contrast, 2-azapentadienyl cations are less reactive, adopting the valence isomeric structure of 1-vinyl-2-azaallenium ions.[4] The general stability of such isomeric cations is well explained qualitatively by the "topology charge stabilization" principle, developed by Gimarc for neutral heterocycles.[5]



Scheme 1

One predominant monomolecular way to overcome the inherent electronic destabilization of 1-aza- and 1-oxapentadienyl cations is a cyclization reaction. This results in five-

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membered heterocyclic allyl cations with additional donor stabilization, and these produce aromatic systems after proton elimination. The analogous reaction of the 3-hydroxypentadienyl cation is known as the Nazarov cyclization.[6,7] In this report we describe for the first time the structural and electronic properties predicted for such reactive cations by quantum chemical calculations, together with the synthesis of their precursors, their in situ generation, and their transformation into cyclic products. The study is then extended to the generation of 1-aza- and 1-oxaheptatrienyl cations **3** and **4**, and their corresponding cyclization reactions.

Quantum Chemical Calculations

In comparison to the pentadienyl and heptatrienyl cations,[8−10] the 1-aza- and 1-oxapentadienyl cations **1** and **2** and the 1-aza- and 1-oxaheptatrienyl cations **3** and **4** display strong polarization of their electronic structures, due to the electronegative heteroatoms. As Figure 1 (AM1 results) demonstrates, quite substantial deviations from the symmetrical electron density distribution of the parent systems are indicated by the HOMO-1[11] (for **1a**, **2b**, **4b**) or HOMO (for **3a**) coefficients obtained by quantum chemical calculations, resulting in enhanced electron density at the heteroatom and decreased electron density at C^2. In the oxygen systems **2b** and **4b**, carbon atoms C^3, which in the pentadienyl system represents the position of the nodal plane, bear quite significant HOMO-1 coefficients. In contrast, the LUMOs of **1−4** closely resemble those of the pentadienyl and heptatrienyl cations, but have smaller coefficients at the heteroatoms. According to the AM1 charge distribution for planar,[12] *all-trans* cations (MOPAC 93[13]), the picture is clearly that of an acceptor-substituted allyl or pentadienyl cation, with electrophilic centers in position C^3, C^5, and C^7 (for heptatrienyl systems) (Table 1). Other quantum chemical methods and population analyses give similar results.

The 1-azapentadienyl cation **1** may in principle adopt eight conformations (Scheme 2, Table 2). For the isolated ion in the gas phase, B3LYP/6−31+G* calculations (GAUSSIAN 98[14]) predict the W-shaped structure **1a** with the NH group in the *exo* position as the global minimum, followed by sickle-type structures **1c** and **1d**, also with *exo*-NH units. The *endo*-NH isomers **1b**, **1e**, and **1f** are higher in energy (5−9 kcal/mol).

The electrocyclization reaction of the W-shaped 1-azapentadienyl cation **1a** experiences a series of two subsequent bond rotations to reach a sufficiently bent conformation capable of undergoing the ring-closure reaction (see Figure 2) to form the *C*-protonated pyrrole **5**. These bond rotations have quite different activation barriers. According to DFT calculations, rotation about C^2-C^3 has barriers of 8.0 and 9.9 kcal/mol (through **TS1c-5**,**TS1a-1d**); here, the favorable allyl cation is preserved during the rotation of the C=N group. Rotation around C^3-C^4 is much more difficult to achieve. The calculated barriers of 25.5 (through **TS1a-1c**) and 27.4 kcal/mol (through **TS1d-5**) are due to the much less favorable 1-azaallyl-type moiety, which is formed in the transition state during the vinyl group rotation. Interestingly, the five-membered heterocycle is formed from both transition states (**TS1c-5**, **TS1d-**5), which would be expected to connect the sickle type structures **1c** and **1d** through U-type structures, but without involvement of such defined U-shaped minimum structures (**1g**, **1h**). Structures **1g** and **1h** do not correspond to minima on the energy hypersurface, and the electrocyclization proceeds without any additional barrier. For the parent compound, this data indicates only slow ring-formation at room temperature. The derivatives studied experimentally contain additional substituents, which are well suited to lower the rotation barriers.

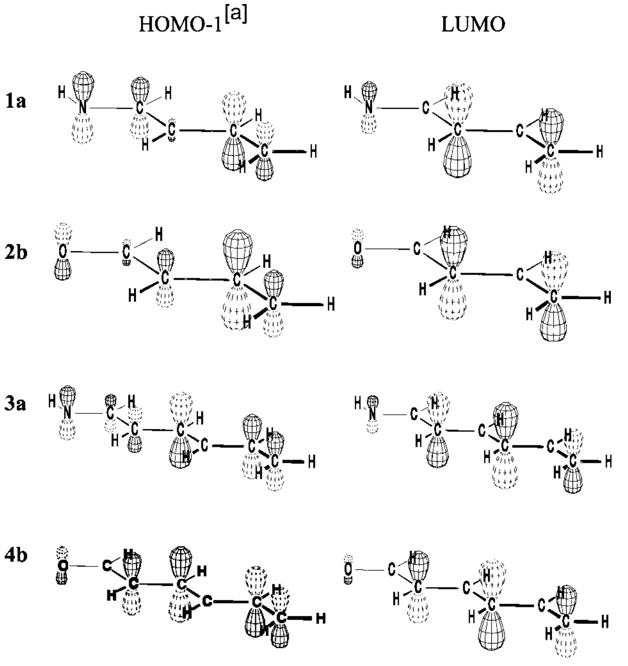


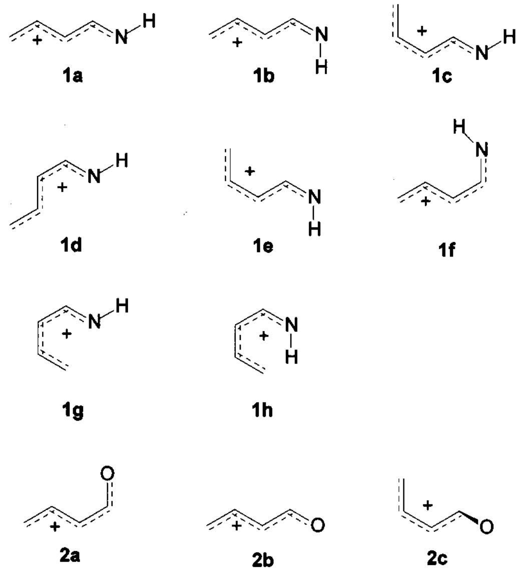
Figure 1. Graphic presentation of the frontier π-orbitals of **1a**, **2b**, **3a**, and **4b** obtained from AM1 calculations (Program PERGRA: R. Sustmann, W. Sicking, Univ. Essen); [a] For **3a** the HOMO is shown; the HOMOs of **1a**, **2b**, and **4b** correspond to the lone pairs centered at N or O, respectively

As well as 1,5-electrocyclization reactions, 1,3-ring-closure reactions giving azirinium or cyclopropyl cation intermediates **6** or **7** also have to be taken into account (Scheme 3).[15,16] Whereas the azirinium ion **6** is calculated to be higher in energy than **1a** by 13.8 kcal/mol, the bicyclic iminium system **7**, which is predicted to be formed subsequently after the 1,3-ring closure, has a total energy similar to that of **1a** (1.2 kcal/mol higher), despite the ring strain in this system. However, the barrier to the formation of the intermediate cyclopropyl cation is calculated to be high (35.8 kcal/mol).

In contrast to the W-shaped structure of **1**, the 1-oxapentadienyl cation **2** is predicted to have the sickle-shape structure **2a** as the lowest-energy conformer (Scheme 2, Table 3). The W conformation **2b** is slightly higher in energy (0.4 kcal/mol). In analogy to the 1-azapentadienyl cation, **1a**,

Table 1. AM1 group charges, calculated for the cations **1a** and **2b** ($X{-}C^2H{-}C^3H{-}C^4H{-}C^5H_2^+$) and for the cations **3a** and **4b** ($X{-}C^2H{-}C^3H{-}C^4H{-}C^5H{-}C^6H{-}C^7H_2^+$)

No.	X	C^2H	C^3H	C^4H	C^5H/C^5H_2	C^6H	C^7H_2
1a (X = NH)	0.1448	0.0211	0.4365	−0.0887	0.4863		
3a (X = NH)	0.0860	0.0282	0.3268	−0.0854	0.3582	−0.0820	0.3682
2b (X = O)	−0.1206	0.3128	0.3281	−0.0718	0.5515		
4b (X = O)	−0.1618	0.3096	0.1958	−0.0531	0.3789	−0.0822	0.4128



Scheme 2

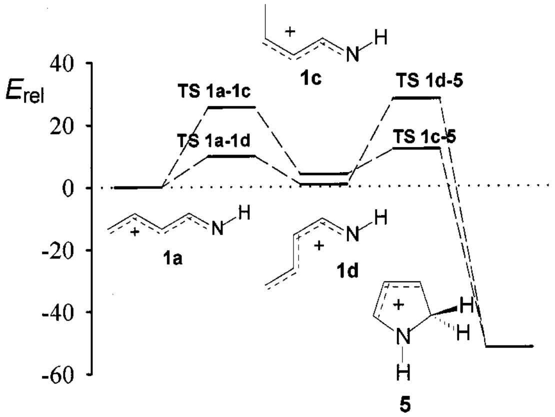


Figure 2. Energy diagram for the conversion of *all-trans*-**1a** into **5** according to DFT calculations (B3LYP/6−31+G*//B3LYP/6−31+G*)

2a is able to undergo a quite exothermic electrocyclization reaction to give the 2*H*-furyl cation **8**. However, the less pronounced electron donor capacity of oxygen, relative to nitrogen, is reflected in the smaller calculated reaction enthalpy for this process ($E_{rel} = -40.0$ kcal/mol). As with the 1-azapentadienyl cation **1a**, two barriers have to be overcome for cyclization of **2a**. Again, rotation about the $C^2{-}C^3$ bond (**TS2a-2b**; allyl cation in the transition state) has a very low barrier of only 0.9 kcal/mol, whereas rotation about $C^3{-}C^4$ is more difficult, with a calculated barrier of 21.0 to 21.8 kcal/mol (**TS2b-2c, TS2a-2c**; 2*H*-oxirenium contribution in the transition state). The transition state for the cyclization of **2c** to **8** is calculated to be only 3.3 kcal/mol higher than **2a**.

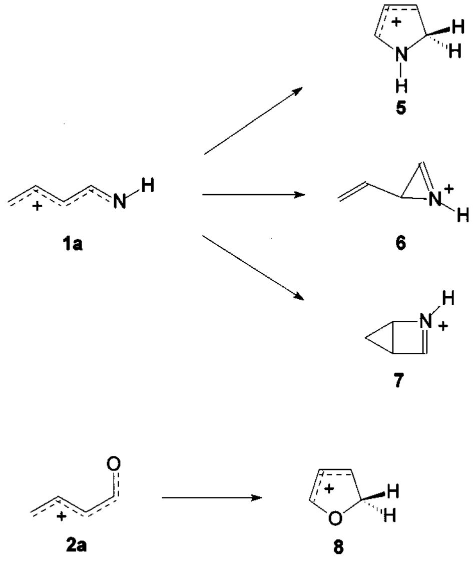
Like the 1-azapentadienyl cation **1,** the 1-azaheptatrienyl cation **3** prefers the *all-trans* W-shaped structure **3a** with an *exo*-NH bond (Scheme 4, Table 4). Among the many (32 !) possible conformers, some sickle-type structures (**3b**,**c**,**e**,**i**,**j**,**k**) are also low in energy (0.6−5 kcal/mol), whereas U-

Table 2. Torsion angles [°], total energies E_{tot} [a.u.] (with number of imaginary frequencies), energies at 0 K ($E_0 = E_{tot}$ + ZPE) [a.u.], and relative energies E^0_{rel} at 0 K [kcal/mol] for various conformations of **1**, for **5−7**, and related transition states (B3LYP/6−31+G*//B3LYP/6−31+G*)

No.	Torsion angles along $H{-}N{-}CH{-}CH{-}CH{-}CH_2^+$	E_{tot}	E_0	E^0_{rel}
1a	180/180/180	−210.43686 (0)	−210.34553	0.00
1b	0/180/180	−210.42762 (0)	−210.33661	5.59
1c	180/180/0	−210.43045 (0)	−210.33913	4.02
1d	180/0/180	−210.43585 (0)	−210.34443	0.70
1e	0/180/0	−210.42231 (0)	−210.33122	8.98
1f	−1.04/8.45/−179.92	−210.42242 (0)	−210.33164	8.72
5	180/0/0	−210.52358 (0)	−210.42830	−51.94
6	170/17/−102.06/−164.54	−210.41357 (0)	−210.32362	13.75
7	163.5/1.00/−113.1	−210.43717 (0)	−210.34358	1.22
TS 1a-1c	179.34/175.58/93.06	−210.39306 (1)	−210.30491	25.49
TS 1a-1d	180.24/−89.10/176.65	−210.41930 (1)	−210.32975	9.90
TS 1c-5	178.88/96.31/−1.47	−210.41593 (1)	−210.32638	12.02
TS 1d-5	181.00/−3.44/ 94.92	−210.38876 (1)	−210.30067	28.15

Table 3. Torsion angles [°], total energies E_{tot} [a.u.] (with number of imaginary frequencies), energies at 0 K ($E_0 = E_{tot}$ + ZPE) [a.u.], and relative energies E^0_{rel} at 0 K [kcal/mol] for various conformations of **2**, for **8**, and related transition states (B3LYP/6−31+G*//B3LYP/6−31+G*)

No.	Torsion angles along $O-CH-CH-CH-CH_2^+$	E_{tot}	E_0	E_{0rel}
2a	0/180	−230.28750 (0)	−230.20957	0.00
2b	180/180	−230.28680 (0)	−230.20893	0.40
2c	101.20/9.55	−230.28186 (0)	−230.20415	3.40
8	0/0	−230.35550 (0)	−230.27326	−39.97
TS 2a-2b	70.65/−175.27	−230.28563 (1)	−230.20812	0.91
TS 2b-2c	94.28/102.24	−230.25166 (1)	−230.17476	21.84
TS 2a-2c	−96.61/87.42	−230.25291 (1)	−230.17618	20.95
TS 2c-8	−25.04/62.58	−230.28166 (1)	−230.20426	3.33

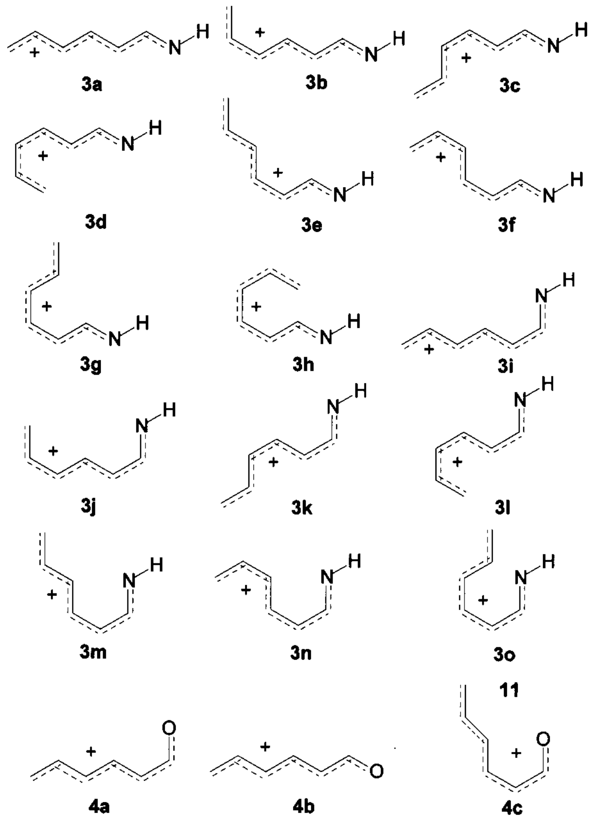


Scheme 3

shaped structures (**3d**,**g**,**h**,**l**,**m**,**o**) are mostly energy-rich (8−15 kcal/mol, except **3n**). The *all-cis* isomer collapses during optimization, forming the seven-membered ring system **9**.

Three possible reaction channels have been investigated computationally: the formation from their respective conformers of a seven-membered *C*-protonated azepine **9** and of two five-membered systems, the cationic 2-vinyldihydropyrrole derivative **10** and the cyclopentenyl cation **11** (Scheme 5). The most stable cyclization product is the seven-membered ring **9** (−32.9 kcal/mol relative to **3a**), followed by the protonated pyrrole **10** (−25.0 kcal/mol; a cyclic amino-substituted allyl cation), whereas the cyclopentenyl system **11** is similar to **3a** in energy (−3.9 kcal/mol, no stabilization by the heteroatom). The ring-opening of **11** affords the highest transition state energy (22.7 kcal/mol, relative to **3a**), that of **9** is 18.1 kcal/mol, whereas the ring-opening of **10** represents the kinetically preferred reaction, with a calculated transition state energy of only 4.3 kcal/mol.

In analogy to **2a**, the oxaheptatrienyl cation **4** also adopts a minimum-energy structure (**4a**) with an *s-cis* arrangement of the C=O group. According to the calculations, the *all-trans* structure **4b** should be slightly higher in energy (0.3 kcal/mol, Scheme 4). The cyclic isomers of the 1-oxaheptatrienyl cation **4a** differ little in energy. All three are lower than **4a**: by 15.8 kcal/mol [2*H*-oxepinium ion **12**, due to the longer conjugated π-electron systems (thermodynamic control)], 12.5 kcal/mol (2-vinyl-2*H*-furanyl cation **13**), and by 11.5 kcal/mol (4-formylcyclopentenyl cation **14**) (Scheme 6, Table 5). The transition state energies relative to **4a** for ring-opening reactions amount to 13.6 kcal/mol for the seven-membered ring **12**, to 15.1 kcal/mol for 4-formylcyclopentenyl cation **14**, and to 1.9 kcal/mol for ring-opening of the 2-vinyl-2*H*-furanyl cation **13**, kinetically the most readily accessible isomer.

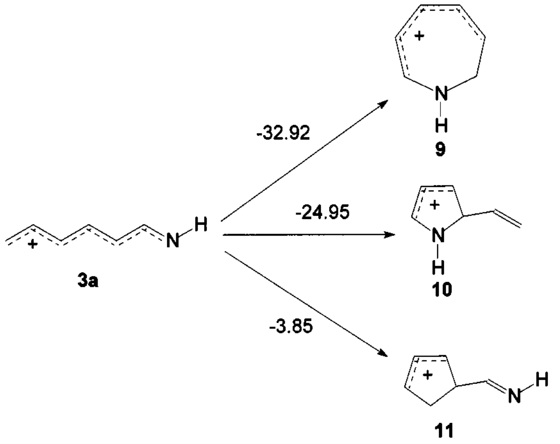


Scheme 4

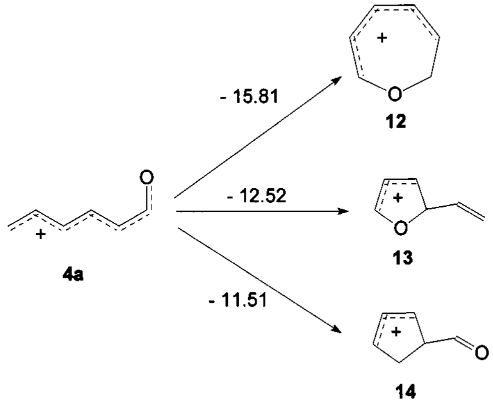
Table 4. Torsion angles [°], total energies E_{tot} [a.u.] (with number of imaginary frequencies), energies at 0 K ($E_0 = E_{tot}$ + ZPE) [a.u.], and relative energies E^0_{rel} at 0 K [kcal/mol] for various conformations of **3**, for **9−11**, and related transition states (B3LYP/6−31+G*//B3LYP/6−31+G*)

No.	Torsion angles along H−N−CH−CH−CH−CH−CH−CH_2^+	E_{tot}	E_0	E^0_{rel}
3a	180/180/180/180/180	−287.87741(0)	−287.75185	0.00
3b	180/180/180/180/0	−287.87111(0)	−287.74559	3.93
3c	180/180/180/0/180	−287.87216(0)	−287.74652	3.34
3d	−179.85/−179.18/−177.30/22.64/29.36	−287.86398(0)	−287.73846	8.40
3e	180/180/0/180/180	−287.87099(0)	−287.74538	4.06
3f	180/180/0/180/0	−287.86497(0)	−287.73941	7.81
3g	−179.85/−177.18/9.42/14.72/−179.98	−287.86164(0)	−287.73589	10.01
3h	177.63/178.32/13.29/29.12/28.26	−287.85345(0)	−287.72807	14.92
3i	180/0/180/180/180	−287.87640(0)	−287.75077	0.68
3j	180/0/180/180/0	−287.87106(0)	−287.74536	4.07
3k	180/0/180/0/180	−287.87018(0)	−287.74453	4.60
3l	179.54/2/19/−179.38/24.68/29.66	−287.86224(0)	−287.73670	9.51
3m	179.86/17.97/3.58/−173.93/179.97	−287.87315(0)	−287.74756	2.69
3n	−179.60/22.82/5.76/−170.58/6.11	−287.86661(0)	−287.74108	6.76
3o	180/0/0/0/180	−287.86404(0)	−287.73790	8.75
9	−171.20/32.00/−4.39/−28.27/−5.42	−287.93538(0)	−287.80431	−32.92
10	178.91/−0.63/0.07/124.98/−103.98	−287.91989(0)	−287.79161	−24.95
11	−179.63/0.02/126.56/−0.92/−1.17	−287.88466(0)	−287.75798	−3.85
TS 9[a]	−176.17/2.20/−11.33/−41.03/−19.75	−287.84800(1)	−287.72309	18.05
TS 10[b]	173.17/−17.62/−8.13/145.21/172.42	−287.87030(1)	−287.74507	4.25
TS 11[c]	0.31/163.16/154.38/−15.57/−17.89	−287.84022(1)	−287.71562	22.73

[a] Transition state for ring-opening of **9**. [b] Transition state for ring-opening of **10**. [c] Transition state for ring-opening of **11**.



Scheme 5



Scheme 6

Results and Discussion

For experimental investigation of intermediate 1-aza- and 1-oxapentadienyl cations **1** and **2**, two classes of possible precursors were envisaged: 1-aza- and 1-oxapentadienes with leaving groups either in the 3- or in the 5-position (Scheme 7). Because of their expected low stability, *N*-halodienamines (leaving group in 1-position) were regarded as less valuable starting compounds for 1-azapentadienyl cations.

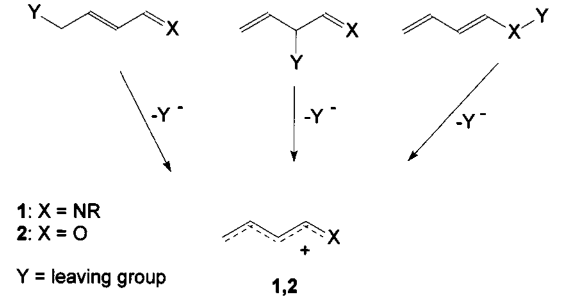
For the synthesis of precursors with a leaving group in 3-position, a three-step procedure starting from crotonaldehyde (**15**) was planned. Epoxidation and subsequent imination afforded the oxiranylimine **16**, which was expected to give the allyl alcohol 3-hydroxy-*N*-isopropyl-1-azapenta-1,4-diene (**17**) upon base-induced oxirane ring-opening (Scheme 8). However, treatment of **16** with LDA or LDA/KO*t*Bu gave the aziridine **18**, which is interpreted as the result of a base-induced heterochiral dimerization by an aza Darzens mechanism.[17] This reaction seems to be induced by a deprotonation at the oxirane ring at the position α to the imino group.

1-Oxa-1,4-pentadienes with acetoxy groups at their 3-positions are accessible from 1,2-diketones by treatment with vinylmagnesium bromide, as described by Trost et al.[18] In our experiments, however, benzil (**19**) gave the allyl acetate **20** only in a small yield of 11% (41−76% had been reported). The main product of these experiments (56%) was the stilbene derivative **21**, which was not reported by Trost et al. (Scheme 9). The structure of **21** was elucidated by X-ray crystallography. The formation of **21** may be explained

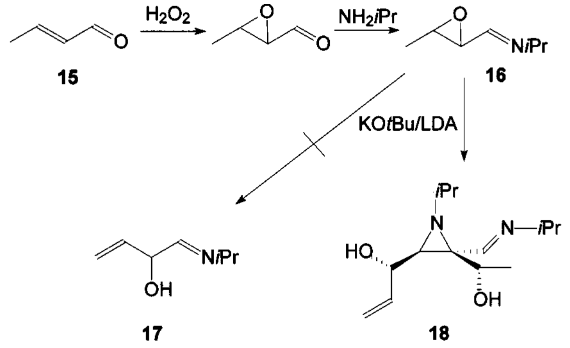
Table 5. Torsion angles [°], total energies E_{tot} [a.u.] (with number of imaginary frequencies), energies at 0 K ($E_0 = E_{tot}$ + ZPE) [a.u.], and relative energies E^0_{rel} at 0 K [kcal/mol] for various conformations of **4**, for **12–14**, and related transition states (B3LYP/6−31+G*//B3LYP/6−31+G*)

No.	Torsion angles along O−CH−CH−CH−CH−CH−CH$_2^+$	E_{tot}	E_0	E^0_{rel}
4a	0/180/180/180	−307.73621(0)	−307.62373	0.00
4b	180/180/180/180	−307.73561(0)	−307.62321	0.33
4c	−19.00/−1.26/173.27/−179.66	−307.73518(0)	−307.62265	0.68
12	−31.04/8.24/25.21/4.62	−307.76613(0)	−307.64863	−15.81
13	0.60/−0.71/−119.53/−130.10	−307.75878(0)	−307.64368	−12.52
14	77.62/−98.17/−6.27/−5.95	−307.75636(0)	−307.64208	−11.51
TS 4a-4b	−88.75/174.18/177.81/179.80	−307.72972(1)	−307.61810	3.53
TS 4a-4c	47.43/90.00/155.56/−176.68	−307.69176(1)	−307.58067	27.02
TS 12[a]	8.65/−7.32/−48.16/−15.45	−307.71380(1)	−307.60210	13.57
TS 13[b]	−14.50/−4.70/142.11/176.96	−307.73319(1)	−307.62077	1.86
TS 14[c]	−164.98/154.12/−16.13/−16.56	−307.71123(1)	−307.59971	15.07

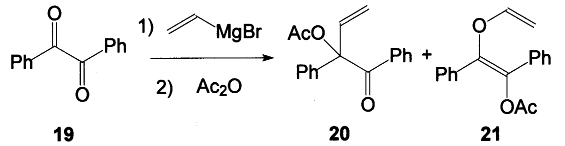
[a] Transition state for ring-opening of **12**. [b] Transition state for ring-opening of **13**. [c] Transition state for ring-opening of **14**.



Scheme 7



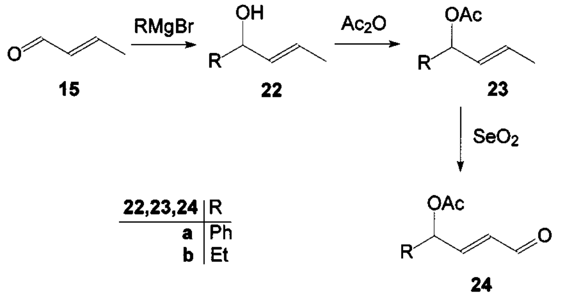
Scheme 8



Scheme 9

in terms of an electron-transfer reduction from vinylmagnesium to benzil, giving the benzil radical anion (or magnesium bromide compound) and subsequent radical combination either on the carbon or on the oxygen atom of the intermediate benzil radical anion. We therefore did not continue with this route for the synthesis of 1-oxa- and 1-azapentadienyl precursors.

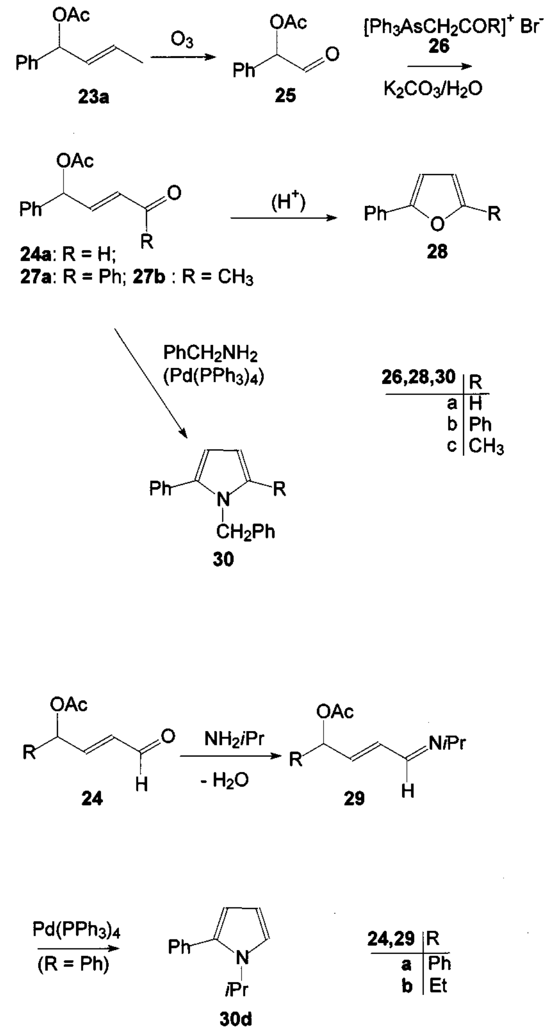
In contrast, precursor α,β-unsaturated aldehydes with leaving groups in their γ-positions were successfully synthesized from crotonaldehyde (**15**) by a route summarized in Scheme 10. The corresponding allyl alcohols **22** were obtained by the addition of Grignard reagents. After acetylation, the allyl acetates **23** were oxidized with selenium dioxide to give the aldehydes **24**.



22,23,24	R
a	Ph
b	Et

Scheme 10

Alternatively, for the corresponding α,β-unsaturated aldehydes and ketones, a straightforward reaction sequence (Scheme 11) starting from allyl acetate **23a** was used. This compound was converted into α-acetoxy aldehyde **25** by ozonolysis[19] and transformed into the α,β-unsaturated carbonyl compounds **24a** and **27** by an arsa Wittig reaction as introduced by Huang et al.[20–22] Here, for the olefination, we took advantage of the high acidity of arsonium salts **26** in comparison to phosphonium salts, which allowed the use of potassium carbonate in combination with traces of water.[23] These conditions did not affect the rather sensitive α-acetoxy aldehydes, which otherwise easily rearranged to the corresponding α-acetoxy ketones. The ketones **27a** and **27b** were obtained in yields of 30 and 62%. The aldehyde **24a**, however, was subject to further homologation, which diminished its yield and caused separation problems. Consequently, the first method (SeO$_2$ oxidation) was better suited (see above) for **24a**.

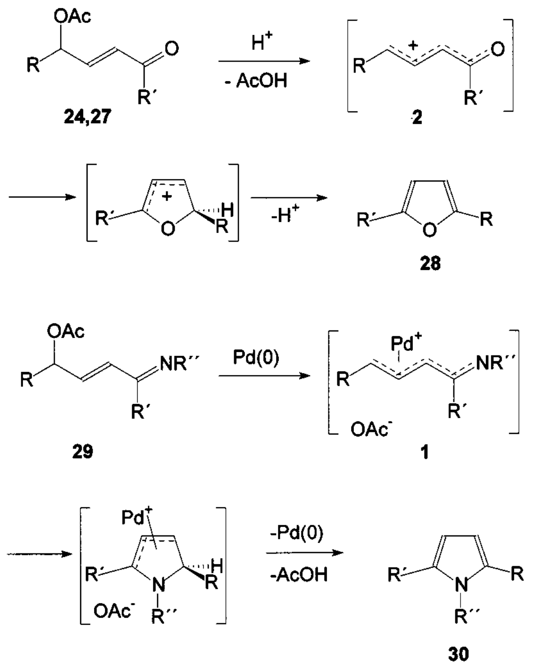


Scheme 11

As predicted by the quantum chemical calculations, the enones **24** and **27** proved to be valuable precursors for electrocyclization reactions. Treatment of these with aqueous sulfuric acid yielded the furans **28** in 32−77% yield after workup. Obviously, under the reaction conditions, the ester was subject to solvolysis, producing the 1-oxapentadienylium intermediate, and isomerism to the sickle- or U-shaped cation then took place. The electrocyclization reaction and a final proton elimination were the subsequent steps in this sequence.

For the synthesis of pyrroles by electrocyclization, the aldehydes **24** were first converted into the imines **29** by molecular sieve assisted condensation with primary amines. Treatment of aldimine **29a** with catalytic amounts of tetrakis(triphenylphosphane)palladium in refluxing toluene provided the corresponding pyrrole **30d** in low yield (ca. 10%, Scheme 12). We assume the intermediate formation of a cationic (1-azapentadienyl)palladium complex, which undergoes the cyclization reaction. Polymeric products were also formed.

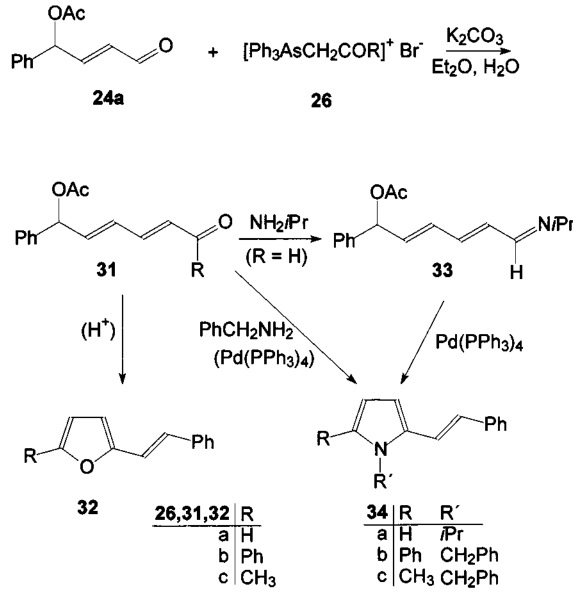
We were not able to isolate satisfactorily pure ketimines from ketones **27** and primary amines. However, the corresponding pyrroles **30a−c** were obtained directly from the carbonyl compounds when a mixture of these with benzylamine was treated with the palladium catalyst as suggested by Trost[18,24] for an isomeric α-acetoxy-β,γ-unsaturated carbonyl compound. The mechanism was probably similar to that mentioned above, involving an initial Pd-catalyzed nucleophilic substitution and a subsequent ring-closure reaction. Removal of acetic acid and of Pd affords the observed pyrroles. As in Trost's work, we observed much better yields for ketones than for aldehydes.



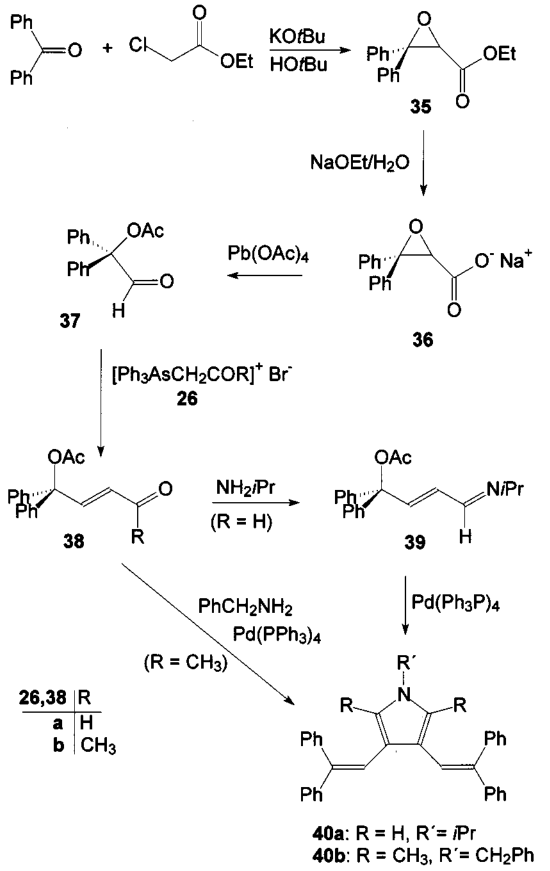
Scheme 12

In a further experiment we also tried to extend the cationic electrocyclization method to 2,4-hexadien-1-ones with leaving groups at their 6-positions (Scheme 13). When starting from the corresponding anions (or lithium compounds), we had previously observed the formation of seven-membered rings (dihydroazepines).[25,26] The arsa Wittig reaction served as an excellent homologization tool for the synthesis of the 6-acetoxy-2,4-hexadien-1-ones **31a−c** from the aldehyde **24a**. On treatment with dilute sulfuric acid, the 2-vinyl-substituted furans **32a−c** were obtained in moderate yield. As predicted by the quantum chemical results, no formation of the seven-membered ring systems (oxepines) was observed. Similarly, the 1-azahexadiene **33**, obtained from the aldehyde **31a** by amine condensation, afforded the 2-vinylpyrrole **34a** in low yield (5%) upon treatment with tetrakis(triphenylphosphane)palladium. Polymeric residues were the main products of this reaction. Much better yields of pyrroles **34b** and **34c** were again obtained from the ketones **31b** and **31c** upon treatment with benzylamine and tetrakis(triphenylphosphane)palladium in refluxing toluene (45 and 58%).

All the electrocyclization reactions so far reported here were accompanied by final proton elimination from the 2-position to produce the aromatic furan and pyrrole electron



Scheme 13



Scheme 14

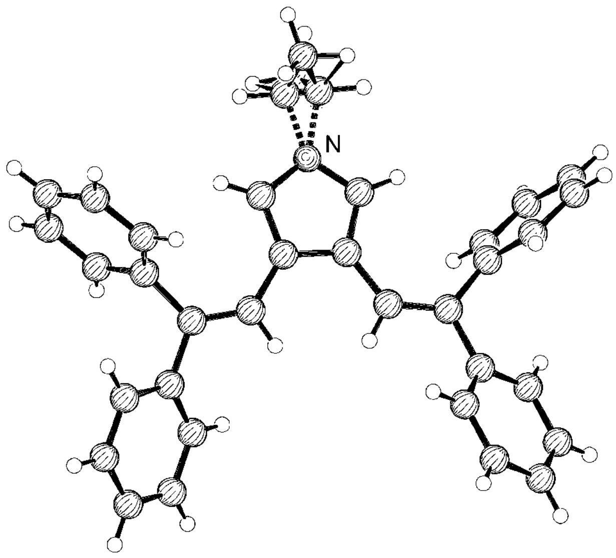


Figure 3. Molecular structure of **40a** obtained by X-ray crystallography; selected bond lengths [Å], bond angles [°], and torsion angles [°]: N1−C2 1.369(3), N1−C*i*Pr 1.522(5), C2−C3 1.381(3), C3−C4 1.437(4), C3−C_α 1.455(3), C_α−C_β 1.346(3), C_β−C_{Ph} 1.490(3); N1−C2−C3 108.49(23), C2−N1−C*i*Pr 111.72(20), C2−N1−C*i*Pr A 138.64(23) (mean 125.18), C2−C3−C_α 128.93(21), C_β−C_α−C3 131.68(21), C_α−C_β−C_{Ph} 119.83(19); N1−C2−C3−C_α −175.59(0.21), C2−C3−C_α−C_β −1.23(0.44), C3−C_α−C_β−C_{Ph} 174.39(0.23), C*i*Pr−N1−C2−C3 175.11(0.29); large thermal displacement parameters indicate splitting of the central carbon atom of the isopropyl group (*i*Pr, *i*Pr A)

systems. We were interested in investigating which reaction products might be observed if no proton was available for elimination. To answer this question, the aldehyde **38a** and the ketone **38b** were prepared as depicted in Scheme 14, according to procedures reported by Johnson[27] (Darzens reaction and saponification) for **35** and **36** and by Kulkarni and Rao[28] (oxidative decarboxylation with lead tetraacetate) for the preparation of **37**. The diphenyl-substituted α,β-unsaturated carbonyl compounds **38** were again synthesized by an arsa Wittig route. Condensation with isopropylamine produced the 1-azabutadiene **39**. The conformation and configuration of **39** in the solid state were determined by X-ray crystallography.[29]

Treatment of **39** with the tetrakis(triphenylphosphane)palladium catalyst in toluene surprisingly once again produced a pyrrole derivative **40a**, in 28% yield. Its structure in the crystalline state (X-ray diffraction) is shown in Figure 3. The formation of **40a** includes a dimerization of **39** and loss of an amine unit, probably by a redox process. However, the mechanism of this unexpected reaction remains to be clarified. Pyrrole **40b** was obtained in low yield (12%) directly from ketone **38b** by treatment with benzylamine in the presence of the Pd catalyst.

Conclusion

Through the use of quantum chemical DFT calculations we have investigated the structural, thermodynamic, and kinetic aspects of electrocyclization reactions of 1-aza- and 1-oxapentadienyl and -hepatrienyl cations **1**, **2** and **3**, **4**. Experimentally, suitable precursors for such cations were found to be α,β-unsaturated carbonyl compounds and imines with leaving groups at the γ-position for **1** and **2** and α,β,γ,δ-unsaturated carbonyl compounds and imines with leaving groups at the ε-position for **3** and **4**. Cyclization reactions were induced by protonation and solvolysis or by Pd^0 catalysis. 1,5-Cyclization reactions yielding furans **28** and **32** and pyrroles **30** and **34** were favored over 1,7-cyclization to give seven-membered heterocycles, which was not observed. 5,5-Diphenyl-substituted α,β-unsaturated carbonyl compounds and imines with leaving groups at their γ-positions surprisingly underwent dimerization to give 3,4-bis(diphenylvinyl)-substituted pyrroles **40**.

Experimental Section

Materials and Methods: IR: Perkin−Elmer PE 298. ^1H NMR: Bruker WM 300 (300.13 MHz) and Varian Unity plus (599.86 MHz), internal reference tetramethylsilane. ^{13}C NMR: Bruker WM 300 (75.47 MHz), Bruker AM 360 (360.13 MHz) and Varian Unity plus (150.85 MHz), internal reference tetramethylsilane or solvent. GC: Hewlett−Packard 6890 with HP5 quartz capillary (30 m). GC/MS: Varian MAT CH7A with GC Varian 1400 plus data system SS 200; Varian MAT 8230 with GC Varian 3400 plus data system SS 300. CHN: Perkin−Elmer Dia CHN 240. Column chromatography: Kieselgel 60 (Merck), 0.063−0.200 mm. Melting points are uncorrected. All solvents were rigorously dried by standard methods. When necessary, the experiments were carried out with complete exclusion of moisture (argon, septum-syringe technique) in glassware that had been thoroughly dried by repeated heating under argon and subsequent evacuation.

(*E*)-1-Acetoxy-2-vinyloxystilbene (21): Under argon, a solution of vinylmagnesium bromide (1 M solution in THF, 45.7 mL, 45.7 mmol) was added dropwise to a solution of benzil (**19**, 9.60 g, 45.7 mmol) in THF (50 mL). The reaction mixture was then heated to reflux for 2 h. After the mixture had cooled to room temperature, a saturated aqueous solution of ammonium chloride (50 mL) was slowly added. Hydrochloric acid (2 N) was added dropwise until the precipitate had dissolved completely, and the layers were separated. The aqueous layer was extracted with three portions (30 mL) of diethyl ether. The combined organic layers were dried with magnesium sulfate. After removal of the solvent under reduced pressure, the crude product was dissolved in dichloromethane (100 mL). This solution was cooled to 0 °C and treated with triethylamine (5.50 g, 54.5 mmol), acetic anhydride (5.55 g, 54.5 mmol), and 4-(dimethylamino)pyridine (0.500 g, 4.1 mmol), and stirred for 10 h. After addition of water (20 mL) and diethyl ether (50 mL) and stirring for 10 min, the layers were separated. The organic layer was washed with hydrochloric acid (2 M, 20 mL), sodium hydrogen carbonate solution (10%), and water. After drying of the organic layer with magnesium sulfate, the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, petroleum ether/ethyl acetate, 5:1). Colorless crystals, 5.79 g (20.7 mmol, 45%). M.p. 98 °C, R_f (TLC) = 0.37 (silica gel, petroleum ether/ethyl acetate, 5:1), R_t (GC) = 17.66 min [40−10/min-280(5)]. As a minor product, **20**[18] was isolated in a yield of 11%. IR (KBr): $\tilde{\nu}$ = 3067 (w) cm^{-1}, 1962 (w), 1896 (w), 1758 (vs), 1626 (s), 1598 (m) 1575 (m), 1494 (s), 1448 (vs), 1427 (m), 1371 (s), 1323 (m), 1313 (m), 1261 (m), 1224 (vs), 1178 (s), 1095 (s), 1072 (s), 1043 (m), 1028 (m), 1007 (m), 1000 (m). ^1H NMR (400 MHz, $CDCl_3$): δ = 2.08 (s, 3 H, CH_3), 4.22 (dd, ^3J = 16.4, ^2J = 2.0 Hz, 1 H, HCH_{trans}=CH), 4.60 (dd, ^3J = 14.0, ^2J = 2.0 Hz, 1 H, HCH_{cis}=CH), 6.31 (dd, ^3J = 14.0, ^3J = 16.4 Hz, 1 H, HCH=C*H*), 7.28−7.42 (m, 6 H, $CH_{arom.}$), 7.51 (m, 2 H, $CH_{arom.}$), 7.61 (m, 2 H, $CH_{arom.}$). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.8 (CH_3), 93.4 (CH_2), 126.9 ($CH_{arom.}$, 2 C), 128.1 ($CH_{arom.}$, 2 C), 128.2 ($CH_{arom.}$, 2 C), 128.25 ($CH_{arom.}$, 1 C), 128.3 ($CH_{arom.}$, 2 C), 128.8 ($CH_{arom.}$, 1 C), 133.2 (C_q), 133.3 (C_q), 137.3 (C_q), 144.0 (C_q), 149.1 ($CH_{olef.}$), 169.3 (C=O). GC-MS (70 eV): *m/z* (%) = 280 (8) [M^+], 238 (84), 223 (14), 178 (4), 165 (25), 105 (100), 77 (43), 51 (8), 43 (12).$C_{18}H_{16}O_3$ (280.32): calcd. C 77.12, H 5.75; found C 77.09, H 5.82. This compound has also been characterized in the solid state by X-ray crystallography.[29]

(2*E*)-4-Acetoxy-4-phenylbut-2-enal (24a): 1-Acetoxy-1-phenylbut-2-ene [**23a**, 15.2 g, 79.9 mmol, produced from crotonaldehyde (**15**) and phenylmagnesium bromide and subsequent acetylation] was dissolved in dry toluene (60 mL) and treated with selenium dioxide (13.3 g, 120 mmol). The reaction mixture was heated for 2 h at reflux under argon. The selenium was filtered off and the solvent was removed under reduced pressure. The product was purified by column chromatography (petroleum ether/ethyl acetate, 5:1). Light yellow oil, 2.25 g (11.0 mmol, 14%), b.p. 140 °C/0.2 mbar, R_f (TLC) = 0.35 (silica gel, petroleum ether/ethyl acetate, 5:1), R_t (GC) = 13.72 min [40−10/min-280(5)]. IR (neat): $\tilde{\nu}$ = 3020 (w) cm^{-1}, 2920 (w), 2810 (w), 2730 (w), 1730 (vs, O=C−O), 1685 (vs, CHO), 1630 (m), 1600 (sh), 1490 (w), 1440 (w), 1370 (m), 1300 (sh), 1220 (s), 1190 (sh), 1120 (m), 1020 (m). ^1H NMR (600 MHz, $CDCl_3$): δ = 2.14 (s, 3 H, CH_3C=O), 6.28 (dd, ^3J = 7.6, ^3J = 15.8 Hz, 1 H, (CH=C*H*CHO), 6.49 (d, ^3J = 4.6 Hz, 1 H, CH−Ph), 6.86 (dd, ^3J = 4.6, ^3J = 15.8 Hz, 1 H, C*H*=CHCHO), 7.33−7.45 (m, 5 H, $CH_{arom.}$), 9.57 (d, ^3J = 7.6 Hz, 1 H, CHO). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 20.9 (CH_3), 74.0 (CH−Ph), 127.4 (*o*/*m*-$CH_{arom.}$), 128.9 (*o*/*m*-$CH_{arom.}$), 129.0 (*p*-$CH_{arom.}$), 131.2 (*C*HCHO), 136.5 (C_{ipso}), 152.7 (*C*H=CHCHO), 169.5 (O=C−O), 192.7 (CHO). GC-MS (70 eV): *m/z* (%) = 204 (1) [M^+], 175 (11), 162 (72), 144 (45), 133 (86), 116 (32), 115 (100), 105 (38), 91 (14), 77 (23), 55 (14), 43 (81). $C_{12}H_{12}O_3$ (204.22): calcd. C 70.57, H 5.92; found C 70.34, H 6.12.

(2*E*)-4-Acetoxy-hex-2-enal (24b): This compound was prepared in a similar manner by literature procedures.[37,38]

General Procedure for the Synthesis of Unsaturated Carbonyl Compounds 27 and 31: The aldehyde (1.4−20.0 mmol) was dissolved in diethyl ether (10−50 mL). Triphenylarsonium bromide (**26**, 1.5 equiv.), potassium carbonate (1.5 equiv.), and water (2 equiv.) were added. The reaction mixture was stirred under argon at room temperature for 14 h. The inorganic salts were removed by filtration through silica gel, with diethyl ether as eluent. The crude product was purified by column chromatography.

(2*E*)-4-Acetoxy-1,4-diphenylbut-2-en-1-one (27a): Treatment of aldehyde **25**[19] (1.78 g, 10.0 mmol) with (2-oxo-2-phenylethyl)triphenylarsonium bromide (**26b**, from triphenylarsane and α-bromoacetophenone in refluxing dioxane, compare ref.[32]) (7.58 g, 15.0 mmol) afforded **27a** as colorless crystals (1.74 g, 6.2 mmol, 62%) after column chromatography (petroleum ether/ethyl acetate, 5:1). M.p. 76 °C, R_f (TLC) = 0.35 (silica gel, petroleum ether/ethyl acetate, 5:1), R_t (GC) = 20.34 min [40−10/min-280(5)]. IR (neat): $\tilde{\nu}$ = 3064 (w) cm^{-1}, 2938 (w), 1739 (vs), 1653 (s), 1624 (s), 1594 (m), 1578 (m), 1494 (m), 1448 (w), 1373 (m), 1335 (m), 1287 (s), 1231 (vs), 1211 (s), 1089 (m), 1070 (m), 1010 (w). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.16 (CH_3), 6.50 (m, 1 H, PhCH), 7.06 (m, 2 H, $CH_{olef.}$), 7.29−7.59 (m, 8 H, $CH_{arom.}$), 7.90 (m, 2 H, *o*-$CH_{arom.}$). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.0 (CH_3), 74.7 (PhCH), 125.7 [CH−C(O)−Ph], 127.4 (*o*/*m*-$CH_{arom.}$), 128.6 (*o*/*m*-$CH_{arom.}$, 4 C), 128.7 (*p*-$CH_{arom.}$), 128.8 (*o*/*m*-$CH_{arom.}$), 133.0 (*p*-$CH_{arom.}$), 137.4 (C_{ipso}), 137.5 (C_{ipso}), 144.3 (PhCH*C*H), 169.6 (CH_3−*C*O_2), 190.1 [CH−*C*(O)−Ph]. GC-MS (70 eV): *m/z* (%) =

280 (0) [M$^+$], 262 (13), 238 (6) [M$^+$ − Ac + H$^+$], 221 (19) [M$^+$ − OAc], 209 (4), 191 (4), 133 (19), 115 (24), 105 (100), 91 (3), 77 (38), 51 (10), 43 (22). $C_{16}H_{18}O_3$ (280.32): calcd. C 77.12, H 5.75; found C 76.87, H 5.87.

(3*E*)-5-Acetoxy-5-phenylpent-3-en-2-one (27b): Treatment of aldehyde **25**[19] (3.56 g, 20.0 mmol) with (2-oxopropyl)triphenylarsonium bromide (**26c**,[22,30] 13.3 g, 30.0 mmol) afforded **27b** (1.31 g, 6.00 mmol, 30%) as a yellow oil[31] after column chromatography (petroleum ether/ethyl acetate, 5:1). R_f (TLC) = 0.33 (silica gel, petroleum ether/ethyl acetate, 5:1), R_t (GC) = 14.60 min [40−10/min-280(5)]. IR (neat): $\tilde{\nu}$ = 3010 (w) cm^{-1}, 2980 (w), 2900 (w), 1720 (s), 1660 (s), 1620 (s), 1480 (w), 1415 (w), 1350 (m), 1220 (s), 1160 (sh), 1060 (m), 1010 (m). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.12 (s, 3 H, CH$_3$−CO$_2$), 2.25 [s, 3 H, CH−C(O)−C*H*$_3$], 6.25 (dd, ^3J = 16.2, ^4J = 1.6 Hz, 1 H, CH−C=O), 6.40 (dd, ^3J = 5.2, ^4J = 1.6 Hz, 1 H, PhCH), 6.81 (dd, ^3J = 16.2, ^3J = 5.2 Hz, 1 H, PhCHC*H*), 7.28−7.42 (m, 5 H, CH$_{\text{arom.}}$). ^{13}C NMR (75 MHz, CDCl$_3$): δ = 20.9 (*C*H$_3$−CO$_2$), 27.2 [CH−C(O)−*C*H$_3$], 72.2 (PhCH), 127.3 (*o*/*m*-CH$_{\text{arom.}}$), 128.7 (*p*-CH$_{\text{arom.}}$), 128.8 (*o*/*m*-CH$_{\text{arom.}}$), 130.1 [*C*H−C(O)−CH$_3$], 137.2 (C$_{ipso}$), 143.2 (PhCH*C*H), 169.5 (CH$_3$−*C*O$_2$), 197.7 [CH−*C*(O)−CH$_3$]. GC-MS (70 eV): *m*/*z* (%) = 218 (1) [M$^+$], 200 (6), 176 (93), 158 (100), 147 (100), 133 (100), 117 (48), 115 (100), 105 (100), 91 (28), 77 (54), 43 (100).

(2*E*,4*E*)-6-Acetoxy-6-phenylhexa-2,4-dienal (31a): Treatment of aldehyde **24a** (290 mg, 1.42 mmol) with (2-oxoethyl)triphenylarsonium bromide (**26a**, 914 mg, 2.13 mmol) afforded **31a** (110 mg, 0.48 mmol, 34%) as an oil after column chromatography (petroleum ether/ethyl acetate, 10:1). R_f (TLC) = 0.29 (silica gel, petroleum ether/ethyl acetate, 5:1), R_t (GC) = 16.65 min [40−10/min-280(5)]. IR (neat): $\tilde{\nu}$ = 3020 (m, Ph) cm^{-1}, 2980 (w, CH$_3$), 2800 (w, CHO), 2720 (w, CHO), 1725 (s, O=C−O), 1670 (s, CHO), 1630 (s, C=C), 1595 (m, Ph), 1485 (m, Ph), 1440 (m), 1360 (s, CH$_3$), 1220 (s, O−C=O), 1150 (s), 1110 (m), 1010 (s). ^{1}H NMR (600 MHz, CDCl$_3$): δ = 2.13 (s, 3 H, C*H*$_3$), 6.17 (dd, ^3J = 7.8, ^3J = 15.6 Hz, 1 H, C*H*CHO), 6.34 [dd, ^3J = 15.2, ^3J = 6.0 Hz, 1 H, PhC(OAc)HC*H*], 6.38 [d, ^3J = 6.0 Hz, 1 H, PhC(OAc)*H*], 6.50 (dd, ^3J = 10.7, ^3J = 15.2 Hz, 1 H, C*H*CHCHCHO), 7.08 (dd, ^3J = 10.7, ^3J = 15.6 Hz, 1 H, C*H*CHCHO), 7.30−7.42 (m, 5 H, CH$_{\text{arom.}}$), 9.54 (d, ^3J = 7.8 Hz, 1 H, C*H*O). ^{13}C NMR (150 MHz, CDCl$_3$): δ = 21.1 (CH$_3$), 74.9 (Ph*C*OAc), 127.2 (*o*/*m*-CH$_{\text{arom.}}$), 128.7 (*p*-CH$_{\text{arom.}}$), 128.8 (*o*/*m*-CH$_{\text{arom.}}$), 129.1 (*C*HCHCHCHO), 132.8 (*C*HCHO), 137.8 (C$_{ipso}$), 141.3 (*C*HCHCHCHCHO), 150.2 (*C*HCHCHO), 169.7 (*C*OOCH$_3$), 193.3 (CHO). GC-MS (70 eV): *m*/*z* (%) = 230 (2) [M$^+$], 201 (19) [M$^+$ − CHO], 188 (20) [M$^+$ − OAc + H$^+$], 170 (12) [M$^+$ − CHO − OAc], 159 (100), 142 (27), 141 (42), 115 (38), 105 (50), 91 (30), 81 (92), 77 (25), 43 (91). $C_{14}H_{14}O_3$ (230.26): calcd. C 73.03, H 6.13; found C 72.44, H 6.10.

(2*E*,4*E*)-6-Acetoxy-1,6-diphenylhexa-2,4-dien-1-one (31b): Treatment of aldehyde **24a** (1.02 g, 5.0 mmol) with (2-oxo-2-phenylethyl)triphenylarsonium bromide (**26b**, 3.79 g, 7.50 mmol) afforded **31b** (579 mg, 1.89 mmol, 38%) as a yellow oil after column chromatography (petroleum ether/ethyl acetate, 5:1). R_f (TLC) = 0.30 (silica gel, petroleum ether/ethyl acetate, 5:1), R_t (GC) = 22.55 min [40−10/min-280(5)]. IR (neat): $\tilde{\nu}$ = 3038 (m) cm^{-1}, 1700 (s), 1684 (s), 1600 (m), 1577 (m), 1494 (m). ^{1}H NMR (600 MHz, CDCl$_3$): δ = 2.13 (s, 3 H, CH$_3$), 6.31 (dd, ^3J = 6.0, ^3J = 15.0 Hz, 1 H, PhCHC*H*), 6.38 (d, ^3J = 6.0 Hz, 1 H, PhCH), 6.50 (dd, ^3J = 10.8, ^3J = 15.0 Hz, 1 H, PhCHCHC*H*), 7.00 [d, ^3J = 15.0 Hz, 1 H, C*H*C(O)Ph], 7.29−7.58 (m, 9 H, PhCHCHCHC*H*, CH$_{\text{arom.}}$), 7.92 (m, 2 H, CH$_{\text{arom.}}$). ^{13}C NMR (150 MHz, CDCl$_3$): δ = 21.1 (CH$_3$), 75.2 [Ph*C*H(OAc)], 126.9 [*C*HC(O)Ph], 127.2, 128.3, 128.4, 128.5, 128.6, 128.7, (CH$_{\text{arom.}}$), 130.1 (PhCHCH*C*H), 132.7, 137.9 (C$_{ipso}$), 138.2 (C$_{ipso}$), 140.4 (PhCH*C*H), 143.0 (PhCHCHCH*C*H), 169.7 (O=C−OCH$_3$), 190.3 (Ph−C=O). GC-MS (70 eV): *m*/*z* (%) = 306 (1) [M$^+$], 264 (26), 159 (63), 105 (100), 77 (56), 43 (44). $C_{20}H_{18}O_3$ (306.36): calcd. C 78.41, H 5.92; found C 78.30, H 5.59.

(3*E*,5*E*)-7-Acetoxy-7-phenylhepta-3,5-dien-2-one (31c): Treatment of aldehyde **24a** (1.03 g, 5.05 mmol) with (2-oxopropyl)triphenylarsonium bromide (**26c**, 3.32 g, 7.50 mmol) afforded **31c** (692 mg, 2.83 mmol, 56%) as a yellow oil after column chromatography (petroleum ether/ethyl acetate, 5:1). R_f (TLC) = 0.24 (silica gel, petroleum ether/ethyl acetate, 5:1), R_t (GC) = 17.52 min [40−10/min-280(5)]. IR (neat): $\tilde{\nu}$ = 3010 (w) cm^{-1}, 2980 (w), 2900 (w), 1720 (s), 1660 (s), 1620 (s), 1480 (w), 1415 (w), 1350 (m), 1220 (s), 1160 (sh), 1060 (m), 1010 (m). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.12 (s, CH$_3$−CO$_2$), 2.25 [s, 3 H, CH−C(O)−C*H*$_3$], 6.17 [d, ^3J = 15.7 Hz, 1 H, C*H*−C(O)−CH$_3$], 6.25 (dd, ^3J = 15.5, ^3J = 5.5 Hz, 1 H, PhCHC*H*), 6.36 (d, ^3J = 5.5 Hz, 1 H, PhC*H*), 6.37 (dd, ^3J = 15.5, ^3J = 10.0 Hz, 1 H, PhCHCHC*H*), 7.08 [dd, ^3J = 15.7, ^3J = 10.0 Hz, 1 H, C*H*CHC(O)−CH$_3$], 7.28−7.42 (m, 5 H, CH$_{\text{arom.}}$). ^{13}C NMR (75 MHz, CDCl$_3$): δ = 20.9 (*C*H$_3$−CO$_2$), 27.2 [CH−C(O)−*C*H$_3$], 72.2 (PhCH), 127.1 (*o*/*m*-CH$_{\text{arom.}}$), 128.5 (*p*-CH$_{\text{arom.}}$), 128.7 (*o*/*m*-CH$_{\text{arom.}}$), 129.7 (PhCHCH*C*H), 131.6 [*C*H−C(O)−CH$_3$], 138.1 (C$_{ipso}$), 140.0 (PhCH*C*H), 141.6 [*C*HCH−C(O)−CH$_3$], 169.7 (CH$_3$−*C*O$_2$), 198.0 [CH−*C*(O)−CH$_3$]. GC-MS (70 eV): *m*/*z* (%) = 218 (1) [M$^+$], 200 (6), 176 (93), 158 (100), 147 (100), 133 (100), 117 (48), 115 (100), 105 (100), 91 (28), 77 (54), 43 (100).

General Procedure for the Synthesis of Furans 28 and 32. 2-Phenylfuran (28a): Compound **24a** (328 mg, 1.61 mmol) was dissolved in dioxane (10 mL) and water (10 mL) and added to 2 M sulfuric acid (10 mL). The reaction mixture was heated to reflux for 30 min. After this had cooled to room temperature, diethyl ether (30 mL) was added. The layers were separated and the organic layer was washed with water (10 mL) and saturated sodium hydrogen carbonate solution (10 mL) and dried with magnesium sulfate. Column chromatography (petroleum ether/ethyl acetate, 10:1) yielded the furan **28a** (74 mg, 0.51 mmol, 32%) as a yellow oil.[33] R_f (TLC) = 0.74 (silica gel, petroleum ether/ethyl acetate, 5:1), R_t (GC) = 9.54 min [40−10/min-280(5)]. IR (neat): $\tilde{\nu}$ = 3100 (sh) cm^{-1}, 3040 (w), 2940 (m), 2850 (sh), 1600 (m), 1500 (w), 1465 (m), 1435 (w), 1270 (w), 1250 (s), 1210 (w), 1150 (m), 1060 (m), 1000 (vs), 950 (sh). ^{1}H NMR: (300 MHz, CDCl$_3$): δ = 6.46 (dd, ^3J = 1.7, ^3J = 3.3 Hz, 1 H, 4-H), 6.64 (dd, ^3J = 3.3, ^4J = 0.7 Hz, 1 H, 3-H), 7.25 (m, 1 H, C$_{\text{arom.}}$), 7.37 (m, 2 H, C$_{\text{arom.}}$), 7.46 (dd, ^3J = 1.7, ^4J = 0.7 Hz, 1 H, 5-H), 7.67 (m, 2 H, C$_{\text{arom.}}$). ^{13}C NMR: (75 MHz, CDCl$_3$): δ = 104.9 (C^3), 111.6 (C^4), 123.8 (*o*/*m*-C$_{\text{arom.}}$), 127.3 (*p*-C$_{\text{arom.}}$), 128.7 (*o*/*m*-C$_{\text{arom.}}$), 131.0 (C$_{ipso}$), 142.0 (C^5), 154.0 (C^2). GC-MS (70 eV): *m*/*z* (%) = 144 (94) [M$^+$], 116 (38), 115 (100), 89 (23), 77 (5), 63 (22).

2,5-Diphenylfuran (28b): This compound was synthesized from **27a** (200 mg, 0.71 mmol). Colorless crystals, 121 mg (0.55 mmol, 77%), m.p. 87 °C, R_f (TLC) = 0.77 (silica gel, petroleum ether/ethyl acetate, 5:1). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 6.67 (s, 2 H, CH$_{\text{furan}}$), 7.24 (m, 2 H, *p*-CH$_{\text{arom.}}$), 7.36 (m, 4 H, *o*/*m*-CH$_{\text{arom.}}$), 7.71 (m, 4 H, *o*/*m*-CH$_{\text{arom.}}$). ^{13}C NMR (75 MHz, CDCl$_3$): δ = 107.2 (CH$_{\text{furan}}$), 126.7 (*o*-CH$_{\text{arom.}}$), 127.3 (*p*-CH$_{\text{arom.}}$), 128.6 (*m*-CH$_{\text{arom.}}$), 130.8 (C$_{ipso\text{,arom.}}$), 153.4 (C$_{ipso\text{,furan}}$).

5-Methyl-2-phenylfuran (28c): This compound was synthesized from **27b** (200 mg, 0.92 mmol). Light yellow crystals, 72 mg (0.46 mmol, 50%), m.p. 38 °C (ref.:[34] 38−39 °C), R_f (TLC) = 0.77 (silica gel, petroleum ether/ethyl acetate, 5:1), R_t (GC) = 10.79 min [40−10/min-280(5)]. IR (neat): $\tilde{\nu}$ = 3059 (w) cm^{-1}, 2919 (w), 1596 (m), 1549 (s), 1488 (m), 1446 (w), 1204 (w), 1068 (w), 1022 (s). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.05 (s, 3 H, CH$_3$), 6.03 (d, ^3J = 3.3 Hz, 1 H, CH$_{\text{furan}}$), 6.51 (d, ^3J = 3.3 Hz, 1 H, CH$_{\text{furan}}$), 7.19 (m, 1 H, CH$_{\text{arom.}}$), 7.33 (m, 2 H, CH$_{\text{arom.}}$), 7.62 (m, 2 H, CH$_{\text{arom.}}$). ^{13}C NMR (75 MHz, CDCl$_3$): δ = 13.6 (CH$_3$), 105.8 (CH$_{\text{furan}}$), 107.7 (CH$_{\text{furan}}$), 123.3 (*o*/*m*-CH$_{\text{arom.}}$), 126.7 (*p*-CH$_{\text{arom.}}$), 128.6 (*o*/*m*-CH$_{\text{arom.}}$), 131.2 (C$_{ipso\text{,arom.}}$), 151.9 (C$_{ipso\text{, furan}}$), 152.3 (C$_{ipso\text{,furan}}$). GC-MS (70 eV): *m*/*z* (%) = 158 (100) [M$^+$], 129 (16), 115 (51), 105 (19), 89 (8), 79 (17), 77 (21), 64 (12), 51 (26), 43 (70).

(*E*)-2-(2-Phenylvinyl)furan (32a):[35] This compound was synthesized from **31a** (230 mg, 1.00 mmol). Light yellow oil, 14 mg (0.082 mmol, 8.2%), R_f (TLC) = 0.64 (silica gel, petroleum ether/ethyl acetate, 5:1), R_t (GC) = 13.02 min [40−10/min-280(5)]. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 6.35 (m, 1 H, 3-H$_{\text{furan}}$), 6.42 (dd, ^3J = 3.3, ^4J = 1.7 Hz, 1 H, 4-H$_{\text{furan}}$), 6.89 (d, ^3J = 16.2 Hz, 1 H, CH$_{\text{olef.}}$), 7.04 (d, ^3J = 16.2 Hz, 1 H, CH$_{\text{olef.}}$), 7.20−7.49 (m, 6 H, CH$_{\text{arom.}}$, 5-H$_{\text{furan}}$). GC-MS (70 eV): *m*/*z* (%) = 170 (100) [M$^+$], 141 (81), 46 (115), 105 (8), 57 (36).

(*E*)-5-Phenyl-2-(2-phenylvinyl)furan (32b):[36] This compound was synthesized from **31b** (360 mg, 1.18 mmol). White crystals, 51 mg (0.207 mmol, 18%), m.p. 86 °C (ref.[36] 87−88 °C), R_f (TLC) = 0.79 (silica gel, petroleum ether/ethyl acetate, 5:1), R_t (GC) = 20.64 min [40−10/min-280(5)]. IR (neat): ṽ = 3060 (w) cm^{-1}, 3024 (w), 2918 (w), 2860 (w), 1675 (w), 1600 (m), 1482 (s), 1450 (s), 1260 (w), 1072 (m), 1023 (s). ^{1}H NMR (360 MHz, CDCl$_3$): δ = 6.46 (d, ^3J = 3.2 Hz, 1 H, CH$_{\text{furan}}$), 6.71 (d, ^3J = 3.2 Hz, 1 H, CH$_{\text{furan}}$), 6.93 (d, ^3J = 16.2 Hz, 1 H, CHC*H*Ph), 7.16 (d, ^3J = 16.2 Hz, 1 H, C*H*CHPh), 7.22−7.58 (m, 8 H, CH$_{\text{arom.}}$), 7.76 (m, 2 H, CH$_{\text{arom.}}$). ^{13}C NMR (90 MHz, CDCl$_3$): δ = 107.3 (CH$_{\text{furan}}$), 111.1 (CH$_{\text{furan}}$), 116.4 (*C*HCHPh), 123.8 (*o*/*m*-CH$_{\text{arom.}}$), 126.3 (*o*/*m*-CH$_{\text{arom.}}$), 127.0, 127.4, 127.5 (2 *p*-CH$_{\text{arom.}}$, CH*C*HPh), 128.7 (4 *o*/*m*-CH$_{\text{arom.}}$), 130.6 (C$_{ipso\text{,arom.}}$), 137.1 (C$_{ipso\text{,arom.}}$), 152.8 (C$_{ipso\text{,furan}}$), 153.5 (C$_{ipso\text{,furan}}$). GC-MS (70 eV): *m*/*z* (%) = 246 (100) [M$^+$], 217 (21), 202 (15), 168 (13), 141 (32), 123 (20), 115 (26), 105 (50), 77 (46), 51 (14).

(*E*)-5-Methyl-2-(2-phenylvinyl)furan (32c):[34] This compound was synthesized from **31c** (140 mg, 0.57 mmol). Light yellow oil, 30 mg (0.16 mmol, 28%), R_f (TLC) = 0.68 (silica gel, petroleum ether/ethyl acetate, 5:1), R_t (GC) = 14.32 min [40−10/min-280(5)]. IR (neat): ṽ = 3024 (w) cm^{-1}, 2962 (m), 2930 (m), 2856 (w), 1645 (w), 1597 (m), 1576 (w), 1532 (w), 1494 (m), 1447 (s), 1364 (w), 1260 (s), 1184 (m), 1028 (s). ^{1}H NMR (600 MHz, CDCl$_3$): δ = 2.36 (s, 3 H, CH$_3$), 6.01 (d, ^3J = 3.2 Hz, 1 H, CH$_{\text{furan}}$), 6.24 (d, ^3J = 3.2 Hz, 1 H, CH$_{\text{furan}}$), 6.83 (d, ^3J = 16.2 Hz, 1 H, CHC*H*Ph), 6.95 (d, ^3J = 16.2 Hz, 1 H, C*H*CHPh), 7.22 (m, 1 H, CH$_{\text{arom.}}$), 7.33 (m, 2 H, CH$_{\text{arom.}}$), 7.45 (m, 2 H, CH$_{\text{arom.}}$). ^{13}C NMR (150 MHz, CDCl$_3$): δ = 13.8 (CH$_3$), 107.8 (CH$_{\text{furan}}$), 109.9 (CH$_{\text{furan}}$), 116.7 (*C*HCHPh), 125.4 (CH*C*HPh), 126.1 (*o*/*m*-CH$_{\text{arom.}}$), 127.2 (*p*-CH$_{\text{arom.}}$), 128.6 (*o*/*m*-CH$_{\text{arom.}}$), 137.3 (C$_{ipso\text{,arom.}}$), 151.7 (C$_{ipso\text{,furan}}$), 152.3 (C$_{ipso\text{,furan}}$). GC-MS (70 eV): *m*/*z* (%) = 184 (76) [M$^+$], 169 (29), 165 (12), 155 (16), 141 (100), 129 (13), 115 (45), 103 (6), 92 (7), 77 (19), 63 (11), 51 (13), 43 (36).

General Procedure for the Synthesis of Imines 29 and 33. (1*E*,3*E*)-5-Acetoxy-*N*-isopropyl-5-phenyl-1-azapenta-1,3-diene (29a): Compound **24a** (0.500 g, 2.45 mmol) was dissolved in dichloromethane (20 mL). Molecular sieves (4Å, 1 g) were added. At −10 °C the reaction mixture was treated with isopropylamine (0.159 g, 2.70 mmol). After 10 h, the molecular sieves were removed by filtration and washed with dichloromethane. The solvent was removed under reduced pressure. The crude product was of good purity; it was used for the pyrrole synthesis without further purification. Light brown oil, 0.593 g (2.42 mmol, 99%). IR (neat): ṽ = 3020 (w) cm^{-1}, 2950 (s), 2840 (m), 1730 (vs, O=C−O), 1650 (m), 1620 (m), 1490 (w), 1450 (m), 1360 (m), 1220 (vs), 1150 (w), 1060 (w), 1015 (m). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.17 [d, ^3J = 6.2 Hz, 6 H, (C*H*$_3$)$_2$−CH], 2.11 (s, 3 H, CH$_3$C=O), 3.34 [sept, ^3J = 6.2 Hz, 1 H, (CH$_3$)$_2$−C*H*], 6.25 (m, 1 H, CHN−CH=C*H*), 6.34−6.44 (m, 2 H, CHN−C*H*=CH−C*H*), 7.28−7.38 (m, 5 H, CH$_{\text{arom.}}$), 7.89 (d, ^3J = 8.4 Hz, 1 H, CHN). ^{13}C NMR (150 MHz, CDCl$_3$): δ = 21.0 (*C*H$_3$−C=O), 23.9 [(*C*H$_3$)$_2$−CH], 61.2 [(CH$_3$)$_2$−*C*H], 74.7 (*C*H-Ph), 127.2 (*o*/*m*-C$_{\text{arom.}}$), 128.4 (*p*-C$_{\text{arom.}}$), 128.7 (*o*/*m*-C$_{\text{arom.}}$), 131.0 (*C*H−CHN), 137.9 (C$_{ipso}$), 140.5 (CHN−CH=*C*H), 158.8 (CHN), 169.7 (O=C−O). GC-MS (70 eV): *m*/*z* (%) = 245 (6) [M$^+$], 230 (4) [M$^+$ − CH$_3$], 203 (31) [M$^+$ + H −C(O)−CH$_3$], 186 (100) [M$^+$ − O−CO−CH$_3$], 174 (21), 170 (23) [186 − CH$_4$], 160 (25), 144 (44), 143 (30), 115 (38), 105 (7), 98 (20), 91 (9), 82 (9), 77 (8), 43 (35).

(1*E*,3*E*)-5-Acetoxy-*N*-isopropyl-1-azahepta-1,3-diene (29b): This compound was synthesized from **24b**[37,38] (293 mg, 1.88 mmol) and isopropylamine (133 mg, 2.25 mmol), in almost quantitative yield and good purity (^{1}H NMR). Colorless crystals were obtained after recrystallization from chloroform/petroleum ether. 351 mg (1.78 mmol, 95%), m.p. 91 °C, R_t (GC) = 10.57 min [40−10/min-280(5)]. IR (neat): ṽ = 2950 (s) cm^{-1}, 2920 (m), 2850 (m), 1730 (vs), 1680 (sh), 1650 (m), 1610 (m), 1450 (m), 1430 (sh), 1360 (s), 1305 (w), 1230 (vs), 1120 (m), 1100 (w), 1070 (w), 1040 (sh), 1010 (m). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.93 (t, ^3J = 7.4 Hz, 3 H, C*H*$_3$CH$_2$), 1.18 [d, ^3J = 6.2 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.70 (m, 2 H, CH$_2$), 2.08 (m, 3 H, CH$_3$C=O), 3.35 [sept, ^3J = 6.2 Hz, 6 H, C*H*(CH$_3$)$_2$], 5.33 (m, 1 H, *H*COAc), 6.08 (dd, ^3J = 15.7, ^3J = 5.5 Hz, 1 H, C*H*CHCHN), 6.34 (dd, ^3J = 15.7, ^3J = 8.8 Hz, 1 H, C*H*CHN), 7.88 (d, ^3J = 8.8 Hz, 1 H, CHN). ^{13}C NMR (75 MHz, CDCl$_3$): δ = 9.3 (*C*H$_3$CH$_2$), 21.0 (*C*H$_3$C=O), 24.0 [CH(*C*H$_3$)$_2$], 27.1 (CH$_2$), 61.1 [*C*H(CH$_3$)$_2$], 74.1 (CH−OAc), 131.1 (*C*HCHN), 140.7 (*C*HCHCHN), 158.9 (CHN), 170.1 (O−C=O). GC-MS (70 eV): *m*/*z* (%) = 197 (1) [M$^+$], 182 (4), 155 (100), 154 (62), 140 (42), 138 (77), 126 (33), 122 (28), 112 (84), 98 (65), 96 (50), 82 (33), 56 (16), 43 (69).

(1*E*,3*E*,5*E*)-7-Acetoxy-*N*-isopropyl-7-phenyl-1-azahepta-1,3,5-triene (33): This compound was synthesized from **31a** (110 mg, 0.48 mmol), dissolved in dichloromethane (10 mL), molecular sieves (4 Å, 260 mg) and isopropylamine (32 mg, 0.54 mmol) at −5 °C. Light brown oil, 128 mg (0.47 mmol, 98%), R_t (GC) = 18.43 min [40−10/min-280(5)]. IR (neat): ṽ = 3020 (w, Ph) cm^{-1}, 2966 (m), 2927 (m), 2861 (m), 1739 (vs), 1630 (s), 1520 (w), 1466 (m), 1370 (m), 1232 (vs). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.18 [d, ^3J = 6.4 Hz, 6 H, CH(C*H*$_3$)$_2$], 2.10 (s, 3 H, C*H*$_3$C=O), 3.35 [sept, ^3J = 6.4 Hz, 1 H, C*H*(CH$_3$)$_2$], 6.02 (dd, ^3J = 15.0, ^3J = 6.6 Hz, 1 H, C*H*CHCHCHCHN), 6.35 (d, 1 H, PhCH), 6.35 (dd, 1 H, C*H*CHN), 6.40 (dd, ^3J = 10.7 Hz, 1 H, C*H*CHCHCHN), 6.55 (dd, ^3J = 15.3, ^3J = 10.7 Hz, 1 H, C*H*CHCHN), 7.27−7.40 (CH$_{\text{arom.}}$), 7.88 (d, ^3J = 8.9 Hz, 1 H, CHN). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 21.0 (CH$_3$), 24.0 [(*C*H$_3$)$_2$CH], 61.2 [(CH$_3$)$_2$*C*H], 75.3 (PhCH), 126.9 (*o*/*m*-CH$_{\text{arom.}}$), 128.2 (*p*-CH$_{\text{arom.}}$), 128.5 (*o*/*m*-CH$_{\text{arom.}}$), 130.9 (*C*HCHCHCHN), 133.1 (*C*HCHN), 135.0 (*C*HCHCHCHCHN), 138.6 (C$_{ipso}$), 139.4 (*C*HCHCHN), 159.3 (C=N), 169.6 (*C*OOCH$_3$). GC-MS (70 eV): *m*/*z* (%) = 271 (0.3) [M$^+$], 211 (17), 196 (4), 168 (22), 141 (10), 122 (100), 105 (5), 80 (92).

1-Isopropyl-2-phenylpyrrole (30d): Compound **29a** (245 mg, 1.00 mmol) was dissolved in dry toluene (10 mL) and treated under argon with tetrakis(triphenylphosphane)palladium(0) (0.116 g, 0.10 mmol). The reaction mixture was stirred at room temperature for 20 min and then heated to reflux for 1 h. The solvent was removed under reduced pressure. The crude product was purified by column chromatography. Yellow oil,[39] 18.7 mg (0.10 mmol, 10%), R_f (TLC) = 0.74 (silica gel, petroleum ether/ethyl acetate, 5:1), R_t (GC) = 12.16 min [40−10/min-280(5)]. IR (neat): ṽ = 3058 (w) cm^{-1}, 3029 (w), 2965 (m), 2924 (m), 2862 (w), 1596 (m), 1579 (m), 1509 (s), 1491 (s), 1465 (s), 1383 (w), 1365 (w), 1316 (m), 1287 (m), 1176 (m), 1084 (w), 1008 (w). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.40 [d, ^3J = 6.9 Hz, 6 H, $(C\mathit{H}_3)_2{-}CH$], 4.49 [sept, ^3J = 6.9 Hz, 1 H, $(CH_3)_2{-}C\mathit{H}$], 6.14 (dd, ^3J = 3.3, ^4J = 1.7 Hz, 3-H$_{\text{pyrrole}}$), 6.26 (dd, ^3J = 3.3, ^3J = 2.9 Hz, 4-H$_{\text{pyrrole}}$), 6.89 (dd, ^3J = 2.9, ^4J = 1.7 Hz, 5-H$_{\text{pyrrole}}$), 7.29−7.44 (m, 5 H, CH$_{\text{arom.}}$). ^{13}C NMR (75 MHz, CDCl$_3$): δ = 24.1 [$(\mathit{C}H_3)_2{-}CH$], 47.1 [$(CH_3)_2{-}\mathit{C}H$], 108.1 (CH$_{\text{pyrrole}}$), 108.3 (CH$_{\text{pyrrole}}$), 117.1 (CH$_{\text{pyrrole}}$), 126.9 (*p*-C$_{\text{arom.}}$), 128.3 (*o*/*m*-C$_{\text{arom.}}$), 129.3 (*o*/*m*-C$_{\text{arom.}}$), 134.0 (C$_q$), 134.0 (C$_q$). GC-MS (70 eV): *m*/*z* (%) = 185 (76) [M$^+$], 170 (12) [M$^+$ − CH$_3$], 143 (100) [M$^+$ − C$_3$H$_6$], 115 (45) 89 (8), 77 (6).

General Procedure for the Synthesis of Pyrroles 30 and 34. 1-Benzyl-2-phenylpyrrole (30a): Compound **24a** (300 mg, 1.47 mmol) was dissolved in dry toluene (10 mL) and treated with benzylamine (270 mg, 2.52 mmol) and tetrakis(triphenylphosphane)palladium(0) (174 mg, 0.15 mmol). The reaction mixture was stirred at room temperature for 20 min and then heated to reflux for 1 h. The solvent was removed under reduced pressure. The crude product is purified by column chromatography (petroleum ether/ethyl acetate, 50:1). Yellow oil,[40] 41 mg (0.18 mmol, 12%), R_f (TLC) = 0.78 (silica gel, petroleum ether/ethyl acetate, 5:1), R_t (GC) = 17.58 min [40−10/min-280(5)]. IR (neat): ṽ = 3061 (w, Ph) cm^{-1}, 3028 (w), 2924 (w), 1602 (m), 1587 (m), 1495 (s), 1471 (m), 1451 (s), 1416 (w), 1356 (w), 1310 (w), 1074 (w), 1028 (w). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 5.06 (s, 2 H, CH$_2$), 6.19 (m, 1 H, CH$_{\text{pyrrole}}$), 6.20 (m, 1 H, CH$_{\text{pyrrole}}$), 6.66 (t, ^3J = 2.2 Hz, 1 H, CH$_{\text{pyrrole}}$), 6.90−6.95 (m, 2 H, *o*-CH$_{\text{benzyl}}$), 7.14−7.26 (m, 8 H, CH$_{\text{arom.}}$). ^{13}C NMR (150 MHz, CDCl$_3$): δ = 50.7 (CH$_2$), 108.5 (CH$_{\text{pyrrole}}$), 108.9 (CH$_{\text{pyrrole}}$), 122.9 (C^{5}H$_{\text{pyrrole}}$), 126.5 (CH$_{\text{arom.}}$), 126.9 (CH$_{\text{arom.}}$), 127.3 (CH$_{\text{arom.}}$), 128.4 (CH$_{\text{arom.}}$), 128.7 (CH$_{\text{arom.}}$), 128.9 (CH$_{\text{arom.}}$), 133.3 (C$_q$), 135.0 (C$_q$), 138.8 (C$_q$). GC-MS (70 eV): *m*/*z* (%) = 233 (55) [M$^+$], 155 (5), 142 (9), 115 (15), 99 (17), 91 (100), 85 (11), 83 (15), 81 (10), 77 (6), 71 (20), 69 (24), 57 (36), 55 (37).

1-Benzyl-2,5-diphenylpyrrole (30b): This compound was synthesized from **27b** (224 mg, 0.80 mmol), benzylamine (145 mg, 1.36 mmol), and tetrakis(triphenylphosphane)palladium(0) (92 mg, 0.08 mmol). Colorless solid after column chromatography (petroleum ether/ethyl acetate, 10:1).[41,42] 0.142 g (0.46 mmol, 57%), m.p. 140 °C (ref.[42] 144 °C), R_f (TLC) = 0.58 (silica gel, petroleum ether/ethyl acetate, 5:1), R_t (GC) = 22.48 min [40−10/min-280(5)]. IR (neat): ṽ = 3065 (w) cm^{-1}, 3026 (w), 1602 (m), 1495 (m), 1482 (m), 1463 (w), 1450 (s), 1433 (m), 1394 (w), 1361 (m), 1322 (m), 1218 (w), 1185 (w), 1120 (w), 1074 (m), 1055 (w), 1030 (m). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 5.22 (s, 2 H, CH$_2$), 6.35 (s, 2 H, CH$_{\text{pyrrole}}$), 6.64 (m, 2 H, *o*-CH$_{\text{benzyl}}$), 7.05−7.40 (m, 13 H, CH$_{\text{arom.}}$). ^{13}C NMR (75 MHz, CDCl$_3$): δ = 48.7 (CH$_2$), 109.7 (CH$_{\text{pyrrole}}$), 126.0 (*o*/*m*-CH$_{\text{benzyl}}$), 126.7 (*p*-CH$_{\text{benzyl}}$), 127.0 (*o*/*m*-CH$_{\text{benzyl}}$), 128.3 (CH$_{\text{arom.}}$, 6 C), 129.1 (CH$_{\text{arom.}}$, 4 C), 133.8 (C$_q$), 136.8 (C$_q$), 139.3 (C$_q$). GC-MS (70 eV): *m*/*z* (%) = 309 (71) [M$^+$], 277 (18), 218 (100), 165 (5), 91 (38), 77 (12), 65 (20), 57 (17).

1-Benzyl-5-methyl-2-phenylpyrrole (30c): This compound was synthesized from **24c** (180 mg, 0.825 mmol), dissolved in dry toluene (5 mL), tetrakis(triphenylphosphane)palladium(0) (113 mg, 0.098 mmol), and benzylamine (150 mg, 1.40 mmol). Purification by kugelrohr distillation. Light yellow oil, 133 mg (0.538 mmol, 65%), b.p. 150 °C/0.1 mbar, R_t (GC) = 18.38 min [40−10/min-280(5)]. IR (neat): ṽ = 3061 (m) cm^{-1}, 3029 (m), 2931 (w), 2914 (w), 1602 (m), 1513 (m), 1495 (m), 1476 (m), 1452 (s), 1444 (s), 1438 (m), 1402 (s), 1355 (m), 1313 (m), 1197 (w), 1184 (w), 1119 (w), 1074 (w), 1028 (m). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.14 (s, 3 H, CH$_3$), 5.13 (s, 2 H, CH$_2$), 6.05 (d, ^3J = 3.3 Hz, 1 H, CH$_{\text{pyrrole}}$), 6.23 (d, ^3J = 3.3 Hz, 1 H, CH$_{\text{pyrrole}}$), 6.93 (m, 2 H, *o*-CH$_{\text{benzyl}}$), 7.17−7.34 (m, 8 H, CH$_{\text{arom.}}$). ^{13}C NMR (75 MHz, CDCl$_3$): δ = 12.6 (CH$_3$), 47.7 (CH$_2$), 107.2 (CH$_{\text{pyrrole}}$), 108.0 (CH$_{\text{pyrrole}}$), 125.6 (CH$_{\text{arom.}}$, 2 C), 126.6 (CH$_{\text{arom.}}$, 2 C), 127.0 (CH$_{\text{arom.}}$, 1 C), 128.3 (CH$_{\text{arom.}}$, 2 C), 128.7 (CH$_{\text{arom.}}$, 3 C), 130.4 (C$^5_{\text{pyrrole}}$), 133.9 (C$_q$), 134.7 (C$_q$), 139.0 (C$_q$). GC-MS (70 eV): *m*/*z* (%) = 247 (100) [M$^+$], 156 (71), 128 (8), 91 (58), 65 (5). C$_{18}$H$_{17}$N (247.33): calcd. C 87.41, H 6.93, N 5.66; found C 87.55, H 7.39, N 5.82.

(*E*)-1-Isopropyl-2-(2-phenylvinyl)pyrrole (34a): This compound was synthesized from **33** (480 mg, 1.77 mmol) and tetrakis(triphenylphosphane)palladium(0) (204 mg, 0.177 mmol), dissolved in dry toluene (10 mL). Reflux under argon for 2 h. Purification by column chromatography (petroleum ether/ethyl acetate, 10:1). Yellow oil, 20 mg (0.094 mmol, 5.3%), R_f (TLC) = 0.75 (silica gel, petroleum ether/ethyl acetate, 5:1), R_t (GC) = 16.67 min [40−10/min-280(5)]. IR (neat): ṽ = 3024 (w) cm^{-1}, 2973 (m), 2928 (m), 2870 (sh), 1625 (w), 1596 (m), 1576 (m), 1493 (m), 1464 (s), 1367 (w), 1288 (s), 1236 (w), 1176 (w), 1069 (w). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.48 [d, ^3J = 6.7 Hz, 6 H, $CH(C\mathit{H}_3)_2$], 4.53 [sept, ^3J = 6.4 Hz, 1 H, $C\mathit{H}(CH_3)_2$], 6.19 (m, 1 H, CH$_{\text{pyrrole}}$), 6.48 (m, 1 H, CH$_{\text{pyrrole}}$), 6.80 (m, 1 H, CH$_{\text{pyrrole}}$), 6.89 (d, ^3J = 16.0 Hz, 1 H, C*H*CH), 7.02 (d, ^3J = 16.0 Hz, 1 H, CHC*H*), 7.16−7.48 (m, 5 H, CH$_{\text{arom.}}$). ^{13}C NMR (150 MHz, CDCl$_3$): δ = 23.7 [$(\mathit{C}H_3)_2{-}CH$], 47.0 [$(CH_3)_2{-}\mathit{C}H$], 106.3 (CH$_{\text{pyrrole}}$), 108.4 (CH$_{\text{pyrrole}}$), 117.1, 117.7 (*C*H$_{\text{pyrrol}}$, *C*HCHPh), 126.0 (*o*/*m*-CH$_{\text{arom.}}$), 126.3, 126.9 (*p*-CH$_{\text{arom.}}$, CH*C*HPh), 128.6 (*o*/*m*-CH$_{\text{arom.}}$), 131.1 (C$_{\textit{ipso},\text{pyrrole}}$), 138.0 (C$_{\textit{ipso},\text{arom.}}$). GC-MS (70 eV): *m*/*z* (%) = 211 (99) [M$^+$], 196 (10), [M$^+$ − CH$_3$], 169 (40) [M$^+$ − C$_3$H$_6$], 168 (100), 167 (39), 154 (5), 152 (4), 141 (14), 139 (8), 120 (21), 115 (13), 80 (7), 77 (5).

(*E*)-1-Benzyl-5-phenyl-2-(2-phenylvinyl)pyrrole (34b): This compound was synthesized from **31b** (300 mg, 0.98 mmol), benzylamine (170 mg, 1.59 mmol), and tetrakis(triphenylphosphane)palladium(0) (105 mg, 0.09 mmol). Yellow solid after column chromatography, 190 mg (0.57 mmol, 58%), m.p. 105 °C, R_f (TLC) = 0.62 (silica gel, petroleum ether/ethyl acetate, 5:1). IR (neat): ṽ = 3020 (m) cm^{-1}, 2922 (s), 1627 (m), 1598 (m), 1575 (m), 1494 (m), 1456 (s), 1416 (w), 1360 (w), 1224 (w). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 5.23 (CH$_2$), 6.35 (d, ^3J = 3.8 Hz, 1 H, CH$_{\text{pyrrole}}$), 6.66 (d, ^3J = 3.8 Hz, 1 H, CH$_{\text{pyrrole}}$), 6.80 (d, ^3J = 16.2 Hz, 1 H, CH*C*HPh), 6.90 (d, ^3J = 16.2 Hz, 1 H, *C*HCHPh), 7.02 (m, 2 H, CH$_{\text{arom.}}$), 7.25 (m, 13 H, CH$_{\text{arom.}}$). ^{13}C NMR (75 MHz, CDCl$_3$): δ = 47.9 (CH$_2$), 107.2 (CH$_{\text{pyrrole}}$), 109.9 (CH$_{\text{pyrrole}}$), 117.6 (PhCH*C*H), 125.7, 125.9, 126.5, 126.9, 127.1, 127.2, 128.4, 128.5, 128.7, 128.8 (CH$_{\text{arom.}}$, Ph*C*HCH), 133.1 (C$_q$), 133.4 (C$_q$), 136.6 (C$_q$), 137.8 (C$_q$), 138.8 (C$_q$). C$_{25}$H$_{21}$N (335.44): calcd. C 89.51, H 6.31, N 4.18; found C 89.08, H 6.81, N 3.98.

(*E*)-1-Benzyl-5-methyl-2-(2-phenylvinyl)pyrrole (34c): This compound was synthesized from **31c** (202 mg, 0.827 mmol) in dry toluene (5 mL), tetrakis(triphenylphosphane)palladium(0) (113 mg, 0.098 mmol), and benzylamine (150 mg, 1.40 mmol). Light yellow needles after column chromatography (petroleum ether/ethyl acetate, 10:1). 102 mg (0.373 mmol, 45%), m.p. 104 °C, R_f (TLC) = 0.73 (silica gel, petroleum ether/ethyl acetate, 5:1), R_t (GC) = 21.85 min [40−10/min-280(5)]. IR (KBr): ṽ = 3078 (w) cm^{-1}, 3062 (w), 3027 (m), 2931 (m), 2909 (w), 1628 (m), 1596 (m), 1494 (m), 1478 (s), 1452 (s), 1442 (m), 1413 (s), 1356 (m), 1308 (m), 1025 (w). ^{1}H NMR (600 MHz, CDCl$_3$): δ = 2.11 (s, 3 H, CH$_3$), 5.13 (s, 2 H, CH$_2$), 6.00 (d, ^3J = 3.3 Hz, 1 H, 4-H$_{\text{pyrrole}}$), 6.51 (d, ^3J = 3.3 Hz, 1 H, 3-H$_{\text{pyrrole}}$), 6.81−6.85 (m, 2 H, CHCHPh), 6.95−7.02 (m, 2 H, *o*-CH$_{\text{benzyl}}$), 7.10−7.17 (m, 1 H, CH$_{\text{arom.}}$), 7.20−7.34 (m, 7 H, CH$_{\text{arom.}}$). ^{13}C NMR (150 MHz, CDCl$_3$): δ = 12.5 (CH$_3$), 46.7 (CH$_2$), 105.9 (CH$_{\text{pyrrole}}$), 107.9 (CH$_{\text{pyrrole}}$), 117.5 (*C*HCHPh), 125.1 (CH*C*HPh), 125.69 (*p*-CH$_{\text{arom.}}$), 125.74 (*o*/*m*-CH$_{\text{arom.}}$), 126.6 (*p*-CH$_{\text{arom.}}$), 127.2 (*o*/*m*-CH$_{\text{arom.}}$), 128.5 (*o*/*m*-CH$_{\text{arom.}}$), 128.8 (*o*/*m*-CH$_{\text{arom.}}$), 130.7 (C^{5}H$_{\text{pyrrole}}$), 131.4 (C^{2}H$_{\text{pyrrole}}$), 137.9 (C$_{ipso\text{,arom.}}$), 138.1 (C$_{ipso\text{,arom.}}$). GC-MS (70 eV): *m*/*z* (%) = 273 (88) [M$^+$], 182 (79), 167 (100), 152 (5), 139 (6), 115 (8), 91 (33), 77 (2), 65 (6).

Ethyl 2,3-Epoxy-3,3-diphenylpropionate (35):[27] A solution of potassium *tert*-butoxide (9.25 g, 83 mmol) in *tert*-butyl alcohol (65 mL) was added dropwise at 10 °C to a solution of benzophenone (13.6 g, 75 mmol) in ethyl chloroacetate (10.1 g, 82.4 mmol). After this was stirred for 10 h, the solvent was removed under reduced pressure, and the residue was dissolved in diethyl ether and washed with water. The organic layer was dried with magnesium sulfate. After removal of the solvent under reduced pressure, the crude product was purified by distillation. Colorless oil, 13.82 g (51.5 mmol, 69%), b.p. 110 °C/0.02 mbar (ref.[43] 152−153 °C/1 Torr), R_t (GC) = 17.87 min [40−10/min-280(5)]. IR (neat): ṽ = 3061 (m) cm^{-1}, 3030 (w), 2982 (m), 2936 (w), 1756 (s), 1728 (s), 1665 (w), 1600 (w), 1497 (m), 1449 (s), 1402 (m), 1387 (m), 1369 (m), 1276 (s), 1200 (s), 1156 (w), 1031 (s). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.95 (t, ^3J = 7.2 Hz, 3 H, CH$_3$), 3.96 (s, 1 H, CH), 3.97 (q, ^3J = 7.2 Hz, 2 H, CH$_2$), 7.25−7.48 (m, 10 H, CH$_{\text{arom.}}$). ^{13}C NMR (75 MHz, CDCl$_3$): δ = 13.7 (CH$_3$), 61.1 (CH$_2$), 61.9 (CH), 66.3 (C$_q$), 126.8 (CH$_{\text{arom.}}$, 2 C), 127.9 (CH$_{\text{arom.}}$, 2 C), 128.0 (CH$_{\text{arom.}}$, 2 C), 128.2 (CH$_{\text{arom.}}$, 1 C), 128.4 (CH$_{\text{arom.}}$, 3 C), 135.4 (C$_{ipso}$), 138.8 (C$_{ipso}$), 166.7 (C=O). GC-MS (70 eV): *m*/*z* (%) = 267 (5) [M$^+$ − 1], 252 (7), 240 (14), 207 (13), 194 (75), 165 (100), 152 (14), 105 (24), 77 (14), 51 (5).

Sodium 2,3-Epoxy-3,3-diphenylpropionate (36):[27] Compound **35** (6.30 g, 23.5 mmol) and water (0.45 g, 25 mmol) were added to a solution of sodium ethoxide [from sodium (0.58 g, 25 mmol) and anhydrous ethanol (12 mL)]. After the mixture was stirred for 5 min, a colorless precipitate had formed, and this was filtered off, washed with diethyl ether, and dried at 60 °C. Colorless solid, 5.68 g (21.6 mmol, 92%). M.p. 271 °C (decomp.). ^{1}H NMR (300 MHz, D$_2$O/[D$_6$]acetone): δ = 3.83 (s, 1 H, CH), 7.15−7.45 (m, 10 H, CH$_{\text{arom.}}$). ^{13}C NMR (75 MHz, D$_2$O/[D$_6$]acetone): δ = 65.1 (CH), 67.23 (C$_q$), 127.9 (CH$_{\text{arom.}}$, 2 C), 128.6 (CH$_{\text{arom.}}$, 2 C), 129.1 (CH$_{\text{arom.}}$, 1 C), 129.3 (CH$_{\text{arom.}}$, 3 C), 129.6 (CH$_{\text{arom.}}$, 2 C), 138.0 (C$_{ipso}$), 141.4 (C$_{ipso}$), 173.9 (COO$^-$).

2-Acetoxy-2,2-diphenylethanal (37): See also ref.[28] A mixture of **36** (5.24 g, 20 mmol), pyridine (1.58 g, 20 mmol), lead tetraacetate (8.86 g, 20 mmol), and dry toluene (80 mL) was stirred under argon for 30 min and then heated to reflux for 70 min. The reaction mixture was treated with ethylene glycol in order to decompose surplus lead tetraacetate. The precipitate was filtered off and the filtrate was washed with water, 2 M hydrochloric acid solution, and again with water. The organic layer was dried with magnesium sulfate. The solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, petroleum ether/ethyl acetate, 5:1). Colorless crystals at 0° C, oil at room temperature, 3.21 g (12.6 mmol, 63%) (ref.:[28] 55%), R_f (TLC) = 0.38 (silica gel, petroleum ether/ethyl acetate, 5:1), R_t (GC) = 17.08 min [40−10/min-280(5)]. IR (neat): ṽ = 3040 (w) cm^{-1}, 2800 (w), 2700 (w), 1720 (vs), 1480 (m), 1440 (m), 1360 (s), 1230 (vs), 1170 (s), 1010 (s). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.20 (s, 3 H, CH$_3$), 7.28−7.48 (m, 10 H, CH$_{\text{arom.}}$), 9.70 (s, 1 H, CHO). ^{13}C NMR (75 MHz, CDCl$_3$): δ = 21.0 (CH$_3$), 87.7 (C$_q$), 127.9 (*o*/*m*-CH$_{\text{arom.}}$), 128.4 (*o*/*m*-CH$_{\text{arom.}}$), 128.5 (*p*-CH$_{\text{arom.}}$), 137.3 (C$_{ipso}$), 169.6 (O=C−O), 192.4 (CHO). GC-MS (70 eV): *m*/*z* (%) = 225 (18) [M$^+$ − CHO], 183 (100) [M$^+$ − CHO − C(O)CH$_3$], 166 (36) [M$^+$ − CHO − O=C−OCH$_3$], 105 (71) [Ph$_2$CO$^+$], 77 (35) [Ph$^+$], 51 (7) [C$_4$H$_4$$^+$].

(2*E*)-4-Acetoxy-4,4-diphenylbut-2-enal (38a): Compound **26a** (2.57 g, 6.00 mmol) and potassium carbonate (840 mg, 6.00 mmol) were added to a solution of **37** (1.016 g, 4.00 mmol) in diethyl ether (20 mL) and water (0.2 mL). After the mixture was stirred overnight (argon) the triphenylarsinic oxide was removed by column filtration. The crude product was purified by column chromatography (silica gel, petroleum ether/ethyl acetate, 5:1). Colorless oil, 0.274 g (0.98 mmol, 24%). R_f (TLC) = 0.45 (silica gel, petroleum ether/ethyl acetate, 5:1), R_t (GC) = 19.04 min [40−10/min-280(5)]. IR (neat): ṽ = 3040 (w) cm^{-1}, 3010 (w), 2950 (w), 2910 (w), 2800 (w), 2700 (w), 1730 (vs), 1680 (vs), 1480 (m), 1440 (m), 1360 (s), 1230 (vs), 1170 (sh), 1130 (m), 1110 (m), 1060 (m), 1010 (s). ^{1}H NMR: (300 MHz, CDCl$_3$): δ = 2.16 (s, 3 H, CH$_3$), 5.93 (dd, ^3J = 7.6, ^3J = 16.0 Hz, 1 H, CHCHO), 7.20−7.45 (m, 10 H, CH$_{\text{arom.}}$), 7.77 (d, ^3J = 16.0 Hz, 1 H, CHC$_q$), 9.67 (d, ^3J = 7.6 Hz, 1 H, CHO). ^{13}C NMR (75 MHz, CDCl$_3$): δ = 21.8 (CH$_3$), 85.7 (C$_q$), 126.9 (*o*/*m*-CH$_{\text{arom.}}$), 128.0 (*p*-CH$_{\text{arom.}}$), 128.3 (*o*/*m*-CH$_{\text{arom.}}$), 133.7 (*C*H−CHO), 141.2 (C$_{ipso}$), 155.7 (C$_q$-*C*H), 168.6 (O=C−O), 192.9 (CHO). GC-MS (70 eV): *m*/*z* (%) = 280 (12) [M$^+$], 251 (8) [M$^+$ − CHO], 238 (10), 220 (23), 209 (60), 207 (36), 192 (156), 191 (59), 178 (39), 165 (39), 133 (38), 115 (60), 105 (100), 91 (19), 77 (39), 43 (59). C$_{18}$H$_{16}$NO$_2$ (280.32): calcd. C 77.12, H 5.75; found C 76.89, H 5.85.

(3*E*)-5-Acetoxy-5,5-diphenylpent-3-en-2-one (38b): Compound **37** (2.54 g, 10.0 mmol), dissolved in diethyl ether (30 mL), was treated with **26c**, (6.65 g, 15.0 mmol), potassium carbonate (2.07 g, 15.0 mmol), and water (540 mg, 30.0 mmol). The reaction mixture was stirred under argon for 14 h. Inorganic salts were removed by column filtration (diethyl ether). The crude product was purified by column chromatography (silica gel, petroleum ether/ethyl acetate, 5:1). Light brown solid, 1.90 g (6.45 mmol, 65%), m.p. 101 °C, R_f (TLC) = 0.40 (silica gel, petroleum ether/ethyl acetate, 5:1), R_t (GC) = 19.46 min [40−10/min-280(5)]. IR (KBr): ṽ = 3055 (w) cm^{-1}, 1748 (vs), 1678 (vs), 1593 (w), 1497 (w), 1488 (w), 1368 (m), 1448 (m), 1256 (s), 1228 (vs), 1204 (m), 1175 (m), 1131 (m), 1068 (w), 1000 (s). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.15 [s, 3 H, CH−C(O)−C*H*$_3$], 2.30 (s, 3 H, CH$_3$−CO$_2$), 5.87 (d, ^3J = 16.2 Hz, 1 H, Ph$_2$CCHC*H*), 7.22−7.38 (m, 10 H, CH$_{\text{arom.}}$), 7.73 (d, ^3J = 16.2 Hz, 1 H, Ph$_2$CCH). ^{13}C NMR (75 MHz, CDCl$_3$): δ = 22.0 (*C*H$_3$−CO$_2$), 27.3 [CH−C(O)−*C*H$_3$], 86.0 (Ph$_2$C$_q$), 127.0 (*o*/*m*-CH$_{\text{arom.}}$), 127.9 (*p*-CH$_{\text{arom.}}$), 128.3 (*o*/*m*-CH$_{\text{arom.}}$), 132.2 [*C*H−C(O)−CH$_3$], 141.8 (C$_{ipso}$), 146.5 (Ph$_2$C$_q$*C*H), 168.7 (CH$_3$−*C*O$_2$), 198.2 [CH−*C*(O)−CH$_3$]. GC-MS (70 eV): *m*/*z* (%) = 294 (5) [M$^+$], 252 (6), 251 (11), 234 (15), 209 (100), 193 (80), 191 (67), 178 (28), 147 (44), 115 (51), 105 (34), 91 (19), 77 (15), 43 (61). C$_{19}$H$_{18}$O$_3$ (294.35): calcd. C 77.53, H 6.16; found C 77.40, H 6.12. This compound has also been characterized in the solid state by X-ray crystallography.[29]

(1*E*,3*E*)-5-Acetoxy-*N*-isopropyl-5,5-diphenyl-1-azapenta-1,3-diene (39): A mixture of **38a** (0.231 g, 0.824 mmol), dissolved in dry dichloromethane (10 mL), and molecular sieves (4 Å, 1 g) was treated at −10 °C, with slow stirring, with isopropylamine (53 mg, 0.90 mmol). After the mixture was stirred overnight, the molecular sieves were filtered off and washed with dichloromethane. The solvent was removed under reduced pressure. The crude product was of good purity (^{1}H NMR) and was used without further purification. Recrystallisation from dichloromethane/petroleum ether yielded colorless rectangular crystals, 0.252 mg (0.784 mmol, 95%). m.p. 115−118 °C. IR (neat): ṽ = 3040 (w) cm^{-1}, 3010 (w), 2940 (s), 2910 (w), 2840 (w), 1730 (vs), 1635 (w), 1600 (m), 1480 (m), 1460 (w), 1440 (m), 1360 (m), 1230 (vs), 1200 (m), 1140 (w), 1080 (w), 1060 (w), 1010 (m). ^{1}H NMR: (300 MHz, $\mathrm{CDCl_3}$): δ = 1.15 [d, ^{3}J = 6.4 Hz, 6 H, $\mathrm{CH{-}(C}H_3)_2$], 2.12 (s, 3 H, $\mathrm{O{=}C{-}CH_3}$), 3.34 [sept, ^{3}J = 6.4 Hz, 1 H, $C\mathrm{H{-}(CH_3)_2}$], 5.99 (dd, ^{3}J = 9.0, ^{3}J = 16.0 Hz, 1 H, C*H*CHN), 7.20−7.38 (m, 11 H, $\mathrm{CH_{arom.}}$, $\mathrm{C_q{-}CH}$), 8.00 (d, ^{3}J = 9.0 Hz, 1 H, CHN). ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$): δ = 22.0 ($C\mathrm{H_3C{=}O}$), 23.9 [$\mathrm{CH{-}(}C\mathrm{H_3)_2}$], 61.1 [$C\mathrm{H{-}(CH_3)_2}$], 86.6 ($\mathrm{C_q}$), 126.9 ($o/m$-$\mathrm{CH_{arom.}}$), 128.0 ($p$-$\mathrm{CH_{arom.}}$), 128.3 ($o/m$-$\mathrm{CH_{arom.}}$), 133.7 ($\mathrm{C}_{ipso}$), 141.2, 155.7 (*C*H=*C*H−CHO), 159.2 (CHN), 168.8 (O=C−O). MS (70 eV): m/z (%) = 321 (46) [$\mathrm{M^+}$], 279 (40), 278 (56), 263 (20), 262 (26), 250 (31), 236 (65), 220 (24), 209 (18), 203 (19), 192 (49), 191 (100), 178 (14), 174 (31), 167 (33), 165 (25), 139 (16), 115 (46), 105 (43), 91 (14), 77 (30), 70 (33). $\mathrm{C_{21}H_{23}NO_2}$ (321.41): calcd. C 78.47, H 7.21, N 4.36; found C 77.61, H 7.31, N 3.99. This compound has also been characterized in the solid state by X-ray crystallography.[29]

3,4-Bis(2,2-diphenylvinyl)-1-isopropylpyrrole (40a): Under argon, compound **39** (180 mg, 0.56 mmol), dissolved in dry toluene (10 mL), was treated with tetrakis(triphenylphosphane)palladium(0) (65 mg, 0.056 mmol). The reaction mixture was stirred at room temperature for 20 min. The mixture was then heated to reflux for 2 h. The solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, petroleum ether/ethyl acetate, 50:1). Colorless solid, 37 mg (0.079 mmol, 28%), m.p. 170 °C. IR (neat): $\tilde{\nu}$ = 3075 (w) $\mathrm{cm^{-1}}$, 3025 (w), 2969 (m), 2926 (w), 1661 (w), 1617 (w), 1593 (m), 1487 (s), 1445 (s), 1418 (s), 1368 (m), 1277 (w), 1188 (m), 1135 (m), 1071 (m), 1031 (w). ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ = 0.97 [d, ^{3}J = 6.7 Hz, 6 H, $\mathrm{CH(C}H_3)_2$], 3.60 [sept, ^{3}J = 6.7 Hz, 1 H, $C\mathrm{H(CH_3)_2}$], 5.46 (s, 2 H, $\mathrm{CH_{pyrrole}}$), 6.69 (s, 1 H,), 7.10−7.80 (m, 22 H, $\mathrm{CH_{arom.}}$, $\mathrm{CH_{olef.}}$). ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$): δ = 23.1 ($\mathrm{CH_3}$), 46.7 [$\mathrm{CH(}C\mathrm{H_3)_2}$], 117.5, 119.6, 120.3 ($\mathrm{C_{q,\ pyrrol}}$), 126.5, 126.8 ($o/m$-$\mathrm{CH_{arom.}}$), 126.9, 128.1 ($o/m$-$\mathrm{CH_{arom.}}$), 128.8 ($o/m$-$\mathrm{CH_{arom.}}$), 130.2 ($o/m$-$\mathrm{CH_{arom.}}$), 137.7 ($\mathrm{C_q}$), 142.1 ($\mathrm{C_q}$), 143.3 ($\mathrm{C_q}$). MS (70 eV): m/z (%) = 465 (100) [$\mathrm{M^+}$], 422 (3), 344 (3), 167 (5), 57 (9). $\mathrm{C_{35}H_{31}N}$ (465.63): calcd. C 90.28, H 6.71, N 3.01; found C 89.63, H 6.67, N 2.65.

X-ray Crystal Structure Analysis of 40a:[29] Empirical formula $\mathrm{C_{35}H_{31}N}$, M = 465.61, colorless crystal 0.35 × 0.20 × 0.05 mm, a = 6.022(2), b = 18.801(5), c = 23.227(4) Å, V = 2629.8(12) $\mathrm{Å^3}$, $\rho_{\mathrm{calcd.}}$ = 1.176 g $\mathrm{cm^{-3}}$, μ = 5.08 $\mathrm{cm^{-1}}$, no absorption correction ($0.842 \leq T \leq 0.975$), Z = 4, orthorhombic, space group *Pbcn* (No. 60), λ = 1.54178 Å, T = 223 K, ω/2θ scans, 2691 reflections collected ($+h$, $-k$, $-l$), [(sinθ)/λ] = 0.62 $\mathrm{Å^{-1}}$, 2691 independent and 1800 observed reflections [$I \geq 2\,\sigma(I)$], 169 refined parameters, R = 0.074, wR^2 = 0.182, max. residual electron density 0.43 (−0.33) e $\mathrm{Å^{-3}}$, due to symmetry disorder in the isopropyl group, hydrogen atoms calculated and refined as riding atoms.

1-Benzyl-3,4-bis(2,2-diphenylvinyl)-2,5-dimethylpyrrole (40b): Compound **38b** (738 mg, 2.51 mmol), dissolved in dry toluene (10 mL), was treated with tetrakis(triphenylphosphane)palladium(0) (400 mg, 0.35 mmol) and benzylamine (455 mg, 4.25 mmol). The reaction mixture was heated to reflux for 1 h. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography (silica gel, petroleum ether/ethyl acetate, 10:1). Yellow oil, 84 mg (0.155 mmol, 12%), R_{f} (TLC) = 0.58 (silica gel, petroleum ether/ethyl acetate, 5:1). IR (neat): $\tilde{\nu}$ = 3055 (w) $\mathrm{cm^{-1}}$, 3025 (w), 2973 (m), 2926 (m), 2854 (m), 1596 (m), 1494 (s), 1453 (s), 1408 (m), 1382 (m), 1373 (m), 1351 (m), 1118 (m), 1078 (w), 1029 (w). ^{1}H NMR (600 MHz, $\mathrm{CDCl_3}$): δ = 1.57 (s, 6 H, $\mathrm{CH_3}$), 4.76 (s, 2 H, $\mathrm{CH_2}$), 6.66 (m, 2 H, o-$\mathrm{CH_{benzyl}}$), 6.69 (s, 1 H, $\mathrm{CH_{olef.}}$), 7.10−7.30 (m, 23 H, $\mathrm{CH_{arom.}}$). ^{13}C NMR (150 MHz, $\mathrm{CDCl_3}$): δ = 10.9 ($\mathrm{CH_3}$), 46.7 ($\mathrm{CH_2}$), 118.1 (C^{3}_{pyrrole}), 123.5 ($\mathrm{CH_{olef.}}$), 124.9 ($C^{2}_{\mathrm{pyrrole}}\mathrm{{-}CH_3}$), 125.5 ($o$-$\mathrm{CH_{benzyl}}$), 126.2 (2 C), 126.8 (2 C), 126.9 (p-$\mathrm{CH_{benzyl}}$), 127.79 (o/m-$\mathrm{CH_{phenyl}}$), 127.80 (o/m-$\mathrm{CH_{phenyl}}$), 128.1 (o/m-$\mathrm{CH_{phenyl}}$), 128.5 (2 C), 130.8 (o/m-$\mathrm{CH_{phenyl}}$), 138.0 ($\mathrm{CH_2C}_{ipso}$), 141.2 ($\mathrm{C}_{ipso\mathrm{,phenyl}}$), 141.9 ($\mathrm{C}_{ipso\mathrm{,phenyl}}$), 144.2 ($\mathrm{C_{q,olef.}}$). MS (70 eV): m/z (%) = 541 (100) [$\mathrm{M^+}$], 450 (5), 435 (7), 167 (31), 105 (21), 91 (50), 77 (13), 57 (19), 55 (10). MS (high resolution, 70 eV): calcd. 541.27698; found 541.27571. As a by-product, 5,5-diphenylpent-4-en-2-one[44] was separated by column chromatography. White solid, 65 mg (0.275 mmol, 11%), R_{f} (TLC) = 0.45 (silica gel, petroleum ether/ethyl acetate, 5:1). ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ = 2.09 (s, 3 H, $\mathrm{CH_3}$), 3.25 (d, ^{3}J = 7.3 Hz, 2 H, $\mathrm{CH_2}$), 6.28 (t, ^{3}J = 7.3 Hz, 2 H, $C\mathrm{HCH_2}$), 7.10−7.39 (m, 10 H, $\mathrm{CH_{arom.}}$). ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$): δ = 29.8 ($\mathrm{CH_3}$), 44.7 ($\mathrm{CH_2}$), 120.5 ($\mathrm{CH_{olef.}}$), 127.3 ($\mathrm{CH_{arom.}}$, 4 C), 128.1 ($\mathrm{CH_{arom.}}$, 2 C), 128.4 ($\mathrm{CH_{arom.}}$, 2 C), 129.6 ($\mathrm{CH_{arom.}}$, 2 C), 139.5 (C_{ipso}), 141.9 (C_{ipso}), 144.9 ($C_{\mathrm{q}}\mathrm{CHCH_2}$), 206.4 (C=O).

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[1] N. De Kimpe, R. Verhé, L. De Buyck, N. Schamp, *Tetrahedron Lett.* **1982**, *23*, 2853−2856.

[2] R. Flammang, S. Lacombe, A. Laurent, A. Maquestiau, B. Marquet, S. Novkova, *Tetrahedron* **1986**, *42*, 315−328.

[3] X. Creary, *Chem. Rev.* **1991**, *91*, 1625−1678.

[4] J.-P. Moldenhauer, M. H. Möller, U. Rodewald, E.-U. Würthwein, *Liebigs Ann.* **1995**, 1015−1025.

[5] B. Gimarc, *J. Am. Chem. Soc.* **1983**, *105*, 1979−1984.

[6] K. L. Habermas, S. E. Denmark, T. K. Jones, *Org. React.* **1994**, *54*, 1−158.

[7] D. A. Smith, C. W. Ulmer, II, *J. Org. Chem.* **1997**, *62*, 5110−5115.

[8] T. S. Sorensen in: G. A. Olah *Carbonium Ions* (Ed.: P. v. R. Schleyer), **1970**, vol. 2, §19, p. 807−835.

[9] E. A. Kallel, K. N. Houk, *J. Org. Chem.* **1989**, *54*, 6006−6008.

[10] L. M. Pratt, A. Streitwieser, *J. Org. Chem.* **2000**, *65*, 290−294.

[11] The AM1-HOMOs of **1a, 2b**, and **4b** correspond to lone pairs at the heteroatoms.

[12] Full AM1 geometry optimizations of **2a** and **4a** produce non-planar structures with perpendicular conformations of the C=O groups, which is in contrast to the DFT results (see Table 2).

[13] MOPAC93: J. J. P. Stewart, Fujitsu Limited, Tokyo, Japan, **1993**.

[14] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, *Gaussian98, Revision A.6*, Gaussian, Inc., Pittsburgh, PA, **1998**, and earlier versions of this program.

[15] E.-U. Würthwein, *J. Org. Chem.* **1984**, *49*, 2971−2978.

[16] D. Bonnet-Delpon, M. Charpentier-Morize, *Chem. Phys. Lett.* **1985**, *116*, 478−481.

[17] D. Alickmann, R. Fröhlich, E.-U. Würthwein, *Org. Lett.* **2001**, *3*, 1527–1530.

[18] B. M. Trost, E. Keinan, *J. Org. Chem.* **1980**, *45*, 2741–2746.

[19] S. Vettel, C. Lutz, A. Diefenbach, G. Haderlein, S. Hammerschmidt, K. Kühling, M.-R. Mofid, T. Zimmermann, P. Knochel, *Tetrahedron: Asymmetry* **1997**, *8*, 779–800.

[20] L. Shi, W. Xia, J. Yang, X. Wen, Y. Huang, *Tetrahedron Lett.* **1987**, *28*, 2155–2158.

[21] Y. Huang, L. Shi, J. Yang, *Tetrahedron Lett.* **1985**, *26*, 6447–6448.

[22] Y. Huang, L. Shi, J. Yang, *J. Org. Chem.* **1987**, *52*, 3558–3560.

[23] Z.-H. Peng, Y.-L. Li, W.-L. Wu, C.-X. Liu, Y.-L. Wu, *J. Chem. Soc., Perkin Trans. 1* **1996**, 1057–1066.

[24] B. M. Trost, *Angew. Chem.* **1989**, *101*, 1199–1219.

[25] S. Klötgen, E.-U. Würthwein, *Tetrahedron Lett.* **1995**, *36*, 7065–7068.

[26] S. Klötgen, R. Fröhlich, E.-U. Würthwein, *Tetrahedron* **1996**, *52*, 14801–14812.

[27] W. S. Johnson, J. S. Belew, L. J. Chinn, R. H. Hunt, *J. Am. Chem. Soc.* **1953**, *75*, 4995–5001.

[28] B. D. Kulkarni, A. S. Rao, *Synthesis* **1976**, 454–455.

[29] CCDC-169310 (**21**), -169311 (**38b**), -169309 (**39**), and -165936 (**40a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

[30] I. Gosney, D. Lloyd, *Tetrahedron* **1973**, *29*, 1697–1710.

[31] J. B. Baudin, S. A. Julia, R. Lorne, *Bull. Soc. Chim. Fr.* **1992**, *129*, 440–456.

[32] G. Aksnes, J. Songstad, *Acta Chem. Scand.* **1964**, *18*, 655–661.

[33] S. P. Tanis, M. V. Deaton, L. A. Dixon, M. C. McMills, J. W. Raggon, M. A. Collins, *J. Org. Chem.* **1998**, *63*, 6914–6928.

[34] Z. G. Hajos, M. P. Wachter, H. M. Werblood, *Synth. Commun.* **1989**, *19*, 3295–3300.

[35] B. Hofmann, H.-U. Reißig, *Chem. Ber.* **1994**, *127*, 2327–2335.

[36] N. D. Obushak, N. I. Ganushchak, A. I. Lesyuk, L. M. Dzikovskaya, P. P. Kisilitsa, *J. Org. Chem. USSR (Engl. Transl.)* **1990**, *26*, 748–753.

[37] A. Ishida, T. Mukaiyama, *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2077–2081.

[38] P. Allevi, M. Anastasia, F. Cajone, P. Ciuffreda, A. M. Sanvito, *J. Org. Chem.* **1993**, *58*, 5000–5002.

[39] H. Aoyama, *J. Chem. Soc., Perkin Trans. 1* **1997**, 1851–1854.

[40] T. Nishio, *Helv. Chim. Acta* **1998**, *81*, 1207–1214.

[41] J. V. Cooney, W. E. McEwen, *J. Org. Chem.* **1981**, *46*, 2570–2573.

[42] K. E. Schulte, J. Reisch, H. Walker, *Chem. Ber.* **1965**, *98*, 98–103.

[43] F. F. Blicke, J. A. Faust, *J. Am. Chem. Soc.* **1954**, *76*, 3156–3159.

[44] A. R. Katritzky, J. Li, M. F. Gordeev, *J. Org. Chem.* **1993**, *58*, 3038–3041.

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