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Electrophilicities of Symmetrically Substituted 1,3-Diarylallyl Cations

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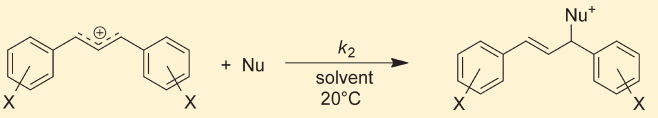
Supporting Information

ABSTRACT: Kinetics of the reactions of nine symmetrically substituted 1,3-diarylallyl cations with different nucleophiles were studied photometrically in dichloromethane, acetonitrile, and DMSO solutions. The second-order rate constants k_2 were found to follow the correlation log $k_2 = s_N(N + E)$. The electrophilicity parameters E of the title cations were derived, using the known values of s_N and N of the nucleophilic reaction partners, and compared with the electrophilicities of analogously substituted benzhydrylium ions. Good linear correlations were found between the electrophilicities E and the quantum chemically calculated gas-phase methyl anion affinities of the allyl cations and the σ^+ constants of the substituents X.



INTRODUCTION

Nucleophilic substitutions of allyl derivatives not only give products where the nucleofuge is directly displaced by the nucleophile but also may proceed with allylic rearrangement.[1] While concerted S_N2' reactions are rare or do not exist,[2] allylic rearrangements via addition−elimination reactions are well-established.[3] Of particular interest are allylic rearrangements via intermediate allyl cations, i.e., S_N1 reactions. Because of the possibility of internal return at both termini of the allylic system, allyl solvolyses provide detailed information on the nature of ion pairs, which cannot be derived from solvolyses of other S_N1 substrates.

Goering's pioneering studies on the solvolyses of optically active allyl derivatives using titrimetric, polarimetric, and isotope exchange methods made it possible to differentiate various steps of the multistep solvolytic processes.[4] However, a comprehensive model, which explains the mechanistic changes caused by structural modifications of the substrates and the solvent, remained elusive.

In recent work, we have demonstrated that knowledge of the absolute rate constants for the reactions of carbocations with leaving groups (ion recombination) and other nucleophiles (e.g., solvents) allows one not only to predict whether solvolyses will proceed with or without common ion return[5] but also to define the border between S_N1 and S_N2 mechanisms.[6] Key to these analyses was the linear free energy relationship (eq 1), where E is an electrophilicity parameter, N is a nucleophilicity parameter, and s_N is a nucleophile-specific sensitivity parameter (previously termed s).[7]

$$\log k_2(20\ ^\circ\mathrm{C}) = s_N(N + E) \quad (1)$$

By defining diarylmethyl (benzhydryl) cations and a set of C-nucleophiles as reference compounds, we have succeeded in arranging a large variety of electrophiles and nucleophiles in electrophilicity and nucleophilicity scales.[8−10]

We have now studied the reactions of nine symmetrically substituted 1,3-diarylallyl cations **1(a−i)** with nucleophiles **2(a−u)** in order to derive the electrophilicity parameters E of these carbocations, which we will employ in subsequent work for elucidating solvolysis mechanisms[4] of allyl derivatives and for investigating the effect of palladium coordination in the intermediates of Tsuji−Trost reactions.[11] The resulting E parameters can also be used for designing new synthetic procedures as well as for better understanding of known reactions via intermediate 1,3-diarylallyl cations, e.g., catalytic S_N1-type reactions of alcohols, which are relevant for designing environmentally benign processes.[12]

RESULTS AND DISCUSSION

Synthesis of 1,3-Diarylallyl Cations 1(a−i). Cations **1(a−f)** cannot be stored as stable salts; they were generated in solution either by treatment of the corresponding chlorides **1-Cl** or trimethylsilyl ethers **1-OTMS** with Lewis acids or by laser-flash photolysis of the corresponding phosphonium salts **1-$PPh_3^+BF_4^-$** or **1-$PPh_3^+TfO^-$** as illustrated in Scheme 1.[13] The diarylallyl tetrafluoroborates **1(g−i)-BF_4** were obtained as stable salts by treatment of the corresponding alcohols **1(g−i)-OH** with $HBF_4 \cdot OEt_2$ or AcOH/$NaBF_4$ as described in the Experimental Section. All allyl cations **1(a−i)** were characterized by UV−vis spectroscopy (Table 1).

As shown in Supplementary Figure SX1 of the Supporting Information, the UV−vis spectrum of cation **1e**, generated photolytically from (*E*)-(1,3-diphenylallyl)triphenylphosphonium triflate in dichloromethane, was identical to that of **1e**, generated from (*E*)-((1,3-diphenylallyl)oxy)trimethylsilane and trimethylsilyl triflate in the same solvent.

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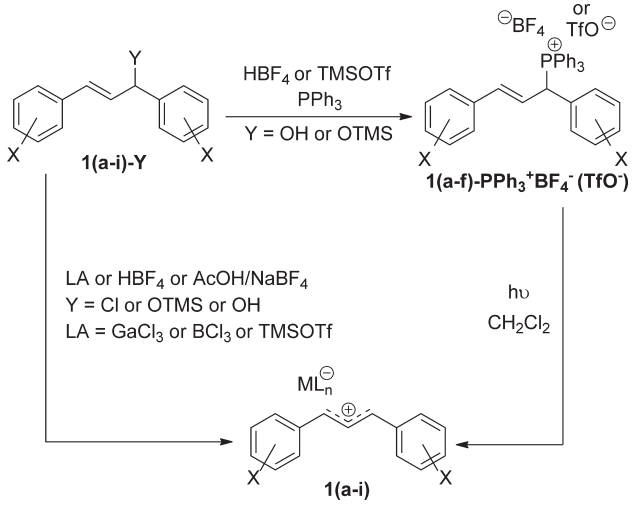
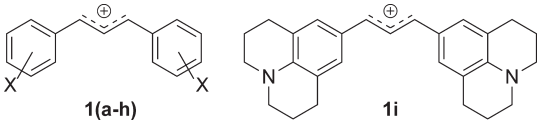
Scheme 1. Generation of Allyl Cations 1(a−i)[a]



[a] For definition of X see Table 1.

Table 1. Cations 1(a−i) and Their UV−vis Maxima in Different Solvents



	X	conditions	λ_{max}/nm	log ε
1a	*m,m*-F_2	**1a-OH**/conc H_2SO_4	496	
1b	*m*-F	**1b-OH**/conc H_2SO_4	500	
1c	*p*-Br	**1c-Cl**/$GaCl_3$/CH_2Cl_2	551	∼5.16
		1c-OH/conc H_2SO_4	527	
1d	*p*-Cl	**1d-OH**/AcOH	530	
1e	H	**1e-OTMS**/TMSOTf/CH_2Cl_2	503	5.16
		1e-OH/AcOH	488	
1f	*p*-Me	**1f-OTMS**/TMSOTf/CH_2Cl_2	532	5.25
1g	*p*-OMe	**1g-BF_4**/CH_2Cl_2	578	5.26
1h	*p*-NMe_2	**1h-BF_4**/CH_3CN	693	5.31
		1h-BF_4/CH_2Cl_2	704	
1i	jul[a]	**1i-BF_4**/CH_3CN	730	5.34
		1i-BF_4/CH_2Cl_2	740	

[a] For structure, see heading of this table.

In addition, the stable cations **1(g−i)** were identified by NMR spectroscopy and HRMS (see Experimental Section). ^{1}H NMR spectra of **1h-BF_4** taken at different temperatures allow determination of the barrier of rotation around the C2−C3 bond in the allyl cation **1h** (Figure 1). From the coalescence temperature[14] of H^a and $H^{a\prime}$ at −10 °C and for H^b and $H^{b\prime}$ at −20 °C, one derives rotational barriers of 50.5 ± 2 and 52 ± 2 kJmol^{-1}, respectively. The structure of **1h-BF_4** was also confirmed by X-ray analysis.[15]

Product Studies. As the nature of the reaction products can be expected not to depend on the substituents X of the aryl groups of **1(a−i)**, product studies were performed with only one representative electrophile for each nucleophile.

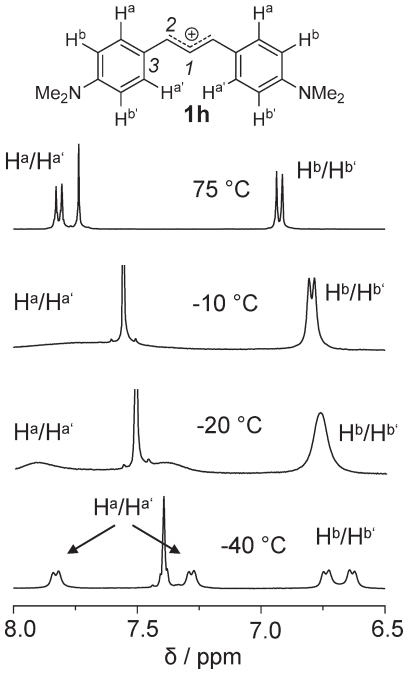
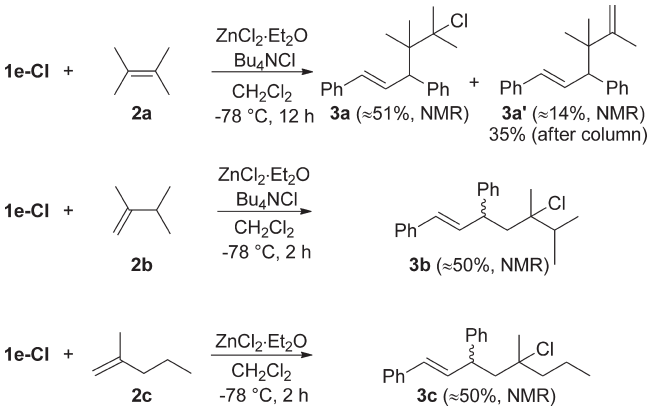


Figure 1. ^{1}H NMR spectra of **1h-BF_4** taken at different temperatures.

Scheme 2



The zinc chloride catalyzed reaction of 2,3-dimethylbut-2-ene (**2a**) with **1e-Cl** provided a complex product mixture, which was not identified. When the reaction was carried out in the presence of tetrabutylammonium chloride, a mixture of only two products, (*E*)-(5-chloro-4,4,5-trimethylhex-1-ene-1,3-diyl)dibenzene (**3a**) and (*E*)-(4,4,5-trimethylhexa-1,5-diene-1,3-diyl)dibenzene (**3a′**), was formed (Scheme 2). Pure **3a′** (35% yield) was obtained by column chromatography of the crude product; as the isolated yield of **3a′** was higher than its content in the crude mixture, one can conclude that **3a** eliminates HCl on silica.

Under the same conditions, the reaction of **1e-Cl** with 2,3-dimethylbut-1-ene (**2b**) gave (*E*)-(5-chloro-5,6-dimethylhept-1-ene-1,3-diyl)dibenzene as a mixture of two diastereomers (dr ca. 1.4: 1, ^{1}H NMR) contaminated by small amounts of byproducts.

In the case of 2-methylpent-1-ene (**2c**), the addition of Bu_4NCl is not necessary, and the major product of the reaction with **1e-Cl** can be unambiguously identified as (*E*)-(5-chloro-5-methyloct-1-ene-1,3-diyl)dibenzene (**3c**, 1.4:1 mixture of two

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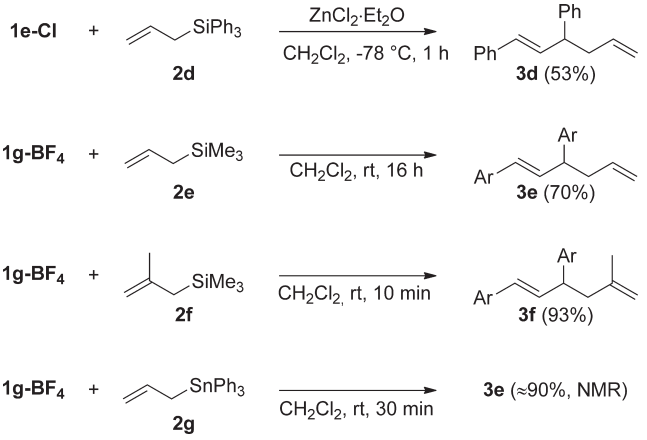
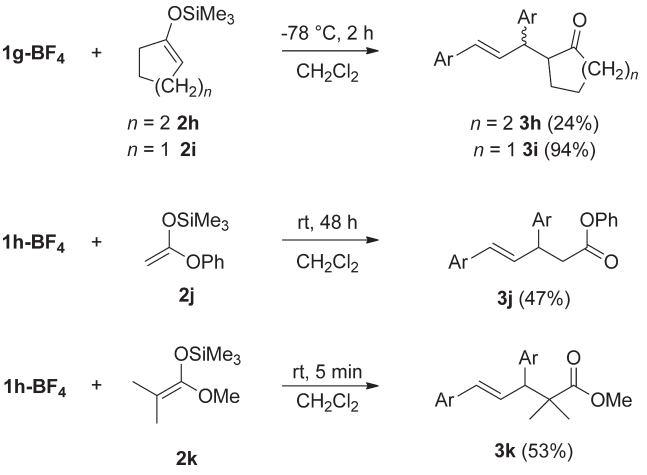
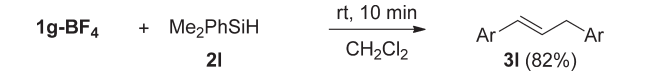
Scheme 3



Scheme 4



Scheme 5



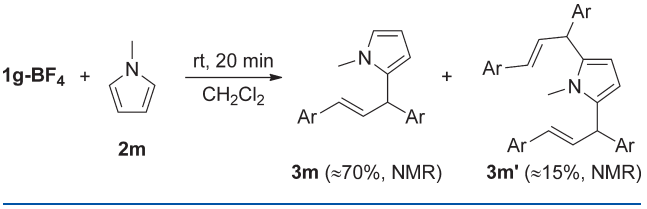
diastereomers, ^{1}H NMR). Additional signals between δ 4.5 and 6.0 ppm in the ^{1}H NMR spectrum indicate the formation of dienes, which may be produced via proton elimination from the intermediate carbocation.

The combinations of allylsilanes **2**(**d**−**f**) and of allyltriphenylstannane (**2g**) with **1e** or **1g** afforded the S_E2' products **3**(**d**−**f**) with moderate to good yields (Scheme 3). Similar results were previously reported for the reaction of **1e-OH** with **2e** under polymer-supported Brønsted acid catalysis.[16]

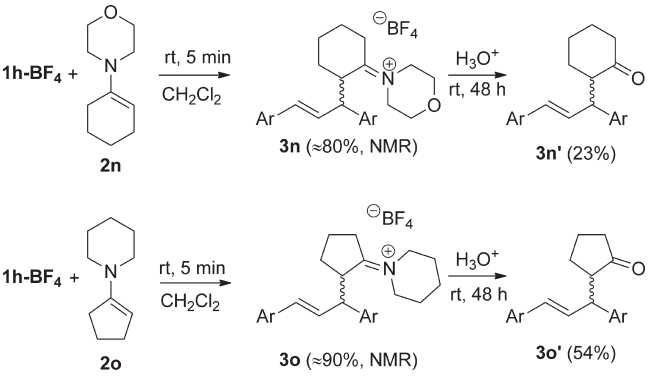
Silyl enol ethers and ketene acetals **2**(**h**−**k**) react with the allylium tetrafluoroborates **1g-BF$_4$** and **1h-BF$_4$** to form the corresponding carbonyl compounds **3**(**h**−**k**) (Scheme 4). The low yield of the reaction of **1g-BF$_4$** with **2h** is probably due to decomposition of **3h** on the silica column, as the same phenomenon was also observed for the structurally analogous compound **3n**′ (see below). The substituted cyclic ketones **3h** and **3i** were formed as mixtures of diastereomers with dr of 1.3:1 and 1.9:1, respectively (based on the ^{1}H NMR spectra of the crude products).

Dimethylphenylsilane (**2l**) reduces **1g-BF$_4$** to yield 82% of (*E*)-4,4′-(prop-1-ene-1,3-diyl)bis(methoxybenzene) (**3l**, Scheme 5).

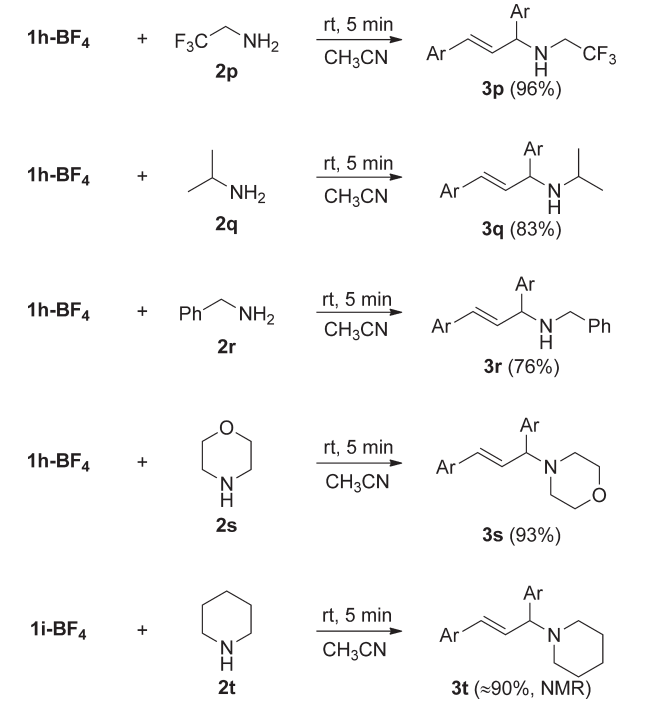
Scheme 6



Scheme 7



Scheme 8



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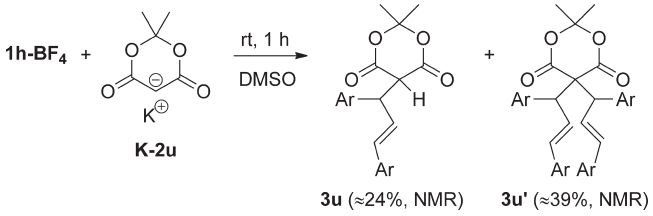
Scheme 9



Slow addition of a suspension of **1g-BF$_4$** in CH_2Cl_2 to 10 equiv of 1-methyl-1*H*-pyrrole (**2m**) leads to a 9:1 mixture of (*E*)-2-(1,3-bis(4-methoxyphenyl)allyl)-1-methyl-1*H*-pyrrole (**3m**) and 2,5-bis((*E*)-1,3-bis(4-methoxyphenyl)allyl)-1-methyl-1*H*-pyrrole (**3m′**) (Scheme 6). The formation of the disubstituted product **3m′** even in the presence of a high excess of **2m** can be explained by mixing control,[17] i.e., the diffusional separation of **3m** from the sparsely soluble crystals of **1g-BF$_4$** is slow compared with the reaction of **1g-BF$_4$** with **3m** ($k_2 > 10^5$ M^{-1} s^{-1}).

The enamines **2n** and **2o** react with the allylium tetrafluoroborate **1h-BF$_4$** to form the iminium salts **3(n,o)-BF$_4$** (characterized by NMR and HRMS) as mixtures of diastereomers (dr ca. 1.2:1, ^{1}H NMR); their hydrolysis with aqueous acetic acid affords (*E*)-2-(1,3-bis(4-(dimethylamino)phenyl)allyl)-cyclohexanone (**3n′**, 23%) and (*E*)-2-(1,3-bis(4-(dimethylamino)-phenyl)allyl)cyclopentanone (**3o′**, 54%) (Scheme 7). The low yield of **3n′** must be due to its partial decomposition on silica, as its precursor **3n** is formed almost quantitatively (^{1}H NMR).

Amines **2(p−t)** react with **1h-BF$_4$** and **1i-BF$_4$** to form (*E*)-1,3-diarylallylamines **3(p−t)** in good yields (Scheme 8).

The combination of **1h-BF$_4$** with 5 equiv of the potassium salt of Meldrum's acid (**K-2u**) affords (*E*)-5-(1,3-bis(4-(dimethylamino)phenyl)allyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (**3u**) and 5,5-bis((*E*)-1,3-bis(4-(dimethylamino)phenyl)allyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (**3u′**) in 24% and 39% yield, respectively (Scheme 9). Obviously, **3u** is deprotonated under the reaction conditions and then reacts with a second equivalent of **1h** to yield **3u′**. The formation of the double-alkylation product **3u′** indicates that the anion formed by deprotonation of **3u** is more reactive than **2u**. The bisadduct **3u′** is formed exclusively (85% yield of isolated **3u′**) when Meldrum's acid is combined with 2 equiv of **1h-BF$_4$** in the presence of 2 equiv of potassium *tert*-butoxide.

Kinetic Experiments. For the investigations of the reactivities of the carbenium ions **1(g−i)**, stock solutions of the isolated tetrafluoroborate salts were used; cations **1(a−f)** were generated in solution as described above. Most of the reactions were studied at 20 °C; in some cases the k_2 values for 20 °C were obtained from the Eyring activation parameters derived from a series of low-temperature measurements. All reactions were studied in those solvents to which the *N* and s_N parameters of the nucleophiles refer: π-nucleophiles in dichloromethane, amines in acetonitrile, and the carbanion **2u** in DMSO.

The rates were determined by monitoring the decays of the absorbances of the corresponding carbocations in the UV−vis spectra. In case of slow reactions ($\tau_{1/2} > 3$ s), conventional UV−vis spectrophotometry was used, fast reactions (20 ms < $\tau_{1/2}$ < 3 s) were followed with stopped-flow devices, and very fast reactions ($\tau_{1/2}$ < 1 ms) were investigated by generating the cations by laser-flash irradiation.[13]

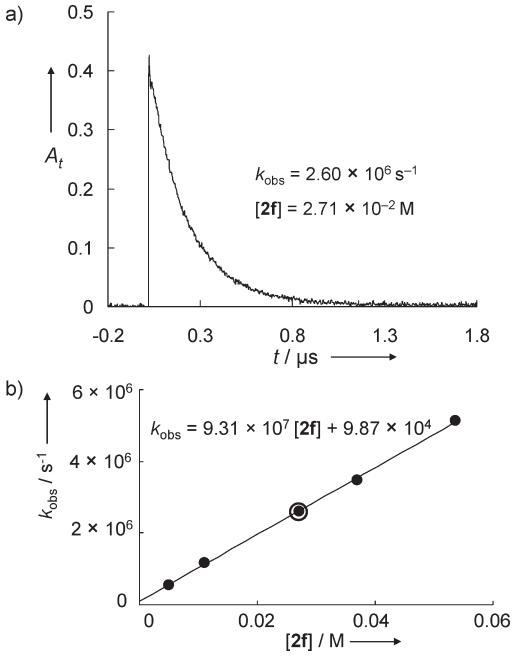


Figure 2. (a) Exponential decay of the absorbance A_t (λ = 500 nm) and (b) correlation between the pseudo-first-order rate constants k_{obs} and the concentration of **2f** for the reaction between (2-methylallyl)trimethylsilane (**2f**) and the cation **1b** generated by laser-flash photolysis from **1b-PPh$_3$$^+BF_4$$^-$** (dichloromethane, 20 °C).

All kinetics were performed under pseudo-first-order conditions using the nucleophiles in high excess, resulting in the monoexponential decays of the electrophiles' absorbances. The pseudo-first-order rate constants (k_{obs}) were obtained by least-squares fitting of the time-dependent absorbances (A_t) to the monoexponential function $A_t = A_0\ e^{-k_{obs}t} + C$ (Figure 2a). The plots of the k_{obs} values versus the nucleophile concentrations were linear (Figure 2b), and their slopes yielded the second-order rate constants (k_2), which are summarized in Table 2.

In order to examine whether the rate constants depend on the nature of the counterions, the reaction of **1e** with the cyclohexanone-derived silyl enol ether **2h** was studied with **1e-PPh$_3$$^+BF_4$$^-$** and **1e-PPh$_3$$^+TfO^-$** as precursors. The very small difference between the resulting rate constants $k_2(BF_4^-) = 6.41 \times 10^7$ M^{-1} s^{-1} and $k_2(TfO^-) = 6.57 \times 10^7$ M^{-1} s^{-1} confirms the independence of k_2 of the counterion, as previously found for analogous reactions with benzhydrylium ions.[18]

Determination of the Electrophilicity Parameters *E*. Figure 3 shows plots of (log k_2)/s_N versus *N* for the reactions of the allyl cations **1(a−i)** with the nucleophiles **2(a−u)**. Slopes of 1 were enforced in the drawn correlation lines, as required by eq 1. The electrophilicity parameters *E* (Table 2) of the cations **1(a−i)** were calculated by minimizing the sum of the squared deviations $\Delta^2 = \Sigma(\log k_2 - s_N(N + E))^2$ using the nonlinear solver "What's Best!".[19] The good correlations shown in Figure 3, which include rate constants determined in different solvents, confirm that in 1,3-diarylallyl cations, as in benzhydrylium ions, differential solvation of the carbocations is negligible, which allows us to use the same electrophilicity parameters *E* in different solvents. As explicitly explained in ref 7, the solvent effects on the rate constants are fully incorporated in the nucleophile-specific parameters *N* and s_N.

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Table 2. Second-Order Rate Constants for the Reactions of 1,3-Diarylallylium Ions 1(a−i) and Nucleophiles 2(a−u) at 20 °C

1,3-diarylallylium ion	generation of **1(a−i)**	E^a	nucleophile/solvent	N, $s_N{}^a$	k_2/M^{-1} s^{-1}	$k_{calc}{}^a$/M^{-1} s^{-1}	k_2/k_{calc}
1a (X = *m,m*-F_2)	*b*	6.11	**2a**/CH_2Cl_2	−1.00, 1.40	3.56×10^7	1.41×10^7	2.52
	b		**2b**/CH_2Cl_2	0.54, 1.00	1.98×10^6	4.43×10^6	0.45
	b		**2c**/CH_2Cl_2	0.96, 1.00	9.11×10^6	1.16×10^7	0.78
	b		**2e**/CH_2Cl_2	1.79, 0.94	2.03×10^7	2.64×10^7	0.77
	b		**2f**/CH_2Cl_2	4.41, 0.96	5.88×10^{8c}	*d*	
	b		**2h**/CH_2Cl_2	5.21, 1.00	1.06×10^{9c}	*d*	
1b (X = *m*-F)	*b*	4.15	**2e**/CH_2Cl_2	1.79, 0.94	6.99×10^5	3.86×10^5	1.81
	b		**2f**/CH_2Cl_2	4.41, 0.96	9.31×10^7	1.66×10^8	0.56
1c (X = *p*-Br)	*e*	2.85	**2d**/CH_2Cl_2	−0.13, 1.21	2.93×10^{3f}	1.98×10^3	1.48
	g		**2f**/CH_2Cl_2	4.41, 0.96	8.65×10^6	9.43×10^6	0.92
	g		**2h**/CH_2Cl_2	5.21, 1.00	7.86×10^7	1.16×10^8	0.68
1d (X = *p*-Cl)	*b*	2.69	**2f**/CH_2Cl_2	4.41, 0.96	6.57×10^6		
1e (X = H)	*h*	2.70	**2c**/CH_2Cl_2	0.96, 1.00	2.88×10^{3f}	4.59×10^3	0.63
	h		**2d**/CH_2Cl_2	−0.13, 1.21	2.53×10^{3f}	1.29×10^3	1.96
	g		**2f**/CH_2Cl_2	4.41, 0.96	5.94×10^6	6.71×10^6	0.88
	b		**2h**/CH_2Cl_2	5.21, 1.00	6.41×10^{7b}	8.15×10^7	0.79
	g		**2h**/CH_2Cl_2	5.21, 1.00	6.54×10^{7g}	8.15×10^7	0.80
1f (X = *p*-Me)	*h*	1.23	**2c**/CH_2Cl_2	0.96, 1.00	5.01×10^1	1.54×10^2	0.33
	h		**2d**/CH_2Cl_2	−0.13, 1.21	4.98×10^1	2.12×10^1	2.35
	h		**2e**/CH_2Cl_2	1.79, 0.94	5.03×10^{2f}	6.85×10^2	0.73
	b		**2f**/CH_2Cl_2	4.41, 0.96	2.24×10^5	2.58×10^5	0.87
	b		**2h**/CH_2Cl_2	5.21, 1.00	4.56×10^6	2.73×10^6	1.67
1g (X = *p*-OMe)	*i*	−1.45	**2e**/CH_2Cl_2	1.79, 0.94	6.68×10^{-1}	2.08	0.32
	i		**2f**/CH_2Cl_2	4.41, 0.96	5.53×10^2	6.90×10^2	0.80
	i		**2g**/CH_2Cl_2	3.09, 0.90	3.69×10^1	2.98×10^1	1.24
	i		**2h**/CH_2Cl_2	5.21, 1.00	6.15×10^3	5.72×10^3	1.08
	i		**2i**/CH_2Cl_2	6.57, 0.93	1.13×10^5	5.74×10^4	1.97
	i		**2l**/CH_2Cl_2	3.27, 0.73	4.94^c	2.12×10^1	0.23
	j		**2m**/CH_2Cl_2	5.85, 1.03	4.91×10^4	3.38×10^4	1.45
1h (X = *p*-NMe_2)	*i*	−7.50	**2i**/CH_2Cl_2	6.57, 0.93	7.82×10^{-2}	1.37×10^{-1}	0.57
	i		**2j**/CH_2Cl_2	8.23, 0.81	1.88	3.90	0.48
	i		**2k**/CH_2Cl_2	9.00, 0.98	1.10×10^2	2.95×10^1	3.73
	i		**2n**/CH_2Cl_2	11.40, 0.83	8.51×10^{3c}	1.73×10^3	4.93
	i		**2p**/CH_3CN	10.13, 0.75	1.29×10^2	9.39×10^1	1.37
	i		**2r**/CH_3CN	14.29, 0.67	2.22×10^4	3.54×10^4	0.63
	i		**2s**/CH_3CN	15.65, 0.74	9.34×10^5	1.07×10^6	0.87
1i (X = jul) [k]	*i*	−9.78	**2o**/CH_2Cl_2	15.06, 0.82	8.30×10^{4c}	2.14×10^4	3.88
	i		**2q**/CH_3CN	13.77, 0.70	4.67×10^2	6.22×10^2	0.75
	i		**2s**/CH_3CN	15.65, 0.74	2.85×10^4	2.21×10^4	1.29
	i		**2t**/CH_3CN	17.35, 0.68	1.54×10^5	1.41×10^5	1.09
	i		**2u**/DMSO	13.91, 0.86	3.38×10^3	3.57×10^3	0.95

[a] The E parameters for **1(a−i)** result from the least-squares minimization of $\Delta^2 = \Sigma(\log k_2 - s_N(N+E))^2$, which uses the second-order rate constants k_2 (this table) and the N and s_N parameters of the nucleophiles **2(a−u)** given in ref 10 and listed in this table. E values with more decimals than given in this table were used for the calculation of k_{calc} by eq 1 and for the correlations in Figures 5, 7, and 9. The use of E parameters given in this table leads to slightly deviating results. [b] Laser-flash photolysis of **1-PPh$_3$$^+BF_4$$^-$**. [c] Values were not used for determination of E. [d] Diffusion limit approached. [e] From **1-Cl** and $GaCl_3$. [f] Extrapolated from rate constants at lower temperature by using the Eyring equation (for details see the Supporting Information). [g] Laser-flash photolysis of **1-PPh$_3$$^+TfO^-$**. [h] From **1-OTMS** and TMSOTf, BCl_3, or $GaCl_3$. [i] Isolated tetrafluoroborate salt (**1-BF$_4$**). [j] From **1g-OMe** and TMSOTf. [k] See Table 1 for definition.

Though the three-parameter eq 1, which can be employed to predict absolute rate constants in a reactivity range of 40 orders of magnitude can only be expected to be reliable within a factor of 10−100,[8a] some systematic deviations within this range shown in Figure 3 prompt us also to comment on their possible origin.

In the combinations of **1a** with **2f** and **2h** the diffusion limit is approached; therefore the k_2 values of these reactions were not used for the determination of E.

Dimethylphenylsilane (**2l**) reacts with the (*E*)-1,3-bis(4-methoxyphenyl)allyl cation (**1g**) 4.3 times more slowly than

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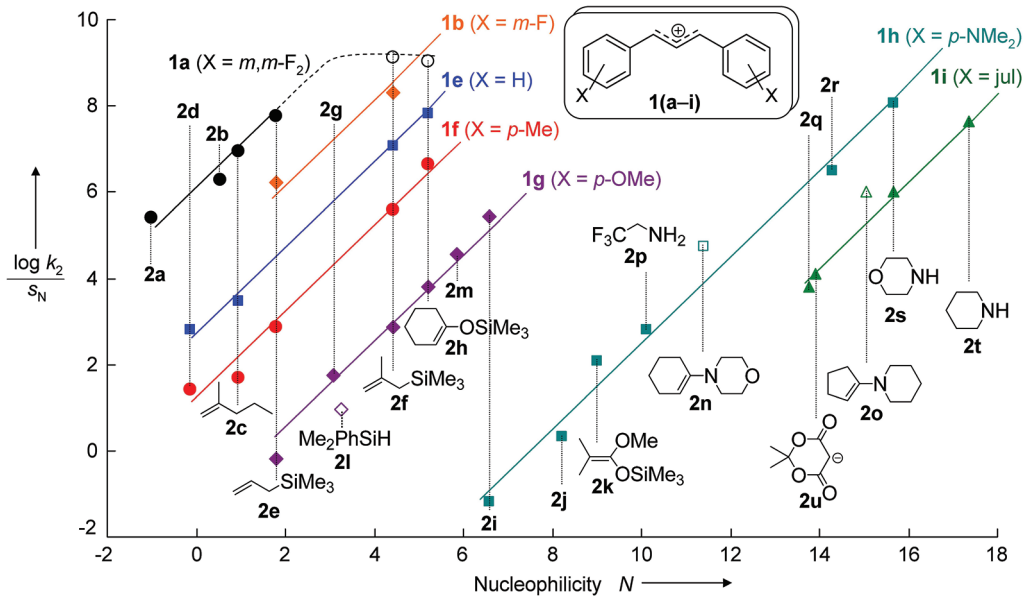

Figure 3. Plot of $(\log k_2)/s_N$ versus N for the reactions of the 1,3-diarylallyl cations **1(a–i)** with the nucleophiles **2(a–u)** (solvents are specified in Table 2). The data points shown with open symbols were not used for the determination of E (see text). The data for cations **1(c–d)** are omitted for clarity.

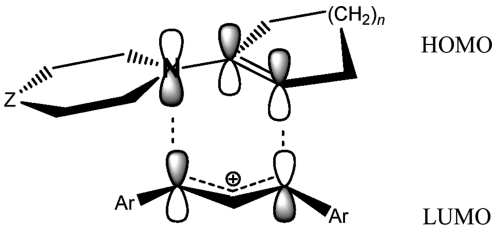

Figure 4. Weak transition state stabilization in reactions between enamines and 1,3-diarylallyl cations.

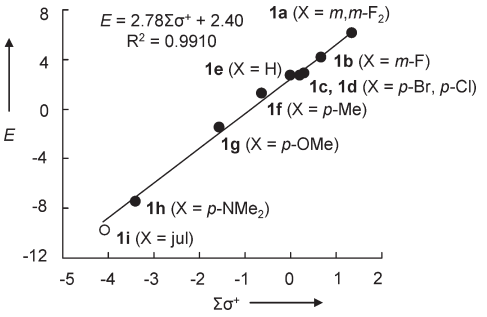

Figure 5. Correlation of the electrophilicity parameters E of the carbocations **1(a–i)** with the sum of the σ^+ parameters[25] of the corresponding aryl substituents. Open symbol: **1i** is not included in the correlation, as σ^+ for the julolidyl moiety of **1i** was estimated from the electrophilicities of benzhydrylium ions.[8a]

calculated by eq 1 from the E parameter of **1g** (derived from its reactions with carbon nucleophiles) and the N and s_N parameters of **2l**, which were derived from its reactions with benzhydrylium ions. Similar trends were observed for the reactions of hydride donors with tropylium[20] and 1,1,3-triarylallylium ions.[21] Obviously, hydride donors react generally faster with benzhydrylium ions than with more highly delocalized carbocations.

The amino-substituted allyl cations **1h** and **1i** react with the enamines **2n** and **2o** about 4.5 times faster than expected from their E parameters. Possibly, interaction of the nitrogen lone-pair with the other allyl terminus, comparable to the transition state of the aza-Claisen rearrangement,[22] accounts for the slightly increased reactivity of the enamines (Figure 4).

These deviations are quite moderate, however, so that the inclusion of the rate constants in the least-squares minimization mentioned above would not significantly change the E parameters derived for the 1,3-diarylallyl cations.

Because of the low thermodynamic driving force of the reaction of **1h** with 2,2,2-trifluoroethylamine (**2p**), the nucleophile had to be used in very high excess (over 5000 equiv). Under such conditions, the kinetics may be affected by traces of impurities present in the reagent. However, the good fit of this rate constant to the correlation line indicates the reliability of the value determined in this way.

The relevance of the electrophilicity parameters listed in Table 2 for predicting reaction rates can be examined by comparison with independently determined rate constants. Miranda, Scaiano, and co-workers[23] reported rate constants of the reactions of cation **1e** with a series of nucleophiles, two of which have been characterized by N and s_N. Substitution of E(**1e**) = 2.70 (Table 2) and N = 1.23, s_N = 0.92 for 2,2,2-trifluoroethanol[24] and N = 10.3, s_N = 0.60 for Cl^- in trifluoroethanol[5a] in eq 1 yield k_{calc}(trifluoroethanol) = 4.1×10^3 s^{-1} and k_{calc} (Cl^- in trifluoroethanol) = 6.3×10^7 M^{-1} s^{-1}, respectively. As these numbers agree within factors 1.9 and 3.5 with the experimental data reported in Table 1 of ref 23 (8.0×10^3 s^{-1} and 2.2×10^8 M^{-1} s^{-1}, respectively), the applicability of electrophilicity parameters E derived in this work has been demonstrated.

Figure 5 shows the correlation between the E parameters of **1(a–i)** and Hammett-Brown's σ^+ (σ_m in case of F) parameters[25] of the corresponding substituents. The quality of this correlation is comparable to that for benzhydrylium ions.[8a]

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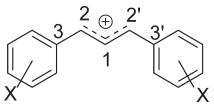
Table 3. Characteristic Bond Lengths Between Aromatic and Allylic Carbons in the 1,3-Diarylallyl Cations 1(a−i) Optimized at the B3LYP/6-31G(d,p) Level of Theory and $\Sigma\sigma^+$ ($\Sigma\sigma_m$) of the Corresponding Substituents



cation	X	$\Sigma\sigma^{+a}$	$r_{C2-C3}{}^b$/Å	$r_{C1-C2}{}^b$/Å
1a	*m,m*-F_2	1.36[c]	1.428	1.39022
1b	*m*-F	0.68[c]	1.427	1.39037
1c	*p*-Br	0.30	1.424	1.39087
1d	*p*-Cl	0.22	1.424	1.39090
1e	H	0.00	1.425	1.39067
1f	*p*-Me	−0.62	1.423	1.39089
1g	*p*-OMe	−1.56	1.419	1.39134
1h	*p*-NMe_2	−3.40	1.415	1.39192
1i	jul	−4.06[d]	1.414	1.39219

[a] From ref 25. [b] Values of *r* with more decimals than given in the table were used for the correlations in Figure 6 and Figure SX2 in Supporting Information. The use of the bond lengths given in this table leads to slightly deviating results. [c] σ_m. [d] Estimated value from ref 8a.

Quantum Chemical Calculations. It has been shown[9a] that the electrophilicities *E* of differently substituted benzhydryl cations correlate well with their methyl anion affinities calculated at the B3LYP/6-31G(d,p) level of theory. Thus, it was of interest to examine the analogous correlation for 1,3-diarylallyl cations. As recent work has shown the higher reliability of the MP2 method for such comparisons,[26] the methyl anion affinities (eq 2) of the cations **1(a−i)** have now been calculated at the MP2(FC)/6-31+G(2d,p)//B3LYP/6-31G(d,p) level of theory.[27]

(2)

The geometrical parameters listed in Table 3 refer to the most stable conformers of diarylallyl cations **1(a−i)**. In contrast to benzhydryl[9a] and trityl cations,[27] the calculated structures for **1(a−i)** are completely planar (all dihedral angles between ring and allyl carbons and hydrogens deviate by less than 1.5° from 0° or 180°), in line with the X-ray analysis of **1h-BF$_4$**.[15]

Table 3 shows that the C2−C3 bond lengths (r_{C2-C3} = $r_{C2'-C3'}$) of the cations **1(a−i)** decrease, while the C1−C2 bond lengths (r_{C1-C2} = $r_{C1-C2'}$) increase with higher electron-donating ability of the substituents. Figure 6 depicts linear correlations of the bond lengths r_{C2-C3} and r_{C1-C2} with Hammett-Brown's σ^+ parameters of the corresponding substituents (σ_m in case of F).[8a,25] From the significantly higher absolute value of the slope in Figure 6a compared with that in Figure 6b one can derive that substituent variation affects the bonds of the allylic termini to the aryl rings much more than the bond lengths in the allylic fragment. The strong double-bond character of the C2−C3 bond in the 1,3-diarylallyl cations **1** is also reflected by the high rotational barrier (51 ± 2 kJ mol^{-1}) for **1h** derived by dynamic NMR spectroscopy (see above).

The bond lengths in the crystal structure of **1h-BF$_4$**[15] are slightly smaller than those calculated for the gas phase (Figure SX2 in the Supporting Information).

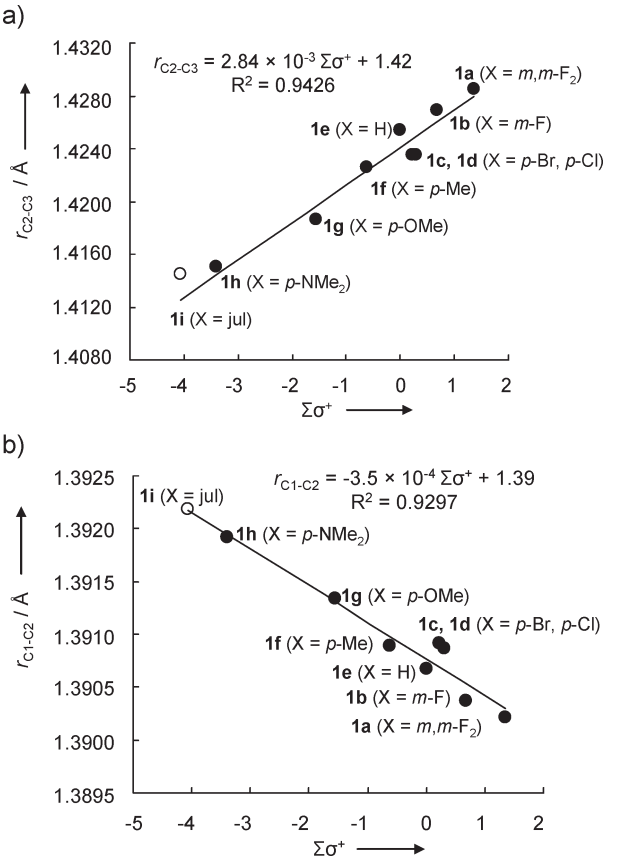


Figure 6. Correlation of the bond lengths (a) r_{C2-C3} and (b) r_{C1-C2} in cations **1(a−i)** with the sum of the σ^+ parameters of the corresponding substituents.[8a,25]

Details of the determinations of the gas-phase methyl anion affinities (ΔH_{298}, ΔG_{298}, Table 4) defined by eq 2 are given on pages S21−S29 of the Supporting Information. Single point calculations were performed at the MP2(FC)/6-31+G(2d,p) level of theory for all allyl cations **1(a−i)** and the corresponding methyl anion adducts **1(a−i)-Me** using the geometries optimized at the B3LYP/6-31G(d,p) level. The resulting MP2 energies were converted to H_{298} and G_{298} using the thermochemical corrections calculated with B3LYP/6-31G(d,p). As cations **1b**, **1g**, and **1i** as well as all (*E*)-1,3-diarylbut-1-enes **1(a−i)-Me** have several minima in the conformational space, the Boltzmann distribution was used to calculate their averaged energies.

As expected, the absolute values of ΔH_{298} and ΔG_{298} decrease with increasing electron donating ability of the substituents. Both ΔH_{298} and ΔG_{298} correlate linearly with the sum of the σ^+ parameters of the corresponding substituents[8a,25] (Figure SX3 in the Supporting Information).

The correlation between the electrophilicity parameters *E* of the allyl cations **1(a−i)** and their ΔH_{298} values (Figure 7) shows that quantum chemically calculated methyl anion affinities can be used for deriving *E* parameters of further 1,3-diarylallyl cations.

The correlation in eq 3

$$\delta E = -0.0769\delta\Delta H_{298} \quad (3)$$

(δ describes the effect of a substituent), which is derived from Figure 7, can be transformed into the relationship (eq 4)

$$\delta\Delta G^{\ddagger} = 0.432 s_N \delta\Delta H_{298} \quad (4)$$

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Table 4. Gas-Phase Methyl Anion Affinities (ΔH_{298}, ΔG_{298} of eq 2) in kJ mol^{-1} Calculated at MP2(FC)/6-31+G(2d,p)//B3LYP/6-31G(d,p)[a]

cation	X	ΔH_{298}[b]	ΔG_{298}[b]
1a	*m*,*m*-F_2	−962.44	−976.53
1b	*m*-F	−931.19	−945.91
1c	*p*-Br	−912.92	−927.61
1d	*p*-Cl	−916.12	−930.84
1e	H	−901.07	−915.29
1f	*p*-Me	−877.42	−891.91
1g	*p*-OMe	−847.22	−861.40
1h	*p*-NMe_2	−782.87	−797.04
1i	jul	−753.03	−767.30

[a] Total energies and thermochemical corrections for the reactants and products can be found in the Supporting Information. [b] The values of ΔH_{298} and ΔG_{298} with more decimals than given in the table were used for the correlations in Figure 7 and Supplementary Figure SX3. The use of ΔH_{298} given in this table leads to slightly deviating results.

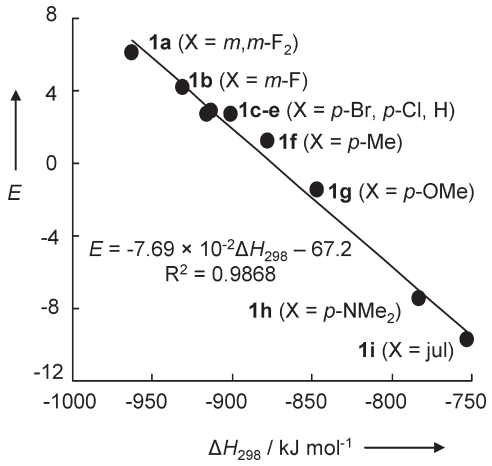


Figure 7. Correlation of the electrophilicities E of the cations **1**(**a**−**i**) with their gas-phase methyl anion affinities ΔH_{298} (calculated at MP2-(FC)/6-31+G(2d,p)//B3LYP/6-31G(d,p)).

by using eq 1 and the Eyring equation. If one assumes that the substituent effects on the diarylallyl cations in the gas phase ($\delta\Delta H_{298}$) are attenuated to 62% in dichloromethane solution, as previously shown for the analogous benzhydrylium ions,[9a] one can derive a Brønsted coefficient expressed in eq 5 by dividing the slope of eq 4 by 0.62.

$$\alpha = 0.70 s_N \qquad (5)$$

Details of this procedure have been described in ref 9a.

Comparison with Benzhydryl Cations. The reactivity range covered by 1,3-diarylallyl cations **1**(**a**−**i**) (16 orders of magnitude) is slightly smaller than that for analogously substituted diarylmethyl cations[8] (Figure 8). While amino-substituted 1,3-diarylallyl and diarylmethyl cations show almost identical electrophilicities, 1,3-diarylallyl cations substituted with weaker electron donors are increasingly less electrophilic than analogously substituted diarylmethyl cations.

As illustrated in Figure 9, the E parameters of 1,3-diarylallyl cations correlate linearly with those of analogously substituted

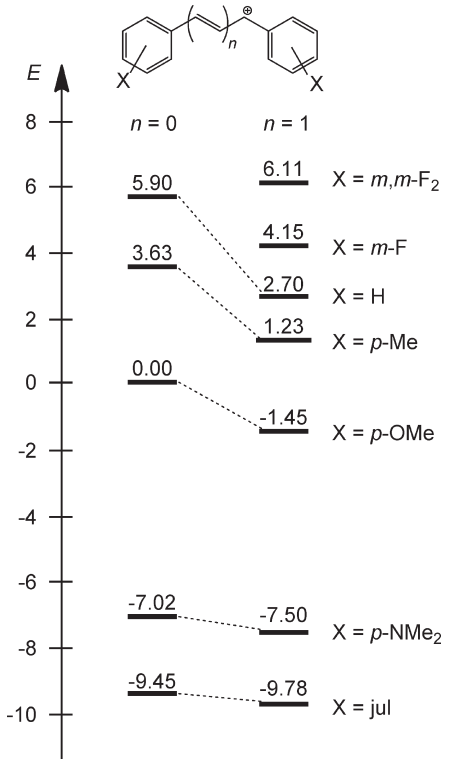


Figure 8. Electrophilicities E of the 1,3-diarylallyl cations (n = 1, from Table 2) compared with those of the corresponding benzhydrylium ions (n = 0).[8]

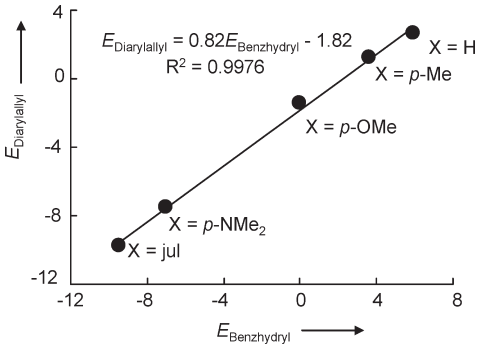


Figure 9. Linear correlation between the E parameters of analogously substituted 1,3-diarylallyl and benzhydryl cations (formula see Figure 8).

benzhydrylium ions (Figure 9). The slope of this correlation (0.82) reflects that the stabilization of 1,3-diarylallyl cations is less affected by the substituents at the aryl rings, which may be explained by the charge delocalization between C1 and C3 in diarylallyl cations, which reduces the electron demand of the carbenium centers.

CONCLUSIONS

The rate constants of the reactions of 1,3-diarylallyl cations **1**(**a**−**i**) with nucleophiles of a large structural variety can be described by the linear free-energy relationship log k_2(20 °C) = $s_N(N + E)$ (eq 1) using N and s_N parameters that have previously been derived from the reactions of the corresponding

nucleophiles with benzhydrylium ions.[8,10] The fact that the correlations used for the determination of the electrophilicity parameters E of **1(a−i)** include rate constants determined in different solvents (CH_2Cl_2, CH_3CN, DMSO) shows that the E parameters listed in Table 2 can be treated as solvent-independent. As pointed out previously,[7] this does not mean that all allyl cations **1(a−i)** are solvated to the same extent but that the solvent effects on these rate constants are fully taken account of in the solvent-dependent nucleophile-specific parameters N and s_N of their reaction partners. As the electrophilicity parameters E of **1(a−i)** correlate linearly with the quantum chemically calculated gas-phase methyl anion affinities of these cations and Hammett-Brown's substituent constants σ^+, these correlations may be employed to estimate reactivities of further 1,3-diarylallyl cations.

EXPERIMENTAL SECTION

Materials for Synthesis. Substituted acetophenones and benzaldehydes with the exception of fluorinated ones (synthesis described below) were purchased. The substituted chalcones (**1(a−g)-O**) and chalcols (**1(a−f)-OH**) were synthesized using the general procedures described below. Synthetic procedures have not been optimized for high yields.

Materials for Kinetic Measurements. Dichloromethane (p.a. grade) was subsequently treated with concentrated sulfuric acid, water, 10% $NaHCO_3$ solution, and again water. After predrying with anhydrous $CaCl_2$, it was freshly distilled over CaH_2. Acetonitrile (HPLC grade) and DMSO (99.7% purity) were used as received.

Gallium chloride was sublimed in a vacuum and stored under glovebox conditions (dry Ar atmosphere). Trimethylsilyl triflate was used as received.

NMR Spectroscopy. In the ^1H and ^{13}C NMR spectra chemical shifts are expressed in δ (ppm) and refer to $CDCl_3$ (δ_H 7.26, δ_C 77.0), CD_2Cl_2 (δ_H 5.32, δ_C 54.0), CD_3CN (δ_H 1.94, δ_C 1.39), nitrobenzene (δ_H 7.50, δ_C 148.1), or TMS (δ_H 0.00, δ_C 0.0) as internal standards. The coupling constants are given in Hz. Abbreviations used are s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). In the case of ^{13}C NMR spectra, these abbreviations refer to the multiplicity in proton-decoupled spectra, and hydrogen multiplicity (based on DEPT or HSQC experiments) is shown as CH_3, CH_2, CH, or C to avoid ambiguity.

3,5-Difluorobenzaldehyde. Prepared according to Olah's procedure:[28] To 1-bromo-3,5-difluorobenzene (28.9 g, 150 mmol) was slowly added a solution of *s*-BuMgCl·LiCl in THF (1.07 M, 140 mL, 150 mmol) to keep the temperature of the reaction mixture below 30 °C. The resulting reaction mixture was further stirred at room temperature. GC−MS analysis[28b] indicated full conversion after 3 h. The reaction mixture was then cooled to −40 °C before DMF (12.7 mL, 12.1 g, 165 mmol) was added dropwise. After the mixture stirred overnight at −40 °C, diethyl ether was added. The resulting mixture was successively washed with saturated ammonium chloride solution, water, and brine before it was dried ($MgSO_4$). Evaporation of solvents followed by distillation under vacuum (75 mbar, 90−110 °C) afforded 3,5-difluorobenzaldehyde (11.2 g, 78.8 mmol, 53%). The ^1H NMR spectrum of the product agreed with previously published data.[29]

3-Fluoroacetophenone. A small portion of 1-bromo-3-fluorobenzene was added to Mg turnings (1.67 g, 68.5 mmol) and LiCl (2.91 g, 68.5 mmol) in dry THF (35 mL). To initiate the reaction, DIBAL-H (1 M solution in hexane, 2.1 mL, 2.1 mmol) was added. After the exothermic process had started, the remaining portion of 1-bromo-3-fluorobenzene (12.0 g, 68.6 mmol in total) was added dropwise keeping the THF gently boiling. The reaction mixture was kept refluxing until full conversion of 1-bromo-3-fluorobenzene was reached (GC−MS monitoring analogous to the method described in ref 28b), then cooled to room temperature, and added to a suspension of $ZnCl_2$ (4.67 g, 34.3 mmol) in THF (15 mL). After stirring for 3 h, the resulting solution was added dropwise to a solution of acetyl chloride (5.38 g, 68.5 mmol) and $[Pd(PPh_3)_4]$ (50 mg, 0.042 mmol, 0.06 mol %) in diethyl ether (500 mL). Stirring was continued for 12 h before saturated aqueous NH_4Cl solution (250 mL) was added. The organic layer was separated, washed with water and brine, and dried ($MgSO_4$). Evaporation of solvents followed by distillation (75 mbar) afforded 3-fluoroacetophenone (4.18 g, 30.2 mmol, 44%) as a colorless liquid. The ^1H NMR spectrum agreed with literature data[30] but showed some impurities (probably owing to the product of $ZnCl_2$-catalyzed attack of acetyl chloride on THF).

3,5-Difluoroacetophenone. Synthesized analogously to 3-fluoroacetophenone from 1-bromo-3,5-difluorobenzene (24.6 g, 128 mmol), a solution of *s*-BuMgCl·LiCl in THF (1.07 M, 120 mL, 128 mmol), zinc chloride (8.70 g, 63.8 mmol), and acetyl chloride (9.2 mL, 10 g, 0.13 mol) to give 3,5-difluoroacetophenone (13.2 g, 84.2 mmol, 66%).

General Method for the Synthesis of (*E*)-1,3-Diarylprop-2-en-1-ones (1-O). According to Manolov's procedure,[31] substituted acetophenones (1 equiv) and benzaldehydes (1 equiv) were dissolved in ethanol (ca. 200 mL ethanol per mole substrate) before an 11% (w/w) aqueous NaOH solution was added (333 mL per mole acetophenone). The resulting mixtures were stirred until precipitates formed (usually after 2 h, otherwise the reaction mixtures were cooled with an ice bath for further 3 h), which were filtered and washed with water until the washing water reacted neutral. Recrystallization of crude products from ethanol gave (*E*)-1,3-diarylprop-2-en-1-ones in 64−88% yields.

(*E*)-1,3-Bis(3,5-difluorophenyl)prop-2-en-1-one (1a-O). From 3,5-difluoroacetophenone (7.18 g, 46.0 mmol) and 3,5-difluorobenzaldehyde (6.53 g, 46.0 mmol) in ethanol (10 mL) and 11% (w/w) aqueous NaOH solution (15 mL): 8.26 g (29.5 mmol, 64%), yellow needles (mp 159.0−160.1 °C). ^1H NMR ($CDCl_3$, 300 MHz): δ 6.89 (tt, $^2J_{HF}$ = 8.7, $^4J_{HH}$ = 2.3 Hz, 1 H, H_{Ar}), 7.06 (tt, $^2J_{HF}$ = 8.4, $^4J_{HH}$ = 2.4 Hz, 1 H, H_{Ar}), 7.11−7.20 (m, 2 H, H_{Ar}), 7.38 (d, $^3J_{HH}$ = 15.7 Hz, 1 H, ArCHC*H*COAr), 7.46−7.57 (m, 2 H, H_{Ar}), 7.72 (d, $^3J_{HH}$ = 15.7 Hz, 1 H, ArC*H*CHCOAr). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 106.1 (t, J_{CF} = 25.4 Hz, CH), 108.5 (t, J_{CF} = 25.4 Hz, CH), 110.9−111.7 (m, 2 × CH), 123.1 (CH), 137.6 (t, J_{CF} = 9.5 Hz, C), 140.6 (t, J_{CF} = 7.6 Hz, C), 143.4 (t, J_{CF} = 3.0 Hz, CH), 163.1 (dd, J_{CF} = 252, J_{CF} = 11.0 Hz, C), 163.3 (dd, J_{CF} = 250, J_{CF} = 12.7 Hz, C), 187.1 ppm (t, J_{CF} = 2.5 Hz, C). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −108.7 to −108.6 (m), −107.7 to −107.6 ppm (m). HRMS (EI; positive): calcd 280.0506 ($C_{15}H_8F_4O$), found 280.0505.

(*E*)-1,3-Bis(3-fluorophenyl)prop-2-en-1-one (1b-O). From 3-fluoroacetophenone (3.00 g, 21.7 mmol) and 3-fluorobenzaldehyde (2.70 g, 21.7 mmol) in ethanol (5 mL) and 11% (w/w) aqueous NaOH solution (7.5 mL): 3.85 g (15.7 mmol, 65% yield with correction for 10% impurities), yellow solid. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.09−7.17 (m, 1 H, H_{ar}), 7.26−7.53 (m, 5 H, H_{ar}) superimposed with 7.46 (d, $^3J_{HH}$ = 15.7 Hz, 1 H, ArCHC*H*COAr), 7.68−7.72 (m, 1 H, H_{ar}), 7.78 (d, $^3J_{HH}$ = 15.7 Hz, 1 H, ArC*H*CHCOAr) superimposed with 7.78−7.82 ppm (m, 1 H, H_{ar}); unknown impurities, which might be the products of the reaction between impurities in 3-fluoroacetophenone and some reagents used for the condensation reaction (NaOH etc.), caused additional resonances in the range of 2−6 ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 114.5 (d, J_{CF} = 21.9 Hz, CH), 115.3 (d, J_{CF} = 22.4 Hz, CH), 117.6 (d, J_{CF} = 21.5 Hz, CH), 120.0 (d, J_{CF} = 21.5 Hz, CH), 122.6 (CH), 124.2 (d, J_{CF} = 3.0 Hz, CH), 124.6 (d, J_{CF} = 2.9 Hz, CH), 130.3 (d, J_{CF} = 7.7 Hz, CH), 130.5 (d, J_{CF} = 8.3 Hz, CH), 136.9 (d, J_{CF} = 7.7 Hz, C), 140.0 (d, J_{CF} = 6.3 Hz, C), 144.0 (d, J_{CF} = 2.8 Hz, CH), 162.9 (d, J_{CF} = 248 Hz, C), 163.0 (d, J_{CF} = 247 Hz, C), 188.7 ppm (d, J_{CF} = 2.2 Hz, C). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −112.34 to −112.26 (m),

−111.64 to −111.56 ppm (m). HRMS (EI, positive): calcd 244.0694 ($C_{15}H_{10}F_2O$), found 244.0694.

General Method for the Synthesis of (*E*)-1,3-Diarylprop-2-en-1-ols (1-OH). Similarly to the procedure by Dickinson et al.,[32] (*E*)-1,3-diarylprop-2-enones (**1-O**) were dissolved in methanol (ca. 80 mM solutions, in some cases heating or refluxing of the reaction mixture was needed to achieve a homogeneous solution). Subsequently, sodium borohydride (0.5−2 equiv) was added in small portions until the TLC spots of (*E*)-1,3-diarylprop-2-enone disappeared. After evaporation of the methanol the residue was dissolved in EtOAc, washed with water (2 ×), and dried ($MgSO_4$). Drying in a vacuum afforded (*E*)-1,3-diarylprop-2-en-1-ols in yields of 89−98%. The resulting alcohols were used without further purification for subsequent syntheses because the excellent crystallization ability of phosphonium salts allows for purification of the cation precursors at the final stage of the synthesis.

(*E*)-1,3-Bis(3,5-difluorophenyl)prop-2-en-1-ol (1a-OH). From **1a-O** (4.99 g, 17.8 mmol): 4.62 g (16.4 mmol, 92%), colorless oil. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 2.20 (br. s, 1 H, OH), 5.36 (d, $^3J_{HH}$ = 6.4 Hz, 1 H, ArCHCHC*H*(OH)Ar), 6.29 (dd, $^3J_{HH}$ = 15.8, 6.4 Hz, 1 H, ArCHC*H*CH(OH)Ar), 6.54−6.81 (m, 3 H, ArC*H*CHCH(OH)Ar, H_{Ar}), 6.82−7.06 ppm (m, 4 H, H_{Ar}).

(*E*)-1,3-Bis(3-fluorophenyl)prop-2-en-1-ol (1b-OH). From **1b-O** (1.00 g, 4.09 mmol): 893 mg (3.62 mmol, 89%), colorless oil. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 2.07 (br. s, 1 H, OH), 5.37 (d, $^3J_{HH}$ = 6.4 Hz, 1 H, ArCHCHC*H*(OH)Ar), 6.33 (dd, $^3J_{HH}$ = 15.9, 6.4 Hz, 1 H, ArCHC*H*CH(OH)Ar), 6.66 (d, $^3J_{HH}$ = 15.9 Hz, 1 H, ArC*H*CHCH(OH)Ar), 6.88−7.39 ppm (m, 8 H, H_{ar}).

(*E*)-1,3-Bis(4-bromophenyl)prop-2-en-1-ol (1c-OH). From **1c-O** (5.00 g, 13.7 mmol): 3.76 g (10.2 mmol, 75%), colorless solid. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 2.13 (br. s, 1 H, OH), 5.33 (d, $^3J_{HH}$ = 6.3 Hz, 1 H, ArCHCHC*H*(OH)Ar), 6.31 (dd, $^3J_{HH}$ = 15.8, 6.3 Hz, 1 H, ArCHC*H*CH(OH)Ar), 6.61 (d, $^3J_{HH}$ = 15.8 Hz, 1 H, ArC*H*CHCH(OH)Ar), 7.19−7.32 (m, 4 H, H_{ar}), 7.37−7.53 ppm (m, 4 H, H_{ar}).

(*E*)-4,4′-(3-Chloroprop-1-ene-1,3-diyl)bis(bromobenzene) (1c-Cl). Synthesized from **1c-OH** (1.00 g, 2.70 mmol) and concentrated HCl by using a procedure described in ref 33: 0.732 g (1.89 mmol, 70%), colorless solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.61 (d, $^3J_{HH}$ = 7.2 Hz, 1 H, ArCHCHC*H*(Cl)Ar), 6.47 (dd, $^3J_{HH}$ = 15.6, 7.2 Hz, 1 H, ArCHC*H*CH(Cl)Ar), 6.58 (d, $^3J_{HH}$ = 15.6 Hz, 1 H, ArC*H*CHCH(Cl)Ar), 7.25−7.29 (m, 2 H, H_{Ar}), 7.35−7.38 (m, 2 H, H_{Ar}), 7.43−7.50 (m, 2 H, H_{Ar}), 7.50−7.60 (m, 2 H, H_{Ar}). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 62.6 (CH), 122.3 (C), 122.5 (C), 128.3 (CH), 129.0 (CH), 129.2 (CH), 131.3 (CH), 131.8 (CH), 131.9 (CH), 134.5 (C), 139.0 ppm (C). Some impurities gave rise to additional resonances in the ^{1}H and ^{13}C NMR spectra of **1c-Cl** and could not be removed by distillation or recrystallization. However, these impurities cannot influence the determination of the second-order rate constants (k_2) because in each kinetic run the same cation precursor concentration was used, so that possible side reactions with these impurities should cause the positive intercept of the k_{obs} vs [Nu] plot and do not affect the slope.

(*E*)-((1,3-Diphenylallyl)oxy)trimethylsilane (1e-OTMS). Prepared using a procedure analogous to that described in ref 34: Triethylamine (0.83 g, 8.2 mmol) and chlorotrimethylsilane (0.96 mL, 0.82 g, 7.6 mmol) were successively added to a solution of **1e-OH** (1.33 g, 6.32 mmol) in dichloromethane (25 mL) under N_2 atmosphere. The reaction mixture was stirred for a further 10 h at ambient temperature. The precipitate formed after addition of diethyl ether (45 mL) was filtered off, and the filtrate was dried in the vacuum providing **1e-OTMS** (1.45 g, 5.12 mmol, 81%) as a yellow oil. The ^{1}H and ^{13}C NMR spectra of **1e-OTMS** were in agreement with those described in ref 35.

(*E*)-((1,3-Bis(4-methylphenyl)allyl)oxy)trimethylsilane (1f-OTMS). Analogously to **1e-OTMS**. From **1f-OH** (5.89 g, 24.7 mmol), chlorotrimethylsilane (3.22 g, 29.6 mmol), and triethylamine (3.25 g, 32.1 mmol): 5.89 g (19.0 mmol, 77%), colorless solid (mp 36.5−38 °C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.16 (m, 9 H, OTMS), 2.34, 2.36 (2 s, 6 H, 2 × CH_3), 5.33 (d, $^3J_{HH}$ = 6.5 Hz, 1 H, ArCHCHC*H*(OTMS)Ar), 6.27 (dd, $^3J_{HH}$ = 15.8, 6.6 Hz, 1 H, ArCHC*H*CH(OTMS)Ar), 6.58 (d, $^3J_{HH}$ = 15.8, 1 H, ArC*H*CHCH(OTMS)Ar), 7.12 (d, $^3J_{HH}$ = 8.0 Hz, 2 H, H_{Ar}), 7.16 (d, $^3J_{HH}$ = 8.2 Hz, 2 H, H_{Ar}), 7.27−7.32 ppm (m, 4 H, H_{Ar}). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 0.3 (CH_3), 21.09 (CH_3), 21.14 (CH_3), 75.5 (CH), 126.2 (CH), 126.4 (CH), 128.95 (CH), 129.03 (CH), 129.2 (CH), 132.0 (CH), 134.2 (C), 136.7 (C), 137.2 (C), 140.8 ppm (C). HRMS (EI, positive): calcd 310.1747 ($C_{20}H_{26}OSi$), found 310.1747.

(*E*)-(1,3-Bis(4-bromophenyl)allyl)oxy)trimethylsilane (1c-OTMS). Prepared analogously to **1e**-OTMS and used for further synthesis without purification and characterization.

General Procedure for the Synthesis of (*E*)-(1,3-Diarylallyl)triphenylphosphonium Tetrafluoroborates (1-PPh$_3^+$BF$_4^-$). Analogously to ref 13, triphenylphosphine was dissolved in dichloromethane (5 mL), and 50% w/w tetrafluoroboric acid solution in diethyl ether was added (1 equiv). After 5 min of stirring at rt, the corresponding diarylallyl alcohol (1 equiv) was added, and the reaction mixture was stirred for a further 30 min. Evaporation of the solvents followed by recrystallization from a CH_2Cl_2/Et_2O mixture afforded the desired products.

(*E*)-(1,3-Bis(3,5-difluorophenyl)allyl)triphenylphosphonium Tetrafluoroborate (1a-PPh$_3^+$BF$_4^-$). From **1a-OH** (97.0 mg, 0.343 mmol): 117 mg (0.205 mmol, 60%), colorless crystals (mp 225.2−226.3 °C). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 6.11 (dd, $^2J_{HP}$ = 15.9, $^3J_{HH}$ = 9.2 Hz, 1 H, ArCHCHC*H*(P$^+$Ph$_3$)Ar), 6.15−6.27 (m, 1 H, ArCHC*H*CH(P$^+$Ph$_3$)Ar), 6.59−6.72 (m, 2 H, H_{Ar}), 6.71−6.78 (m, 1 H, H_{Ar}), 6.79−6.91 (m, 3 H, H_{Ar}), 6.98 ppm (dd, $^3J_{HH}$ = 15.4, $^4J_{HP}$ = 4.6 Hz, 1 H, ArC*H*CHCH(P$^+$Ph$_3$)Ar), 7.61−7.68 (m, 6 H, H_{Ar}), 7.68−7.75 (m, 6 H, H_{Ar}), 7.82−7.95 ppm (m, 3 H, H_{Ar}). ^{13}C NMR (CD_2Cl_2, 101 MHz): δ 45.8 (dt, J_{CP} = 45.7, J_{CF} = ca. 2 Hz, CH), 104.7 (t, J_{CF} = 25.7 Hz, CH), 105.6 (td, J_{CF} = 25.0, J_{CP} = 2.5 Hz, CH), 110.0−110.4 (m, CH), 113.8−114.2 (m, CH), 116.8 (d, J_{CP} = 83.1 Hz, C), 121.4 (d, J_{CP} = 6.4 Hz, CH), 131.1 (d, J_{CP} = 12.5 Hz, CH), 135.1 (d, J_{CP} = 9.1 Hz, CH), 135.7−136.0 (m, C), 136.3 (d, J_{CP} = 3.1 Hz, CH), 138.4 (dt, J_{CP} = 12.9, J_{CF} = 3.0 Hz, CH), 139.0−139.3 (m, C), 162.4−162.6 (m, C), 164.9−165.1 ppm (m, C). ^{19}F NMR (CD_2Cl_2, 282 MHz): δ −151.10 to −151.05 (m, 3 F, BF_4^-), −151.03 to −151.00 (m, 1 F, BF_4^-), −113.6 to −113.5, −110.7 to −110.6 ppm (2 m, 4 F, F_{Ar}). ^{31}P NMR (CD_2Cl_2, 162 MHz): δ 23.5 ppm. HRMS (ESI, positive): calcd 527.1546 ($C_{33}H_{24}F_4P^+$), found 527.1543.

(*E*)-(1,3-Bis(3-fluorophenyl)allyl)triphenylphosphonium Tetrafluoroborate (1b-PPh$_3^+$BF$_4^-$). From **1b-OH** (298 mg, 1.21 mmol): 520 mg (0.899 mmol, 74%), colorless crystals (mp 176.3−177.3 °C). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 5.94 (dd, $^2J_{HP}$ = 16.3, $^3J_{HH}$ = 8.9 Hz, 1 H, ArCHCHC*H*(P$^+$Ph$_3$)Ar), 6.24−6.31 (m, 1 H, ArCHC*H*CH(P$^+$Ph$_3$)Ar), 6.76 (ddd, $^3J_{HF}$ = 9.7, $^3J_{HH}$ = 2.0, 2.0 Hz, 1 H, H_{Ar}), 6.90−6.98 (m, 4 H, ArC*H*CHCH(P$^+$Ph$_3$)Ar, H_{Ar}), 7.06−7.09 (m, 1 H, H_{Ar}), 7.09−7.13 (m, 1 H, H_{Ar}), 7.23−7.33 (m, 2 H, 6-H, H_{Ar}), 7.57−7.62 (m, 6 H, H_{Ar}), 7.66−7.71 (m, 6 H, H_{Ar}), 7.83−7.87 ppm (m, 3 H, H_{Ar}). ^{13}C NMR (CD_2Cl_2, 101 MHz): δ: 46.6 (dd, J_{CP} = 45.0, J_{CF} = 1.9 Hz, CH), 113.6 (dd, J_{CF} = 22.0, J_{CP} = 1.8 Hz, CH), 116.3 (dd, J_{CF} = 21.4, J_{CP} = 1.1 Hz, CH), 117.05 (d, J_{CP} = 82.8 Hz, C), 117.06 (dd, J_{CF} = 20.9, J_{CP} = 3.0 Hz, CH), 117.6 (dd, J_{CF} = 23.0, J_{CP} = 5.9 Hz, CH), 120.6 (d, J_{CP} = 6.3 Hz, CH), 123.5 (dd, J_{CF} = 2.8, J_{CP} = 1.9 Hz, CH), 126.7 (dd, J_{CP} = 6.1, J_{CF} = 3.1 Hz, CH), 130.95 (d, J_{CP} = 12.4 Hz, CH), 130.99 (dd, J_{CF} = ca. 8, J_{CP} = 1.0 Hz, CH), 131.9 (dd, J_{CF} = 8.2, J_{CP} = 2.5 Hz, CH), 134.4 (dd, J_{CF} = 7.4, J_{CP} = 5.3 Hz, C), 135.2 (d, J_{CP} = 9.0 Hz, CH), 136.1 (d, J_{CP} = 3.1 Hz, CH), 138.1 (dd, J_{CF} = 7.7, J_{CP} = 3.0 Hz, C), 138.8 (dd, J_{CP} = 13.0, J_{CF} = 2.6 Hz, CH), 163.4 (dd, J_{CF} = 249, J_{CP} = 2.5 Hz, C), 163.5 ppm (dd, J_{CF} = 246, J_{CP} = 1.1 Hz, C). ^{19}F NMR (CD_2Cl_2, 282 MHz): δ −150.93 to −150.90 (m, 3 F, BF_4^-), −150.87 to −150.85 (m, 1 F, BF_4^-), −113.6 to −113.5, −110.7 to −110.6 ppm (2 m, 2 F, F_{Ar}). ^{31}P NMR (CD_2Cl_2, 162 MHz): δ 23.1 ppm. HRMS (ESI, positive): calcd 491.1735 ($C_{33}H_{26}F_2P^+$), found 491.1732.

(*E*)-(1,3-Bis(4-chlorophenyl)allyl)triphenylphosphonium Tetrafluoroborate (1d-PPh$_3^+$BF$_4^-$). From **1d-OH** (600 mg, 2.15 mmol): 721 mg (1.18 mmol, 55%), colorless crystals (149.6−150.4 °C). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 5.96 (dd, $^2J_{HP}$ = 16.3, $^3J_{HH}$ = 9.0 Hz, 1 H, ArCHCHC*H*(P^+Ph_3)Ar), 6.24−6.32 (m, 1 H, ArCHC*H*CH(P^+Ph_3)Ar), 6.92 (dd, $^3J_{HH}$ = 15.4, $^4J_{HP}$ = 4.5 Hz, 1 H, ArC*H*CHCH(P^+Ph_3)Ar), 6.99−7.09 (m, 2 H, H_{Ar}), 7.21−7.27 (m, 6 H, H_{Ar}), 7.59−7.64 (m, 6 H, H_{Ar}), 7.66−7.71 (m, 6 H, H_{Ar}), 7.83−7.88 ppm (m, 3 H, H_{Ar}). ^{13}C NMR (CD_2Cl_2, 101 MHz): δ 46.4 (d, J_{CP} = 44.6 Hz, CH), 117.1 (d, J_{CP} = 82.6 Hz, C), 119.9 (d, J_{CP} = 6.1 Hz, CH), 128.6 (d, J_{CP} = 1.8 Hz, CH), 129.4 (d, J_{CP} = 0.9 Hz, CH), 130.1 (d, J_{CP} = 2.4 Hz, CH), 130.7 (d, J_{CP} = 5.3 Hz, C), 130.9 (d, J_{CP} = 12.3 Hz, CH), 132.1 (d, J_{CP} = 5.9 Hz, CH), 134.5 (d, J_{CP} = 2.9 Hz, C), 135.1 (d, J_{CP} = 9.0 Hz, CH superimposed with signal for C (can be seen in HMBC spectrum)), 135.9 (d, J_{CP} = 3.7 Hz, C), 136.0 (d, J_{CP} = 3.0 Hz, CH), 138.6 ppm (d, J_{CP} = 13.1 Hz, CH). ^{31}P NMR (CD_2Cl_2, 162 MHz): δ 22.8 ppm. HRMS (ESI, positive): calcd 523.1144 ($C_{33}H_{26}{}^{35}Cl_2P$), found 523.1142; calcd 525.1114 ($C_{33}H_{26}{}^{35}Cl^{37}ClP$), found 525.1115; calcd 527.1084 ($C_{33}H_{26}{}^{37}Cl_2P$), found 527.1089.

(*E*)-(1,3-Diphenylallyl)triphenylphosphonium Tetrafluoroborate (1e-PPh$_3^+$BF$_4^-$). From **1e-OH** (310 mg, 1.26 mmol): 671 mg (1.24 mmol, 98%), colorless crystals (mp 202.6−203.5 °C). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 5.77 (dd, $^2J_{HP}$ = 16.3 Hz, $^3J_{HH}$ = 8.7 Hz, 1 H, ArCHCHC*H*(P^+Ph_3)Ar), 6.31−6.39 (m, 1 H, ArCHC*H*CH(P^+Ph_3)Ar), 6.88 (dd, $^3J_{HH}$ = 15.7, $^4J_{HP}$ = 3.9 Hz, 1 H, ArC*H*CHCH(P^+Ph_3)Ar), 7.06−7.08 (m, 2 H, H_{Ar}), 7.24−7.33 (m, 7 H, H_{Ar}), 7.39−7.49 (m, 1 H, H_{Ar}), 7.53−7.59 (m, 6 H, H_{Ar}), 7.65−7.70 (m, 6 H, H_{Ar}), 7.83−7.88 ppm (m, 3 H, H_{Ar}). ^{13}C NMR (CD_2Cl_2, 101 MHz): δ 47.6 (d, J_{CP} = 44.2 Hz, CH), 117.3 (d, J_{CP} = 82.5 Hz, C), 119.7 (d, J_{CP} = 6.4 Hz, CH), 127.2 (d, J_{CP} = 1.9 Hz, CH), 129.3 (d, J_{CP} = 1.0 Hz, CH), 129.5 (d, J_{CP} = 1.2 Hz, CH), 130.07 (d, J_{CP} = 3.1 Hz, CH), 130.10 (d, J_{CP} = 2.3 Hz, CH), 130.7 (d, J_{CP} = 6.1 Hz, CH), 130.8 (d, J_{CP} = 12.3 Hz, CH), 131.9 (d, J_{CP} = 5.4 Hz, C), 135.2 (d, J_{CP} = 8.9 Hz, CH), 135.9 (d, J_{CP} = 3.1 Hz, CH), 136.0 (d, J_{CP} = 3.1 Hz, C), 139.5 ppm (d, J_{CP} = 13.0 Hz, CH). HRMS (ESI, positive): calcd 455.1923 ($C_{33}H_{28}P^+$), found 455.1924.

(*E*)-(1,3-Di-*p*-tolylallyl)triphenylphosphonium Tetrafluoroborate (1f-PPh$_3^+$BF$_4^-$). From **1f-OH** (1.00 g, 4.24 mmol): 1.68 g (2.95 mmol, 69%), colorless crystals (mp 188.9−189.9 °C). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 2.30 (s, 3 H, CH_3), 2.35 (d, $^7J_{HP}$ = 2.0 Hz, 3 H, CH_3), 5.68 (dd, $^2J_{HP}$ = 16.2, $^3J_{HH}$ = 8.6 Hz, 1 H, ArCHCHC*H*(P^+Ph_3)Ar), 6.24−6.31 (m, 1 H, ArCHC*H*CH(P^+Ph_3)Ar), 6.79 (dd, $^3J_{HH}$ = 15.7, $^4J_{HP}$ = 4.8 Hz, 1 H, ArC*H*CHCH(P^+Ph_3)Ar), 6.91−6.95 (m, 2 H, H_{Ar}), 7.07−7.15 (m, 4 H, H_{Ar}), 7.15−7.19 (m, 2 H, H_{Ar}), 7.52−7.58 (m, 6 H, H_{Ar}), 7.65−7.70 (m, 6 H, H_{Ar}), 7.83−7.88 ppm (m, 3 H, H_{Ar}). ^{13}C NMR (CD_2Cl_2, 101 MHz): δ 21.4 (d, J_{CP} = 1.1 Hz, CH_3), 21.5 (s, CH_3), 47.4 (d, J_{CP} = 43.9 Hz, CH), 117.5 (d, J_{CP} = 82.3 Hz, C), 118.6 (d, J_{CP} = 6.2 Hz, CH), 127.1 (d, J_{CP} = 1.9 Hz, CH), 128.7 (d, J_{CP} = 5.4 Hz, C), 129.9 (d, J_{CP} = 1.0 Hz, CH), 130.5 (d, J_{CP} = 6.0 Hz, CH), 130.7 (d, J_{CP} = ca. 1.9 Hz, CH) superimposed with 130.8 (d, J_{CP} = 12.2 Hz, CH), 133.1 (d, J_{CP} = 3.0 Hz, C), 135.2 (d, J_{CP} = 8.8 Hz, CH), 135.9 (d, J_{CP} = 3.0 Hz, CH), 139.2 (d, J_{CP} = 13.1 Hz, CH), 139.7 (d, J_{CP} = 1.4 Hz, C), 140.4 ppm (d, J_{CP} = 3.3 Hz, C). ^{31}P NMR (CD_2Cl_2, 162 MHz): δ 22.1 ppm. HRMS (ESI, positive): calcd 483.2236 ($C_{35}H_{32}P^+$), found 483.2235.

General Procedure for the Synthesis of (*E*)-(1,3-Diarylallyl)triphenylphosphonium Triflates (1-PPh$_3^+$TfO$^-$). Triphenylphosphine (1 equiv) and trimethylsilyl triflate (1.2 equiv) were successively added to a dichloromethane solution of (*E*)-((1,3-diarylallyl)oxy)trimethylsilane (**1-OTMS**). The reaction mixture was stirred for 30 min at rt. After evaporation of the solvent, the crude product was recrystallized from a CH_2Cl_2/Et_2O mixture, affording the (diarylallyl) triphenylphosphonium triflate.

(*E*)-(1,3-Bis(4-bromophenyl)allyl)triphenylphosphonium Triflate (1c-PPh$_3^+$TfO$^-$). From **1c-OTMS** (620 mg, 1.41 mmol): 730 mg (0.957 mmol, 68%), colorless crystals (mp 228.8−229.9 °C). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 6.19−6.28 (m, 2 H, ArCHCHC*H*(P^+Ph_3)Ar, ArCHC*H*CH(P^+Ph_3)Ar), 6.91−7.00 (m, 3 H, ArC*H*CHCH(P^+Ph_3)Ar, H_{Ar}), 7.16 (d, $^3J_{HH}$ = 8.4 Hz, 2 H, H_{Ar}), 7.42 (d, $^3J_{HH}$ = 8.4 Hz, 4 H, H_{Ar}), 7.61−7.69 (m, 12 H, H_{Ar}), 7.82−7.87 ppm (m, 3 H, H_{Ar}). ^{13}C NMR (CD_2Cl_2, 101 MHz): δ 45.9 (d, J_{CP} = 44.4 Hz, CH), 117.3 (d, J_{CP} = 82.6 Hz, C), 120.0 (d, J_{CP} = 6.2 Hz, CH), 121.6 (q, J_{CF} = 321.0 Hz, $CF_3SO_3^-$), 123.4 (d, J_{CP} = 1.6 Hz, C), 124.2 (d, J_{CP} = 3.9 Hz, C), 128.9 (d, J_{CP} = 1.8 Hz, CH), 130.9 (d, J_{CP} = 12.3 Hz, CH), 131.3 (d, J_{CP} = 5.3 Hz, C), 132.4 (d, J_{CP} = 1.8 Hz, CH), 132.5 (d, J_{CP} = 3.2 Hz, CH), 133.1 (d, J_{CP} = 2.4 Hz, CH), 135.0 (d, J_{CP} = 2.9 Hz, C), 135.2 (d, J_{CP} = 9.0 Hz, CH), 136.0 (d, J_{CP} = 3.1 Hz, CH), 138.9 ppm (d, J_{CP} = 13.1 Hz, CH). ^{31}P NMR (CD_2Cl_2, 162 MHz): δ 22.6 ppm. HRMS (ESI, positive): calcd 611.0133 ($C_{33}H_{26}{}^{79}Br_2P^+$), found 611.0136; calcd 613.0113 ($C_{33}H_{26}{}^{79}Br^{81}BrP^+$), found 613.0113; calcd 615.0092 ($C_{33}H_{26}{}^{81}Br_2P^+$), found 615.0098.

(*E*)-(1,3-Diphenylallyl)triphenylphosphonium Triflate (1e-PPh$_3^+$TfO$^-$). From **1e-OTMS** (603 mg, 2.14 mmol): 1.01 g (1.66 mmol, 78%), colorless solid (mp 201.8−202.9 °C). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 5.98 (dd, $^2J_{HP}$ = 16.4, $^3J_{HH}$ = 8.7 Hz, 1 H, ArCHCHC*H*(P^+Ph_3)Ar), 6.30−6.38 (m, 1 H, ArCHC*H*CH(P^+Ph_3)Ar), 6.91 (dd, $^3J_{HH}$ = 15.7, $^4J_{HP}$ = 4.8 Hz, 1 H, ArC*H*CHCH(P^+Ph_3)Ar), 7.07−7.11 (m, 2 H, H_{Ar}), 7.24−7.31 (m, 7 H, H_{Ar}), 7.38−7.42 (m, 1 H, H_{Ar}), 7.56−7.61 (m, 6 H, H_{Ar}), 7.64−7.68 (m, 6 H, H_{Ar}), 7.82−7.87 ppm (m, 3 H, H_{Ar}). ^{13}C NMR (CD_2Cl_2, 101 MHz): δ 47.2 (d, J_{CP} = 43.9 Hz, CH), 117.5 (d, J_{CP} = 82.5 Hz, C), 119.7 (d, J_{CP} = 6.4 Hz, CH), 121.6 (q, J_{CF} = 321.0 Hz, $CF_3SO_3^-$), 127.2 (d, J_{CP} = 1.9 Hz, CH), 129.3 (d, J_{CP} = 0.9 Hz, CH), 129.5 (d, J_{CP} = 1.2 Hz, CH), 130.0 (d, J_{CP} = 3.3 Hz, CH), 130.1 (d, J_{CP} = 2.3 Hz, CH), 130.7 (d, J_{CP} = 6.0 Hz, CH), 130.8 (d, J_{CP} = 12.2 Hz, CH), 132.1 (d, J_{CP} = 5.4 Hz, C), 135.2 (d, J_{CP} = 8.9 Hz, CH), 135.9 (d, J_{CP} = 3.0 Hz, CH), 136.0 (d, J_{CP} = 3.0 Hz, C), 139.5 ppm (d, J_{CP} = 13.0 Hz, CH). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 22.7 ppm. HRMS (ESI, positive): calcd 455.1923 ($C_{33}H_{28}P^+$), found 455.1921

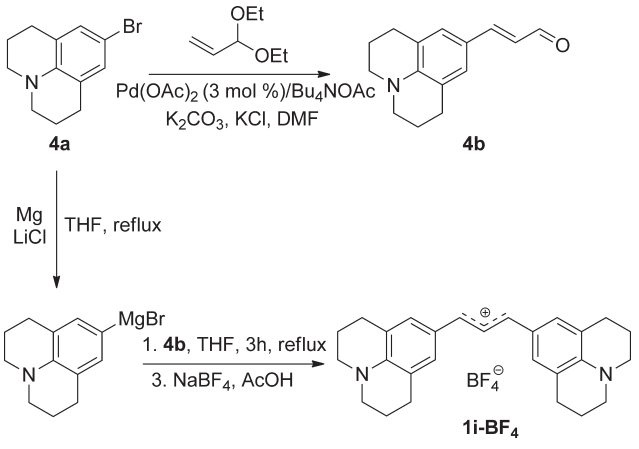
(*E*)-1,3-Bis(4-methoxyphenyl)allylium Tetrafluoroborate (1g-BF$_4$). (*E*)-1,3-Bis(4-methoxyphenyl)prop-2-enone **1g-O** (5.00 g, 18.6 mmol) was dissolved in MeOH (250 mL). Sodium borohydride (ca. 1.5 g, ca. 40 mmol) was added in small portions to the resulting solution until complete disappearance of the (*E*)-1,3-bis(4-methoxyphenyl)prop-2-enone spot (TLC). Methanol was evaporated from the reaction solution, and the remaining solid was dissolved in diethyl ether and slowly added to a 50% w/w HBF_4 solution in diethyl ether (40 mL, 250 mmol). The resulting suspension was stirred for 1 h at rt, and then the precipitate was filtered and washed with diethyl ether. Recrystallization from a dichloromethane/pentane mixture gave **1g-BF$_4$** (3.42 g, 10.1 mmol, 54%) as violet crystals. The product is water- and air-sensitive, but it can be stored for several months under glovebox conditions (dry Ar atmosphere). ^{1}H NMR (CD_3CN, 400 MHz): δ 4.07 (s, 6 H, OMe), 7.24 (d, $^3J_{HH}$ = 8.7 Hz, 4 H, H_{Ar}), 8.18−8.29 (m, 5 H, $H_{Ar,}$ ArCHC*H*CH$^+$Ar), 8.54 ppm (d, $^3J_{HH}$ = 13.5 Hz, 2 H, ArC*H*CHC*H*$^+$Ar). ^{13}C NMR (CD_3CN, 101 MHz): δ 58.3 (CH_3), 114.5 (CH), 127.0 (CH), 130.7 (C), 141.4 (CH), 172.9 (C), 176.3 ppm (CH). HRMS (FAB, positive): calcd 253.1229 ($C_{17}H_{17}O_2^+$), found 253.1226. The ^{1}H NMR spectrum of **1g** in 96% H_2SO_4 has previously been reported.[36]

(*E*)-1,3-Bis(4-methoxyphenyl)allyl Methyl Ether (1g-OMe). A solution of **1g-BF$_4$** (24.1 g, 71.0 mmol) in dichloromethane (250 mL) was cooled to −70 °C before a 5.4 M sodium methoxide solution in methanol (20.0 mL, 110 mmol) was added. The reaction mixture was slowly brought to 0 °C using an ice bath and stirred overnight at this temperature. The formed precipitate was filtered off, and the filtrate was quenched with 2 M aqueous ammonia. The organic layer was separated, and the water layer was extracted with diethyl ether (5×). The organic phases were combined, and the solvents were removed in a rotary evaporator. The crude product was purified by Kugelrohr distillation (250 °C, 10^{-3} mbar) affording **1g-OMe** (6.0 g, 21 mmol, 30%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.36 (s, 3 H, OMe), 3.80, 3.81 (2 s, 2 × 3 H, 2 × OMe), 4.74 (d, $^3J_{HH}$ = 7.0 Hz, 1 H, ArCHCHC*H*(OMe)Ar), 6.16 (dd, $^3J_{HH}$ = 15.9, 7.0 Hz, 1 H, ArCHC*H*CH(OMe)Ar), 6.55 (d, $^3J_{HH}$ = 15.9 Hz, 1 H, ArC*H*CHCH(OMe)Ar), 6.81−6.87 (m, 2 H, H_{Ar}), 6.88−6.94 (m, 2 H, H_{Ar}), 7.30−7.34 ppm (m, 4 H, H_{Ar}). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 55.24 (CH_3), 55.25 (CH_3), 56.2 (CH_3), 84.0 (CH), 113.87 (CH), 113.92 (CH), 127.7 (CH), 128.1 (CH), 128.2 (CH), 129.4 (C), 130.8 (CH), 133.4 (C), 159.1 (C), 159.3 ppm (C). Anal. Calcd for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 76.29; H, 7.03.

(*E*)-1,3-Bis(4-dimethylaminophenyl)allylium Tetrafluoroborate (1h-BF$_4$). Synthesized using Brieskorn's procedure.[37] 4-Bromo-*N*,*N*-dimethylaniline (9.11 g, 45.5 mmol) was added dropwise under Ar atmosphere to lithium (1.20 g, 173 mmol) in dry diethyl ether (100 mL) at ambient temperature. After 18 h of stirring, unreacted lithium was filtered off, and (*E*)-3-(4-(dimethylamino)phenyl)propenal (6.00 g, 34.2 mmol) was added dropwise to the filtrate (rt). After refluxing for 3 h, subsequent cooling to rt, and dissolving in conc acetic acid (250 mL), the reaction mixture was added to a 20% w/w aq solution of sodium tetrafluoroborate (500 mL). A green precipitate formed which was filtered, washed with water and diethyl ether, and dried in the vacuum. Recrystallization from dichloromethane/pentane afforded **1h-BF$_4$** (7.04 g, 19.2 mmol, 56%) as a green powder with metallic gloss (mp 177−178 °C, decomp). In order to obtain crystals suitable for X-ray diffraction analysis, **1h-BF$_4$** was recrystallized from acetonitrile. ^{1}H NMR (CD_3CN, 400 MHz): δ 3.22 (s, 12 H, 2 × NMe_2), 6.79−6.95 (m, 4 H, H_{Ar}), 7.65−7.86 ppm (m, 7 H). ^{13}C NMR (CD_3CN, 101 MHz): δ 41.4 (CH_3), 115.0 (CH), 121.2 (CH), 126.2 (C), 137.3 (weak broad peak which becomes sharper at 50 °C, CH), 157.7 (C), 161.5 ppm (CH). HRMS (ESI, positive): calcd 279.1856 ($C_{19}H_{23}N_2^+$), found 279.1855.

(*E*)-1,3-Bis(julolidin-9-yl)allylium Tetrafluoroborate (1i-BF$_4$). Synthesized using the following scheme:



9-Bromo-1,2,3,5,6,7-hexahydropyrido[3,2,1-*ij*]quinoline (4a). Julolidine (19.1 g, 110 mmol) was reacted with bromine (5.65 mL, 17.6 g, 110 mmol) in dichloromethane.[38] Workup as described in ref 38 afforded **4a** (22.3 g, 88.3 mmol, 80%). The ^{1}H NMR spectrum of **4a** agreed with that described in the literature.[39]

(*E*)-3-(1,2,3,5,6,7-Hexahydropyrido[3,2,1-*ij*]quinolin-9-yl)acrylaldehyde (4b). 9-Bromojulolidine **4a** (5.00 g, 19.8 mmol) was reacted with acrolein diethylacetal (7.74 g, 59.4 mmol) in the presence of tetrabutylammonium acetate (8.97 g, 29.7 mmol), potassium acetate (0.97 g, 9.9 mmol), potassium carbonate (4.11 g, 29.7 mmol), potassium chloride (2.96 g, 39.7 mmol), and palladium acetate (133 mg, 0.595 mmol) following a procedure as described in ref 40. The reaction progress was monitored by TLC. After workup, the crude product was purified by column chromatography (silica gel, hexane/EtOAc/NEt_3 = 91/7/2) affording **4b** (870 mg, 3.82 mmol, 19%). The ^{1}H NMR spectrum of **4b** was in accord with the one described in ref 41.

(*E*)-1,3-Bis(julolidin-9-yl)allylium Tetrafluoroborate (1i-BF$_4$). Magnesium (145 mg, 5.95 mmol) and lithium chloride (315 mg, 7.44 mmol) were slurried in THF (5 mL). Then DIBAL-H (1 M solution in hexane, 220 μL, 0.223 mmol) was added to the resulting mixture followed by dropwise addition of freshly sublimated (160 °C, 5 × 10^{-3} mbar) **4a** (1.87 g, 7.44 mmol). After completion of addition, the resulting mixture was kept gently boiling until GC−MS analysis (analogous to the method described in reference 28b) showed complete conversion of **4a**. A solution of **4b** (780 mg, 3.43 mmol) in THF was added dropwise to the reaction solution, and the resulting mixture was refluxed for 3 h. After dissolving in conc acetic acid (60 mL), the reaction mixture was poured into a 20% w/w aq solution of sodium tetrafluoroborate (120 mL). A green precipitate formed which was filtered, washed with water and diethyl ether, and dried in the vacuum to yield **1i-BF$_4$** (0.95 g, 2.0 mmol, 59%) of as dark green powder (mp 151.6−152.5 °C, decomp). ^{1}H NMR (nitrobenzene-d_5, 400 MHz, 100 °C): δ 1.96−2.02 (m, 8 H, $NCH_2CH_2CH_2$), 2.73−2.79 (m, 8 H, $NCH_2CH_2CH_2$), 3.49−3.55 (m, 8 H, $NCH_2CH_2CH_2$), 7.31 (s, 4 H, H_{Ar}), 7.43 (d, $^3J_{HH}$ = 13.3 Hz, 2 H, ArC*H*CHCH$^+$Ar), 7.67 ppm (t, $^3J_{HH}$ = 13.3 Hz, 1 H, ArCHC*H*CH$^+$Ar). ^{13}C NMR (nitrobenzene-d_5, 101 MHz, 100 °C): δ 20.6 (CH_2), 26.9 (CH_2), 51.0 (CH_2), 119.0 (CH), 123.5 (C), 125.1 (C), 132.5 (CH), 151.1 (C), 156.5 ppm (CH). HRMS (ESI, positive): calcd 383.2482 ($C_{27}H_{31}N_2^+$), found 383.2479.

Product Studies

Reaction of 1,3-Diphenylallyl Cation (1e) with 2,3-Dimethylbut-2-ene (2a). Zinc chloride (300 mg, 1.84 mmol), tetrabutylammonium chloride (608 mg, 2.19 mmol), diethyl ether (0.30 mL), and **2a** (402 mg, 4.78 mmol) were dissolved in dichloromethane (5 mL) and cooled to −78 °C. Then **1e-Cl** (500 mg, 2.18 mmol) in dichloromethane (4 mL) was added dropwise. The reaction solution was stirred at −78 °C for 2 h and then kept in a −60 °C fridge for another 12 h. The resulting mixture was quenched with 2 M aqueous ammonia. Diethyl ether was added to the organic phase followed by washing with water and brine, drying ($MgSO_4$), and evaporation of the solvents in a vacuum. The crude mixture (534 mg) contained (*E*)-(5-chloro-4,4,5-trimethylhex-1-ene-1,3-diyl)dibenzene (**3a**) (ca. 350 mg, ca. 1.1 mmol, ∼50%), (*E*)-(4,4,5-trimethylhexa-1,5-diene-1,3-diyl)-dibenzene (**3a′**) (ca. 85 mg, ca. 0.3 mmol, ∼14%) and <20% of other products (all ratios are based on the ^{1}H NMR spectrum of the crude mixture). A portion of the crude product (298 mg) was purified by column chromatography (silica gel, pentane/EtOAc = 99.3/0.7) affording **3a′** (116 mg, 0.418 mmol). Assuming the same column efficiency for the purification of the whole amount of the crude product one would expect 35% (210 mg, 0.758 mmol) overall yield of **3a′**.

The reaction under identical conditions but without Bu_4NCl afforded a complicated product mixture, which could not be resolved by using column chromatography or distillation.

3a. ^{1}H NMR ($CDCl_3$, 599 MHz): δ 1.02, 1.28 (2 s, 2 × 3 H, 2 × CH_3), 1.64, 1.66 (2 s, 2 × 3 H, 2 × CH_3), 3.87 (d, $^3J_{HH}$ = 10.2 Hz, 1 H, PhCHCHC*H*(R)Ph), 6.36 (d, $^3J_{HH}$ = 15.7 Hz, 1 H, PhC*H*CHCH(R)Ph), 6.71 (dd, $^3J_{HH}$ = 15.7, 10.2 Hz, 1 H, PhCHC*H*CH(R)Ph), 7.16−7.20 (m, 2 H, H_{Ar}), 7.23−7.31 (m, 6 H, H_{Ar}), 7.31−7.34 ppm (m, 2 H, H_{Ar}). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 20.9 (CH_3), 23.7 (CH_3), 30.0 (CH_3), 30.2 (CH_3), 45.7 (C), 55.8 (CH), 80.6 (br. s, C), 126.1 (CH), 126.2 (CH), 127.1 (CH), 128.1 (CH), 128.5 (CH), 129.5 (CH), 130.6 (CH), 132.3 (CH), 137.7 (C), 143.9 ppm (C). ^{1}H and ^{13}C NMR spectra for **3a** were obtained by comparing the spectra of the crude mixture and those of isolated **3a′**. HRMS of the crude mixture (EI, positive): calcd 312.1639 ($C_{21}H_{25}{}^{35}Cl$, **3a**), found 312.1631; calcd 276.1873 ($C_{21}H_{24}$, **3a′**), found 276.1877.

3a′. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.01, 1.11 (2 s, 2 × 3 H, 2 × CH_3), 1.77−1.78 (m, 3 H, CH_3), 3.52 (d, $^3J_{HH}$ = 9.0 Hz, 1 H, PhCHCHC*H*(R)Ph), 4.69−4.74 (m, 1 H, RR′C=CH_2), 4.77−4.82

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(m, 1 H, RR′C=CH_2), 6.35 (d, $^3J_{HH}$ = 15.7 Hz, 1 H, PhC*H*CHCH(R)Ph), 6.57 (dd, $^3J_{HH}$ = 15.7, 9.0 Hz, 1H, PhCHC*H*CH(R)Ph), 7.16−7.23 (m, 4 H, H_{Ar}), 7.24−7.29 (m, 4 H, H_{Ar}), 7.32−7.34 ppm (m, 2 H, H_{Ar}). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 20.1 (CH_3), 24.1 (CH_3), 25.7 (CH_3), 42.8 (C), 56.2 (CH), 111.3 (CH_2), 126.1 (2 × CH, superimposed), 127.0 (CH), 127.6 (CH), 128.4 (CH), 129.7 (CH), 130.7 (CH), 131.2 (CH), 137.9 (C), 142.1 (C), 151.2 ppm (C). HRMS (EI, positive): calcd 276.1873 ($C_{21}H_{24}$), found 276.1872.

(*E*)-(5-Chloro-5,6-dimethylhept-1-ene-1,3-diyl)dibenzene (3b). Zinc chloride (300 mg, 1.84 mmol), tetrabutylammonium chloride (555 mg, 1.99 mmol), diethyl ether (0.30 mL), and 2,3-dimethylbut-1-ene (**2b**) (370 mg, 4.40 mmol) were dissolved in dichloromethane (5 mL). The mixture was cooled to −78 °C followed by dropwise addition of **1e-Cl** (455 mg, 1.99 mmol) in dichloromethane (4 mL). After stirring for 30 min, the reaction was quenched with 2 M aq NH_3. Diethyl ether was added to the organic phase followed by washing with water and brine, drying ($MgSO_4$), and evaporation of the solvents in the vacuum to afford **3b** (481 mg) as a mixture of two diastereomers (dr ca. 1.4: 1) in ca. 70% purity (^{1}H NMR). Due to the presence of impurities in the crude product the yield could only be estimated to be ∼50%. ^{1}H NMR ($CDCl_3$, 300 MHz): 0.96 (d, $^3J_{HH}$ = 6.69 Hz, 1.29 H, CH(CH_3)$_2$), 1.03 (d, $^3J_{HH}$ = 6.73 Hz, 3.42 H, CH(CH_3)$_2$), 1.08 (d, $^3J_{HH}$ = 6.69 Hz, 1.29 H, CH(CH_3)$_2$), 1.40 (s, 1.71 H, CH_3), 1.48 (s, 1.29 H, CH_3), 1.94−2.10 (m, 1 H, C*H*(CH_3)$_2$), 2.28−2.48 (m, 2 H, CH_2), 3.83−3.92 (m, 1 H, ArCHCHC*H*(R)Ar), 6.28−6.47 (m, 2 H, ArC*H*C*H*CH(R)Ar), 7.15−7.38 ppm (m, 10 H, H_{Ar}). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 18.07 (CH_3), 18.12 (CH_3), 18.16 (CH_3), 18.23 (CH_3), 27.7 (CH_3), 38.8 (CH), 39.2 (CH), 45.9 (CH), 46.2 (CH), 47.7 (CH_2), 48.2 (CH_2), 79.3 (C), 79.5 (C), 126.1 (CH), 126.3 (CH), 126.4 (CH), 127.09 (CH), 127.14 (CH), 127.6 (CH), 127.7 (CH), 128.4 (CH), 128.5 (CH), 128.69 (CH), 128.71 (CH), 129.1 (CH), 129.5 (CH), 134.9 (CH), 135.1 (CH), 137.4 (C), 145.1 (C), 145.4 ppm (C). HRMS (EI, positive): calcd 312.1639 ($C_{21}H_{25}{}^{35}Cl$), found 312.1635.

(*E*)-(5-Chloro-5-methyloct-1-ene-1,3-diyl)dibenzene (3c). According to procedure described in ref 42, **1e-Cl** (1.25 g, 5.45 mmol) was dissolved in dichloromethane (8 mL). This solution was added dropwise to a mixture of 2-methylpent-1-ene (**2c**) (0.671 g, 7.96 mmol), zinc chloride (300 mg, 1.84 mmol), diethyl ether (0.3 mL), and dichloromethane (10 mL) at −78 °C. After stirring for 30 min, the solution was allowed to warm up and quenched with 2 M aq NH_3. The organic phase was separated, washed with water and brine, and dried ($MgSO_4$). Evaporation of solvents in the vacuum afforded **3c** (1.29 g) as a mixture of two diastereomers (dr ca. 1.4: 1) of ca. 70% purity (^{1}H NMR). Due to the presence of impurities in the crude product the yield could only be estimated to be ∼50%. ^{1}H NMR ($CDCl_3$, 599 MHz): δ 0.84 (t, $^3J_{HH}$ = 7.4 Hz, 1.74 H, $CH_2CH_2CH_3$), 0.87 (t, $^3J_{HH}$ = 7.3 Hz, 1.26 H, $CH_2CH_2CH_3$), 1.34−1.52 (m, 2 H, $CH_2CH_2CH_3$), 1.45 (s, 1.26 H, CH_3), 1.53 (s, 1.74 H, CH_3), 1.65−1.82 (m, 2 H, $CH_2CH_2CH_3$), 2.31−2.44 (m, 2 H, CH_2), 3.78−3.93 (m, 1 H, PhCHCHC*H*(R)Ph), 6.35−6.41 (m, 2 H, PhC*H*C*H*CH(R)Ph), 7.16−7.39 ppm (m, 10 H, H_{ar}). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 14.07 (CH_3), 14.10 (CH_3), 18.1 (CH_2), 30.6 (CH_3), 30.8 (CH_3), 46.15 (CH), 46.21 (CH), 46.7 (CH_2), 47.1 (CH_2), 49.5 (CH_2), 49.7 (CH_2), 75.0 (C), 75.1 (C), 126.1 (CH), 126.34 (CH), 126.36 (CH), 127.11 (CH), 127.14 (CH), 127.66 (CH), 127.67 (CH), 128.40 (CH), 128.42 (CH), 128.67 (CH), 128.70 (CH), 129.3 (CH), 129.5 (CH), 134.75 (CH), 134.81 (CH), 137.4 (C), 137.5 (C), 145.0 (C), 145.1 ppm (C). HRMS (EI, positive): calcd 312.1639 ($C_{21}H_{25}{}^{35}Cl$), found 312.1638. Tables SX1 and SX2 of the Supporting Information compare the ^{1}H and ^{13}C resonances found for **3c** with those of the structurally related **3b**.

(*E*)-Hexa-1,5-diene-1,3-diyldibenzene (3d). The allylium ion precursor **1e-Cl** (315 mg, 1.38 mmol) was dissolved in dichloromethane (5 mL). This solution was added dropwise to a mixture of allyltriphenylsilane (**2d**) (436 mg, 1.45 mmol), zinc chloride (100 mg, 0.612 mmol), diethyl ether (0.1 mL), and dichloromethane (7 mL) at −78 °C. After stirring for 30 min, the solution was allowed to warm up and quenched with 2 M aq NH_3. The organic phase of the resulting mixture was separated, washed with water and brine, and dried ($MgSO_4$) followed by evaporation of solvents. The residue was dissolved in pentane and filtered through a paper filter. The filtrate was freed from the solvent and purified by column chromatography (silica gel, pentane/EtOAc = 98.4/1.6) affording **3d** (171 mg, 0.729 mmol, 53%) as a colorless oil. The ^{1}H and ^{13}C NMR spectra of **3d** agreed with those described in ref 16. HRMS (EI, positive): calcd 234.1403 ($C_{18}H_{18}$), found 234.1418. Anal. Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.10; H, 7.97.

(*E*)-4,4′-(Hexa-1,5-diene-1,3-diyl)bis(methoxybenzene) (3e). Allyltrimethylsilane (**2e**) (913 mg, 7.99 mmol) was added to a solution of **1g-BF$_4$** (1.36 g, 4.01 mmol) in dichloromethane (20 mL) at ambient temperature. After stirring for 16 h, the reaction mixture was hydrolyzed using 2 M aq NH_3 and extracted with dichloromethane (2 ×). The combined organic phases were washed with water and dried ($MgSO_4$). Evaporation of the solvents in the vacuum afforded **3e** (0.92 g, 3.1 mmol, 70%) as an oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.51−2.56 (m, 2 H, CH_2), 3.45 (ddd, $^3J_{HH}$ = 7.4, 7.4, 7.3 Hz, 1 H, ArCHCHC*H*(R)Ar), 3.78 (2 s, 2 × 3 H, 2 × CH_3), 4.97 (d, $^3J_{HH}$ = 10.2 Hz, 1 H, CH=C*H*$_2$), 5.03 (d, $^3J_{HH}$ = 17.1 Hz, 1 H, CH=C*H*$_2$), 5.70−5.81 (m, 1 H, C*H*=CH_2), 6.19 (dd, $^3J_{HH}$ = 15.8, 7.3 Hz, 1 H, ArCHC*H*CH(R)Ar), 6.30 (d, $^3J_{HH}$ = 15.9 Hz, 1 H, ArC*H*CHCH(R)Ar), 6.77−6.88 (m, 4 H, H_{Ar}), 7.13−7.18 (m, 2 H, H_{Ar}), 7.23−7.28 ppm (m, 2 H, H_{Ar}). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 40.4 (CH_2), 48.0 (CH), 55.2 (CH_3), 55.3 (CH_3), 113.86 (CH), 113.89 (CH), 116.1 (CH_2), 127.2 (CH), 128.6 (CH), 128.8 (CH), 130.4 (C), 131.7 (CH), 136.1 (CH), 136.8 (C), 158.0 (C), 158.9 ppm (C). Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.77; H, 7.55.

*Formation of **3e** from **1g-BF$_4$** and **2g**.* Allyltriphenylstannane (**2g**) (385 mg, 0.985 mmol) was added successively to a dichloromethane solution of **1g-BF$_4$** (196 mg, 0.577 mmol) at room temperature. After stirring for 30 min, the reaction mixture was hydrolyzed using 1 M aq NH_3 and then extracted with dichloromethane (2 ×). The combined organic phases were washed with water, dried ($MgSO_4$) and freed from solvents in the vacuum to yield the crude product (164 mg) for which ^{1}H and ^{13}C NMR spectra showed signals of **3e** and some impurities (see pp S163−S164 of the Supporting Information).

(*E*)-4,4′-(5-Methylhexa-1,5-diene-1,3-diyl)bis(methoxybenzene) (3f). (2-Methylallyl)-trimethylsilane (**2f**) (168 mg, 1.31 mmol) was added to a solution of **1g-BF$_4$** (223 mg, 0.656 mmol) in dichloromethane (10 mL) at ambient temperature. After fading of the violet color, the reaction mixture was filtered through a short column filled with alumina, and the solvent was evaporated in the vacuum to yield **3f** (190 mg, 0.616 mmol, 93%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.72 (s, 3 H, CH_3), 2.50 (d, $^3J_{HH}$ = 7.7 Hz, 2 H, CH_2), 3.60 (td, $^3J_{HH}$ = 7.7, 6.8 Hz, 1 H, ArCHCHC*H*(R)Ar), 3.79, 3.80 (2 s, 2 × 3 H, 2 × OCH_3), 4.67−4.68, 4.73−4.74 (2 m, 2 × 1 H, C=C*H*$_2$), 6.18 (dd, $^3J_{HH}$ = 15.8, 6.8 Hz, 1 H, ArCHC*H*CH(R)Ar), 6.28 (d, $^3J_{HH}$ = 15.9 Hz, 1 H, ArC*H*CHCH(R)Ar), 6.79−6.83 (m, 2 H, H_{Ar}), 6.85−6.88 (m, 2 H, H_{Ar}), 7.15−7.19 (m, 2 H, H_{Ar}), 7.23−7.28 ppm (m, 2 H, H_{Ar}). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 22.5 (CH_3), 44.5 (CH_2), 46.1 (CH), 55.2 (CH_3), 55.3 (CH_3), 112.4 (CH_2), 113.8 (CH), 113.9 (CH), 127.2 (CH), 128.5 (CH), 128.6 (CH), 130.4 (C), 132.1 (CH), 136.4 (C), 143.5 (C), 158.0 (C), 158.8 ppm (C). HRMS (EI, positive): calcd 308.1771 ($C_{21}H_{24}O_2$), found 308.1762.

(*E*)-2-(1,3-Bis(4-methoxyphenyl)allyl)cyclohexanone (3h). 1-(Trimethylsiloxy)cyclohexene (**2h**) (1.00 mL, 204 mg, 1.92 mmol) was added to a stirred solution of **1g-BF$_4$** (204 mg, 0.600 mmol) in dichloromethane (10 mL) at −78 °C. After the solution had changed the color from intensive violet to red, the mixture was allowed to warm, filtered through aluminum oxide using dichloromethane as solvent, and freed from solvents in the vacuum. The crude mixture contained mainly **3h** as mixture of diastereomers (dr 1.3:1, based on ^{1}H NMR).

Purification of the crude product by column chromatography (silica gel, pentane/EtOAc = 85/15) afforded **3h** in three fractions (overall yield of isolated **3h**: 24%).

First Diastereomer of ***3h***. Colorless oil, 20.4 mg (58.2 μmol, 10%). ^{1}H NMR ($CDCl_3$, 599 MHz): δ 1.37−1.43 (m, 1 H, CH_2), 1.57−1.64 (m, 1 H, CH_2), 1.73−1.86 (m, 3 H, CH_2), 1.90−1.98 (m, 1 H, CH_2), 2.33−2.38 (m, 1 H, CH_2), 2.42−2.46 (m, 1 H, CH_2), 2.79−2.83 (m, 1 H, CH), 3.77 (s, 3 H, OCH_3), 3.79 (s, 3 H, OCH_3), 3.80−3.81 (m, 1 H, ArCHCHC*H*(R)Ar), 6.25 (d, $^3J_{HH}$ = 15.9 Hz, 1 H, ArC*H*CHCH-(R)Ar), 6.29 (dd, $^3J_{HH}$ = 15.9, 6.5 Hz, 1 H, ArCHC*H*CH(R)Ar), 6.78−6.80 (m, 2 H, H_{Ar}), 6.85−6.87 (m, 2 H, H_{Ar}), 7.14−7.17 (m, 2 H, H_{Ar}), 7.22−7.25 ppm (m, 2 H, H_{Ar}). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 23.8 (CH_2), 28.5 (CH_2), 32.0 (CH_2), 42.1 (CH_2), 47.4 (CH), 55.21 (CH_3), 55.24 (CH_3), 56.1 (CH), 113.8 (CH), 113.9 (CH), 127.3 (CH), 129.4 (CH), 129.5 (CH), 130.0 (CH), 130.2 (C), 134.1 (C), 158.1 (C), 158.8 (C), 212.7 ppm (C). HRMS (EI, positive): calcd 350.1876 ($C_{23}H_{26}O_3$), found 350.1864.

Second Diastereomer of ***3h***. Colorless oil, 16.0 mg (45.7 μmol, 8%). ^{1}H NMR ($CDCl_3$, 599 MHz): δ 1.62−1.70 (m, 2 H, CH_2), 1.70−1.80 (m, 1 H, CH_2), 1.88−1.94 (m, 1 H, CH_2), 1.95−2.01 (m, 1 H, CH_2), 2.14−2.18 (m, 1 H, CH_2), 2.24−2.29 (m, 1 H, CH_2), 2.35−2.39 (m, 1 H, CH_2), 2.81−2.85 (m, 1 H, CH), 3.77 (s, 3 H, OCH_3), 3.79 (s, 3 H, OCH_3), 3.90 (dd, $^3J_{HH}$ = 8.9, 8.9 Hz, 1 H, ArCHCHC*H*(R)Ar), 6.09 (dd, $^3J_{HH}$ = 15.7, 9.3 Hz, 1 H, ArCHC*H*CH(R)Ar), 6.37 (d, $^3J_{HH}$ = 15.7 Hz, 1 H, ArC*H*CHCH(R)Ar), 6.80−6.84 (m, 4 H, H_{Ar}), 7.18−7.20 (m, 2 H, H_{Ar}), 7.25−7.28 ppm (m, 2 H, H_{Ar}). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 24.3 (CH_2), 28.4 (CH_2), 31.8 (CH_2), 42.3 (CH_2), 47.6 (CH), 55.2 (CH_3), 55.3 (CH_3), 55.9 (CH), 113.85 (CH), 113.87 (CH), 127.3 (CH), 128.8 (CH), 129.1 (CH), 130.1 (C), 130.3 (CH), 135.4 (C), 157.9 (C), 158.9 (C), 212.0 ppm (C). HRMS (EI, positive): calcd 350.1876 ($C_{23}H_{26}O_3$), found 350.1873.

Mixture of First and Second Diastereomer of ***3h***. Colorless oil (12.8 mg, 36.5 μmol, 6%). ^{1}H and ^{13}C NMR spectra are superpositions of the corresponding spectra of both separately characterized diastereomers.

(*E*)-2-(1,3-Bis(4-methoxyphenyl)allyl)cyclopentanone (3i). Prepared analogously to **3h** from **1g-BF$_4$** (250 mg, 0.735 mmol) and 1-(trimethylsiloxy)cyclopentene (**2i**, 264 mg, 1.69 mmol) as a mixture of diastereomers (dr 1:1.9, based on ^{1}H NMR of the crude product). After column chromatography (silica gel, pentane/EtOAc = 85/15), three fractions were obtained (overall yield of isolated **3i**: 94%).

First Diastereomer of ***3i***. Colorless oil, 28.9 mg (0.0859 mmol, 11%). ^{1}H NMR ($CDCl_3$, 599 MHz): δ 1.60−1.68 (m, 1 H, CH_2), 1.69−1.73 (m, 1 H, CH_2), 1.76−1.82 (m, 1 H, CH_2), 1.86−1.92 (m, 1 H, CH_2), 2.08−2.13 (m, 1 H, CH_2), 2.22−2.27 (m, 1 H, CH_2), 2.59−2.63 (m, 1 H, CH), 3.78 (s, 3 H, OCH_3), 3.80 (s, 3 H, OCH_3), 4.00−4.02 (m, 1 H, ArCHCHC*H*(R)Ar), 6.36 (d, $^3J_{HH}$ = 16.0 Hz, 1 H, ArC*H*CHCH-(R)Ar), 6.43 (dd, $^3J_{HH}$ = 16.0, 6.9 Hz, 1 H, ArCHC*H*CH(R)Ar), 6.82−6.85 (m, 4 H, H_{Ar}), 7.12−7.15 (m, 2 H, H_{Ar}), 7.29−7.31 ppm (m, 2 H, H_{Ar}). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 20.5 (CH_2), 26.3 (CH_2), 38.8 (CH_2), 46.7 (CH), 53.8 (CH), 55.2 (CH_3), 55.3 (CH_3), 113.6 (CH), 113.9 (CH), 127.3 (CH), 129.53 (CH), 129.54 (CH), 129.9 (CH), 130.2 (C), 133.5 (C), 158.2 (C), 158.9 (C), 219.6 ppm (C). HRMS (EI, positive): calcd 336.1720 ($C_{22}H_{24}O_3$), found 336.1719.

Second Diastereomer of ***3i***. Colorless oil, 4.2 mg (0.012 mmol, 2%). ^{1}H NMR ($CDCl_3$, 599 MHz): δ 1.71−1.76 (m, 1 H, CH_2), 1.91−2.06 (m, 3 H, CH_2), 2.16−2.23 (m, 1 H, CH_2), 2.28−2.33 (m, 1 H, CH_2), 2.53−2.57 (m, 1 H, CH), 3.79 (s, 3 H, OCH_3), 3.80 (s, 3 H, OCH_3), 4.03 (dd, $^3J_{HH}$ = 8.4, 4.1 Hz, 1 H, ArCHCHC*H*(R)Ar), 6.23 (dd, $^3J_{HH}$ = 15.7, 8.4 Hz, 1 H, ArCHC*H*CH(R)Ar), 6.33 (d, $^3J_{HH}$ = 15.7 Hz, 1 H, ArC*H*CHCH(R)Ar), 6.80−6.83 (m, 2 H, H_{Ar}), 6.85−6.88 (m, 2 H, H_{Ar}), 7.20−7.24 (m, 2 H, H_{Ar}), 7.24−7.29 ppm (m, 2 H, H_{Ar}). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 20.7 (CH_2), 25.9 (CH_2), 38.9 (CH_2), 47.0 (CH), 55.0 (CH), 55.25 (CH_3), 55.29 (CH_3), 113.86 (CH), 113.91 (CH), 127.2 (CH), 127.4 (CH), 128.9 (CH), 130.1 (C), 131.4 (CH), 135.1 (C), 158.1 (C), 159.0 (C), 219.3 ppm (C). HRMS (EI, positive): calcd 336.1720 ($C_{22}H_{24}O_3$), found 336.1717.

Mixture of First and Second Diastereomer of ***3i***. Total 214 mg (0.635 mmol, 81%). ^{1}H and ^{13}C NMR spectra are superpositions of the corresponding spectra of both separately characterized diastereomers.

(*E*)-Phenyl 3,5-Bis(4-(dimethylamino)phenyl)pent-4-enoate (3j). 1-Phenoxy-1-(trimethylsiloxy)ethene (**2j**) (340 μL, 341 mg, 1.64 mmol) was added to a suspension of **1h-BF$_4$** (462 mg, 1.22 mmol) in dichloromethane (5 mL). The mixture was stirred for 48 h and then hydrolyzed with diluted aq NH_3. The organic layer was separated, and the aqueous phase was extracted with dichloromethane (2×). The combined organic phases were washed with water and dried ($MgSO_4$). Evaporation of solvents followed by column chromatography (silica gel, *n*-hexane/Et_2O = 3/1) afforded **3j** (248 mg, 59.7 mmol, 47%) as an oily solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.94, 2.95 (2 s, 2 × 6 H, 2 × NMe_2), 2.96−3.08 (m, 2 H, CH_2), 4.03−4.08 (m, 1 H, ArCHCHC*H*-(R)Ar), 6.21 (dd, $^3J_{HH}$ = 15.8, 7.5 Hz, 1 H, ArCHC*H*CH(R)Ar), 6.43 (d, $^3J_{HH}$ = 15.8 Hz, 1 H, ArC*H*CHCH(R)Ar), 6.66−6.70 (m, 2 H, H_{Ar}), 6.73−6.79 (m, 2 H, H_{Ar}), 6.90−6.93 (m, 2 H, H_{Ar}), 7.16−7.33 ppm (m, 7 H, H_{Ar}). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 40.6 (CH_3), 46.8 (CH_3), 41.3 (CH_2), 44.5 (CH), 112.6 (CH), 113.1 (CH), 121.6 (CH), 125.6 (CH), 126.0 (C), 127.2 (CH), 128.1 (CH), 128.2 (CH), 129.3 (CH), 129.6 (CH), 131.0 (C), 149.5 (C), 149.9 (C), 150.7 (C), 170.7 ppm (C). HRMS (EI, positive): calcd 414.2302 ($C_{27}H_{30}N_2O_2$), found 414.2308.

(*E*)-Methyl 3,5-Bis(4-(dimethylamino)phenyl)-2,2-dimethylpent-4-enoate (3k). 1-Methoxy-2-methyl-1-(trimethylsiloxy)propene (**2k**) (175 mg, 1.01 mmol) was added to a suspension of **1h-BF$_4$** in dichloromethane (10 mL) at room temperature. After stirring for 5 min, the reaction mixture was washed with saturated aq $NaHCO_3$ (3 ×), dried ($MgSO_4$), and freed from the solvent. Recrystallization of the residue from acetonitrile afforded **3k** (192 mg, 0.505 mmol, 53%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.15, 1.21 (2 s, 2 × 3 H, 2 × CH_3), 2.92, 2.94 (2 s, 2 × 6 H, 2 × NMe_2), 3.60 (s, 3 H, OCH_3), 3.65 (dd, $^3J_{HH}$ = 5.7, $^4J_{HH}$ = 3.0 Hz, 1 H, ArCHCHC*H*(R)Ar), 6.29−6.40 (m, 2 H, ArC*H*C*H*CH(R)Ar), 6.65−6.70 (m, 4 H, H_{Ar}), 7.09−7.12 (m, 2 H, H_{Ar}), 7.23−7.26 ppm (m, 2 H, H_{Ar}). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 22.3 (CH_3), 23.2 (CH_3), 40.6 (CH_3), 40.7 (CH_3), 47.6 (C), 51.5 (CH_3), 56.1 (CH), 112.4 (CH), 112.5 (CH), 125.0 (CH), 126.5 (C), 127.1 (CH), 129.0 (C), 129.8 (CH), 131.7 (CH), 149.3 (C), 149.8 (C), 177.9 ppm (C). Anal. Calcd for $C_{24}H_{32}N_2O_2$: C, 75.75; H, 8.48; N, 7.36. Found: C, 75.53; H, 8.55; N, 7.38.

(*E*)-1,3-Bis(4-methoxyphenyl)prop-2-ene (3l). Dimethylphenylsilane (**2l**) (1.40 mL, 1.25 g, 9.15 mmol) was added to a stirred suspension of **1g-BF$_4$** (1.06 g, 3.11 mmol) in dichloromethane at rt. After complete decolorization, the reaction mixture was hydrolyzed with water and extracted with dichloromethane (2×). The combined organic phases were dried ($MgSO_4$) and freed from solvent. Kugelrohr distillation of the crude product (240−250 °C, 1.1 × 10^{-2} mbar) gave **3l** (0.648 g, 2.55 mmol, 82%) as an oil. The ^{1}H and ^{13}C NMR spectra agreed with those described in ref 43. Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.61; H, 7.07.

Reaction between 1g-BF$_4$ and 1-Methyl-1*H*-pyrrole (2m). A suspension of **1g-BF$_4$** (162 mg, 0.478 mmol) in dichloromethane was added dropwise to a solution of 1-methyl-1*H*-pyrrole (**2m**) (578 mg, 7.13 mmol) in dichloromethane (10 mL) at −78 °C. The resulting mixture was allowed to warm, then washed with brine and water, dried ($MgSO_4$), and freed from solvents in the vacuum. Based on its ^{1}H NMR spectrum the crude mixture (183 mg) contained (*E*)-2-(1,3-bis(4-methoxyphenyl)allyl)-1-methyl-1*H*-pyrrole (**3m**) (ca. 120 mg, 0.36 mmol, ∼70%), 2,5-bis((*E*)-1,3-bis(4-methoxyphenyl)allyl)-1-methyl-1*H*-pyrrole (**3 m′**) (ca. 20 mg, 0.039 mmol, ∼15%), unreacted 1-methyl-1-*H*-pyrrole (**2m**, ca. 9 mg, 0.1 mmol), and some impurities (ca. 10% w/w).

3m. ^{1}H NMR ($CDCl_3$, 599 MHz): δ 3.42 (s, 3 H, NCH_3), 3.81 (s, 3 H, OCH_3), 3.82 (s, 3 H, OCH_3), 4.80 (d, $^3J_{HH}$ = 6.9 Hz, ArCHCHC*H*-(R)Ar), 5.93−5.98 (m, 1 H, H_{Ar}), 6.10−6.13 (m, 1 H, H_{Ar}), 6.19 (d,

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$^3J_{HH}$ = 15.8 Hz, 1 H, ArC*H*CHCH(R)Ar), 6.47 (dd, $^3J_{HH}$ = 15.8, 6.9 Hz, 1 H, ArCHC*H*CH(R)Ar), 6.60−6.63 (m, 1 H, H_{Ar}), 6.82−6.90 (m, 4 H, H_{Ar}), 7.09−7.15 (m, 2 H, H_{Ar}), 7.28−7.34 ppm (m, 2 H, H_{Ar}). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 33.9 (CH_3), 45.7 (CH), 55.2 (CH_3), 55.3 (CH_3), 106.4 (CH), 107.6 (CH), 113.8 (CH), 113.9 (CH), 122.0 (CH), 127.4 (CH), 129.4 (CH), 129.6 (CH), 130.0 (CH), 130.1 (C), 134.1 (C), 134.2 (C), 158.2 (C) 158.9 ppm (C). HRMS (ESI, positive): calcd 333.1729 ($C_{22}H_{23}NO_2$), found 333.1720.

3 m′. ^{1}H NMR ($CDCl_3$, 599 MHz): δ 3.61 (s, 3 H, NCH_3), 3.81, 3.82 (2 s, 2 × 6 H, 4 × OCH_3), 4.70 (d, $^3J_{HH}$ = 7.6 Hz, 2 H, ArCHCHC*H*-(R)Ar), 6.34 (s, 2 H, H_{Ar}) overlapped with 6.36 (d, $^3J_{HH}$ = 15.7 Hz, 2 H, ArC*H*CHCH(R)Ar), 6.48 (dd, $^3J_{HH}$ = 15.7, 7.6 Hz, 2 H, ArCHC*H*CH-(R)Ar), 6.82−6.90 (m, 8 H, H_{Ar}), 7.21−7.28 (m, 4 H, H_{Ar}), 7.30−7.35 ppm (m, 4 H, H_{Ar}). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 36.1 (CH_3), 46.6 (CH), 55.21 (CH_3), 55.24 (CH_3), 113.6 (CH), 113.8 (CH), 119.8 (CH), 127.0 (C), 127.3 (CH), 128.8 (CH), 129.2 (CH), 130.5 (C), 131.9 (CH), 137.0 (C), 157.9 (C), 158.7 ppm (C).

(*E*)-4-(2-(1,3-Bis(4-(dimethylamino)phenyl)allyl)cyclohexylidene)morpholin-4-ium Tetrafluoroborate (3n, mixture of diastereomers). The allylium tetrafluoroborate **1h-BF$_4$** (68.1 mg, 0.186 mmol) and 1-(*N*-morpholino)cyclohexene (**2n**) (32.5 mg, 0.194 mmol) were mixed in CD_2Cl_2. The resulting solution was analyzed by NMR and HRMS. ^{1}H NMR (CD_2Cl_2, 400 MHz, only characteristic resonances): δ 2.90, 2.93, 2.93, 2.94 (4 s, 12 H, 4 × NMe_2), 5.93 (dd, $^3J_{HH}$ = 15.7, 9.9 Hz, 0.48 H, ArCHC*H*CH(R)Ar), 6.18 (dd, $^3J_{HH}$ = 15.6, 9.5 Hz, 0.52 H, ArCHC*H*CH(R)Ar), 6.30 (d, $^3J_{HH}$ = 15.7 Hz, 0.48 H, ArC*H*CHCH(R)Ar), 6.49 ppm (d, $^3J_{HH}$ = 15.6 Hz, 0.52 H, ArC*H*CHCH(R)Ar). ^{13}C NMR (CD_2Cl_2, 101 MHz, only characteristic resonances): δ 40.6, 40.7, 40.78, 40.82, (4 × CH_3, 2 × NMe_2), 48.0, 48.9 (2 × CH, CHC=N^+), 50.8, 51.7 (2 × CH, ArCHCHC*H*(R)Ar), 124.0, 124.8 (2 × CH, ArC*H*CHCH(R)Ar), 131.6, 133.5 (2 × CH, ArCHCHCH(R)Ar), 195.6, 195.7 ppm (2 × C, *C*=N^+); the chemical shifts of C=N^+ are close to those for products of reactions between benzhydrylium ions and **2n** (δ 195.1 ppm, see ref 8a). HRMS (ESI, positive): calcd 446.3166 ($C_{29}H_{40}N_3O$), found 446.3163. Tables SX3 and SX4 of the Supporting Information compare the characteristic ^{1}H and ^{13}C resonances of compound **3n** listed above with those of the hydrolyzed product **3n′**.

(*E*)-2-(1,3-Bis(4-(dimethylamino)phenyl)allyl)cyclohexanone (3n′). A solution of **1h-BF$_4$** (268 mg, 0.736 mmol) in dichloromethane (30 mL) was prepared. Subsequently, 1-(*N*-morpholino)-cyclohexene (**2n**) (129 mg, 0.772 mmol) and aqueous acetic acid (50 mL of a ca. 2% v/v solution) were added. The resulting mixture was stirred for 48 h at rt. The aqueous phase was separated and extracted with dichloromethane (2×). The combined organic phases were then dried ($MgSO_4$) and freed from solvents. The crude product was purified by column chromatography (silica gel, pentane/EtOAc = 3/1) affording **3n′** in three fractions:

*First Diastereomer of **3n′***. Yellowish oil, 15.3 mg (0.0406 mmol, 6%). ^{1}H NMR ($CDCl_3$, 599 MHz): δ 1.43−1.50 (m, 1 H, CH_2), 1.54−1.63 (m, 1 H, CH_2), 1.70−1.80 (m, 1 H, CH_2), 1.78−1.87 (m, 2 H, CH_2), 1.87−1.95 (m, 1 H, CH_2), 2.28−2.37 (m, 1 H, CH_2), 2.40−2.49 (m, 1 H, CH_2), 2.76−2.83 (m, 1 H, CH), 2.91, 2.92 (2 s, 2 × 6 H, 2 × NMe_2), 3.77 (dd, $^3J_{HH}$ = 9.5, 6.0 Hz, 1 H, ArCHCHC*H*(R)Ar), 6.16−6.26 (m, 2 H, ArC*H*C*H*CH(R)Ar), 6.60−6.65 (m, 2 H, H_{Ar}), 6.68−6.74 (m, 2 H, H_{Ar}), 7.09−7.14 (m, 2 H, H_{Ar}), 7.17−7.21 ppm (m, 2 H, H_{Ar}). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 23.4 (CH_2), 28.5 (CH_2), 31.7 (CH_2), 40.6 (CH_3), 40.7 (CH_3), 41.9 (CH_2), 47.4 (CH), 56.3 (CH), 112.5 (CH), 112.8 (CH), 126.3 (C), 127.1 (CH), 128.2 (CH), 129.0 (CH), 129.5 (CH), 130.2 (C), 149.2 (C), 149.8 (C), 213.2 ppm (C). HRMS (EI, positive): calcd 376.2509 ($C_{25}H_{32}N_2O$), found 376.2492.

*Second Diastereomer of **3n′***. Colorless solid, 36.5 mg (0.0969 mmol, 13%). ^{1}H NMR ($CDCl_3$, 599 MHz): δ 1.59−1.69 (m, 1 H, CH_2), 1.69−1.77 (m, 1 H, CH_2), 1.77−1.86 (m, 1 H, CH_2), 1.86−2.00 (m, 2 H, CH_2), 2.09−2.17 (m, 1 H, CH_2), 2.21−2.30 (m, 1 H, CH_2), 2.35−2.43 (m, 1 H, CH_2), 2.80−2.85 (m, 1 H, CH), 2.91, 2.94 (2 s, 2 × 6 H, 2 × NMe_2), 3.88 (dd, $^3J_{HH}$ = 9.0, 8.9 Hz, 1 H, ArCHCHC*H*-(R)Ar), 6.03 (dd, $^3J_{HH}$ = 15.6, 9.0 Hz, 1 H, ArCHC*H*CH(R)Ar), 6.35 (d, $^3J_{HH}$ = 15.6 Hz, 1 H, ArC*H*CHCH(R)Ar), 6.66 (d, $^3J_{HH}$ = 8.8 Hz, 2 H, H_{Ar}), 6.69 (d, $^3J_{HH}$ = 8.7 Hz, 2 H, H_{Ar}), 7.16 (d, $^3J_{HH}$ = 8.7 Hz, 2 H, H_{Ar}), 7.24 ppm (d, $^3J_{HH}$ = 8.8 Hz, 2 H, H_{Ar}). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 23.9 (CH_2), 28.4 (CH_2), 31.5 (CH_2), 40.6 (CH_3), 40.7 (CH_3), 42.0 (CH_2), 47.5 (CH), 56.0 (CH), 112.5 (CH), 112.8 (CH), 126.2 (C), 127.0 (CH), 127.5 (CH), 128.4 (CH), 130.4 (CH), 131.4 (C), 149.0 (C), 149.8 (C), 212.5 ppm (C). HRMS (EI, positive): calcd 376.2509 ($C_{25}H_{32}N_2O$), found 376.2502.

*Mixture of First and Second Diastereomer of **3n′***. Yellowish oil, 12.4 mg (0.0239 mmol, 4%). ^{1}H and ^{13}C NMR spectra are superpositions of the corresponding spectra of both separately characterized diastereomers.

Overall yield of **3n′**: 23%. As the ^{1}H NMR spectrum of the crude product (286 mg, ca. 100%) contains mainly the signals corresponding to the mixture of two diastereomers described above, the much lower yield of isolated material can be explained by purification problems (partial decomposition of **3n′** on the column).

(*E*)-1-(2-(1,3-Bis(4-(dimethylamino)phenyl)allyl)cyclopentylidene)piperidin-1-ium Tetrafluoroborate (3o, mixture of diastereomers). The allylium tetrafluoroborate **1h-BF$_4$** (70.2 mg, 0.192 mmol) and 1-(*N*-piperidino)cyclopentene (**2o**) (30.3 mg, 0.200 mmol) were mixed in CD_2Cl_2. The resulting solution was analyzed by NMR and HRMS. ^{1}H NMR (CD_2Cl_2, 400 MHz, only characteristic resonances): δ 2.92, 2.93, 2.94, 2.95 (4 s, 12 H, 4 × NMe_2), 6.06 (dd, $^3J_{HH}$ = 15.6, 9.2 Hz, 0.48 H, ArCHC*H*CH(R)Ar), 6.20 (dd, $^3J_{HH}$ = 15.6, 8.9 Hz, 0.52 H, ArCHC*H*CH(R)Ar), 6.31 (d, $^3J_{HH}$ = 15.6 Hz, 0.48 H, ArC*H*CHCH(R)Ar), 6.42 (d, $^3J_{HH}$ = 15.6 Hz, 0.52 H, ArC*H*CHCH-(R)Ar), 6.62−6.75 (m, 4 H, H_{Ar}), 7.06−7.11 (m, 1.04 H, H_{Ar}), 7.11−7.16 (m, 0.96 H, H_{Ar}), 7.21−7.25 (m, 0.96 H, H_{Ar}), 7.26−7.31 ppm (m, 1.04 H, H_{Ar}). ^{13}C NMR (CD_2Cl_2, 101 MHz, only characteristic resonances): δ 40.61, 40.68, 40.80, 40.83 (4 × CH_3), 50.2, 51.3 (2 × CH, ArCHCHCH-(R)Ar), 52.0, 52.3 (2 × CH, *C*HC=N^+), 123.7, 125.4 (2 × CH, ArCHCHCH(R)Ar), 132.0, 133.3 (2 × CH, ArCHCHCH(R)Ar), 198.4, 198.7 ppm (2 × C, *C*=N^+). HRMS (ESI, positive): calcd 430.3217 ($C_{29}H_{40}N_3$), found 430.3219. Tables SX5 and SX6 of the Supporting Information compare the characteristic ^{1}H and ^{13}C resonances of compound **3o** listed above with those of the hydrolyzed product **3o′**.

(*E*)-2-(1,3-Bis(*N*,*N*-dimethylaminophenyl)allyl)cyclopentanone (3o′). Analogously to **3n′**; from **1h-BF$_4$** (208 mg, 0.568 mmol) and 1-(*N*-piperidino)cyclopentene (**2o**) (90.2 mg, 0.597 mmol). The crude product was purified by column chromatography (silica gel, pentane/EtOAc = 3/1) affording three fractions of **3o′** (overall yield of isolated **3o′**, 54%).

*First Diastereomer of **3o′***. Colorless oil, 18.6 mg (0.0513 mmol, 9%). ^{1}H NMR ($CDCl_3$, 599 MHz): δ 1.65−1.73 (m, 2 H, CH_2), 1.73−1.80 (m, 1 H, CH_2), 1.81−1.92 (m, 1 H, CH_2), 2.07−2.17 (m, 1 H, CH_2), 2.16−2.27 (m, 1 H, CH_2), 2.56−2.66 (m, 1 H, CH), 2.91 (s, 6 H, NMe_2), 2.94 (s, 6 H, NMe_2), 3.99−4.02 (m, 1 H, ArCHCHC*H*(R)Ar), 6.31−6.38 (m, 2 H, ArC*H*C*H*CH(R)Ar), 6.63−6.70 (m, 4 H, H_{Ar}), 7.05−7.10 (m, 2 H, H_{Ar}), 7.23−7.28 ppm (m, 2 H, H_{Ar}). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 20.6 (CH_2), 26.2 (CH_2), 38.9 (CH_2), 40.6 (CH_3), 40.7 (CH_3), 46.6 (CH), 54.0 (CH), 112.5 (CH), 112.6 (CH), 126.3 (C), 127.1 (CH), 127.9 (CH), 129.5 (CH), 129.6 (CH), 129.7 (C), 149.2 (C), 149.8 (C), 220.2 ppm (C). HRMS (EI, positive): calcd 362.2353 ($C_{24}H_{30}N_2O$), found 362.2363.

*Second Diastereomer of **3o′***. Colorless oil, 54.8 mg (0.151 mmol, 27%). ^{1}H NMR ($CDCl_3$, 599 MHz): δ 1.67−1.77 (m, 1 H, CH_2), 1.93−2.07 (m, 3 H, CH_2), 2.13−2.22 (m, 1 H, CH_2), 2.25−2.33 (m, 1 H, CH_2), 2.50−2.58 (m, 1 H, CH), 2.93, 2.93 (2 s, 2 × 6 H, 2 × NMe_2), 4.01 (dd, $^3J_{HH}$ = 8.5, 3.8 Hz, 1 H, ArCHCHC*H*(R)Ar), 6.16 (dd, $^3J_{HH}$ = 15.7, 8.5 Hz, 1 H, ArCHC*H*CH(R)Ar), 6.31 (d, $^3J_{HH}$ = 15.7 Hz, 1 H,

ArC*H*CHCH(R)Ar), 6.62−6.69 (m, 2 H, H_{Ar}), 6.69−6.77 (m, 2 H, H_{Ar}), 7.17−7.21 (m, 2 H, H_{Ar}), 7.21−7.24 ppm (m, 2 H, H_{Ar}). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 20.8 (CH_2), 25.7 (CH_2), 39.0 (CH_2), 40.6 (CH_3), 40.8 (CH_3), 46.9 (CH), 55.1 (CH), 112.4 (CH), 112.8 (CH), 125.5 (CH), 126.2 (C), 127.1 (CH), 128.5 (CH), 131.3 (C), 131.5 (CH), 149.2 (C), 149.9 (C), 219.9 ppm (C). HRMS (EI, positive): calcd 362.2353 ($C_{24}H_{30}N_2O$), found 362.2352.

Mixture of First and Second Diastereomer of ***3o′***. Colorless oil, 36.8 mg (0.101 mmol, 18%). ^1H and ^{13}C NMR spectra are superpositions of the corresponding spectra of both separately characterized diastereomers.

(*E*)-*N*-(1,3-Bis(4-(dimethylamino)phenyl)allyl)-2,2,2-trifluoroethylamine (3p). Obtained from **1h-BF$_4$** (134 mg, 0.365 mmol), 2,2,2-trifluoroethylamine (**2p**) (75.6 mg, 0.763 mmol), and potassium carbonate (529 mg, 3.83 mmol) by using a procedure described in ref 44: yellow oil, 133 mg (0.352 mmol, 96%). ^1H NMR (CD_2Cl_2, 400 MHz): δ 1.74 (s, 1 H, NH), 2.96, 2.96 (2 s, 2 × 6 H, 2 × NMe_2), 3.29−3.14 (m, 2 H, CH_2), 4.38 (d, $^3J_{HH}$ = 7.7 Hz, 1 H, ArCHCHC*H*(R)Ar), 6.07 (dd, $^3J_{HH}$ = 15.8, 7.7 Hz, 1 H, ArCHC*H*CH(R)Ar), 6.51 (d, $^3J_{HH}$ = 15.8 Hz, 1 H, ArC*H*CHCH(R)Ar), 6.65−6.73 (m, 2 H, H_{Ar}), 6.73−6.80 (m, 2 H, H_{Ar}), 7.18−7.38 ppm (m, 4 H, H_{Ar}). ^{13}C NMR ($CDCl_3$, 101 MHz): 40.8 (CH_3), 41.0 (CH_3), 48.3 (q, $^2J_{CF}$ = 30.9 Hz, CH_2), 64.8 (CH), 112.8 (CH), 113.3 (CH), 125.7 (C), 126.7 (q, $^1J_{CF}$ = 278.5 Hz, CF_3), 127.9 (CH), 128.2 (CH), 128.5 (CH), 130.7 (C), 131.0 (CH), 150.8 (C), 150.9 ppm (C). ^{19}F NMR (CD_2Cl_2, 376 MHz) δ −71.7 to −71.6 ppm (m). HRMS (EI, positive): calcd 377.2073 ($C_{21}H_{26}F_3N_3$), found 377.2074.

(*E*)-*N*-(1,3-Bis(4-(dimethylamino)phenyl)allyl)isopropylamine (3q). Obtained analogously to **3p** from isopropylamine **2q** (129 mg, 1.74 mmol) and **1h-BF$_4$** (366 mg, 0.871 mmol) without use of K_2CO_3: red oily solid, 243 mg (0.721 mmol, 83%). ^1H NMR ($CDCl_3$, 599 MHz): δ 1.08 (d, $^3J_{HH}$ = 6.3 Hz, 3 H, CH_3), 1.10 (d, $^3J_{HH}$ = 6.3 Hz, 3 H, CH_3), 1.35 (br. s, 1 H, NH), 2.83 (qq, $^3J_{HH}$ = 6.3 Hz, 6.3 Hz, 1 H, C*H*(CH_3)$_2$), 2.94, 2.94 (2 s, 2 × 6 H, 2 × NMe_2), 4.40 (d, $^3J_{HH}$ = 7.4 Hz, 1 H, ArCHCHC*H*(R)Ar), 6.12 (dd, $^3J_{HH}$ = 15.8, 7.4 Hz, 1 H, ArCHC*H*CH(R)Ar), 6.41 (d, $^3J_{HH}$ = 15.8 Hz, 1 H, ArC*H*CHCH(R)Ar), 6.63−6.69 (m, 2 H, H_{Ar}), 6.72−6.76 (m, 2 H, H_{Ar}), 7.24−7.29 ppm (m, 4 H, H_{Ar}). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 23.0 (CH_3), 23.4 (CH_3), 40.5 (CH_3), 40.7 (CH_3), 45.4 (CH), 61.9 (CH), 112.4 (CH), 112.7 (CH), 125.9 (C), 127.2 (CH), 127.9 (CH), 129.1 (CH), 129.6 (CH), 131.8 (C), 149.7 (C), 149.8 ppm (C). HRMS (EI, positive): calcd 337.2512 ($C_{22}H_{31}N_3$), found 337.2512.

(*E*)-*N*-(1,3-Bis(4-(dimethylamino)phenyl)allyl)benzylamine (3r). Obtained analogously to **3q** from benzylamine **2r** (150 mg, 1.40 mmol) and **1h-BF$_4$** (251 mg, 0.685 mmol). Recrystallization of the crude product from diethyl ether/pentane afforded **3r** (201 mg, 0.522 mmol, 76%) as a pale red solid (mp 88.2−90.0 °C, decomp). Evaporation of the solvents from the solution which was left after recrystallization afforded additional 60 mg (0.16 mmol, 23%) of **3r** in lower quality as yellow oil. ^1H NMR ($CDCl_3$, 599 MHz): δ 1.83 (br. s, 1 H, NH), 2.96, 2.97 (2 s, 2 × 6 H, 2 × NMe_2), 3.81 (d, 1 H, $^2J_{HH}$ = 14.3 Hz, CH_2), 3.84 (d, $^2J_{HH}$ = 14.3 Hz, 1 H, CH_2), 4.33 (d, $^3J_{HH}$ = 7.6 Hz, 1 H, ArCHCHC*H*(R)Ar), 6.17 (dd, $^3J_{HH}$ = 15.7, 7.6 Hz, 1 H, ArCHC*H*CH(R)Ar), 6.50 (d, $^3J_{HH}$ = 15.7 Hz, 1 H, ArC*H*CHCH(R)Ar), 6.68−6.71 (m, 2 H, H_{Ar}), 6.74−6.82 (m, 2 H, H_{Ar}), 7.15−7.50 ppm (m, 9 H, H_{Ar}). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 40.5 (CH_3), 40.7 (CH_3), 51.3 (CH_2), 64.1 (CH), 112.4 (CH) 112.7 (CH), 125.7 (C), 126.7 (CH), 127.2 (CH), 128.0 (CH), 128.1 (CH), 128.3 (CH), 128.8 (CH), 129.7 (CH), 131.3 (C), 140.7 (C), 149.8 (C), 149.9 ppm (C). HRMS (EI, positive): calcd 385.2513 ($C_{26}H_{31}N_3$), found 385.2528. Anal. Calcd for $C_{26}H_{31}N_3$: C, 81.00; H, 8.10; N, 10.90. Found: C, 80.61; H, 8.27; N, 10.65.

(*E*)-*N*-(1,3-Bis(4-(dimethylamino)phenyl)allyl)morpholine (3s). Obtained analogously to **3q** from morpholine **2s** (328 mg, 3.77 mmol) and **1h-BF$_4$** (329 mg, 0.897 mmol). Pentane (10 mL) was added to the crude product, and the resulting suspension was treated with ultrasound for 30 min. Then the solid residue was filtered and dried in the vacuum affording **3s** (304 mg, 0.831 mmol, 93%) as a pale gray solid (mp 76.8−78.1 °C, decomp). ^1H NMR ($CDCl_3$, 300 MHz): δ 2.37−2.44 (m, 2 H, NCH_2), 2.53−2.60 (m, 2 H, NCH_2), 2.95 (s, 12 H, 2 × NMe_2), 3.68 (d, $^3J_{HH}$ = 8.9 Hz, 1 H, ArCHCHC*H*(R)Ar), 3.72 (t, $^3J_{HH}$ = 4.7 Hz, 4 H, CH_2O), 6.10 (dd, $^3J_{HH}$ = 15.7, 8.9 Hz, 1 H, ArCHC*H*CH(R)Ar), 6.45 (d, $^3J_{HH}$ = 15.7 Hz, 1 H, ArC*H*CHCH(R)Ar), 6.67 (d, $^3J_{HH}$ = 8.8 Hz, 2 H, H_{Ar}), 6.73 (d, $^3J_{HH}$ = 8.8 Hz, 2 H, H_{Ar}), 7.26 (d, $^3J_{HH}$ = 8.8 Hz, 2 H, H_{Ar}), 7.27 ppm (d, $^3J_{HH}$ = 8.8 Hz, 2 H, H_{Ar}). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 40.5 (CH_3), 40.7 (CH_3), 52.2 (CH_2), 67.2 (CH_2), 74.4 (CH), 112.4 (CH), 112.7 (CH), 125.7 (C), 127.2 (CH), 127.4 (CH), 128.7 (CH), 129.7 (C), 130.9 (CH), 149.8 (C), 150.0 ppm (C). Anal. Calcd for $C_{23}H_{31}N_3O$: C, 75.58; H, 8.55; N, 11.50. Found: C, 75.37; H, 8.60; N, 11.21.

(*E*)-9,9′-(3-(Piperidin-1-yl)prop-1-ene-1,3-diyl)bis(1,2,3,5,6,7-hexahydropyrido[3,2,1-*ij*]quinoline) (3t). Piperidine **2t** (12.0 mg, 0.141 mmol) was added to a stirred slurry of **1i-BF$_4$** (30.6 mg, 65.1 μmol) and potassium carbonate (98.5 mg, 0.713 mmol) in acetonitrile (10 mL). After fading of the green color, the mixture was diluted with diethyl ether, washed with 2 M NaOH solution and dried ($MgSO_4$). Evaporation of the solvent gave the crude product that was analyzed by NMR spectroscopy. Because of the high instability of **3t** in the presence of proton sources (reaction between **1i** and piperidine is reversible) further attempts to purify **3t** were not made. ^1H NMR (CD_3CN, 400 MHz): δ 1.36−1.45 (m, 2 H, CH_2), 1.46−1.56 (m, 4 H, CH_2), 1.85−1.92 (m, 8 H, CH_2), 2.30−2.46 (m, 4 H, CH_2), 2.64−2.70 (m, 8 H, CH_2), 3.06−3.11 (m, 8 H, CH_2), 3.47 (d, $^3J_{HH}$ = 8.9 Hz, 1 H, ArCHCHC*H*(R)Ar), 5.93 (dd, $^3J_{HH}$ = 15.9, 8.9 Hz, 1 H, ArCHC*H*CH(R)Ar), 6.20 (d, $^3J_{HH}$ = 15.9 Hz, 1 H, ArC*H*CHCH(R)Ar), 6.68 (s, 2 H, H_{Ar}), 6.74 ppm (s, 2 H, H_{Ar}). ^{13}C NMR (CD_3CN, 101 MHz): δ 23.0 (CH_2), 23.2 (CH_2), 25.7 (CH_2), 27.1 (CH_2), 28.4 (CH_2), 28.5 (CH_2), 50.7 (CH_2), 50.8 (CH_2), 53.4 (CH_2), 75.3 (CH), 122.4 (C), 122.5 (C), 125.75 (C), 125.81 (CH), 127.3 (CH), 128.8 (CH), 130.9 (CH), 131.3 (C), 142.9 (C), 143.4 ppm (C). Though signals of excess piperidine and some other impurities are present in the NMR spectra, these spectra still allow unambiguous identification of **3t** as the major product formed in the reaction.

5,5-Bis((*E*)-1,3-bis(4-(dimethylamino)phenyl)allyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (3u′). A solution of Meldrum's acid (**H-2u**) (62.4 mg, 0.432 mmol) and potassium *tert*-butoxide (110 mg, 0.900 mmol) in DMSO (2 mL) was added to a suspension of **1h-BF$_4$** (317 mg, 0.866 mmol) in DMSO at rt. The reaction mixture was stirred for 10 min followed by addition of water. The precipitate was filtered and dried in the vacuum affording **3u′** (255 mg, 0.366 mmol, 85%) as a pale green solid. ^1H NMR (CD_2Cl_2, 400 MHz): δ 0.66 (s, 6 H, 2 × CH_3), 2.85 (s, 12 H, NMe_2), 2.97 (s, 12 H, NMe_2), 4.18 (d, $^3J_{HH}$ = 10.1 Hz, 2 H, ArCHCHC*H*(R)Ar), 6.30 (d, $^3J_{HH}$ = 15.7 Hz, 2 H, ArC*H*CHCH(R)Ar), 6.56−6.67 (m, 4 H, H_{Ar}), 6.68−6.75 (m, 4 H, H_{Ar}), 6.86 (dd, $^3J_{HH}$ = 15.7, 10.1 Hz, 2 H, ArCHC*H*CH(R)Ar), 7.02−7.12 (m, 4 H, H_{Ar}), 7.26−7.34 ppm (m, 4 H, H_{Ar}). ^{13}C NMR (CD_2Cl_2, 101 MHz): δ 29.0 (CH_3), 40.88 (CH_3), 40.92 (CH_3), 54.6 (CH), 65.1 (C), 106.3 (C), 112.9 (CH), 113.3 (CH), 122.3 (CH), 126.4 (C), 128.0 (CH), 128.3 (C), 130.3 (CH), 134.5 (CH), 150.8 (2 × C), 168.1 ppm (C). HRMS (EI, positive): calcd 700.3983 ($C_{44}H_{52}N_4O_4$), found 700.3998.

Reaction of 1h-BF$_4$ with the potassium salt of Meldrum's acid (K-2u). According to ref 45, a solution of **1h-BF$_4$** (104 mg, 0.285 mmol) in DMSO was added dropwise to a solution of **K-2u** (253 mg, 1.39 mmol) in the same solvent at rt. After decolorization followed by addition of water, the precipitate was filtered, washed with water, and dried in the vacuum affording a mixture of (*E*)-5-(1,3-bis(4-(dimethylamino)phenyl)allyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (**3u**) (29 mg, 0.069 mmol, 24%) and **3u′** (39 mg, 0.056 mmol, 39%). The yields of **3u** and

3u′ are based on the signal ratios in the ^{1}H NMR spectrum and the mass (68.5 mg) of the crude product mixture. **3u**: ^{1}H NMR (CD_2Cl_2, 400 MHz): 1.51, 1.71 (2 s, 2 × 3 H, 2 × CH_3), 2.91, 2.94 (2 s, 2 × 6 H, 2 × NMe_2), 3.95 (br. s, 1 H, COC*H*CO), 4.55−4.57 (br. m, 1 H, ArCHCHC*H*-(R)Ar), 6.49 (d, $^3J_{HH}$ = 16.1 Hz, 1 H, ArC*H*CHCH(R)Ar), 6.55−6.80 (m overlapped with signals of **3u′**, 5 H, ArCHC*H*CH(R)Ar, H_{Ar}), 7.19−7.36 (m overlapped with signals of **3u′**, 4 H, H_{Ar}). ^{13}C NMR (CD_2Cl_2, 101 MHz): δ 28.1 (CH_3), 28.7 (CH_3), 40.8 (CH_3), 40.9 (CH_3), 47.7 (CH), 53.4 (CH), 105.7 (C), 112.8 (CH), 113.0 (CH), 124.8 (CH), 125.7 (C), 127.8 (CH), 128.4 (C), 129.5 (CH), 132.9 (CH), 150.4 (C), 150.8 (C), 165.30 (C), 165.33 ppm (C). The ^{1}H and ^{13}C NMR spectra of **3u** were obtained comparing the corresponding spectra of the crude mixture with those of isolated **3u′**. HRMS (EI, positive): calcd 422.2200 ($C_{25}H_{30}N_2O_4$), found 422.2193.

■ ASSOCIATED CONTENT

Supporting Information. Details of the kinetic experiments, quantum chemical calculations, NMR spectra of all characterized compounds, and crystallographic data in CIF format for the compound **1h-BF$_4$**. This material is available free of charge via the Internet at http://pubs.acs.org.

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