# Determination of the electrophilic reactivities of 1,1,3-triarylallyl cations † ‡

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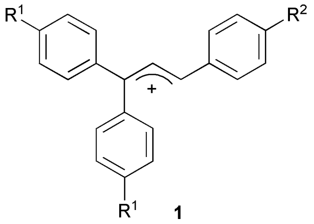
The 1,1,3-triphenylallyl cation and its *p*-methoxy and *p*-dimethylamino substituted derivatives have been generated in dichloromethane solution or as stable salts. Allylsilanes, allylstannanes, silylated enol ethers and ketene acetals, as well as enamines attack the sterically less hindered 3-position of the allyl cation as derived from the structures of the reaction products. Kinetic investigations of these reactions revealed that they follow the equation $\log k(20\ ^\circ\mathrm{C}) = s(N + E)$, which allows one to derive the electrophilicity parameters $E$ of $\mathrm{Ph_2C{=}CH{-}CH^+Ph}$ ($E = +0.98 \pm 0.20$), $(p\text{-}\mathrm{MeOC_6H_4})_2\mathrm{C{=}CH{-}CH^+Ph}$ ($E = -2.67 \pm 0.30$), $(p\text{-}\mathrm{Me_2NC_6H_4})_2\mathrm{C{=}CH{-}CH^+Ph}$ ($E = -8.97 \pm 0.32$) and $(p\text{-}\mathrm{Me_2NC_6H_4})_2\mathrm{C{=}CH{-}CH^+}(p\text{-}\mathrm{Me_2NC_6H_4})$ ($E = -9.84 \pm 0.21$).

## Introduction

1,1,3-Triaryl substituted allyl cations **1**, diversely substituted at the *p*-positions of the aromatic moieties have been known since 1941.[1–4] Their use as sensitisers in electrophotographical materials has been described.[5]



**1**

**1a** $R^1 = R^2 = H$
**1b** $R^1 = OMe, R^2 = H$
**1c** $R^1 = NMe_2, R^2 = H$
**1d** $R^1 = R^2 = NMe_2$

In a series of papers,[6–9] we have recently demonstrated that the rates of the reactions of carbocations with nucleophiles are given by the three-parameter eqn. (1),

$$\log k\ (20\ ^\circ\mathrm{C}) = s\ (N + E) \qquad (1)$$

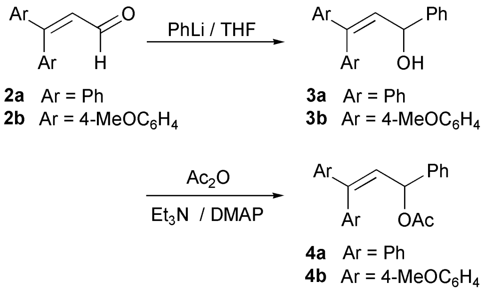
where $s$ = nucleophile-specific slope parameter, $N$ = nucleophilicity parameter and $E$ = electrophilicity parameter, and we have defined reference nucleophiles,[6] which are recommended for the characterisation of further electrophiles.

We now report on the kinetics of the reactions of the triarylallyl cations **1a**–**d** with different types of nucleophiles and employ these data for determining the $E$ parameters of **1a**–**d**.

## Results and discussion

### Synthesis of the triarylallyl cations 1a–d

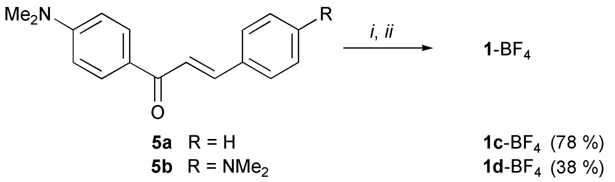
Following a reaction sequence described by Williams *et al.*,[10] the 3,3-diarylpropenals **2a**,**b**[11] were combined with phenyllithium in THF to give the triarylallyl alcohols **3a**,**b**. Acylation with acetic anhydride in the presence of triethylamine and 4-(dimethylamino)pyridine (DMAP) converted the alcohols **3a**,**b** into the acetates **4a**,**b**[10,12] (Scheme 1).



**Scheme 1** Syntheses of the acetates **4**

Because of their tendency to undergo cyclisation to indanyl cations,[13,14] the cations **1a** and **1b** were generated at low temperature from the corresponding precursors **4a** or **4b** with trimethylsilyl triflate (TMSOTf) in dichloromethane and combined with the nucleophilic reaction partners below −40 °C.

The 1,3-diarylpropenones **5a**,**b** were obtained from *p*-(dimethylamino)acetophenone[15] and the corresponding benzaldehydes by aldol condensation.[16] Treatment with *p*-(dimethylamino)phenyllithium,[17–19] subsequent acidification and addition of aqueous sodium tetrafluoroborate solution led to the precipitation of **1c**–$BF_4$ and **1d**–$BF_4$,[1] respectively, which could be purified by recrystallisation from dichloromethane–pentane mixtures (Scheme 2).



**Scheme 2** *Conditions*: i, 4-bromo-*N*,*N*-dimethylaniline, lithium, $Et_2O$–THF; ii, AcOH, $NaBF_4$, $H_2O$.

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† Dedicated to Professor W. Beck on the occasion of his 70th birthday.

‡ Electronic supplementary information (ESI) available: UV–VIS spectra of cations **1a**–**d**; synthesis of compounds **17**, **18**, **20**–**22**, **24**, **26**, **28**; rate constants and experimental conditions of the individual kinetic experiments. See http://www.rsc.org/suppdata/p2/b2/b203554e/

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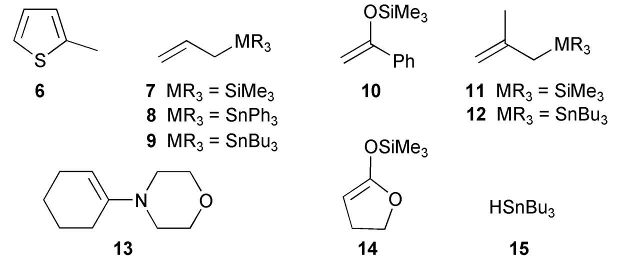
**Table 1** Products and kinetics of the reactions of the triarylallyl cations **1a**–**d** with various nucleophiles

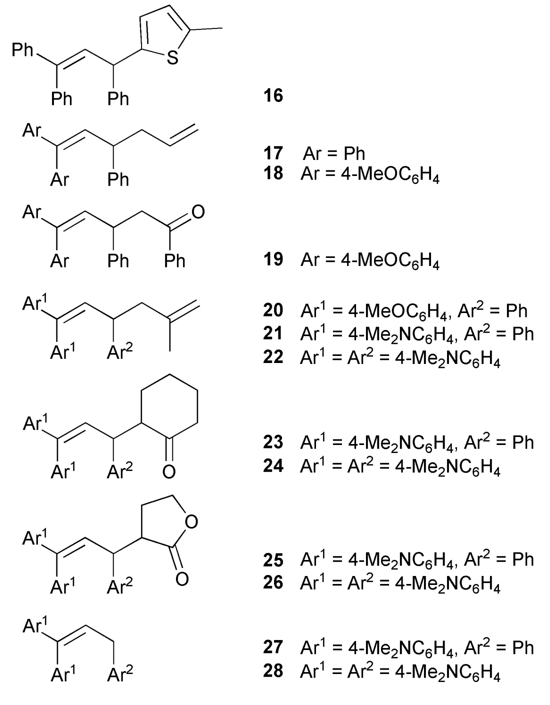
| Electrophile | Nucleophile | Product (yield) | $\Delta H^{\ddagger}$/kJ mol$^{-1\,a}$ | $\Delta S^{\ddagger}$/J mol$^{-1}$ K$^{-1\,a}$ | $k$(20 °C)/l mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|---|---|
| **1a** | **6** | **16** (75%) | 24.17 ± 0.87 | −116.4 ± 4.1 | $2.51 \times 10^{2}$ |
| | **7** | **17** (64%) | 27.05 ± 1.22 | −106.3 ± 5.9 | $2.58 \times 10^{2}$ |
| | **8** | **17** (66%) | 20.40 ± 1.24 | −106.4 ± 5.8 | $3.93 \times 10^{3}$ |
| **1b** | **9** | **18** (40%) | 32.66 ± 1.72 | −77.3 ± 7.9 | $8.48 \times 10^{2}$ |
| | **10** | **19** (21%) | 27.57 ± 1.12 | −90.0 ± 5.3 | $1.50 \times 10^{3}$ |
| | **11** | **20** (42%) | 31.12 ± 1.75 | −106.7 ± 8.1 | $4.67 \times 10^{1}$ |
| | **12** | **20** (40%) | 20.87 ± 0.94 | −95.6 ± 4.5 | $1.18 \times 10^{4}$ |
| **1c** | **12** | **21** (52%) | — | — | $6.58 \times 10^{-2}$ |
| | **13** | **23** (24%, 65 : 35) | 28.79 ± 2.19 | −105.2 ± 8.8 | $1.46 \times 10^{2}$ |
| | **14** | **25** (67%, 53 : 47) | 30.19 ± 0.60 | −100.4 ± 2.5 | $1.46 \times 10^{2}$ |
| | **15** | **27** (24%) | — | — | $5.77 \times 10^{-1}$ |
| **1d** | **12** | **22** (37%) | — | — | $1.16 \times 10^{-2}$ |
| | **13** | **24** (5%, 71 : 29) | 18.03 ± 2.03 | −158.2 ± 8.0 | $2.05 \times 10^{1}$ |
| | **14** | **26** (37%, 58 : 42) | 29.37 ± 0.48 | −112.2 ± 2.0 | $4.92 \times 10^{1}$ |
| | **15** | **28** (30 %) | — | — | $1.69 \times 10^{-1}$ |

[a] Since the standard deviations of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ do not include systematic errors, the actual uncertainties are greater than indicated in this column. For that reason the listed decimals are meaningless by themselves but are needed to reproduce the rate constants given.

## Reactions with nucleophiles

Treatment of the triphenylallyl acetate **4a** with trimethylsilyl triflate and the nucleophiles **6**–**8** at −70 °C gave rise to the formation of compounds **16** and **17** indicating the exclusive nucleophilic attack at the monosubstituted allylic terminus of **1a**[20] (Table 1). An analogous reaction pathway was derived from the formation of compounds **18**–**20** from the trimethylsilyl triflate induced reactions of **4b** with **9**–**12** at −45 °C. Though only moderate yields of the pure products were isolated, we did not find evidence for nucleophilic attack at the diaryl substituted allylic terminus.





Products **21**–**28** were obtained by combining the stable tetrafluoroborate salts of **1c** and **1d** with the nucleophiles **12**–**15** at 20 °C. Low diastereoselectivities were observed in the reactions of the prochiral electrophiles **1c**,**d** with the prochiral π-systems **13** and **14**. While the five-membered ring compound **14** gave rise to a ratio of diastereoisomers of *ca.* 1 : 1, morpholinocyclohexene **13** gave 2 : 1 mixtures of diastereomers which were not separated. Since only low yields of **23**–**26** were isolated, an interpretation of these diastereomeric ratios is not possible.

## Kinetics

The rate constants of the reactions of the triarylallyl cations **1a**–**d** with the nucleophiles **6**–**15** were determined by monitoring the decay of the electrophile absorbances, using the equipment and the data evaluation procedures described previously.[21]

Because of the previously mentioned tendency of the allyl cations **1a** and **1b** to undergo cyclisation, solutions of **1a**,**b**-OTf were generated from the allyl acetates **4a**,**b** and trimethylsilyl triflate in dichloromethane at $T < -40$ °C. Kinetic investigations of the reactions of **1a**,**b**-OTf with the nucleophiles **6**–**12** were performed at −70 °C to −50 °C and monitored at $\lambda = 510 \pm 5$ nm (**1a**) or 470 ± 5 nm (**1b**).[22] The rate constants referring to 20 °C (Table 1) were then calculated from the Eyring activation parameters determined in the low-temperature range. Since the allyl cations **1c** and **1d** do not undergo intramolecular cyclisation reactions,[23] the kinetics of their reactions with the π-nucleophiles **12**–**14** as well as with tributylstannane (**15**) could be studied in a wider temperature range or even at 20 °C at $\lambda$ = 675 nm for **1c** and 600 nm for **1d**.[22] In analogy to the reactions of benzhydrylium triflates and tetrafluoroborates with the nucleophiles **6**–**15**,[6] all reactions listed in Table 1 follow second-order kinetics, first order with respect to carbenium ion concentration and first order with respect to nucleophile concentration. Since kinetic investigations of the reactions of benzhydrylium triflates and tetrafluoroborates with **6**–**15** showed independence of the rate constants of the nature of the counterions,[21,24,25] rate-determining electrophile–nucleophile combination can also be assumed for the reactions of **1a**,**b**-OTf and **1c**,**d**–$BF_4$ with **6**–**15**.

Except for the hydride donor **15**, all nucleophiles **6**–**14** which were used for kinetic investigations in this work (Table 1) belong to a list of reference nucleophiles which have recently been recommended as reaction partners for the determination of further *E* parameters.[6] Therefore, the rate constants of the reactions of the π-nucleophiles **6**–**14** with the allyl cations **1a**–**d** given in Table 1 have been selected for the calculation of *E* parameters for **1a**–**d**. Table 2 demonstrates that for each allyl cation the *E* parameters derived from reactions with different nucleophiles are in close agreement, corroborating that the

**Table 2** Determination of the electrophilicity parameters $E$ of **1a**–**d** from reactions with different reference nucleophiles

| Electrophile | Nucleophile | $N^a$ | $s^a$ | log ($k$/l mol$^{-1}$ s$^{-1}$) | $E$ |
|---|---|---|---|---|---|
| **1a** | **6** | 1.26 | 0.96 | 2.40 | +1.25 |
| | **7** | 1.79 | 0.94 | 2.41 | +0.77 |
| | **8** | 3.09 | 0.90 | 3.59 | +0.89 |
| | | | | | $E$(**1a**) = +0.98 ± 0.20$^b$ |
| **1b** | **9** | 5.46 | 0.89 | 2.93 | −2.16 |
| | **10** | 6.22 | 0.96 | 3.18 | −2.90 |
| | **11** | 4.41 | 0.96 | 1.67 | −2.68 |
| | **12** | 7.48 | 0.89 | 4.07 | −2.90 |
| | | | | | $E$(**1b**) = −2.67 ± 0.30$^b$ |
| **1c** | **12** | 7.48 | 0.89 | −1.18 | −8.81 |
| | **13** | 11.40 | 0.83 | 2.16 | −8.79 |
| | **14** | 12.56 | 0.70 | 2.16 | −9.47 |
| | | | | | $E$(**1c**) = −8.97 ± 0.32$^b$ |
| **1d** | **12** | 7.48 | 0.89 | −1.94 | −9.65 |
| | **13** | 11.40 | 0.83 | 1.31 | −9.82 |
| | **14** | 12.56 | 0.70 | 1.69 | −10.14 |
| | | | | | $E$(**1d**) = −9.84 ± 0.21$^b$ |

[a] From ref. 6. [b] The $E$ parameter is obtained by minimizing $\Delta^2 = \Sigma[\log k_i - s_i(E + N_i)]^2$ and deviates slightly from the arithmetic mean of $E$ derived from the individual reactions. The calculations were actually performed with more decimals of log $k$, $N$, and $s$ than indicated in the table. The use of log $k$, $N$, and $s$ given in the table leads to slightly deviating results.

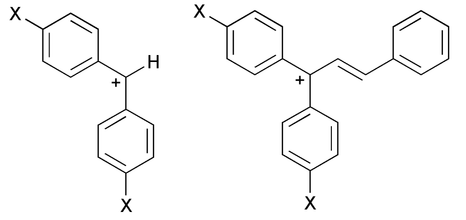
nucleophilicity parameters derived from reactions with benzhydrylium ions[6] also hold for the reactions with this class of electrophiles.

The wide applicability of these reactivity parameters is further demonstrated by the fact that the rate constants for the hydride transfer from tributylstannane (**15**) to **1c** ($k_{calc}$ = 3.50 l mol$^{-1}$ s$^{-1}$) and **1d** ($k_{calc}$ = 1.16 l mol$^{-1}$ s$^{-1}$), calculated from eqn. (1) using the $E$ values of these electrophiles (Table 2) and the reactivity parameters of hydride donor **15** ($N$ = 9.96, $s$ = 0.55)[6] deviate by less than a factor of 7 from the experimental numbers in Table 1.

The triarylallyl cations **1a**–**d** can be considered as vinylogous tritylium ions. Because steric effects have to be considered, reactions of tritylium ions with π-nucleophiles cannot be treated by eqn. (1), but for reactions with hydride donors an electrophilicity parameter of $E(Ph_3C^+) = -0.69$ has been derived.[26] Comparison with the $E$ value of the triphenylallyl cation **1a** indicates that the electrophilicity of $Ph_3C^+$ is enhanced by 1.7 logarithmic units upon insertion of an additional double bond.

Replacement of the benzhydryl hydrogen in benzhydrylium ions by a styryl group reduces the electrophilicity by 2 to 5 orders of magnitude (Table 3). As expected, the effect is largest for the unsubstituted benzhydrylium ion ($\Delta E = -4.92$) and shrinks to $\Delta E = -2.67$ and $-1.95$ for the methoxy and dimethylamino substituted systems because of the reduced electron demand in the latter carbenium ions.

**Table 3** Comparison of the electrophilicities of the triarylallyl cations with those of structurally analogous benzhydrylium ions



| X | $E^a$ | $E^b$ | $\Delta E$ |
|---|---|---|---|
| H | +5.90 | +0.98 | −4.92 |
| OMe | 0.00 | −2.67 | −2.67 |
| $NMe_2$ | −7.02 | −8.97 | −1.95 |

[a] From ref. 6. [b] This work.

Remarkably, replacement of phenyl by $p$-(dimethylamino)-phenyl (**1c**⟶**1d**) reduces the electrophilicity by less than one order of magnitude. This difference is comparable to that between malachite green [($p$-$Me_2NC_6H_4)_2PhC^+$] and crystal violet [($p$-$Me_2NC_6H_4)_3C^+$],[27] though in the case of the tritylium ions, the introduction of a third strongly donating arene ring is accompanied by a reduction of the π-overlap with the other two rings.

As the reduction of electrophilicity due to replacement of $p$-methoxy by $p$-dimethylamino turned out to be comparable in the benzhydryl and the 1,1-diaryl-3-phenylallyl series (Table 3), one can expect that the exchange of the $p$-dimethylaminophenyl groups in **1c** by stronger electron donors such as the julolidin-9-yl or the lilolidin-8-yl group would have similar effects as in the benzhydryl series.[6] Sterically non-shielded carbocations with electrophilicity parameters as low as $E = -12$ would thus become available for kinetic investigations of stronger nucleophiles.

## Experimental

### General

NMR spectra were recorded with Varian Mercury 200, Bruker ARX 300, Varian VRX 400S, and Varian INOVA-400 spectrometers. $^1$H NMR chemical shifts refer to tetramethylsilane ($\delta_H$ 0.00) and $^{13}$C NMR chemical shifts refer to the solvent as internal standard ($CDCl_3$: $\delta$ 77.0; $CD_3CN$: $\delta$ 1.3). Coupling constants $J$ are given in Hz. Mass spectra (EI, 70 eV) were obtained with a Varian MAT 90 or MAT 95 instrument. Melting points (uncorrected) were determined with a Reichert Thermovar apparatus.

The UV–VIS photometers used for the kinetic studies were Schölly KGS III with band-pass filters by Corion[21] and J&M TIDAS DAD with insertion probes by Hellma.[28] The kinetic measurements and the data-evaluation were carried out as described previously.[21]

All reactions were performed with exclusion of moisture in an atmosphere of dry nitrogen in carefully dried Schlenk glassware. Dichloromethane was freshly distilled from $CaH_2$

before use. THF and diethyl ether were dried over KOH and Na–benzophenone. Pentane was dried over KOH and Na.

Allyl acetate **4a**,[10] allylsilane **11**,[25] allylstannane **12**,[25] and silyl ketene acetal **14**[29] were synthesised according to literature methods. All other nucleophiles are commercially available.

### Synthesis of 3,3-bis(4-methoxyphenyl)-1-phenylallyl acetate (4b)

In analogy to the report by Williams *et al.*,[10] reaction of aldehyde **2b**[11,30] with phenyllithium yielded alcohol **3b** which was converted into the acetate **4b**. Alcohol **3b** (0.54 g, 1.6 mmol) was dissolved in a mixture of acetic anhydride (0.22 ml, 2.3 mmol), triethylamine (0.35 ml, 2.5 mmol), 4-(dimethylamino)pyridine (40 mg, 0.33 mmol), and dichloromethane (30 ml). The solution was stirred at ambient temperature for 22 h and then worked up as described[10] to yield **4b** (0.51 g, 82%) as an orange oil; $\delta_H$ (300 MHz; $CDCl_3$)[31] 2.06 (3 H, s, $CH_3$), 3.77, 3.84 (2 × 3 H, 2 s, 2 × OMe), 6.17 (1 H, d, *J* 9.4, 2-H), 6.31 (1 H, d, *J* 9.4, 1-H), 6.76–6.83, 6.89–6.94, 7.10–7.14, 7.15–7.19 (4 × 2 H, 4 m, ArH), 7.26–7.34 (5 H, m, ArH); $\delta_C$ (75.5 MHz, $CDCl_3$)[31] 21.4 (q, $CH_3$), 55.2, 55.3 (2 q, OMe), 74.4 (d, C-1), 113.4, 113.5 (2 d, Ar), 124.2 (d, C-2), 126.9, 127.9, 128.6, 128.8, 130.9 (5 d, Ar), 131.3, 134.3, 140.5, 143.9, 158.6, 158.9 (6 s, C-3 and Ar), 169.8 (COO); *m*/*z* 388 ($M^+$, 24%), 345 (16), 329 (100), 221 (14).

### Synthesis of 3,3-bis(4-dimethylaminophenyl)-1-phenylallyl tetrafluoroborate (1c–$BF_4$)

A solution of 4-(dimethylamino)phenyllithium in diethyl ether (45 ml) was prepared from 4-bromo-*N*,*N*-dimethylaniline (9.91 g, 49.5 mmol) and lithium (0.64 g, 92 mmol) as described in the literature.[17,18] Then a solution of ketone **5a**[16] (5.00 g, 19.9 mmol) in dry THF (20 ml) was added at ambient temperature over 1.5 h. The mixture was stirred for another 30 min, then it was acidified with glacial acetic acid (30 ml) and poured into a 2 M aqueous solution of $NaBF_4$ (200 ml). Small portions of the mixture were diluted with water to precipitate a blue solid which was filtered off, washed with water and dried *in vacuo*. Recrystallisation from $CH_2Cl_2$–*n*-pentane yielded **1c**–$BF_4$ (6.83 g, 78%) as blue metallic needles, mp 146–147 °C (decomp.); $\delta_H$ ($CD_2Cl_2$, 300 MHz)[31] 3.30 (12 H, s, 2 × $NMe_2$), 6.91–6.96 (4 H, m, ArH), 7.20 (1 H, d, *J* 15.5, 1-H), 7.48–7.50 (3 H, m, ArH), 7.58–7.62 (4 H, m, ArH), 7.69–7.73 (2 H, m, ArH), 7.79 (1 H, d, *J* 15.5 Hz, 2-H); $\delta_C$ ($CD_2Cl_2$, 75.5 MHz)[31] 41.0 (q, $NMe_2$), 113.8 (d, Ar), 126.9 (s, Ar), 128.1 (d, C-2), 129.6, 129.7, 132.3 (3 d, Ar), 135.9 (s, Ar), 139.3 (d, Ar), 153.8 (d, C-1), 157.1 (s, Ar), 173.8 (s, C-3).

### Synthesis of 1,3,3-tris(4-dimethylaminophenyl)allyl tetrafluoroborate (1d–$BF_4$)

A solution of 4-(dimethylamino)phenyllithium in diethyl ether (20 ml) was prepared from 4-bromo-*N*,*N*-dimethylaniline (4.81 g, 24.0 mmol) and lithium (0.42 g, 61 mmol) as described in the literature.[17,18] Excess lithium was removed after the reaction had been stirred for 21 h at ambient temperature. Then a suspension of ketone **5b**[16] (5.89 g, 20.0 mmol) in dry THF (80 ml) was added. The mixture was heated to reflux for 3 h, then it was cooled to ambient temperature, acidified with glacial acetic acid (30 ml) and poured into a 5 M aqueous solution of $NaBF_4$ (200 ml). Small portions of the mixture were diluted with water and neutralised with aq. $NaHCO_3$ to precipitate a blue solid which was filtered off and dried *in vacuo*. Recrystallisation from $CH_2Cl_2$–*n*-hexane yielded **1d**–$BF_4$ (3.69 g, 38%) as golden needles, mp 134–138 °C; $\delta_H$ (400 MHz, $CD_2Cl_2$)[31] 3.20 (18 H, br s, 3 × $NMe_2$), 6.79–6.84 (6 H, m, ArH), 7.37 (1 H, d, *J* 14.4, 1-H), 7.47–7.50 (4 H, m, ArH), 7.63 (1 H, d, *J* 14.4, 2-H), 7.67–7.69 (2 H, m, ArH); $\delta_C$ (100.6 MHz, $CD_2Cl_2$)[31] 40.6, 40.7 (2 q, $NMe_2$), 112.6, 113.3 (2 d, Ar), 121.7 (d, C-2), 125.2, 126.6 (2 s, Ar), 134.9, 137.1 (2 d, Ar), 155.5 (s, Ar), 158.7 (d, C-1), 174.2 (s, C-3).

### 2-Methyl-5-(1,3,3-triphenylprop-2-enyl)thiophene (16)

Compound **4a** (0.65 g, 2.0 mmol) was dissolved in dichloromethane (10 ml) under nitrogen and cooled to −70 °C. Trimethylsilyl triflate (0.39 ml, 2.2 mmol) was added to give a red solution of **1a**-OTf. After the addition of arene **6** (0.25 ml, 2.6 mmol) the solution was stirred at −70 °C until the red colour of **1a** disappeared (3 d). The mixture was allowed to warm to ambient temperature and hydrolysed over 15 min by adding aq. $NaHCO_3$ solution (30 ml).[32] The aqueous layer was separated and extracted with dichloromethane (10 ml). The combined organic layers were dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* to yield the crude product which was recrystallised to give **16** (0.55 g, 75%) as light brown crystals, mp 127–129 °C (from diethyl ether–*n*-pentane) (Found: C, 85.31; H, 6.08; S, 8.64. $C_{26}H_{22}S$ requires C, 85.20; H, 6.05; S, 8.75 %); $\delta_H$ ($CDCl_3$, 400 MHz) 2.40 (3 H, s, 2-Me), 4.89 (1 H, d, *J* 10.4, 5-C*H*CH=C), 6.49–6.56 (3 H, m, 3-H, 4-H, and 5-CHC*H*=C), 7.19–7.39 (15 H, m, ArH); $\delta_C$ ($CDCl_3$, 100.6 MHz) 15.31 (q, 2-Me), 46.51 (d, 5-*C*HCH=C), 124.27, 124.66 (2 d, C-3, C-4), 126.64, 127.31, 127.36, 127.52, 127.92, 128.11, 128.30, 128.56, 129.76 (9 d, Ar), 130.45 (d, 5-CH*C*H=C), 138.59 (s, C-2), 139.40, 141.54, 142.03, 143.91 (4 s, Ar and 5-CHCH=*C*), 146.22 (s, C-5); *m*/*z* 366 ($M^+$, 100%), 351 (10), 289 (12), 275 (16), 268 (19), 187 (19).

### 1,1,3-Triphenylhexa-1,5-diene (17)

As described above for the formation of **16**, acetate **4a** (0.35 g, 1.1 mmol), trimethylsilyl triflate (0.06 ml, 0.3 mmol) and allylsilane **7** (0.22 ml, 0.16 g, 1.4 mmol) reacted for 21 h. Work-up gave a crude product which was purified by chromatography on neutral alumina with *n*-hexane–diethyl ether (5 : 2) as eluent to yield **17** (0.22 g, 64%) as a yellow oil which crystallised on standing, mp 56–57 °C (lit.,[33] 53–55 °C); $\delta_H$ ($CDCl_3$, 400 MHz)[31] 2.48–2.52 (2 H, m, 4-$H_2$), 3.48–3.55 (1 H, m, 3-H), 4.93–5.02 (2 H, m, 6-$H_2$), 5.61–5.71 (1 H, m, 5-H), 6.24 (1 H, d, *J* 10.5, 2-H), 7.12–7.37 (15 H, m, ArH); $\delta_C$ ($CDCl_3$, 100.6 MHz)[31] 41.70 (t, C-4), 45.12 (d, C-3), 116.22 (t, C-6), 126.11, 127.05, 127.29, 127.38, 128.06, 128.15, 128.50, 129.87 (8 d, Ar), 132.26 (d, C-2), 136.32 (d, C-5), 140.04, 141.46, 142.46, 144.70 (4 s, C-1 and Ar).

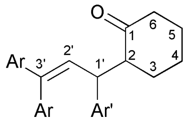
### 5,5-Bis(4-methoxyphenyl)-1,3-diphenylpent-4-en-1-one (19)

Compound **4b** (0.12 g, 0.31 mmol) was dissolved in dichloromethane (10 ml) under nitrogen and cooled to −70 °C. Trimethylsilyl triflate (80 µl, 0.44 mmol) was added to give a red solution of **1b**-OTf. After the addition of silyl enol ether **10** (80 µl, 0.39 mmol) the stirred solution was allowed to warm to −45 °C. After 3 d the reaction mixture was worked up as above, and the crude product was purified by chromatography on neutral alumina with *n*-hexane–diethyl ether (10 : 1) as eluent to yield **19** (29.2 mg, 21%) as an orange oil; $\delta_H$ (300 MHz, $CDCl_3$)[31] 3.31 (1 H, dd, $^2J$ 15.3, *J* 7.9, 2-H), 3.42 (1 H, dd, $^2J$ 15.3, *J* 6.7, 2-H), 3.76, 3.82 (2 × 3 H, 2 s, 2 × OMe), 4.12–4.20 (1 H, m, 3-H), 6.14 (1 H, d, *J* 10.4, 4-H), 6.73–6.84 (4 H, m, ArH), 6.89–6.98, 7.05–7.11 (2 × 2 H, 2 m, ArH), 7.15–7.31 (5 H, m, ArH), 7.33–7.40 (2 H, m, ArH), 7.45–7.53 (1 H, m, ArH), 7.80–7.84 (2 H, m, ArH); $\delta_C$ (75.5 MHz, $CDCl_3$)[31] 41.88 (d, C-3), 46.41 (t, C-2), 55.18, 55.24 (2 q, 2 × OMe), 113.38, 113.53, 126.33, 127.29, 128.17, 128.45, 128.49, 128.65 (8 d, Ar), 128.98 (d, C-4), 130.76 (d, Ar), 132.10 (s), 132.82 (d, Ar), 135.19, 137.01 (2 s), 141.18, 144.32, 158.61, 158.92 (4 s), 198.33 (s, C-1); *m*/*z* (EI) 448 ($M^+$, 8%), 330 (24), 329 (100), 328 (72), 221 (17), 121 (14) (HRMS: Found *m*/*z* 448.2031. $C_{31}H_{28}O_3$ requires 448.2038).

### 1,1-Bis(4-methoxyphenyl)-5-methyl-3-phenylhexa-1,5-diene (20)

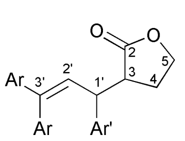
As described for the formation of **19**, compound **4b** (0.12 g, 0.31 mmol), trimethylsilyl triflate (70 µl, 0.39 mmol), and allylstannane **12** (0.19 g, 0.55 mmol) reacted for 4 h while the temperature was raised from −70 °C to ambient. The crude product was purified by chromatography on neutral alumina with *n*-hexane–diethyl ether (15 : 1) as eluent to yield **20** (47.6 mg, 40%) as a colourless oil (Found C, 84.20; H, 7.64. $C_{27}H_{28}O_2$ requires C, 84.34; H, 7.34%); $\delta_H$ (300 MHz, $CDCl_3$)[31] 1.52 (3 H, br s, 5-Me), 2.43 (2 H, d, *J* 7.5, 4-$H_2$), 3.61 (1 H, dt, *J* 10.3, *J* 7.5, 3-H), 3.76, 3.83 (2 × 3 H, 2 s, 2 × OMe), 4.65–4.71 (2 H, m, 6-$H_2$), 6.08 (2 H, d, *J* 10.3, 2-H), 6.76–6.80, 6.86–6.89, 6.99–7.04 (3 × 2 H, 3 m, ArH), 7.11–7.31 (7 H, m, Ar); $\delta_C$ (75.5 MHz, $CDCl_3$)[31] 22.22 (q, 5-Me), 43.56 (d, C-3), 46.59 (t, C-4), 55.18, 55.24 (2 q, 2 × OMe), 112.27 (t, C-6), 113.38, 125.94, 127.36, 128.46, 128.48 (5 d, Ar), 130.71 (d, C-2), 131.01 (d, Ar), 132.54, 135.73, 140.32, 143.61, 145.63, 158.57, 158.79 (7 s, C-1, C-5 and Ar); *m*/*z* (EI) 384 ($M^+$, 2), 330 (27), 329 (100), 221 (13).

### 2-[3,3-Bis(4-dimethylaminophenyl)-1-phenylprop-2-enyl]cyclohexanone (23)



A solution of **1c**–$BF_4$ (0.27 g, 0.61 mmol) and enamine **13** (0.27 g, 1.6 mmol) in dichloromethane (10 ml) was stirred for 7 d at ambient temperature. Then 2 M HCl (10 ml) and water (30 ml) were added. The phases were separated, and the aqueous layer was extracted with dichloromethane (10 ml). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (2 × 10 ml) and water (2 × 10 ml), dried ($MgSO_4$) and filtered, and the solvent was evaporated *in vacuo*. The residue was purified by chromatography[34] on neutral alumina (activity III) with *n*-hexane–diethyl ether (1 : 1) as eluent to yield **23** (67 mg, 24%) as a colourless oil, ratio of diastereomers 65 : 35 (determined by $^1H$ NMR spectroscopy) (Found C, 82.16; H, 8.24; N, 5.82. $C_{31}H_{36}N_2O$ requires C, 82.26; H, 8.02; N, 6.19%); $\delta_H$ (300 MHz, $CDCl_3$)[31] 1.42–1.80 (6 H, m, 3-$H_2$, 4-$H_2$, 5-$H_2$), 2.10–2.20 (2 H, m, 6-$H_2$), 2.66–2.90 (1 H, m, 2-H), 2.89 (6 H, s, $NMe_2$), 2.99 (0.65 × 6 H, s, $NMe_2$, major diastereomer), 3.00 (0.35 × 6 H, s, $NMe_2$, minor diastereomer), 3.86–3.94 (1 H, m, 1′-H), 5.94 (0.35 H, d, *J* 10.7, 2′-H, minor diastereomer), 6.07 (0.65 H, d, *J* 10.5, 2′-H, major diastereomer), 6.57–6.62, 6.68–6.77 (2 × 2 H, 2 m, ArH), 6.94–7.32 (9 H, m, ArH and Ar′H); $\delta_C$ (75.5 MHz, $CDCl_3$)[31] major diastereomer: 21.68 (t, C-4), 27.91 (t, C-5), 30.17 (t, C-3), 40.41 (t, C-6), 40.55 (br q, $NMe_2$), 44.97 (d, C-1′), 57.89 (d, C-2), 111.80, 112.02, 112.08 (3 d, Ar), 126.01 (d, Ar′), 126.11 (d, C-2′), 128.19 (d), 128.32 (s), 128.47, 128.50, 130.92 (3 d), 131.83, 141.73, 143.50, 149.45, 149.79 (5 s), 213.31 (C-1), additional signals of the minor diastereomer: 23.61 (t, C-4), 28.50 (t, C-5), 32.01 (t, C-3), 41.94 (t, C-6), 44.94 (d, C-1′), 57.05 (d, C-2), 125.86 (d), 126.50 (d, C-2′), 127.83, 127.97, 128.31 (3 d), 128.40 (s), 130.68 (d), 131.47, 142.10, 144.02, 149.43, 149.73 (5 s), 212.19 (s, C-1); *m*/*z* (EI) 452 ($M^+$, 8%), 356 (26), 355 (100).

### 3-[3,3-Bis(4-dimethylaminophenyl)-1-phenylprop-2-enyl]-dihydrofuran-2-one (25)



A solution of **1c**–$BF_4$ (0.24 g, 0.54 mmol) and silyl ketene acetal **14** (0.21 g, 1.3 mmol) in dichloromethane (10 ml) was stirred for 2 d at ambient temperature. Then the solvent was removed *in vacuo* and the residue was purified by chromatography on neutral alumina with *n*-hexane–ethyl acetate (3 : 2) as eluent to yield **25** (0.16 g, 67%) as a yellow-greenish oil, ratio of diastereomers 53 : 47 (determined by $^1H$ NMR spectroscopy); $\delta_H$ (400 MHz, $CDCl_3$)[31] 1.90–2.31 (2 H, m, 4-$H_2$), 2.91/2.92 (6 H, s, $NMe_2$), 2.93–2.95 (1 H, m, 3-H), 2.96/2.97 (6 H, s, $NMe_2$), 3.92–4.14 (3 H, m, 5-$H_2$ and 1′-H), 6.20 (0.53 H, d, *J* 10.6, 2′-H, major diastereomer) and 6.30 (0.47 H, d, *J* 10.7, 2′-H, minor diastereomer), 6.60–6.72 (4 H, m, ArH), 6.92–6.99, 7.12–7.19 (2 × 2 H, 2 m, ArH), 7.20–7.33 (5 H, m, Ar′H); $\delta_C$ (100.6 MHz, $CDCl_3$)[31] 26.21, 26.29 (2 t, C-4), 40.48*, 40.51, 40.54 (3 q, $NMe_2$), 45.04, 45.25 (2 d, C-1′), 45.19, 45.47 (2 d, C-3), 66.33 (2 t, C-5), 111.93*, 111.97, 112.00 (3 d, Ar), 122.90, 123.57 (2 d, C-2′), 126.54, 126.56 (2 d, Ar′), 127.92 (s, Ar), 128.00, 128.27, 128.36, 128.46, 128.50, 128.58, 130.56* (7 d, Ar and Ar′), 131.28, 131.39, 142.33, 142.47, 143.31, 143.62, 149.53, 149.91 (8 s, C-3′, Ar and Ar′), 177.27, 177.29 (2 s, C-2), signals with double intensity are marked with an asterisk; *m*/*z* (EI): 440 ($M^+$, 27%), 355 (100), 234 (11), 210 (11) (HRMS: Found *m*/*z* 440.2451. $C_{29}H_{32}N_2O_2$ requires 440.2464).

### 1,1-Bis(4-dimethylaminophenyl)-3-phenylprop-1-ene (27)

A solution of **1c**–$BF_4$ (0.27 g, 0.61 mmol) and stannane **15** (0.18 ml, 0.20 g, 0.68 mmol) in dichloromethane (10 ml) was stirred for 4 d at ambient temperature. Then the solvent was removed *in vacuo* and the residue was purified by chromatography on neutral alumina with *n*-hexane–diethyl ether (1 : 1) as eluent to yield **27** (52.9 mg, 24%) as colourless crystals, mp 98–99 °C (Found: C, 83.92; H, 7.89; N, 7.69. $C_{25}H_{28}N_2$ requires C, 84.23; H, 7.92; N, 7.86%); $\delta_H$ (300 MHz, $CDCl_3$) 2.91, 2.96 (2 × 6 H, 2 s, 2 × $NMe_2$), 3.51 (2 H, d, *J* 7.5, 3-$H_2$), 6.04 (1 H, t, *J* 7.5, 2-H), 6.60–6.64, 6.65–6.75 (2 × 2 H, 2 m, ArH), 7.10–7.30 (9 H, m, ArH); $\delta_C$ (75.5 MHz, $CDCl_3$) 35.98 (t, C-3), 40.54, 40.58 (2 q, 2 × $NMe_2$), 112.01, 112.08 (2 d, Ar), 123.55 (d, C-2), 125.65, 128.27, 128.28, 128.42, 130.78 (5 d, ArH), 131.82, 141.97, 142.24, 149.41, 149.66 (5 s); *m*/*z* (EI): 356 ($M^+$, 100%), 355 (53), 312 (14), 235 (10), 234 (11), 149 (10).

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