Domino reactions initiated by intramolecular hydride transfers from tri(di)arylmethane fragments to ketenimine and carbodiimide functions†‡

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The ability of triarylmethane and diarylmethane fragments to behave as hydride donors participating in thermal [1,5]-H shift/6π-ERC tandem processes involving ketenimine and carbodiimide functions is disclosed. *C*-Alkyl-*C*-phenyl ketenimines *N*-substituted by a triarylmethane substructure convert into a variety of 3,3,4,4-tetrasubstituted-3,4-dihydroquinolines, as structurally related carbodiimides transform into 3,4,4-trisubstituted-3,4-dihydroquinazolines *via* transient *ortho*-azaxylylenes. The first step of these one-pot conversions, the [1,5]-H shift, is considered to be a hydride migration on the basis of the known hydricity of the tri(di)arylmethane fragment and the electrophilicity of the central heterocumulenic carbon atom, whereas the final electrocyclization involves the formation of a sterically congested C–C or C–N bond. In the cases of *C*,*C*-diphenyl substituted triarylmethane-ketenimines the usual 6π-ERC becomes prohibited by the presence of two phenyl rings at each end of the azatrienic system. This situation opens new reaction channels: (a) following the initial hydride shift, the tandem sequence continues with an alternative electrocyclization mode to give 9,10-dihydroacridines, (b) the full sequence is initiated by a rare 1,5 migration of an electron-rich aryl group, followed by a 6π-ERC which leads to 2-aryl-3,4-dihydroquinolines, or (c) a different [1,5]-H shift/6π-ERC sequence involving the initial migration of a hydrogen atom from a methyl group at the *ortho* position to the nitrogen atom of the ketenimine function. Diarylmethane-ketenimines bearing a methyl group at the benzylic carbon atom experience a tandem double [1,5]-H shift, the first one being the usual benzylic hydride transfer whereas the second one involves the methyl group at the initial benzylic carbon atom, the reaction products being 2-aminostyrenes. Diarylmethane-ketenimines lacking such a methyl group convert into 3,4-dihydroquinolines by the habitual tandem [1,5]-H shift/6π-ERC processes.

Introduction

C–H Bond functionalization, the direct and selective replacement of C–H bonds with new C–C or C–heteroatom bonds, is an important and long-standing goal in organic chemistry.[1] A series of transformations for C–H bond functionalization initiated by an intramolecular hydride transfer and followed by cyclization of the resulting intermediates have been recently disclosed.[2] Such hydride shift/cyclization sequences, serving for the efficient buildup of complex polycyclic systems, are in some sense related to those based upon the well-known *tert*-amino effect.[3] In this context, while investigating new reactions of nitrogenated heterocumulenes, we recently found that 1,3-dioxolane-ketenimines **1** (X = O; Y = CR^2R^3), 1,3-dioxolane-carbodiimides **1** (X = O; Y = NAr) and 1,3-dithiolane-ketenimines **1** (X = S; Y = CR^2R^3) transform, under mild thermal treatment, into spiroquinolines **3** (X = O, S; Y = CR^2R^3) and spiroquinazolines **3** (X = O; Y = NAr), *via* a tandem sequence consisting of a [1,5]-H shift followed by a 6π electrocyclic ring closure (6π-ERC) (Scheme 1).[4] On the other hand, when 1,3-oxathiolane-ketenimines **4** (Y = CR^2R^3) and 1,3-oxathiolane-carbodiimides **4** (Y = NAr) were submitted to mild heating the 2,1-benzisothiazol-3-ones **6** were formed, a transformation which seems to occur through a formal [1,5]-H shift/1,5 electrocyclization/[3+2] cycloreversion tandem process, with the concomitant formation of ethylene (Scheme 1).[5] The [1,5]-H shifts from the acetalic functions to the electrophilic central carbon atom of the ketenimine or carbodiimide moieties, presumably providing the transient *ortho*-azaxylylenes **2** and **5**, were characterized as intramolecular hydride transfers by means of computational DFT studies. In fact, the computed NBO analysis of heterocumulenes **1** and **4** shows the weakening and polarization of the acetalic C–H bond by hyperconjugative interactions of its σ* C–H orbital with the lone pair electrons at the vicinal heteroatoms. These results demonstrated the hydride donor ability (hydricity) of the 2-monosubstituted 1,3-dioxolane, 1,3-oxathiolane and 1,3-dithiolane functions. Additionally, the experimental work and the computational calculations showed that the hydricity-imparting character of these acetalic functions decreases in the order: 1,3-dioxolane > 1,3-oxathiolane > 1,3-dithiolane.

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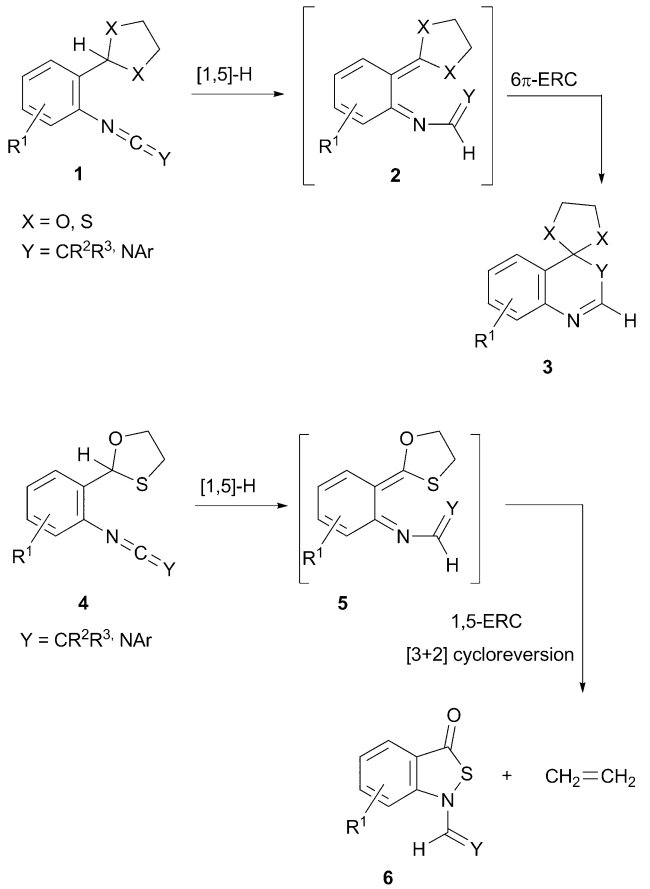
† Dedicated to Professor José Elguero with respect and admiration.

‡ Electronic supplementary information (ESI) available: Comprehensive experimental section. ^{1}H and ^{13}C NMR spectra of compounds **11**, **13**, **18**, **20**, **22**, **25**, **27**, **30**, **32** and **34**. ^{31}P NMR spectra of compounds **11**, **27** and **32**. Cif files of **13e**, **13k**, **18a** and **20b**. CCDC reference numbers 779905–779908. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0ob00193g



Scheme 1 Proposed mechanisms for the conversions **1** → **3** and **4** → **6**.

The main class of compounds possessing hydricity is the metal hydrides.[6] Nevertheless several types of organic compounds are also considered to exhibit this property. For example, NADH model compounds,[7] triarylmethanes[8] and some 1,3-dinitrogenated heterocyclic systems, such as *N*,*N*-dimethylbenzimidazoles,[9] 2-benzoyl-*N*,*N*-dimethylperhydropyrimidine[10] and orthoformamides,[11] are generally appreciated as good hydride donors.

Based on the known hydricity of the triarylmethanes, we targeted the preparation of a series of these compounds bearing a ketenimine or carbodiimide function linked by its nitrogen atom to the *ortho* position of one of the three aryl groups (Fig. 1). Our aim was to examine the viability of the [1,5]-H transfer from the sp^3 methine carbon to the electron-deficient central carbon atom of the ketenimine or carbodiimide fragment, and therefore the participation of this type of heterocumulene in

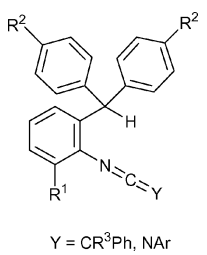


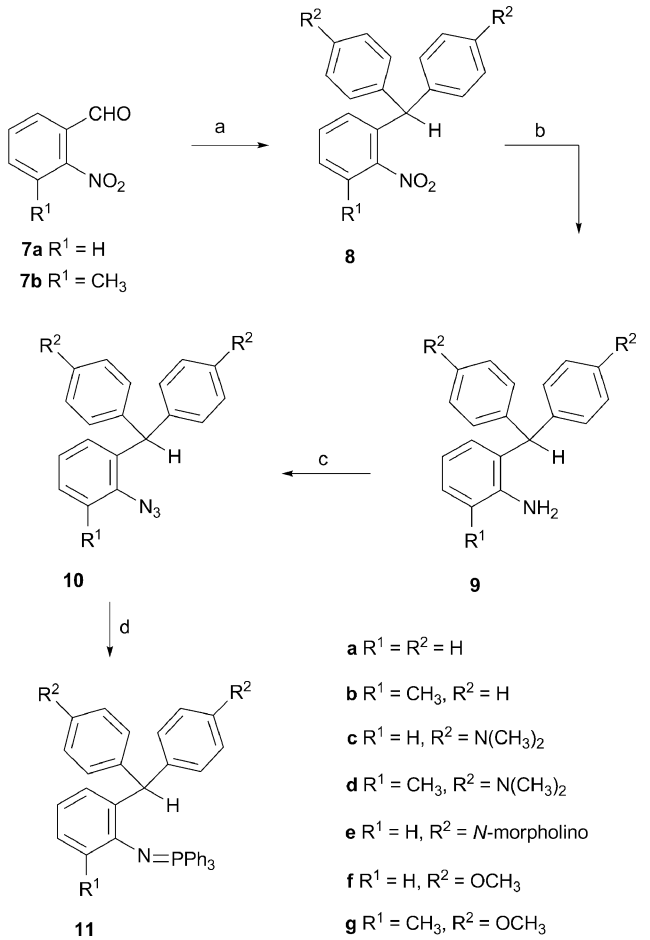
Fig. 1 General structure of triarylmethane-ketenimines and triarylmethane-carbodiimides.

[1,5]-H shift/6π-ERC tandem processes closely related to those described for compounds **1**. As result of this experimental work we here disclose that such triarylmethane-ketenimines converted under thermal conditions into substituted quinolines or acridines through tandem processes that involve as the first mechanistic step either the expected [1,5]-H transfer or an unusual [1,5] sigmatropic migration of an aryl group, and as the second step different modes of electrocyclic ring closure in the resulting 3-azahexatriene intermediates. The electrocyclization mode at this second step seems to depend on the nature of the substituents at the aryl rings (R^1 and R^2) and at the *C*-terminal carbon atom of the starting ketenimine function (R^3). In addition, we report that under similar conditions triarylmethane-carbodiimides simply undergo 1,5 migration of the hydrogen at the sp^3 methine carbon atom and subsequent 6π-ERC to afford quinazolines.

Results and discussion

The synthetic strategy for the preparation of the triarylmethane-ketenimines and triarylmethane-carbodiimides starts with a Friedel–Crafts acylation in which two equivalents of benzene or a monosubstituted benzene react with one equivalent of 2-nitrobenzaldehyde **7a** or 3-methyl-2-nitrobenzaldehyde **7b**, to provide nitrotriarylmethanes **8** (36–73%). These reactions were run under different conditions depending on the nature of R^2. In the cases where R^2 = H (**8a,b**) the acylation reaction was carried out by treating benzene solutions of the 2-nitrobenzaldehydes **7** with anhydrous aluminium chloride.[12] When $R^2 = N(CH_3)_2$ (**8c,d**) or *N*-morpholino (**8e**) mixtures of the 2-nitrobenzaldehydes **7** and *N*,*N*-dimethylaniline or *N*-phenylmorpholine were treated with anhydrous zinc chloride.[13] The synthesis of the nitro derivatives **8f** and **8g** in which $R^2 = OCH_3$ was achieved by reaction of the 2-nitrobenzaldehydes **7** with anisole in the presence of aluminium chloride.[14] Next, the reduction of compounds **8** with molecular hydrogen in the presence of Pd on activated charcoal, using ethanol as solvent, yielded the anilines **9** (65–88%). The diazotation of anilines **9** followed by the addition of sodium azide provided azides **10**. For this latter conversion different reaction conditions were also used in accordance with the nature of R^2. For R^2 = H or OCH_3 the corresponding azides **10a,b,f,g** were readily obtained (80–92%) by sequential treatment of sulfuric acid/1,4-dioxane solutions of amines **9a,b,f,g** with sodium nitrite and sodium azide.[13] For the cases where $R^2 = N(CH_3)_2$ or *N*-morpholino suspensions of the amines **9c–e** in 6 N hydrochloric acid were first treated with a solution of sodium nitrite in water, and then with an aqueous solution of sodium azide and sodium acetate (45–72%).[15] The imination reaction of triphenylphosphine with the azides **10**, in anhydrous diethyl ether at room temperature, provided the triphenyliminophosphoranes **11** (86–99%) (Scheme 2).

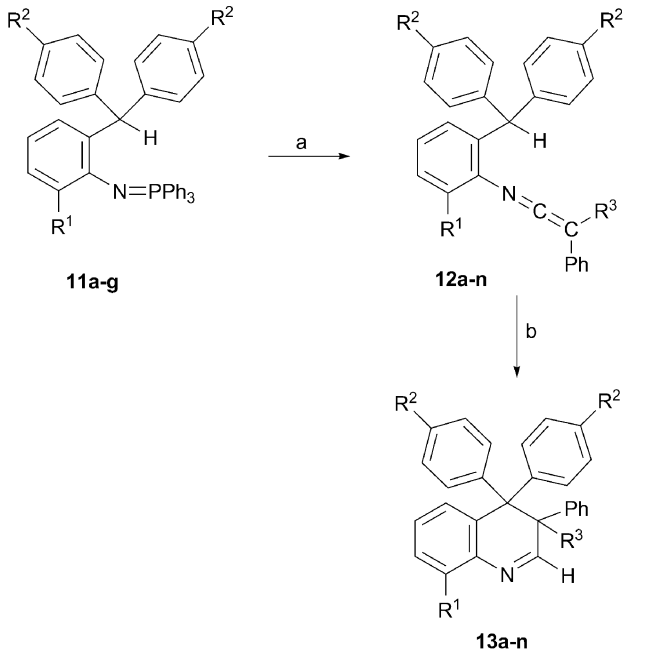
The aza-Wittig reaction of iminophosphoranes **11** with ethylphenylketene and methylphenylketene, in dichloromethane solution at room temperature, led to the formation of the triarylmethane-ketenimines **12** (Scheme 3, Table 1), which were separated from the triphenylphosphine oxide by column chromatography on a short pad of silica gel, checked by IR (strong absorption near 2000 cm^{-1}) and immediately submitted to the next reaction step for preventing its partial hydrolysis.[16] It is relevant to note that compounds **12** bear a phenyl group and an ethyl or methyl substituent at the sp^2 terminal carbon atom of the



Scheme 2 *Reagents and conditions*: (a) R^2 = H C_6H_6, $AlCl_3$, 60 °C, 6 h; R^2 = $N(CH_3)_2$, *N*-morpholino $C_6H_5R^2$, $ZnCl_2$, 80 °C, 6 h; R^2 = OCH_3 $C_6H_5OCH_3$, $AlCl_3$, r.t., 12 h (36–73%). (b) H_2, Pd/C, EtOH, r.t., 24 h (65–88%). (c) R^2 = H, OCH_3 (1) $NaNO_2$, H_2SO_4 (4 N)/1,4-dioxane, 0 °C, 30 min (2) NaN_3, H_2SO_4 (4 N)/1,4-dioxane, r.t., 16 h; R^2 = $N(CH_3)_2$, *N*-morpholino (1) $NaNO_2$, HCl/H_2O, 0 °C, 30 min (2) NaN_3, NaOAc, HCl/H_2O, r.t., 1 h (45–92%). (d) PPh_3, Et_2O, r.t., 16 h (86–99%).

Table 1 Ketenimines **12** and Quinolines **13**

entry	R^1	R^2	R^3	**12** Yield (%)	**13** Yield (%)
a	H	H	CH_3	88	60
b	H	H	CH_2CH_3	80	15
c	CH_3	H	CH_3	40	99
d	CH_3	H	CH_2CH_3	38	61
e	H	$N(CH_3)_2$	CH_3	92	63
f	H	$N(CH_3)_2$	CH_2CH_3	71	80
g	CH_3	$N(CH_3)_2$	CH_3	90	78
h	CH_3	$N(CH_3)_2$	CH_2CH_3	67	75
i	H	*N*-morpholino	CH_3	79	65
j	H	*N*-morpholino	CH_2CH_3	97	60
k	H	OCH_3	CH_3	74	57
l	H	OCH_3	CH_2CH_3	86	52
m	CH_3	OCH_3	CH_3	70	85
n	CH_3	OCH_3	CH_2CH_3	97	99



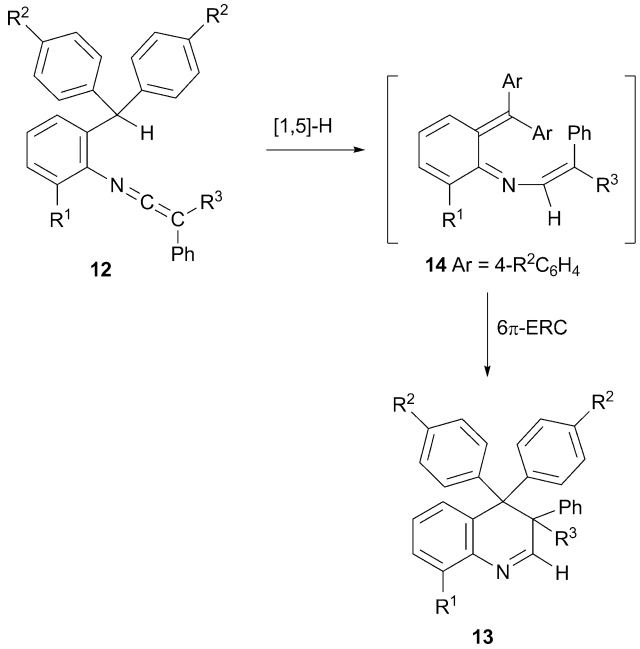
Scheme 3 *Reagents and conditions*: (a) PhR^3CCO, CH_2Cl_2, r.t., 30 min. (b) Toluene or *ortho*-xylene, reflux, 5–144 h.

ketenimine function. When toluene or *ortho*-xylene solutions of ketenimines **12** were heated at reflux temperature, during periods of time ranging from 5 to 144 h, the 3-ethyl(methyl)-3,4,4-triaryl-3,4-dihydroquinolines **13** were formed, and isolated in moderate to good yields (Scheme 3, Table 1).

The structural determination of the 3-alkyl-3,4,4-triaryl-3,4-dihydroquinolines **13** was carried out following their analytical and spectral data. In their ^{1}H NMR spectra the C(2)H proton resonates as a singlet at δ = 8.21–8.68 ppm. Relevant ^{13}C NMR data of compounds **13** are the chemical shifts of the quaternary carbon C3 at δ = 48.0–52.0 ppm, the quaternary carbon C4 at δ = 59.7–62.9 ppm and the methine C2 at δ = 166.2–169.4 ppm. Moreover, the structures of compounds **13e** (R^1 = H; R^2 = $N(CH_3)_2$; R^3 = CH_3) and **13k** (R^1 = H; R^2 = OCH_3; R^3 = CH_3) were determined by X-ray crystal diffraction (see Electronic supplementary information). The main feature of these two structures is the relatively long bond distance of the C3–C4 bond (C8–C9 bond in the crystallographic study), 1.598 Å in compound **13e** and 1.604 Å in **13k**. These long distances are most probably due to the steric repulsion between the bulky substituents at the C3 and C4 carbon atoms.[17]

The transformation **12** → **13** should proceed by a mechanism involving as the first step the cleavage of the C–H bond of the triarylmethane fragment *via* a 1,5 hydride shift to give the transient *ortho*-azaxylylene **14** (Scheme 4). Subsequent 6π electrocyclic ring closure should afford the sterically congested 3,4-dihydroquinolines **13**. The denotation of the first mechanistic step as a hydride shift relies on the known hydricity of the triarylmethane C–H bond and the electrophilicity of the central ketenimine carbon atom.

The presence of a methyl substituent at the *ortho* position to the keteniminic nitrogen atom (R^1 = CH_3) has a significant influence on the reactivity of the triarylmethane-ketenimines **12**: in general, compounds **12** with R^1 = CH_3 afforded the corresponding 3,4-dihydroquinolines **13** in the best chemical yields and in the shortest reaction times. This enhancement of reactivity could be rationalized by considering that the presence of this methyl group shifts the conformational equilibrium of compounds **12** to the



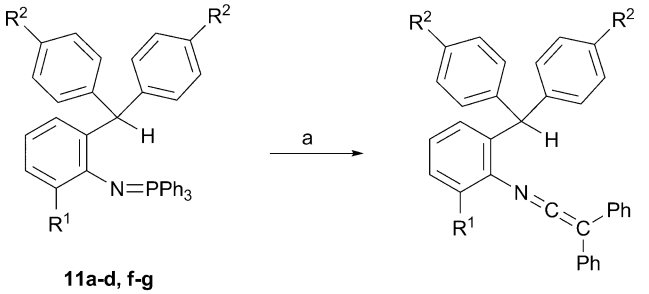
Scheme 4 Proposed mechanism for the conversion **12** → **13**.

C_{aryl}–N rotational isomer that locates the electrophilic central carbon atom of the ketenimine function close to the hydrogen atom that is going to translate in the 1,5 hydride migration.[18] In addition, we have observed that the presence of strong electron-releasing groups (R^2 = $N(CH_3)_2$, *N*-morpholino and OCH_3) at the *para* position of the two other aryl rings facilitates the conversion of ketenimines **12** by shortening the reaction time. These groups are known to increase the hydricity of the triarylmethane C–H bond.[8] In most of the cases, placing an ethyl group instead of a methyl one at the terminal carbon atom of the ketenimine function results in a lower yield of the tandem process converting ketenimines **12** into quinolines **13**, a fact that could be attributed to the slightly higher steric hindrance that makes more difficult the electrocyclization step.

We next approached the study of similar tandem processes in which the future C3–C4 bond of the putative final quinolines is more sterically congested by the presence of four aryl substituents at the extremes of that bond. To this end we prepared the *C*,*C*-diphenyl ketenimines **15** (60–92%) by reacting iminophosphoranes **11a–d** and **11f,g** with diphenylketene, in dichloromethane solution at room temperature (Scheme 5).

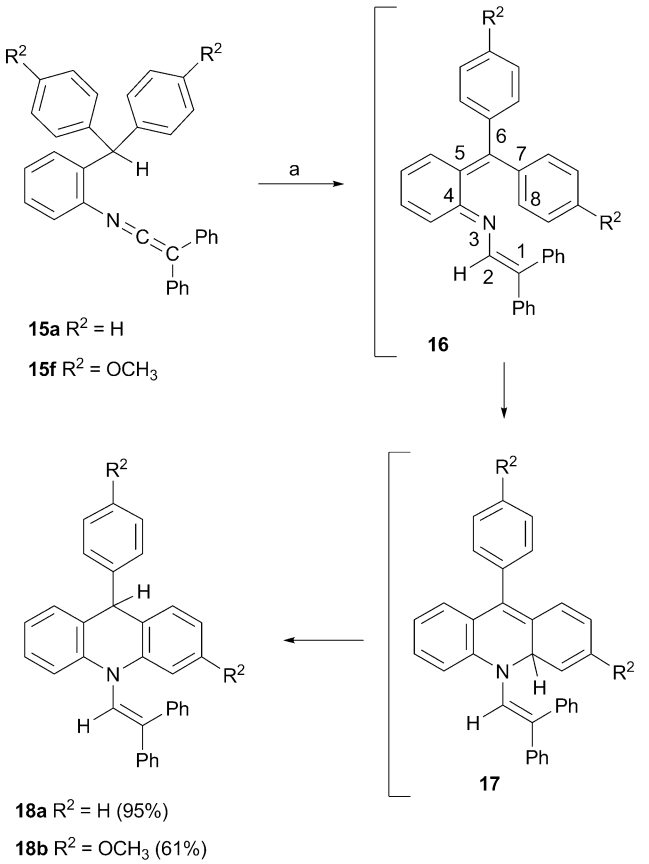
When toluene solutions of ketenimines **15** were heated at reflux temperature for several days these heterocumulenes remained unaltered. Under more severe thermal conditions (*ortho*-xylene, 180 °C, sealed tube) and longer reaction times we were able to achieve the transformation of **15** into different heterocyclic compounds depending on the nature of the substituents R^1 and R^2.

Thus, the thermal treatment of *C*,*C*-diphenyl ketenimines **15a** (R^1 = R^2 = H) and **15f** (R^1 = H; R^2 = OCH_3) under such reaction conditions (5–7 days) yielded 9,10-dihydroacridines **18** (Scheme 6). The structural determination of compounds **18** was achieved following their spectral data, and confirmed by X-ray diffraction of a monocrystal of compound **18a** (R^1 = R^2 = H) (see Electronic supplementary information).



15a R^1 = R^2 = H (87%)
15b R^1 = CH_3, R^2 = H (60%)
15c R^1 = H, R^2 = $N(CH_3)_2$ (84%)
15d R^1 = CH_3, R^2 = $N(CH_3)_2$ (89%)
15f R^1 = H, R^2 = OCH_3 (90%)
15g R^1 = CH_3, R^2 = OCH_3 (92%)

Scheme 5 *Reagents and conditions*: (a) Ph_2CCO, CH_2Cl_2, r.t., 30 min.

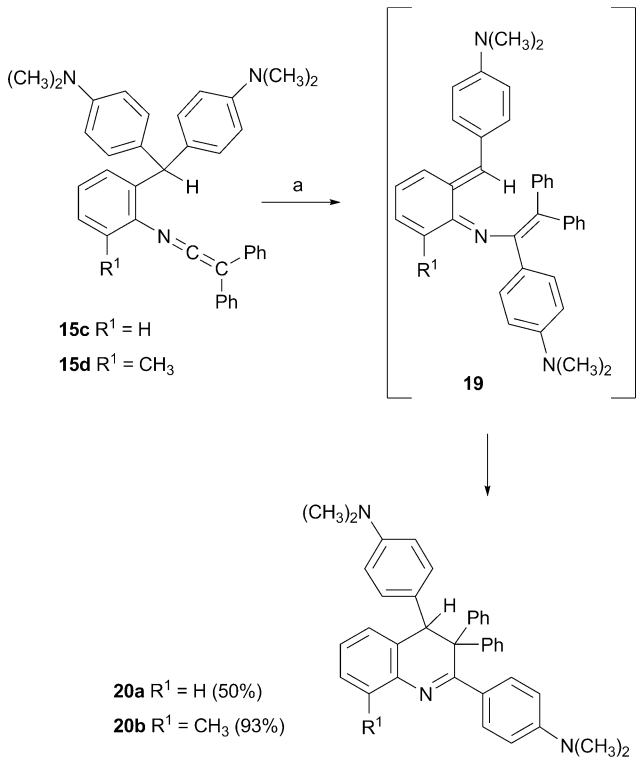


Scheme 6 *Reagents and conditions*: (a) *ortho*-Xylene, 180 °C, sealed tube, 5–7 d.

The formation of dihydroacridines **18** could be explained by assuming the initial formation of the *ortho*-azaxylylene intermediates **16** *via* a 1,5 hydride shift. The further cyclization of these intermediates through a 6π electrocyclic ring closure involving the N3–C4–C5–C6–C7–C8 1-azatriene fragment should afford the final species **18**. The alternative 6π-electrocyclization of the *ortho*-azaxylylenes **16** that would involve the closure of the

C1–C2–N3–C4–C5–C6 3-azatriene system *via* C1–C6 bond formation, that was initially expected and is similar to those presented above, is probably made difficult by the presence of two phenyl rings at each end (C1 and C6) of the azatrienic system, which should result in a severe steric congestion at the transition state of such an electrocyclization thus preventing its occurrence.[19]

In the cases of the *C*,*C*-diphenyl ketenimines **15c** and **15d**, where the R^2 substituent is a dimethylamino group, the reaction products obtained from their thermal treatment were the 2-aryl substituted 3,4-dihydroquinolines **20** (Scheme 7).

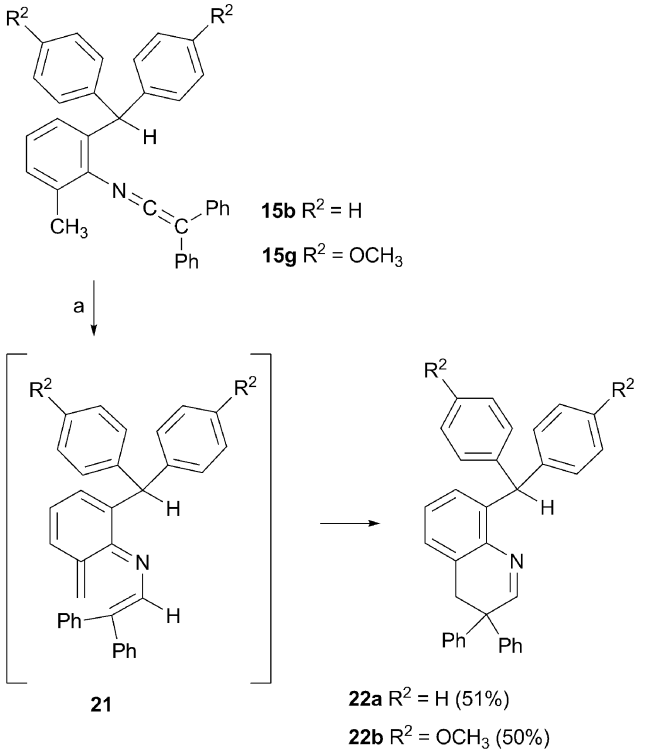


Scheme 7 *Reagents and conditions*: (a) *ortho*-Xylene, 180 °C, sealed tube, 1–2 d.

Quinolines **20** were characterized following their spectral data, IR, ^{1}H and ^{13}C NMR and mass spectrometry, and additionally by an X-ray crystal structure of example **20b** (R^1 = CH_3) (see Electronic supplementary information). In the solid state the C3–C4 bond distance of compound **20b** (C7–C8 in the crystallographic numbering) is also larger (1.588 Å) than a standard Csp^3–Csp^3 bond, and slightly shorter than those shown by quinolines **13e** and **13k**.

The formation of compounds **20** is apparently explained as occurring by a tandem process in which the first step is the rare 1,5 migration of one electron-rich 4-dimethylaminophenyl group[20] to the central carbon atom of the ketenimine function leading to the transient *ortho*-azaxylylene **19**, followed by the habitual 6π-ERC process.

C,*C*-Diphenyl ketenimines **15b** (R^1 = CH_3; R^2 = H) and **15g** (R^1 = CH_3; R^2 = OCH_3), both bearing a methyl group in the *ortho* position to the keteniminic nitrogen atom (R^1 = CH_3), when heated under the standard reaction conditions for extended periods of time (14–21 days), converted into the new 4-unsubstituted 3,4-dihydroquinolines **22a** (R^2 = H) and **22b** (R^2 = OCH_3), respectively (Scheme 8). The spectral data of quinolines **22** are fully consistent with their proposed structures.



Scheme 8 *Reagents and conditions*: (a) *ortho*-Xylene, 180 °C, sealed tube, 14–21 d.

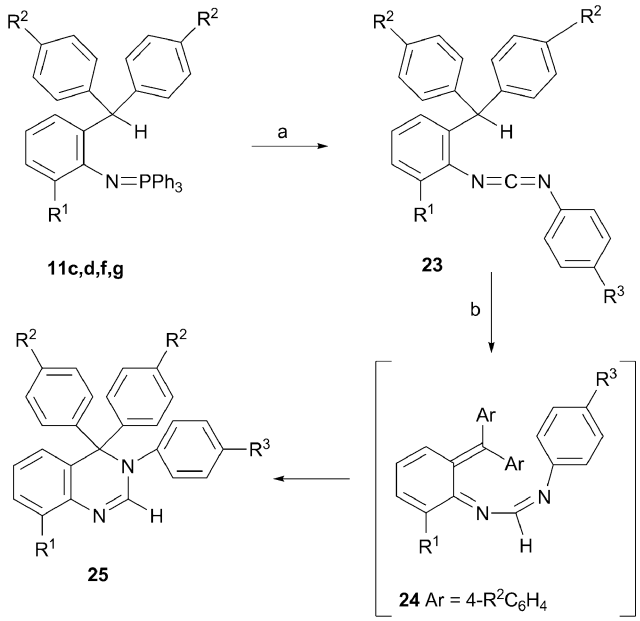
The conversions **15** → **22** should be initiated by a 1,5 migration of one of the hydrogen atoms of the methyl group to give the transient *ortho*-azaxylylenes **21**, which undergo subsequent 6π-electrocyclization to quinolines **22** (Scheme 8). Amongst the various [1,5]-H shift/6π-ERC tandem processes that could undergo ketenimines **15b** and **15g** the one leading to **22** became the most viable reaction pathway, probably because it involves a facile 6π-electrocyclization step *via* a non congested transition state as the 3-azatriene intermediate experiencing the cyclization is unsubstituted at one of its carbon termini. Although the alternative [1,5]-H shift/6π-ERC sequences initiated by the [1,5]-H transfer from the methine carbon atom of the triarylmethane fragment should reasonably have a quite lower activation energy for this first step, when compared with the [1,5]-H shift from the methyl group, the further putative electrocyclizations must have notably higher activation barriers, instead.

The ability of triarylmethane fragments as hydride donors participating in [1,5]-H shift/6π-ERC tandem processes involving carbodiimide functions as the acceptor units was also evaluated. The reaction of iminophosphoranes **11c,d,f,g** with arylisocyanates, in dichloromethane solution at room temperature, gave triarylmethane-carbodiimides **23**. The heating at 180 °C in a sealed tube of *ortho*-xylene solutions of carbodiimides **23**, during periods of time ranging from 2 to 5 days, yielded the 3,4,4-triaryl-3,4-dihydroquinazolines **25** (Scheme 9, Table 2).

The structural characterization of quinazolines **25** relies on their spectroscopic data. Their IR spectra show an absorption band at 1606–1614 cm^{-1} attributed to the vibration of the N–C bond. In

Table 2 Triarylmethane-carbodiimides **23** and quinazolines **25**

entry	R^1	R^2	R^3	**23** Yield (%)	**25** Yield (%)
a	H	$N(CH_3)_2$	Br	53	82
b	CH_3	$N(CH_3)_2$	Cl	60	84
c	CH_3	$N(CH_3)_2$	CH_3	90	76
d	H	OCH_3	Cl	45	78
e	CH_3	OCH_3	Br	56	61



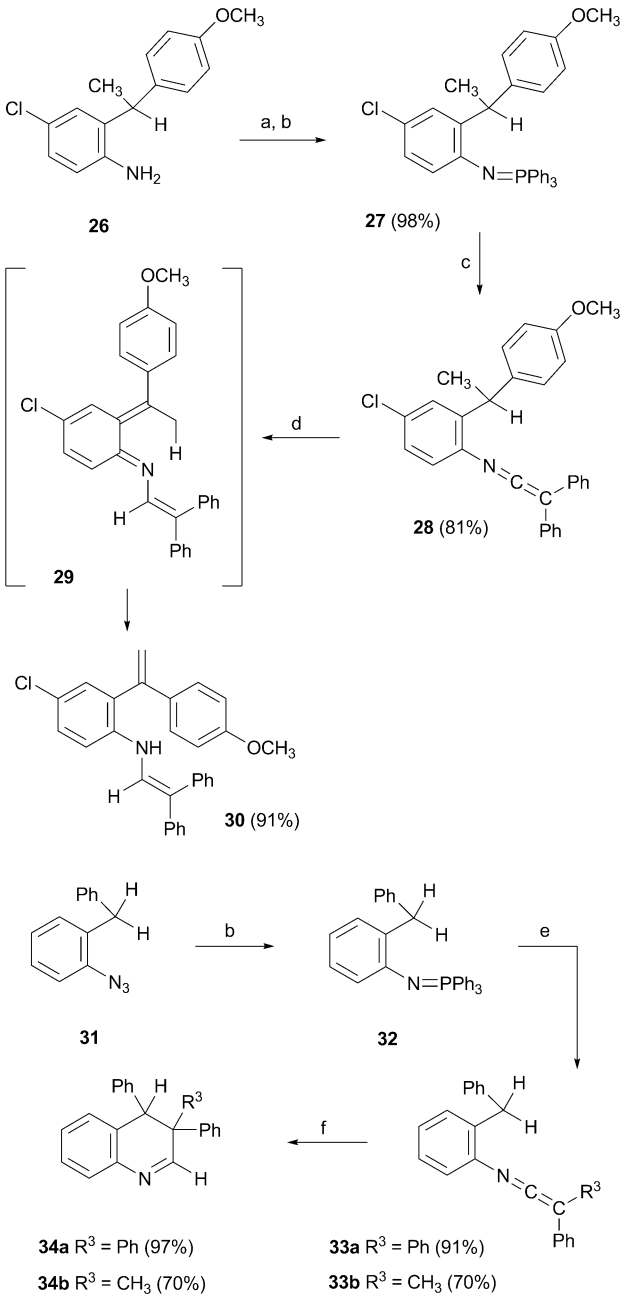
Scheme 9 *Reagents and conditions*: (a) 4-R^3-C_6H_4NCO, CH_2Cl_2, r.t., 30 min. (b) *ortho*-Xylene, 180 °C, sealed tube, 2–5 d.

their ^{1}H NMR spectra the signal of the C(2)H proton appears as a singlet at δ = 7.64–7.73 ppm. Their ^{13}C NMR spectra show the signals of the aliphatic quaternary carbon atom C4 and the methine carbon C2 at δ = 71.8–71.9 ppm and δ = 146.3–147.4 ppm, respectively.

Obviously, the formation of the dihydroquinazolines **25** from carbodiimides **23** can be rationalized as resulting from a [1,5]-H shift/6π-ERC sequence that involves the diazatriene intermediates **24**.

It is worth noting that the thermal activation of triarylmethane-carbodiimides **23** yields a single type of products, the quinazolines **25**, in contrast with the variety of heterocyclic compounds formed in the thermal cyclization of *C*,*C*-diphenyl ketenimines **15**. This difference is explained by the relatively easy electrocyclization of the 1,3-diazatriene fragment of intermediates **24**, which should occur through a less sterically congested transition state than the similar process of the C1–C2–N3–C4–C5–C6 3-azatriene fragment in species **16**. Moreover, it is conceivable that the lone pair at the terminal nitrogen atom of the 1,3-diazatriene moiety of **24** may also assist the 6π-ERC step by conferring a certain degree of pseudopericyclic character to its transition state.[21]

At this point, we were also interested in exploring whether the C–H bond of a diarylmethane fragment would be similarly activated as a formal hydride donor in related tandem processes. With this aim and following the usual sequence of reactions, as shown in Scheme 10, we prepared diarylmethane-ketenimines **28**



Scheme 10 *Reagents and conditions*: (a) (1) $NaNO_2$, H_2SO_4/H_2O, 0 °C, 30 min (2) NaN_3, H_2SO_4/H_2O, r.t., 16 h. (b) PPh_3, Et_2O, r.t., 16 h. (c) Ph_2CCO, CH_2Cl_2, r.t., 30 min. (d) *ortho*-Xylene, reflux, 3 h. (e) PhR^3CCO, CH_2Cl_2, r.t., 30 min. (f) Toluene, 160 °C, sealed tube, 36 h.

and **33a,b**, the first one bearing a methyl group at the benzylic carbon atom, and the second one lacking this substituent.

The heating of ketenimine **28** in refluxing toluene provided the substituted 2-aminostyrene **30**, isolated as the unique reaction product in 91% yield. In contrast, the thermal activation of ketenimines **33** in toluene solution at 160 °C, in a sealed tube, led to the quinolines **34** (Scheme 10). Quinoline **34b**, in which R^3 is a methyl group was obtained as a pair of *cis* and *trans* diastereoisomers in a ratio close to 1 : 1.5.

The conversion **28** → **30** probably proceeds by a tandem double [1,5]-H shift, the first one being the usual benzylic hydride transfer

whereas the second one involves the migration of one of the methyl protons towards the nitrogen atom of the intermediate *ortho*-azaxylylene **29**. This result demonstrated the ability of $-(Ar)_2C-H$ hydrogen atoms to engage in intramolecular hydride shifts but also reveals a limitation of the tandem [1,5]-H shift/6π-ERC methodology here developed for the preparation of polynuclear heterocycles: a primary (or secondary) alkyl group placed at the benzylic carbon atom from which the hydride departs in the first step interrupts the habitual tandem sequence at the 6π-ERC stage, as their H atoms become involved in a competitive, and clearly more successful, [1,5]-H shift for the final recovery of the aromaticity at the benzene nucleus of the *ortho*-azaxylylene. Notwithstanding, in the absence of such an alkyl group the habitual tandem [1,5]-H shift/6π-ERC sequence is fully operative when starting from diarylmethane hydride-donor fragments, as the transformation of ketenimines **33** into quinolines **34** clearly proves.

Conclusions

We here disclosed a novel synthetic protocol for converting *C*-alkyl-*C*-phenyl ketenimines *N*-substituted by triarylmethane substructures into a variety of 3,3,4,4-tetrasubstituted-3,4-dihydroquinolines, which is also valid for transforming structurally related carbodiimides into 3,4,4-trisubstituted-3,4-dihydroquinazolines. This protocol is based on the hydride donor ability of the triarylmethane C–H fragment which, by thermal activation in solution, promotes a tandem [1,5]-H shift/6π-ERC sequence leading from the heterocumulenes to the heterocyclic products. In the first step, a hydrogen atom translates from the benzylic position to the central carbon atom of the heterocumulenic function. The last mechanistic step, the 6π electrocyclization, is also noteworthy as it implies the formation of sterically congested C–C or C–N bonds. Only when the new putative C–C bond would be tetraaryl substituted the usual 6π-ERC is prevented and the tandem sequence continues with a second 6π-electrocyclization mode leading to 9,10-dihydroacridines. Alternatively, the full sequence either becomes a new tandem process of the type [1,5]-Ar shift/6π-ERC which leads to 2-aryl substituted 3,4-dihydroquinolines initiated by the rare migration of an electron-rich aryl group, or is replaced by another [1,5]-H shift/6π-ERC process involving the initial migration of a hydrogen atom from the methyl group *ortho* to the N atom of the ketenimine. We have also demonstrated the ability of diarylmethane fragments for promoting similar transformations and the interruption of the final electrocyclization in the cases where a methyl group is placed at the benzylic H-donor carbon atom. New investigations are currently underway in our laboratories aimed to extend the applicability of this synthetic methodology by replacing the acceptor heterocumulene units by other functions bearing electrophilic carbon atoms.

Experimental

All melting points are uncorrected. Infrared (IR) spectra were recorded neat or as Nujol emulsions. ^{1}H NMR spectra were recorded in $CDCl_3$ at 300 or 400 MHz. ^{13}C NMR spectra were recorded in $CDCl_3$ at 75 or 100 MHz. The chemical shifts are expressed in ppm, relative to Me_4Si at $\delta = 0.00$ ppm for ^{1}H, while the chemical shifts for ^{13}C are reported relative to the resonance of $CDCl_3$ $\delta = 77.1$ ppm. *J* values are given in Hz.

Preparation of the quinolines 13

To a solution of iminophosphorane **11** (1 mmol) in anhydrous dichloromethane (15 mL) ethylphenylketene (0.15 g, 1 mmol) or methylphenylketene (0.13 g, 1 mmol) in the same solvent (5 mL) was added. The reaction mixture was stirred at room temperature for 30 min. Then, the solvent was removed under reduced pressure and the resulting crude material was chromatographed on a silica gel column, using hexanes/diethyl ether (9 : 1, v/v) as eluent, to give the corresponding ketenimine **12**.

A solution of the ketenimine **12** (0.5 mmol) in anhydrous toluene (20 mL) was heated at reflux temperature under an atmosphere of nitrogen for 5–144 h. After cooling at room temperature, the solvent was removed under reduced pressure and the resulting material was purified by column chromatography on silica gel.

3-Methyl-3,4,4-triphenyl-3,4-dihydroquinoline 13a. Yield = 0.11 g, 60%; mp 194–195 °C (colourless prisms from diethyl ether–hexane); ν_{max}(Nujol)/cm^{-1} 1633; δ_H(300 MHz; $CDCl_3$) 1.83 (3 H, s), 6.61 (2 H, d, *J* 7.5), 6.90 (4 H, t, *J* 7.2), 6.98–7.06 (4 H, m), 7.10–7.21 (6 H, m), 7.45 (1 H, dd, *J* 7.5 and 1.2), 7.55–7.58 (2 H, m), 8.21 (1 H, s); δ_C(75 MHz; $CDCl_3$) 20.2, 48.5 (s), 61.4 (s), 126.2, 126.3, 126.6, 126.7, 127.2, 127.5, 127.6, 127.9, 128.4, 128.6, 129.2, 131.8, 135.1 (s), 138.2 (s), 140.8 (s), 141.7 (s), 146.1 (s), 167.8; HRMS (ESI): Calcd for $C_{28}H_{24}N$ $[M + H]^+$ 374.1903, found 374.1907.

3-Ethyl-3,4,4-triphenyl-3,4-dihydroquinoline 13b. Yield = 0.03 g, 15%; yellow oil; ν_{max}(neat)/cm^{-1} 1625; δ_H(300 MHz; $CDCl_3$) 0.80 (3 H, t, *J* 7.2), 2.00–2.10 (1 H, m), 2.53–2.62 (1 H, m), 6.61 (2 H, d, *J* 7.6), 6.93–7.25 (14 H, m), 7.41–7.46 (3 H, m), 8.63 (1 H, s); δ_C(75 MHz; $CDCl_3$) 8.8, 24.8, 51.6 (s), 62.6 (s), 126.5, 126.6, 126.7, 126.8, 127.2, 127.3, 127.4, 127.8, 128.3, 129.0, 130.4, 130.5, 131.7, 135.2 (s), 135.3 (s), 141.8 (s), 142.3 (s), 144.0 (s), 167.7; HRMS (ESI): Calcd for $C_{29}H_{26}N$ $[M + H]^+$ 388.2060, found 388.2066.

3,8-Dimethyl-3,4,4-triphenyl-3,4-dihydroquinoline 13c. Yield = 0.19 g, 99%; mp 195–196 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1633; δ_H(400 MHz; $CDCl_3$) 1.81 (3 H, s), 2.56 (3 H, s), 6.65 (2 H, d, *J* 10.0), 6.86–7.04 (10 H, m), 7.09–7.24 (4 H, m), 7.54–7.57 (2 H, m), 8.25 (1 H, s); δ_C(100 MHz; $CDCl_3$) 18.5, 20.6, 48.0 (s), 61.8 (s), 126.3, 126.6, 126.7, 127.1, 127.4, 127.5, 128.0, 128.8, 128.9, 132.1, 135.0 (s), 135.9 (s), 138.5 (s), 140.1 (s), 141.4 (s), 146.2 (s), 167.4; HRMS (ESI): Calcd for $C_{29}H_{26}N$ $[M + H]^+$ 388.2060, found 388.2066.

3-Ethyl-8-methyl-3,4,4-triphenyl-3,4-dihydroquinoline 13d. Yield = 0.12 g, 61%; mp 145–147 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1628; δ_H(400 MHz; $CDCl_3$) 0.78 (3 H, t, *J* 9.6), 1.96–2.08 (1 H, m), 2.54 (3 H, s), 2.58–2.63 (1 H, m), 6.57 (2 H, d, *J* 9.0), 6.91–7.20 (14 H, m), 7.43 (2 H, d, *J* 9.0), 8.68 (1 H, s); δ_C(100 MHz; $CDCl_3$) 8.80, 18.4, 24.9, 50.9 (s), 62.9 (s), 126.4, 126.5, 126.7, 126.8, 126.9, 127.1, 127.2, 127.3, 129.0, 130.4, 130.6, 131.9, 134.9 (s), 135.5 (s), 140.6 (s), 142.0 (s), 144.2 (s), 166.2; HRMS (ESI): Calcd for $C_{30}H_{28}N$ $[M + H]^+$ 402.2216, found 402.2219.

4,4-Bis[4-(*N*,*N*-dimethylamino)phenyl]-3-methyl-3-phenyl-3,4-dihydroquinoline 13e. Yield = 0.14 g, 63%; mp 190–191 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1613;

δ_H(300 MHz; $CDCl_3$) 1.77 (3 H, s), 2.90 (12 H, s), 6.37 (2 H, d, *J* 9.0), 6.50 (2 H, d, *J* 9.0), 6.65 (2 H, d, *J* 8.1), 6.72 (2 H, d, *J* 8.1), 6.93 (2 H, t, *J* 7.5), 6.99–7.04 (2 H, m), 7.10–7.20 (2 H, m), 7.37–7.42 (3 H, m), 8.23 (1 H, s); δ_C(75 MHz; $CDCl_3$) 20.6, 40.3, 40.7, 49.0 (s), 59.9 (s), 110.5, 111.2, 126.4, 126.6, 127.3, 127.8, 128.2, 129.0, 129.8, 132.6, 134.0 (s), 136.6 (s), 139.1 (s), 141.8 (s), 148.8 (s), 148.9 (s), 169.4 (s); HRMS (ESI): Calcd for $C_{32}H_{34}N_3$ $[M + H]^+$ 460.2747, found 460.2751.

4,4-Bis[4-(*N*,*N*-dimethylamino)phenyl]-3-ethyl-3-phenyl-3,4-dihydroquinoline 13f. Yield = 0.19 g, 80%; mp 171–172 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1610; δ_H(400 MHz; $CDCl_3$) 0.74 (3 H, t, *J* 7.3), 1.98–2.07 (1 H, m), 2.45–2.54 (1 H, m), 2.85 (6 H, s), 2.91 (6 H, s), 6.37 (2 H, d, *J* 9.1), 6.53 (2 H, d, *J* 9.1), 6.70 (2 H, d, *J* 7.7), 6.76 (2 H, d, *J* 7.7), 7.00–7.09 (4 H, m), 7.14–7.20 (2 H, m), 7.24–7.26 (2 H, m), 7.40 (1 H, dd, *J* 7.6 and 1.3), 8.63 (1 H, s); δ_C(100 MHz; $CDCl_3$) 9.0, 25.6, 40.4, 40.5, 52.0 (s), 60.9 (s), 110.5, 110.8, 126.4, 126.7, 127.1, 127.5, 128.0, 128.9, 129.9 (s), 130.6, 131.3 (s), 131.7, 132.2, 136.4 (s), 136.5 (s), 142.3 (s), 148.9 (s), 149.0 (s), 168.5; HRMS (ESI): Calcd for $C_{33}H_{36}N_3$ $[M + H]^+$ 474.2904, found 474.2910.

4,4-Bis[4-(*N*,*N*-dimethylamino)phenyl]-3,8-dimethyl-3-phenyl-3,4-dihydroquinoline 13g. Yield = 0.18 g, 78%; mp 170–171 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1610; δ_H(400 MHz; $CDCl_3$) 1.75 (3 H, s), 2.54 (3 H, s), 2.87 (6 H, s), 2.88 (6 H, s), 6.36 (2 H, d, *J* 8.8), 6.48–6.51 (2 H, m), 6.62 (2 H, d, *J* 7.6), 6.71 (2 H, d, *J* 8.8), 6.88–7.04 (6 H, m), 7.37–7.39 (2 H, m), 8.27 (1 H, s); δ_C(100 MHz; $CDCl_3$) 18.5, 20.9, 40.4, 40.7, 48.3 (s), 60.3 (s), 110.5, 111.2, 126.4, 126.8, 127.1, 127.3, 128.4, 129.1, 129.6 (s), 130.1, 132.7, 134.0 (s), 135.4 (s), 136.4 (s), 139.3 (s), 140.1 (s), 148.8 (s), 148.9 (s), 167.9; HRMS (ESI): Calcd for $C_{33}H_{36}N_3$ $[M + H]^+$ 474.2904, found 474.2909.

4,4-Bis[4-(*N*,*N*-dimethylamino)phenyl]-3-ethyl-8-methyl-3-phenyl-3,4-dihydroquinoline 13h. Yield = 0.18 g, 75%; mp 165–167 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1610; δ_H(300 MHz; $CDCl_3$) 0.72 (3 H, t, *J* 7.2), 1.94–2.06 (1 H, m), 2.45–2.50 (1 H, m), 2.53 (3 H, s), 2.86 (6 H, s), 2.92 (6 H, s), 6.36 (2 H, d, *J* 9.0), 6.53 (2 H, d, *J* 9.0), 6.67 (2 H, d, *J* 8.1), 6.76 (2 H, d, *J* 8.1), 6.91–7.08 (6 H, m), 7.23–7.26 (2 H, m), 8.68 (1 H, s); δ_C(75 MHz; $CDCl_3$) 15.4, 18.4, 25.7, 40.5, 40.6, 51.4 (s), 61.2 (s), 110.4, 110.7, 126.3, 126.7, 126.9, 127.1, 128.4, 130.2 (s), 130.6, 131.7 (s), 131.8, 132.4, 135.1 (s), 136.2 (s), 136.8 (s), 140.6 (s), 148.9 (s), 149.0 (s), 167.0; HRMS (ESI): Calcd for $C_{34}H_{38}N_3$ $[M + H]^+$ 488.3060, found 488.3065.

3-Methyl-4,4-bis[4-(*N*-morpholino)phenyl]-3-phenyl-3,4-dihydroquinoline 13i. Yield = 0.18 g, 65%; mp 221–222 °C (orange prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1608 and 1512; δ_H(400 MHz; $CDCl_3$) 1.79 (3 H, s), 3.06–3.09 (8 H, m), 3.79–3.85 (8 H, m), 6.55 (2 H, d, *J* 8.4), 6.65–6.67 (4 H, m), 6.78 (2 H, d, *J* 8.4), 6.93 (2 H, t, *J* 7.6), 7.03 (2 H, t, *J* 8.4), 7.17 (2 H, t, *J* 7.6), 7.45 (3 H, m), 8.23 (1 H, s); δ_C(100 MHz; $CDCl_3$) 20.1, 48.2, 48.4 (s), 48.8, 59.7 (s), 66.4, 66.5, 112.9, 113.6, 126.2, 126.5, 127.0, 127.5, 127.9, 128.3 (s), 128.4, 128.5, 129.3, 131.8 (s), 132.2, 135.6 (s), 136.7 (s), 138.3 (s), 141.4 (s), 148.9 (s), 149.1 (s), 168.6; HRMS (ESI): Calcd for $C_{36}H_{38}N_3O_2$ $[M + H]^+$ 544.2959, found 544.2963.

3-Ethyl-4,4-bis[4-(*N*-morpholino)phenyl]-3-phenyl-3,4-dihydroquinoline 13j. Yield = 0.17 g, 60%; mp 184–185 °C (orange prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1713 and 1608; δ_H(400 MHz; $CDCl_3$) 0.76 (3 H, t, *J* 6.8), 1.94–2.04 (1 H, m), 2.45–2.52 (1 H, m), 3.07–3.16 (8 H, m), 3.81–3.86 (8 H, m), 6.54 (2 H, d, *J* 8.8), 6.67–6.72 (4 H, m), 6.80 (2 H, d, *J* 7.6), 7.00–7.11 (4 H, m), 7.15–7.21 (2 H, m), 7.29 (2 H, d, *J* 8.8), 7.41 (1 H, d, *J* 7.6), 8.60 (1 H, s); δ_C(100 MHz; $CDCl_3$) 8.4, 22.0, 48.3, 48.5, 51.4 (s), 60.6 (s), 66.4, 66.5, 112.7, 113.1, 126.1, 126.5, 126.8, 127.2, 127.6, 128.4, 130.1, 131.2, 131.8, 132.7 (s), 134.1 (s), 135.4 (s), 135.7 (s), 141.8 (s), 148.9 (s), 149.0 (s), 167.7; HRMS (ESI): Calcd for $C_{37}H_{40}N_3O_2$ $[M + H]^+$ 558.3115, found 558.3122.

4,4-Bis(4-methoxyphenyl)-3-methyl-3-phenyl-3,4-dihydroquinoline 13k. Yield = 0.12 g, 57%; mp 168–170 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1606; δ_H(400 MHz; $CDCl_3$) 1.78 (3 H, s), 3.72 (3 H, s), 3.75 (3 H, s), 6.54 (2 H, d, *J* 9.0), 6.62 (2 H, d, *J* 7.7), 6.67 (2 H, d, *J* 9.0), 6.78 (2 H, d, *J* 8.4), 6.93 (2 H, t, *J* 7.7), 7.01–7.06 (2 H, m), 7.15–7.19 (2 H, m), 7.43–7.46 (3 H, m), 8.21 (1 H, s); δ_C(100 MHz; $CDCl_3$) 20.5, 48.8 (s), 55.2, 55.3, 60.2 (s), 111.8, 112.9, 126.7, 127.1, 127.6, 128.0, 128.5, 128.8, 128.9, 130.0, 132.9, 133.1 (s), 136.0 (s), 138.3 (s), 138.6 (s), 141.8 (s), 158.0 (s), 158.1 (s), 169.0; HRMS (ESI): Calcd for $C_{30}H_{28}NO_2$ $[M + H]^+$ 434.2115, found 434.2119.

3-Ethyl-4,4-bis(4-methoxyphenyl)-3-phenyl-3,4-dihydroquinoline 13l. Yield = 0.12 g, 52%; mp 187–188 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1606; δ_H(400 MHz; $CDCl_3$) 0.77 (3 H, t, *J* 7.3), 1.96–2.05 (1 H, m), 2.45–2.55 (1 H, m), 3.73 (3 H, s), 3.78 (3 H, s), 6.55 (2 H, d, *J* 9.1), 6.67 (2 H, d, *J* 7.7), 6.71 (2 H, d, *J* 9.1), 6.82 (2 H, d, *J* 7.7), 7.01–7.05 (2 H, m), 7.07–7.10 (2 H, m), 7.15 (1 H, dd, *J* 7.8 and 1.3), 7.19 (1 H, td, *J* 7.4 and 1.4), 7.31 (2 H, d, *J* 8.5 Hz), 7.42 (1 H, dd, *J* 7.7 and 1.2), 8.63 (1 H, s); δ_C(100 MHz; $CDCl_3$) 8.9, 25.4, 51.8 (s), 55.2, 55.3, 61.2 (s), 111.8, 112.3, 126.7, 127.1, 127.3, 127.8, 128.2, 128.8, 130.4, 131.8, 132.6, 134.0, 135.7 (s), 135.8 (s), 135.9 (s), 142.2 (s), 158.1 (s), 158.3 (s), 168.1; HRMS (ESI): Calcd for $C_{31}H_{30}NO_2$ $[M + H]^+$ 448.2271, found 448.2273.

4,4-Bis(4-methoxyphenyl)-3,8-dimethyl-3-phenyl-3,4-dihydroquinoline 13m. Yield = 0.19 g, 85%; mp 158–160 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1629; δ_H(300 MHz; $CDCl_3$) 1.76 (3 H, s), 2.55 (3 H, s), 3.72 (3 H, s), 3.74 (3 H, s), 6.53 (2 H, d, *J* 8.4), 6.59 (2 H, d, *J* 7.8), 6.67 (2 H, d, *J* 8.7), 6.76 (2 H, d, *J* 7.8), 6.92–7.02 (6 H, m), 7.44 (2 H, d, *J* 8.4), 8.26 (1 H, s); δ_C(75 MHz; $CDCl_3$) 18.5, 20.7, 48.1 (s), 55.1, 55.2, 60.5 (s), 111.6, 112.7, 126.6, 126.7, 127.3, 127.5, 128.8, 128.9, 130.1, 133.0, 133.5 (s), 135.7 (s), 135.8 (s), 138.2 (s), 138.7 (s), 140.0 (s), 157.9 (s), 158.0 (s), 167.6; HRMS (ESI): Calcd for $C_{31}H_{30}NO_2$ $[M + H]^+$ 448.2271, found 448.2276.

3-Ethyl-4,4-bis(4-methoxyphenyl)-8-methyl-3-phenyl-3,4-dihydroquinoline 13n. Yield = 0.23 g, 99%; colourless oil; ν_{max}(neat)/cm^{-1} 1606; δ_H(400 MHz; $CDCl_3$) 0.75 (3 H, t, *J* 7.2), 1.99 (1 H, m), 2.49 (1 H, m), 2.53 (3 H, s), 3.71 (3 H, s), 3.76 (3 H, s), 6.54 (2 H, d, *J* 8.8), 6.64 (2 H, d, *J* 7.6), 6.70 (2 H, d, *J* 8.8), 6.81 (2 H, d, *J* 8.0), 6.95–7.09 (6 H, m), 7.31 (2 H, d, *J* 8.0), 8.67 (1 H, s); δ_C(100 MHz; $CDCl_3$) 8.9, 18.3, 25.5, 51.1 (s), 55.1, 55.2, 61.4 (s), 111.7, 112.2, 126.5, 126.6, 127.1, 127.3, 128.9, 130.4, 131.9, 132.7, 134.2 (s), 135.4 (s), 135.5 (s), 135.9 (s), 136.2 (s), 140.5 (s), 158.0 (s), 158.2 (s), 166.6; HRMS (ESI): Calcd for $C_{32}H_{32}NO_2$ $[M + H]^+$ 462.2428, found 462.2436.

Preparation of acridines 18, 2-arylquinolines 20 and quinolines 22

To a solution of iminophosphorane **11** (1 mmol) in anhydrous dichloromethane (15 mL) a solution of diphenylketene (0.19 g, 1 mmol) in the same solvent (5 mL) was added. The reaction mixture was stirred at room temperature under nitrogen for 30 min. Next the solvent was removed under reduced pressure and the resulting material was purified by column chromatography on silica gel, using hexanes/diethyl ether (9 : 1; v/v) as eluent, to provide the expected ketenimine **15**.

A deoxygenated solution of the ketenimine **15** (0.5 mmol) in anhydrous *ortho*-xylene (20 mL) was heated in a sealed tube at 180 °C during 2–21 d. After cooling, the solvent was removed under reduced pressure. The resulting material was purified by column chromatography on silica gel.

10-(2,2-Diphenylethenyl)-9-phenyl-9,10-dihydroacridine 18a. Yield = 0.21 g, 95%; mp 191–192 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1589; δ_H(300 MHz; $CDCl_3$) 5.22 (1 H, s), 6.61 (1 H, s), 6.83–6.88 (4 H, m), 7.07–7.21 (14 H, m), 7.37–7.41 (3 H, m), 7.48–7.51 (2 H, m); δ_C(75 MHz; $CDCl_3$) 47.9, 114.0, 121.5, 124.0, 124.7 (s), 126.1, 127.2, 127.5, 127.8, 128.2, 128.3, 128.5, 128.6, 129.0, 129.6, 137.7 (s), 140.1 (s), 145.5 (s), 147.3 (s); HRMS (ESI): Calcd for $C_{33}H_{26}N$ [M + H]$^+$ 436.2060, found 436.2064.

10-(2,2-Diphenylethenyl)-3-methoxy-9-(4-methoxyphenyl)-9,10-dihydroacridine 18b. Yield = 0.15 g, 61%; mp 150–151 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1595 and 1508; δ_H(400 MHz; $CDCl_3$) 3.72 (3 H, s), 3.73 (3 H, s), 5.12 (1 H, s), 6.42 (1 H, dd, *J* 8.4 and 2.8), 6.59 (1 H, s), 6.62–6.65 (2 H, m), 6.74 (1 H, d, *J* 2.4), 6.76–6.78 (2 H, m), 6.85 (1 H, m), 6.98 (1 H, d, *J* 8.0), 7.08 (2 H, d, *J* 7.2), 7.10–7.21 (6 H, m), 7.38–7.41 (3 H, m), 7.46–7.49 (2 H, m); δ_C(100 MHz; $CDCl_3$) 46.3, 55.3, 55.4, 100.5, 106.4, 113.9, 114.0, 117.8, 121.5, 123.9, 125.4 (s), 127.0, 127.8, 128.1, 128.2, 128.4, 128.5, 128.6, 129.0, 129.5, 130.2, 137.8 (s), 139.9 (s), 140.0 (s), 140.3 (s), 141.0 (s), 145.7 (s), 157.8 (s), 158.9 (s); HRMS (ESI): Calcd for $C_{35}H_{30}NO_2$ [M + H]$^+$ 496.2271, found 496.2275.

2,4-Bis[4-(*N*,*N*-dimethylamino)phenyl]-3,3-diphenyl-3,4-dihydroquinoline 20a. Yield = 0.13 g, 50%; colourless oil; ν_{max}(neat)/cm^{-1} 1608; δ_H(400 MHz; $CDCl_3$) 2.82 (6 H, s), 2.89 (6 H, s), 4.56 (1 H, s), 6.31 (2 H, d, *J* 7.6), 6.40–6.43 (4 H, m), 6.57 (2 H, d, *J* 8.8), 6.79 (2 H, t, *J* 8.4), 6.93–6.98 (3 H, m), 7.08–7.18 (2 H, m), 7.21–7.23 (2 H, m), 7.31 (2 H, d, *J* 9.2), 7.40 (1 H, d, *J* 8.0), 7.63 (2 H, d, *J* 8.0); δ_C(100 MHz; $CDCl_3$) 40.1, 40.6, 54.6, 59.0 (s), 110.5, 112.2, 125.6, 125.9, 126.5, 126.7, 126.9, 127.2, 127.3 (s), 127.6, 127.9, 128.8 (s), 129.7, 131.1, 131.2, 131.4, 131.8, 142.0 (s), 142.1 (s), 144.1 (s), 149.6 (s), 150.7 (s), 171.7 (s); HRMS (ESI): Calcd for $C_{37}H_{36}N_3$ [M + H]$^+$ 522.2904, found 522.2908.

2,4-Bis[4-(*N*,*N*-dimethylamino)phenyl]-8-methyl-3,3-diphenyl-3,4-dihydroquinoline 20b. Yield = 0.25 g, 93%; mp 234–235 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1610 and 1519; δ_H(300 MHz; $CDCl_3$) 2.46 (3 H, s), 2.80 (6 H, s), 2.89 (6 H, s), 4.51 (1 H, s), 6.32 (2 H, d, *J* 7.5), 6.41 (4 H, t, *J* 8.7), 6.54 (2 H, d, *J* 8.7), 6.76–6.84 (4 H, m), 6.93–6.98 (2 H, m), 7.11–7.23 (3 H, m), 7.40 (2 H, d, *J* 9.0), 7.61 (2 H, d, *J* 7.5); δ_C(75 MHz; $CDCl_3$) 17.9, 40.2, 40.7, 55.0, 58.4 (s), 110.3, 112.3, 125.1, 125.6, 125.9, 126.2, 126.8, 127.7 (s), 127.8, 128.5, 129.2 (s), 129.7, 131.1, 131.3, 131.4, 134.8 (s), 142.3 (s), 142.4 (s), 142.5 (s), 149.5 (s), 150.5 (s), 168.6 (s); HRMS (ESI): Calcd for $C_{38}H_{38}N_3$ [M + H]$^+$ 536.3060, found 536.3062.

3,3-Diphenyl-8-diphenylmethyl-3,4-dihydroquinoline 22a. Yield = 0.11 g, 51%; mp 159–161 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1599, 1581 and 1493; δ_H(400 MHz; $CDCl_3$) 3.47 (2 H, s), 6.55 (1 H, s), 6.81 (1 H, d, *J* 7.6), 6.95 (1 H, d, *J* 7.6), 7.00–7.07 (9 H, m), 7.17–7.28 (12 H, m), 8.22 (1 H, s); δ_C(100 MHz; $CDCl_3$) 38.1, 48.7 (s), 50.4, 125.9, 126.1, 126.5 (s), 127.4, 127.7, 127.8, 128.1, 128.7, 129.8, 140.0 (s), 140.8 (s), 143.8 (s), 144.3 (s), 166.7; HRMS (ESI): Calcd for $C_{34}H_{28}N$ [M + H]$^+$ 450.2216, found 450.2222.

8-Bis(4-methoxyphenyl)methyl-3,3-diphenyl-3,4-dihydroquinoline 22b. Yield = 0.13 g, 50%; mp 147–149 °C (colourless prisms from diethyl ether–hexane); ν_{max}(Nujol)/cm^{-1} 1610; δ_H(400 MHz; $CDCl_3$) 3.43 (2 H, s), 3.78 (6 H, s), 6.39 (1 H, s), 6.75–6.78 (4 H, m), 6.90–6.95 (5 H, m), 6.99 (1 H, d, *J* 7.6), 7.01–7.04 (5 H, m), 7.16–7.24 (6 H, m), 8.21 (1 H, s); δ_C(100 MHz; $CDCl_3$) 38.1, 48.6 (s), 48.7, 55.3, 113.5, 125.9, 126.4 (s), 126.7, 127.3, 127.8, 128.4, 128.5, 130.6, 136.9 (s), 140.6 (s), 140.7 (s), 143.8 (s), 157.7 (s), 166.6; HRMS (ESI): Calcd for $C_{36}H_{32}NO_2$ [M + H]$^+$ 510.2428, found 510.2433.

Preparation of quinazolines 25

To a solution of iminophosphorane **11** (1 mmol) in anhydrous dichloromethane (15 mL) a solution of the aryl isocyanate (1 mmol) in the same solvent (5 mL) was added. The reaction mixture was stirred at room temperature for 30 min. The solvent was removed under reduced pressure, and the oily residue was chromatographed on a silica gel column using hexanes/diethyl ether (7 : 3, v/v) as eluent to give the corresponding carbodiimide **23**.

A solution of the carbodiimide **23** (0.5 mmol) in anhydrous *o*-xylene (20 mL) was heated a 180 °C, in a sealed tube, for 2–5 d. After cooling at room temperature, the solvent was removed under reduced pressure and the resulting material was purified by silica gel column chromatography.

3-(4-Bromophenyl)-4,4-bis[4-(*N*,*N*-dimethylamino)phenyl]-3,4-dihydroquinazoline 25a. Yield = 0.22 g, 82%; mp 193–194 °C (colourless prisms from diethyl ether–hexane); ν_{max}(Nujol)/cm^{-1} 1608; δ_H(400 MHz; $CDCl_3$) 2.89 (12 H, s), 6.54–6.56 (4 H, m), 6.76–6.79 (3 H, m), 6.98–7.01 (1 H, m), 7.13–7.24 (8 H, m), 7.64 (1 H, s); δ_C(100 MHz; $CDCl_3$) 40.3, 71.9 (s), 111.3, 118.5 (s), 124.1, 125.3, 127.1, 127.2, 127.6, 129.0, 130.4, 131.2, 133.0 (s), 140.7 (s), 142.0 (s), 147.4, 149.3 (s); HRMS (ESI): Calcd for $C_{30}H_{30}BrN_4$ [M + H]$^+$ 525.1648, found 525.1655.

3-(4-Chlorophenyl)-4,4-bis[4-(*N*,*N*-dimethylamino)phenyl]-8-methyl-3,4-dihydroquinazoline 25b. Yield = 0.21 g, 84%; mp 230–231 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1614 and 1574; δ_H(300 MHz; $CDCl_3$) 2.41 (3 H, s), 2.90 (12 H, s), 6.52–6.57 (4 H, m), 6.61 (1 H, d, *J* 7.8), 6.83–6.87 (2 H, m), 6.91 (1 H, d, *J* 7.8), 7.00–7.04 (3 H, m), 7.11–7.16 (4 H, m), 7.70 (1 H, s); δ_C(75 MHz; $CDCl_3$) 17.8, 40.4, 71.9 (s), 111.3, 124.7, 125.1, 126.6, 128.3, 129.0, 129.2 (s), 130.3 (s), 130.4, 131.9 (s), 133.0 (s), 139.1 (s), 141.7 (s), 146.5, 149.3 (s); HRMS (ESI): Calcd for $C_{31}H_{32}ClN_4$ [M + H]$^+$ 495.2310, found 495.2317.

4,4-Bis[4-(*N*,*N*-dimethylamino)phenyl]-8-methyl-3-(4-methylphenyl)-3,4-dihydroquinazoline 25c. Yield = 0.18 g, 76%; mp 255–257 °C (yellow prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1606; δ_H(400 MHz; $CDCl_3$) 2.19 (3 H, s), 2.42 (3 H, s), 2.88 (12 H, s), 6.53–6.56 (4 H, m), 6.59 (1 H, d, *J* 7.6), 6.79–6.81 (2 H, m), 6.85–6.89 (3 H, m), 7.01 (1 H, d, *J* 7.6), 7.14–7.18 (4 H, m), 7.73 (1 H, s); δ_C(75 MHz; $CDCl_3$) 17.9, 20.8, 40.5, 71.8 (s), 111.3, 124.3, 125.1, 125.5, 128.8, 128.9, 129.9 (s), 130.6, 131.7 (s), 133.0 (s), 134.4 (s), 139.5 (s), 140.6 (s), 147.3, 149.2 (s); HRMS (ESI): Calcd for $C_{32}H_{35}N_4$ [M + H]$^+$ 475.2856, found 475.2860.

3-(4-Chlorophenyl)-4,4-bis(4-methoxyphenyl)-3,4-dihydroquinazoline 25d. Yield = 0.18 g, 78%; mp 96–97 °C (colourless prisms from diethyl ether–hexane); ν_{max}(Nujol)/cm^{-1} 1608; δ_H(300 MHz; $CDCl_3$) 3.71 (6 H, s), 6.72–6.82 (7 H, m), 7.01–7.06 (3 H, m), 7.19–7.26 (6 H, m), 7.66 (1 H, s); δ_C(75 MHz; $CDCl_3$) 55.3, 71.9 (s), 113.2, 124.4, 125.7, 126.9, 127.0, 128.1, 128.5, 130.8, 131.1 (s), 132.3 (s), 133.4 (s), 140.6 (s), 141.1 (s), 147.4, 158.8 (s); HRMS (ESI): Calcd for $C_{28}H_{24}ClN_2O_2$ [M + H]$^+$ 455.1521, found 455.1527.

3-(4-Bromophenyl)-4,4-bis(4-methoxyphenyl)-8-methyl-3,4-dihydroquinazoline 25e. Yield = 0.16 g, 61%; mp 83–85 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1608; δ_H(400 MHz; $CDCl_3$) 2.42 (3 H, s), 3.76 (6 H, s), 6.55 (1 H, d, *J* 7.6), 6.73–6.77 (6 H, m), 6.93 (1 H, t, *J* 7.6), 7.06 (1 H, d, *J* 7.6), 7.17–7.22 (6 H, m), 7.70 (1 H, s); δ_C(100 MHz; $CDCl_3$) 15.3, 55.3, 71.9 (s), 113.2, 118.6 (s), 124.9, 125.1, 126.8, 129.5, 130.8, 131.4, 132.3 (s), 132.4 (s), 133.4 (s), 139.1 (s), 141.8 (s), 146.3, 158.8 (s); HRMS (ESI): Calcd for $C_{29}H_{26}BrN_2O_2$ [M + H]$^+$ 513.1172, found 513.1174.

Preparation of 4-chloro-2-[1-(4-methoxyphenyl)vinyl]-*N*-(2,2-diphenylvinyl)aniline 30

To a solution of iminophosphorane **27** (0.8 g, 1.5 mmol) in anhydrous dichloromethane (15 mL) a solution of diphenylketene (0.24 g, 1.5 mmol) in the same solvent (5 mL) was added. The reaction mixture was stirred at room temperature under nitrogen for 30 min. Next the solvent was removed under reduced pressure and the resulting material was purified by column chromatography on silica gel, using hexanes/diethyl ether (9.5 : 0.5; v/v) as eluent, to provide the ketenimine **28** (81% yield).

A solution of the ketenimine **28** (0.33 g, 0.75 mmol) in anhydrous *ortho*-xylene (20 mL) was heated at reflux temperature under nitrogen for 3 h. After cooling, the solvent was removed under reduced pressure and the resulting material was purified by column chromatography on silica gel, using hexanes/diethyl ether (9 : 1, v/v) as eluent.

4-Chloro-2-[1-(4-methoxyphenyl)vinyl]-*N*-(2,2-diphenylvinyl)-aniline 30. Yield = 0.30 g, 91%; orange oil; ν_{max}(neat)/cm^{-1} 1659; δ_H(300 MHz; $CDCl_3$) 3.79 (3 H, s), 5.07 (1 H, d, *J* 0.9), 5.53 (1 H, d, *J* 0.9), 6.10 (1 H, d, *J* 12.0), 6.71–6.75 (2 H, m), 6.88–6.96 (3 H, m), 6.99–7.04 (2 H, m), 7.08–7.13 (3 H, m), 7.18–7.25 (7 H, m), 7.29–7.38 (1 H, m); δ_C(75 MHz; $CDCl_3$) 55.3, 112.7, 114.1, 115.4, 118.4 (s), 123.9, 124.0 (s), 125.6, 126.2, 126.8, 127.6, 128.3, 128.8, 129.0, 129.8, 130.5, 130.7 (s), 137.9 (s), 138.7 (s), 141.6 (s), 144.5 (s), 159.8 (s); HRMS (ESI): Calcd for $C_{29}H_{25}ClNO$ [M + H]$^+$ 438.1619, found 438.1619.

Preparation of quinolines 34

To a solution of 1-phenylmethyl-2-triphenylphosphoranylideneaminobenzene **32** (0.5 g, 1.1 mmol) in anhydrous dichloromethane (15 mL) a solution of diphenylketene (1.1 mmol) or methylphenylketene (1.1 mmol) in the same solvent (5 mL) was added. The reaction mixture was stirred at room temperature under nitrogen for 30 min. Next the solvent was removed under reduced pressure and the resulting material was purified by column chromatography on silica gel, using hexanes/diethyl ether (9.5 : 0.5; v/v) as eluent, to provide ketenimine **33a** (91% yield) or ketenimine **33b** (70% yield), respectively.

A deoxygenated solution of ketenimine **33** (0.5 mmol) in anhydrous toluene (20 mL) was heated in a sealed tube at 160 °C during 36 h. After cooling, the solvent was removed under reduced pressure. The resulting material was purified by column chromatography on silica gel, using hexanes/diethyl ether (4 : 1) as eluent.

3,3,4-Triphenyl-3,4-dihydroquinoline 34a. Yield = 0.17 g, 97%; mp 192–194 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1614; δ_H(400 MHz; $CDCl_3$) 4.75 (1 H, s), 6.56 (2 H, d, *J* 7.2), 6.76–6.78 (2 H, m), 6.92–7.00 (3 H, m), 7.03–7.06 (3 H, m), 7.21–7.23 (4 H, m), 7.25–7.29 (2 H, m), 7.30–7.34 (2 H, m), 7.45 (1 H, d, *J* 7.2), 8.54 (1 H, s); δ_C(100 MHz; $CDCl_3$) 50.8, 54.2 (s), 126.3, 126.4, 127.0, 127.6, 127.7, 127.8, 127.9, 128.2, 128.4, 128.5, 128.9, 129.1, 130.1 (s), 139.6 (s), 141.8 (s), 143.1 (s), 144.3 (s), 165.5; HRMS (ESI): Calcd for $C_{27}H_{22}N$ [M + H]$^+$ 360.1747, found 360.1751.

3-Methyl-3,4-diphenyl-3,4-dihydroquinoline 34b. Yield = 0.10 g, 70%; colourless oil; ν_{max}(neat)/cm^{-1} 1622; δ_H(300 MHz; $CDCl_3$) 1.30 (3 H, s, minor isomer), 1.62 (3 H, s, major isomer), 4.02 (1 H, s, major isomer), 4.28 (1 H, s, minor isomer), 6.47–6.49 (3 H, m), 6.89–7.36 (23 H, m), 7.49 (1 H, d, *J* 7.5, minor isomer), 7.56 (1 H, d, *J* 7.8, major isomer), 7.90 (1 H, s, minor isomer), 8.05 (1 H, s, major isomer); δ_C(75 MHz; $CDCl_3$) 20.5 (minor isomer), 23.2 (major isomer), 45.4 (s, minor isomer), 46.3 (s, major isomer), 54.0 (minor isomer), 54.7 (major isomer), 126.6, 126.9, 127.0, 127.1, 127.3, 127.4, 127.6, 127.7, 127.89, 127.94, 128.0, 128.1, 128.4, 128.5, 128.8, 129.6, 129.8, 138.5 (s), 139.1 (s), 140.7 (s), 142.1 (s), 142.2 (s), 144.1 (s), 168.8; HRMS (ESI): Calcd for $C_{22}H_{20}N$ [M + H]$^+$ 298.1590, found 298.1594.

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