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1,5-(H, RO, RS) shift/6π-electrocyclic ring closure tandem processes on *N*-[(α-heterosubstituted)-2-tolyl]-ketenimines: a case study of relative migratory aptitudes and activating effects†

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A number of *N*-aryl ketenimines, substituted at the *ortho* position either with different non-cyclic acetalic functions (acetals, monothioacetals, dithioacetals) or with only one alkoxymethyl or (alkylthio)methyl group, have been prepared and submitted to thermal treatment in toluene solution. Under smooth heating the ketenimines bearing non-cyclic acetals converted into 3,4-dihydroquinolines following two competitive tandem sequences that involve the alternative 1,5 migration of a hydride or alkoxy group as the first mechanistic step, followed by subsequent 6π electrocyclic ring closure. The heterocumulenes bearing acyclic monothioacetal and dithioacetal functions converted *via* a unique consecutive process involving the selective migration of the alkanethiolate group. Ketenimines bearing only one ether or thioether group transformed exclusively by the tandem sequence initiated by a 1,5 hydride shift. All these transformations provided as final reaction products a variety of quinoline derivatives with a range of substitution patterns. From these experiments the following order of propensity to migration can be extracted: RS > RO > H. It was also possible to estimate the following order of relative activating activities: RO > RS > H.

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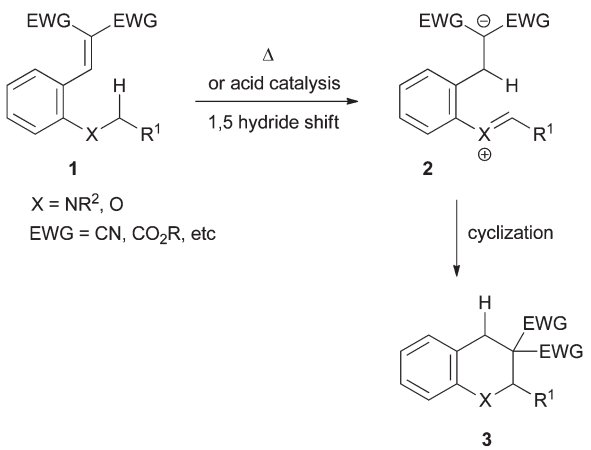
Introduction

The development of new methodologies for the selective replacement of the carbon–hydrogen bond with new bonds (C–H functionalization) has provided a powerful tool in synthetic organic chemistry,[1] allowing the production of numerous complex molecules.[2] Recently, much attention on this research topic has been devoted to the functionalization of C(sp^3)–H bonds *via* the so-called "internal redox process" (Scheme 1).[3] This type of process involves as the first step the cleavage of a C–H bond α to a heteroatom *via* a 1,5 hydride shift to give a zwitterionic intermediate **2**. Subsequent recombination of the reduced and oxidized parts of the molecule takes place to afford heterocyclic compounds **3**. Moreover, the participation in this type of reaction of benzylic C–H bonds[4] without adjacent heteroatoms and even of aliphatic non-benzylic C–H bonds[5] has been also reported. These internal redox processes are commonly activated either thermally or by Brønsted and Lewis acid catalysis.[6]



Scheme 1 Typical internal redox process.

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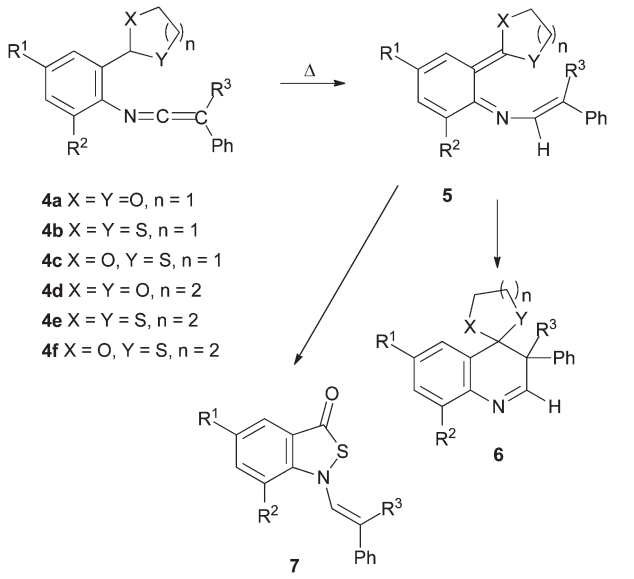
†Electronic supplementary information (ESI) available: ORTEP representation of the crystal structure of *cis*-**20e**. Copy of ^{1}H and ^{13}C NMR spectra of compounds **10**, **12**, **13**, **17**, **20**, **21**, **26**, **28**, **31**, **34**, **37** and **39**. Copy of ^{31}P NMR spectra of compounds **10**, **17**, **26**, **31** and **37**. Cif files of *cis*-**20e**. CCDC 905526. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ob27010b



Scheme 2 Cyclic acetalic fragments facilitating tandem sequences promoted by initial 1,5 hydride shifts.

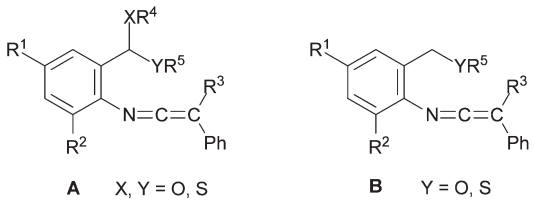


Fig. 1 General structure of ketenimines bearing non-cyclic acetalic functions (**A**) and ether or thioether groups (**B**).

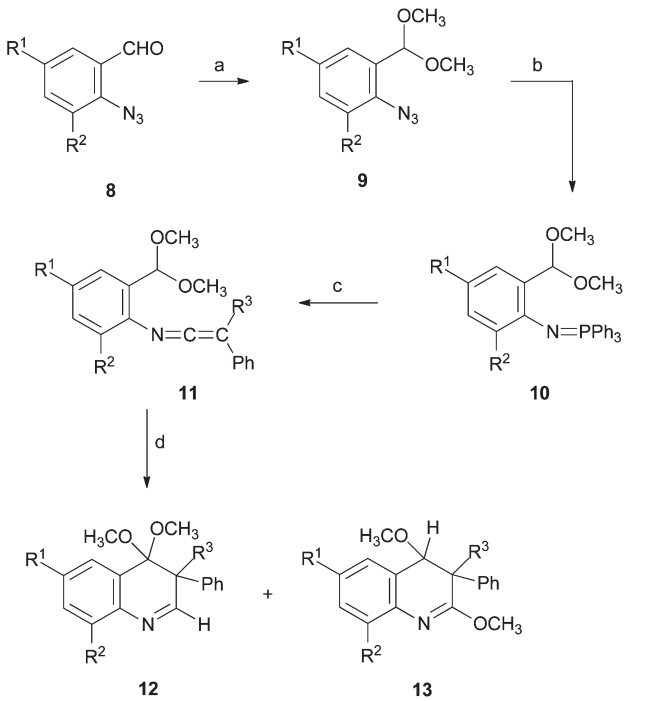
Recently, as part of our research program for developing new reactions involving ketenimines we discovered that under thermal activation the acetal-ketenimines **4** converted into quinolones **6** (Scheme 2).[7] In these conversions the acetalic C–H bond serves as a hydride source for translating its H atom to the central carbon of the pendant ketenimine moiety. After the hydride transfer, the resulting *ortho*-azaxylylene intermediates **5** undergo 6π electrocyclic ring closure (6π-ERC) to form the quinoline ring system. The C(sp^3)–H activation step occurring in these tandem processes is facilitated by the hydricity (hydride donor ability) of the acetalic functions. Only in one particular case (X = O, Y = S, *n* = 1) the course of the one-pot thermal transformation changed, the final products being species **7**, but the result was also explained by postulating an initial 1,5 hydride shift.[8] We have also previously conducted similar sequences onto ketenimines bearing triarylmethane fragments as hydride donors.[9]

Stimulated by these results we became interested in the exploration of the thermally-activated transformation that could undergo *N*-aryl ketenimines **A** bearing non-cyclic acetalic functions at the *ortho* position of the keteniminic nitrogen atom, such as acetals, monothioacetals and dithioacetals, and structurally related *N*-aryl ketenimines **B** supporting only one ether or thioether function at the benzylic carbon (Fig. 1). It is well known that under high temperature conditions (FVP conditions) oxoketenimines undergo anionotropic 1,3 migration of electron-donor RO, RS and R_2N groups from the carbonyl carbon to the central heterocumulenic carbon atom, thus equilibrating with imidoylketenes.[10] In our hands *N*-phenyl ketenimines substituted at the *ortho* position of their *N*-phenyl ring with different carboxylic –C(O)Z functions (Z = RS, ArS, ArSe, ArO and R_2N) undergo cyclization, under mild thermal conditions, initiated by 1,5-shifts of these electron-donor fragments *Z* to the ketenimine central carbon atom.[11] In contrast, structurally related ketenimines bearing $ArCH_2O$ groups at the carbonyl carbon experience evolution by a different pathway: the addition of the non-carbonylic oxygen atom of the ester group to the ketenimine followed by oxygen-to-carbon migration of the benzyl unit.[12] Several examples of related 1,5 RO migrations have been also reported involving the electrophilic carbon atom of carbodiimides as the migration terminus.[13] However, in the thermally-induced tandem transformations of ketenimines **4** bearing cyclic acetalic fragments we always obtained products derived from the exclusive migration of the benzylic H atom. Most probably, the conformational restrictions imposed on the system by the cyclic nature of the acetalic groups prevent the alternative anionotropic migration of the RO and/or RS fragments from the acetalic carbon atom by making more difficult the subsequent cyclization. We thus reasoned that the acyclic acetalic functions of ketenimines **A** in Fig. 1 would probably allow the competitive migration of all atoms (or groups of atoms) at the acetalic carbon, and, if so, to establish the relative order of migratory aptitude of these atoms in such tandem processes, in combination with the study of the more simple related substrates **B**.

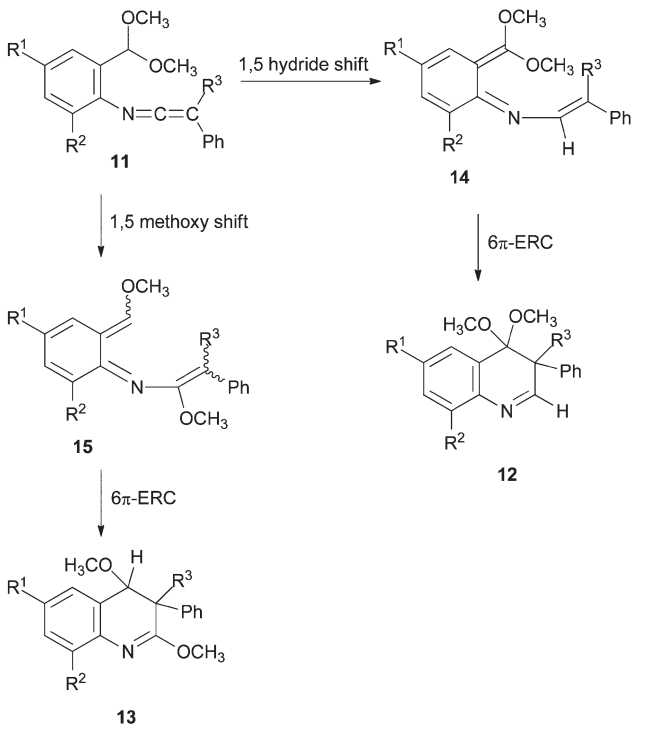
Herein we disclose that under thermal treatment several examples of ketenimines **A** bearing non-cyclic acetal functions (X = Y = O) converted into mixtures of 4,4-dialkoxyquinolines and 2,4-dialkoxyquinolines, following two competitive tandem sequences involving the respective 1,5 migration of hydride and alkoxy groups. We also document that in similar reactions of ketenimines **A** supporting acyclic dithioacetals (X = Y = S) and monothioacetals (X = O, Y = S) the alkanethiolate group selectively migrated to give 2-alkylthioquinolines. We also show that ketenimines **B** bearing one ether or thioether group transformed, on heating, exclusively into the quinolines resulting from a tandem sequence having as the first step a 1,5 hydride shift.

Results and discussion

Dimethoxyacetal-ketenimines **11** designed for the initial studies were prepared *via* a three step sequence initiated by the treatment of methanolic solutions of the easily available 2-azidobenzaldehydes **8** with methyl orthoformate, in the presence of a catalytic amount of *para*-toluenesulfonic acid at room temperature, to provide α,α-dimethoxy-2-tolylazides **9**. The Staudinger reaction of acetal-azides **9** with triphenylphosphine, in anhydrous diethyl ether at room temperature,



Scheme 3 *Reagents and conditions*: (a) $HC(OCH_3)_3$, *p*-TsOH cat., CH_3OH, r.t., 24 h. (b) PPh_3, Et_2O, r.t., 16 h. (c) PhR^3CCO, toluene, r.t., 30 min. (d) Toluene, reflux, 3–24 h.



Scheme 4 Alternative reaction pathways for the conversion of **11** into **12** and **13**.

Table 1 4,4-Dimethoxyquinolines **12** and 2,4-dimethoxyquinolines **13**

Entry	R^1	R^2	R^3	Combined yield (%)	**12** : **13** Ratio
a	H	H	Ph	82	41 : 59
b	H	CH_3	Ph	88	41 : 59
c	Cl	H	Ph	89	27 : 73
d	CH_3	H	Ph	64	61 : 39
e	H	H	CH_3	90	33 : 66
f	H	CH_3	CH_3	75	33 : 66

afforded the acetal-iminophosphoranes **10**. When toluene solutions of compounds **10** were treated, at room temperature, with diphenylketene and methylphenylketene the acetal-ketenimines **11** were formed, as corroborated by recording FT-IR spectra of the final solutions which showed very strong absorption bands around 2000 cm^{-1} distinctive of the ketenimine grouping. By simply heating at reflux temperature for a few hours the toluene solutions containing heterocumulenes **11**, a clean reaction occurred to provide mixtures of the 4,4-dimethoxy-3,4-dihydroquinolines **12** and the 2,4-dimethoxy-3,4-dihydroquinolines **13** (Scheme 3, Table 1).

The determination of the structure of dihydroquinolines **12** and **13** was carried out following their spectral data: IR, ^1H and ^{13}C NMR and mass spectrometry. In the ^1H NMR of the 4,4-dimethoxy derivatives **12a–d** the protons of both methoxy groups resonate as one singlet at δ = 2.82–2.91 ppm, whereas in examples **12e,f**, bearing a chiral C3 carbon atom, the diastereotopic methoxy groups appear as two singlets at very close chemical shifts, δ = 2.89–2.95 ppm. In these compounds the C(2)H proton appears at δ = 7.82–8.49 ppm. Significant ^{13}C NMR data of quinolines **12** are the chemical shifts of the C4 aliphatic quaternary carbon at δ = 99.9–100.6 ppm and that of the C2 methine carbon at δ = 170.5–172.6 ppm. The ^1H NMR spectra of quinolines **13** show two neatly different methoxy groups, that linked to C2 resonates at δ = 3.92–3.99 ppm and that to C4 at δ = 3.01–3.41 ppm. In their ^{13}C NMR spectra the quaternary C2 resonates at δ = 165.9–169.7 ppm, whereas the signal of the methine C4 appears at δ = 84.6–85.9 ppm, considerably shifted upfield with respect to the signal of the same carbon in the isomeric quinolines **12** bearing two methoxy groups at that carbon.

The 2,4-dimethoxy-3,4-dihydroquinolines **13e,f** in which R^3 is a methyl group were obtained as mixtures of the two possible racemic diastereoisomers in relative ratios close to 1 : 1, as calculated by integration in the ^1H NMR spectra of the final reaction mixtures. These mixtures were resolved by column chromatography and both diastereoisomers of compounds **13e,f** could be isolated in a pure form. Thus we were able to measure two-dimensional NOESY spectra of both diastereoisomers, but the data extracted from these experiments were not conclusive enough in order to assign the relative *cis*/*trans* configuration of the two stereocenters in each isomer.

Obviously two competitive reaction pathways operate in the thermal conversion of acetal-ketenimines **11** (Scheme 4). A 1,5 hydride-like migration of the acetalic H to the central carbon atom of the ketenimine grouping followed by a 6π electrocyclization of the resulting 3-azatriene **14** explains the formation of 4,4-dimethoxy-3,4-dihydroquinolines **12**. A similar

sequence involving the alternative 1,5 shift of one of the methoxy substituents of the acetalic function in turn explains the formation of 2,4-dimethoxy-3,4-dihydroquinolines **13**.

Most of the entries of Table 1 show that quinolines **13** slightly predominate over **12** in the final reaction mixtures (the only rare exception is entry d). For briefly analysing these results we must bring into play the results of our previous computational analyses on the closely related two-step processes shown in Scheme 2, showing that the first step, the hydride transfer from the benzylic carbon to the central one of the ketenimine, is always the rate-determining one with the higher activation energy.[7,8] Thus, in a reasonable approximation our analysis will deal with the first migratory step. In our interpretation of the experimental results in Table 1, the composition of the mixtures of compounds **12** and **13** obtained from **11** should be explained as resulting from a combination of two electronic effects: first, the "pushing" power of the substituents at the benzylic carbon for contributing to "expel" the migrating atom or group in an anion-like form, and second, the anionotropic migratory aptitude of the "expelled" atom or group. The first one can be also viewed as the ability of the atoms or groups at the benzylic carbon to stabilise the developing electronic deficiency at that atom. In this respect the ability of an RO group to stabilise positive charges, *via* lone pair conjugation, at the carbon atom to which it is linked is well known. In other words, the lone pairs at the oxygen atoms of **11** contribute to detach the migrating group (H or CH_3O) from the benzylic carbon in an anion-like form.[14] By contrast, the H atom should not play a comparable activating role in this respect. Concerning the second electronic effect, the migratory aptitude of the groups in anion-like form, it is also of fundamental chemical knowledge that electronegative atoms, such as oxygen, better accommodate negative charges than the simplest H atom. The results of the thermal conversions of ketenimines **11**, yielding mixtures of quinolines **12** and **13** not very far from the 1 : 1 ratio, should thus be reasoned as resulting from a compromise situation between the facilitation of the H migration path by the two methoxy groups, and the better migratory aptitude of the detached CH_3O when compared with H, but in this last case being activated by only one methoxy group. This compromise situation between the two alternative reaction paths seems to be slightly unbalanced toward the second one in most of the cases collected in Table 1.

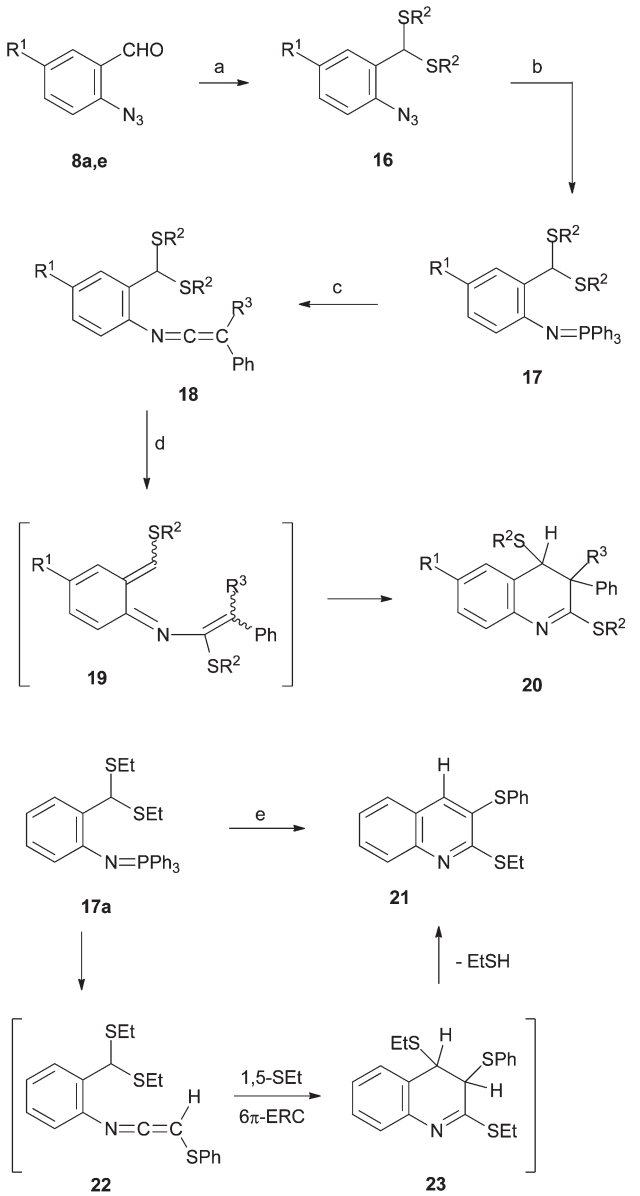
We next examined the thermal evolution of ketenimines bearing non-cyclic dithioacetal functionalities. The reaction of 2-azidobenzaldehydes **8a,e** with ethanethiol or 2-phenylethanethiol, in anhydrous chloroform at room temperature in the presence of trimethylsilyl chloride, yielded the corresponding dithioacetal-azides **16**, which in a further step by treatment with triphenylphosphine, in diethyl ether solution at room temperature, were converted into the iminophosphoranes **17**. The dithioacetal-ketenimines **18** were prepared by the usual methodology, the aza-Wittig reaction of the iminophosphoranes **17** with diphenylketene or methylphenylketene. The thermal conditions required to promote the conversion of the dithioacetal-ketenimines **18** were dependent on the nature of the R^3 substituent. Whereas ketenimines **18a–c** bearing R^3 = Ph required heating in refluxing toluene, those with $R^3 = CH_3$ **18d,e** transformed just by keeping their dichloromethane solution at room temperature. The reaction products obtained in the thermal treatment of dithioacetal-ketenimines **18** were, in all the cases, the 2,4-dialkylthio-3,4-dihydroquinolines **20** (Scheme 5, Table 2), which formed by the habitual two-step sequence: the selective 1,5 shift of one alkanethiolate group from the acetalic carbon to the ketenimine central carbon atom followed by the 6π electrocyclization of the 3-azahexatriene intermediates **19**.

With the aim of extending the synthetic scope of this 1,5-SR shift/6π-ERC tandem process to the preparation of additional quinolines with different substitution patterns, a mixture of iminophosphorane **17a** and *S*-phenyl 2-diazoethanethiolate in anhydrous toluene was heated at 80 °C, giving rise to the 2-ethylthio-3-phenylthioquinoline **21**. The full mechanistic sequence explaining the formation of quinoline **21** is also shown in Scheme 5, involving as the last step the aromatization of the pyridine ring of the 1,5-SR/6π-ERC product **23** by the β-elimination of volatile ethanethiol.

Quinolines **20d,e** ($R^3 = CH_3$) having two sterocenters, C3 and C4 carbon atoms, were obtained as mixtures of the *cis* and *trans* diastereoisomers in unexpectedly good diastereomeric ratios (up to 90 : 10). The fractional crystallization of the major isomer of compound **20e** yielded good quality single crystals suitable for X-ray structure determination. The X-ray structural data indicate that in this diastereoisomer of **20e** the phenyl group at C3 and the ethylthio group at C4 are in a relative *cis* disposition (see ESI†). A relative *cis* configuration was also assigned to the major diastereoisomer of quinoline **20d** as it showed ^1H and ^{13}C NMR data similar to those of *cis*-**20e**.

As shown in Scheme 5 and Table 2, the migrating group in the thermal conversion of dithioacetal-ketenimines **18** is always an alkylthio group, whereas products derived from the alternative migration of the acetalic H atom were neither isolated nor even detected in the reaction crudes, in sharp contrast with the results obtained with acetal-ketenimines **11**. From the exclusive formation of 3,4-dihydroquinolines **20** by thermal treatment of dithioacetal-ketenimines **18**, and also by taking our background in this research into account, we can estimate that the RS groups of ketenimines **18** possess better migratory aptitude than the CH_3O of ketenimines **11**. To reach this conclusion, one key point is that we have previously proved that a cyclic dithioacetal fragment is less effective than a similar cyclic acetal in promoting the 1,5 H migrations represented in Scheme 2. That is, alkoxy groups have better "pushing" ability than their thioanalogues in order to "expel" the migrating atom or group. This is why the contrasting results of the thermal treatment of ketenimines **11** and **18** can be rationalized by accounting for the poorer activating power of the RS groups in comparison with that of the methoxy group, and the better migratory aptitude of the RS ones.[15]

Nevertheless, with the aim of directly testing the above estimations on the relative migratory aptitudes of the different

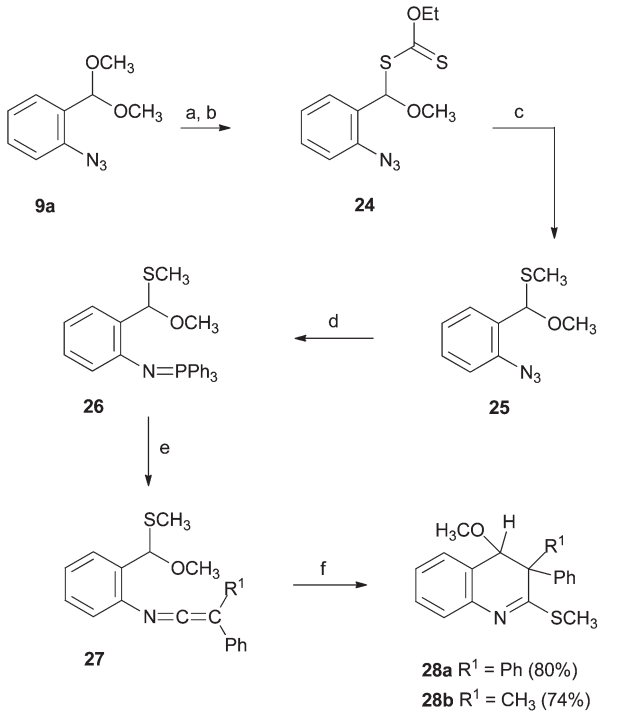


Scheme 5 *Reagents and conditions*: (a) R^2SH, TMSCl, $CHCl_3$, r.t., 1 h. (b) PPh_3, Et_2O, r.t., 16 h. (c) PhR^3CCO, toluene, r.t., 30 min. (d) **18a–c**: toluene, reflux, 1 h; **18d,e**: CH_2Cl_2, r.t., 3–16 h. (e) $PhSC(O)CH(N_2)$, toluene, 80 °C, 1 h.

Table 2 2,4-Dialkylthioquinolines **20**

Compound	R^1	R^2	R^3	Yield (%)	*Cis*/*trans* ratio
20a	H	CH_3CH_2	Ph	94	
20b	Br	CH_3CH_2	Ph	81	
20c	H	$PhCH_2CH_2$	Ph	99	
20d	H	CH_3CH_2	CH_3	97	90 : 10
20e	Br	CH_3CH_2	CH_3	99	72 : 28

groups, we next tackled the preparation of ketenimines bearing non-cyclic monothioacetal functions, substrates with one hydrogen atom, one alkoxy group and one alkylthio group simultaneously placed at the migration origin, the benzylic

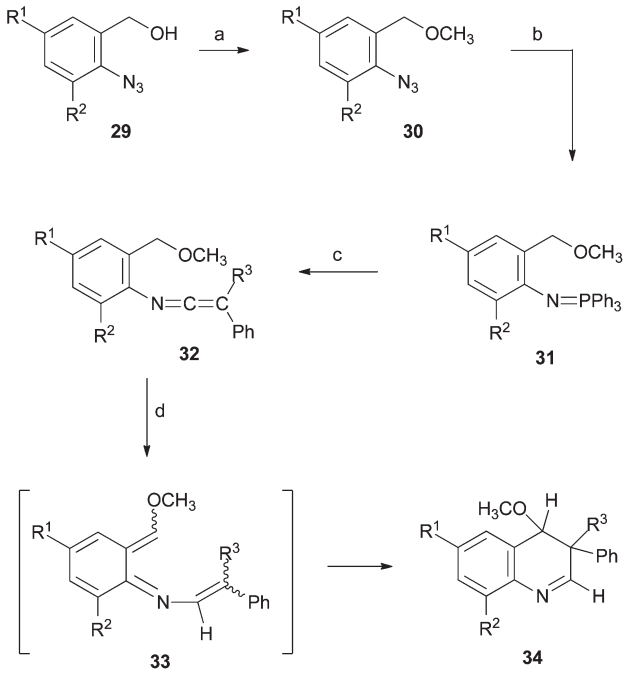


Scheme 6 *Reagents and conditions*: (a) $SOCl_2$, r.t., 16 h. (b) KSC(S)OEt, Et_2O, reflux, 1 h. (c) CH_3I, $NaOCH_3$, Et_2O, 15 °C, 5 h. (d) PPh_3, Et_2O, r.t., 16 h. (e) PhR^1CCO, toluene, r.t., 30 min. (f) Toluene, reflux, 1 h.

carbon atom. Thus, hemithioacetal-ketenimines **27** were prepared in a simple five-step synthetic sequence starting from α,α-dimethoxy-2-tolylazide **9a**. The consecutive treatment of compound **9a** with thionyl chloride and potassium *O*-ethyl dithiocarbonate afforded the xanthate **24**. Next, xanthate **24** was reacted with methyl iodide in the presence of sodium methoxide leading to hemithioacetal-azide **25**, which by the habitual methodology was converted into a pair of hemithioacetal-ketenimines **27**. The heating at reflux temperature of toluene solutions of ketenimines **27** provided 4-methoxy-2-methylthioquinolines **28** as the only reaction products (Scheme 6). The 3-methyl-3,4-dihydroquinoline **28b** ($R^1 = CH_3$) was obtained as a mixture of the two expected *cis*/*trans* diastereoisomers, in a relative ratio close to 2 : 1, which could be separated by column chromatography on silica gel. Unfortunately, the recorded NMR experiments for both diastereoisomers of compound **28b** did not allow us a reliable stereochemical assignment of the relative *cis*/*trans* configuration of the two stereocenters in each isomer.

Clearly the conversions summarized in Scheme 6 took place through the exclusive 1,5 migration of the methylthio group. These results are in accord with our previous estimations: the most favourable 1,5 anionotropic shift should be the one involving the best migrating group, methylthio, being promoted by the most powerful activating one, the methoxy group.

All 1,5-X shift/6π-ERC tandem sequences examined so far in this work deal with acetalic substrates, that is species bearing one hydrogen atom and two heteroatom-linked groups (RO,



Scheme 7 *Reagents and conditions*: (a) CH_3I, KOH, DMSO, r.t., 30 min. (b) PPh_3, Et_2O, r.t., 16 h. (c) PhR^3CCO, toluene, r.t., 30 min. (d) Toluene, reflux, 12–36 h.

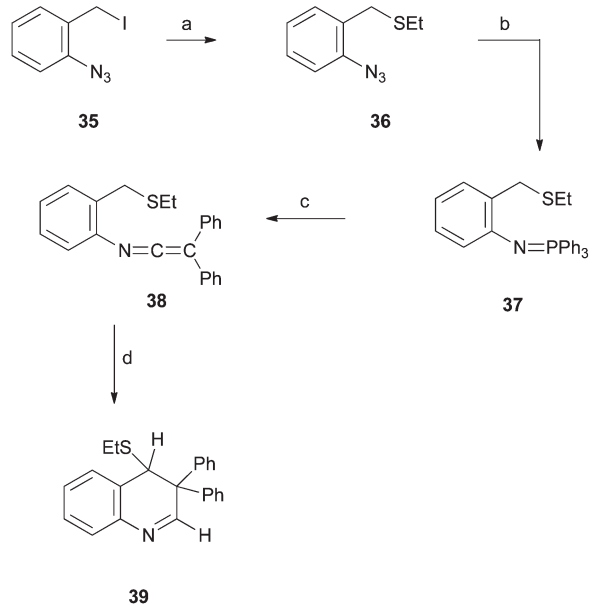
Table 3 4-Methoxyquinolines **34**

Compound	R^1	R^2	R^3	Yield (%)
34a	H	H	Ph	51
34b	H	CH_3	Ph	99
34c	Cl	H	Ph	70
34d	CH_3	H	Ph	61
34e[a]	H	H	CH_3	69
34f[a]	H	CH_3	CH_3	50

[a] Obtained as mixtures of diastereoisomers in a relative ratio close to 2 : 1.

RS) at the benzylic carbon. In all cases, at least one of these groups could migrate in the first step whereas the second one activates the migration by the participation of the lone pairs at its heteroatom. Still some questions remained unanswered. If the ketenimine bears only one of these groups, would it be able to experience the 1,5 shift in the absence of the second RO or RS as the activating group? Only if this group is the one with the best migratory aptitude? Would the H migration compete? The following, final experiments were carried out aiming to answer these questions, by using substrates bearing only one alkoxy or alkylthio group at the benzylic carbon atom.[16]

Methylation of the hydroxyl group of the 2-azidobenzyl alcohols **29**, followed by consecutive treatment of the resulting azido-ethers **30** with triphenylphosphine and methylphenylketene or diphenylketene under the usual conditions afforded ketenimines **32**. 4-Methoxy-3,4-dihydroquinolines **34** were the only products formed when toluene solutions of ketenimines



Scheme 8 *Reagents and conditions*: (a) EtSH, KOH, DMSO, r.t., 2 h. (b) PPh_3, Et_2O, r.t., 16 h. (c) Ph_2CCO, toluene, r.t., 30 min. (d) Toluene, reflux, 6 d (50%) or *ortho*-xylene, reflux, 24 h (85%).

32 were heated at reflux temperature. The conversions of **32** into **34** were complete in an interval of 12–36 h (Scheme 7, Table 3).

The formation of dihydroquinolines **34** is the consequence of tandem 1,5-H/6π-ERC processes, these results proving that in the absence of a second heteroatom-linked group able to facilitate the migration placed at the benzylic carbon, the methoxy group remained at that position playing the role of an activating group.

Ketenimine **38**, prepared similarly to **32** and containing the good-migrating ethylthio group, heated in toluene solution at reflux temperature gave rise, after 6 days, to a 50% yield of 4-ethylthio-3,4-dihydroquinoline **39**, as a result of a tandem 1,5-H/6π-ERC process (Scheme 8). A better yield, 85%, was obtained when carrying out the thermal treatment in refluxing *ortho*-xylene for 24 h.

It became thus clear that even a group with good migratory aptitude, such as EtS, would require the activation of a second heteroatom-linked group at the benzylic position for undergoing a 1,5 shift to the central ketenimine carbon of this type of heterocumulene. Otherwise, the H migration promoted by the activating group is the only observed shift. By comparing the reaction conditions of the **32** into **34** and **38** into **39** transformations, the better activating characteristics of the alkoxy groups over the alkylthio ones are once again highlighted.

Conclusions

In conclusion, ketenimines bearing acyclic acetal functions as hydride donor units have been shown to undergo competitive 1,5-H/6π-ERC and 1,5-OR/6π-ERC tandem processes, leading to

quinolines, whereas their monothioacetal and dithioacetal analogues experience cyclization through tandem processes involving as the first step the selective migration of an alkylthio group. We have herein also demonstrated that a single ether or thioether function is also able to impart hydricity facilitating intramolecular H shifts, but in no case the migration of the heteroatom-based function is amenable. Thus the thermal treatment of *N*-aryl ketenimines, supporting one ether or thioether function at the benzylic carbon at the *ortho* position, provides the quinolines resulting from the exclusive 1,5-H migration in the first mechanistic step. The analysis of all these experiments revealed the following order of migratory aptitude RS > RO > H, accounting for the anionotropic nature of the migratory step. The order of activating power follows the sequence RO > RS > H, reflecting the relative power for stabilizing the developing carbocationic characteristics at the benzylic carbon atom in the rearrangement.

Experimental

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

2-Azidobenzaldehyde **8a**,[17] 2-azido-3-methylbenzaldehyde **8b**,[18] 2-azido-5-chlorobenzaldehyde **8c**,[19] 2-azido-5-methylbenzaldehyde **8d**,[18] 2-azido-5-bromobenzaldehyde **8e**,[19] 2-azidobenzyl alcohol **29a**,[20] 2-azido-3-methylbenzyl alcohol **29b**,[18] 2-azido-5-chlorobenzyl alcohol **29c**,[21] 2-azido-5-methylbenzylalcohol **29d**,[18] 2-azidobenzyl iodide **35**,[21] methylphenylketene[22] and diphenylketene[23] were prepared following published experimental procedures.

Preparation of 2-azido-1-(dimethoxymethyl)benzenes 9

To a solution of the 2-azidobenzaldehyde **8** (10 mmol) in anhydrous methanol (15 mL) methyl orthoformate (2.12 g, 20 mmol) and a catalytic amount of *para*-toluenesulfonic acid (0.01 g) were added. The reaction mixture was stirred at room temperature for 24 h. Then, the solvent was removed under reduced pressure, and the crude material was purified by column chromatography on silica gel.

2-Azido-1-(dimethoxymethyl)benzene 9A (R^1 = R^2 = H). Eluent for column chromatography: hexanes–diethyl ether (4 : 1, v/v); (1.83 g, 95%); yellow oil; ν_{max}(neat)/cm^{-1} 2127 (vs), 2089 (s); δ_H (400 MHz, $CDCl_3$) 3.35 (6 H, s), 5.52 (1 H, s), 7.14–7.18 (2 H, m), 7.37 (1 H, ddd, *J* 8.2, 7.2, 1.6), 7.57–7.59 (1 H, m); δ_C (100 MHz, $CDCl_3$) 53.6, 99.3, 118.2, 124.5, 127.9, 129.1 (s), 129.9, 137.8 (s).

2-Azido-1-(dimethoxymethyl)-3-methylbenzene 9B (R^1 = H; R^2 = CH_3). Eluent for column chromatography: hexanes–diethyl ether (9 : 1, v/v); (1.51 g, 73%); colourless oil; ν_{max}(neat)/cm^{-1} 2113 (vs); δ_H (400 MHz, $CDCl_3$) 2.41 (3 H, s), 3.37 (6 H, s), 5.60 (1 H, s), 7.11–7.18 (2 H, m), 7.41–7.44 (1 H, m); δ_C (100 MHz, $CDCl_3$) 18.1, 53.8, 100.8, 125.5, 125.7, 131.6, 131.9 (s), 132.9 (s), 136.4 (s).

2-Azido-5-chloro-1-(dimethoxymethyl)benzene 9C (R^1 = Cl; R^2 = H). Eluent for column chromatography: hexanes–diethyl ether (7 : 3, v/v); (2.25 g, 99%); colourless oil; ν_{max}(neat)/cm^{-1} 2129 (vs), 2098 (vs); δ_H (400 MHz, $CDCl_3$) 3.35 (6 H, s), 5.47 (1 H, s), 7.09 (1 H, d, *J* 8.5), 7.33 (1 H, dd, *J* 8.5, 2.5), 7.57 (1 H, d, *J* 2.5); δ_C (100 MHz, $CDCl_3$) 53.6, 98.7, 119.5, 128.2, 130.2 (s), 130.7 (s), 136.4 (s).

2-Azido-1-(dimethoxymethyl)-5-methylbenzene 9D (R^1 = CH_3; R^2 = H). Eluent for column chromatography: hexanes–diethyl ether (4 : 1, v/v); (2.03 g, 98%); yellow oil; ν_{max}(neat)/cm^{-1} 2129 (vs), 2105 (vs); δ_H (300 MHz, $CDCl_3$) 2.33 (3 H, s), 3.35 (6 H, s), 5.49 (1 H, s), 7.05 (1 H, d, *J* 8.1), 7.17 (1 H, dd, *J* 8.1, 1.9), 7.38 (1 H, d, *J* 1.9); δ_C (75 MHz, $CDCl_3$) 21.0, 53.8, 99.5, 118.1, 128.3, 128.8 (s), 130.5, 134.4 (s), 135.0 (s).

Preparation of 1-(dimethoxymethyl)-2-triphenylphosphoranylideneaminobenzenes 10

To a solution of 2-azido-1-(dimethoxymethyl)benzene **9** (5 mmol) in anhydrous diethyl ether (20 mL), under nitrogen at room temperature, triphenylphosphine (1.30 g, 5 mmol) was added in small portions. The reaction mixture was stirred at room temperature for 16 h. Then the precipitated compounds **10** were isolated by filtration and washed with anhydrous diethyl ether (10 mL). These compounds were used in the following step without further purification.

For analytical samples iminophosphoranes **10** were recrystallized from diethyl ether.

1-(Dimethoxymethyl)-2-triphenylphosphoranylideneaminobenzene 10A (R^1 = R^2 = H). (2.09 g, 98%); mp 125–126 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 1435 (vs), 1321 (vs), 1103 (s); δ_H (400 MHz, $CDCl_3$) 3.36 (6 H, s), 6.16 (1 H, s), 6.47 (1 H, d, *J* 8.0), 6.68 (1 H, t, *J* 7.4), 6.83 (1 H, t, *J* 7.4), 7.41–7.45 (7 H, m), 7.48–7.54 (3 H, m), 7.73–7.78 (6 H, m); δ_C (100 MHz, $CDCl_3$) 54.1, 101.9, 117.3, 121.8 (d, *J* 9.6), 126.8, 128.3, 128.6 (d, *J* 12.0), 131.6 (d, *J* 2.4), 131.7 (d, *J* 99.7) (s), 131.8 (s), 132.6 (d, *J* 9.7), 149.4 (s); δ_P (161.9 MHz, $CDCl_3$, H_3PO_4) 1.5; HRMS (ESI): Calcd for $C_{27}H_{27}NO_2P$ $[M + H]^+$ 428.1774, found 428.1780.

1-(Dimethoxymethyl)-3-methyl-2-triphenylphosphoranylideneaminobenzene 10B (R^1 = H; R^2 = CH_3). (2.03 g, 92%); mp 118–119 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 1435 (vs), 1381 (vs), 1105 (s); δ_H (400 MHz, $CDCl_3$) 1.90 (3 H, s), 2.95 (6 H, s), 5.56 (1 H, s), 6.72 (1 H, td, *J* 7.4, 2.1), 6.96 (1 H, d, *J* 7.4), 7.26 (1 H, d, *J* 7.4), 7.36–7.40 (6 H, m), 7.44–7.52 (3 H, m), 7.58–7.68 (6 H, m); δ_C (100 MHz, $CDCl_3$) 21.3, 52.9, 101.3, 118.7 (d, *J* 3.2), 124.4 (d, *J* 1.9), 128.3 (d, *J* 12.0), 130.1 (d, *J* 2.5), 131.2 (d, *J* 2.4), 132.4 (d, *J* 9.5), 132.6 (d, *J* 100.8) (s), 133.5 (d, *J* 4.0) (s), 147.1 (s); δ_P (161.9 MHz, $CDCl_3$, H_3PO_4) – 3.8; HRMS (ESI): Calcd for $C_{28}H_{29}NO_2P$ $[M + H]^+$ 442.1930, found 442.1936.

5-Chloro-1-(dimethoxymethyl)-2-triphenylphosphoranylideneaminobenzene 10C (R^1 = Cl; R^2 = H). (2.10 g, 91%); mp 117–118 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 1346 (vs), 1321 (s), 1108 (s); δ_H (400 MHz, $CDCl_3$) 3.35 (6 H, s), 6.06 (1 H, s), 6.36 (1 H, dd, *J* 8.5, 1.4), 6.77 (1 H, dd, *J* 8.5, 2.8), 7.39–7.53 (10 H, m),

7.70–7.75 (6 H, m); δ_C (100 MHz, $CDCl_3$) 54.0, 101.2, 122.1 (s), 122.6 (d, *J* 9.6), 126.8, 128.1, 128.7 (d, *J* 11.9), 131.1 (d, *J* 99.3) (s), 131.8 (d, *J* 2.4), 32.5 (d, *J* 9.6), 133.2 (d, *J* 20.1) (s), 148.1 (s); δ_P (161.9 MHz, $CDCl_3$, H_3PO_4) 2.7; HRMS (ESI): Calcd for $C_{27}H_{26}ClNO_2P$ $[M + H]^+$ 462.1384, found 462.1389.

1-(Dimethoxymethyl)-5-methyl-2-triphenylphosphoranylideneaminobenzene **10D** (R^1 = CH_3; R^2 = H). (1.85 g, 84%); mp 128–129 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 1489 (vs), 1344 (s), 1107 (s); δ_H (400 MHz, $CDCl_3$) 2.19 (3 H, s), 3.37 (6 H, s), 6.14 (1 H, s), 6.39 (1 H, dd, *J* 81, 1.4), 6.65 (1 H, dd, *J* 8.1, 2.0), 7.23–7.25 (1 H, m), 7.40–7.44 (6 H, m), 7.47–7.49 (3 H, m), 7.72–7.77 (6 H, m); δ_C (100 MHz, $CDCl_3$) 20.7, 54.2, 101.9, 121.5 (d, *J* 9.3), 126.4 (s), 127.2, 128.5 (d, *J* 11.9), 129.0, 131.5 (d, *J* 2.5), 131.8 (d, *J* 99.6) (s), 132.6 (d, *J* 9.6), 146.6 (s); δ_P (161.9 MHz, $CDCl_3$, H_3PO_4) 1.6; HRMS (ESI): Calcd for $C_{28}H_{29}NO_2P$ $[M + H]^+$ 442.1930, found 442.1936.

Preparation of 4,4-dimethoxyquinolines 12 and 2,4-dimethoxyquinolines 13

To a solution of the 1-(dimethoxymethyl)-2-triphenylphosphoranylideneaminobenzene **10** (1 mmol) in anhydrous toluene (20 mL) a solution of methylphenylketene (0.13 g, 1 mmol) or diphenylketene (0.19 g, 1 mmol) in the same solvent (5 mL) was added. The reaction mixture was stirred under nitrogen at room temperature for 30 min, and next heated at reflux temperature for 3–24 h. After cooling at room temperature, the solvent was removed under reduced pressure, and the resulting crude material was purified by column chromatography on silica gel.

4,4-Dimethoxy-3,3-diphenyl-3,4-dihydroquinoline **12A** (R^1 = R^2 = H; R^3 = Ph). Eluent for column chromatography: hexanes–diethyl ether (4 : 1, v/v); (0.12 g, 34%); mp 131–132 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 1628 (m); δ_H (400 MHz, $CDCl_3$) 2.82 (6 H, s), 7.09–7.12 (6 H, m), 7.13–7.17 (3 H, m), 7.32–7.36 (4 H, m), 7.67–7.70 (1 H, m), 8.38 (1 H, s); δ_C (100 MHz, $CDCl_3$) 50.9, 59.0 (s), 100.2 (s), 126.1, 127.0, 127.1, 127.2, 127.5, 129.3, 129.4 (s), 131.1, 141.4 (s), 143.2 (s), 172.0; HRMS (ESI): Calcd for $C_{23}H_{22}NO_2$ $[M + H]^+$ 344.1645, found 344.1649.

4,4-Dimethoxy-8-methyl-3,3-diphenyl-3,4-dihydroquinoline **12B** (R^1 =H; R^2 = CH_3; R^3 = Ph). Eluent for column chromatography: hexanes–diethyl ether (9 : 1, v/v); (0.13 g, 36%); colourless oil; ν_{max}(neat)/cm^{-1} 1587 (m); δ_H (300 MHz, $CDCl_3$) 2.33 (3 H, s), 2.88 (6 H, s), 7.05–7.09 (2 H, m), 7.14–7.16 (6 H, m), 7.40–7.43 (4 H, m), 7.57–7.60 (1 H, m), 8.49 (1 H, s); δ_C (75 MHz, $CDCl_3$) 17.4, 50.9, 58.5 (s), 100.6 (s), 123.8, 126.6, 127.0, 127.5, 129.1 (s), 131.1, 131.2, 134.9 (s), 141.3 (s), 141.7 (s), 170.5; HRMS (ESI): Calcd for $C_{24}H_{24}NO_2$ $[M + H]^+$ 358.1802, found 358.1817.

6-Chloro-4,4-dimethoxy-3,3-diphenyl-3,4-dihydroquinoline **12C** (R^1 = Cl; R^2 = H; R^3 = Ph). Eluent for column chromatography: hexanes–diethyl ether (9 : 1, v/v); (0.09 g, 24%); colourless oil; ν_{max}(neat)/cm^{-1} 1621 (m); δ_H (300 MHz, $CDCl_3$, 55 °C) 2.91 (6 H, s), 7.12–7.23 (8 H, m), 7.38–7.41 (4 H, m), 7.75 (1 H, d, *J* 2.2), 8.46 (1 H, s); δ_C (75 MHz, $CDCl_3$, 55 °C) 51.0, 58.8 (s), 99.9 (s), 126.3, 127.3, 127.7, 128.2, 129.3, 131.0, 131.2 (s), 133.0 (s), 140.9 (s), 141.8 (s), 172.6; HRMS (ESI): Calcd for $C_{23}H_{21}ClNO_2$ $[M + H]^+$ 378.1255, found 378.1262.

4,4-Dimethoxy-6-methyl-3,3-diphenyl-3,4-dihydroquinoline **12D** (R^1 = CH_3; R^2 = H; R^3 = Ph). Eluent for column chromatography: hexanes–diethyl ether (1 : 1, v/v); (0.14 g, 39%); mp 113–114 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 1621 (m); δ_H (400 MHz, $CDCl_3$, 57 °C) 2.36 (3 H, s), 2.90 (6 H, s), 7.03 (1 H, dd, *J* 7.8, 1.2), 7.10 (1 H, d, *J* = 7.8), 7.16–7.18 (6 H, m), 7.40–7.43 (4 H, m), 7.56–7.57 (1 H, m), 8.39 (1 H, s); δ_C (100 MHz, $CDCl_3$) 21.6, 50.9, 59.1 (s), 100.3 (s), 126.6, 126.8, 127.0, 127.5, 129.0 (s), 129.8, 131.1, 137.1 (s), 141.0 (s), 141.5 (s), 170.9; HRMS (ESI): Calcd for $C_{24}H_{24}NO_2$ $[M + H]^+$ 358.1802, found 358.1808.

4,4-Dimethoxy-3-methyl-3-phenyl-3,4-dihydroquinoline **12E** (R^1 = R^2 = H; R^3 = CH_3). Eluent for column chromatography: dichloromethane; (0.08 g, 30%); colourless oil; ν_{max}(neat)/cm^{-1} 1610 (m); δ_H (400 MHz, $CDCl_3$) 1.52 (3 H, s), 2.91 (3 H, s), 2.95 (3 H, s), 7.26–7.44 (6 H, m), 7.54–7.57 (2 H, m), 7.64–7.66 (1 H, m), 7.82 (1 H, s); δ_C (100 MHz, $CDCl_3$) 16.9, 50.5, 51.0, 51.2 (s), 100.0 (s), 126.7, 127.1, 127.3, 127.4, 127.5 (s), 127.8, 129.6, 129.9, 140.2 (s), 172.2.

4,4-Dimethoxy-3,8-dimethyl-3-phenyl-3,4-dihydroquinoline **12F** (R^1 = H; R^2 = CH_3; R^3 = CH_3). Eluent for column chromatography: hexanes–diethyl ether (9 : 1, v/v); (0.07 g, 25%); colourless oil; ν_{max}(neat)/cm^{-1} 1630 (m); δ_H (300 MHz, $CDCl_3$) 1.50 (3 H, s), 2.52 (3 H, s), 2.89 (3 H, s), 2.92 (3 H, s), 7.14–7.22 (1 H, m), 7.23–7.38 (4 H, m), 7.48–7.51 (1 H, m), 7.56–7.59 (2 H, m), 7.85 (1 H, s); δ_C (100 MHz, $CDCl_3$) 16.9, 17.8, 50.4, 50.6 (s), 51.0, 100.2 (s), 124.3, 126.7, 127.2, 128.7, 129.9, 131.3, 134.9 (s), 140.4 (s), 140.5 (s), 170.7; HRMS (ESI): Calcd for $C_{19}H_{22}NO_2$ $[M + H]^+$ 296.1645, found 296.1655.

2,4-Dimethoxy-3,3-diphenyl-3,4-dihydroquinoline **13A** (R^1 = R^2 = H; R^3 = Ph). Eluent for column chromatography: hexanes–diethyl ether (9 : 1, v/v); (0.16 g, 48%); mp 146–147 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 1629 (vs); δ_H (400 MHz, $CDCl_3$) 3.01 (3 H, s), 3.92 (3 H, s), 4.63 (1 H, s), 6.96–7.00 (1 H, m), 7.03–7.05 (1 H, m), 7.09–7.13 (9 H, m), 7.21 (1 H, d, *J* 7.4), 7.24–7.26 (2 H, m); δ_C (100 MHz, $CDCl_3$) 54.2, 58.5 (s), 58.7, 84.9, 124.6, 125.1, 125.9, 126.8, 127.0, 127.3, 127.9 (s), 128.0, 128.8, 128.9, 130.7, 139.3 (s), 141.5 (s), 141.9 (s), 167.5 (s); HRMS (ESI): Calcd for $C_{23}H_{22}NO_2$ $[M + H]^+$ 344.1645, found 344.1655.

2,4-Dimethoxy-8-methyl-3,3-diphenyl-3,4-dihydroquinoline **13B** (R^1 = H; R^2 = CH_3; R^3 = Ph). Eluent for column chromatography: hexanes–diethyl ether (9 : 1, v/v); (0.18 g, 52%); mp 173–174 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 1666 (m); δ_H (400 MHz, $CDCl_3$) 2.32 (3 H, m), 3.07 (3 H, m), 3.99 (3 H, m), 4.65 (1 H, s), 6.94 (1 H, t, *J* 7.4), 7.05 (1 H, d, *J* 7.4), 7.12 (1 H, d, *J* 7.4), 7.17–7.21 (8 H, m), 7.30–7.33 (2 H, m); δ_C (100 MHz, $CDCl_3$) 17.3, 54.0, 58.2 (s), 58.6, 85.2, 123.7, 124.1, 126.7, 126.9, 127.2, 127.4 (s), 127.9, 128.9, 130.3, 130.7, 133.3 (s), 139.7 (s), 139.8 (s), 141.6 (s), 165.9 (s); HRMS (ESI): Calcd for $C_{24}H_{24}NO_2$ $[M + H]^+$ 358.1802, found 358.1806.

6-Chloro-2,4-dimethoxy-3,3-diphenyl-3,4-dihydroquinoline **13C** (R^1 = Cl; R^2 = H; R^3 = Ph). Eluent for column chromatography: hexanes–diethyl ether (9 : 1, v/v); (0.25 g, 65%); mp 150–151 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 1614 (vs); δ_H (400 MHz, $CDCl_3$)

3.01 (3 H, s), 3.98 (3 H, s), 4.71 (1 H, s), 7.03 (1 H, d, *J* 8.3), 7.13–7.15 (3 H, m), 7.18–7.24 (6 H, m), 7.29–7.33 (3 H, m); δ_C (100 MHz, $CDCl_3$) 54.4, 58.4 (s), 59.3, 84.9, 125.5, 126.3, 127.1, 127.2, 127.5, 128.1, 128.6, 129.0, 129.8 (s), 130.1 (s), 130.5, 138.5 (s), 140.4 (s), 141.3 (s), 168.0 (s); HRMS (ESI): Calcd for $C_{23}H_{21}ClNO_2$ $[M + H]^+$ 378.1255, found 378.1263.

2,4-Dimethoxy-6-methyl-3,3-diphenyl-3,4-dihydroquinoline **13d** (R^1 = CH_3; R^2 = H; R^3 = Ph). Eluent for column chromatography: hexanes–diethyl ether (9 : 1, v/v); (0.09 g, 25%); mp 176–177 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 1630 (vs); δ_H (400 MHz, $CDCl_3$) 2.31 (3 H, s), 3.07 (3 H, s), 3.97 (3 H, s), 4.67 (1 H, s), 6.98–7.01 (2 H, m), 7.09–7.10 (1 H, m), 7.17–7.21 (8 H, m), 7.31–7.33 (2 H, m); δ_C (100 MHz, $CDCl_3$) 21.3, 54.1, 58.5 (s), 58.8, 85.1, 124.9, 126.5, 126.8, 127.0, 127.2, 127.7 (s), 127.9, 129.0, 129.3, 130.7, 134.2 (s), 139.3 (s), 139.4 (s), 141.7 (s), 166.8 (s); HRMS (ESI): Calcd for $C_{24}H_{24}NO_2$ $[M + H]^+$ 358.1802, found 358.1806.

Diastereoisomer 1 of 2,4-dimethoxy-3-methyl-3-phenyl-3,4-dihydroquinoline **13e** (R^1 = R^2 = H; R^3 = CH_3). Eluent for column chromatography: dichloromethane; (0.08 g, 30%); colourless oil; ν_{max}(neat)/cm^{-1} 1630 (s); δ_H (400 MHz, $CDCl_3$) 1.66 (3 H, s), 3.19 (3 H, s), 3.99 (3 H, s), 4.15 (1 H, s), 6.89–6.94 (2 H, m), 7.00 (1 H, d, *J* 5.1), 7.06–7.20 (6 H, m); δ_C (100 MHz, $CDCl_3$) 20.5, 49.1 (s), 53.9, 56.6, 84.6, 123.9, 125.0, 125.1 (s), 126.2, 126.9, 128.4, 128.5, 129.3, 141.2 (s), 143.3 (s), 169.0 (s); HRMS (ESI): Calcd for $C_{18}H_{20}NO_2$ $[M + H]^+$ 282.1489, found 282.1495.

Diastereoisomer 2 of 2,4-dimethoxy-3-methyl-3-phenyl-3,4-dihydroquinoline **13e** (R^1 = R^2 = H; R^3 = CH_3). Eluent for column chromatography: dichloromethane; (0.08 g, 30%); colourless oil; ν_{max}(neat)/cm^{-1} 1625 (s); δ_H (400 MHz, $CDCl_3$) 1.63 (3 H, s), 3.41 (3 H, s), 3.93 (3 H, s), 4.14 (1 H, s), 7.06 (1 H, td, *J* 6.8, 0.8), 7.16–7.23 (6 H, m), 7.25–7.28 (2 H, m); δ_C (100 MHz, $CDCl_3$) 21.8, 48.8 (s), 54.0, 59.9, 85.4, 124.7, 124.9, 125.6, 126.9, 127.6, 127.9 (s), 128.4, 128.7, 138.5 (s), 142.3 (s), 169.7 (s); HRMS (ESI): Calcd for $C_{18}H_{20}NO_2$ $[M + H]^+$ 282.1489, found 282.1499.

Diastereoisomer 1 of 2,4-dimethoxy-3,8-dimethyl-3-phenyl-3,4-dihydroquinoline **13f** (R^1 = H; R^2 = R^3 = CH_3). Eluent for column chromatography: hexanes–diethyl ether (9 : 1, v/v); (0.07 g, 25%); colourless oil; ν_{max}(neat)/cm^{-1} 1633 (vs); δ_H (300 MHz, $CDCl_3$) 1.66 (3 H, s), 2.39 (3 H, s), 3.20 (3 H, s), 3.98 (3 H, s), 4.11 (1 H, s), 6.79–6.85 (2 H, m), 7.05–7.20 (6 H, m); δ_C (75 MHz, $CDCl_3$) 17.5, 20.5, 48.8 (s), 53.7, 56.8, 85.1, 123.4, 124.8 (s), 126.1, 126.2, 126.9, 128.4, 130.8, 133.2 (s), 141.2 (s), 141.4 (s), 167.5 (s); HRMS (ESI): Calcd for $C_{19}H_{22}NO_2$ $[M + H]^+$ 296.1645, found 296.1651.

Diastereoisomer 2 of 2,4-dimethoxy-3,8-dimethyl-3-phenyl-3,4-dihydroquinoline **13f** (R^1 = H; R^2 = R^3 = CH_3). Eluent for column chromatography: hexanes–diethyl ether (9 : 1, v/v); (0.07 g, 25%); colourless oil; ν_{max}(neat)/cm^{-1} 1633 (vs); δ_H (300 MHz, $CDCl_3$) 1.59 (3 H, s), 2.42 (3 H, s), 3.34 (3 H, s), 3.92 (3 H, s), 4.05 (1 H, s), 6.93–7.00 (1 H, m), 7.02 (1 H, d, *J* 6.0), 7.11–7.14 (1 H, m), 7.16–7.24 (3 H, m), 7.26–7.30 (2 H, m); δ_C (75 MHz, $CDCl_3$) 17.4, 21.7, 48.4 (s), 53.8, 59.6, 85.9, 123.5, 124.1, 126.8, 127.3 (s), 127.5, 128.5, 130.1, 133.1 (s), 138.8 (s), 140.0 (s), 168.2 (s); HRMS (ESI): Calcd for $C_{19}H_{22}NO_2$ $[M + H]^+$ 296.1645, found 296.1652.

Preparation of 2-azido-1-[bis(alkylthio)methyl]benzenes 16

To a solution of the 2-azidobenzaldehyde **8** (8 mmol) in anhydrous chloroform (20 mL) at room temperature ethanethiol (0.99 g, 16 mmol) or 2-phenylethanethiol (2.21 g, 16 mmol) was added. Next, trimethylchlorosilane (1.19 g, 11 mmol) was added dropwise for 20 min, and the stirring at room temperature was continued for 1 h. Then Na_2CO_3 5% aqueous solution (50 mL) was added. The organic phase was separated and dried over anhydrous magnesium sulphate. The solvent was removed under reduced pressure and the resulting material was purified by column chromatography on silica gel, using hexanes–dichloromethane (7 : 3, v/v) as the eluent.

2-Azido-1-[bis(ethylthio)methyl]benzene **16a** (R^1 = H; R^2 = CH_3CH_2). (2.00 g, 99%); colourless oil; ν_{max}(neat)/cm^{-1} 2121 (vs), 2088 (vs); δ_H (300 MHz, $CDCl_3$) 1.24 (6 H, t, *J* 7.4), 2.46–2.67 (4 H, m), 5.32 (1 H, s), 7.10–7.17 (2 H, m), 7.28 (1 H, td, *J* 7.7, 1.6), 7.67 (1 H, dd, *J* 7.7, 1.6); δ_C (75 MHz, $CDCl_3$) 14.4, 26.3, 45.6, 117.9, 125.1, 128.8, 129.3, 132.0 (s), 136.7 (s).

2-Azido-5-bromo-1-[bis(ethylthio)methyl]benzene **16b** (R^1 = Br; R^2 = CH_3CH_2). (2.47 g, 93%); colourless oil; ν_{max}(neat)/cm^{-1} 2125 (vs), 2086 (vs); δ_H (400 MHz, $CDCl_3$) 1.25 (6 H, t, *J* 7.4), 2.50–2.58 (2 H, m), 2.60–2.65 (2 H, m), 5.23 (1 H, s), 6.99 (1 H, d, *J* 8.5), 7.39 (1 H, dd, *J* 8.5, 2.3), 7.80 (1 H, d, *J* 2.3); δ_C (75 MHz, $CDCl_3$) 14.3, 26.4, 118.2 (s), 119.5, 131.8, 132.3, 134.1 (s), 136.0 (s).

2-Azido-1-[bis(2-phenylethylthio)methyl]benzene **16c** (R^1 = H; R^2 = $PhCH_2CH_2$). (3.21 g, 99%); colourless oil; ν_{max}(neat)/cm^{-1} 2121 (vs), 2088 (vs); δ_H (400 MHz, $CDCl_3$) 2.68–2.77 (2 H, m), 2.80–2.88 (6 H, m), 5.29 (1 H, s), 7.09–7.15 (6 H, m), 7.18–7.21 (2 H, m), 7.25–7.28 (5 H, m), 7.64 (1 H, d, *J* 7.7, 1.4); δ_C (100 MHz, $CDCl_3$) 33.7, 36.0, 46.5, 118.0, 125.2, 126.4, 128.5, 128.6, 129.1, 129.4, 131.7 (s), 136.8 (s), 140.3 (s).

Preparation of 1-[bis(alkylthio)methyl]-2-triphenylphosphoranylideneaminobenzenes 17

To a solution of the 2-azido-1-[bis(alkylthio)methyl]benzene **16** (5 mmol) in anhydrous diethyl ether (20 mL), under nitrogen at room temperature, triphenylphosphine (1.30 g, 5 mmol) was added in small portions. The reaction mixture was stirred at room temperature for 16 h. Then the precipitated compounds **17** were isolated by filtration and washed with anhydrous diethyl ether (10 mL). These compounds were used in the following step without further purification.

For analytical samples iminophosphoranes **17** were recrystallized from diethyl ether.

1-[Bis(ethylthio)methyl]-2-triphenylphosphoranylideneaminobenzene **17a** (R^1 = H; R^2 = CH_3CH_2). (2.07 g, 85%); mp 106–107 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 1580 (s), 1110 (s); δ_H (400 MHz, $CDCl_3$) 1.18 (6 H, t, *J* 7.4), 2.48–2.64 (4 H, m), 6.34 (1 H, s), 6.42 (1 H, d, *J* 7.0), 6.66 (1 H, t, *J* 7.0), 6.74 (1 H, td, *J* 7.5, 1.8), 7.40–7.45 (6 H, m), 7.48–7.52 (3 H, m), 7.55 (1 H, dt, *J* 7.5, 2.2), 7.73–7.78 (6 H, m); δ_C (100 MHz, $CDCl_3$) 14.8, 26.2, 46.5, 117.6, 120.9 (d, *J* 10.0), 127.2, 128.4, 128.6 (d, *J* 11.9), 131.4 (d, *J* 99.0)

(s), 131.7 (d, *J* 2.4), 132.5 (d, *J* 9.7), 133.9 (d, *J* 21.5) (s), 148.4 (s); δ_P (161.9 MHz, $CDCl_3$, H_3PO_4) 1.9; HRMS (ESI): Calcd for $C_{29}H_{31}NPS_2$ $[M + H]^+$ 488.1630, found 488.1634.

1-[Bis(ethylthio)methyl]-5-bromo-2-triphenylphosphoranylideneaminobenzene **17B** (R^1 = Br; R^2 = CH_3CH_2). (2.49 g, 88%); mp 117–118 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 1436 (vs), 1112 (vs); δ_H (300 MHz, $CDCl_3$) 1.18 (6 H, t, *J* 7.4), 2.46–2.65 (4 H, m), 6.23 (1 H, s), 6.25 (1 H, dd, *J* 8.5, 1.2), 6.81 (1 H, dd, *J* 8.5, 2.6), 7.41–7.47 (6 H, m), 7.50–7.55 (3 H, m), 7.65 (1 H, t, *J* 2.6), 7.69–7.76 (6 H, m); δ_C (75 MHz, $CDCl_3$) 14.7, 26.2, 46.1, 109.5 (s), 122.1 (d, *J* 10.0), 128.7 (d, *J* 11.9), 130.1, 130.8 (d, *J* 99.5) (s), 131.0 (d, *J* 1.0), 131.9 (d, *J* 2.8), 132.5 (d, *J* 9.7), 136.2 (d, *J* 21.8) (s), 147.7 (s); δ_P (161.9 MHz, $CDCl_3$, H_3PO_4) 3.8; HRMS (ESI): Calcd for $C_{29}H_{30}BrNPS_2$ $[M + H]^+$ 566.0735, found 566.0740.

1-[Bis(2-phenylethylthio)methyl]-2-triphenylphosphoranylideneaminobenzene **17C** (R^1 = H; R^2 = $PhCH_2CH_2$). (2.24 g, 70%); mp 109–110 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 1436 (vs), 1110 (vs); δ_H (400 MHz, $CDCl_3$) 2.75–2.89 (8 H, m), 6.42 (1 H, d, *J* 7.5), 6.52 (1 H, s), 6.68 (1 H, t, *J* 7.5), 6.76 (1 H, td, *J* 7.5, 1.7), 7.00–7.02 (4 H, m), 7.10–7.14 (6 H, m), 7.34–7.39 (6 H, m), 7.45–7.49 (3 H, m), 7.59 (1 H, dt, *J* 7.5, 2.1), 7.69–7.74 (6 H, m); δ_C (100 MHz, $CDCl_3$) 33.7, 36.3, 46.9, 117.7, 120.9 (d, *J* 10.1), 126.0, 127.5, 128.3, 128.6, 128.7 (d, *J* 12.0), 131.2 (d, *J* 98.9) (s), 131.7, 132.5 (d, *J* 9.6), 133.5 (d, *J* 22.0) (s), 141.1 (s), 148.6 (s); δ_P (161.9 MHz, $CDCl_3$, H_3PO_4) 3.0; HRMS (ESI): Calcd for $C_{41}H_{39}NPS_2$ $[M + H]^+$ 640.2256, found 640.2264.

Preparation of 2,4-bis(alkylthio)quinolines 20a–c

To a solution of the 1-[bis(alkylthio)methyl]-2-triphenylphosphoranylideneaminobenzene **17** (1 mmol) in anhydrous toluene (20 mL) a solution of diphenylketene (0.19 g, 1 mmol) in the same solvent (5 mL) was added. The reaction mixture was stirred under nitrogen at room temperature for 30 min. Next, the solution was heated at reflux temperature for 1 h. After cooling at room temperature, the solvent was removed under reduced pressure, and the resulting crude material was purified by column chromatography on silica gel, using hexanes–diethyl ether (9 : 1, v/v) as the eluent.

2,4-Bis(ethylthio)-3,3-diphenyl-3,4-dihydroquinoline **20A** (R^1 = H; R^2 = CH_3CH_2; R^3 = Ph). (0.38 g, 94%); colourless oil; ν_{max}(neat)/cm^{-1} 1552 (vs); δ_H (400 MHz, $CDCl_3$) 1.15 (3 H, t, *J* 7.4), 1.35 (3 H, t, *J* 7.4), 2.27–2.38 (2 H, m), 3.10–3.25 (2 H, m), 4.69 (1 H, s), 7.10–7.14 (1 H, m), 7.20–7.34 (10 H, m), 7.47–7.50 (2 H, m), 7.63 (1 H, d, *J* 7.4); δ_C (100 MHz, $CDCl_3$) 13.7, 14.5, 26.0, 28.3, 54.5, 60.2 (s), 125.2, 125.9, 126.6, 127.3, 127.4, 127.5, 128.0, 129.1 (s), 130.3, 130.4, 137.3 (s), 142.1 (s), 143.1 (s), 173.7 (s); HRMS (ESI): Calcd for $C_{25}H_{26}NS_2$ $[M + H]^+$ 404.1501, found 404.1504.

2,4-Bis(ethylthio)-6-bromo-3,3-diphenyl-3,4-dihydroquinoline **20B** (R^1 = Br; R^2 = CH_3CH_2; R^3 = Ph). (0.39 g, 81%); colourless oil; ν_{max}(neat)/cm^{-1} 1566 (vs); δ_H (400 MHz, $CDCl_3$) 1.10 (3 H, t, *J* 7.4), 1.28 (3 H, t, *J* 7.4), 2.22–2.34 (2 H, m), 3.03–3.17 (2 H, m), 4.58 (1 H, s), 7.04–7.07 (1 H, m), 7.17–7.19 (3 H, m), 7.26–7.32 (6 H, m), 7.39–7.43 (2 H, m), 7.77 (1 H, s); δ_C (100 MHz, $CDCl_3$) 13.6, 14.4, 26.0, 28.5, 54.3, 59.9 (s), 119.0 (s), 126.8, 127.5, 127.6, 128.6, 129.5, 130.2, 130.3, 131.0, 131.5 (s), 136.7 (s), 141.7 (s), 142.0 (s), 174.8 (s); HRMS (ESI): Calcd for $C_{25}H_{25}BrNS_2$ $[M + H]^+$ 482.0606, found 482.0608.

2,4-Bis(2-phenylethylthio)-3,3-diphenyl-3,4-dihydroquinoline **20C** (R^1 = H; R^2 = $PhCH_2CH_2$; R^3 = Ph). (0.55 g, 99%); colourless oil; ν_{max}(neat)/cm^{-1} 1552 (vs); δ_H (400 MHz, $CDCl_3$) 2.41–2.48 (2 H, m), 2.63–2.70 (2 H, m), 2.93–2.98 (2 H, m), 3.28–3.42 (2 H, m), 4.69 (1 H, s), 7.01–7.29 (20 H, m), 7.42–7.48 (3 H, m), 7.54–7.56 (1 H, m); δ_C (100 MHz, $CDCl_3$) 32.8, 35.2, 35.5, 36.0, 55.2, 60.3 (s), 125.4, 126.1, 126.4, 126.7, 127.4, 127.5, 128.1, 128.5, 128.7, 129.0 (s), 130.3, 130.5, 137.2 (s), 140.2 (s), 140.9 (s), 142.1 (s), 142.9 (s), 173.0 (s); HRMS (ESI): Calcd for $C_{35}H_{34}NS_2$ $[M + H]^+$ 556.2127, found 556.2132.

Preparation of 2,4-bis(alkylthio)quinolines 20d,e

To a solution of the 1-[bis(alkylthio)methyl]-2-triphenylphosphoranylideneaminobenzene **17** (1 mmol) in anhydrous dichloromethane (20 mL) a solution of methylphenylketene (0.13 g, 1 mmol) in the same solvent (5 mL) was added. The reaction mixture was stirred under nitrogen at room temperature for 3–16 h. Next, the solvent was removed under reduced pressure, and the resulting crude material was purified by column chromatography on silica gel, using hexanes–diethyl ether (9 : 1, v/v) as the eluent.

cis-2,4-Bis(ethylthio)-3-methyl-3-phenyl-3,4-dihydroquinoline **20D** (R^1 = H; R^2 = CH_3CH_2; R^3 = CH_3). (0.33 g, 97%); colourless oil; ν_{max}(neat)/cm^{-1} 1581 (vs); δ_H (400 MHz, $CDCl_3$) 1.14 (3 H, t, *J* 7.4), 1.30 (3 H, t, *J* 7.4), 1.87 (3 H, s), 2.21–2.32 (2 H, m), 3.12 (2 H, q, *J* 7.2), 3.92 (1 H, s), 7.11–7.15 (1 H, m), 7.16–7.19 (3 H, m), 7.24–7.29 (3 H, m), 7.33 (1 H, d, *J* 7.6), 7.45–7.47 (1 H, m); δ_C (100 MHz, $CDCl_3$) 13.9, 14.8, 24.6, 24.9, 27.6, 49.9 (s), 55.4, 125.7, 126.2, 127.5, 127.6, 127.7 (s), 127.8, 128.0, 128.2, 138.0 (s), 142.9 (s), 175.1 (s); HRMS (ESI): Calcd for $C_{20}H_{24}NS_2$ $[M + H]^+$ 342.1345, found 342.1352.

cis-2,4-Bis(ethylthio)-6-bromo-3-methyl-3-phenyl-3,4-dihydroquinoline **20E** (R^1 = Br; R^2 = CH_3CH_2; R^3 = CH_3). (0.30 g, 72%); mp 94–95 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 1593 (vs); δ_H (300 MHz, $CDCl_3$) 1.19 (3 H, t, *J* 7.4), 1.29 (3 H, t, *J* 7.4), 1.87 (3 H, s), 2.33 (2 H, q, *J* 7.4), 3.09 (2 H, q, *J* 7.4), 3.86 (1 H, s), 7.18–7.26 (6 H, m), 7.40 (1 H, dd, *J* 8.2, 2.0), 7.62–7.63 (1 H, m); δ_C (75 MHz, $CDCl_3$) 13.8, 14.8, 24.6, 25.0, 27.9, 49.6 (s), 55.1, 119.3 (s), 127.2, 127.7, 127.8, 127.9, 130.2 (s), 130.8, 131.2, 137.5 (s), 142.1 (s), 176.2 (s); HRMS (ESI): Calcd for $C_{20}H_{23}BrNS_2$ $[M + H]^+$ 420.0450, found 420.0453.

Preparation of quinoline 21

To a solution of 1-[bis(ethylthio)methyl]-2-triphenylphosphoranylideneaminobenzene **17a** (0.25 g, 0.5 mmol) in anhydrous toluene, heated at 80 °C, under nitrogen, a solution of *S*-phenyl 2-diazoethanethiolate (0.1 g, 0.5 mmol) in the same solvent (10 mL) was added dropwise for 10 min, and the heating at 80 °C was continued for 1 h. After cooling at room temperature the solvent was removed under reduced pressure. The resulting material was purified by column chromatography on silica gel using hexanes–diethyl ether (9.5 : 0.5, v/v) as the eluent.

2-Ethylthio-3-phenylthioquinoline 21. (0.14 g, 91%); colourless oil; ν_{max}(neat)/cm^{-1} 1612 (s); δ_H (400 MHz, $CDCl_3$) 1.42 (3 H, t, *J* 7.6), 3.33 (2 H, q, *J* 7.6), 7.23–7.35 (5 H, m), 7.38 (1 H, d, *J* 8.0), 7.57 (1 H, d, *J* 8.0), 7.61 (1 H, t, *J* 8.0), 7.84 (1 H, s), 7.92 (1 H, d, *J* 8.0); δ_C (100 MHz, $CDCl_3$) 14.2, 25.2, 125.5, 126.1 (s), 127.2, 127.5, 127.8, 128.4 (s), 129.5, 129.8, 130.7, 134.1 (s), 138.5, 147.2 (s), 160.9 (s); HRMS (ESI): Calcd for $C_{17}H_{16}NS_2$ $[M + H]^+$ 298.0719, found 298.0725.

Preparation of xanthate 24

A mixture of 2-azido-1-(dimethoxymethyl)benzene **9a** (2.91 g, 15 mmol) and thionyl chloride (15 mL) was heated at reflux temperature for 30 min, followed by stirring at room temperature for 16 h. Then the remaining thionyl chloride was removed to dryness under reduced pressure to give 2-azido-1-[(1′-chloro)methoxymethyl]benzene, which was used in the following step without further purification.

A mixture of 2-azido-1-[(1′-chloro)methoxymethyl]benzene (2.97 g, 15 mmol) and potassium *O*-ethyl dithiocarbonate (2.43 g, 15 mmol) in anhydrous diethyl ether (30 mL) was heated at reflux temperature for 1.5 h. After cooling at room temperature water (50 mL) was added. The organic phase was separated and dried over anhydrous magnesium sulphate. The solvent was removed under reduced pressure and the crude material was purified by column chromatography on silica gel, using hexanes–diethyl ether (9.5 : 0.5, v/v) as the eluent.

Xanthate 24. (3.27 g, 77%); colourless oil; ν_{max}(neat)/cm^{-1} 2127 (vs), 2096 (vs); δ_H (300 MHz, $CDCl_3$) 1.45 (3 H, t, *J* 7.1), 3.52 (3 H, s), 4.70 (2 H, q, *J* 7.1), 6.60 (1 H, s), 7.12–7.16 (2 H, m), 7.32–7.38 (1 H, m), 7.51–7.54 (1 H, m); δ_C (75 MHz, $CDCl_3$) 13.8, 57.4, 70.0, 87.6, 118.3, 125.0, 127.9, 129.0 (s), 129.9, 136.8 (s), 212.6 (s).

Preparation of 2-azido-1-[(1′-methoxy)methylthiomethyl]-benzene 25

To a solution of xanthate **24** (1.42 g, 5 mmol) in anhydrous diethyl ether (25 mL), at 15 °C, a solution of methyl iodide (1.06 g, 7.5 mmol) in the same solvent (20 mL) was added dropwise for 20 min. Next, the reaction mixture was stirred at room temperature for 30 min and sodium methoxide (0.49 g, 9 mmol) was added. The stirring at room temperature was continued for 5 h before the addition of water (25 mL). The organic phase was separated and dried over anhydrous magnesium sulphate. The solvent was removed under reduced pressure and the resulting oil was purified by column chromatography on silica gel, using hexanes–diethyl ether (9.5 : 0.5, v/v) as the eluent.

2-Azido-1-[(1′-methoxy)methylthiomethyl]benzene 25. (0.75 g, 72%); colourless oil; ν_{max}(neat)/cm^{-1} 2127 (vs); δ_H (300 MHz, $CDCl_3$) 1.95 (3 H, s), 3.44 (3 H, s), 5.57 (1 H, s), 7.11–7.16 (2 H, m), 7.28–7.34 (1 H, m), 7.45–7.48 (1 H, m); δ_C (75 MHz, $CDCl_3$) 10.9, 56.2, 82.0, 118.1, 124.3, 127.2, 128.8, 130.6 (s), 135.9 (s).

Preparation of 1-[(1′-methoxy)methylthiomethyl]-2-triphenylphosphoranylideneaminobenzene 26

To a solution of 2-azido-1-[methoxy(methylthio)methyl]-benzene **25** (0.62 g, 3 mmol) in anhydrous diethyl ether (15 mL), under nitrogen at room temperature, triphenylphosphine (0.80 g, 3 mmol) was added in small portions. The reaction mixture was stirred at room temperature for 16 h. Then the solvent was removed under reduced pressure and the crude material was purified by column chromatography on silica gel deactivated with triethylamine, using hexanes–diethyl ether (1 : 1, v/v) as the eluent.

1-[(1′-Methoxy)methylthiomethyl]-2-triphenylphosphoranylideneaminobenzene 26. (0.88 g, 66%); colourless oil; ν_{max}(neat)/cm^{-1} 1591 (vs), 1351 (vs), 1107 (vs); δ_H (300 MHz, $CDCl_3$) 1.99 (3 H, s), 3.45 (3 H, s), 6.22 (1 H, s), 6.43–6.46 (1 H, m), 6.67 (1 H, t, *J* 7.5), 6.80 (1 H, td, *J* 7.5, 1.7), 7.32–7.35 (1 H, m), 7.40–7.51 (9 H, m), 7.72–7.79 (6 H, m); δ_C (75 MHz, $CDCl_3$) 11.6, 56.4, 84.5, 117.0, 121.4 (d, *J* 9.7), 126.2 (d, *J* 1.7), 127.5, 128.6 (d, *J* 11.9), 131.5 (d, *J* 99.1) (s), 131.6 (d, *J* 2.8), 132.6 (d, *J* 9.7), 132.8 (d, *J* 20.4 (s), 147.7 (s); δ_P (161.9 MHz, $CDCl_3$, H_3PO_4) 2.2; HRMS (ESI): Calcd for $C_{27}H_{27}NOPS$ $[M + H]^+$ 444.1545, found 444.1564.

Preparation of 4-methoxy-2-methylthioquinolines 28

To a solution of 1-[(1′-methoxy)methylthiomethyl]-2-triphenylphosphoranylideneaminobenzene **26** (0.58 g, 1.3 mmol) in anhydrous toluene (15 mL) a solution of methylphenylketene (0.17 g, 1.3 mmol) or diphenylketene (0.25 g, 1.3 mmol) in the same solvent (5 mL) was added. The reaction mixture was stirred under nitrogen at room temperature for 30 min. Next, the solution was heated at reflux temperature for 1 h. After cooling at room temperature, the solvent was removed under reduced pressure, and the resulting crude material was purified by column chromatography on silica gel, using hexanes–diethyl ether (9 : 1, v/v) as the eluent.

4-Methoxy-2-methylthio-3,3-diphenyl-3,4-dihydroquinoline 28A (R^1 = Ph). (0.37 g, 80%); mp 146–147 °C (from Et_2O); ν_{max}-(Nujol)/cm^{-1} 1554 (vs), 1539 (vs); δ_H (300 MHz, $CDCl_3$) 2.49 (3 H, s), 3.36 (3 H, s), 4.98 (1 H, s), 6.96 (1 H, td, *J* 7.3, 1.0), 7.09 (1 H, d, *J* 7.3), 7.14–7.23 (10 H, m), 7.44–7.46 (2 H, m); δ_C (100 MHz, $CDCl_3$) 14.8, 58.7, 60.6 (s), 83.8, 125.0, 125.3, 125.4, 127.3, 127.4, 127.9, 128.0 (s), 128.6, 129.6, 131.2, 138.7 (s), 140.7 (s), 143.1 (s), 175.2 (s); HRMS (ESI): Calcd for $C_{23}H_{22}NOS$ $[M + H]^+$ 360.1417, found 360.1421.

Diastereoisomer 1 of 4-methoxy-3-methyl-2-methylthio-3-phenyl-3,4-dihydroquinoline 28B (R^1 = CH_3). (0.19 g, 50%); mp 100–101 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 1554 (vs); δ_H (400 MHz, $CDCl_3$) 1.59 (3 H, s), 2.48 (3 H, s), 3.31 (3 H, s), 4.01 (1 H, s), 7.11 (1 H, td, *J* 7.2, 1.4), 7.15–7.17 (1 H, m), 7.21–7.25 (3 H, m), 7.31 (1 H, td, *J* 7.7, 1.7), 7.35 (1 H, dd, *J* 7.7, 1.3), 7.39–7.42 (2 H, m); δ_C (100 MHz, $CDCl_3$) 13.8, 22.2, 51.2 (s), 59.1, 84.3, 125.7, 125.8, 126.3, 127.0 (s), 127.3, 127.4, 128.9, 129.4, 138.1 (s), 142.4 (s), 176.6 (s); HRMS (ESI): Calcd for $C_{18}H_{20}NOS$ $[M + H]^+$ 298.1260, found 298.1267.

Diastereoisomer 2 of 4-methoxy-3-methyl-2-methylthio-3-phenyl-3,4-dihydroquinoline 28B (R^1 = CH_3). (0.09 g, 24%); yellow oil; ν_{max}(neat)/cm^{-1} 1556 (vs); δ_H (400 MHz, $CDCl_3$) 1.71 (3 H, s), 2.55 (3 H, s), 3.18 (3 H, s), 4.29 (1 H, s), 7.02–7.06 (1 H, m), 7.07–7.09 (1 H, m), 7.17–7.30 (6 H, m), 7.32–7.34 (1 H, m); δ_C (100 MHz, $CDCl_3$) 13.5, 19.9, 51.5 (s), 57.7, 84.4, 125.3, 125.5, 125.6 (s), 127.1, 127.2, 127.6, 128.3, 129.3, 141.2 (s), 142.9 (s), 176.0 (s); HRMS (ESI): Calcd for $C_{18}H_{20}NOS$ $[M + H]^+$ 298.1260, found 298.1265.

Preparation of azido-methoxymethylbenzenes 30

To a suspension of potassium hydroxide (1.12 g, 20 mmol) in dimethylsulfoxide (20 mL) the corresponding 2-azidobenzyl alcohol **29** (5 mmol) and methyl iodide (1.42 g, 10 mmol) were added, and the reaction mixture was stirred at room temperature for 30 min. Next, water was added (100 mL) and the mixture was extracted with dichloromethane (3 × 50 mL). The combined organic phase was washed with water (3 × 50 mL) and dried over anhydrous magnesium sulphate. The solvent was removed under reduced pressure and the resulting material was purified by column chromatography on silica gel.

1-Azido-2-methoxymethylbenzene 30A (R^1 = R^2 = H). Eluent for column chromatography: hexanes–diethyl ether (4 : 1, v/v); (0.77 g, 94%); yellow oil; ν_{max}(neat)/cm^{-1} 2125 (vs); δ_H (400 MHz, $CDCl_3$) 3.41 (3 H, s), 4.42 (2 H, s), 7.12–7.17 (2 H, m), 7.31–7.36 (1 H, m), 7.38–7.41 (1 H, m); δ_C (100 MHz, $CDCl_3$) 58.4, 69.9, 118.0, 124.7, 129.0, 129.5 (s), 129.7, 138.0 (s).

2-Azido-1-methoxymethyl-3-methylbenzene 30B (R^1 = H; R^2 = CH_3). Eluent for column chromatography: hexanes–diethyl ether (9 : 1, v/v); (0.50 g, 56%); yellow oil; ν_{max}(neat)/cm^{-1} 2107 (vs); δ_H (300 MHz, $CDCl_3$) 2.36 (3 H, s), 3.40 (3 H, s), 4.49 (2 H, s), 7.02–7.10 (2 H, m), 7.18–7.21 (1 H, m); δ_C (75 MHz, $CDCl_3$) 17.9, 58.2, 71.1, 125.6, 127.5, 130.8, 131.8 (s), 132.3 (s), 136.6 (s).

1-Azido-4-chloro-2-methoxymethylbenzene 30C (R^1 = Cl; R^2 = H). Eluent for column chromatography: hexanes–diethyl ether (9 : 1, v/v); (0.70 g, 71%); yellow oil; ν_{max}(neat)/cm^{-1} 2131 (vs), 2090 (vs); δ_H (300 MHz, $CDCl_3$) 3.39 (3 H, s), 4.32 (2 H, s), 6.99 (1 H, dd, *J* 8.5), 7.22 (1 H, dd, *J* 8.5, 2.4), 7.37 (1 H, d, *J* 2.4); δ_C (75 MHz, $CDCl_3$) 58.4, 69.1, 118.9, 128.4, 128.8, 130.1 (s), 131.3 (s), 135.9 (s).

1-Azido-2-methoxymethyl-4-methylbenzene 30D (R^1 = CH_3; R^2 = H). Eluent for column chromatography: hexanes–diethyl ether (7 : 3, v/v); (0.57 g, 64%); yellow oil; ν_{max}(neat)/cm^{-1} 2142 (vs), 2084 (vs); δ_H (400 MHz, $CDCl_3$) 2.32 (3 H, s), 3.40 (3 H, s), 4.38 (2 H, s), 7.03 (1 H, d, *J* 8.1), 7.12 (1 H, d, *J* 81, 1.7), 7.19–7.20 (1 H, m); δ_C (100 MHz, $CDCl_3$) 20.8, 58.5, 69.9, 118.0, 129.1 (s), 129.6, 130.4, 134.5 (s), 135.2 (s).

Preparation of methoxymethyl-triphenylphosphoranylideneaminobenzenes 31

To a solution of the azido-methoxymethylbenzene **30** (5 mmol) in anhydrous diethyl ether (20 mL), under nitrogen at room temperature, triphenylphosphine (1.3 g, 5 mmol) was added in small portions. The reaction mixture was stirred at room temperature for 16 h. Then the precipitated compounds **31** were isolated by filtration and washed with anhydrous diethyl ether (10 mL). These compounds were used in the following step without further purification.

For analytical samples iminophosphoranes **31** were recrystallized from diethyl ether.

1-Methoxymethyl-2-triphenylphosphoranylideneaminobenzene 31A (R^1 = R^2 = H). (1.81 g, 91%); mp 127–128 °C (from Et_2O); ν_{max}-(Nujol)/cm^{-1} 1324 (vs), 1105 (vs); δ_H (400 MHz, $CDCl_3$) 3.45 (3 H, s), 4.83 (2 H, s), 6.46 (1 H, dd, *J* 7.9, 1.1), 6.68 (1 H, d, *J* 7.3), 6.81 (1 H, t, *J* 7.3), 7.30 (1 H, d, *J* 7.3), 7.40–7.45 (6 H, m), 7.47–7.52 (3 H, m), 7.72–7.77 (6 H, m); δ_C (75 MHz, $CDCl_3$) 58.3, 72.2, 117.4, 121.1 (d, *J* 9.8), 127.2, 127.7, 128.6 (d, *J* 12.0), 131.6 (d, *J* 2.5), 131.7 (d, *J* 99.6) (s), 132.4 (s), 132.6 (d, *J* 9.6), 148.8 (s); δ_P (161.9 MHz, $CDCl_3$, H_3PO_4) 0.9; HRMS (ESI): Calcd for $C_{26}H_{25}NOP$ $[M + H]^+$ 398.1668, found 398.1670.

1-Methoxymethyl-3-methyl-2-triphenylphosphoranylideneaminobenzene 31B (R^1 = H; R^2 = CH_3). (1.54 g, 75%); mp 100–101 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 1379 (vs), 1109 (vs); δ_H (400 MHz, $CDCl_3$) 1.92 (3 H, d, *J* 1.5), 3.00 (3 H, s); 4.22 (2 H, s); 6.72 (1 H, td, *J* 7.4, 2.4), 6.94 (1 H, d, *J* 7.4), 7.09 (1 H, d; *J* 7.4), 7.37–7.42 (6 H, m), 7.47–7.49 (3 H, m), 7.55–7.61 (6 H, m); δ_C (100 MHz, $CDCl_3$) 21.0, 57.7, 73.1, 119.0 (d, *J* 3.3), 125.5 (d, *J* 2.2), 128.4 (d, *J* 12.1), 129.2 (d, *J* 2.7), 131.3 (d, *J* 2.5), 132.4 (d, *J* 9.5), 132.8 (d, *J* 101.1) (s), 133.1 (d, *J* 7.4) (s), 133.4 (d, *J* 6.2) (s), 146.4 (d, *J* 2.1) (s); δ_P (161.9 MHz, $CDCl_3$, H_3PO_4) – 4.5; HRMS (ESI): Calcd for $C_{27}H_{27}NOP$ $[M + H]^+$ 412.1825, found 412.1830.

4-Chloro-2-methoxymethyl-1-triphenylphosphoranylideneaminobenzene 31C (R^1 = Cl; R^2 = H). (1.88 g, 87%); mp 103–104 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 1374 (vs), 1105 (vs); δ_H (400 MHz, $CDCl_3$) 3.45 (3 H, s), 4.75 (2 H, s), 6.33 (1 H, dd, *J* 8.4, 1.4), 6.74 (1 H, dd, *J* 8.4, 2.7), 7.28 (1 H, t, *J* 2.7), 7.41–7.46 (6 H, m), 7.49–7.54 (3 H, m), 7.68–7.74 (6 H, m); δ_C (100 MHz, $CDCl_3$) 58.5, 71.7, 121.7 (d, *J* 9.6), 122.2 (s), 126.7, 127.1, 128.7 (d, *J* 11.9), 131.2 (d, *J* 99.1) (s), 131.8 (d, *J* 2.5), 132.5 (d, *J* 9.6), 134.3 (d, *J* 20.7) (s), 147.3 (s); δ_P (161.9 MHz, $CDCl_3$, H_3PO_4) 2.3; HRMS (ESI): Calcd for $C_{26}H_{23}ClNOP$ $[M + H]^+$ 432.1279, found 432.1291.

2-Methoxymethyl-4-methyl-1-triphenylphosphoranylideneaminobenzene 31D (R^1 = CH_3; R^2 = H). (1.81 g, 88%); mp 119–121 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 1437 (vs), 1107 (vs); δ_H (400 MHz, $CDCl_3$) 2.20 (3 H, s), 3.45 (3 H, s), 4.80 (2 H, s), 6.37 (1 H, d, *J* 8.0), 6.62 (1 H, dd, *J* 8.0, 1.7), 7.13 (1 H, s), 7.39–7.44 (6 H, m), 7.47–7.51 (3 H, m), 7.71–7.76 (6 H, m); δ_C (100 MHz, $CDCl_3$) 20.7, 58.3, 72.1, 120.8 (d, *J* 9.4), 126.4 (s), 127.7, 128.4, 128.5 (d, *J* 11.9), 131.5 (d, *J* 2.5), 131.8 (d, *J* 99.1) (s), 132.1 (s), 132.6 (d, *J* 9.6), 146.0 (s); δ_P (161.9 MHz, $CDCl_3$, H_3PO_4) 0.5; HRMS (ESI): Calcd for $C_{27}H_{27}NOP$ $[M + H]^+$ 412.1825, found 412.1828.

Preparation of 4-methoxyquinolines 34

To a solution of methoxymethyl-triphenylphosphoranylideneaminobenzene **31** (1.5 mmol) in anhydrous toluene (15 mL) a solution of methylphenylketene (0.2 g, 1.5 mmol) or diphenylketene (0.29 g, 1.5 mmol) in the same solvent (5 mL) was added. The reaction mixture was stirred under nitrogen at

room temperature for 30 min and next heated at reflux temperature for 12–36 h. Then, after cooling at room temperature, the solvent was removed under reduced pressure, and the resulting crude material was purified by column chromatography on silica gel.

4-Methoxy-3,3-diphenyl-3,4-dihydroquinoline **34a** (R^1 = R^2 = H; R^3 = Ph). Eluent for column chromatography: hexanes–diethyl ether (4 : 1, v/v); (0.24 g, 51%); colourless oil; ν_{max}(neat)/cm^{-1} 1596 (s); δ_H (400 MHz, $CDCl_3$) 3.08 (3 H, s), 4.66 (1 H, s), 7.14–7.34 (14 H, m), 8.50 (1 H, d, *J* 1.1); δ_C (100 MHz, $CDCl_3$) 54.9 (s), 58.0, 81.9, 126.9, 127.0, 127.1, 127.2 (s), 127.4, 127.7, 128.1, 128.3, 128.4, 129.2, 129.3, 141.3 (s), 142.1 (s), 142.2 (s), 167.2; HRMS (ESI): Calcd for $C_{22}H_{20}NO$ $[M + H]^+$ 314.1539, found 314.1545.

4-Methoxy-8-methyl-3,3-diphenyl-3,4-dihydroquinoline **34b** (R^1 = H; R^2 = CH_3; R^3 = Ph). Eluent for column chromatography: hexanes–diethyl ether (9 : 1, v/v); (0.49 g, 99%); mp 95–96 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 1620 (s); δ_H (400 MHz, $CDCl_3$) 2.44 (3 H, s), 3.07 (3 H, s), 4.59 (d, 1 H, *J* 1.1), 7.10–7.18 (8 H, m), 7.19–7.24 (1 H, m), 7.26–7.30 (2 H, m), 7.32–7.35 (2 H, m), 8.55 (1 H, d, *J* 1.1); δ_C (100 MHz, $CDCl_3$) 17.6, 54.3 (s), 57.9, 82.0, 124.9, 126.6 (s), 126.8, 127.0, 127.3, 128.1, 128.2, 128.3, 129.2, 131.1, 135.5 (s), 140.0 (s), 141.6 (s), 142.2 (s), 165.8; HRMS (ESI): Calcd for $C_{23}H_{22}NO$ $[M + H]^+$ 328.1696, found 328.1702.

6-Chloro-4-methoxy-3,3-diphenyl-3,4-dihydroquinoline **34c** (R^1 = Cl; R^2 = H; R^3 = Ph). Eluent for column chromatography: hexanes–diethyl ether (7 : 3, v/v); (0.36 g, 70%); mp 125–126 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 1620 (s); δ_H (400 MHz, $CDCl_3$) 3.09 (3 H, s), 4.64 (1 H, s), 7.14–7.32 (13 H, m), 8.49 (1 H, s); δ_C (100 MHz, $CDCl_3$) 54.6 (s), 58.6, 81.8, 126.6, 127.1, 127.3, 128.2, 128.3, 128.5, 128.7, 129.1, 129.2, 133.1 (s), 140.4 (s), 140.5 (s), 142.0 (s), 167.7; HRMS (ESI): Calcd for $C_{22}H_{19}ClNO$ $[M + H]^+$ 348.1150, found 348.1155.

4-Methoxy-6-methyl-3,3-diphenyl-3,4-dihydroquinoline **34d** (R^1 = CH_3; R^2 = H; R^3 = Ph). Eluent for column chromatography: hexanes–diethyl ether (4 : 1, v/v); (0.30 g, 61%); mp 123–124 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 1624 (s); δ_H (400 MHz, $CDCl_3$) 2.36 (3 H, s), 3.08 (3 H, s), 4.61 (1 H, s), 7.09–7.34 (13 H, m), 8.45 (1 H, s); δ_C (100 MHz, $CDCl_3$) 21.5, 54.8 (s), 58.0, 81.8, 126.7 (s), 126.9, 127.0, 127.3, 127.7, 128.1, 128.3, 128.4, 129.3, 129.7, 137.7 (s), 139.7 (s), 141.4 (s), 142.2 (s), 166.1; HRMS (ESI): Calcd for $C_{23}H_{22}NO$ $[M + H]^+$ 328.1696, found 328.1701.

4-Methoxy-3-methyl-3-phenyl-3,4-dihydroquinoline **34e** (R^1 = R^2 = H; R^3 = CH_3) (mixture of diastereoisomers in a 2 : 1 *cis*/*trans* ratio). Eluent for column chromatography: hexanes–diethyl ether (9 : 1, v/v); (0.26 g, 69%); colourless oil; ν_{max}(neat)/cm^{-1} 1609 (s); Major Diastereoisomer: δ_H (300 MHz, $CDCl_3$) 1.27 (3 H, s), 2.93 (3 H, s), 3.85 (1 H, s), 8.10 (1 H, s); Minor Diastereoisomer: δ_H (300 MHz, $CDCl_3$) 1.49 (3 H, s), 3.06 (3 H, s), 4.18 (1 H, s), 7.83 (1 H, s); HRMS (ESI): Calcd for $C_{17}H_{18}NO$ $[M + H]^+$ 252.1383, found 252.1390.

4-Methoxy-3,8-dimethyl-3-phenyl-3,4-dihydroquinoline **34f** (R^1 = H; R^2 = CH_3; R^3 = CH_3) (mixture of diastereoisomers in a 2 : 1 *cis*/*trans* ratio). Eluent for column chromatography: hexanes–diethyl ether (9 : 1, v/v); (0.20 g, 50%); colourless oil; ν_{max}(neat)/cm^{-1} 1620 (s); Major Diastereoisomer: δ_H (300 MHz, $CDCl_3$) 1.33 (3 H, s), 2.53 (3 H, s), 2.99 (3 H, s), 3.88 (1 H, d, *J* 1.5), 8.23 (1 H, d, *J* 1.5); Minor Diastereoisomer: δ_H (300 MHz, $CDCl_3$) 1.57 (3 H, s), 2.51 (3 H, s), 3.15 (3 H, s), 4.22 (1 H, d, *J* 1.5), 7.92 (1 H, d, *J* 1.5); HRMS (ESI): Calcd for $C_{18}H_{20}NO$ $[M + H]^+$ 266.1539, found 266.1545.

Preparation of 1-azido-2-(ethylthio)methylbenzene 36

To a solution of potassium hydroxide (0.44 g, 8 mmol) in dimethylsulfoxide (20 mL) was added, dropwise for 20 min, a mixture of 2-azidobenzyl iodide **35** (4.16 g, 16 mmol) and ethanethiol (0.48 g, 8 mmol) in the same solvent (25 mL). The reaction mixture was stirred at room temperature for 2 h. Then water (40 mL) and dichloromethane (40 mL) were added. The organic phase was separated and dried over anhydrous magnesium sulphate. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel, using hexanes–ethyl acetate (9 : 1, v/v) as the eluent.

1-Azido-2-(ethylthio)methylbenzene 36. (1.28 g, 83%); yellow oil; ν_{max}(neat)/cm^{-1} 2127 (vs); δ_H (400 MHz, $CDCl_3$) 1.25 (3 H, t, *J* 7.4), 2.49 (2 H, q, *J* 7.4), 3.68 (2 H, s), 7.08 (1 H, td, *J* 7.7, 1.1), 7.14 (1 H, dd, *J* 7.7, 1.1), 7.25–7.30 (2 H, m); δ_C (100 MHz, $CDCl_3$) 14.5, 25.8, 31.0, 118.4, 124.7, 128.4, 130.2 (s), 138.2 (s).

Preparation of 2-(ethylthio)methyl-1-triphenylphosphoranylideneaminobenzene 37

To a solution of 1-azido-2-(ethylthio)methylbenzene **36** (1.16 g, 6 mmol) in anhydrous diethyl ether (20 mL), under nitrogen at room temperature, triphenylphosphine (1.55 g, 6 mmol) was added in small portions. The reaction mixture was stirred at room temperature for 16 h. Then the solvent was removed under reduced pressure and the crude material was purified by column chromatography on silica gel deactivated with triethylamine, using hexanes–diethyl ether (1 : 1, v/v) as the eluent.

2-(Ethylthio)methyl-1-triphenylphosphoranylideneaminobenzene 37. (2.46 g, 96%); yellow oil; ν_{max}(neat)/cm^{-1} 1348 (vs), 1112 (vs); δ_H (400 MHz, $CDCl_3$) 1.20 (3 H, t, *J* 7.4), 2.51 (2 H, q, *J* 7.4), 4.08 (2 H, s), 6.46 (1 H, d, *J* 7.5), 6.61 (1 H, t, *J* 7.5), 6.77 (1 H, t, *J* 7.5), 7.22–7.24 (1 H, m), 7.38–7.42 (6 H, m), 7.45–7.48 (3 H, m), 7.74–7.79 (6 H, m); δ_C (100 MHz, $CDCl_3$) 15.0, 25.7, 33.1, 117.1, 121.2 (d, *J* 9.9), 126.9, 128.5 (d, *J* 11.9), 129.6, 131.5 (d, *J* 98.8) (s), 131.6 (d, *J* 2.0), 132.6 (d, *J* 9.6), 132.7 (s), 149.4 (s); δ_P (161.9 MHz, $CDCl_3$, H_3PO_4) 1.1; HRMS (ESI): Calcd for $C_{27}H_{26}NPS$ $[M + H]^+$ 428.1596, found 428.1602.

Preparation of 4-ethylthio-3,3-diphenyl-3,4-dihydroquinoline 39

To a solution of 2-(ethylthio)methyl-1-triphenylphosphoranylideneaminobenzene **37** (0.51 g, 1.2 mmol) in anhydrous *ortho*-xylene (15 mL) a solution of diphenylketene (0.23 g, 1.2 mmol) in the same solvent (5 mL) was added. The reaction mixture was stirred under nitrogen at room temperature for 30 min and next heated at reflux temperature for 24 h. Then, after cooling at room temperature, the solvent was removed under

reduced pressure, and the resulting crude material was purified by column chromatography on silica gel, using hexanes–diethyl ether (7 : 3, v/v) as the eluent.

4-Ethylthio-3,3-diphenyl-3,4-dihydroquinoline 39. (0.35 g, 85%); mp 99–101 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 1616 (s); δ_H (400 MHz, $CDCl_3$) 0.94 (3 H, t, *J* 7.4), 1.88–1.98 (2 H, m), 4.60 (1 H, s), 7.13–7.18 (3 H, m), 7.20–7.23 (2 H, m), 7.24–7.30 (3 H, m), 7.31–7.33 (5 H, m), 7.40–7.42 (1 H, m), 8.63 (1 H, s); δ_C (100 MHz, $CDCl_3$) 14.1, 26.2, 50.2, 53.3 (s), 127.0, 127.3, 127.5, 127.8, 128.0, 128.1, 128.2, 128.3, 128.4, 128.5 (s), 128.9, 141.2 (s), 142.1 (s), 143.0 (s), 165.4; HRMS (ESI): Calcd for $C_{23}H_{22}NS$ $[M + H]^+$ 344.1467, found 344.1472.

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