Pergamon

Tetrahedron 58 (2002) 1415–1424

TETRAHEDRON

Carbon–hydrogen bond insertion reactions of 3-acetoxyaminoquinazolin-4(3*H*)-ones with cyclic dienes: stereochemistry and mechanism

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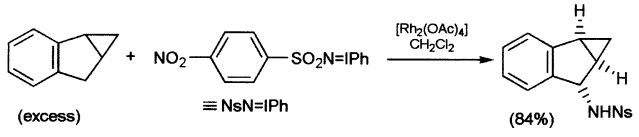
Received 3 October 2001; revised 16 November 2001; accepted 13 December 2001

Abstract—Reaction of 2-substituted-3-acetoxyaminoquinazolin-4(3*H*)-ones (QNHOAc) with cyclohexa-1,3-diene or cyclohexa-1,4-diene (2 equiv.) gives, besides the expected aziridination products, stable dihydroaromatic by-products formally arising by insertion of [QN̈:] into one of the doubly allylic C–H bonds. An analogous insertion into the methylene C–H bonds of 9,10-dihydroanthracene or xanthene (1.5–2 equiv.) occurs. Using 3-acetoxyamino-2-[(*S*)-2,2-dimethyl-1-hydroxypropyl]quinazolin-4(3*H*)-one **2** (Q^1NHOAc) in the presence of titanium(IV) *t*-butoxide, insertion into cyclohexa-1,3-diene takes place completely diastereoselectively and the configuration at the cyclohexadienyl ring carbon has been correlated with that at the 6-position of the major aziridine diastereoisomer co-produced in the reaction. A mechanism involving concerted insertion into the C–H bond of the diene by QNHOAc is proposed with *endo*-overlap of both double bonds of the diene with the Q group in the transition state.

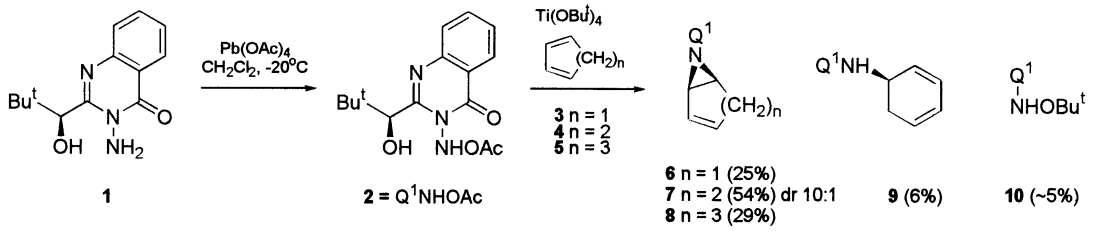
Direct insertion reactions into carbon–hydrogen bonds to form carbon–nitrogen bonds are less well known than the corresponding reactions to form carbon–carbon or carbon–oxygen bonds. Insertion by a small number of nitrenes in their singlet states takes place stereospecifically with retention of configuration.[1] Other examples all involve metal catalysed reactions of PhI=NSO_2Ar compounds[2] where yields can be as high as 84% in favourable cases (Scheme 1)[3] with retention of configuration in the product.



Scheme 1.

Cyclic dienes **3**–**5** were previously shown to react with 3-acetoxyaminoquinazolinone **2** (Q^1NHOAc) in the presence of titanium(IV) *t*-butoxide (TTB) to give monoaziridines as major products: aziridines **6** and **8** were separated as single diastereoisomers in crystalline form without the need for chromatography because the decomposition products of Q^1NHOAc were not present in the recovered products.[4,5]

However, whereas the aziridinations of cyclopentadiene and cycloheptadiene were highly diastereoselective, that of cyclohexa-1,3-diene was less so (dr 10:1–4:1). A further difference in the aziridination of cyclohex-1,3-diene was the isolation of a by-product (6%) by chromatography identified as the dienylamine **9** but not separated from a further by-product, 3-*t*-butoxyamino-quinazolinone **10** (Scheme 2).[5] Dienylamine **9** is the formal insertion product



1 2 = Q^1NHOAc

Scheme 2.

Keywords: insertion reactions; cyclohexadienes; acetoxyaminoquinazolinones.
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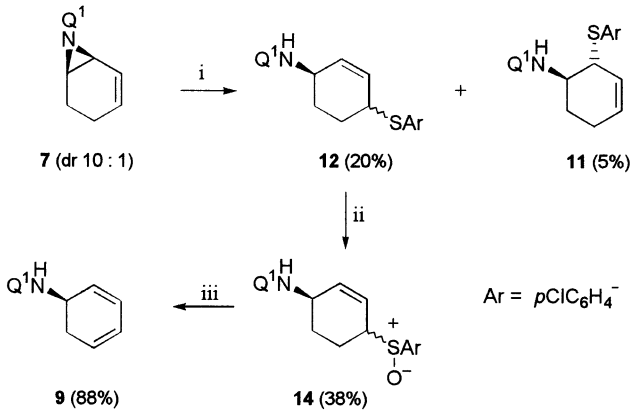


Scheme 3. *Reagents*: i, *p*-ClC_6H_5SH, CH_2Cl_2, 90°C, 2 h; ii, H_2O_2, AcOH; iii, Δ, CCl_4, 2 h.

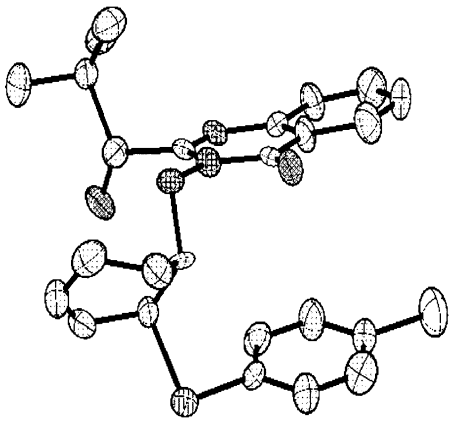


Figure 1. Molecular structure of **11**, showing 50% displacement probability ellipsoids. Hydrogen atoms are omitted for clarity.

of [$Q^1\ddot{N}$:] into a doubly allylic C–H bond of the diene: no evidence for the formation of analogous insertion products was found from the reactions of cyclopenta- or cyclohepta-1,3-diene.

Since insertion products of QNHOAc compounds into σ bonds had not previously been observed, we have investigated whether analogous reaction products could be obtained with other dienes. Evidence for the mechanism of the insertion reaction to form dienylamine **9** is presented.

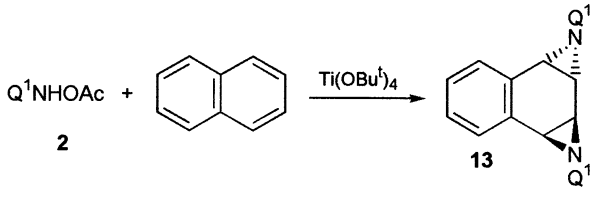
The major diastereoisomer of aziridine **7** was the only one isolated when aziridination of cyclohexa-1,3-diene was carried out in acetonitrile.[5] Conversion of this major diastereoisomer of aziridine **7** into dienylamine **9** was accomplished as shown in Scheme 3. Aziridine ring-opening with thiophenol gave thioether **12** as the major product from S_N2' attack but of unknown configuration at the C–SAr chiral centre. The minor product **11**, presumably formed by direct S_N2 attack, was separated by chromatography and an X-ray structure determination[†] on one of a very small number of crystals of the compound formed confirmed the *trans* relationship between the two substituents on the cyclohexene ring (Fig. 1).[‡]

Surprisingly, in the crystal form, both substituents are in axial positions with the quinazolinone and *p*-chlorothiophenol rings oriented almost parallel, suggesting the presence of an attractive interaction between their two π-systems.

Surprisingly also, the space group of the crystal ($P\bar{1}$) showed that the compound it contained was racemic in spite of the fact that the bulk of the material after removal of the crystals had a significant rotation [$(\alpha)_D$=+25.3 (*c*=1, EtOH)]. Although the enantiopurity of the bulk of this material is unknown we believe it is high since the starting material Q^1NH_2 **1** is of high enantiopurity and racemisation either in the aziridination step or in the conversion of aziridine **7** into thioether **12** seems unlikely. The enantiopurity of Q^1NHOAc **2** was confirmed by using it to bis-aziridinate naphthalene to give the 1,2,3,4-tetrasubstituted-tetrahydronaphthalene **13** (Scheme 4) whose ^1H and ^{13}C NMR spectra showed the presence of a single diastereoisomer.[§]

The two chiral centres in the $Bu^tCH(OH)$ groups, therefore, must have the same configuration leading to C_{2v} symmetry in bis-aziridine **13** and since (*S*)-*tert*-leucine was the starting material for the preparation of Q^1NH_2 **1**, this configuration is presumably (*S*). Oxidation of thioether **12** to the sulfoxide **14** followed by thermal elimination of sulfenic acid gave a pure sample of dienylamine **9** identical with that isolated as a mixture with Q^1NHOBu^t **10** from the reaction of Q^1NHOAc **2** with cyclohexa-1,3-diene–TTB (Scheme 2).

This conversion strongly suggested that dienylamine **9** was formed as a single diastereoisomer, a conclusion supported by synthesis of a mixture of diastereoisomers of **9** (given later).

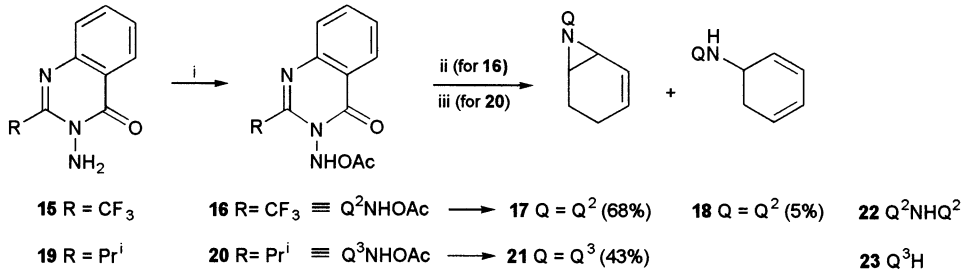


Scheme 4.

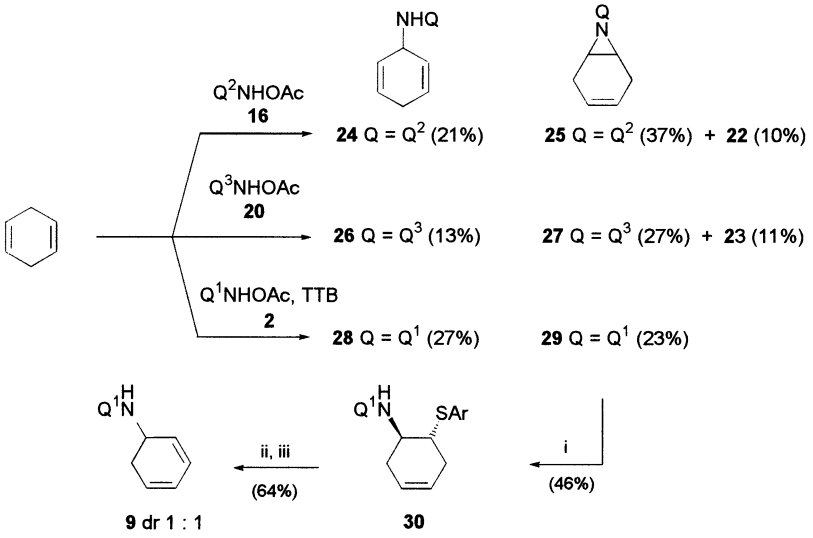
[†] Data were measured on a Siemens P4 diffractometer with graphite monochromated Mo Kα radiation (λ=0.7107 Å) using an ω-scan technique. Three standard reflections monitored every 100 scans showed no significant variation in intensity, the reflections were corrected for Lorentz and polarisation effects. The structures were solved by direct methods and refined by full-matrix least squares on F^2 using the program SHELXL-97. All hydrogen atoms were included in calculated positions (C–H=0.96 Å) using a riding model. All crystals were poor diffractors, as a consequence there was insufficient observed data to refine all atoms with anisotropic displacement parameters and the carbon atoms of the quinazoline ring were refined as isotropic. All other non-hydrogen atoms were refined as anisotropic. *Crystal data for* **11**. $C_{25}H_{28}ClN_3O_2S$, *M*=470.01, triclinic, space group *P*1, *a*=7.335(2), *b*=11.349(4), *c*=15.583(2) Å, α=72.64(2), β=89.82(2), γ=74.40(3)°, *V*=1188.2(5) $Å^3$, *T*=200 K, *Z*=2, μ(Mo Kα)=0.276 mm^{-1} colourless plate, crystal dimensions 0.40×0.15×0.04 mm^3. Full matrix least squares based on F^2 gave *R*1=0.122 for 1551 observed data ($F>4\sigma(F)$) and *wR*2=0.232 for all 4078 data, GOF=1.054 for 249 parameters [CCDC No. 160875].

[‡] The conformation of this thioether in solution, however, could not be determined from the coupling constant between the two Q^1NH*C*H*C*H*S*Ar protons in its NMR spectrum because these signals overlapped to give a narrow multiplet.

[§] The two aziridine rings in **13** are *trans* but their orientations are arbitrarily assigned.

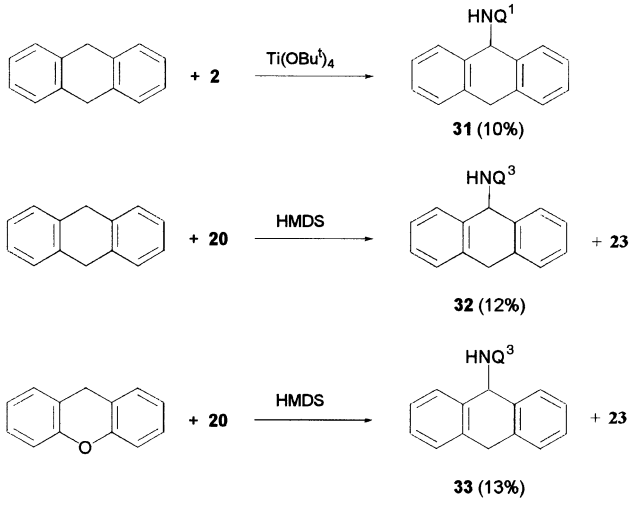


Scheme 5. *Reagents*: i, LTA, CH_2Cl_2; ii, cyclohexa-1,3-diene; iii, cyclohexa-1,3-diene, hexamethyldisilazane.



Scheme 6. *Reagents*: i, *p*-ClC_6H_5SH, NaOH, CH_3CN, 80°C; ii, H_2O_2, AcOH; iii, Δ, CCl_4, 2 h.

A similarly small yield of dienylamine **18** was obtained,[5] along with major product **17**, in reaction of the 2-trifluoromethyl-substituted Q^2NHOAc **16**[6] with cyclohexa-1,3-diene (Scheme 5) but no analogous dienylamine was isolated in aziridination of this diene with 3-acetoxyamino-2-isopropylquinazolinone **20** (in the presence of hexamethyldisilazane):[7] minor amounts of *N*,*N*-bis-(3,4-dihydro-4-oxoquin-azolin-3-yl)amine **22** and 3-H-quinazolinone **23**, known decomposition products of Q^2NHOAc **16** and Q^3NHOAc **20**, respectively, were also isolated in these reactions.

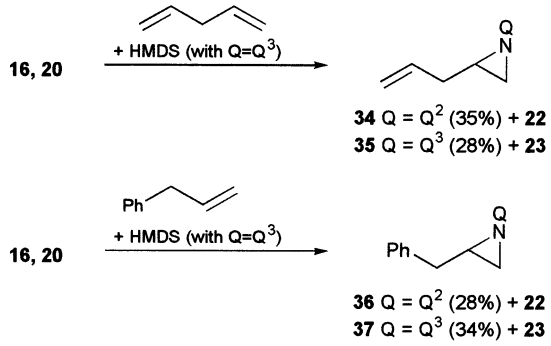


Scheme 7.

Significantly greater yields of insertion products were obtained using cyclohexa-1,4-diene: with Q^1NHOAc **2**–TTB the yield of dienylamine **28** exceeded that of aziridine **29**; some insertion product **26** was obtained even using Q^3NHOAc **20** (Scheme 6).

Confirmation of the diastereopurity of the dienylamine **9**, prepared from cyclohexa-1,3-diene and Q^1NHOAc **2**–TTB in Scheme 2, was obtained by the conversion of aziridine **29** into a 1:1 mixture of dienylamine diastereoisomers **9** as shown in Scheme 6: some of the corresponding protons in these two diastereoisomers resonated at different chemical shifts in the NMR spectrum of the mixture and only one set were present in the spectrum of the product **9** obtained in Scheme 3. The conversion of aziridine **29** to thioether **30** by thiophenolate anion is another example of the ability of the Q group to facilitate nucleophilic ring-opening of the three-membered ring.[8]

The reactions of 9,10-dihydroanthracene with Q^1NHOAc **2**–TTB and of 9,10-dihydroanthracene and xanthene with Q^3NHOAc **20** were examined with the expectation that aziridination of the aromatic double bonds would not compete with insertion. Although this turned out to be the case (Scheme 7), the yields of insertion products did not exceed 13% in any case; the major product again was the



Scheme 8.

3*H*-quinazolinone **23** using Q^3NHOAc **20**. In the ^{1}H NMR spectrum of the product **32**, there were additional signals present consistent with the presence of hindered rotation around the 9(C)–N bond.[9]

The *N*,*N*-bis-(3,4-dihydro-4-oxoquinazolin-3-yl)amine **22** and 3*H*-quinazolinone **23** were the only products isolated from attempts to react Q^2NHOAc **16** and Q^3NHOAc **20**, respectively, with fluorene, anthrone, diphenylmethane or 9,10-dihydrophenanthrene. Penta-1,4-diene and allylbenzene reacted to give only the corresponding aziridines **34**–**37** in addition to Q^2NHQ^2 **22** and Q^3H **23** (Scheme 8).

Thus the scope of this reaction at present seems to be limited to six-membered ring-contained dienes although the double bonds may be contained in benzene rings as in dihydroanthracene and in xanthene.

1. Mechanism of insertion

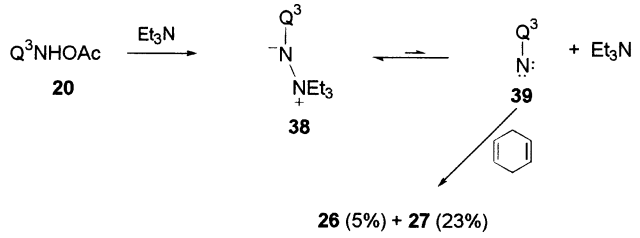
Concerted insertion with retention of configuration into C–H bonds is reminiscent of the behaviour of reactive singlet nitrenes (given earlier). We have shown previously that (3,4-dihydro-4-oxoquinazolin-3-yl)nitrenes [QN̈:], the species formally derived by elimination of acetic acid from QNHOAc are also aziridinating agents with a reactivity profile very similar to, but identifiably different from, that of the corresponding QNHOAc compounds.[10]

To exclude the possibility that these insertion products using QNHOAc in fact arose from reaction of the corresponding QN̈: compounds[¶] we reacted cyclohexa-1,4-diene with the Q^3N intermediate **39** generated from the corresponding nitrogen ylide **38** (Scheme 9).

The ratio of dienylamine **26**–aziridine **27** was much reduced by comparison with the corresponding reaction of Q^3NHOAc **19** with this diene (Scheme 6) and thus the species effecting the insertion is unlikely to be the nitrene Q^3N̈–**39**.

The available evidence, therefore, suggests that in the formation of these insertion products, the reacting species is QNHOAc and that the reaction occurs concertedly.

[¶] Insertion into C–H bonds had not previously been observed in reactions of QN̈:.



Scheme 9.

Since dienylamine **9** is formed as a single diastereoisomer, we assume that it is formed with retention of configuration since if a hydride or hydrogen atom were removed from one face of the diene by Q^1NHOAc, the resulting pentadienyl cation or radical would be unlikely to recombine with the co-produced Q^1NH_2 or Q^1ṄH exclusively from the opposite face. It seems likely, moreover, that the insertion is concerted since, if it were to proceed, for example, via hydride transfer to give, albeit transiently, a pentadienyl cation–Q^1NH_2 intermediate species **40**, attack at both ends of the cation would be anticipated and, using Q^1NHOAc–TTB, lead to a mixture of diastereoisomers (Scheme 10).

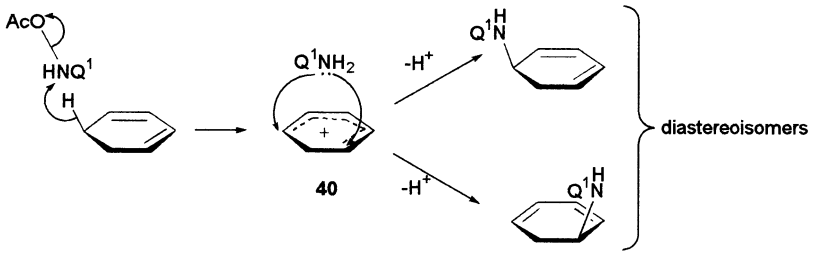
When the aziridination of cyclohexa-1,4-diene in Scheme 6 was carried out using Q^1NDOAc, prepared by LTA oxidation of Q^1ND_2, the NMR spectrum of the crude product showed the presence of an N*H* of integral value one proton for the dienylamine **9**. This result excludes a species such as **40** or at least one in which rapid interchange of the two NH_2 proton environments occurs.

The fact that reactions of cyclohexa-1,3- and cyclohexa-1,4-diene with Q^1NHOAc–TTB lead to no product in common also militates against the intervention of a cyclohexadienyl radical or cation since only a small separation from the co-generated QṄH or QNH_2 species would be expected to lead to indistinguishable cation–radical intermediates from either diene and identical product(s) on recombination.

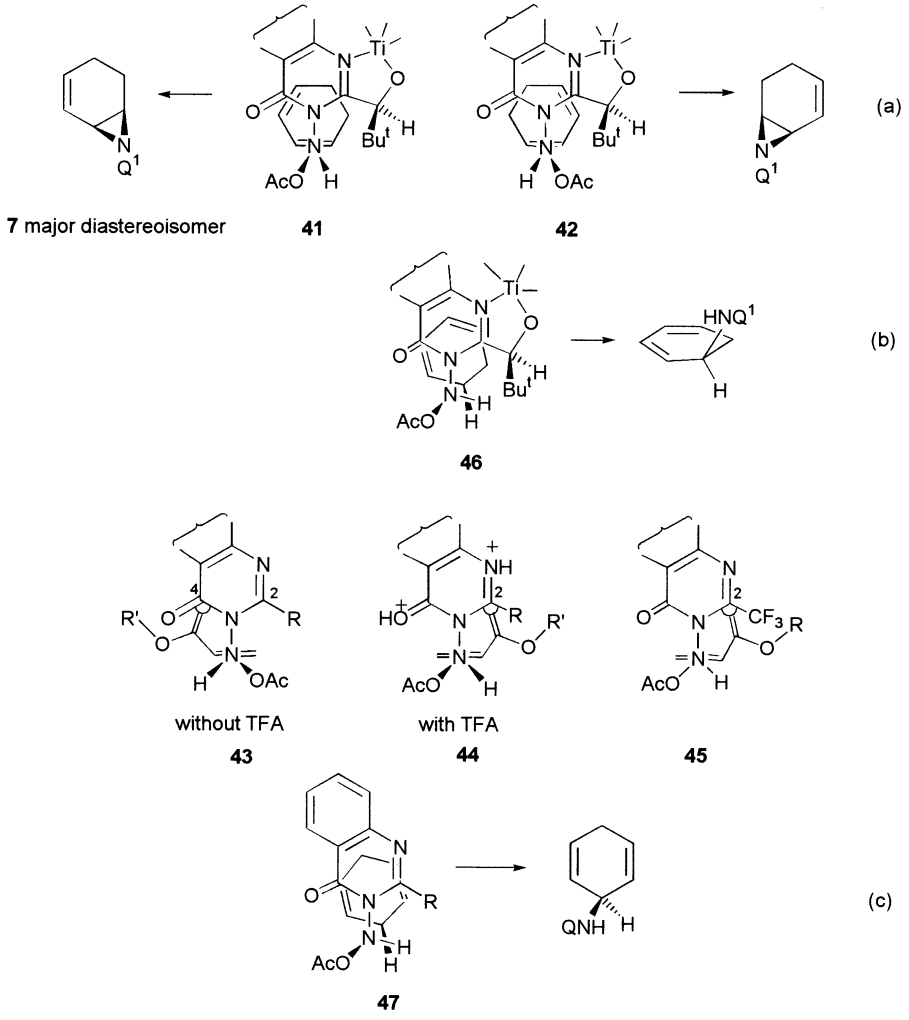
In aziridination of these cyclic dienes, **3**, **4** and **5**, a key factor in bringing about diastereoselectivity is *endo*-overlap of the unreacting double bond with the carbonyl group of the quinazolinone as in transition state (TS[#]) **41** for the formation of the major diastereoisomer of aziridine **7** (Scheme 11a).[8] The less than complete diastereoselectivity in aziridination of cyclohexa-1,3-diene with Q^1NHOAc **2**–TTB can be accounted for by some competition from TS[#] **42**.

We have proposed elsewhere[11] that, in aziridination of α,β-unsaturated *esters*, an analogous switch from *endo*-overlap of the ester carbonyl oxygen with (Q)*C*═O **43** to (Q)C═N **44** occurs as a result of addition of trifluoroacetic acid (TFA) to the reaction mixture. The effect of TFA is believed to result from protonation of the quinazolinone at N-1 thereby increasing the electrophilicity at (Q)C-2. With an electron-withdrawing trifluoromethyl group at (Q)C-2 as in Q^2NHOAc **16**, *endo*-overlap of the ester carbonyl oxygen with (Q)*C*═N as in **45** was favoured even in the absence of TFA.

The effect of chelation of N-1 by titanium as in TS[#] **42** is to simulate, to some degree, the effect of protonation at N-1



Scheme 10.



Scheme 11.

and it is assumed that formation of some of the minor diastereoisomer of aziridine **7** takes place via TS# **42** for this reason.

Formation of dienylamine **9** could proceed via TS# **46** (Scheme 11b), which resembles both TS#s **41** and **42** having *endo*-overlap of one diene double bond with (Q^1)C=O and one with (Q^1)C=N.

For insertions into the bis-allylic C–H bond of cyclohexa-1,4-diene, a similar TS# **47** can be envisaged (Scheme 11c).

It is significant that only Q^1NHOAc **2**–TTB and Q^2NHOAc **16**, but not Q^3NHOAc **20**, gave insertion products with cyclohexa-1,3-diene: Q^3NHOAc **20** lacks the electron-withdrawing factors present in the other two reagents which facilitate *endo*-overlap with the C=N bond. On the other hand, Q^3NHOAc **20** does insert into an allylic C–H bond of cyclohexa-1,4-diene: presumably this diene is more reactive because *endo*-interaction of both double bonds of the diene as in TS# **47** does not entail the loss of some resonance which accompanies, for example, TS# **42**.

endo-Overlap of the unreacting double bond in *aziridination* of dienes by QNHOAc is thought to require its conjugation with the reacting double bond[11] and thus no *endo*-overlap is expected to be present in the aziridination of cyclohexa-1,4-diene.[‖] Consequently, the relatively higher ratio of insertion/aziridination using this diene (Scheme 6) can be ascribed to the presence of TS$^{\#}$-stabilising *endo*-interactions only in formation of the insertion products.

In this mechanistic interpretation, two double bonds in the diene are required to complex with the Q-double bonds (TS$^{\#}$s **46** and **47**) and thus locate the bis-allylic C–H bond in the geometry required for insertion to occur: the presence of both double bonds, however, could also stabilise any charge development in the (concerted) TS$^{\#}$ for insertion.

Although the yields in these insertion reactions are low, the substrate dienes are only used in twofold excess (cf. Scheme 1). Stable allylically functionalised dihydroaromatic compounds, e.g. **28**, are unusual and potentially very useful compounds; stereoselective attack on the double bonds could be facilitated by the allylic substituent. The challenge is to find analogous QNHX compounds having an enhanced insertion/aziridination reactivity ratio with dienes or even with allyl derivatives.

2. Experimental

2.1. General

For details of instrumentation and other experimental details see Ref. 8. Preparation of dienylamines **9** and **18** have been reported previously.[5]

2.1.1. Correlation of the major diastereoisomer of aziridine 7 with dienylamine 9. A pure sample of aziridine **7** obtained from aziridination of cyclohexa-1,3-diene in acetonitrile[5] (100 mg, 0.3 mmol) was dissolved in dichloromethane (2 cm^3) containing 4-chlorothiophenol (89 mg, 0.61 mmol) and heated at 90°C in a sealed Young's tube for 2 h. After cooling, saturated sodium hydrogen carbonate solution (10 cm^3) was added and the mixture extracted with dichloromethane (10 cm^3), the organic layer separated, dried and the solvent removed under reduced pressure to give a light brown solid. Column chromatography (6:1 light petroleum–ethyl acetate) gave 4-chlorothiophenol followed by a mixture of ring-opened aziridine products which was re-chromatographed using kieselgel (8:1 light petroleum–ethyl acetate) to give allylsulphide **11** (7 mg, 10%) (based on recovered starting material) R_f 0.21, as a colourless crystalline solid, mp 91–93°C (from ethanol). $[\alpha]_D$=+25.3 (c=1.0, EtOH); (Found: MH$^+$ 470.1669. $C_{25}H_{28}ClN_3O_2S$ requires *MH* 470.1669); ν_{max} (cm^{-1}) 1695 m, 1680 s, 1670 m and 1595 s; δ_H (300 MHz) 0.85 [9H, s, $(CH_3)_3$], 1.78 (1H, m, C*H*H), 1.98–2.30 (3H, struct. m, C*HH*C*H*H), 3.38 (2H, m, C*H*NH and C*H*SAr), 3.53 (1H, d, J=10.1 Hz, CHO*H*), 4.98 (1H, d, J=10.1 Hz, C*H*OH), 5.16 (1H, br s, NH), 5.81 (1H, d br, J~10 Hz, C*H*=CH), 5.99 (1H, d br, J~10 Hz, CH=C*H*), 6.55 (2H, d, J=8.4 Hz, 2×CH(Ar)], 6.86 [2H, d, J=8.4 Hz, 2×CH(Ar)], 7.46 [1H, ddd, J=8.1, 6.9, 1.1 Hz, H-6(Q)], 7.70 [1H, dd, J=8.1, 1.1 Hz, H-8(Q)], 7.76 [1H, ddd, J=8.1, 6.9, 1.1 Hz, H-7(Q)] and 7.99 [1H, dd, J=8.1, 1.1 Hz, H-5(Q)]; *m/z* (%) 470 (MH$^+$, 100), 231 (71), 222 (98).

Further elution gave allylsulphide **12** (28 mg, 40%) (based on recovered starting material) as a colourless oil, R_f 0.18; (Found: MH$^+$ 470.1669. $C_{25}H_{28}ClN_3O_2S$ requires *MH* 470.1669); ν_{max} (cm^{-1}) 1690 m, 1675 s, 1665 m and 1590 s; δ_H (300 MHz) 0.89 [9H, s, $(CH_3)_3$], 1.60 (2H, m, 2×C*H*), 2.04 (1H, struct. m, C*H*), 2.18 (1H, struct. m, C*H*), 3.53 (1H, d, J=9.9 Hz, CHO*H*), 3.75 (2H, m, C*H*NH, C*H*SAr), 4.96 (1H, d, J=9.9 Hz, C*H*OH), 5.38 (1H, d, J=5.5 Hz, NH), 5.53 (1H, m, incl. J=9.5 Hz, CH=C), 5.91 (1H, dd, J=9.5, 2.5 Hz, C=CH), 7.28 [2H, d, J=8.4 Hz, 2×CH(Ar)], 7.33 [2H, d, J=8.4 Hz, 2×CH(Ar)], 7.43 [1H, ddd, J=8.1, 6.9, 1.0 Hz, H-6(Q)], 7.63 [1H, dd, J=8.1, 1.0 Hz, H-8(Q)], 7.71 [1H, ddd, J=8.1, 6.9, 1.1 Hz, H-7(Q)] and 8.18 [1H, dd, J=8.1, 1.1 Hz, H-5(Q)]; *m/z* (%) 470 (MH$^+$, 100), 307 (87) and 231 (54).

Further elution gave aziridine **7** (27 mg, 27% recovered), R_f 0.18.

2.1.2. Oxidation of sulphide 12 to sulfoxide 14 and thermal elimination to dienylamine 9. Allylsulphide **12** (20 mg, 42.5 μmol) was stirred in glacial acetic acid (1 cm^3) containing hydrogen peroxide (1.4 mg/5 μl, 42.5 μmol) for 2 h. Ethyl acetate (1.5 cm^3) was added and the solution washed with saturated sodium hydrogen carbonate solution (1 cm^3), dried and evaporated to give the crude product as a colourless oil. Column chromatography (4:1 light petroleum–ethyl acetate) gave sulfoxide **14** (8 mg, 38%) as a colourless oil, R_f 0.40.

Sulfoxide **14** (8 mg, 16 μmol) was heated at reflux in carbon tetrachloride (1 cm^3) under nitrogen for 2 h. On cooling, ethyl acetate (1 cm^3) was added to the reaction mixture and the solution washed with saturated sodium hydrogen carbonate solution (1 cm^3), dried and evaporated to give the crude product as a colourless oil. Column chromatography (4:1 light petroleum–ethyl acetate) gave dienylamine **9** (4 mg, 88%) R_f 0.35, as a colourless oil whose NMR spectrum showed the presence of a single diastereoisomer identical with that isolated in a mixture with **10** as a by-product in reaction of cyclohexa-1,3-diene with Q^{1}NHOAc **2**–TTB.[5]

2.1.3. Aziridination of naphthalene with (*S*)-3-acetoxyamino-2-(1-hydroxy-2,2-dimethylprop-1-yl)-quinazolin-4(3*H*)-one 2. General aziridination procedure A (given later) was followed using LTA (1.116 g, 2.56 mmol), (*S*)-3-amino-2-(1-hydroxy-2,2-dimethylprop-1-yl)-quinazolin-4(3*H*)-one **1** (0.600 g, 2.42 mmol), naphthalene (0.310 g, 2.42 mmol) and HMDS (1.162 g, 7.26 mmol) in dichloromethane (6 cm^3). The crude product was dissolved in ethanol and cooled in ice to give bis-aziridine **13** as a colourless crystalline solid (53 mg, 70%), mp 221–222°C (from acetonitrile). $[\alpha]_D^{20}$=+131.4 (c=1.0, EtOH); (Found: M$^+$ 619.3033. $C_{36}H_{38}N_6O_4$ requires *M* 619.3033); ν_{max} (cm^{-1}) 3450 w, 1665 s and 1580 m; δ_H 1.87 [18H, s, 2×C$(CH_3)_3$],

[‖] The yield of aziridine **37** is little more than is obtained with hex-1-ene suggesting that there is little stabilisation of the TS$^{\#}$ by *endo*-overlap of the phenyl ring with Q[3].

3.55 (2H, d, J=10.0 Hz, 2×CHO*H*), 3.72 (2H, d, J=7.5 Hz, azir. NC*H*C*H*N), 4.60 [2H, d, J=7.5 Hz, 2×azir. NCH(Ar)], 4.96 (2H, d, J=10.0 Hz, 2×C*H*OH), 7.38–7.55 (4H) and 7.62–7.87 (6H), [2×m, 6×CH(Q), 4×CH(Ar)] and 8.33 [2H, d, J=9.5 Hz, 2×H-5(Q)]; δ_C (75 MHz) 26.3 [2×$(CH_3)_3$], 38.5 [2×*C*$(CH_3)_3$], 48.0, 48.3 (4×NCH), 75.0 (2×CHOH), 121.9 [2×*C*CO(Q)], 127.1, 127.4, 129.7 [6×CH(Ar)–Q], 130.8 (2×C), 131.6, 134.5 [4×CH(Ar)–Q], 145.2 [2×*C*N=C(Q)] and 157.7, 159.7 [2×C=N(Q), 2×CO(Q)]; *m*/*z* (%) 619 (MH^+, 72), 374 (52), 245 (66), 231 (38) and 128 (100).

2.1.4. Reaction of cyclohexa-1,4-diene with Q^{3}NHOAc 20 (general procedure A). Dry dichloromethane (6 cm^3) in a dry ice–acetone bath held at −12°C was magnetically stirred and lead tetra-acetate (LTA) (687 mg, 1.54 mmol) added in one portion. When the LTA had dissolved, the temperature of the bath was lowered to −20°C and 3-aminoquinazolinone **19**[12] (300 mg, 1.47 mmol) added continuously in small portions over 10–15 min at this temperature, stirring throughout. The temperature of the bath was allowed to rise to −10°C and the cold solution containing Q^{3}NHOAc **20** rapidly filtered into a flask maintained at −10°C to remove insoluble lead di-acetate (on a small scale a Pasteur pipette can be used). To this filtered solution, cyclohexa-1,4-diene (235 mg, 0.28 cm^{-1}, 2.94 mmol) and hexamethyldisilazane (474 mg, 2.94 mmol) were added and the temperature allowed to reach ambient, stirring throughout. The reaction mixture was washed with aqueous saturated sodium hydrogen carbonate, dried and the solvent evaporated under reduced pressure to give the product as a yellow oil. Column chromatography (4:1 light petroleum–ethyl acetate) gave dienylamine **26** (52 mg, 13%) as a colourless oil, R_f 0.47. (Found: MH^+ 282.1606. $C_{17}H_{19}N_3O$ requires *MH* 282.1606); ν_{max} (cm^{-1}) 1675 s and 1615 m; δ_H 1.33 (6H, d, J=6.7 Hz, C*H*$_3$CHC*H*$_3$), 2.50–2.85 (2H, m, CH_2), 3.80 [1H, h, J=6.7 Hz, C*H*$(CH_3)_2$], 4.13 (1H, m, incl. J=5.9, 1.6 Hz, C*H*NH), 5.78 (3H, m, N*H*, 2×C=C*H*), 5.98 (2H, struct. m, 2×C=C*H*), 7.42 [1H, ddd, J=8.2, 6.3, 1.2 Hz, H-6(Q)], 7.62–7.76 [2H, m, H-7 and H-8(Q)] and 8.23 [1H, dd, J=8.2, 1.0 Hz, H-5(Q)]; δ_C 27.0 (CH_2), 31.2 [$(CH_3)_2$], 45.9 [*C*H$(CH_3)_2$], 54.7 (CNH), 120.9 [*C*CO(Q)], 124.6, 126.5, 127.0, 127.7, 128.5 [3×CH(Q), 2×H*C*=*C*H], 134.5 [CH(Q)], 147.6 [*C*N=C(Q)] and 162.5, 163.4 [CN(Q), CO(Q)]; *m*/*z* (%) 282 (MH^+, 36), 204 (100) and 189 (31).

Further elution gave aziridine **27** (113 mg, 27%) R_f 0.39, as a colourless solid mp 95–96°C (from light petroleum–ethyl acetate). (Found: C, 72.6; H, 6.8; N, 15.0%. $C_{17}H_{19}N_3O$ requires C, 72.6; H, 6.8; N, 14.9%); ν_{max} (cm^{-1}) 1660 s and 1570 s; δ_H 1.42 (6H, d, J=6.6 Hz, 2×CH_3), 2.53 (2H, dd, J=17.1, 2.5 Hz, 2×C*H*H), 2.88 (2H, dd, J=17.1, 2.2 Hz, 2×CH*H*), 2.89 (2H, s br, 2×azir. NCH), 3.62 [1H, h, J=6.6 Hz, C*H*$(CH_3)_2$], 5.60 (2H, br s, *H*C=C*H*), 7.38 [1H, ddd, J=8.2, 6.3, 1.2 Hz, H-6(Q)], 7.58–7.70 [2H, m, H-7, H-8(Q)] and 8.17 [1H, dd, J=8.2, 1.0 Hz, H-5(Q)]; δ_C 21.6 [$(CH_3)_2$], 23.4 (2×CH_2), 31.3 [*C*H$(CH_3)_2$], 45.9 (2×C–N), 121.6 [*C*CO(Q)], 122.7 (H*C*=*C*H), 126.4, 126.9, 127.7, 133.8 [4×CH(Q)], 146.5 [*C*N=C(Q)] and 160.5, 161.5 [CN(Q), CO(Q)]; *m*/*z* (%) 281 (M^+, 14), 227 (100), 214 (66) and 203 (56).

Further elution gave Q^{3}H **23** (27 mg, 11%) as a colourless solid, R_f 0.10.

2.1.5. Reaction of cyclohexa-1,4-diene with Q^{2}NHOAc 16. General aziridination procedure A was followed in this reaction using Q^{2}NH$_2$ **15**[5] (300 mg, 1.44 mmol), LTA (638 mg, 1.44 mmol) and cyclohexa-1,4-diene (210 mg, 2.62 mmol) in dichloromethane (6 cm^3). Crystallisation of the crude product from ethyl acetate–light petroleum removed Q^{2}NHQ^2 **22** (57 mg, 10%).[6] Evaporation of the mother liquor and trituration of the resultant paste with light petroleum, gave aziridine **25** (151 mg, 37%) as a colourless solid, mp 88–91°C (from ethyl acetate–light petroleum). (Found: MH^+ 308.1011. $C_{15}H_{12}F_3N_3O$ requires *MH* 308.1011); ν_{max} (cm^{-1}) 1685 s and 1595 s; δ_H 2.44 (2H, d, J∼19 Hz, 2×C*H*), 2.77 (2H, d, J∼19 Hz, 2×C*H*), 3.51 (2H, s, 2×azir. C*H*), 5.56 (2H, s, *H*C=C*H*), 7.59 [1H, ddd, J=8.2, 4.4, 4.4 Hz, H-6(Q)], 7.78–7.82 [2H, m, H-7 and H-8(Q)] and 8.23 [1H, d, J=8.2 Hz, H-5(Q)]; δ_C 23.4 (2×CH_2), 42.2 (2×CN), 120.8 [*C*CO(Q)], 122.4 (*C*=*C*), 123.2 (CF_3), 126.9, 128.8, 129.5, 134.9 [4×CH(Q)], 144.3 [*C*N=C(Q)] and 160.7, 160.8 [CN(Q), CO(Q)]; *m*/*z* (%) 308 (MH^+, 100), 229 (22), 154 (48) and 136 (33).

Evaporation of the mother liquor gave dienylamine **24** (84 mg, 21%) as a colourless oil. (Found: MH^+ 308.1011. $C_{15}H_{12}F_3N_3O$ requires *MH*308.1011); ν_{max} (cm^{-1}) 1680 s and 1605 s; δ_H 2.68 (2H, m, C*H*$_2$), 4.16 (1H, m, C*H*NH), 5.50 (1H, d, J=7.6 Hz, NH), 5.55 (2H, ddd, J=10.3, 1.6, 1.6 Hz, *H*C=CH), 5.98 (2H, ddd, J=10.3, 1.4, 1.4 Hz, HC=C*H*), 7.64 [1H, ddd, J=8.0, 3.2, 3.2 Hz, H-6(Q)], 7.84–7.88 [2H, m, H-7 and H-8(Q)] and 8.33 [1H, dd, J=8.0, 1.0 Hz, H-5(Q)]; δ_C 26.9 (CH_2), 55.9 (CHNH), 120.8 [*C*CO(Q)], 124.9, 127.4, 128.3, 129.2, 129.6, 135.5 [4×CH(Q), HC=*C*H], 143.5 [*C*N=C(Q)] and 162.3, 162.4 [CN(Q), CO(Q)]—(*C*F_3 missing); *m*/*z* (%) 308 (MH^+, 23), 230 (48), 154 (100) and 136 (59).

2.1.6. Reaction of cyclohexa-1,4-diene with Q^{1}NHOAc 2–TTB (general procedure B). A solution of Q^{1}NHOAc **2** in dichloromethane (6 cm^3) at −20°C (bath temp.) was prepared using 3-aminoquinazolinone **1** (245 mg, 0.98 mmol) and LTA (458 mg, 1.04 mmol) as described for Q^{3}NHOAc **20** in general procedure A and the cold solution freed from lead di-acetate by filtering rapidly through a cotton wool plug into a flask maintained at −20°C (bath temp.). Titanium(IV) *t*-butoxide (598 mg, 2.00 mmol) was added, the solution stirred for 2 min, then cyclohexa-1,4-diene (156 mg, 1.96 mmol) added and the temperature of the reaction mixture allowed to rise to ambient by removal of the cooling bath. Saturated aqueous sodium hydrogen carbonate was added to the vigorously stirred reaction mixture and the gelatinous precipitate formed was removed by filtration through celite. The organic layer was separated, washed with brine, dried and the solvent removed under reduced pressure. Column chromatography (3:1 light petroleum–ethyl acetate) of the crude product gave dienylamine **28** (86 mg, 27%) R_f 0.56, as a colourless solid mp 105–107°C (from ethanol). $[\alpha]_D^{20}$=+135.4 (c=1.5, EtOH); (Found: C, 70.1; H, 7.3; N, 12.8%. $C_{19}H_{24}O_2N_3$ requires C, 70.1; H, 7.1; N, 12.9%); ν_{max} (cm^{-1}) 3500 w, 1670 s and 1590 s; δ_H 0.99 [9H, s, $(CH_3)_3$], 2.66 (2H, struct. m, CH_2), 3.63 (1H, d, J=10.4 Hz, CHO*H*), 4.16 (1H, struct. m,

C*H*NH), 5.14 (1H, d, *J*=10.4 Hz, C*H*OH), 5.69 (1H, d, *J*=5.4 Hz, NH), 5.71–5.88 (2H, struct. m, 2×C=C*H*), 5.93–6.04 (2H, struct. m, 2×C=C*H*), 7.48 [1H, ddd, *J*=8.2, 6.9, 1.5 Hz, H-6(Q)], 7.69 [1H, dd, *J*=8.2, 1.5 Hz, H-8(Q)], 7.78 [1H, ddd, *J*=8.2, 6.9, 1.0 Hz, H-7(Q)] and 8.27 [1H, dd, *J*=8.2, 1.0 Hz, H-5(Q)]; δ_C 25.9 [$C(CH_3)_3$], 26.6 (CH_2), 37.9 [$C(CH_3)_3$], 54.4 (CNH), 74.7 (COH), 120.7 [*C*CO(Q)], 123.7, 124.0, 126.8, 126.9, 127.3, 128.6, [3×CH(Q), 2×H*C*=*C*H], 134.5 [CH(Q)], 145.9 [*C*N=C(Q)] and 158.7, 161.8 [CN(Q), CO(Q)]; *m/z* (%) 326 (MH^+, 78), 248 (72), 233 (100) and 215 (54).

Further elution gave aziridine **29** (74 mg, 23%) R_f 0.40, as a colourless solid mp 59–60°C (from ethanol). $[\alpha]_D^{20}=+72.4$ (*c*=1.0, EtOH); (Found: MH^+ 326.1868. $C_{19}H_{24}O_2N_3$ requires *M* 326.1869); ν_{max} (cm^{-1}) 3480 m, 1665 s and 1590 s; δ_H 1.03 [9H, s, $C(CH_3)_3$], 2.52 (2H, m, incl. *J*~20 Hz, 2×C*H*), 2.80 (1H, m, incl. *J*~20 Hz, C*H*), 3.00 (2H, struct. m, C*H* and azir. C*H*), 3.15 (1H, dd, *J*=7.9 Hz, 4.4, azir. NCH), 3.80 (1H, d, *J*=10.0 Hz, CHO*H*), 5.01 (1H, d, *J*=10.0 Hz, C*H*OH), 5.59 (2H, s br, C*H*=C*H*), 7.45 [1H, ddd, *J*=8.2, 6.9, 1.2 Hz, H-6(Q)], 7.64 [1H, dd, *J*=8.2, 1.0 Hz, H-8(Q)], 7.71 [1H, ddd, *J*=8.2, 6.9, 1.0 Hz, H-7(Q)] and 8.21 [1H, dd, *J*=8.2, 1.2 Hz, H-5(Q)]; δ_C 23.6 (2×CH_2), 26.5 [$C(CH_3)_3$], 38.6 [$C(CH_3)_3$], 44.6, 47.0 (2×C–N), 75.2 (COH), 121.8 [*C*CO(Q)], 123.5, 126.7, 127.2, 127.3, 134.3 [4×CH(Q), H*C*=*C*H], 145.1 [*C*N=C(Q)] and 157.7, 160.3 [CN(Q), CO(Q)]; *m/z* (%) 326 (MH^+, 60), 268 (24), 233 (100) and 215 (59).

2.1.7. Reaction of cyclohexa-1,4-diene with (3,4-dihydro-4-oxo-2-isopropylquinazolin-3-yl)nitrene Q^3N 39. A solution of 3-acetoxyaminoquinazolinone Q^3NHOAc **20** in dichloromethane (6 cm^3) was prepared from QNH_2 **19** (300 mg, 1.47 mmol) and LTA (687 mg, 1.55 mmol) according to general procedure A and filtered to remove lead di-acetate at −20°C. Following the published procedure,[10] triethylamine (1.47 g, 14.7 mmol) was added and the solution set aside at −20°C for 10 min before addition of cyclohexa-1,4-diene (235 mg, 0.28 cm^{-1}, 2.94 mmol). After warming to room temperature, the reaction was worked up as described under general procedure A. Column chromatography (4:1 light petroleum–ethyl acetate) of the crude product gave dienylamine **26** (5%) as a colourless oil, R_f 0.44 identical with that isolated previously. Further elution gave aziridine **27** (23%) as a colourless oil, R_f 0.38 identical with that isolated previously. Further elution gave Q^3H **23** (25 mg, 10%) as a colourless solid, R_f 0.10.

2.1.8. Reaction of Q^2NDOAc with cyclohexa-1,4-diene. 3-Amino-2-trifluoromethylquinazolinone **15** (70 mg, 0.3 mmol) was dissolved in $CDCl_3$ (2 cm^3) and D_2O (2 equiv., 11 μl) added. After stirring for 20 min NMR analysis showed the N*H*$_2$ protons had been replaced by **D**, the spectrum containing signals at δ 7.62 [1H, ddd, *J*=8.0, 4.5, 1.0 Hz, H-6(Q)], 7.80–7.90 [2H, m, H-7, H-8(Q)] and 8.27 [1H, d, *J*=8.0 Hz, H-5(Q)].

Aziridination of cyclohexa-1,4-diene using this deuterated material was carried out according to general procedure A using LTA (146 mg, 0.33 mmol), cyclohexa-1,4-diene (48 mg, 0.6 mmol), HMDS (121 mg, 0.75 mmol) in $CDCl_3$ (2 cm^3) as solvent. After stirring at ambient temperature for 1 h, a sample of the reaction mixture analysed by NMR showed a ~3:2 mixture of aziridine **25** and dienylamine **24** was present with the latter exhibiting signals at δ 5.45 (d, *J*=7.5 Hz, NH) and 4.10 (m, C*H*NH) with a relative integration of 1:1.

2.1.9. Ring-opening of aziridine 29 with thiophenolate. Aziridine **29** (108 mg, 0.33 mmol) was dissolved in acetonitrile (1 cm^3) containing 4-chlorothiophenol (48 mg, 0.33 mmol) and sodium hydroxide (10 mg, 0.25 mmol), and heated at 90°C in a sealed Young's tube for 1 h. During this period the solution turned cloudy. After cooling, saturated sodium hydrogen carbonate solution (10 cm^3) was added and the mixture extracted with ethyl acetate (2×10 cm^3) giving the crude product as a light brown solid after drying and evaporation of the solvent. Column chromatography (6:1 light petroleum–ethyl acetate) gave a mixture of the ring-opened product and excess 4-chlorothiophenol. Re-chromatography using kieselgel (8:1 light petroleum–ethyl acetate) gave 4-chlorothiophenol (R_f 0.68). Further elution gave arylsulphide **30** (71 mg, 46%) as a colourless oil, R_f 0.31. (Found: MH^+ 470.1669. $C_{25}H_{29}O_2N_3ClS$ requires *M* 470.1669); ν_{max} (cm^{-1}) 3400 w, 1695 s, 1680 s, 1670 m and 1595 s; δ_H (300 MHz) 0.92 [9H, s, $(CH_3)_3$], 2.05 (2H, m, incl. *J*=12.0, 6.0 Hz, NHCHCH_2), 2.09 (1H, ddd, *J*=18.0, 15.8, 2.0 Hz, C*H*HCHSAr), 2.61 (1H, dd, *J*=18.0, 5.5 Hz, CH*H*CHSAr), 3.35 (1H, ddd, *J*=15.8, 9.0, 5.5 Hz, CHSAr), 3.58 (1H, d, *J*=10.1 Hz, CHO*H*), 3.67 (1H, ddd, *J*=9.0, 6.0, 2.3 Hz, C*H*NH), 5.19 (1H, d, *J*=10.1 Hz, C*H*OH), 5.53 (1H, dd, *J*=9.9, 1.8 Hz, CH=C), 5.60 (1H, dd, *J*=9.9, 2.0 Hz, C=CH), 6.11 (1H, d, *J*=2.3 Hz, NH), 7.32 [2H, d, *J*=8.4 Hz, 2×CH(Ar)], 7.50 [1H, ddd, *J*=8.1, 6.9, 1.1 Hz, H-6(Q)], 7.57 [2H, d, *J*=8.4 Hz, 2×CH(Ar)], 7.70 [1H, d, *J*=8.2 Hz, H-8(Q)], 7.79 [1H, ddd, *J*=8.2, 6.9, 1.1 Hz, H-7(Q)] and 8.28 [1H, dd, *J*=8.1, 1.1 Hz, H-5(Q)]; *m/z* (%) 470 (MH^+, 100) and 307 (87).

2.1.10. Oxidation of sulphide 30 to the sulfoxide and thermal elimination to give a 1:1 mixture of dienylamine 9 diastereoisomers. Arylsulphide **30** (102 mg, 0.22 mmol) was stirred in glacial acetic acid (10 cm^3) containing hydrogen peroxide (7 mg/23 μl, 0.22 mmol) for 2 h. Addition of ethyl acetate (10 cm^3) and washing with saturated sodium hydrogen carbonate solution (10 cm^3) gave the crude product as a colourless oil after separation, drying and evaporation of the solvent. Column chromatography (6:1 light petroleum–ethyl acetate) gave the corresponding sulfoxide (49 mg, 46%) as a colourless oil, R_f 0.41.

The sulfoxide was heated at reflux in carbon tetrachloride (1 cm^3) under nitrogen for 2 h. After cooling, dichloromethane (10 cm^3) was added, the solution washed with saturated sodium hydrogen carbonate solution (10 cm^3), dried and evaporated to give the crude product as a colourless oil. Column chromatography (3:1 light petroleum–ethyl acetate) gave dienylamine **9** (21 mg, 64%) as a colourless oil, R_f 0.51, whose NMR spectrum showed the presence of a 1:1 mixture of diastereoisomers by comparison with that of **9** obtained above with observable signals for the additional diastereoisomer at δ 0.95 [9H, s, $(CH_3)_3$], 2.23 (1H, dddd, *J*=18.6, 6.6, ~3, ~3 Hz, C*H*H), 2.29 (1H, ddd, *J*=18.6, 4.8, 4.8 Hz, C*H*H), 3.56 (1H, d br, *J*~10 Hz, CHO*H*), 3.76 (1H,

struct. m, C*H*NH), 5.06 (1H, d, *J*=10.4 Hz, C*H*OH), 5.16 (1H, d, *J*=2.4 Hz, NH) and 6.22 (1H, dd, *J*~10, ~3 Hz, C*H*=C). A COSY spectrum showed that the signal at δ 3.76 was coupled to those at δ 2.23, 2.29, 5.16 and 5.93.

2.1.11. Reaction of 9,10-dihydroanthracene with Q^{3}NHOAc 20. General aziridination procedure A was followed in this reaction using Q^{3}NH$_2$ **19** (300 mg, 1.47 mmol), LTA (687 mg, 1.54 mmol), HMDS (474 mg, 2.94 mmol) and 9,10-dihydroanthracene (529 mg, 2.94 mmol) in dichloromethane (6 cm^3). Column chromatography (4:1 light petroleum–ethyl acetate) of the crude product (831 mg) gave unreacted 9,10-dihydroanthracene (428 mg, 81% recovered), R_f 0.68.

Further elution gave 9-(Q^3-amino)-9,10-dihydroanthracene **32** (60 mg, 12%) as a yellow oil, R_f 0.47. (Found: MH$^+$ 382.1914. $C_{25}H_{24}ON_3$ requires *M* 382.1914); ν_{max} (cm^{-1}) 1680 s, 1595 s and 1480 m; δ_H 0.66 (3H, d, *J*=6.9 Hz, C*H*$_3$CHCH$_3$), 0.94 (3H, d, *J*=6.9 Hz, CH$_3$CHC*H*$_3$), 2.75 [1H, h, *J*=6.9 Hz, C*H*(CH$_3$)$_2$], 3.97 (1H, d, *J*=18.2 Hz, C*H*H), 4.39 (1H, d, *J*=18.2 Hz, C*H*H), 5.40–5.44 (1H, m, C*H*NH), 5.52 (1H, d, *J*=1.9 Hz, NH), 6.69 [1H, d, *J*=7.3 Hz, CH(Ar)], 7.01 [1H, dd, *J*=7.3, 7.3 Hz, CH(Ar)], 7.17–7.41 [5H, m, 5×CH(Ar)], 7.41 [1H, ddd, *J*=8.2, 6.9, 1.2 Hz, H-6(Q)], 7.66 [1H, dd, *J*=8.2, 1.2 Hz, H-8(Q)], 7.74 [1H, ddd, *J*=8.2, 6.9, 1.2 Hz, H-7(Q)], 7.77–7.81 [1H, m, CH(Ar)] and 8.35 [1H, dd, *J*=8.2, 1.2 Hz, H-5(Q)]—additional unassigned signals were present at δ 8.17 (~0.1H, dd, *J*=8.0, ~2 Hz) and 8.30 (~0.2H, four lines); δ_C 18.8, 22.1 (2×CH$_3$), 30.7 [*C*H(CH$_3$)$_2$], 35.7 (CH$_2$), 63.0 (C–N), 121.1 [*C*CO(Q)], 126.5, 126.8, 127.4 [3×CH(Q)], 127.6, 127.9, 128.1, 128.3, 128.6, 128.8, 129.4, 129.6 [8×CH(Ar)], 134.5 [CH(Q)], 134.7, 135.0, 138.7, 138.8 [4×C(Ar)], 147.8 [*C*N=C(Q)], 162.7, 164.3 [CN(Q), CO(Q)]; *m*/*z* (%) 382 (MH$^+$, 100), 189 (27) and 181 (24).

2.1.12. Reaction of 9,10-dihydroanthracene with Q^{1}NHOAc 2–TTB. General aziridination procedure B was followed in this reaction using Q^{1}NH$_2$ **1** (100 mg, 0.41 mmol), LTA (188 mg, 0.43 mmol) and 9,10-dihydroanthracene (110 mg, 0.61 mmol) in dichloromethane (3 cm^3). After work up the crude product was isolated as a yellow solid (194 mg). Column chromatography (4:1 light petroleum–ethyl acetate) gave unreacted 9,10-dihydroanthracene (92 mg, 84% recovered), R_f 0.75. Further elution gave 9-(Q^1-amino)-9,10-dihydroanthracene **31** (17 mg, 10%) as a yellow oil, R_f 0.47. $[\alpha]_D^{20}$=+75.5 (*c*=1.0, EtOH); (Found: MH$^+$ 426.2182. $C_{27}H_{28}ON_3$ requires *M* 426.2182); ν_{max} (cm^{-1}) 1680 s, 1595 s and 1480 m; δ_H 0.71 [9H, s, (CH$_3$)$_3$], 2.58 (1H, d, *J*=8.5 Hz, CHO*H*), 4.05 (1H, d, *J*=18.5 Hz, C*H*H), 4.18 (1H, d, *J*=8.5 Hz, C*H*OH), 4.41 (1H, d br, *J*=18.5 Hz, CH*H*), 5.34 (1H, narrow struct. m, C*H*NH), 5.49 (1H, d, *J*=1.9 Hz, NH), 6.65 [1H, d, *J*=7.2 Hz, CH(Ar)], 7.00 [1H, dd, *J*=7.6, 7.6 Hz, CH(Ar)], 7.30–7.82 [9H, m, 3×CH(Q) and 6×CH(Ar)] and 8.28 [1H, dd, *J*=8.2, 1.0 Hz, H-5(Q)]; *m*/*z* (%) 426 (M$^+$, 100).

2.1.13. Reaction of Q^{3}NHOAc 20 with xanthene. General aziridination procedure A was followed in this reaction using Q^{3}NH$_2$ **19** (266 mg, 1.31 mmol), LTA (609 mg, 1.38 mmol), HMDS (528 mg, 3.20 mmol), xanthene (398 mg, 2.62 mmol) and dichloromethane (6 cm^3). Column chromatography (4:1 light petroleum–ethyl acetate) gave unreacted xanthene, R_f 0.74.

Further elution gave (Q^3)-amine-substituted xanthene **33** (59 mg, 13%) as a pale yellow oil, R_f 0.4. (Found: MH$^+$ 384.1711. $C_{24}H_{22}O_2N_3$ requires *M* 384.1712); ν_{max} (cm^{-1}) 1675 s, 1610 m, 1590 s and 1480 m; δ_H 0.61 (3H, d, *J*=6.8 Hz, C*H*$_3$CHCH$_3$), 0.76 (3H, d, *J*=6.8 Hz, CH$_3$CHC*H*$_3$), 2.63 [1H, h, *J*=6.8 Hz, C*H*(CH$_3$)$_2$], 5.29 (1H, d, *J*=2.0 Hz, C*H*NH), 5.38 (1H, d, *J*=2.0 Hz, NH), 6.44 [1H, d, *J*=7.5 Hz, CH(Ar)], 6.78 [1H, dd, *J*=7.2, 7.2 Hz, CH(Ar)], 7.01–7.26 [5H, m, 5×CH(Ar)], 7.33 [1H, ddd, *J*=8.0, 6.9, 1.3 Hz, H-6(Q)], 7.54 [1H, dd, *J*=8.2, 1.3 Hz, H-8(Q)], 7.57–7.63 [2H, m, H-7(Q) and CH(Ar)] and 8.18 [1H, dd, *J*=8.0, 1.3 Hz, H-5(Q)]; δ_C 18.8, 22.1 (2×CH$_3$), 30.9 [CH(CH$_3$)$_2$], 55.6 (C–N), 117.2, 118.4 [2×CH(Ar)], 120.4, 120.6, 121.1 [2×C–N(Ar), *C*CO(Q)], 123.7, 124.2, 126.6, 126.8 [4×CH(Ar–Q)], 127.2 [C–O(Ar)], 128.1, 129.8, 130.2, 130.4, 134.8, 135.2 [6×CH(Ar–Q)], 147.9 [*C*N=C(Q)], 153.2 [C–O(Ar)] and 162.7, 164.4 [CN(Q), CO(Q)]; *m*/*z* (%) 384 (MH$^+$, 1), 359 (23), 331 (28) and 330 (100).

2.1.14. Aziridination of 1,4-pentadiene with Q^{3}NHOAc 20. General aziridination procedure A was followed in this reaction using Q^{3}NH$_2$ **19** (200 mg, 0.96 mmol), LTA (459 mg, 1.03 mmol) and 1,4-pentadiene (118 mg/0.18 cm^3, 1.97 mmol) in dichloromethane (4 cm^3). The bulk of the major product, 3*H*-quinazolinone **23** was separated by trituration with ethyl acetate and the aziridine **35** obtained as a crystalline solid, containing <10% of **23** by evaporation of the ethyl acetate. A pure sample of aziridine **35** (73 mg, 28%) R_f 0.47, was obtained by column chromatography (3:1 light petroleum–ethyl acetate) as a colourless crystalline solid mp 42–44°C (from light petroleum–ethyl acetate). (Found: M$^+$ 269.1528. $C_{16}H_{19}ON_3$ requires *M* 269.1528); ν_{max} (cm^{-1}) 1670 s, 1620 m and 1590 s; δ_H 1.39 (3H, d, *J*=6.6 Hz, C*H*$_3$CHCH$_3$), 1.42 (3H, d, *J*=6.6 Hz, CH$_3$CHC*H*$_3$), 2.34 (1H, dddd, *J*~15, ~7, ~2, ~2 Hz, C*H*H), 2.46 (1H, dd, *J*=5.6, 1.9 Hz, azir. NC*H*), 2.51 (1H, dd, *J*=7.5, 1.5 Hz, azir. NC*H*), 2.87 (1H, dddd, *J*~15, ~7, ~2, ~2 Hz, CH*H*), 2.93–3.20 (1H, struct. m, azir. NCH), 3.71 [1H, sept, *J*=6.6 Hz, C*H*(CH$_3$)$_2$], 5.14 [1H, d, further split, *J*~10 Hz CH=C*H*H(*cis*)], 5.18 (1H, ddd, *J*~16, 3.5, 1.5 Hz, C=CH*H*), 5.91 (1H, ddt, *J*=16.2, 10.8, 6.9 Hz, C*H*=CH$_2$), 7.38 [1H, ddd, *J*=8.2, 6.6, 1.2 Hz, H-6(Q)], 7.58–7.70 [2H, struct. m, H-7 and H-8(Q)] and 8.17 [1H, dd, *J*=8.2, 1.2 Hz, H-5(Q)]; δ_C 21.1, 21.8 (2×CH$_3$), 31.2 [*C*H(CH$_3$)$_2$], 35.8 (CH$_2$), 40.9 (NCH$_2$), 45.3 (NCH), 117.9 (C=*C*H$_2$), 121.7 [*C*CO(Q)], 126.5, 127.1, 127.3, 133.7, 133.9 [4×CH(Q) and *C*=CH$_2$), 146.6 [*C*N=C(Q)] and 160.7, 161.6 [CN(Q), CO(Q)]; *m*/*z* (%) 269 (M$^+$, 41), 226 (37), 214 (100) and 213 (84).

2.1.15. Aziridination of 1,4-pentadiene with Q^{2}NHOAc 16. General aziridination procedure A was followed in this reaction using Q^{2}NH$_2$ **15** (225 mg, 0.98 mmol), LTA (459 mg, 1.03 mmol), HMDS (318 mg, 1.97 mmol) and 1,4-pentadiene (118 mg/0.18 cm^3, 1.97 mmol) in dichloromethane (5 cm^3). Column chromatography (3:1 light petroleum–ethyl acetate) of the crude product (156 mg) gave aziridine **34** (103 mg, 35%) R_f 0.71, as a colourless solid mp 44–45°C (from light petroleum–ethyl acetate). (Found:

M^+ 295.0932. $C_{14}H_{12}ON_3F_3$ requires *M* 295.0932); ν_{max} (cm^{-1}) 1690 s and 1610 m; δ_H 2.18 (1H, dd, *J*=4.7, 1.5 Hz, azir. NC*H*H), 2.28 (1H, dddd, *J*~15, ~7, ~2, ~2 Hz, C*H*H), 2.55 (1H, dddd, *J*~15, ~7, ~2, ~2 Hz, CH*H*), 3.41 (1H, d br, *J*=7.5 Hz, azir. NCH*H*), 3.72 (1H, 5 broad lines, azir. NCH), 5.10 (1H, d, further split, *J*=9.9 Hz, C=C*H*H), 5.15 (1H, d, further split, *J*=17.0 Hz, C=CH*H*), 5.86 (1H, ddt, *J*=17.0, 10.0, 6.6 Hz, C*H*=CH_2), 7.57 [1H, ddd, *J*=8.2, 4.4, 4.1 Hz, H-6(Q)], 7.79 [2H, 2 lines, br, *J*=4.0 Hz, H-7 and H-8(Q)] and 8.19 [1H, d, *J*=8.2 Hz, H-5(Q)]; δ_C 34.8, 36.0 (2×CH_2), 39.2 (NCH), 117.7 (C=*C*H_2), 123.4 [*C*CO(Q)], 126.8, 128.8, 129.4, 133.8, 135.0 [4×CH(Q), C=*C*H], 143.8 [CN(Q)], 144.3 [*C*N=C(Q)] and 161.2 [CO(Q)]—(*C*F_3 not visible); *m*/*z* (%) 296 (M^+, 100) and 214 (62).

2.1.16. Aziridination of allylbenzene with Q^3NHOAc 20. General aziridination procedure A was followed in this reaction using Q^3NH_2 **19** (266 mg, 1.31 mmol), LTA (609 mg, 1.38 mmol), HMDS (528 mg, 3.28 mmol) and allylbenzene (310 mg, 2.62 mmol) in dichloromethane (6 cm^3). Column chromatography (3:1 light petroleum–ethyl acetate) of the crude product (280 mg) gave aziridine **37** (117 mg, 34%) as a yellow oil, R_f 0.58. (Found: M^+ 319.1684. $C_{20}H_{21}ON_3$ requires *M* 319.1684); ν_{max} (cm^{-1}) 1670 s, 1620 m and 1595 s; δ_H 1.53 (3H, d, *J*=6.9 Hz, C*H*$_3$CHCH$_3$), 1.58 (3H, d, *J*=6.9 Hz, CH$_3$CHC*H*$_3$), 2.67 (1H, dd, *J*=6.0, 1.5 Hz, azir. NC*H*H), 2.69 (1H, dd, *J*=7.8, 1.5 Hz, azir. NCH*H*), 2.96 (1H, dd, *J*=14.2, 7.0 Hz, C*H*H), 3.33 (1H, dddd, *J*=7.8, 7.0, 6.0, 4.4 Hz, azir. NCH), 3.75 (1H, dd, *J*=14.2, 4.4 Hz, CH*H*), 3.83 [1H, h, *J*=6.9 Hz, C*H*(CH$_3$)$_2$], 7.47 [5H, struct. m, 5×CH(Ar)], 7.58 [1H, ddd, *J*=8.0, 6.6, 1.8 Hz, H-6(Q)], 7.77–7.90 [2H, m, H-7 and H-8(Q)] and 8.37 [1H, dd, *J*=8.0, 1.0 Hz, H-5(Q)]; δ_C 21.2, 21.7 [CH(*C*H$_3$)$_2$], 31.2 [*C*H(CH$_3$)$_2$], 37.9 (CH_2), 41.4 (NCH_2), 46.7 (NCH), 121.7 [*C*CO(Q)], 126.5, 127.1, 127.4, 128.8, 129.0, 129.5, 134.0 [5×CH(Ar) and 4×CH(Q)], 137.7 [C(Ar)], 146.7 [*C*N=C(Q)] and 160.8, 161.6 [CN(Q), CO(Q)]; *m*/*z* (%) 319 (M^+, 100) and 214 (48).

2.1.17. Aziridination of allylbenzene with Q^2NHOAc 16. General aziridination procedure A was followed in this reaction using Q^2NH_2 **15** (300 mg, 1.31 mmol), LTA (609 mg, 1.38 mmol) and allylbenzene (310 mg, 2.62 mmol) in dichloromethane (6 cm^3). Column chromatography (3:1 light petroleum–ethyl acetate) of the crude product (281 mg) gave aziridine **36** (154 mg, 28%) as a yellow oil, R_f 0.67. (Found: M^+ 345.1089. $C_{18}H_{14}ON_3F_3$ requires *M* 345.1088); ν_{max} (cm^{-1}) 1690 s and 1610 m; δ_H 2.14 (1H, dd, *J*=4.8, 1.2 Hz, azir. NC*H*H), 2.61 (1H, dd, *J*=14.5, 7.3 Hz, C*H*H), 3.15 (1H, dd, *J*=14.5, 5.3 Hz, CH*H*), 3.33 (1H, dd, *J*=7.3, 1.2 Hz, azir. NCH*H*), 3.84 (1H, 5 lines, br, azir. NCH), 7.16 [5H, struct. m, 5×CH(Ar)], 7.38–7.52 [1H, m, H-6(Q)], 7.62–7.75 [2H, struct. m, H-7 and H-8(Q)] and 8.09 [1H, d, *J*=7.8 Hz, H-5(Q)]; δ_C 35.1, 37.9 (2×CH_2), 40.4 (NCH), 123.1 [*C*CO(Q)], 126.5, 126.6, 128.5, 128.6, 128.9, 134.7 [5×CH(Ar) and 4×CH(Q)], 137.6 [C(Ar)], 143.3, 144.0 [CN(Q), *C*N=C(Q)] and 160.8 [CO(Q)]—(CF_3 not visible); *m*/*z* (%) 345 (M^+, 48), 214 (26) and 130 (100).

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