Thermal decomposition of *tert*-butyl *o*-(phenoxy)- and *o*-(anilino)-phenyliminoxyperacetates

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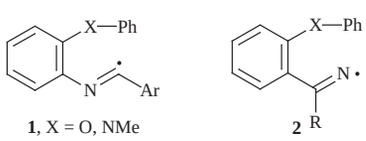
Some *o*-phenoxy- and *o*-anilino-substituted aryliminyl radicals have been generated by thermal decomposition of suitable *tert*-butyl iminoxyperacetates. The iminyls show no disposition to give 7-membered cyclisation on the phenyl group. In some cases, products have been found that can be rationalised through a 1,6-spirocyclisation of the iminyl radicals followed by homolytic 1,5-migration of the phenyl group from the aminic to the iminic nitrogen: this seems to be the first instance of such a process. Evidence has been found for the formation of imines through hydrogen abstraction by the iminyls; with two *o*-phenoxy-substituted peresters these imines have been unexpectedly isolated. The reactions have also afforded significant—in some cases major—amounts of other products (acridine, quinazolinone and indole derivatives) presumably deriving from carbon radicals: mechanisms are suggested to account for the formation of these compounds. The structure of the quinazolinone compound has been determined by X-ray crystallographic analysis.

Introduction

In the last decades, there has been an extraordinary growth in the chemistry of organic free-radicals, due to their remarkable potential in organic synthesis. The availability of a great body of kinetic data and a fine control of the regioselectivity and, very recently, the stereoselectivity of radical reactions have allowed the design of novel, exciting radical-based synthetic strategies.[1]

Among the various radical species investigated, we have drawn special attention to imidoyls; several papers have appeared dealing both with mechanistic aspects of their chemistry and their application to the synthesis of heterocyclic compounds.[2] Recently, we have investigated the possibility of 1,6- or 1,7-cyclisation on the aromatic ring of *o*-aryloxy- and *o*-arylamino benzimidoyl radicals **1** in the liquid phase.[3] The oxygen



1, X = O, NMe **2**

a: X = O, R = H **g**: X = NMe, R = H
b: X = O, R = Me **h**: X = NMe, R = Me
c: X = O, R = Ph **i**: X = NMe, R = Ph
d: X = NH, R = H **j**: X = NPh, R = H
e: X = NH, R = Me **k**: X = NPh, R = Me
f: X = NH, R = Ph **l**: X = NPh, R = Ph

derivatives furnished dibenzoxazepines, *via* 1,7-ring closure, and comparable amounts of benzophenones, through 1,6-spirocyclisation followed by 1,5-translocation of an aryl radical.

This result prompted us to address our studies to analogous iminyl radicals **2**. These species, almost completely neglected by organic chemists till the eighties,[4] are growing more popular mostly due to the work by Forrester,[5] McNab[6] and Zard,[7] who have proved their usefulness in synthetically interesting transformations.[8]

Iminyl radicals have been generated by many different methodologies, *i.e.* pyrolytic or photochemical reactions,[5,6,8b,d] addition of carbon radicals to nitriles,[8c,e,g–m] reduction of *N*-chloroketimines,[4a] hydrogen abstraction from imines,[4c] and reactions of tin radicals with oxime benzoates,[7f,h,i] sulfenimides,[7e,i] xanthic hydrazones,[7g,i,j,k] Barton esters[7c,e,i] and benzotriazolylimines.[8n] Although the sulfenimide method has been widely employed for synthetic purposes, it has been reported that sulfenimides of aromatic ketones are not readily accessible.[9] Therefore, according to the method of Forrester,[5] we decided to generate the iminyls **2** by thermal decomposition of suitable *tert*-butyl iminoxyperacetates. Here we report the data obtained by pyrolysis of a series of peresters and we discuss the fate of the resulting iminyls **2** and the possible intermediacy of other radical species.[10]

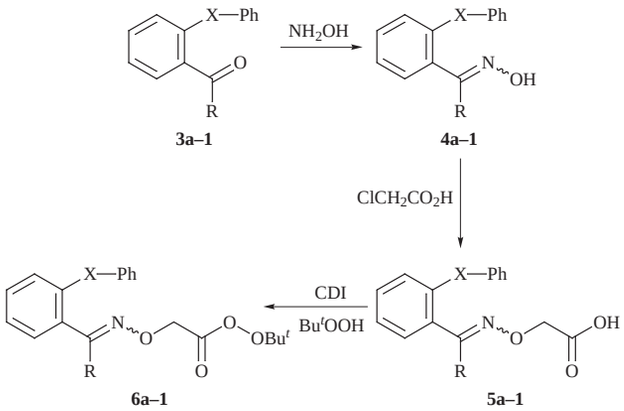
Results and discussion

The peracetates **6a**–**l** were prepared from the corresponding carbonyl compounds **3a**–**l** according to the literature.[5] The only exception was that the esterification was carried out directly by treatment of the acids with *tert*-butyl hydroperoxide and *N*,*N*′-carbonyldiimidazole (CDI) (Scheme 1).

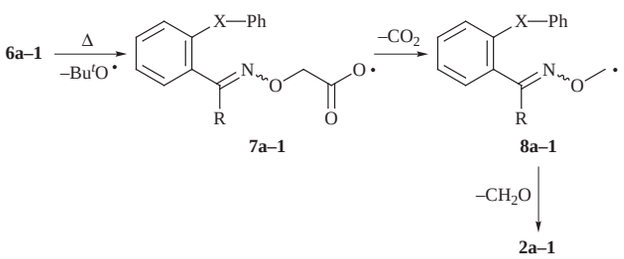
Thermal decomposition of the peresters **6a**–**l** furnishes the corresponding iminyls **2a**–**l** according to Scheme 2.

The easy homolysis of the oxygen–oxygen bond of **6a**–**l** followed by facile decarboxylation of **7a**–**l** generates radicals **8a**–**l**; in contrast, the loss of formaldehyde from **8a**–**l** seems to be not very fast. Indeed, the first attempts at decomposition of **6a**–**l**, performed under the conditions already reported (*i.e.* boiling benzene),[5] afforded products **9a**–**l** arising almost exclusively from coupling between **8a**–**l** and *tert*-butoxyl radicals (Scheme 3).

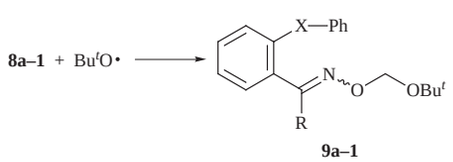
Further attempts at higher temperatures showed a decrease of the yields of **9a**–**l** with concomitant appearance of some other compounds. Therefore we decided to carry out the



Scheme 1

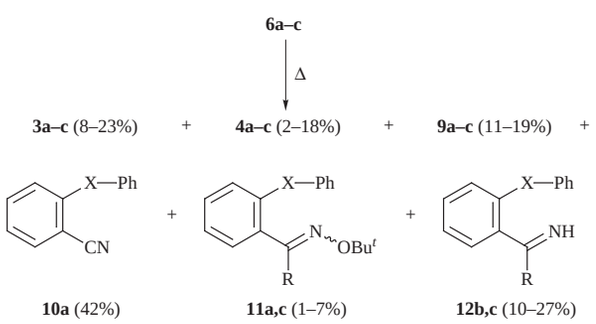


Scheme 2



Scheme 3

decompositions in boiling 0.02 M bromobenzene solutions.[11] Under these conditions, the oxygenated peresters **6a**–**c** gave the compounds shown in Scheme 4.

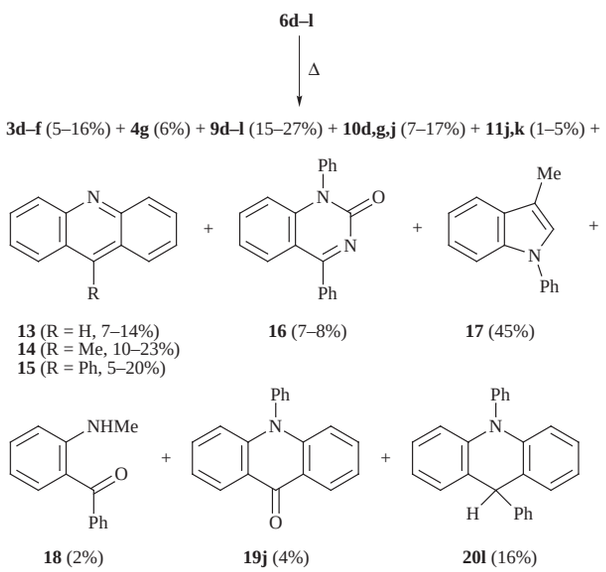


Scheme 4

With the exception of compounds **9a**–**c**, already discussed, all the other products can be accounted for through the corresponding iminyls **2a**–**c**. The carbonyl derivatives **3a**–**c** are probably the result of partial hydrolysis of the imines **12a**–**c**, which can derive from the iminyls **2a**–**c** by hydrogen abstraction. On the other hand, **3a**–**c** cannot arise from other imine derivatives, *e.g.* **4a**–**c**, **9a**–**c** or **11a**–**c**, because these compounds are completely stable under chromatographic conditions. The nitrile **10a** can be easily rationalised by an assisted β-fragmentation of the C–H bond of iminyl **2a**. The oximes **4a**–**c** could be the result of an oxidation process of the corresponding iminyl radicals, whereas the recombination of iminyls **2a**–**c** and *tert*-butoxyl radicals can lead to the *O*-*tert*-butyl oximes **11a**–**c**.

As far as the imines **12b**,**c** are concerned, their isolation was quite astonishing for at least two reasons. First, *N*-unsubstituted imines are generally very easily hydrolysed by column chromatography and, in fact, analogous derivatives were never isolated from peresters **6d–l** (see below). Second, it is amazing that iminyl radicals can abstract a hydrogen atom in the apparent absence of a true hydrogen donor. A possible explanation for their reasonable stability might be an efficient six-membered intramolecular hydrogen bonding between nitrogen and oxygen atoms. This is strongly supported by spectral evidence, *i.e.* the extremely broad N–H absorption band in the IR spectrum and the very high chemical shift value of the N–H proton (>14 δ) in the ^{1}H NMR spectrum. Furthermore, the mass spectra of the corresponding acids **5b**,**c** show a first important fragmentation involving loss of carbon dioxide and formaldehyde, which leads to the radical cations of the imines; it is worth noting that, from this point on, these spectra are identical to those of the imines **12b**,**c**.[12] It remains rather obscure which is the actual species acting as a hydrogen donor.

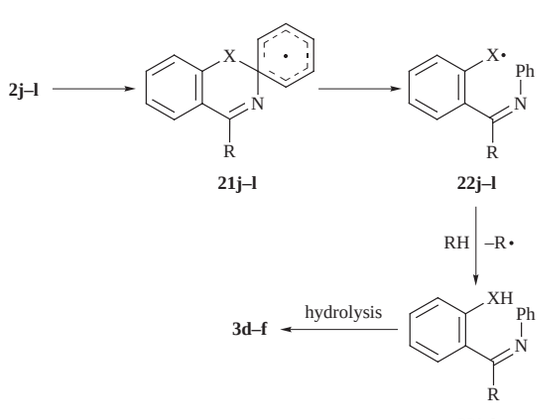
When the peresters **6d–l** were allowed to decompose under the same conditions, they afforded a wider set of products, as shown in Scheme 5.



Scheme 5

As far as compounds **3**, **4**, **9**, **10** and **11** are concerned, they can be accounted for as previously reported for the decomposition of the peresters **6a**–**c**. Nevertheless, it is worth pointing out that the carbonyl derivatives **3d**–**f** were also obtained from the peresters **6j**–**l**; this means that the aminic nitrogen has lost one of the two *N*-phenyl rings present in the starting materials. This is probably the result of an *ipso*-substitution process by the iminyl, as reported in Scheme 6.

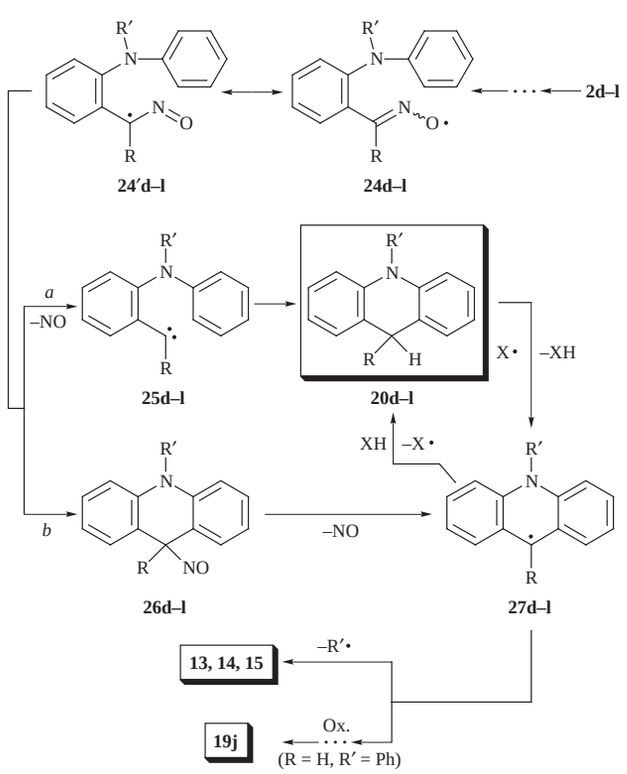
The spirocyclohexadienyl **21**, obtained by 1,6-cyclisation



Scheme 6

of the corresponding iminyl, can rearrange through a 1,5-migration of the phenyl ring from the aminic to the iminic nitrogen; the resulting aminyl **22** gives rise to the carbonyl compound **3** by hydrogen abstraction followed by hydrolysis of the imine **23**. An analogous rearrangement has been already suggested to explain some products obtained from *o*-(aryloxy)iminyls by flash vacuum pyrolysis (FVP)[10a] and from *o*-(aryloxy)imidoyls in solution.[3a,b] Radical migrations of phenyl rings are in general rather uncommon, particularly when involving heteroatoms.[13] To our knowledge, this result seems to be the first example concerning a 1,5-radical translocation of a phenyl group from nitrogen to nitrogen. The very small amounts of the ketone **18**, obtained from the perester **6i**, could also be explained with the same mechanism.

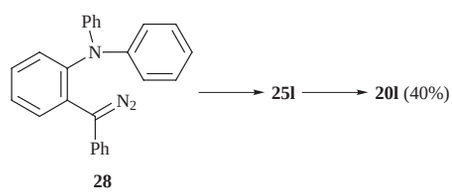
All the peresters **6d–l** gave rise to variable amounts of acridines **13**, **14** and **15**; these derivatives are always formed with loss of the substituent on the aminic nitrogen (H, Me, Ph) and retention of the substituent on the iminic carbon. The formation of these compounds is a very intriguing problem. The first mechanism considered was an electrocyclic one, similar to that initially suggested for analogous derivatives obtained by FVP.[10b] Nevertheless, the intervention of such a mechanism under our conditions is very unlikely. Furthermore, the isolation of compounds **19** and **20** from peresters **6j** and **6l**, respectively, led us to invent another pathway that could account for the formation of all the acridine derivatives (Scheme 7).



Scheme 7

If the oximes are the result of an oxidation process of the iminyls, as suggested above, their formation should involve the iminoxyl radicals **24**, whose mesomeric form **24′** can follow two different routes. In the first case (path *a*) **24′** can lose nitric oxide leading to the carbene **25**, whose cyclisation gives the dihydroacridines **20**, isolated in the case R = R′ = Ph (**20l**). Due to hydrogen abstraction from **20**, which produces radicals **27**, the acridines **13**, **14** and **15** can arise by loss of the radical R′, whereas **19j** can be the result of an oxidation process. Alternatively, **24′** can cyclise to **26** (path *b*); loss of nitric oxide from **26** leads to radicals **27** and thence to all the acridine derivatives.

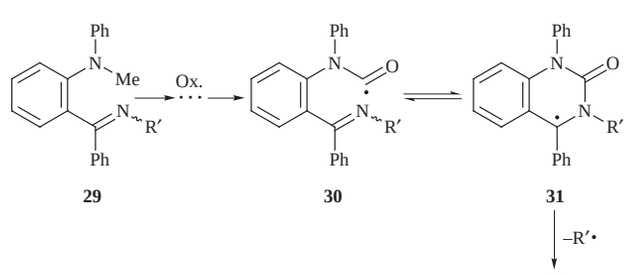
The importance of the mesomeric structure **24′** is evidenced by the higher yields of acridines when R is a phenyl group. In addition, in the case of perester **6k** a GC-MS analysis of the reaction mixture showed the presence of trace amounts of 9-methylene-10-phenyl-9,10-dihydroacridine: such a compound can very likely derive from **27k** by hydrogen abstraction from the methyl group. Finally, the carbene **25l** was generated by an independent route starting from the diazo compound **28**. From this experiment we obtained the dihydroacridine **20l** as a major product (Scheme 8). This result clearly shows the importance



Scheme 8

of carbene **25** in the formation of the acridine derivatives, although we cannot exclude the intervention to some extent of path *b*.[14]

The quinazolinone **16**, whose structure was confirmed by X-ray diffractometry (Fig. 1), was obtained from the peresters **6f**,**i**,**l**. In the case of **6i**, **16** could be accounted for by cyclisation of the carbamoyl radical **30** on an iminic double bond (Scheme 9).



Scheme 9

Indeed, it has been reported that, under our conditions, *N*-Me moieties are easily oxidised to carbamoyl radicals;[3b] moreover, an analogous mechanism has been already suggested for the formation of similar compounds in the oxidation of *N*-arylidene-*o*-(methylanilino)anilines.[3b] If this mechanism may be straightforward for the decomposition of **6i**, on the other hand it is rather difficult to understand how **16** can be formed from **6f**,**l**. Nevertheless, under these conditions we can postulate the intervention of such aminyl radicals as **32** (Scheme 10); these species can be generated from **6f**,**l** by hydrogen abstraction and 1,5-migration of a phenyl group, respectively (see Scheme 6). Although at such high temperatures *tert*-butoxyl radicals are known to generate methyl radicals easily, we did not expect to find products derived from coupling of the methyl radicals. On the other hand, the structure of **16** was unambiguously estab-

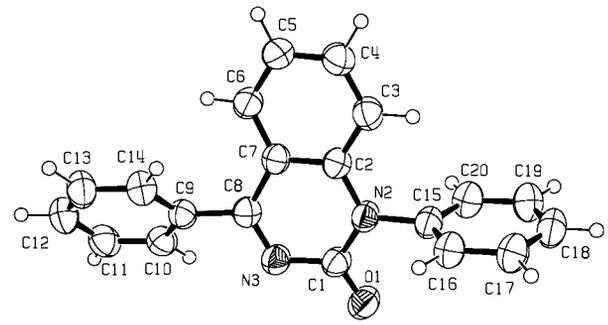
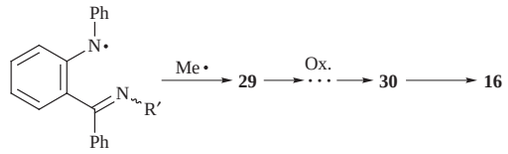


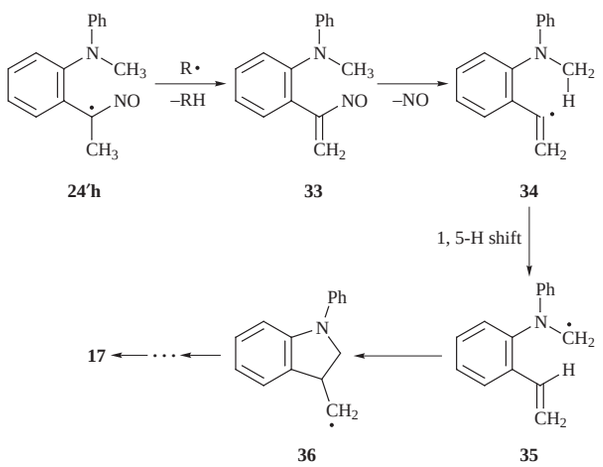
Fig. 1 The X-ray crystal structure of 1,4-diphenyl-1,2-dihydroquinazolin-2-one (**16**) showing the atom-numbering scheme



Scheme 10

lished and, as one can see, it contains one carbon atom more by comparison with the corresponding iminyls. This suggests that the aminyls **32** and the methyl radicals fulfil the kinetic conditions of the Ingold–Fischer effect for their coupling.[15] It is worth noting that **16** was exclusively obtained when R was a phenyl: this is probably due to the greater stability attained by radical **31** when a phenyl ring is linked to the carbon atom.

The last compound we have to account for is the indole derivative **17**, whose structure was unambiguously confirmed by spectral data comparison with an authentic specimen. It is not clear how it can be formed, especially in the light of the fact that it was isolated exclusively from the perester **6h**, *i.e.* only when the starting material bears two methyl groups. Our hypothesis that takes this evidence into account is shown in Scheme 11.



Scheme 11

The nitroso radical **24′h**, already suggested for the formation of the acridine derivatives (see Scheme 7), might undergo hydrogen abstraction to give the corresponding alkene **33** and, after loss of nitric oxide, the radical **34**; 1,5-hydrogen shift leads to radical **35**, which can account for **17** through a 5-*exo*-trig cyclisation process. Although this mechanism is not supported by any experimental evidence, nevertheless the intermediacy of radical **24′h** and its possibility of furnishing the alkene **33** have been shown in the discussion of the acridine compounds. The formation of **17** could be also accounted for through an intramolecular insertion of a carbene (**25h**) into the *N*-methyl group.[16] Although the intermediacy of the corresponding carbenic species has been suggested for the reaction of perester **6l** (see above), this conjecture would not explain why an analogous indole derivative was not obtained, for instance, from perester **6i** (R = Ph), *i.e.* when the formation of a carbene should be more favoured. We believe that the mechanism of Scheme 11 is the only plausible pathway accounting for the simultaneous presence of the two methyl groups.

Conclusions

In the light of these results, we can say that iminyl radicals **2a**–**l** are unable to give seven-membered cyclisation onto both the phenoxy and the phenylamino moieties. In a few cases (**2i**–**l**) we observed products that can be accounted for through 1,6-spirocyclisation followed by homolytic 1,5-migration of a phenyl group from the aminic nitrogen to the iminic one. This process resembles the behaviour already reported for *o*-(phenoxy)arylimidoyl radicals and, to our knowledge, it is unprecedented. Evidence was found for the formation of the imines **12** through hydrogen abstraction by the iminyls; surprisingly, we isolated two of them in the case of iminyls **2b**,**c**. The presence of hydrogen-abstraction products in a very poor hydrogen donor medium lets us suppose that the homolytic aromatic substitution should be a very slow reaction. Finally, from decomposition of the peresters **6a**–**l** some other products were isolated, probably as a result of carbon-centred radicals; mechanisms were suggested to account for their formation. Studies are underway to investigate the behaviour of the same iminyl radicals when generated under milder, non-oxidative conditions, *i.e.* from the corresponding oxime benzoates with tributyltin radicals.[7f,h,i] Studies are also in progress on analogous sulfur-containing iminyls to investigate the possibility of intramolecular homolytic substitution at the sulfur atom.

Experimental

General procedures

Melting points were determined on an Electrothermal capillary apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded in deuterochloroform on Varian EM 360L (60 MHz), Gemini 200 (200 MHz) or Gemini 300 (300 MHz) instruments, using tetramethylsilane as an internal standard. Coupling constants *J* are given in Hz. Low and high resolution mass spectra were performed with a VG 7070E spectrometer by electron impact with a beam energy of 70 eV. GC-MS analyses were carried out on a Carlo Erba AUTO/HRGC/MS-QMD 1000 instrument equipped with a Quadrex capillary column (007, 25 m × 0.25 mm i.d.) and a NIST/NBS library. IR spectra were recorded in chloroform solution on a Perkin-Elmer 257 spectrophotometer. Column chromatography was carried out on silica gel (ICN Silica, 63–200, 60 Å), using light petroleum (bp 40–70 °C) and a light petroleum–diethyl ether gradient (from 0 up to 100% diethyl ether) as eluent. All the organic phases were dried over anhydrous sodium sulfate. Previously reported reaction products were identified by spectral comparison and mixed mp determination with authentic specimens. When elemental analyses were not performed, the purity of the compounds was confirmed by the absence of any significant extraneous peak in the ^{1}H NMR spectra and/or by GC-MS analysis.

Starting materials

2-Chlorobenzophenone, *N*-methylaniline and 2-chlorobenzoic acid were commercially available (Aldrich). 2-Phenoxybenzaldehyde (**3a**),[17] 1-(2-phenoxyphenyl)ethan-1-one oxime (**4b**),[18] 2-anilinobenzaldehyde (**3d**),[19] 1-(2-anilinophenyl)ethan-1-one (**3e**),[20] (2-anilinophenyl)(phenyl)methanone (**3f**),[20] 1-(2-iodophenyl)ethan-1-one,[21] 2-(diphenylamino)benzaldehyde (**3j**),[22] [2-(diphenylamino)phenyl](phenyl)methanone (**3l**)[23] and tosylhydrazine[24] were prepared according to the literature.

(2-Phenoxyphenyl)(phenyl)methanone 3c

Phenol (18.8 g, 200 mmol) was dissolved in a solution of KOH (11.2 g, 200 mmol) in absolute ethanol (100 cm^3). 2-Chlorobenzophenone (34.3 g, 159 mmol) was then added and the solvent was removed under vacuum. The resulting mixture was kept overnight at 200–210 °C. After cooling, dichloromethane and water were added and the organic phase separated and dried. The residue was chromatographed to give **3c** (20.4 g, 47%) as an oil (Found: C, 83.4; H, 5.15. $C_{19}H_{14}O_2$ requires C, 83.2; H, 5.15%); ν_{max}/cm^{-1} 3000, 1670, 1600, 1480, 1450, 1320 and 1300; δ_H(200 MHz) 6.77–6.86 (2 H, m), 6.94–7.10 (2 H, m), 7.16–7.30 (3 H, m), 7.36–7.60 (5 H, m) and 7.79–7.87 (2 H, m); *m*/*z* 274.1000 (M$^+$, 100%. $C_{19}H_{14}O_2$ requires 274.0994), 273 (86), 197 (92), 105 (85), 77 (87) and 51 (33).

N-Methyl-N-phenylanthranilic acid

Following the procedure by Allen and McKee,[25] a mixture of *N*-methylaniline (177.7 g, 1.66 mol), 2-chlorobenzoic acid (41.0 g, 0.26 mol), anhydrous potassium carbonate (41.0 g, 0.30 mol) and copper powder (1.0 g) was kept at 200 °C for 3 h. The excess of *N*-methylaniline was evaporated off and the residue was refluxed for 15 min with water (500 cm^3) and activated carbon. The hot suspension was filtered and conc. hydrochloric acid was added to the filtrate up to a slightly acid pH value. The solution was extracted with dichloromethane, the organic phase was dried, the solvent removed and the residue chromatographed to give the title compound (47.2 g, 80%), mp 103–105 °C (lit.,[26] 104–104.5 °C).

Methyl N-methyl-N-phenylanthranilate

Methyl iodide (11.7 g, 87.0 mmol) was added dropwise at r.t. to a stirred solution of potassium carbonate (10.7 g, 77.9 mmol) and *N*-methyl-*N*-phenylanthranilic acid (17.7 g, 77.9 mmol) in DMF (174 cm^3). The mixture was mechanically stirred for 12 h. The solvent was evaporated and the residue extracted with diethyl ether; the organic phase was dried and the solvent removed to give the title compound (17.8 g, 94%) as an oil (Found: C, 75.0; H, 6.3; N, 5.8. $C_{15}H_{15}NO_2$ requires C, 74.7; H, 6.3; N, 5.8%); ν_{max}/cm^{-1} 3050, 3000, 2950, 2880, 1720 and 1600; δ_H(60 MHz) 3.23 (3 H, s, N-Me), 3.53 (3 H, s, COOMe) and 6.53–7.97 (9 H, m, Ar-H); *m/z* 241.1112 (M^+, 100%. $C_{15}H_{15}NO_2$ requires 241.1103), 226 (6), 210 (27), 208 (28), 195 (9), 182 (22), 180 (27), 167 (19) and 77 (25).

[2-(Methylanilino)phenyl]methanol

A solution of methyl *N*-methyl-*N*-phenylanthranilate (23.0 g, 95.7 mmol) in anhydrous THF was added dropwise at 0 °C to a stirred solution of $LiAlH_4$ (4 × 1 g pellets, 105.3 mmol) in THF. After 1 h, ethyl acetate (30 cm^3) and then water (20 cm^3) were added cautiously to the solution. After filtration and removal of the solvent, the residue was extracted with diethyl ether; the organic phase was dried and the solvent removed to give the title compound (16.9 g, 83%) as an oil (Found: C, 79.1; H, 7.1; N, 6.6. $C_{14}H_{15}NO$ requires C, 78.8; H, 7.1; N, 6.6%); ν_{max}/cm^{-1} 3600, 3400, 3050, 2950, 2890, 1600 and 1490; δ_H(300 MHz) 2.62 (1 H, br s, CH_2OH), 3.27 (3 H, s, N-Me), 4.60 (2 H, s, CH_2OH), 6.63 (2 H, m, Ar-H), 6.81 (1 H, dddd, J_1, J_2 7.4, J_3, J_4 0.9, Ar-H), 7.17–7.27 (3 H, m, Ar-H), 7.31–7.43 (2 H, m, Ar-H) and 7.54–7.59 (1 H, m, Ar-H); *m/z* 213.1158 (M^+, 98%. $C_{14}H_{15}NO$ requires 213.1154), 195 (18), 194 (100), 182 (13), 180 (46), 167 (17) and 77 (26).

2-(Methylanilino)benzaldehyde 3g

A solution of [2-(methylanilino)phenyl]methanol (10.0 g, 47.1 mmol) in dichloromethane (95 cm^3) was added dropwise at r.t. to a stirred suspension of CrO_3 (28.3 g, 282 mmol) in pyridine (45 cm^3) and dichloromethane (700 cm^3). After 1 h, the mixture was filtered on silica gel, the solvent was evaporated and the residue chromatographed to give **3g** (5.0 g, 50%), mp 39.5–40.5 °C (Found: C, 80.0; H, 6.2; N, 6.6. $C_{14}H_{13}NO$ requires C, 79.6; H, 6.2; N, 6.6%); ν_{max}/cm^{-1} 3000, 1690, 1600 and 1480; δ_H(60 MHz) 3.28 (3 H, s, N-Me), 6.62–8.10 (9 H, m, Ar-H) and 10.20 (1 H, s, CHO); *m/z* 211.0995 (M^+, 79%. $C_{14}H_{13}NO$ requires 211.0997), 198 (18), 197 (37), 181 (28), 180 (100), 168 (47), 167 (21) and 77 (31).

1-[2-(Methylanilino)phenyl]ethan-1-one 3h

A mixture of *N*-methylaniline (35.5 g, 180 mmol), 2-iodoacetophenone (44.1 g, 180 mmol), potassium carbonate (17.7 g), copper powder (1.5 g) and di-*n*-butyl ether (125 cm^3) was refluxed for 24 h under a nitrogen atmosphere. The hot mixture was filtered and the solvent was removed. The residue was chromatographed to give **3h** (37.7 g, 93%) as an oil (Found: C, 80.3; H, 6.7; N, 6.2. $C_{15}H_{15}NO$ requires C, 80.0; H, 6.7; N, 6.2%); ν_{max}/cm^{-1} 3000, 1680, 1600, 1480 and 1340; δ_H(300 MHz) 2.42 (3 H, s, COMe), 3.30 (3 H, s, N-Me), 6.70–6.76 (2 H, m, Ar-H), 6.79–6.86 (1 H, m, Ar-H), 7.20–7.34 (4 H, m, Ar-H), 7.49–7.56 (1 H, m, Ar-H) and 7.66 (1 H, ddd, J_1 7.6, J_2 1.5, J_3 0.4, Ar-H); *m/z* 225.1156 (M^+, 100%. $C_{15}H_{15}NO$ requires 225.1154), 210 (70), 208 (46), 195 (9), 193 (9), 182 (19), 180 (16), 167 (27) and 77 (39).

[2-(Methylanilino)phenyl](phenyl)methanol

A solution of bromobenzene (5.7 g, 36 mmol) in anhydrous THF was added dropwise under a nitrogen atmosphere to a stirred suspension of activated magnesium turnings (0.87 g, 36 mmol) in THF. The resulting mixture was refluxed until a homogeneous solution was obtained. After cooling with an ice-bath, a solution of **3g** (7.6 g, 36 mmol) in THF was added dropwise at 0 °C. The resulting mixture was refluxed for 2 h and then quenched with water and aqueous ammonium chloride. After extraction with diethyl ether, the organic phase was dried, the solvent was removed and the residue chromatographed to give the title compound (9.7 g, 93%) as an oil (Found: C, 82.7; H, 6.6; N, 4.8. $C_{20}H_{19}NO$ requires C, 83.0; H, 6.6; N, 4.8%); ν_{max}/cm^{-1} 3600, 3400, 2980, 2880, 1600 and 1490; δ_H(300 MHz) 2.63 (1 H, br s, CHO*H*), 2.90 (3 H, s, N-Me), 5.92 (1 H, s, C*H*OH), 6.52–6.59 (2 H, m, Ar-H), 6.77 (1 H, dddd, J_1, J_2 7.2, J_3, J_4 0.7, Ar-H), 7.08–7.40 (10 H, m, Ar-H) and 7.62–7.68 (1 H, m, Ar-H); *m/z* 289.1471 (M^+, 50%. $C_{20}H_{19}NO$ requires 289.1467), 270 (100), 256 (17), 194 (58), 181 (11), 167 (12), 105 (21), 91 (14) and 77 (35).

[2-(Methylanilino)phenyl](phenyl)methanone 3i

Following the procedure previously described for **3g**, the ketone **3i** was isolated (1.8 g, 31%). Better yields were obtained by methylation of **3f** (see above) according to the following procedure. Finely powdered potassium hydroxide (15.9 g) was added to a solution of **3f** in acetone (135 cm^3) and the resulting mixture was refluxed for 10 min. After cooling, dimethyl sulfate (26.8 g) was added dropwise. After a 15 min reflux, the mixture was poured into water and extracted with diethyl ether. The organic phase was dried, the solvent was removed and the residue chromatographed to give **3i** (14.3 g, 79%), mp 107–108.5 °C (Found: C, 83.9; H, 5.95; N, 4.9. $C_{20}H_{17}NO$ requires C, 83.6; H, 5.95; N, 4.9%); ν_{max}/cm^{-1} 3000, 1660, 1600 and 1480; δ_H(300 MHz) 3.05 (3 H, s, N-Me), 6.46–6.52 (2 H, m, Ar-H), 6.70 (1 H, dddd, J_1, J_2 7.2, J_3, J_4 1.0, Ar-H), 7.02–7.09 (2 H, m, Ar-H), 7.26–7.34 (4 H, m, Ar-H), 7.45 (1 H, dddd, J_1 7.3, J_2 6.7, J_3, J_4 1.2, Ar-H) and 7.50–7.58 (4 H, m, Ar-H); *m/z* 287.1312 (M^+, 100%. $C_{20}H_{17}NO$ requires 287.1310), 270 (100), 210 (21), 182 (9), 180 (10), 167 (16), 105 (12), 91 (17) and 77 (49).

1-[2-(Diphenylamino)phenyl]ethan-1-one 3k

The procedure previously described for **3h** was followed (see above), with the exception that, after 5 days at reflux, additional 5 equiv. of K_2CO_3, iodobenzene and copper were added and the mixture was refluxed for another week. Under these conditions, ketone **3e** (13.1 g, 62 mmol) gave **3k** (8.1 g, 46%), mp 72–74 °C (from light petroleum) (Found: C, 84.0; H, 5.95; N, 4.9. $C_{20}H_{17}NO$ requires C, 83.6; H, 5.95; N, 4.9%); ν_{max}/cm^{-1} 2920, 1680, 1590, 1570, 1470 and 1440; δ_H(200 MHz) 2.37 (3 H, s, Me), 6.93–7.05 (6 H, m, Ar-H), 7.12–7.28 (6 H, m, Ar-H), 7.43 (1 H, ddd, J_1 7.8, J_2 7.4, J_3 1.7, Ar-H) and 7.52 (1 H, dd, J_1 7.6, J_2 1.6, Ar-H); *m/z* 287.1315 (M^+, 100%. $C_{20}H_{17}NO$ requires 287.1310), 272 (23), 244 (58), 243 (11), 242 (6), 241 (7), 196 (11), 194 (11), 167 (14), 166 (13) and 77 (7).

General procedure for the synthesis of the oximes 4a,c–l

According to a standard procedure,[27] a solution of the carbonyl compound and hydroxylamine hydrochloride (same amount in weight as the former) in a 10:1 v/v mixture of ethanol and pyridine (with the latter in the same amount in volume as the carbonyl derivative) was refluxed under mechanical stirring for a few hours. The mixture was poured into ice–water, acidified to

pH ~ 5 with conc. hydrochloric acid and extracted with diethyl ether. The organic phase was dried, the solvent was removed and the residue chromatographed or crystallised.

2-Phenoxybenzaldehyde oxime 4a. After 1 h and without chromatography, **3a** (19.0 g, 96 mmol) gave **4a** (20.0 g, 98%), mp 78–80 °C (from light petroleum–benzene) (Found: C, 73.0; H, 5.2; N, 6.6. $C_{13}H_{11}NO_2$ requires C, 73.2; H, 5.2; N, 6.6%); ν_{max}/cm^{-1} 3580, 3320, 1590, 1480 and 1450; δ_H(200 MHz) 6.91 (1 H, dd, J_1 8.1, J_2 1.0, Ar-H), 6.96–7.02 (2 H, m, Ar-H), 7.08–7.20 (2 H, m, Ar-H), 7.29–7.40 (3 H, m, Ar-H), 7.85 (1 H, dd, J_1 7.7, J_2 1.6, Ar-H), 8.45 (1 H, br s, OH) and 8.51 (1 H, s, CH=N); *m/z* 213.0786 (M$^+$, 57%. $C_{13}H_{11}NO_2$ requires 213.0790), 196 (50), 181 (22), 167 (15), 91 (100), 77 (61) and 51 (35).

(2-Phenoxyphenyl)(phenyl)methanone oxime 4c. After 1 h and without chromatography, **3c** (20.4 g, 75 mmol) yielded **4c** (20.0 g, 93%), mp 138–140 °C (from light petroleum–benzene) (Found: C, 79.1; H, 5.2; N, 4.8. $C_{19}H_{15}NO_2$ requires C, 78.9; H, 5.2; N, 4.8%); ν_{max}/cm^{-1} 3580, 3300, 3000, 1600, 1580, 1480, 1450, 1320, 1310, 1160, 990 and 910; δ_H(200 MHz) 6.87–7.07 (4 H, m, Ar-H), 7.15–7.44 (8 H, m, Ar-H), 7.45–7.53 (2 H, m, Ar-H) and 8.88 (1 H, br s, OH); *m/z* 289.1105 (M$^+$, 51%. $C_{19}H_{15}NO_2$ requires 289.1103), 272 (100), 196 (20), 181 (19), 105 (56), 91 (68), 77 (72) and 51 (42).

2-Anilinobenzaldehyde oxime 4d. After 1 h, **3d** (16.8 g, 85 mmol) gave **4d** (15.0 g, 83%), mp 47–49 °C (Found: C, 73.9; H, 5.7; N, 13.15. $C_{13}H_{12}N_2O$ requires C, 73.6; H, 5.7; N, 13.2%); ν_{max}/cm^{-1} 3570, 3300, 3000, 1600, 1570, 1460 and 1320; δ_H(300 MHz) 6.82 (1 H, ddd, J_1, J_2 7.1, J_3 1.3, Ar-H), 7.09 (1 H, dddd, J_1, J_2 7.0, J_3, J_4 1.0, Ar-H), 7.12–7.40 (8 H, m, Ar-H + OH), 8.30 (1 H, s, CH=N) and 8.82 (1 H, br s, NH); *m/z* 212.0947 (M$^+$, 100%. $C_{13}H_{12}N_2O$ requires 212.0950), 195 (80), 194 (24), 193 (14), 180 (79), 167 (31), 166 (10) and 77 (21).

1-(2-Anilinophenyl)ethan-1-one oxime 4e. After 1 h, **3e** (10.0 g, 47 mmol) yielded **4e** (17.2 g, 85%) as an oil (Found: C, 74.6; H, 6.25; N, 12.35. $C_{14}H_{14}N_2O$ requires C, 74.3; H, 6.25; N, 12.4%); ν_{max}/cm^{-1} 3580, 3300, 3000, 1600, 1580 and 1450; δ_H(300 MHz) 2.40 (3 H, s, Me), 6.87–6.93 (1 H, m, Ar-H), 7.00–7.06 (1 H, m, Ar-H), 7.16–7.35 (5 H, m, Ar-H), 7.38 (1 H, dd, J_1 8.3, J_2 1.3, Ar-H), 7.47 (1 H, dd, J_1 7.9, J_2 1.6, Ar-H), 7.85 (1 H, br s) and 8.85 (1 H, br s); *m/z* 226.1108 (M$^+$, 100%. $C_{14}H_{14}N_2O$ requires 226.1106), 209 (74), 208 (31), 207 (35), 194 (60), 180 (38), 167 (46), 166 (21) and 77 (27).

(2-Anilinophenyl)(phenyl)methanone oxime 4f. After 1 h, **3f** (19.2 g, 70 mmol) yielded **4f** (17.2 g, 85%), mp 143–145 °C (Found: C, 79.3; H, 5.6; N, 9.75. $C_{19}H_{16}N_2O$ requires C, 79.1; H, 5.6; N, 9.7%); ν_{max}/cm^{-1} 3560, 3400, 3000, 1600, 1580, 1500, 1450 and 1310; δ_H(200 MHz) 6.13 (1 H, br s, OH), 6.85–7.60 (14 H, m, Ar-H) and 9.70 (1 H, br s, NH); *m/z* 288.1266 (M$^+$, 76%. $C_{19}H_{16}N_2O$ requires 288.1263), 269 (100), 256 (38), 196 (17), 167 (28) and 77 (21).

2-(Methylanilino)benzaldehyde oxime 4g. After 30 min and without chromatography, **3g** (10.6 g, 50 mmol) yielded **4g** (9.7 g, 86%), mp 107–109 °C (from light petroleum–benzene) (Found: C, 74.6; H, 6.25; N, 12.35. $C_{14}H_{14}N_2O$ requires C, 74.3; H, 6.25; N, 12.4%); ν_{max}/cm^{-1} 3580, 3320, 3000, 1600, 1490 and 1340; δ_H(300 MHz) 3.25 (3 H, s, Me), 6.60–6.66 (2 H, m, Ar-H), 6.76–6.82 (1 H, m, Ar-H), 7.16–7.33 (4 H, m, Ar-H), 7.41–7.48 (1 H, m, Ar-H), 7.88–7.93 (1 H, m, Ar-H), 8.16 (1 H, s, OH) and 8.24 (1 H, s, N=CH); *m/z* 226.1102 (M$^+$, 39%. $C_{14}H_{14}N_2O$ requires 226.1106), 209 (100), 194 (87), 180 (61) and 77 (26).

1-[2-(Methylanilino)phenyl]ethan-1-one oxime 4h. After 30 min and without chromatography, **3h** (19.8 g, 88 mmol) yielded **4h** (17.2 g, 81%) as an oil (Found: C, 74.8; H, 6.7; N, 11.65. $C_{15}H_{16}N_2O$ requires C, 75.0; H, 6.7; N, 11.7%); δ_H(200 MHz) 2.06 (3 H, s, C-Me), 3.19 (3 H, s, N-Me), 6.66–6.83 (3 H, m, Ar-H), 7.14–7.48 (6 H, m, Ar-H) and 8.78 (1 H, br s, OH); *m/z* 240.1266 (M$^+$, 31%. $C_{15}H_{16}N_2O$ requires 240.1263), 223 (62), 208 (100), 194 (44), 193 (16), 180 (14) and 77 (20).

[2-(Methylanilino)phenyl](phenyl)methanone oxime 4i. After 30 min, **3i** (9.5 g, 33 mmol) yielded **4i** (7.6 g, 80%) as a mixture of the *E*- and *Z*-isomers, which were partially separated by chromatography (Found: C, 79.65; H, 6.0; N, 9.25. $C_{20}H_{18}N_2O$ requires C, 79.4; H, 6.0; N, 9.3%). Major isomer, mp 119–121 °C; ν_{max}/cm^{-1} 3570, 3300, 3000, 1605, 1595 and 1490; δ_H(200 MHz) 2.90 (3 H, s, NMe), 6.52–6.60 (2 H, m, Ar-H), 6.70 (1 H, dddd, J_1 7.4, J_2 7.2, J_3, J_4 0.9, Ar-H), 7.02–7.12 (2 H, m, Ar-H), 7.20–7.54 (9 H, m, Ar-H) and 8.22 (1 H, br s, OH); *m/z* 302.1422 (M$^+$, 74%. $C_{20}H_{18}N_2O$ requires 302.1419), 285 (100), 270 (79), 256 (22), 193 (14), 180 (21), 167 (12), 91 (17) and 77 (31). Minor isomer, mp 182–184 °C; ν_{max}/cm^{-1} 3580, 3300, 3000, 1605, 1595 and 1500; δ_H(200 MHz) 2.67 (3 H, s, NMe), 6.26–6.34 (2 H, m, Ar-H), 6.70 (1 H, dddd, J_1 7.4, J_2 7.2, J_3, J_4 1.0, Ar-H), 7.03–7.38 (9 H, m, Ar-H), 7.48 (1 H, ddd, J_1, J_2 7.7, J_3 1.5, Ar-H), 7.63 (1 H, dd, J_1 7.1, J_2 1.2, Ar-H) and 8.20 (1 H, br s, OH); *m/z* 302.1423 (M$^+$, 22%. $C_{20}H_{18}N_2O$ requires 302.1419), 285 (100), 270 (63), 256 (15), 193 (15), 180 (30), 167 (22), 91 (51) and 77 (71).

2-(Diphenylamino)benzaldehyde oxime 4j. After 1 h, **3j** (11.9 g, 43 mmol) yielded **4j** (10.5 g, 84%), mp 123–125 °C (from light petroleum–benzene) (Found: C, 79.2; H, 5.6; N, 9.7. $C_{19}H_{16}N_2O$ requires C, 79.1; H, 5.6; N, 9.7%); ν_{max}/cm^{-1} 3580, 3320, 1590 and 1490; δ_H(300 MHz) 6.92–7.02 (6 H, m, Ar-H), 7.11–7.26 (6 H, m, Ar-H), 7.34–7.42 (1 H, m, Ar-H), 7.81 (1 H, dd, J_1 7.7, J_2 1.2, Ar-H) and 8.22–8.28 (2 H, s + br s, N=CH + OH); *m/z* 288.1266 (M$^+$, 100%. $C_{19}H_{16}N_2O$ requires 288.1263), 271 (64), 270 (24), 269 (17), 256 (99), 243 (13), 180 (22), 167 (16), 77 (22) and 51 (21).

1-[2-(Diphenylamino)phenyl]ethan-1-one oxime 4k. After 12 h, **3k** (8.1 g, 28 mmol) gave **4k** (8.5 g, 99%) as a glassy solid, 5 : 1 mixture of the *E*- and *Z*-isomers (Found: C, 79.6; H, 6.0; N, 9.25. $C_{20}H_{18}N_2O$ requires C, 79.4; H, 6.0; N, 9.3%); δ_H(200 MHz) 1.75 (3 H, s, C-Me, minor isomer), 1.95 (3 H, s, C-Me, major isomer), 6.90–7.38 (14 H, m, Ar-H) and 7.74 (1 H, br s, OH, both isomers); *m/z* 302.1424 (M$^+$, 100%. $C_{20}H_{18}N_2O$ requires 302.1419), 285 (48), 270 (80), 256 (12), 243 (13), 210 (16), 195 (17), 167 (17), 77 (21) and 51 (15).

[2-(Diphenylamino)phenyl](phenyl)methanone oxime 4l. After 24 h, **3l** (8.7 g, 25 mmol) yielded **4l** (7.0 g, 77%) as a mixture of the *E*- and *Z*-isomers, which were partially separated by chromatography (Found: C, 82.6; H, 5.5; N, 7.7. $C_{25}H_{20}N_2O$ requires C, 82.4; H, 5.5; N, 7.7%). Major isomer, mp 145–147 °C (from light petroleum–benzene); ν_{max}/cm^{-1} 3560, 3300, 1590 and 1480; δ_H(300 MHz) 6.80–7.42 (19 H, m, Ar-H) and 8.05 (1 H, br s, OH); *m/z* 364.1577 (M$^+$, 92%. $C_{25}H_{20}N_2O$ requires 364.1576), 347 (36), 332 (100), 272 (20), 256 (13), 196 (10), 167 (12), 77 (16) and 51 (9). Minor isomer, mp 158–159 °C (from light petroleum–benzene); ν_{max}/cm^{-1} 3560, 3300, 1590 and 1480; δ_H(300 MHz) 6.67–7.50 (19 H, m, Ar-H) and 8.16 (1 H, br s, OH); *m/z* 364.1578 (M$^+$, 98%. $C_{25}H_{20}N_2O$ requires 364.1576), 347 (39), 332 (100), 272 (22), 256 (12), 196 (10), 167 (11), 77 (13) and 51 (6).

General procedure for the synthesis of the iminoxyacetic acids 5a–l

According to the reported procedure,[5b] a mixture of oxime (30 mmol), chloroacetic acid (1.6 equiv.) and sodium hydroxide (3 equiv.) in water (25 cm^3)–ethanol (13 cm^3) was refluxed for several hours. Then it was poured into ice–water and neutralised with conc. hydrochloric acid. The mixture was extracted with dichloromethane, the organic phase was dried, the solvent removed and the residue chromatographed.

2-({[1-(2-Phenoxyphenyl)methylidene]amino}oxy)acetic acid 5a. After 16 h, **4a** (20.0 g, 94 mmol) gave **5a** (21.0 g, 78%), mp 101–103 °C (from light petroleum–benzene) (Found: C, 66.5; H, 4.8; N, 5.1. $C_{15}H_{13}NO_4$ requires C, 66.4; H, 4.8; N, 5.1%); ν_{max}/cm^{-1} 3500, 3050, 1740, 1590, 1480 and 1090; δ_H(200 MHz) 4.80 (2 H, s, CH_2), 6.90–7.05 (3 H, m, Ar-H), 7.10–7.20 (2 H, m, Ar-H), 7.30–7.45 (3 H, m, Ar-H), 7.93 (1 H, dd, J_1 7.8, J_2 1.4, Ar-H) and 8.63 (1 H, s, N=CH); *m/z* 271.0851 (M$^+$, 9%.

$C_{15}H_{13}NO_4$ requires 271.0845), 197 (73), 196 (100), 195 (84), 181 (13), 167 (32), 120 (10), 77 (67) and 51 (36).

2-({[1-(2-Phenoxyphenyl)ethylidene]amino}oxy)acetic acid 5b. After 16 h, **4b** (11.9 g, 52 mmol) yielded **5b** (9.50 g, 64%) as a 6.4:1 mixture of the *E*- and *Z*-isomers, mp 90–93 °C (from light petroleum–benzene) (Found: C, 67.5; H, 5.3; N, 4.9. $C_{16}H_{15}NO_4$ requires C, 67.4; H, 5.3; N, 4.9%); ν_{max}/cm^{-1} 3500, 3060, 1770, 1740, 1600, 1490 and 1100; δ_H(200 MHz) 2.18 (3 H, s, Me, minor isomer), 2.28 (3 H, s, Me, major isomer), 4.55 (2 H, s, CH_2, minor isomer), 4.72 (2 H, s, CH_2, major isomer), 6.85–7.40 (9 H, m, Ar-H), 7.46 (1 H, dd, J_1 7.5, J_2 1.6, Ar-H, major isomer) and 10.81 (1 H, s, OH); *m/z* 285.1006 (M^+, 14%. $C_{16}H_{15}NO_4$ requires 285.1001), 211 (47), 210 (100), 196 (59), 120 (18), 91 (16), 77 (51) and 51 (24).

2-({[1-(2-Phenoxyphenyl)-1-phenylmethylidene]amino}oxy)-acetic acid 5c. After 16 h, **4c** (20.0 g, 69 mmol) yielded **5c** (11.4 g, 48%), mp 146–148 °C (from light petroleum–benzene) (Found: C, 72.9; H, 4.9; N, 4.0. $C_{21}H_{17}NO_4$ requires C, 72.6; H, 4.9; N, 4.0%); ν_{max}/cm^{-1} 3340, 3060, 3000, 1770, 1730, 1590, 1580, 1480, 1450, 1350, 1330 and 1090; δ_H(200 MHz) 4.74 (2 H, s, CH_2), 6.90–7.12 (4 H, m, Ar-H), 7.22–7.47 (8 H, m, Ar-H) and 7.50–7.58 (2 H, m, Ar-H); *m/z* 347.1164 (M^+, 12%. $C_{21}H_{17}NO_4$ requires 347.1158), 273 (73), 272 (100), 196 (40), 180 (31), 77 (76) and 51 (29).

2-({[1-(2-Anilinophenyl)methylidene]amino}oxy)acetic acid 5d. After 16 h, **4d** (14.4 g, 68 mmol) yielded **5d** (12.0 g, 65%), mp 143–145 °C (from light petroleum–benzene) (Found: C, 66.85; H, 5.2; N, 10.35. $C_{15}H_{14}N_2O_3$ requires C, 66.7; H, 5.2; N, 10.4%); ν_{max}/cm^{-1} 3300, 3000, 1740, 1610, 1600, 1570 and 1320; δ_H(300 MHz) 4.78 (2 H, s, CH_2), 6.81 (1 H, ddd, J_1 7.9, J_2 7.0, J_3 1.2, Ar-H), 7.07 (1 H, dddd, J_1, J_2 7.0, J_3, J_4 1.2, Ar-H), 7.18–7.37 (7 H, m, Ar-H), 8.38 (1 H, s, N=CH) and 8.65 (1 H, br s, NH); *m/z* 270.1008 (M^+, 71%. $C_{15}H_{14}N_2O_3$ requires 270.1004), 195 (100), 194 (32), 180 (24), 167 (36) and 77 (19).

2-({[1-(2-Anilinophenyl)ethylidene]amino}oxy)acetic acid 5e. After 16 h, **4e** (9.3 g, 41 mmol) yielded **5e** (7.30 g, 63%), mp 103–104 °C (from light petroleum–benzene) (Found: C, 67.8; H, 5.7; N, 9.9. $C_{16}H_{16}N_2O_3$ requires C, 67.6; H, 5.7; N, 9.85%); ν_{max}/cm^{-1} 3300, 3000, 1740, 1600 and 1450; δ_H(300 MHz) 2.40 (3 H, s, Me), 4.75 (2 H, s, CH_2), 6.81–6.88 (1 H, m, Ar-H), 6.89–6.96 (1 H, m, Ar-H), 7.07–7.42 (7 H, m, Ar-H) and 9.00 (2 H, br s, NH + OH); *m/z* 284.1163 (M^+, 86%. $C_{16}H_{16}N_2O_3$ requires 284.1161), 209 (100), 208 (30), 207 (23), 194 (20), 193 (14), 180 (17), 167 (52), 166 (13) and 77 (14).

2-({[1-(2-Anilinophenyl)-1-phenylmethylidene]amino}oxy)-acetic acid 5f. After 16 h, **4f** (20.0 g, 69 mmol) yielded **5f** (16.6 g, 69%), mp 178–180 °C (by addition of light petroleum to an ice-cold diethyl ether solution) (Found: C, 73.1; H, 5.2; N, 8.1. $C_{21}H_{18}N_2O_3$ requires C, 72.8; H, 5.2; N, 8.1%); ν_{max}/cm^{-1} 3350, 3000, 1740, 1600, 1500 and 1310; δ_H(300 MHz) 4.90 (2 H, br s, CH_2), 6.78–7.60 (14 H, m, Ar-H) and 8.57 (2 H, br s, NH + OH); *m/z* 346.1322 (M^+, 78%. $C_{21}H_{18}N_2O_3$ requires 346.1317), 271 (79), 270 (61), 269 (100), 255 (11), 167 (40) and 77 (22).

2-[({1-[2-(Methylanilino)phenyl]methylidene}amino)oxy]-acetic acid 5g. After 16 h, **4g** (11.5 g, 50 mmol) yielded **5g** (12.8 g, 91%), mp 87–88 °C (Found: C, 67.8; H, 5.7; N, 9.8. $C_{16}H_{16}N_2O_3$ requires C, 67.6; H, 5.7; N, 9.85%); ν_{max}/cm^{-1} 3500, 3050, 3000, 2920, 1770, 1730, 1600, 1480, 1340 and 1110; δ_H(300 MHz) 3.50 (3 H, s, Me), 4.98 (2 H, s, CH_2), 6.84–6.89 (2 H, m, Ar-H), 7.03 (1 H, dddd, J_1, J_2 7.0, J_3, J_4 1.0, Ar-H), 7.40–7.57 (4 H, m, Ar-H), 7.67–7.74 (1 H, m, Ar-H), 8.17 (1 H, dd, J_1 7.7, J_2 1.4, Ar-H) and 8.55 (1 H, s, N=CH); *m/z* 284.1160 (M^+, 22%. $C_{16}H_{16}N_2O_3$ requires 284.1161), 209 (100), 208 (48), 207 (32), 194 (67), 180 (46) and 77 (26).

2-[({1-[2-(Methylanilino)phenyl]ethylidene}amino)oxy]acetic acid 5h. After 16 h, **4h** (15.6 g, 65 mmol) gave **5h** (16.8 g, 87%), mp 49–53 °C (Found: C, 68.7; H, 6.1; N, 9.35. $C_{17}H_{18}N_2O_3$ requires C, 68.4; H, 6.1; N, 9.4%); δ_H(200 MHz) 2.10 (3 H, s, C-Me), 3.20 (3 H, s, N-Me), 4.70 (2 H, s, CH_2), 6.65–6.85 (3 H, m, Ar-H), 7.15–7.50 (6 H, m, Ar-H) and 8.95 (1 H, br s, OH); *m/z* 298 (M^+, 1%), 253 (<1), 224 (31), 223 (22), 221 (42), 209 (77), 208 (76), 207 (40), 206 (16), 193 (23), 180 (12), 167 (10), 119 (52), 104 (88) and 77 (100).

2-[({1-[2-(Methylanilino)phenyl]-1-phenylmethylidene}amino)-oxy]acetic acid 5i. After 16 h, **4i** (12.4 g, 41 mmol) yielded **5i** (12.4 g, 84%) as a 2:1 mixture of the *E*- and *Z*-isomers, oil (Found: C, 73.55; H, 5.6; N, 7.8. $C_{22}H_{20}N_2O_3$ requires C, 73.3; H, 5.6; N, 7.8%); ν_{max}/cm^{-1} 3500, 3060, 1770, 1730, 1600, 1490, 1350 and 1100; δ_H(200 MHz) 2.72 (3 H, s, Me, minor isomer), 2.92 (3 H, s, Me, major isomer), 4.68 (2 H, s, CH_2, major isomer), 4.70 (2 H, s, CH_2, minor isomer), 6.30–6.37 (2 H, m, Ar-H, minor isomer), 6.55–6.63 (2 H, m, Ar-H, major isomer), 6.69–6.78 (1 H, m, Ar-H, minor isomer), 7.03–7.14 (1 H, m, Ar-H, major isomer), 7.20–7.70 (11 H, m, Ar-H) and 10.40 (1 H, br s, COOH); *m/z* 360.1480 (M^+, 11%. $C_{22}H_{20}N_2O_3$ requires 360.1474), 285 (28), 270 (69), 269 (100), 165 (29) and 77 (24).

2-[({1-[2-(Diphenylamino)phenyl]methylidene}amino)oxy]-acetic acid 5j. After 16 h, **4j** (9.1 g, 32 mmol) yielded **5j** (5.5 g, 50%), mp 134–136 °C (from light petroleum–benzene) (Found: C, 73.15; H, 5.2; N, 8.1. $C_{21}H_{18}N_2O_3$ requires C, 72.8; H, 5.2; N, 8.1%); ν_{max}/cm^{-1} 3500, 3050, 1780, 1740, 1590, 1490 and 1100; δ_H(300 MHz) 4.60 (2 H, s, CH_2), 6.92–7.00 (6 H, m, Ar-H), 7.12 (1 H, dd, J_1 7.8, J_2 1.1, Ar-H), 7.18–7.26 (5 H, m, Ar-H), 7.36–7.42 (1 H, m, Ar-H), 7.82 (1 H, dd, J_1 7.8, J_2 1.4, Ar-H) and 8.30 (1 H, s, N=CH); *m/z* 346.1320 (M^+, 5%. $C_{21}H_{18}N_2O_3$ requires 346.1317), 270 (100), 269 (30), 256 (15), 167 (14), 135 (11), 77 (12) and 51 (11).

2-[({1-[2-(Diphenylamino)phenyl]ethylidene}amino)oxy]acetic acid 5k. After 9 h, **4k** (8.5 g, 28 mmol) gave **5k** (6.0 g, 59%) as a 5:1 mixture of the *E*- and *Z*-isomers, oil (Found: C, 73.45; H, 5.6; N, 7.8. $C_{22}H_{20}N_2O_3$ requires C, 73.3; H, 5.6; N, 7.8%); ν_{max}/cm^{-1} 3500, 3060, 3000, 1770, 1740, 1590, 1480 and 1100; δ_H(200 MHz) 1.55 (3 H, s, Me, minor isomer), 2.05 (3 H, s, Me, major isomer), 4.23 (2 H, s, CH_2, minor isomer), 4.40 (2 H, s, CH_2, major isomer) and 6.92–7.42 (14 H, m, Ar-H); *m/z* 360.1473 (M^+, 19%. $C_{22}H_{20}N_2O_3$ requires 360.1474), 286 (55), 285 (29), 271 (17), 195 (100), 167 (14), 77 (26) and 51 (14).

2-[({1-[2-(Diphenylamino)phenyl]-1-phenylmethylidene}-amino)oxy]acetic acid 5l. After 21 h, **4l** (16.4 g, 45 mmol) yielded **5l** (12.2 g, 64%) as a 4:1 mixture of the *E*- and *Z*-isomers, mp 158–162 °C (from light petroleum–benzene) (Found: C, 77.1; H, 5.25; N, 6.6. $C_{27}H_{22}N_2O_3$ requires C, 76.8; H, 5.25; N, 6.6%); ν_{max}/cm^{-1} 3460, 3040, 1760, 1730, 1590, 1430 and 1090; δ_H(300 MHz) 4.38 (2 H, s, CH_2, major isomer), 4.48 (2 H, s, CH_2, minor isomer), 6.65–7.51 (19 H, m, Ar-H); *m/z* 422.1636 (M^+, 6%. $C_{27}H_{22}N_2O_3$ requires 422.1630), 348 (69), 347 (100), 271 (8), 256 (15), 77 (19) and 51 (6).

General procedure for the synthesis of the iminoxyperacetates 6a–l

According to the reported procedure,[28] the iminoxyacetic acid (10 mmol) was added at r.t. and under nitrogen to a stirred solution of CDI (1 equiv) in anhydrous THF (15 cm^3). After 1 h, a solution of *tert*-butyl hydroperoxide (2.2 equiv.) in light petroleum (30 cm^3) was added dropwise at 0 °C and the mixture was kept at 0–5 °C for 4 h. The mixture was poured into water and extracted with diethyl ether. The organic phase was washed twice with cold water and dried. After removal of the solvent the residue was chromatographed. Due to very low (or absent) molecular ions (with the exception of **6d**) and their decomposition hazard, neither high resolution mass spectra nor elemental analyses were obtained for the peresters **6a–l**; their purity was however confirmed by the complete absence of any significant extraneous peak in the ^1H NMR spectra.

CAUTION: Since hydroperoxides and peresters are potentially hazardous compounds, they must be handled with due care; avoid exposure to strong heat or light, mechanical shock, oxidisable organic materials, or transition metal ions. No par-

ticular difficulties were experienced in handling any of the new peresters synthesised in this work using the procedure described above. Their column chromatography did not give any problems, even on a 10 g scale; however, we advise performing the separation with extreme care, evaporating the solvent under reduced pressure with a water bath kept below 20 °C.

***tert*-Butyl 2-({[1-(2-phenoxyphenyl)methylidene]amino}oxy)-peracetate 6a.** Starting from **5a** (8.1 g, 30 mmol), **6a** was obtained (9.15 g, 89%) as an oil; ν_{max}/cm^{-1} 3000, 2940, 1780, 1590, 1480, 1450, 1240 and 1080; δ_H(200 MHz) 1.33 (9 H, s, Bu^t), 4.78 (2 H, s, CH_2), 6.88 (1 H, dd, J_1 8.1, J_2 1.0, Ar-H), 6.92–7.02 (2 H, m, Ar-H), 7.06–7.16 (2 H, m, Ar-H), 7.28–7.40 (3 H, m, Ar-H), 7.88 (1 H, dd, J_1 7.7, J_2 1.6, Ar-H) and 8.58 (1 H, s, N=CH); *m*/*z* 344 (M^+ + 1, <1%), 299 (1), 213 (10), 196 (44), 195 (100), 167 (48), 77 (64) and 57 (31).

***tert*-Butyl 2-({[1-(2-phenoxyphenyl)ethylidene]amino}oxy)-peracetate 6b.** Starting from **5b** (9.5 g, 33 mmol), **6b** was obtained (10.0 g, 84%) as an oil; ν_{max}/cm^{-1} 2980, 2930, 1780, 1590, 1480, 1450 and 1370; δ_H(200 MHz) 1.24 (9 H, s, Bu^t), 2.21 (3 H, s, Me), 4.71 (2 H, s, CH_2), 6.82 (1 H, dd, J_1 7.9, J_2 1.1, Ar-H), 6.86–6.95 (2 H, m, Ar-H), 6.98–7.08 (2 H, m, Ar-H), 7.18–7.34 (3 H, m, Ar-H) and 7.38 (1 H, dd, J_1 7.5, J_2 1.7, Ar-H); *m*/*z* 357 (M^+, <1%), 313 (8), 283 (17), 227 (32), 210 (100), 195 (33), 185 (26), 134 (23), 91 (41), 77 (42) and 57 (100).

***tert*-Butyl 2-({[1-(2-phenoxyphenyl)-1-phenylmethylidene]-amino}oxy)peracetate 6c.** Starting from **5c** (8.7 g, 25 mmol), **6c** was obtained (8.3 g, 79%) as a 11:8 mixture of the *E*- and *Z*-isomers, oil; ν_{max}/cm^{-1} 2990, 2970, 2880, 1770, 1590, 1580, 1480, 1450, 1370 and 1090; δ_H(200 MHz) 1.27 (9 H, s, Bu^t, major isomer), 1.29 (9 H, s, Bu^t, minor isomer), 4.68 (2 H, s, CH_2, major isomer), 4.76 (2 H, s, CH_2, minor isomer), 6.68–6.76 (2 H, m, Ar-H, both isomers) and 6.82–7.60 (26 H, m, Ar-H, both isomers); *m*/*z* 345 (M^+ − 74, 15%), 289 (19), 272 (100), 196 (53), 105 (28), 77 (42) and 57 (93).

***tert*-Butyl 2-({[1-(2-anilinophenyl)methylidene]amino}oxy)-peracetate 6d.** Starting from **5d** (5.4 g, 20 mmol), **6d** was obtained (6.0 g, 90%), mp 39–41 °C; δ_H(200 MHz) 1.20 (9 H, s, Bu^t), 4.70 (2 H, s, CH_2), 6.66–6.76 (1 H, m, Ar-H), 6.93–7.03 (1 H, m, Ar-H), 7.06–7.30 (7 H, m, Ar-H), 8.26 (1 H, s, N=CH) and 8.54 (1 H, br s, NH); *m*/*z* 342.1586 (M^+, 5%. $C_{19}H_{22}N_2O_4$ requires 342.1580), 298 (63), 268 (4), 212 (45), 195 (100), 180 (74), 167 (22) and 57 (82).

***tert*-Butyl 2-({[1-(2-anilinophenyl)ethylidene]amino}oxy)-peracetate 6e.** Starting from **5e** (5.4 g, 19 mmol), **6e** was obtained (6.4 g, 95%), mp 34–35 °C; ν_{max}/cm^{-1} 3370, 3000, 1780, 1600, 1450, 1370 and 1100; δ_H(60 MHz) 1.30 (9 H, s, Bu^t), 2.10 (3 H, s, Me), 4.67 (2 H, s, CH_2), 6.70–7.58 (9 H, m, Ar-H) and 8.88 (1 H, br s, NH); *m*/*z* 356 (M^+, <1%), 312 (73), 282 (6), 227 (5), 226 (29), 209 (100), 208 (23), 194 (61), 180 (19), 167 (35), 77 (14) and 57 (68).

***tert*-Butyl 2-({[1-(2-anilinophenyl)-1-phenylmethylidene]-amino}oxy)peracetate 6f.** Starting from **5f** (5.4 g, 15 mmol), **6f** was obtained (6.2 g, 96%), mp 94.5–95.5 °C; ν_{max}/cm^{-1} 3330, 2990, 1780, 1600, 1500, 1450, 1370, 1310 and 1090; δ_H(200 MHz) 1.37 (9 H, s, Bu^t), 4.90 (2 H, s, CH_2) and 6.90–7.60 (14 H, m, Ar-H); *m*/*z* 374 (M^+ − 44, 2%), 344 (<1), 271 (11), 269 (5), 256 (4), 196 (1), 167 (2), 59 (30) and 44 (100).

***tert*-Butyl 2-[({1-[2-(methylanilino)phenyl]methylidene}-amino)oxy]peracetate 6g.** Starting from **5g** (7.8 g, 27 mmol), **6g** was obtained (8.8 g, 92%) as an oil; ν_{max}/cm^{-1} 2980, 1770, 1600, 1520 and 1180; δ_H(300 MHz) 1.35 (9 H, s, Bu^t), 3.25 (3 H, s, Me), 4.75 (2 H, s, CH_2), 6.58–6.64 (2 H, m, Ar-H), 6.79 (1 H, dd, J_1, J_2 7.1, Ar-H), 7.15–7.32 (4 H, m, Ar-H), 7.45 (1 H, ddd, J_1, J_2 7.7, J_3 1.6, Ar-H), 7.94 (1 H, dd, J_1 7.9, J_2 1.6, Ar-H) and 8.30 (1 H, s, N=CH); *m*/*z* 356 (M^+, <1%), 312 (7), 282 (3), 209 (91), 208 (48), 207 (31), 194 (100), 193 (93), 180 (25), 77 (27), 59 (81), 57 (86) and 44 (70).

***tert*-Butyl 2-[({1-[2-(methylanilino)phenyl]ethylidene}-amino)oxy]peracetate 6h.** Starting from **5h** (7.1 g, 24 mmol), **6h** was obtained (7.5 g, 86%) as a 9:2 mixture of the *E*- and *Z*-isomers, oil; δ_H(200 MHz) 1.35 (9 H, s, Bu^t, minor isomer), 1.37 (9 H, s, Bu^t, major isomer), 2.10 (3 H, s, C-Me, major isomer), 2.32 (3 H, s, C-Me, minor isomer), 3.20 (3 H, s, N-Me, major isomer), 3.30 (3 H, s, N-Me, minor isomer), 4.77 (2 H, s, CH_2, major isomer), 4.85 (2 H, s, CH_2, minor isomer), 6.70–6.85 (3 H, m, Ar-H) and 7.15–7.70 (6 H, m, Ar-H, both isomers); *m*/*z* 370 (M^+, <1%), 326 (6), 296 (1), 223 (33), 208 (100), 207 (49), 206 (34), 194 (10), 77 (14) and 57 (35).

***tert*-Butyl 2-[({1-[2-(methylanilino)phenyl]-1-phenylmethyl-idene}amino)oxy]peracetate 6i.** Starting from **5i** (7.0 g, 20 mmol), **6i** was obtained (7.2 g, 85%) as a 2:1 mixture of the *E*- and *Z*-isomers, oil; ν_{max}/cm^{-1} 2920, 1780 and 1600; δ_H(200 MHz) 1.33 (9 H, s, Bu^t, both isomers), 2.80 (3 H, s, N-Me, minor isomer), 2.93 (3 H, s, N-Me, major isomer), 4.68 (2 H, s, CH_2, major isomer), 4.73 (2 H, s, CH_2, minor isomer), 6.30–6.38 (2 H, m, Ar-H, minor isomer), 6.50–6.60 (2 H, m, Ar-H, major isomer), 6.66–6.76 (1 H, m, Ar-H, minor isomer), 7.00–7.12 (1 H, m, Ar-H, major isomer) and 7.15–7.70 (11 H, m, Ar-H, both isomers); *m*/*z* 388 (M^+ − 44, 19%), 285 (59), 270 (100), 269 (84), 165 (28), 77 (15) and 57 (40).

***tert*-Butyl 2-[({1-[2-(diphenylamino)phenyl]methylidene}-amino)oxy]peracetate 6j.** Starting from **5j** (9.4 g, 27 mmol), **6j** was obtained (6.8 g, 60%), mp 64–68 °C; ν_{max}/cm^{-1} 2980, 1780, 1590, 1480 and 1080; δ_H(200 MHz) 1.30 (9 H, s, Bu^t), 4.67 (2 H, s, CH_2), 6.92–7.45 (13 H, m, Ar-H), 7.89 (1 H, dd, J_1 7.7, J_2 1.6, Ar-H) and 8.30 (1 H, s, N=CH); *m*/*z* 375 (M^+ − 43, 14%), 345 (M^+ − 73, 11), 271 (100), 270 (34), 257 (30), 167 (12), 77 (14), 57 (26), 51 (11) and 44 (27).

***tert*-Butyl 2-[({1-[2-(diphenylamino)phenyl]ethylidene}-amino)oxy]peracetate 6k.** Starting from **5k** (6.0 g, 17 mmol), **6k** was obtained (5.4 g, 76%) as a 5:1 mixture of the *E*- and *Z*-isomers, oil; ν_{max}/cm^{-1} 2980, 1780, 1590, 1480, 1370 and 1090; δ_H(200 MHz) 1.20 (9 H, s, Bu^t, both isomers), 1.73 (3 H, s, Me, minor isomer), 1.90 (3 H, s, Me, major isomer), 4.18 (2 H, s, CH_2, minor isomer), 4.38 (2 H, s, CH_2, major isomer) and 6.82–7.30 (14 H, m, Ar-H, both isomers); *m*/*z* 432 (M^+, 1%), 388 (100), 358 (15), 302 (22), 285 (70), 270 (79), 256 (13), 243 (10), 195 (18), 167 (10), 77 (7) and 57 (22).

***tert*-Butyl 2-[({1-[2-(diphenylamino)phenyl]-1-phenylmethyl-idene}amino)oxy]peracetate 6l.** Starting from **5l** (9.7 g, 23 mmol), **6l** was obtained (6.7 g, 59%) as an oil; ν_{max}/cm^{-1} 2980, 1770, 1590, 1480, 1370 and 1090; δ_H(200 MHz) 1.25 (9 H, s, Bu^t), 4.40 (2 H, br s, CH_2) and 6.70–7.45 (19 H, m, Ar-H); *m*/*z* 451 (M^+ − 43, 47%), 421 (M^+ − 73, 24), 378 (8), 364 (11), 348 (54), 347 (100), 332 (74), 256 (25), 77 (12) and 57 (9).

General procedure for the decomposition of peresters 6a–l

A bromobenzene (50 cm^3) solution of the perester (10 mmol) was added dropwise in 1 h to 450 cm^3 of boiling bromobenzene. After one additional hour at reflux, the solution was cooled, the solvent was evaporated and the residue chromatographed.

From 6a. Perester **6a** (9.5 mmol) gave in order of elution **3a** (0.40 g, 21%); 2-*phenoxybenzaldehyde* O-(tert-*butyl*)*oxime* **11a** (0.03 g, 1%), oil; ν_{max}/cm^{-1} 2980, 2930, 1590, 1480, 1450, 1370 and 960; δ_H(200 MHz) 1.32 (9 H, s, Bu^t), 6.86–6.97 (3 H, m, Ar-H), 7.02–7.18 (2 H, m, Ar-H), 7.24–7.36 (3 H, m, Ar-H), 7.96 (1 H, dd, J_1 7.8, J_2 1.6, Ar-H) and 8.38 (1 H, s, N=CH); *m*/*z* 269.1418 (M^+, 15%. $C_{17}H_{19}NO_2$ requires 269.1416), 213 (31), 196 (25), 181 (25), 91 (45), 77 (25) and 57 (100); 2-*phenoxybenzaldehyde* O-(tert-*butoxymethyl*)*oxime* **9a** (0.32 g, 11%), oil; ν_{max}/cm^{-1} 2980, 1600, 1480, 1450 and 1000; δ_H(200 MHz) 1.25 (9 H, s, Bu^t), 5.34 (2 H, s, CH_2), 6.84–7.40 (8 H, m, Ar-H), 8.00 (1 H, dd, J_1 7.9, J_2 1.6, Ar-H) and 8.46 (1 H, s, N=CH); *m*/*z* 299.1526 (M^+, 9%. $C_{18}H_{21}NO_3$ requires 299.1521), 269 (6), 213 (26), 196 (70), 77 (19) and 57 (100); 2-*phenoxybenzonitrile* **10a** (0.96 g, 42%), oil [lit.,[29] bp (6 mbar) 150–154 °C]; ν_{max}/cm^{-1} 3000, 2230, 1600, 1480, 1450 and 1250; *m*/*z* 195 (M^+, 100%), 167 (50), 77 (45) and 51 (38); **4a** (0.03 g, 2%).

From 6b. Perester **6b** (10 mmol) yielded in order of elution 1-(2-*phenoxyphenyl*)*ethan*-1-*imine* **12b** (0.21 g, 10%), mp 82–

84 °C (Found: C, 80.0; H, 6.2; N, 6.6. $C_{14}H_{13}NO$ requires C, 79.6; H, 6.2; N, 6.6%); ν_{max}/cm^{-1} 3000, 1620, 1600, 1580, 1490, 1450, 1370 and 1310; δ_H(200 MHz) 2.35 (3 H, s, Me), 6.85–6.96 (3 H, m, Ar-H), 7.03 (1 H, dd, J_1 8.2, J_2 1.1, Ar-H), 7.20 (1 H, dddd, J_1, J_2 7.3, J_3, J_4 1.1, Ar-H), 7.33–7.46 (3 H, m, Ar-H), 7.64 (1 H, dd, J_1 8.0, J_2 1.6, Ar-H) and 14.32 (1 H, br s, NH); δ_C(50 MHz) 17.5, 118.6, 118.7, 120.2, 121.8, 125.3, 129.4, 129.6, 133.5, 147.5, 162.5 and 171.7; *m*/*z* 211.1000 (M$^+$, 88%. $C_{14}H_{13}NO$ requires 211.0997), 210 (77), 196 (89), 120 (32), 77 (100) and 51 (40); **3c** (0.48 g, 23%); 1-(2-*phenoxyphenyl*)*ethan*-1-*one* O-(tert-*butoxymethyl*)*oxime* **9b** (0.60 g, 19%), oil; ν_{max}/cm^{-1} 2980, 1590, 1480, 1450, 1370 and 990; δ_H(200 MHz) 1.24 (9 H, s, Bu^t), 2.21 (3 H, s, Me), 5.35 (2 H, s, CH_2), 6.88–7.00 (3 H, m, Ar-H), 7.03–7.12 (1 H, m, Ar-H), 7.14 (1 H, dd, J_1 7.4, J_2 1.1, Ar-H), 7.26–7.37 (3 H, m, Ar-H) and 7.51 (1 H, dd, J_1 7.4, J_2 1.8, Ar-H); *m*/*z* 313.1680 (M$^+$, 5%. $C_{19}H_{23}NO_3$ requires 313.1678), 283 (10), 227 (20), 210 (80), 195 (20), 185 (18), 134 (16), 91 (31), 77 (21) and 57 (100); **4b** (0.40 g, 18%).

From 6c. Perester **6c** (10 mmol) afforded in order of elution (2-*phenoxyphenyl*)(*phenyl*)*methanimine* **12c** (0.73 g, 27%), mp 135–137 °C (Found: C, 83.7; H, 5.5; N, 5.1. $C_{19}H_{15}NO$ requires C, 83.5; H, 5.5; N, 5.1%); ν_{max}/cm^{-1} 3000, 1600, 1480 and 1450; δ_H(200 MHz) 6.70–6.80 (3 H, m, Ar-H), 6.90–7.45 (11 H, m, Ar-H) and 14.52 (1 H, br s, NH); δ_C(50 MHz) 118.1, 120.0, 122.5, 124.8, 128.3, 128.6, 128.9, 129.0, 132.4, 133.4, 134.2, 147.0, 162.7 and 173.5; *m*/*z* 273.1157 (M$^+$, 100%. $C_{19}H_{15}NO$ requires 273.1154), 272 (88), 256 (6), 196 (46), 180 (26), 77 (92) and 51 (33); **3c** (0.21 g, 8%); (2-*phenoxyphenyl*)(*phenyl*)-*methanone* O-(tert-*butyl*)*oxime* **11c** (0.24 g, 7%), oil; ν_{max}/cm^{-1} 2980, 1590, 1580, 1480, 1450, 1400, 1370, 1330, 1150, 1100, 1000, 950 and 870; δ_H(200 MHz) 1.18 (9 H, s, Bu^t), 6.83–7.39 (12 H, m, Ar-H) and 7.50–7.60 (2 H, m, Ar-H); *m*/*z* 345.1727 (M$^+$, 12%. $C_{23}H_{23}NO_2$ requires 345.1729), 289 (20), 272 (85), 196 (44), 105 (32), 91 (18), 77 (27) and 57 (100); (2-*phenoxyphenyl*)(*phenyl*)*methanone* O-(tert-*butoxymethyl*)*oxime* **9c** (0.59 g, 16%), oil; ν_{max}/cm^{-1} 2980, 1590, 1580, 1480, 1450, 1400, 1370, 1330, 1150, 1100, 1000, 950 and 870; δ_H(200 MHz) 1.21 (9 H, s, Bu^t), 5.29 (2 H, s, CH_2), 6.83–7.40 (12 H, m, Ar-H) and 7.53–7.62 (2 H, m, Ar-H); *m*/*z* 375.1830 (M$^+$, 5%. $C_{24}H_{25}NO_3$ requires 375.1834), 345 (14), 289 (97), 272 (80), 180 (23), 170 (31), 77 (42) and 57 (100); **4c** (0.26 g, 9%).

From 6d. Perester **6d** (8.2 mmol) gave in order of elution **3d** (0.08 g, 5%); 2-*anilinobenzaldehyde* O-(tert-*butoxymethyl*)*oxime* **9d** (0.46 g, 19%), mp 36–37 °C (Found: C, 72.7; H, 7.4; N, 9.35. $C_{18}H_{22}N_2O_2$ requires C, 72.5; H, 7.4; N, 9.4%); δ_H(200 MHz) 1.40 (9 H, s, Bu^t), 5.45 (2 H, s, CH_2), 6.82–6.94 (1 H, m, Ar-H), 7.12–7.21 (1 H, m, Ar-H), 7.24–7.50 (7 H, m, Ar-H), 8.37 (1 H, s, N=CH) and 9.22 (1 H, br s, NH); δ_C(50 MHz) 29.1, 75.1, 93.0, 113.7, 116.2, 118.1, 122.0, 123.3, 129.6, 130.7, 133.3, 141.6, 144.3 and 153.2; *m*/*z* 298.1683 (M$^+$, 50%. $C_{18}H_{22}N_2O_2$ requires 298.1681), 212 (43), 195 (71), 194 (29), 193 (19), 180 (66), 167 (19), 77 (12) and 57 (100); 2-*anilinobenzonitrile* **10d** (0.16 g, 10%), mp 47–49 °C (lit.,[30] 47–48 °C); *acridine* **13** (0.12 g, 8%), mp 107–110 °C (lit.,[31] 108–110 °C).

From 6e. Perester **6e** (10 mmol) yielded in order of elution **3e** (0.27 g, 13%); 1-(2-*anilinophenyl*)*ethan*-1-*one* O-(tert-*butoxymethyl*)*oxime* **9e** (0.69 g, 22%), oil; ν_{max}/cm^{-1} 3700, 2980, 1600, 1570, 1500, 1450, 1370, 1320 and 990; δ_H(200 MHz) 1.30 (9 H, s, Bu^t), 2.35 (3 H, s, Me), 5.40 (2 H, s, CH_2), 6.83–6.93 (1 H, m, Ar-H), 6.95–7.03 (1 H, m, Ar-H), 7.18–7.52 (7 H, m, Ar-H) and 9.57 (1 H, br s, NH); δ_C(50 MHz) 14.7, 28.9, 75.0, 92.5, 116.1, 118.7, 119.9, 121.7, 121.8, 129.4, 129.5, 142.4, 142.5 and 157.2; *m*/*z* 312.1841 (M$^+$, 85%. $C_{19}H_{24}N_2O_2$ requires 312.1838), 282 (4), 226 (35), 209 (100), 208 (27), 207 (17), 194 (64), 180 (23), 167 (35), 77 (15) and 57 (96); 9-*methylacridine* **14** (0.44 g, 23%), mp 132–133.5 °C (lit.,[32] 132.5 °C).

From 6f. Perester **6f** (10 mmol) afforded in order of elution **3f** (0.27 g, 10%); (2-*anilinophenyl*)(*phenyl*)*methanone* O-(tert-*butoxymethyl*)*oxime* **9f** (1.01 g, 27%) as a 4.4:1 mixture of the *E*- and *Z*-isomers, oil (Found: C, 77.2; H, 7.0; N, 7.5. $C_{24}H_{26}N_2O_2$ requires C, 77.0; H, 7.0; N, 7.5%); major isomer, ν_{max}/cm^{-1} 3400, 2980, 1600, 1580, 1500, 1450, 1310 and 950; δ_H(200 MHz) 1.32 (9 H, s, Bu^t), 5.52 (2 H, s, CH_2), 6.20 (1 H, br s, NH), 6.90–7.16 (5 H, m, Ar-H), 7.22–7.44 (6 H, m, Ar-H), 7.53 (1 H, br d, *J* 8.0, Ar-H) and 7.62–7.70 (2 H, m, Ar-H); δ_C(50 MHz) 29.2, 75.7, 93.7, 118.6, 121.3, 125.2, 128.3, 128.7, 128.9, 130.1, 130.3, 136.1, 141.5, 144.0 and 157.5; *m*/*z* 374.1999 (M$^+$, 77%. $C_{24}H_{26}N_2O_2$ requires 374.1994), 344 (9), 288 (32), 271 (52), 270 (46), 269 (76), 256 (72), 196 (30), 189 (12), 167 (30), 77 (17) and 57 (100); minor isomer, ν_{max}/cm^{-1} 3260, 2960, 1600, 1450, 1320, 1100 and 950; δ_H(200 MHz) 1.18 (9 H, s, Bu^t), 5.32 (2 H, s, CH_2), 6.64–6.72 (1 H, m, Ar-H), 6.90 (1 H, dd, J_1 7.6, J_2 1.2, Ar-H), 6.97–7.07 (1 H, m, Ar-H), 7.15–7.52 (11 H, m, Ar-H) and 9.68 (1 H, br s, NH); δ_C(50 MHz) 29.1, 75.4, 93.1, 115.8, 118.5, 120.8, 121.4, 122.4, 128.5, 129.1, 129.5, 129.7, 130.1, 132.8, 134.7, 142.7, 143.9 and 160.0; *m*/*z* 374.1996 (M$^+$, 56%. $C_{24}H_{26}N_2O_2$ requires 374.1994), 344 (2), 288 (22), 273 (35), 272 (49), 271 (64), 270 (65), 269 (100), 256 (47), 196 (24), 180 (10), 167 (44), 77 (31) and 57 (65); 9-*phenylacridine* **15** (0.51 g, 20%), mp 180–182 °C (lit.,[33] 181–182 °C); 1,4-*diphenyl*-1,2-*dihydroquinazolin*-2-*one* **16** (0.24 g, 8%), mp 180–183 °C; ν_{max}/cm^{-1} 1660, 1600, 1370 and 1320; δ_H(300 MHz) 6.76 (1 H, d, *J* 8.4), 7.18–7.28 (1 H, m), 7.36–7.42 (2 H, m), 7.50–7.67 (7 H, m), 7.78–7.84 (2 H, m) and 7.89 (1 H, dd, J_1 8.1, J_2 1.3); δ_C(50 MHz) 116.1, 116.4, 122.9, 128.9, 129.1, 129.7, 130.0, 130.2, 130.9, 131.2, 135.3, 137.0, 137.5, 145.7 and 176.2; *m*/*z* 298.1105 (M$^+$, 69%. $C_{20}H_{14}N_2O$ requires 298.1106), 297 (100), 256 (18) and 77 (10); the structure of **16** was also confirmed by X-ray diffractometry (Fig. 1): see below for experimental details.

From 6g. Perester **6g** (10 mmol) gave in order of elution 2-(*methylanilino*)*benzaldehyde* O-(tert-*butoxymethyl*)*oxime* **9g** (0.48 g, 15%), oil; ν_{max}/cm^{-1} 2950, 1600, 1480 and 1000; δ_H(300 MHz) 1.50 (9 H, s, Bu^t), 3.50 (3 H, s, Me), 5.60 (2 H, s, CH_2), 6.82–6.91 (2 H, m, Ar-H), 6.99–7.06 (1 H, m, Ar-H), 7.40–7.58 (4 H, m, Ar-H), 7.64–7.72 (1 H, m, Ar-H), 8.26–8.32 (1 H, m, Ar-H) and 8.44 (1 H, s, N=CH); δ_C(50 MHz) 28.7, 40.3, 74.8, 92.5, 114.0, 118.0, 126.4, 127.3, 128.0, 129.0, 130.3, 131.5, 147.1, 147.7 and 149.4; *m*/*z* 312.1836 (M$^+$, 12%. $C_{19}H_{24}N_2O_2$ requires 312.1838), 209 (100), 194 (81), 180 (15), 77 (8) and 57 (49); 2-(*methylanilino*)*benzonitrile* **10g** (0.14 g, 7%), oil; ν_{max}/cm^{-1} 3000, 2220, 1600 and 1480; δ_H(300 MHz) 3.40 (3 H, s, Me), 6.87–6.93 (2 H, m, Ar-H), 6.97 (1 H, dddd, J_1, J_2 7.2, J_3, J_4 1.0, Ar-H), 7.18 (1 H, ddd, J_1, J_2 7.6, J_3 0.9, Ar-H), 7.24–7.33 (3 H, m, Ar-H), 7.55 (1 H, ddd, J_1 8.2, J_2 7.4, J_3 1.5, Ar-H) and 7.64 (1 H, ddd, J_1 7.6, J_2 1.6, J_3 0.4, Ar-H); *m*/*z* 208.1003 (M$^+$, 100%. $C_{14}H_{12}N_2$ requires 208.1001), 207 (52), 194 (15), 192 (11), 180 (8), 167 (7), 131 (16) and 77 (20); **4g** (0.14 g, 6%); **13** (0.25 g, 14%).

From 6h. Perester **6h** (10 mmol) yielded in order of elution 3-*methyl*-1-*phenyl*-1H-*indole* **17** (0.93 g, 45%), oil;[34] **3h** (0.18 g, 8%); 1-[2-(*methylanilino*)*phenyl*]*ethan*-1-*one* O-(tert-*butoxymethyl*)*oxime* **9h** (0.49 g, 15%) as a 5.7:1 mixture of the *E*- and *Z*-isomers, oil; ν_{max}/cm^{-1} 2960 and 1600; δ_H(200 MHz) 0.98 (9 H, s, Bu^t, minor isomer), 1.00 (9 H, s, Bu^t, major isomer), 1.78 (3 H, s, C-Me, major isomer), 1.81 (3 H, s, C-Me, minor isomer), 2.92 (3 H, s, N-Me, minor isomer), 2.95 (3 H, s, N-Me, major isomer), 4.91 (2 H, s, CH_2, minor isomer), 5.10 (2 H, s, CH_2, major isomer), 6.40–6.58 (3 H, m, Ar-H, both isomers), 6.88–7.30 (6 H, m, Ar-H, both isomers); *m*/*z* 326.1999 (M$^+$, 8%. $C_{20}H_{26}N_2O_2$ requires 326.1994), 223 (31), 208 (100), 194 (7), 77 (13) and 57 (30); **14** (0.23 g, 12%).

From 6i. Perester **6i** (10 mmol) afforded in order of elution [2-(*methylanilino*)*phenyl*](*phenyl*)*methanone* O-(tert-*butoxymethyl*)*oxime* **9i** (0.66 g, 17%) as a 13:4 mixture of the *E*- and *Z*-isomers, oil; major isomer, ν_{max}/cm^{-1} 3000, 1600, 1480, 1350, 1090, 1000 and 950; δ_H(200 MHz) 1.28 (9 H, s, Bu^t), 2.92 (3 H, s, Me), 5.28 (2 H, s, CH_2), 6.54–6.62 (2 H, m, Ar-H), 6.72 (1 H, dddd, J_1, J_2 7.2, J_3, J_4 0.8, Ar-H), 7.04–7.15 (2 H, m, Ar-H) and 7.20–7.52 (9 H, m, Ar-H); *m*/*z* 388.2150 (M$^+$, 46%. $C_{25}H_{28}N_2O_2$ requires 388.2151), 285 (80), 270 (100), 194 (8), 180 (8), 167 (6),

77 (11) and 57 (40); minor isomer, ν_{max}/cm^{-1} 3000, 1600, 1490, 1350, 1100, 1010 and 950; δ_H(200 MHz) 1.20 (9 H, s, Bu^t), 2.65 (3 H, s, Me), 5.25 (2 H, s, CH_2), 6.28–6.37 (2 H, m, Ar-H), 6.63–6.72 (1 H, m, Ar-H), 7.03–7.38 (9 H, m, Ar-H), 7.47 (1 H, ddd, J_1, J_2 7.3, J_3 1.8, Ar-H) and 7.70 (1 H, dd, J_1 7.3, J_2 1.7, Ar-H); *m*/*z* 388.2153 (M^+, 8%. $C_{25}H_{28}N_2O_2$ requires 388.2151), 285 (82), 270 (100), 194 (6), 180 (7), 167 (3), 77 (8) and 57 (34); **15** (0.45 g, 18%); [2-(*methylamino*)*phenyl*](*phenyl*)*methanone* **18** (0.03 g, 2%), mp 68.5–70 °C (lit.,[35] 69 °C); **16** (0.22 g, 7%).

From 6j. Perester **6j** (9.5 mmol) gave in order of elution 10-*phenyl*-9,10-*dihydroacridin*-9-*one* **19j** (0.10 g, 4%), mp 274–276 °C (lit.,[36] 276 °C); 2-(*diphenylamino*)*benzaldehyde* O-(tert-*butyl*)*oxime* **11j** (0.15 g, 5%), oil; ν_{max}/cm^{-1} 2980, 1590, 1480 and 960; δ_H(200 MHz) 1.22 (9 H, s, Bu^t), 6.90–7.40 (13 H, m, Ar-H), 7.94 (1 H, dd, J_1 7.8, J_2 1.5, Ar-H) and 8.14 (1 H, s, N=CH); *m*/*z* 344.1895 (M^+, 73%. $C_{23}H_{24}N_2O$ requires 344.1889), 288 (7), 271 (33), 256 (100), 180 (10), 77 (8) and 57 (36); **3d** (0.25 g, 13%); **3j** (0.35 g, 13%); 2-(*diphenylamino*)*benzaldehyde* O-(tert-*butoxymethyl*)*oxime* **9j** (0.60 g, 17%), oil; ν_{max}/cm^{-1} 2960, 1590, 1480 and 1000; δ_H(300 MHz) 1.12 (9 H, s, Bu^t), 5.23 (2 H, s, CH_2), 6.91–7.28 (12 H, m, Ar-H), 7.38 (1 H, td, J_t 7.5, J_d 1.4, Ar-H), 7.98 (1 H, dd, J_1 7.7, J_2 1.2, Ar-H) and 8.22 (1 H, s, N=CH); *m*/*z* 374.1996 (M^+, 38%. $C_{24}H_{26}N_2O_2$ requires 374.1994), 271 (31), 270 (14), 256 (100), 77 (7) and 57 (56); 2-(*diphenylamino*)-*benzonitrile* **10j** (0.44 g, 17%), mp 106–108 °C (Found: C, 84.8; H, 5.2; N, 10.35. $C_{19}H_{14}N_2$ requires C, 84.4; H, 5.2; N, 10.4%); ν_{max}/cm^{-1} 2220, 1590, 1480, 1440 and 1270; δ_H(200 MHz) 7.02–7.35 (12 H, m), 7.43–7.53 (1 H, m) and 7.58 (1 H, dd, J_1 7.7, J_2 1.6); *m*/*z* 270.1155 (M^+, 100%. $C_{19}H_{14}N_2$ requires 270.1157), 269 (30), 192 (4), 167 (9), 135 (10), 77 (10) and 51 (11); **13** (0.12 g, 7%).

From 6k. Perester **6k** (8.0 mmol) gave in order of elution 1-[2-(*diphenylamino*)*phenyl*]*ethan*-1-*one* O-(tert-*butyl*)*oxime* **11k** (0.04 g, 1%) as a 5:1 mixture of the *E*- and *Z*-isomers, oil; δ_H(200 MHz) 1.06 (9 H, s, Bu^t, minor isomer), 1.08 (9 H, s, Bu^t, major isomer), 1.70 (3 H, s, Me, minor isomer), 1.90 (3 H, s, Me, major isomer) and 6.75–7.45 (14 H, m, Ar-H); *m*/*z* 358.2044 (M^+, 91%. $C_{24}H_{26}N_2O$ requires 358.2045), 302 (8), 285 (56), 270 (100), 256 (18), 243 (10), 210 (14), 196 (16), 180 (11), 167 (17), 77 (19), 57 (47) and 51 (11); **3e** (0.17 g, 10%); 1-[2-(*diphenylamino*)*phenyl*]*ethan*-1-*one* O-(tert-*butoxymethyl*)*oxime* **9k** (0.68 g, 22%) as a 5:1 mixture of the *E*- and *Z*-isomers, oil; δ_H(200 MHz) 1.13 (9 H, s, Bu^t, major isomer), 1.15 (9 H, s, Bu^t, minor isomer), 1.78 (3 H, s, Me, minor isomer), 1.99 (3 H, s, Me, major isomer), 4.85 (2 H, s, CH_2, minor isomer), 5.10 (2 H, s, CH_2, major isomer) and 6.85–7.45 (14 H, m, Ar-H, both isomers); *m*/*z* 388.2155 (M^+, 21%. $C_{25}H_{28}N_2O_2$ requires 388.2151), 285 (44), 270 (78), 256 (12), 167 (16), 77 (26), 57 (100) and 51 (22); **14** (0.15 g, 10%).

From 6l. Perester **6l** (8.0 mmol) afforded in order of elution 9,10-*diphenyl*-9,10-*dihydroacridine* **20l** (0.43 g, 16%), mp 171–173 °C (lit.,[36] 175–175.5 °C); **3f** (0.36 g, 16%); **3l** (0.08 g, 3%); [2-(*diphenylamino*)*phenyl*](*phenyl*)*methanone* O-(tert-*butoxymethyl*)*oxime* **9l** (0.54 g, 15%) as a 13:2 mixture of the *E*- and *Z*-isomers; major isomer, mp 123–126 °C (from light petroleum–benzene) (Found: C, 80.3; H, 6.7; N, 6.2. $C_{30}H_{30}N_2O_2$ requires C, 80.0; H, 6.7; N, 6.2%); δ_H(200 MHz) 1.20 (9 H, s, Bu^t), 4.97 (2 H, s, CH_2) and 6.72–7.35 (19 H, m, Ar-H); *m*/*z* 451 ($M^+ + 1$, 94%), 421 (21), 364 (15), 347 (52), 332 (100), 272 (16), 256 (18), 243 (14), 196 (14), 167 (9), 77 (12) and 57 (65); minor isomer, oil (Found: C, 80.4; H, 6.7; N, 6.2. $C_{30}H_{30}N_2O_2$ requires C, 80.0; H, 6.7; N, 6.2%); δ_H(200 MHz) 1.15 (9 H, s, Bu^t), 5.12 (2 H, s, CH_2) and 6.65–7.60 (19 H, m, Ar-H); *m*/*z* 451 ($M^+ + 1$, 100%), 421 (27), 364 (25), 347 (77), 332 (95), 272 (23), 256 (23), 243 (16), 196 (10), 167 (11), 77 (15) and 57 (63); **15** (0.11 g, 5%); **16** (0.17 g, 7%).

N′-{1-[2-(Diphenylamino)phenyl]-1-phenylmethylidene}-4-methylbenzene-1-sulfonohydrazide

A solution of **3l** (5.0 g, 14 mmol), tosylhydrazine (2.9 g, 16 mmol) and conc. hydrochloric acid (2 drops) in absolute ethanol (30 cm^3) was refluxed for 3 days; additional tosylhydrazine (~1 g) and conc. HCl (2 drops) were added every 24 h. After removal of the solvent, the residue was chromatographed to give mostly starting material and the title compound (0.37 g, 5%), mp 191–194 °C (decomp.) (Found: C, 74.25; H, 5.25; N, 8.15; S, 6.2. $C_{32}H_{27}N_3O_2S$ requires C, 74.25; H, 5.3; N, 8.1; S, 6.2%); ν_{max}/cm^{-1} 3300, 1590, 1490, 1380, 1320 and 1160; δ_H(200 MHz) 2.38 (3 H, s, Me), 6.40–6.55 (4 H, m + A part of AA′BB′, *J* 8.3, Ar-H), 6.66–7.40 (17 H, m, Ar-H) and 7.58–7.74 (3 H, m + B part of AA′BB′, *J* 8.3, Ar-H); *m*/*z* 517.1830 (M^+, 6%. $C_{32}H_{27}N_3O_2S$ requires 517.1824), 489 (6), 362 (<1), 334 (72), 332 (86), 256 (100), 254 (21), 91 (21) and 77 (11).

Decomposition of the above hydrazide *via* the diazo compound 28[37]

A solution of methyllithium (1.6 M, 0.5 cm^3) in anhydrous THF (5 cm^3) was added dropwise at r.t. under a nitrogen atmosphere to a solution of the hydrazide (0.5 g, 0.9 mmol) in THF (10 cm^3). After 4 h, the solution was refluxed for 5 h and kept overnight at r.t. The mixture was poured into ice–water and extracted with dichloromethane. The organic phase was dried, the solvent was removed and the residue chromatographed to give **20l** (0.11 g, 40%) and 0.04 g of an unidentified product, δ_H(200 MHz) 5.79 (1 H, s), 6.74–6.88 (6 H, m), 6.95–7.22 (11 H, m) and 7.42–7.52 (1 H, m); *m*/*z* 393 (M^+, <1%), 365 (<1), 351 (74), 332 (100), 272 (13), 256 (23), 244 (6), 181 (5), 167 (9), 105 (9) and 77 (15).

X-Ray crystal structure analysis of quinazolinone 16

Crystal data. $C_{20}H_{14}N_2O$, $M = 298.33$. Triclinic, $a = 9.287(1)$, $b = 10.625(2)$, $c = 9.192(2)$ Å, $\alpha = 95.42(3)$, $\beta = 117.95(2)$, $\gamma = 69.42(2)°$, $V = 747.4(2)$ Å^3 (by least squares fitting of the setting angles of 28 automatically centred reflections in the range $15.7 \leqslant \theta \leqslant 40.7°$), $\lambda = 1.541\,78$ Å, space group $P\bar{1}$, $Z = 2$, $D = 1.326$ g cm^{-3}, μ(CuKα) = 0.658 mm^{-1}.

Data collection and processing. Pale yellow prismatic crystal (0.08 × 0.19 × 0.46 mm^3), Siemens AED diffractometer, θ–2θ scans, scan width $(1.2 + 0.34 \tan\theta)°$, scan speed 0.05–0.16° s^{-1}, graphite monochromated CuKα radiation ($\lambda = 1.541\,78$ Å), crystal orientation and stability checked by two standard reflections measured every 100 reflections, 2828 reflections collected ($4 \leqslant \theta \leqslant 70°$, $-11 \leqslant h \leqslant 11$, $-12 \leqslant k \leqslant 12$, $0 \leqslant l \leqslant 11$), of which 2156 showing $I > 2\sigma(I)$, no absorption correction performed.

Structure analysis and refinement. The structure was solved by direct methods with SIR92[38] and refined by full-matrix least squares on F^2 with SHELXL93.[39] The hydrogen atoms were located in a ΔF map and positionally refined with $U_{iso} = 0.1$ Å^2. The final residuals were $R_1 = 0.0385$ and $wR_2 = 0.1077$ for 2156 unique reflections having $I > 2\sigma(I)$ and $R_1 = 0.0512$ and $wR_2 = 0.1178$, $S = 1.00$ for all 2828 data and 251 refined parameters. Maximal $\Delta/\sigma = -0.002$ and maximum and minimum residual peak in the final difference Fourier map 0.211 and −0.124 e Å^{-3} respectively. The molecular structure is shown in Fig. 1.[40] Atomic coordinates, thermal parameters, bond lengths and bond angles have been deposited at the Cambridge Crystallographic Data Centre. Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, available *via* the RSC Web page (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/212.

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