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New Stable *N*-H Oxaziridines – Synthesis and Reactivity

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A number of stable new *N*-H oxaziridines have been designed and prepared, and their reactivity as electrophilic sources of nitrogen investigated. 3-*tert*-Butyl-3-phenyloxaziridine is the most efficient and stable and has potential for use as a general reagent for this purpose.

Introduction

Chemical reactions involving electrophilic sources of nitrogen commonly require toxic or otherwise undesirable reagents, including tosyl azide, nitroso compounds, diimides, or azodicarboxylates, and new reagents are therefore desirable; indeed, the use of green sources of electrophilic nitrogen has been identified as an "aspirational reaction" by the pharmaceutical manufacturers.[1] Oxaziridines, characterized by a reactive strained C,N,O three-membered ring, have shown interesting reactivities as nitrogen and oxygen atom transfer reagents, and the synthesis and chemistry of oxaziridines has been widely studied.[2] It has been established that the attack of a nucleophile occurs at either the oxygen or the nitrogen atoms of the ring, depending upon the nature of the nucleophile and the substituents on the oxaziridine, especially at the nitrogen atom. For example, oxaziridines bearing electron-withdrawing substituents on the nitrogen atom or on both the nitrogen and the carbon atoms of the three-membered ring have been developed for their ability to transfer oxygen atoms to nucleophiles. In particular, *N*-(fluoroalkyl)oxaziridines,[3] *N*-phosphanyloxaziridines[4] and *N*-sulfonyloxaziridines[5] have proved to be efficient reagents for the oxidation of sulfides to sulfoxides, the asymmetric hydroxyation of enolates, and the stereoselective epoxidation of olefins. Davis in particular has shown that *N*-substituted camphoryl oxaziridines transfer oxygen to various nucleophiles with very good stereoselectivity, perhaps due to the steric hindrance close to the oxaziridine ring.[6] Oxygen transfer may also be performed with hindered oxaziridines and hindered nucleophiles,[7] and may be promoted by acid, forming an *N*-protonated oxaziridine which is believed to be the active oxidizing species.[8]

Nitrogen transfer has also been performed, mainly using *N*-H, *N*-alkyl-, *N*-aryl-, *N*-acyl-, *N*-carboxamido- or *N*-(alkoxycarbonyl)oxaziridines, with sulfur, nitrogen, phosphorus and carbon nucleophiles.[9] However, few electrophilic aminations have been carried out with enantiomerically pure chiral *N*-substituted oxaziridines.[10] To date, only a handful of reports of enantiomerically pure chiral *N*-acyloxaziridines have been published.[10,11]

N-H oxaziridines, first reported in the early 1960s,[12] can be effective for the amination of nitrogen, oxygen, sulfur and carbon nucleophiles,[13] and are potentially of great value today as relatively "green" sources of electrophilic nitrogen. Due to their general instability, however, very few *N*-H oxaziridines have been prepared, and fewer used for their ability to transfer nitrogen.[14] N-H oxaziridines also offer the attractive additional potential as enantioselective nitrogen transfer agents by incorporation of chiral elements into their structure.

The first enantiomerically pure chiral *N*-H oxaziridines **1** and **2**, which were prepared in our laboratories, were derived from (*R*,*R*)-(+)-camphor and the related (–)-fenchone respectively.[15] These two *N*-H oxaziridines showed remarkable stability, and may readily be functionalized at nitrogen using a range of standard electrophilic reagents; for example, reaction of **1** with cyclohexyl isocyanate gives oxaziridine **3** in 67% yield. They are able to transfer their nitrogen atom to carbon nucleophiles such as anions derived from esters and nitriles.[16] In these reactions, a new carbon–nitrogen bond is formed, but the camphor or fenchone unit is retained in the product structure through an imine linkage, and the ester or nitrile moiety is hydrolysed and in some cases decarboxylated, we believe as a consequence of the reaction mechanism (e.g. Scheme 1), in which cleavage of the N–O bond of the oxaziridine induced by attack of the nucleophile is followed by cyclization; ring-opening and tautomerization leads to the observed products. Moderate

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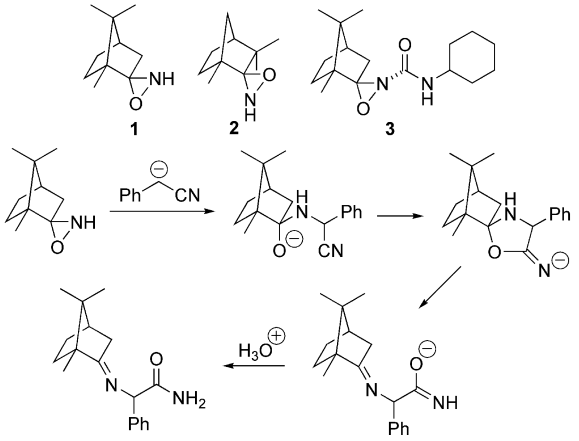
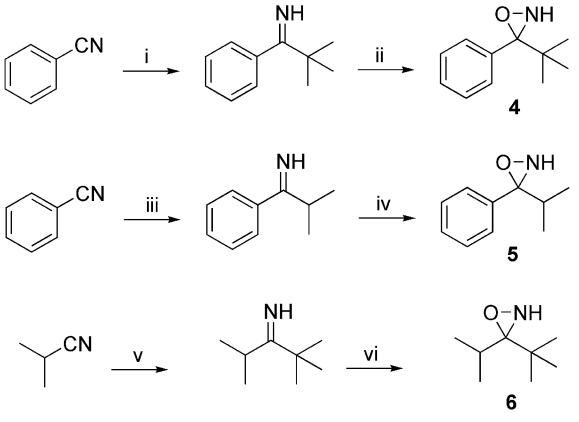
stereoselectivity is observed. We report here the synthesis of a number of new stable *N*-H oxaziridines, together with their reactivity as sources of electrophilic nitrogen towards carbon nucleophiles.



Scheme 1. Nitrogen transfer to nucleophiles.

Results and Discussion

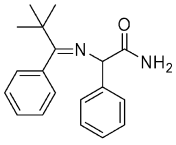
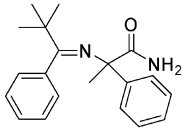
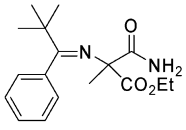
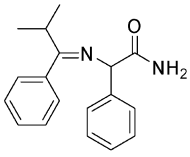
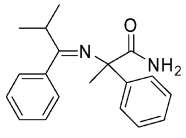
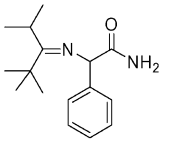
Because of the dearth of reports of stable *N*-H oxaziridines, we initiated an investigation into the optimum steric and electronic requirements for the synthesis of stable *N*-H oxaziridines that might be used as effective nitrogen transfer reagents. 3,3-Di-*tert*-butyloxaziridine and 3,3-diphenyl oxaziridine have previously been reported,[17] and we prepared *N*-H oxaziridines related to these two structures, as it appeared that the presence of at least one *tert*-butyl or phenyl group was necessary for stability in these simple cases. Three new *N*-H oxaziridines, the *tert*-butyl/phenyl **4**, isopropyl/phenyl **5**, and isopropyl/*tert*-butyl **6**, were prepared using a straightforward two-step procedure using the corresponding nitrile as the starting material, by addition of alkyllithium or Grignard reagents to nitriles to give the corresponding primary imines after work-up,[18] followed by oxidation with *m*CPBA (Scheme 2). These new oxaziridines have proved to be stable in the laboratory for months at room temperature.



Scheme 2. Generation of *N*-H oxaziridines **4**–**6**. (i) *t*BuLi, THF, 78 °C to room temp., 15 h; NH_3, –78 °C to room temp.; 70%; (ii) *m*CPBA, –40 °C, CH_2Cl_2; 79%; (iii) *i*PrMgCl, THF, Δ, 15 h; NH_3, –78 °C to room temp.; 65%; (iv) *m*CPBA, –40 °C, CH_2Cl_2; 30%; (v) *t*BuLi, THF, –78 °C to room temp., 15 h; NH_3, –78 °C to room temp.; (vi) *m*CPBA, –40 °C, CH_2Cl_2; 67% (two steps).

An unusual feature of nitrogen-containing three-membered heterocycles is that there is rather a high barrier to inversion at nitrogen.[19] Indeed, each of our three new *N*-H oxaziridines displays pairs of signals in their ^1H NMR spectra at room temperature, presumably corresponding to slow inversion at the pyramidal nitrogen atom, with the ra-

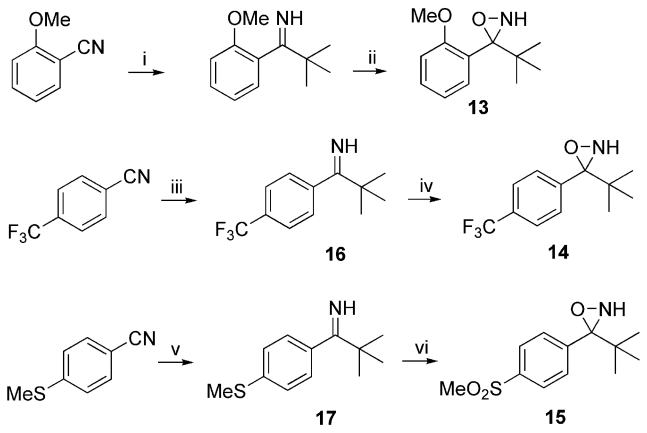
Table 1. Electrophilic amination of nitriles using *N*-H oxaziridines **4**–**6**.[a]

Oxaziridine	Nitrile	Product	% Yield
4	phenylacetonitrile	 **7**	78
4	α-methyl phenylacetonitrile	 **8**	80
4	ethyl-2-cyanopropionate	 **9**	56
5	phenylacetonitrile	 **10**	70
5	α-methyl phenylacetonitrile	 **11**	50
6	phenylacetonitrile	 **12**	85

[a] Conditions: i) LHMDS, nitrile, THF, –78 °C, 1 h; ii) oxaziridine addition at –78 °C, then room temp.

tios: **4** (4:1); **5** (2.3:1); **6** (1.2:1). These three oxaziridines were then used in the electrophilic amination of three nitriles (Table 1) by deprotonation α to the nitrile using lithium hexamethyldisilazide followed by addition of the *N*-H oxaziridine in THF solution at –78 °C, conditions that are very successful for the "parent" camphor *N*-H oxaziridine **1**.

Each oxaziridine was effective for nitrogen transfer to the nitriles. After work-up and purification, the products **7**–**12** were obtained in moderate to good yields as the corresponding primary amides, as we have previously observed. In the case of the product **9**, it was interesting to note that only the nitrile group is attacked and hydrolysed, and not the ester moiety. This result shows a difference of reactivity between these new *N*-unprotected oxaziridines and *N*-H camphor oxaziridine **1**, where both hydrolysis of the nitrile and hydrolysis/decarboxylation of the ester were observed as reaction pathways.[15,16]



Scheme 3. Generation of *N*-H oxaziridines **13**–**15**. (i) *t*BuLi, THF, –78 °C to room temp., 15 h; NH_3, –78 °C to room temp.; 64%; (ii) *m*CPBA, –40 °C, CH_2Cl_2; 38%; (iii) *t*BuLi, THF, –78 °C to room temp., 15 h; NH_3, –78 °C to room temp.; (iv) *m*CPBA, –40 °C, CH_2Cl_2; 43% (two steps); (v) *t*BuLi, THF, –78 °C to room temp., 15 h; NH_3, –78 °C to room temp.; (vi) *m*CPBA, –40 °C, CH_2Cl_2; 60% (two steps).

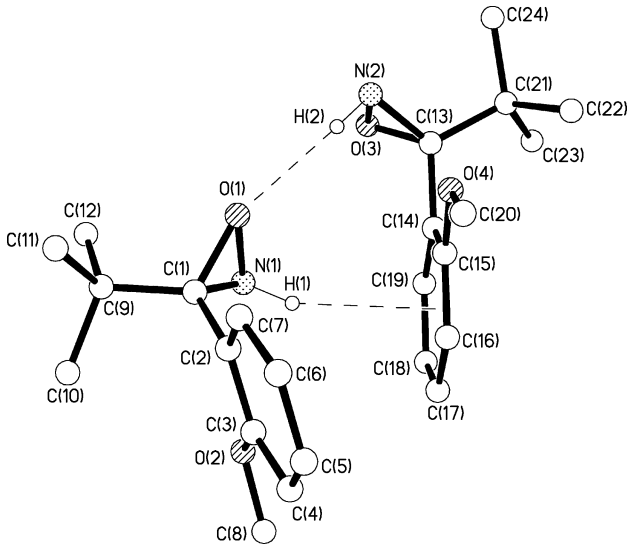
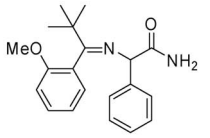
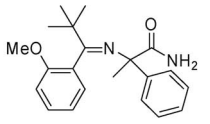
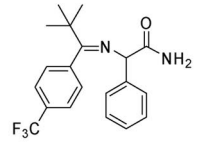
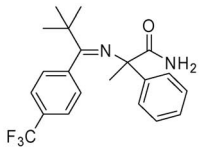
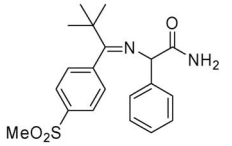
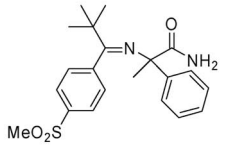


Figure 1. Structure of *N*-H oxaziridine **13** with two molecules in the asymmetric unit linked via N–H···O and N–H···π interactions.

3-*tert*-Butyl-3-phenyloxaziridine (**4**) was the most stable and appears to be the best general reagent for nitrogen transfer. Other structures based on oxaziridine **4** were therefore investigated; for example, substituents were added at the phenyl group in an attempt to increase reactivity. Three further new *N*-H oxazirdines **13**–**15** were synthesized following the procedure described for **4**–**6** (Scheme 3).

2,2-Dimethyl-1-[4-trifluoromethyl)phenyl]propan-1-imine (**16**) and propanimine **17** were not sufficiently stable to be

Table 2. Electrophilic amination of nitriles using *N*-H oxaziridines **13**–**15**.[a]

Oxaziridine	Nitrile	Product	% Yield
13	phenylacetonitrile	 **18**	30
13	α-methyl phenylacetonitrile	 **19**	25
14	phenylacetonitrile	 **20**	50
14	α-methyl phenylacetonitrile	 **21**	53
15	phenylacetonitrile	 **22**	60
15	α-methyl phenylacetonitrile	 **23**	40

[a] Conditions: i) LHMDS, nitrile, THF, –78 °C, 1 h; ii) oxaziridine addition at –78 °C, then room temp.

purified and were used directly in the oxidation step without further purification. All of these oxaziridines again display pairs of signals in their ^{1}H NMR spectra at room temperature, with ratios: **13** (7.3:1); **14** (2.3:1); **15** (1.5:1), and are air-stable, no decomposition being observed over several days at room temperature. While all of the other oxaziridines described here are colourless oils, oxaziridine **13** was isolated as a colourless crystalline material, and was subjected to single-crystal X-ray analysis (Figure 1). The crystal structure shows hydrogen bonding between the NH hydrogen atom of one molecule and the oxygen atom of another, plus a possible interaction between the NH hydrogen atom of one molecule and the aromatic ring of the other.

These oxaziridines were used as described above for electrophilic amination reactions of two nitriles (Table 2).

While these new *N*-H oxaziridines were all able to transfer nitrogen to give products **18**–**23**, no improvement in yields or reactivity over 3-*tert*-butyl-3-phenyloxaziridine (**4**) was observed. The electron-donating character of the methoxy group may explain the reduced reactivity of the 3-*tert*-butyl-3-(2-methoxyphenyl)-1,2-oxaziridine (**13**).

Conclusions

We have developed a new range of chiral *N*-H oxaziridines capable of electrophilic amination of nitrile derivatives. 3-*tert*-Butyl-3-phenyloxaziridine (**4**) is the most efficient and stable and has potential for use as a general reagent for this purpose.

Experimental Section

General Procedure for the Synthesis of Imines: A solution of nitrile in dry THF (1 mL/mmol) cooled to –78 °C was added dropwise to a solution of *tert*-butyllithium (1.5 equiv., 1.7 M in pentane) or a Grignard reagent (1.5 equiv., 2 M or 3 M in THF) and the mixture stirred at room temperature (when *tert*-butyllithium was used), or under reflux (when Grignard reagents were used), for 15 h. After cooling to –78 °C, ammonia gas was bubbled through and the reaction was stirred vigorously for 15 min. The mixture was allowed to reach room temperature, the white precipitate removed by filtration, and the solvent removed under reduced pressure. Purification by kugelrohr distillation afforded the desired imines.

General Procedure for the Synthesis of Oxaziridines from Imines: A solution of purified *m*CPBA (1 equiv.) in dry dichloromethane (5 mL/mmol) was cooled to between –30 °C and –40 °C, causing some of the peracid to crystallize from the solution. Upon addition of a solution of the imine in dry dichloromethane (3 mL/mmol) to the reaction mixture over a period of 4–5 min, the solution became homogeneous. The reaction mixture was stirred overnight at between –30 and –40 °C, and allowed to reach room temperature. The reaction mixture was stirred at room temperature for a further two hours until all of the peracid had reacted, by which time much of the *m*-chlorobenzoic acid by-product had crystallized from the solution. The solution was concentrated under reduced pressure until approximately 25% of the original volume remained. Petroleum ether was added and the solution again concentrated under reduced pressure until approximately 25% of the original volume remained. This process was repeated once more, and finally petroleum ether (5 mL/mmol) was added to the mixture. The precipitated *m*-chlorobenzoic acid was removed by filtration, and the rest of this by-product washed from the resulting solution with aqueous sodium hydroxide. The organic phase was dried ($MgSO_4$), and the solvent removed under reduced pressure to give the crude product, which was purified by column chromatography on silica gel (light petroleum/ethyl acetate) to afford the desired oxaziridine.

General Procedure for the Reaction of Oxaziridines with Phenylacetonitrile or α-Methylphenylacetonitrile: A solution of phenylacetonitrile or α-methylphenylacetonitrile in THF (5 mL/mmol) was added dropwise to a cooled (–78 °C) stirring solution of lithium bis(trimethylsilyl)amide (1.0 M in THF, 1.1 equiv.) in dry THF (2.5 mL/mmol). After one hour at –78 °C, a solution of oxaziridine (1.5 equiv.) in dry THF (2 mL/mmol) was added dropwise, and the reaction allowed to reach room temperature over a period of two hours. Saturated aqueous ammonium chloride (10 mL/mmol) was added, and the mixture extracted with dichloromethane (3×10 mL/mmol). The combined organic extracts were dried ($MgSO_4$), and the solvents removed under reduced pressure to give an oil, which was purified by column chromatography on silica gel (light petroleum/ethyl acetate). The product was recrystallized from a mixture of chloroform and hexane to afford the desired product.

3-*tert*-Butyl-3-phenyloxaziridine (4): Prepared according to the general procedure using (300 mg, 1.64 mmol) of the corresponding imine, the title compound **4** was isolated as a colourless oil (231 mg, 79%). IR (neat): $\tilde{\nu}_{max.}$ = 3202 (NH), 2969, 1481, 1329, 1128, 902, 735, 702 cm^{-1}. Oxaziridine **4** shows in its ^{1}H NMR spectrum a signal pair of diastereoisomers (A and B) at N-H in a 4:1 ratio (the major isomer is represented by A). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.31 (m, C*H*Ar, 5 H_A, 5 H_B), 4.41 (br. s, N*H*, 1 H_B), 3.86 (br. s, N*H*, 1 H_A), 1.07 (s, CCH_3, 9 H_B), 1.02 (s, CCH_3, 9 H_A) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.9 (C_{Aq}Ar), 136.5 (C_{Bq}Ar), 128.5 (*C*HAr), 128.1 (*C*HAr), 128.0 (*C*HAr), 127.7 (*C*HAr), 127.6 (*C*HAr), 127.4 (*C*HAr), 86.26 (N-C_{Bq}-O), 86.23 (N-C_{Aq}-O), 35.2 ($C_{Bq}CH_3$), 35.0 ($C_{Aq}CH_3$), 25.55 (CC$_A$H$_3$), 25.48 (CC$_B$H$_3$) ppm. MS (FAB$^+$): *m*/*z* = 178 [M + H]$^+$, 105, 77. HRMS (FAB$^+$) $C_{11}H_{16}NO$ [M + H]$^+$ calcd. 178.12319; found 178.12342.

3-Isopropyl-3-phenyloxaziridine (5): Prepared according to the general procedure using (1.25 g, 4.85 mmol) of the corresponding imine, the title compound **5** was isolated as a colourless oil (243 mg, 30%). IR (neat): $\tilde{\nu}_{max.}$ = 3200 (NH), 2969, 1577, 1469, 1294, 756, 699 cm^{-1}. Oxaziridine **5** shows in its ^{1}H NMR spectrum a signal pair of diastereoisomers (A and B) at N-H in a 2.3:1 ratio (the major isomer is represented by A). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.13 (m, C*H*Ar, 5 H_A, 5 H_B), 4.14 (br. s, N*H*, 1 H_B), 3.69 (br. s, N*H*, 1 H_A), 2.30 (septet, *J* = 6.9 Hz, C*H*CH$_3$, 1 H_A), 2.29 (septet, *J* = 6.9 Hz, C*H*CH$_3$, 1 H_B), 0.948 (d, *J* = 6.9 Hz, CHCH_3, 3 H_B), 0.946 (d, *J* = 6.9 Hz, CHCH_3, 3 H_B), 0.91 (d, *J* = 6.9 Hz, CHCH_3, 3 H_A), 0.89 (d, *J* = 6.9 Hz, CHCH_3, 3 H_A) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.9 (C_{Aq}Ar), 136.5 (C_{Bq}Ar), 128.8 (*C*HAr), 128.6 (*C*HAr), 128.5 (*C*HAr), 128.1 (*C*HAr), 127.0 (*C*HAr), 126.1 (*C*HAr), 83.6 (N-C_{Bq}-O), 83.7 (N-C_{Aq}-O), 33.8 (C_BCH_3), 32.3 (C_AHCH_3), 17.8 (CC$_A$H$_3$), 17.5 (CHC_BH$_3$), 17.1 (CHC_BH$_3$), 16.4 (CC$_A$H$_3$) ppm. MS (FAB$^+$): *m*/*z* = 164 [M + H]$^+$, 105, 91, 77. HRMS (FAB$^+$) $C_{10}H_{14}NO$ [M + H]$^+$ calcd. 164.10754; found 164.10721.

3-*tert*-Butyl-3-isopropyloxaziridine (6): A solution of isobutyronitrile (1.35 mL, 15 mmol) in THF (2.5 mL) cooled to –78 °C, was added dropwise to a solution of *tert*-butyllithium (1.7 M in pentane, 13.2 mL, 22.5 mmol) and the mixture was stirred at room temperature for 15 h. After cooling to –78 °C, ammonia gas was bubbled through and the reaction was stirred vigorously for 15 min. The

mixture was then allowed to reach room temperature, the precipitate was filtered and the solvent was removed under reduced pressure to afford the imine which was used immediately due to its instability. Then, prepared according to the general procedure, the title compound **6** was isolated as a colourless oil (1.45 g, 67% over two steps). IR (neat): $\tilde{\nu}_{max.}$ = 3220 (NH), 2968, 1481, 1465, 1368, 1286, 969, 896 cm^{-1}. Oxaziridine **6** shows in its ^1H NMR spectrum a signal pair of diastereoisomers (A and B) at N-H in a 1.2:1 ratio (the major isomer is represented by A). ^1H NMR (400 MHz, $CDCl_3$): δ = 3.81 (br. s, N*H*, 1 H_B), 3.56 (br. s, N*H*, 1 H_A), 2.43 (septet, J = 6.9 Hz, C*H*CH_3, 1 H_A), 2.28 (septet, J = 6.8 Hz, C*H*CH_3, 1 H_B), 0.96 (s, CC*H*$_3$, 9 H_B), 0.92 (s, CC*H*$_3$, 9 H_A), 0.93–0.91 (m, CHC*H*$_3$, 6 H_A), 0.78 (d, J = 6.8 Hz, CHC*H*$_3$, 3 H_B), 1.32 (J = 6.8 Hz, CHC*H*$_3$, 3 H_B) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 86.4 (N-C_{Aq}-O), 86.2 (N-C_{Bq}-O), 36.0 (N-C_{Bq}-O), 35.9 ($C_{Aq}CH_3$), 26.7 (C_BHCH_3), 26.5 (C_AHCH_3), 25.2 (CC_AH_3), 20.1 (CC_BH_3), 20.4 (CHC_AH_3), 20.2 (CHC_AH_3), 18.3 (CHC_BH_3), 17.6 (CHC_BH_3) ppm. MS (FAB^+): m/z = 143 $[M]^+$, 128, 101, 84, 70, 57. HRMS (FAB^+) $C_8H_{17}NO$ $[M]^+$ calcd. 143.13101; found 143.13151.

3-*tert*-Butyl-3-(2-methoxyphenyl)-1,2-oxaziridine (13): Prepared according to the general procedure using (920 mg, 4.8 mmol) of the corresponding imine, the title compound **13** was recrystallized from a mixture of chloroform/hexane and isolated as a colourless crystalline material (385 mg, 38%), m.p. 52–53 °C. IR (neat): $\tilde{\nu}_{max.}$ = 3220 (NH), 2977, 1599 cm^{-1}. Oxaziridine **13** shows in its ^1H NMR spectrum a signal pair of diastereoisomers (A and B) at N-H in a 7.3:1 ratio (the major isomer is represented by A). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.29 (m, C*H*Ar, 2 H_A, 2 H_B), 6.97–6.88 (m, C*H*Ar, 2 H_A, 2 H_B), 4.44 (br. s, N*H*, 1 H_B), 4.00 (br. s, N*H*, 1 H_A), 3.83 (s, OC*H*$_3$, 3 H_A, 3 H_B), 1.06 (s, CC*H*$_3$, 9 H_B), 1.00 (s, CC*H*$_3$, 9 H_A) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.8 (C_qAr), 129.8 (*C*HAr), 129.7 (*C*HAr), 126.37 (C_qAr), 119.8 (*C*HAr), 110.41 (*C*HAr), 83.5 (N-C_q-O), 55.11 (O*C*H_3), 35.8 (C_qCH_3), 25.3 (C*C*H_3) ppm. MS (FAB^+): m/z = 208 $[M + H]^+$, 190, 175, 135, 91, 77. HRMS (FAB^+) $C_{12}H_{18}NO_2$ $[M + H]^+$ calcd. 208.13375; found 208.13375. $C_{12}H_{17}NO_2$ (207.27): calcd. C 69.54, H 8.27, N 6.76; found C 69.63, H 8.34, N 9.97.

CCDC-757772 (for **13**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3-*tert*-Butyl-3-[4-(trifluoromethyl)phenyl]-1,2-oxaziridine (14): A solution of 4-(trifluoromethyl)benzonitrile (735 mg, 4.3 mmol) in THF (2.5 mL) cooled to –78 °C, was added dropwise to a solution of *tert*-butyllithium (1.7 M in pentane, 3.8 mL, 6.5 mmol) and the mixture was stirred overnight at room temperature. After cooling to –78 °C, ammonia gas was bubbled through and the reaction was stirred vigorously for 15 min. Then, the mixture was allowed to reach room temperature, the white precipitate was filtered and the solvent was removed under reduced pressure to afford the imine as a black foam. Because of its instability, the imine was not purified and was used immediately. Prepared according to the general procedure, the title compound **14** was isolated as a yellow oil (455 mg, 43% over two steps). IR (neat): $\tilde{\nu}_{max.}$ = 3206 (NH), 2969, 2872, 1619 cm^{-1}. Oxaziridine **14** shows in its ^1H NMR spectrum a signal pair of diastereoisomers (A and B) at N-H in a 2.3:1 ratio (the major isomer is represented by A). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.64–7.59 (m, C*H*Ar, 2 H_A, 2 H_B), 7.52–7.49 (m, C*H*Ar, 3 H_A, 3 H_B), 7.10 (d, J = 7.6 Hz, C*H*Ar, 1 H_A, 1 H_B), 4.45 (br. s, N*H*, 1 H_B), 3.87 (br. s, N*H*, 1 H_A), 1.08 (s, CC*H*$_3$, 9 H_B), 1.03 (s, CC*H*$_3$, 9 H_A) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.7 (C_{Aq}Ar), 140.4 (C_{Bq}Ar), 130.8 (q, $^2J_{C\text{-}F}$ = 32.5 Hz, C_{Aq}ArCF3), 130.6 (q, $^2J_{C\text{-}F}$ = 32.3 Hz, C_{Bq}ArCF3), 128.5 (C_BHAr), 128.1 (C_AHAr), 124.7 (q, $^3J_{C\text{-}F}$ = 3.7 Hz, $C_AHArCCF_3$), 124.5 (q, $^3J_{C\text{-}F}$ = 3.8 Hz, $C_BHArCCF_3$), 124.0 (q, $J_{C\text{-}F}$ = 270.5 Hz, $C_{Bq}F_3$), 123.8 (q, $J_{C\text{-}F}$ = 270.6 Hz, $C_{Aq}F_3$), 86.0 (N-C_{Bq}-O), 85.9 (N-C_{Aq}-O), 35.1 ($C_{Bq}CH_3$), 35.0 ($C_{Aq}CH_3$), 25.4 (CC_AH_3), 25.3 (CC_BH_3) ppm. MS (FAB^+): m/z = 246 $[M + H]^+$, 228, 199, 172, 145. HRMS (FAB^+) $C_{12}H_{15}NOF_3$ $[M + H]^+$ calcd. 246.10275; found 246.11120.

3-*tert*-Butyl-3-[4-(methylsulfonyl)phenyl]-1,2-oxaziridine (15): A solution of 4-(methylthio)benzonitrile (865 mg, 5.8 mmol) in THF (2.5 mL) cooled to –78 °C in dry diethyl ether was added dropwise to a solution of *tert*-butyllithium (1.7 M in pentane, 5.1 mL, 8.7 mmol) and the mixture was stirred overnight at room temperature. After cooling to –78 °C, ammonia gas was bubbled through and the reaction was stirred vigorously for 15 min. Then, the mixture was allowed to reach room temperature, the white precipitate was filtered and the solvent was removed under reduced pressure to afford the imine as an orange oil. Because of its instability, the imine was not purified and was used immediately. Prepared according to the general procedure, the title compound **15** was isolated as a colourless solid (881 mg, 60% over two steps), m.p. 143–144 °C. IR (neat): $\tilde{\nu}_{max.}$ = 3202 (NH), 2970, 2871, 1482 cm^{-1}. Oxaziridine **15** shows in its ^1H NMR spectrum a signal pair of diastereoisomers (A and B) at N-H in a 1.5:1 ratio (the major isomer is represented by A). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.96–7.92 (m, C*H*Ar, 2 H_A, 2 H_B), 7.64–7.58 (m, C*H*Ar, 2 H_A, 2 H_B), 4.48 (br. s, N*H*, 1 H_B), 3.87 (br. s, N*H*, 1 H_A), 3.08 (s, SO_2CH_3, 3 H_A), 3.04 (s, SO_2CH_3, 3 H_B), 1.09 (s, CC*H*$_3$, 9 H_B), 1.04 (s, CC*H*$_3$, 9 H_A) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.6 (C_{Aq}Ar), 142.5 (C_{Bq}Ar), 140.7 (C_{Aq}Ar SO2CH$_3$), 140.3 (C_{Bq}Ar SO_2CH_3), 129.2 (C_BHAr), 128.7 (C_AHAr), 126.9 (C_AHAr), 126.7 (C_BHAr), 85.9 (N-C_{Bq}-O), 85.8 (N-C_{Aq}-O), 44.5 ($SO_2C_BH_3$), 44.4 ($SO_2C_AH_3$), 35.0 ($C_{A+Bq}CH_3$), 25.4 (CC_AH_3), 25.3 (CC_BH_3) ppm. MS (FAB^+): m/z = 256 $[M + H]^+$, 154, 107, 77, 57. HRMS (FAB^+) $C_{12}H_{18}NO_3S$ $[M + H]^+$ calcd. 256.10095; found 256.10074. $C_{12}H_{17}NO_3S{\cdot}0.1H_2O$ (257.14): calcd. C 56.04, H 6.75, N 5.44; found C 55.92, H 6.51, N 5.16.

2-(2,2-Dimethyl-1-phenylpropylidenamino)-2-phenylacetamide (7): Prepared according to the general procedure using phenylacetonitrile (132 µL, 1.15 mmol), the title compound **7** was isolated as a yellow solid (265 mg, 78%), m.p. 142–143 °C. IR (DCM): $\tilde{\nu}_{max.}$ = 3265 (NH_2), 3058, 2965, 1682 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.24–7.09 (m, 9 H, C*H*Ar), 6.92 (br. s, 1 H, C*H*Ar), 6.38 (br. s, 1 H, NH_2), 5.75 (br. s, 1 H, NH_2), 4.41 (s, 1 H, PhC*H*CO), 1.12 (s, 9 H, CC*H*$_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 181.2 (C_q=O), 175.0 (C_q=N), 140.19 (C_qAr), 136.0 (C_qAr), 128.3 (*C*HAr), 128.0 (*C*HAr), 127.4 (*C*HAr), 127.0 (*C*HAr), 126.9 (*C*HAr), 69.2 (Ph*C*HCO), 40.5 (C_qCH_3), 28.3 (CCH_3) ppm. MS (FAB^+): m/z = 295 $[M + H]^+$, 317, 250, 162, 106, 91. HRMS (FAB^+): calcd. for $C_{19}H_{23}N_2O$ $[M + H]^+$ 295.18109; found 295.18130. $C_{19}H_{22}N_2O$ (294.17): calcd. C 77.50, H 7.54, N 9.51; found C 77.02, H 7.47, N 9.50.

2-(2,2-Dimethyl-1-phenylpropylidenamino)-2-phenylpropanamide (8): Prepared according to the general procedure using α-methylphenylacetonitrile (93 µL, 0.67 mmol), the title compound **8** was isolated as a white solid (165 mg, 80%), m.p. 157–158 °C. IR (DCM): $\tilde{\nu}_{max.}$ = 3164 (NH_2), 3053, 2967, 1686 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.65 (br. s, 1 H, N*H*), 7.22–7.18 (m, 1 H, C*H*Ar), 7.13–7.063 (m, 4 H, C*H*Ar), 6.97–6.91 (m, 4 H, C*H*Ar), 6.72–6.68 (m, 1 H, C*H*Ar), 5.69 (br. s, 1 H, N*H*), 1.47 (s, 3 H, PhCC*H*$_3$), 1.11 (s, 9 H, CC*H*$_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.2 (C_q=O), 179.0 (C_q=N), 144.25 (C_qAr), 136.9 (C_qAr), 128.0 (*C*HAr), 127.6 (*C*HAr), 127.2 (*C*HAr), 126.8

(*C*HAr), 126.7 (*C*HAr), 126.4 (*C*HAr), 126.3 (*C*HAr), 67.7 (Ph$C_q$$CH_3$), 41.9 ($C_q$$CH_3$), 28.5 (C$CH_3$), 21.8 (PhC$CH_3$) ppm. MS (FAB$^+$) *m*/*z* 309 [M + H]$^+$, 331, 264, 162, 105, 91. HRMS (FAB$^+$) $C_{20}H_{25}N_2O$ [M + H]$^+$ calcd. 309.19669; found 309.19625. $C_{20}H_{24}N_2O$ (308.42): calcd. C 77.87, H 7.85, N 9.08; found C 77.77, H 7.78, N 9.07.

Ethyl 3-Amino-2-(2,2-dimethyl-1-phenylpropylidenamino)-2-methyl-3-oxopropanoate (9): A solution of ethyl 2-cyanopropionate (157 μL, 1.2 mmol) in THF (2.5 mL) was added dropwise to a cooled (–78 °C) stirring solution of lithium bis(trimethylsilyl)amide (1.0 M in THF, 1.45 mL, 1.2 mmol) in dry THF (2.5 mL). After 1 h at –78 °C, a solution of **4** (200 mg, 1.12 mmol) in dry THF (1 mL) was added dropwise and the reaction was allowed to reach room temperature over a period of two hours. Saturated aqueous ammonium chloride (20 mL) was added and the mixture extracted with DCM (3×25 mL). The combined organic extracts were dried ($MgSO_4$) and the solvent removed under reduced pressure to give a yellow oil which was purified by column chromatography on silica gel (light petroleum/ethyl acetate, 6:4) to afford the title compound **9** (204 mg, 56%) as a colourless solid, m.p. 119–120 °C. IR (DCM): $\tilde{\nu}_{max.}$ = 3401, 3170 (NH_2), 2966, 1731 (C=O ester), 1689 (C=O amide), 1361, 1258, 1134, 715 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (br. s, 1 H, N*H*), 7.33–7.27 (m, 3 H, C*H*Ar), 6.99 (br. s, 1 H, C*H*Ar), 6.90–6.87 (m, 1 H, C*H*Ar), 6.17 (br. s, 1 H, N*H*), 3.81–3.73 (quintet, *J* = 7.1 Hz, 1 H, OC$H_2$$CH_3$), 3.80–3.70 (quintet, *J* = 7.1 Hz, 1 H, OC$H_2$$CH_3$), 1.44 (s, 3 H, C$H_3$), 1.15 (s, 9 H, CC$H_3$), 1.12–1.07 (t, *J* = 7.1 Hz, 3 H, OCH$_2$CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.9 (C_q), 176.4 (C_q), 170.2 (C_q), 135.4 (C_qAr), 128.4 (*C*HAr), 128.3 (*C*HAr), 128.0 (*C*HAr), 127.5 (*C*HAr), 127.2 (*C*HAr), 70.5 ($CH_3C_qCO_2CH_2CH_3$), 61.2 (OCH_2CH_3), 41.9 ($C_q$$CH_3$), 28.5 (C$CH_3$), 23.2 (*C*$H_3$), 13.7 (OCH$_2$*C*$H_3$) ppm. MS (NSI$^+$): *m*/*z* = 305 [M + H]$^+$, 260, 162. HRMS (NSI$^+$) $C_{17}H_{24}N_2O_3$ [M + H]$^+$ calcd. 305.1860; found 305.1859. $C_{17}H_{24}N_2O_3$ (304.38): calcd. C 67.06, H 7.96, N 9.20; found C 67.11, H 8.06, N 9.04.

2-(2-Methyl-1-phenylpropylideneamino)-2-phenylacetamide (10): Prepared according to the general procedure using phenylacetonitrile (172 μL, 1.49 mmol), the title compound **10** was isolated as a red solid (289 mg, 70%), m.p. 137–138 °C. IR (DCM): $\tilde{\nu}_{max.}$ = 3406 (NH_2), 2963, 1683 (C=O), 1596, 1453, 1224, 708 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.22 (m, 8 H, C*H*Ar), 6.88–6.84 (m, 2 H, C*H*Ar), 5.90 (br. s, 2 H, NH_2), 4.70 (s, 1 H, PhC*H*CO), 2.85 (septet, *J* = 6.8 Hz, 1 H, C*H*CH_3), 1.23 (d, *J* = 6.8 Hz, 3 H, CHCH_3), 1.12 (d, *J* = 6.8 Hz, 3 H, CHCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.6 (C_q=O), 175.1 (C_q=N), 140.3 (C_qAr), 137.1 (C_qAr), 128.5 (*C*HAr), 128.4 (*C*HAr), 128.3 (*C*HAr), 127.5 (*C*HAr), 126.9 (*C*HAr), 126.3 (*C*HAr), 69.0 (Ph*C*HCO), 39.0 (*C*HCH$_3$), 20.2 (CH*C*H$_3$), 19.8 (CH*C*H$_3$) ppm. MS (FAB$^+$): *m*/*z* = 281 [M + H]$^+$, 236, 106, 91. HRMS (FAB$^+$) $C_{18}H_{21}N_2O$ [M + H]$^+$ calcd. 281.16539; found 281.16558. $C_{18}H_{20}N_2O{\cdot}0.2H_2O$ (283.96): calcd. C 76.12, H 7.25, N 9.86; found C 76.11, H 7.01, N 10.13.

2-(2-Methyl-1-phenylpropylidenamino)-2-phenylpropanamide (11): Prepared according to the general procedure using α-methylphenylacetonitrile (122 μL, 0.918 mmol), the title compound **11** was isolated as a colourless solid (135 mg, 50%), m.p. 156–157 °C. IR (DCM): $\tilde{\nu}_{max.}$ = 3398 (NH_2), 2963, 1686 (C=O), 1597 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.64 (br. s, 1 H, NH_2), 7.38–7.33 (m, 1 H, C*H*Ar), 7.16–6.99 (m, 7 H, C*H*Ar), 6.38 (m, 2 H, C*H*Ar), 5.86 (br. s, 1 H, NH_2), 2.67 (septet, *J* = 6.8 Hz, 1 H, C*H*CH$_3$), 1.46 (s, 3 H, PhCCH_3), 1.18 (d, *J* = 6.8 Hz, 3 H, CHCH_3), 1.07 (d, *J* = 6.8 Hz, 3 H, CHCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.5 (C_q=O), 177.2 (C_q=N), 144.6 (C_qAr), 139.3 (C_qAr), 128.5 (*C*HAr), 128.1 (*C*HAr), 127.2 (*C*HAr), 127.2 (*C*HAr), 126.8 (*C*HAr), 126.4 (*C*HAr), 67.7 (Ph$C_q$$CH_3$), 41.3 (*C*HCH$_3$), 21.9 (PhC*C*H$_3$), 20.2 (CH*C*H$_3$), 20.0 (CH*C*H$_3$) ppm. MS (FAB$^+$): *m*/*z* = 295 [M + H]$^+$, 250, 148, 91. HRMS (FAB$^+$): $C_{19}H_{23}N_2O$ [M + H]$^+$ calcd. 295.18104; found 295.18062. $C_{19}H_{22}N_2O$ (294.39): calcd. C 77.50, H 7.55, N 9.52; found C 77.21, H 7.52, N 9.51.

2-Phenyl-2-(2,2,4-trimethylpentan-3-ylidenamino)acetamide (12): Prepared according to the general procedure using phenylacetonitrile (40 μL, 0.35 mmol), the title compound **12** was isolated as a colourless solid (77 mg, 85%), m.p. 187–188 °C. IR (DCM): $\tilde{\nu}_{max.}$ = 3145 (NH_2), 2965, 1691 (C=O), 1653 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.50 (m, 2 H, C*H*Ar), 7.33–7.25 (m, 3 H, C*H*Ar), 7.00 (br. s, 1 H, NH_2), 5.73 (br. s, 1 H, NH_2), 5.48 (s, 1 H, PhC*H*CO), 2.97 (septet, *J* = 7.4 Hz, 1 H, C*H*CH_3), 1.26 (d, *J* = 7.4 Hz, 3 H, CHCH_3), 1.20 (s, 9 H, CCH_3), 0.99 (d, *J* = 7.4 Hz, 3 H, CHCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 183.1 (C_q=O), 175.3 (C_q=N), 140.2 (C_qAr), 128.4 (C_qAr), 127.4 (*C*HAr), 126.5 (*C*HAr), 67.0 (Ph*C*HCO), 42.3 ($C_q$$CH_3$), 29.9 (*C*HCH$_3$), 27.7 (C*C*H$_3$), 20.4 (CH*C*H$_3$), 20.3 (CH*C*H$_3$) ppm. MS (FAB$^+$): *m*/*z* = 261 [M + H]$^+$, 283, 217, 216, 203. HRMS (FAB$^+$) $C_{16}H_{25}N_2O$ [M + H]$^+$ calcd. 261.19662; found 261.19652. $C_{16}H_{24}N_2O$ (260.37): calcd. C 73.79, H 9.30, N 10.76; found C 73.82, H 9.25, N 10.74.

2-[1-(2-Methoxyphenyl)-2,2-dimethylpropylidenamino]-2-phenylacetamide (18): Prepared according to the general procedure using phenylacetonitrile (78 μL, 0.67 mmol), the title compound **18** was isolated as a yellow solid (65 mg, 30%), m.p. 168–170 °C. IR: $\tilde{\nu}_{max.}$ = (DCM) 3432 (NH_2), 2965, 1689 (C=O) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (br. s, 1 H, C*H*Ar), 7.30–7.17 (m, 6 H, C*H*Ar), 6.96–6.92 (m, 1 H, C*H*Ar), 6.87 (d, *J* = 8.4 Hz, 1 H, NH_2), 5.59 (br. s, 1 H, NH_2), 4.47 (s, 1 H, PhC*H*CO), 3.05 (s, 3 H, OCH_3), 1.19 (s, 9 H, CCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.5 (C_q=O), 175.2 (C_q=N), 155.5 (C_qAr), 139.9 (C_qAr), 129.5 (*C*HAr), 127.3 (*C*HAr), 127.5 (*C*HAr), 127.03 (*C*HAr), 127.00 (*C*HAr), 125.18 (C_qArOMe), 120.0 (*C*HAr), 110.3 (*C*HAr), 69.5 (Ph*C*HCO), 54.0 (O*C*H$_3$), 40.8 ($C_q$$CH_3$), 28.3 (C*C*H$_3$) ppm. MS (FAB$^+$): *m*/*z* = 325 [M + H]$^+$, 347, 280. HRMS (FAB$^+$) $C_{20}H_{25}N_2O_2$ [M + H]$^+$ calcd. 325.19160; found 325.19208. $C_{20}H_{24}N_2O_2$ (324.42): calcd. C 74.10, H 7.53, N 8.97; found C 74.03, H 7.47, N 8.63.

2-[1-(2-Methoxyphenyl)-2,2-dimethylpropylidenamino]-2-phenylpropanamide (19): Prepared according to the general procedure using α-methylphenylacetonitrile (66 μL, 0.48 mmol), the title compound **19** was isolated as a white solid (40 mg, 25%), m.p. 164–166 °C. IR (DCM): $\tilde{\nu}_{max.}$ = 3410 (NH_2), 2965, 1687 (C=O) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.67 (br. s, 1 H, NH_2), 8.50 (br. s, 1 H, NH_2′), 7.97–7.15 (m, 10 H, C*H*Ar and C*H*′Ar), 6.93–6.91 (m, 2 H, C*H*Ar and C*H*′Ar), 6.83–6.75 (m, 3 H, C*H*Ar and C*H*′Ar), 6.37–6.33 (td, *J* = 7.46, *J* = 0.92 Hz, 1 H, C*H*Ar), 6.25 (d, *J* = 8.39 Hz, 1 H, C*H*′Ar), 5.76 (br. s, 2 H, NH_2 and NH_2′), 5.56 (dd, *J* = 7.46, *J* = 1.6 Hz, 1 H, C*H*Ar), 3.77 (s, 3 H, OCH_3), 3.13 (s, 3 H, OCH_3′), 1.59 (s, 3 H, Me), 1.41 (s, 3 H, Me′), 1.12 (s, 18 H, CCH_3 and CCH_3′) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.2 (C_q=O), 179.9 (C'_q=O), 177.2 (C_q=N and C'_q=N), 155.3 (C_qAr), 154.8 (C'_qAr), 144.8 (C_qArOMe), 141.4 (C'_qArOMe), 129.0 (*C*HAr), 128.6 (*C*′HAr), 128.2 (*C*HAr), 128.0 (*C*′HAr), 127.9 (*C*HAr), 127.0 (*C*′HAr), 126.9 (*C*HAr), 126.7 (*C*′HAr), 126.4 (*C*HAr), 126.1 (*C*′HAr), 119.2 (*C*HAr), 118.5 (*C*′HAr), 109.4 (*C*HAr), 109.2 (*C*′HAr), 68.6 (Ph$C_q$$CH_3$), 67.6 (Ph$C_q$′$CH_3$), 54.6 (O*C*H$_3$), 53.6 (O*C*′H$_3$), 41.9 ($C_q$$CH_3$), 41.8 (*C*q′CH3), 28.6 (C*C*H$_3$), 28.4 (C*C*′H$_3$), 22.9 (PhC*C*H$_3$), 19.1 (PhC*C*′H$_3$) ppm. MS (FAB$^+$): *m*/*z* = 339 [M + H]$^+$, 361, 294, 192, 148, 120, 103. HRMS

(FAB$^+$) $C_{21}H_{27}N_2O_2$ [M + H]$^+$ calcd. 339.20725; found 339.20740. $C_{21}H_{26}N_2O_2$ (338.44): calcd. C 74.72, H 7.73, N 8.69; found C 74.45, H 7.75, N 8.28.

2-[2,2-Dimethyl-1-(4-trifluoromethylphenyl)propylidenamino]-2-phenylacetamide (20): Prepared according to the general procedure using phenylacetonitrile (47 μL, 0.4 mmol), the title compound **20** was isolated as a colourless foam (70 mg, 50%), m.p. 65–66 °C. IR (DCM): $\tilde{\nu}_{max.}$ = 3446 (NH_2), 2968, 1692 (C=O) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (br. s, 1 H, C*H*Ar), 7.44 (br. s, 1 H, C*H*Ar), 7.29–7.22 (m, 4 H, C*H*Ar), 7.17 –7.15 (m, 3 H, C*H*Ar), 6.57 (br. s, 1 H, N*H*$_2$), 5.51 (br. s, 1 H, N*H*$_2$), 4.40 (s, 1 H, PhC*H*CO), 1.21 (s, 9 H, CC*H*$_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.9 (C_q=O), 174.3 (C_q=N), 139.7 (C_qAr), 128.5 (*C*HAr), 127.7 (*C*HAr), 126.8 (*C*HAr), 69.4 (Ph*C*HCO), 40.6 (C_qCH_3), 28.2 (C*C*H$_3$) ppm. MS (EI$^+$): *m*/*z* = 361 [M – H]$^+$, 347, 318, 261, 14, 106, 91. HRMS (EI+) $C_{20}H_{21}F_3N_2O$ (M$^+$) calcd. 362.16060; found 362.16145. $C_{20}H_{21}F_3N_2O$ (362.39): calcd. C 66.27, H 5.85, N 7.73; found C 66.60, H 5.89, N 7.57.

2-[2,2-Dimethyl-1-(4-trifluoromethylphenyl)propylidenamino]-2-phenylpropionamide (21): Prepared according to the general procedure using α-methylphenylacetonitrile (27 μL, 0.20 mmol), the title compound **21** was isolated as a colourless foam (40 mg, 53%), m.p. 181–183 °C. IR: $\tilde{\nu}_{max.}$ = (DCM) 3415 (NH_2), 2967, 1682 (C=O) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.53 (br. s, 1 H, C*H*Ar), 7.48 (d, *J* = 8.4 Hz, 1 H, C*H*Ar), 7.16–7.04 (m, 4 H, C*H*Ar), 6.92–6.88 (m, 3 H, 2C*H*Ar), 5.84 (br. d, *J* = 7.6 Hz, 2 H, N*H*$_2$), 1.51 (s, 3 H, PhCC*H*$_3$), 1.14 (s, 9 H, CC*H*$_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.3 (C_q=O), 177.8 (C_q=N), 143.5 (C_qAr), 140.5 (C_qAr), 128.1 (*C*HAr), 127.7 (*C*HAr), 127.6 (*C*HAr), 127.1 (*C*HAr), 126.4 (*C*HAr), 123.6 (*C*HAr), 123.5 (*C*HAr), 68.0 (PhC_qCH_3), 41.8 (C_qCH_3), 28.4 (C*C*H$_3$), 22.2 (PhC*C*H$_3$) ppm. MS (FAB$^+$): *m*/*z* = 377 [M + H]$^+$, 332, 230, 148, 120, 91. HRMS (FAB$^+$) $C_{21}H_{24}F_3N_2O$ [M + H]$^+$ calcd. 377.18407; found 377.18425. $C_{21}H_{23}F_3N_2O{\cdot}0.2C_6H_{14}$ (393.66): calcd. C 67.7, H 6.61, N 7.12; found C 67.92, H 6.21, N 7.19.

2-{2,2-Dimethyl-1-[4-(methylsulfonyl)phenyl]propylidenamino}-2-phenylacetamide (22): Prepared according to the general procedure using phenyl acetonitrile (52 μL, 0.45 mmol), the title compound **22** was isolated as a colourless solid (100 mg, 60%), m.p. 191–192 °C. IR (DCM): $\tilde{\nu}_{max.}$ = 3443 (NH_2), 2967, 1693 (C=O) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 7.1 Hz, 1 H, C*H*Ar), 7.77 (d, *J* = 6.8 Hz, 1 H, N*H*$_2$), 7.30–7.14 (m, 7 H, C*H*Ar), 6.67 (d, *J* = 6.9 Hz, 1 H, N*H*$_2$), 5.83 (br. s, 1 H, C*H*Ar), 4.38 (s, 1 H, PhC*H*CO), 3.10 (s, 3 H, SO_2CH_3), 1.21 (s, 9 H, CC*H*$_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.3 (C_q=O), 174.2 (C_q=N), 141.8 (C_qAr), 140.3 (C_qAr), 139.4 (C_qAr), 128.6 (*C*HAr), 127.8 (*C*HAr), 126.7 (*C*HAr), 69.4 (Ph*C*HCO), 44.5 (SO_2CH_3), 40.6 (C_qCH_3), 28.1 (C*C*H$_3$) ppm. MS (FAB$^+$): *m*/*z* = 373 [M + H]$^+$, 328, 154, 106, 91. HRMS (FAB$^+$) $C_{20}H_{25}N_2O_3S$ [M + H]$^+$ calcd. 373.15859; found 373.15859. $C_{20}H_{24}N_2O_3S{\cdot}0.3H_2O$ (377.88): calcd. C 63.55, H 6.57, N 7.45; found C 63.55, H 6.37, N 7.25.

2-{2,2-Dimethyl-1-[4-(methylsufonyl)phenyl]propylidenamino}-2-phenylpropanamide (23): Prepared according to the general procedure using α-methylphenylacetonitrile (61 μL, 0.46 mmol), the title compound **23** was isolated as a colourless solid (70 mg, 40%), m.p. 218–219 °C. IR (DCM): $\tilde{\nu}_{max.}$ = 3416 (NH_2), 2965, 1682 (C=O) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46 (d, *J* = 5.6 Hz, 1 H, N*H*$_2$), 7.80 (dd, *J* = 8.0, *J* = 1.8 Hz, 1 H, C*H*Ar), 7.23 (dd, *J* = 8.0, *J* = 1.8 Hz, 1 H, C*H*Ar), 7.15–7.13 (m, 2 H, C*H*Ar), 7.08–7.05 (m, 2 H, C*H*Ar), 6.90–6.87 (m, 2 H, C*H*Ar), 6.38 (d, *J* = 5.3 Hz, 1 H, N*H*$_2$), 5.95 (dd, *J* = 8.0, *J* = 1.3 Hz, 1 H, C*H*Ar), 3.03 (s, 3 H, SO_2CH_3), 2.04 (s, 3 H, PhCC*H*$_3$), 1.12 (s, 9 H, CC*H*$_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.3 (C_q=O), 177.2 (C_q=N), 143.4 (C_qAr), 142.8 (C_qArCF_3), 138.8 (C_qAr), 128.3 (*C*HAr), 128.2 (*C*HAr), 128.1 (*C*HAr), 127.2 (*C*HAr), 126.5 (*C*HAr), 125.5 (*C*HAr), 125.4 (*C*HAr), 68.0 (Ph*C*CH$_3$), 44.4 (SO_2CH_3), 41.9 (C_qCH_3), 28.4 (C*C*H$_3$), 22.4 (PhC*C*H$_3$) ppm. MS (FAB$^+$): *m*/*z* = 387 [M + H]$^+$, 342, 240, 148, 120, 91. HRMS (FAB$^+$) $C_{21}H_{27}N_2O_3S$ [M + H]$^+$ calcd. 387.17424; found 387.17375. $C_{21}H_{26}N_2O_3S{\cdot}0.2H_2O$ (390.11): calcd. C 64.64, H 6.83, N 7.17; found C 64.64, H 6.83, N 6.84.

Supporting Information (see also the footnote on the first page of this article): Selected crystal structure determination data for **13**.

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