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A New Protocol for the Synthesis of *N*(1)-Unsubstituted 2-Substituted 2-Imidazolines

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Abstract—Lateral metallation at C-2(α) of 1-*tert*-butoxycarbonyl-2-methyl-2-imidazoline followed by reaction with a range of C-electrophiles and deprotection with TFA reliably affords *N*(1)-unsubstituted 2-substituted 2-imidazolines; P- or Se-electrophiles lead to 2-alkenyl-2-imidazolines via Wadsworth–Emmons or selenoxide elimination protocols. © 2000 Elsevier Science Ltd. All rights reserved.

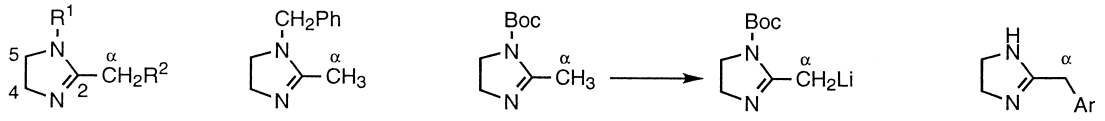
Introduction

We have for a number of years been engaged in a programme to utilise the heterocycle 2-imidazoline (4,5-dihydroimidazole; **1**) as a vehicle for carbon atom-transfer,[1] and have reported protocols for transfer of C_1,[2] C_2,[3] CCN[4] and CNC[5] fragments. In addition, these methodologies provide access to new derivatives of the imidazoline pharmacophore observed in many bioactive molecules, for example in the cardiovascular arena.[6] A key component in this work has been elaboration at C-2 via lateral metallation of a C-2 substituent, and our early reports utilised lithiation at C-2(α) of 1-benzyl-2-methyl-2-imidazoline **2** to achieve this.[3] In combination with a dissolving metal *N*-debenzylation, this provided a route to *N*(1)-unsubstituted imidazolines,[3a] and for successive functionalisations at C-2(α) and N-1 of imidazolines.[7]

Recently we have uncovered limitations to this debenzylation and we now report a much more widely applicable protocol using *tert*-butoxycarbonyl (Boc) as the N-1 protecting group in **3** for elaboration of an imidazoline C-2(α) nucleophile **4** with a range of electrophiles to generate ultimately *N*(1)-unsubstituted imidazolines. Protection at N-1 is necessary, as we[7] and others[8] have found that *efficient* simultaneous double metallation at N-1 and C-2(α) is limited to 2-arylmethyl-2-imidazolines such as **5** (Scheme 1).

Results and Discussion

Limitations to our earlier sequence of C-2(α) elaboration and *N*-debenzylation were highlighted by attempts to prepare 2-(3-butenyl)-2-imidazoline **7** by treatment of the 1-benzyl derivative **6** with Na–NH_3(l.). This led to low recoveries of **7** along with 2-butyl-2-imidazoline **8** (e.g. with 2.5 equiv. Na, a 2:1 mixture of **7** and **8** in 31% yield). Imidazoline **8** is possibly derived by an intramolecular electron-transfer reduction from the benzyl substituent before debenzylation.[9] In line with our previous report,[7] attempts to avoid *N*-protection by double deprotonation of commercial 2-methyl-2-imidazoline **9** (2 equiv. *n*-BuLi, THF, 20°C) met with mixed success. For example, quenching with 3-bromobut-1-ene (1 equiv.) did give C-alkylation product **7** but only in low yield (10%), and 2 equiv. of the bromide afforded N,C-dialkylation product **11** in only a moderate 45% yield (1 equiv. each of base and halide leads exclusively to the *N*-alkylation product **10**). In contrast, similar treatment of 2-benzyl-2-imidazoline **12**



Scheme 1.

Keywords: *N*(1)-unsubstituted imidazolines; 2-alkenyl imidazolines; Wadsworth–Emmons protocols; selenoxide elimination protocols.
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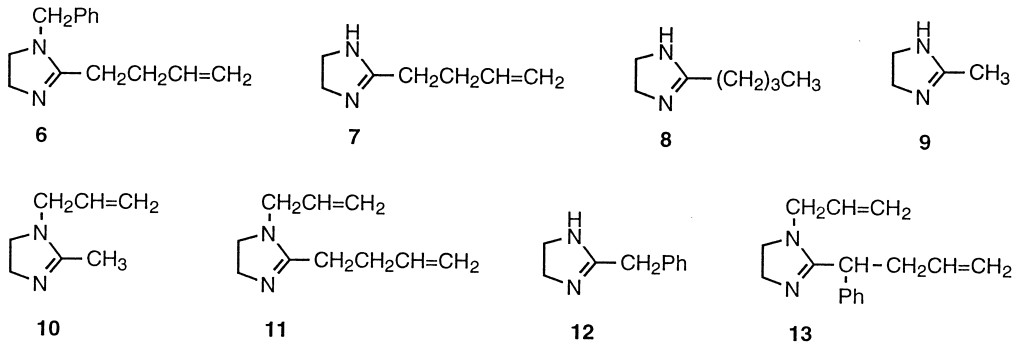


Scheme 2.

resulted in efficient N,C-dialkylation to afford imidazoline **13** (91%), confirming that the extra stabilisation afforded by a 2-arylmethyl group is needed to effectively support a dimetallated species (Scheme 2).[8]

A suitable alternative *N*-protecting group was found to be *tert*-butoxycarbonyl (Boc).[10] 1-*tert*-Butoxycarbonyl-2-methyl-2-imidazoline **3** was easily prepared from 2-methyl-2-imidazoline **9** (Boc_2O, Et_3N, CH_2Cl_2, 0→20°C; 77%) and metallated using *sec*-BuLi (THF, TMEDA, -78°C) to afford a bright yellow solution of lithio-derivative **4**. Use of n-BuLi or LDA, or the absence of TMEDA, produced much less satisfactory results. The lithiomethyl derivative **4** may be stabilised by interaction with the carbamate carbonyl group (Fig. 1). Alkylation was readily accomplished by reaction with a range of haloalkanes (Scheme 3), to afford the imidazolines **14a**–**h** in good yields (64–92%), Table 1 entries 1–8. It was possible to complete a second alkylation under the same conditions to give C-2(α)-branched imidazolines **15a**–**c** (Scheme 3), Table 1 entries 9–11. Treatment of the *N*-Boc-2-methylimidazoline **3** with 2.2 equiv. each of *sec*-BuLi and 3-bromopropene (THF, TMEDA, −78°C) afforded a mixture of monoalkylated material **14b** (56%) and dialkylated imidazoline **15a** (22%), Table 1 entry 12. Attempts at a third alkylation by deprotonation of **15** were not successful.[11] Deprotection of the C-alkylated imidazolines **14** and **15** was achieved using acidic conditions (TFA, 20°C) to afford NH-heterocycles **16a**–**k** in good yields (65–87%), Table 1. This completes a simple and robust sequence for elaboration of 2-methyl-2-imidazoline **9**.

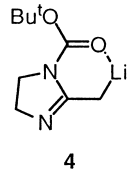
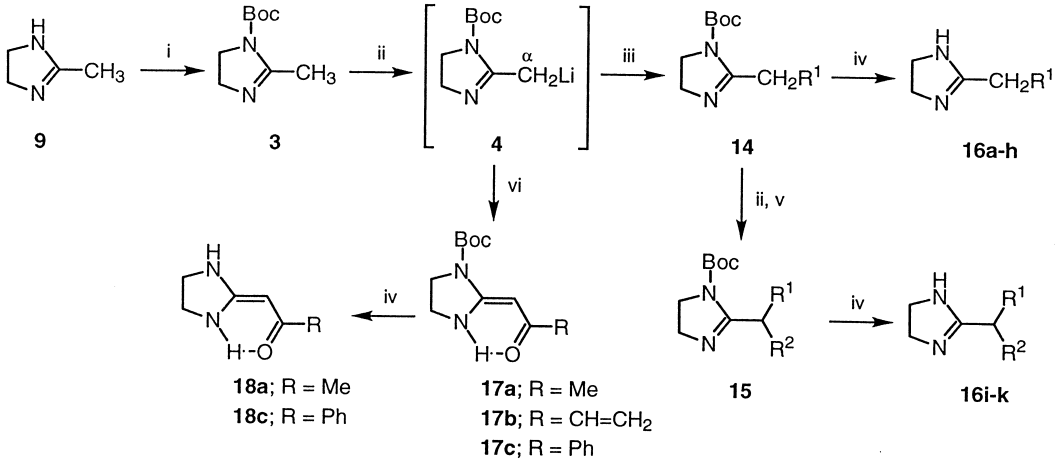


Figure 1.

The lithio derivative **4** could be quenched with a range of other electrophiles. Acylation with the esters ethyl acetate, methyl propenoate and methyl benzoate afforded the enaminoketones **17a**–**c** (72, 42 and 64%, respectively) (Scheme 3). Formulation as the enaminoketone tautomers is supported by spectroscopic data, e.g. δ_C(CO) 185–195, and by an X-ray crystal structure determination for **17c** (Fig. 2).[12,13] Enediamines **17a** and **17c** were efficiently deprotected, again using TFA at 20°C, to afford **18a** and **18c** as crystalline solids (81 and 90%).

A major target for our C-2 elaboration is to generate *N*-unsubstituted 2-(1-alkenyl)-2-imidazolines, to be accessed via C-2(α)-heteroatom-substituted derivatives. We have earlier reported synthesis of the *N*-benzyl analogues, from



Scheme 3. Reagents: (i) Boc_2O, Et_3N, CH_2Cl_2, 0→20°C; (ii) *sec*-BuLi, THF, TMEDA, −78°C; (iii) R^1Hal, −78→20°C; (iv) TFA, 20°C; (v) R^2Hal, −78→20°C; (vi) MeCOOEt (for **17a**), CH_2=CHCOOMe (for **17b**) or $PhCO_2Me$ (for **17c**), −78→20°C.

Table 1. Alkylation of *N*-Boc-2-imidazoline **3** and deprotection of imidazolines **14** and **15**

Entry	R^1Hal	Imidazoline **14** (yield %)	R^2Hal	Imidazoline **15** (yield %)	Imidazoline **16** (yield %)
1	$MeCH_2CH_2I$	**14a** (86)	–	–	**16a** (87)
2	$CH_2{=}CHCH_2Br$	**14b** (82)	–	–	**16b** (82)
3	$CH_2{=}CHCH_2CH_2Br$	**14c** (64)	–	–	–
4	$CH_2{=}CHCH{=}CHCH_2Br$	**14d** (67)	–	–	–
5	$MeCH{=}CHCH{=}CHCH_2Br$	**14e** (81)	–	–	**16e** (67)
6	$PhCH_2Br$	**14f** (92)	–	–	**16f** (73)
7	$2\text{–}PhC_6H_4CH_2Br$	**14g** (81)	–	–	**16g** (80)
8	$2\text{–}FurylCH_2Cl$	**14h** (71)	–	–	**16h** (65)
9	–	**14b**	$CH_2{=}CHCH_2Br$	**15a** (84)	**16i** (67)
10	–	**14b**	$PhCH_2Br$	**15b** (76)	**16j** (67)
11	–	**14c**	$CH_2{=}CHCH_2Br$	**15c** (87)	**16k** (81)
12	$CH_2{=}CHCH_2Br$ (2.2 equiv.)	**14b** (56)		**15a** (22)	

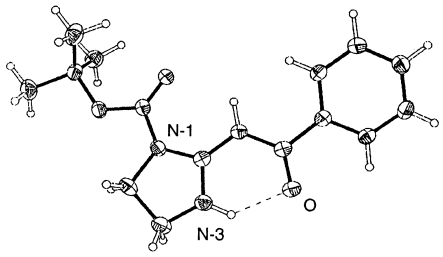
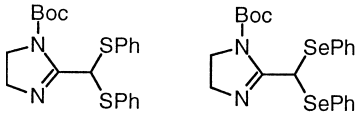


Figure 2. X-Ray crystal structure of acylation product **17c**.

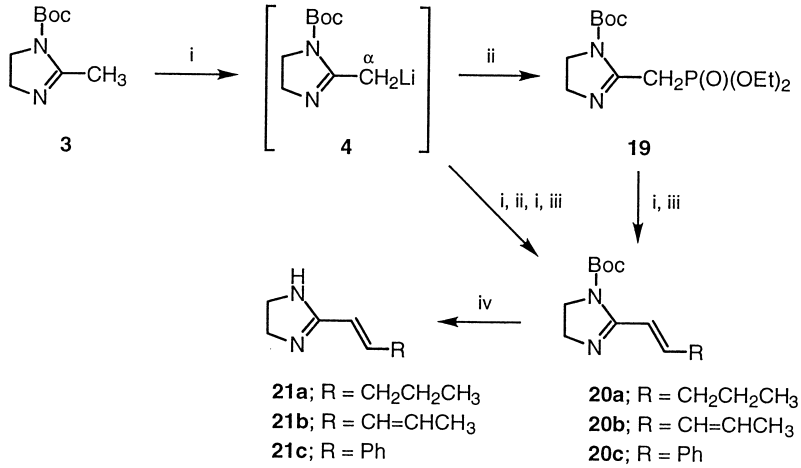
reaction of 1-benzyl-2-diethylphosphonomethyl-2-imidazoline,[14] but removal of the *N*-benzyl group proved impossible. These targets could be prepared from lithiomethyl intermediate **4** through reaction with heteroatom electrophiles. Treatment with diethyl chlorophosphate afforded the phosphonomethyl imidazoline **19** (51%) (Scheme 4). Deprotonation of phosphonate **19** under the same conditions (*sec*-BuLi, THF, TMEDA, −78°C), followed by addition of an aldehyde gave the 2-(1-alkenyl)imidazolines **20a–c** as products of Wadsworth–Emmons condensation (67, 65 and 66%, using butanal, 2-butenal or benzaldehyde, respectively). The products **20b,c** were isolated as *E*-isomers of the new double bond, whereas **20a** was initially isolated as a 2:1 mixture *E*:*Z* which slowly (several days) converted to *E*-isomer on standing at 20°C. The phosphonylation-condensation could also be performed in one-pot without isolation of the phosphonomethylimidazoline **19**, but in slightly lower overall yield. Again, deprotection with TFA cleanly afforded the NH compounds **21a–c** in good yields (82, 64 and 91%, respectively), providing chromatography was performed on alumina rather than silica.[14]

Using other heteroatom electrophiles, the lithiomethyl imidazoline **4** was quenched with diphenyl disulphide to afford the mono-sulphenylated product **24** (42%) (Scheme 5), along with the disubstituted derivative **22** (28%). Deprotection of the imidazoline **24** (TFA, 20°C) afforded 2-phenylthiomethyl-2-imidazoline **25** (81%). Use of diphenyl diselenide as electrophile led to 2-phenylselenomethyl-2-imidazoline **26** (52%), again accompanied by a low yield (8%) of the disubstituted product **23**.

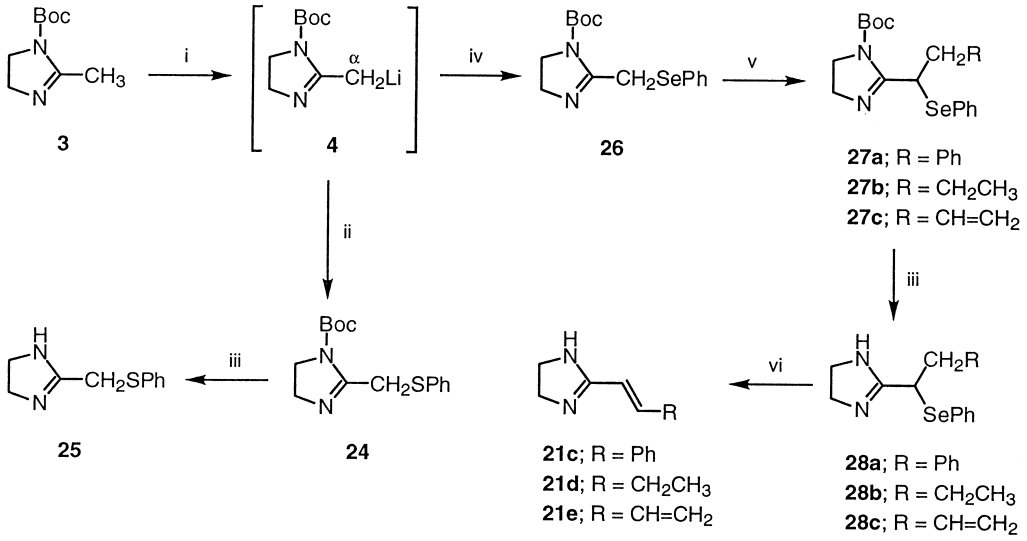


22 **23**

In an alternative approach to 2-(1-alkenyl)-2-imidazolines, when the phenylselenomethyl derivative **26** was deprotonated (*sec*-BuLi, THF, TMEDA, −78°C) and treated with a haloalkane (1-iodopropane, 3-bromopropene or benzyl bromide) the C-2(α) alkylated products **27a–c** were formed (79, 80 and 90%, respectively) (Scheme 5). Attempts to



Scheme 4. Reagents: (i) *sec*-BuLi, THF, TMEDA, −78°C; (ii) $(EtO)_2P(O)Cl$, −78→20°C; (iii) RCHO, −78→20°C; (iv) TFA, 20°C.



Scheme 5. Reagents: (i) *sec*-BuLi, THF, TMEDA, −78°C; (ii) PhSSPh, −78°C→20°C; (iii) TFA, 20°C; (iv) PhSeSePh, −78°C→20°C; (v)*sec*-BuLi, THF, TMEDA, −78°C, RCH_2Hal; (vi) mCPBA, CH_2Cl_2, 0°C→20°C.

form the selenoxides from imidazolines **27** were unsuccessful. On the other hand, when the *N-tert*-butoxycarbonyl group was removed (TFA, 20°C), the imidazolines **28a–c** were isolated in good yields (71, 91 and 80%, respectively). Selenium oxidation (mCPBA, CH_2Cl_2, 0°→20°C) followed by spontaneous elimination[15] now proceeded smoothly to afford in high yield the 2-(1-alkenyl)imidazolines **21c–e** (90, 92 and 92%, respectively), that again had to be purified over alumina.

We have thus demonstrated the use of 1-*tert*-butyloxycarbonyl-2-(lithiomethyl)-2-imidazoline **4** (prepared by metallation of 1-*tert*-butyloxycarbonyl-2-methyl-2-imidazoline **3**) in a simple and reliable protocol for the elaboration at C-2(α) of 2-methyl-2-imidazoline.

Experimental

General

Melting points were measured on a Kofler hot-stage and are uncorrected. IR spectra were recorded on a Perkin–Elmer 1710 FTIR spectrometer in chloroform unless otherwise stated. NMR spectra were recorded in deuteriochloroform unless otherwise stated (internal standard TMS) on JEOL LAMBDA300 or JEOL EX400 spectrometers; ^1H spectra at 300 or 400 MHz and ^{13}C spectra at 75 MHz or 100 MHz, respectively. Low resolution mass spectra were obtained using an AEI MS902 spectrometer in EI-positive mode. Solvents were dried and distilled before use: chloroform and dichloromethane from CaH_2; tetrahydrofuran (THF) from K immediately before use. Column chromatography was performed under medium pressure using silica gel (Kieselgel 60; 220–440 mesh) or neutral alumina (150 mesh) as indicated. Organic extracts were dried over anhydrous $MgSO_4$ for 20 min.

1-*tert*-Butyloxycarbonyl-2-methyl-2-imidazoline 3. Triethylamine (19.78 cm^3, 0.14 mol) was added dropwise to 2-methyl-2-imidazoline (10.00 g, 0.12 mol) in dichloromethane (120 cm^3) at 0°C. Di-*tert*-butyl dicarbonate (31.11 g, 0.14 mol) was added in small portions and the reaction mixture stirred at 0°C for 10 min. The ice-bath was removed and the reaction stirred at 20°C overnight. Water was added and the organic layer extracted with dichloromethane (3×100 cm^3). The combined organic extracts were washed with saturated aq. $NaHCO_3$ (100 cm^3), dried and concentrated. The crude product was distilled under reduced pressure and the *title compound* obtained as a white solid (16.75 g, 77%), bp 82–86°C at 0.15 mmHg, mp 44–46°C (Found: M^+ 184.1212: $C_9H_{16}N_2O_2$ requires: *M* 184.1212); ν_{max}(film)/cm^{-1} 2995, 1714; δ_H (400 MHz) 1.45 [9H, s, $C(CH_3)_3$], 2.28 (3H, s, CH_3), 3.68 (4H, s, NCH_2CH_2N); δ_C (100 MHz), 17.9 (2-CH_3), 28.1 [$C(CH_3)_3$], 46.4 and 51.7 (NCH_2), 81.4 [$C(CH_3)_3$], 150.9 (CO), 158.1 (NCN); *m/z* 184 (M^+, 7%), 128 (7), 84 (20), 70 (24), 57 (100).

1-Benzyl-2-(but-3-enyl)-2-imidazoline 6. *n*-Butyllithium (14 cm^3 of a 1.8 M solution in hexanes, 25.28 mmol) was injected into 1-benzyl-2-methyl-2-imidazoline **2** (4.00 g, 23.00 mmol) in dry THF (80 cm^3) stirred at −78°C under nitrogen. The solution was stirred at −78°C for 30 min and 3-bromobut-1-ene (2.18 cm^3, 25.28 mmol) was injected. The reaction mixture was stirred at −78°C for 4 h and at 20°C for 1.5 h, before wet diethyl ether (50 cm^3) was added followed by water (100 cm^3). The layers were separated and the aqueous phase was extracted with diethyl ether (3×100 cm^3). The combined organic extracts were washed with brine (100 cm^3), dried and concentrated. The crude product was purified by column chromatography on silica gel eluting with isopropylamine:chloroform (1:99 v/v) to give the *title compound* as a yellow oil (3.85 g, 78%) (Found: MH^+ 213.1392. $C_{14}H_{13}N_2$ requires: *MH* 213.1392); ν_{max}(film)/cm^{-1} 3065, 2934, 2863, 1612, 1496, 1453, 1274, 737; δ_H (300 MHz) 2.39–2.49 (4H, br m, $CH_2CH_2CH{=}CH_2$), 3.20 and 3.69 (each 2H, t, *J*=9.7 Hz, NCH_2CH_2N), 4.28 (2H, s, CH_2Ph), 4.98–5.10 (2H, m, $CH{=}CH_2$), 5.82–5.93 (1H, m, $CH{=}CH_2$), 7.22–7.37 (5H, m, Ar-H); δ_C (75 MHz) 27.3 and 30.5 (CH_2), 50.3 (NCH_2) 50.7 (CH_2Ph), 53.5 (NCH_2), 115.4 ($CH{=}CH_2$),

127.2, 127.4 and 128.8 (ArCH), 137.4 (*C*H=CH_2), 137.8 (ArC), 166.4 (NCN); *m/z* 214 (M^+, 1%) 213 (2), 203 (1), 190 (1), 174 (3), 160 (1), 149 (2), 133 (41), 120 (59), 106 (21), 91 (100), 77 (3), 65 (15).

1-(Prop-2-enyl)-2-methyl-2-imidazoline 10. *n*-Butyllithium (14.28 cm^3 of a 2.0 M solution in hexanes, 28.57 mmol) was injected into 2-methyl-2-imidazoline (2.00 g, 23.80 mmol) in dry THF (150 cm^3) stirred at 20°C under nitrogen. The yellow suspension was stirred at 20°C for 50 min. The reaction mixture was cooled to 0°C and 3-bromopropene (2.47 cm^3, 28.57 mmol) was injected. The reaction mixture was stirred at 0°C for 15 min. and at 20°C overnight before the reaction was quenched with water (100 cm^3). The organic layer was extracted with diethyl ether (3×100 cm^3), the combined organic extracts were washed successively with brine (100 cm^3) and water (100 cm^3), dried and concentrated. The crude product was purified by column chromatography on silica gel (0:100→3:97 v/v isopropylamine:ethyl acetate) to give the *title compound* as a yellow oil (1.30 g, 44%) (Found: M^+ 124.0999. $C_7H_{12}N_2$ requires: *M* 124.1000); ν_{max}(film)/cm^{-1} 2934, 2866, 1616, 1490, 1420, 1258, 934; δ_H (400 MHz) 1.93 (3H, s, CH_3), 3.26–3.31 and 3.63–3.68 (each 2H, t, *J*=9.8 Hz, NCH_2CH_2N), 3.72 (2H, d, *J*= 5.8 Hz, N*C*H_2CH=CH_2), 5.17–5.22 (2H, m, CH=C*H*$_2$), 5.72–5.82 (1H, m, C*H*=CH_2); δ_C (100 MHz), 13.9 (CH_3), 49.4, 49.9 and 51.9 (NCH_2), 117.1 (CH=*C*H_2), 133.1 (*C*H=CH_2), 164.3 (NCN); *m/z* 124 (M^+, 27%), 110 (1), 97 (5), 83 (24), 67 (19), 54 (100), 42 (30), 28 (17).

2-(But-3-enyl)-1-(prop-2-enyl)-2-imidazoline 11. Prepared by the method described above for **10**, but using *n*-butyllithium (25.88 cm^3 of a 1.8 M solution in pentanes, 46.62 mmol), 2-methyl-2-imidazoline **3** (1.78 g, 21.19 mmol) and 3-bromopropene (4.00 cm^3, 46.62 mmol). A milky suspension was observed before addition of the bromide, when a clear solution was formed. Column chromatography on silica gel (0:100→4:96 v/v isopropylamine:ethyl acetate) gave the *title compound* as a yellow oil (1.56 g, 45%) (Found: M^+ 165.1391. $C_{10}H_{16}N_2$ requires: *M* 165.1391); ν_{max}(film)/cm^{-1} 2977, 2932, 2862, 1642, 1615, 1486, 1418, 1258, 1213, 995, 915; δ_H (300 MHz) 2.24–2.29 (2H, m, CH_2CH_2CH=CH_2), 2.37–2.44 (2H, m, CH_2CH_2CH=CH_2), 3.27 and 3.69 (each 2H, t, *J*=9.7 Hz, NCH_2CH_2N), 3.71 (2H, d, *J*=4.0 Hz, N*C*H_2CH=CH_2), 4.97–5.10 (2H, m, CH_2CH_2CH=CH_2), 5.15–5.22 (2H, m, NCH_2CH=CH_2), 5.71–5.92 (2H, m, 2×C*H*=CH_2); δ_C (75 MHz), 27.1 and 30.4 (CH_2), 49.2, 50.1 and 52.2 (NCH_2), 115.1 and 117.0 (CH=*C*H_2), 133.8 and 137.5 (*C*H=CH_2), 166.5 (NCN); *m/z* 164 (M^+, 1%), 163 (4), 149 (4), 135 (2), 123 (10), 109 (3), 98 (2), 83 (32), 70 (100), 55 (29), 41 (65).

2-(1-Phenylbut-3-enyl)-1-(prop-2-enyl)-2-imidazoline 13. Prepared by the method described above for **10**, but using *n*-butyllithium (15.70 cm^3 of a 2.5 M solution in hexanes, 39.37 mmol), 2-benzyl-2-imidazoline **12** (3.00 g, 18.75 mmol) and 3-bromopropene (3.40 cm^3, 39.37 mmol). A yellow suspension was observed before addition of the bromide, when a clear yellow solution was formed. Column chromatography gave the *title compound* as a yellow oil (4.10 g, 91%) (Found: C, 78.72; H, 8.36; N, 11.41%; $(M-H)^+$ 239.1545. $C_{16}H_{20}N_2{\cdot}0.2H_20$ requires: C, 78.81; H, 8.37; N, 11.49%; *M*−*H* 239.1548); ν_{max}(film)/cm^{-1} 2932, 2862, 1641, 1611, 1416, 1210, 1074, 917, 702; δ_H (400 MHz) 2.49–2.56 and 2.84–2.91 (each 1H, m, $CHCH_2$), 3.13–3.21 and 3.26–3.33 (each 1H, dd, *J*=8.8 and 17.1 Hz, N*C*H_2CH=CH_2), 3.43–3.49 (2H, m, N*C*H_2CH_2N), 3.60–3.65 (1H, dd, *J*=5.9 and 15.2 Hz, C*H*CH_2), 3.69–3.84 (2H, m, NCH_2CH_2N), 4.92–4.97 (2H, m, $CHCH_2CH$=CH_2), 5.01–5.07 (2H, m, NCH_2CH=CH_2), 5.40–5.50 (1H, m, $CHCH_2CH$=CH_2), 5.69–5.75 (1H, m, NCH_2CH=CH_2), 7.20–7.32 (5H, m, Ar-H); δ_C (100 MHz) 39.8 (CH_2), 44.5 (CH), 49.1, 50.2 and 52.6 (NCH_2), 116.5 and 117.1 (CH=*C*H_2), 127.1, 128.2 and 128.8 (Ar-C), 134.0 and 136.7 (*C*H=CH_2), 140.6 (Ar-C), 167.3 (NCN); *m/z* 240 (M^+, 51%), 226 (5), 211 (11), 199 (43), 184 (5), 170 (8), 156 (17), 149 (31), 135 (9), 129 (13), 121 (14), 103 (13), 91 (24), 82 (15), 77 (23).

General method for synthesis of 2-substituted 1-*tert*-butyloxycarbonyl-2-imidazolines 14 and 15

sec-Butyllithium (solution in hexanes) was injected into 1-*tert*-butyloxycarbonyl-2-methyl-2-imidazoline **3** or 1-*tert*-butyloxycarbonyl-2-substituted-2-imidazoline **14** in dry THF/TMEDA (25–30:1 v/v; 0.1 M in imidazoline) stirred at −78°C under nitrogen. The bright yellow solution produced was stirred for 20 min at −78°C. The organohalide electrophile was injected (when liquid) or added by cannula as a solution in THF (when solid) to the reaction mixture at −78°C under nitrogen. The reaction was allowed to warm to 20°C overnight. The reaction was quenched with water (100 cm^3), the organic layer was extracted with diethyl ether (3×100 cm^3) and the combined extracts were washed successively with saturated aq. $NaHCO_3$ (100 cm^3), water (100 cm^3) and brine (100 cm^3), dried and concentrated. The crude product was purified by column chromatography on silica (1:9→2:3 v/v ethyl acetate:hexane) to give the compound **14** or **15**, respectively.

2-Butyl-1-*tert*-butyloxycarbonyl-2-imidazoline 14a. Prepared by the general method, using 1-*tert*-butyloxycarbonyl-2-methyl-2-imidazoline **3** (2.00 g, 10.86 mmol), *sec*-butyllithium (9.19 cm^3 of a 1.3 M solution in hexanes, 11.95 mmol) and 1-iodopropane (1.16 cm^3, 11.95 mmol). The *title compound* was obtained as a colourless oil (2.10 g, 86%) (Found: C, 63.29; H, 9.42; N, 12.29%; M^+ 226.1681. $C_{12}H_{22}N_2O_2$ requires: C, 63.69; H, 9.80; N, 12.38%; *M* 226.1681); ν_{max}(film)/cm^{-1} 2960, 2875, 1722, 1642, 1369, 1322, 1151, 1004; δ_H (400 MHz) 0.92 (3H, t, *J*=7.3 Hz, CH_2CH_3), 1.40 (2H, m, CH_2CH_3), 1.50 [9H, s, $C(CH_3)_3$] 1.63 (2H, m, C$H_2CH_2CH_3$), 2.72 (2H, t, *J*=8.0 Hz, C$H_2CH_2CH_2CH_3$), 3.75 (4H, s, NCH_2CH_2N); δ_C (75 MHz), 13.9 (CH_2CH_3), 22.5 (CH_2), 28.2 [$C(CH_3)_3$], 28.7 and 30.6 (CH_2), 46.7 and 51.80 (NCH_2), 81.5 [$C(CH_3)_3$], 150.8 (CO), 161.6 (NCN); *m/z* 226 (M^+, 0.8%), 184 (1), 171 (2), 128 (2), 85 (3), 58 (8).

2-(But-3-enyl)-1-*tert*-butyloxycarbonyl-2-imidazoline 14b. Prepared by the general method, using 1-*tert*-butyloxycarbonyl-2-methyl-2-imidazoline **3** (4.00 g, 21.74 mmol), *sec*-butyllithium (26.08 cm^3 of a 1 M solution in hexanes, 26.08 mmol) and 3-bromo-1-propene (2.25 cm^3, 26.08 mmol). The *title compound* was obtained as a colourless

oil (4.00 g, 82%) (Found: C, 63.20; H, 8.78; N, 12.72%; MH^+ 225.1603. $C_{12}H_{20}N_2O_2{\cdot}0.2H_2O$ requires: C, 63.24; H, 9.02; N, 12.29%; *MH* 225.1603); ν_{max}(film)/cm^{-1} 2960, 2934, 1720, 1640, 1369, 1150; δ_H (400 MHz) 1.50 [9H, s, $C(CH_3)_3$], 2.40 (2H, q, *J*=8.0 Hz, $CH_2CH{=}CH_2$), 2.78 (2H, t, *J*=8.0 Hz, $CH_2CH_2CH{=}CH_2$), 3.77 (4H, s, NCH_2CH_2N), 5.00–5.10 (2H, m, $CH{=}CH_2$), 5.84 (1H, m, $CH{=}CH_2$); δ_C (100 MHz) 27.9 [$C(CH_3)_3$], 30.0 and 30.4 (CH_2), 46.6 and 51.8 (NCH_2), 81.4 [$C(CH_3)_3$], 114.8 ($CH{=}CH_2$), 137.3 ($CH{=}CH_2$), 150.7 (CO), 160.57 (NCN); *m/z* 225 (MH^+, 0.9%), 208 (1), 169 (17), 124 (12), 97 (4), 84 (5), 58 (16).

1-*tert*-Butyloxycarbonyl-2-(pent-4-enyl)-2-imidazoline 14c. Prepared by the general method, using 1-*tert*-butyloxycarbonyl-2-methyl-2-imidazoline **3** (1.50 g, 8.15 mmol), *sec*-butyllithium (6.89 cm^3 of a 1.3 M solution in hexanes, 8.96 mmol) and 4-bromobut-1-ene (0.91 cm^3, 8.96 mmol). The *title compound* was obtained as a colourless oil (1.25 g, 64%) (Found: MH^+ 239.1759. $C_{13}H_{22}N_2O_2$ requires: *MH* 239.1759); ν_{max}(film)/cm^{-1} 2977, 2934, 1719, 1641, 1369, 1148; δ_H (400 MHz) 1.50 [9H, s, $C(CH_3)_3$], 1.73–1.80 (2H, m, $CH_2CH_2CH{=}CH_2$), 2.13–2.18 (2H, m, $CH_2CH{=}CH_2$), 2.71 (2H, t, J 7.5, $CH_2CH_2CH_2CH{=}CH_2$), 3.73 (4H, s, NCH_2CH_2N), 4.97–5.07 (2H, m, $CH{=}CH_2$), 5.78–5.88 (1H, m, $CH{=}CH_2$); δ_C (100 MHz), 25.7 (CH_2), 28.0 [$C(CH_3)_3$], 30.3 and 33.4 (CH_2), 46.6 and 51.8 (NCH_2), 81.6 [$C(CH_3)_3$], 114.9 ($CH{=}CH_2$), 138.3 ($CH{=}CH_2$), 150.9 (CO), 161.5 (NCN); *m/z* 239 (MH^+, 3%), 201 (9), 183 (26), 157 (16), 140 (26), 129 (10), 88 (18), 57 (100).

1-*tert*-Butyloxycarbonyl-2-(hexa-3,5-dienyl)-2-imidazoline 14d. Prepared by the general method, using 1-*tert*-butyloxycarbonyl-2-methyl-2-imidazoline **3** (1.20 g, 6.52 mmol), *sec*-butyllithium (6.01 cm^3 of a 1.3 M solution in hexanes, 7.82 mmol) and 1-bromopenta-2,4-diene (1.l5 g, 7.82 mmol). The *title compound* was obtained as a colourless oil (1.09 g, 67%) (Found: C, 65.70; H, 8.84; N, 10.94%; MH^+ 251.1755. $C_{14}H_{22}N_2O_2{\cdot}0.4H_2O$ requires: C, 65.42; H, 8.86; N, 10.88%; *MH* 251.1759); ν_{max}(film)/cm^{-1} 2977, 1718, 1643, 1369, 1317, 1256, 1143, 1005, 768; δ_H (300 MHz) 1.50 [9H, s, $C(CH_3)_3$], 2.48 (2H, q, *J*=7.1 Hz, $CH{=}CHCH_2CH_2$), 2.79 (2H, t, *J*=7.8 Hz, $CH{=}CHCH_2CH_2$), 3.74 (4H, s, NCH_2CH_2N), 4.97 (1H, dd, *J*=1.2 and 11.6 Hz, $CH{=}CH$), 5.10 (1H, dd, *J*=1.2 and 16.8 Hz, $CH{=}CH$), 5.72–5.81, 6.05–6.14 and 6.10–6.34 (each 1H, m, $CH{=}CHCH{=}CH_2$); δ_C (75 MHz) 28.2 [$C(CH_3)_3$], 29.4 and 30.5 (CH_2), 46.8 and 52.0 (NCH_2), 81.6 [$C(CH_3)_3$], 115.2 ($CH_2{=}CH$), 130.9, 133.7 and 137.1 ($CH{=}CHCH{=}CH_2$), 150.9 (CO), 160.7 (NCN); *m/z* 251 (MH^+, 100%), 195 (21), 185 (10), 151 (11), 135 (2), 129 (4), 99 (2), 85 (9).

1-*tert*-Butyloxycarbonyl-2-(hepta-3,5-dienyl)-2-imidazoline 14e. Prepared by the general method, using 1-*tert*-butyloxycarbonyl-2-methyl-2-imidazoline **3** (1.50 g, 8.15 mmol), *sec*-butyllithium (6.89 cm^3 of a 1.3 M solution in hexanes, 8.96 mmol) and 1-bromohexa-2,4-diene (1.44 g, 8.96 mmol). The *title compound* was obtained as a mixture of geometric isomers (4:1 *E,E*:*E,Z*) as a colourless oil (1.55 g, 81%) (Found: M^+ 264.1474. $C_{15}H_{24}N_2O_2$ requires: *M* 264.1473); ν_{max}(film)/cm^{-1} 2977, 2934, 1718, 1644, 1479, 1369, 1331, 1222, 1147, 1000; for *E,E*-isomer δ_H (400 MHz) 1.50 [9H, s, $C(CH_3)_3$], 1.71 (3H, d, *J*=6.8 Hz, $CH_3CH{=}CH$), 2.42 (2H, q, *J*=7.2 Hz, $CH{=}CHCH_2CH_2$), 2.76 (2H, t, *J*=8.0 Hz, $CH{=}CHCH_2CH_2$), 3.72 (4H, s, NCH_2CH_2N), 5.58–5.63 and 5.98–6.10 (each 2H, m, $CH{=}CHCH{=}CH$); δ_C (100 MHz) 17.9 ($CH_3CH{=}CH$), 28.2 [$C(CH_3)_3$], 29.3 and 30.6 (CH_2), 46.7 and 51.9 (NCH_2), 81.5 [$C(CH_3)_3$], 127.2, 130.2, 130.8 and 131.4 (CH), 150.8 (CO), 160.7 (N=C–N); for *E,Z*-isomer δ_H (400 MHz) 1.11 (3H, d, *J*=6.8 Hz, $CH_3CH{=}CH$), 1.50 [9H, s, $C(CH_3)_3$], 2.42 (2H, q, *J*=7.2 Hz, $CH{=}CHCH_2CH_2$), 2.76 (2H, t, *J*=8.0 Hz, $CH{=}CHCH_2CH_2$), 3.72 (4H, s, NCH_2CH_2N), 4.97 (1H, d, *J*=10.2 Hz, $CH{=}CHCH{=}CH$), 5.12 (1H, d, *J*=17.1 Hz, $CH{=}CHCH{=}CH$), 5.98–6.10 and 6.28–6.35 (each 1H, m, $CH{=}CHCH{=}CH$); δ_C (100 MHz) 17.9 ($CH_3CH{=}CH$), 28.2 [$C(CH_3)_3$], 34.3 and 37.5 (CH_2), 46.7 and 51.9 (NCH_2), 81.5 [$C(CH_3)_3$], 127.1, 128.5, 137.6 and 139.1 (CH), 150.8 (CO), 160.7 (NCN); *m/z* 264 (M^+, 0.7%), 208 (65), 193 (35), 179 (23), 149 (33), 135 (19), 123 (20), 109 (48), 83 (39), 57 (100).

1-*tert*-Butyloxycarbonyl-2-(2-phenylethyl)-2-imidazoline 14f. Prepared by the general method, using 1-*tert*-butyloxycarbonyl-2-methyl-2-imidazoline **3** (1.00 g, 5.43 mmol), *sec*-butyllithium (0.71 cm^3 of a 1.3 M solution in hexanes, 5.97 mmol) and benzyl bromide (0.71 cm^3, 5.97 mmol). The *title compound* was obtained as a colourless oil (1.36 g, 92%) (Found: C, 70.04; H, 8.07; N, 10.16%; M^+ 274.1681. $C_{16}H_{22}N_2O_2$ requires: C, 70.04; H, 8.08; N, 10.21; *M* 274.1681); ν_{max}(film)/cm^{-1} 2977, 2934, 1718, 1644, 1370, 1143; δ_H (400 MHz) 1.50 [9H, s, $C(CH_3)_3$], 3.00 (4H, br s, CH_2CH_2Ph), 3.75 (4H, s, NCH_2CH_2N), 7.20–7.50 (5H, m, Ar-H); δ_C (100 MHz) 28.2 [$C(CH_3)_3$], 32.5 and 32.6 (CH_2), 46.8 and 52.0 (NCH_2), 81.5 [$C(CH_3)_3$], 125.9, 128.3, 128.4 and 141.3 (Ar-C), 151.0 (CO), 160.90 (NCN); *m/z* 274 (M^+, 0.6%), 218 (49), 174 (8), 145 (6), 97 (11).

1-*tert*-Butyloxycarbonyl-2-[2-(2-phenyl)phenylethyl]-2-imidazoline 14g. Prepared by the general method, using 1-*tert*-butyloxycarbonyl-2-methyl-2-imidazoline **3** (1.00 g, 5.43 mmol), *sec*-butyllithium (5.43 cm^3 of a 1.1 M solution in hexanes, 5.97 mmol) and 2-phenylbenzyl bromide (1.09 cm^3, 5.97 mmol). The *title compound* was obtained as a colourless oil (1.55 g, 81%) (Found: C, 74.79; H, 7.52; N, 7.53%; M^+ 350.1995. $C_{22}H_{26}N_2O_2{\cdot}0.1H_2O$ requires: C, 75.00; H, 7.44; N, 7.95%; *M* 350.1994); ν_{max}(film)/cm^{-1} 2977, 2934, 1718, 1642 1480, 1370, 1145; δ_H (400 MHz) 1.47 [9H, s, $C(CH_3)_3$], 2.85 (2H, t, *J*=8.0 Hz, CH_2Ar), 2.98 (2H, t, *J*=8.0 Hz, CH_2CH_2Ar), 3.65 (4H, s, NCH_2CH_2N), 7.15–7.40 (9H, m, Ar-H); δ_C (100 MHz) 28.0 [$C(CH_3)_3$], 29.5 and 32.3 (CH_2), 46.6 and 51.9 (NCH_2), 81.4 [$C(CH_3)_3$], 125.9, 126.7, 127.5, 128.1, 129.2, 130.1, 138.7, 141.7 and 141.9 (Ar-C), 150.8 (CO), 160.7 (NCN); *m/z* 350 (M^+, 9%), 294 (48), 249 (60), 217 (12), 165 (39), 115 (97), 97 (11), 71 (14), 57 (100).

1-*tert*-Butyloxycarbonyl-2-[2-(2-furyl)ethyl]-2-imidazoline 14h. Prepared by the general method, using 1-*tert*-butyloxycarbonyl-2-methyl-2-imidazoline **3** (2.00 g, 10.86 mmol), *sec*-butyllithium (14.94 cm^3 of a 0.8 M solution in hexanes, 11.95 mmol) and furfuryl chloride (1.20 g, 11.97 mmol). The *title compound* was obtained as a colourless oil (2.03 g, 71%) (Found: C, 60.88; H, 7.48; N, 10.08%; M^+ 264.1474. $C_{14}H_{20}N_2O_2{\cdot}0.8H_2O$ requires: C, 60.34; H,

7.18, N, 10.05%; *M* 264.1473); ν_{max}(film)/cm^{-1} 2977, 2934, 1718, 1644, 1479, 1369, 1331, 1222, 1147, 1000; δ_H (400 MHz) 1.45 [9H, s, C(CH$_3$)$_3$], 2.92–3.02 (4H, br m, C*H*$_2$C*H*$_2$Furyl), 3.68 (4H, s, NCH$_2$CH$_2$N), 5.95 (1H, d, *J*=2.9 Hz, Furyl H-3), 6.18 (1H, dd, *J*=1.5 and 2.9 Hz, Furyl H-4), 7.28 (1H, d, *J*=1.5 Hz, Furyl H-5); δ_C (100 MHz) 25.0 (CH$_2$), 28.2 [C(*C*H$_3$)$_3$], 29.5 (CH$_2$), 46.8 and 51.9 (NCH$_2$), 81.8 [*C*(CH$_3$)$_3$], 105.0, 110.1 and 140.9 (Furyl-C), 150.8 (CO), 154.9 (Furyl-C), 160.4 (NCN); *m/z* 264 (M$^+$, 2%), 208 (68), 191 (16), 163 (41), 135 (55), 121 (24), 94 (17), 84 (15), 81 (33), 70 (14), 58 (100).

1-*tert*-Butyloxycarbonyl-2-[1-(prop-2-enyl)but-3-enyl]-2-imidazoline 15a. Prepared by the general method, using 2-(but-3-enyl)-1-*tert*-butyloxycarbonyl-2-imidazoline **14b** (0.60 g, 2.67 mmol), *sec*-butyllithium (2.67 cm^3 of a 1.1 M solution in hexanes, 2.94 mmol) and 3-bromopropene (0.25 cm^3, 2.94 mmol). The *title compound* was obtained as a colourless oil (0.59 g, 84%) (Found: MH$^+$ 265.1916. $C_{15}H_{24}N_2O_2$ requires: *M* 265.1916); ν_{max}(film)/cm^{-1} 2996, 2972, 1720, 1644, 1483, 1369, 1329, 1149, 1010, 915; δ_H (400 MHz) 1.52 [9H, s, C(CH$_3$)$_3$], 2.29–2.35 and 2.40–2.50 (4H, 2×m, 2×C*H*$_2$CH=CH$_2$), 3.58 (1H, apparent t, *J*=6.6 Hz, C*H*CH$_2$CH=CH$_2$), 3.77 (4H, s, NCH$_2$CH$_2$N), 4.98–5.08 (4H, m, 2×CH=C*H*$_2$), 5.75–5.86 (2H, m, 2×C*H*=CH$_2$); δ_C (75 MHz), 28.3 [C(*C*H$_3$)$_3$], 36.6 and 37.8 (CH$_2$), 47.1 and 51.9 (NCH$_2$), 81.7 [*C*(CH$_3$)$_3$], 116.6 (CH=*C*H$_2$), 136.1 (*C*H=CH$_2$), 150.8 (CO), 163.6 (NCN); *m/z* 265 (MH$^+$, 2%), 209 (19), 191 (5), 165 (27), 154 (14), 149 (14), 123 (25), 108 (8), 83 (3), 57 (100).

1-*tert*-Butyloxycarbonyl-2-(1-phenylmethylbut-3-enyl)-2-imidazoline 15b. Prepared by the general method, using 2-(but-3-enyl)-1-*tert*-butyloxycarbonyl-2-imidazoline **14b** (0.30 g, 1.34 mmol), *sec*-butyllithium (1.47 cm^3 of a 1.0 M solution in hexanes, 1.47 mmol) and benzyl bromide (0.18 cm^3, 1.47 mmol). The *title compound* was obtained as a yellow oil (0.32 g, 76%) (Found: C, 71.82; H, 8.38; N, 9.45%; M$^+$ 314.1995. $C_{14}H_{18}N_2$ requires: C, 71.49; H, 8.67; N, 9.26%; *M* 314.1994); ν_{max}(film)/cm^{-1} 2976, 1669, 1610, 1296, 1200, 1178, 1130; δ_H (400 MHz) 1.50 [9H, s, C(CH$_3$)$_3$], 2.27–2.34 and 2.40–2.47 (each 1H, m, C*H*$_2$CH=CH$_2$), 2.78–2.84 (1H, dd, *J*=7.8 and 13.6 Hz, C*H*HPh), 3.02–3.07 (1H, dd, *J*=7.6 and 13.6 Hz, CH*H*Ph), 3.60–3.77 (4H, m, NCH$_2$CH$_2$N), 3.87–3.92 (1H, m, C*H*CH$_2$Ph), 5.00–5.05 (2H, m, CH=C*H*$_2$), 5.65–5.75 (1H, m, C*H*=CH$_2$), 7.15–7.28 (5H, m, Ar-H); δ_C (100 MHz), 28.2 [C(*C*H$_3$)$_3$], 36.6 and 38.8 (CH$_2$), 39.6 (CH), 46.9 and 51.8 (NCH$_2$), 81.5 [*C*(CH$_3$)$_3$], 116.6 (CH=*C*H$_2$), 126.0, 128.1 and 129.3 (Ar-C), 135.9 (*C*H=CH$_2$), 139.9 (Ar-C), 150.6 (CO), 163.5 (NCN); *m/z* 315 (MH$^+$, 2%), 259 (24), 217 (26), 213 (15), 173 (24), 167 (28), 123 (26), 91 (21), 57 (100).

1-*tert*-Butyloxycarbonyl-2-[1-(prop-2-enyl)pent-4-enyl]-2-imidazoline 15c. Prepared by the general method, using 1-*tert*-butyloxycarbonyl-2-(pent-4-enyl)-2-imidazoline **14c** (0.77 g, 3.23 mmol), *sec*-butyllithium (2.73 cm^3 of a 1.3 M solution in hexanes, 3.55 mmol) and 3-bromopropene (0.31 cm^3, 3.55 mmol). The *title compound* was obtained as a yellow oil (0.78 g, 87%) (Found: C, 67.14; H, 9.18, N, 9.81%; MH$^+$ 279.2084. $C_{16}H_{26}N_2O_2{\cdot}0.5H_20$ requires: C, 66.89, H, 9.05, N, 9.75%; *MH* 279.2072); ν_{max} (film)/cm^{-1} 3076, 2977, 2933, 2878, 1718, 1640, 1479, 1455, 1363, 1321, 1215, 1175, 1157, 1005; δ_H (400 MHz) 1.50 [9H, s, C(CH$_3$)$_3$], 1.60–1.70 and 1.77–1.84 (each 1H, m, C*H*$_2$CH$_2$CH=CH$_2$), 2.03–2.15 (2H, m, CH$_2$C*H*$_2$CH=CH$_2$), 2.26–2.34 and 2.39–2.49 (each 1H, m, CHC*H*$_2$CH=CH$_2$), 3.50–3.58 (1H, m, C*H*CH$_2$CH=CH$_2$), 3.77 (4H, s, NCH$_2$CH$_2$N), 4.90–5.07 (4H, m, 2×CH=C*H*$_2$), 5.75–5.86 (2H, m, 2×C*H*=CH$_2$); δ_C (100 MHz), 28.5 [C(*C*H$_3$)$_3$], 31.4, 31.5 and 37.4 (CH$_2$), 37.7 (CH), 47.2 and 51.9 (NCH$_2$), 114.7 and 116.7 (CH=*C*H$_2$), 136.1 and 138.9 (*C*H=CH$_2$), 151.0 (CO), 164.1 (NCN); *m/z* 279 (MH$^+$, 12%), 223 (82), 179 (14), 168 (12), 137 (8), 123 (9), 97 (13), 67 (11), 57 (100).

General method for synthesis of 2-alkyl-substituted 2-imidazolines 16

TFA was added to the 2-substituted 1-*tert*-butyloxycarbonyl-2-imidazoline **14** or **15** and the resulting solution was stirred at 20°C for 20–60 min. The TFA was removed under reduced pressure and the imidazoline trifluoroacetate salt was dissolved in dichloromethane (100 cm^3). The solution was then washed with aq. NaOH (10% w/v; 100 cm^3) and the organic layer was dried and concentrated. The crude product was purified by column chromatography on silica (0:100→2:98 v/v isopropylamine:ethyl acetate) to give the imidazoline **16**.

2-Butyl-2-imidazoline 16a. Prepared by the general method, using 2-butyl-1-*tert*-butyloxycarbonyl-2-imidazoline **14a** (1.25 g, 5.53 mmol) and TFA (3 cm^3). The *title compound* was obtained as white crystals (0.61 g, 87%), mp 39–41°C (Found: C, 66.32; H, 10.94; N, 21.96%; MH$^+$ 127.1235. $C_7H_{14}N_2$ requires C, 66.62; H, 11.18; N, 22.20%; *M* 127.1235); ν_{max}(KBr)/cm^{-1} 3230, 2958, 2871, 1615, 1495, 1467, 1289, 1268; δ_H (400 MHz) 0.92 (3H, t, *J*=7.2 Hz, CH$_3$), 1.31–1.41 (2H, m, C*H*$_2$CH$_3$), 1.57–1.64 (2H, m, C*H*$_2$CH$_2$CH$_3$), 2.32 (2H, t, *J*=7.8 Hz, C*H*$_2$CH$_2$CH$_2$CH$_3$), 3.70 (4H, s, NCH$_2$CH$_2$N); δ_C (75 MHz) 13.8 (CH$_3$), 22.5, 28.8 and 29.2 (CH$_2$), 49.9 (NCH$_2$), 168.1 (NCN); *m/z* 127 (M$^+$, 80%), 115 (5), 98 (8), 84 (100), 73 (15), 69 (11), 57 (15), 44 (23).

2-(But-3-enyl)-2-imidazoline 16b. Prepared by the general method, using 2-(but-3-enyl)-1-*tert*-butyloxycarbonyl-2-imidazoline **14b** (1.45 g, 6.47 mmol) and TFA (3 cm^3). The *title compound* was obtained as a white solid (0.66 g, 82%), mp 29–31°C (Found: MH$^+$ 124.1000. $C_7H_{12}N_2$ requires: *M* 124.1000); ν_{max}(film)/cm^{-1} 3200, 2934, 1610, 1540, 1369, 1150; δ_H (400 MHz) 2.37–2.45 (4H, br m, CH$_2$CH$_2$), 3.72 (4H, s, NCH$_2$CH$_2$N), 4.89 (1H, br s, NH), 5.00–5.11 (2H, m, CH=C*H*$_2$), 5.78–5.87 (1H, m, C*H*=CH$_2$); δ_C (75 MHz) 28.6 and 30.5 (CH$_2$), 49.7 (NCH$_2$), 115.4 (CH=*C*H$_2$), 137.3 (*C*H=CH$_2$), 167.2 (NCN); *m/z* 124 (M$^+$, 2%) 123 (87), 113 (22), 109 (9), 84 (21), 67 (24), 55 (49), 43 (51).

2-(Hepta-3,5-dienyl)-2-imidazoline 16e. Prepared by the general method, using 1-*tert*-butyloxycarbonyl-2-(hepta-3,5-dienyl)-2-imidazoline **14e** (1.20 g, 4.54 mmol) and TFA (3 cm^3). The *title compound* was obtained as a mixture of geometric isomers (4:1 *E*,*E*:*E*,*Z*) as a white solid (0.50 g, 67%), mp 68–70°C (Found: M$^+$ 164.1317. $C_{10}H_{16}N_2$

requires: *M* 164.1313); ν_{max}(KBr)/cm^{-1} 3154, 3017, 2932, 2862, 1606, 1505, 1475, 1451, 1376, 1284, 1146; for *E*,*E*-isomer δ_H (400 MHz) 1.73 (3H, d, *J*=6.8 Hz, C*H*$_3$CH=CH), 2.28–2.42 (4H, m, CH=CHC*H*$_2$C*H*$_2$), 3.58 (4H, s, NCH$_2$CH$_2$N), 3.80 (1H, br s, NH), 5.52–5.68 and 5.98–6.10 (each 2H, m, CH=CHCH=CH); δ_C (100 MHz), 18.0 (CH$_3$), 29.2 and 29.4 (CH$_2$), 49.9 (NCH$_2$), 127.9, 130.3, 131.3 and 136.9 (CH), 167.4 (NCN); for *E*,*Z*-isomer δ_H (400 MHz) 1.08 (3H, d, *J*=6.8 Hz, C*H*$_3$CH=CH), 2.28–2.42 (4H, m, CH=CHC*H*$_2$C*H*$_2$), 3.58 (4H, s, NCH$_2$CH$_2$N), 3.80 (1H, br s, NH), 5.04 (1H, d, *J*=10.2 Hz, CH=C*H*CH=CH), 5.12 (1H, d, *J*=17.2 Hz, CH=CHC*H*=CH), 5.98–6.10 and 6.24–6.34 (each 1H, m, C*H*=CHCH=C*H*); δ_C (100 MHz), 20.1 (CH$_3$), 29.2 and 29.4 (CH$_2$), 49.9 (NCH$_2$), 115.9, 130.3, 131.3 and 139.1 (CH), 166.5 (NCN); *m*/*z* 164 (M$^+$, 57%), 149 (93), 135 (57), 123 (25), 97 (22), 84 (100), 79 (44), 54 (35).

2-(2-Phenylethyl)-2-imidazoline 16f. Prepared by the general method, using 1-*tert*-butyloxycarbonyl-2-(2-phenylethyl)-2-imidazoline **14f** (2.00 g, 7.29 mmol) and TFA (4 cm^3). The *title compound* was obtained as a white solid (0.93 g, 73%), mp 102–104°C (Found: C, 75.83; H, 8.12; N, 15.86%; M$^+$ 174.1146. C$_{11}$H$_{14}$N$_2$ requires: C, 75.82; H, 8.10; N, 16.07%; *M* 174.1157); ν_{max}(KBr)/cm^{-1} 3158, 3059, 3001, 2926, 2859, 1606, 1498, 1286; δ_H (400 MHz) 2.52–2.56 (2H, t, *J*=7.9 Hz, CH$_2$C*H*$_2$Ph), 2.94–2.98 (2H, t, *J*=7.9 Hz, C*H*$_2$CH$_2$Ph), 3.56 (4H, br s, NCH$_2$CH$_2$N), 7.20–7.50 (5H, m, Ar-H); δ_C (100 MHz) 31.1 and 32.8 (CH$_2$), 49.4 (NCH$_2$), 126.2, 128.2, 128.4 and 141.1 (Ar-C), 167.2 (NCN); *m*/*z* 174 (M$^+$, 33%), 173 (100), 144 (8), 117 (16), 97 (38), 91 (25), 84 (10), 65 (33).

2-[2-(2-Phenyl)phenylethyl]-2-imidazoline 16g. Prepared by the general method, using 2-[2-(2-phenyl)phenylethyl]-1-*tert*-butyloxycarbonyl-2-imidazoline **14g** (1.38 g, 3.94 mmol) and TFA (3 cm^3). The *title compound* was obtained as a white solid (0.79 g, 80%), mp 118–120°C (Found: C, 81.68; H, 7.25; N, 11.17%; (M−H)$^+$ 249.1382. C$_{22}$H$_{26}$N$_2$O$_2$ requires: C, 81.56; H, 7.25; N, 11.18%; *M*−*H* 249.1392); ν_{max}(film)/cm^{-1} 3152, 3104, 2932, 1608, 1558, 1538, 1505, 1479, 1310, 1279; δ_H (400 MHz) 2.30–2.33 (2H, t, *J*=8.0 Hz, CH$_2$C*H*$_2$Ar), 2.92–2.95 (2H, t, *J*=8.0 Hz, C*H*$_2$CH$_2$Ar), 3.47 (4H, s, NCH$_2$CH$_2$N), 4.11 (1H, br s, NH), 7.15–7.40 (9H, m, Ar-H); δ_C (100 MHz), 30.2 and 30.7 (CH$_2$), 50.2 (NCH$_2$), 126.3, 127.0, 127.6, 128.2, 129.1, 129.2, 130.2, 138.3, 141.5 and 141.8 (Ar-C), 167.1 (NCN); *m*/*z* 250 (M$^+$, 33%), 249 (100), 173 (30), 165 (40), 152 (13), 115 (10), 97 (25), 71 (22).

2-[2-(2-Furyl)ethyl]-2-imidazoline 16h. Prepared by the general method, using 1-*tert*-butyloxy-carbonyl-2-[2-(2-furyl)ethyl]-2-imidazoline **14h** (0.300 g, 1.13 mmol) and TFA (1 cm^3). The *title compound* was obtained as a white solid (0.12 g, 65%), mp 98–100°C (Found: M$^+$ 164.0950. C$_9$H$_{12}$N$_2$ requires: *M* 164.0949); ν_{max}(KBr)/cm^{-1} 3165, 3118, 2927, 2862, 1606, 1511, 1377, 1289, 1001; δ_H (400 MHz) 2.48–2.52 (2H, t, *J*=7.8 Hz, CH$_2$C*H*$_2$Furyl), 2.88–2.93 (2H, t, *J*=7.8 Hz, C*H*$_2$CH$_2$Furyl), 3.48 (4H, s, NCH$_2$CH$_2$N), 4.31 (1H, br s, NH), 5.95 (1H, d, *J*=3.0 Hz, Furyl H-3), 6.21 (1H, dd, *J*=3.0 and 1.9 Hz, Furyl H-4), 7.29 (1H, d, *J*=1.9 Hz, Furyl H-5); δ_C (100 MHz), 25.1 and 27.8 (CH$_2$), 49.8 (NCH$_2$), 105.3, 110.2, 141.1 and 154.6 (Furyl-C), 166.7 (NCN); *m*/*z* 164 (M$^+$, 100%), 135 (92), 121 (40), 110 (11), 94 (17), 84 (65), 54 (37).

2-[1-(Prop-2-enyl)but-3-enyl]-2-imidazoline 16i. Prepared by the general method, using 1-*tert*-butyloxycarbonyl-2-[1-(prop-2-enyl)but-3-enyl]-2-imidazoline **15a** (1.20 g, 4.54 mmol) and TFA (3 cm^3). The *title compound* was obtained as a yellow oil (0.50 g, 67%) (Found: MH$^+$ 165.1388. C$_{10}$H$_{16}$N$_2$ requires: *MH* 165.1392); ν_{max}(film)/cm^{-1} 3196, 3077, 2977, 2864, 1642, 1612, 1495, 1472, 1452, 1288; δ_H (400 MHz) 2.25–2.35 (4H, m, 2×CHC*H*$_2$CH=CH$_2$), 2.46 (1H, m, C*H*CH$_2$CH=CH$_2$), 3.52 (4H, s, NCH$_2$CH$_2$N), 3.95 (1H, br s, NH), 4.95–5.10 (4H, m, CH=C*H*$_2$), 5.70–5.86 (2H, m, C*H*=CH$_2$); δ_C (100 MHz) 36.9 (CH$_2$), 39.7 (CH), 49.5 (NCH$_2$), 116.8 (CH=*C*H$_2$), 135.9 (*C*H=CH$_2$), 169.9 (NCN); *m*/*z* 165 (MH$^+$, 100%), 149 (14), 135 (14), 121 (34), 110 (10), 94 (4), 82 (9), 67 (6).

2-(1-Phenylmethylbut-3-enyl)-2-imidazoline 16j. Prepared by the general method, using 2-(1-phenylmethylbut-3-enyl)-1-*tert*-butyloxycarbonyl-2-imidazoline **15b** (0.20 g, 0.64 mmol) and TFA (1 cm^3). The *title compound* was obtained as a white solid (0.09 g, 67%), mp 76–78°C (Found: M$^+$ 214.1470. C$_{14}$H$_{18}$N$_2$ requires: *M* 214.1470); ν_{max}(KBr)/cm^{-1} 3120, 2976, 1669, 1610, 1296, 1200, 1178, 1130; δ_H (400 MHz) 2.35–2.41 and 2.48–2.56 (each 1H, m, CHC*H*$_2$CH=CH$_2$), 2.91–2.98 and 3.02–3.09 (each 1H, dd, *J*=7.6 and 13.6 Hz, CHC*H*$_2$Ph), 3.20–3.30 (1H, m, C*H*CH$_2$), 3.99–3.87 (4H, m, NCH$_2$CH$_2$N), 5.05 (1H, d, *J*=10.2 Hz, CH=C*H*H), 5.15 (1H, d, *J*=17.1 Hz, CH=CH*H*), 5.65–5.75 (1H, m, C*H*=CH$_2$), 7.15–7.30 (5H, m, Ar-H); δ_C (100 MHz) 36.1 and 37.8 (CH$_2$), 40.2 (CH), 44.7 (NCH$_2$), 118.2 (CH=*C*H$_2$), 126.9, 128.6, 128.9 (Ar-C), 133.81 (*C*H=CH$_2$), 137.4 (Ar-C), 173.3 (NCN); *m*/*z* 214 (M$^+$, 18%), 213 (36), 173 (61), 171 (24), 167 (10), 137 (16) 123 (100), 108 (12), 91 (38), 77 (10), 65 (20), 57 (57).

2-[1-(Prop-2-enyl)pent-4-enyl)-2-imidazoline 16k. Prepared by the general method, using 1-*tert*-butyloxycarbonyl-2-[1-(prop-2-enyl)pent-4-enyl)-2-imidazoline **15c** (0.50 g, 1.80 mmol) and TFA (2 cm^3). The *title compound* was obtained as a pale yellow oil (0.26 g, 81%) (Found: MH$^+$ 179.1548. C$_{11}$H$_{18}$N$_2$ requires: *MH* 179.1548); ν_{max}(film)/cm^{-1} 3176, 3077, 2976, 2933, 2863, 1641, 1611, 1495, 1472, 1455, 1289; δ_H (400 MHz) 1.58–176 (2H, m, CHC*H*$_2$CH$_2$), 2.05–2.15 and 2.26–2.34 (each 2H, m, C*H*$_2$CH=CH$_2$), 2.38–2.44 (1H, m, C*H*CH$_2$), 3.56 (4H, s, NCH$_2$CH$_2$N), 4.08 (1H, br s, NH), 4.95–5.10 (4H, m, 2×CH=C*H*$_2$), 5.72–5.86 (2H, m, 2×C*H*=CH$_2$); δ_C (100 MHz), 31.3, 31.8 and 37.6 (CH$_2$), 39.4 (CH), 49.6 (NCH$_2$), 114.4 and 116.5 (CH=*C*H$_2$), 135.9 and 138.1 (*C*H=CH$_2$), 169.9 (NCN); *m*/*z* 178 (M$^+$, 9%), 163 (18), 135 (32), 124 (86), 123 (100), 109 (28), 97 (49), 67 (21).

General method for synthesis of 1-*tert*-butyloxycarbonyl-2-(2-oxoalkylidene)imidazolidines 17

sec-Butyllithium (solution in hexanes) was injected into 1-*tert*-butyloxycarbonyl-2-methyl-2-imidazoline **3** in dry THF/TMEDA (20:1 v/v; 0.1 M in imidazoline) stirred at −78°C under nitrogen. The bright yellow solution produced

was stirred for 20 min at −78°C. Freshly distilled ester electrophile was injected to the reaction mixture at −78°C under nitrogen. The mixture was allowed to warm to 20°C overnight. The reaction was quenched with water (100 cm^3), the organic layer was extracted with diethyl ether (3×50 cm^3) and the combined extracts were washed successively with saturated aq. $NaHCO_3$ (100 cm^3), water (100 cm^3) and brine (100 cm^3), dried and concentrated. The crude product was purified by column chromatography on silica gel (1:9→1:1 v/v ethyl acetate:hexane) to give the compound **17**.

1-*tert*-Butyloxy-2-(2-oxopropylidene)imidazolidine 17a. Prepared by the general method, using 1-*tert*-butyloxycarbonyl-2-methyl-2-imidazoline **3** (0.55 g, 2.99 mmol), *sec*-butyllithium (3.58 cm^3 of a 1.0 M solution in hexanes, 3.58 mmol) and ethyl acetate (0.70 cm^3, 6.00 mmol). The *title compound* was obtained as white crystals (0.49 g, 72%), mp 125–127°C (Found: C, 58.12; H, 8.11; N, 12.11%; M^+ 226.1317. $C_{11}H_{18}N_2O_3$ requires: C, 58.39; H, 8.02; N, 12.37%; *M* 226.1317); ν_{max}(KBr)/cm^{-1} 3253, 2976, 2936, 1725, 1622, 1557, 1318, 1253, 1149; δ_H (400 MHz) 1.45 [9H, s, $C(CH_3)_3$], 2.03 (3H, s, CH_3), 3.57 and 3.80 (each 2H, t, *J*=9.0 Hz, NCH_2CH_2N), 5.92 (1H, s, CH), 9.96 (1H, br s, NH); δ_C (100 MHz) 28.0 [$C(CH_3)_3$], 29.3 (CH_3), 41.1 and 44.9 (NCH_2), 81.6 (CH), 82.7 [$C(CH_3)_3$], 150.4 (CO), 157.6 (NCN), 195.2 (CO); *m/z* 226 (M^+, 10%), 170 (32), 153 (10), 126 (31), 111 (68), 84 (41), 70 (12), 57 (100), 43 (29).

1-*tert*-Butyloxy-2-(2-oxobut-3-enylidene)imidazolidine 17b. Prepared by the general method, using 1-*tert*-butyloxycarbonyl-2-methyl-2-imidazoline **3** (2.00 g, 10.87 mmol), *sec*-butyllithium (11.95 cm^3 of a 1.0 M solution in hexanes, 11.95 mmol) and methyl propenoate (1.86 cm^3, 11.95 mmol). The *title compound* was obtained as white crystals (1.05 g, 42%), mp 145–147°C (Found: C, 60.63; H, 7.69; N, 11.77%; MH^+ 239.1383. $C_{12}H_{17}N_2O_3$ requires: C, 60.74; H, 7.22; N, 11.80%; *MH* 239.1396); ν_{max}(KBr)/cm^{-1} 3245, 2971, 2930, 1732, 1601, 1541, 1514, 1476, 1313, 1250, 1151, 1040; δ_H (400 MHz) 1.55 [9H, s, $C(CH_3)_3$], 3.67 and 3.88 (each 2H, t, *J*=7.8 Hz NCH_2CH_2N), 5.44–5.47 (1H, dd, *J*=2.0 and 10.4 Hz, CH=C*H*H), 6.06 (1H, s, C=CHCO), 6.11–6.16 (1H, dd, *J*=2.0 and 16.2 Hz, CH=CH*H*), 6.34–6.41 (1H, dd, *J*=10.4 and 17.2 Hz, C*H*=CH_2), 10.48 (1H, br s, NH); δ_C (100 MHz) 28.0 [$C(CH_3)_3$], 41.3 and 44.0 (NCH_2), 81.9 (C=*C*HCO), 83.0 [$C(CH_3)_3$], 122.1 (CH=*C*H_2), 138.3 (*C*H=CH_2), 150.4 (CO), 159.1 (NCN), 186.3 (CO); *m/z* 239 (M^+, 5%), 183 (12), 165 (3), 149 (5), 139 (12), 123 (2), 108 (6), 87 (5), 57 (100).

1-*tert*-Butyloxy-2-(2-oxo-2-phenylethylidene)imidazolidine 17c. Prepared by the general method, using 1-*tert*-butyloxycarbonyl-2-methyl-2-imidazoline **3** (2.00 g, 10.86 mmol), *sec*-butyllithium (10.86 cm^3 of a 1.1 M solution in hexanes, 11.95 mmol) and methyl benzoate (1.48 cm^3, 11.95 mmol). The *title compound* was obtained as white crystals (2.00 g, 64%), mp 170–172°C (Found: C, 66.50; H, 7.00; N, 9.63%; MH^+ 289.1545. $C_{16}H_{20}N_2O_3$ requires: C, 66.65; H, 6.99; N, 9.71%; *MH* 289.1552); ν_{max}(KBr)/cm^{-1} 3253, 2979, 1733, 1608, 1557, 1581, 1532, 1358, 1317, 1146; δ_H (300 MHz) 1.57 [9H, s, $C(CH_3)_3$], 3.67 and 3.88 (each 2H, t, *J*=8.5 Hz, NCH_2CH_2N), 6.69 (1H, s, CH), 7.86–7.95 (5H, m, Ar-H), 10.47 (1H, br s, NH); δ_C (75 MHz) 28.1 [$C(CH_3)_3$], 41.2 and 45.1 (NCH_2), 78.8 (CH), 82.9 [$C(CH_3)_3$], 126.9, 128.1, 130.4 and 140.5 (Ar-C), 150.5 (CO), 159.1 (NCN), 188.2 (CO); *m/z* 288 (M^+, 11%), 232 (22), 215 (8), 204, (7), 187 (100), 159 (24), 146 (3), 131 (8), 111 (41), 105 (33), 77 (34).

X-Ray crystal structure data for 17c.[16] $C_{16}H_{20}N_2O_3$, *M*=288.34, orthorhombic, *a*=10.6561(2), *b*=15.5737(3), *c*=17.8997(3) Å, *U*=2970.54(9) $Å^3$, *T*=162(2) K, space group *Pbca*, monochromated Mo-*K*α radiation, λ=0.71073 Å, *Z*=8, D_c=1.289 Mg m^{-3}, *F*(000)=1232, colourless bipyramid crystals, dimensions 0.20×0.20×0.20 mm, μ(Mo−*K*α)=0.090 mm^{-1}, $2.58<2\theta<26.00°$, 23802 reflections measured, 2910 unique reflections. The structure was solved by direct methods and refined by full-matrix least-squares on F^2. The final cycle (for 270 parameters) converged with *R*1=0.0467, *wR*2=0.0947 (for all data) and *R*1=0.0356, *wR*2=0.0893 [$F^2>2\sigma(F^2)$].

2-(2-Oxopropylidene)imidazolidine 18a. TFA (1 cm^3) was added to 1-*tert*-butyloxy-2-(2-oxopropyl-idene)-2-imidazoline **17a** (0.20 g, 0.88 mmol) and the resulting solution was stirred at 20°C for 60 min. The TFA was removed under reduced pressure, the imidazolidine salt dissolved in dichloromethane (20 cm^3), and the solution then washed with aq. NaOH (20 cm^3, 10% w/v). The organic layer was dried and concentrated, and the crude product purified by column chromatography on silica (0:100→3:97 v/v isopropylamine:chloroform) to give the *title compound* as a yellow solid (0.09 g, 81%), mp 157–159°C (Found: M^+ 126.0793. $C_6H_{10}N_2O$ requires: *M* 126.0793); ν_{max}(KBr)/cm^{-1} 3279, 3116, 1605, 1557, 1490, 1323; δ_H (400 MHz) 1.98 (3H, s, CH_3), 3.55 and 3.70 (each 2H, t, *J*=7.8 Hz, NCH_2CH_2N), 4.77 (1H, s, CH), 5.40 and 9.20 (each 1H, br s, NH); δ_C [100 MHz; $(CD_3)_2SO$] 28.5 (CH_3), 41.8 and 43.5 (NCH_2), 76.0 (CH), 164.4 (NCN), 188.1 (CO); *m/z* 126 (M^+, 44%), 111 (100), 97 (12), 84 (39), 70 (23), 54 (40), 43 (73).

2-(2-Oxo-2-phenylethylidene)imidazolidine 18c. Prepared by the method described above for **18a**, using TFA (4 cm^3) and 1-*tert*-butyloxy-2-(2-oxo-2-phenylethylidene)imidazolidine **17c** to give the *title compound* as white crystals (0.70 g, 90%), mp 203–205°C (lit.[17] 208°C) (Found: C, 69.88; H, 6.48; N, 14.73%; $(M-H)^+$ 187.0864. $C_{11}H_{12}N_2O$ requires: C, 70.19; H, 6.43; N, 14.88%; *M*−*H* 187.0871); ν_{max}(KBr)/cm^{-1} 3310, 2987, 2860, 1603, 1582, 1554, 1503, 1477, 1451, 1332, 1290, 1213, 1054, 720; δ_H [300 MHz; $(CD_3)_2SO$] 3.45 and 3.59 (each 2H, t, *J*=8.0 Hz, NCH_2CH_2N), 5.54 (1H, s, CH), 7.30–7.39 (3H, m, Ar-H), 7.69–7.75 (2H, m, Ar-H), 9.28 (1H, br s, NH); δ_C [75 MHz; $(CD_3)_2SO$], 41.8 and 43.5 (NCH_2), 73.1 (CH), 126.1, 127.9, 129.4 and 141.5 (Ar-C), 165.4 (NCN), 181.9 (CO); *m/z* 188 (M^+, 67%), 159 (30), 131 (18), 111 (100), 105 (37), 81 (8), 77 (85).

1-*tert*-Butyloxycarbonyl-2-(diethylphosphonomethyl)-2-imidazoline 19. *sec*-Butyllithium (18.39 cm^3 of a 1.3 M solution in hexanes, 23.91 mmol) was injected into 1-*tert*-butyloxycarbonyl-2-methyl-2-imidazoline **3** (4.00 g, 21.74 mmol) in dry THF (200 cm^3) and TMEDA (5 cm^3) stirred at −78°C under nitrogen. The bright yellow solution produced

was stirred for 20 min at −78°C under nitrogen before diethyl chlorophosphate (3.45 cm^3, 23.91 mmol) was injected into the reaction mixture. The mixture was allowed to warm to 20°C overnight and the reaction was quenched with water (100 cm^3). The organic layer was extracted with diethyl ether (3×100 cm^3) and the combined organic extracts were washed successively with saturated aq. $NaHCO_3$ (100 cm^3), water (50 cm^3) and brine (50 cm^3), dried and concentrated. The crude product was purified by column chromatography on silica gel (0:100→1:99 v/v isopropylamine:chloroform) to give the *title compound* as a yellow oil (3.56 g, 51%) (Found: C, 45.14; H, 7.86; N, 7.90%; M^+ 320.1501. $C_{13}H_{25}N_2O_5P{\cdot}1.5H_2O$ requires: C, 44.95; H, 8.13; N, 8.06%; *M* 320.1501); ν_{max}(film)/cm^{-1} 2981, 2935, 1713, 1639, 1371, 1254, 1165, 1028; δ_H (400 MHz) 1.31–1.34 (6H, t, *J*=7.2 Hz, 2×C*H*$_3$CH$_2$), 1.50 [9H, s, C(CH$_3$)$_3$], 3.56–3.62 (2H, d, *J*=22.0 Hz, CH$_2$P), 3.80 (4H, s, NCH$_2$CH$_2$N), 4.14–4.21 (4H, q, *J*=7.6 Hz, CH$_3$C*H*$_2$); δ_C (100 MHz) 16.1 (*C*H$_3$CH$_2$), 27.9 [C(*C*H$_3$)$_3$], 40.2 (CH$_3$*C*H$_2$), 46.6 and 52.2 (NCH$_2$), 62.6 (CH$_2$P), 82.1 [*C*(CH$_3$)$_3$], 150.8 (CO), 153.6 (NCN); *m/z* 321 (MH^+, 2%), 220 (18), 192 (8), 179 (8), 166 (11), 138 (8), 123 (2), 110 (9), 84 (95), 57 (100).

General method for the synthesis of 1-*tert*-butyloxycarbonyl-2-alkenyl-2-imidazolines 20

sec-Butyllithium (solution in cyclohexane) was added dropwise to 1-*tert*-butyloxycarbonyl-2-(diethylphos-phonomethyl)-2-imidazoline **19** in dry THF/TMEDA (25:1 v/v; 0.1 M in imidazoline) stirred at −78°C under nitrogen. The red solution produced was stirred for 20 min at −78°C. Freshly distilled aldehyde electrophile was injected rapidly into the reaction mixture at −78°C under nitrogen. The reaction was allowed to warm to 20°C overnight. The reaction was quenched with water (100 cm^3), the organic layer extracted with diethyl ether (3×100 cm^3) and the combined organic extracts were washed successively with saturated aq. $NaHCO_3$ (100 cm^3) and brine (100 cm^3), dried and concentrated. The crude product was purified by column chromatography on silica gel (ethyl acetate:hexane) to give the compound **20**.

1-*tert*-Butyloxycarbonyl-2-(pent-1-enyl)-2-imidazoline 20a. Prepared by the general method, using 1-*tert*-butyloxycarbonyl-2-(diethylphosphonomethyl)-2-imidazoline **19** (0.50 g, 1.56 mmol), *sec* butyl-lithium (1.72 cm^3 of a 1 M solution in cyclohexane, 1.72 mmol) and butanal (0.15 cm^3, 1.72 mmol). The *title compound* was obtained after chromatography on silica gel (1:9→1:1 v/v ethyl acetate:hexane) as a colourless oil (0.25 g, 67%; 0.19 g of *E*-isomer and 0.06 g of *Z*-isomer) (Found: C, 63.51; H, 9.22; N, 11.74%; MH^+ 239.1760. $C_{13}H_{22}N_2O_2{\cdot}0.4.H_2O$ requires: C, 63.31; H, 9.25; N, 11.36%; *MH* 239.1759). The *Z*-isomer converts to the *E*-isomer upon standing; data for *E*-isomer: ν_{max}(film)/cm^{-1} 2961, 2932, 1718, 1654, 1614, 1370, 1149, 1014; δ_H (400 MHz) 0.93 (3H, t, *J*=7.2 Hz, C*H*$_3$CH$_2$), 1.48–1.53 (2H, m, CH$_3$C*H*$_2$), 1.52 [9H, s, C(CH$_3$)$_3$], 2.15–2.20 (2H, dt, *J*=7.2 and 7.6 Hz, C*H*$_2$CH=CH), 3.78 (4H, s, NCH$_2$CH$_2$N), 6.72 (2H, s, CH=CH); δ_C (100 MHz), 13.9 (CH$_3$), 21.7 (CH$_2$), 28.2 [C(*C*H$_3$)$_3$], 35.3 (CH$_2$), 46.8 and 52.0 (NCH$_2$), 81.6 [*C*(CH$_3$)$_3$], 119.6 and 141.8 (CH=CH), 151.1 (CO), 157.3 (NCN). Data for *Z*-isomer: δ_H (400 MHz) 0.92 (3H, t, *J*=7.2 Hz, C*H*$_3$CH$_2$), 1.48–1.53 (2H, m, CH$_3$C*H*$_2$), 1.52 [9H, s, C(CH$_3$)$_3$], 2.42–2.47 (2H, q, *J*=7.6 Hz, C*H*$_2$CH=CH), 3.71–3.76 and 3.86–3.90 (each 2H, t, *J*=9.2 Hz, NCH$_2$CH$_2$N), 5.92 (1H, m, CH$_2$C*H*=CH), 6.42 (1H, d, *J*=11.6 Hz, CH$_2$CH=C*H*); δ_C (100 MHz) 13.9 (CH$_3$), 22.5 (CH$_2$), 28.2 [C(*C*H$_3$)$_3$], 31.4 (CH$_2$), 45.9 and 52.8 (NCH$_2$), 81.6 [*C*(CH$_3$)$_3$], 118.8 and 141.3 (CH=CH), 151.1 (CO), 155.8 (NCN); *m/z* 239 (MH^+, 100%), 183 (84), 167 (16), 139 (39), 123 (14), 109 (25), 84 (5), 81 (11), 57 (99).

1-*tert*-Butyloxycarbonyl-2-(penta-1,3-dienyl)-2-imidazoline 20b. Prepared by the general method, using 1-*tert*-butyloxycarbonyl-2-(diethylphosphonomethyl)-2-imidazoline **19** (1.42 g, 4.44 mmol), *sec*-butyllithium (6.10 cm^3 of a 0.8 M solution in cyclohexane, 4.48 mmol) and 2-butenal (0.40 ml, 4.48 mmol). The *title compound* was obtained after chromatography on silica gel (1:9→2:8 v/v ethyl acetate:hexane) as an orange solid (0.68 g, 65%), mp 58–60°C (Found: C, 65.82; H, 8.56; N: 11.43%; MH^+ 237.1603. $C_{13}H_{20}N_2O_2$ requires: C, 66.07; H, 8.53; N, 11.85%; *MH* 237.1603); ν_{max}(KBr)/cm^{-1} 2977, 2934, 1714, 1646, 1617, 1596, 1375, 1166, 1140, 1011; δ_H (400 MHz) 1.52 [9H, s, C(C*H*$_3$)$_3$], 1.83 (3H, d, *J*=6.8 Hz, C*H*$_3$CH), 3.80 (4H, s, NCH$_2$CH$_2$N), 5.96–6.01 (1H, m, CH$_3$C*H*), 6.20 (1H, dd, *J*=13.0 and 13.2 Hz, CH$_3$CH=C*H*), 6.78–6.82 (1H, d, *J*=15.6 Hz, CH$_3$CH=CHCH=C*H*), 7.15–7.21 (1H, dd, *J*=13.2 and 15.6 Hz, CH$_3$CH=CHC*H*); δ_C (100 MHz) 18.5 (CH$_3$), 28.3 [C(*C*H$_3$)$_3$], 46.9 and 52.1 (NCH$_2$), 81.7 [*C*(CH$_3$)$_3$], 117.9, 131.1, 135.7 and 139.3 (CH), 151.2 (CO), 157.5 (NCN); *m/z* 237 (MH^+, 18%), 221 (49), 181 (38), 165 (100), 135 (17), 121 (52), 107 (12), 83 (92), 57 (100).

1-*tert*-Butyloxycarbonyl-2-(2-phenylethenyl)-2-imidazoline 20c. Prepared by the general method, using 1-*tert*-butyloxycarbonyl-2-(diethylphosphonomethyl)-2-imidazoline **19** (0.50 g, 1.56 mmol), *sec* butyllithium (1.72 cm^3 of a 1 M solution in cyclohexane, 1.72 mmol) and benzaldehyde (0.17 cm^3, 1.72 mmol). The *title compound* was obtained after chromatography on silica gel (1:9→2:3 v/v ethyl acetate:hexane) as a white solid (0.28 g, 66%), mp 63–65°C (Found: C, 69.90; H, 7.45; N, 9.89%; M^+ 272.1525. $C_{16}H_{20}N_2O_2{\cdot}0.1H_2O$ requires: C, 70.08; H, 7.37; N, 10.22%; *M* 272.1525); ν_{max}(KBr)/cm^{-1} 2979, 1713, 1641, 1608, 1371, 1316, 1148, 1015, 756; δ_H (400 MHz) 1.50 [9H, s, C(C*H*$_3$)$_3$], 3.80 (4H, s, NCH$_2$CH$_2$N), 7.22–7.32 (4H, m, PhC*H*=CH, and Ar-H), 7.47 (3H, m PhCH=C*H* and Ar-H); δ_C (100 MHz), 28.2 [C(*C*H$_3$)$_3$], 46.9 and 52.1 (NCH$_2$), 81.7 [*C*(CH$_3$)$_3$], 117.2 (Ph*C*H), 127.5, 128.6, 128.9 and 135.9 (Ar-C), 138.2 (PhCH=*C*H), 151.1 (CO), 157.4 (NCN); *m/z* 272 (M^+, 13%), 244 (13), 215 (100), 199 (25), 171 (100), 143 (29), 115 (55), 107 (62), 91 (73), 79 (71), 57 (100).

General method for the one-pot synthesis of 1-*tert*-butyloxycarbonyl-2-alkenyl-2-imidazolines 20

sec-Butyllithium (1.3 M solution in cyclohexane) was injected into 1-*tert*-butyloxycarbonyl-2-methyl-2-imidazoline **3** in dry THF/TMEDA stirred at −78°C under nitrogen. The bright yellow solution produced was stirred at −78°C for 20 min, when diethyl chlorophosphate was injected and

the pale yellow solution produced was stirred at −78°C for 1 h and at 20°C for 4 h under nitrogen. The reaction mixture was cooled to −78°C and a second equiv. of *sec*-butyllithium (1.3 M solution in cyclohexane) was added. The bright red solution produced was stirred at −78°C for 20 min and freshly distilled aldehyde was injected into it. The reaction mixture was stirred overnight and allowed to warm to 20°C. The reaction was quenched with water (100 cm^3), the organic layer was extracted with diethyl ether (3×100 cm^3) and the combined organic extracts were washed successively with saturated aq. $NaHCO_3$ (100 cm^3), water (50 cm^3) and brine (50 cm^3), dried and concentrated. The crude product was purified by column chromatography on silica gel (1:4→2:3 v/v ethyl acetate:hexane) to give the imidazoline **20**.

One-pot synthesis of 1-*tert*-butyloxycarbonyl-2-(pent-1-enyl)-2-imidazoline 20a. Prepared by the general method, using 1-*tert*-butyloxycarbonyl-2-methyl-2-imidazoline **3** (2.00 g, 10.86 mmol), *sec* butyllithium (2×9.19 cm^3 of a 1.3 M solution in cyclohexane, 2×11.95 mmol), diethyl chlorophosphate (1.32 cm^3, 10.86 mmol) and butanal (1.05 cm^3, 11.95 mmol) in THF (108 cm^3) and TMEDA (3 cm^3). The title compound was obtained as a yellow oil (0.85 g, 33%; 0.68 g of *trans* isomer and 0.17 g of *cis* isomer), identical to that reported above.

One-pot synthesis of 1-*tert*-butyloxycarbonyl-2-(penta-1,3-dienyl)-2-imidazoline 20b. Prepared by the general method, using 1-*tert*-butyloxycarbonyl-2-methyl-2-imidazoline **3** (4.00 g, 21.70 mmol), *sec*-butyllithium (2×18.4 cm^3 of a 1.3 M in cyclohexane, 2×23.90 mmol), diethyl chlorophosphate (3.45 cm^3, 23.90 mmol) and 2-butenal (1.98 cm^3, 23.90 mmol) in THF (217 cm^3) and TMEDA (3 cm^3). The title compound was obtained as a white solid (1.75 g, 33%), identical to that reported above.

One-pot synthesis of 1-*tert*-butyloxycarbonyl-2-phenylethenyl-2-imidazoline 20c. Prepared by the general method, using 1-*tert*-butyloxycarbonyl-2-methyl-2-imidazoline **3** (2.00 g, 10.86 mmol), *sec* butyllithium (2×9.19 cm^3 of a 1.3 M solution in cyclohexane, 2×11.95 mmol), diethyl chlorophosphate (1.32 cm^3, 10.86 mmol) and benzaldehyde (1.21 cm^3, 11.95 mmol) in THF (108 cm^3) TMEDA (3 cm^3). The title compound was obtained as a white solid (1.20 g, 40%), identical to that reported above.

General method A for synthesis of 2-alkenyl-2-imidazolines 21

TFA was added to the 2-substituted 1-*tert*-butyloxycarbonyl-2-imidazoline **20** and the resulting solution was stirred at 20°C for 20–60 min. The TFA was removed under reduced pressure and crude product was purified by column chromatography on neutral alumina (activation grade 3) to give the imidazoline **21**.

2-(Pent-1-enyl)-2-imidazoline 21a. Prepared by general method A, using 1-*tert*-butyloxycarbonyl-2-(pent-1-enyl)-2-imidazoline **20a** (0.20 g, 0.84 mmol) and TFA (1 cm^3). The *title compound* was obtained after column chromatography (0:100→2:98 v/v isopropylamine:chloroform) as a white gum (0.095 g, 82%) (Found: M^+ 138.1157. $C_8H_{14}N_2$ requires: *M* 138.1157); ν_{max}(KBr)/cm^{-1} 3197, 2956, 2932, 2871, 1699, 1603, 1580, 1500, 1470, 1278, 973; δ_H (400 MHz) 0.85 (3H, t, *J*=7.2 Hz, C*H*$_3$CH$_2$), 1.37–1.43 (2H, m, CH$_3$C*H*$_2$), 2.07–2.13 (2H, dt, *J*=7.2 and 7.6 Hz, C*H*$_2$CH=CH), 3.60 (4H, s, NCH$_2$CH$_2$N), 5.95–6.00 (1H, d, *J*=16.1 Hz, CH$_2$CH=C*H*), 6.17–6.24 (1H, m, CH$_2$C*H*=CH); δ_C (100 MHz) 13.6 (CH$_3$), 21.7 and 34.6 (CH$_2$), 50.0 (NCH$_2$), 120.9 and 139.9 (CH=CH), 164.2 (NCN); *m*/*z* 138 (M^+, 61%), 123 (31), 109 (100), 94 (37), 81 (96), 67 (26), 56 (34), 41(48).

2-(Penta-1,3-dienyl)-2-imidazoline 21b. Prepared by general method A, using 1-*tert*-butyloxycarbonyl-2-(penta-1,3-dienyl)-2-imidazoline **20b** (0.54 g, 2.28 mmol) and TFA (1 cm^3). The *title compound* was obtained after column chromatography (0:100→2:98 v/v isopropylamine:ethyl acetate) as a white solid (0.20 g, 64%), mp 112–114°C (Found: M^+ 136.1000. $C_8H_{12}N_2$ requires: *M* 136.1000); ν_{max}(KBr)/cm^{-1} 3178, 2936, 2870, 1651, 1630, 1505, 1475, 1276, 988; δ_H (400 MHz) 1.83 (3H, d, *J*=6.8 Hz, C*H*$_3$CH), 3.68 (4H, s, NCH$_2$CH$_2$N), 4.40 (1H, br s, NH), 5.95–6.00 (1H, m, CH$_3$C*H*), 6.02–6.06 (1H, d, *J*=15.6 Hz, CH$_3$CH=CHCH=C*H*), 6.14–6.20 (1H, dd, *J*=13.0 and 13.2 Hz, CH$_3$CH=C*H*CH=CH), 6.72–6.68 (1H, dd, *J*=13.2 and 15.6 Hz, CH$_3$CH=CHC*H*=CH); δ_C (100 MHz) 18.5 (CH$_3$), 49.6 (NCH$_2$), 118.4, 130.5, 135.8 and 138.0 (CH), 164.3 (NCN); *m*/*z* 136 (M^+, 100%), 135 (64), 121 (49), 106 (66), 92 (26), 79 (38), 66 (22), 41 (18), 18 (16).

2-(2-Phenylethenyl)-2-imidazoline 21c. Prepared by general method A, using 1-*tert*-butyloxycarbonyl-2-(2-phenylethenyl)-2-imidazoline **20c** (0.17 g, 0.62 mmol) and TFA (2 cm^3). The *title compound* was obtained after column chromatography (0:100→2:98 v/v isopropylamine:chloroform) as a white solid (0.098 g, 91%), mp 154–156°C (Found: M^+ 172.1000. $C_{11}H_{12}N_2$ requires: *M* 172.1000); ν_{max}(KBr)/cm^{-1} 3171, 2926, 2867, 1651, 1597, 1581, 1501, 1292, 982, 760; δ_H (400 MHz) 3.70 (4H, s, NCH$_2$CH$_2$N), 4.32 (1H, br s, NH), 6.68 and 7.05 (each 1H, d, *J*=16.6 Hz, CH=CH), 7.30 (3H, m, Ar-H), 7.46 (2H, m, Ar-H); δ_C (100 MHz) 50.0 (NCH$_2$), 118.3 (CH), 127.2, 128.8, 128.9 and 135.4 (Ar-C), 136.7 (CH), 164.1 (NCN); *m*/*z* 172 (M^+, 65%), 171 (79), 143 (23), 128 (13), 115 (100), 103 (8), 77 (17), 57 (36).

1-*tert*-Butyloxycarbonyl-2-phenylthiomethyl-2-imidazoline 24 and 1-*tert*-butyloxycarbonyl-2,2-bis(phenylthio)-methyl-2-imidazoline 22. *sec*-Butyllithium (4.97 cm^3 of a 1.2 M solution in cyclohexane, 5.97 mmol) was injected into 1-*tert*-butyloxycarbonyl-2-methyl-2-imidazoline 3 (1.00 g, 5.43 mmol) in dry THF (54 cm^3) and TMEDA (2 cm^3) stirred at −78°C under nitrogen. The bright yellow solution produced was stirred at −78°C for 20 min, when diphenyl disulphide (1.30 g, 5.97 mmol) in THF (20 cm^3) was added via cannula at −78°C under nitrogen. The reaction mixture was allowed to warm to 20°C overnight. The reaction was quenched with water (100 cm^3), the organic layer was extracted with diethyl ether (3×100 cm^3) and the combined organic extracts were washed successively with saturated aq. $NaHCO_3$ (100 cm^3), water (50 cm^3) and brine (50 cm^3), dried and concentrated. The crude product was purified by column chromatography on silica gel

(1:9→2:3 v/v ethyl acetate:hexane) to give the *monosulphenated 2-imidazoline* **24** as a white solid (0.60 g, 38%), mp 77–79°C (Found: C, 61.55; H, 6.98; N, 9.50%; M^+ 292.1245. $C_{15}H_{20}N_2O_2S$ requires: C, 61.62; H, 6.89; N, 9.58%; *M* 292.1245); ν_{max}(KBr)/cm^{-1} 2974, 1703, 1635, 1483, 1379, 1142, 737; δ_H (400 MHz) 1.46 (9H, s, [C(CH$_3$)$_3$], 3.70 (4H, s, NCH$_2$CH$_2$N), 4.07 (2H, s, PhSC*H*$_2$), 7.22–7.35 (3H, m, Ar-H), 7.38–7.42 (2H, m, Ar-H); δ_C (100 MHz) 28.1 [C(*C*H$_3$)$_3$], 34.0 (PhS*C*H$_2$), 46.8 and 52.2 (NCH$_2$), 82.2 [*C*(CH$_3$)$_3$], 126.4, 128.9, 129.8 and 136.0 (Ar-C), 150.6 (CO), 157.7 (NCN); *m/z* 292 (M^+, 8%), 236 (41), 219 (5), 203 (14), 191 (13), 159 (22), 123 (12), 109 (10), 57 (100); and the *disulphenated 2-imidazoline* **22** as a white solid (0.65 g, 28%), mp 91–93°C (Found: C, 62.93; H, 6.13; N, 7.03%; M^+ 400.1279. $C_{15}H_{20}N_2O_2S$ requires: C, 62.97; H, 6.04; N, 6.99%; *M* 400.1279); ν_{max}(KBr)/cm^{-1} 2977, 1698, 1634, 1482, 1364, 1133, 1006, 739; δ_H (400 MHz) 1.52 [9H, s, C(CH$_3$)$_3$], 3.66–3.68 and 3.74–3.77 (each 2H, t, *J*=8.0 Hz, NCH$_2$CH$_2$N), 6.20 (1H, br s, CH), 7.31–7.35 (6H, m, Ar-H), 7.48–7.51 (4H, m, Ar-H); δ_C (100 MHz) 28.7 [C(*C*H$_3$)$_3$], 47.5 and 52.4 (NCH$_2$), 54.5 (CH), 82.7 [*C*(CH$_3$)$_3$], 128.6, 129.2, 132.7 and 134.4 (Ar-C), 150.7 (CO), 157.8 (NCN); *m/z* 400 (M^+, 2%), 291 (19), 235 (100), 191 (38), 139 (43), 121 (27), 110 (21), 97 (80), 77 (18), 70 (23), 57 (85).

2-Phenylthiomethyl-2-imidazoline 25. TFA (2 cm^3) was added to 1-*tert*-butyloxycarbonyl-2-phenylthiomethyl-2-imidazoline **24** (0.30 g, 1.02 mmol) and the solution was stirred at 20°C for 1 h. The TFA was removed under reduced pressure and the imidazoline salt was dissolved in chloroform (10 cm^3). The solution was then washed with aq. NaOH (10% w/v; 10 cm^3) and the organic layer was dried and concentrated. The crude product was then purified by column chromatography on alumina (grade 3) (0:100→1:99 v/v isopropylamine:chloroform) to give the *title compound* as a white solid (0.16 g, 81%), mp 83–85°C (Found: C, 62.38; H, 6.37; N, 14.51%; M^+ 192.0721. $C_{10}H_{12}N_2S$ requires: C, 62.47; H, 6.29; N, 14.56%; *M* 192.0721); ν_{max}(KBr)/cm^{-1} 3207, 3057, 2928, 1613, 1482, 1464, 1448, 1439, 1292, 1278, 1094, 980, 734; δ_H (400 MHz) 3.57 (4H, s, NCH$_2$CH$_2$N), 3.75 (2H, s, PhSC*H*$_2$), 4.58 (1H, br s, NH), 7.22–7.35 (3H, m, Ar-H), 7.42–7.45 (2H, m, Ar-H); δ_C (100 MHz) 31.9 (PhS*C*H$_2$), 50.2 (NCH$_2$), 126.5, 128.8, 129.3 and 135.0 (Ar-C), 164.3 (NCN); *m/z* 192 (M^+, 100%), 177 (5), 159 (55), 123 (9), 109 (39), 81 (50), 65 (25), 54 (74).

1-*tert*-Butyloxycarbonyl-2-phenylselenomethyl-2-imidazoline 26 and 1-*tert*-butyloxycarbonyl-2,2-bis(phenylseleneno)methyl-2-imidazoline 23. *sec*-Butyllithium (12.32 cm^3 of a 1.3 M solution in cyclohexane, 16.02 mmol) was injected into 1-*tert*-butyloxycarbonyl-2-methyl-2-imidazoline 3 (2.95 g, 16.02 mmol) in dry THF (100 cm^3) and TMEDA (0.5 cm^3) stirred at −78°C under nitrogen. The bright yellow solution produced was stirred at −78°C for 20 min, when diphenyl diselenide (5.00 g, 16.02 mmol) in THF (60 cm^3) was added via cannula. The reaction mixture was allowed to warm to 20°C overnight. The reaction was quenched with water (100 cm^3) and the organic layer was extracted with diethyl ether (3×100 cm^3) and the combined organic extracts were washed successively with saturated aq. NaHCO$_3$ (100 cm^3), water (50 cm^3) and brine (50 cm^3), dried and concentrated. The crude product was purified by column chromatography on silica gel (1:9→2:3 v/v ethyl acetate:hexane) to give the *monoselenenated 2-imidazoline* 26 as a white solid (2.86 g, 52%), mp 76–78°C (Found: C, 53.13; H, 6.03; N, 8.29%; M^+ 340.0689. $C_{15}H_{20}N_2O_2Se$ requires: C, 53.10; H, 5.94; N, 8.26%; *M* 340.0689); ν_{max}(KBr)/cm^{-1} 2974, 1702, 1636, 1480, 1380, 1141, 732; δ_H (400 MHz) 1.55 [9H, s, C(CH$_3$)$_3$], 3.76 (4H, s, NCH$_2$CH$_2$N), 4.05 (2H, s, PhSeC*H*$_2$), 7.25 (3H, m, Ar-H), 7.60 (2H, m, Ar-H); δ_C (100 MHz) 26.2 (PhSe*C*H$_2$), 28.5 [C(*C*H$_3$)$_3$], 46.6 and 52.2 (NCH$_2$), 82.2 [*C*(CH$_3$)$_3$], 127.5, 128.7, 130.6 and 133.3 (Ar-C), 150.7 (CO), 159.1 (NCN); *m/z* 340 (M^+, 1.5%), 282 (12), 215 (17), 203 (11), 159 (45), 127 (7), 91 (8), 57 (100); and the *diselenenated 2-imidazoline* 23 as a yellow oil (0.63 g, 8%) (Found: C, 51.58; H, 4.85; N, 5.59%; M^+ 496.0163. $C_{21}H_{24}N_2O_2Se_2$ requires: C, 51.02; H, 4.89; N, 5.67%; *M* 496.0168); ν_{max}(film)/cm^{-1} 2977, 2930, 1708, 1628, 1477, 1371, 1141, 1002; δ_H (300 MHz) 1.47 [9H, s, C(CH$_3$)$_3$], 3.63 and 3.68 (each 2H, t, *J*=7.0 Hz, NCH$_2$CH$_2$N), 6.14 (1H, br s, CH), 7.25–7.29 (6H, m, Ar-H), 7.59–7.71 (4H, m, Ar-H); δ_C (75 MHz) 28.2 [C(*C*H$_3$)$_3$], 37.5 (CH), 47.3 and 51.9 (NCH$_2$), 82.1 [*C*(CH$_3$)$_3$], 128.7, 129.1, 135.1 and 131.5 (Ar-C), 150.4 (CO), 159.1 (NCN); *m/z* 494 (M^+, 2%), 439 (1), 397 (1), 395 (1), 339 (2), 314 (12) 283 (11), 234 (7), 157 (100), 130 (8), 117 (21), 97 (18), 77 (100).

1-*tert*-Butyloxycarbonyl-2-(1-phenylseleneno-2-phenylethyl)-2-imidazoline 27a. *sec*-Butyllithium (0.62 cm^3 of a 1.2 M solution in cyclohexane, 0.74 mmol) was injected into 1-*tert*-butyloxycarbonyl-2-phenylselenenomethyl-2-imidazoline **26** (0.21 g, 0.62 mmol) in dry THF (7 cm^3) and TMEDA (0.5 cm^3) stirred at −78°C under nitrogen. The brown solution produced was stirred for 20 min at −78°C, when benzyl bromide (0.09 cm^3, 0.74 mmol) was injected to the reaction mixture. The reaction mixture was allowed to warm to 20°C overnight. The reaction was quenched with water (100 cm^3) and the organic layer was extracted with diethyl ether (3×100 cm^3) and the combined organic extracts were washed successively with saturated aq. NaHCO$_3$ (100 cm^3), water (100 cm^3) and brine (100 cm^3), dried and concentrated. The crude product was purified by column chromatography on silica gel (1:9→2:3 v/v ethyl acetate:hexane) to give the *title compound* as a yellow oil (0.21 g, 79%) (Found: C, 60.66; H, 6.27; N, 6.33%; M^+ 430.1159. $C_{22}H_{26}N_2O_2Se{\cdot}0.2H_2O$ requires: C, 60.86; H, 6.08; N, 6.45%; *M* 430.1159); ν_{max}(film)/cm^{-1} 2977, 1713, 1630, 1370, 1144, 999, 766, 696; δ_H (400 MHz) 1.48 [9H, s, C(CH$_3$)$_3$], 3.10–3.18 (1H, m, C*H*HPh), 3.38–3.48 (1H, dd, *J*=6.8 and 13.8 Hz, CH*H*Ph), 3.60–3.77 (4H, m, NCH$_2$CH$_2$N), 5.15 (1H, br s, CH), 7.15–7.40 (8H, m, Ar-H), 7.53 (2H, m, Ar-H); δ_C (100 MHz) 28.2 [C(*C*H$_3$)$_3$], 39.0 (*C*H$_2$Ph), 39.2 (CH), 46.8 and 51.8 (NCH$_2$), 81.8 [*C*(CH$_3$)$_3$], 126.3, 128.1, 128.4, 128.6, 128.8, 136.5, 137.1 and 139.4 (Ar-C), 150.5 (CO), 160.8 (NCN); *m/z* 430 (M^+, 1%), 374 (5), 324 (5), 293 (3), 217 (32), 173 (24), 141 (19), 123 (31), 77 (18), 57 (100).

1-*tert*-Butyloxycarbonyl-2-(1-phenylselenenobutyl)-2-imidazoline 27b. Prepared by the general method, using *sec*-butyllithium (5.38 cm^3 of a 1.3 M solution in cyclohexane, 7.00 mmol), 1-*tert*-butyloxycarbonyl-2-

phenylselenenomethyl-2-imidazoline **26** (2.00 g, 5.89 mmol) and 1-iodopropane (0.70 cm^3, 7.00 mmol) to give the *title compound* as a yellow oil (1.80 g, 80%) (Found: C, 56.98; H, 7.23; N, 7.48%; M^+ 382.1158. $C_{18}H_{26}N_2O_2Se$ requires: C, 56.69; H, 6.87; N, 7.34; *M* 382.1158); ν_{max}-(film)/cm^{-1} 2960, 1713, 1613, 1368, 1146; δ_H (400 MHz) 0.82 (3H, t, *J*=7.2 Hz, CH_3), 1.45 (2H, m, CH_3CH_2), 1.52 [9H, s, $C(CH_3)_3$], 1.68–1.75 and 1.83–1.91 (each 1H, m, CH_2CH), 3.57–3.80 (4H, m, NCH_2CH_2N), 4.71 (1H, br s, CH), 7.25 (3H, m, Ar-H), 7.53 (2H, m, Ar-H); δ_C (100 MHz) 13.6 (CH_3), 21.0 (CH_2), 28.2 [$C(CH_3)_3$], 33.6 (CH_2), 38.8 (CH), 46.8 and 51.8 (NCH_2), 81.8 [$C(CH_3)_3$], 128.4, 128.5, 128.8 and 136.8 (Ar-C), 150.68 (CO), 161.3 (NCN); *m/z* 382 (M^+, 7%), 326 (33), 284 (15), 245 (32), 201 (27), 169 (30), 141 (14), 125 (58), 123 (13), 78 (9), 57 (100).

1-*tert*-Butyloxycarbonyl-2-(1-phenylselenenobut-3-enyl)-2-imidazoline 27c. Prepared by the general method, using *sec*-butyllithium (3.09 cm^3 of a 1.1 M solution in cyclohexane, 3.4 mmol), 1-*tert*-butyloxycarbonyl-2-phenylselenenomethyl-2-imidazoline **26** (1.05 g, 3.09 mmol) and 3-bromopropene (0.29 cm^3, 3.40 mmol) to give the *title compound* as a yellow oil (1.06 g, 90%) (Found: M^+ 380.1002. $C_{18}H_{24}N_2O_2Se$ requires: *M* 380.1002); ν_{max}(film)/cm^{-1} 2977, 1714, 1631, 1478, 1147; δ_H (400 MHz) 1.52 [9H, s, $C(CH_3)_3$], 2.45–2.52 and 2.67–2.74 (each 1H, m, $CH_2CH{=}CH_2$), 3.60–3.80 (4H, m, NCH_2CH_2N), 4.75 (1H, br s, PhSeC*H*), 5.00–5.09 (2H, m, $CH{=}CH_2$), 5.80–5.90 (1H, m, $CH{=}CH_2$), 7.25 (3H, m, Ar-H), 7.55 (2H, m, Ar-H); δ_C (100 MHz) 28.2 [$C(CH_3)_3$], 37.7 (CH_2), 38.3 (PhSe*C*H), 46.9 and 51.8 (NCH_2), 81.8 [$C(CH_3)_3$], 116.6 ($CH{=}CH_2$), 128.2, 128.4 and 128.5 (Ar-C), 135.8 ($CH{=}CH_2$), 136.8 (Ar-C), 150.6 (CO), 160.6 (NCN); *m/z* 380 (M^+, 1%), 243 (10), 224 (6), 169 (49), 141 (16), 123 (56), 78 (8), 70 (10), 57 (100).

2-(1-Phenylseleneno-2-phenylethyl)-2-imidazoline 28a: TFA (4 cm^3) was added to 1-*tert*-butyloxycarbonyl-2-(1-phenylseleneno-2-phenylethyl)-2-imidazoline **27a** (1.25 g, 2.91 mmol) and the solution was stirred at 20°C for 1 h. The TFA was removed under reduced pressure and the imidazoline salt was dissolved in dichloromethane (20 cm^3). The solution was then washed with aq. NaOH (10% w/v; 30 cm^3) and the organic layer was dried and concentrated. The crude product was purified by column chromatography on silica gel (ethyl acetate) to give the *title compound* as a white solid (0.68 g, 71 %), mp 103-105°C (Found: C, 61.27; H, 5.53; N, 8.91%; M^+ 330.0634. $C_{17}H_{18}N_2Se{\cdot}0.2H_2O$ requires C, 61.14; H, 5.51; N, 8.39%; *M* 330.0634); ν_{max}(film)/cm^{-1} 3061, 2926, 1601, 1498, 1270, 740, 693; δ_H (400 MHz) 3.00–3.10 and 3.26–3.35 (each 1H, dd, *J*=6.8 and 13.7 Hz, CH_2Ph), 3.42 (4H, m, NCH_2CH_2N), 4.03 (1H, t, *J*=6.8 Hz, PhSeC*H*), 7.10–7.28 (8H, m, Ar-H), 7.48 (2H, m, Ar-H); δ_C (100 MHz) 39.3 (CH_2), 42.1 (*C*H), 50.1 (NCH_2), 126.7, 128.2, 128.4, 128.9, 129.0, 134.4, 134.9 and 138.7 (Ar-C), 167.4 (NCN); *m/z* 330 (M^+, 6%), 249 (62), 239 (26), 173 (100), 158 (12), 132 (14), 115 (15), 105 (26), 91 (22), 77 (22).

2-(1-Phenylselenenobutyl)-2-imidazoline 28b. Prepared by the general method, using TFA (3 cm^3) and 1-*tert*-butyloxycarbonyl-2-(1-phenylselenenobutyl)-2-imidazoline **27b** (1.50 g, 3.93 mmol) to give the *title compound* as a yellow solid (1.00 g, 91%), mp 67–69°C (Found: C, 55.55; H, 6.56; N, 9.96%; M^+ 282.0635. $C_{13}H_{18}N_2Se$ requires: C, 55.52; H, 6.45; N, 9.96%; *M* 282.0635); ν_{max}(KBr)/cm^{-1} 3176, 2955, 1605, 1495, 1466, 1276, 978, 746, 694; δ_H (400 MHz) 0.87 (3H, t, *J*=7.4 Hz, CH_3), 1.34–1.52 (2H, m, CH_3CH_2), 1.70–1.80 and 1.86–1.96 (each 1H, m, CH_2CH), 3.45 (4H, s, NCH_2CH_2N), 3.85 (1H, t, *J*=8.8 Hz, CH_2CH), 4.40 (1H, br s, NH), 7.28 (3H, m, Ar-H), 7.52 (2H, m, Ar-H); δ_C (100 MHz) 13.5 (CH_3), 21.4 and 35.1 (CH_2), 41.0 (CH), 50.1 (NCH_2), 127.9, 128.5, 128.9 and 134.5 (Ar-C), 167.8 (NCN); *m/z* 282 (M^+, 3.5%), 253 (2), 240 (2), 201 (11), 160 (7), 125 (5), 97 (7), 84 (9).

2-(1-Phenylselenenobut-3-enyl)-2-imidazoline 28c. Prepared by the general method, using TFA (1 cm^3) and 1-*tert*-butyloxycarbonyl-2-(1-phenylselenenobut-3-enyl)-2-imidazoline **27c** (0.29 g, 0.76 mmol). Column chromatography on silica gel (0:100→4:96 v/v isopropylamine:ethyl acetate) gave the *title compound* as a yellow oil (0.17 g, 80%) which solidified upon standing, mp 41–43°C (Found: C, 55.00; H, 5.72; N, 9.40%; M^+ 280.0478. $C_{13}H_{16}N_2Se{\cdot}0.2H_2O$ requires: C, 54.99; H, 5.78; N; 9.87%; *M* 280.0478); ν_{max}(film)/cm^{-1} 3175, 3073, 2932, 1607, 1477, 1438, 1286, 919, 740; δ_H (400 MHz) 2.55–2.60 and 2.70–2.80 (each 1H, m, $CH_2CH{=}CH_2$), 3.50 (4H, s, NCH_2CH_2N), 3.90 (1H, t, *J*=8.8 Hz, PhSeC*H*), 4.75 (1H, br s, NH), 5.10–5.20 (2H, m, $CH{=}CH_2$), 5.80–5.90 (1H, m, $CH{=}CH_2$), 7.26–7.32 (3H, m, Ar-H), 7.57 (2H, m, Ar-H); δ_C (100 MHz), 37.2 (CH_2), 40.2 (CH), 50.1 (NCH_2), 117.4 ($CH{=}CH_2$), 128.2, 129.1 and 134.9 (Ar-C), 135.2 ($CH{=}CH_2$), 137.5 (Ar-C), 167.4 (NCN); *m/z* 280 (M^+, 9%), 279, (17), 239 (13), 199 (61), 157 (12), 123 (100), 97 (14), 77 (19), 67 (16).

General method B for synthesis of 2-alkenyl-2-imidazolines 21

A solution of 3-chloroperbenzoic acid in dry dichloromethane was added via cannula to the 2-(1-seleneno)-2-imidazoline **28** in dry dichloromethane at 0°C under nitrogen. The resulting yellow solution was stirred at 0°C for 1 h and at room temperature for a further 2 h. The dichloromethane was removed under reduced pressure and the crude product was purified by column chromatography on neutral alumina (activation grade 3) to give the 2-alkenyl-2-imidazolines **21**.

2-(2-Phenylethenyl)-2-imidazoline 21c. Prepared by general method B, using 2-(1-phenylseleneno-2-phenylethyl)-2-imidazoline **28a** (0.30 g, 0.91 mmol) and 3-chloroperbenzoic acid (0.17 g, 1.00 mmol). Chromatography on alumina (0:100→3:97 v/v isopropylamine:ethyl acetate) afforded the title compound as a white solid (0.16 g, 90%), m.p 154–156°C, identical to that reported above, method A.

2-(But-1-enyl)-2-imidazoline 21d. Prepared by general method B, using 2-(1-phenylselenenobutyl)-2-imidazoline **28b** (0.30 g, 1.06 mmol) and 3-chloroperbenzoic acid (0.20 g, 1.17 mmol). Chromatography on alumina (0:100→5:95 v/v isopropylamine:ethyl acetate) gave the *title compound* as a thick colourless oil (0.12 g, 92%) (Found: M^+ 124.1000. $C_7H_{12}N_2$ requires: *M* 124.1000);

ν_{max}(film)/cm^{-1} 3197, 2965, 2864, 2873, 1663, 1602, 1500, 1461, 1274, 986; δ_H (400 MHz) 1.00 (3H, t, J= 7.2 Hz, CH_3), 2.10–2.20 (2H, m, CH_2), 3.60 (4H, s, NCH_2CH_2N), 3.95 (1H, br s, NH), 5.98 (1H, d, J= 16.6 Hz, C*H*=CHCH$_2$), 6.23–6.32 (1H, m, CH=C*H*CH$_2$); δ_C (100 MHz) 12.6 (CH_3), 25.6 (CH_2), 51.6 (NCH_2), 119.9 (*C*H=CHCH$_2$), 141.3 (CH=*C*HCH$_2$), 164.0 (NCN); *m/z* 124 (M^+, 84%), 123 (55), 109 (56), 94 (88), 80 (29), 67 (100).

2-(Buta-1,3-dienyl)-2-imidazoline 21e. Prepared by general method B, using 2-(1-phenylseleneno-but-3-enyl)-2-imidazoline **28c** (0.30 g, 1.07 mmol) and 3-chloroperbenzoic acid (0.22 g, 1.29 mmol). Chromatography on alumina (0:100→2:98 v/v isopropylamine:ethyl acetate) gave the *title compound* as a white solid (0.12 g, 92%), mp 220°C (decomp.) (Found: M^+ 122.0844. $C_7H_{10}N_2$ requires M 122.0844); ν_{max}(KBr)/cm^{-1} 3176, 2936, 2864, 1643, 1614, 1566, 1497, 1276, 1000, 982; δ_H (400 MHz) 3.70 (4H, s, NCH_2CH_2N), 4.40 (1H, br s, NH), 5.35–5.40 (1H, d, J=10.0 Hz, CH=C*H*H), 5.50 (1H, d, J=16.6 Hz, CH=CH*H*), 6.20–6.26 (1H, d, J=16.6 Hz, C*H*=CHCH=CH$_2$), 6.43–6.55 (1H, m, C*H*=CH$_2$), 6.71–6.80 (1H, dd, J=10.0 and 16.2 Hz, CH=C*H*CH=CH$_2$); δ_C (100 MHz) 50.4 (NCH_2), 121.9 (CH=*C*H$_2$), 122.4, 135.7 and 137.0 (CH), 163.8 (NCN); *m/z* 122 (M^+, 100%), 121 (52), 106 (16), 93 (75), 66 (57), 53 (23).

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