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PAPER

Cycloaddition of homochiral dihydroimidazoles: A 1,3-dipolar cycloaddition route to optically active pyrrolo[1,2-*a*]imidazoles†

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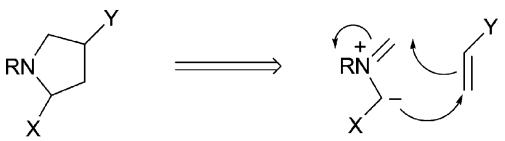
N-Alkylation of optically active 1-benzyl-4-phenyl-4,5-dihydroimidazole with active alkyl halides and treatment of the so-formed 4,5-dihydroimidazolium ions with DBU in the presence of a range of electron-deficient alkene dipolarophiles, constitutes a 'one-pot' cascade terminating in a 1,3-dipolar cycloaddition reaction that affords optically active pyrrolo[1,2-*a*]imidazoles. Three bonds of the so-formed pyrrolidine moiety are constructed in this cascade. The cycloaddition follows an *endo* approach of dipole and dipolarophile with *anti* geometry of the dipole and facial selectivity derived from the phenyl substituent. Inter- and intramolecular cycloaddition modes are observed.

Introduction

The five-membered saturated nitrogen heterocyclic pyrrolidine ring system is a common sub-unit in many natural products and synthetic molecules of biological significance.[1] The use of azomethine ylides **1** as 1,3-dipoles in cycloaddition reactions with alkenes is a valuable method for the assembly of pyrrolidines (Scheme 1).[2] These pericyclic reactions have well-defined transition states, ideally suited to the asymmetric synthesis of such molecules. Simple naturally occurring pyrrolidines with interesting biological properties include the marine metabolites kainic acid **2** and acromelic acid **3**,[3] and pyrrolidine dicarboxylic acid **4**, a potent inhibitor of glutamate transport.[4]



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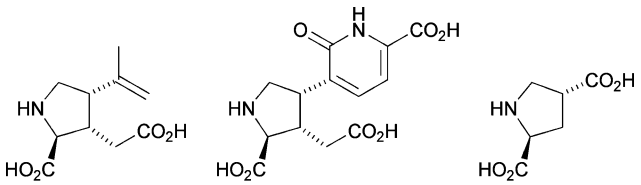
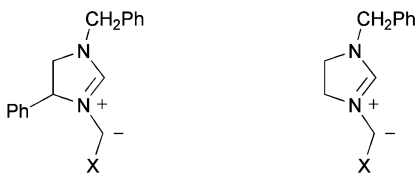
Scheme 1 1,3-Dipolar cycloaddition of azomethine ylides to generate pyrrolidines (X, Y usually electron-withdrawing).





Our approach to achieving stereocontrol in such dipolar cycloadditions is to attach a chiral auxiliary to nitrogen, but to restrict rotational freedom about the N-to-auxiliary bond by constraining the auxiliary in a ring, affording optically active 4,5-dihydroimidazolium (imidazolinium) ylides **5**. The facial selectivity of the ylides in cycloadditions is thus fully predictable; the phenyl substituent facilitates ultimate removal of the templating atoms. The ylides are generated *in situ* from dihydroimidazoles and a suitable alkylating agent, and undergo enantioselective cycloaddition to afford optically active pyrrolo[1,2-*a*]imidazoles as potential precursors to the corresponding pyrrolidines.[5,6] In these sequences three of the bonds in the newly-formed pyrrolidine ring are made during the alkylation-deprotonation-cycloaddition cascade. In a previous publication we have detailed the diasteroselective cycloadditions of achiral dihydroimidazolium ylides **6**;[7] we now report in full the results of our investigations in this area using the optically active ylides **5**. Related studies of

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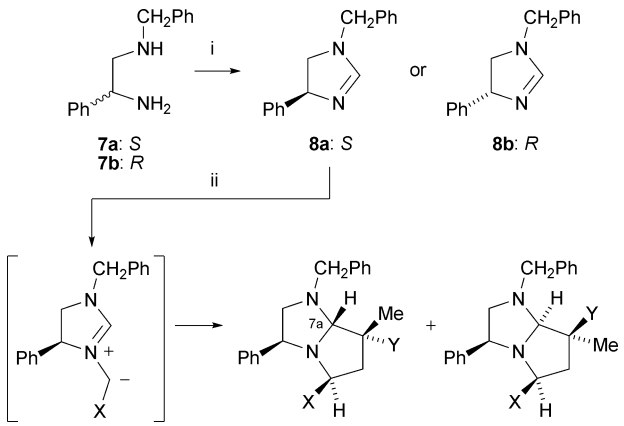
asymmetric induction in azomethine ylide cycloaddition by an auxiliary rotationally constrained at nitrogen have been disclosed by others.[8]

Results and Discussion

The precursors to the ylides **5** are the dihydroimidazoles **8a,b**. These were prepared from the enantiomerically pure diamines **7a,b** (themselves prepared from commercially available enantiomers of phenylglycine as we have reported earlier[9]) by heating at reflux in triethyl orthoformate with catalytic *p*-toluenesulfonic acid. Initial attempts at quaternisation proved very slow, being incomplete after several days at 20 °C, or 23 h at reflux in THF, even with active halides such as methyl bromoacetate; addition of KI had no effect. This led to the development of a revised 'one-pot' procedure whereby the salt is consumed by deprotonation and cycloaddition as it is formed.[10] Thus, imidazolines **8a,b** were separately mixed with an alkylating agent and a dipolarophile (3 mol equiv.) in dry THF and heated to reflux, when 1 mol equiv. of 1,8-diazabicyclo[5.4.0]undec-8-ene (DBU) was added dropwise over 4 h followed by a further 2 h at reflux. Isolation then provided the hexahydropyrrolo[1,2-*a*]imidazole cycloadducts, forming *three* of the five bonds of the new pyrrolidine ring in one pot (Scheme 2).



Scheme 2 Preparation of pyrroloimidazoles **9** by dipolar cycloaddition of azomethine ylides derived from optically active dihydroimidazoles **8** Reagents: i, $(EtO)_3CH$, *p*-TsOH; ii, $BrCH_2X$, $CH_2{=}C(Me)Y$, THF reflux, then DBU.

A variety of alkylating agents and dipolarophiles were employed in these reactions. Thus, with methyl bromoacetate as alkylating agent, smooth reactions occurred with methyl 2-methylpropenoate as dipolarophile, affording cycloadducts **9a** (53%) and **9b** (55%) from **8a** and **8b**, respectively (Scheme 2; only 3*S*-series cycloadducts shown). Employing 2-methylpropenonitrile as dipolarophile gave cycloadducts **9c** (34%) and **9d** (56%). The absolute stereochemistry of the cycloadducts is as illustrated and was secured by ^{1}H NOE difference spectroscopy to determine relative stereochemistry, as exemplified in Fig. 1, combined with the fixed

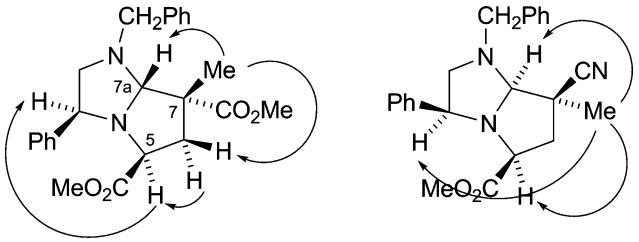


Fig. 1 n.O.e correlations to determine relative stereochemistry of cycloadducts **9a** and **9e**.

configuration of C-3 derived originally from phenylglycine. For example, for cycloadduct **9a**, NOE enhancements were observed between protons on the following carbon atoms: C-5→C-3, C-6(pro-*S*)→C-5, C-7(Me)→C-6(pro-*R*), C-7(Me)→C-7a. This stereochemical outcome of the cycloaddition is consistent with an *endo* approach of the dipole and dipolarophile, with the dipole having the *anti* geometry and facial selectivity provided by the 4-phenyl substituent in the dipole, as summarised in the transition state model illustrated in Fig. 2.[5] We did not generally observe any other cycloadduct diastereoisomers with ester-activated dipolarophiles, but with nitrile-based dipolarophiles a minor isomer corresponding to *exo* approach could sometimes be isolated. Thus, nitrile **9c** was isolated along with small amounts of **9e** (*endo* : *exo* 8 : 1), and nitrile **9d** with small amounts of **9f** (*endo* : *exo* 11 : 1). Interestingly, however, ^{1}H NOE difference spectroscopy (*e.g.* Fig. 1 for adduct **9e**) showed that the stereochemistry at C-7a in the *exo* adducts was opposite to what would be predicted for *exo* addition by our transition state model. It is likely that *exo* addition occurs in the expected fashion and is followed by an epimerisation at C-7a, since the alternative antarafacial addition across the dipole is energetically disfavoured.[11] A possible mechanism for this reversible epimerisation would involve protonation at N-1 of the predicted *exo*-adduct **10** followed by ring opening to produce an *N*-substituted pyrrolidinium species. Such species would be capable of ring closing from the opposite face to the ring opening and so provide the epimerised *exo*-adduct **9e** (Scheme 3).

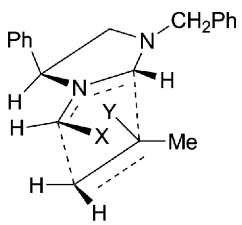
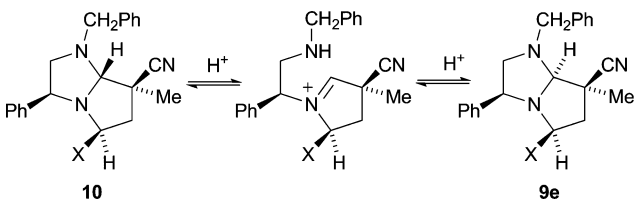


Fig. 2 Transition state model for cycloaddition to give **9a** (X = Y = CO_2Me).



Scheme 3 Mechanism proposed for epimerisation at C-7a of pyrroloimidazoles.

Using *t*-butyl bromoacetate as alkylating agent permitted smooth cycloaddition with a variety of dipolarophiles. With methyl 2-methylpropenoate adducts **9g** (from **8a**) and **9h** (from **8b**) were isolated as single stereoisomers. Once again the stereochemical outcome of the cycloaddition was in agreement with our transition state model. It proved possible to crystallise pyrroloimidazole **9g**, and a single crystal X-ray analysis (Fig. 3) confirmed the structure to be as shown, in agreement with our ^{1}H NOE studies. As in the previous examples, reaction with 2-methylpropenonitrile was slightly less stereoselective, affording adducts **9i** (from **8a**) and **9j** (from **8b**) along with a small amount of the product of *exo* addition: **9i** with **9k** (*endo* : *exo* 8 : 1); **9j** with **9l** (*endo* : *exo* 8 : 1).

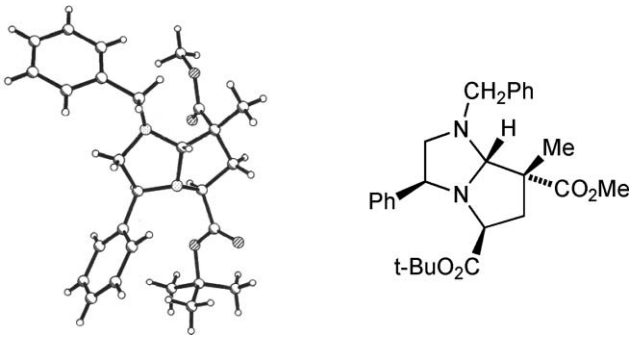
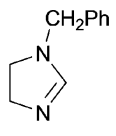


Fig. 3 X-Ray crystal structure of cycloadduct **9g**.

Seeking an approach to natural products that contain a 2,4-disubstituted pyrrolidine skeleton, we were interested in achieving cycloadditions with dipolarophiles lacking a substituent α to the activating group; in particular, we were concerned about the stereochemical integrity of the resulting C-7 substituent. Our work with the achiral imidazoline **11** had shown that cycloadducts such as **12** existed as an inseparable mixture of epimers at C-7, presumably *via* elimination (through ring-opening, *cf.* Scheme 3, and proton loss) and conjugate addition across C(7)–C(7a).[5] Gratifyingly, methyl and *t*-butyl propenoates with the appropriate dihydroimidazoles **8a** or **8b** and *t*-butyl bromoacetate as alkylating agent, gave single stereoisomers of bicycles **13a** (65%) and its enantiomer **13b** (63%), and **13c** (59%) and its enantiomer **13d** (49%) (Scheme 4). Once again we were able to support our ^{1}H NOE studies with a single crystal X-ray analysis of adduct **13a** (Fig. 4), which was in agreement with our transition state model. In the case of *t*-butyl propenoate, some of the *exo* isomer was also produced. Hence **13c** was isolated along with **13e** (*endo* : *exo* 20 : 1) and **13d** with **13f** (*endo* : *exo* 25 : 1). Once again, ^{1}H NOE studies showed that the *exo* adducts had the opposite stereochemistry at C-7a to that predicted by our transition state model.



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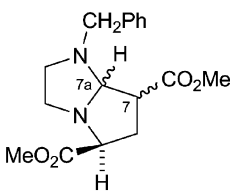

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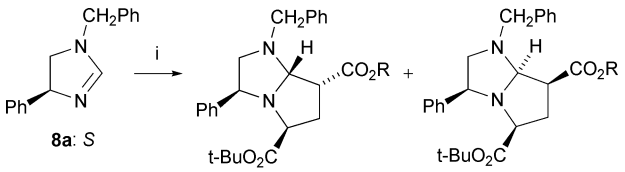
It was pleasing to find that these cycloadditions using *t*-butyl bromoacetate as alkylating agent were the most efficient to date. Using this alkylating agent it was possible to extend



R = Me **13a**
13b (from *R*-enantiomer **8b**)
R = t-Bu **13c** **13e**
13d (from *R*-enantiomer **8b**) **13f**

Scheme 4 Cycloaddition of azomethine ylides formed from dihydroimidazoles **8** using t-butyl bromoacetate as alkylating agent Reagents: i, $BrCH_2CO_2t$-Bu, $CH_2{=}CHCO_2R$, THF reflux, then DBU.

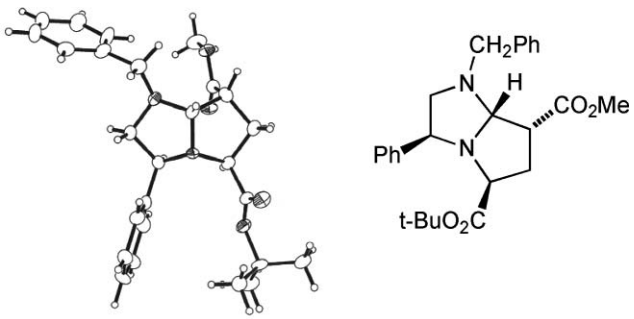
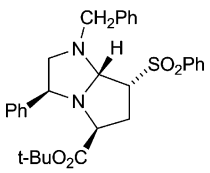


Fig. 4 X-Ray crystal structure of cycloadduct **13a**.

the range of dipolarophiles to those incorporating sulfone and ketone activating groups. Hence phenyl ethenyl sulfone gave **14** (33%)[12] and but-3-en-2-one afforded **15** (81%), both from (*S*)-dihydroimidazole **8a**. Employing secondary bromides as alkylating agents also afforded cycloadducts, although the yields were low. In cycloadditions with dihydroimidazole **8a** and methyl 2-methylpropenoate, ethyl 2-bromopropanoate afforded the adduct **16a** (29%) having quaternary centres at both C-5 and C-7, whilst *t*-butyl 2-bromopropanoate afforded adduct **16b** (23%). Both of these cycloadducts were formed as single stereoisomers, with the more bulky ester function of the dipole adopting an *anti* disposition and the dipolarophile approaching *endo* as in previous examples.



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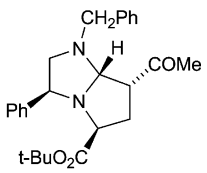

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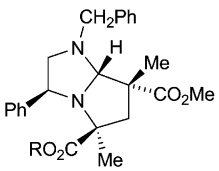
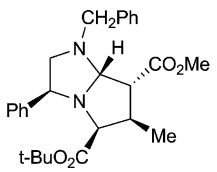


16a; R = Et
16b; R = t-Bu

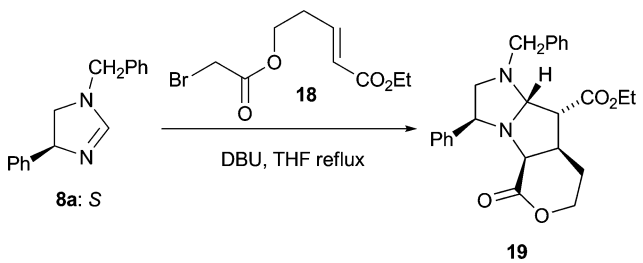


17a
17b (enantiomer of **17a**)

A number of key metabolites with interesting biological profiles, in particular neuroexcitatory properties, feature a 2,3,4-trisubstituted pyrrolidine ring.[3] Clearly to approach such systems we needed to achieve cycloaddition with 1,2-disubstituted alkene dipolarophiles, and we selected methyl (*E*)-but-2-enoate

for our initial experiments. Although this dipolarophile afforded encouraging yields of bicycles **17a** (46%) and **17b** (26%, not optimised) from **8a** and **8b**, respectively, we were unable to obtain cycloadducts with any of the other cyclic and acyclic 1,2-disubstituted dipolarophiles which were investigated. These included ethyl (*E*)-5-hydroxypent-2-enoate, ethyl (*E*)-5-(*t*-butyldimethylsilyloxy)pent-2-enoate, diethyl glutaconate, 2(5*H*)-furanone and 5,6-dihydro-2*H*-pyran-2-one.

Success using 1,2-disubstituted alkene dipolarophiles finally came with an intramolecular variant of the cycloaddition reaction.[13] Employing one equivalent of ethyl (*E*)-5-(bromoacetoxy)pent-2-enoate **18** whose convenient synthesis we have reported previously[13] and which contains, tethered, both an alkylating agent and a dipolarophile, led to the crystalline tricyclic cycloadduct **19** from dihydroimidazole **8a** (35%) as a single stereoisomer (Scheme 5); the enantiomer of **19** was also isolated (30% from **8b**) but not fully characterised.[14] The stereochemical outcome of this cycloaddition reaction was confirmed by an X-ray crystal structure analysis of **19** (Fig. 5). Once again the stereochemical result of the cycloaddition is fully consistent with our transition state model, furnishing a precursor to the desired 2,3,4-trisubstituted pyrrolidines with complete stereocontrol. Disappointingly the (*Z*)-bromoacetate failed to undergo the cycloaddition reaction, with a competing polymerisation processes appearing to dominate under the reaction conditions.



Scheme 5 Intramolecular cycloaddition of a dihydroimidazolium ylide.

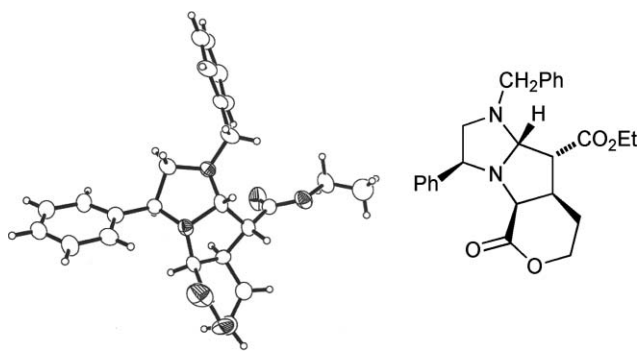


Fig. 5 X-Ray crystal structure of cycloadduct **19**.

We have thus shown that optically active dihydroimidazoles, *via* dihydroimidazolium ylides, are useful precursors to optically active pyrrolo[1,2-*a*]imidazoles though an alkylation-deprotonation-cycloaddition cascade. The cycloaddition gives predictable stereochemistry and can operate in inter- and intramolecular modes. The cycloadducts are potential precursors of enantiopure pyrrolidines, as we have shown in preliminary form and will report in detail.[15]

Experimental

Melting points were obtained on a Gallenkamp capillary or a Reichert hot stage and are uncorrected. IR spectra were recorded using Pye Unicam SP1000, Pye Unicam SP3-100 or Perkin-Elmer 1820X FT spectrometers. Mass spectra were recorded using AEI MS902 or VG 8080E spectrometers. ^{1}H NMR spectra were obtained using the following spectrometers: Perkin Elmer R32 or Jeol FX90Q at 90 MHz; Bruker WM200 at 200 MHz; Bruker WM250 at 250 MHz; Bruker AM400 or Jeol EX400 at 400 MHz. ^{13}C NMR spectra were recorded using the following instruments: Jeol FX90Q spectrometer at 22.8 MHz; Bruker WM200 at 50.3 MHz; Bruker WM250 at 62.9 MHz; Jeol EX280 at 68 MHz; Bruker AM400 or Jeol EX400 at 100.6 or 100.4 MHz, respectively. ^{1}H NMR spectra were determined in deuteriochloroform solution unless indicated, and chemical shifts are quoted in parts per million (ppm) from tetramethylsilane as internal standard; coupling constants are quoted in Hz. ^{13}C NMR spectra were determined in deuteriochloroform solution and chemical shifts quoted in ppm from tetramethylsilane as internal standard or from tetramethylsilane using $CDCl_3$ as internal standard. Column chromatography was carried out at medium pressure using Merck Kieselgel 60 (Art. 9385). Thin layer chromatography (TLC) was carried out on silica plates (Kieselgel 60, F254, Merck Art. 5554). Solvent extracts were dried over anhydrous magnesium sulfate or sodium sulfate for at least 10 min. Ether refers to diethyl ether and petroleum ether corresponds to the fraction with b.p. 40–60 °C. Tetrahydrofuran (THF) and ether were distilled from lithium aluminium hydride or potassium immediately prior to use. Other dry solvents were prepared as described in Perrin *et al.*[16]

(*S*)-1-Benzyl-4-phenyl-4,5-dihydroimidazole (8a). Prepared from (*S*)-1-phenyl-2-benzylaminoethylamine (**7a**, 7.0 g, 31 mmol) by the method described below for the preparation of (*R*)-enantiomer **8b** but using triethyl orthoformate (18.34 g, 0.124 mol), to afford the title compound as a colourless oil (1.55 g, 41%): b.p. 148 °C/0.1 mmHg; $[\alpha]_D^{23}$ −172.0 (*c* 1.03; EtOH); ν_{max}(film)/cm^{-1} 3060, 3027, 2925, 2846, 1672, 1600, 1581, 1493, 1453, 1169, 757; δ_H (400 MHz; $CDCl_3$) 2.96 (1H, t, J = 9.3, PhCHC*H*H), 3.57 (1H, dd, J = 9.3, 10.8, PhCHCH*H*), 4.20, 4.34 (each 1H, d, J = 14.8, PhCH_2), 5.13 (1H, m, PhC*H*CH$_2$), 7.09 (1H, d, J = 1.6, NCHN), 7.31 (10H, m, Ar–H); δ_C (100 MHz; $CDCl_3$) 51.7 (Ph*C*H$_2$), 55.4 (PhCH*C*H$_2$), 69.95 (Ph*C*HCH$_2$), 126.6, 127.0, 127.7, 127.75, 128.45, 128.7 (6 × Ar-*C*H), 136.7, 143.8 (2 × Ar-*C*) and 157.0 (NCHN); m/z 236 (M$^+$, 36%), 120 (53), 91(100). HRMS: (EI) M$^+$ 236.1334; $C_{16}H_{16}N_2$ requires M$^+$ 236.1313. Found: C, 81.4; H, 7.1; N, 11.8%; $C_{16}H_{16}N_2$ requires C, 81.3; H, 6.8; N, 11.85%.

(*R*)-1-Benzyl-4-phenyl-4,5-dihydroimidazole (8b). (*R*)-1-Phenyl-2-benzylaminoethylamine (**7b**, 6 g, 26.5 mmol) and *p*-toluenesulfonic acid (0.04 g, 0.22 mmol) in triethyl orthoformate (15.72 g, 0.106 mol) was heated at reflux for 20 h. After cooling to room temperature, aqueous sodium hydroxide (5% w/v, 5 cm^3) was added and the mixture was extracted with chloroform (3 × 25 mL). The combined organic phase was dried (Na_2SO_4) and evaporated under reduced pressure. The residue was purified by column chromatography, eluting with ethyl acetate : triethylamine (99 : 1 v/v) and fractionally distilled under vacuum to yield the title compound as a colourless oil (5.40 g, 86%): b.p.

146–148 °C/0.08 mmHg; $[\alpha]_D^{23}$ 168.9 (*c* 1.01; EtOH); ν_{max}(film)/cm^{-1} 3061, 3028, 2924, 2844, 1670, 1600, 1581, 1493, 1453, 1168, 757; δ_H (250 MHz; $CDCl_3$) 2.96 (1H, t, *J* = 9.2, PhCHC*H*H), 3.58 (1H, dd, *J* = 9.2, 10.7, PhCHCH*H*), 4.20, 4.36 (each 1H, d, *J* = 14.9, PhCH_2), 5.14 (1H, m, PhC*H*CH$_2$), 7.10 (1H, d, *J* = 1.8, NCHN), 7.28 (10H, m, Ar–H); δ_C (68 MHz; $CDCl_3$) 51.3 (Ph*C*H$_2$), 55.55 (PhCH*C*H$_2$), 69.7 (Ph*C*HCH$_2$) 126.3, 126.7, 127.4, 127.5, 128.2, 128.4 (6 × Ar-*C*H), 136.4, 143.5 (2 × Ar–C), 156.7 (NCHN); *m*/*z* 236 (M$^+$, 39%), 120 (52), 91(100). HRMS: (EI) M$^+$ 236.1294; $C_{16}H_{16}N_2$ requires M$^+$ 236.1313. Found: C, 81.3; H, 7.1; N, 11.9%; $C_{16}H_{16}N_2$ requires C, 81.3; H, 6.8; N, 11.85%.

(3*S*,5*S*,7*R*,7a*S*)-1-Benzyl-5,7-bis(methoxycarbonyl)-7-methyl-3-phenylhexahydropyrrolo[1,2-*a*]imidazole (9a). Methyl bromoacetate (1.29 g, 0.80 mL, 8.46 mmol) was added to (*S*)-1-benzyl-4-phenyl-4,5-dihydroimidazole (**8a**, 2.00 g, 8.46 mmol) in tetrahydrofuran (50 mL) stirred at reflux under nitrogen. Methyl 2-methylpropenoate (2.54 g, 2.72 mL, 25.39 mmol) was added in one portion followed by the dropwise addition over 4 h of DBU (1.29 g, 1.27 mL, 8.46 mmol). Stirring at reflux was continued for 2 h. The solvent was evaporated under reduced pressure and the residue partitioned between chloroform (3 × 40 mL) and water (40 mL). The combined organic phase was dried (Na_2SO_4), evaporated under reduced pressure and the residue purified by column chromatography eluting with hexane : ethyl acetate (4 : 1 v/v) to afford the title compound as a colourless oil (1.80 g, 52%): $[\alpha]_D^{22}$ –15.6 (*c* 1.04; EtOH); ν_{max}(film)/cm^{-1} 3062, 3028, 2949, 2804, 1731, 1454, 1265, 1205, 1132, 700; δ_H (250 MHz; $CDCl_3$) 1.50 (3H, s, CH_3), 2.20 (1H, dd, *J* = 9.9, 13.2, 6-C*H*H), 2.44 (1H, dd, *J* = 9.2, 10.0, PhCHC*H*H), 2.77 (1H, dd, *J* = 6.8, 13.2, 6-CH*H*), 3.21 (2H, m, PhC*H*H and PhCHCH*H*), 3.34, 3.81 (each 3H, s, OCH_3), 4.08 (1H, dd, *J* = 6.8, 9.9, 5-CH), 4.13 (2H, m, PhCH*H* and PhC*H*CH$_2$), 4.31 (1H, s, 7a-CH), 7.25 (10H, m, Ar–H); δ_C (100 MHz; $CDCl_3$) 23.0 (CH_3), 43.3 (6-CH_2), 51.5, 51.9 (2 × OCH_3), 53.3 (7-C), 58.4 (Ph*C*H$_2$), 64.7 (PhCH*C*H$_2$), 67.0 (5-CH), 69.4 (Ph*C*HCH$_2$), 96.2 (7a-CH), 127.0, 127.1, 127.2, 128.0, 128.2, 128.8 (6 × Ar-*C*H), 138.4, 141.3 (2 × Ar-*C*), 174.6, 175.3 (2 × CO); *m*/*z* 408 (M$^+$, 4%), 309 (29), 308 (100), 249 (36), 217 (13), 130 (12), 104 (34), 91 (87). HRMS: (EI) M$^+$ 408.2001; $C_{24}H_{28}N_2O_4$ requires M$^+$ 408.2049. Found: C, 70.85; H, 7.2; N, 6.9%; $C_{24}H_{28}N_2O_4$ requires C, 70.6; H, 6.9; N, 6.9%.

(3*R*,5*R*,7*S*,7a*R*)-1-Benzyl-5,7-bis(methoxycarbonyl)-7-methyl-3-phenylhexahydropyrrolo[1,2-*a*]imidazole (9b). Prepared from (*R*)-1-benzyl-4-phenyl-4,5-dihydroimidazole (**8b**, 2.00 g, 8.46 mmol) by the method described above for the preparation of **9a** but using methyl bromoacetate (1.29 g, 0.80 mL, 8.46 mmol), methyl 2-methylpropenoate (2.54 g, 2.72 mL, 25.39 mmol) and DBU (1.29 g, 1.27 mL, 8.46 mmol). Purification by column chromatography eluting with hexane : ethyl acetate (4 : 1 v/v) yielded the title compound as a colourless oil (1.90 g, 55%): $[\alpha]_D^{22}$ 16.8 (*c* 1.20; EtOH); ν_{max}(film)/cm^{-1} 3027, 2948, 2804, 1731, 1453, 1265, 1205, 1178, 701; δ_H (400 MHz; $CDCl_3$) 1.50 (3H, s, CH_3), 2.20 (1H, dd, *J* = 9.8, 13.3, 6-C*H*H), 2.44 (1H, t, *J* = 9.6, PhCHC*H*H), 2.77 (1H, dd, *J* = 7.0, 13.3, 6-CH*H*), 3.22 (2H, m, PhC*H*H and PhCHCH*H*), 3.34, 3.80 (each 3H, s, OCH_3), 4.06 (1H, dd, *J* = 7.0, 9.8, 5-CH), 4.12 (2H, m, PhCH*H* and PhC*H*CH$_2$), 4.31 (1H, s, 7a-CH), 7.24 (10H, m, Ar–H); δ_C (68 MHz; $CDCl_3$) 22.8 (CH3), 43.2 (6-CH_2), 51.3, 51.75 (2 × OCH_3), 53.1 (7-C), 58.2 (Ph*C*H$_2$), 64.5 (PhCH*C*H$_2$), 66.8 (5-CH), 69.2 (Ph*C*HCH$_2$), 96.0 (7a-CH), 126.8, 126.9, 127.0, 127.9, 128.1, 128.7 (6 × Ar-*C*H), 138.2 141.1 (2 × Ar–C), 174.45, 175.1 (2 × CO); *m*/*z* 408 (M$^+$, 2%), 309 (29), 308 (67), 249 (56), 217 (22), 130 (24), 113 (26), 104 (52), 91 (100). HRMS: (EI) M$^+$ 408.2002; $C_{24}H_{28}N_2O_4$ requires M$^+$ 408.2049. Found: C, 70.6; H, 7.2; N, 6.7%; $C_{24}H_{28}N_2O_4$ requires C, 70.6; H, 6.9; N, 6.9%.

(3*S*,5*S*,7*R*,7a*S*)-1-Benzyl-7-cyano-5-methoxycarbonyl-7-methyl-3-phenylhexahydropyrrolo[1,2-*a*]imidazole (9c). Prepared from (*S*)-1-benzyl-4-phenyl-4,5-dihydroimidazole (**8a**, 0.30 g, 1.27 mmol) by the method described above for the preparation of **9a** but using methyl bromoacetate (0.19 g, 0.12 mL, 1.27 mmol), 2-methylpropenonitrile (0.26 g, 0.32 mL, 3.81 mmol) and DBU (0.19 g, 0.19 mL, 1.27 mmol). Purification by column chromatography, eluting with hexane : ethyl acetate (3 : 1 v/v) yielded the *exo*-adduct (**9e**) as a colourless solid (18 mg, 4%): m.p. 103–105 °C; ν_{max}(film)/cm^{-1} 3030, 2951, 2815, 2235, 1747, 1455, 1437, 1206, 1181, 701; δ_H (250 MHz; $CDCl_3$) 1.51 (3H, s, CH_3), 2.42 (1H, dd, *J* 6.0, 12.8, 6-C*H*H), 2.63 (1H, dd, *J* = 9.2, 10.1, PhCHC*H*H), 2.81 (1H, dd, *J* = 10.4, 12.8, 6-CH*H*), 3.35 (3H, s, OCH_3), 3.38 (1H, m, PhCHCH*H*), 3.46 (1H, d, *J* = 13.1, PhC*H*H), 3.56 (1H, dd, *J* = 6.0, 10.4, 5-CH), 4.01 (1H, dd, *J* = 5.5, 10.1, PhC*H*CH$_2$), 4.08 (1H, d, *J* = 13.1, PhCH*H*), 4.75 (1H, s, 7a-CH), 7.26 (10H, m, Ar–H); δ_C (68 MHz; $CDCl_3$) 20.0 (CH_3), 38.6 (7-C), 43.0 (6-CH2), 51.8 (OCH_3), 57.7 (Ph*C*H$_2$), 64.2 (5-CH), 64.3 (PhCH*C*H$_2$), 69.7 (Ph*C*HCH$_2$), 91.6 (7a-CH), 123.1 (CN), 126.9, 127.4, 127.6, 128.2, 128.5, 128.7 (6 × Ar-*C*H), 137.4, 140.0 (2 × Ar-*C*), 172.6 (CO); *m*/*z* 375 (M$^+$, 3%), 309 (24), 308 (100), 249 (59), 217 (19), 130 (12), 104 (31), 91 (90). HRMS: (EI) M$^+$ 375.1948; $C_{23}H_{25}N_3O_2{\cdot}0.33H_2O$ requires M$^+$ 375.1947. Found: C, 72.25; H, 6.7; N, 10.9%. $C_{23}H_{25}N_3O_2{\cdot}0.33H_2O$ requires C, 72.4; H, 6.8; N, 11.0%; and the title compound (**9c**) as a colourless oil (0.16 g, 34%): $[\alpha]_D^{22}$ –43.5 (*c* 0.69; EtOH); ν_{max}(film)/cm^{-1} 3028, 2950, 2236, 1745, 1495, 1453, 1175; δ_H (250 MHz; $CDCl_3$) 1.42 (3H, s, CH_3), 2.36 (1H, dd, *J* = 10.1, 13.1, 6-C*H*H), 2.64 (1H, t, *J* = 9.6, PhCHC*H*H), 2.75 (1H, dd, *J* = 6.2, 13.1, 6-CH*H*), 3.36 (3H, s, OCH_3), 3.50 (2H, m, PhC*H*H and PhCHCH*H*), 3.84 (1H, dd, *J* = 6.2, 10.1, 5-CH), 4.06 (1H, d, *J* = 12.8, PhCH*H*), 4.20 (1H, s, 7a-CH), 4.32 (1H, dd, *J* = 5.7, 9.9, PhC*H*CH$_2$), 7.23 (10H, m, Ar–H); δ_C (68 MHz; $CDCl_3$) 22.1 (CH_3), 43.8 (6-CH_2), 44.5 (7-C), 51.7 (OCH_3), 58.5 (Ph*C*H$_2$), 64.5 (PhCH*C*H$_2$), 65.1 (5-CH), 69.3 (Ph*C*HCH$_2$), 93.5 (7a-CH), 122.2 (CN), 126.8, 127.3, 127.4, 128.1, 128.4, 128.9 (6 × Ar-*C*H), 137.9, 140.3 (2 × Ar-*C*), 172.7 (CO); *m*/*z* 375 (M$^+$, 1%), 309 (13), 308 (66), 249 (39), 217 (13), 146 (15), 130 (11), 104 (46), 91 (100). HRMS: (EI) M$^+$ 375.1950; $C_{23}H_{25}N_3O_2$ requires M$^+$ 375.1947. Found: C, 73.2; H, 6.9; N, 10.9%; $C_{23}H_{25}N_3O_2$ requires C, 73.6; H, 6.7; N, 11.1%.

(3*R*,5*R*,7*S*,7a*R*)-1-Benzyl-7-cyano-5-methoxycarbonyl-7-methyl-3-phenylhexahydropyrrolo[1,2-*a*]imidazole (9d). Prepared from (*R*)-1-benzyl-4-phenyl-4,5-dihydroimidazole (**8b**, 0.50 g, 2.12 mmol) by the method described above for the preparation of **9a** but using methyl bromoacetate (0.32 g, 0.20 mL, 2.12 mmol), 2-methylpropenonitrile (0.43 g, 0.53 mL, 6.36 mmol) and DBU (0.32 g, 0.32 mL, 2.12 mmol). Purification by column chromatography, eluting with hexane : ethyl acetate (4 : 1 v/v) yielded the *exo*-adduct (**9f**) as a colourless solid (38 mg, 5%), m.p. 100–102 °C: ν_{max} KBr/cm^{-1} 3062, 3029, 2950, 2815, 2234, 1745, 1454, 1204, 1180, 700; δ_H (250 MHz; $CDCl_3$) 1.51 (3H, s, CH_3),

2.42 (1H, dd, J = 6.0, 12.8, 6-C*H*H), 2.63 (1H, dd, J = 9.2, 10.0, PhCHC*H*H), 2.81 (1H, dd, J = 10.4, 12.8, 6-CH*H*), 3.34 (3H, s, OCH_3) 3.36 (1H, m, PhCHCH*H*), 3.46 (1H, d, J = 13.1, PhC*H*H), 3.56 (1H, dd, J = 6.0, 10.4, 5-CH), 4.01 (1H, dd, J = 5.5, 10.0, PhC*H*CH_2), 4.08 (1H, d, J = 13.0, PhCH*H*), 4.75 (1H, s, 7a-CH), 7.26 (10H, m, Ar–H); δ_C (68 MHz; $CDCl_3$) 20.0 (CH_3), 38.6 (7-C), 43.0 (6-CH_2), 51.8 (OCH_3), 57.7 (Ph*C*H_2), 64.2 (5-CH), 64.3 (PhCH*C*H_2), 69.7 (Ph*C*HCH_2), 91.6 (7a-CH), 123.1 (CN), 126.9, 127.4, 127.55, 128.1, 128.45, 128.7 (6 × Ar-*C*H), 137.4, 140.0 (2 × Ar-*C*), 172.6 (CO); m/z 375 (M^+, 1%), 308 (82), 249 (52), 217 (19), 130 (13), 104 (39) and 91 (100). HRMS: (EI) M^+ 375.1951; $C_{23}H_{25}N_3O_2$ requires M^+ 375.1947. Found: C, 73.7; H, 6.9; N, 11.5%; $C_{23}H_{25}N_3O_2$ requires C, 73.6; H, 6.7; N, 11.2%; and the title compound (**9d**) as a colourless solid (1.78 g, 56%), m.p. 67–69 °C: $[\alpha]_D^{22}$ 43.5 (c 0.63; EtOH); ν_{max} KBr/cm^{-1} 3028, 2948, 2811, 2236, 1744, 1454, 1204, 1176, 701; δ_H (250 MHz; $CDCl_3$) 1.41 (3H, s, CH_3), 2.35 (1H, dd, J = 10.1, 13.1, 6-C*H*H), 2.63 (1H, t, J = 9.7, PhCHC*H*H), 2.72 (1H, dd, J = 6.1, 13.1, 6-CH*H*), 3.35 (3H, s, OCH_3), 3.50 (2H, m, PhC*H*H and PhCHCH*H*), 3.83 (1H, dd, J = 6.1, 10.1, 5-CH), 4.04 (1H, d, J = 12.9, PhCH*H*), 4.18 (1H, s, 7a-CH), 4.30 (1H, dd, J = 5.7, 9.7, PhC*H*CH_2), 7.33 (10H, m, Ar–H); δ_C (68 MHz; $CDCl_3$) 22.1 (CH_3), 43.8 (6-CH_2), 44.6 (7-C), 51.75 (OCH_3), 58.5 (Ph*C*H_2), 64.5 (PhCH*C*H_2), 65.1 (5-CH), 69.4 (Ph*C*HCH_2), 93.55 (7a-CH), 122.2 (CN), 126.85, 127.4, 127.4, 128.1, 128.4, 128.9 (6 × Ar-*C*H), 137.9, 140.3 (2 × Ar-*C*), 172.8 (CO); m/z 375 (M^+, 2%), 309 (26), 308 (94), 249 (59), 217 (21), 104 (54), 91 (100). HRMS: (EI) M^+ 375.1977; $C_{23}H_{25}N_3O_2$ requires M^+ 375.1947. Found: C, 73.9; H, 6.6; N, 11.3%; $C_{23}H_{25}N_3O_2$ requires C, 73.6; H, 6.7; N, 11.2%.

(3*S*,5*S*,7*R*,7a*S*)-1-Benzyl-5-*t*-butoxycarbonyl-7-methoxycarbonyl-7-methyl-3-phenylhexahydropyrrolo[1,2-*a*]imidazole (9g). Prepared from (*S*)-1-benzyl-4-phenyl-4,5-dihydroimidazole (**8a**, 2.0 g, 8.46 mmol) by the method described above for the preparation of **9a** but using *t*-butyl bromoacetate (1.65 g, 1.37 mL, 8.46 mmol), methyl 2-methylpropenoate (2.54 g, 2.72 mL, 25.39 mmol) and DBU (1.29 g, 1.27 mL, 8.46 mmol). Purification by column chromatography, eluting with petroleum ether (b.p. 40–60 °C) : ethyl acetate (5 : 1 v/v) yielded the title compound as a colourless oil (1.95 g, 51%): ν_{max}(film)/cm^{-1} 3061, 3027, 2976, 2803, 1731, 1453, 1366, 1263, 1151, 700; δ_H (250 MHz; $CDCl_3$) 1.12 (9H, s, $C(CH_3)_3$), 1.49 (3H, s, 7-CH_3), 2.18 (1H, dd, J = 9.8, 13.2, 6-C*H*H), 2.41 (1H, t, J = 9.7, PhCHC*H*H), 2.71 (1H, dd, J = 6.6, 13.2, 6-CH*H*), 3.20 (2H, m, PhC*H*H and PhCHCH*H*), 3.80 (3H, s, OCH_3), 3.90 (1H, dd, J = 6.6, 9.8, 5-CH), 4.10 (2H, m, PhCH*H* and PhC*H*CH_2), 4.31 (1H, s, 7a-CH), 7.28 (10H, m, Ar–H); δ_C (68 MHz; $CDCl_3$) 23.0 (7-CH_3), 27.5 (C(*C*H_3)$_3$), 43.3 (6-CH_2), 51.8 (OCH_3), 53.2 (7-C), 58.4 (Ph*C*H_2), 64.9 (PhCH*C*H_2), 68.2 (5-CH), 69.4 (Ph*C*HCH_2), 80.3 (*C*(CH_3)$_3$), 96.4 (7a-CH), 127.0, 127.1, 127.3, 128.0, 128.1, 128.8 (6 × Ar-*C*H), 138.4, 141.8 (2 × Ar-*C*), 173.5, 175.5 (2 × CO); m/z 450 (M^+, 7%), 350 (57), 294 (45), 249 (39), 131 (42), 104 (40), 91 (100). HRMS: (EI) M^+ 450.2491; $C_{27}H_{34}N_2O_4$ requires M^+ 450.2519. Found: C, 72.1; H, 7.9; N, 6.1%; $C_{27}H_{34}N_2O_4$ requires C, 72.0; H, 7.6; N, 6.2%.

Crystal data for **9g**: $C_{27}H_{34}N_2O_4$, M = 450.6, colourless block, 0.70 × 0.59 × 0.30 mm; orthorhombic, $P2_12_12_1$; a = 8.046(1), b = 14.280(2), c = 22.646(3) Å, U = 2602(1) $Å^3$; T = 293 K, μ(Mo-Kα) = 0.08 mm^{-1}, D_c = 1.15 g cm^{-3}; Z = 4, F(000) = 968, $2\theta_{max}$ = 50°; 299 parameters, wR = 0.1034 for all 2620 data, R = 0.042 for 1393 data with $F_o > 4\sigma(F_o)$.

(3*R*,5*R*,7*S*,7a*R*)-1-Benzyl-5-*t*-butoxycarbonyl-7-methoxycarbonyl-7-methyl-3-phenylhexahydropyrrolo[1,2-*a*]imidazole (9h). Prepared from (*R*)-1-benzyl-4-phenyl-4,5-dihydroimidazole (**8b**, 1.0 g, 4.23 mmol) by the method described above for the preparation of **9a** but using *t*-butyl bromoacetate (0.83 g, 0.68 mL, 4.23 mmol), methyl 2-methylpropenoate (1.27 g, 1.36 mL, 12.70 mmol) and DBU (0.64 g, 0.63 mL, 4.23 mmol). Purification by column chromatography, eluting with petroleum ether (b.p. 40–60 °C) : ethyl acetate (5 : 1 v/v) yielded the title compound as a colourless oil (1.95 g, 51%): ν_{max}(film)/cm^{-1} 2978, 1732, 1455, 1264, 1152, 701; δ_H (400 MHz; $CDCl_3$) 1.12 (9H, s, $C(CH_3)_3$), 1.49 (3H, s, 7-CH_3), 2.18 (1H, dd, J = 9.8, 13.2, 6-C*H*H), 2.41 (1H, t, J = 9.7, PhCHC*H*H), 2.71 (1H, dd, J = 6.6, 13.2, 6-CH*H*), 3.21 (2H, m, PhC*H*H and PhCHCH*H*), 3.80 (3H, s, OCH_3), 3.90 (1H, dd, J = 6.6, 9.8, 5-CH), 4.11 (2H, m, PhCH*H* and PhC*H*CH_2), 4.31 (1H, s, 7a-CH), 7.29 (10H, m, Ar–H); δ_C (68 MHz; $CDCl_3$) 22.9 (7-CH_3), 27.3 (C(*C*H_3)$_3$), 43.2 (6-CH_2), 51.6 (OCH_3), 53.0 (7-C), 58.2 (Ph*C*H_2), 64.8 (PhCH*C*H_2), 68.0 (5-CH), 69.3 (Ph*C*HCH_2), 80.1 (*C*(CH_3)$_3$), 96.3 (7a-CH), 126.8, 126.9, 127.1, 127.85, 128.0, 128.6 (6 × Ar-*C*H), 138.2, 141.65 (2 × Ar-*C*), 173.2, 175.2 (2 × CO); m/z 450 (M^+, 1%), 350 (44), 294 (48), 249 (33), 104 (38), 91 (100). HRMS: (EI) M^+ 450.2521; $C_{27}H_{34}N_2O_4$ requires M^+ 450.2519. Found: C, 72.1; H, 7.9; N, 6.1%; $C_{27}H_{34}N_2O_4$ requires C, 72.0; H, 7.6; N, 6.2%.

(3*S*,5*S*,7*R*,7a*S*)-1-Benzyl-5-*t*-butoxycarbonyl-7-cyano-7-methyl-3-phenylhexahydropyrrolo[1,2-*a*]imidazole (9i). This compound was prepared from (*S*)-1-benzyl-4-phenyl-4,5-dihydroimidazole (**8a**, 1.0 g, 4.23 mmol) by the method described above for the preparation of **9a** but using *t*-butyl bromoacetate (0.83 g, 0.68 mL, 4.23 mmol), 2-methylpropenonitrile (0.85 g, 1.07 mL, 12.70 mmol) and DBU (0.64 g, 0.63 mL, 4.23 mmol). Purification by column chromatography, eluting with petroleum ether (b.p. 40–60 °C) : ethyl acetate (5 : 1 v/v) yielded the *exo*-adduct (**9k**) as a colourless solid (62 mg, 4%), m.p. 100–102 °C [from petroleum ether (b.p. 40–60 °C)]: ν_{max} ($CHCl_3$)/cm^{-1} 2822, 2236, 1732, 1369, 1153; δ_H (250 MHz; $CDCl_3$) 1.13 (9H, s, $C(CH_3)_3$), 1.50 (3H, s, 7-CH_3), 2.38 (1H, dd, J = 5.8, 12.7, 6-C*H*H), 2.62 (1H, apparent t, J = 9.5, PhCHC*H*H), 2.77 (1H, dd, J = 10.7, 12.7, 6-CH*H*), 3.35 (1H, dd, J = 5.5, 8.9, PhCHCH*H*), 3.45 (2H, m, PhC*H*H and 5-CH), 3.99 (1H, dd, J = 5.5, 9.9, PhC*H*CH_2), 4.08 (1H, d, J = 13.0, PhCH*H*), 4.75 (1H, s, 7a-CH), 7.27 (10H, m, Ar–H); δ_C (68 MHz; $CDCl_3$) 20.15 (7-CH_3), 27.4 (C(*C*H_3)$_3$), 38.5 (7-C), 43.4 (6-CH_2), 57.8 (Ph*C*H_2), 64.7 (PhCH*C*H_2), 65.6 (5-CH), 69.8 (Ph*C*HCH_2), 81.3 (*C*(CH_3)$_3$), 92.0 (7a-CH), 123.4 (CN), 127.2, 127.4, 127.5, 128.2, 128.4, 128.7 (6 × Ar-*C*H), 137.6, 140.5 (2 × Ar-*C*), 171.4 (CO); m/z 350 (39%), 316 (12), 294 (48), 249 (32), 104 (40), 91 (100). Found: C, 74.85; H, 7.7; N, 10.0%; $C_{26}H_{31}N_3O_2$ requires C, 74.8; H, 7.5; N, 10.1%; and the title compound (**9i**) as a colourless solid (0.47 g, 27%), m.p. 118–119 °C [from petroleum ether (b.p. 40–60 °C)]: $[\alpha]_D^{22}$ −15.8 (c 0.48; EtOH); ν_{max} (KBr)/cm^{-1} 3072, 3029, 2981, 2959, 2943, 2234, 1736, 1454, 1443, 1366, 1215, 1152, 1079, 702; δ_H (400 MHz; $CDCl_3$) 1.13 (9H, s, $C(CH_3)_3$), 1.41 (3H, s, 7-CH_3), 2.32 (1H, dd, J = 10.1, 13.1, 6-C*H*H), 2.59 (1H, apparent t, J = 9.5, PhCHC*H*H), 2.67 (1H, dd, J = 6.0, 13.1, 6-CH*H*), 3.47 (2H, m, PhC*H*H and PhCHCH*H*), 3.71 (1H, dd, J = 6.0, 10.1, 5-CH), 4.04 (1H, d, J = 12.7, PhCH*H*), 4.17

(1H, s, 7a-CH), 4.29 (1H, dd, J = 5.8, 9.8, PhCHCH$_2$), 7.31 (10H, m, Ar–H); δ_C (68 MHz; $CDCl_3$) 22.25 (7-CH_3), 27.4 (C(CH_3)$_3$), 43.9 (6-CH2), 44.4 (7-C), 58.5 (PhCH_2), 64.7 (PhCHCH_2), 66.4 (5-CH), 69.4 (PhCHCH$_2$), 81.1 (C(CH_3)$_3$), 93.8 (7a-CH), 122.4 (CN), 127.1, 127.3, 127.3, 128.1, 128.3, 128.9 (6 × Ar-CH), 138.0, 140.9 (2 × Ar-C), 171.45 (CO); m/z (FAB) 418 (MH^+, 5%), 350 (48), 316 (17), 294 (57), 249 (32), 130 (16), 104 (44), 104 (100). HRMS: (EI) M^+ 417.2424; $C_{26}H_{31}N_3O_2$ requires M^+ 417.2416. Found: C, 74.75; H, 7.8; N, 10.1%; $C_{26}H_{31}N_3O_2$ requires C, 74.8; H, 7.5; N, 10.1%.

(3*R*,5*R*,7*S*,7a*R*)-1-Benzyl-5-*t*-butoxycarbonyl-7-cyano-7-methyl-3-phenylhexahydropyrrolo[1,2-*a*]imidazole (9j). This compound was prepared from (*R*)-1-benzyl-4-phenyl-4,5-dihydroimidazole (**8b**, 0.50 g, 2.12 mmol) by the method described above for the preparation of **9a** but using *t*-butyl bromoacetate (0.41 g, 0.34 mL, 2.12 mmol), 2-methylpropenonitrile (0.43 g, 0.53 mL, 6.35 mmol) and DBU (0.32 g, 0.32 mL, 2.12 mmol). Purification by column chromatography, eluting with petroleum ether (b.p. 40–60 °C) : ethyl acetate (5 : 1 v/v) yielded the *exo*-adduct (**9l**) as a colourless solid (24 mg, 3%), m.p. 99–101 °C: ν_{max} (KBr)/cm^{-1} 2981, 2233, 1724, 1636, 1366, 1162, 698; δ_H (400 MHz; $CDCl_3$) 1.13 (9H, s, C(CH_3)$_3$), 1.49 (3H, s, 7-CH_3), 2.38 (1H, dd, J = 5.9, 12.8, 6-CHH), 2.62 (1H, t, J = 9.2, PhCHCHH), 2.76 (1H, dd, J = 10.8, 12.8, 6-CHH), 3.35 (1H, dd, J = 5.5, 9.2, PhCHCHH), 3.44 (2H, m, PhCHH and 5-CH), 3.99 (1H, dd, J = 5.5, 10.0, PhCHCH$_2$), 4.07 (1H, d, J = 13.1, PhCHH), 4.75 (1H, s, 7a-CH), 7.39 (10H, m, Ar–H); δ_C (68 MHz; $CDCl_3$) 20.1 (7-CH_3), 27.4 (C(CH_3)$_3$), 38.5 (7-C), 43.4 (6-CH_2), 57.8 (PhCH_2), 64.7 (PhCHCH_2), 65.6 (5-CH), 69.8 (PhCHCH$_2$), 81.3 (C(CH_3)$_3$), 91.95 (7a-CH), 123.4 (CN), 127.2, 127.4, 127.5, 128.2, 128.4, 128.7 (6 × Ar-CH), 137.6, 140.5 (2 × Ar-C), 171.4 (CO); m/z 350 (15%), 294 (20), 249 (17), 120 (35), 104 (15), 91 (100). Found: C, 75.0; H, 7.7; N, 10.3%; $C_{26}H_{31}N_3O_2$ requires C, 74.8; H, 7.5; N, 10.1%; and the title compound (**9j**) as a colourless solid (194 mg, 22%), m.p. 119–120 °C: $[\alpha]_D^{22}$ 15.7 (*c* 1.07; EtOH); ν_{max} (KBr)/cm^{-1} 2978, 1732, 1455, 1264, 1152 and 701; δ_H (400 MHz; $CDCl_3$) 1.13 (9H, s, C(CH_3)$_3$), 1.45 (3H, s, 7-CH_3), 2.35 (1H, dd, J = 9.7, 13.2, 6-CHH), 2.65 (1H, t, J = 9.7, PhCHCHH), 2.78 (1H, dd, J = 6.4, 13.2, 6-CHH), 3.53 (2H, m, PhCHH and PhCHCHH), 3.78 (1H, dd, J = 6.4, 9.7, 5-CH), 4.12 (1H, d, J = 12.9, PhCHH), 4.23 (1H, s, 7a-CH), 4.35 (1H, dd, J = 5.9, 9.7, PhCHCH$_2$), 7.29 (10H, m, Ar–H); δ_C (68 MHz; $CDCl_3$) 22.1 (7-CH_3), 27.2 (C(CH_3)$_3$), 43.7 (6-CH_2), 44.2 (7-C), 58.3 (PhCH_2), 64.55 (PhCHCH_2), 66.25 (5-CH), 69.2 (PhCHCH$_2$), 80.8 (C(CH_3)$_3$), 93.6 (7a-CH), 122.2 (CN), 126.9, 127.1, 127.15, 128.0, 128.2, 128.7 (6 × Ar-CH), 137.9, 140.75 (2 × Ar-C), 171.25 (CO); m/z (FAB) 418 (MH^+, 63%), 350 (100), 316 (19), 294 (37), 249 (17), 208 (22). HRMS: (FAB) MH^+ 418.2507; $C_{26}H_{31}N_3O_2$ requires MH^+ 418.2494. Found: C, 74.7; H, 7.5; N, 9.9%; $C_{26}H_{31}N_3O_2$ requires C, 74.8; H, 7.5; N, 10.1%.

(3*S*,5*S*,7*R*,7a*S*)-1-Benzyl-5-*t*-butoxycarbonyl-7-methoxycarbonyl-3-phenylhexahydropyrrolo[1,2-*a*]imidazole (13a). Prepared from (*S*)-1-benzyl-4-phenyl-4,5-dihydroimidazole (**8a**, 1.0 g, 4.23 mmol) by the method described above for the preparation of **9a** but using *t*-butyl bromoacetate (0.83 g, 0.68 mL, 4.23 mmol), methyl propenoate (1.09 g, 1.14 mL, 12.70 mmol) and DBU (0.64 g, 0.63 mL, 4.23 mmol). Purification by column chromatography, eluting with petroleum ether (b.p. 40–60 °C) : ethyl acetate (5 : 1 v/v) yielded the title compound as a colourless solid (1.21 g, 65%), m.p. 98–99 °C [from petroleum ether (b.p. 40–60 °C)]: $[\alpha]_D^{22}$ –22.8 (*c* 1.08; EtOH); ν_{max} (KBr)/cm^{-1} 3032, 2980, 2946, 1728, 1367, 1166, 1152, 697; δ_H (400 MHz; $CDCl_3$) 1.22 (9H, s, C(CH_3)$_3$), 2.26 (1H, m, 6-CHH), 2.40 (1H, t, J = 9.6, PhCHCHH), 2.58 (1H, m, 6-CHH), 3.27 (3H, m, PhCHH, 7-CH and PhCHCHH), 3.72 (3H, s, OCH_3), 3.80 (1H, t, J = 6.8, 5-CH), 4.08 (1H, d, J = 12.9, PhCHH), 4.13 (1H, m, PhCHCH$_2$), 4.68 (1H, d, J = 6.6, 7a-CH), 7.27 (10H, m, Ar–H); δ_C (68 MHz; $CDCl_3$) 27.4 (C(CH_3)$_3$), 32.6 (6-CH2), 47.9 (7-CH), 51.3 (OCH_3), 58.2 (PhCH_2), 64.0 (PhCHCH_2), 66.8 (5-CH), 68.6 (PhCHCH$_2$), 80.1 (C(CH_3)$_3$), 88.4 (7a-CH), 126.7, 126.9, 127.8, 128.0, 128.3 (6 × Ar-CH), 138.2, 141.2 (2 × Ar-C), 172.7, 173.0 (2 × CO); m/z 436 (M^+, 2%), 350 (36), 335 (15) 294 (41), 249 (33), 120 (24), 104 (52), 91 (100). HRMS: (EI) M^+ 436.2377; $C_{26}H_{32}N_2O_4$ requires M^+ 436.2362. Found: C, 71.6; H, 7.6; N, 6.4%; $C_{26}H_{32}N_2O_4$ requires C, 71.5; H, 7.4; N, 6.4%.

A crystal was mounted on a thin glass fibre and transferred into the cold stream of the diffractometer low temperature device. *Crystal data* for **13a**: $C_{26}H_{32}N_2O_4$, M = 436.54, monoclinic, $P2_1$; a = 10.276(2), b = 5.799(3), c = 20.259(5) Å, β = 103.07(2)°, U = 1175.9(7) Å^3, T = 150(2) K, μ(Mo-Kα) = 0.083 mm^{-1}, D_c = 1.233 g cm^{-3}, Z = 2, 2284 unique data (R_{int} 0.072) were used in all calculations. Final R_1 [1639 $F > 4\sigma(F)$] = 0.0734 and wR(all F^2) was 0.146.

(3*R*,5*R*,7*S*,7a*R*)-1-Benzyl-5-*t*-butoxycarbonyl-7-methoxycarbonyl-3-phenylhexahydropyrrolo[1,2-*a*]imidazole (13b). Prepared from (*R*)-1-benzyl-4-phenyl-4,5-dihydroimidazole (**8b**, 1.0 g, 4.23 mmol) by the method described above for the preparation of **9a** but using *t*-butyl bromoacetate (0.83 g, 0.68 mL, 4.23 mmol), methyl propenoate (1.09 g, 1.14 mL, 12.70 mmol) and DBU (0.64 g, 0.63 mL, 4.23 mmol). Purification by column chromatography, eluting with petroleum ether (b.p. 40–60 °C) : ethyl acetate (5 : 1 v/v) yielded the title compound as a colourless solid (1.17 g, 63%), m.p. 92–94 °C [from petroleum ether (b.p. 40–60 °C)]: $[\alpha]_D^{22}$ 22.8 (*c* 1.08; EtOH); ν_{max} (KBr)/cm^{-1} 3032, 2980, 2946, 1728, 1367, 1166, 1152, 697; δ_H (270 MHz; $CDCl_3$) 1.21 (9H, s, C(CH_3)$_3$), 2.27 (1H, m, 6-CHH), 2.40 (1H, t, J = 9.6, PhCHCHH), 2.58 (1H, m, 6-CHH), 3.28 (3H, m, PhCHH, 7-CH and PhCHCHH), 3.70 (3H, s, OCH_3), 3.82 (1H, t, J = 6.9, 5-CH), 4.08 (1H, d, J = 13.2, PhCHH), 4.13 (1H, m, PhCHCH$_2$), 4.68 (1H, d, J = 6.3, 7a-CH), 7.28 (10H, m, Ar–H); δ_C (68 MHz; $CDCl_3$) 27.4 (C(CH_3)$_3$), 32.65 (6-CH2), 48.0 (7-CH), 51.4 (OCH_3), 58.3 (PhCH_2), 64.0 (PhCHCH_2), 66.8 (5-CH), 68.7 (PhCHCH$_2$), 80.2 (C(CH_3)$_3$), 88.45 (7a-CH), 126.8, 127.0, 127.9, 128.0, 128.3 (6 × Ar-CH), 138.3, 141.3 (2 × Ar-C), 172.8, 173.1 (2 × CO); m/z 436 (M^+, 4%), 350 (43), 335 (16), 294 (48), 249 (37), 120 (32), 104 (58), 91 (100). HRMS: (EI) M^+ 436.2345; $C_{26}H_{32}N_2O_4$ requires M^+ 436.2362. Found: C, 71.3; H, 7.5; N, 6.3%; $C_{26}H_{32}N_2O_4$ requires C, 71.5; H, 7.4; N, 6.4%.

(3*S*,5*S*,7*R*,7a*S*)-1-Benzyl-5,7-bis(t-butoxycarbonyl)-3-phenylhexahydropyrrolo[1,2-*a*]imidazole (13c). Prepared from (*S*)-1-benzyl-4-phenyl-4,5-dihydroimidazole (**8a**, 1.0 g, 4.23 mmol) by the method described above for the preparation of **9a** but using *t*-butyl bromoacetate (0.83 g, 0.68 mL, 4.23 mmol), *t*-butyl propenoate (1.19 g, 1.26 mL, 9.73 mmol) and DBU (0.64 g, 0.63 mL, 4.23 mmol). Purification by column chromatography, eluting with petroleum ether (b.p. 40–60 °C) : ethyl acetate (5 : 1 v/v) yielded the title compound as a colourless solid (1.20 g, 59%), m.p. 102–104 °C [from petroleum ether (b.p. 40–60 °C)],

$[\alpha]_D^{22}$ −27.0 (*c* 0.97; EtOH): ν_{max} (KBr)/cm^{-1} 2927, 1734, 1628, 1384, 1369, 1145, 702; δ_H (400 MHz; $CDCl_3$) 1.22, 1.49 (18H, 2 × s, 2 × $C(CH_3)_3$), 2.22 (1H, m, 6-C*H*H), 2.43 (1H, t, *J* = 9.5, PhCHC*H*H), 2.52 (1H, m, 6-CH*H*), 3.16 (1H, dd, *J* = 6.5, 11.8, 7-CH), 3.26 (2H, m, PhC*H*H and PhCHCH*H*), 3.71 (1H, t, *J* = 7.0, 5-CH), 4.13 (2H, m, PhCH*H* and PhC*H*CH_2), 4.61 (1H, d, *J* = 6.5, 7a-CH), 7.26 (10H, m, Ar–H); δ_C (68 MHz; $CDCl_3$) 27.5, 27.75 (2 × $C(CH_3)_3$), 33.1 (6-CH_2), 49.2 (7-CH), 58.35 (Ph*C*H_2), 63.9 (PhCH*C*H_2), 67.0 (5-CH), 68.9 (Ph*C*HCH$_2$), 80.1, 80.5 (2 × *C*$(CH_3)_3$), 88.4 (7a-CH), 126.8, 126.9, 127.0, 127.9, 129.0 (6 × Ar-*C*H), 137.9, 141.6 (2 × Ar-*C*), 171.6, 173.15 (2 × CO); *m*/*z* 478 (M^+, 5%), 350 (53), 294 (62), 249 (35), 235 (25), 120 (17), 104 (42), 91 (100). HRMS: (EI) M^+ 478.2853; $C_{29}H_{38}N_2O_4$ requires M^+ 478.2832. Found: C, 72.6; H, 8.25; N, 6.0%; $C_{29}H_{38}N_2O_4$ requires C, 72.8; H, 8.0; N, 5.9%; and the *exo*-adduct (**13e**) as a colourless oil (70 mg, 3%): ν_{max} (KBr)/cm^{-1} 3062, 3028, 2977, 2931, 1732, 1628, 1367, 1150, 700; δ_H (400 MHz; $CDCl_3$) 1.14, 1.47 (18H, 2 × s, 2 × $C(CH_3)_3$), 2.31 (1H, t, *J* = 9.5, PhCHC*H*H), 2.46, 2.56 (2H, 2 × m, 6-CH_2), 2.99 (1H, m, 7-CH), 3.21 (1H, d, *J* = 12.9, PhC*H*H), 3.32 (1H, dd, *J* = 6.3, 9.3, PhCHCH*H*), 3.58 (1H, dd, *J* = 6.2, 9.4, 5-CH), 4.06 (2H, m, PhCH*H* and PhC*H*CH_2), 4.39 (1H, d, *J* = 4.5, 7a-CH), 7.26 (10H, m, Ar–H); δ_C (68 MHz; $CDCl_3$) 27.5, 28.05 (2 × $C(CH_3)_3$), 34.0 (6-CH_2), 50.5 (7-CH), 56.6 (Ph*C*H_2), 64.0 (PhCH*C*H_2), 68.75 (Ph*C*HCH$_2$), 69.0 (5-CH), 80.7, 81.0 (2 × *C*$(CH_3)_3$), 89.6 (7a-C), 126.9, 126.9, 127.1, 128.1, 128.1, 128.8 (6 × Ar-*C*H), 138.35, 142.6 (2 × Ar-*C*), 171.7, 171.9 (2 × CO); *m*/*z* 478 (M^+, 21%), 350 (85), 294 (71), 249 (38), 235 (30), 104 (27), 91 (100). HRMS: (EI) M^+ 478.2848; $C_{29}H_{38}N_2O_4$ requires M^+ 478.2832. Found: C, 72.1; H, 8.1; N, 5.7%; $C_{29}H_{38}N_2O_4 \cdot 0.2H_2O$ requires C, 72.1; H, 8.2; N, 5.7%.

(3*R*,5*R*,7*S*,7a*R*)-1-Benzyl-5,7-bis(t-butoxycarbonyl)-3-phenylhexahydropyrrolo[1,2-*a*]imidazole (13d). Prepared from (*R*)-1-benzyl-4-phenyl-4,5-dihydroimidazole (**8b**, 0.50 g, 2.12 mmol) by the method described above for the preparation of **9a** but using *t*-butyl bromoacetate (0.41 g, 0.34 mL, 2.12 mmol), *t*-butyl propenoate (0.81 g, 0.93 mL, 6.35 mmol) and DBU (0.32 g, 0.32 mL, 2.12 mmol). Purification by column chromatography, eluting with petroleum ether (b.p. 40–60 °C) : ethyl acetate (5 : 1 v/v) yielded the title compound as a colourless solid (0.49 g, 49%), m.p. 95–98 °C [from petroleum ether (b.p. 40–60 °C)], $[\alpha]_D^{22}$ 27.1 (*c* 0.98; EtOH): ν_{max} (KBr)/cm^{-1} 3031, 2975, 2935, 1733, 1369, 1146, 702; δ_H (400 MHz; $CDCl_3$) 1.21, 1.48 (18H, 2 × s, 2 × $C(CH_3)_3$), 2.23 (1H, m, 6-C*H*H), 2.43 (1H, t, *J* = 9.6, PhCHC*H*H), 2.55 (1H, m, 6-CH*H*), 3.16 (1H, dd, *J* = 6.5, 11.9, 7-CH), 3.26 (2H, m, PhC*H*H and PhCHCH*H*), 3.73 (1H, t, *J* = 6.9, 5-CH), 4.13 (2H, m, PhCH*H* and PhC*H*CH_2), 4.62 (1H, d, *J* = 6.5, 7a-CH), 7.27 (10H, m, ArH); δ_C (68 MHz; $CDCl_3$) 27.5, 28.2 (2 × $C(CH_3)_3$), 33.1 (6-CH_2), 49.2 (7-CH), 58.4 (Ph*C*H_2), 63.9 (PhCH*C*H_2), 67.0 (5-CH), 69.0 (Ph*C*HCH$_2$), 80.2, 80.5 (2 × *C*$(CH_3)_3$), 88.5 (7a-CH), 126.8, 126.95, 127.0, 127.9, 129.0 (6 × Ar-*C*H), 138.0, 141.6 (2 × Ar-*C*), 171.6, 173.2 (2 × CO); *m*/*z* 478 (M^+, 4%), 350 (73), 294 (76), 249 (45), 235 (34), 120 (17), 104 (38), 91 (100). HRMS: (EI) M^+ 478.2827; $C_{29}H_{38}N_2O_4$ requires M^+ 478.2832. Found: C, 72.5; H, 8.1; N, 5.8%; $C_{29}H_{38}N_2O_4$ requires C, 72.8; H, 8.0; N, 5.9%; and the *exo*-adduct (**13f**) as a colourless oil (22 mg, 2%): ν_{max}(film)/cm^{-1} 2977, 1729, 1367, 1150, 700; δ_H (400 MHz; $CDCl_3$) 1.14, 1.47 (18H, 2 × s, 2 × $C(CH_3)_3$), 2.30 (1H, t, *J* = 9.5, PhCHC*H*H), 2.46, 2.57 (2H, 2 × m, 6-C*H*H), 2.97 (1H, m, 7-CH), 3.20 (1H, d, *J* = 12.9, PhC*H*H), 3.32 (1H, dd, *J* = 6.3, 9.2, PhCHCH*H*), 3.58 (1H, dd, *J* = 6.2, 9.4, 5-CH), 4.09 (2H, m, PhCH*H* and PhC*H*CH_2), 4.38 (1H, d, *J* = 4.5, 7a-CH), 7.26 (10H, m, Ar–H); δ_C (100 MHz; $CDCl_3$) 27.5, 28.1 (2 × $C(CH_3)_3$), 34.05 (6-CH_2), 50.7 (7-CH), 56.7 (Ph*C*H_2), 64.1 (PhCH*C*H_2), 68.9 (Ph*C*HCH$_2$), 69.1 (5-CH), 80.7, 81.0 (2 × *C*$(CH_3)_3$), 89.6 (7a-CH), 126.85, 126.9, 127.0, 128.1, 128.3, 128.8 (6 × Ar-*C*H), 138.6, 142.7 (2 × Ar-*C*), 171.8, 171.9 (2 × CO); *m*/*z* 478 (M^+, 25%), 350 (96), 294 (83), 249 (42), 235 (33), 104 (29), 91 (100). HRMS: (EI) M^+ 478.2837; $C_{29}H_{38}N_2O_4$ requires M^+ 478.2832.

(3*S*,5*S*,7*R*,7a*S*)-1-Benzyl-5-*t*-butoxycarbonyl-3-phenyl-3-phenylsulfonylhexahydropyrrolo[1,2-*a*]imidazole (14). t-Butyl bromoacetate (0.83 g, 0.68 mL, 4.23 mmol) was added to a solution of (*S*)-1-benzyl-4-phenyl-4,5-dihydroimidazole (**8a**, 1.0 g, 4.23 mmol) and phenyl ethenyl sulfone (2.14 g, 12.70 mmol) in dry tetrahydrofuran (30 mL), stirred at reflux under nitrogen. DBU (0.64 g, 0.63 mL, 4.23 mmol) was added dropwise over 4 h, and stirring at reflux was continued for 1.5 h. The solvent was evaporated under reduced pressure and the residue was partitioned between chloroform (3 × 30 mL) and water (30 mL). The organic phase was dried (Na_2SO_4), evaporated under reduced pressure and the residue was purified by column chromatography, eluting with petroleum ether (b.p. 40–60 °C) : ethyl acetate (5 : 1 v/v) to yield the title compound as a colourless solid (0.72 g, 33%), m.p. 142–145 °C (from ethyl acetate): ν_{max} (KBr)/cm^{-1} 2927, 1734, 1628, 1384, 1145; δ_H (250 MHz; $CDCl_3$) 1.20 (9H, s, $C(CH_3)_3$), 2.18 (1H, m, 6-C*H*H), 2.46 (2H, m, PhCHC*H*H and 6-CH*H*), 3.32 (2H, m, PhC*H*H and PhCHCH*H*), 3.67 (1H, t, *J* = 6.5, PhC*H*CH_2), 3.98 (1H, dd, *J* = 6.2, 13.7, 7-CH), 4.18 (1H, dd, *J* = 5.5, 10.1, 5-CH), 4.62 (1H, d, *J* = 11.9, PhCH*H*), 4.97 (1H, d, *J* = 6.2, 7a-CH), 7.59 (15H, m, Ar–H); δ_C (68 MHz; $CDCl_3$) 27.55 (C(*C*$H_3)_3$), 32.0 (6-CH_2), 59.1 (Ph*C*H_2), 63.45 (PhCH*C*H_2), 64.6 (Ph*C*HCH$_2$), 66.45 (7-CH), 67.8 (5-CH), 81.0 (*C*$(CH_3)_3$), 87.7 (7a-CH), 126.9, 127.2, 128.1, 128.3, 129.1, 129.2 (9 × Ar-*C*H), 133.2, 138.3, 140.6 (3 × Ar-*C*), 171.9 (CO); *m*/*z* 461 (M^+–C_4H_9, 6%), 417 (11), 350 (61), 294 (63), 249 (45), 235 (36), 120 (50), 104 (59), 91 (100). HRMS: (EI) M^+–C_4H_9 461.1536; $C_{30}H_{34}N_2O_4S$ requires M^+–C_4H_9 461.1535. Found: C, 69.4; H, 6.9; N, 5.5%; $C_{30}H_{34}N_2O_4S$ requires C, 69.5; H, 6.6; N, 5.4%.

(3*S*,5*S*,7*R*,7a*S*)-7-Acetyl-1-Benzyl-5-*t*-butoxycarbonyl-3-phenylhexahydropyrrolo[1,2-*a*]imidazole (15). Prepared from (*S*)-1-benzyl-4-phenyl-4,5-dihydroimidazole (**8a**, 1.0 g, 4.23 mmol) by the method described above for the preparation of **9a** but using *t*-butyl bromoacetate (0.83 g, 0.68 mL, 4.23 mmol), but-3-en-2-one (0.89 g, 1.06 mL, 12.70 mmol) and DBU (0.64 g, 0.63 mL, 4.23 mmol). The residue was extracted with petroleum ether (b.p. 40–60 °C) to yield the title compound as a yellow oil (1.27 g, 71%): δ_H (270 MHz; $CDCl_3$) 1.14 (9H, s, $C(CH_3)_3$), 2.07 (3H, s, $COCH_3$), 2.42 (3H, m, PhCHC*H*H and 6-CH_2), 3.01 (1H, m, 7-CH), 3.41 (2H, m, PhC*H*H and PhCHCH*H*), 3.59 (1H, dd, *J* = 6.3, 8.9, 5-CH), 3.73 (1H, d, *J* = 12.9, PhCH*H*), 4.11 (1H, dd, *J* = 6.3, 9.6, PhC*H*CH_2), 4.46 (1H, d, *J* = 4.3, 7a-CH), 7.29 (10H, m, Ar–H); δ_C (68 MHz; $CDCl_3$) 27.4 (C(*C*$H_3)_3$), 28.8 (CO*C*H_3), 33.9 (6-CH_2), 57.0 (Ph*C*H_2), 57.1 (7-CH), 64.5 (PhCH*C*H_2), 68.8 (Ph*C*HCH$_2$), 69.1 (5-CH), 80.7 (*C*$(CH_3)_3$), 88.2 (7a-CH), 126.8, 127.1, 128.0, 128.2, 128.8 (6 × Ar-*C*H), 138.2, 142.5 (2 × Ar-*C*), 171.5, 173.15 (2 × CO).

(3*S*,5*S*,7*R*,7a*S*)-1-Benzyl-5,7-dimethyl-5-ethoxycarbonyl-7-methoxycarbonyl-3-phenylhexahydropyrrolo[1,2-*a*]imidazole (16a). Prepared from (*S*)-1-benzyl-4-phenyl-4,5-dihydroimidazole (**8a**, 1.00 g, 4.24 mmol) by the method described above for the preparation of **9a** but using ethyl 2-bromopropanoate (767 mg, 4.24 mmol), methyl 2-methylpropenoate (1.36 mL, 1.27 g, 12.7 mmol) and DBU (0.63 mL, 0.64 g, 4.22 mmol). Purification by column chromatography, eluting with petroleum ether (b.p. 40–60 °C) : ethyl acetate (3 : 1 v/v), yielded the title compound (530 mg, 29%) as a colourless oil, $[\alpha]_D^{22}$ 12.3 (*c* 1.00; $CHCl_3$): ν_{max}(film)/cm^{-1} 2981, 2949, 1733, 1495, 1454, 1252, 1135, 702; δ_H (400 MHz; $CDCl_3$) 1.25–1.28 (6H, m, C*H*$_3$CH$_2$ and 5-CH$_3$), 1.37 (3H, s, 7-CH$_3$), 2.24 (1H, d, *J* = 13.6, 6-C*H*H), 2.30-2.32 (1H, m, PhCHC*H*H), 2.88 (1H, d, *J* = 13.6, 6-CH*H*), 3.16 (1H, dd, *J* = 5.5, 9.0, PhCHCH*H*), 3.38 (1H, d, *J* = 12.7, PhC*H*H), 3.72 (3H, s, OCH$_3$), 4.12-4.20 (3H, m, CH$_3$C*H*$_2$O and PhCH*H*), 4.33 (1H, s, 7a-CH), 4.54 (1H, dd, *J* = 5.5, 9.4, PhC*H*CH$_2$), 7.14–7.28 (8H, m, Ar–H), 7.42 (2H, d, *J* = 8.0, Ar–H); δ_C (100.6 MHz; $CDCl_3$) 14.2, 21.35, 23.95 (3 × CH$_3$), 48.1 (6-CH$_2$), 51.9 (OCH$_3$), 54.3 (7-C), 59.7 (Ph*C*H$_2$), 60.8 (CH$_3$*C*H$_2$), 62.0 (Ph*C*HCH$_2$), 64.35 (PhCH*C*H$_2$), 68.0 (5-C), 97.4 (7a-CH), 126.6, 126.9, 128.1, 128.6 (6 × Ar-*C*H, overlapping), 138.7, 143.1 (2 × Ar-*C*), 176.0, 176.4 (2 × CO); *m*/*z* 436 (M$^+$, 1%), 405 (6), 363 (9), 337 (33), 336 (100), 263 (49), 91 (89). HRMS: (EI) M$^+$ 436.2336; $C_{26}H_{32}N_2O_4$ requires M$^+$ 436.2362.

(3*S*,5*S*,7*R*,7a*S*)-1-Benzyl-5-*t*-butoxycarbonyl-5,7-dimethyl-7-methoxycarbonyl-3-phenylhexahydropyrrolo[1,2-*a*]imidazole (16b). Prepared from (*S*)-1-benzyl-4-phenyl-4,5-dihydroimidazole (**8a**, 2.00 g, 8.48 mmol) by the method described above for the preparation of **9a** but using *t*-butyl 2-bromopropanoate (1.85 g, 8.48 mmol), methyl 2-methylpropenoate (2.72 mL, 2.55 g, 25.4 mmol) and DBU (1.26 mL, 1.28 g, 8.43 mmol). Purification by column chromatography, eluting with petroleum ether (b.p. 40–60 °C) : ethyl acetate (3 : 1 v/v), yielded the title compound (910 mg, 23%) as a colourless oil, $[\alpha]_D^{22}$ 2.35 (*c* 2.06; CH_2Cl_2): ν_{max} (KBr)/cm^{-1} 3028, 2977, 2876, 2813, 1728 (s, br), 1603, 1498, 1367, 1251, 1137, 1031, 702; δ_H (400 MHz; $CDCl_3$) 1.15 (3H, s, 5-CH$_3$), 1.40 (3H, s, 7-CH$_3$), 1.47 (9H, s, C(CH$_3$)$_3$), 2.21 (1H, d, *J* = 13.6, 6-C*H*H), 2.30 (1H, t, *J* = 9.3, PhCHC*H*H), 2.83 (1H, d, *J* = 13.6, 6-CH*H*), 3.15 (1H, dd, *J* = 5.5, 9.3, PhCHCH*H*), 3.37 (1H, d, *J* = 12.7, PhC*H*H), 3.72 (3H, s, OCH$_3$), 4.12 (1H, d, *J* = 12.7, PhCH*H*), 4.31 (1H, s, 7a-CH), 4.55 (1H, dd, *J* = 5.5, 9.3, PhC*H*CH$_2$), 7.15–7.45 (10H, m, Ar–H); δ_C (100.6 MHz; $CDCl_3$) 21.3, 23.9 (2 × CH$_3$), 27.8 (C(*C*H$_3$)$_3$), 47.9 (6-CH$_2$), 52.0 (OCH$_3$), 54.2 (7-C), 60.2 (Ph*C*H$_2$), 61.9 (Ph*C*HCH$_2$), 64.3 (PhCH*C*H$_2$), 68.3 (5-C), 80.25 (*C*(CH$_3$)$_3$), 97.4 (7a-CH), 126.7, 126.7, 126.8, 128.0, 128.1, 128.55 (6 × Ar-*C*H), 138.7, 143.2 (2 × Ar-*C*), 175.4, 176.1 (2 × CO); *m*/*z* (FAB) 465 (MH$^+$, 13%), 463 (32), 407 (30), 365 (28), 364 (84), 363 (23), 308 (32), 263 (25), 237 (18), 210 (23), 208 (17), 104 (35), 91 (100). HRMS: (FAB) MH$^+$ 465.2746; $C_{28}H_{36}N_2O_4$ requires MH$^+$ 465.2753.

(3*S*,5*S*,6*R*,7*R*,7a*S*)-1-Benzyl-5-*t*-butoxycarbonyl-7-methoxycarbonyl-6-methyl-3-phenylhexahydropyrrolo[1,2-*a*]imidazole (17a). Prepared from (*S*)-1-benzyl-4-phenyl-4,5-dihydroimidazole (**8a**, 1.0 g, 4.23 mmol) by the method described above for the preparation of **9a** but using *t*-butyl bromoacetate (0.83 g, 0.68 mL, 4.23 mmol), methyl (*E*)-but-2-enoate (1.27 g, 1.35 mL, 12.70 mmol) and DBU (0.64 g, 0.63 mL, 4.23 mmol). Purification by column chromatography, eluting with petroleum ether (b.p. 40–60 °C) : ethyl acetate (10 : 1 v/v) yielded the title compound as a colourless solid (0.87 g, 46%), m.p. 138–139 °C: ν_{max} (KBr)/cm^{-1} 2971, 1724, 1714, 1258, 1156, 1028, 698; δ_H (400 MHz; C_6D_6) 1.09 (3H, d, *J* = 6.8, 6-CH$_3$), 1.29 (9H, s, C(CH$_3$)$_3$), 2.17 (1H, dd, *J* = 9.2, 9.9, PhCHC*H*H), 2.98 (1H, d, *J* = 13.2, PhC*H*H), 3.14 (2H, m, PhCHCH*H* and 6-CH), 3.38 (4H, m, OCH$_3$ and 7-CH), 3.53 (1H, d, *J* = 7.5, 5-CH), 3.96 (1H, dd, *J* = 5.3, 9.9, PhC*H*CH$_2$), 4.08 (1H, d, *J* = 13.2, PhCH*H*), 4.86 (1H, d, *J* = 6.9, 7a-CH), 7.17 (10H, m, Ar–H); δ_C (68 MHz; C_6D_6) 14.1 (6-CH$_3$), 28.0 (C(*C*H$_3$)$_3$), 36.8 (6-CH), 51.1 (OCH$_3$), 56.45 (7-CH), 59.3 (Ph*C*H$_2$), 62.7 (PhCH*C*H$_2$), 68.4 (Ph*C*HCH$_2$), 70.75 (5-CH), 80.2 (*C*(CH$_3$)$_3$), 87.5 (7a-CH), 127.2, 127.2, 127.4, 128.4, 128.5, 128.85 (6 × Ar-*C*H), 139.5, 141.7 (2 × Ar-*C*), 171.6, 172.0 (2 × CO); *m*/*z* 450 (M$^+$, 3%), 350 (29), 294 (36), 120 (23), 104 (32), 91 (100). HRMS: (EI) M$^+$ 450.2520; $C_{27}H_{34}N_2O_4$ requires M$^+$ 450.2519. Found: C, 71.9; H, 7.6; N, 6.1%; $C_{27}H_{34}N_2O_4$ requires C, 72.0; H, 7.6; N, 6.2%.

(3*R*,5*R*,6*S*,7*S*,7a*R*)-1-Benzyl-5-*t*-butoxycarbonyl-7-methoxycarbonyl-6-methyl-3-phenylhexahydropyrrolo[1,2-*a*]imidazole (17b). Prepared from (*R*)-1-benzyl-4-phenyl-4,5-dihydroimidazole (**8b**, 1.0 g, 4.23 mmol) by the method described above for the preparation of **9a** but using *t*-butyl bromoacetate (0.83 g, 0.68 mL, 4.23 mmol), methyl (*E*)-but-2-enoate (1.27 g, 1.35 mL, 12.70 mmol) and DBU (0.64 g, 0.63 mL, 4.23 mmol). Purification by column chromatography, eluting with petroleum ether (b.p. 40–60 °C) : ethyl acetate (10 : 1 v/v) yielded the title compound as a colourless solid (0.50 g, 26%), m.p. 139–140 °C: ν_{max} (KBr)/cm^{-1} 3027, 2974, 2960, 1725, 1714, 1258, 1156, 1028, 698; δ_H (270 MHz; C_6D_6) 1.09 (3H, d, *J* = 6.6, 6-CH$_3$), 1.30 (9H, s, C(CH$_3$)$_3$), 2.17 (1H, dd, *J* = 8.9, 9.9, PhCHC*H*H), 2.99 (1H, d, *J* = 13.2, PhC*H*H), 3.18 (2H, m, PhCHCH*H* and 6-CH), 3.40 (4H, m, OCH$_3$ and 7-CH), 3.52 (1H, d, *J* = 7.6, 5-CH), 3.96 (1H, dd, *J* = 5.3, 9.9, PhC*H*CH$_2$), 4.08 (1H, d, *J* = 13.2, PhCH*H*), 4.85 (1H, d, *J* = 6.7, 7a-CH), 7.19 (10H, m, Ar–H); δ_C (68 MHz; C_6D_6) 14.1 (6-CH$_3$), 28.0 (C(*C*H$_3$)$_3$), 36.8 (6-CH), 51.1 (OCH$_3$), 56.5 (7-CH), 59.3 (Ph*C*H$_2$), 62.7 (PhCH*C*H$_2$), 68.4 (Ph*C*HCH$_2$), 70.8 (5-CH), 80.2 (*C*(CH$_3$)$_3$), 87.5 (7a-CH), 127.2, 127.2, 127.4, 128.5, 128.8, 128.85 (6 × Ar-*C*H), 139.5, 141.75 (2 × Ar-*C*), 171.6, 172.0 (2 × CO); *m*/*z* (FAB) 451 (MH$^+$, 22%), 350 (15), 210 (14), 154 (37), 136 (35), 120 (23), 107 (27), 91 (78). HRMS: (FAB) MH$^+$ 451.2540; $C_{27}H_{34}N_2O_4$ requires MH$^+$ 451.2597. Found: C, 72.1; H, 7.8; N, 6.2%; $C_{27}H_{34}N_2O_4$ requires C, 72.0; H, 7.6; N, 6.2%.

Decahydropyrano[3,4-*b*]pyrrolo[1,2-*a*]imidazole (19). Prepared from (*S*)-1-benzyl-4-phenyl-4,5-dihydroimidazole (**8a**, 1.69 g, 7.17 mmol) by the method described above for the preparation of **9a** but using ethyl (*E*)-5-(bromoacetoxy)pent-2-enoate **18** (1.9 g, 7.17 mmol) and DBU (1.09 g, 1.07 mL, 7.17 mmol) added dropwise over 5 h, followed by stirring at reflux for a further hour. Purification by column chromatography, eluting with ethyl acetate : hexane (3 : 1 v/v) afforded the title compound (1.06 g, 35%) as colourless plates, m.p. 109–111 °C (from diethyl ether), $[\alpha]_D^{22}$ 34.7 (*c* 1.23; $CHCl_3$): ν_{max} (KBr)/cm^{-1} 3026, 2963, 2806, 1754(s), 1724(s), 1496, 1455, 1378, 1304, 1256, 1219, 1175, 1138, 1053, 1038, 758, 703; δ_H (400 MHz; $CDCl_3$) 1.21 (3H, t, *J* = 7.2, CH$_3$), 1.63–1.72, 2.18–2.25 (each 1H, m, C*H*$_2$CH$_2$O), 2.39 (1H, t, *J* = 9.0, PhCHC*H*H), 2.98 (1H, t, *J* = 7.0, C*H*CO$_2$Et), 3.24 (1H, d, *J* = 13.2, NC*H*HPh), 3.29 (1H, dd, *J* = 5.9, 9.0, PhCHCH*H*), 3.39–3.47 (1H, m, C*H*CH$_2$CH$_2$), 3.86 (1H, d, *J* = 7.8, CHCO$_2$), 4.06

(1H, d, J = 13.2, NCHHPh), 4.10–4.30 (4H, m, PhCHCH$_2$, CH$_2$CHHO, OCH_2CH$_3$), 4.40–4.45 (1H, m, CH$_2$CHHO), 4.65 (1H, d, J = 7.0, NCHN), 7.20–7.30 (8H, m, Ar–H), 7.40 (2H, d, J = 8.1, Ar–H); δ_C (100.6 MHz; $CDCl_3$) 13.9 (CH_3), 27.6 (CH_2CH_2O), 38.2 ($CHCH_2CH_2$), 56.7 ($CHCO_2Et$), 58.2 ($PhCH_2N$), 60.8 (CO_2CH_2), 62.8 ($PhCHCH_2$), 64.9 ($CHCO_2$), 66.45 (CH_2CH_2O), 68.3 ($PhCHCH_2$), 86.8 (NCHN), 126.4, 126.9, 127.1, 128.1, 128.15, 128.2 (6 × Ar-CH), 138.1, 140.5 (2 × Ar-C), 170.8, 171.3 (2 × CO); m/z 420 (M^+, 28%), 374 (37), 245 (30), 235 (59), 120 (44), 104 (71), 91 (100), 77 (60). Found: C, 71.75; H, 7.0; N, 6.9; $C_{25}H_{28}N_2O_4$ requires C, 71.4; H, 6.7; N, 6.7).

A crystal was mounted on a glass fibre and transferred to the diffractometer. *Crystal data* for **19**: $C_{25}H_{28}N_2O_4$, M = 420.49, monoclinic, a = 11.351(2), b = 9.7612(10), c = 19.942(3) Å, β = 91.07(2), U = 2209.1(4) Å^3, T = 298(2) K, space group $P2_1$ (No. 4), Z = 4, D_c = 1.265 g cm^{-3}, μ(Mo-Kα) = 0.050 mm^{-1}, 3081 unique reflections measured, of which 3072 were used in all calculations. Final R_1 [2091 $F > 4\sigma(F)$] = 0.0494 and wR(all F^2) was 0.141.

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