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Organic & Biomolecular Chemistry

Cite this: Org. Biomol. Chem., 2011, 9, 297

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

Raymond C. F. Jones, *^{*a*} Kevin J. Howard, ^{*b*} John S. Snaith, \ddagger^{b} Alexander J. Blake, ^{*b*} Wang-Shei Li^{*b*} and Peter J. Steel^{*c*}

Received 2nd August 2010, Accepted 27th September 2010 DOI: 10.1039/c0ob00529k

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



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

^aDepartment of Chemistry, Loughborough University, Loughborough, Leics, UK LE11 3TU. E-mail: r.c.f.jones@lboro.ac.uk; Fax: +44 1509 223925; Tel: +44 1509 222557

[‡] Present address: School of Chemistry, University of Birmingham, Birmingham B15 2TT



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 4,5dihydroimidazolium (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

^bDepartment of Chemistry, University of Nottingham, University Park, Nottingham, UK NG7 2RD

^eDepartment of Chemistry, University of Canterbury, Private Bag 4800, Christchurch, 8140, New Zealand

[†] Electronic supplementary information (ESI) available: X-Ray crystallographic data tables. CCDC reference numbers 787234–787236. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0ob00529k

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 earlier⁹) 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 'onepot' 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, BrCH₂X, CH₂=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 ¹H 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: $C-5\rightarrow C-3$, C-6(pro-S) \rightarrow C-5, C-7(Me) \rightarrow C-6(pro-R), C-7(Me) \rightarrow C-7a. This stereochemical outcome of the cvcloaddition is consistent with an endo approach of the dipole and dipolarophile, with the dipole having the anti geometry and facial selectivity provided by the 4phenyl 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, ¹H 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 ¹H NOE studies. As in the previous examples, reaction with 2methylpropenonitrile was slightly less stereoselective, affording adducts 9i (from 8a) and 9i (from 8b) along with a small amount of the product of exo addition: 9i with 9k (endo: exo 8:1); 9i with 91 (endo: exo 8:1).



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

Seeking an approach to natural products that contain a 2,4disubstituted 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 ¹H 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, ¹H NOE studies showed that the exo adducts had the opposite stereochemistry at C-7a to that predicted by our transition state model.



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



Scheme 4 Cycloaddition of azomethine ylides formed from dihydroimidazoles 8 using t-butyl bromoacetate as alkylating agent Reagents: i, BrCH₂CO₂t-Bu, CH₂=CHCO₂R, 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 2methylpropenoate, 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.



A number of key metabolites with interesting biological profiles, in particular neuroexcitatory properties, feature a 2,3,4trisubstituted 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(5H)-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 previously13 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 stereo-chemistry 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. ¹H 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. ¹³C 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. ¹H 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. ¹³C NMR spectra were determined in deuteriochloroform solution and chemical shifts quoted in ppm from tetramethylsilane as internal standard or from tetramethylsilane using CDCl₃ 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); $v_{\text{max}}(\text{film})/\text{cm}^{-1}$ 3060, 3027, 2925, 2846, 1672, 1600, 1581, 1493, 1453, 1169, 757; $\delta_{\rm H}$ (400 MHz; CDCl₃) 2.96 (1H, t, J = 9.3, PhCHCHH), 3.57 (1H, dd, J = 9.3, 10.8, PhCHCHH), 4.20, 4.34 (each 1H, d, J = 14.8, PhCH₂), 5.13 (1H, m, PhCHCH₂), 7.09 (1H, d, J = 1.6, NCHN), 7.31 (10H, m, Ar–H); $\delta_{\rm C}$ (100 MHz; CDCl₃) 51.7 (PhCH₂), 55.4 (PhCHCH₂), 69.95 (PhCHCH₂), 126.6, 127.0, 127.7, 127.75, 128.45, 128.7 (6 × Ar-CH), 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; C₁₆H₁₆N₂ requires M⁺ 236.1313. Found: C, 81.4; H, 7.1; N, 11.8%; C₁₆H₁₆N₂ 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 cm³) was added and the mixture was extracted with chloroform (3×25 mL). The combined organic phase was dried (Na₂SO₄) 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); v_{max} (film)/cm⁻¹ 3061, 3028, 2924, 2844, 1670, 1600, 1581, 1493, 1453, 1168, 757; $\delta_{\rm H}$ (250 MHz; CDCl₃) 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, PhC*H*₂), 5.14 (1H, m, PhC*H*CH₂), 7.10 (1H, d, *J* = 1.8, NCHN), 7.28 (10H, m, Ar–H); $\delta_{\rm c}$ (68 MHz; CDCl₃) 51.3 (PhCH₂), 55.55 (PhCHCH₂), 69.7 (PhCHCH₂) 126.3, 126.7, 127.4, 127.5, 128.2, 128.4 (6 × Ar-CH), 136.4, 143.5 (2 × Ar–C), 156.7 (NCHN); *m/z* 236 (M⁺, 39%), 120 (52), 91(100). HRMS: (EI) M⁺ 236.1294; C₁₆H₁₆N₂ requires M⁺ 236.1313. Found: C, 81.3; H, 7.1; N, 11.9%; C₁₆H₁₆N₂ requires C, 81.3; H, 6.8; N, 11.85%.

(3S,5S,7R,7aS)-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)-1benzyl-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 $(3 \times 40 \text{ mL})$ and water (40 mL). The combined organic phase was dried (Na₂SO₄), 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%): $[\alpha]_{\rm D}^{22}$ -15.6 (c 1.04; EtOH); $v_{\rm max}$ (film)/cm⁻¹ 3062, 3028, 2949, 2804, 1731, 1454, 1265, 1205, 1132, 700; $\delta_{\rm H}$ (250 MHz; CDCl₃) 1.50 (3H, s, CH₃), 2.20 (1H, dd, J = 9.9, 13.2, 6-CHH), 2.44 (1H, dd, J = 9.2, 10.0, PhCHCHH), 2.77 (1H, dd, J = 6.8, 13.2, 6-CHH), 3.21 (2H, m, PhCHH and PhCHCHH), 3.34, 3.81 (each 3H, s, OCH₃), 4.08 (1H, dd, J = 6.8, 9.9, 5-CH), 4.13 (2H, m, PhCHH and PhCHCH₂), 4.31 (1H, s, 7a-CH), 7.25 (10H, m, Ar–H); $\delta_{\rm C}$ (100 MHz; CDCl₃) 23.0 (CH₃), 43.3 (6-CH₂), 51.5, 51.9 (2 × OCH₃), 53.3 (7-C), 58.4 (Ph CH_2), 64.7 (Ph $CHCH_2$), 67.0 (5-CH), 69.4 (PhCHCH₂), 96.2 (7a-CH), 127.0, 127.1, 127.2, 128.0, 128.2, 128.8 (6 × Ar-CH), 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; C₂₄H₂₈N₂O₄ requires M⁺ 408.2049. Found: C, 70.85; H, 7.2; N, 6.9%; C₂₄H₂₈N₂O₄ requires C, 70.6; H, 6.9; N, 6.9%.

(3R,5R,7S,7aR)-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 2methylpropenoate (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); v_{max} (film)/cm⁻¹ 3027, 2948, 2804, 1731, 1453, 1265, 1205, 1178, 701; $\delta_{\rm H}$ (400 MHz; CDCl₃) 1.50 (3H, s, CH₃), 2.20 (1H, dd, J = 9.8, 13.3, 6-CHH), 2.44 (1H, t, J = 9.6, PhCHCHH), 2.77 (1H, dd, J = 7.0, 13.3, 6-CHH), 3.22 (2H, m, PhCHH and PhCHCHH), 3.34, 3.80 (each 3H, s, OCH₃), 4.06 (1H, dd, J = 7.0, 9.8, 5-CH), 4.12 (2H, m, PhCHH and PhCHCH₂), 4.31 (1H, s, 7a-CH), 7.24 (10H, m, Ar–H); $\delta_{\rm C}$ (68 MHz; CDCl₃) 22.8 (CH3), 43.2 (6-CH₂), 51.3, 51.75 (2 × OCH₃), 53.1 (7-C), 58.2 (PhCH₂),

64.5 (PhCHCH₂), 66.8 (5-CH), 69.2 (PhCHCH₂), 96.0 (7a-CH), 126.8, 126.9, 127.0, 127.9, 128.1, 128.7 (6 × Ar-CH), 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; C₂₄H₂₈N₂O₄ requires M⁺ 408.2049. Found: C, 70.6; H, 7.2; N, 6.7%; C₂₄H₂₈N₂O₄ requires C, 70.6; H, 6.9; N, 6.9%.

(3S,5S,7R,7aS)-1-Benzyl-7-cvano-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; v_{max}(film)/cm⁻¹ 3030, 2951, 2815, 2235, 1747, 1455, 1437, 1206, 1181, 701; $\delta_{\rm H}$ (250 MHz; CDCl₃) 1.51 (3H, s, CH₃), 2.42 (1H, dd, J 6.0, 12.8, 6-CHH), 2.63 (1H, dd, J = 9.2, 10.1, PhCHCHH), 2.81 (1H, dd, J = 10.4, 12.8, 6-CHH), 3.35 (3H, s, OCH₃), 3.38 (1H, m, PhCHCHH), 3.46 (1H, d, J = 13.1, PhCHH), 3.56 (1H, dd, J = 6.0, 10.4, 5-CH), 4.01 (1H, dd, J = 5.5, 10.1, PhCHCH₂), 4.08 (1H, d, J = 13.1, PhCHH), 4.75 (1H, s, 7a-CH), 7.26 (10H, m, Ar–H); δ_c (68 MHz; CDCl₃) 20.0 (CH₃), 38.6 (7-C), 43.0 (6-CH2), 51.8 (OCH₃), 57.7 (PhCH₂), 64.2 (5-CH), 64.3 (PhCHCH₂), 69.7 (PhCHCH₂), 91.6 (7a-CH), 123.1 (CN), 126.9, 127.4, 127.6, 128.2, 128.5, 128.7 (6 × Ar-CH), 137.4, 140.0 $(2 \times \text{Ar-}C)$, 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; C₂₃H₂₅N₃O₂·0.33H₂O requires M⁺ 375.1947. Found: C, 72.25; H, 6.7; N, 10.9%. C23H25N3O2.0.33H2O requires C, 72.4; H, 6.8; N, 11.0%; and the title compound (9c) as a colourless oil $(0.16 \text{ g}, 34\%): [\alpha]_{D}^{22} -43.5 \ (c \ 0.69; \text{ EtOH}); \ v_{\text{max}}(\text{film})/\text{cm}^{-1} \ 3028,$ 2950, 2236, 1745, 1495, 1453, 1175; $\delta_{\rm H}$ (250 MHz; CDCl₃) 1.42 $(3H, s, CH_3)$, 2.36 (1H, dd, J = 10.1, 13.1, 6-CHH), 2.64 (1H, dd, J = 10.1, 13.1, 1t, J = 9.6, PhCHCHH), 2.75 (1H, dd, J = 6.2, 13.1, 6-CHH), 3.36 (3H, s, OCH₃), 3.50 (2H, m, PhCHH and PhCHCHH), 3.84 (1H, dd, J = 6.2, 10.1, 5-CH), 4.06 (1H, d, J = 12.8, PhCHH), 4.20 (1H, s, 7a-CH), 4.32 (1H, dd, J = 5.7, 9.9, PhCHCH₂), 7.23 (10H, m, Ar–H); $\delta_{\rm C}$ (68 MHz; CDCl₃) 22.1 (CH₃), 43.8 (6-CH₂), 44.5 (7-C), 51.7 (OCH₃), 58.5 (PhCH₂), 64.5 (PhCHCH₂), 65.1 (5-CH), 69.3 (PhCHCH₂), 93.5 (7a-CH), 122.2 (CN), 126.8, 127.3, 127.4, 128.1, 128.4, 128.9 (6 × Ar-CH), 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; C₂₃H₂₅N₃O₂ requires M⁺ 375.1947. Found: C, 73.2; H, 6.9; N, 10.9%; C₂₃H₂₅N₃O₂ requires C, 73.6; H, 6.7; N, 11.1%.

(3*R*,5*R*,7*S*,7*aR*)-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: v_{max} KBr/cm⁻¹ 3062, 3029, 2950, 2815, 2234, 1745, 1454, 1204, 1180, 700; $\delta_{\rm H}$ (250 MHz; CDCl₃) 1.51 (3H, s, CH₃), 2.42 (1H, dd, J = 6.0, 12.8, 6-CHH), 2.63 (1H, dd, J = 9.2, 10.0, PhCHCHH), 2.81 (1H, dd, J = 10.4, 12.8, 6-CHH), 3.34 (3H, s, OCH₃) 3.36 (1H, m, PhCHCHH), 3.46 (1H, d, J = 13.1, PhCHH), 3.56 (1H, dd, J = 6.0, 10.4, 5-CH), 4.01 (1H, dd, J = 5.5, 10.0, PhCHCH₂), 4.08 (1H, d, J = 13.0, PhCHH), 4.75 (1H, s, 7a-CH), 7.26 (10H, m, Ar–H); $\delta_{\rm C}$ (68 MHz; CDCl₃) 20.0 (CH₃), 38.6 (7-C), 43.0 (6-CH₂), 51.8 (OCH₃), 57.7 (PhCH₂), 64.2 (5-CH), 64.3 (PhCHCH₂), 69.7 (PhCHCH₂), 91.6 (7a-CH), 123.1 (CN), 126.9, 127.4, 127.55, 128.1, 128.45, 128.7 (6 × Ar-CH), 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; C₂₃H₂₅N₃O₂ requires M⁺ 375.1947. Found: C, 73.7; H, 6.9; N, 11.5%; C₂₃H₂₅N₃O₂ 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); v_{max} KBr/cm⁻¹ 3028, 2948, 2811, 2236, 1744, 1454, 1204, 1176, 701; $\delta_{\rm H}$ (250 MHz; CDCl₃) 1.41 (3H, s, CH_3), 2.35 (1H, dd, J = 10.1, 13.1, 6-CHH), 2.63 (1H, t, J = 9.7, PhCHCHH), 2.72 (1H, dd, J = 6.1, 13.1, 6-CHH),3.35 (3H, s, OCH₃), 3.50 (2H, m, PhCHH and PhCHCHH), 3.83 (1H, dd, J = 6.1, 10.1, 5-CH), 4.04 (1H, d, J = 12.9, PhCHH), 4.18 (1H, s, 7a-CH), 4.30 (1H, dd, J = 5.7, 9.7, PhCHCH₂), 7.33 (10H, m, Ar–H); δ_c (68 MHz; CDCl₃) 22.1 (CH₃), 43.8 (6-CH₂), 44.6 (7-C), 51.75 (OCH₃), 58.5 (PhCH₂), 64.5 (PhCHCH₂), 65.1 (5-CH), 69.4 (PhCHCH₂), 93.55 (7a-CH), 122.2 (CN), 126.85, 127.4, 127.4, 128.1, 128.4, 128.9 (6 × Ar-CH), 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; C₂₃H₂₅N₃O₂ requires M⁺ 375.1947. Found: C, 73.9; H, 6.6; N, 11.3%; C₂₃H₂₅N₃O₂ requires C, 73.6; H, 6.7; N, 11.2%.

(3S,5S,7R,7aS)-1-Benzyl-5-t-butoxycarbonyl-7-methoxycarbonyl-7-methyl-3-phenylhexahydropyrrolo[1,2-a]imidazole (9g). from (S)-1-benzyl-4-phenyl-4,5-dihydroimidazole Prepared (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%): v_{max} (film)/cm⁻¹ 3061, 3027, 2976, 2803, 1731, 1453, 1366, 1263, 1151, 700; $\delta_{\rm H}$ (250 MHz; CDCl₃) 1.12 (9H, s, C(CH₃)₃), 1.49 (3H, s, 7-CH₃), 2.18 (1H, dd, J = 9.8, 13.2, 6-CHH), 2.41 (1H, t, J = 9.7, PhCHCHH), 2.71 (1H, dd, J = 6.6, 13.2, 6-CHH), 3.20 (2H, m, PhCHH and PhCHCHH), $3.80 (3H, s, OCH_3), 3.90 (1H, dd, J = 6.6, 9.8, 5-CH), 4.10 (2H, 3.80 (3H, s, OCH_3)), 3.90 (1H, dd, J = 6.6, 9.8, 5-CH), 4.10 (2H, 3.80 (3H, s, OCH_3)), 3.90 (1H, dd, J = 6.6, 9.8, 5-CH), 4.10 (2H, 3.80 (3H, s, OCH_3)), 3.90 (1H, dd, J = 6.6, 9.8, 5-CH), 4.10 (2H, 3.80 (3H, s, OCH_3)), 3.90 (1H, dd, J = 6.6, 9.8, 5-CH), 4.10 (2H, 3.80 (3H, s, OCH_3)), 3.90 (3H, s, OCH_3))$ m, PhCHH and PhCHCH₂), 4.31 (1H, s, 7a-CH), 7.28 (10H, m, Ar–H); δ_c (68 MHz; CDCl₃) 23.0 (7-CH₃), 27.5 (C(CH₃)₃), 43.3 (6-CH₂), 51.8 (OCH₃), 53.2 (7-C), 58.4 (PhCH₂), 64.9 (PhCHCH₂), 68.2 (5-CH), 69.4 (PhCHCH₂), 80.3 (C(CH₃)₃), 96.4 (7a-CH), 127.0, 127.1, 127.3, 128.0, 128.1, 128.8 (6 × Ar-CH), 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; C₂₇H₃₄N₂O₄ requires M⁺ 450.2519. Found: C, 72.1; H, 7.9; N, 6.1%; C₂₇H₃₄N₂O₄ 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) Å³; T = 293 K, μ (Mo-K α) = 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 $F_{\circ} > 4\sigma(F_{\circ})$.

(3R,5R,7S,7aR)-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%): v_{max} (film)/cm⁻¹ 2978, 1732, 1455, 1264, 1152, 701; $\delta_{\rm H}$ (400 MHz; CDCl₃) 1.12 (9H, s, C(CH₃)₃), 1.49 (3H, s, 7-CH₃), 2.18 (1H, dd, J = 9.8, 13.2, 6-CHH), 2.41 (1H, t, J = 9.7, PhCHCHH), 2.71 (1H, dd, J = 6.6, 13.2, 6-CHH), 3.21 (2H, m, PhCHH and PhCHCHH), 3.80 (3H, s, OCH₃), 3.90 (1H, dd, J = 6.6, 9.8, 5-CH), 4.11 (2H, m, PhCHH and PhCHCH₂), 4.31 (1H, s, 7a-CH), 7.29 (10H, m, Ar-H); $\delta_{\rm C}$ (68 MHz; CDCl₃) 22.9 (7-CH₃), 27.3 (C(CH₃)₃), 43.2 (6-CH₂), 51.6 (OCH₃), 53.0 (7-C), 58.2 (PhCH₂), 64.8 (PhCHCH₂), 68.0 (5-CH), 69.3 (PhCHCH₂), 80.1 (C(CH₃)₃), 96.3 (7a-CH), 126.8, 126.9, 127.1, 127.85, 128.0, 128.6 (6 × Ar-CH), 138.2, 141.65 $(2 \times \text{Ar-}C)$, 173.2, 175.2 $(2 \times \text{CO})$; m/z 450 (M⁺, 1%), 350 (44), 294 (48), 249 (33), 104 (38), 91 (100). HRMS: (EI) M⁺ 450.2521; C₂₇H₃₄N₂O₄ requires M⁺ 450.2519. Found: C, 72.1; H, 7.9; N, 6.1%; C₂₇H₃₄N₂O₄ requires C, 72.0; H, 7.6; N, 6.2%.

(3S,5S,7R,7aS)-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)]: v_{max} (CHCl₃)/cm⁻¹ 2822, 2236, 1732, 1369, 1153; $\delta_{\rm H}$ (250 MHz; CDCl₃) 1.13 (9H, s, C(CH₃)₃), 1.50 (3H, s, 7-CH₃), 2.38 (1H, dd, J = 5.8, 12.7, 6-CHH), 2.62 (1H, apparent t, J = 9.5, PhCHCHH), 2.77 (1H, dd, J = 10.7, 12.7, 6-CHH), 3.35 (1H, dd, J = 5.5, 8.9, PhCHCHH), 3.45 (2H, m, PhCHH and 5-CH), 3.99 (1H, dd, J = 5.5, 9.9, PhCHCH₂), 4.08 (1H, d, J = 13.0, PhCHH), 4.75 (1H, s, 7a-CH), 7.27 (10H, m, Ar-H); $\delta_{\rm C}$ (68 MHz; CDCl₃) 20.15 (7-CH₃), 27.4 (C(CH₃)₃), 38.5 (7-C), 43.4 (6-CH₂), 57.8 (PhCH₂), 64.7 (PhCHCH₂), 65.6 (5-CH), 69.8 (PhCHCH₂), 81.3 (C(CH₃)₃), 92.0 (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 (39%), 316 (12), 294 (48), 249 (32), 104 (40), 91 (100). Found: C, 74.85; H, 7.7; N, 10.0%; C₂₆H₃₁N₃O₂ 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); v_{max} (KBr)/cm⁻¹ 3072, 3029, 2981, 2959, 2943, 2234, 1736, 1454, 1443, 1366, 1215, 1152, 1079, 702; $\delta_{\rm H}$ (400 MHz; CDCl₃) 1.13 (9H, s, C(CH₃)₃), 1.41 (3H, s, 7-CH₃), 2.32 (1H, dd, J = 10.1, 13.1, 6-CHH), 2.59 (1H, apparent t, J = 9.5, PhCHCHH), 2.67 (1H, dd, J = 6.0, 13.1, 6-CHH), 3.47 (2H, m, PhCHH and PhCHCHH), 3.71 (1H, dd, J = 6.0, 10.1, 5-CH), 4.04 (1H, d, J = 12.7, PhCHH), 4.17 (1H, s, 7a-CH), 4.29 (1H, dd, J = 5.8, 9.8, PhCHCH₂), 7.31 (10H, m, Ar–H); $\delta_{\rm C}$ (68 MHz; CDCl₃) 22.25 (7-CH₃), 27.4 (C(CH₃)₃), 43.9 (6-CH2), 44.4 (7-C), 58.5 (PhCH₂), 64.7 (PhCHCH₂), 66.4 (5-CH), 69.4 (PhCHCH₂), 81.1 (C(CH₃)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; C₂₆H₃₁N₃O₂ requires M⁺ 417.2416. Found: C, 74.75; H, 7.8; N, 10.1%; C₂₆H₃₁N₃O₂ requires C, 74.8; H, 7.5; N, 10.1%.

(3R,5R,7S,7aR)-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 exoadduct (91) as a colourless solid (24 mg, 3%), m.p. 99–101 °C: v_{max} (KBr)/cm⁻¹ 2981, 2233, 1724, 1636, 1366, 1162, 698; $\delta_{\rm H}$ (400 MHz; CDCl₃) 1.13 (9H, s, C(CH₃)₃), 1.49 (3H, s, 7-CH₃), 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, PhCHCH₂), 4.07 (1H, d, J = 13.1, PhCHH), 4.75 (1H, s, 7a-CH), 7.39 (10H, m, Ar–H); $\delta_{\rm C}$ (68 MHz; CDCl₃) 20.1 (7-CH₃), 27.4 (C(CH₃)₃), 38.5 (7-C), 43.4 (6-CH₂), 57.8 (PhCH₂), 64.7 (PhCHCH₂), 65.6 (5-CH), 69.8 (PhCHCH₂), 81.3 (C(CH₃)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%; C₂₆H₃₁N₃O₂ 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); v_{max} (KBr)/cm⁻¹ 2978, 1732, 1455, 1264, 1152 and 701; $\delta_{\rm H}$ (400 MHz; CDCl₃) 1.13 (9H, s, $C(CH_3)_3$, 1.45 (3H, s, 7-CH₃), 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-CH*H*), 3.53 (2H, m, PhC*H*H and PhCHCH*H*), 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, PhC*H*CH₂), 7.29 (10H, m, Ar–H); $\delta_{\rm C}$ (68 MHz; CDCl₃) 22.1 (7-CH₃), 27.2 (C(CH₃)₃), 43.7 (6-CH₂), 44.2 (7-C), 58.3 (PhCH₂), 64.55 (PhCHCH₂), 66.25 (5-CH), 69.2 (PhCHCH₂), 80.8 (C(CH₃)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; C₂₆H₃₁N₃O₂ requires MH⁺ 418.2494. Found: C, 74.7; H, 7.5; N, 9.9%; C₂₆H₃₁N₃O₂ requires C, 74.8; H, 7.5; N, 10.1%.

(3*S*,5*S*,7*R*,7*aS*)-1-Benzyl-5-*t*-butoxycarbonyl-7-methoxycarbonyl-3-phenylhexahydropyrrolo[1,2-*a*]imidazole (13a). Prepared from (*S*)-1-benzyl-4-phenyl-4,5-dihydroimidazole (13a). Prepared mol) 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); v_{max} (KBr)/cm⁻¹ 3032, 2980, 2946, 1728, 1367, 1166, 1152, 697; δ_H (400 MHz; CDCl₃) 1.22 (9H, s, C(CH₃)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, OCH₃), 3.80 (1H, t, *J* = 6.8, 5-CH), 4.08 (1H, d, *J* = 12.9, PhCHH), 4.13 (1H, m, PhCHCH₂), 4.68 (1H, d, *J* = 6.6, 7a-CH), 7.27 (10H, m, Ar–H); δ_C (68 MHz; CDCl₃) 27.4 (C(CH₃)₃), 32.6 (6-CH2), 47.9 (7-CH), 51.3 (OCH₃), 58.2 (PhCH₂), 64.0 (PhCHCH₂), 66.8 (5-CH), 68.6 (PhCHCH₂), 80.1 (*C*(CH₃)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; C₂₆H₃₂N₂O₄ requires M⁺ 436.2362. Found: C, 71.6; H, 7.6; N, 6.4%; C₂₆H₃₂N₂O₄ 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**: C₂₆H₃₂N₂O₄, *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) Å³, *T* = 150(2) K, μ (Mo-K α) = 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 σ (*F*)] = 0.0734 and *wR*(all *F*²) was 0.146.

(3R,5R,7S,7aR)-1-Benzyl-5-t-butoxycarbonyl-7-methoxycarbonyl-3-phenylhexahydropyrrolo[1,2-alimidazole (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); v_{max} (KBr)/cm⁻¹ 3032, 2980, 2946, 1728, 1367, 1166, 1152, 697; δ_H (270 MHz; CDCl₃) 1.21 (9H, s, C(CH₃)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, OCH₃), 3.82 (1H, t, J = 6.9, 5-CH), 4.08 (1H, d, J = 13.2, PhCHH), 4.13 (1H, m, PhCHCH₂), 4.68 (1H, d, J = 6.3, 7a-CH), 7.28 (10H, m, Ar–H); δ_{C} (68 MHz; CDCl₃) 27.4 (C(CH₃)₃), 32.65 (6-CH2), 48.0 (7-CH), 51.4 (OCH₃), 58.3 (PhCH₂), 64.0 (PhCHCH₂), 66.8 (5-CH), 68.7 (PhCHCH₂), 80.2 (C(CH₃)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%; C₂₆H₃₂N₂O₄ requires C, 71.5; H, 7.4; N, 6.4%.

(3*S*,5*S*,7*R*,7*aS*)-1-Benzyl-5,7-bis(t-butoxycarbonyl)-3-phenylhexahydropyrrolo[1,2-*a*]imidazole (13c). Prepared from (*S*)-1benzyl-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)], $[\alpha]_{\rm D}^{22}$ -27.0 (c 0.97; EtOH): $v_{\rm max}$ (KBr)/cm⁻¹ 2927, 1734, 1628, 1384, 1369, 1145, 702; $\delta_{\rm H}$ (400 MHz; CDCl₃) 1.22, 1.49 (18H, 2×s, 2× $C(CH_3)_3$, 2.22 (1H, m, 6-CHH), 2.43 (1H, t, J = 9.5, PhCHCHH), 2.52 (1H, m, 6-CHH), 3.16 (1H, dd, J = 6.5, 11.8, 7-CH), 3.26 (2H, m, PhCHH and PhCHCHH), 3.71(1H, t, J = 7.0, 5-CH), 4.13(2H, J)m, PhCHH and PhCHCH₂), 4.61 (1H, d, J = 6.5, 7a-CH), 7.26 (10H, m, Ar–H); $\delta_{\rm C}$ (68 MHz; CDCl₃) 27.5, 27.75 (2 × C(CH₃)₃), 33.1 (6-CH₂), 49.2 (7-CH), 58.35 (PhCH₂), 63.9 (PhCHCH₂), 67.0 (5-CH), 68.9 (PhCHCH₂), 80.1, 80.5 ($2 \times C(CH_3)_3$), 88.4 (7a-CH), 126.8, 126.9, 127.0, 127.9, 129.0 (6 × Ar-CH), 137.9, 141.6 $(2 \times \text{Ar-}C)$, 171.6, 173.15 $(2 \times \text{CO})$; m/z 478 (M⁺, 5%), 350 (53), 294 (62), 249 (35), 235 (25), 120 (17), 104 (42), 91 (100). HRMS: (EI) M⁺ 478.2853; C₂₉H₃₈N₂O₄ requires M⁺ 478.2832. Found: C, 72.6; H, 8.25; N, 6.0%; C₂₉H₃₈N₂O₄ requires C, 72.8; H, 8.0; N, 5.9%; and the *exo*-adduct (13e) as a colourless oil (70 mg, 3%): v_{max} (KBr)/cm⁻¹ 3062, 3028, 2977, 2931, 1732, 1628, 1367, 1150, 700; $\delta_{\rm H}$ (400 MHz; CDCl₃) 1.14, 1.47 (18H, 2 × s, 2 × C(CH₃)₃), 2.31 $(1H, t, J = 9.5, PhCHCHH), 2.46, 2.56 (2H, 2 \times m, 6-CH_2), 2.99$ (1H, m, 7-CH), 3.21 (1H, d, J = 12.9, PhCHH), 3.32 (1H, dd, J = 6.3, 9.3, PhCHCHH), 3.58 (1H, dd, J = 6.2, 9.4, 5-CH), 4.06 (2H, m, PhCHH and PhCHCH₂), 4.39 (1H, d, J = 4.5, 7a-CH), 7.26 (10H, m, Ar–H); δ_{C} (68 MHz; CDCl₃) 27.5, 28.05 (2 × C(CH₃)₃), 34.0 (6-CH₂), 50.5 (7-CH), 56.6 (PhCH₂), 64.0 (PhCHCH₂), 68.75 (Ph*C*HCH₂), 69.0 (5-CH), 80.7, 81.0 (2 × *C*(CH₃)₃), 89.6 (7a-C), 126.9, 126.9, 127.1, 128.1, 128.1, 128.8 (6×Ar-CH), 138.35, 142.6 $(2 \times \text{Ar-}C)$, 171.7, 171.9 $(2 \times \text{CO})$; m/z 478 (M⁺, 21%), 350 (85), 294 (71), 249 (38), 235 (30), 104 (27), 91 (100). HRMS: (EI) M⁺ 478.2848; C₂₉H₃₈N₂O₄ requires M⁺ 478.2832. Found: C, 72.1; H, 8.1; N, 5.7%; C₂₉H₃₈N₂O₄·0.2H₂O requires C, 72.1; H, 8.2; N, 5.7%.

(3R,5R,7S,7aR)-1-Benzyl-5,7-bis(t-butoxycarbonyl)-3-phenylhexahydropyrrolo[1,2-a]imidazole (13d). Prepared from (R)-1benzyl-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): v_{max} (KBr)/cm⁻¹ 3031, 2975, 2935, 1733, 1369, 1146, 702; $\delta_{\rm H}$ (400 MHz; CDCl₃) 1.21, 1.48 (18H, 2 × s, 2 × C(CH₃)₃), 2.23 (1H, m, 6-CHH), 2.43 (1H, t, J = 9.6, PhCHCHH), 2.55 (1H, m, 6-CHH), 3.16 (1H, dd, J = 6.5, 11.9, 7-CH), 3.26 (2H, m, PhCHH and PhCHCHH), 3.73 (1H, t, J = 6.9, 5-CH), 4.13 (2H, m, PhCHH and PhCHCH₂), 4.62 (1H, d, J = 6.5, 7a-CH), 7.27 (10H, m, ArH); $\delta_{\rm C}$ (68 MHz; CDCl₃) 27.5, 28.2 (2 × C(CH₃)₃), 33.1 (6-CH₂), 49.2 (7-CH), 58.4 (PhCH₂), 63.9 (PhCHCH₂), 67.0 (5-CH), 69.0 (PhCHCH₂), 80.2, 80.5 (2 × C(CH₃)₃), 88.5 (7a-CH), 126.8, 126.95, 127.0, 127.9, 129.0 (6 × Ar-CH), 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; C₂₉H₃₈N₂O₄ requires M⁺ 478.2832. Found: C, 72.5; H, 8.1; N, 5.8%; C₂₉H₃₈N₂O₄ requires C, 72.8; H, 8.0; N, 5.9%; and the exo-adduct (13f) as a colourless oil (22 mg, 2%): $v_{\text{max}}(\text{film})/\text{cm}^{-1}$ 2977, 1729, 1367, 1150, 700; $\delta_{\rm H}$ (400 MHz; CDCl₃) 1.14, 1.47 $(18H, 2 \times s, 2 \times C(CH_3)_3), 2.30 (1H, t, J = 9.5, PhCHCHH), 2.46,$ 2.57 (2H, 2 × m, 6-CHH), 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*CH₂), 4.38 (1H, d, J = 4.5, 7a-CH), 7.26 (10H, m, Ar–H); $\delta_{\rm C}$ (100 MHz; CDCl₃) 27.5, 28.1 (2 × C(CH₃)₃), 34.05 (6-CH₂), 50.7 (7-CH), 56.7 (PhCH₂), 64.1 (PhCHCH₂), 68.9 (PhCHCH₂), 69.1 (5-CH), 80.7, 81.0 (2 × C(CH₃)₃), 89.6 (7a-CH), 126.85, 126.9, 127.0, 128.1, 128.3, 128.8 (6 × Ar-CH), 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; C₂₉H₃₈N₂O₄ requires M⁺ 478.2832.

(3S,5S,7R,7aS)-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 $(3 \times 30 \text{ mL})$ and water (30 mL). The organic phase was dried (Na₂SO₄), 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): v_{max} (KBr)/cm⁻¹ 2927, 1734, 1628, 1384, 1145; $\delta_{\rm H}$ (250 MHz; CDCl₃) 1.20 (9H, s, C(CH₃)₃), 2.18 (1H, m, 6-CHH), 2.46 (2H, m, PhCHCHH and 6-CHH), 3.32 (2H, m, PhCHH and PhCHCHH), 3.67 (1H, t, J = 6.5, PhCHCH₂), 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, PhCHH), 4.97 (1H, d, J = 6.2, 7a-CH), 7.59 (15H, m, Ar–H); $\delta_{\rm C}$ (68 MHz; CDCl₃) 27.55 (C(CH₃)₃), 32.0 (6-CH₂), 59.1 (PhCH₂), 63.45 (PhCHCH₂), 64.6 (PhCHCH₂), 66.45 (7-CH), 67.8 (5-CH), 81.0 (C(CH₃)₃), 87.7 (7a-CH), 126.9, 127.2, 128.1, 128.3, 129.1, 129.2 (9 × Ar-CH), 133.2, 138.3, 140.6 $(3 \times \text{Ar-}C)$, 171.9 (CO); m/z 461 (M⁺-C₄H₉, 6%), 417 (11), 350 (61), 294 (63), 249 (45), 235 (36), 120 (50), 104 (59), 91 (100). HRMS: (EI) M^+ -C₄H₉ 461.1536; C₃₀H₃₄N₂O₄S requires M^+ -C₄H₉ 461.1535. Found: C, 69.4; H, 6.9; N, 5.5%; C₃₀H₃₄N₂O₄S requires C, 69.5; H, 6.6; N, 5.4%.

(3S,5S,7R,7aS)-7-Acetyl-1-Benzyl-5-t-butoxycarbonyl-3-phenylhexahydropyrrolo[1,2-a]imidazole (15). Prepared from (S)-1benzyl-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-2one (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%): $\delta_{\rm H}$ (270 MHz; CDCl₃) 1.14 (9H, s, C(CH₃)₃), 2.07 (3H, s, COCH₃), 2.42 (3H, m, PhCHCHH and 6-CH₂), 3.01 (1H, m, 7-CH), 3.41 (2H, m, PhCHH and PhCHCHH), 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, PhCHCH₂), 4.46 (1H, d, J = 4.3, 7a-CH), 7.29 (10H, m, Ar–H); $\delta_{\rm C}$ (68 MHz; CDCl₃) 27.4 (C(CH₃)₃), 28.8 (COCH₃), 33.9 (6-CH₂), 57.0 (PhCH₂), 57.1 (7-CH), 64.5 (PhCHCH₂), 68.8 (PhCHCH₂), 69.1 (5-CH), 80.7 (C(CH₃)₃), 88.2 (7a-CH), 126.8, 127.1, 128.0, 128.2, 128.8 (6 × Ar-CH), 138.2, 142.5 (2 × Ar-C), 171.5, 173.15 $(2 \times CO).$

(3S,5S,7R,7aS)-1-Benzyl-5,7-dimethyl-5-ethoxycarbonyl-7methoxycarbonyl-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; CHCl₃): $v_{\rm max}$ (film)/cm⁻¹ 2981, 2949, 1733, 1495, 1454, 1252, 1135, 702; $\delta_{\rm H}$ (400 MHz; CDCl₃) 1.25–1.28 (6H, m, CH₃CH₂ and 5-CH₃), 1.37 (3H, s, 7-CH₃), 2.24 (1H, d, J = 13.6, 6-CHH), 2.30-2.32 (1H, m, PhCHCHH), 2.88 (1H, d, J = 13.6, 6-CHH), 3.16 (1H, dd, J = 5.5, 9.0, PhCHCHH), 3.38 (1H, d, J = 12.7, PhCHH), 3.72 (3H, s, OCH₃), 4.12-4.20 (3H, m, CH₃CH₂O and PhCHH), 4.33 (1H, s, 7a-CH), 4.54 (1H, dd, J = 5.5, 9.4, PhCHCH₂), 7.14–7.28 (8H, m, Ar–H), 7.42 (2H, d, J = 8.0, Ar–H); $\delta_{\rm C}$ (100.6 MHz; CDCl₃) 14.2, 21.35, 23.95 (3×CH₃), 48.1 (6-CH₂), 51.9 (OCH₃), 54.3 (7-C), 59.7 (PhCH₂), 60.8 (CH₃CH₂), 62.0 (PhCHCH₂), 64.35 (PhCHCH₂), 68.0 (5-C), 97.4 (7a-CH), 126.6, 126.9, 128.1, 128.6 (6 × Ar-CH, 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; C₂₆H₃₂N₂O₄ requires M⁺ 436.2362.

(3S,5S,7R,7aS)-1-Benzyl-5-t-butoxycarbonyl-5,7-dimethyl-7methoxycarbonyl-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; CH₂Cl₂): v_{max} (KBr)/cm⁻¹ 3028, 2977, 2876, 2813, 1728 (s, br), 1603, 1498, 1367, 1251, 1137, 1031, 702; $\delta_{\rm H}$ (400 MHz; CDCl₃) 1.15 (3H, s, 5-CH₃), 1.40 (3H, s, 7-CH₃), 1.47 (9H, s, C(CH₃)₃), 2.21 (1H, d, J = 13.6, 6-CHH), 2.30 (1H, t, J = 9.3, PhCHCHH), 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, PhCHH), 3.72 (3H, s, OCH₃), 4.12 (1H, d, J=12.7, PhCHH), 4.31 (1H, s, 7a-CH), 4.55 (1H, dd, J = 5.5, 9.3, PhCHCH₂), 7.15-7.45 (10H, m, Ar–H); $\delta_{\rm C}$ (100.6 MHz; CDCl₃) 21.3, 23.9 (2 × CH₃), 27.8 (C(CH₃)₃), 47.9 (6-CH₂), 52.0 (OCH₃), 54.2 (7-C), 60.2 (PhCH₂), 61.9 (PhCHCH₂), 64.3 (PhCHCH₂), 68.3 (5-C), 80.25 (C(CH₃)₃), 97.4 (7a-CH), 126.7, 126.7, 126.8, 128.0, 128.1, 128.55 (6 × Ar-CH), 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; C₂₈H₃₆N₂O₄ requires MH⁺ 465.2753.

(3S,5S,6R,7R,7aS)-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: v_{max} (KBr)/cm⁻¹ 2971, 1724, 1714, 1258, 1156, 1028, 698; $\delta_{\rm H}$ (400 MHz; C₆D₆) 1.09 (3H, d, J = 6.8, 6-CH₃), 1.29 (9H, s, C(CH₃)₃), 2.17 (1H, dd, J = 9.2, 9.9, PhCHCHH), 2.98 (1H, d, J = 13.2, PhCHH), 3.14 (2H, m, PhCHCHH and 6-CH), 3.38 (4H, m, OCH₃ and 7-CH), 3.53 (1H, d, J = 7.5, 5-CH), 3.96 (1H, dd, J = 5.3, 9.9, PhCHCH₂), 4.08 (1H, d, J = 13.2, PhCHH), 4.86 (1H, d, J = 6.9, 7a-CH), 7.17 (10H, m, Ar-H); δ_{C} (68 MHz; $C_{6}D_{6}$) 14.1 (6-CH₃), 28.0 (C(CH₃)₃), 36.8 (6-CH), 51.1 (OCH₃), 56.45 (7-CH), 59.3 (PhCH₂), 62.7 (PhCHCH₂), 68.4 (PhCHCH₂), 70.75 (5-CH), 80.2 (C(CH₃)₃), 87.5 (7a-CH), 127.2, 127.2, 127.4, 128.4, 128.5, 128.85 (6 × Ar-CH), 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; C₂₇H₃₄N₂O₄ requires M⁺ 450.2519. Found: C, 71.9; H, 7.6; N, 6.1%; C₂₇H₃₄N₂O₄ requires C, 72.0; H, 7.6; N, 6.2%.

(3R, 5R, 6S, 7S, 7aR)-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: *v*_{max} (KBr)/cm⁻¹ 3027, 2974, 2960, 1725, 1714, 1258, 1156, 1028, 698; $\delta_{\rm H}$ (270 MHz; C₆D₆) 1.09 (3H, d, J = 6.6, 6-CH₃), 1.30 (9H, s, $C(CH_3)_3$, 2.17 (1H, dd, J = 8.9, 9.9, PhCHCHH), 2.99 (1H, d, J = 13.2, PhCHH), 3.18 (2H, m, PhCHCHH and 6-CH), 3.40 (4H, m, OCH₃ and 7-CH), 3.52 (1H, d, J = 7.6, 5-CH), 3.96 (1H, dd, J = 5.3, 9.9, PhCHCH₂), 4.08 (1H, d, J = 13.2, PhCHH), 4.85 $(1H, d, J = 6.7, 7a-CH), 7.19 (10H, m, Ar-H); \delta_{C} (68 MHz; C_6D_6)$ 14.1 (6-CH₃), 28.0 (C(CH₃)₃), 36.8 (6-CH), 51.1 (OCH₃), 56.5 (7-CH), 59.3 (PhCH₂), 62.7 (PhCHCH₂), 68.4 (PhCHCH₂), 70.8 (5-CH), 80.2 (C(CH₃)₃), 87.5 (7a-CH), 127.2, 127.2, 127.4, 128.5, 128.8, 128.85 (6 × Ar-CH), 139.5, 141.75 (2 × Ar-C), 171.6, 172.0 $(2 \times CO); m/z$ (FAB) 451 (MH⁺, 22%), 350 (15), 210 (14), 154 (37), 136 (35), 120 (23), 107 (27), 91 (78). HRMS: (FAB) MH⁺ 451.2540; C₂₇H₃₄N₂O₄ requires MH⁺ 451.2597. Found: C, 72.1; H, 7.8; N, 6.2%; C₂₇H₃₄N₂O₄ 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; CHCl₃): *v*_{max} (KBr)/cm⁻¹ 3026, 2963, 2806, 1754(s), 1724(s), 1496, 1455, 1378, 1304, 1256, 1219, 1175, 1138, 1053, 1038, 758, 703; $\delta_{\rm H}$ (400 MHz; CDCl₃) 1.21 (3H, t, J = 7.2, CH₃), 1.63– 1.72, 2.18–2.25 (each 1H, m, CH_2CH_2O), 2.39 (1H, t, J = 9.0, PhCHCHH), 2.98 (1H, t, J = 7.0, CHCO₂Et), 3.24 (1H, d, J =13.2, NCHHPh), 3.29 (1H, dd, J = 5.9, 9.0, PhCHCHH), 3.39-3.47 (1H, m, CHCH₂CH₂), 3.86 (1H, d, J = 7.8, CHCO₂), 4.06 (1H, d, J = 13.2, NCH*H*Ph), 4.10–4.30 (4H, m, PhC*H*CH₂, CH₂C*H*HO, OC*H*₂CH₃), 4.40–4.45 (1H, m, CH₂CH*H*O), 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); $\delta_{\rm c}$ (100.6 MHz; CDCl₃) 13.9 (CH₃), 27.6 (CH₂CH₂O), 38.2 (CHCH₂CH₂), 56.7 (CHCO₂Et), 58.2 (PhCH₂N), 60.8 (CO₂CH₂), 62.8 (PhCHCH₂), 64.9 (CHCO₂), 66.45 (CH₂CH₂O), 68.3 (PhCHCH₂), 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; C₂₅H₂₈N₂O₄ 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**: C₂₅H₂₈N₂O₄, M = 420.49, monoclinic, a = 11.351(2), b = 9.7612(10), c = 19.942(3) Å, $\beta = 91.07(2)$, U = 2209.1(4) Å³, T = 298(2) K, space group $P2_1$ (No. 4), Z = 4, $D_c = 1.265$ g cm⁻³, μ (Mo-K α) = 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.

Acknowledgements

We thank EPSRC for postdoctoral funding (J. S. S., K. J. H.), University of Nottingham for a studentship (K. J. H.), Rhone-Poulenc Agriculture for additional financial support (K. J. H.), Dr D. Hawkins for helpful discussions, and the EPSRC National Mass Spectrometry Service Centre (Swansea) for some MS data.

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