1,7-Electrocyclisation of non-stabilised α,β:γ,δ-unsaturated azomethine ylides

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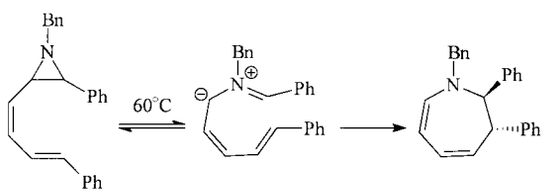
The generation of α,β:γ,δ-unsaturated azomethine ylides **8** is described, starting from *N*-substituted α-amino acids **7** and aldehydes **6**, **12**. These azomethine ylides undergo a 1,7-electrocyclisation, followed by a [1,5]-hydrogen shift, to give the dihydrobenzazepines **10a**–**f** and **13**.

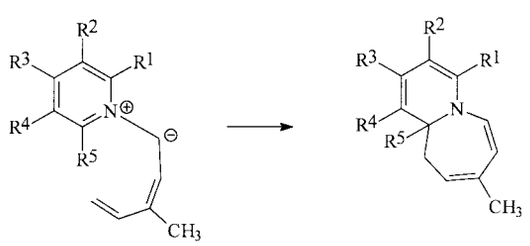
The 1,7-electrocyclisation of dipolar intermediates constitutes a general route to a variety of seven-membered heterocycles.[1] Very few examples of the 1,7-electrocyclisations of azomethine ylides have, however, been reported. Azomethine ylides have been postulated as intermediates in some complex, multi-step rearrangements but the only definitive examples are the thermal ring-opening of the aziridine **1** to give the azomethine ylide **2**, which subsequently cyclises to the dihydroazepine **3** (Scheme 1),[2] and the recent report by Marx and Eberbach on



1 2 3

Scheme 1

the 1,7-electrocyclisations of butadienyl ylides **4** to dihydropyrido[2,1-*a*]azepines **5** (Scheme 2).[3]



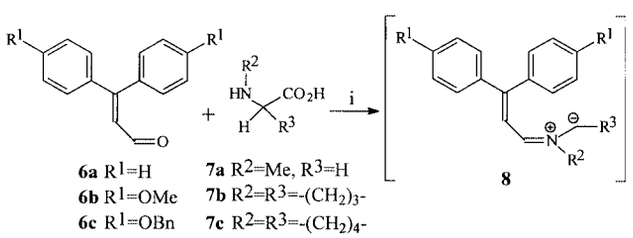
4 5

Scheme 2

We wish to report here the generation of non-stabilised α,β:γ,δ-unsaturated azomethine ylides by the decarboxylation method, and their subsequent cyclisation to dihydro-2-benzazepines.[4]

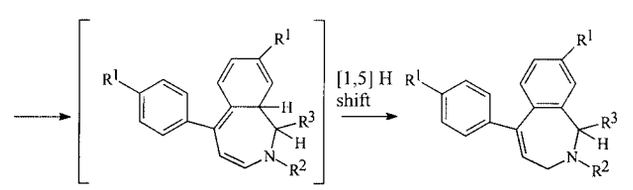
Results and discussion

Our initial studies involved the generation of non-stabilised azomethine ylides **8** by the decarboxylation method,[5] involving



6a R1=H **7a** R2=Me, R3=H
6b R1=OMe **7b** R2=R3=-(CH2)3-
6c R1=OBn **7c** R2=R3=-(CH2)4-

8



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10a R1=H, R2=Me, R3=H
10b R1=OMe, R2=Me, R3=H
10c R1=OBn, R2=Me, R3=H
10d R1=H, R2=R3=-(CH2)3-
10e R1=OBn, R2=R3=-(CH2)3-
10f R1=H, R2=R3=-(CH2)4-

Scheme 3 *Reagents and conditions*: i, *p*-xylene, reflux.

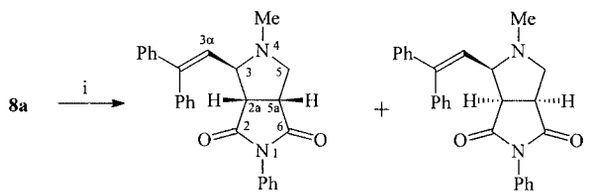
the condensation of *N*-substituted α-amino acids **7** with 3,3-diarylpropenals **6** (Scheme 3). For example, when a mixture of β-phenylcinnamaldehyde **6a** and sarcosine **7a** was refluxed for 30 h in *p*-xylene, the 2,3-dihydro-2-methyl-5-phenyl-1*H*-2-benzazepine **10a** was obtained in 85% yield, after column chromatography on neutral alumina. The dihydrobenzazepine **10a** arises from a 1,7-electrocyclisation, to give the intermediate **9**, followed by a [1,5]-hydrogen shift, leading to the re-aromatisation of the benzene ring.

The intermediacy of an azomethine ylide in this process was shown by the trapping of ylide **8a** with *N*-phenylmaleimide to give the two isomeric cycloadducts **11a** and **11b** (*exo*:*endo* ratio 1:1) (Scheme 4). The structure and stereochemistry of the *exo*-cycloadduct **11a** was established by 2D-COSY and ^{1}H NOE experiments. The irradiation of H-3α gave a large enhancement of H-2a and one of the H-5 methylene protons—while the irradiation of H-3 gave an enhancement of only the *N*-Me singlet.

The use of the 4-alkoxy substituted derivatives **6b**,**c**, prepared from the corresponding substituted benzophenone and

Table 1 Reaction times and % yields for 1,7-electrocyclisations of azomethine ylides **7**

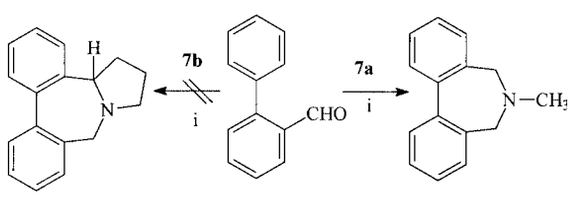
Azomethine ylide **8**	Dihydrobenzazepine **10**	Reaction time/h	Yield (%)
8a	**10a**	30	85
8b	**10b**	26	94
8c	**10c**	24	95
8d	**10d**	28	42
8e	**10e**	28	38
8f	**10f**	30	33



Scheme 4 *Reagents and conditions*: i, *N*-phenylmaleimide, $PhCH_3$, reflux, 3 h.

diethyl 2-(cyclohexylamino)vinylphosphonate by the method of Nagata *et al.*,[6] with sarcosine **7a** also gave azomethine ylides, which subsequently gave the corresponding 2,3-dihydro-2-methyl-1*H*-2-benzazepines **10b**,**c** in excellent yields (Table 1).

We next chose to form the azomethine ylides from the propenals **6** and the cyclic secondary α-amino acids proline **7b** or pipecolinic acid **7c**, allowing the formation of the pyrrolo-[2,1-*a*][2]benzazepine **10d**,**e** or pyrido[2,1-*a*][2]benzazepine **10f** ring systems in a single step (Scheme 3). The moderate yields



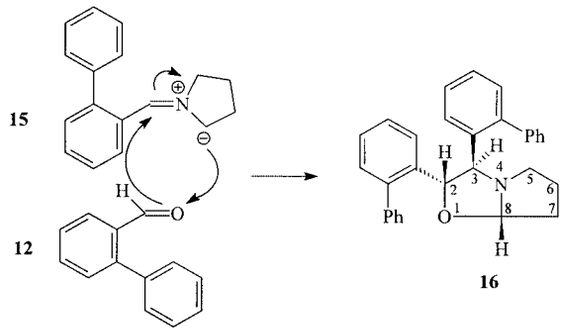
Scheme 5 *Reagents and conditions*: i, *p*-xylene, reflux.

(Table 1) for the formation of these more complex ring systems are due to decomposition on chromatographic separation, even on neutral alumina.

We have attempted to extend this work to the reaction of biphenyl-2-carbaldehyde **12**, prepared by the method of Cullen and Sharp,[7] with either sarcosine **7a** or proline **7b** (Scheme 5). The reaction of aldehyde **12** with sarcosine **7a** gave the corresponding dihydrodibenz[*c*,*e*]azepine **13**[8] in low yield—the lower yield for this process presumably resulting from a combination of the losses upon chromatography and the loss of aromaticity in two aromatic rings on undergoing the initial 1,7-electrocyclisation. The reaction of the aldehyde **12** with proline gave a product which was not the expected dihydrodibenz[*c*,*e*]azepine **14**. Spectroscopic analysis revealed that this new product was an oxazolidine **16** (obtained as a single isomer), resulting from the 1,3-cycloaddition of the azomethine ylide **15** to the precursor aldehyde **12** (Scheme 6). The stereochemistry of the oxazolidine **16** was confirmed by comparison of the ^1H chemical shifts and coupling constants with those of analogues prepared previously.[9] All attempts to obtain the dihydrodibenz[*c*,*e*]azepine **14**, *e.g.* by utilising higher dilution conditions, were unsuccessful.

Experimental

Mps were determined on a Gallenkamp apparatus and are



Scheme 6

uncorrected. Elemental analyses were performed on a Perkin-Elmer 240C or Carlo Erba 1106 Elemental Analyser. IR spectra were recorded on a Perkin-Elmer 1600 series FTIR or Unicam research series FTIR spectrophotometer using sodium chloride plates. ^1H NMR spectra were acquired on a JEOL GSX 270 FT NMR at 270 MHz. Coupling constants are given in Hz and all chemical shifts are relative to an internal standard of tetramethylsilane. ^{13}C NMR spectra were obtained on a JEOL GFX 270 FT NMR (68 MHz) spectrometer. Low resolution electron impact mass spectra were obtained on a Trio 2000 VG spectrometer. High resolution spectra were obtained on a VG ZAB-E spectrometer (EPSRC Mass Spectrometry Service Centre, Swansea). Thin layer chromatography was performed on Merck silica gel $60F_{254}$. All solvents were purified according to standard procedures. Diethyl ether and tetrahydrofuran were freshly distilled over sodium wire with a trace of benzophenone. *p*-Xylene was distilled from, and stored over, sodium wire. Fisons silica gel 60 (35–70 micron) was used for wet flash chromatography. The samples were applied in liquid form or were pre-adsorbed onto silica gel 60 (35–70 micron) from dichloromethane solutions. The 4-alkoxy substituted propenals **6b**,**c** were prepared from the corresponding substituted benzophenone and diethyl 2-(cyclohexylamino)vinylphosphonate by the method of Nagata *et al.*,[6] and biphenyl-2-carbaldehyde **12** was prepared by the method of Cullen and Sharp.[7]

1,7-Electrocyclisations of azomethine ylides—general procedure

A solution of the *N*-substituted α-amino acid (1 mmol) and β-phenylcinnamaldehyde (0.5 mmol) was refluxed in *p*-xylene (5 cm^3) for 24–30 h, under nitrogen. After cooling, the solvent was evaporated under reduced pressure. The residue was purified using column chromatography on neutral alumina, with petrol–ethyl acetate 2:1 as the eluent, to give the dihydrobenzazepine.

2,3-Dihydro-2-methyl-5-phenyl-1*H*-2-benzazepine 10a

A solution of sarcosine **7a** and β-phenylcinnamaldehyde **6a** in *p*-xylene was refluxed for 30 h. Chromatography gave the title compound as a pale yellow oil (85%) (Found: MH^+, 236.144. Calc. for $C_{17}H_{18}N$: *M*, 236.144); ν_{max} (liquid film)/cm^{-1} 1600 (C=C); δ_H(270 MHz, $CDCl_3$) 2.47 (3H, s, NCH_3), 2.90 (2H, d, *J* 7.3, H-3), 3.61 (2H, s, H-1), 6.47 (1H, t, *J* 7.3, H-4), 7.10 (1H, m, ArH), 7.25–7.35 (7H, m, Ar-H), 7.39 (1H, m, Ar-H); δ_C(68 MHz, $CDCl_3$) 43.0 (NCH_3), 51.8 (CH_2), 58.0 (CH_2), 124.0 (CH), 127.4 (CH), 127.6 (CH), 127.8 (CH), 128.2 (2 × CH), 128.4 (2 × CH), 129.1 (CH), 129.8 (CH), 136.8 (quat.), 140.3 (quat.), 140.9 (quat.), 147.0 (quat.); *m/z* 236 (MH^+, 82%), 235 (M^+, 100), 234 (87), 193 (30), 144 (31); *picrate salt of* ***10a***, mp 202 °C (lit.[10] mp 209–210 °C) (Found: C, 59.4; H, 4.4; N, 12.1. $C_{23}H_{20}N_4O_7$ requires C, 59.5; H, 4.3; N, 12.1%).

1,3-Dipolar cycloaddition between *N*-phenylmaleimide and azomethine ylide 8a—derived from β-phenylcinnamaldehyde 6a and sarcosine 7a

Sarcosine **7a** (44 mg, 0.49 mmol), β-phenylcinnamaldehyde **6a**

(102 mg, 0.49 mmol) and *N*-phenylmaleimide (84 mg, 0.49 mmol) were dissolved in toluene (5 cm^3) and the solution was refluxed for 3 h. After 1 h more sarcosine (44 mg, 0.49 mmol) was added to the reaction mixture. When the reaction was complete, the solvent was removed *in vacuo* and the ^1H NMR spectrum of the residue gave the *syn-exo*-**11a**:*syn-endo*-**11b** isomer ratio as 1:1. The two isomers were separated by column chromatography to give the *syn-exo* isomer **11a** as a white powder (65 mg, 32%), mp 157–158 °C (Found: M^+, 408.184. Calc. for $C_{27}H_{24}N_2O_2$: *M*, 408.184); ν_{max} (liquid film)/cm^{-1} 1704 (C=O); δ_H(270 MHz, $CDCl_3$) 2.26 (3H, s, NCH_3), 2.35 (1H, m, H-5), 2.99 (1H, m, H-5), 3.22 (2H, m, H-2a and H-5a), 3.49 (1H, d, *J* 9.5, H-3), 5.93 (1H, d, *J* 9.5, H-3α), 7.21–7.50 (15H, m, 3 × Ph); δ_C(68 MHz, $CDCl_3$) 39.6 (NCH_3), 44.1 (CH_2), 49.5 (CH), 58.5 (CH), 67.5 (CH), 125.8 (C=CH), 126.5 (CH), 127.5 (CH), 128.2 (CH), 128.5 (CH), 129.1 (CH), 129.5 (CH), 132.2 (quat.), 139.9 (quat.), 141.5 (quat.), 146.4 (quat.), 178.3 (2 × C=O); *m*/*z* 408 (M^+, 30%), 393 (10), 331 (20), 317 (20), 241 (12), 235 (43), 220 (35), 158 (100).

The *syn-endo* isomer **11b** was also obtained as a white powder (54 mg, 27%), mp 117–118 °C (Found: M^+, 408.184. Calc. for $C_{27}H_{24}N_2O_2$: *M*, 408.184); ν_{max} (liquid film)/cm^{-1} 1708 (C=O); δ_H(270 MHz, $CDCl_3$) 2.25 (3H, s, NCH_3), 2.75 (1H, dd, *J* 9.9, 4.6, H-3), 3.36 (2H, m), 3.55 (2H, m), 6.08 (1H, d, *J* 9.9, H-3α), 7.19–7.49 (15H, m, 3 × Ph); δ_C(68 MHz, $CDCl_3$) 38.0 (NCH_3), 44.4 (CH_2), 51.6 (CH), 56.5 (CH), 66.3 (CH), 125.0 (CH), 126.5 (CH), 127.4 (CH), 127.6 (CH), 127.9 (CH), 128.3 (CH), 128.6 (CH), 129.1 (CH), 131.9 (quat.), 138.7 (quat.), 141.6 (quat.), 147.3 (quat.), 175.8 (2 × C=O); *m*/*z* 408 (M^+, 65%), 393 (24), 331 (48), 317 (25), 241 (48), 235 (88), 220 (62), 158 (100), 115 (25), 82 (31).

2,3-Dihydro-8-methoxy-5-(4′-methoxyphenyl)-2-methyl-1*H*-2-benzazepine 10b

A solution of sarcosine **7a** and 3,3-bis(4′-methoxyphenyl)-propenal **6b** was refluxed for 26 h. Chromatography gave the title compound as a pale yellow oil (94%) (Found: MH^+, 296.165. Calc. for $C_{19}H_{22}NO_2$: *M*, 296.165); ν_{max} (liquid film)/cm^{-1} 1604 (C=C); δ_H(270 MHz, $CDCl_3$) 2.48 (3H, s, NCH_3), 2.91 (2H, d, *J* 7.3, H-3), 3.59 (2H, s, H-1), 3.82 (3H, s, OCH_3), 3.85 (3H, s, OCH_3), 6.32 (1H, t, *J* 7.3, H-4), 6.86 (2H, d, *J* 8.6, H-3′,5′), 6.85 (1H, dd, *J* 8.6, 2.6, H-7), 6.94 (1H, d, *J* 2.6, H-9), 7.06 (1H, d, *J* 8.6, H-6), 7.23 (2H, d, *J* 8.6, H-2′,6′); δ_C(68 MHz, $CDCl_3$) 42.9 (NCH_3), 51.8 (CH_2), 55.3 (2 × MeO), 58.0 (CH_2), 113.25 (CH), 113.6 (2 × CH), 115.0 (CH), 120.7 (CH), 129.5 (2 × CH), 130.4 (CH), 132.9 (quat.), 133.6 (quat.), 138.0 (quat.), 146.5 (quat.), 159.0 (quat.), 159.5 (quat.); *m*/*z* 296 (MH^+, 55%), 295 (87), 294 (55), 188 (25), 174 (33), 41 (55), 29 (100).

2,3-Dihydro-8-benzyloxy-5-(4′-benzyloxyphenyl)-2-methyl-1*H*-2-benzazepine 10c

A solution of sarcosine **7a** and 3,3-bis(4′-benzyloxyphenyl)-propenal **6c** was refluxed for 24 h. Chromatography gave the title compound as a pale yellow oil (95%) (Found: MH^+, 448.228. Calc. for $C_{31}H_{30}NO_2$: *M*, 448.228); ν_{max} (liquid film)/cm^{-1} 1604 (C=C); δ_H(270 MHz, $CDCl_3$) 2.43 (3H, s, NCH_3), 2.85 (2H, d, *J* 7.3, H-3), 3.54 (2H, s, H-1), 5.07 (2H, s, OCH_2), 5.10 (2H, s, OCH_2), 6.32 (1H, t, *J* 7.3, H-4), 6.90 (2H, m, Ar-H), 7.05 (2H, m, Ar-H), 7.23 (2H, d, *J* 7.9, Ar-H), 7.30–7.46 (10H, m, Ar-H), 7.78 (1H, d, *J* 9.2, Ar-H); δ_C(68 MHz, $CDCl_3$) 43.2 (NCH_3), 52.1 (CH_2), 58.3 (CH_2), 70.1 (2 × OCH_2), 113.9 (CH), 114.4 (2 × CH), 114.6 (2 × CH), 115.9 (CH), 121.6 (CH), 127.5 (CH), 128.0 (CH), 128.2 (2 × CH), 128.6 (3 × CH), 129.5 (2 × CH), 130.4 (CH), 132.2 (CH), 133.3 (quat.), 134.1 (quat.), 136.9 (quat.), 137.0 (quat.), 138.6 (quat.), 146.0 (quat.), 158.1 (quat.), 158.7 (quat.); *m*/*z* 448 (MH^+, 30%), 447 (40), 395 (18), 356 (80), 264 (18), 250 (18), 211 (12), 91 (100).

7-Phenyl-2,3,5,11b-tetrahydro-1*H*-pyrrolo[2,1-*a*][2]benzazepine 10d

A solution of proline **7b** and β-phenylcinnamaldehyde **6a** was refluxed for 28 h. Chromatography gave the title compound as a pale yellow oil (42%) (Found: M^+, 261.152. Calc. for $C_{19}H_{19}N$: *M*, 261.152); ν_{max} (liquid film)/cm^{-1} 1600; δ_H(270 MHz, $CDCl_3$) 1.26 (2H, m, H-2), 2.11 (2H, m, H-1), 2.50 (2H, m, H-3), 2.95 (1H, br m, H-5), 3.38 (1H, dd, *J* 11.9, 7.2, H-11b), 4.21 (1H, br m, H-5), 6.52 (1H, t, *J* 6.6, H-6), 7.08 (1H, dd, *J* 7.3, 1.3, H-11), 7.21–7.39 (8H, m, H-8, 9, 10 + Ph); δ_C(68 MHz, $CDCl_3$) 24.0 (CH_2), 26.5 (CH_2), 49.7 (CH_2), 52.1 (CH_2), 62.0 (CH), 125.7 (CH), 126.7 (CH), 127.4 (CH), 127.6 (2 × CH), 128.2 (2 × CH), 128.3 (2 × CH), 129.5 (CH), 139.0 (quat.), 140.1 (quat.), 141.6 (quat.), 146.0 (quat.); *m*/*z* 262 (50%), 261 (M^+, 62), 260 (49), 149 (62), 41 (38), 29 (100).

10-Benzyloxy-7-(4′-benzyloxyphenyl)-2,3,5,11b-tetrahydro-1*H*-pyrrolo[2,1-*a*][2]benzazepine 10e

A solution of proline **7b** and 3,3-bis(4′-benzyloxyphenyl)-propenal **6c** was refluxed for 28 h. Chromatography gave the title compound as a pale brown oil (38%) (Found: $(M - H)^+$, 472.228. Calc. for $C_{33}H_{30}NO_2$: *M*, 472.226); ν_{max} (liquid film)/cm^{-1} 1604; δ_H(270 MHz, $CDCl_3$) 1.20 (2H, m, H-2), 1.95 (2H, m, H-1), 2.32 (2H, m, H-3), 2.68 (1H, br m, H-5), 4.22 (2H, m, H-5 and H-11b), 5.08 (2H, s, CH_2), 5.12 (2H, s, CH_2), 6.57 (1H, t, *J* 7.0, H-6), 6.87 (1H, d, *J* 7.9, H-9), 7.01 (2H, d, *J* 7.9, H-3′,5′), 7.16 (2H, d, *J* 7.9, H-2′,6′), 7.22 (1H, d, *J* 7.9, H-8), 7.24 (1H, s, H-11), 7.41 (10H, m, ArH); δ_C(68 MHz, $CDCl_3$) 29.7 (CH_2), 30.0 (CH_2), 51.2 (CH_2), 63.6 (CH_2), 68.5 (CH), 70.0 (2 × CH_2), 114.6 (2 × CH), 114.7 (2 × CH), 123.5 (CH), 124.3 (CH), 127.5 (2 × CH), 127.6 (2 × CH), 128.0 (2 × CH), 128.2 (CH), 128.6 (4 × CH), 129.0 (quat.), 129.2 (CH), 129.4 (quat.), 131.8 (quat.), 132.0 (quat.), 136.9 (quat.), 156.6 (quat.), 158.9 (quat.); *m*/*z* (rel. intensity, %): 473 (6%), 472 (23), 471 (25), 288 (10), 92 (11), 91 (100).

8-Phenyl-1,2,3,4,6,12b-hexahydropyrido[2,1-*a*][2]benzazepine 10f

A solution of pipecolinic acid **7c** and β-phenylcinnamaldehyde **6c** was refluxed for 30 h. Chromatography gave the title compound as a pale brown oil (33%) (Found: MH^+, 276.175. Calc. for $C_{20}H_{22}N$: *M*, 276.175); ν_{max} (liquid film)/cm^{-1} 1446; δ_H(270 MHz, $CDCl_3$) 0.86 (2H, m, CH_2), 1.35 (2H, m, CH_2), 1.61 (1H, m, CH_2), 1.72 (2H, m, CH_2), 1.96 (1H, m, CH_2), 3.05 (3H, m, H-6 and H-12b), 6.49 (1H, t, *J* 7.3, H-7), 7.03 (1H, d, *J* 7.9, ArH), 7.21–7.39 (7H, m, ArH), 7.53 (1H, d, *J* 7.9, ArH); δ_C(68 MHz, $CDCl_3$) 25.0 (CH_2), 26.5 (CH_2), 29.0 (CH_2), 30.8 (CH_2), 52.6 (CH_2), 61.5 (CH), 125.6 (CH), 125.8 (quat.), 126.8 (CH), 127.2 (CH), 127.7 (CH), 127.9 (CH), 128.2 (3 × CH), 128.3 (2 × CH), 128.6 (quat.), 131.6 (quat.); *m*/*z* 276 (86%), 275 (M^+, 100), 274 (55), 247 (43), 218 (18), 193 (31), 184 (20), 110 (23), 41 (22).

6,7-Dihydro-6-methyl-5*H*-dibenz[*c*,*e*]azepine 13

A solution of 2-phenylbenzaldehyde **12** (0.915 g, 5 mmol) and sarcosine **7a** (0.890 g, 10 mmol) in *p*-xylene (20 cm^3) was refluxed for 24 h. Chromatography (eluent EtOAc to 90% EtOAc–10% MeOH) gave the title compound **13** as a yellow oil (0.088 g, 9%) (Found: M^+, 209.123. Calc. for $C_{15}H_{15}N$: *M*, 209.120. Found: $(M - H)^+$, 208.114. Calc. for $C_{15}H_{14}N$: *M*, 208.113); ν_{max} (liquid film)/cm^{-1} 1450; δ_H(270 MHz, $CDCl_3$), 2.51 (3H, s, NCH_3), 3.44 (4H, s, 2 × CH_2), 7.30–7.50 (8H, m, Ar-H); δ_C(68 MHz, $CDCl_3$) 42.1 (NCH_3), 57.1 (2 × CH_2), 127.6 (4 × CH), 128.1 (2 × CH), 129.7 (2 × CH), 134.2 (2 × quat.), 141.0 (2 × quat.); *m*/*z* 209 (M^+, 89%), 208 (100), 166 (89), 165 (93).

2,3-Bis(biphenyl-2′-yl)-2,3,5,6,7,8-hexahydropyrrolo[2,1-*b*]-oxazole 16

A solution of 2-phenylbenzaldehyde **12** (0.915 g, 5 mmol) and proline **7b** (1.150 g, 10 mmol) in *p*-xylene (20 cm^3), was heated to reflux under an atmosphere of argon for 24 h. Chromatography (eluent EtOAc to 90% EtOAc–10% MeOH) gave the title compound **16** as a yellow oil (0.409 g, 35%) (Found: MH^+, 418.217. Calc. for $C_{30}H_{28}NO$: *M*, 418.217); ν_{max} (liquid film)/cm^{-1} 1477; δ_H(270 MHz, $CDCl_3$) 1.90 (2H, m, H-7), 2.67 (2H, dt, *J* 10.55, 6.3, H-6), 3.05 (2H, dt, *J* 10.55, 6.3, H-5), 4.03 (1H, d, *J* 8.4, H-3), 4.84 (1H, d, *J* 8.4, H-2), 5.15 (1H, dd, *J* 4.2, 2.6, H-8), 7.0–7.7 (18H, m, Ar-H); δ_C(68 MHz, $CDCl_3$) 24.0 (C-6), 31.7 (C-7), 55.3 (C-5), 74.8 (C-3), 85.4 (C-2), 98.6 (C-8), 126.3 (CH), 126.4 (CH), 126.45 (CH), 127.15 (CH), 127.25 (CH), 127.3 (CH), 127.6 (CH), 128.0 (CH), 128.4 (CH), 128.7 (quat.), 129.1 (CH), 129.2 (CH), 129.35 (CH), 129.7 (quat.), 135.1 (quat.), 140.6 (quat.), 141.0 (quat.), 142.25 (quat.); *m*/*z* 419 (35%), 418 (MH^+, 100%), 282 (35), 264 (97), 236 (87), 235 (74), 183 (100), 70 (85), 43 (86).

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