

(CH₃)₂, 32.01 and 29.33 (C(CH₃)₂), 14.57 (OHCH₂CH₃); IR (Nujol) 3355, 1650, 1428 (s) cm⁻¹; MS (EI) *m/e* (relative intensity) 314 (87, M⁺), 299 (100, M⁺ - CH₃). Anal. Calcd for C₁₈H₂₆N₂O₂: C, 72.58; H, 8.34; N, 8.91. Found: C, 72.56; H, 8.33; N, 8.93.

4-(*N*-Methylamino)-6,7-(1,2,3,4-tetrahydro-1,1,4,4-tetramethylbenzo)indole (16). A solution of indole 4 (20.0 g, 0.063 mol) in dry THF (280 mL) under argon was treated over 1/2 h at room temperature via syringe with LiAlH₄ (127 mL, 1.0 M in THF, gas evolution was noted upon addition), and the resulting light yellow suspension refluxed for 1/2 h. TLC revealed the absence of indole 4 (*R*_f 0.4 in B) and the presence of amine 16, which had an identical *R*_f (0.4 in B), but which had staining characteristics different from the starting carbamate. The solution was cooled to 0 °C, and the remaining LiAlH₄ was destroyed with a mixture of Na₂SO₄·10H₂O–Celite (1:1). The thick slurry was filtered through a Celite pad, the pad was washed with several portions of 5:1 THF–NEt₃ and EtOAc, and the filtrate was concentrated. The solid remaining was purified by chromatography using 3:1 hexane/EtOAc as eluant to yield 15.0 g (92%) of amine 16: mp 197–199 °C (dec, purple crystals/CH₂Cl₂–hexane); ¹H NMR δ 8.19 (s, 1 H, NH), 7.03 (t, *J* = 2.4 Hz, 1 H, NCH=), 6.36 (dd, *J* = 2.4 Hz, 1 H, ArCH=), 6.27 (s, 1 H, ArH), 2.96 (s, 3 H, NCH₃), 1.72 (m, complex, 4 H, CH₂CH₂C(CH₃)₂), 1.44 (s, 6 H, C(CH₃)₂), 1.28 (s, 6 H, C(CH₃)₂); ¹³C NMR δ 140.28 (Ar), 140.15 (Ar), 134.31 (Ar), 121.37 (Ar), 117.66 (ArNCH=), 116.27 (ArCH=C), 98.25 (Ar), 98.11 (Ar), 37.62 and 35.68 (C(CH₃)₂CH₂CH₂), 34.66 and 33.24 ((CH₃)₂C), 32.19 ((CH₃)₂C), 28.19 (NCH₃), 29.69 ((CH₃)₂C); MS (EI) *m/e* (relative intensity) 256 (55, M⁺), 241 (100, M⁺ - CH₃). Anal. Calcd for C₁₇H₂₄N₂: C, 79.63; H, 9.44; N, 10.93. Found: C, 79.31; H, 9.43; N, 10.84.

(*S*)-4-(Methyl(1-((phenylmethyl)oxy)carbonyl)-2-methylpropyl)amino)-6,7-(1,2,3,4-tetrahydro-1,1,4,4-tetramethylbenzo)indole (17). A mixture of indole 16 (1.20 g, 4.68 mmol) and (*R*)-2-((trifluoromethyl)sulfonyl)oxy-3-methylbutanoic acid benzyl ester^{7a} (1.55 g, 5.61 mmol) in ClCH₂CH₂Cl (20 mL) and 2,6-lutidine (0.7 mL, 6.08 mmol) was refluxed for 12 h. TLC revealed the absence of 16 (*R*_f 0.4 in B) and the presence of indole 17 (*R*_f 0.6 in B). The solvent was evaporated, and the residue was partitioned between EtOAc and saturated aqueous NaHCO₃. The organic layer was dried (MgSO₄), filtered, and concentrated. The residue was purified by chromatography using 3:1 hexane/EtOAc as eluant to yield 1.95 g (93%) of 17: mp 138–140 °C (purple crystals/CH₂Cl₂–hexanes); ¹H NMR δ 8.21 (br s, 1 H, NH), 7.25 (m, 3 H, ArH), 7.11 (d, *J* = 3 Hz, 1 H, ArCH=), 7.08 (m, 2 H, ArH), 6.64 (s, 1 H, ArH), 6.61 (dd, *J* = 2 Hz, 1 H, NCH=), 5.07 (q, *J* = 12 Hz, 2 H, ArCH₂), 4.02 (d, *J* = 11 Hz, 1 H, CH₃NCHiPr), 3.00 (s, 3 H, NCH₃), 2.39 (m, complex (9 lines), 1 H, CH(CH₃)₂), 1.75 (m, 2 H, (CH₃)₂CCH₂), 1.66 (m, 2 H, (CH₃)₂CCH₂), 1.48 (s, 3 H, C(CH₃)₂), 1.46 (s, 3 H, C(CH₃)₂), 1.25 (s, 3 H, C(CH₃)₂), 1.23 (s, 3 H, C(CH₃)₂), 1.12 (d, *J* = 6 Hz, 3 H, CH(CH₃)₂), 0.93 (d, *J* = 6 Hz, 3 H, CH(CH₃)₂); ¹³C NMR δ 171.97 (CO₂Bn), 143.47 (Ar), 139.41 (Ar), 135.87 (Ar), 135.19 (Ar), 128.33 (Ar), 127.95 (Ar), 127.88 (Ar), 121.42 (Ar), 120.98 (ArNCH=), 119.79 (ArC=), 107.56 (Ar), 101.21 (Ar), 70.66 (CO₂CH₂Ar), 65.74 (CH₃NC(iPr)CO₂Bn), 37.67 and 35.47 ((CH₃)₂CCH₂), 34.51 and 34.14 ((CH₃)₂C), 33.31 (CH(CH₃)₂), 32.12, 29.58, 29.50 and 27.92 ((CH₃)₂C), 19.87 and 19.38 (CH(CH₃)₂); MS (EI) *m/e* (relative intensity) 446 (73, M⁺), 431 (10, M⁺ - CH₃), 403 (50, M⁺ - C₃H₇), 311 (100, M⁺ - PhCH₂OC=O). Anal. Calcd for C₂₉H₃₈N₂O₂: C, 77.98; H, 8.58; N, 6.28. Found: C, 78.13; H, 8.62; N, 6.24.

Ethyl (*S*)-3-(4-(Methyl(1-((phenylmethyl)oxy)carbonyl)-2-methylpropyl)amino)-6,7-(1,2,3,4-tetrahydro-1,1,4,4-tetramethylbenzo)-1*H*-indol-3-yl)-2-oximidopropionate (18). A suspension of 17 (10.0 g, 0.022 mol) in CH₂Cl₂ (28 mL), ethyl 3-bromo-2-oximidopropionate²³ (4.72 g, 0.022 mol), and Na₂CO₃ (1.0 g) was stirred for 12 h. TLC revealed the absence of 17 (*R*_f 0.45 in B) and the presence of oxime 18 (*R*_f 0.1 in B). The dark suspension was diluted with EtOAc, filtered, and concentrated. The oil remaining was purified by chromatography using 3:1 hexane/EtOAc and then 1:1 hexane/EtOAc as eluant to yield 6.43 g (50%) of 18 as a white solid: mp 128–131 °C (CH₂Cl₂/hexanes); ¹H NMR δ 9.38 (br s, 1 H, exch, NOH), 8.02 (br s, 1 H, no exch, ArNHCH=C), 7.26 (m, 3 H, CH₂ArH), 7.17 (m, 2 H, CH₂ArH), 6.93 (s, 1 H, ArH), 6.72 (s, 1 H, ArNHCH=C), 5.09 (B part, AB q, *J* = 12 Hz, 1 H, CH₂Ar), 4.95 (A part, AB q,

J = 12 Hz, 1 H, CH₂Ar), 4.45 (B part, AB q, *J* = 15 Hz, 1 H, CH₂C=NOH), 4.37 (A part, AB q, *J* = 15 Hz, 1 H, CH₂C=NOH), 4.24 (B part AB q, *J* = 6 Hz, 1 H, OCH₂CH₃), 4.22 (A part, AB q, *J* = 6 Hz, 1 H, OCH₂CH₃), 3.72 (d, *J* = 8.5 Hz, 1 H, NCH(iPr)CO₂Bn), 2.94 (s, 3 H, NCH₃), 2.31 (m, complex, 1 H, CH(CH₃)₂), 1.71 (m, complex, 2 H, C(CH₃)₂CH₂), 1.65 (m, complex, 2 H, C(CH₃)₂CH₂), 1.429 (s, 3 H, C(CH₃)₂), 1.423 (s, 3 H, C(CH₃)₂), 1.24 (t, *J* = 6 Hz, 3 H, OCH₂CH₃) overlapping 1.24 (s, 3 H, C(CH₃)₂), 1.23 (s, 3 H, C(CH₃)₂), 1.13 (d, *J* = 6.5 Hz, 3 H, CH(CH₃)₂), 0.93 (d, *J* = 6.5 Hz, 3 H, CH(CH₃)₂); ¹³C NMR δ 173.10 (CO₂Et), 163.72 (CO₂Bn), 152.75 (C=NOH), 144.70 (Ar), 139.28 (Ar), 135.99 (Ar), 135.74 (Ar), 128.34 (Ar), 128.29 (Ar), 128.00 (Ar), 123.74 (Ar), 120.98 (ArNHCH=), 120.09 (Ar), 112.51 (Ar), 108.73 (ArC=CHN), 72.48 (OCH₂CH₃), 65.98 (CO₂Bn), 61.70 (CH₂C=NOH), 37.66, 35.31, 34.47, 33.38, 32.08, 29.43, 29.12, 28.80, 22.47, 20.24, 28.98, 14.03 (OCH₂CH₃); MS (EI) *m/e* (relative intensity) 575.2 (100, M⁺), 532.2 (20, M⁺ - C₃H₇), 440.2 (62, M⁺ - CO₂Bn). Anal. Calcd for C₃₄H₄₆N₃O₅: C, 70.92; H, 7.88; N, 7.28. Found: C, 70.93; H, 7.77; N, 7.27.

(*S,R* and *S,S*)-Ethyl 3-(4-Methyl(1-((phenylmethyl)oxy)carbonyl)-2-methylpropyl)amino)-6,7-(1,2,3,4-tetrahydro-1,1,4,4-tetramethylbenzo)-1*H*-indol-3-yl)-2-amino-propionates (20 and 21). A solution of oxime 18 (11.0 g, 0.019 mol) in dry THF (250 mL) was treated with aluminum foil (5 g, 0.19 mol) that had been cut into small pieces and immersed successively in 2% aqueous HgCl₂, distilled H₂O, and THF. The dark gray suspension was stirred for 12 h at room temperature, at which time TLC revealed the absence of 18 (*R*_f 0.5 in A) and the presence of amino esters 20 and 21 (*R*_f 0.20 and 0.15 in A, respectively). The suspension was filtered and concentrated to yield 7.8 g (75%) of a mixture of the amines as a light yellow oil. Analytical samples of each of the amino esters was provided by chromatography over silica gel using 1:1 hexane/EtOAc to give the *S,R* diastereomer 20 as an oil: ¹H NMR δ 8.14 (s, 1 H, NH), 7.23 (q, *J* = 3 Hz, 3 H, CH₂ArH), 7.05 (m, 2 H, CH₂ArH), 6.96 (d, *J* = 3 Hz, 1 H, ArNHCH=), 6.90 (s, 1 H, ArH), 5.00 (B part, AB q, *J* = 12 Hz, 1 H, ArCH₂), 4.82 (A part, AB q, *J* = 12 Hz, 1 H, ArCH₂), 4.11 (q, *J* = 6 Hz, 2 H, CH₃CH₂O), 3.81 (q, *J* = 3 Hz, 1 H, NCH(iPr)CO₂Bn), 3.68 (br s, 1 H, H₂NCHCO₂Et), 3.33 (AB q, *J* = 6, 9 Hz, 2 H, CH₂CH(NH₂)CO₂Et), 2.87 (br s, 3 H, NCH₃), 2.34 (sextet, *J* = 9 Hz, 1 H, (iPr)CH), 1.73 (m, complex, 2 H, C(CH₃)₂CH₂), 1.65 (m, complex, 2 H, C(CH₃)₂CH₂), 1.62 (br s, 2 H, exch, NH₂), 1.46 (s, 3 H, C(CH₃)₂), 1.45 (s, 3 H, C(CH₃)₂), 1.26 (s, 3 H, C(CH₃)₂), 1.22 (s, 3 H, C(CH₃)₂), 1.16 (t, *J* = 6 Hz, 3 H, CH₃CH₂O), 1.12 (d, *J* = 6 Hz, 3 H, (CH₃)₂CH), 0.96 (m, complex, 3 H, (CH₃)₂CH); ¹³C NMR δ 175.77, 172.47, 144.74, 139.03, 135.86, 135.72, 128.28, 128.02, 127.82, 123.85, 121.45, 121.27, 112.13, 111.49, 72.44 (CHCO₂Bn), 65.83 (CH₃CH₂O), 60.53 (ArCH₂), 56.38 (CH₂CH(NH₂)CO₂Et), 37.74, 35.32, 34.48, 33.38, 32.52, 32.20, 32.09, 32.05, 29.55, 28.90, 28.75, 20.35, 14.11; MS (FAB) *m/e* (relative intensity) 562.2 (100, MH⁺); high-resolution MS calcd for C₃₄H₄₆N₃O₄ 562.3644, found 562.3690. Further elution gave the *S,S* diastereomer 21 as an oil: ¹H NMR δ 8.15 (s, 1 H, NH), 7.21 (m, 3 H, CH₂ArH), 6.98 (m, 2 H, CH₂ArH), overlapping 6.94 (m, 1 H, ArNHCH=), 6.91 (s, 1 H, ArH), 5.02 (B part, AB q, *J* = 12 Hz, 1 H, ArCH₂), 4.74 (A part, AB q, *J* = 12 Hz, 1 H, ArCH₂), 4.17 (q, *J* = 6 Hz, 2 H, CH₃CH₂O), 3.96 (br s, 1 H), 3.66 (br s, 1 H), 3.62 (dd, *J* = 3 Hz, 1 H), 2.92 (m, 1 H) overlapping 2.88 (br s, 3 H, NCH₃), 2.33 (sextet, *J* = 6 Hz, (iPr)CH), 1.74 (m, complex, 2 H, C(CH₃)₂CH₂), 1.67 (m, complex, 2 H, C(CH₃)₂CH₂), 1.48 (s, 3 H, C(CH₃)₂) overlapping 1.48 (br s, 2 H, exch, NH₂), 1.47 (s, 3 H, C(CH₃)₂), 1.29 (s, 3 H, C(CH₃)₂), 1.25 (t, *J* = 6 Hz, 3 H, CH₃CH₂O), 1.24 (s, 3 H, C(CH₃)₂), 1.15 (d, *J* = 9 Hz, 3 H, CH(CH₃)₂), 0.90 (m, complex, 3 H, CH(CH₃)₂); ¹³C NMR δ 175.44, 139.21, 136.14, 135.64, 128.22, 127.94, 127.87, 123.80, 122.05, 120.97, 110.98, 72.53 (CHCO₂Bn), 65.83 (CH₃CH₂O), 60.54 (BnCH₂O), 54.75 (CH₂C(NH₂)CO₂Et), 37.61, 35.29, 34.49, 33.39, 32.10, 31.96, 29.70, 28.92, 28.62, 20.41, 14.18; MS (FAB) *m/e* (relative intensity) 562.2 (100, MH⁺); high-resolution MS calcd for C₃₄H₄₆N₃O₄ 562.3644, found 562.3674.

(*S,S*)- and (*S,R*)-1,3,4,5,7,8,10,11,12,13-Decahydro-4-(ethoxycarbonyl)-8,10,10,13,13-pentamethyl-7-(1-methylethyl)-6*H*-benzo[*g*][1,4]diazonino[7,6,5-*cd*]indol-6-one (23 and 24). A solution of a mixture of amines 20 and 21 (4.50 g, 8.17 mmol), 10% Pd/C (0.5 g), and camphorsulfonic acid (0.1 g) in EtOH (50 mL) was hydrogenated at 40 psi on a Parr shaker apparatus. After