Supporting Information

Reaction of α -(*N*-Carbamoyl)alkylcuprates with Enantioenriched Propargyl Electrophiles: Synthesis of Enantioenriched 3-Pyrrolines

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General. NMR spectra were recorded as CDCl_3 solutions. The ^1H NMR (300MHz) chemical shifts are reported as δ values in parts per million (ppm) relative to tetramethylsilane (TMS) or CHCl_3 (7.24 ppm) as internal standard. The ^{13}C NMR (75 MHz) chemical shifts are reported as δ values in parts per million (ppm) downfield from TMS and referenced with respect to the CDCl_3 signal (triplet, centerline $\delta = 77.0$ ppm). Infrared spectra (IR) were recorded as neat samples (liquid films on NaCl plates) unless otherwise noted. Gas chromatography/mass spectrometry measurements were performed on a GC coupled to a mass selective detector at 70 eV. Analytical thin-layer chromatography (TLC) was performed on silica gel plates, 200 mesh with F-254 indicator. Visualization was accomplished by UV light (254 nm), 4% ethanol solution of phosphomolybdic acid, 5% *p*-anisaldehyde, or 5% H_2SO_4 -90% EtOH solution. Flash column chromatography was performed with 200-400 mesh silica gel. Bulb-to-bulb distillations were performed on a micro-distillation oven model GKR-51; boiling points were recorded as the oven temperature and are not corrected. Elemental analyses were determined from doubly purified samples involving column chromatography followed by kugelrohr distillation.

Materials. Anhydrous tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium benzophenone ketyl. Dichloromethane (CH_2Cl_2), *N, N, N, N*-tetramethylethylenediamine (TMEDA) and chlorotrimethylsilane were distilled from CaH_2 under a positive N_2 atmosphere. CuCN was used without further purification. *sec*-BuLi (1.5 M in cyclohexane) was prepared from *sec*-BuCl and FMC's Stabi-Li-ze lithium powder and titrated using *sec*-BuOH and 1,10-phenanthroline monohydrate in THF.¹ All round bottom flasks used for the preparation of the organocopper and cuprate reagents were cleaned with 48% hydrobromic acid, followed by rinsing with copious amounts of water, acetone and then oven dried (100 °C) overnight. All glassware was flamed-dried under high vacuum and purged with argon and then cooled under a dry nitrogen atmosphere. The LiCl was weighed into a flame-dried

flask and flamed-dried under vacuum (0.05 mm Hg) and purged with argon and then cooled under a dry nitrogen atmosphere. All copper reactions were conducted under a positive, dry nitrogen atmosphere in anhydrous solvents in flasks fitted with a rubber septum. The nitrogen gas was passed through concentrated sulfuric acid, potassium hydroxide, and indicating and non-indicating Drierite before being introduced into the reaction flask. Low temperature baths (-78 °C or warmer) were prepared using shallow thermoflasks with a cyrocool machine, or dry ice-isopropanol slush bath mixtures. Flask to flask transfer of air and moisture sensitive intermediates was completed using double-tipped needles (cannula) under a positive argon pressure maintained by double layered balloons filled with argon.

All alkynes and $\text{Zn}(\text{OTf})_2$ were purchased from commercial vendors. All aldehydes are commercially available and were redistilled if necessary. The carbamates were prepared from their free amines and stored in the freezer and redistilled if the color turned yellow before use. (+)-*N*-methylephedrine and (-)-*N*-methylephedrine were purchased.

General Procedure A: Preparation of Racemic Propargylic Alcohols. A solution of alkyne (1.0 mmol) in dry THF (10 mL) was treated with lithium diisopropylamide (1.1 mmol) at -30 °C for 40 minutes, followed by the addition of aldehyde (1.1 mmol) at -30 °C. The mixture was warmed to room temperature over two hours, quenched with saturated NH_4Cl (aq), and extracted with diethyl ether three times. The combined organic extractions were dried over MgSO_4 , filtered, and concentrated under vacuum to afford crude material, which was purified by flash column chromatography (silica gel, ethyl acetate/petroleum ether, 1:5, v/v) to give colorless oils.

General Procedure C: Propargyl Alcohol Benzoylation (for Chiral HPLC Analysis). The propargylic alcohol (1.0 mmol) was dissolved in dry CH_2Cl_2 (4.0 mL), followed by the addition of Et_3N (0.150 g, 1.5 mmol) and benzoyl chloride (0.16 g, 1.2 mmol) at 0 °C. The reaction mixture was warmed to room temperature over two hours, then quenched with saturated NaHCO_3 at room temperature, and stirred for another 30 minutes. The aqueous phase was extracted with CH_2Cl_2 and the organic phase was dried over anhydrous Na_2SO_4 . The organic solvent was concentrated under vacuum to afford crude product, which was purified by flash column chromatography (silica gel, ethyl acetate/petroleum ether, v/v, 1/10) to give products as colorless oils.

General Procedure D: Preparation of Enantioenriched Propargylic Alcohols with Catalytic Amounts of $\text{Zn}(\text{OTf})_2$ and Chiral Ligands Under Solvent Free Conditions.² Following the procedure of Jiang,² under argon, to a solution of $\text{Zn}(\text{OTf})_2$ (0.2 equiv., 0.20 mmol) and chiral ligand

[0.22 equiv., 0.22 mmol, (1*S*, 2*S*) or (1*R*, 2*R*)-3-*t*-butyldimethylsilyloxy)-2-(*N,N*,-dimethylamino)-1-(*p*-nitrophenyl)propan-1-ol] in alkyne (3.0 equiv., 3.0 mmol) was added triethylamine (0.3 equiv., 0.30 mmol) at room temperature for 2.0 hours. Then the aldehyde (1.0 equiv., 1.0 mmol) was added dropwise by syringe. The reaction mixture was heated for 48 hours at 70 °C, then cooled to room temperature, diluted with petroleum ether, and washed with HCl (control pH > 4). The organic phase was washed with brine, dried over MgSO₄, and concentrated under vacuum to afford crude product, which was purified by flash chromatograph (silica gel, ethyl acetate/petroleum ether, 1:5, v/v).

General Procedure E: Preparation of Propargylic Alcohols with Catalytic Amounts of Zn(OTf)₂ and Chiral Ligands in Toluene.³ Following the procedure Jiang,³ to a solution of Zn(OTf)₂ (0.20 equiv) and chiral ligand [0.22 equiv., 0.22 mmol, (1*S*, 2*S*) or (1*R*, 2*R*)-3-*t*-butyldimethylsilyloxy)-2-(*N,N*,-dimethylamino)-1-(*p*-nitrophenyl)propan-1-ol] in distilled toluene (0.5 M) under argon was added triethylamine (0.5 equiv.) at room temperature. Alkyne (1.1 equiv.) was then added to the reaction mixture via syringe. After 15 minutes stirring, the aldehyde (1.0 equiv.) was added dropwise via syringe. After addition was complete, the reaction mixture was stirred for 6 hours at 50 °C, then quenched with saturated NH₄Cl (aq), and extracted with petroleum ether (3 x 10 mL). The combined organic extracts were dried over MgSO₄ and concentrated under vacuum to afford crude product, which was purified by flash chromatograph (silica gel, ethyl acetate/petroleum ether, 1:5, v/v).

General Procedure F: Preparation of Enantioenriched Propargylic Alcohols with Stoichiometric Amounts of Zn(OTf)₂ and Chiral Ligand in Toluene.⁴ Following the procedure of Carreira,⁴ a solution of aldehyde (e.g., isobutyraldehyde, 0.072 g, 1.0 mmol) and alkyne (e.g., phenylacetylene 0.10 g, 1.0 mmol) in toluene (2.0 mL) was treated with Et₃N (0.122 g, 1.2 mmol), (+)-*N*-methylephedrine, (0.400 g, 1.1 mmol) and Zn(OTf)₂, (0.22 g, 1.2 mmol) at room temperature under argon. The reaction mixture was stirred for 12 hours at room temperature, then quenched with saturated NH₄Cl (aq), and extracted with petroleum ether (3 x 10 mL). The combined organic extracts were dried over MgSO₄, and concentrated under vacuum to afford crude product, which was purified by flash column chromatography (silica gel, ethyl acetate/petroleum ether, 1:5, v/v).

4-Methyl-1-phenyl-1-pentyn-3-ol (3a*R*). Employing General Procedure D with phenyl acetylene (3.0 equiv., 0.612 g, 6.0 mmol), Zn(OTf)₂ (0.2 equiv., 0.146 g, 0.40 mmol), (1*S*, 2*S*)-3-(*t*-butyldimethylsilyloxy)-2-*N,N*-dimethylamino-1-(*p*-nitrophenyl)propan-1-ol chiral ligand (0.22 equiv., 0.156 g, 0.44 mmol), triethylamine (0.3 equiv., 61 mg, 0.60 mmol), and isobutyraldehyde (1.0 equiv.,

0.144 g, 2.0 mmol) gave **3aR** (0.28 g, 81%) after purification by flash column chromatography (silica gel, ethyl acetate/petroleum ether, 1:5, v/v): ^1H NMR (CDCl_3) δ 1.04 (d, $J = 6.9$ Hz, 3H), 1.06 (d, $J = 6.9$ Hz, 3H), 1.95 (oct, $J = 6.9$ Hz, 1H), 1.69 (s, 1H), 1.95 (sex, $J = 6.8$ Hz, 1H), 4.37 (d, $J = 6.0$ Hz, 1H), 7.22-7.48 (m, 5H); ^{13}C NMR (CDCl_3) δ 17.5, 18.2, 34.6, 68.4, 85.6, 88.9, 122.7, 128.3, 131.7, 145.1.

The enantiomeric purity of **3aR** was determined by chiral HPLC analysis of the corresponding benzoate ester on a CHIRACEL OD column [cellulose tris(3,5-dimethylphenylcarbamate) on silica gel] to be 81% ee (hexane/ i PrOH, 99.7:0.3 (v/v), flow rate = 0.35 mL/min, detection at $\lambda = 210$ nm. The (*R*)-enantiomer (major) eluted first with a retention time of 21.1 min followed by the (*S*)-isomer (minor) at 21.9 min.

4-Methyl-1-phenyl-1-pentyn-3-ol, methanesulfonate (3bR). General Procedure B was employed with propargyl alcohol **3aR** (0.278 g, 1.61 mmol) to afford crude product **3bR** (0.34 g, 84%), which was used without further purification: ^1H NMR (CDCl_3) δ 1.09 (d, $J = 6.9$ Hz, 3H), 1.11 (d, $J = 6.9$ Hz, 3H), 2.19 (oct, $J = 6.8$ Hz, 1H), 3.14 (s, 3H), 5.19 (d, $J = 5.4$ Hz, 1H), 7.24-7.45 (m, 5H); ^{13}C NMR (CDCl_3) δ 17.5, 17.9, 33.6, 39.1, 75.3, 83.2, 89.1, 128.4, 129.2, 131.8, 141.6.

2-Methyl-8-phenyl-4-octyn-3-ol (4aR). Employing General Procedure D with 5-phenyl-1-pentyne (0.864 g, 6.0 mmol) and isobutyraldehyde (0.114 g, 2.0 mmol) gave **4aR** (0.367 g, 1.7 mmol, 85%) as a colorless oil after purification by flash column chromatography (silica gel, ethyl acetate/petroleum ether, 1:5, v/v): ^1H NMR (CDCl_3) δ 1.00 (d, $J = 6.9$ Hz, 3H), 1.02 (d, $J = 6.9$ Hz, 3H), 1.71-1.94 (m, 4H), 2.24 (dt, $J = 6.8, 2.1$ Hz, 2H), 2.71 (t, $J = 7.4$ Hz, 2H), 4.19 (dd, $J = 6.8, 2.1$ Hz, 1H), 7.15-7.31 (m, 5H); ^{13}C NMR (CDCl_3) δ 17.4, 18.1 (2 carbon over lap), 30.3, 34.6, 34.8, 68.0, 80.3, 85.5, 125.8, 128.3, 128.4, 141.5.

The enantiomeric purity of **4aR** was determined by chiral HPLC analysis of the corresponding benzoate ester on a CHIRACEL OD column [cellulose tris(3,5-dimethylphenylcarbamate) on silica gel] to be 93% ee (hexane/ i PrOH, 99.5:0.5 (v/v), flow rate = 0.5 mL/min, detection at $\lambda = 210$ nm. The (*R*)-enantiomer (major) eluted first with a retention time of 14.4 min followed by the (*S*)-isomer (minor) at 17.1 min.

2-Methyl-8-phenyl-4-octyn-3-ol, methanesulfonate (4bR). General Procedure B was employed with **4aR** (0.210 g, 0.98 mmol) to give **4bR** (0.295 g, 99 %): IR (neat) 3382, 2957, 1462, 1041, 759, 699 (cm^{-1}); ^1H NMR (CDCl_3) δ 1.05 (d, $J = 6.9$ Hz, 3H), 1.07 (d, $J = 6.9$ Hz, 3H), 1.84 (quint, $J = 6.9$ Hz, 2H),

2.10 (oct, $J = 6.9$ Hz, 1H), 2.28 (td, $J = 6.8, 2.1$ Hz, 2H), 2.76 (t, $J = 6.9$ Hz, 2H), 3.12 (s, 3H), 5.05 (dd, $J = 6.8, 2.1$ Hz, 1H), 7.12-7.36 (m, 5H); ^{13}C NMR (CDCl_3) δ 17.4, 17.9, 18.0, 29.9, 33.6, 34.7, 39.0, 75.1, 77.4, 89.9, 126.0, 128.4, 129.6, 141.0.

6-Methyl-3-heptyn-1, 5-diol, 1-benzoate (5aR). General Procedure D with **1a** and **2c** on a 2.0 mmol scale gave **5aR** (0.428 g, 0.174 mmol, 87%) after column chromatography (silica gel, ethyl acetate/petroleum ether, 1:5, v/v): ^1H NMR (CDCl_3) δ 1.01 (d, $J = 6.9$ Hz, 3H), 1.03 (d, $J = 6.9$ Hz, 3H), 1.74-1.92 (m, 1H), 2.15 (s, 1H), 2.68 (dt, $J = 6.9, 1.9$ Hz, 2H), 4.10-4.21 (m, 1H), 4.40 (t, $J = 6.8$ Hz, 2H), 7.37-7.62 (m, 3H), 7.95-8.10 (m, 2H); ^{13}C NMR (CDCl_3) δ 17.3, 18.0, 19.3, 34.3, 62.7, 67.8, 81.4, 81.6, 128.3, 129.6, 133.0, 166.3.

The enantiomeric purity of **5aR** was determined by chiral HPLC analysis of the corresponding benzoate ester on a CHIRACEL OD column [cellulose tris(3,5-dimethylphenylcarbamate) on silica gel] to be 99% ee (hexane/ i PrOH, 99.7:0.3 (v/v), flow rate = 0.5 mL/min, detection at $\lambda = 210$ nm. The (*R*)-enantiomer (major) eluted first with a retention time of 35.5 min followed by the (*S*)-isomer (minor) at 36.2 min.

1-Benzoyloxy-6-Methyl-3-heptyn-5-ol, 5-methanesulfonate (5bR). Employing General Procedure B with **5aR** (0.313 g, 1.26 mmol) gave clean crude mesylate **5bR** (0.412 g, 95%): ^1H NMR (CDCl_3) δ 1.07 (d, $J = 6.9$ Hz, 3H), 1.09 (d, $J = 6.9$ Hz, 3H), 2.05 (oct, $J = 6.8$ Hz, 1H), 2.75 (dt, $J = 6.8, 2.1$ Hz, 2H), 3.10 (s, 3H), 4.43 (t, $J = 6.8$ Hz, 2H), 4.96 (dd, $J = 6.8, 2.1$ Hz, 1H), 7.44-7.61 (m, 5H); ^{13}C NMR (CDCl_3) δ 17.3, 18.0, 19.7, 33.6, 39.3, 62.8, 76.3, 76.9, 86.3, 128.6, 129.8, 129.6, 133.5, 166.1.

7-[(1,1-Dimethylethyl)dimethylsilyl]oxy]-2-methyl-4-heptyn-3-ol (6aR). Employing general procedure D with **1a** and alkyne **2d** on a 2.0 mmol scale afforded **6aR** (0.435 g 85%) as a colorless liquid after purification by flash column chromatography (silica gel, ethyl acetate/petroleum ether, 1:5, v/v): ^1H NMR (CDCl_3) δ 0.10 (s, 6H), 0.92 (s, 9H), 1.04 (d, $J = 6.9$ Hz, 3H), 1.06 (d, $J = 6.9$ Hz, 3H), 1.80-1.91 (m, 1H), 2.45 (dt, $J = 7.2, 2.1$ Hz, 2H), 3.74 (t, $J = 7.2$ Hz, 2H), 4.12-4.18 (m, 1H); ^{13}C NMR (CDCl_3) δ -0.49, 17.5, 18.3, 23.1, 25.6, 34.6, 61.9, 68.1, 77.2, 83.1.

The enantiomeric purity of **6aR** was determined by chiral HPLC analysis of the corresponding benzoate ester on a CHIRACEL OD column [cellulose tris(3,5-dimethylphenylcarbamate) on silica gel] to be 90% ee (hexane/ i PrOH, 99.5:0.5 (v/v), flow rate = 0.5 mL/min, detection at $\lambda = 210$ nm. The (*R*)-

enantiomer (major) eluted first with a retention time of 8.1 min followed by the (*S*)-isomer (minor) at 9.1 min.

2,2-Dimethyl-7-phenyl-4-heptyn-3-ol (7aR). Employing General procedure D with 5-phenyl-1-pentyne (3.0 equiv., 0.864 g, 6.0 mmol) and pivalaldehyde (0.181 g, 2.0 mmol) gave **7aR** (0.419 g, 91%) after purification by flash column chromatography (silica gel, ethyl acetate/petroleum ether, 1:5, v/v): IR (neat) 3426 (br), 2954 s, 2852 s, 1604, 1448, 1352, 1036, 993, 741, 693 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.02 (s, 9H), 1.68 (s, 1H), 1.86 (quint, $J = 7.2$ Hz, 2H), 2.27 (dt, $J = 7.2, 2.1$ Hz, 2H), 2.75 (t, $J = 7.2$ Hz, 2H), 4.04 (t, $J = 2.1$ Hz, 1H), 7.20-7.34 (m, 5H); ^{13}C NMR (CDCl_3) δ 18.2, 25.3, 30.4, 34.9, 35.9, 71.6, 80.4, 80.8, 125.9, 128.4, 128.5, 141.6; mass spectrum m/z (relative intensity) EI 230 (1, M^+), 173 (23), 155 (10), 129 (27), 117 (17), 104 (20), 91 (37), 70 (17), 57 (100).

The enantiomeric purity of **7aR** was determined by chiral HPLC analysis of the corresponding benzoate ester on a CHIRACEL OD column [cellulose tris(3,5-dimethylphenylcarbamate) on silica gel] to be 99% ee (hexane/ i PrOH, 99:1 (v/v), flow rate = 0.5 mL/min, detection at $\lambda = 210$ nm. The (*R*)-enantiomer eluted first with a retention time of 21.6 min followed by the (*S*)-isomer (minor) at 27.0 min.

2,2-Dimethyl-8-phenyl-4-octyn-3-ol, methanesulfonate (7bR). Employing General Procedure B with **7aR** (0.345 g, 1.5 mmol) gave mesylate **7bR** (0.439 g, 95%). Crude **7bR** was used without purification: IR (neat) 2951, 2929, 733, 2852, 2355, 2322, 2219, 1355 (vs), 1170 (vs), 913 (vs), 847, 694, 520 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.99 (s, 9H), 1.79 (quint, $J = 7.2$, 2H), 2.21 (dt, $J = 7.2, 2.1$ Hz, 2H), 2.65 (t, $J = 7.2$, 2H), 3.03 (s, 3H), 4.78 (t, $J = 2.1$, 1H); 7.08-7.25 (m, 5H); ^{13}C NMR (CDCl_3) δ 18.2, 25.5, 30.2, 34.9, 36.1, 39.2, 75.4, 80.9, 89.9, 126.2, 128.5, 128.6, 141.2; mass spectrum m/z (relative intensity) EI 308 (1, M^+), 264 (1), 197 (3), 173 (21), 155 (6), 129 (21), 104 (18), 91 (37), 77 (15), 57 (100).

1,6-Diphenyl-2-hexyn-1-ol (8aR). Employing General Procedure D with 5-phenyl-1-pentyne (0.288 g, 6.0 mmol) and benzaldehyde (0.212 g, 2.0 mmol) gave **8aR** (0.265 g, 53%) after purification by flash column chromatography (silica gel, ethyl acetate/petroleum ether, 1:5, v/v): ^1H NMR (CDCl_3) δ 1.91 (quint, $J = 7.2$ Hz, 2H), 2.34 (dt, $J = 7.2, 2.1$ Hz, 2H), 2.77 (t, $J = 7.2$ Hz, 2H), 6.76 (t, $J = 2.1$, 1H), 7.18-7.69 (m, 10H); ^{13}C NMR (CDCl_3) δ 18.3, 30.1, 34.9, 64.9, 77.2, 87.2, 125.9, 126.6, 128.3, 128.5, 128.6 141.5.

The enantiomeric purity of **8aR** was determined by chiral HPLC analysis of the corresponding benzoate ester on a CHIRACEL OD column [cellulose tris(3,5-dimethylphenylcarbamate) on silica gel]

to be 90% ee (hexane/ⁱPrOH, 99:1 (v/v), flow rate = 1.0 mL/min, detection at λ = 210 nm. The (*R*)-enantiomer eluted first with a retention time of 21.5 min followed by the (*S*)-isomer at 23.0 min.

1,6-Diphenyl-2-hexyn-1-ol, 2,3,4,5,6-pentafluorobenzoate (8cR). Employing General Procedure C with **8aR** (0.50 g, 2.0 mmol) and pentafluorobenzoyl chloride (0.738 g, 3.0 mmol) gave benzoate **8cR** (0.728 g, 82%) after column chromatography: IR (neat) 3033, 2945 (s), 2230, 1732 (vs), 1748 (vs), 1334 (vs), 1213 (vs), 1011 (vs), 951 (s), 891 (s), 749, 694 cm⁻¹; ¹H NMR (CDCl₃) δ 1.90 (quint, *J* = 7.2 Hz, 2H), 2.33 (dt, *J* = 7.2, 2.1 Hz, 2H), 2.76 (t, *J* = 7.2 Hz, 2H), 6.71 (t, *J* = 2.1, 1H), 7.17-7.66 (m, 10H); ¹³C NMR (CDCl₃) δ 18.2, 29.9, 34.9, 68.9, 76.3, 89.5, 125.9, 126.0, 126.6, 127.8, 128.3, 128.4, 128.5, 128.6, 128.7, 129.3, 136.4, 141.3, 187.8; mass spectrum, *m/z* (relative intensity), EI, 429 (6), 400 (11), 296 (100), 281 (19), 115 (41), 91 (26).

1-Phenyl-4-tridecyn-6-ol (9aR). Employing General Procedure F with 5-phenyl-1-pentyne (0.864 g, 6.0 mmol) and *n*-octaldehyde (0.281 g, 2.0 mmol) gave **9aR** (0.299 g, 55%) after purification by flash column chromatography (silica gel, ethyl acetate/petroleum ether, 1:5, v/v): IR (neat) 3322, 2929 (vs), 2852 (vs), 2355, 2328, 1448, 1022, 694 (s) cm⁻¹; ¹H NMR (CDCl₃) δ 0.88-0.92 (m, 5H), 1.28-1.32 (m, 8H), 1.45-1.47 (m, 1H), 1.66-1.75 (m, 2H), 1.81-1.90 (m, 2H), 2.25 (dt, *J* = 6.9, 2.1 Hz, 2H), 2.74 (t, *J* = 7.0 Hz, 2H), 4.35-4.42 (m, 1H), 7.19-7.30 (m, 5H); ¹³C NMR (CDCl₃) δ 14.1, 18.2, 22.6, 22.7, 25.3, 29.3, 30.2, 31.8, 34.8, 38.2, 62.8, 81.9, 84.9, 125.9, 128.4, 128.5, 141.6.

The enantiomeric purity of **9aR** was determined by chiral HPLC analysis of the corresponding benzoate ester on a CHIRACEL OD column [cellulose tris(3,5-dimethylphenylcarbamate) on silica gel] to be 90% ee (hexane/ⁱPrOH, 99.5:0.5 (v/v), flow rate = 0.5 mL/min, detection at λ = 210 nm. The (*R*)-enantiomer eluted first with a retention time of 21.3 min followed by the (*S*)-isomer at 21.9 min.

1-Phenyl-4-tridecyn-6-ol, methanesulfonate (9bR). General Procedure B was employed with **9aR** (0.281 g, 1.0 mmol) to afford mesylate **9bR** (0.334 g, 95%), which was used without purification: ¹H NMR (CDCl₃) δ 0.92 (t, *J* = 6.9 Hz, 3H), 1.25-1.47 (m, 8H), 1.57 (quint, *J* = 7.7 Hz, 2H), 1.81-1.98 (m, 4H), 2.27 (dt, *J* = 6.8, 2.1 Hz, 2H), 2.75 (t, *J* = 7.4 Hz, 2H), 3.12 (s, 3H), 5.21 (tt, *J* = 6.6, 2.1 Hz, 1H), 7.20-7.35 (m, 5H); ¹³C NMR (CDCl₃) δ 14.1, 18.1, 22.6, 24.9, 28.9, 29.1, 29.9, 31.7, 34.8, 36.1, 39.1, 72.7, 76.6, 89.5, 126.1, 128.5, 128.5, 141.1.

Carbamic acid, methyl[2-phenyl-5-methyl-2,3-hexadienyl], 1,1-dimethylethyl ester (12S). Employing General Procedure G with *N*-Boc-*N,N*-dimethylamine (0.145 g, 1.0 mmol,) and **3bR** (0.252 g, 1.0 mmol,) gave **12S** (0.292 g, 78%) as a colorless oil after purification by flash column chromatography (silica gel, ether/petroleum ether, 1/5, v/v): ¹H NMR (CDCl₃) δ 1.11 (d, *J* = 6.7 Hz, 6H), 1.48 (s, 9H), 2.38-2.54 (m, 1H), 2.77-2.91 (m, 3H), 4.17-4.50 (m, 2H), 5.59-5.68 (m, 1H), 7.14-7.47 (m, 5H); ¹³C NMR (CDCl₃) δ 22.6, 28.4 (28.7), 33.7, 48.5 (49.2), 79.8 (80.1), 103.1 (103.2), 104.1, 126.0, 126.8, 128.4, 135.5 (135.7), 155.5 (155.7), 202.1 (202.3) (rotamers).

The enantiomeric purity of **12S** was determined by chiral HPLC analysis on a CHIRACEL OD column [cellulose tris(3,5-dimethylphenylcarbamate) on silica gel] to be 81% ee. (hexane/ⁱPrOH, 99.65:0.35 (v/v), flow rate = 0.37 mL/min, detection at λ = 210 nm. The (*S*)-enantiomer (major) eluted first with a retention time of 27.1 min followed by the (*R*)-isomer (minor) at 29.2 min.

Carbamic acid, methyl[2-(3-phenylpropyl-5-methyl-2,3-hexadienyl], 1,1-dimethylethyl ester (13S). Employing General Procedure G with *N*-Boc-*N,N*-dimethylamine (0.217 g, 1.5 mmol) and **4bR** (0.441 g, 1.5 mmol) afforded **13S** (0.40 g, 78%) as a colorless oil after purification by flash column chromatography (silica gel, ether/petroleum ether, 1:5, v/v): [α]_D²² = - 11.3° (*c* 0.011, CH₂Cl₂); IR 2960 (s), 2925 (s), 2864 (s), 1964 (w), 1702 (s), 1463 (s), 1395 (s), 1300 (s), 1247 (s), 1151 (s), 880 (s), 697 (s) cm⁻¹; ¹H NMR (CDCl₃) δ 1.03 (d, *J* = 6.8 Hz, 6H), 1.46 (s, 9H), 1.70-1.85 (m, 2H), 1.86-1.99 (m, 2H), 2.24-2.37 (m, 1H), 2.66 (t, *J* = 7.5 Hz, 2H), 2.83 (s, 3H), 3.68-3.89 (m, 2H), 5.19-5.30 (m, 1H), 7.13- 7.34 (m, 5H); ¹³C NMR (CDCl₃) δ 22.6, 28.3, 29.2, 33.5, 33.9, 35.5, 50.8, 51.4, 79.0 (79.2), 100.9 (101.0), 101.9 (102.1), 125.6, 128.2, 128.3, 142.2, 155.5 (155.7), 199.1 (199.3) (rotamers); mass spectrum *m/z* (relative intensity) EI 288 (18), 287 (90), 170 (11), 211 (4), 183 (14), 169 (8), 144 (8), 108 (21), 96 (10), 88 (40), 57 (100).

The enantiomeric purity of **13S** was determined by chiral HPLC analysis on a CHIRACEL OD column [cellulose tris(3,5-dimethylphenylcarbamate) on silica gel] to be 93% ee (hexane/ⁱPrOH, 99.8:0.2 (v/v), flow rate = 0.33 mL/min, detection at λ = 210 nm. The (*S*)-enantiomer (major) eluted first with a retention time of 30.3 min followed by the (*R*)-isomer (minor) at 32.7 min.

Carbamic acid, [2-(2-benzoyloxy)ethyl-5-methyl-2,3-hexadienyl]methyl, 1,1-dimethylethyl ester (14S). Employing General procedure G with *N*-Boc-*N,N*-dimethylamine (0.145 g 1.0 mmol) and **5bR** (0.328 g, 1.0 mmol) afforded **14S** (0.275 g, 74%) as a colorless oil after purification by flash column chromatography (silica gel, ether/petroleum ether, 1:5, v/v): IR (neat) 2969 (s), 1964 (w), 1711 (s),

1606 (m), 1457 (s), 1387 (s), 1274 (s), 1154 (s), 865 (s), 767 (s), 720 (s) cm^{-1} ; ^1H NMR (CDCl_3) δ 0.95 (d, $J = 6.7$ Hz, 6H), 1.44 (s, 9H), 2.16-2.29 (m, 1H), 2.35 (td, $J = 6.8, 2.9$ Hz, 2H), 2.81 (s, 3H), 3.72-3.96 (m, 2H), 4.40 (t, $J = 6.8$ Hz, 2H), 5.16-5.31 (m, 1H), 7.30-7.57 (m, 3H), 7.90-8.14 (m, 2H); ^{13}C NMR (CDCl_3) δ 22.4, 28.2, 28.3, 29.0, 34.2, 51.4, 51.7, 67.9, 79.6, 98.2, 101.6, 128.2, 129.5, 130.0, 132.8, 156.2, 166.4, 199.3 (rotamers); mass spectrum m/z (relative intensity) EI 317 (24), 258 (5), 195 (13), 180 (10), 105 (75), 93 (26), 77 (32), 57 (100).

The enantiomeric purity of **14S** was determined by chiral HPLC analysis on a CHIRACEL OD column [cellulose tris(3,5-dimethylphenylcarbamate) on silica gel] to be 99% ee. (hexane/ i PrOH/TFA, 99.4:0.5:0.1 (v/v), flow rate = 1.00 mL/min, detection at $\lambda = 210$ nm. The (*S*)-enantiomer (minor) eluted first with a retention time of 5.5 min followed by the (*R*)-isomer (major) at 14.8 min.

Carbamic Acid, methyl[4-phenyl-2-(3-phenylpropyl)-2,3-butadienyl], 1,1-dimethylethyl ester (16S). Employing General Procedure G on *N*-Boc-*N,N*-dimethylamine (0.145 g, 1.0 mmol) and **8cR** (0.429 g, 1.0 mmol) afforded **16S** (0.263 g, 77%) as a colorless oil after purification by flash column chromatography (silica gel, ether/petroleum ether, 1:5, v/v): IR (neat) 2978, 2912, 1945, 1683 (vs), 1495, 1394, 1148 (vs), 875, 744, 684 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.48 (1.51) (s, 9H) (rotamer), 1.84-1.91 (m, 2H), 2.11-2.23 (m, 2H), 2.74 (t, $J = 7.5$ Hz, 2H), 2.93 (2.90) (s, 3H), 3.87-4.22 (m, 2H), 6.33 (s, 1H), 7.18-7.42 (m, 10 H); ^{13}C NMR (CDCl_3) δ 28.4, 29.4, 29.6, (34.0) 34.5, 35.7, 50.8 (51.3), 79.4 (79.6), 97.0 (97.4), 105.4, 105.6, 125.8, 126.8, 128.4, 128.5, 128.6, 135.0, 142.2, 155.6 (155.8), 202.1 (202.4); mass spectrum, m/z (relative intensity), EI, 341 (3), 312 (11), 269 (54), 229 (26), 129 (100), 91 (72).

The enantiomeric purity of **16S** was determined by chiral HPLC analysis on a CHIRACEL OD column [cellulose tris(3,5-dimethylphenylcarbamate) on silica gel] to be 90% ee (hexane/ i PrOH, 99.5:0.5 (v/v), flow rate = 0.5 mL/min, detection at $\lambda = 210$ nm. The (*R*)-enantiomer eluted first with a retention time of 16.4 min followed by the (*S*)-isomer (minor) at 17.2 min.

Carbamic acid, methyl[2-(3-phenylpropyl)-2,3-undecadienyl], 1,1-dimethylethyl ester (17S). Employing General Procedure G on *N*-Boc-*N,N*-dimethylamine (0.145 g, 1.0 mmol) and **9bR** (0.350 g, 1.0 mmol) afforded **17S** (0.315 g, 79%) as a colorless oil after purification by flash column chromatography (silica gel, ether/petroleum ether, 1:5, v/v): IR (neat) 2920 (vs), 2369, 2325, 1940 (w), 1701 (vs), 1458, 1384, 1154, 877, 690 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.91 (t, $J = 7.0$ Hz, 3H), 1.47 (br s, 8H), 1.38-1.50 (m, 2H), 1.47 (s, 9H), 1.73-1.86 (m, 2H), 1.90-1.99 (m, 2H), 1.97-2.06 (m, 2H), 2.66 (t, $J = 7.6$ Hz, 2H), 2.83 (s, 3H), 3.78-3.86 (br s, 2H), 5.19-5.25 (m, 1H), 7.19-7.32 (m, 5H); ^{13}C NMR (CDCl_3)

δ 14.1, 22.7, 28.5, 29.2, 29.3, 29.4, 31.8, 33.5, 33.8, 35.6, 50.9, 51.5, 79.3, 93.4, 100.5, 125.7, 128.3, 128.5, 142.4, 155.7, 201.2; mass spectrum m/z (relative intensity) 399 (1, M^+), 343 (100), 326 (190), 88 (35), 57 (100).

The enantiomeric purity of **17S** was determined by chiral HPLC analysis on a CHIRACEL OD column [cellulose tris(3,5-dimethylphenylcarbamate) on silica gel] to be 90% ee (hexane/*i*PrOH, 99.5:0.5 (v/v), flow rate = 0.5 mL/min, detection at λ = 210 nm. The (*S*)-enantiomer eluted first with a retention time of 14.0 min followed by the (*R*)-isomer at 14.7 min.

Deprotection of *N*-Boc Carbamates with Trimethylsilyltrifluoromethane Sulfonate (TMSOTf) in CH_2Cl_2 : Isomerization Studies. To a solution of **12S** (380 mg, 1.26 mmol, 78% ee) in dichloromethane (20 mL) was added trimethylsilyltriflate (280 mg, 1.26 mmol) at $-40^\circ C$, and the solution was allowed to warm to room temperature ($\sim 20^\circ C$) over three hours. After 3 hours, saturated aqueous K_2CO_3 (20 mL) was added to each reaction mixture. After stirring for 2-3 minutes the reaction mixture was transferred to a separatory funnel, shaken well, and the layers were separated. The aqueous layer was extracted with dichloromethane (25 mL), and the combined organic layers were washed with brine (25 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo to give crude material (233 mg, 92% yield). 1H and ^{13}C NMR of the crude material indicated it to be **18S** uncontaminated with the cyclised product **24S**. The **18S**, thus obtained, was cyclised using the standard $AgNO_3$ procedure to give **24S** in 55% yield (128 mg), which showed an ee of 78% (same as the starting **12S**).

Another reaction was setup with **12S** (487 mg, 1.62 mmol, 81% ee), dichloromethane (20 mL) and trimethylsilyltriflate (360 mg, 1.62 mmol) using same procedure. After stirring for 20 minutes, the second reaction was worked up in similar way to give crude material (305 mg, 94% yield). 1H and ^{13}C NMR showed it to be 67:33 mixture of **18S**: **24S**. The crude was again dissolved in dichloromethane (25 mL) and saturated aqueous K_2CO_3 (25 mL) was added and the biphasic mixture was stirred for 12 hours. The organic layer was separated, dried over anhydrous $MgSO_4$, and concentrated in vacuo to give crude material (256 mg). 1H and ^{13}C NMR analysis showed it to be 33:67 mixture of **18S**: **24S**. **24S** [106 mg, 62% (based on the amount present in the crude material)] was isolated by silica gel column chromatography using 30% ethyl acetate in hexane. This isolated **24S** had an ee of 73% compared to an 81% ee for the starting **12S**.

***N*-Methyl-2-phenyl-5-methyl-2,3-hexadienyl-1-amine (18S).** General Procedure H was employed on **12S** (0.885 g, 2.94 mmol) to afford product **18S** (0.582 g, 99%), which was pure by both 1H and ^{13}C

NMR analysis: IR (neat) 2962 (s), 2868 (s), 2783 (s), 1940, 1600 (s), 1498 (s), 1447 (s), 1290 (s), 1106 (s), 919 (m), 761 (s), 697 (s) cm^{-1} ; ^1H NMR (CDCl_3) δ 1.12 (d, $J = 6.8$ Hz, 6H), 1.64 (s, 1H), 2.35-2.66 (m, 4H), 3.64 (s, 2H), 5.59-5.68 (m, 1H), 7.12-7.49 (m, 5H); ^{13}C NMR (CDCl_3) δ 22.6, 22.7, 28.6, 35.8, 51.4, 102.6, 105.3, 125.7, 126.5, 128.3, 135.9, 201.6; mass spectrum m/z (relative intensity) EI 202 (6, $\text{M}^+ + 1$), 201 (34, M^+), 186 (100), 141 (30), 128 (30), 115 (58), 102 (14), 91 (24), 77 (30), 51 (26).

***N*-Methyl-2-(3-phenylpropyl)-5-methyl-2,3-hexadienyl-1-amine (19S).** Employing General Procedure H with **13S** (0.613 g, 2.13 mmol) afforded **19S** (0.490 g, 95 %), which was pure by both ^1H and ^{13}C NMR analysis: IR (neat) 3432 (m), 2965 (s), 2871 (s), 2794 (m), 1940 (w), 1649 (w), 1497 (s), 1470 (s), 1108 (s), 916 (s), 732 (s), 692 (s) cm^{-1} ; ^1H NMR (CDCl_3) δ 1.02 (d, $J = 6.7$ Hz, 6H), 1.50 (s, 1H), 1.70-1.86 (m, 2H), 1.94-2.06 (m, 2H), 2.23-2.39 (m, 1H), 2.43 (s, 3H), 2.66 (t, $J = 7.5$ Hz, 2H), 3.13 (s, 2H), 5.22- 5.32 (m, 1H), 7.12-7.34 (m, 5H); ^{13}C NMR (CDCl_3) δ 22.7, 22.8, 28.4, 29.3, 30.1, 35.5, 53.8, 101.2, 103.9, 125.6, 128.2, 128.4, 142.4, 198.4; mass spectrum, m/z (relative intensity), EI 243 (11, M^+) 228 (28), 201 (30), 186 (11), 139 (51), 124 (24), 104 (24), 91 (100), 84 (91), 77 (49), 65 (41), 51 (21).

***N*-Methyl-2-[1-(2-benzoyloxy)ethyl]-5-methyl-2,3-hexadien-1-amine (20S).** General Procedure H was employed on **14S** (0.174 g, 0.55 mmol) to afford amino allene **20S** (0.480 g, 95%) which was pure by both ^1H and ^{13}C NMR analysis: IR (neat) 3327 (w), 3061 (w), 2965 (s), 2864 (s), 2794 (m), 1964 (w), 1712 (s), 1615 (m), 1457 (s), 1387 (s), 1290 (s), 1183 (s), 1123 (s), 1020 (s), 968 (m), 915 (s), 819 (s), 723 (s) cm^{-1} ; ^1H NMR (CDCl_3) δ 0.94 (d, $J = 6.7$ Hz, 6H), 1.63 (s, 1H), 2.15-2.30 (m, 1H), 2.30-2.47 (m, 4H), 3.17 (s, 2H), 4.39 (t, $J = 6.9$ Hz, 2H), 5.23 (td, $J = 5.7, 2.7$ Hz, 1H), 7.34-7.55 (m, 3H), 7.95-8.04 (m, 2H); ^{13}C NMR (CDCl_3) δ 22.4, 22.5, 28.2, 29.7, 35.7, 53.8, 63.3, 98.0, 100.3, 101.5, 128.1, 129.4, 130.2, 166.4, 198.8; mass spectrum, m/z (relative intensity) EI 273 (5, M^+), 258 (44), 168 (6), 151 (45), 136 (44), 105 (80), 91 (22), 77 (100), 51 (28).

***N*-methyl-4-phenyl-2-(3-phenylpropyl)-2, 3-butadien-1-amine (22S).** General Procedure H was employed on **16S** (0.377 g, 1.0 mmol,) to afford **22S** (0.269 g, 97 %) which was pure by both ^1H and ^{13}C NMR analysis: IR (neat): 3333 (br), 2929, 2852, 1940, 1498, 902, 826, 749 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.82 (br s, 1H), 1.86-1.97 (m, 2H), 2.18-2.28 (m, 2H), 2.51 (s, 3H), 2.75 (t, $J = 7.5$ Hz, 2H), 3.35 (br s, 2H), 6.37 (t, $J = 2.1$ Hz, 1H), 7.19-7.42 (m, 10H); ^{13}C NMR (CDCl_3) δ 29.5, 30.4, 35.7, 36.1, 53.7, 97.2, 107.4, 125.8, 126.7, 126.8, 128.4, 128.5, 128.7, 135.4, 142.3, 201.6; mass spectrum, m/z (relative intensity), EI, 277 (8, M^+), 200 (21), 170 (59), 158 (45), 91 (100).

N*-Methyl-2-(3-phenylpropyl)-2,3-undecadien-1-amine (23*S*)**. General Procedure H was employed on **17*S (0.399 g, 1.0 mmol) to afford **23*S*** (0.282 g, 95 %) which was pure by both ^1H and ^{13}C NMR analysis: IR (neat) 2833, 1940 (w), 1449 (s), 689 (s) cm^{-1} ; ^1H NMR (CDCl_3) δ 0.90 (t, $J = 6.5$ Hz, 3H), 1.20-1.36 (m, 10 H), 1.36-1.49 (m, 2H), 1.78 (quint, $J = 7.6$ Hz, 2H), 2.02-2.11 (m, 2H), 2.54 (br s, 3H), 2.67 (t, $J = 7.5$ Hz, 2H), 3.30 (br s, 2H), 3.40 (br s, 1H), 5.32 (t, $J = 2.4$ Hz, 1H), 7.17-7.29 (m, 5H); ^{13}C NMR (CDCl_3) δ 14.1, 22.7, 29.15, 29.18, 29.2, 29.3, 29.4, 30.1, 31.8, 35.4, 52.4, 77.2, 94.8, 98.9, 125.7, 128.3, 128.4, 142.3, 201.5; mass spectrum m/z (relative intensity) 297 (M^+ , 23), 212 (15), 193 (100), 122 (16), 120 (14), 109 (46), 108 (44), 91 (11).

1-Methyl-2-isopropyl-4-phenyl-2,5-dihydro-1H-pyrrole (24*S*). Employing General Procedure I on **18*S*** (0.101 g, 0.5 mmol) afforded **24*S*** (55 mg, 55%) as a slight yellow liquid after purified by flash column chromatography (silica gel, 100% diethyl ether as eluent): IR 2960 (s), 2868 (s), 2774 (s), 1496 (s), 1467 (s), 1452 (s), 1387 (s), 1357 (m), 912 (s), 740 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 0.93 (d, $J = 6.7$ Hz, 3H), 1.03 (d, $J = 6.9$ Hz, 3H), 1.72-1.88 (m, 1H), 2.54 (s, 3H), 3.31-3.42 (m, 1H), 3.57-3.65 (m, 1H), 4.21-4.32 (m, 1H), 6.08 (d, $J = 1.5$ Hz, 1H), 7.24-7.44 (m, 5H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 18.0, 19.9, 31.9, 43.0, 63.4, 79.6, 123.6, 125.4, 127.4, 128.4, 134.4, 138.9; mass spectrum m/z (relative intensity) EI 201 (2, M^+), 200 (6, $\text{M}^+ - 1$), 199 (32, $\text{M}^+ - 2$), 184 (97), 158 (100), 143 (19), 128 (11), 115 (17), 91 (99), 77 (98), 51 (7). Anal Calcd for $\text{C}_{14}\text{H}_{19}\text{N}$: C, 83.58; H, 9.45. Found: C, 83.31; H, 9.65.

The enantiomeric purity of **24*S*** was determined by chiral HPLC analysis on a CHIRACEL OD column [cellulose tris(3,5-dimethylphenylcarbamate) on silica gel] to be 81% ee (hexane/ i PrOH/diethylamine, 99.55:0.35:0.10 (v/v), flow rate = 0.37 mL/min, detection at $\lambda = 254$ nm. The (*S*)-enantiomer (major) eluted first with a retention time of 12.4 min followed by the (*R*)-isomer (minor) at 13.6 min.

1-Methyl-2-isopropyl-4-(3-phenylpropyl)-2,5-dihydro-1H-pyrrole (25*S*). General Procedure I was employed on **19*S*** (0.134 g, 0.55 mmol) to afford **25*S*** (0.082g, 61%) after purification by flash column chromatography (silica gel, ether/petroleum ether, 1/1): IR (neat) 3055 (s), 3027 (s), 2940 (s), 2770 (s), 1661 (m), 1596 (s), 1493 (s), 1454 (s), 1383 (s), 1350 (s), 1170 (s), 1105 (s), 914 (s), 733 (s), 689 (s) cm^{-1} ; ^1H NMR (CDCl_3) δ 0.88 (d, $J = 6.7$ Hz, 3H), 0.96 (d, $J = 6.8$ Hz, 3H), 1.62-1.89 (m, 3H), 2.12-2.28 (m, 2H), 2.46 (s, 3H), 2.65 (t, $J = 7.5$ Hz, 2H), 3.25-3.31 (m, 2H), 3.71-3.83 (m, 1H), 5.32(s, 1H), 7.16-7.36 (m, 5H); ^{13}C NMR (CDCl_3) δ 17.8, 19.9, 28.5, 29.3, 31.8, 35.5, 42.9, 65.4, 79.0, 121.9, 125.6, 128.2, 128.4, 140.8, 142.2; mass spectrum, m/z (relative intensity), EI 243 (3, M^+), 241 (13), 200 (100),

137 (77), 122 (27), 108 (15), 91 (79), 82 (23), 77 (12), 65 (16). Anal. Calcd for C₁₇H₂₅N: C, 83.95; H, 10.29. Found: C, 83.40; H, 10.32.

The enantiomeric purity of **25S** was determined by chiral HPLC analysis on a CHIRACEL OD column [cellulose tris(3,5-dimethylphenylcarbamate) on silica gel] to be 93% ee (hexane/ⁱPrOH/diethylamine, 99:0.5:0.5 (v/v), flow rate = 0.35 mL/min, detection at λ = 235 nm. The (*S*)-enantiomer (major) eluted first with a retention time of 11.9 min followed by the (*R*)-isomer (minor) at 14.9 min.

1-Methyl-2-isopropyl-4-(2-benzoyloxyethyl)-3-pyrroline (26S). General Procedure I was employed with **26S** (0.147 g, 0.54 mmol) afforded **26S** (85 mg, 57%) after purification by flash column chromatography (silica gel, ether/petroleum ether, 3/1, v/v): IR (neat) 3415 (s), 3061 (m), 2961 (s), 2873 (s), 2780 (s), 1719 (s), 1611 (m), 1462 (s), 1387 (s), 1278 (s), 1190 (s), 1116 (s), 1029 (s), 969 (m), 719 (s) cm⁻¹; ¹H NMR (CDCl₃) δ 0.80 (d, *J* = 6.8 Hz, 3H), 0.89 (d, *J* = 6.9 Hz, 3H), 1.58-1.70 (m, 1H), 2.41 (s, 3H), 2.47-2.58 (m, 2H), 3.07-3.25 (m, 2H), 3.74-3.86 (m, 1H), 4.40 (td, *J* = 6.7, 0.8 Hz, 2H), 5.40 (s, 1H), 7.35-7.57 (m, 3H), 7.96-8.05 (m, 2H); ¹³C NMR (CDCl₃) δ 17.7, 19.8, 28.5, 31.6, 42.8, 63.0, 65.4, 79.0, 124.1, 128.2, 129.5, 130.2, 132.8, 136.9, 166.4; mass spectrum, *m/z* (relative intensity), EI 273 (0.5, M⁺), 272 (1), 271 (3), 230 (9), 149 (24), 134 (42), 108 (100), 94 (14), 77 (28). Anal. Calcd for C₁₇H₂₃NO₂: C, 74.73; H, 8.42. Found: C, 74.75; H, 8.49.

The enantiomeric purity of **26S** was determined by chiral HPLC analysis on a CHIRACEL OD column [cellulose tris(3,5-dimethylphenylcarbamate) on silica gel] to be 99% ee (hexane/ⁱPrOH/diethylamine, 99:0.5:0.5 (v/v), flow rate = 0.5 mL/min, detection at λ = 215 nm. The (*S*)-enantiomer (major) eluted first with a retention time of 40.9 min followed by the (*R*)-isomer (minor) at 41.3 min.

1-Methyl-2-phenyl-4-(3-phenylpropyl)-3-pyrroline (28R). General Procedure I was employed on **16S** (0.277 g, 0.5 mmol) to afford **28R** (109 mg, 79%) after purification by flash column chromatography (silica gel, ether/petroleum ether, 1/1): IR (neat): 2934, 2858, 2770, 1487, 1448, 1345, 1055, 886, 847, 755, 689 cm⁻¹; ¹H NMR (CDCl₃) δ 1.91 (quint, *J* = 7.5 Hz, 2H), 2.18-2.38 (m, 2H), 2.41 (s, 3H), 2.76 (t, *J* = 7.5 Hz, 2H), 3.31-3.37 (m, 1H), 3.66-3.92 (m, 1H), 4.31 (br s, 1H), 5.41 (s, 1H), 7.21-7.36 (m, 10H); ¹³C NMR (CDCl₃) δ 28.6, 29.3, 35.6, 41.3, 65.1, 76.9, 124.7, 125.9, 127.7, 127.8, 128.4, 128.5, 128.6, 142.2, 142.4, 142.8; mass spectrum, *m/z* (relative intensity), EI, 277 (23, M⁺), 200 (29), 179 (63), 158 (49), 91 (100). High resolution mass spectrum *m/z* 277.1827 (M⁺) (calcd. for C₂₀H₂₃N 277.1830).

The enantiomeric purity of **28R** was determined by chiral HPLC analysis on a CHIRACEL OD column [cellulose tris(3,5-dimethylphenylcarbamate) on silica gel] to be 90% ee (hexane/ⁱPrOH/diethylamine, 99:0.5:0.5 (v/v), flow rate = 0.5 mL/min, detection at λ = 215 nm. The (*R*)-enantiomer (major) eluted first with a retention time of 15.1 min followed by the (*S*)-isomer (minor) at 18.2 min.

1-Methyl-2-(1-heptyl)-4-(3-phenylpropyl)-3-pyrroline (29S). General Procedure I was employed on **23S** (0.148 g, 0.5 mmol) to afford **29S** (99 mg, 66%) after purification by flash column chromatography (silica gel, ether/petroleum ether, 1/1): IR (neat) 2833, 1380 (vs), 689 (s) cm^{-1} ; ¹H NMR (CDCl_3) δ 0.90 (t, J = 6.5 Hz, 3H), 1.18-1.49 (m, 12H), 1.50-1.62 (m, 1H), 1.80-1.83 (m, 2H), 2.09-2.19 (m, 2H), 2.66 (t, J = 7.5 Hz, 2H), 2.83 (s, 3H), 3.26-3.45 (m, 1H), 3.63 (br s, 1H), 4.12-4.31 (m, 1H), 5.45 (d, J = 1.4 Hz, 1H), 7.13-7.36 (m, 5H); ¹³C NMR (CDCl_3) δ 14.1, 22.6, 26.4, 28.1, 28.8, 29.1, 29.5, 31.7, 35.5, 64.8, 75.2, 77.2, 122.4, 126.0, 128.4, 128.4, 140.1, 141.5; mass spectrum m/z (relative intensity) 299 (22), 212 (13), 193 (100), 122 (20), 109 (47), 108 (46), 91 (16). High resolution mass spectrum m/z 299.2609 (M^+) (calcd. for $\text{C}_{21}\text{H}_{33}\text{N}$ 299.2613).

The enantiomeric purity of **29S** was determined by chiral HPLC analysis on a CHIRACEL OD column [cellulose tris(3,5-dimethylphenylcarbamate) on silica gel] to be 90% ee (hexane/ⁱPrOH/diethylamine, 99:0.5:0.5 (v/v), flow rate = 0.5 mL/min, detection at λ = 210 nm. The (*S*)-enantiomer (major) eluted first with a retention time of 14.1 min followed by the (*R*)-isomer (minor) at 16.8 min.

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Carbamic acid, [2-(2-benzoyloxy)ethyl-5-methyl-2,3-hexadienyl]methyl, 1,1-dimethylethyl ester (14S)

Carbanic acid, [2-(2-benzoyloxy)ethyl-5-methyl-2,3-hexadienyl]methyl, 1,1-dimethylethyl ester (14S)

Carbamic acid, methyl[2-(3-phenylpropyl-5-methyl-2,3-hexadienyl), 1,1-dimethylethyl ester (15S)

7.300
7.287
7.216
7.201

2.849

1.801

1.482

1.071

Carbamic acid, methyl[2-(3-phenylpropyl-5-methyl-2,3-hexadienyl), 1,1-dimethylethyl] ester (15S)

7.370
7.355
7.321
7.296
7.280
7.277
7.259
7.247
7.223
7.198
6.333

4.124
4.077
4.044
3.936
3.885
2.925
2.898
2.762
2.737
2.712
2.190
2.165
2.148
2.138
2.103
2.018
1.967
1.945
1.939
1.921
1.914
1.897
1.888
1.873
1.863
1.550
1.548
1.508
1.478
1.359
1.349
1.325
1.323
1.301

Carbamic acid, methyl(2-3(3-phenylpropyl)-2,3-undecadienyl)-2,3-undecadienyl, 1,1-dimethylethyl ester (16S)

Carbamic acid, methyl[2-(3-phenylpropyl)-2,3-undecadienyl] 1,1-dimethylethyl ester (17S)

N-methyl-2-(3-phenylpropyl)-2,3-undecadien-1-amine (235)

1-Methyl-2-isopropyl-4-(2-benzoyloxyethyl)-3-pyrroline (26S)