SUPPORTING INFORMATION

Enantioselective Carbolithiation Initiated Cascade Reactions

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Materials and methods

All commercially available solvents and reagents were used as supplied unless otherwise stated. Cumene was distilled over calcium hydride and stored over 4 Å molecular sieves. Benzonitrile, 2,2-diethoxypropionitrile, *N*-methoxy-*N*-methyl-acetamide and γ -butyrolactone were distilled prior to use. (-)-Sparteine was stored over potassium hydroxide. Anhydrous TMEDA was used as supplied. *n*-Butyllithium was purchased as 2.5 M solution in hexanes, phenyllithium as 2.0 M or 1.8 M solution in di-*n*-butylether, *n*-hexyllithium as 2.3 M solution in hexane and ethyllithium as 0.5 M solution in 90/10 benzene/cyclohexane. The exact concentration of the organolithium solution was determined by titration with diphenylacetic acid in THF prior to use¹. THF and diethyl ether were distilled from sodium benzophenone ketyl, under nitrogen, immediately prior to use. Reactions were carried out in oven dried or flame dried glassware. Low temperatures were obtained with an acetone/solid CO₂ bath or ice/salt bath. Chromatography was performed on silica gel 60 PF₂₅₄ or aluminium oxide 90. ¹H and ¹³C NMR spectrum were recorded on a 300 MHz instrument.

1. Kofran, W.G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879.

Procedure for synthesis of benzyl-(2-propenyl-phenyl)-amines 1a-b.

A solution of tetrakis(triphenylphosphine)palladium(0) (5 mol%) and benzyl-(2-bromophenyl)-amine (8 mmol) in DME (40 ml) was stirred at room temperature under nitrogen, in the dark, for 20 min. *trans*-1-Propen-1-ylboronic acid (10 mmol), sodium carbonate (8 mmol) and water (10 ml) were added and the mixture heated at reflux for 20 h. The reaction mixture was cooled to room temperature and the DME was evaporated. The aqueous layer was extracted with dichloromethane (2 x 20 ml). The combined organic layers were dried over sodium sulfate and concentrated to dryness. Gravity chromatography eluting with cyclohexane/diethyl ether gave the purified product.

Benzyl-(2-propenyl-phenyl)-amine (1a).

Colorless oil (92% yield). ^1H NMR (CDCl_3 , 300 MHz) δ : 7.40-7.26 (m, 5H), 7.22 (m, 1H), 7.10 (m, 1H), 6.70 (m, 1H), 6.60 (d, 1H, $J = 8.1$ Hz), 6.42 (d, 1H, $J = 15.4$ Hz), 6.07 (dq, 1H, $J = 15.4/6.5$ Hz), 4.35 (s, 2H), 4.14 (bs, 1H), 1.88 (m, 3H). ^{13}C NMR (CDCl_3 , 75 MHz) δ : 144.9, 139.5, 128.7, 128.6, 128.2, 127.6, 127.5, 127.3, 126.7, 124.6, 117.6, 110.8, 48.4, 19.0. IR (neat): 1452, 1503, 1600, 2849, 2912, 3028, 3062, 3436 cm^{-1} . EI-MS: m/z 224.2 $[\text{M}+\text{H}]^+$. HRMS $[\text{M}+\text{H}]^+$: 224.1431, $\text{C}_{16}\text{H}_{18}\text{N}$ requires 224.1439.

Benzyl-(4-methoxy-2-propenyl-phenyl)-amine (1b).

Pale yellow oil (72% yield). ^1H NMR (CDCl_3 , 300 MHz) δ : 7.40-7.24 (m, 5H), 6.84 (m, 1H), 6.70 (m, 1H), 6.57 (d, 1H, $J = 8.6$ Hz), 6.44 (d, 1H, $J = 15.5$ Hz), 6.08 (dq, 1H, $J = 15.5/6.5$ Hz), 4.30 (s, 2H), 3.75 (s, 3H), 1.88 (m, 3H). ^{13}C NMR (CDCl_3 , 75 MHz) δ : 152.1, 139.7, 139.2, 128.7, 128.6, 128.6, 127.6, 127.1, 126.5, 126.0, 113.2, 112.3, 55.6, 49.2, 18.8. IR (neat): 1217, 1452, 1504, 2831, 2912, 2933, 3026, 3060, 3425 cm^{-1} . EI-MS: m/z 254.1 $[\text{M}+\text{H}]^+$. HRMS $[\text{M}+\text{H}]^+$: 254.1542, $\text{C}_{17}\text{H}_{20}\text{NO}$ requires 254.1545. Anal. calcd for $\text{C}_{17}\text{H}_{19}\text{NO}$: C, 80.62; H, 7.56; N, 5.53. Found: C, 80.26; H, 7.50; N, 5.35.

Procedure for synthesis of indoles 3a-i.

Phenyllithium (0.50 mmol) was added to a solution of **1** (0.50 mmol) in cumene (2 ml) and stirred at room temperature for 15 min. This solution was added dropwise, over 15 min to a premixed solution of alkyllithium (1.0 mmol)¹ and (-)-sparteine² (1.50 mmol) in cumene (2 ml) at -15°C. The mixture was stirred at -15°C for a further 4 h and treated with the electrophile (5.0 mmol). The bath was removed and the reaction stirred at room temperature for 30 min (with DMF and γ -butyrolactone as electrophile) or 3 h (with benzonitrile, 2,2-diethoxypropionitrile, *N*-methoxy-*N*-methyl-acetamide as electrophile). Hydrochloric acid³ (2M, 10 ml) was added and stirred at room temperature for 10 min. The organic layer was separated and the aqueous layer extracted with diethyl ether (2 x 10 ml). Combined organic layers were dried over sodium sulfate and concentrated to dryness. Gravity chromatography eluting with pentane/diethyl ether gave the purified product.

1. For ethyllithium 2.5 mmol used.
2. The racemic mixture was generated by replacing (-)-sparteine with *N,N,N',N'*-tetramethylethylenediamine (TMEDA).
3. For **3d** saturated ammonium chloride solution (10 ml) was added and stirred at room temperature for 10 min. The aqueous layer was separated, hydrochloric acid (5M, 10 ml) was added to the organic layer and stirring continued for 30 min.

1-Benzyl-3-(1-methyl-pentyl)-1*H*-indole (3a).

Colorless oil. ¹H NMR (CDCl₃, 300 MHz) δ : 7.65 (d, 1H, *J* = 7.7 Hz), 7.30-7.22 (m, 4H), 7.16-7.05 (m, 4H), 6.87 (s, 1H), 5.27 (s, 2H), 3.03 (m, 1H), 1.78 (m, 1H), 1.61 (m, 1H), 1.34 (d, 3H, *J* = 6.9 Hz), 1.26 (m, 4H), 0.86 (m, 3H). ¹³C NMR (CDCl₃, 75 MHz) δ : 138.0, 136.8, 128.7, 127.6, 127.4, 126.7, 124.2, 122.1, 121.5, 119.6, 118.6, 109.6, 49.8, 37.5, 30.8, 30.0, 22.9, 21.5, 14.1. IR (neat): 1453, 1467, 2869, 2926, 2956, 3030, 3058 cm⁻¹. EI-MS: *m/z* 292.3 [M+H]⁺. HRMS [M+H]⁺: 292.2053, C₂₁H₂₆N requires 292.2065. [α]_D²⁰ = +4° (c = 0.2, CH₂Cl₂, 20°C). The enantiomeric excess was determined using a Chiracel OD-H column (99.75/0.25 pentane/isopropanol, 0.4 ml/min), peaks fully defined

using PeakFit v4 software with retention times of isomers: 48.0 min (8%) and 49.2 min (92%). A racemic mixture generated with TMEDA gave retention times 48.0 min (50%) and 49.2 min (50%).

1-Benzyl-2-methyl-3-(1-methyl-pentyl)-1*H*-indole (3b).

Colorless solid (mp 108-110°C). ¹H NMR (CDCl₃, 300 MHz) δ: 7.69 (d, 1H, *J* = 7.6 Hz), 7.25-7.17 (m, 4H), 7.05 (m, 2H), 6.92 (m, 2H), 5.30 (s, 2H), 2.98 (m, 1H), 2.27 (s, 3H), 1.87 (m, 1H), 1.74 (m, 1H), 1.43 (d, 3H, *J* = 7.0 Hz), 1.23 (m, 4H), 0.82 (t, 3H, *J* = 6.7 Hz). ¹³C NMR (CDCl₃, 75 MHz) δ: 138.3, 136.8, 131.7, 128.7, 127.1, 126.7, 125.9, 120.3, 119.6, 118.4, 116.7, 109.0, 46.4, 36.9, 31.7, 30.7, 22.8, 21.6, 14.2, 10.5. IR (KBr disk): 1456, 2858, 2922, 2954 cm⁻¹. EI-MS: *m/z* 306.2 [M+H]⁺. HRMS [M+H]⁺: 306.2234, C₂₂H₂₈N requires 306.2222. Anal. calcd. for C₂₂H₂₇N: C, 86.51; H, 8.91; N, 4.59. Found: C, 86.15; H, 8.77; N, 4.47. [α]_D²⁰ = +26° (c = 0.1, CH₂Cl₂, 20°C). The enantiomeric excess was determined using a Chiracel OD column (99/1 pentane/isopropanol, 0.6 ml/min), retention times of isomers: 14.6 min (7%) and 15.4 min (93%). A racemic mixture generated with TMEDA gave retention times 14.6 min (50%) and 15.4 min (50%).

1-Benzyl-3-(1-methyl-pentyl)-2-phenyl-1*H*-indole (3c).

Colorless oil. ¹H NMR (CDCl₃, 300 MHz) δ: 7.80 (m, 1H), 7.37 (m, 3H), 7.26 (m, 2H), 7.21-7.09 (m, 6H), 6.89 (m, 2H), 5.14 (s, 2H), 2.84 (m, 1H), 1.89 (m, 1H), 1.65 (m, 1H), 1.40 (d, 3H, *J* = 7.0 Hz), 1.14 (m, 4H), 0.78 (t, 3H, *J* = 6.6 Hz). ¹³C NMR (CDCl₃, 75 MHz) δ: 138.5, 137.5, 137.1, 132.5, 130.9, 128.5, 128.1, 128.1, 126.9, 126.6, 126.0, 121.4, 120.6, 118.9, 118.7, 110.3, 47.4, 36.8, 31.6, 30.6, 22.7, 22.0, 14.1. IR (neat): 1461, 2856, 2926, 2956, 3030, 3061 cm⁻¹. EI-MS: *m/z* 368.2 [M+H]⁺. HRMS [M+H]⁺: 368.2391, C₂₇H₃₀N requires 368.2378. [α]_D²⁰ = +15° (c = 0.1, CH₂Cl₂, 20°C). The enantiomeric excess was determined using a Chiracel OD column (99.5/0.5 pentane/isopropanol, 0.6 ml/min), retention times of isomers: 11.9 min (93%) and 14.0 min (7%). A racemic mixture generated with TMEDA gave retention times 11.9 min (50%) and 14.0 min (50%).

1-[1-Benzyl-3-(1-methyl-pentyl)-1*H*-indol-2-yl]-ethanone (3d).

Colorless oil. ^1H NMR (CDCl_3 , 300 MHz) δ : 7.88 (d, 1H, $J = 8.1$ Hz), 7.32-7.15 (m, 5H), 7.09 (m, 1H), 6.95 (m, 2H), 5.54 (s, 2H), 3.41 (m, 1H), 2.51 (s, 3H), 1.99 (m, 1H), 1.87 (m, 1H), 1.52 (d, 3H, $J = 7.1$ Hz), 1.25 (m, 3H), 1.14 (m, 1H), 0.83 (t, 3H, $J = 6.9$ Hz). ^{13}C NMR (CDCl_3 , 75 MHz) δ : 194.6, 139.4, 138.6, 134.2, 128.5, 128.0, 127.0, 126.2, 125.2, 125.1, 123.2, 119.7, 111.0, 48.0, 36.9, 32.6, 31.8, 30.7, 22.8, 21.5, 14.1. IR (neat): 1454, 1658, 2856, 2870, 2927, 2956, 3032, 3060 cm^{-1} . EI-MS: m/z 334.3 $[\text{M}+\text{H}]^+$. HRMS $[\text{M}+\text{H}]^+$: 334.2187, $\text{C}_{23}\text{H}_{28}\text{NO}$ requires 334.2171. Anal. calcd. for $\text{C}_{23}\text{H}_{27}\text{NO}$: C 82.84; H 8.16; N 4.20. Found: C 82.69; H 8.16; N 4.14. $[\alpha]_{\text{D}} = -6^\circ$ ($c = 0.2$, CH_2Cl_2 , 20°C). The enantiomeric excess was determined using a Chiracel OD column (99.5/0.5 pentane/isopropanol, 0.6 ml/min), retention times of isomers: 28.5 min (92%) and 30.6 min (8%). A racemic mixture generated with TMEDA gave retention times 28.5 min (50%) and 30.6 min (50%).

3-[1-Benzyl-3-(1-methyl-pentyl)-1*H*-indol-2-yl]-propan-1-ol (3e).

Pale yellow oil. ^1H NMR (CDCl_3 , 300 MHz) δ : 7.71 (d, 1H, $J = 7.1$ Hz), 7.26-7.13 (m, 4H), 7.06 (m, 2H), 6.91 (m, 2H), 5.34 (s, 2H), 3.63 (t, 2H, $J = 6.2$ Hz), 2.96 (m, 1H), 2.78 (m, 2H), 1.89 (m, 1H), 1.79 (m, 1H), 1.71 (m, 2H), 1.50 (bs, 1H), 1.44 (d, 3H, $J = 6.9$ Hz), 1.24 (m, 4H), 0.84 (t, 3H, $J = 6.6$ Hz). ^{13}C NMR (CDCl_3 , 75 MHz) δ : 138.4, 137.1, 135.5, 128.7, 127.1, 126.5, 125.8, 120.6, 120.0, 118.6, 117.2, 109.5, 62.1, 46.4, 36.9, 33.4, 31.9, 30.9, 22.9, 21.8, 21.0, 14.2. IR (neat): 1465, 2871, 2924, 2955, 3056, 3348 cm^{-1} . EI-MS: m/z 348.3 $[\text{M}-\text{H}]^-$. HRMS $[\text{M}+\text{H}]^+$: 350.2472, $\text{C}_{24}\text{H}_{32}\text{NO}$ requires 350.2484. HRMS $[\text{M}-\text{H}]^-$: 348.2314, $\text{C}_{24}\text{H}_{30}\text{NO}$ requires 348.2327. Anal. calcd. for $\text{C}_{24}\text{H}_{31}\text{NO}$: C 82.47; H 8.94; N 4.01. Found: C 82.20; H 8.90; N 3.90. $[\alpha]_{\text{D}} = +7^\circ$ ($c = 0.1$, CH_2Cl_2 , 20°C). The enantiomeric excess was determined using a Chiracel OD column (95/5 pentane/isopropanol, 0.6 ml/min), retention times of isomers: 33.0 min (8%) and 39.9 min (92%). A racemic mixture generated with TMEDA gave retention times 33.0 min (50%) and 39.9 min (50%).

1-Benzyl-3-sec-butyl-1H-indole (3f).

Colorless oil. ^1H NMR (CDCl_3 , 300 MHz) δ : 7.66 (d, 1H, $J = 7.5$ Hz), 7.31-7.22 (m, 4H), 7.17-7.06 (m, 4H), 6.88 (s, 1H), 5.27 (s, 2H), 2.97 (m, 1H), 1.81 (m, 1H), 1.65 (m, 1H), 1.34 (d, 3H, $J = 6.9$ Hz), 0.91 (t, 3H, $J = 7.5$ Hz). ^{13}C NMR (CDCl_3 , 75 MHz) δ : 138.0, 136.8, 128.7, 127.6, 127.4, 126.7, 124.3, 121.7, 121.5, 119.6, 118.6, 109.7, 49.8, 32.5, 30.4, 21.0, 12.2. IR (neat): 1454, 1466, 2871, 2922, 2959, 3029, 3060 cm^{-1} . EI-MS: m/z 264.2 $[\text{M}+\text{H}]^+$. HRMS $[\text{M}+\text{H}]^+$: 264.1746, $\text{C}_{19}\text{H}_{22}\text{N}$ requires 264.1752. $[\alpha]_{\text{D}} = +3^\circ$ ($c = 0.3$, CH_2Cl_2 , 20°C).

1-Benzyl-3-(1-methyl-heptyl)-1H-indole (3g).

Colorless oil. ^1H NMR (CDCl_3 , 300 MHz) δ : 7.65 (d, 1H, $J = 7.8$ Hz), 7.26 (m, 4H), 7.11 (m, 4H), 6.87 (s, 1H), 5.27 (s, 2H), 3.03 (m, 1H), 1.77 (m, 1H), 1.58 (m, 1H), 1.34 (d, 3H, $J = 6.9$ Hz), 1.26 (m, 8H), 0.86 (t, 3H, $J = 6.5$ Hz). ^{13}C NMR (CDCl_3 , 75 MHz) δ : 138.0, 136.8, 128.7, 127.6, 127.4, 126.7, 124.2, 122.1, 121.5, 119.6, 118.6, 109.6, 49.8, 37.8, 31.9, 30.9, 29.5, 27.7, 22.7, 21.5, 14.1. IR (neat): 1454, 1467, 2855, 2925, 2955, 3030, 3056 cm^{-1} . EI-MS: m/z 320.2 $[\text{M}+\text{H}]^+$. HRMS $[\text{M}+\text{H}]^+$: 320.2387, $\text{C}_{23}\text{H}_{30}\text{N}$ requires 320.2378. Anal. calcd. for $\text{C}_{23}\text{H}_{29}\text{N}$: C 86.47; H 9.15; N 4.38. Found: C 86.48; H 9.17; N 4.29. $[\alpha]_{\text{D}} = +4^\circ$ ($c = 0.3$, CH_2Cl_2 , 20°C). The enantiomeric excess was determined using a Chiracel OD column (99.8/0.2 pentane/isopropanol, 0.6 ml/min), retention times of isomers: 90.1 min (8%) and 93.2 min (92%). A racemic mixture generated with TMEDA gave retention times 90.1 min (50%) and 93.2 min (50%).

1-Benzyl-5-methoxy-3-(1-methyl-pentyl)-1H-indole (3h).

Colorless oil. ^1H NMR (CDCl_3 , 300 MHz) δ : 7.26 (m, 3H), 7.08 (m, 4H), 6.86 (s, 1H), 6.80 (m, 1H), 5.23 (s, 2H), 3.85 (s, 3H), 2.98 (m, 1H), 1.77 (m, 1H), 1.58 (m, 1H), 1.43-1.28 (m, 4H), 1.33 (d, 3H, $J = 7.0$ Hz), 0.87 (m, 3H). ^{13}C NMR (CDCl_3 , 75 MHz) δ : 153.5, 138.1, 132.2, 128.7, 127.9, 127.4, 126.6, 125.0, 121.5, 111.4, 110.4, 101.8, 56.0, 50.0, 37.4, 30.7, 30.0, 22.9, 21.4, 14.2. IR (neat): 1224, 1452, 1485, 2858, 2926, 2954, 3029, 3061 cm^{-1} . EI-MS: m/z 322.2 $[\text{M}+\text{H}]^+$. HRMS $[\text{M}+\text{H}]^+$: 322.2186, $\text{C}_{22}\text{H}_{28}\text{NO}$ requires 322.2171. $[\alpha]_{\text{D}} = -21^\circ$ ($c = 0.1$, CH_2Cl_2 , 20°C). The enantiomeric excess was determined using a Chiracel OD column (99.8/0.2 pentane/isopropanol, 0.8 ml/min),

retention times of isomers: 97.8 min (93%) and 103.7 min (7%). A racemic mixture generated with TMEDA gave retention times 97.8 min (50%) and 103.7 min (50%).

3-[1-Benzyl-5-methoxy-3-(1-methyl-pentyl)-1*H*-indol-2-yl]-propan-1-ol (3i).

Pale yellow oil. ^1H NMR (CDCl_3 , 300 MHz) δ : 7.22 (m, 4H), 7.03 (d, 1H, $J = 8.9$ Hz), 6.89 (m, 2H), 6.74 (m, 1H), 5.29 (s, 2H), 3.85 (s, 3H), 3.62 (t, 2H, $J = 6.0$ Hz), 2.90 (m, 1H), 2.74 (m, 2H), 1.87 (m, 1H), 1.77 (m, 1H), 1.70 (m, 2H), 1.60 (bs, 1H), 1.43 (m, 3H), 1.26 (m, 4H), 0.84 (t, 3H, $J = 7.2$ Hz). ^{13}C NMR (CDCl_3 , 75 MHz) δ : 153.2, 138.5, 136.4, 132.4, 128.7, 127.1, 126.8, 125.8, 116.7, 110.0, 109.8, 103.0, 62.1, 56.1, 46.5, 36.6, 33.4, 31.8, 30.8, 22.9, 21.6, 21.1, 14.2. IR (neat): 1228, 1453, 1481, 2870, 2924, 2957, 3030, 3061, 3409 cm^{-1} . EI-MS: m/z 378.2 $[\text{M}-\text{H}]^-$. HRMS $[\text{M}+\text{H}]^+$: 380.2579, $\text{C}_{25}\text{H}_{34}\text{NO}_2$ requires 380.2590. $[\alpha]_{\text{D}} = +9^\circ$ ($c = 0.2$, CH_2Cl_2 , 20°C). The enantiomeric excess was determined using a Chiracel OD column (95/5 pentane/isopropanol, 0.6 ml/min), retention times of isomers: 43.9 min (8%) and 53.8 min (92%). A racemic mixture generated with TMEDA gave retention times of 43.9 min (50%) and 53.8 min (50%).

Procedure for synthesis of anilines 4a-d.

Phenyllithium (0.50 mmol) was added to a solution of **1** (0.50 mmol) in cumene (2 ml) and stirred at room temperature for 15 min. This solution was added dropwise, over 15 min, to a premixed solution of alkyllithium¹ (1.00 mmol) and (-)-sparteine¹ (1.50 mmol) in cumene (2 ml) at -15°C. The mixture was stirred at -15°C for a further 4 h and treated with methanol (1 ml). The reaction mixture was washed with hydrochloric acid (1M, 10 ml) and the aqueous layer extracted with diethyl ether (2 x 10 ml). The combined organic layers were dried over sodium sulfate and concentrated to dryness. Gravity chromatography eluting with cyclohexane/diethyl ether gave the purified product.

1. For ethyllithium 2.5 mmol used.
2. The racemic mixture was generated by replacing (-)-sparteine with *N,N,N',N'*-tetramethylethylenediamine (TMEDA).

Benzyl-[2-(2-methyl-hexyl)-phenyl]-amine (4a).

Colorless oil. ¹H NMR (CDCl₃, 300 MHz) δ: 7.39-7.24 (m, 5H), 7.12-7.00 (m, 2H), 6.66 (m, 2H), 4.36 (s, 2H), 3.95 (bs, 1H), 2.54 (dd, 1H, *J* = 14.3/ 5.9 Hz), 2.24 (dd, 1H, *J* = 14.3/ 8.4 Hz), 1.76 (m, 1H), 1.27 (m, 6H), 0.87 (m, 6H). ¹³C NMR (CDCl₃, 75 MHz) δ: 145.8, 139.6, 130.5, 128.7, 127.4, 127.2, 127.1, 125.4, 117.0, 110.6, 48.4, 39.3, 37.0, 32.4, 29.5, 22.9, 20.0, 14.1. IR (neat): 1507, 2857, 2924, 2955, 3030, 3063 cm⁻¹. EI-MS: *m/z* 282.3 [M+H]⁺. HRMS [M+H]⁺: 282.2220, C₂₀H₂₈N requires 282.2222. Anal. calcd. for C₂₀H₂₇N: C, 85.35; H, 9.67; N, 4.98. Found: C, 85.10; H, 9.39; N, 5.02. [α]_D²⁰ = -3° (c = 0.7, CH₂Cl₂, 20°C). The enantiomeric excess was determined using a Chiracel OD column (99/1 pentane/isopropanol, 0.6 ml/min), retention times of isomers: 25.4 min (S, 92%) and 32.5 min (R, 8%). A racemic mixture generated with TMEDA gave retention times 25.4 min (50%) and 32.5 min (50%).

Benzyl-[2-(2-methyl-butyl)-phenyl]-amine (4b).

Colorless oil. ^1H NMR (CDCl_3 , 300 MHz) δ : 7.38-7.23 (m, 5H), 7.09 (m, 1H), 7.02 (m, 1H), 6.68 (m, 1H), 6.62 (m, 1H), 4.37 (s, 2H), 3.95 (bs, 1H), 2.53 (dd, 1H, $J = 14.3/6.0$ Hz), 2.26 (dd, 1H, $J = 14.3/8.1$ Hz), 1.71 (m, 1H), 1.43 (m, 1H), 1.20 (m, 1H), 0.89 (m, 6H). ^{13}C NMR (CDCl_3 , 75 MHz) δ : 145.8, 139.7, 130.5, 128.7, 127.4, 127.2, 127.1, 125.4, 117.1, 110.6, 48.4, 38.9, 34.0, 29.7, 19.5, 11.6. IR (neat): 1505, 2871, 2923, 2959, 3030, 3064, 3428 cm^{-1} . EI-MS: m/z 254.1 $[\text{M}+\text{H}]^+$. HRMS $[\text{M}+\text{H}]^+$: 254.1906, $\text{C}_{18}\text{H}_{24}\text{N}$ requires 254.1909. $[\alpha]_{\text{D}} = -7^\circ$ ($c = 0.1$, CH_2Cl_2 , 20°C). The enantiomeric excess was determined using a Chiracel OD column (99/1 pentane/isopropanol, 0.6 ml/min), retention times of isomers: 23.9 min (S, 93%) and 43.2 min (R, 7%). A racemic mixture generated with TMEDA gave retention times 23.9 min (50%) and 43.2 min (50%).

Benzyl-[2-(2-methyl-octyl)-phenyl]-amine (4c).

Colorless oil. ^1H NMR (CDCl_3 , 300 MHz) δ : 7.39-7.24 (m, 5H), 7.08 (m, 1H), 7.01 (m, 1H), 6.68 (m, 1H), 6.62 (m, 1H), 4.35 (s, 2H), 3.96 (bs, 1H), 2.53 (dd, 1H, $J = 14.4/5.7$ Hz), 2.24 (dd, 1H, $J = 14.4/8.2$ Hz), 1.76 (m, 1H), 1.26 (m, 10H), 0.87 (m, 6H). ^{13}C NMR (CDCl_3 , 75 MHz) δ : 145.8, 139.6, 130.5, 128.7, 127.4, 127.2, 127.1, 125.5, 117.1, 110.6, 48.5, 39.3, 37.3, 32.4, 31.9, 29.6, 27.2, 22.7, 20.0, 14.1. IR (neat): 1507, 2853, 2924, 2954 cm^{-1} . EI-MS: m/z 310.2 $[\text{M}+\text{H}]^+$. HRMS $[\text{M}+\text{H}]^+$: 310.2527, $\text{C}_{22}\text{H}_{32}\text{N}$ requires 310.2535. $[\alpha]_{\text{D}} = -7^\circ$ ($c = 0.3$, CH_2Cl_2 , 20°C). The enantiomeric excess was determined using a Chiracel OD column (99.5/0.5 pentane/isopropanol, 0.6 ml/min), retention times of isomers: 37.9 min (S, 92%) and 44.7 min (R, 8%). A racemic mixture generated with TMEDA gave retention times 37.9 min (50%) and 44.7 min (50%).

Benzyl-[4-methoxy-2-(2-methyl-hexyl)-phenyl]-amine (4d).

Red/orange oil. ^1H NMR (CDCl_3 , 300 MHz) δ : 7.31 (m, 5H), 6.66 (m, 2H), 6.57 (m, 1H), 4.32 (s, 2H), 3.74 (s, 3H), 3.65 (bs, 1H), 2.53 (dd, 1H, $J = 14.1/6.0$ Hz), 2.22 (dd, 1H, $J = 14.1/8.5$ Hz), 1.76 (m, 1H), 1.26 (m, 6H), 0.88 (m, 6H). ^{13}C NMR (CDCl_3 , 75 MHz) δ : 151.6, 140.2, 139.9, 128.7, 128.6, 127.5, 127.1, 117.4, 111.7, 111.3, 55.7, 49.2, 39.4, 36.9, 32.5, 29.4, 22.9, 19.9, 14.1. IR (neat): 1222, 1510, 2870, 2925, 2954, 3029, 3061,

3418 cm^{-1} . EI-MS: m/z 312.3 $[\text{M}+\text{H}]^+$. HRMS $[\text{M}+\text{H}]^+$: 312.2325, $\text{C}_{21}\text{H}_{30}\text{NO}$ requires 312.2327. $[\alpha]_{\text{D}} = -6^\circ$ ($c = 0.1$, CH_2Cl_2 , 20°C).

Determination of Absolute Stereochemistry.

4a was converted into (*S*)-3-methyl-heptanoic acid following the literature procedure.¹

The absolute stereochemistry of all other products was assigned by analogy.

1. (a) Norsikian, S.; Marek, I.; Normant, J.F. *Tetrahedron Lett.* **1997**, 38, 7523. (b) Norsikian, S.; Marek, I.; Klien, S.; Poisson, J.F.; Normant, J.F. *Chem. Eur. J.* **1999**, 5, 2055.

Benzyl-(2-propenyl-phenyl)-amine (1a)

Benzyl-(4-methoxy-2-propenyl-phenyl)-amine (1b)

1-Benzyl-3-(1-methyl-pentyl)-1*H*-indole (3a)

1-Benzyl-2-methyl-3-(1-methyl-pentyl)-1*H*-indole (3b)

1-Benzyl-3-(1-methyl-pentyl)-2-phenyl-1*H*-indole (3c)

1-[1-Benzyl-3-(1-methyl-pentyl)-1*H*-indol-2-yl]-ethanone (3d)

3-[1-Benzyl-3-(1-methyl-pentyl)-1*H*-indol-2-yl]-propan-1-ol (3e)

1-Benzyl-3-*sec*-butyl-1*H*-indole (3f)

1-Benzyl-3-(1-methyl-heptyl)-1*H*-indole (3g)

1-Benzyl-5-methoxy-3-(1-methyl-pentyl)-1*H*-indole (3h)

3-[1-Benzyl-5-methoxy-3-(1-methyl-pentyl)-1*H*-indol-2-yl]-propan-1-ol (3i)

Benzyl-[2-(2-methyl-hexyl)-phenyl]-amine (4a)

Benzyl-[2-(2-methyl-butyl)-phenyl]-amine (4b)

Benzyl-[2-(2-methyl-octyl)-phenyl]-amine (4c)

Benzyl-[4-methoxy-2-(2-methyl-hexyl)-phenyl]-amine (4d)