Supporting Information

Intramolecular Pd-Mediated Processes of Amino-Tethered Aryl Halides and Ketones: Insight into the Ketone α -Arylation and Carbonyl-Addition Dichotomy. A New Class of Four-Membered Azapalladacycles

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General Methods. ^1H - and ^{13}C NMR spectra were recorded in CDCl_3 solution, using Me_4Si as internal standard. Chemical shifts are reported in ppm downfield (δ) from Me_4Si . ^{31}P NMR spectra were recorded in CDCl_3 with external H_3PO_4 as reference. IR spectra were recorded on a Nicolet 205 FT infrared spectrophotometer and only noteworthy absorptions are listed. Melting points were determined in a capillary tube and are uncorrected. TLC was carried out on SiO_2 (silica gel 60 F₂₅₄, Merck), and the spots were located with UV light, iodoplatinate reagent or 1% aqueous KMnO_4 . Chromatography refers to flash chromatography and was carried out on SiO_2 (silica gel 60, SDS, 230-400 mesh ASTM). Drying of organic extracts during workup of reactions was performed over anhydrous Na_2SO_4 . Evaporation of solvents was accomplished with a rotatory evaporator. Microanalyses and HRMS were performed by Centro de Investigación y Desarrollo (CSIC), Barcelona.

Representative Procedures for the Pd-Catalyzed Intramolecular Coupling of 2-Haloanilines and Ketones.

Method A: To a solution of ketone **1a** (100 mg, 0.25 mmol) in dry THF (10 mL) were added $\text{Pd}(\text{PPh}_3)_4$ (60 mg, 0.05 mmol) and $\text{KO}^t\text{-Bu}$ (0.75 mmol, 0.75 mL of 1M solution in *t*-butyl alcohol). The solution was heated at reflux for 3.5 h. After cooling to room temperature, the mixture was diluted with ether and washed with saturated aqueous NaHCO_3 . The aqueous layer was extracted with ether, and the combined organic extracts were dried and concentrated. The residue was purified by chromatography (CH_2Cl_2) to give ketone **2** (58 mg, 84%).

Method B: To a solution of ketone **3** (102 mg, 0.28 mmol) in dry THF (10 mL) were added $\text{PdCl}_2(\text{PPh}_3)_2$ (39 mg, 0.05 mmol) and Cs_2CO_3 (276 mg, 0.85 mmol). The mixture was stirred at 100 °C in a sealed tube for 24 h. After cooling to room temperature, the mixture was diluted with ether and washed with saturated aqueous NaHCO_3 . The aqueous layer was extracted with ether, and the combined organic extracts were dried and concentrated. The residue was purified by chromatography

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(from CH₂Cl₂ to 98:2 CH₂Cl₂/MeOH) to give ketone **4** (21 mg, 33%) and 4-(*N*-Acetyl-*N*-phenylamino)cyclohexanone (3 mg, 5%).

Method C: To a solution of ketone **1a** (100 mg, 0.25 mmol) in dry THF (10 mL) were added Pd(PPh₃)₄ (60 mg, 0.05 mmol) and K₃PO₄ (160 mg, 0.75 mmol). The mixture was stirred at 110 °C in a sealed tube for 24 h. After cooling to room temperature, the mixture was diluted with ether and washed with saturated aqueous NaHCO₃. The aqueous layer was extracted with ether, and the combined organic extracts were dried and concentrated. The residue was purified by chromatography (CH₂Cl₂) to give ketone **2** (52 mg, 76%).

1-Benzyl-2,3,4,6-tetrahydro-2,6-methano-1*H*-1-benzazocin-5-one (2)

¹H NMR (CDCl₃, 300 MHz) δ 1.80-1.94 (m, 1H), 2.15-2.30 (m, 3H), 2.36-2.54 (m, 2H), 3.70-3.77 (m, 2H), 4.61 (d, *J* = 17.4 Hz, 1H, NCH₂Ar), 4.79 (d, *J* = 17.4 Hz, 1H, NCH₂Ar), 6.56 (d, *J* = 8.4 Hz, 1H), 6.59 (td, *J* = 7.5 and 1 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 1H), 7.05 (ddd, *J* = 8.4, 7.5, and 1.5 Hz, 1H), 7.24-7.38 (m, 5H). ¹³C NMR (CDCl₃, 75.5 MHz) δ 29.4 (CH₂), 33.6 (CH₂), 34.5 (CH₂), 51.5 (CH), 51.8 (CH), 52.5 (CH₂), 110.2 (CH), 115.7 (CH), 118.5 (C), 125.9 (CH), 127.0 (CH), 128.7 (CH), 128.8 (CH), 129.0 (CH), 138.2 (C), 144.6 (C), 209.8 (C). IR (KBr) 1706 cm⁻¹. Anal. Calcd for C₁₉H₁₉NO (277.4)·1/4H₂O: C, 80.96; H, 6.97; N, 4.97. Found: C, 80.88; H, 6.95; N, 4.93.

1-Acetyl-2,3,4,6-tetrahydro-2,6-methano-1*H*-1-benzazocin-5-one (4)

¹H NMR (CDCl₃, 300 MHz) δ 1.99-2.46 (m, 6H), 2.45 (s, 3H, CH₃), 3.70 (br s, 1H), 4.89 (br s, 1H), 7.03 (td, *J* = 7.5 and 1 Hz, 1H), 7.15 (dd, *J* = 7.5 and 1.5 Hz, 1H), 7.25 (td, *J* = 7.5 and 1.5 Hz, 1H), 7.82 (br, 1H). ¹³C NMR (CDCl₃, 75.5 MHz) δ 25.1 (CH₃), 30.3 (CH₂), 31.8 (CH₂), 34.2 (CH₂), 48.1 (CH), 51.1 (CH), 122.7 (CH), 123.8 (CH), 125.4 (C), 127.8 (CH), 129.1 (CH), 138.0 (C), 170.8 (C), 208.6 (C). Anal. Calcd for C₁₄H₁₅NO₂ (229.3)·1/3H₂O: C, 71.47; H, 6.71; N, 5.95. Found: C, 71.43; H, 6.91; N, 5.65.

4-(*N*-Acetyl-*N*-phenylamino)cyclohexanone

¹H NMR (CDCl₃, 300 MHz, mixture of rotamers) δ 1.53 (dtd, *J* = 13.2, 12, and 4.5 Hz, 2H), 1.78 and 1.99 (2 s, 3H, CH₃ *E* (major) and *Z* (minor) rotamer, respectively), 2.10-2.20 (m, 2H), 2.36 (dm, *J* = 14.7 Hz, 2H), 2.54 (td, *J* = 14.7 and 6 Hz, 2H), 4.43 and 5.13 (2 tt, *J* = 12 and 3.6 Hz, 1H, H-4 *Z* (minor) and *E* (major) rotamer, respectively), 7.05-7.15 (m, 2H), 7.38-7.50 (m, 3H). ¹³C NMR (CDCl₃, 75.5 MHz) δ *E* (major) rotamer 23.4 (CH₃), 30.4 (CH₂), 39.9 (CH₂), 51.5 (CH), 128.7 (CH), 129.5 (CH), 129.9 (CH), 138.9 (C), 170.3 (C), 209.4 (C). *Z* (minor) rotamer 24.3 (CH₃), 31.0 (CH₂), 39.8 (CH₂), 55.5 (CH), 171.5 (C), 210.0 (C). IR (KBr) 1714 cm⁻¹.

1-(Methoxycarbonyl)-2,3,4,6-tetrahydro-2,6-methano-1*H*-1-benzazocin-5-one (6)

Chromatography: from hexane to 3:2 hexane-EtOAc.

¹H NMR (CDCl₃, 300 MHz) δ 1.97 (tdd, *J* = 13.5, 6, and 3 Hz, 1H), 2.17 (dm, *J* = 13.2 Hz, 1H), 2.22 (dm, *J* = 18 Hz, 1H), 2.28 (dt, *J* = 13.2 and 2.7 Hz, 1H), 2.31-2.52 (m, 2H), 3.66 (br s, 1H), 3.88 (s, 3H, OCH₃), 4.82 (br s, 1H), 6.96 (td, *J* = 7.5 and 1.2 Hz, 1H), 7.10 (dd, *J* = 7.5 and 1.8 Hz, 1H), 7.26 (ddd, *J* = 8.7, 7.5, and 1.8 Hz, 1H), 8.43 (d, *J* = 8.7 Hz, 1H). ¹³C NMR (CDCl₃, 75.5 MHz) δ 30.0 (CH₂), 33.0 (CH₂), 34.2 (CH₂), 48.7 (CH), 51.4 (CH), 53.1 (OCH₃), 120.9 (CH), 122.5 (CH), 124.4 (C), 128.3 (CH), 129.0 (CH), 138.1 (C), 154.7 (C), 209.0 (C). IR (film) 1666, 1713 cm⁻¹. HRMS Calcd for C₁₄H₁₅NO₃ 245.1051. Found 245.1041.

4-Acetyl-1-benzyl-1,2,3,4-tetrahydroquinoline (8)

Chromatography: from hexane to 4:1 hexane-EtOAc.

¹H NMR (CDCl₃, 300 MHz) δ 2.05 (dm, *J* = 13.2 Hz, 1H), 2.19 (s, 3H), 2.35 (ddd, *J* = 13.2, 4.8, and 4.2 Hz, 1H), 3.28 (dtd, *J* = 11.7, 4.8, and 0.9 Hz, 1H), 3.41 (ddd, *J* = 11.7, 10.2, and 4.2 Hz, 1H), 3.78 (t, *J* = 4.8 Hz, 1H), 4.49 (s, 2H), 6.58 (d, *J* = 8.4 Hz, 1H), 6.63 (td, *J* = 7.5 and 1 Hz, 1H), 7.02 (d, *J* = 7.5 Hz, 1H), 7.06 (ddd, *J* = 8.4 and 7.5 Hz, 1H), 7.20-7.40 (m, 6H). ¹³C NMR (CDCl₃, 75.5 MHz) δ 24.1 (CH₂), 28.5 (CH₃), 46.5 (CH₂), 51.1 (CH), 54.8 (CH₂), 111.5 (CH), 115.9 (CH), 118.7 (C), 126.3 (CH), 126.7 (CH), 128.4 (CH), 128.5 (CH), 129.7 (CH), 138.2 (C), 145.0 (C), 209.9 (C). IR (film) 1711 cm⁻¹. HRMS Calcd for C₁₈H₁₉NO 265.1467. Found 265.1466.

4-Acetyl-1-benzyl-1,2,3,4-tetrahydro-4-quinolinol (9)

Chromatography: from hexane to 4:1 hexane-EtOAc.

¹H NMR (CDCl₃, 300 MHz) δ 1.86 (dt, *J* = 12.9 and 3.3 Hz, 1H), 2.16 (s, 3H), 2.32 (td, *J* = 12.9 and 4.5 Hz, 1H), 3.36 (ddd, *J* = 11.7, 4.2, and 3.3 Hz, 1H), 3.61 (ddd, *J* = 12.9, 11.7, and 3.3 Hz, 1H), 4.57 (s, 2H), 4.63 (s, 1H, OH), 6.64 (td, *J* = 7.8 and 1 Hz, 1H), 6.68 (dd, *J* = 7.8 and 1 Hz, 1H), 6.79 (dd, *J* = 7.8 and 1.5 Hz, 1H), 7.11 (td, *J* = 7.8 and 1.5 Hz, 1H), 7.25-7.40 (m, 5H). ¹³C NMR (CDCl₃, 75.5 MHz) δ 24.5 (CH₃), 33.5 (CH₂), 45.0 (CH₂), 55.4 (CH₂), 76.8 (C), 112.6 (CH), 116.9 (CH), 120.6 (C), 126.6 (CH), 127.0 (CH), 128.1 (CH), 128.6 (CH), 129.8 (CH), 138.1 (C), 145.6 (C), 210.6 (C). IR (film) 3390 (br), 1705 cm⁻¹. HRMS Calcd for C₁₈H₁₉NO₂ 281.1416. Found 281.1418.

5-(*N*-Benzyl-*N*-phenylamino)-2-pentanone (10)

Chromatography: from hexane to 4:1 hexane-EtOAc.

¹H NMR (CDCl₃, 300 MHz) δ 1.92 (tt, *J* = 7.5 and 6.9 Hz, 2H), 2.10 (s, 3H), 2.46 (t, *J* = 6.9 Hz, 2H), 3.39 (t, *J* = 7.5 Hz, 2H), 4.53 (s, 2H), 6.67 (tm, *J* = 7.2 Hz, 1H), 6.72 (dm, *J* = 8.5 Hz, 2H), 7.15-7.34

(m, 7H). ^{13}C NMR (CDCl_3 , 75.5 MHz) δ 21.2 (CH_2), 30.0 (CH_3), 40.7 (CH_2), 50.2 (CH_2), 54.4 (CH_2), 112.2 (CH), 116.3 (CH), 126.5 (CH), 126.7 (CH), 128.5 (CH), 129.2 (CH), 138.8 (C), 148.4 (C), 208.0 (C). IR (film) 1708 cm^{-1} . HRMS Calcd for $\text{C}_{18}\text{H}_{21}\text{NO}$ 267.1623. Found 267.1611.

1-Benzyl-4-methyl-1,2,3,4-tetrahydro-4-quinolinol (12)

Chromatography: from hexane to 4:1 hexane-EtOAc. ^1H NMR (CDCl_3 , 500 MHz) δ 1.65 (s, 3H, CH_3), 1.85 (s, 1H, OH), 2.02-2.11 (m, 2H, CH_2), 3.37 (ddd, $J = 12, 7$, and 5 Hz, 1H, NCH_2), 3.51 (ddd, $J = 12, 7.5$, and 5 Hz, 1H, NCH_2), 4.52 (s, 2H, NCH_2Ar), 6.55 (dd, $J = 8$ and 1 Hz, 1H, H-8), 6.69 (td, $J = 7.5$ and 1 Hz, 1H, H-6), 7.07 (ddd, $J = 8, 7.5$, and 1.5 Hz, 1H, H-7), 7.24-7.36 (m, 5H), 7.49 (dd, $J = 7.5$ and 1.5 Hz, 1H, H-5). ^{13}C NMR (CDCl_3 , 75.5 MHz) δ 29.5 (CH_3), 37.4 (C-3), 46.3 (C-2), 55.2 (NCH_2Ar), 68.2 (C-4), 111.4 (C-8), 116.0 (C-6), 125.6 (C-5), 126.4 (o-C), 126.8 (p-C), 127.5 (C-4a), 128.6 (m-C), 128.8 (C-7), 138.4 (ipso-C), 144.2 (C-8a). IR (film) $1604, 3396\text{ (br)}\text{ cm}^{-1}$. HRMS Calcd for $\text{C}_{17}\text{H}_{19}\text{NO}$ 253.1467. Found 253.1465. Anal. Calcd for $\text{C}_{17}\text{H}_{19}\text{NO}$: C, 80.60; H, 7.56; N, 5.53. Found: C, 80.73; H, 7.66; N, 5.84.

1-Acetyl-4-methyl-1,2,3,4-tetrahydro-4-quinolinol (14)

Chromatography: from CH_2Cl_2 to 98:2 $\text{CH}_2\text{Cl}_2/\text{MeOH}$.

^1H NMR (CDCl_3 , 200 MHz) δ 1.54 (s, 3H, CH_3), 2.01-2.11 (m, 2H), 2.24 (s, 3H, CH_3), 2.47 (br s, 1H, OH), 3.63 (dt, $J = 13.2$ and 6.6 Hz, 1H), 4.07 (br dt, $J = 13.2$ and 6.2 Hz, 1H), 7.15-7.32 (m, 3H), 7.56-7.64 (m, 1H). ^{13}C NMR (CDCl_3 , 50 MHz) δ 23.4 (CH_3), 29.0 (CH_3), 39.7 (CH_2), 41.0 (CH_2), 69.1 (C), 124.3 (CH), 125.4 (CH), 125.5 (CH), 127.4 (CH), 137.0 (C), 169.9 (C). IR (film) $1636, 3400\text{ (br)}\text{ cm}^{-1}$. HRMS Calcd for $\text{C}_{12}\text{H}_{15}\text{NO}_2$ 205.1103. Found 205.1113.

1-(Methoxycarbonyl)-4-methyl-1,2,3,4-tetrahydro-4-quinolinol (16)

Chromatography: from CH_2Cl_2 to 98:2 $\text{CH}_2\text{Cl}_2/\text{MeOH}$. ^1H NMR (CDCl_3 , 200 MHz) δ 1.58 (s, 3H, CH_3), 1.96 (br s, 1H, OH), 2.04 (dd, $J = 6.2$ and 5.6 Hz, 2H), 3.70 (ddd, $J = 13.2, 6.2$, and 5.6 Hz, 1H), 3.80 (s, 3H, OCH_3), 4.01 (ddd, $J = 13.2, 6.2$, and 5.6 Hz, 1H), 7.12 (td, $J = 7.5$ and 1.5 Hz, 1H), 7.25 (ddd, $J = 8.2, 7.5$, and 1.8 Hz, 1H), 7.55 (dd, $J = 7.5$ and 1.8 Hz, 1H), 7.72 (dd, $J = 8.2$ and 1.5 Hz, 1H). ^{13}C NMR (CDCl_3 , 50 MHz) δ 29.4 (CH_3), 39.0 (CH_2), 41.8 (CH_2), 53.0 (OCH_3), 68.8 (C), 123.6 (CH), 124.1 (CH), 125.5 (CH), 127.6 (CH), 134.8 (C), 136.4 (C), 155.0 (C). IR (film) $1713, 3439\text{ (br)}\text{ cm}^{-1}$. Anal. Calcd for $\text{C}_{12}\text{H}_{15}\text{NO}_3$ (221.3): C, 65.14; H, 6.83; N, 6.33. Found: C, 65.04; H, 6.89; N, 6.10.

3-Acetyl-1-(methoxycarbonyl)indole (17)

Chromatography: from CH_2Cl_2 to 98:2 $\text{CH}_2\text{Cl}_2/\text{MeOH}$.

^1H NMR (CDCl_3 , 200 MHz) δ 2.57 (s, 3H, CH_3), 4.12 (s, 3H, CH_3), 7.29-7.47 (m, 2H), 8.13-8.20 (m, 1H), 8.26 (s, 1H), 8.35-8.41 (m, 1H). ^{13}C NMR (CDCl_3 , 50 MHz) δ 27.8 (CH_3), 54.5 (OCH_3), 114.8 (CH), 121.3 (C), 122.7 (CH), 124.6 (CH), 125.7 (CH), 127.8 (C), 129.0 (C), 131.9 (CH), 147.5 (C), 193.7 (C). IR (film) 1666, 1752 cm^{-1} . HRMS Calcd for $\text{C}_{12}\text{H}_{11}\text{NO}_3$: 217.0739. Found: 217.0732.

1-Benzyl-4-ethyl-1,2,3,4-tetrahydro-4-quinolinol (19)

Chromatography: from hexane to 4:1 hexane-EtOAc.

^1H NMR (CDCl_3 , 300 MHz) δ 0.94 (t, J = 7.5 Hz, 3H), 1.80 (br s, 1H, OH), 1.92 (q, J = 7.5 Hz, 2H), 1.93 (ddd, J = 13.2, 7.8, and 4.2 Hz, 1H), 2.09 (ddd, J = 13.2, 7.8, and 4.5 Hz, 1H), 3.32 (ddd, J = 12, 7.8, and 4.2 Hz, 1H), 3.44 (ddd, J = 12, 7.8, and 4.5 Hz, 1H), 4.48 (s, 2H, NCH_2Ar), 6.52 (dd, J = 8.4 and 1 Hz, 1H), 6.65 (ddd, J = 7.8, 7.2, and 1 Hz, 1H), 7.03 (ddd, J = 8.4, 7.2, and 1.5 Hz, 1H), 7.20-7.35 (m, 5H), 7.38 (dd, J = 7.8 and 1.5 Hz, 1H). ^{13}C NMR (CDCl_3 , 75.5 MHz) δ 8.2 (CH_3), 33.7 (CH_2), 33.8 (CH_2), 46.0 (CH_2), 55.1 (CH_2), 70.4 (C), 111.4 (CH), 115.9 (CH), 125.6 (CH), 126.4 (CH), 126.8 (CH), 126.9 (C), 128.5 (CH), 128.6 (CH), 138.4 (C), 144.6 (C). IR (film) 1604, 3421 (br) cm^{-1} . Anal. Calcd for $\text{C}_{18}\text{H}_{21}\text{NO}$ (267.4): C, 80.86; H, 7.92; N, 5.24. Found: C, 80.72; H, 8.00; N, 5.18.

4-Ethyl-1-(methoxycarbonyl)-1,2,3,4-tetrahydro-4-quinolinol (21)

Chromatography: from CH_2Cl_2 to 98:2 $\text{CH}_2\text{Cl}_2/\text{MeOH}$.

^1H NMR (CDCl_3 , 300 MHz) δ 0.88 (t, J = 7.5 Hz, 3H, CH_3), 1.70 (br s, 1H, OH), 1.75-1.96 (m, 2H), 1.90 (ddd, J = 13.8, 7.2 and 4.5 Hz, 1H), 2.13 (ddd, J = 13.8, 8.7, and 4.8 Hz, 1H), 3.53 (ddd, J = 12.9, 8.7, and 4.5 Hz, 1H), 3.80 (s, 3H, OCH_3), 4.09 (ddd, J = 12.9, 7.2, and 4.8 Hz, 1H), 7.12 (ddd, J = 7.8, 7.2 and 1.5 Hz, 1H), 7.24 (ddd, J = 8.4, 7.2, and 1.5 Hz, 1H), 7.49 (dd, J = 7.8 and 1.5 Hz, 1H), 7.70 (d, J = 8.4 Hz, 1H). ^{13}C NMR (CDCl_3 , 50 MHz) δ 8.3 (CH_3), 33.5 (CH_2), 35.7 (CH_2), 41.5 (CH_2), 52.9 (OCH_3), 71.0 (C), 123.5 (CH), 124.0 (CH), 125.4 (CH), 127.3 (CH), 134.5 (C), 136.7 (C), 154.9 (C). IR (film) 1711, 3458 (br) cm^{-1} . HRMS Calcd for $\text{C}_{13}\text{H}_{17}\text{NO}_3$: 235.1208. Found: 235.1209.

4-tert-Butyl-1-methyl-1,2,3,4-tetrahydro-4-quinolinol (23)

Chromatography: from hexane to 4:1 hexane-EtOAc.

^1H NMR (CDCl_3 , 300 MHz) δ 0.98 (s, 9H), 1.60 (br s, 1H, OH), 1.83 (ddd, J = 13.8, 11.4, and 6.9 Hz, 1H), 2.48 (ddd, J = 13.8, 5.4, and 4.2 Hz, 1H), 2.85 (s, 3H), 3.16 (ddd, J = 11.4, 6.9, and 4.2 Hz, 1H), 3.34 (td, J = 11.4 and 5.4 Hz, 1H), 6.56 (dd, J = 8.4 and 1 Hz, 1H), 6.66 (ddd, J = 7.5, 7.2, and 1 Hz, 1H), 7.15 (ddd, J = 8.4, 7.2, and 1.5 Hz, 1H), 7.44 (dd, J = 7.5 and 1.5 Hz, 1H). ^{13}C NMR (CDCl_3 , 75.5 MHz) δ 26.1 (CH_3), 35.5 (CH_2), 38.3 (CH_3), 38.9 (C), 48.7 (CH_2), 74.0 (C), 110.2 (CH), 115.0 (CH), 127.0 (C), 127.1 (CH), 128.0 (CH), 146.4 (C). IR (film) 1604, 3547 (br) cm^{-1} . Anal. Calcd for $\text{C}_{14}\text{H}_{21}\text{NO}$ (219.3)· $1/4\text{H}_2\text{O}$: C, 75.13; H, 9.68; N, 6.26. Found: C, 75.17; H, 9.63; N, 5.87.

***trans*-5-Methyl-5,6,6a,7,8,9,10,10a-octahydro-10a-phenanthridinol (25-*trans*)**

Chromatography: from hexane to 4:1 hexane-EtOAc: **25-*trans*** eluted in first place.

¹H NMR (CDCl₃, 300 MHz) δ 1.24-1.88 (m, 9H), 2.49 (dm, *J* = 14.1 Hz, 1H), 2.93 (s, 3H), 2.93 (dd, *J* = 12 and 4.8 Hz, 1H), 3.23 (t, *J* = 12 Hz, 1H), 6.60-6.68 (m, 2H), 7.18 (ddd, *J* = 8.1, 7.5, and 1.5 Hz, 1H), 7.35 (dd, *J* = 7.2 and 1.5 Hz, 1H). ¹³C NMR (CDCl₃, 75.5 MHz) δ 21.7 (CH₂), 25.2 (CH₂), 25.3 (CH₂), 35.2 (CH₂), 38.9 (CH₃), 40.2 (CH), 52.2 (CH₂), 67.8 (C), 111.2 (CH), 115.5 (CH), 124.4 (CH), 127.3 (C), 129.1 (CH), 145.5 (C).

***cis*-5-Methyl-5,6,6a,7,8,9,10,10a-octahydro-10a-phenanthridinol (25-*cis*)**

Chromatography: from hexane to 4:1 hexane-EtOAc: **25-*cis*** eluted in second place.

¹H NMR (CDCl₃, 300 MHz) δ 1.13-1.44 (m, 3H), 1.52-1.88 (m, 6H), 2.47 (ddd, *J* = 12.5, 4.2, and 3.3 Hz, 1H), 2.94 (s, 3H), 2.96 (dd, *J* = 11.5 and 3.9 Hz, 1H), 3.63 (dd, *J* = 11.5 and 3.9 Hz, 1H), 6.62 (dd, *J* = 8.1 and 1 Hz, 1H), 6.67 (td, *J* = 7.5 and 1 Hz, 1H), 7.18 (ddd, *J* = 8.1, 7.5, and 1.5 Hz, 1H), 7.37 (dd, *J* = 7.5 and 1.5 Hz, 1H). ¹³C NMR (CDCl₃, 75.5 MHz) δ 23.7 (CH₂), 24.7 (CH₂), 27.7 (CH₂), 37.2 (CH₂), 39.4 (CH₃), 41.0 (CH), 52.1 (CH₂), 70.3 (C), 111.2 (CH), 116.0 (CH), 124.0 (C), 125.9 (CH), 129.0 (CH), 145.4 (C).

1,2-Dihydro-1-(methoxycarbonyl)-2'-oxo-3-spirocyclohexylindole (28)

Chromatography: from CH₂Cl₂ to 98:2 CH₂Cl₂/MeOH: ketone **28** eluted in first place.

¹H NMR (CDCl₃, 300 MHz, 50°C) δ 1.82 (m, 1H), 1.92-2.16 (m, 5H), 2.51 (dt, *J* = 14 and 7 Hz, 1H), 2.68 (dt, *J* = 14 and 6.7 Hz, 1H), 3.82 (d, *J* = 11.1 Hz, 1H), 3.84 (s, 3H), 4.38 (d, *J* = 11.1 Hz, 1H), 7.01 (td, *J* = 7.5 and 1.2 Hz, 1H), 7.24 (td, *J* = 7.5 and 1.2 Hz, 1H), 7.30 (d, *J* = 7.5 Hz, 1H), 7.77 (br, 1H). ¹³C NMR (CDCl₃, 75.5 MHz, 50°C) δ 21.9 (CH₂), 26.9 (CH₂), 39.4 (CH₂), 39.8 (CH₂), 52.6 (CH₃), 56.3 (CH₂), 57.6 (C), 115.1 (CH), 120.1 (C), 122.5 (CH), 124.9 (CH), 128.8 (CH), 132.7 (C), 153.3 (C), 207.9 (C). IR (film) 1710 cm⁻¹. Mp: 98-100.3 °C. Anal. Calcd for C₁₅H₁₇NO₃ (259.3)·1/4H₂O: C, 68.29; H, 6.69; N, 5.31. Found: C, 68.54; H, 6.67; N, 5.18.

***trans*-5-(Methoxycarbonyl)-5,6,6a,7,8,9,10,10a-octahydro-10a-phenanthridinol (27-*trans*)**

Chromatography: from CH₂Cl₂ to 98:2 CH₂Cl₂/MeOH: **27-*trans*** eluted in second place.

¹H NMR (CDCl₃, 300 MHz) δ 1.28 (m, 1H), 1.43-1.86 (m, 8H), 2.44 (dm, *J* = 12.9 Hz, 1H), 3.43 (t, *J* = 12.3 Hz, 1H), 3.80 (s, 3H), 3.81 (dd, *J* = 12.3 and 5.4 Hz, 1H), 7.06 (ddd, *J* = 7.8, 7.2, and 1.2 Hz, 1H), 7.27 (ddd, *J* = 8.4, 7.2, and 1.5 Hz, 1H), 7.40 (dd, *J* = 7.8 and 1.5 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H). ¹³C NMR (CDCl₃, 75.5 MHz) δ 21.5 (CH₂), 25.1 (CH₂), 25.6 (CH₂), 35.4 (CH₂), 41.3 (CH), 46.3 (CH₂), 52.9 (CH₃), 67.7 (C), 123.3 (CH), 123.6 (CH), 123.8 (CH), 128.1 (CH), 134.1 (C), 137.0 (C), 155.2 (C). IR

(film) 3470 (br), 1712 cm^{-1} . Mp: 106.7-109 °C. Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_3 \cdot 1/4\text{H}_2\text{O}$: C, 67.78; H, 7.39; N, 5.27. Found: C, 68.12; H, 7.35; N, 5.07.

cis-5-(Methoxycarbonyl)-5,6,6a,7,8,9,10,10a-octahydro-10a-phenanthridinol (27-cis)

Chromatography: from CH_2Cl_2 to 98:2 $\text{CH}_2\text{Cl}_2/\text{MeOH}$: **27-cis** eluted in third place.

^1H NMR (CDCl_3 , 300 MHz) δ 1.15-1.86 (m, 8H), 1.93 (tt, J = 9.3 and 4.2 Hz, 1H), 2.32 (m, 1H), 3.80 (s, 3H), 3.88 (dd, J = 13.2 and 3.9 Hz, 1H), 3.98 (dd, J = 13.2 and 5.4 Hz, 1H), 7.11 (ddd, J = 8.1, 7.5, and 1.5 Hz, 1H), 7.26 (ddd, J = 8.1, 7.5, and 1.5 Hz, 1H), 7.51 (dd, J = 7.5 and 1.5 Hz, 1H), 7.84 (dd, J = 7.5 and 1.5 Hz, 1H). ^{13}C NMR (CDCl_3 , 75.5 MHz) δ 23.0 (CH_2), 23.5 (CH_2), 26.1 (CH_2), 37.2 (CH_2), 41.4 (CH), 45.8 (CH_2), 53.0 (CH_3), 70.6 (C), 123.4 (CH), 124.1 (CH), 125.6 (CH), 127.8 (CH), 131.9 (C), 137.0 (C), 155.5 (C). IR (film) 3458 (br), 1712 cm^{-1} . HRMS Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_3$: 261.1356. Found: 261.1372.

1-Benzyl-3-methyl-2,3-dihydro-1H-indol-3-ol (30)

^1H NMR (CDCl_3 , 200 MHz, from the crude reaction mixture) δ 1.62 (s, 3H), 2.36 (s, 1H, OH), 3.23 (d, J = 10.2 Hz, 1H), 3.38 (d, J = 10.2 Hz, 1H), 4.25 (d, J = 14.6 Hz, 1H), 4.39 (d, J = 14.6 Hz, 1H), 6.61 (d, J = 7.6 Hz, 1H), 6.76 (td, J = 7.4 and 1.5 Hz, 1H). ^{13}C NMR (CDCl_3 , 75.5 MHz, from the crude reaction mixture) δ 25.6 (CH_3), 52.5 (CH_2), 67.3 (CH_2), 76.3 (C), 107.7 (CH), 117.9 (CH), 122.5 (CH), 127.1 (CH), 127.7 (CH), 128.4 (CH), 129.4 (CH), 134.3 (C), 137.8 (C), 151.0 (C).

1-Benzyl-3-methylindole¹ (31)

To a solution of crude alcohol **30** in dichloromethane (200 mL) TFA (1 mL) was dropwise added. After 2 h at room temperature, the mixture was washed with saturated aqueous NaHCO_3 , and the organic layer was dried and concentrated. The residue was purified by chromatography (from hexane to 4:1 hexane-EtOAc) to give indole **31**.

^1H NMR (CDCl_3 , 200 MHz) δ 2.33 (s, 3H), 5.27 (s, 2H), 6.90 (s, 1H), 7.08-7.38 (m, 8H), 7.60 (d, J = 7.5 Hz, 1H).

9-Benzyl-2,3,4,4a,9,9a-hexahydro-1H-carbazol-4a-ol (33)

^1H NMR (CDCl_3 , 200 MHz, from the crude reaction mixture) δ 1.20-2.16 (m, 8H), 3.35 (t, J = 5.8 Hz, 1H), 4.13 (d, J = 15.4 Hz, 1H, NCH_2Ar), 4.44 (d, J = 15.4 Hz, 1H, NCH_2Ar), 6.49 (d, J = 8 Hz, 1H), 6.76 (td, J = 7.6 and 1.5 Hz, 1H), 7.13 (ddd, J = 8, 7.6, and 1.5 Hz, 1H). ^{13}C NMR (CDCl_3 , 50 MHz, from the crude reaction mixture) δ 21.2 (CH_2), 21.6 (CH_2), 25.0 (CH_2), 33.4 (CH_2), 49.8 (CH_2), 70.9 (CH), 77.6

¹ Solé, D.; Cancho, Y.; Llebaria, A.; Moretó, J. M.; Delgado, A. *J. Org. Chem.* **1996**, *61*, 5895-5904.

(C), 108.5 (CH), 118.1 (CH), 121.7 (CH), 126.9 (CH), 127.3 (CH), 128.4 (CH), 129.0 (CH), 133.3 (C), 139.7 (C), 150.5 (C).

9-Benzyl-2,3,4,9-tetrahydro-1H-carbazole² (34)

Chromatography: from hexane to 4:1 hexane-EtOAc.

¹H NMR (CDCl₃, 300 MHz) δ 1.80-1.95 (m, 4H), 2.62 (tm, J = 5.7 Hz, 2H), 2.76 (tm, J = 5.7 Hz, 2H), 5.23 (s, 2H, NCH₂Ar), 6.96-7.28 (m, 8H), 7.48-7.52 (m, 1H). ¹³C NMR (CDCl₃, 75.5 MHz) δ 21.1 (CH₂), 22.2 (CH₂), 23.2 (CH₂), 23.3 (CH₂), 46.2 (CH₂), 108.9 (CH), 109.8 (C), 117.7 (CH), 118.8 (CH), 120.7 (CH), 126.1 (CH), 127.1 (CH), 127.4 (C), 128.6 (CH), 135.5 (C), 136.4 (C), 138.2 (C). IR (film) 1466, 2927 cm⁻¹.

2-Benzyl-1,2,3,4,5,7-hexahydro-3,7-methano-2-benzazonin-6-one (36)

Chromatography: from hexane to 4:1 hexane-EtOAc.

¹H NMR (CDCl₃, 300 MHz) δ 1.96 (dddd, J = 13.8, 9.9, 6.9, and 3 Hz, 1H), 2.18-2.32 (m, 2H), 2.35 (dddd, J = 15.3, 6.9, 3.6, and 0.7 Hz, 1H), 2.68 (dtd, J = 15, 3.6, and 1.2 Hz, 1H), 2.91 (ddd, J = 15.3, 9.9, and 7.5 Hz, 1H), 3.12 (br s, 1H), 3.61 (d, J = 16.2 Hz, 1H), 3.64 (d, J = 15 Hz, 1H, NCH₂Ar), 3.60-3.75 (masked, 1H), 4.06 (d, J = 15 Hz, 1H, NCH₂Ar), 4.12 (d, J = 16.2 Hz, 1H), 6.79 (d, J = 7.2 Hz, 1H), 7.05 (td, J = 7.5 and 1.5 Hz, 1H), 7.15 (td, J = 7.5 and 1.5 Hz, 1H), 7.18-7.42 (m, 6H). ¹³C NMR (CDCl₃, 75.5 MHz) δ 29.8 (CH₂), 31.4 (CH₂), 34.9 (CH₂), 53.4 (CH), 54.7 (CH₂), 55.1 (CH), 59.1 (CH₂), 126.4 (CH), 126.5 (CH), 126.7 (CH), 127.9 (CH), 128.3 (CH), 129.0 (CH), 130.7 (CH), 137.3 (C), 139.0 (C), 139.4 (C), 210.7 (C). IR (film) 1704 cm⁻¹. HRMS Calcd for C₂₀H₂₁NO: 291.1623. Found: 291.1621.

5-Acetyl-2-benzyl-2,3,4,5-tetrahydro-1H-2-benzazepine (38)

Chromatography: from hexane to 3:2 hexane-EtOAc.

¹H NMR (CDCl₃, 300 MHz) δ 2.01 (dddd, J = 14.5, 9.9, 4.5, and 3 Hz, 1H), 2.10 (s, 3H, CH₃), 2.29 (dddd, J = 14.5, 6.6, 4.5, and 3.6 Hz, 1H), 2.88 (dt, J = 13.2 and 4.5 Hz, 1H), 3.19 (ddd, J = 13.2, 9.9, and 3.6 Hz, 1H), 3.48 (d, J = 13.5 Hz, 1H), 3.54 (d, J = 13.5 Hz, 1H), 3.72 (d, J = 15 Hz, 1H), 3.78 (dd, J = 6.6 and 3 Hz, 1H), 3.83 (d, J = 15 Hz, 1H), 6.97 (dd, J = 7 and 1.5 Hz, 1H), 7.11 (dd, J = 7.2 and 1.5 Hz, 1H), 7.16-7.34 (m, 7H). ¹³C NMR (CDCl₃, 75.5 MHz) δ 29.6 (CH₃), 26.5 (CH₂), 53.8 (CH₂), 58.2 (CH), 58.5 (CH₂), 58.6 (CH₂), 126.9 (CH), 127.0 (CH), 127.2 (CH), 128.1 (CH), 128.9 (CH), 129.7 (CH), 130.3 (CH), 138.8 (C), 139.0 (C), 139.7 (C), 208.7 (C). IR (film) 1709 cm⁻¹. Anal. Calcd for C₁₉H₂₁NO (279.4)·1/4H₂O: C, 80.38; H, 7.63; N, 4.93. Found: C, 80.36; H, 7.54; N, 4.91.

² El-Hamamy, A. A.; Hill, J.; Townend, J. J. *Chem. Soc., Perkin Trans. I* **1983**, 573-580.

4-Acetyl-2-benzyl-1,2,3,4-tetrahydroisoquinoline (40)

Chromatography: from CH₂Cl₂ to 98:2 CH₂Cl₂/MeOH.

¹H NMR (CDCl₃, 300 MHz) δ 2.08 (s, 3H), 2.74 (dd, *J* = 11.7 and 5.1 Hz, 1H), 3.15 (ddd, *J* = 11.7, 3.3, and 1.2 Hz, 1H), 3.46 (d, *J* = 15 Hz, 1H), 3.62 (d, *J* = 12.9 Hz, 1H), 3.68 (d, *J* = 12.9 Hz, 1H), 3.63-3.71 (m, 1H), 3.87 (d, *J* = 15 Hz, 1H), 7.02-7.40 (m, 9H). ¹³C NMR (CDCl₃, 75.5 MHz) δ 28.7 (CH₃), 53.1 (CH₂), 53.7 (CH), 55.8 (CH₂), 62.5 (CH₂), 126.3 (CH), 126.8 (CH), 126.9 (CH), 127.2 (CH), 128.2 (CH), 128.9 (CH), 129.1 (CH), 131.8 (C), 135.1 (C), 137.7 (C), 210.1 (C). IR (film) 1709 cm⁻¹.

4-Acetyl-2-benzyl-2*H*-isoquinolin-1-one³ (41)

Chromatography: from CH₂Cl₂ to 98:2 CH₂Cl₂/MeOH.

¹H NMR (CDCl₃, 300 MHz) δ 2.49 (s, 3H), 5.30 (s, 2H), 7.29-7.42 (m, 5H), 7.55 (ddd, *J* = 8.1, 7.2, and 1.2 Hz, 1H), 7.74 (ddd, *J* = 8.1, 7.2, and 1.5 Hz, 1H), 7.93 (s, 1H), 8.48 (dd, *J* = 8.1 and 1.5 Hz, 1H), 8.91 (dd, *J* = 8.1 and 1.2 Hz, 1H). ¹³C NMR (CDCl₃, 75.5 MHz) δ 27.7 (CH₃), 52.2 (CH₂), 115.5 (C), 125.2 (C), 125.9 (CH), 127.5 (CH), 127.7 (CH), 127.9 (CH), 128.1 (CH), 128.9 (CH), 133.2 (CH), 133.6 (C), 135.6 (C), 139.6 (CH), 161.9 (C), 195.4 (C). IR (film) 1660 cm⁻¹. HRMS Calcd for C₁₈H₁₅NO₂: 277.1103. Found: 277.1107.

1-Acetyl-2-benzylisoindol (44)

Chromatography: CH₂Cl₂.

¹H NMR (CDCl₃, 300 MHz) δ 2.71 (s, 3H), 5.94 (s, 2H), 7.10-7.42 (m, 7H), 7.48 (s, 1H), 7.66 (dt, *J* = 8.4 and 1 Hz, 1H), 7.90 (dd, *J* = 8.7 and 1 Hz, 1H). ¹³C NMR (CDCl₃, 75.5 MHz) δ 30.7 (CH₃), 54.7 (CH₂), 120.0 (CH), 121.0 (CH), 121.8 (CH), 124.2 (CH), 126.0 (CH), 127.2 (CH), 127.6 (CH), 128.5 (CH), 137.2 (CH), 186.2 (C). IR (film) 1713 cm⁻¹. MS(ESP⁺) 250 (M+H)⁺.

Azapalladacycle 46

A solution of iodoaniline **7** (200 mg, 0.51 mmol), Pd₂(dba)₃ (256 mg, 0.28 mmol), and PPh₃ (134 mg, 0.51 mmol) in benzene (10 mL) was stirred at room temperature for 48 h. The reaction mixture was filtered through Celite, washed carefully with Et₂O, and concentrated *in vacuo*. The residue was purified by "flash" chromatography (SiO₂, from hexane to 1:1 hexane-EtOAc) to give palladium complex **46** (327 mg, 84%) as a brown solid. Crystallization from hexane-EtOAc afforded crystals suitable for X-ray analysis.

Decomposition point 150.2-153.4 °C. The signals in the ¹H and ¹³C NMR spectra were unambiguously assigned with the aid of 2D-NMR experiments (COSY, HSQC, and HMBC) and NOESY. The *J* (¹H-³¹P) were unambiguously established from the ¹H{³¹P} NMR spectrum. ¹H NMR (CDCl₃, 300 MHz) δ

³ Kimura, M.; Waki, I.; Deguchi, Y.; Amemiya, K.; Maeda, T. *Chem. Pharm. Bull.* **1983**, *31*, 1277-1282.

1.86 (m, 1H, H-4), 2.13 (s, 3H, CH₃), 2.47 (ddd, J = 17.5, 8.4, and 6.6 Hz, 1H, H-3), 2.67 (ddd, J = 17.5, 8.4, and 5.6 Hz, 1H, H-3), 2.88 (m, 1H, H-4), 3.27 (tdd, J (¹H-¹H) = 11.2 and 9 Hz, and J (¹H-³¹P) = 4.8 Hz, 1H, H-5), 3.51 (td, J = 11.2 and 4 Hz, 1H, H-5), 4.09 (dd, J (¹H-¹H) = 11.4 Hz and J (¹H-³¹P) = 8 Hz, 1H, NCH₂Ar), 4.54 (d, J = 11.4 Hz, 1H, NCH₂Ar), 5.60 (d, J = 7.6 Hz, 1H, H-3'), 6.48 (ddt, J = 7.6, 7.4, and 1.2 Hz, 1H, H-4'), 6.92 (dd, J = 7.8 and 1.2 Hz, 1H, H-6'), 7.02 (ddd, J = 7.8, 7.4, and 1.2 Hz, 1H, H-5'), 7.22-7.46 (m, 18H), 7.58 (m, 2H). ¹³C NMR (CDCl₃, 75.5 MHz) δ 23.3 (s, CH₂, C-4), 30.0 (s, CH₃), 41.2 (s, CH₂, C-3), 58.3 (s, CH₂, C-5), 64.3 (s, NCH₂Ar), 120.3 (s, CH, C-6'), 124.9 (s, CH, C-5'), 125.2 (d, J (¹³C-³¹P) = 3.6 Hz, CH, C-4'), 127.3 (d, J (¹³C-³¹P) = 12.8 Hz, C, C-2'), 127.9 (s, CH), 128.0 (s, CH), 128.0 (d, J (¹³C-³¹P) = 10.9 Hz, CH PPh₃), 128.3 (d, J (¹³C-³¹P) = 1.9 Hz, CH, C-3'), 130.6 (d, J (¹³C-³¹P) = 2.8 Hz, CH PPh₃), 131.7 (d, J (¹³C-³¹P) = 51.5 Hz, C PPh₃), 132.8 (s, CH), 134.9 (d, J (¹³C-³¹P) = 11.9 Hz, CH PPh₃), 135.4 (s, C), 157.2 (d, J (¹³C-³¹P) = 4.1 Hz, C, C-1'), 207.9 (s, C, C-2). ³¹P NMR (CDCl₃, 121.5 MHz) δ 38.5. IR (KBr) 1713 cm⁻¹. MS (ESP⁺) 761 (M⁺), 634 (M⁺-I). Anal. Calcd for C₃₆H₃₅INOPPd (761.9)·H₂O: C, 55.44; H, 4.78; N, 1.80. Found: C, 55.28; H, 4.57; N, 1.79.

Azapalladacycle 47

A solution of iodoaniline **7** (50 mg, 0.13 mmol) and Pd(PPh₃)₄ (167 mg, 0.14 mmol) in benzene (10 mL) was stirred at room temperature for 96 h. The reaction mixture was filtered through Celite, washed carefully with Et₂O, and concentrated *in vacuo*. The residue was purified by "flash" chromatography (SiO₂, from hexane to 4:6 hexane-EtOAc) to give palladium complex **46** (56 mg, 56%) and palladium complex **47** (13 mg, 15%) isolated as a yellow solid.

¹H NMR (CDCl₃, 300 MHz) δ 1.97 (m, 1H), 2.11 (s, 3H, CH₃), 2.52 (ddd, J = 17.7, 8.1, and 6.3 Hz, 1H), 2.75 (ddd, J = 17.7, 8.1, 5.7 Hz, 1H), 2.85 (m, 1H), 3.21 (m, 1H), 3.46 (td, J = 11.4 and 4.5 Hz, 1H), 4.06 (dd, J = 11.4 and 8 Hz, 1H), 4.52 (d, J = 11.4 Hz, 1H), 5.51 (d, J = 7.5 Hz, 1H), 6.46 (m, 1H), 6.90-7.06 (m, 2H), 7.20-7.50 (m, 18H), 7.54 (m, 2H). ¹³C NMR (CDCl₃, 75.5 MHz) δ 23.2 (s, CH₂), 29.9 (s, CH₃), 41.3 (s, CH₂), 57.5 (s, CH₂), 63.4 (s, CH₂), 119.4 (s, CH), 124.8 (s, CH), 125.1 (d, J (¹³C-³¹P) = 3 Hz, CH), 126.1 (d, J (¹³C-³¹P) = 8.2 Hz, C), 127.9 (s, CH), 128.0 (d, J (¹³C-³¹P) = 11.2 Hz, CH PPh₃), 128.4 (d, J (¹³C-³¹P) = 11.7 Hz, CH), 129.1 (d, J (¹³C-³¹P) = 8 Hz, CH), 130.5 (d, J (¹³C-³¹P) = 51.2 Hz, C PPh₃), 130.6 (d, J (¹³C-³¹P) = 2.6 Hz, CH PPh₃), 132.8 (s, CH), 134.7 (d, J (¹³C-³¹P) = 12.2 Hz, CH PPh₃), 135.7 (s, C), 156.8 (d, J (¹³C-³¹P) = 4.1 Hz, C), 207.9 (s, C). ³¹P NMR (CDCl₃, 121.5 MHz) δ 35.2. IR (KBr) 1713 cm⁻¹. MS (ESP⁺) 1304 (M⁺, dimer), 635 (M⁺-OH). Anal. Calcd for C₃₆H₃₆NO₂PPd (652.1): C, 66.31; H, 5.56; N, 2.15. Found: C, 66.79; H, 5.23; N, 1.76.

Azapalladacycle 48

A solution of iodoaniline **1a** (50 mg, 0.12 mmol), Pd₂(dba)₃ (60 mg, 0.066 mmol), and PPh₃ (33 mg, 0.13 mmol) in benzene (10 mL) was stirred at room temperature for 24 h. The reaction mixture was

filtered through Celite, washed carefully with Et₂O, and concentrated *in vacuo*. The residue was purified by “flash” chromatography (SiO₂, from CH₂Cl₂ to 98:2 CH₂Cl₂-MeOH) to give palladium complex **48** (63 mg, 65%). Crystallization from CH₂Cl₂-Et₂O afforded crystals suitable for X-ray analysis.

Decomposition point 166.5-168.7 °C. ¹H NMR (CDCl₃, 300 MHz) δ 1.79 (qd, *J* = 12.6 and 4.5 Hz, 1H), 2.22 (tdd, *J* = 11.7, 10.8, and 7.5 Hz, 1H), 2.42-2.57 (m, 3H), 2.64 (td, *J* = 14.4 and 6.3 Hz, 1H), 2.79 (dm, *J* = 11.7 Hz, 1H), 3.74 (m, 1H), 4.20 (tm, *J* = 11.7 Hz, 1H), 4.38 (dd, *J* = 11.1 and 8.1 Hz, 1H), 4.51 (d, *J* = 11.1 Hz, 1H), 5.64 (d, *J* = 7.5 Hz, 1H), 6.48 (m, 1H), 6.99 (d, *J* = 4.2 Hz, 2H), 7.22-7.44 (m, 18H), 7.62 (dd, *J* = 8.1 and 1.5 Hz, 2H). ¹³C NMR (CDCl₃, 75.5 MHz) δ 27.6 (s, CH₂), 32.8 (s, CH₂), 39.5 (s, CH₂), 39.9 (s, CH₂), 60.6 (s, CH₂), 64.9 (s, CH), 123.1 (s, CH), 124.5 (s, CH), 125.4 (d, *J* (¹³C-³¹P) = 3.9 Hz, CH), 127.8 (s, CH), 127.9 (d, *J* (¹³C-³¹P) = 10.9 Hz, CH PPh₃), 128.1 (s, CH), 128.6 (d, *J* (¹³C-³¹P) = 9.4 Hz, CH), 130.6 (d, *J* (¹³C-³¹P) = 2.5 Hz, CH PPh₃), 131.6 (d, *J* (¹³C-³¹P) = 51.6 Hz, C PPh₃), 133.1 (s, CH), 134.7 (d, *J* (¹³C-³¹P) = 12 Hz, CH PPh₃), 135.6 (s, C), 154.6 (s, C), 209.8 (s, C). One C signal was not observed. ³¹P NMR (CDCl₃, 121.5 MHz) δ 38.3. Anal. Calcd for C₃₇H₃₅INOPPd (773.9)·CH₂Cl₂: C, 53.14; H, 4.34; N, 1.63. Found: C, 53.37; H, 4.38; N, 1.62.

Azapalladacycle 49

Crystallization from CH₂Cl₂-Et₂O afforded pale brown crystals.

¹H NMR (CDCl₃, 300 MHz) δ 2.11 (m, 1H), 2.23-2.72 (m, 6H), 3.60 (m, 1H), 4.02 (m, 1H), 4.23 (dd, *J* = 11.2 and 8.4 Hz, 1H), 4.58 (d, *J* = 11.2 Hz, 1H), 5.54 (d, *J* = 7.4 Hz, 1H), 6.47 (m, 1H), 6.97-7.02 (m, 2H), 7.20-7.45 (m, 18H), 7.58 (dm, *J* = 8.1 Hz, 2H). ¹³C NMR (CDCl₃, 75.5 MHz) δ 28.4 (s, CH₂), 31.9 (s, CH₂), 39.3 (s, CH₂), 39.8 (s, CH₂), 59.9 (s, CH₂), 63.8 (s, CH), 121.9 (s, CH), 124.4 (s, CH), 125.4 (d, *J* (¹³C-³¹P) = 2.8 Hz, CH), 127.0 (d, *J* (¹³C-³¹P) = 9.4 Hz, C), 127.8 (s, CH), 127.9 (s, CH), 128.0 (d, *J* (¹³C-³¹P) = 11.0 Hz, CH PPh₃), 129.4 (d, *J* (¹³C-³¹P) = 8.8 Hz, CH), 130.2 (d, *J* (¹³C-³¹P) = 51.6 Hz, C PPh₃), 130.6 (s, CH PPh₃), 132.9 (s, CH), 134.6 (d, *J* (¹³C-³¹P) = 12 Hz, CH PPh₃), 135.8 (s, C), 154.5 (d, *J* (¹³C-³¹P) = 3.9 Hz, C), 209.8 (s, C). ³¹P NMR (CDCl₃, 121.5 MHz) δ 35.3. IR (film) 1714 cm⁻¹. Anal. Calcd for C₃₇H₃₆NO₂PPd (664.1)·CH₂Cl₂: C, 60.94; H, 5.11; N, 1.87. Found: C, 60.94; H, 5.09; N, 1.87.

Azapalladacycle 54

A solution of iodoaryl ketone **37a** (102 mg, 0.25 mmol) and Pd(PPh₃)₄ (294 mg, 0.25 mmol) in benzene (10 mL) was stirred at room temperature for 72 h. The reaction mixture was concentrated *in vacuo*, and the residue was purified by “flash” chromatography (SiO₂, CH₂Cl₂) to give palladium complex **54** (190 mg, 99%).

¹H NMR (CDCl₃, 300 MHz) δ 2.12 (s, 3H), 2.20 (m, 1H), 2.44 (m, 1H), 2.60-2.90 (m, 3H), 3.78 (br t, *J* = 12.9 Hz, 1H), 3.87 (dd, *J* = 14.4 and 3.3 Hz, 1H), 4.44-4.56 (m, 3H), 6.26 (t, *J* = 7.5 Hz, 1H), 6.36 (t, *J*

= 7.5 Hz, 1H), 6.84 (t, J = 7 Hz, 1H), 7.02 (d, J = 7.2 Hz, 1H), 7.26-7.44 (m, 14H), 7.70-7.80 (m, 6H). ^{13}C NMR (CDCl_3 , 75.5 MHz) δ 22.8 (s, CH_2), 30.0 (s, CH_3), 40.9 (s, CH_2), 58.3 (s, CH_2), 62.2 (s, CH_2), 62.5 (s, CH_2), 122.6 (s, CH), 124.1 (s, CH), 124.6 (d, J (^{13}C - ^{31}P) = 6.6 Hz, CH), 127.9 (d, J (^{13}C - ^{31}P) = 10.5 Hz, CH PPh_3), 128.0 (s, CH), 128.2 (s, CH), 130.3 (d, J (^{13}C - ^{31}P) = 2.2 Hz, CH PPh_3), 131.8 (s, CH), 132.5 (d, J (^{13}C - ^{31}P) = 50.6 Hz, C PPh_3), 132.6 (s, C), 135.1 (d, J (^{13}C - ^{31}P) = 11.6 Hz, CH PPh_3), 136.5 (d, J (^{13}C - ^{31}P) = 12 Hz, CH), 149.1 (d, J (^{13}C - ^{31}P) = 2.2 Hz, C), 154.7 (d, J (^{13}C - ^{31}P) = 3.9 Hz, C), 208.1 (s, C). ^{31}P NMR (CDCl_3 , 121.5 MHz) δ 39.2.

Azapalladacycle 55

A solution of iodoaryl ketone **43a** (70 mg, 0.18 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (222 mg, 0.19 mmol) in benzene (10 mL) was stirred at room temperature for 72 h. The reaction mixture was concentrated *in vacuo*, and the residue was purified by “flash” chromatography (SiO_2 , from hexane to 1:1 hexane/EtOAc) to give palladium complex **55** (49 mg, 35%).

^1H NMR (CDCl_3 , 300 MHz) δ 2.18 (s, 3H), 3.53 (dd, J = 18 and 7.5 Hz, 1H), 3.71 (dd, J = 13.5 and 3.5 Hz, 1H), 4.43 (d, J = 13.5 Hz, 1H), 4.67 (d, J = 13.5 Hz, 1H), 5.04 (d, J = 13.5 Hz, 1H), 5.10 (d, J = 18 Hz, 1H), 6.34 (td, J = 7.8 and 1.5 Hz, 1H), 6.41 (t, J = 7.8 Hz, 1H), 6.88 (t, J = 7.8 Hz, 1H), 7.03 (d, J = 7.8 Hz, 1H), 7.25-7.45 (m, 14H), 7.90-8.10 (m, 6H). ^{13}C NMR (CDCl_3 , 75.5 MHz) δ 29.3 (s, CH_3), 59.9 (s, CH_2), 61.9 (s, CH_2), 66.6 (s, CH_2), 122.8 (s, CH), 124.0 (s, CH), 124.7 (d, J (^{13}C - ^{31}P) = 6.6 Hz, CH), 127.9 (d, J (^{13}C - ^{31}P) = 10.4 Hz, CH PPh_3), 128.3 (s, CH), 128.4 (s, CH), 130.2 (d, J (^{13}C - ^{31}P) = 2.3 Hz, CH PPh_3), 131.8 (s, C), 131.9 (s, CH), 132.9 (d, J (^{13}C - ^{31}P) = 50.6 Hz, C PPh_3), 135.1 (d, J (^{13}C - ^{31}P) = 11.6 Hz, CH PPh_3), 136.6 (d, J (^{13}C - ^{31}P) = 12 Hz, CH), 148.0 (s, C), 154.9 (d, J (^{13}C - ^{31}P) = 5 Hz, C), 203.8 (s, C). ^{31}P NMR (CDCl_3 , 121.5 MHz) δ 39.8.

Palladium Complex 56

A solution of iodoaryl ketone **50** (100 mg, 0.34 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (402 mg, 0.35 mmol) in benzene (10 mL) was stirred at room temperature for 96 h. The reaction mixture was concentrated *in vacuo*, and the residue was purified by “flash” chromatography (SiO_2 , from hexane to EtOAc) to give palladium complex **56** (285 mg, 91%). Crystallization from CH_2Cl_2 -Et₂O afforded yellow crystals.

Decomposition point 143-147 °C. ^1H NMR (CDCl_3 , 300 MHz) δ 1.19 (m, 2H), 2.06 (s, 3H, CH_3), 2.14 (t, J = 7.5 Hz, 2H), 2.36 (t, J = 8.1 Hz, 2H), 6.20 (d, J = 7.5 Hz, 1H), 6.28 (t, J = 7.5 Hz, 1H), 6.52 (t, J = 7.5 Hz, 1H), 6.82 (dm, J = 7.5 Hz, 1H), 7.18-7.27 (m, 12H), 7.28-7.36 (m, 6H), 7.38-7.47 (m, 12H). ^{13}C NMR (CDCl_3 , 75.5 MHz) δ 22.5 (s, CH_2), 29.9 (s, CH_3), 38.5 (s, CH_2), 44.0 (s, CH_2), 123.0 (s, CH), 124.6 (s, CH), 127.6 (t, J (^{13}C - ^{31}P) = 5.2 Hz, CH PPh_3), 128.0 (s, CH), 129.7 (s, CH PPh_3), 131.9 (t, J (^{13}C - ^{31}P) = 23 Hz, C PPh_3), 134.5 (t, J (^{13}C - ^{31}P) = 6.6 Hz, CH), 134.8 (t, J (^{13}C - ^{31}P) = 6.1 Hz, CH PPh_3), 143.8 (s, C), 159.3 (s, C), 208.6 (s, C). ^{31}P NMR (CDCl_3 , 121.5 MHz) δ 20.2. IR (film) 1712 cm^{-1} .

¹. FAB-MS *m/z* 791 (M⁺-I) (10), 531 (40), 423 (100). Anal. Calcd for C₄₇H₄₃IOP₂Pd (919.1): C, 61.42; H, 4.72. Found: C, 61.05; H, 4.77.

Palladium Complex 57

A solution of iodoaryl ketone **51** (100 mg, 0.36 mmol) and Pd(PPh₃)₄ (424 mg, 0.37 mmol) in benzene (10 mL) was stirred at room temperature for 72 h. The reaction mixture was concentrated *in vacuo*, and then the palladium complex **57** (260 mg, 80%) was precipitated as a brown solid from EtOAc-MeOH. Crystallization from benzene afforded brown crystals.

Melting point 191-193 °C. ¹H NMR (CDCl₃, 300 MHz) δ 1.82 (dd, *J* = 8.4 and 8.1 Hz, 2H), 1.97 (s, 3H, CH₃), 2.62 (dd, *J* = 8.4 and 8.1 Hz, 2H), 6.10 (d, *J* = 7.5 Hz, 1H), 6.35 (t, *J* = 7.5 Hz, 1H), 6.53 (t, *J* = 7.5 Hz, 1H), 6.93 (dm, *J* = 7.5 Hz, 1H), 7.20-7.58 (m, 30H). ¹³C NMR (CDCl₃, 75.5 MHz) δ 29.8 (s, CH₃), 32.8 (br m, CH₂), 42.7 (s, CH₂), 123.1 (s, CH), 124.5 (s, CH), 127.7 (t, *J* (¹³C-³¹P) = 5.2 Hz, CH PPh₃), 128.1 (s, CH), 129.7 (s, CH PPh₃), 131.9 (t, *J* (¹³C-³¹P) = 23.1 Hz, C PPh₃), 134.5 (t, *J* (¹³C-³¹P) = 6 Hz, CH), 134.8 (t, *J* (¹³C-³¹P) = 6 Hz, CH PPh₃), 143.4 (s, C), 159.5 (s, C), 208.0 (s, C). ³¹P NMR (CDCl₃, 121.5 MHz) δ 19.9. IR (film) 1713 cm⁻¹. Anal. Calcd for C₄₆H₄₁IOP₂Pd (905.1)·C₆H₆: C, 63.52; H, 4.82. Found: C, 63.65; H, 4.74.

Palladium Complex 58

A solution of iodoaryl ketone **52**⁴ (100 mg, 0.38 mmol) and Pd(PPh₃)₄ (445 mg, 0.39 mmol) in benzene (10 mL) was stirred at room temperature for 72 h. The reaction mixture was concentrated *in vacuo*, and the palladium complex **58** (330 mg, 97%) was precipitated as a pale brown solid from Et₂O.

¹H NMR (CDCl₃, 300 MHz) δ 1.61 (s, 3H, CH₃), 3.63 (s, 2H), 6.26 (t, *J* = 7.5 Hz, 1H), 6.34 (d, *J* = 7.5 Hz, 1H), 6.54 (t, *J* = 7.5 Hz, 1H), 6.75 (dm, *J* = 7.5 Hz, 1H), 7.18-7.50 (m, 30H). ¹³C NMR (CDCl₃, 75.5 MHz) δ 29.3 (s, CH₃), 54.0 (s, CH₂), 122.9 (s, CH), 125.6 (s, CH), 127.8 (t, *J* (¹³C-³¹P) = 4.9 Hz, CH PPh₃), 129.8 (s, CH PPh₃), 130.0 (s, CH), 131.8 (t, *J* (¹³C-³¹P) = 23.2 Hz, C PPh₃), 134.6 (t, *J* (¹³C-³¹P) = 6.5 Hz, CH), 134.9 (t, *J* (¹³C-³¹P) = 6.1 Hz, CH PPh₃), 137.4 (t, *J* (¹³C-³¹P) = 3.7 Hz, C), 159.9 (s, C), 206.2 (s, C). ³¹P NMR (CDCl₃, 121.5 MHz) δ 23.1. IR (film) 1716 cm⁻¹.

Palladium Complex 59

A solution of iodoaryl ketone **53** (100 mg, 0.33 mmol) and Pd(PPh₃)₄ (373 mg, 0.32 mmol) in benzene (10 mL) was stirred at room temperature for 72 h. The reaction mixture was concentrated *in vacuo*, and the palladium complex **59** (109 mg, 35%) was precipitated as a yellow solid from EtOAc-MeOH.

Melting point 181-183 °C. ¹H NMR (CDCl₃, 300 MHz) δ 0.90-1.25 (m, 2H), 1.42-1.66 (m, 2H), 1.74 (m, 1H), 1.82-2.10 (m, 4H), 2.29 (br d, *J* = 13.5 Hz, 1H), 3.19 (dd, *J* = 14.5 and 4 Hz, 1H), 6.15 (d, *J* = 7.4

⁴ Negishi, E.; Copéret, C.; Sugihara, T.; Shimoyama, I.; Zhang, Y.; Wu, G.; Tour, J. M. *Tetrahedron* **1994**, *50*, 425-436.

Hz, 1H), 6.28 (t, $J = 7.4$ Hz, 1H), 6.48 (t, $J = 7.4$ Hz, 1H), 6.87 (dm, $J = 7.4$ Hz, 1H), 7.20-7.52 (m, 30H). ^{13}C NMR (CDCl_3 , 75.5 MHz) δ 24.8 (s, CH_2), 28.0 (s, CH_2), 34.4 (s, CH_2), 39.1 (s, CH_2), 42.1 (s, CH_2), 49.7 (s, CH), 122.7 (s, CH), 124.3 (s, CH), 127.6 (m, CH PPh_3), 129.6 (s, CH), 129.7 (s, CH PPh_3), 131.6-132.4 (m, C PPh_3), 134.9 (m, CH PPh_3), 135.9 (t, $J(^{13}\text{C}-^{31}\text{P}) = 5.5$ Hz, CH), 142.7 (s, C), 159.6 (s, C), 212.2 (s, C). ^{31}P NMR (CDCl_3 , 121.5 MHz) δ 21.9. IR (film) 1704 cm^{-1} .

SYNTHESIS OF THE STARTING MATERIALS

4-[(2-Iodophenyl)amino]cyclohexanone ethylene acetal (60a)

A solution of 2-iodoaniline (5.04 g, 23 mmol) and 1,4-cyclohexanedione monoethylene acetal (3.94 g, 25.3 mmol) in toluene (180 mL) was heated at reflux in a Dean-Stark apparatus for 48 h. The solvent was removed *in vacuo* and the residue was dissolved in MeOH (100 mL). The resulting solution was cooled to $0\text{ }^\circ\text{C}$, and NaBH_4 (1.75 g, 46.3 mmol) was added. After stirring at room temperature for 15 h, the solvent was removed *in vacuo* and the residue was dissolved in dichloromethane. The solution was poured into saturated aqueous NH_4Cl , basified with NaHCO_3 , and extracted with dichloromethane. The organic extracts were washed with water, dried, and concentrated. Chromatography (CH_2Cl_2) of the residue yielded aniline **60a** (4.77 g, 60%).

^1H NMR (CDCl_3 , 300 MHz) δ 1.55-1.73 (m, 4H), 1.75-1.88 (m, 2H), 1.97-2.12 (m, 2H), 3.43 (m, 1H, H-4), 3.96 (s, 4H), 4.17 (br d, $J = 7.2$ Hz, 1H, NH), 6.40 (td, $J = 7.5$ and 1.5 Hz, 1H, H-4'), 6.59 (dd, $J =$

8.1 and 1.5 Hz, 1H, H-6'), 7.18 (ddd, J = 8.1, 7.5, and 1.5 Hz, 1H, H-5'), 7.64 (dd, J = 7.5 and 1.5 Hz, 1H, H-3'). ^{13}C NMR (CDCl_3 , 75.5 MHz) δ 29.6 (CH_2), 32.7 (CH_2), 50.2 (CH), 64.2 (CH_2), 64.3 (CH_2), 85.9 (C), 108.1 (C), 111.0 (CH), 118.2 (CH), 129.3 (CH), 139.1 (CH), 146.1 (C). IR (KBr) 1509, 1588, 3375 cm^{-1} . Anal. Calcd for $\text{C}_{14}\text{H}_{18}\text{INO}_2$ (359.2): C, 46.81; H, 5.05; N, 3.90. Found: C, 46.81; H, 5.08; N, 3.91.

4-[(2-Bromophenyl)amino]cyclohexanone ethylene acetal (60b)

Operating as in the preparation of **60a**, starting from 2-bromoaniline, aniline **60b** was obtained after chromatography (CH_2Cl_2).

^1H NMR (CDCl_3 , 300 MHz) δ 1.52-1.74 (m, 4H), 1.78-1.88 (m, 2H), 2.00-2.10 (m, 2H), 3.41 (m, 1H, H-4), 3.97 (s, 4H), 4.25 (m, 1H, NH), 6.53 (ddd, J = 7.8, 7.5, and 1.5 Hz, 1H, H-4'), 6.65 (dd, J = 8.1 and 1.5 Hz, 1H, H-6'), 7.15 (ddd, J = 8.1, 7.5, and 1.5 Hz, 1H, H-5'), 7.40 (dd, J = 7.8 and 1.5 Hz, 1H, H-3'). ^{13}C NMR (CDCl_3 , 75.5 MHz) δ 29.8 (CH_2), 33.0 (CH_2), 50.0 (CH), 64.3 (CH_2), 64.4 (CH_2), 108.2 (C), 109.9 (C), 111.7 (CH), 117.4 (CH), 128.4 (CH), 132.5 (CH), 143.9 (C). IR (KBr) 1510, 1588, 3370 cm^{-1} .

4-[N-Benzyl-N-(2-iodophenyl)amino]cyclohexanone ethylene acetal (61a)

To a solution of aniline **60a** (2.8 g, 7.8 mmol) in CH_3CN (100 mL) were added benzyl bromide (5 mL, 42.1 mmol), Lil (0.28 g, 2.1 mmol), and K_2CO_3 (11.66 g, 84.4 mmol). After stirring at reflux for 48 h, the solvent was removed *in vacuo* and the residue was partitioned between dichloromethane and water. The organic extracts were dried and concentrated. Chromatography (CH_2Cl_2) of the residue yielded aniline **61a** (3.12 g, 90%).

^1H NMR (CDCl_3 , 300 MHz) δ 1.48-1.62 (m, 2H), 1.75-1.93 (m, 4H), 1.95-2.07 (m, 2H), 3.14 (tt, J = 11.1 and 3.6 Hz, 1H, H-4), 3.94 (m, 4H, $\text{OCH}_2\text{CH}_2\text{O}$), 4.30 (s, 2H, NCH_2Ar), 6.69 (td, J = 7.5 and 1.5 Hz, 1H, H-4'), 7.03-7.32 (m, 7H), 7.80 (dd, J = 7.5 and 1.5 Hz, 1H, H-3'). ^{13}C NMR (CDCl_3 , 75.5 MHz) δ 26.0 (CH_2), 33.8 (CH_2), 50.4 (CH_2), 61.1 (CH), 64.2 (CH_2), 64.3 (CH_2), 101.6 (C), 108.4 (C), 125.4 (CH), 125.5 (CH), 126.5 (*p*-C), 127.9 and 128.4 (*o*-C and *m*-C), 128.0 (CH), 139.1 (C), 140.1 (CH), 151.1 (C). IR (KBr) 1467 cm^{-1} . Anal. Calcd for $\text{C}_{21}\text{H}_{24}\text{INO}_2$ (449.3): C, 56.13; H, 5.38; N, 3.12. Found: C, 56.18; H, 5.45; N, 3.14.

4-[N-Benzyl-N-(2-bromophenyl)amino]cyclohexanone ethylene acetal (61b)

Operating as in the preparation of **61a**, starting from 2-bromoaniline **60b**, aniline **61b** (91%) was obtained after chromatography (CH_2Cl_2).

^1H NMR (CDCl_3 , 300 MHz) δ 1.49-1.62 (m, 2H), 1.75-1.92 (m, 4H), 1.92-2.02 (m, 2H), 3.22 (m, 1H, H-4), 3.93 (m, 4H), 4.32 (s, 2H, NCH_2Ar), 6.80 (m, 1H), 7.06-7.31 (m, 7H), 7.51 (dd, J = 7.8 and 1 Hz, 1H). ^{13}C NMR (CDCl_3 , 75.5 MHz) δ 26.1 (CH_2), 33.9 (CH_2), 49.8 (CH_2), 60.9 (CH), 64.2 (CH_2), 64.3 (CH_2), 108.3 (C), 122.8 (C), 124.4 (CH), 125.4 (CH), 126.4 (*p*-C), 127.1 (CH), 127.9 (*o*-C and *m*-C),

133.7 (CH), 139.3 (C), 148.3 (C). IR (KBr) 1472 cm^{-1} . HRMS Calcd for $\text{C}_{21}\text{H}_{24}\text{BrNO}_2$ 401.0990. Found 401.1003.

4-[*N*-Benzyl-*N*-(2-iodophenyl)amino]cyclohexanone (**1a**)

To a solution of acetal **61a** (2.13 g, 4.7 mmol) in THF (25 mL) was added 10% aqueous HCl (95 mL). After stirring at 50 °C for 24 h, the mixture was basified with Na_2CO_3 and extracted with dichloromethane. The organic extracts were dried and concentrated. Chromatography (CH_2Cl_2) of the residue yielded aniline **1a** (1.98 g, 99%).

^1H NMR (CDCl_3 , 300 MHz) δ 2.03 (dtd, J = 13.5, 9.6, and 4.5 Hz, 2H, H-3ax and H-5ax), 2.22 (dm, J = 13.5 Hz, 2H, H-3eq and H-5eq), 2.30 (m 2H, H-2ax and H-6ax), 2.50 (dt, J = 14.4 and 4.5 Hz, 2H, H-2eq and H-6eq), 3.54 (tt, J = 9.6 and 3.3 Hz, 1H, H-4), 4.26 (s, 2H, NCH_2Ar), 6.76 (ddd, J = 7.8, 7, and 1.5 Hz, 1H, H-4'), 6.99 (dd, J = 7.8 and 1.5 Hz, 1H, H-6'), 7.10-7.26 (m, 6H), 7.85 (dd, J = 7.8 and 1.5 Hz, 1H, H-3'). ^{13}C NMR (CDCl_3 , 75.5 MHz) δ 28.4 (CH_2), 39.3 (CH_2), 51.7 (CH_2), 58.1 (CH), 101.8 (C), 126.0 (CH), 126.1 (CH), 127.0 (*p*-C), 128.0 and 128.7 (*o*-C and *m*-C), 128.1 (CH), 137.8 (C), 140.2 (CH), 150.3 (C), 210.9 (CO). IR (KBr) 1714 cm^{-1} . Anal. Calcd for $\text{C}_{19}\text{H}_{20}\text{INO}$ (405.3): C, 56.30; H, 4.97; N, 3.46. Found: C, 56.09; H, 4.98; N, 3.45.

4-[*N*-Benzyl-*N*-(2-bromophenyl)amino]cyclohexanone (**1b**)

Operating as in the preparation of **1a**, starting from 2-bromoaniline **61b**, aniline **1b** (76%) was obtained after chromatography (CH_2Cl_2).

^1H NMR (CDCl_3 , 300 MHz) δ 1.94-2.10 (m, 2H, H-3ax and H-5ax), 2.15-2.27 (m, 2H, H-3eq and H-5eq), 2.27-2.40 (m 2H, H-2ax and H-6ax), 2.49 (dm, J = 14.1 Hz, 2H, H-2eq and H-6eq), 3.62 (tt, J = 9.9 and 3.3 Hz, 1H, H-4), 4.29 (s, 2H, NCH_2Ar), 6.89 (ddd, J = 8.1, 7.2, and 1.8 Hz, 1H, H-4'), 7.05 (dd, J = 8.1 and 1.8 Hz, 1H, H-6'), 7.10-7.27 (m, 6H), 7.57 (dd, J = 8.1 and 1.8 Hz, 1H, H-3'). ^{13}C NMR (CDCl_3 , 75.5 MHz) δ 28.6 (CH_2), 39.4 (CH_2), 51.1 (CH_2), 58.4 (CH), 123.1 (C), 125.2 (CH), 126.2 (CH), 126.8 (*p*-C), 127.3 (CH), 128.0 and 128.3 (*o*-C and *m*-C), 133.9 (CH), 138.3 (C), 147.6 (C), 210.8 (CO). IR (KBr) 1711 cm^{-1} . Anal. Calcd for $\text{C}_{19}\text{H}_{20}\text{BrNO}$ (358.3): C, 63.70; H, 5.63; N, 3.91. Found: C, 63.73; H, 5.64; N, 3.94.

4-[*N*-Acetyl-*N*-(2-iodophenyl)amino]cyclohexanone (**3**)

To a solution of aniline **60a** (756 mg, 2.1 mmol) in dichloromethane (30 mL) were added triethylamine (0.73 mL, 6.2 mmol) and acetyl chloride (0.37 mL, 5.2 mmol). After stirring at room temperature for 72 h, the mixture was washed with 1 N aqueous NaOH. The organic layer was dried and concentrated. The residue was dissolved in THF (10 mL) and 18% aqueous HCl (40 mL) was added. After stirring at room temperature for 24 h, the mixture was basified with NaHCO_3 and extracted with dichloromethane. The organic extracts were dried and concentrated. Chromatography (95:5 CH_2Cl_2 -MeOH) of the residue yielded acetanidide **3** (650 mg, 87%).

^1H NMR (CDCl_3 , 300 MHz) δ 1.32 (dtd, J = 13.5, 12.6, and 4.8 Hz, 1H, H-3ax or H-5ax), 1.66-1.88 (m, 1H, H-3ax or H-5ax), 1.81 (s, 3H, CH_3), 2.22-2.64 (m, 6H), 4.91 (tt, J = 12 and 3.3 Hz, 1H, H-4), 7.11 (td, J = 7.8 and 1.5 Hz, 1H, H-4'), 7.21 (dd, J = 7.8 and 1.5 Hz, 1H, H-6'), 7.44 (td, J = 7.8 and 1.5 Hz, 1H, H-5'), 7.97 (dd, J = 7.8 and 1.5 Hz, 1H, H-3'). ^{13}C NMR (CDCl_3 , 75.5 MHz) δ 23.8 (CH_3), 29.1 (CH_2), 31.0 (CH_2), 39.9 (CH_2), 53.8 (CH), 103.3 (C), 129.5 (CH), 130.0 (2 CH), 140.5 (CH), 142.5 (C), 170.1 (CON), 209.4 (CO). IR (film) 1662, 1716 cm^{-1} . HRMS Calcd for $\text{C}_{14}\text{H}_{16}\text{INO}_2$ 357.0226. Found 357.0228.

4-[*N*-(2-iodophenyl)-*N*-(methoxycarbonyl)amino]cyclohexanone ethylene acetal (62)

A solution of iodoaniline **60a** (150 mg, 0.42 mmol) and K_2CO_3 (120 mg, 0.87 mmol) in methyl chloroformate (2 mL) was heated at reflux for 12 h. The mixture was poured into water and extracted with dichloromethane. The organic extracts were dried and concentrated to give carbamate **62** (174 mg, 99%).

^1H NMR (CDCl_3 , 300 MHz) δ 1.18 (dtd, J = 12.7, 12.3, and 5.4 Hz, 1H, H-3ax or H-5ax), 1.58-1.83 (m, 5H), 1.89 (dm, J = 12.7 Hz, 1H, H-3eq or H-5eq), 2.10-2.25 (m, 1H), 3.64 (br s, 3H, CH_3), 3.78-3.94 (m 4H), 4.22 (br s, 1H, H-4), 7.01 (td, J = 7.8 and 1.5 Hz, 1H, H-4'), 7.20 (dd, J = 7.8 and 1.5 Hz, 1H, H-6'), 7.37 (td, J = 7.8 and 1.5 Hz, 1H, H-5'), 7.88 (dd, J = 7.8 and 1.5 Hz, 1H, H-3'). ^{13}C NMR (CDCl_3 , 75.5 MHz) δ 27.1 (CH_2), 29.6 (CH_2), 33.9 (CH_2), 52.8 (OCH_3), 56.5 (CH), 64.1 (CH_2), 64.2 (CH_2), 103.2 (C), 107.5 (C), 128.8 (CH), 128.9 (CH), 129.7 (CH), 139.5 (CH), 141.5 (C), 154.8 (CON). Anal. Calcd for $\text{C}_{16}\text{H}_{20}\text{INO}_4$ (417.2): C, 46.06; H, 4.83; N, 3.36. Found: C, 45.91; H, 4.85; N, 3.30.

4-[*N*-(2-iodophenyl)-*N*-(methoxycarbonyl)amino]cyclohexanone (5)

To a solution of acetal **62** (174 mg, 0.41 mmol) in THF (2 mL) was added 18% aqueous HCl (8 mL). After stirring at room temperature for 24 h, the mixture was basified with Na_2CO_3 and extracted with dichloromethane. The organic extracts were dried and concentrated. Chromatography (99:1 CH_2Cl_2 -MeOH) of the residue yielded ketone **5** (134 mg, 86%).

^1H NMR (CDCl_3 , 300 MHz) δ 1.41 (dtd, J = 13.5, 12.6, and 5 Hz, 1H, H-3ax or H-5ax), 1.65-2.01 (m, 2H), 2.19-2.29 (m, 1H), 2.33 (dtd, J = 15, 5, and 2.5 Hz), 2.39-2.61 (m, 3H), 3.68 and 3.69 (2 s, 3H, OCH_3), 4.60 (br t, J = 12 Hz, 1H, H-4), 7.05 (ddd, J = 8, 7.5 and 1.5 Hz, 1H, H-4'), 7.17 (dd, J = 7.8 and 1.5 Hz, 1H, H-6'), 7.37 (ddd, J = 7.8, 7.5, and 1.5 Hz, 1H, H-5'), 7.90 (dd, J = 8 and 1.5 Hz, 1H, H-3'). ^{13}C NMR (CDCl_3 , 75.5 MHz) δ 29.1 (CH_2), 31.4 (CH_2), 39.6 (CH_2), 39.7 (CH_2), 53.0 (OCH_3), 55.7 (CH), 102.9 (C), 128.8 (CH), 129.2 (CH), 129.5 (CH), 139.7 (CH), 141.3 (C), 154.7 (CON), 209.1 (CO). IR (film) 1712 cm^{-1} . HRMS Calcd for $\text{C}_{14}\text{H}_{16}\text{INO}_3$ 373.0174. Found 373.0167.

5-[N-Benzyl-N-(2-iodophenyl)amino]-2-pentanone (**7**)

To a solution of 3-(2-methyl-[1,3]dioxolan-2-yl)propionaldehyde (2 g, 13.8 mmol) in dichloromethane (100 mL) were added 2-iodoaniline (2.6 g, 11.6 mmol), AcOH (2 mL, 35.5 mmol), and NaBH(OAc)₃ (6 g, 28 mmol). After one night at room temperature, the reaction mixture was poured into saturated aqueous NaHCO₃ solution and extracted with dichloromethane. The organic extracts were dried and concentrated. The resulting residue was dissolved in CH₃CN (100 mL) and were added benzyl bromide (6.5 mL, 54.7 mmol), K₂CO₃ (15.3 g, 110.6 mmol), and a catalytic amount of LiI. After 48 h at reflux, the solvent was removed *in vacuo* and the residue was partitioned between dichloromethane and water. The organic layer was dried and concentrated. Chromatography (hexane to 6:4 hexane-EtOAc) afforded 5-[N-benzyl-N-(2-iodophenyl)amino]-2-pentanone ethylene acetal (3 g, 50%). ¹H NMR (CDCl₃, 200 MHz) δ 1.23 (s, 3H), 1.40-1.70 (m, 4H), 2.94 (t, *J* = 7.2 Hz, 2H), 3.80-3.90 (m, 4H), 4.10 (s, 2H), 6.80 (ddd, *J* = 8.1, 7.5, and 1.5 Hz, 1H), 7.04 (dd, *J* = 8.1 and 1.5 Hz, 1H), 7.20-7.41 (m, 6H), 7.85 (dd, *J* = 8.1 and 1.5 Hz, 1H). ¹³C NMR (CDCl₃, 50 MHz) δ 21.4 (CH₂), 23.7 (CH₃), 36.3 (CH₂), 52.0 (CH₂), 59.2 (CH₂), 64.5 (CH₂), 100.7 (C), 109.8 (C), 124.2 (CH), 125.8 (CH), 126.9 (CH), 128.0 and 128.8 (*o*-C and *m*-C), 128.6 (CH), 138.0 (C), 139.9 (CH), 151.7 (C).

To a solution of the above acetal (3g, 6.9 mmol) in THF (40 mL) was added 18% aqueous HCl. After 24 h at room temperature, the mixture was basified with NaHCO₃ and extracted with dichloromethane. The organic extracts were dried and concentrated. Chromatography (hexane to 8:2 hexane-EtOAc) yielded ketone **7** (2.56 g, 94%).

¹H NMR (CDCl₃, 300 MHz) δ 1.63 (quintuplet, *J* = 7.2 Hz, 2H), 2.08 (s, 3H), 2.47 (t, *J* = 7.2 Hz, 2H), 2.92 (t, *J* = 7.2 Hz, 2H), 4.07 (s, 2H), 6.83 (ddd, *J* = 8.1, 7.5, and 1.5 Hz, 1H), 7.03 (dd, *J* = 8.1 and 1.5 Hz, 1H), 7.23-7.40 (m, 6H), 7.89 (dd, *J* = 8.1 and 1.5 Hz, 1H). ¹³C NMR (CDCl₃, 75.5 MHz) δ 20.8 (CH₂), 30.0 (CH₃), 41.0 (CH₂), 50.5 (CH₂), 59.6 (CH₂), 100.6 (C), 124.4 (CH), 126.1 (CH), 127.0 (*p*-C), 128.0 and 128.9 (*o*-C and *m*-C), 128.7 (CH), 137.6 (C), 139.9 (CH), 151.3 (C), 208.6 (CO). IR (film) 1713 cm⁻¹. HRMS Calcd for C₁₈H₂₀INO 393.0590. Found 393.0600.

4-[N-Benzyl-N-(2-iodophenyl)amino]-2-butanone (11a)

To a solution of 2-iodoaniline (0.2 g, 0.9 mmol) in MeOH (5 mL) were added methyl vinyl ketone (0.17 mL, 2 mmol) and triethylamine (0.18 mL, 1.33 mmol), and the mixture was stirred for 72 h. Additional methyl vinyl ketone (80 μL , 0.45 mmol) was added at 24 h and 48 h. The solvent was removed *in vacuo*, the resulting residue was dissolved in CH_3CN (5 mL), and were added benzyl bromide (0.53 mL, 4.44 mmol) and K_2CO_3 (0.37 g, 2.68 mmol). After 48 h at room temperature, the solvent was removed *in vacuo* and the residue was partitioned between Et_2O and water. The organic layer was dried and concentrated. Chromatography (CH_2Cl_2) yielded 2-iodoaniline **11a** (0.28 g, 80%).

^1H NMR (CDCl_3 , 200 MHz) δ 2.03 (s, 3H, CH_3), 2.51 (t, J = 7.8 Hz, 2H, CH_2CO), 3.24 (t, J = 7.8 Hz, 2H, NCH_2), 4.07 (s, 2H, NCH_2Ar), 6.84 (ddd, J = 8, 7.2, and 1.6 Hz, 1H, H-4'), 7.04 (dd, J = 8 and 1.6 Hz, 1H, H-6'), 7.20-7.43 (m, 6H), 7.89 (dd, J = 8 and 1.6 Hz, 1H, H-3'). ^{13}C NMR (CDCl_3 , 75.5 MHz) δ 30.3 (CH_3), 41.5 (CH_2), 47.3 (CH_2), 59.9 (CH_2), 101.2 (C), 124.4 (CH), 126.5 (CH), 127.2 (CH), 128.1 and 129.0 (*o*-C and *m*-C), 128.8 (CH), 137.5 (C), 140.1 (CH), 151.3 (C), 207.7 (CO). IR (film) 1714 cm^{-1} . Anal. Calcd for $\text{C}_{17}\text{H}_{18}\text{INO}$ (379.2): C, 53.84; H, 4.78; N, 3.69. Found: C, 53.76; H, 4.76; N, 3.72.

4-[N-Benzyl-N-(2-bromophenyl)amino]-2-butanone (11b)

Operating as in the preparation of **11a**, starting from 2-bromoaniline (0.96 g, 5.55 mmol), aniline **11b** (76%) was obtained after chromatography (hexane to 9:1 hexane- CH_2Cl_2).

^1H NMR (CDCl_3 , 300 MHz) δ 2.02 (s, 3H, CH_3), 2.53 (t, J = 7.2 Hz, 2H, CH_2CO), 3.29 (t, J = 7.2 Hz, 2H, NCH_2), 4.15 (s, 2H, NCH_2Ar), 6.95 (ddd, J = 8, 7.5, and 1.5 Hz, 1H, H-4'), 7.05 (dd, J = 8 and 1.5 Hz, 1H, H-6'), 7.19-7.38 (m, 6H), 7.60 (dd, J = 8 and 1.5 Hz, 1H, H-3'). ^{13}C NMR (CDCl_3 , 75.5 MHz) δ 30.2 (CH_3), 41.4 (CH_2), 46.6 (CH_2), 59.0 (CH_2), 122.2 (C), 124.4 (CH), 125.3 (CH), 127.1 (CH), 127.8 (CH), 128.1 and 128.6 (*o*-C and *m*-C), 137.7 (C), 133.8 (CH), 148.4 (C), 207.7 (CO). IR (film) 1715 cm^{-1} . Anal. Calcd for $\text{C}_{17}\text{H}_{18}\text{BrNO}$ (332.2): C, 61.46; H, 5.46; N, 4.22. Found: C, 61.50; H, 5.46; N, 4.22.

4-[*N*-Acetyl-*N*-(2-iodophenyl)amino]-2-butanone (**13**)

To a solution of 2-iodoaniline (1.13 g, 5.2 mmol) in MeOH (25 mL) were added methyl vinyl ketone (0.46 mL, 5.7 mmol) and triethylamine (1.1 mL, 7.8 mmol), and the mixture was stirred for 72 h. Additional methyl vinyl ketone (0.23 mL, 2.85 mmol) was added at 24 h and 48 h. The solvent was removed *in vacuo* affording crude 4-[*N*-(2-iodophenyl)amino]-2-butanone (1.5 g, quantitative), which was used in the next step without purification.

A solution of 4-[*N*-(2-iodophenyl)amino]-2-butanone (0.75 g, 2.6 mmol) in acetic anhydride (5 mL) was stirred at room temperature for 24 h. The reaction mixture was poured into water (20 mL) and stirring was continued until only one phase was observed. The mixture was basified with 2N aqueous NaOH and extracted with dichloromethane. The organic extracts were dried and concentrated. Chromatography (49:1 EtOAc-DEA) afforded amide **13** (0.45 g, 52%).

¹H NMR (CDCl₃, 300 MHz) δ 1.78 (s, 3H, CH₃CON), 2.17 (s, 3H, CH₃), 2.76 (ddd, *J* = 16.8, 8.4, and 5.7 Hz, 1H, CH₂CO), 2.87 (ddd, *J* = 16.8, 8.4, and 6.6 Hz, 1H, CH₂CO), 3.46 (ddd, *J* = 14.1, 8.4, and 5.7 Hz, 1H, NCH₂), 4.30 (ddd, *J* = 14.1, 8.4, and 6.6 Hz, 1H, NCH₂), 7.09 (ddd, *J* = 8.1, 7.8, and 1.5 Hz, 1H, H-4'), 7.24 (dd, *J* = 7.8 and 1.5 Hz, 1H, H-6'), 7.43 (td, *J* = 7.8 and 1.5 Hz, 1H, H-5'), 7.95 (dd, *J* = 8.1 and 1.5 Hz, 1H, H-3'). ¹³C NMR (CDCl₃, 75.5 MHz) δ 22.8 (CH₃), 30.0 (CH₃), 41.6 (CH₂), 44.0 (CH₂), 100.1 (C), 129.6 (CH), 129.8 (CH), 129.9 (CH), 140.2 (CH), 144.9 (C), 170.2 (CON), 206.8 (CO). IR (film) 1663, 1713 cm⁻¹. Anal. Calcd for C₁₂H₁₄INO₂ (331.2): C, 43.52; H, 4.26; N, 4.23. Found: C, 43.70; H, 4.45; N, 4.08.

4-[*N*-(2-iodophenyl)-*N*-methoxycarbonylamino]-2-butanone (**15**)

To a solution of 2-iodoaniline (1.13 g, 5.2 mmol) in MeOH (25 mL) were added methyl vinyl ketone (0.46 mL, 5.7 mmol) and triethylamine (1.1 mL, 7.8 mmol), and the mixture was stirred for 72 h. Additional methyl vinyl ketone (0.23 mL, 2.85 mmol) was added at 24 h and 48 h. The solvent was removed *in vacuo*, the residue was dissolved in dichloromethane (30 mL), and were added methyl chloroformate (0.8 mL, 10.4 mmol) and DIPEA (1.8 mL, 10.4 mmol). The mixture was stirred at room temperature for 40 h and then heated to reflux for 3 h. The reaction mixture was poured into water and extracted with dichloromethane. The organic extracts were washed with saturated aqueous NaHCO₃, dried, and concentrated. Chromatography (4:1 hexane-EtOAc) yielded carbamate **15** (1.3 g, 73%).

¹H NMR (CDCl₃, 300 MHz) δ 2.17 (s, 3H, CH₃), 2.86 (t, *J* = 7.2 Hz, 2H, CH₂CO), 3.65 (s, 3H, OCH₃), 3.70 (dt, *J* = 14.1 and 7.2 Hz, 1H, NCH₂), 4.05 (dt, *J* = 14.1 and 7.2 Hz, 1H, NCH₂), 7.04 (ddd, *J* = 7.8, 7.5, and 1.5 Hz, 1H, H-4'), 7.20 (dd, *J* = 7.8 and 1.5 Hz, 1H, H-6'), 7.39 (ddd, *J* = 7.8, 7.5, and 1.5 Hz, 1H, H-5'), 7.89 (dd, *J* = 7.8 and 1.5 Hz, 1H, H-3'). ¹³C NMR (CDCl₃, 75.5 MHz) δ 30.0 (CH₃), 41.9 (CH₂), 45.5 (CH₂), 53.0 (OCH₃), 100.1 (C), 129.0 (CH), 129.1 (CH), 129.2 (CH), 139.5 (CH), 143.6 (C), 155.1 (COO), 206.6 (CO). IR (film) 1712 cm⁻¹. HRMS Calcd for C₁₂H₁₄INO₃: 347.0018. Found: 347.0011.

1-[N-Benzyl-N-(2-iodophenyl)amino]-3-pentanone (18)

A solution of 2-iodoaniline (0.5 g, 2.3 mmol), ethyl vinyl ketone (0.25 mL, 2.5 mmol), and Et₃N (0.64 mL, 4.6 mmol) in MeOH (10 mL) was stirred at room temperature for 24 h. Ethyl vinyl ketone was added (0.25 mL, 2.5 mmol) and stirring was maintained for 24 h at room temperature. The solvent was removed *in vacuo*, the residue was dissolved in CH₃CN (30 mL), and benzyl bromide (0.82 mL, 6.9 mmol) and K₂CO₃ (0.95 g, 6.9 mmol). After 48 h at 50 °C, the solvent was removed *in vacuo* and the residue was partitioned between dichloromethane and water. The organic layer was dried and concentrated. Chromatography (hexane to 8:2 hexane-EtOAc) yielded iodoaniline **18** (0.7 g, 77%).

¹H NMR (CDCl₃, 300 MHz) δ 0.96 (t, *J* = 7.5 Hz, 3H), 2.29 (q, *J* = 7.5 Hz, 2H), 2.49 (t, *J* = 7.5 Hz, 2H), 3.25 (t, *J* = 7.5 Hz, 2H), 4.08 (s, 2H), 6.83 (ddd, *J* = 7.8, 7.2, and 1.5 Hz, 1H), 7.03 (dd, *J* = 7.8 and 1.5 Hz, 1H), 7.20-7.41 (m, 6H), 7.88 (dd, *J* = 7.8 and 1.5 Hz, 1H). ¹³C NMR (CDCl₃, 75.5 MHz) δ 7.6 (CH₃), 36.2 (CH₂), 40.1 (CH₂), 47.3 (CH₂), 59.8 (CH₂), 101.1 (C), 124.4 (CH), 126.3 (CH), 127.1 (CH), 128.1 and 128.9 (*o*-C and *m*-C), 128.7 (CH), 137.5 (C), 140.0 (CH), 151.2 (C), 210.1 (CO). IR (film) 1712 cm⁻¹. Anal. Calcd for C₁₈H₂₀INO (393.3): C, 54.98; H, 5.13; N, 3.56. Found: C, 54.86; H, 5.06; N, 3.62.

1-[N-(2-Iodophenyl)-N-methoxycarbonylamino]-3-pentanone (20)

A solution of 2-iodoaniline (0.76 g, 3.5 mmol), ethyl vinyl ketone (0.38 mL, 3.8 mmol), and Et₃N (0.95 mL, 6.8 mmol) in MeOH (15 mL) was stirred at room temperature for 24 h. Ethyl vinyl ketone was added (0.38 mL, 3.8 mmol) and stirring was maintained for 24 h at room temperature. The solvent was removed *in vacuo*, the residue was dissolved in methyl chloroformate (10 mL) and K₂CO₃ (1g, 7 mmol) was added. After 12 h at 60 °C, the mixture was poured into water and extracted with dichloromethane. The organic extracts were dried and concentrated. Chromatography (hexane to 1:1 hexane-EtOAc) yielded carbamate **20** (0.97 g, 77%).

¹H NMR (CDCl₃, 300 MHz) δ 1.03 (t, *J* = 7.2 Hz, 3H, CH₃), 2.44 (m, 2H), 2.82 (t, *J* = 7.5 Hz, 2H), 3.64 (s, 3H, OCH₃), 3.70 (dt, *J* = 14.4 and 7.5 Hz, 1H, NCH₂), 4.04 (dt, *J* = 14.4 and 7.5 Hz, 1H, NCH₂), 7.02 (ddd, *J* = 7.8, 7.5, and 1.5 Hz, 1H, H-4'), 7.19 (dd, *J* = 7.8 and 1.2 Hz, 1H, H-6'), 7.37 (ddd, *J* = 7.8, 7.5, and 1.5 Hz, 1H, H-5'), 7.88 (dd, *J* = 7.8 and 1.2 Hz, 1H, H-3'). ¹³C NMR (CDCl₃, 75.5 MHz) δ 7.6 (CH₃), 36.0 (CH₂), 40.7 (CH₂), 45.7 (CH₂), 53.1 (OCH₃), 100.2 (C), 129.0 (CH), 129.1 (CH), 129.3 (CH), 139.6 (CH), 143.8 (C), 155.2 (COO), 209.3 (CO). IR (film) 1713 cm⁻¹. Anal. Calcd for C₁₃H₁₆INO₃ (361.2): C, 43.23; H, 4.46; N, 3.88. Found: C, 43.38; H, 4.44; N, 3.87.

1-[N-(2-Iodophenyl)-N-methylamino]-4,4-dimethyl-3-pentanone (**22**)

Sodium (1 g, 44.3 mmol) was slowly added to MeOH (25 mL). Once the evolution of hydrogen had ceased, 2-iodoaniline (2 g, 9.1 mmol) was added and the resulting solution was poured onto a suspension of paraformaldehyde (0.39 g, 13 mmol) in MeOH (10 mL). The resulting mixture was stirred at room temperature for 5 h and then hydrolyzed with cool water and extracted with Et₂O. The organic extracts were washed with water, dried, and concentrated *in vacuo*, taking care that the temperature remained below 25 °C. The resulting *N*-(Methoxymethyl)-2-iodoaniline^{5,6} was dissolved in dichloromethane (15 mL) and the solution was cooled to -78 °C. A solution of BF₃·Et₂O (1.2 mL, 9.5 mmol) in dichloromethane (10 mL) was added dropwise, the resulting mixture was stirred at -78 °C for 5 min and then a solution of pinacolone trimethylsilyl enol ether (1 mL, 4.6 mmol) in dichloromethane (10 mL) was added. After 4 h at -78 °C, the reaction mixture was allowed to reach room temperature, poured into brine, and extracted with dichloromethane. The organic extracts were dried and concentrated. Chromatography (hexane to 8:2 hexane-EtOAc) afforded a 1:1.1 mixture of 2-iodoaniline and 1-[*N*-(2-iodophenyl)amino]-4,4-dimethyl-3-pentanone. The mixture was dissolved in CH₃CN (40 mL) and K₂CO₃ (0.94 g, 6.8 mmol) and iodomethane (2.8 mL, 45 mmol) were added. After 24 h at 50 °C, iodomethane (1.5 mL, 24 mmol) was added, and heating was maintained for 24 h. The solvent was removed *in vacuo* and the residue was partitioned between dichloromethane and water. The organic extracts were dried and concentrated. Chromatography (hexane to 9:1 hexane-EtOAc) yielded ketone **22** (0.82 g, 52%).

¹H NMR (CDCl₃, 300 MHz) δ 1.11 (s, 9H), 2.70 (s, 3H), 2.74 (t, *J* = 7.5 Hz, 2H), 3.22 (t, *J* = 7.5 Hz, 2H), 6.79 (ddd, *J* = 7.8, 7.2, and 1.5 Hz, 1H), 7.10 (dd, *J* = 8.1 and 1.5 Hz, 1H), 7.31 (ddd, *J* = 8.1, 7.2, and 1.5 Hz, 1H), 7.84 (dd, *J* = 7.8 and 1.5 Hz, 1H). ¹³C NMR (CDCl₃, 75.5 MHz) δ 26.3 (CH₃), 35.1 (CH₂), 43.0 (CH₃), 44.3 (C), 51.7 (CH₂), 99.2 (C), 121.9 (CH), 125.5 (CH), 128.9 (CH), 139.9 (CH),

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153.7 (C), 214.5 (CO). IR (film) 1704 cm^{-1} . Anal. Calcd for $\text{C}_{14}\text{H}_{20}\text{INO}$ (345.2): C, 48.71; H, 5.84; N, 4.06. Found: C, 48.74; H, 5.88; N, 4.05.

2-[*N*-(2-Iodophenyl)aminomethyl]cyclohexanone (**63**)

Sodium (1.1 g, 47 mmol) was slowly added to MeOH (80 mL). Once the evolution of hydrogen had ceased, 2-iodoaniline (2 g, 9.1 mmol) was added and the resulting solution was poured onto a suspension of paraformaldehyde (0.39 g, 13 mmol) in MeOH (10 mL). The resulting mixture was stirred at room temperature for 5 h and then hydrolyzed with cool water and extracted with Et_2O . The organic extracts were washed with water, dried, and concentrated *in vacuo*, taking care that the temperature remained below 25 °C. The resulting *N*-(Methoxymethyl)-2-iodoaniline was dissolved in dichloromethane (15 mL) and the solution was cooled to -78 °C. A solution of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (2 mL, 15.8 mmol) in dichloromethane (20 mL) was added dropwise, the resulting mixture was stirred at -78 °C for 5 min and then a solution of 1-cyclohexenyloxytrimethylsilane (1.5 mL, 7.7 mmol) in dichloromethane (10 mL) was added. After 4 h at -78 °C, the reaction mixture was allowed to reach room temperature, poured into brine, and extracted with dichloromethane. The organic extracts were dried and concentrated. Chromatography (hexane to 8:2 hexane-EtOAc) afforded aniline **63** (1.6 g) unpurified with a small amount of cyclohexanone.

2-[[*N*-(2-Iodophenyl)-*N*-methylamino]methyl]cyclohexanone (**24**)

To a solution of aniline **63** (1 g, 3 mmol) in CH_3CN (50 mL) were added K_2CO_3 (1.26 g, 9.1 mmol) and methyl iodide (2 mL, 32.1 mmol). The resulting mixture was heated at 50 °C for 36 h, additional portions of methyl iodide (2 mL) being added every 8 h. The solvent was removed *in vacuo* and the residue was partitioned between water and dichloromethane. The organic layer was dried and concentrated. Chromatography (hexane to 94:6 hexane-EtOAc) yielded amine **24** (0.72 g, 70%).

^1H NMR (CDCl_3 , 300 MHz) δ 1.37 (qm, J = 11.7 Hz, 1H), 1.55 (qt, J = 11.7 and 3.3 Hz, 1H), 1.65 (qdd, J = 11.7, 4.5, and 3.3 Hz, 1H), 1.83 (dm, J = 11.7 Hz, 1H), 2.01 (dm, J = 9.6 Hz, 1H), 2.20-2.53 (m, 4H), 2.61 (s, 3H), 2.85 (dd, J = 13 and 9 Hz, 1H), 3.50 (dd, J = 13 and 4 Hz, 1H), 6.78 (ddd, J = 7.8, 7.2, and 1.5 Hz, 1H), 7.11 (dd, J = 7.8 and 1.5 Hz, 1H), 7.28 (ddd, J = 7.8, 7.2, and 1.5 Hz, 1H), 7.82 (dd, J = 7.8 and 1.5 Hz, 1H). ^{13}C NMR (CDCl_3 , 75.5 MHz) δ 24.6 (CH_2), 27.9 (CH_2), 32.5 (CH_2), 42.1 (CH_2), 44.3 (CH_3), 48.8 (CH), 55.0 (CH_2), 99.7 (C), 122.5 (CH), 125.7 (CH), 129.0 (CH), 139.7 (CH), 153.9 (C), 212.5 (CO). Anal. Calcd for $\text{C}_{14}\text{H}_{18}\text{INO}$ (343.2): C, 48.99; H, 5.29; N, 4.08. Found: C, 48.88; H, 5.24; N, 4.09.

2-[[*N*-(2-Iodophenyl)-*N*-methoxycarbonylamino]methyl]cyclohexanone (**26**)

To a solution of aniline **63** (0.56 g, 1.7 mmol) in methyl chloroformate (12 mL) was added K_2CO_3 (0.47 g, 3.36 mmol). After 12 h at 60 °C, the mixture was poured into water and extracted with

dichloromethane. The organic extracts were dried and concentrated. Chromatography (hexane to 7:3 hexane-EtOAc) yielded carbamate **26** (0.42 g, 64%).

^1H NMR (CDCl_3 , 200 MHz) δ 1.44-2.14 (5H), 2.20-2.58 (m, 3H), 2.74 (m, 1H), 3.49 (dd, J = 14.6 and 7 Hz, 0.5H), 3.57 (dd, J = 14.6 and 7.4 Hz, 0.5H), 3.63 (s, 3H), 3.92 (dd, J = 14.6 and 7.4 Hz, 0.5H), 4.20 (dd, J = 14.6 and 7 Hz, 0.5H), 7.02 (m, 1H), 7.18 (dd, J = 7.8 and 1.5 Hz, 0.5H), 7.29 (dd, J = 7.8 and 1.5 Hz, 0.5H), 7.38 (m, 1H), 7.86 (dd, J = 7.8 and 1.5 Hz, 0.5H), 7.88 (dd, J = 7.8 and 1.5 Hz, 0.5H). ^{13}C NMR (CDCl_3 , 50 MHz) δ 24.1 (CH_2), 24.8 (CH_2), 27.8 (CH_2), 27.9 (CH_2), 32.4 (CH_2), 32.6 (CH_2), 41.5 (CH_2), 42.2 (CH_2), 49.3 (CH), 49.7 (CH), 50.0 (CH_2), 51.2 (CH_2), 53.2 (CH_3), 99.9 (C), 100.5 (C), 128.9 (CH), 129.1 (CH), 129.3 (CH), 129.4 (CH), 129.9 (CH), 139.5 (CH), 139.7 (CH), 144.1 (C), 144.3 (C), 155.6 (COO), 156.0 (COO), 211.5 (CO), 212.1 (CO). IR (film) 1711 cm^{-1} . Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{INO}_3$ (387.2): C, 46.53; H, 4.69; N, 3.62. Found: C, 46.52; H, 4.61; N, 3.55.

1-[*N*-Benzyl-*N*-(2-iodophenyl)amino]-2-propanol (**64**)

To a cooled (0 °C) solution of *N*-benzyl-2-iodoaniline (0.78 g, 2.5 mmol) in dichloromethane (10 mL) was added AlEt_3 (2 mL, 3.8 mmol) in the dark.⁷ After 30 min at 0 °C, the mixture was allowed to reach room temperature, and propylene oxide (0.26 mL, 3.7 mmol) was added. The mixture was stirred at room temperature for 24 h. After cooling to 0 °C, were added NaF (0.45 g, 11 mmol) and water (0.3 mL, 16.6 mmol), and the mixture was stirred for 1 h. The reaction mixture was filtered through Celite, washing carefully with dichloromethane, and the solution was washed with brine. The organic layer was dried and concentrated. Chromatography (hexane to 6:4 hexane-EtOAc) yielded alcohol **64** (0.7 g, 75%).

^1H NMR (CDCl_3 , 200 MHz) δ 1.06 (d, J = 6.2 Hz, 3H), 2.68 (dd, J = 12.8 and 10.2 Hz, 1H), 3.08 (dd, J = 12.8 and 2.6 Hz, 1H), 3.24 (s, 1H, OH), 3.65 (dq, J = 10.2, 6.2, and 2.6 Hz, 1H), 4.02 (d, J = 13.8 Hz, 1H), 4.16 (d, J = 13.8 Hz, 1H), 6.88 (ddd, J = 8, 7.2, and 1.5 Hz, 1H), 6.95 (dd, J = 8.4 and 1.5 Hz, 1H), 7.18-7.34 (m, 6H), 7.89 (dd, J = 8 and 1.5 Hz, 1H). ^{13}C NMR (CDCl_3 , 50 MHz) δ 19.7 (CH_3), 59.9 (CH_2), 60.4 (CH_2), 63.7 (CH), 101.5 (C), 125.4 (CH), 127.1 (CH), 127.5 (CH), 128.2 and 129.6 (o-C and m-C), 129.0 (CH), 136.3 (C), 139.8 (CH), 151.1 (C).

⁷ Overman, L. E.; Sugai, S. *J. Org. Chem.* **1985**, 50, 4154-4155.

1-[*N*-Benzyl-*N*-(2-iodophenyl)amino]-2-propanone (29)

To a cooled (-78 °C) solution of oxalyl chloride (0.4 mL, 4.6 mmol) in dichloromethane (10 mL) was added DMSO (0.57 mL, 8 mmol). After 30 min at -78 °C, a solution of alcohol **64** (0.7 g, 1.9 mmol) in dichloromethane (15 mL) was added. The mixture was stirred at -78 °C for 1 h and Et₃N (1.9 mL, 13.6 mmol) was added. The solution was stirred at -78 °C for 15 min and then allowed to reach room temperature. The reaction mixture was partitioned between dichloromethane and saturated aqueous NaHCO₃. The organic layer was washed with brine, dried, and concentrated. Chromatography (hexane to 8:2 hexane-EtOAc) afforded ketone **29** (0.59 g, 85%).

¹H NMR (CDCl₃, 300 MHz) δ 2.04 (s, 3H), 3.77 (s, 2H), 4.30 (s, 2H), 6.79 (ddd, *J* = 7.8, 7.2, and 1.8 Hz, 1H), 7.19 (dd, *J* = 7.8 and 1.5 Hz, 1H), 7.22-7.44 (m, 6H), 7.86 (dd, *J* = 7.8 and 1.5 Hz, 1H). ¹³C NMR (CDCl₃, 75.5 MHz) δ 27.7 (CH₃), 58.6 (CH₂), 62.0 (CH₂), 98.5 (C), 124.7 (CH), 126.0 (CH), 127.4 (CH), 128.3 and 128.9 (*o*-C and *m*-C), 128.8 (CH), 137.1 (C), 140.1 (CH), 151.1 (C), 207.4 (CO). IR (film) 1714 cm⁻¹. HRMS Calcd for C₁₆H₁₆INO: 365.0277. Found: 365.0271.

trans-2-[*N*-Benzyl-*N*-(2-iodophenyl)amino]cyclohexanol (65)

To a cooled (0 °C) solution of *N*-benzyl-2-iodoaniline (0.5 g, 1.6 mmol) in dichloromethane (10 mL) was added AlEt₃ (1.3 mL, 2.5 mmol) in the dark. After 30 min at 0 °C, the mixture was allowed to reach room temperature, and cyclohexene oxide (0.25 mL, 2.5 mmol) was added. The mixture was stirred at room temperature for 24 h. After cooling to 0 °C, were added NaF (285 mg, 6.8 mmol) and water (0.18 mL, 10.2 mmol), and the mixture was stirred for 1 h. The reaction mixture was filtered through Celite, washing carefully with dichloromethane, and the organic solution was washed with brine. The organic layer was dried and concentrated, and the resulting residue was crystallized (hexane) to yield alcohol **65** (855 mg, 86%).

¹H NMR (CDCl₃, 300 MHz) δ 1.12 (qt, *J* = 12.6 and 3.3 Hz, 1H), 1.27 (qt, *J* = 12.6 and 3.3 Hz, 1H), 1.30-1.44 (m, 1H), 1.51 (qd, *J* = 12.6 and 3.6 Hz, 1H), 1.66-1.79 (m, 2H), 1.94 (dm, *J* = 12.6 Hz, 1H), 2.18 (dm, *J* = 12.6 Hz, 1H), 2.90 (ddd, *J* = 12.6, 9.9, and 3.3 Hz, 1H), 3.85 (td, *J* = 9.9 and 3.6 Hz, 1H), 3.88 (br s, 1H, OH), 4.21 (d, *J* = 14.1 Hz, 1H, N CH₂Ar), 4.38 (d, *J* = 14.1 Hz, 1H, N CH₂Ar), 6.74 (ddd, *J* = 7.8, 7, and 1.8 Hz, 1H, H-4'), 7.07-7.30 (m, 7H), 7.78 (dd, *J* = 7.8 and 1.5 Hz, 1H, H-3'). ¹³C NMR (CDCl₃, 75.5 MHz) δ 24.3 (CH₂), 24.6 (CH₂), 25.4 (CH₂), 34.2 (CH₂), 50.1 (CH₂), 69.0 (CH), 71.0 (CH), 101.4 (C), 126.5 (CH), 126.8 (CH), 126.9 (CH), 128.0 and 128.6 (*o*-C and *m*-C), 128.2 (CH), 138.1 (C), 140.2 (CH), 149.6 (C). IR (KBr) 3747 cm⁻¹. mp 99-100°C. Anal. Calcd for C₁₉H₂₂INO (407.3): C, 56.03; H, 5.44; N, 3.44. Found: C, 56.14; H, 5.48; N, 3.37.

2-[*N*-Benzyl-*N*-(2-iodophenyl)amino]cyclohexanone (32)

To a cooled (-78 °C) solution of oxalyl chloride (0.34 mL, 3.9 mmol) in dichloromethane (10 mL) was added DMSO (0.5 mL, 7 mmol). After 30 min at -78 °C, a solution of alcohol **65** (0.91 g, 2.23 mmol) in

dichloromethane (11 mL) was added. The mixture was stirred at -78 °C for 1 h and Et₃N (1.6 mL, 11.8 mmol) was added. The solution was stirred at -78 °C for 15 min and then allowed to reach room temperature. The reaction mixture was partitioned between dichloromethane and saturated aqueous NaHCO₃. The organic layer was washed with brine, dried, and concentrated. Chromatography (hexane to 9:1 hexane-EtOAc) afforded ketone **32** (0.79 g, 87%).

¹H NMR (CDCl₃, 300 MHz) δ 1.58-1.78 (m, 2H), 1.86-2.04 (m, 3H), 2.16-2.30 (m, 1H), 2.38-2.57 (m, 2H), 3.91 (dd, *J* = 10.5 and 5.1 Hz, 1H, H-2), 4.26 (d, *J* = 15 Hz, 1H, N CH₂Ar), 4.70 (d, *J* = 15 Hz, 1H, N CH₂Ar), 6.68 (ddd, *J* = 7.8, 7.2, and 1.5 Hz, 1H), 7.08-7.38 (m, 7H), 7.76 (dd, *J* = 7.8 and 1.5 Hz, 1H). ¹³C NMR (CDCl₃, 75.5 MHz) δ 24.4 (CH₂), 27.6 (CH₂), 32.6 (CH₂), 41.8 (CH₂), 52.4 (CH₂), 70.2 (CH), 100.4 (C), 125.6 (CH), 126.6 (CH), 126.8 (CH), 127.8 and 128.6 (*o*-C and *m*-C), 128.2 (CH), 138.6 (C), 139.7 (CH), 150.2 (C), 211.2 (CO). IR (KBr) 1712 cm⁻¹. mp 108.8-109.5°C. Anal. Calcd for C₁₉H₂₀INO (405.3): C, 56.31; H, 4.97; N, 3.46. Found: C, 56.31; H, 4.97; N, 3.49.

4-[N-Benzyl-N-(2-iodobenzyl)amino]cyclohexanone (**35a**)

To a solution of 4-(*N*-benzylamino)cyclohexanone ethylene acetal⁸ (0.77 g, 3.1 mmol) in CH₃CN (50 mL) were added K₂CO₃ (0.86 g, 6.2 mmol), 2-iodobenzyl chloride (0.95 g, 3.8 mmol), and LiI (150 mg). The mixture was stirred at 60 °C for 24 h. The solvent was removed *in vacuo* and the residue was partitioned between dichloromethane and water. The organic extracts were concentrated, the residue dissolved in THF (80 mL), and 10% aqueous HCl (80 mL) added. After 16 h at room temperature, the mixture was basified with Na₂CO₃ and extracted with dichloromethane. The organic extracts were dried and concentrated. Chromatography (CH₂Cl₂) yielded amine **35a** (1 g, 77%).

¹H NMR (CDCl₃, 200 MHz) δ 1.81 (m, 2H), 2.14-2.50 (m, 6H), 2.99 (tt, *J* = 11.4 and 4.8 Hz, 1H, H-4), 3.68 (s, 2H), 3.69 (s, 2H), 6.91 (td, *J* = 7.5 and 1.8 Hz, 1H), 7.20-7.42 (m, 6H), 7.55 (dd, *J* = 7.8 and 1.8 Hz, 1H), 7.77 (dd, *J* = 8.2 and 1.2 Hz, 1H). ¹³C NMR (CDCl₃, 50 MHz) δ 27.5 (CH₂), 40.1 (C CH₂), 54.1 (CH₂), 56.4 (CH), 58.6 (CH₂), 99.9 (C), 126.9 (CH), 128.1 (CH), 128.2 (CH), 128.6 (CH), 128.5 (CH), 139.1 (CH), 139.7 (C), 141.7 (C), 210.8 (CO). IR (film) 1714 cm⁻¹. Anal. Calcd for C₂₀H₂₂INO (419.3)·1/4 H₂O: C, 56.68; H, 5.35; N, 3.31. Found: C, 56.67; H, 5.23; N, 3.32.

⁸ Quirante, J.; Escolano, C.; Massot, M.; Bonjoch, J. *Tetrahedron* **1997**, 53, 1391-1402.

4-[*N*-Benzyl-*N*-(2-bromobenzyl)amino]ciclohexanone (**35b**)

Operating as in the preparation of **35a** and using 2-bromobenzyl bromide as the alkylating agent, amine **35b** (68%) was obtained after chromatography (CH₂Cl₂).

¹H NMR (CDCl₃, 300 MHz) δ 1.76-1.94 (m, 2H), 2.17-2.48 (m, 6H), 3.01 (tt, J = 11.4 and 3.3 Hz, 1H, H-4), 3.70 (s, 2H), 3.76 (s, 2H), 7.08 (td, J = 7.5 and 1.5 Hz, 1H), 7.20-7.41 (m, 6H), 7.50 (dd, J = 8 and 1.5 Hz, 1H), 7.60 (dd, J = 7.8 and 1.5 Hz, 1H). ¹³C NMR (CDCl₃, 75.5 MHz) δ 27.4 (CH₂), 40.1 (CH₂), 53.5 (CH₂), 54.1 (CH₂), 56.3 (CH), 124.0 (C), 126.8 (CH), 127.2 (CH), 128.1 (CH), 128.2 (CH), 128.3 (CH), 130.2 (CH), 132.4 (CH), 138.9 (C), 139.8 (C), 210.8 (CO). IR (film) 1716 cm⁻¹. Anal. Calcd for C₂₀H₂₂BrNO (372.3)·3/4H₂O: C, 62.26; H, 6.14; N, 3.63. Found: C, 61.90; H, 5.72; N, 3.52.

5-(*N*-Benzylamino)-2-pentanone ethylene acetal (**66**)

A mixture of 5-iodo-2-pentanone ethylene acetal⁹ (5.7 g, 22.4 mmol), benzylamine (12 mL, 109 mmol), and K₂CO₃ (6.2 g, 44.9 mmol) was stirred at 70 °C for 24 h. The reaction mixture was partitioned between dichloromethane and saturated aqueous NaHCO₃. The organic extracts were dried and concentrated. Chromatography (9:1 CH₂Cl₂-MeOH) yielded amine **66** (4.7 g, 89%).

¹H NMR (CDCl₃, 300 MHz) δ 1.31 (s, CH₃), 1.44 (s, 1H, NH), 1.55-1.75 (m, 4H), 2.63 (t, J = 6.9 Hz, 2H), 3.78 (s, 2H, NCH₂Ar), 3.82-3.98 (m, 4H), 7.18-7.35 (m, 5H). ¹³C NMR (CDCl₃, 75.5 MHz) δ 23.7 (CH₃), 24.6 (CH₂), 36.7 (CH₂), 49.3 (CH₂), 53.8 (CH₂), 64.5 (CH₂), 109.8 (C), 126.7 (CH), 127.9 and 128.2 (*o*-C and *m*-C), 140.3 (C). Anal. Calcd for C₁₄H₂₁NO₂(235.3)·1/4 H₂O: C, 70.11; H, 9.04; N, 5.84. Found: C, 70.50; H, 8.99; N, 5.98.

5-[*N*-Benzyl-*N*-(2-iodobenzyl)amino]-2-pentanone (**37a**)

To a solution of amine **66** (1 g, 4.3 mmol) in CH₃CN (30 mL) were added K₂CO₃ (1.77 g, 12.8 mmol), 2-iodobenzyl chloride (1.4 g, 5.5 mmol), and a catalytic amount of LiI. The mixture was stirred at 65 °C for 24 h. The solvent was removed *in vacuo* and the residue was partitioned between dichloromethane and water. The organic extracts were concentrated, the residue dissolved in THF (20 mL), and 18% aqueous HCl (80 mL) added. After 24 h at room temperature, the mixture was basified with NaHCO₃.

⁹ Chiarello, J.; Joulié, M. M. *Tetrahedron* **1988**, *44*, 41-48.

and extracted with dichloromethane. The organic extracts were dried and concentrated. Chromatography (hexane to 9:1 hexane-EtOAc) yielded amine **37a** (1.49 g, 85%).

^1H NMR (CDCl_3 , 300 MHz) δ 1.76 (quintuplet, $J = 7.2$ Hz, 2H, H-4), 2.04 (s, 3H, CH_3), 2.39 (t, $J = 7.2$ Hz, 2H), 2.44 (t, $J = 7.2$ Hz, 2H), 3.60 (s, 2H), 3.61 (s, 2H), 6.93 (ddd, $J = 8.1$, 7.5, and 1.5 Hz, 1H), 7.20-7.37 (m, 6H), 7.52 (dd, $J = 7.8$ and 1.5 Hz, 1H), 7.81 (dd, $J = 8.1$ and 1.5 Hz, 1H). ^{13}C NMR (CDCl_3 , 75.5 MHz) δ 20.9 (CH_2), 29.9 (CH_3), 41.2 (CH_2), 52.5 (CH_2), 58.3 (CH_2), 62.7 (CH_2), 100.2 (C), 126.9 (CH), 128.0 (CH), 128.1 and 128.8 (*o*-C and *m*-C), 128.6 (CH), 130.2 (CH), 139.2 (C), 139.3 (CH), 141.6 (C), 208.7 (CO). IR (film) 1716 cm^{-1} . Anal. Calcd for $\text{C}_{19}\text{H}_{22}\text{INO}$ (407.3): C, 56.03; H, 5.44; N, 3.44. Found: C, 55.95; H, 5.42; N, 3.44.

5-[*N*-Benzyl-*N*-(2-bromobenzyl)amino]-2-pentanone (**37b**)

Operating as in the preparation of **37a** and using 2-bromobenzyl bromide as the alkylating agent, amine **37b** (75%) was obtained after chromatography (hexane to 8:2 hexane-EtOAc).

^1H NMR (CDCl_3 , 300 MHz) δ 1.76 (quintuplet, $J = 6.9$ Hz, 2H, H-4), 2.04 (s, 3H, CH_3), 2.39 (t, $J = 6.9$ Hz, 2H), 2.44 (t, $J = 6.9$ Hz, 2H), 3.59 (s, 2H), 3.66 (s, 2H), 7.08 (ddd, $J = 8$, 7.5, and 1.8 Hz, 1H), 7.20-7.36 (m, 6H), 7.51 (dd, $J = 8$ and 1.2 Hz, 1H), 7.56 (dd, $J = 7.8$ and 1.5 Hz, 1H). ^{13}C NMR (CDCl_3 , 75.5 MHz) δ 21.1 (CH_2), 29.8 (CH_3), 41.2 (CH_2), 52.7 (CH_2), 57.8 (CH_2), 58.4 (CH_2), 124.2 (C), 126.8 (CH), 127.1 (CH), 128.0 and 128.7 (*o*-C and *m*-C), 128.1 (CH), 130.5 (CH), 132.5 (CH), 138.7 (C), 139.3 (C), 208.6 (CO). IR (film) 1716 cm^{-1} .

4-[*N*-Benzyl-*N*-(2-iodobenzyl)amino]-2-butanone (**39a**)

A solution of *N*-benzyl-*N*-(2-iodobenzyl)amine (1.28 g, 3.96 mmol), methyl vinyl ketone (0.53 mL, 6.34 mmol), and triethylamine (0.88 mL, 6.34 mmol) in MeOH (10 mL) was stirred at room temperature for 18 h. The solvent was removed *in vacuo* and the residue was purified by chromatography (CH₂Cl₂) to yield amine **39a** (0.93 g, 60%).

¹H NMR (CDCl₃, 200 MHz) δ 2.00 (s, 3H), 2.61 (t, *J* = 7 Hz, 2H), 2.83 (t, *J* = 7 Hz, 2H), 3.62 (s, 2H), 3.64 (s, 2H), 6.93 (td, *J* = 7.8 and 1.8 Hz, 1H), 7.18-7.40 (m, 6H), 7.51 (dd, *J* = 6.8 and 1.5 Hz, 1H), 7.82 (dd, *J* = 7.8 and 1.8 Hz, 1H). ¹³C NMR (CDCl₃, 75.5 MHz) δ 29.9 (CH₃), 41.6 (CH₂), 48.5 (CH₂), 58.4 (CH₂), 62.6 (CH₂), 100.1 (C), 127.0 (CH), 128.1 (CH), 128.2 and 128.8 (*o*-C and *m*-C), 128.6 (CH), 130.3 (CH), 138.9 (C), 139.3 (CH), 141.2 (C), 208.0 (CO). IR (film) 1713 cm⁻¹. Anal. Calcd for C₁₈H₂₀INO (393.3): C, 54.97; H, 5.13; N, 3.56. Found: C, 54.97; H, 5.06; N, 3.54.

4-[*N*-Benzyl-*N*-(2-bromobenzyl)amino]-2-butanone (**39b**)

Operating as in the preparation of **39a**, starting from *N*-benzyl-*N*-(2-bromobenzyl)amine, amine **39b** (50%) was obtained after chromatography (CH₂Cl₂).

¹H NMR (CDCl₃, 300 MHz) δ 2.00 (s, 3H), 2.61 (t, *J* = 7.2 Hz, 2H), 2.81 (t, *J* = 7.2 Hz, 2H), 3.60 (s, 2H), 3.67 (s, 2H), 7.08 (ddd, *J* = 7.8, 7.5, and 1.8 Hz, 1H), 7.19-7.36 (m, 6H), 7.48-7.56 (m, 2H). ¹³C NMR (CDCl₃, 75.5 MHz) δ 29.8 (CH₃), 41.6 (CH₂), 48.6 (CH₂), 57.6 (CH₂), 58.5 (CH₂), 124.2 (C), 127.0 (CH), 127.2 (CH), 128.2 and 128.7 (*o*-C and *m*-C), 128.3 (CH), 130.6 (CH), 132.5 (CH), 138.3 (C), 138.9 (C), 208.0 (CO). IR (film) 1713 cm⁻¹.

2-[[*N*-Benzyl-*N*-(2-iodobenzyl)amino]methyl]cyclohexanone (**42**)

To a solution of *N*-benzyl-*N*-(2-iodobenzyl)amine (1 g, 3.1 mmol) in MeOH (4 mL)) was added dropwise 10% HCl/Et₂O (5 mL). The solvent was removed *in vacuo*, the residue was dissolved in AcOH (5 mL), and paraformaldehyde (96 mg, 3.2 mmol) and cyclohexanone (0.65 mL, 6.22 mmol) were added. The resulting solution was stirred at 60 °C for 2.5 h, the solvent removed *in vacuo*, and the residue dissolved in hot acetone (10 mL).¹⁰ A white solid was separated from the cold solution. This solid was dissolved in dichloromethane and the solution was washed with saturated aqueous NaHCO₃. The organic layer was dried and concentrated to give amine **42** (1.34 g, quantitative).

¹H NMR (CDCl₃, 300 MHz) δ 1.24 (dtd, *J* = 10.2, 9.9, and 3.3 Hz, 1H), 1.42-1.74 (m, 3H), 1.89 (dm, *J* = 9 Hz, 1H), 2.15-2.22 (m, 2H), 2.28 (dm, *J* = 13.5 Hz, 1H), 2.40-2.58 (m, 2H), 2.89 (dd, *J* = 12 and 4.5 Hz, 1H), 3.46 (d, *J* = 13.5 Hz, 1H), 3.53 (d, *J* = 14.4 Hz, 1H), 3.65 (d, *J* = 14.4 Hz, 1H), 3.67 (d, *J* = 13.5 Hz, 1H), 6.92 (td, *J* = 7.8 and 1.8 Hz, 1H), 7.18-7.36 (m, 6H), 7.52 (dd, *J* = 7.5 and 1.8 Hz, 1H), 7.80 (dd, *J* = 7.8 and 1.2 Hz, 1H). ¹³C NMR (CDCl₃, 75.5 MHz) δ 24.1 (CH₂), 27.8 (CH₂), 32.2 (CH₂), 41.7 (CH₂), 48.8 (CH), 53.7 (CH₂), 59.1 (CH₂), 63.3 (CH₂), 100.2 (C), 126.9 (CH), 128.0 (CH), 128.1 and 128.9 (*o*-C and *m*-C), 128.5 (CH), 130.4 (CH), 139.1 (C), 139.2 (CH), 141.4 (C), 212.8 (CO). IR

¹⁰ Blicke, F. F.; McCarty, F. J. *J. Org. Chem.* **1959**, *24*, 1069-1076.

(film) 1708 cm⁻¹. Anal. Calcd for C₂₁H₂₄INO (433.3): C, 58.21; H, 5.58; N, 3.23. Found: C, 58.11; H, 5.59; N, 3.27.

1-[*N*-Benzyl-*N*-(2-iodobenzyl)amino]-2-propanone (**43a**)

To a solution of *N*-benzyl-*N*-(2-iodobenzyl)amine (1.5 g, 4.6 mmol) in acetonitrile (25 mL) were added chloroacetone (0.5 mL, 5.9 mmol) and K₂CO₃ (1.3 g, 9.4 mmol). After 72 h at reflux, the solvent was evaporated *in vacuo* and the residue was partitioned between dichloromethane and saturated aqueous NaHCO₃. The organic layer was dried and concentrated. Chromatography (hexane to 7:3 hexane-EtOAc) afforded ketone **43a** (0.59 g, 33%).

¹H NMR (CDCl₃, 300 MHz) δ 2.02 (s, 3H), 3.25 (s, 2H), 3.76 (s, 2H), 3.78 (s, 2H), 6.95 (ddd, *J* = 7.8, 7.5, and 1.5 Hz, 1H), 7.22-7.42 (m, 6H), 7.53 (dd, *J* = 7.8 and 1.5 Hz, 1H), 7.82 (dd, *J* = 7.8 and 1.5 Hz, 1H). ¹³C NMR (CDCl₃, 75.5 MHz) δ 27.7 (CH₃), 58.6 (CH₂), 62.9 (CH₂), 63.0 (CH₂), 100.5 (C), 127.2 (CH), 128.1 (CH), 128.3 and 129.0 (*o*-C and *m*-C), 128.9 (CH), 130.4 (CH), 138.3 (C), 139.4 (CH), 140.8 (C), 208.6 (CO). IR (film) 1713 cm⁻¹. Anal. Calcd for C₁₇H₁₈INO(379.2)·1/2H₂O: C, 52.59; H, 4.93; N, 3.61. Found: C, 52.56; H, 4.65; N, 3.79.

1-[*N*-Benzyl-*N*-(2-bromobenzyl)amino]-2-propanone (**43b**)

Operating as in the preparation of **43a**, starting from *N*-benzyl-*N*-(2-bromobenzyl)amine, amine **43b** (39%) was obtained after chromatography (hexane to 95:5 hexane-EtOAc).

¹H NMR (CDCl₃, 200 MHz) δ 2.05 (s, 3H), 3.25 (s, 2H), 3.75 (s, 2H), 3.82 (s, 2H), 7.02-7.63 (m, 9H). ¹³C NMR (CDCl₃, 75.5 MHz) δ 27.6 (CH₃), 58.3 (CH₂), 58.8 (CH₂), 63.2 (CH₂), 124.6 (C), 127.2 (CH), 127.3 (CH), 128.3 and 128.9 (*o*-C and *m*-C), 128.6 (CH), 130.8 (CH), 132.8 (CH), 137.9 (C), 138.4 (C), 208.4 (CO). IR (film) 1714 cm⁻¹.

trans-2-[*N*-Benzyl-*N*-(2-iodobenzyl)amino]cyclohexanol (**67**)

To a cooled (0 °C) solution of *N*-benzyl-*N*-(2-iodobenzyl)amine (0.36 g, 1.1 mmol) in dichloromethane (10 mL) was added AlEt₃ (0.9 mL, 1.7 mmol) in the dark. After 30 min at 0 °C, the mixture was allowed to reach room temperature, and cyclohexene oxide (0.17 mL, 1.7 mmol) was added. The mixture was stirred at room temperature for 24 h. After cooling to 0 °C, were added NaF (190 mg, 4.5 mmol) and water (0.13 mL, 7.2 mmol), and the mixture was stirred for 1 h. The reaction mixture was filtered through Celite, washing carefully with dichloromethane, and then the organic solution was washed with brine. The organic layer was dried and concentrated, and the resulting residue was purified by chromatography (hexane to 1:1 hexane-EtOAc) to yield alcohol **67** (0.46 g, quantitative).

¹H NMR (CDCl₃, 300 MHz) δ 1.02-1.37 (m, 4H), 1.58-2.15 (m, 4H), 2.29 (ddd, *J* = 11.4, 9.9, and 3.3 Hz, 1H), 3.39 (d, *J* = 13.2 Hz, 1H), 3.51 (td, *J* = 9.9 and 4.2 Hz, 1H), 3.66 (d, *J* = 13.5 Hz, 1H), 3.66 (bb, 1H, OH), 3.77 (d, *J* = 13.5 Hz, 1H), 3.87 (d, *J* = 13.2 Hz, 1H), 6.90 (dt, *J* = 8.1 and 4.5 Hz, 1H), 7.22-7.33 (m, 7H), 7.77 (d, *J* = 7.8 Hz, 1H). ¹³C NMR (CDCl₃, 75.5 MHz) δ 22.5 (CH₂), 24.1 (CH₂), 25.4

(CH₂), 33.2 (CH₂), 53.6 (CH₂), 57.8 (CH₂), 64.2 (CH), 69.0 (CH), 100.7 (C), 127.1 (CH), 128.2 (CH), 128.3 and 129.1 (*o*-C and *m*-C), 128.9 (CH), 130.6 (CH), 139.0 (C), 139.4 (CH), 141.1 (C). IR (film) 2931 cm⁻¹. HRMS Calcd for C₂₀H₂₄INO: 421.0903. Found: 421.0917.

2-[*N*-Benzyl-*N*-(2-iodobenzyl)amino]cyclohexanone (**45**)

To a cooled (-78 °C) solution of oxalyl chloride (0.25 mL, 2.9 mmol) in dichloromethane (10 mL) was added DMSO (0.35 mL, 4.9 mmol). After 30 min at -78 °C, a solution of alcohol **67** (0.5 g, 1.2 mmol) in dichloromethane (11 mL) was added. The mixture was stirred at -78 °C for 1 h and then Et₃N (1.2 mL, 8.6 mmol) was added. The solution was stirred at -78 °C for 15 min and then allowed to reach room temperature. The reaction mixture was partitioned between dichloromethane and saturated aqueous NaHCO₃. The organic layer was washed with brine, dried, and concentrated. Chromatography (hexane to 1:1 hexane-EtOAc) afforded ketone **45** (273 mg, 55%).

¹H NMR (CDCl₃, 300 MHz) δ 1.53-2.05 (m, 5H), 2.13-2.32 (m, 2H), 2.41 (ddt, *J* = 14.1, 3.9, and 2.1 Hz, 1H), 3.33 (ddd, *J* = 12.5, 5.5, and 1 Hz, 1H), 3.77 (d, *J* = 14.4 Hz, 1H), 3.78 (d, *J* = 13.5 Hz, 1H), 4.03 (d, *J* = 14.4 Hz, 1H), 4.04 (d, *J* = 13.5 Hz, 1H), 6.89 (td, *J* = 7.5 and 1.5 Hz, 1H), 7.16-7.40 (m, 6H), 7.61 (dd, *J* = 7.5 and 1.5 Hz, 1H), 7.75 (dd, *J* = 7.8 and 1.5 Hz, 1H). ¹³C NMR (CDCl₃, 75.5 MHz) δ 25.1 (CH₂), 27.1 (CH₂), 31.5 (CH₂), 42.4 (CH₂), 55.2 (CH₂), 59.7 (CH₂), 67.2 (CH), 99.8 (C), 126.7 (CH), 128.0 (CH), 128.1 and 128.4 (*o*-C and *m*-C), 128.3 (CH), 129.9 (CH), 138.9 (CH), 140.2 (C), 142.2 (C), 211.4 (CO). IR (film) 1712 cm⁻¹.

5-(2-Iodophenyl)-2-pentanone (**50**)

To a suspension of NaH (55%, 176 mg, 4 mmol), previously washed with hexane, in EtOH (15 mL) was slowly added a solution of ethyl acetoacetate (0.52 g, 4 mmol) in EtOH (1 mL). After heating at reflux for 1 h, a solution of 2-(2-iodophenyl)ethyl iodide¹¹ (1.5 g, 4.19 mmol) in EtOH (5 mL) was added and maintained at reflux for 24 h. The reaction mixture was diluted with Et₂O and washed with water. The organic layer was dried and concentrated to give ethyl 2-acetyl-4-(2-iodophenyl)butyrate (1.45 g, quantitative). A solution of crude 2-acetyl-4-(2-iodophenyl)butyrate (1.45 g, 4 mmol) in 5% aqueous NaOH was heated at 90 °C for 5 h. A 50% aqueous H₂SO₄ solution (8 mL) was added and the mixture was stirred at 90 °C for 3 h and at room temperature for 24 h.¹² The reaction mixture was extracted with Et₂O, and the organic extracts were dried and concentrated. Chromatography (hexane to 9:1 hexane-EtOAc) afforded ketone **50** (0.44 g, 38%).

¹¹ Ripa, L.; Hallberg, A. *J. Org. Chem.* **1996**, *61*, 7147-7155.

¹² Montgomery, F. C.; Saunders Jr., W. H. *J. Org. Chem.* **1976**, *41*, 2368-2372.

^1H NMR (CDCl_3 , 200 MHz) δ 1.88 (ddt, J = 7.8, 7.6, and 7.2 Hz, 2H), 2.15 (s, 3H), 2.50 (t, J = 7.2 Hz, 2H), 2.72 (dd, J = 7.8 and 7.6 Hz, 2H), 6.88 (ddd, J = 8, 7.5, and 2 Hz, 1H), 7.20 (dd, J = 7.5 and 2 Hz, 1H), 7.27 (td, J = 7.5 and 1.2 Hz, 1H), 7.80 (dd, J = 8 and 1.2 Hz, 1H). ^{13}C NMR (CDCl_3 , 50 MHz) δ 24.1 (CH_2), 30.0 (CH_3), 39.8 (CH_2), 42.8 (CH_2), 100.5 (C), 127.8 (CH), 128.2 (CH), 129.3 (CH), 139.4 (CH), 144.0 (C), 208.4 (C). IR (film) 1714 cm^{-1} . Anal. Calcd for $\text{C}_{11}\text{H}_{13}\text{IO}$ (288.1): C, 45.85; H, 4.55. Found: C, 45.87; H, 4.54.

4-(2-Iodophenyl)-2-butanone (**51**)

A mixture of 2-iodobenzyl chloride (1 g, 3.96 mmol), acetylacetone (0.45 mL, 4.36 mmol), and K_2CO_3 (0.55 g, 4 mmol) in EtOH (10 mL) was heated at reflux for 24 h.¹³ The solvent was removed *in vacuo* and the residue was partitioned between Et_2O and water. The organic layer was dried and concentrated. Chromatography (hexane to 8:2 hexane-EtOAc) yielded ketone **51** (712 mg, 65%).

^1H NMR (CDCl_3 , 200 MHz) δ 2.13 (s, 3H), 2.70 (t, J = 8.2 Hz, 2H), 2.95 (t, J = 8.2 Hz, 2H), 6.85 (ddd, J = 8, 6.2, and 3 Hz, 1H), 7.17-7.30 (m, 2H), 7.75 (dd, J = 8 and 1.2 Hz, 1H). ^{13}C NMR (CDCl_3 , 50 MHz) δ 29.7 (CH_3), 34.4 (CH_2), 43.3 (CH_2), 100.0 (C), 127.7 (CH), 128.1 (CH), 129.2 (CH), 139.0 (CH), 143.1 (C), 206.6 (C). IR (film) 1716 cm^{-1} . Anal. Calcd for $\text{C}_{10}\text{H}_{11}\text{IO}$ (274.1): C, 43.82; H, 4.05. Found: C, 43.81; H, 4.19.

Methyl 1-(2-iodobenzyl)-2-oxocyclohexanecarboxylate (**68**)

To a suspension of NaH (55%, 0.44 g, 10.1 mmol), previously washed with hexane, in THF (50 mL), cooled at $0\text{ }^\circ\text{C}$, was slowly added a solution of methyl 2-oxocyclohexanecarboxylate (1.52 g, 9.73 mmol). The mixture was stirred at room temperature for 30 min and then were added a solution of 2-iodobenzyl chloride (2.94 g, 11.7 mmol) in THF (15 mL) and a catalytic amount of LiI. After 84 h at reflux, the mixture was poured into water and extracted with EtOAc. The organic extracts were

¹³ Boatman, S.; Harris, T. M.; Hauser, C. R. *J. Org. Chem.* **1965**, *30*, 3321-3324.

washed with brine, dried, and concentrated. Chromatography (hexane to 8:2 hexane-EtOAc) yielded β -ketoester **68** (1.87 g, 52%).

^1H NMR (CDCl_3 , 200 MHz) δ 1.55-1.80 (m, 4H), 2.01 (m, 1H), 2.34-2.60 (m, 3H), 3.28 (d, J = 14.5 Hz, 1H), 3.48 (d, J = 14.5 Hz, 1H), 3.70 (s, 3H), 6.88 (td, J = 7.6 and 1.8 Hz, 1H), 7.10 (dd, J = 7.6 and 1.8 Hz, 1H), 7.23 (td, J = 7.6 and 1.2 Hz, 1H), 7.82 (dd, J = 7.6 and 1.2 Hz, 1H). ^{13}C NMR (CDCl_3 , 50 MHz) δ 22.5 (CH_2), 27.4 (CH_2), 35.5 (CH_2), 41.1 (CH_2), 43.0 (CH_2), 52.3 (CH_3), 62.1 (C), 102.6 (C), 127.8 (CH), 128.3 (CH), 130.7 (CH), 139.7 (CH), 139.9 (C), 171.1 (C), 206.6 (C). IR (film) 1713 cm^{-1} . Anal. Calcd for $\text{C}_{15}\text{H}_{17}\text{IO}_3$ (372.2): C, 48.41; H, 4.60. Found: C, 48.02; H, 4.81.

2-(2-Iodobenzyl)cyclohexanone (**53**)

A solution of β -ketoester **68** (1.38 g, 3.7 mmol) and LiI (0.32 g, 7.5 mmol) in dry DMF (15 mL) was heated at 150 $^\circ\text{C}$ for 7 h. The mixture was cooled to room temperature, poured into 5% aqueous NaHCO_3 , and extracted with Et_2O . The organic extracts were washed with brine, dried, and concentrated. Chromatography (hexane to 8:2 hexane-EtOAc) yielded ketone **53** (0.76 g, 65%).

^1H NMR (CDCl_3 , 300 MHz) δ 1.44 (qd, J = 12.3 and 3.3 Hz, 1H), 1.60 (qt, J = 12.3 and 3.3 Hz, 1H), 1.68 (qm, J = 12.3 Hz, 1H), 1.84 (dm, J = 12.3 Hz, 1H), 1.99-2.14 (m, 2H), 2.34 (ddd, J = 13.5, 12.3, and 1.2 Hz, 1H), 2.43 (dm, J = 13.5 Hz, 1H), 2.52 (dd, J = 13.8 and 7.8 Hz, 1H), 2.67 (m, 1H), 3.34 (dd, J = 13.8 and 5.4 Hz, 1H), 6.87 (dm, J = 7.8 Hz, 1H), 7.20-7.28 (m, 2H), 7.79 (d, J = 7.8 Hz, 1H). ^{13}C NMR (CDCl_3 , 75.5 MHz) δ 25.3 (CH_2), 28.1 (CH_2), 33.7 (CH_2), 39.9 (CH_2), 42.2 (CH_2), 50.8 (CH), 100.8 (C), 127.8 (CH), 127.9 (CH), 130.9 (CH), 139.3 (CH), 142.9 (C), 211.7 (C). IR (film) 1709 cm^{-1} . Anal. Calcd for $\text{C}_{13}\text{H}_{15}\text{IO}$ (314.2): C, 49.70; H, 4.81. Found: C, 49.64; H, 4.82.