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Supporting Information for

Synthesis of 2*H*-1-Benzopyrans via Palladacycles with a Metal-Bonded Stereogenic Carbon

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General Methods. Unless otherwise indicated, all NMR data were collected at room temperature in CDCl₃ with internal CHCl₃ as the reference (δ 7.26 ppm for ¹H and 77.00 ppm for ¹³C) and internal (present in a sealed capillary inserted into the NMR tube) H₃PO₄ (δ 0 ppm) as the reference for ³¹P NMR. IR spectra were measured in KBr pellets, or as thin films on salt (NaCl) plates. Melting points are uncorrected and were taken in open capillary tubes. MS were measured under fast atom bombardment (FAB) or electron impact (EI) conditions. Elemental Analyses were performed by Galbraith Laboratories, Knoxville, TN. Analytical thin-layer chromatography (TLC) was carried out on commercial Merck silica gel 60 plates, 0.25 μ m thickness, with fluorescent indicator (F-254) or stained with aqueous KMnO₄ solution. Column chromatography was performed with 40-63 μ m silica gel (Merck) or basic alumina (150 mesh, Brokmann I). Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone. Methylene chloride, 1,2-dichloroethane and DMF were kept over 3Å (8-12 mesh) molecular sieves. Benzene was distilled from CaH₂ and kept over 3Å (8-12 mesh) molecular sieves under an atmosphere of dry argon; other solvents were used as received. Unless otherwise specified, all reactions were carried out under an atmosphere of dry nitrogen or argon in oven-dried (at least 6h at 140 °C) glassware. Single crystals for X-ray analysis were obtained by slow diffusion of hexanes into methylene chloride solutions of the palladium complexes.

General Procedure for the Synthesis of Aryl Iodides 1a,b and 1d,e. To a suspension of *ortho*-iodophenol (1 mmol) and K₂CO₃ (5–9 mmol) in acetone (10 mL) at rt under argon was added the appropriate alkylating agent (2-5 mmol) and the suspension was heated to reflux for the indicated time. Unless stated otherwise, the reaction mixture was filtered and solvents were removed under reduced pressure to give the crude product. The crude product was then separated by flash

chromatography over silica eluting with indicated solvent mixtures to afford the aryl iodides **1a**, **b**, **d**, **e** as clear oils or low melting solids.

(2-Iodophenoxy)acetonitrile (1a). *Ortho*-iodophenol (2.50 g, 11.36 mmol), K_2CO_3 (7.85 g, 56.8 mmol) and bromoacetonitrile (2.3 mL, 3.9 g, 33.0 mmol) were treated for 18 h according to the general procedure described above. Eluting the column with EtOAc/hexane (1 : 9) afforded aryl iodide **1a** (2.85 g, 97%) as a white crystalline solid: mp = 66–67 °C (hexane); R_f = 0.46 (EtOAc/hexane 1 : 5); 1H NMR (400 MHz) δ 7.83 (dd, J = 7.8 Hz, 1.4 Hz, 1 H), 7.37 (td, J = 7.8 Hz, 1.4 Hz, 1 H), 6.99 (d, J = 8.2 Hz, 1 H), 6.86 (t, J = 8.1 Hz, 1 H), 4.82 (s, 2 H); ^{13}C NMR (100 MHz) δ 155.4, 140.2, 129.8, 125.2, 114.6, 113.6, 86.7, 54.7; IR (KBr, cm^{-1}): 2974 (w), 2945 (w), 1613 (w), 1572 (m), 1470 (s), 1442 (s); MS (EI) m/z (relative intensity) 259 (M^+ , 75), 219 (60), 191 (28), 132 (25), 92 (100); HRMS (FAB) calcd for C_8H_6INO (M^+) 258.9494, found 258.9488; Anal. Calcd for C_8H_6INO : C, 37.09; H, 2.33; N, 5.41. Found: C, 35.57; H, 2.42; N, 5.19.

Ethyl (2-iodophenoxy)acetate (1b).¹ *Ortho*-iodophenol (4.00 g, 18.19 mmol), K_2CO_3 (12.55 g, 90.8 mmol) and ethyl bromoacetate (4.0 mL, 6.0 g, 36.07 mmol) were treated for 18 h according to the general procedure described above. Eluting the column with ether/hexane (1 : 20) afforded aryl iodide **1b** (5.43 g, 98%) as a clear oil: R_f = 0.20 (EtOAc/hexane 1 : 20); 1H NMR (400 MHz) δ 7.79 (dd, J = 7.7 Hz, 1.5 Hz, 1 H), 7.29–7.24 (m, 1 H), 6.75 (td, J = 7.6 Hz, 1.2 Hz, 1 H), 6.71 (dd, J = 6.5 Hz, 1.2 Hz, 1 H), 4.67 (s, 2 H), 4.26 (q, J = 7.13 Hz, 2 H), 1.28 (t, J = 7.1 Hz, 3 H); ^{13}C NMR (100 MHz) δ 168.2, 156.5, 139.7, 129.3, 123.4, 112.2, 86.3, 66.2, 61.3, 14.0; IR (neat, cm^{-1}): 1764(s).

1-(Benzyloxy)-2-iodobenzene (1d).² *Ortho*-iodophenol (0.504 g, 2.29 mmol), K_2CO_3 (3.01 g, 21.00 mmol) and benzyl bromide (1.30 mL, 1.87 g, 10.90 mmol) were treated for 9 h according to the general procedure described above. Eluting the column with hexane afforded the aryl iodide **1d** (0.633 g, 89%) as a clear oil: R_f = 0.61 (EtOAc/hexane 1 : 20); 1H NMR (500 MHz) δ 7.81 (dd, J = 7.8 Hz, 1.5 Hz, 1 H), 7.51 (d, J = 7.6 Hz, 2 H), 7.40 (t, J = 7.6 Hz, 2 H), 7.33 (t, J = 7.3 Hz, 1 H), 7.28 (t, J = 8.2 Hz, 1 H), 6.87 (d, J = 8.2 Hz, 1 H), 6.73 (td, J = 7.6 Hz, 1.1 Hz, 1 H), 5.16 (s, 2 H);

^{13}C NMR (125 MHz) δ 157.2, 139.5, 136.5, 129.4, 128.5 (two carbons), 127.8, 126.9 (two carbons), 122.8, 112.7, 86.8, 70.8; IR (neat, cm^{-1}): 1582(s), 1497 (s), 745 (m), 695 (m), 655 (w).

1-Iodo-2-(2-methoxyethoxy)benzene (1e).² *Ortho*-iodophenol (0.755 g, 3.42 mmol), K_2CO_3 (2.58 g, 18.70 mmol) and 2-bromoethyl methyl ether (1.0 mL, 1.47 g, 10.60 mmol) were treated for 8 h according to the general procedure described above. Extraction of the crude reaction mixture between ethyl acetate and 5% aqueous NaOH, and flash chromatography over silica, eluting the column with ether/hexane (1 : 20) afforded the aryl iodide **1e** (0.786 g, 82%) as a clear oil that solidified in refrigerator: mp = 25–26 °C (EtOAc/hexane, 1 : 20); R_f = 0.55 (EtOAc/hexane 1 : 3); ^1H NMR (500 MHz) δ 7.77 (dd, J = 7.8 Hz, 1.4 Hz, 1 H), 7.28 (td, J = 7.8 Hz, 1.2 Hz, 1 H), 6.84 (d, J = 8.2 Hz, 1 H), 6.71 (t, J = 7.6 Hz, 1 H), 4.16 (t, J = 4.9 Hz, 2 H), 3.82 (t, J = 4.9 Hz, 2 H), 3.50 (s, 3 H); ^{13}C NMR (125 MHz) δ 157.5, 139.5, 129.4, 122.8, 112.6, 86.8, 70.8, 69.0, 59.6; IR (neat, cm^{-1}): 1581 (w), 1468 (s), 1277 (s), 748 (m), 651 (w).

(2-Iodophenoxy)-*N,N*-diethylacetamide (1c). To a suspension of NaH (60% dispersion in mineral oil, 0.422 g, 10.55 mmol) in DMF (8.0 mL) and THF (28 mL) at rt under argon was added a solution of the *ortho*-iodophenol (2.08 g, 9.45 mmol) in THF (10 mL) followed by neat *N,N*-diethylchloroacetamide (1.0 mL, 1.09 g, 7.27 mmol). The resulting suspension was stirred for 16 h at rt. The reaction mixture was concentrated under reduced pressure and separated by extraction between ether and 5% aqueous NaOH. Organic layers were combined, and dried (MgSO_4) to afford a crude product. The crude product was purified by flash chromatography over silica eluting with EtOAc/hexane (1 : 2) to yield aryl iodide **1c** (2.24 g, 92%) as a pale yellow oil that solidified on standing at rt: mp = 52–53 °C (EtOAc/hexane, 1 : 2); R_f = 0.20 (EtOAc/hexane 1 : 2); ^1H NMR (400 MHz) δ 7.77 (dd, J = 7.8 Hz, 1.5 Hz, 1 H), 7.28 (d, J = 8.0 Hz, 1 H), 6.92 (dd, J = 8.3 Hz, 1.0 Hz, 1 H), 6.73 (td, J = 7.5 Hz, 1.1 Hz, 1 H), 4.74 (s, 2 H), 3.47 (q, J = 7.1 Hz, 2 H), 3.39 (q, J = 7.1 Hz, 2 H), 1.20 (t, J = 7.1 Hz, 3 H), 1.12 (t, J = 7.1 Hz, 3 H); ^{13}C NMR (100 MHz) δ 166.5, 156.7, 139.6, 129.6, 123.2, 112.5, 85.9, 68.9, 41.6, 40.1, 14.4, 12.7; IR (KBr, cm^{-1}): 1658(s); MS (EI) m/z (relative intensity) 333 (M^+ , 25), 233 (10), 206 (100); HRMS (FAB) calcd for $\text{C}_{12}\text{H}_{17}\text{INO}_2$ ($\text{M}+\text{H}^+$) 334.0304, found 334.0301.

General Procedure for the Synthesis of the Palladium(II)-TMEDA Complexes 2. To a solution of tris(dibenzylideneacetone)dipalladium(0) (Pd_2dba_3) (0.5 mmol) in benzene (20-60 mL per 1 mmol) at rt under argon was added tetramethylethylenediamine (TMEDA) (1.2-2.1 mmol) followed by a solution of the aryl iodide **1** (1.1-1.2 mmol) in benzene (2 mL per 1 mmol). The reaction mixture was stirred at 55 °C (oil bath) for 30 minutes. The suspension was filtered through a plug of Celite, and solvents were removed under reduced pressure. The crude product was deposited on Celite and the material was placed on a top of a short plug of silica. Elution with EtOAc/Hexane (1 : 5) removed excess dibenzylideneacetone (dba), and subsequent elution with EtOAc/Hexane (1 : 1) and/or EtOAc afforded palladium(II) complexes **2** as yellow solids. In certain cases, trituration of the crude product with ether was required to afford pure complexes **3** as yellow solids.

[2-(Cyanomethoxy)phenyl]iodo(tetramethylethylenediamine)palladium (2a). Pd_2dba_3 (2.00 g, 2.18 mmol), TMEDA (0.98 mL, 0.755 g, 6.49 mmol) and iodoaryl **1a** (1.24 g, 4.80 mmol) were treated according to the general procedure described above. Elution with EtOAc/Hexane (1 : 1) afforded the palladium complex **2a** (1.52 g, 72%) as a yellow solid: mp = 174–175 °C decomp. (ether); R_f = 0.40 (EtOAc/hexane 2 : 1); ^1H NMR (400 MHz) δ 7.32 (dd, J = 7.3 Hz, 1.7 Hz, 1 H), 6.86 (td, J = 7.5 Hz, 1.7 Hz, 1 H), 6.80 (td, J = 7.3 Hz, 1.6 Hz, 1 H), 6.70 (dd, J = 7.7 Hz, 1.6 Hz, 1 H), 5.25 (d, J = 15.8 Hz, 1 H), 4.78 (d, J = 15.9 Hz, 1 H), 2.82-2.80 (m, 1 H), 2.77 (s, 3 H), 2.74 (s, 3 H), 2.71-2.66 (m, 1 H), 2.65-2.61 (m, 2 H), 2.41 (s, 3 H), 2.36 (s, 3 H); ^{13}C NMR (125 MHz) δ 159.8, 138.7, 131.8, 124.2, 123.3, 117.3, 116.9, 62.2, 58.6, 56.2, 50.5, 50.2, 50.1, 49.8; IR (KBr, cm^{-1}): 1458 (s), 1177 (s), 802(s); Anal. Calcd for $\text{C}_{14}\text{H}_{22}\text{IN}_3\text{OPd}$: C, 34.91; H, 4.60; N, 8.72. Found: C, 34.96; H, 4.68; N, 8.69.

[2-(Ethoxycarbonylmethoxy)phenyl]iodo(tetramethylethylenediamine)palladium (2b). Pd_2dba_3 (1.05 g, 1.15 mmol), TMEDA (0.70 mL, 0.539 g, 4.63 mmol) and iodoaryl **1b** (0.881 g, 2.87 mmol) were treated according to the general procedure described above. Elution with EtOAc/Hexane (1 : 1), and trituration of the crude product with ether afforded the palladium complex **2b** (0.952 g, 78%) as a yellow solid: mp = 152–153 °C (ether); R_f = 0.23 (EtOAc/hexane

2 : 1); ^1H NMR (400 MHz) δ 7.25 (dd, $J = 7.5$ Hz, 1.6 Hz, 1 H), 6.81 (td, $J = 7.8$ Hz, 1.6 Hz, 1 H), 6.72 (td, $J = 7.3$ Hz, 1.3 Hz, 1 H), 6.49 (dd, $J = 7.8$ Hz, 1.2 Hz, 1 H), 5.05 (d, $J = 16.1$ Hz, 1 H), 4.57 (d, $J = 16.1$ Hz, 1 H), 4.28-4.21 (m, 2 H), 2.89-2.81 (m, 1 H), 2.73 (s, 3 H), 2.71 (s, 3 H), 2.68-2.64 (m, 1 H), 2.60-2.58 (m, 2 H), 2.47 (s, 3 H), 2.41 (s, 3 H), 1.30 (t, $J = 7.1$ Hz, 3 H); ^{13}C NMR (125 MHz) δ 170.6, 160.4, 138.3, 131.2, 123.8, 121.8, 114.3, 67.2, 62.1, 60.6, 58.6, 50.5, 50.2, 49.9, 49.3, 14.3; IR (KBr, cm^{-1}): 1728 (s); Anal. Calcd for $\text{C}_{16}\text{H}_{27}\text{IN}_2\text{O}_3\text{Pd}$: C, 36.35; H, 5.15; N, 5.30. Found: C, 36.32; H, 5.23; N, 5.25.

[2-(*N,N*-Diethylcarbonylmethoxy)phenyl] iodo(tetramethylethylenediamine) palladium (2c). Pd_2dba_3 (0.826 g, 0.901 mmol), TMEDA (0.36 mL, 0.277 g, 2.38 mmol) and iodoaryl **1c** (0.400 g, 1.20 mmol) were treated according to the general procedure described above. Elution with EtOAc afforded the palladium complex **2c** (0.496 g, 74%) as a yellow solid: mp = 157–158 °C (ether); $R_f = 0.26$ (EtOAc); ^1H NMR (500 MHz) δ 7.27 (dd, $J = 7.8$ Hz, 1.5 Hz, 1 H), 6.82 (td, $J = 7.7$ Hz, 1.5 Hz, 1 H), 6.73 (td, $J = 7.3$ Hz, 1.3 Hz, 1 H), 6.59 (dd, $J = 7.8$ Hz, 1.3 Hz, 1 H), 5.37 (d, $J = 13.2$ Hz, 1 H), 4.54 (d, $J = 13.2$ Hz, 1 H), 3.52-3.38 (m, 3 H), 3.35-3.27 (m, 1 H), 2.88-2.81 (m, 1 H), 2.70 (s, 3 H), 2.67 (s, 3 H), 2.61-2.51 (m, 3 H), 2.48 (s, 3 H), 2.39 (s, 3 H), 1.23 (t, $J = 7.1$ Hz, 3 H), 1.17 (t, $J = 7.1$ Hz, 3 H); ^{13}C NMR (125 MHz) δ 168.6, 160.7, 138.4, 131.5, 123.9, 121.9, 115.8, 69.2, 62.1, 58.5, 50.6, 50.3, 49.8, 49.1, 41.5, 40.0, 14.5, 13.0; IR (KBr, cm^{-1}): 1656 (s), 1640(s); Anal. Calcd for $\text{C}_{18}\text{H}_{32}\text{IN}_3\text{O}_2\text{Pd}$: C, 38.90; H, 5.80; N, 7.56. Found: C, 38.83; H, 5.92; N, 7.48.

Iodo[2-(phenylmethoxy)phenyl](tetramethylethylenediamine)palladium (2d). Pd_2dba_3 (0.305 g, 0.333 mmol), TMEDA (0.203 mL, 0.156 g, 1.35 mmol) and iodoaryl **1d** (0.250 g, 0.805 mmol) were treated according to the general procedure described above. Elution with EtOAc/Hexane (1 : 1) and EtOAc, and subsequent trituration of the crude product with ether afforded the palladium complex **2d** (0.222 g, 63%) as an orange solid: mp = 194–195 °C decomp. (ether); $R_f = 0.73$ (EtOAc); ^1H NMR (400 MHz) δ 7.78 (d, $J = 7.3$ Hz, 2 H), 7.37 (t, $J = 7.4$ Hz, 2 H), 7.29 (t, $J = 7.3$ Hz, 1 H), 7.20 (dd, $J = 7.4$ Hz, 1.5 Hz, 1 H), 6.85 (td, $J = 7.6$ Hz, 1.5 Hz, 1 H), 6.71 (td, $J = 7.3$ Hz, 1.2 Hz, 1 H), 6.58 (dd, $J = 7.9$ Hz, 1.1 Hz, 1 H), 5.30 (d, $J = 11.6$ Hz, 1 H),

4.98 (d, $J = 11.6$ Hz, 1 H), 2.72 (s, 3 H), 2.68 (s, 3 H), 2.64-2.52 (m, 3 H), 2.49-2.46 (m, 1 H), 2.44 (s, 3 H), 2.25 (s, 3 H); ^{13}C NMR (125 MHz) δ 161.0, 139.0, 137.6, 130.8, 128.1 (two carbons), 127.5 (two carbons), 127.1, 123.8, 120.9, 112.6, 70.6, 62.0, 58.5, 50.3 (two carbons), 49.6, 49.1; IR (KBr, cm^{-1}): 1557 (w), 1451 (m), 1219(s), 802 (m), 755 (m); HRMS (FAB) calcd for $\text{C}_{19}\text{H}_{31}\text{IN}_3\text{OPd}$ ($\text{M}+\text{NH}_4^+$) 550.0547, found 550.0561.

Iodo[2-(2-methoxyethoxy)phenyl](tetramethylethylenediamine)palladium (2e). Pd_2dba_3 (0.340 g, 0.371 mmol), TMEDA (0.226 mL, 0.174 g, 1.50 mmol) and iodoaryl **1e** (0.249 g, 0.895 mmol) were treated according to the general procedure described above. Elution with EtOAc/Hexane (1 : 1) and EtOAc, and subsequent trituration of the crude product with ether, afforded the palladium complex **2d** (0.262 g, 70%) as an orange solid: mp = 149–150 °C decomp. (ether); $R_f = 0.50$ (EtOAc); ^1H NMR (400 MHz) δ 7.18 (dd, $J = 7.4$ Hz, 1.5 Hz, 1 H), 6.82 (td, $J = 7.5$ Hz, 1.5 Hz, 1 H), 6.68 (td, $J = 7.3$ Hz, 1.3 Hz, 1 H), 6.51 (dd, $J = 7.9$ Hz, 1.2 Hz, 1 H), 4.41-4.36 (m, 1 H), 4.15-4.10 (m, 1 H), 3.98-3.92 (m, 1 H), 3.79-3.74 (m, 1 H), 3.51 (s, 3 H), 2.84-2.78 (m, 1 H), 2.73 (s, 3 H), 2.72 (s, 3 H), 2.68-2.57 (m, 2 H), 2.55-2.49 (m, 1 H), 2.43 (s, 3 H), 2.33 (s, 3 H); ^{13}C NMR (125 MHz) δ 161.0, 137.7, 130.8, 123.7, 120.9, 113.1, 72.2, 68.3, 62.0, 59.1, 58.5, 50.3 (two carbons), 49.6, 48.9; IR (KBr, cm^{-1}): 1559 (w), 1461 (s), 801 (m), 753 (m); HRMS (FAB) calcd for $\text{C}_{15}\text{H}_{28}\text{IN}_2\text{O}_2\text{Pd}$ ($\text{M}+\text{H}^+$) 501.0230, found 501.0232.

General Procedure for the Synthesis of the Palladium(II)- Ph_3P Complexes 3. A solution of the complex **2** (1 mmol) and Ph_3P (2.2 mmol) in methylene chloride (10-30 mL) was stirred for the indicated time at rt under argon. The solvent was removed under reduced pressure and the crude product was trituated with small amounts of ether to afford pure complexes **3** as solids.

***trans*-[2-(Cyanomethoxy)phenyl]iodobis(triphenylphosphine)palladium (3a).** Treatment of the complex **2a** (0.300 g, 0.622 mmol) and Ph_3P (0.369 g, 1.41 mmol) for 2.0 h according to the general procedure described above yielded complex **3a** (0.543 g, 98%) as a pale yellow solid: mp = 176–177 °C (ether); $R_f = 0.43$ (EtOAc/hexane 1 : 2); ^1H NMR (400 MHz) δ 7.55-7.49 (m, 12 H), 7.33-7.29 (m, 6 H), 7.27-7.22 (m, 12 H), 7.03-7.01 (m, 1 H), 6.44 (t, $J = 7.8$ Hz, 1 H), 6.33 (t, $J = 7.3$ Hz, 1 H), 5.36 (d, $J = 8.1$ Hz, 1 H), 3.68 (s, 2 H); ^{13}C NMR (125 MHz) δ 156.6, 147.2, 134.7

(t, $J(^{13}\text{C}-^{31}\text{P}) = 6.2$ Hz), 134.5 (t, $J(^{13}\text{C}-^{31}\text{P}) = 6.4$ Hz), 132.2 (t, $J(^{13}\text{C}-^{31}\text{P}) = 23.4$ Hz), 129.8, 127.8 (t, $J(^{13}\text{C}-^{31}\text{P}) = 6.4$ Hz), 127.6 (t, $J(^{13}\text{C}-^{31}\text{P}) = 5.1$ Hz), 124.1, 121.8, 115.6, 109.4, 52.0 (several signals account for more than one carbon); ^{31}P NMR (202 MHz) δ 23.1 (s, 2 P); IR (KBr, cm^{-1}): 1561 (w), 1480 (w), 1434 (s), 1095 (m), 741 (m), 692 (s), 519 (m); HRMS (FAB) calcd $\text{C}_{44}\text{H}_{36}\text{NOP}_2\text{Pd}$ (M-I^+) 762.1307, found 762.1308; Anal. Calcd for $\text{C}_{44}\text{H}_{36}\text{INOP}_2\text{Pd}$: C, 59.38; H, 4.08. Found: C, 59.17; H, 4.20.

***trans*-[2-(Ethoxycarbonylmethoxy)phenyl]iodobis(triphenylphosphine)palladium (3b).**

Treatment of the complex **2b** (0.879 g, 1.66 mmol) with Ph_3P (0.959 g, 3.65 mmol) for 1.0 h according to the according to the general procedure described above yielded complex **3b** (1.52 g, 98%) as a yellow solid: mp = 192–193 °C decomp. (ether); $R_f = 0.43$ (EtOAc/hexane 1 : 2); ^1H NMR (400 MHz) δ 7.59–7.54 (m, 12 H), 7.29 (t, $J = 7.1$ Hz, 6 H), 7.25–7.21 (m, 12 H), 7.00–6.96 (m, 1 H), 6.37 (t, $J = 7.2$ Hz, 1 H), 6.24 (t, $J = 7.2$ Hz, 1 H), 5.26 (dd, $J = 8.0$ Hz, 1.1 Hz, 1 H), 4.34 (q, $J = 7.1$ Hz, 2 H), 3.50 (s, 2 H), 1.36 (t, $J = 7.1$ Hz, 3 H); ^{13}C NMR (125 MHz) δ 168.7, 157.4, 146.6 (t, $J(^{13}\text{C}-^{31}\text{P}) = 3.5$ Hz), 134.9 (t, $J(^{13}\text{C}-^{31}\text{P}) = 6.2$ Hz), 134.7 (t, $J(^{13}\text{C}-^{31}\text{P}) = 8.1$ Hz), 134.2 (t, $J(^{13}\text{C}-^{31}\text{P}) = 3.8$ Hz), 132.4 (t, $J(^{13}\text{C}-^{31}\text{P}) = 23.0$ Hz), 129.7, 129.5, 127.6 (q, $J(^{13}\text{C}-^{31}\text{P}) = 4.0$ Hz), 127.4 (t, $J(^{13}\text{C}-^{31}\text{P}) = 5.0$ Hz), 123.8, 120.8, 110.0, 64.2, 60.8, 14.4 (several signals account for more than one carbon); ^{31}P NMR (162 MHz) δ 23.3 (s, 2 P); IR (KBr, cm^{-1}): 1752 (s); HRMS (FAB) calcd for $\text{C}_{46}\text{H}_{41}\text{IO}_3\text{P}_2\text{Pd}$ (M-I^+) 809.1566, found 809.1569; Anal. Calcd for $\text{C}_{46}\text{H}_{41}\text{IO}_3\text{P}_2\text{Pd}$: C, 58.96; H, 4.41. Found: C, 58.60; H, 4.67.

***trans*-[2-(*N,N*-Diethylcarbonylmethoxy)phenyl]iodobis(triphenylphosphine)palladium (3c).**

Treatment of the complex **2c** (0.051 g, 0.091 mmol) with Ph_3P (0.051 g, 0.195 mmol) for 1.25 h according to the according to the general procedure described above yielded complex **3c** (0.082 g, 94%) as a pale yellow solid: mp = 184 –185 °C decomp. (ether); $R_f = 0.43$ (EtOAc/hexane 1 : 1); ^1H NMR (400 MHz) δ 7.53–7.45 (m, 12 H), 7.30 (t, $J = 7.2$ Hz, 6 H), 7.22 (t, $J = 7.3$ Hz, 12 H), 6.89–6.87 (m, 1 H), 6.43 (t, $J = 7.6$ Hz, 1 H), 6.18 (t, $J = 7.2$ Hz, 1 H), 5.67 (d, $J = 8.1$ Hz, 1 H), 3.64 (s, 2 H), 3.45–3.40 (m, 2 H), 3.16–3.11 (m, 2 H), 1.17 (t, $J = 7.0$ Hz, 3 H), 1.10 (t, $J = 7.1$ Hz, 3 H); ^{13}C NMR (125 MHz) δ 167.1, 158.3, 146.0 (t, $J(^{13}\text{C}-^{31}\text{P}) = 3.4$ Hz),

135.4 (t, $J(^{13}\text{C}-^{31}\text{P}) = 4.0$ Hz), 134.9 (t, $J(^{13}\text{C}-^{31}\text{P}) = 6.2$ Hz), 134.6 (t, $J(^{13}\text{C}-^{31}\text{P}) = 6.2$ Hz), 132.4 (t, $J(^{13}\text{C}-^{31}\text{P}) = 23.0$ Hz), 129.7, 129.6, 127.7 (t, $J(^{13}\text{C}-^{31}\text{P}) = 4.8$ Hz), 127.5 (t, $J(^{13}\text{C}-^{31}\text{P}) = 5.1$ Hz), 124.1, 120.7, 111.1, 66.9, 41.2, 40.2, 14.4, 13.2 (several signals account for more than one carbon); ^{31}P NMR (202 MHz) δ 23.2 (s, 2 P); IR (KBr, cm^{-1}): 1651 (s); HRMS (FAB) calcd for $\text{C}_{48}\text{H}_{46}\text{NO}_2\text{P}_2\text{Pd}$ (M-I^+) 836.2039, found 836.2037.

***trans*-Iodo[2-(phenylmethoxy)phenyl]bis(triphenylphosphine)palladium (3d).**³ Treatment of the complex **2d** (0.100 g, 0.188 mmol) with Ph_3P (0.108 g, 0.412 mmol) for 17 h according to the general procedure described above yielded complex **3d** (0.175 g, 98%) as a white solid: mp = 187–188 °C decomp. (ether); $R_f = 0.43$ (EtOAc/hexane 1 : 3); ^1H NMR (500 MHz) δ 7.53–7.52 (m, 3 H), 7.41–7.43 (m, 12 H), 7.41–7.37 (m, 2 H), 7.29–7.26 (m, 6 H), 7.16 (t br, $J = 7.4$ Hz, 12 H), 7.04 (dd, $J = 7.2$ Hz, 1.5 Hz, 1 H), 6.44 (t, $J = 6.0$ Hz, 1 H), 6.29 (t, $J = 5.8$ Hz, 1 H), 5.52 (d, $J = 7.9$ Hz, 1 H), 3.92 (2 H); ^{13}C NMR (125 MHz) δ 158.7, 146.2 (t, $J(^{13}\text{C}-^{31}\text{P}) = 3.3$ Hz), 137.6, 134.8 (t, $J(^{13}\text{C}-^{31}\text{P}) = 6.4$ Hz), 134.6 (t, $J(^{13}\text{C}-^{31}\text{P}) = 6.4$ Hz), 134.1 (t, $J(^{13}\text{C}-^{31}\text{P}) = 6.2$ Hz), 132.3 (t, $J(^{13}\text{C}-^{31}\text{P}) = 23$ Hz), 129.5, 128.7 (d, $J(^{13}\text{C}-^{31}\text{P}) = 37.5$ Hz), 127.9, 127.6 (t, $J(^{13}\text{C}-^{31}\text{P}) = 5.0$ Hz), 127.5 (t, $J(^{13}\text{C}-^{31}\text{P}) = 5.0$ Hz), 123.98, 120.2, 110.3, 68.7 (several signals account for more than one carbon); ^{31}P NMR (202 MHz) δ 23.3 (s, 2 P); IR (KBr, cm^{-1}): 1558 (w), 1433 (s), 742 (m), 692 (s).

***trans*-Iodo[2-(2-methoxyethoxy)phenyl]bis(triphenylphosphine)palladium (3e).**

Treatment of the complex **2e** (0.100 g, 0.201 mmol) with Ph_3P (0.115 g, 0.437 mmol) for 1.5 h according to the general procedure described above yielded complex **3e** (0.164 g, 90%) as an orange solid: mp = 160–162 °C decomp. (ether); $R_f = 0.31$ (EtOAc/hexane 1 : 3); ^1H NMR (400 MHz) δ 7.57–7.51 (m, 12 H), 7.29 (t, $J = 7.3$ Hz, 6 H), 7.22 (t, $J = 7.3$ Hz, 12 H), 6.96–6.93 (m, 1 H), 6.35 (t, $J = 7.6$ Hz, 1 H), 6.21 (t, $J = 7.2$ Hz, 1 H), 5.33 (dd, $J = 8.1$ Hz, 1.1 Hz, 1 H), 3.64 (t, $J = 5.2$ Hz, 2 H), 3.56 (s, 3 H), 3.08 (t, $J = 5.2$ Hz, 2 H); ^{13}C NMR (125 MHz) δ 158.2, 146.0 (t, $J(^{13}\text{C}-^{31}\text{P}) = 3.4$ Hz), 134.9 (t, $J(^{13}\text{C}-^{31}\text{P}) = 6.2$ Hz), 133.7 (t, $J(^{13}\text{C}-^{31}\text{P}) = 3.7$ Hz), 132.4 (t, $J(^{13}\text{C}-^{31}\text{P}) = 23.0$ Hz), 129.5, 127.4 (t, $J(^{13}\text{C}-^{31}\text{P}) = 5.0$ Hz), 123.9, 120.0, 109.9, 71.4, 64.9, 59.1 (several signals account for more than one carbon); ^{31}P NMR (202 MHz) δ 23.5 (s, 2 P); IR (KBr, cm^{-1}):

1561 (w), 1433 (s), 1223 (w), 741 (m), 692 (s); HRMS (FAB) calcd for $C_{45}H_{45}NIO_2P_2Pd$ ($M+NH_4^+$) 926.1005, found 926.1022.

General Procedure for the Synthesis of Palladacycles 4a, 4b and 4c (Method B). To the solid reagents including the complex **2** (1 mmol), $AgNO_3$ (1.5 mmol) and solid *t*-BuOK (1.8 mmol) was added THF (40 mL per 1 mmol). Alternatively, to the solid complex **2** (1 mmol) and $AgNO_3$ (1.1 mmol) was injected simultaneously a 1M solution of *t*-BuOK in THF (1.1 mL, 1.1 mmol) and THF (20-30 mL per 1 mmol). The resulting suspension was stirred for 10 minutes at rt under argon. Reaction mixture was filtered through Celite and a small plug of basic alumina eluting with methylene chloride or methanol/methylene chloride (1 : 9). Solvents were removed under reduced pressure and the crude products were triturated with small amounts of ether to afford palladacycles **4a**, **4b** and **4c** as white solids.

(Cyanomethineoxy-1,2-phenylene)(tetramethylethylenediamine)palladium (4a). Complex **2a** (0.500 g, 1.04 mmol), solid *t*-BuOK (0.212 g, 1.89 mmol) and $AgNO_3$ (0.271 g, 1.59 mmol) were treated according to the general procedure described above. Elution with methylene chloride afforded the palladacycle **4a** (0.247 g, 67%) as a white solid: mp = 210–212 °C (ether); R_f = 0.36 (EtOAc); 1H NMR (500 MHz) δ 7.06 (dd, J = 7.5 Hz, 1.3 Hz, 1 H), 6.96 (td, J = 7.3 Hz, 1.5 Hz, 1 H), 6.69–6.64 (m, 2 H), 5.79 (s, 1 H), 2.91 (s, 3 H), 2.82 (s, 3 H), 2.79–2.70 (m, 1 H), 2.70 (s, 3 H), 2.64 (s, 3 H), 2.62–2.50 (m, 3 H); ^{13}C NMR (125 MHz) δ 172.8, 135.5, 133.3, 126.2, 124.3, 118.3, 109.3, 69.9, 61.4, 60.2, 50.7, 50.2, 49.8, 48.0; IR (KBr, cm^{-1}): 2190 (m); HRMS (FAB) calcd for $C_{14}H_{22}N_3OPd$ ($M+H^+$) 353.0798, found 354.0786; Anal. Calcd for $C_{14}H_{21}N_3OPd$: C, 47.53; H, 5.98; N, 11.88. Found: C, 47.33; H, 6.03; N, 11.84.

(Ethoxycarbonylmethineoxy-1,2-phenylene)(tetramethylethylenediamine)palladium

(4b). Complex **2b** (0.957 g, 1.81 mmol), *t*-BuOK (1M solution in THF, 2.0 mL, 2.00 mmol) and $AgNO_3$ (0.337 g, 1.98 mmol) were treated according to the general procedure described above. Elution with methylene chloride afforded the palladacycle **4b** (0.422 g, 73%) as a white solid: mp = 183–184 °C decomp. (ether); R_f = 0.50 (EtOAc); 1H NMR (500 MHz) δ 7.01 (dd, J = 7.5 Hz, 1.2 Hz, 1 H), 6.93 (td, J = 7.7 Hz, 1.2 Hz, 1 H), 6.69 (dd, J = 7.8 Hz, 1.1 Hz, 1 H), 6.60 (td, J = 7.4 Hz,

1.1 Hz, 1 H), 5.78 (s, 1 H), 4.12 (q, $J = 7.1$ Hz, 2 H), 2.96 (td, $J = 12.5$ Hz, 3.1 Hz, 1 H), 2.87 (s, 3 H), 2.87-2.77 (m, 1 H), 2.81 (s, 3 H), 2.73 (s, 3 H), 2.55 (s, 3 H), 2.41 (dt, $J = 13.6$ Hz, 3.0 Hz, 1 H), 2.29 (dt, $J = 12.9$ Hz, 3.0 Hz, 1 H), 1.20 (t, $J = 7.1$ Hz, 3 H); ^{13}C NMR (125 MHz) δ 178.0, 173.9, 136.8, 133.2, 125.7, 117.4, 108.4, 87.2, 61.1, 60.5, 59.5, 51.3, 51.2, 49.5, 46.1, 14.4; IR (KBr, cm^{-1}): 1670 (s); HRMS (FAB) calcd for $\text{C}_{16}\text{H}_{27}\text{N}_2\text{O}_3\text{Pd}$ ($\text{M}+\text{H}^+$) 401.1056, found 401.1084; Anal. Calcd for $\text{C}_{16}\text{H}_{26}\text{N}_2\text{O}_3\text{Pd}$: C, 47.95; H, 6.54; N, 6.99. Found: C, 47.92; H, 6.68; N, 6.99.

(*N,N*-Diethylcarbonylmethineoxy-1,2-phenylene)(tetramethylethylenediamine)palladium (4c). Complex **2c** (0.232 g, 0.418 mmol), *t*-BuOK (1M solution in THF, 0.5 mL, 0.50 mmol) and AgNO_3 (0.079 g, 0.463 mmol) were treated according to the general procedure described above. Elution with methanol/methylene chloride (1 : 9) afforded the palladacycle **4c** (0.118 g, 66%) as a white solid: mp = 188–189 °C decomp. (ether); $R_f = 0.65$ (MeOH/ CH_2Cl_2 1 : 9); ^1H NMR (400 MHz) δ 7.13 (dd, $J = 7.5$ Hz, 1.3 Hz, 1 H), 6.94 (t, $J = 7.5$ Hz, 1 H), 6.64 (td, $J = 6.2$ Hz, 0.9 Hz, 1 H), 6.62 (d, $J = 5.9$ Hz, 1 H), 6.27 (s, 1 H), 3.99 (hex, $J = 7.1$ Hz, 1 H), 3.46 (hex, $J = 7.1$ Hz, 1 H), 3.29 (hex, $J = 6.9$ Hz, 1 H), 3.14 (hex, $J = 6.9$ Hz, 1 H), 2.92 (s, 3 H), 2.83 (s, 3 H), 2.79 (s, 3 H), 2.95-2.79 (m, 2 H), 2.42 (s, 3 H), 2.35 (d, $J = 12.5$ Hz, 1 H), 2.23 (d, $J = 12.5$ Hz, 1 H), 1.15 (t, $J = 7.1$ Hz, 3 H); 1.09 (t, $J = 6.9$ Hz, 3 H); ^{13}C NMR (125 MHz) δ 176.6, 172.8, 137.9, 133.5, 125.6, 117.2, 108.9, 92.6, 61.5, 61.4, 51.4, 51.2, 48.2, 45.4, 42.8, 40.4, 13.8, 13.0; IR (KBr, cm^{-1}): 1586 (s); HRMS (FAB) calcd for $\text{C}_{18}\text{H}_{32}\text{N}_3\text{O}_2\text{Pd}$ ($\text{M}+\text{H}^+$) 428.1529, found 428.1546; Anal. Calcd for $\text{C}_{18}\text{H}_{31}\text{N}_3\text{O}_2\text{Pd}$: C, 50.53; H, 7.30; N, 9.82. Found: C, 50.36; H, 7.41; N, 9.86.

General Procedure for the Synthesis of Palladacycles 5a and 5b (Method C). To a solution of Pd_2dba_3 (0.56 mmol) and Ph_3P (2.2 mmol) in benzene (25 mL) at rt under argon was added a solution of the aryl iodide **1a,b** (1.0 mmol) in benzene (3 mL). The resulting solution was stirred at 55 °C (oil bath) for 30 minutes. After cooling to rt, *t*-BuOK (1M solution in THF, 1.26 mL, 1.26 mmol) was added, and the stirring was continued for additional 30 minutes. The reaction mixture was filtered through Celite and a small plug of basic alumina eluting with ethyl acetate, to afford a

crude product. Trituration of the crude product with small amounts of ether yielded the palladacycles **5a** and **5b** as white and pale yellow solids respectively.

(Cyanomethineoxy-1,2-phenylene)bis(triphenylphosphine)palladium (5a). Treatment of the Pd₂dba₃ (0.196 g, 0.214 mmol), Ph₃P (0.222 g, 0.849 mmol), aryl iodide **1a** (0.100 g, 0.388 mmol) and *t*-BuOK (1M solution in THF, 0.4 mL, 0.400 mmol) according to the general procedure described above afforded the palladacycle **5a** (0.191 g, 65%) as a white solid: mp = 184–186 °C decomp. (ether); R_f = 0.17 (EtOAc/hexane 1 : 3); ¹H NMR (400 MHz) δ 7.51–7.46 (m, 6 H), 7.43–7.36 (m, 6 H), 7.35–7.30 (m, 4 H), 7.24–7.19 (m, 8 H), 7.09 (td, *J* = 7.9 Hz, 1.9 Hz, 6 H), 6.83–6.74 (m, 2 H), 6.47 (tdd, *J* = 7.6 Hz, 3.5 Hz, 1.2 Hz, 1 H), 6.06 (tt, *J* = 6.3 Hz, 1.4 Hz, 1 H), 4.97 (dd, *J* = 8.3 Hz, 6.5 Hz, 1 H); ¹³C NMR (125 MHz) δ 173.4 (t, *J*(¹³C–³¹P) = 4.7 Hz), 146.8 (dd, *J*(¹³C–³¹P) = 103.7, 9.2 Hz), 141.0 (dd, *J*(¹³C–³¹P) = 9.5 Hz, 2.6 Hz), 134.8 (dd, *J*(¹³C–³¹P) = 152.0 Hz, 12.9 Hz), 132.8 (dd, *J*(¹³C–³¹P) = 36.3 Hz, 1.6 Hz), 131.4 (d, *J*(¹³C–³¹P) = 37.0 Hz), 130.1 (dd, *J*(¹³C–³¹P) = 39.2 Hz, 2.0 Hz), 128.1 (dd, *J*(¹³C–³¹P) = 62.6 Hz, 9.7 Hz), 125.9, 122.7 (d, *J*(¹³C–³¹P) = 4.7 Hz), 117.9 (dd, *J*(¹³C–³¹P) = 8.0 Hz, 4.0 Hz), 109.4, 80.6 (dd, *J*(¹³C–³¹P) = 89.5 Hz, 6.3 Hz) (several signals account for more than one carbon); ³¹P NMR (162 MHz) δ 31.7 (d, *J* = 31.6 Hz, 1 P), 23.6 (d, *J* = 31.3 Hz, 1 P); IR (KBr, cm⁻¹): 2194 (m); HRMS (FAB) calcd for C₄₄H₃₅NOP₂Pd (M⁺) 761.1229, found 761.1207; Anal. Calcd for C₄₄H₃₅NOP₂Pd: C, 69.34; H, 4.63. Found: C, 68.86; H, 4.68.

(Ethoxycarbonylmethineoxy-1,2-phenylene)bis(triphenylphosphine) palladium (5b).

Treatment of the Pd₂dba₃ (1.01 g, 1.10 mmol), Ph₃P (1.15 g, 4.39 mmol), aryl iodide **1b** (0.606 g, 1.98 mmol) and *t*-BuOK (1M solution in THF, 2.0 mL, 2.00 mmol) according to the general procedure described above afforded the palladacycle **5b** (1.38 g, 86%) as a pale yellow solid: mp = 173–174 °C decomp. (ether); R_f = 0.26 (EtOAc/hexane 1 : 2); ¹H NMR (500 MHz) δ 7.50 (t, *J* = 9.1 Hz, 6 H), 7.35 (t, *J* = 8.6 Hz, 6 H), 7.27 (td, *J* = 7.3 Hz, 1.1 Hz, 3 H), 7.21 (t, *J* = 7.4 Hz, 3 H), 7.15 (td, *J* = 7.9 Hz, 1.7 Hz, 6 H), 7.05 (t, *J* = 7.5 Hz, 6 H), 6.85–6.77 (m, 2 H), 6.37 (td, *J* = 7.8 Hz, 3.3 Hz, 1 H), 6.02 (tt, *J* = 7.3 Hz, 1.7 Hz, 1 H), 5.43 (dd, *J* = 10.7 Hz, 7.7 Hz, 1 H), 4.25–4.12 (m, 1 H), 3.86–3.79 (m, 1 H), 1.01 (t, *J* = 8.8 Hz, 3 H); ¹³C NMR (125 MHz) δ 176.1, 173.4 (t, *J*(¹³C–

^{31}P) = 4.7 Hz), 147.8 (dd, $J(^{13}\text{C}-^{31}\text{P})$ = 105.1 Hz, 10.6 Hz), 140.7 (dd, $J(^{13}\text{C}-^{31}\text{P})$ = 9.1 Hz, 2.9 Hz), 134.9 (dd, $J(^{13}\text{C}-^{31}\text{P})$ = 99.7 Hz, 13.0 Hz), 133.2 (dd, $J(^{13}\text{C}-^{31}\text{P})$ = 80.5 Hz, 33.5 Hz), 129.7 (d, $J(^{13}\text{C}-^{31}\text{P})$ = 9.8 Hz), 127.8 (dd, $J(^{13}\text{C}-^{31}\text{P})$ = 23.8 Hz, 9.6 Hz), 125.7, 117.4 (dd, $J(^{13}\text{C}-^{31}\text{P})$ = 8.6 Hz, 3.7 Hz), 108.8 (d, $J(^{13}\text{C}-^{31}\text{P})$ = 2.2 Hz), 96.8 (dd, $J(^{13}\text{C}-^{31}\text{P})$ = 83.0 Hz, 6.2 Hz), 58.9, 14.4 (several signals account for more than one carbon); ^{31}P NMR (162 MHz) δ 29.9 (d, J = 28.3 Hz, 1 P), 25.1 (d, J = 28.1 Hz, 1P); IR (KBr, cm^{-1}): 1732 (m), 1708 (s); HRMS (FAB) calcd for $\text{C}_{46}\text{H}_{41}\text{O}_3\text{P}_2\text{Pd}$ ($\text{M}+\text{H}^+$) 809.1566, found 809.1598; Anal. Calcd for $\text{C}_{46}\text{H}_{40}\text{O}_3\text{P}_2\text{Pd}$: C, 68.28; H, 4.98. Found: C, 67.42; H, 5.15.

Preparation of Palladacycles 5a and 5b from complexes 3a and 3b by the use of *t*-BuOK (Method A).

(Cyanomethineoxy-1,2-phenylene)bis(triphenylphosphine)palladium (5a). To a solution of the iodopalladium complex **3a** (0.100 g, 0.112 mmol) in THF (14 mL) at rt under argon was added *t*-BuOK (1 M in THF, 0.12 mL, 0.120 mmol). The reaction mixture was stirred for 5 minutes at rt. The suspension was filtered through a small plug of basic alumina eluting with ethyl acetate. Solvents were removed under reduced pressure, and the crude product was triturated with a small amount of ether to afford palladacycle **5a** (0.050 g, 59%) as a pale yellow solid. Analytical data for palladacycle **5a** are given above.

(Ethoxycarbonylmethineoxy-1,2-phenylene)bis(triphenylphosphine) palladium (5b). To a solution of the iodopalladium complex **3b** (1.000 g, 1.06 mmol) in THF (80 mL) at rt under argon was added *t*-BuOK (1 M in THF, 1.20 mL, 1.20 mmol). The reaction mixture was stirred for 15 minutes at rt. The suspension was filtered through a small plug of Celite. Solvents were removed under reduced pressure, and the crude product was triturated with a small amount of ether to afford palladacycle **5b** (0.760 g, 86%) as a pale yellow solid. Analytical data for palladacycle **5b** are given above.

General Procedure for the Synthesis of Palladacycles 5a-c and 6c via Ligand Exchange. A solution of the palladacycle bearing the TMEDA ligand (1.0 mmol) and the appropriate monodentate or bidentate phosphorus ligand (molar equivalents indicated below) in methylene

chloride (25-40 mL) was stirred for the indicated time at rt under argon. Solvent was removed under reduced pressure and the crude product was triturated with small amounts of ether to afford complexes bearing the phosphorus ligands **5a-c** and **6c** as solids.

(Cyanomethineoxy-1,2-phenylene)bis(triphenylphosphine)palladium (5a). Treatment of the complex **4a** (0.038 g, 0.108 mmol) and Ph_3P (0.130 g, 0.495 mmol) for 1h according to the general procedure described above afforded the palladacycle **5a** (0.072 g, 88%) as a pale yellow solid. Analytical data for complex **5a** are given above.

(Ethoxycarbonylmethineoxy-1,2-phenylene)bis(triphenylphosphine) palladium (5b). Treatment of the complex **4b** (0.292 g, 0.729 mmol) and Ph_3P (0.840 g, 3.20 mmol) for 1h according to the general procedure described above afforded the palladacycle **5b** (0.608 g, 98%) as a white solid. Analytical data for complex **5b** are given above.

(*N,N*-Diethylcarbonylmethineoxy-1,2-phenylene) [1,2-bis(diphenylphosphino)ethane] palladium (5c). Treatment of the complex **4c** (0.020 g, 0.046 mmol) and 1,2-bis(diphenylphosphino)ethane (dppe) (0.020 g, 0.050 mmol) for 45 minutes according to the general procedure described above afforded the palladacycle **5c** (0.024 g, 74%) as a yellow solid: mp = 230–232 °C decomp. (ether); R_f = 0.16 (EtOAc/hexane 1 : 1); ^1H NMR (500 MHz) δ 8.05–7.95 (m, 4 H), 7.73–7.68 (m, 2 H), 7.55–7.47 (m, 6 H), 7.43–7.30 (m, 6 H), 7.29–7.26 (m, 2 H), 6.97 (td, J = 7.5 Hz, 3.7 Hz, 1 H), 6.92–6.86 (m, 2 H), 6.75 (d, J = 9.1 Hz, 1 H), 6.28 (t, J = 7.1 Hz, 1 H), 3.75 (hex, J = 7.3 Hz, 1 H), 2.82 (hex, J = 7.7 Hz, 2 H), 2.48–2.30 (m, 2 H), 2.11–2.04 (m, 2 H), 1.90–1.87 (m, 1 H), 1.05 (t, J = 6.9 Hz, 3 H), 0.88 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (125 MHz) δ 175.5, 174 (t, $J(^{13}\text{C}-^{31}\text{P})$ = 4.6 Hz), 149.5 (dd, $J(^{13}\text{C}-^{31}\text{P})$ = 104.9 Hz, 9.0 Hz), 141.1 (dd, $J(^{13}\text{C}-^{31}\text{P})$ = 11.2 Hz, 2.4 Hz), 134.3 (dd, $J(^{13}\text{C}-^{31}\text{P})$ = 13.2 Hz, 8.5 Hz), 133.5 (d, $J(^{13}\text{C}-^{31}\text{P})$ = 12.6 Hz), 132.8 (d, $J(^{13}\text{C}-^{31}\text{P})$ = 12.6 Hz), 131.4, 131.2 (d, $J(^{13}\text{C}-^{31}\text{P})$ = 2.0 Hz), 131.1, 130.7 (d, $J(^{13}\text{C}-^{31}\text{P})$ = 1.6 Hz), 129.8 (d, $J(^{13}\text{C}-^{31}\text{P})$ = 10.3 Hz), 129.6, 129.3, 129.1 (d, $J(^{13}\text{C}-^{31}\text{P})$ = 9.7 Hz), 128.8 (dd, $J(^{13}\text{C}-^{31}\text{P})$ = 13.6 Hz, 9.8 Hz), 128.1 (d, $J(^{13}\text{C}-^{31}\text{P})$ = 10.0 Hz), 126.0, 117.6 (dd, $J(^{13}\text{C}-^{31}\text{P})$ = 7.9 Hz, 4.5 Hz), 109.5 (d, $J(^{13}\text{C}-^{31}\text{P})$ = 2.0 Hz), 102.9 (dd, $J(^{13}\text{C}-^{31}\text{P})$ = 87.2 Hz, 4.7 Hz), 44.5, 40.9, 30.5 (dd, $J(^{13}\text{C}-^{31}\text{P})$ = 26.5 Hz, 18.3 Hz), 29.2 (dd, $J(^{13}\text{C}-^{31}\text{P})$ = 26.2 Hz, 17.6 Hz), 14.9, 14.2

(several signals account for more than one carbon); ^{31}P NMR (202 MHz) δ 44.0 (d, $J = 16.5$ Hz, 1 P), 40.6 (d, $J = 16.4$ Hz, 1 P); IR (KBr, cm^{-1}): 1607 (s). HRMS (FAB) calcd for $\text{C}_{38}\text{H}_{40}\text{NO}_2\text{P}_2\text{Pd}$ ($\text{M}+\text{H}^+$) 710.1569, found 710.1582; Anal. Calcd for $\text{C}_{38}\text{H}_{39}\text{NO}_2\text{P}_2\text{Pd}$: C, 64.27; H, 5.54; N, 1.97. Found: C, 63.83; H, 5.68; N, 1.99.

(*N,N*-Diethylcarbonylmethineoxy-1,2-phenylene) [1,4-bis(diphenylphosphino)butane] palladium (6c). Treatment of the complex **4c** (0.208 g, 0.487 mmol) and 1,4-bis(diphenylphosphino)butane (dppb) (0.229 g, 0.536 mmol) for 1.25 h according to the general procedure described above (trituration with mixtures of ether/hexane) afforded the palladacycle **6c** (0.328 g, 91%) as a white solid: mp = 157–158 °C (ether/hexane); $R_f = 0.59$ (EtOAc/hexane 2 : 1); ^1H NMR (500 MHz, 50 °C, CDCl_3) δ 7.93–7.85 (m, 4 H), 7.63 (t, $J = 8.7$ Hz, 2 H), 7.50–7.46 (m, 3 H), 7.41 (td, $J = 7.7$ Hz, 1.4 Hz, 2 H), 7.36–7.27 (m, 6 H), 7.22 (td, $J = 7.4$ Hz, 1.2 Hz, 1 H), 7.09 (td, $J = 7.6$ Hz, 1.5 Hz, 2 H), 6.82–6.75 (m, 2 H), 6.68 (dd, $J = 7.8$ Hz, 2.0 Hz, 1 H), 5.88 (t, $J = 7.6$ Hz, 1 H), 3.39–3.21 (s br, 2 H), 3.16–3.11 (m, 2 H), 2.73–2.67 (m, 1 H), 2.46–2.42 (m, 1 H), 2.33–2.20 (m, 2 H), 2.22–1.98 (m, 1 H), 1.88–1.83 (m, 1 H), 1.65–1.57 (m, 2 H), 1.33–1.28 (m, 1 H), 1.03 (t, $J = 7.0$ Hz, 6 H); ^{13}C NMR (125 MHz, run at 50 °C in CDCl_3) δ 175.8, 174.5 (t, $J(^{13}\text{C}-^{31}\text{P}) = 5.1$ Hz), 148.8 (dd, $J(^{13}\text{C}-^{31}\text{P}) = 104.5$ Hz, 9.7 Hz), 140.7 (dd, $J(^{13}\text{C}-^{31}\text{P}) = 10.1$ Hz, 2.8 Hz), 136.6 (d, $J(^{13}\text{C}-^{31}\text{P}) = 33.6$ Hz), 134.8 (d, $J(^{13}\text{C}-^{31}\text{P}) = 13.1$ Hz), 134.6, 134.3, 134.1, 133.7 (d, $J(^{13}\text{C}-^{31}\text{P}) = 12.6$ Hz), 132.9 (dd, $J(^{13}\text{C}-^{31}\text{P}) = 32.1$ Hz, 11.7 Hz), 131.5 (d, $J(^{13}\text{C}-^{31}\text{P}) = 30.1$ Hz), 130.4, 129.9, 129.4, 129.1, 128.3 (dd, $J(^{13}\text{C}-^{31}\text{P}) = 34.1$ Hz, 9.5 Hz), 128.1 (dd, $J(^{13}\text{C}-^{31}\text{P}) = 9.1$ Hz, 5.6 Hz), 125.4, 117.1 (dd, $J(^{13}\text{C}-^{31}\text{P}) = 8.1$ Hz, 4.0 Hz), 108.6, 103.5 (dd, $J(^{13}\text{C}-^{31}\text{P}) = 92.2$ Hz, 5.1 Hz), 41.4 br (two carbons), 29.1 (d, $J(^{13}\text{C}-^{31}\text{P}) = 20.2$ Hz), 27.7 (d, $J(^{13}\text{C}-^{31}\text{P}) = 17.3$ Hz), 25.9 (t, $J(^{13}\text{C}-^{31}\text{P}) = 5.6$ Hz), 23.5 br, 13.7 br (two carbons) (several signals account for more than one carbon, hindered rotation about the amide bond accounts for the broad signals at 41.4 and 13.7 ppm); ^{31}P NMR (202 MHz) δ 21.9 (d, $J = 34.5$ Hz, 1 P), 12.7 (d, $J = 34.1$ Hz, 1 P); IR (KBr, cm^{-1}): 1601 (m); HRMS (FAB) calcd for $\text{C}_{40}\text{H}_{44}\text{NO}_2\text{P}_2\text{Pd}$ ($\text{M}+\text{H}^+$) 738.1882, found 738.1907; Anal. Calcd for $\text{C}_{40}\text{H}_{43}\text{NO}_2\text{P}_2\text{Pd}$: C, 65.09; H, 5.87; N, 1.90. Found: C, 64.60; H, 6.15; N, 1.88.

2-*N,N*-Diethylcarbonyl-3,4-bis(methoxycarbonyl)-2*H*-1-benzopyran (7). To a solution of the palladacycle **6c** (0.150 g, 0.203 mmol) in 1,2-dichloroethane (5.6 mL) at rt under argon was injected dimethyl acetylenedicarboxylate (dmad) as neat liquid (0.055 mL, 0.064 g, 0.447 mmol). The reaction mixture was stirred for 5 h at 80 °C (oil bath) and for additional 16 h at rt. The reaction mixture was concentrated and separated by flash chromatography over silica eluting with EtOAc/hexane (1 : 2), to yield the benzopyran **7** (0.045 g, 64%) as a yellow oil that solidified at rt: mp = 98–100 °C (EtOAc/hexane, 1 : 2); R_f = 0.56 (EtOAc/hexane 1 : 3); ^1H NMR (400 MHz) δ 7.24 (td, J = 7.8 Hz, 1.4 Hz, 1 H), 7.08 (dd, J = 7.8 Hz, 1.5 Hz, 1 H), 6.93 (td, J = 7.6 Hz, 1.0 Hz, 1 H), 6.84 (d, J = 8.2 Hz, 1 H), 5.95 (s, 1 H), 3.96 (s, 3 H), 3.77 (s, 3 H), 3.70–3.55 (m, 2 H), 3.36–3.23 (m, 2 H), 1.33 (t, J = 7.1 Hz, 3 H), 1.06 (t, J = 7.1 Hz, 3 H); ^{13}C NMR (100 MHz) δ 166.9, 166.0, 163.6, 152.5, 138.4, 132.4, 126.7, 122.4, 118.7, 117.9, 116.2, 70.4, 52.7, 52.5, 41.7, 40.4, 14.5, 12.7; IR (neat, cm^{-1}): 1725 (s), 1651 (s); MS (EI) m/z (relative intensity) 347 (M^+ , 10), 316 (50), 288 (53), 261 (50), 247 (50); 100 (100); HRMS (FAB) calcd for $\text{C}_{18}\text{H}_{22}\text{NO}_6$ ($\text{M}+\text{H}^+$) 348.1447, found 348.1463.

2-Ethoxycarbonyl-3,4-bis(methoxycarbonyl)-2*H*-1-benzopyran (8). To a solution of the palladacycle **5b** (0.150 g, 0.186 mmol) in 1,2-dichloroethane (5.6 mL) at rt under argon was injected dmad as neat liquid (0.050 mL, 0.058 g, 0.407 mmol). The reaction mixture was stirred for 1 h at 40 °C (oil bath). Solvent was removed under reduced pressure, and the crude product was triturated with ether to afford bis(triphenylphosphine)(dimethyl acetylenedicarboxylate)palladium⁴ (0.104 g, 72%) as a yellow powder. The filtrate was concentrated under reduced pressure, and separated by flash chromatography over silica eluting with EtOAc/hexane (1 : 3) to yield the benzopyran **8** (0.056 g, 95%) as a yellow oil that solidified at rt: mp = 58–60 °C (EtOAc/hexane, 1 : 3); R_f = 0.39 (EtOAc/hexane 1 : 3); ^1H NMR (400 MHz) δ 7.34 (t, J = 7.7 Hz, 1 H), 7.16 (dd, J = 7.8 Hz, 1.5 Hz, 1 H), 7.06 (dd, J = 8.1 Hz, 0.9 Hz, 1 H), 6.98 (td, J = 7.5 Hz, 1.0 Hz, 1 H), 5.83 (s, 1 H), 4.20–4.06 (m, 2 H), 3.95 (s, 3 H), 3.85 (s, 3 H), 1.18 (t, J = 7.1 Hz, 3 H); ^{13}C NMR (100 MHz) δ 168.4, 166.3, 163.6, 153.5, 137.8, 133.1, 126.6, 122.6, 117.8, 117.4, 117.1, 71.1, 61.9, 52.8, 52.6, 13.9; IR (neat, cm^{-1}): 1760 (m), 1736 (m), 1723(s); MS (EI) m/z (relative intensity) 320 (M^+ ,

25), 289 (27), 261 (50), 247 (100), 219 (48); HRMS (FAB) calcd for $C_{16}H_{17}O_7$ ($M+H^+$) 321.0974, found 321.0970. **Analytical data for bis(triphenylphosphine)(dimethyl acetylenedicarboxylate)palladium:** mp = 128–130 °C decomp. (ether); 1H NMR (400 MHz) δ 7.27–7.20 (m, 20 H), 7.17–7.11 (m, 10 H), 3.23 (s, 6 H); ^{31}P NMR (162 MHz) δ 30.7 (s, 2 P).

General Procedure for the Synthesis of 2*H*-1-Benzopyrans 9-14. To a solution of the palladacycle **5b** (1 mmol) in 1,2-dichloroethane (30 mL) at rt under argon was injected the appropriate alkyne as neat liquid (2.2 mmol) unless indicated otherwise. The reaction mixture was stirred for the indicated time at 80 °C (oil bath) and in several cases for additional 20 h at rt. Crude mixture was separated by flash chromatography over silica eluting with ether/hexane (1 : 6) to afford the 2*H*-1-benzopyrans **9-14** as colorless or yellow oils or solids.

2,3-Bis(ethoxycarbonyl)-4-methyl-2*H*-1-benzopyran (9a). Treatment of the palladacycle **5b** (0.200 g, 0.247 mmol) and ethyl 2-butynoate (0.063 mL, 0.060 g, 0.540 mmol) for 5 h at 80 °C according to the general procedure described afforded a regioisomerically pure benzopyran **9a** (0.022 g, 31%) as a white solid: mp = 44–45 °C (ether/hexane, 1 : 6); R_f = 0.32 (EtOAc/hexane 1 : 3); 1H NMR (500 MHz) δ 7.40 (dd, J = 7.8 Hz, 1.2 Hz, 1 H), 7.28 (td, J = 7.1 Hz, 1.4 Hz, 1 H), 7.02 (d, J = 7.1 Hz, 1 H), 6.98 (t, J = 7.4 Hz, 1 H), 5.84 (s, 1 H), 4.38–4.24 (m, 2 H), 4.17–4.03 (m, 2 H), 2.49 (s, 3 H), 1.35 (t, J = 7.1 Hz, 3 H), 1.15 (t, J = 7.1 Hz, 3 H); ^{13}C NMR (125 MHz) δ 169.6, 165.5, 153.6, 141.2, 131.5, 125.8, 123.1, 122.0, 118.4, 116.7, 72.3, 61.4, 60.8, 15.3, 14.3, 13.9; IR (neat, cm^{-1}): 1756 (s), 1723 (s); MS (EI) m/z (relative intensity) 290 (M^+ , 30), 245 (20), 217 (100), 189 (25), 171 (48), 144 (20), 115 (49); HRMS (FAB) calcd for $C_{16}H_{22}NO_5$ ($M+NH_4^+$) 308.1498, found 308.1511.

2,3-Bis(ethoxycarbonyl)-4-methyl-2*H*-1-benzopyran (9a) and 2,4-Bis(ethoxycarbonyl)-3-methyl-2*H*-1-benzopyran (9b) (6:1 mixture). Treatment of the palladacycle **5b** (0.200 g, 0.247 mmol) and ethyl 2-butynoate (0.063 mL, 0.060 g, 0.540 mmol) for 6 h at 80 °C and for 20 h at rt according to the general procedure described above afforded a mixture of two regioisomeric benzopyrans **9a** and **9b** (0.038 g, 54%) as a colorless oil. The ratio of regioisomers determined from 1H NMR was 6 : 1 (**9a** : **9b**). Analytical data for the mixture of isomers: 1H NMR (500 MHz)

δ 7.40 (dd, $J = 7.8$ Hz, 1.2 Hz, 1 H), 7.28 (td, $J = 7.1$ Hz, 1.4 Hz, 1 H), 7.02 (d, $J = 7.1$ Hz, 1 H), 6.98 (t, $J = 7.4$ Hz, 1 H), 6.37 (s, 0.14 H), 5.84 (s, 0.86 H), 4.38-4.24 (m, 2 H), 4.17-4.03 (m, 2 H), 2.49 (s, 3 H), 1.35 (t, $J = 7.1$ Hz, 3 H), 1.15 (t, $J = 7.1$ Hz, 3 H); ^{13}C NMR (125 MHz) (signals for the minor regioisomer **9b** are in parentheses following the signals for the major isomer) δ 169.6, 165.5 (166.4), 153.6, 141.2 (144.9), 131.5 (132.1), 125.8, 123.1 (124.4), 122.0 (121.6), 118.4 (118.2), 116.7 (111.5), 72.3 (73.6), 61.4 (61.6), 60.8 (60.0), 15.3 (28.6), 14.3 (14.2), 13.9 (14.1).

4-Butyl-2,3-bis(ethoxycarbonyl)-2H-1-benzopyran (10). Treatment of the palladacycle **5b** (0.150 g, 0.185 mmol) and ethyl 2-heptynoate (0.069 mL, 0.063 g, 0.409 mmol)⁵ for 6 h at 80 °C according to the general procedure described above afforded the benzopyran **10** (0.048 g, 79%) as a yellow oil: $R_f = 0.56$ (EtOAc/hexane 1 : 3); ^1H NMR (400 MHz) δ 7.42 (dd, $J = 7.8$ Hz, 1.4 Hz, 1 H), 7.28 (t, $J = 7.6$ Hz, 1 H), 7.03 (d, $J = 8.4$ Hz, 1 H), 6.98 (dd, $J = 7.5$ Hz, 1.0 Hz, 1 H), 5.83 (s, 1 H), 4.37-4.23 (m, 2 H), 4.14-4.03 (m, 2 H), 3.09-3.02 (m, 1 H), 2.94-2.87 (m, 1 H), 1.53-1.42 (m, 4 H), 1.35 (t, $J = 7.1$ Hz, 3 H), 1.15 (t, $J = 7.1$ Hz, 3 H), 0.94 (t, $J = 7.1$ Hz, 3 H); ^{13}C NMR (125 MHz) δ 169.7, 165.2, 154.0, 145.9, 131.5, 125.7, 122.0, 121.9, 117.6, 116.9, 72.3, 61.3, 60.7, 31.7, 28.1, 23.0, 14.2, 13.9, 13.8; IR (neat, cm^{-1}): 1752(s), 1711 (s); MS (EI) m/z (relative intensity) 332 (M^+ , 10), 287 (20), 259 (100), 175 (20); HRMS (FAB) calcd for $\text{C}_{19}\text{H}_{28}\text{NO}_5$ ($\text{M}+\text{NH}_4^+$) 350.1967, found 350.1981.

2,3-Bis(ethoxycarbonyl)-4-phenyl-2H-1-benzopyran (11). Treatment of the palladacycle **5b** (0.150 g, 0.185 mmol) and ethyl phenylpropiolate (0.067 mL, 0.070 g, 0.406 mmol) for 5 h at 80 °C according to the general procedure described above afforded the benzopyran **11** (0.038 g, 76%) as a colorless oil: $R_f = 0.42$ (EtOAc/hexane 1 : 3); ^1H NMR (400 MHz) δ 7.44-7.37 (m, 5 H), 7.26 (td, $J = 10.3$ Hz, 1.6 Hz, 1 H), 7.06 (dd, $J = 8.1$ Hz, 1.0 Hz, 1 H), 6.83 (td, $J = 7.8$ Hz, 1.1 Hz, 1 H), 6.73 (dd, $J = 7.8$ Hz, 1.5 Hz, 1 H), 5.94 (s, 1 H), 4.18 (q, $J = 7.1$ Hz, 2 H), 4.02-3.92 (m, 2 H), 1.20 (t, $J = 7.1$ Hz, 3 H), 0.91 (t, $J = 7.1$ Hz, 3 H); ^{13}C NMR (125 MHz) δ 169.4, 164.8, 153.6, 144.6, 136.5, 131.8, 128.7, 128.8 (br, 4 carbons), 127.7, 122.8, 121.9, 118.3, 116.5, 72.5, 61.6, 60.6, 14.0, 13.5 (some of the signals appeared broad due to a hindered rotation about the bond between the C4 of the benzopyran ring and the phenyl substituent); IR (neat, cm^{-1}): 1756 (s), 1723 (s); MS (EI) m/z

(relative intensity) 352 (M^+ , 10), 307 (25), 279 (100), 251 (30), 178 (10); HRMS (FAB) calcd for $C_{21}H_{21}O_5$ ($M+H^+$) 353.1389, found 353.1411.

2-Ethoxycarbonyl-3-methylcarbonyl-4-phenyl-2H-1-benzopyran (12). Treatment of the palladacycle **5b** (0.149 g, 0.185 mmol) and 4-phenyl-3-butyne-2-one (0.060 mL, 0.0594 g, 0.412 mmol) for 6 h at 80 °C and for 20h at rt according to the general procedure described above afforded the benzopyran **12** (0.035 g, 59%) as an yellow oil: R_f = 0.36 (EtOAc/hexane 1 : 3); 1H NMR (500 MHz) δ 7.51-7.45 (m, 5 H), 7.27 (td, J = 7.7 Hz, 1.5 Hz, 1 H), 7.06 (d, J = 8.1 Hz, 1 H), 6.85 (t, J = 7.8 Hz, 1 H), 6.79 (dd, J = 7.8 Hz, 1.5 Hz, 1 H), 6.01 (s, 1 H), 4.19-4.10 (m, 2 H), 1.71 (s, 3 H), 1.20 (t, J = 7.1 Hz, 3 H); ^{13}C NMR (125 MHz) δ 198.4, 169.6, 153.7, 143.1, 136.0, 132.1, 129.1 (two carbons), 128.9, 128.8 (br, two carbons), 128.6, 127.4, 122.7, 121.9, 116.7, 72.5, 61.5, 30.4, 14.1 (some of the signals appeared broad due to a hindered rotation about the bond between the C4 of the benzopyran ring and the phenyl substituent); IR (neat, cm^{-1}): 1736 (s), 1658 (s); MS (EI) m/z (relative intensity) 322 (M^+ , 20), 279 (45), 249 (100), 205 (20), 178 (20); HRMS (FAB) calcd for $C_{20}H_{19}O_4$ ($M+H^+$) 323.1283 found 323.1298;

4-(1-Cyclohexenyl)-2,3-bis(ethoxycarbonyl)-2H-1-benzopyran (13). Treatment of the palladacycle **5b** (0.147 g, 0.182 mmol) and ethyl-3-(1-cyclohexenyl)-2-propynoate⁶ (0.072 g, 0.403 mmol), added as a solution in 1,2-dichloroethane (1.5 mL), for 5 h at 80 °C and for 20 h at rt according to the general procedure described above afforded the benzopyran **13** (0.037 g, 57%) as a yellow oil: R_f = 0.40 (EtOAc/hexane 1 : 3); 1H NMR (500 MHz, run at 50 °C, $CDCl_3$) δ 7.27 (dd, J = 7.8 Hz, 1.5 Hz, 1 H), 7.25 (t, J = 7.6 Hz, 1 H), 6.98 (dd, J = 8.0 Hz, 1.0 Hz, 1 H), 6.93 (td, J = 7.5 Hz, 1.1 Hz, 1 H), 5.78 (s, 1 H), 5.53 (s, br, 1 H), 4.29-4.21 (m, 2 H), 4.16-4.10 (m, 2 H), 2.26-2.15 (m, 4 H), 1.83-1.76 (m, 2 H), 1.72-1.67 (m, 2 H), 1.32 (t, J = 11.6 Hz, 3 H), 1.18 (t, J = 10.0 Hz, 3 H); ^{13}C NMR (125 MHz, run at 62 °C in $CDCl_3$) δ 169.5, 164.9, 154.0, 147.0, 133.9, 131.6, 127.6, 125.9, 121.9, 121.8, 116.8, 116.5, 72.4, 61.4, 60.6, 28.8 (br), 25.2, 22.7, 22.0, 14.3, 14.0 (spectrum was run at elevated temperature due to the significant line broadening caused by a hindered rotation about the bond between C4 of the benzopyran ring and the cyclohexyl substituent that was observed at 25°C); IR (neat, cm^{-1}): 1752 (m), 1719 (s); 1687 (s); MS (EI) m/z (relative intensity)

356 (M^+ , 25), 237 (20), 283 (100), 203 (10), 175 (15); HRMS (FAB) calcd for $C_{21}H_{25}O_5$ ($M+H^+$) 357.1702 found 357.1706.

2,3-Bis(ethoxycarbonyl)-4-trimethylsilyl-2H-1-benzopyran (14). Treatment of the palladacycle **5b** (0.150 g, 0.185 mmol) and ethyl (3-trimethylsilyl)propynoate (0.077 mL, 0.069 g, 0.405 mmol) for 7 h at 80 °C and for 20 h at rt according to the general procedure described above afforded the benzopyran **14** (0.023 g, 36%) as a yellow solid: mp = 93–94 °C (ether/hexane, 1 : 6); R_f = 0.50 (EtOAc/hexane 1 : 3); 1H NMR (500 MHz) δ 7.25 (dd, J = 8.7 Hz, 1.2 Hz, 1 H), 7.21 (td, J = 7.4 Hz, 1.5 Hz, 1 H), 7.07 (dd, J = 8.1 Hz, 1.2 Hz, 1 H), 6.94 (td, J = 7.6 Hz, 1.2 Hz, 1 H), 5.71 (s, 1 H), 4.40–4.33 (m, 1 H), 4.25–4.17 (m, 1 H), 4.09–4.02 (m, 2 H), 1.36 (t, J = 7.1 Hz, 3 H), 1.13 (t, J = 7.1 Hz, 3 H), 0.29 (s, 9 H); ^{13}C NMR (125 MHz) δ 168.7, 167.1, 152.4, 143.5, 136.0, 130.1, 128.7, 124.9, 121.6, 117.4, 72.4, 61.4 (2 carbons), 14.0, 13.9, 1.3 (3 carbons); IR (neat, cm^{-1}): 1752 (s), 1728 (s), 1707 (s); MS (EI) m/z (relative intensity) 348 (M^+ , 28), 333 (70), 275 (100), 247 (50), 231 (60); HRMS (FAB) calcd for $C_{18}H_{25}O_5Si$ ($M+H^+$) 349.1471, found 349.1455.

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1a
 ^{13}C NMR (125 MHz, CDCl_3)

1a

¹H NMR (500 MHz, CDCl₃)

1c
¹H NMR (400 MHz, CDCl₃)

1c
 ^{13}C NMR (125 MHz, CDCl_3)

2d
 ^1H NMR (500 MHz, CDCl_3)

2d
 ^{13}C NMR (125 MHz, CDCl_3)

2e
¹H NMR (500 MHz, CDCl₃)

2e
 ^{13}C NMR (125 MHz, CDCl_3)

3a
¹H NMR (500 MHz, CDCl₃)

3a
 ^{13}C NMR (125 MHz, CDCl_3)

3b
 ^1H NMR (500 MHz, CDCl_3)

3b
¹³C NMR (125 MHz, CDCl₃)

3c
¹H NMR (400 MHz, CDCl₃)

3c
 ^{13}C NMR (125 MHz, CDCl_3)

3e
¹H NMR (500 MHz, CDCl₃)

3e
 ^{13}C NMR (125 MHz, CDCl_3)

5a
 ^1H NMR (500 MHz, CDCl_3)

5a
 ^{13}C NMR (125 MHz, CDCl_3)

5b
¹H NMR (500 MHz, CDCl₃)

5b

¹³C NMR (125 MHz, CDCl₃)

5c

^1H NMR (500 MHz, CDCl_3)