

## An Efficient Intermolecular Palladium-Catalyzed Synthesis of Aryl Ethers

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### Supporting Information.

**General Considerations.** All reactions were carried out under an argon atmosphere in oven-dried glassware. THF and diethyl ether (Et<sub>2</sub>O) were distilled under argon from the sodium ketyl of benzophenone and toluene was distilled under nitrogen from molten sodium. Alternatively, toluene, THF, and Et<sub>2</sub>O were purchased from J. T. Baker in CYCLE-TAINER<sup>®</sup> solvent delivery kegs, which were vigorously purged with argon for 2 h, and further purified by passing the solvent through two packed columns of neutral alumina and copper (II) oxide under argon pressure. 1-Butanol, benzyl alcohol, and 2-methyl-1-propanol were purchased from Aldrich in Sure-Seal<sup>®</sup> bottles and used without further purification. All other alcohols were purchased from Alfa Aesar or Aldrich, degassed with argon, and stored over 3Å molecular sieves before use. Di-*tert*-butylchlorophosphine, 9-bromoanthracene, 2-bromofluorobenzene, 2-bromochlorobenzene, 2-bromophenol, cyclohexylzinc bromide in THF (0.5 M), magnesium powder (50 mesh) and DMAP were purchased from Aldrich and used without further purification. Anhydrous Cs<sub>2</sub>CO<sub>3</sub> was purchased from Chemetall; the bulk of the material was stored under nitrogen in a Vacuum Atmospheres glovebox. Small portions (1-2 g) were removed from the glovebox in glass vials, stored in the air in desiccators filled with anhydrous calcium sulfate, and weighed in the air. Pd(OAc)<sub>2</sub>, 2,2'-dibromo-1,1'-binaphthyl, *n*-BuLi in hexanes, copper (I) chloride, bis(2-diphenylphosphinophenyl)ether (DPEphos), 2-*N,N*-dimethylamino-2'-diphenylphosphinobiphenyl, 2-di-cyclohexylphosphinobiphenyl and 2-(di-*tert*-butylphosphino)biphenyl were purchased from Strem chemical company and used without further purification. di-*tert*-butyl dicarbonate was purchased from Lancaster and used without further purification. 5-Bromoindole, 6-bromoindole and 5-bromo-7-nitroindole were generously donated

by 3D Pharmaceuticals. 2-(*N,N*-dimethylamino)-2'-di-*tert*-butylphosphinobiphenyl,<sup>1</sup> 2-di-*tert*-butylphosphinobiphenyl-2'-isopropylbiphenyl,<sup>1</sup> 1-(2-di-*tert*-butylphosphino)-*o*-terphenyl,<sup>3</sup> 1-(2-di-*tert*-butylphosphinophenyl)naphthalene,<sup>1</sup> 2-(di-*tert*-butylphosphino)-1,1'-binaphthyl,<sup>2</sup> 2-(*N,N*-Dimethylamino)-2'-di-*tert*-butylphosphino-1,1'-binaphthyl,<sup>3</sup> 2,2'-dibromo-5, 5', 6, 6', 7, 7', 8, 8'-octahydro-1,1'-binaphthyl,<sup>4</sup> 5-bromoindole-1-carboxylic acid *tert*-butyl ester,<sup>5</sup> 3-bromo-benzoic acid-*tert*-butyl ester,<sup>6</sup> 4-bromo-benzoic acid-*tert*-butyl ester,<sup>7</sup> 4-bromo-3-iodoanisole<sup>2</sup> and 1-bromo-2-isopropyl-naphthalene<sup>11</sup> were synthesized according to the known literature procedures. 4-Bromo-3-ethyl-1-methoxybenzene, 4-bromo-3-*n*-propyl-1-methoxybenzene, 4-bromo-3-isopropyl-1-methoxybenzene, and 4-bromo-3-*tert*-butyl-1-methoxybenzene were synthesized from the corresponding *meta*-alkylphenols. Methylation of the phenols with dimethyl sulfate followed by selective bromination *para* to the methoxy group with NBS and silica gel<sup>8</sup> gave the aryl halides in good yield. Silica gel chromatography purifications were performed by flash chromatography using Silicycle ultra pure silica gel (230-400 mesh) or EM Science Silica gel 60 packed columns. Yields refer to isolated yields of compounds greater than 95% purity as determined by capillary gas chromatography (GC), and proton Nuclear Magnetic Resonance spectroscopy (<sup>1</sup>H NMR) analysis. New compounds were also characterized by elemental analysis (Atlantic Microlabs, Norcross, GA). Yields reported in this section refer to a single experiment whereas those reported in Tables 1 and 2 and Scheme 2 are an average of two or more runs. IR spectra were obtained by placing neat samples directly on the DiComp probe of an ASI REACTIR *in situ* IR instrument. Mass Spectra (GC/MS) were recorded on a Hewlett Packard model GCD. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Varian XL 300 or Varian XL 500 with chemical shifts reported in ppm relative to the residual deuterated solvent. Gas chromatography analyses were performed on a Hewlett Packard 5890 instrument with a FID detector and a Hewlett Packard 25 m x 0.2 mm i.d. HP-5 capillary column or a Hewlett Packard 6890 instrument with a FID detector and a Hewlett Packard 10 m x 0.1 mm i.d. HP-1 column. The procedures described in this section are representative; thus, the yields may differ slightly from those given in Tables 1, 2, 3, 4.

## Synthesis of Ligands

### 2-Trimethylsilyl-2'-di<sup>t</sup>-butylphosphino-1,1'-binaphthyl (Table 4, ligand **1**, R' = TMS)

A Schlenk tube was charged with 2,2'-dibromo-1,1'-binaphthyl (412 mg, 1.0 mmol) and capped with a rubber septum. THF (5 ml) was added via syringe. The solution was cooled down to -78°C with dry ice and acetone. n-BuLi in hexane (1.6 M, 0.7 ml, 1.1 mmol) was added dropwise. The resulting mixture was slowly warmed up to -60°C over 2 h. Then TMSCl in THF (1 M, 2.0 ml, 2.0 mmol) was added dropwise at -60°C. The reaction mixture was allowed to warm up to room temperature over 1 h and stirred overnight. The reaction mixture was concentrated *in vacuo*. Chromatography on silica gel with hexane gave white solid 260 mg, consisting of 2-bromo-2'-trimethylsilyl-1,1'-binaphthyl and 2,2'-trimethylsilyl-1,1'-binaphthyl in a 3.2 : 1 ratio determined by GC. A Schlenk tube was charged with the material obtained above and magnesium powder (24 mg, 1.0 mmol), then capped with rubber septum. 2 ml THF was added via syringe. The reaction mixture was heated up to 60°C. At this point, 1,2-dibromoethane (9 µl, 0.1 mmol) was added. The reaction mixture was stirred at 60°C for 2 h and subsequently cooled to 0°C. Copper(I) chloride (50 mg, 0.5 mmol) was added. The reaction mixture was stirred at 0°C for 30 sec, then di-tert-butylchlorophosphine (190 µl, 1.0 mmol) was added via syringe. The mixture was heated up to 60°C and stirred for 15 h. After cooling to room temperature, 30% aqueous NH<sub>4</sub>OH (50 ml) was added into the reaction mixture. The resulting suspension was extracted with ethyl acetate (2 x 30 ml). The combined organic extracts were washed with 30% aqueous NH<sub>4</sub>OH (2 x 50 ml), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated *in vacuo*. Purification of the crude material by flash chromatography on silica gel with 20 : 1 hexane : ethyl acetate followed by recrystallization from methanol gave 70 mg (15%) of the title compound as a white solid. Mp: 166-168 °C (Ether). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>) δ 7.97 (d, 1H, J = 8.4 Hz), 7.77 (d, 1H, J = 8.4 Hz), 7.69 (d, 1H, J = 8.4 Hz), 7.68-7.60 (m, 3H), 7.36 (d, 1H, J = 8.7 Hz), 7.32 (d, 1H, J = 8.4 Hz), 7.24-7.12 (m, 2H), 7.00 (t, 1H, J = 8.4 Hz), 6.90 (t, 1H, J = 8.4 Hz), 1.10 (d, 9H, J<sub>HP</sub> = 11.4 Hz), 1.07 (d, 9H, J<sub>HP</sub> = 11.4 Hz), -0.21 (s, 9H). <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>) δ 150.2, 149.8, 145.2, 145.1, 139.64, 139.62, 136.9, 136.5, 135.6, 135.5, 134.7, 134.6, 134.24, 134.23, 134.1, 132.91,

132.89, 131.0, 129.45, 129.43, 128.99, 128.96, 128.2, 127.6, 127.3, 126.7, 126.6, 126.5, 125.9, 33.8, 33.4, 33.3, 33.0, 32.2, 32.0, 31.6, 31.4, 0.83 (observed complexity due to P-C splitting).  $^{31}\text{P}$  NMR (121 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  22.0. IR (neat,  $\text{cm}^{-1}$ ) 3049, 2954, 2894, 2861, 1499, 1474, 1362, 1248, 880, 832, 810, 747, 685. HRMS (ESI) calcd for  $\text{C}_{31}\text{H}_{39}\text{PSi}$   $[\text{M}+\text{H}]^+$  471.2631, found 471.2647.

**2-Phenyl-2'-di<sup>t</sup>-butylphosphino-1,1'-binaphthyl** (Table 4, ligand **2**, R' = Ph)

A Schlenk tube was charged with 2,2'-dibromo-1,1'-binaphthyl (206 mg, 0.50 mmol), phenylboronic acid (65 mg, 0.53 mmol),  $\text{K}_3\text{PO}_4$  (318 mg, 1.5 mmol),  $\text{Pd}(\text{OAc})_2$  (4.5 mg, 0.020 mmol), 2-N,N-dimethylamino-2'-diphenylphosphinobiphenyl (15.3 mg, 0.040 mmol) and capped with a rubber septum. Toluene (1 ml) was added via syringe. The reaction mixture was heated up to  $85^\circ\text{C}$  and stirred for 15 h. After cooling to room temperature, the reaction mixture was filtered through celite with ether. The filtrate was concentrated *in vacuo* and chromatography on silica gel with hexane gave white solid 123 mg, consisting of 2-bromo-2'-phenyl-1,1'-binaphthyl and 2-phenyl-1,1'-binaphthyl in a 9 : 1 ratio determined by GC. A Schlenk tube was charged with the material obtained above and magnesium powder (15 mg, 0.60 mmol), then capped with rubber septum. 2 ml THF was added via syringe. The reaction mixture was heated up to  $60^\circ\text{C}$ . At this point, 1,2-dibromoethane (6  $\mu\text{l}$ , 0.060 mmol) was added. The reaction mixture was stirred at  $60^\circ\text{C}$  for 2 h and subsequently cooled to  $0^\circ\text{C}$ . Copper(I) chloride (30 mg, 0.30 mmol) was added. The reaction mixture was stirred at  $0^\circ\text{C}$  for 30 sec, then di-tert-butylchlorophosphine (114  $\mu\text{l}$ , 0.60 mmol) was added via syringe. The mixture was heated up to  $60^\circ\text{C}$  and stirred for 15 h. After cooling to room temperature, 30% aqueous  $\text{NH}_4\text{OH}$  (50 ml) was added into the reaction mixture. The resulting suspension was extracted with ethyl acetate (2 x 30 ml). The combined organic extracts were washed with 30% aqueous  $\text{NH}_4\text{OH}$  (2 x 50 ml), dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated *in vacuo*. Purification of the crude material by flash chromatography on silica gel with 20 : 1 hexane : ethyl acetate gave 64 mg (27%) of the title compound as a white solid. Mp:  $179\text{--}181^\circ\text{C}$  (Ether).  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.82 (d, 1H, J = 8.7 Hz), 7.77 (d, 1H, J = 8.7 Hz),

7.69-7.54 (m, 5H), 7.40-7.34 (m, 2H), 7.20 (t, 1H,  $J = 6.9$  Hz), 7.09 (t, 1H,  $J = 7.8$  Hz), 0.79 (d, 9H,  $J_{HP} = 11.1$  Hz), 0.77 (d, 9H,  $J_{HP} = 11.1$  Hz).  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  147.4, 146.9, 144.02, 144.00, 140.35, 140.29, 136.39, 136.35, 136.3, 135.9, 135.5, 135.4, 135.1, 133.73, 133.71, 133.48, 133.45, 133.4, 131.1, 130.1, 129.6, 129.22, 129.19, 129.0, 128.8, 128.5, 127.2, 127.0, 126.7, 126.1, 125.8, 33.5, 33.1, 31.8, 31.7, 31.5, 30.9, 30.7 (observed complexity due to P-C splitting).  $^{31}\text{P}$  NMR (121 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  23.0. IR (neat,  $\text{cm}^{-1}$ ) 3056, 2956, 2892, 1596, 1474, 1362, 1171, 1030, 1021, 820, 762, 698. HRMS (ESI) calcd for  $\text{C}_{34}\text{H}_{35}\text{P}$   $[\text{M}+\text{H}]^+$  475.2549, found 475.2536.

**2-Cyclohexyl-2'-di<sup>t</sup>-butylphosphino-1,1'-binaphthyl** (Table 4, ligand **2**,  $\text{R}' = \text{Cy}$ )

A Schlenk tube was charged with 2,2'-dibromo-1,1'-binaphthyl (1.24 g, 3.0 mmol),  $\text{Pd}_2(\text{DBA})_3$  (69 mg, 0.075 mmol), DPEphos (97 mg, 0.18 mmol) and capped with a rubber septum. Cyclohexylzincbromide in THF (0.5 M, 6.5 ml, 3.3 mmol) was added via syringe. The rubber septum was replaced with a Teflon screw cap under a flow of Argon. The reaction mixture heated up to  $90^\circ\text{C}$  and stirred for 16 h. After cooling to room temperature, the reaction mixture was filtered through celite with ether. The filtrate was concentrated *in vacuo*. Chromatography on silica gel with hexane followed by recrystallization from ether gave white solid 0.73 g, consisting of 2-bromo-2'-cyclohexyl-1,1'-binaphthyl, 2-bromo-1,1'-binaphthyl, 1,1'-binaphthyl and 2,2'-dibromo-1,1'-binaphthyl in a 2.5 : 1 : 2 : 2.5 ratio determined by GC. A Schlenk tube was charged with the material obtained above and magnesium powder (44 mg, 1.8 mmol), then capped with a rubber septum. 3 ml THF was added via syringe. The reaction mixture was heated up to  $60^\circ\text{C}$ . At this point, 1,2-dibromoethane (19  $\mu\text{l}$ , 0.22 mmol) was added. The reaction mixture was stirred at  $60^\circ\text{C}$  for 2 h and subsequently cooled to  $0^\circ\text{C}$ . Copper(I) chloride (110 mg, 1.1 mmol) was added. The reaction mixture was stirred at  $0^\circ\text{C}$  for 30 sec, then di-tert-butylchlorophosphine (350  $\mu\text{l}$ , 1.8 mmol) was added via syringe. The mixture was heated up to  $60^\circ\text{C}$  and stirred for 36 h. After cooling to room temperature, 30% aqueous  $\text{NH}_4\text{OH}$  (50 ml) was added into the reaction mixture. The resulting suspension was extracted with ethyl acetate (2 x 50 ml). The combined

organic extracts were washed with 30% aqueous  $\text{NH}_4\text{OH}$  (2 x 50 ml), dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated *in vacuo*. Purification of the crude material by flash chromatography on silica gel with 20 : 1 hexane : ethyl acetate followed by separation on preparative TLC gave 30 mg (2%) of the title compound as a white solid. Mp: 166-168 °C (Ether).  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  8.04 (d, 1H,  $J = 8.7$  Hz), 7.81 (d, 1H,  $J = 8.7$  Hz), 7.70-7.54 (m, 4H), 7.26 (d, 1H,  $J = 8.7$  Hz), 7.20-7.05 (m, 2H), 6.88-6.72 (m, 3H), 2.83-2.68 (m, 1H), 2.56-2.45 (m, 1H), 1.90-1.60 (m, 3H), 1.50-0.70 (m, 5H), 1.29 (d, 9H,  $J_{\text{HP}} = 11.1$  Hz), 0.86 (d, 9H,  $J_{\text{HP}} = 11.4$  Hz), 0.69-0.52 (m, 1H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  148.2, 147.7, 144.00, 143.98, 137.0, 136.6, 135.4, 135.3, 135.2, 135.1, 134.9, 134.26, 134.24, 133.07, 133.05, 133.00, 129.5, 129.11, 129.08, 129.0, 128.2, 127.2, 126.6, 126.5, 125.6, 125.5, 125.2, 42.23, 42.21, 36.3, 33.6, 33.3, 32.9, 32.61, 32.57, 32.5, 32.3, 31.1, 30.9, 27.1, 26.8 (observed complexity due to P-C splitting).  $^{31}\text{P}$  NMR (121 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  22.5. IR (neat,  $\text{cm}^{-1}$ ) 3056, 2929, 2858, 1507, 1474, 1362, 1171, 1021, 818, 747, 693. HRMS (ESI) calcd for  $\text{C}_{34}\text{H}_{41}\text{P}$   $[\text{M}+\text{H}]^+$  481.3019, found 481.3009.

### **9-(2-Di-*tert*-butylphosphinophenyl)-anthracene** (Table 4, ligand 5)

An oven-dried 100 mL Schlenk tube with stirbar was charged with magnesium turnings (210 mg, 8.5 mmol). The flask was evacuated and back-filled with argon. A solution of 9-bromoanthracene (2.0 g, 7.8 mmol) in 15 mL of 5:1 diethyl ether/THF was added dropwise with constant stirring. The reaction mixture was heated to 45 °C for 5.5 hours and then allowed to cool to room temperature. After the addition of magnesium turnings (160 mg, 6.5 mmol) and 2-bromofluorobenzene (700  $\mu\text{L}$ , 6.5 mmol), the reaction mixture was stirred at room temperature for 16 hours. Copper (I) chloride (770 mg, 7.8 mmol) was added under an argon purge. The tube was charged with di-*tert*-butylchlorophosphine (1.50 mL, 7.8 mmol) and the reaction mixture was heated to 60 °C for 22 hours. The reaction mixture was diluted with 30 mL 1:1 hexane/ethyl acetate, 15 mL water and 8 mL of 30 % aqueous ammonium hydroxide. The layers were separated and the aqueous layer was extracted with 1:1 hexanes/ ethyl acetate (3 x 50 mL). The combined organic extracts were washed with water (1 x 50 mL) and brine (1 x 50 mL), dried over  $\text{MgSO}_4$ , filtered and concentrated

to leave a yellow solid. The crude material was purified by chromatography on silica gel eluting with 4:1 hexanes/toluene and then 4:1 hexanes/ethyl acetate to yield a pale yellow solid. This crude solid was further purified by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/MeOH to yield 130 mg (4 %) of the title compound as a pale yellow crystalline solid, mp 220-221 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.49 (s, 1H), 8.07 (m, 1H), 8.02 (d, *J*<sub>HH</sub> = 8.5 Hz, 2H), 7.54 (m, 3H), 7.51 (s, 1H), 7.41 (t, *J*<sub>HH</sub> = 7 Hz, 3H), 7.27 (t, *J*<sub>HH</sub> = 8.5 Hz, 2H), 1.01 (d, *J*<sub>HP</sub> = 12 Hz, 18H); <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>) δ 22.0; <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 147.4 (d, *J*<sub>CP</sub> = 34 Hz), 139.4 (d, *J*<sub>CP</sub> = 30 Hz), 138.2 (d, *J*<sub>CP</sub> = 6 Hz), 136.4, 132.8 (d, *J*<sub>CP</sub> = 7 Hz), 131.3, 130.7 (d, *J*<sub>CP</sub> = 9 Hz), 128.8, 128.6, 128.5, 126.8, 126.6, 125.0, 124.5, 32.6 (d, *J*<sub>CP</sub> = 25 Hz), 31.3 (d, *J*<sub>CP</sub> = 15 Hz); IR (neat, cm<sup>-1</sup>) 3049, 2977, 2952, 2892, 2863, 1472, 1459, 1385, 1362, 1175, 1156, 1119, 1017, 934, 884, 845, 758, 737. HRMS (EI) calcd for C<sub>28</sub>H<sub>31</sub>P (M<sup>+</sup>) 398.2158, found 398.2158.

#### **1-(2-Di-*tert*-butylphosphinophenyl)-2-isopropyl-naphthalene** (Table 4, ligand **6**)

An oven-dried Schlenk tube was charged with magnesium powder (0.12 g, 5 mmol), 1-bromo-2-isopropyl-naphthalene (0.50g, 2 mmol) and 5 ml THF. The mixture was heated to 60°C, and 1,2-dibromoethane (35 µl, 0.4 mmol) was added dropwise via syringe over 15 min. The mixture was heated at 60°C for 1 h and then 2-bromochlorobenzene (235 µl, 2.0 mmol) was added dropwise. The resulting mixture was heated for 2 h at 60°C and subsequently cooled to 0°C. Copper(I) chloride (200 mg, 2.0 mmol) was added. The reaction mixture was stirred at 0°C for 1 min, then di-*tert*-butylchlorophosphine (760 µl, 4.0 mmol) was added via syringe. The mixture was heated up to 60°C and stirred for 15 h. After cooling to room temperature, 30% aqueous NH<sub>4</sub>OH (50 ml) was added into the reaction mixture. The resulting suspension was extracted with ethyl acetate (2 x 50 ml). The combined organic extracts were washed with 30% aqueous NH<sub>4</sub>OH (2 x 50 ml), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated *in vacuo*. The crude material was passed through a silica gel column with 10 : 1 hexane : ethyl acetate to give 280 mg white solid which was about 90% pure. 80 mg of this white solid was dissolved in 0.5 ml THF and 2 ml of BH<sub>3</sub> in THF (1 M) solution was added dropwise. The mixture was stirred at room temperature for 2 h and then

concentrated *in vacuo*. Chromatography on silica gel with 10 : 1 hexane : ethyl acetate gave a white solid which was further purified by recrystallization from methanol to yield white crystals. The crystals was dissolved in 2 ml triethylamine and stirred overnight. The reaction mixture was concentrated *in vacuo* and chromatography on silica gel with 10 : 1 hexane : ethyl acetate gave 40 mg of the title compound as a white solid. Mp: 141-142 °C (Ether). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>) δ 7.92-7.84 (m, 1H), 7.72 (d, 1H, J = 8.4 Hz), 7.65 (d, 1H, J = 7.5 Hz), 7.43 (d, 1H, J = 8.7 Hz), 7.32 (d, 1H, J = 8.7 Hz), 7.24-7.02 (m, 5H), 3.15 (septet, 1H, J = 6.9 Hz), 1.46 (d, 3H, J = 6.6 Hz), 1.17 (d, 9H, J<sub>HP</sub> = 11.1 Hz), 1.04 (d, 3H, J = 6.9 Hz), 0.87 (d, 9H, J<sub>HP</sub> = 11.1 Hz). <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>) δ 148.8, 148.4, 143.81, 143.79, 138.9, 138.5, 137.8, 137.7, 136.8, 136.7, 134.57, 134.56, 133.3, 133.2, 133.0, 129.02, 129.01, 128.94, 128.92, 126.6, 125.4, 125.2, 124.0, 33.1, 33.0, 32.8, 32.6, 32.0, 31.8, 31.63, 31.60, 31.2, 31.0, 26.0, 22.84, 22.80 (observed complexity due to P-C splitting). <sup>31</sup>P NMR (121 MHz, C<sub>6</sub>D<sub>6</sub>) δ 21.1. IR (neat, cm<sup>-1</sup>) 2962, 2863, 1461, 1362, 1173, 818, 762, 747. HRMS (ESI) calcd for C<sub>27</sub>H<sub>35</sub>P [M+H]<sup>+</sup> 391.2549, found 391.2530.

### **2-Bromo-5, 5', 6, 6', 7, 7' 8, 8'-octahydro-[1,1']-binaphthyl**

An oven-dried 100 mL Schlenk tube with stirbar was charged with dibromide (1.2 g, 2.9 mmol). The flask was evacuated and back-filled with argon. THF (20 mL) was added to dissolve the dibromide. The solution was cooled to -50 °C and *n*-butyl lithium (1.8 mL, 1.6 M in hexanes, 2.9 mmol) was added dropwise. After 1 hour the solution was cooled to -78 °C and 1N HCl (0.45 mL) was added dropwise. The solution was allowed to warm to room temperature slowly over 4 hours. The solution was concentrated and the residue was dissolved in 50 mL of diethyl ether and 25 mL of 1N HCl. The layers were separated and the water layer was extracted with diethyl ether (2 x 15 mL). The combined organic extracts were washed with saturated aqueous sodium bicarbonate (1 x 30 mL), water (1 x 30 mL) and brine (1 x 30 mL). The solution was dried over MgSO<sub>4</sub>, filtered and concentrated to leave a white solid. This crude material was recrystallized

from 1:4 ethyl acetate/95 % ethanol to afford 0.82 g (84 %) of a white crystalline solid. This material was used without further purification.

***rac*-2-(Di-*tert*-butylphosphino)-5, 5', 6, 6', 7, 7', 8, 8'-octahydro-[1,1']-binaphthyl** (Table 4, ligand 7)

An oven-dried 100 mL Schlenk tube with stirbar was charged with magnesium turnings (42 mg, 1.7 mmol). The flask was evacuated and back-filled with argon. A solution of 2-Bromo-5, 5', 6, 6', 7, 7', 8, 8'-octahydro-[1,1']-binaphthyl (0.53 g, 1.6 mmol) in 5 mL of THF was added dropwise with constant stirring. The reaction mixture was heated to 65 °C for 4 hours and then was allowed to cool to room temperature. Copper (I) chloride (190 mg, 1.9 mmol) was added to the reaction mixture under an argon purge. The tube was charged with di-*tert*-butylchlorophosphine (0.36 mL, 1.9 mmol) and additional THF (1 mL). The reaction mixture was heated to 65 °C for 24 hours. The reaction mixture was allowed to cool to room temperature, then 40 mL of 1:1 hexane/ethyl acetate, 20 mL water, and 10 mL of 30 % aqueous ammonium hydroxide were added and the mixture transferred to a separatory funnel. The water layer was extracted with ethyl acetate (2 x 30 mL). The combined organic extracts were washed with water (50 mL) and brine (50 mL), dried over anhydrous sodium sulfate, filtered and concentrated to leave an oily white solid. This crude material was recrystallized from 95:5 ethyl acetate/ethanol to afford 65 mg (10 %) of the title compound as a white crystalline solid, mp 130-131 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.61 (d, *J*<sub>HH</sub> = 7 Hz, 1H), 7.07 (m, 3H), 6.77 (dd, *J*<sub>HH</sub> = 2.5, 7 Hz, 1H), 2.83 (m, 4H), 2.40 (m, 1H), 2.18 (m, 1H), 2.08 (m, 1H), 2.00 (m, 1H), 1.62-1.85 (m, 8H), 1.18 (d, *J*<sub>HP</sub> = 11.5 Hz, 9H), 1.13 (d, *J*<sub>HP</sub> = 11.5 Hz, 9H); <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>) δ 20.8; <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 150.1 (d, *J*<sub>CP</sub> = 33 Hz), 141.4 (d, *J*<sub>CP</sub> = 8 Hz), 138.4, 136.8, 135.8 (d, *J*<sub>CP</sub> = 7 Hz), 135.1, 132.9 (d, *J*<sub>CP</sub> = 25 Hz), 132.6, 128.5, 127.9, 126.9, 124.4, 33.5 (d, *J*<sub>CP</sub> = 24 Hz), 32.5 (d, *J*<sub>CP</sub> = 25 Hz), 31.8 (d, *J*<sub>CP</sub> = 16 Hz), 31.0 (d, *J*<sub>CP</sub> = 15 Hz), 30.3, 30.1, 28.5, 28.0, 23.7, 23.4, 23.3, 22.9; IR (neat, cm<sup>-1</sup>) 2933, 2860, 1580, 1474, 1451, 1362, 1173, 807, 778, 733. HRMS (EI) calcd for C<sub>28</sub>H<sub>39</sub>P (M<sup>+</sup>) 406.2784, found 406.2767.

**2-*N,N*-Dimethylamino-2'-di-*tert*-butylphosphino-5, 5', 6, 6', 7, 7', 8, 8'-octahydro-1,1'-binaphthyl** (Table 4, ligand **8**)

A Schlenk tube was charged with 2,2'-dibromo-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl (0.42 g, 1.0 mmol), Pd<sub>2</sub>(DBA)<sub>3</sub> (18.3 mg, 0.02 mmol), DPEphos (27 mg, 0.05 mmol), NaO<sup>t</sup>-Bu (144 mg, 1.5 mmol) and capped with a rubber septum. Benzophenone imine (235.6 mg, 1.3 mmol) and 2 ml toluene were added via syringe. The rubber septum was replaced with a Teflon screw cap under a flow of Argon. The reaction mixture was heated up to 100°C and stirred for 20 h. After cooling to room temperature, the reaction mixture was concentrated *in vacuo*, followed by the addition of 20 ml THF, 10 ml water and 5 ml of 2 M aqueous HCl solution. The mixture was stirred at room temperature for 1 h. Then 0.5 M aqueous NaOH solution was added to basify the solution. The resulting solution was extracted with dichloromethane (3 x 30 ml). The combined organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated *in vacuo*. Purification of the crude material by flash chromatography on silica gel with 15 : 1 hexane : ethyl acetate gave 227 mg (64%) of 2-amino-2'-bromo-5, 5', 6, 6', 7, 7', 8, 8'-octahydro-1,1'-binaphthyl as a white solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.44 (d, 1H, J = 8.1 Hz), 6.97 (d, 1H, J = 8.4 Hz), 6.96 (d, 1H, J = 8.1 Hz), 6.61 (d, 1H, J = 7.8 Hz), 3.20 (s, 2H), 2.86-2.66 (m, 4H), 2.46-2.16 (m, 3H), 2.08-1.92 (m, 1H), 1.82-1.58 (m, 8H). A Schlenk tube was charged with the material obtained above (214 mg, 0.60 mmol) and Na<sub>2</sub>CO<sub>3</sub> (160 mg, 1.5 mmol), then capped with a rubber septum. 3 ml DMF and iodomethane (256 mg, 1.8 mmol) were added via syringe. The rubber septum was replaced with a Teflon screw cap under a flow of Argon. The reaction mixture was heated up to 50°C and stirred for 12 h. The reaction mixture was cooled to room temperature, diluted with ether and filtered through a pad of celite. The filtrate was concentrated *in vacuo* and purification of the crude material by flash chromatography on silica gel with 15 : 1 hexane : ethyl acetate gave 192 mg (83%) of 2-*N,N*-dimethylamino-2'-bromo-5, 5', 6, 6', 7, 7', 8, 8'-octahydro-1,1'-binaphthyl as a white solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.38 (d, 1H, J = 8.4 Hz), 7.11 (d, 1H, J = 8.1 Hz), 6.98 (d, 1H, J = 8.4 Hz), 6.92 (d, 1H, J = 8.1 Hz), 2.88-2.68 (m, 4H), 2.50 (s, 6H), 2.46-2.30

(m, 2H), 2.10-1.86 (m, 2H), 1.80-1.56 (m, 8H). The white solid (192 mg, 0.50 mmol) and magnesium powder (24 mg, 1.0 mmol) were loaded into a Schlenk tube, and capped with a rubber septum. 2 ml THF was added via syringe. The reaction mixture was heated up to 60°C. At this point, 1,2-dibromoethane (9 µl, 0.10 mmol) was added. The reaction mixture was stirred at 60°C for 1 h and subsequently cooled to 0°C. Copper(I) chloride (50 mg, 0.50 mmol) was added. The reaction mixture was stirred at 0°C for 30 sec, then di-tert-butylchlorophosphine (190 µl, 1.0 mmol) was added via syringe. The mixture was heated up to 60°C and stirred for 40 h. After cooling to room temperature, 30% aqueous NH<sub>4</sub>OH (50 ml) was added into the reaction mixture. The resulting suspension was extracted with ethyl acetate (2 x 50 ml). The combined organic extracts were washed with 30% aqueous NH<sub>4</sub>OH (2 x 50 ml), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated *in vacuo*. Purification of the crude material by flash chromatography on silica gel with 2 : 1 hexane : ethyl acetate gave 55 mg (25%) of the title compound as a white solid. Mp: 201-203 °C (Ether). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>) δ 7.72 (d, 1H, J = 7.5 Hz), 7.02 (d, 1H, J = 8.4 Hz), 6.95 (d, 1H, J = 7.5 Hz), 6.87 (d, 1H, J = 8.4 Hz), 2.80-2.10 (m, 8H), 2.40 (s, 6H), 1.80-1.20 (m, 8H), 1.29 (d, 9H, J<sub>HP</sub> = 10.8 Hz), 1.07 (d, 9H, J<sub>HP</sub> = 11.1 Hz). <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>) δ 149.8, 149.7, 149.0, 148.5, 138.63, 138.62, 137.4, 137.3, 136.6, 134.94, 134.86, 134.7, 134.5, 134.4, 134.3, 131.5, 129.4, 127.2, 117.3, 43.8, 33.3, 32.9, 32.6, 32.20, 32.17, 32.0, 30.9, 30.6, 30.4, 30.3, 29.49, 29.46, 28.9, 24.0, 23.9, 23.7 (observed complexity due to P-C splitting). <sup>31</sup>P NMR (121 MHz, C<sub>6</sub>D<sub>6</sub>) δ 24.4. IR (neat, cm<sup>-1</sup>) 2927, 2856, 2771, 1592, 1474, 1445, 1362, 1314, 1173, 1050, 974, 807. HRMS (ESI) calcd for C<sub>30</sub>H<sub>44</sub>NP [M+H]<sup>+</sup> 450.3284, found 450.3267.

## Synthesis of Substrates

### (2-Bromophenoxy)-triisopropylsilane (Table 1, entry 17)

A clean, dry 50 mL round bottom flask with stirbar was charged with imidazole (0.61 g, 9.0 mmol), 2-bromophenol (0.70 mL, 6.0 mmol) and 12 mL anhydrous DMF. Triisopropylchlorosilane (1.28 mL, 6.0 mmol) was added dropwise with constant stirring. After

19 hours, diethyl ether (80 mL) and water (40 mL) were added. The layers were separated and the organic layer was washed with water (2 x 40 mL), saturated aqueous copper sulfate (1 x 30 mL), water (2 x 20 mL) and brine (1 x 40 mL). The organic layer was dried over magnesium sulfate, filtered and concentrated to leave a pale yellow oil. The crude oil was purified by column chromatography on silica gel eluting with hexanes to afford 1.79 g (90 %) of a colorless liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 (d,  $J_{\text{HH}} = 7.5$  Hz, 1H), 7.15 (t,  $J_{\text{HH}} = 8$  Hz, 1H), 6.90 (d,  $J_{\text{HH}} = 8.5$  Hz, 1H), 6.80 (t,  $J_{\text{HH}} = 8$  Hz, 1H), 1.34 (septet, 3H), 1.14 (d, 18H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  153.2, 133.6, 128.4, 122.1, 119.9, 115.3, 18.2, 13.2; IR (neat,  $\text{cm}^{-1}$ ) 3058, 2926, 2871, 2824, 1567, 1472, 1440, 1114, 1023, 750, 658. Anal. Calcd for  $\text{C}_{15}\text{H}_{25}\text{BrSiO}$ : C, 54.70; H 7.65. Found: C, 54.56; H 7.46.

#### **6-Bromoindole-1-carboxylic acid *tert*-butyl ester** (Table 2, entry 16)

A clean, dry 50 mL Schlenk tube with stirbar was charged with 5-bromo-indole (0.40 g, 2.0 mmol). The flask was evacuated and back-filled with argon. THF (20 mL) was added to dissolve the indole followed by addition of DMAP (2.5 mg, 21  $\mu\text{mol}$ ) and di-*tert*-butyl dicarbonate (0.52 mL, 2.2 mmol). The mixture was stirred at room temperature under argon for 4 hours. The solvent was removed *in vacuo* to leave a golden oil. The crude material was purified by chromatography on silica gel eluting with 8:1 hexane/toluene to afford 0.60 g (99 %) of a white crystalline solid (mp 60-61  $^{\circ}\text{C}$ ).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.37 (br s, 1H), 7.57 (br s, 1H), 7.42 (d,  $J_{\text{HH}} = 8.5$  Hz, 1H), 7.35 (dd,  $J_{\text{HH}} = 2, 8.5$  Hz, 1H), 6.54 (d,  $J_{\text{HH}} = 4$  Hz, 1H), 1.68 (s, 9H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  149.6, 136.0, 129.5, 126.5, 126.1, 122.1, 118.6, 118.1, 107.2, 84.4, 28.3; IR (neat,  $\text{cm}^{-1}$ ) 2979, 1735, 1434, 1370, 1331, 1281, 1248, 1206, 1152, 1086, 1025, 888, 808, 768, 720. Anal. Calcd for  $\text{C}_{13}\text{H}_{14}\text{BrNO}_2$ : C, 52.72; H 4.77. Found: C, 52.75; H 4.77.

#### **1-Bromo-2-*n*-propyl-4-methoxybenzene** (Table 3, entry 4)

An oven-dried 200 mL Schlenk flask with stirbar was charged with *n*-propylanisole, 100 mL  $\text{CCl}_4$ , N-bromosuccinamide (2.0 g, 10 mmol), and silica gel (5.0 g). The flask was wrapped with aluminum foil and allowed to stir vigorously at ambient temperature for 39.5 hours. The reaction mixture was filtered through Celite, washed with water (2 x 100 mL), dried over magnesium sulfate, filtered and concentrated to leave a crude yellow oil. This material was purified by column chromatography on silica gel eluting with hexanes to afford 1.8 g (80 %) of a colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41 (d,  $J_{\text{HH}} = 8.5$  Hz, 1H), 6.77 (d,  $J_{\text{HH}} = 3$  Hz, 1H), 6.62 (dd,  $J_{\text{HH}} = 8.5, 3$  Hz, 1H), 3.79 (s, 3H), 2.67 (t, 2H), 1.65 (sextet, 2H), 0.99 (t, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  159.0, 143.1, 133.3, 116.3, 115.2, 113.0, 55.6, 38.6, 23.3, 14.1; IR (neat,  $\text{cm}^{-1}$ ) 2960, 2933, 2871, 1596, 1573, 1470, 1289, 1252, 1162, 1013, 799. Anal. Calcd for  $\text{C}_{10}\text{H}_{13}\text{BrO}$ : C, 52.42; H 5.72. Found: C, 52.18; H 5.75.

#### **1-Bromo-2-phenyl-4-methoxybenzene** (Table 3, entry 6)

An oven-dried 15 mL, resealable Schlenk tube was charged with  $\text{Pd}(\text{OAc})_2$  (4.5 mg, 20  $\mu\text{mol}$ , 1.0 mol %), 2-dicyclohexylphosphinobiphenyl (14 mg, 40  $\mu\text{mol}$ , 2.0 mol %), phenyl boronic acid (370 mg, 3.0 mmol, 1.5 equiv), and KF (350 mg, 6.0 mmol, 1.5 equiv). The Schlenk tube was evacuated and back-filled with argon and fitted with a rubber septum. THF (1.0 mL) followed by 4-bromo-2-iodoanisole (630 mg, 2.0 mmol) and additional THF (1.0 mL) were added via syringe. The Schlenk tube was then sealed under argon and stirred at 45  $^\circ\text{C}$  for 51 hours. The reaction mixture was diluted with 40 mL diethyl ether and 40 mL of 1 M NaOH. The layers were separated and the aqueous layer was extracted with diethyl ether (2 x 20 mL). The combined organic extracts were washed with brine (1 x 30 mL), dried over  $\text{MgSO}_4$ , filtered and concentrated to leave an orange oil. The resulting oil was purified by flash chromatography on silica gel with an eluent of 95:5 hexanes/toluene to afford 380 mg (72 %) of a colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 (d,  $J_{\text{HH}} = 8.5$  Hz, 1H), 7.43 (m, 5H), 6.89 (d,  $J_{\text{HH}} = 3$  Hz, 1H), 6.79 (dd,  $J_{\text{HH}} = 8.5, 3$  Hz, 1H), 3.82 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  159.0, 143.6, 141.3, 133.9, 129.5, 128.2, 127.9, 116.8, 114.9, 113.3, 55.7; IR (neat,  $\text{cm}^{-1}$ ) 3061, 3003, 2961, 2937, 2837, 1590,

1563, 1467, 1444, 1393, 1320, 1297, 1220, 1177, 1038, 857, 807, 764, 699. Anal. Calcd for  $C_{13}H_{11}BrO$ : C, 59.34; H 4.21. Found: C, 59.10; H 4.14.

## **General Procedures for the Intermolecular Coupling of Alcohols with Aryl Halides**

**General Procedure A.** An oven-dried 15 mL, resealable Schlenk tube was charged with  $Pd(OAc)_2$  (3.4 mg, 15  $\mu$ mol, 2 mol %), ligand **1** (7.5 mg, 18.8  $\mu$ mol, 2.5 mol %) and  $Cs_2CO_3$  (365 mg, 1.12 mmol, 1.5 equiv). The Schlenk tube was evacuated and back-filled with argon and fitted with a rubber septum. Toluene (0.5 mL) followed by aryl halide (0.75 mmol), alcohol (1.5 mmol) and additional toluene (1.0 mL) were added via syringe. The Schlenk tube was then sealed under argon and stirred at ambient temperature until the aryl halide had been consumed as judged by GC analysis. The reaction mixture was diluted with 2 mL of diethyl ether, filtered through a pad of celite, and concentrated to leave a crude oil. The resulting oil was purified by flash chromatography on silica gel with an eluent of 99:1 hexanes/ethyl acetate.

**General Procedure B.** An oven-dried 15 mL, resealable Schlenk tube was charged with  $Pd(OAc)_2$  (2.2 mg, 10  $\mu$ mol, 2 mol %), ligand **1** (5.5 mg, 12.5  $\mu$ mol, 2.5 mol %) and  $Cs_2CO_3$  (244 mg, 0.75 mmol, 1.5 equiv). The Schlenk tube was evacuated and back-filled with argon and fitted with a rubber septum. Toluene (0.5 mL) followed by aryl halide (0.50 mmol), alcohol (1.0 mmol) and additional toluene (0.5 mL) were added via syringe. The Schlenk tube was then sealed under argon and placed on a preheated oil bath at 70 °C until the aryl halide had been consumed as judged by GC analysis. The reaction mixture was cooled to room temperature, diluted with 2 mL of ether, filtered through a pad of celite, and concentrated to leave a crude oil. The resulting oil was purified by flash chromatography on silica gel with an eluent of 99:1 hexanes/ethyl acetate.

**2-Butoxy-1,3-dimethylbenzene** (Table 1, entry 1)

General procedure A was followed for 39 hours to afford 121 mg (90 %) of the title compound as a colorless liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.01 (d,  $J_{\text{HH}} = 7.5$  Hz, 2H), 6.92 (t,  $J_{\text{HH}} = 8$  Hz, 1H), 3.77 (t, 2H), 2.29 (s, 6H), 1.80 (pentet, 2H), 1.56 (sextet, 2H), 1.01 (t, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  156.3, 131.2, 128.9, 123.8, 72.2, 32.7, 19.6, 16.5, 14.2; IR (neat,  $\text{cm}^{-1}$ ) 2957, 2931, 2870, 1476, 1377, 1263, 1204, 1091, 766. Anal. Calcd for  $\text{C}_{12}\text{H}_{18}\text{O}$ : C, 80.85; H 10.18. Found: C, 80.55; H 10.31.

### **Benzyl-2,6-dimethylphenyl ether** (Table 1, entry 2)

General procedure A was followed for 44.5 hours to afford 155 mg (97 %) of the title compound as a colorless liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51 (d,  $J_{\text{HH}} = 7.5$  Hz, 2H), 7.43 (t,  $J_{\text{HH}} = 7$  Hz, 2H), 7.37 (m, 1H), 7.06 (d,  $J_{\text{HH}} = 7$  Hz, 2H), 6.97 (t,  $J_{\text{HH}} = 7.5$  Hz, 1H), 4.84 (s, 2H), 2.33 (s, 6H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  155.9, 137.9, 131.3, 129.1, 128.7, 128.2, 128.0, 124.2, 74.1, 16.6; IR (neat,  $\text{cm}^{-1}$ ) 3031, 2920, 2859, 1476, 1373, 1263, 1198, 1091, 1019, 787, 734, 698. Anal. Calcd for  $\text{C}_{15}\text{H}_{16}\text{O}$ : C, 84.87; H 7.60. Found: C, 84.77; H 7.63.

### **2-(2-Methylpropoxy)-1,3-dimethylbenzene** (Table 1, entry 3)

General procedure A was followed for 38.5 hours to afford 121 mg (90 %) of the title compound as a colorless liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.02 (d,  $J_{\text{HH}} = 7$  Hz, 2H), 6.91 (t,  $J_{\text{HH}} = 8$  Hz, 1H), 3.54 (d, 2H), 2.30 (s, 6H), 2.13 (septet, 1H), 1.09 (d, 6H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  156.1, 131.7, 129.0, 123.8, 78.6, 29.6, 19.6, 16.4; IR (neat,  $\text{cm}^{-1}$ ) 2956, 2925, 1467, 1390, 1264, 1204, 1092, 1022, 766. Anal. Calcd for  $\text{C}_{12}\text{H}_{18}\text{O}$ : C, 80.85; H 10.18. Found: C, 80.65; H 10.31.

### **2-Ethoxy-1, 3-dimethylbenzene** (Table 1, entry 4)

General procedure A was followed for 29 hours to afford 105 mg (93%) of the title compound as a colorless liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.02 (d,  $J_{\text{HH}} = 7$  Hz, 2H), 6.93 (t,  $J_{\text{HH}} = 7.5$  Hz, 1H), 3.86 (q, 2H), 2.30 (s, 6H), 1.44 (t, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  156.3, 131.2,

128.9, 123.8, 68.0, 16.5, 16.0; IR (neat,  $\text{cm}^{-1}$ ) 2976, 2925, 1476, 1384, 1262, 1207, 1041, 907, 767. Anal. Calcd for  $\text{C}_{10}\text{H}_{14}\text{O}$ : C, 79.95; H 9.39. Found: C, 79.67; H 9.33.

### **1-Butoxynaphthalene** (Table 1, entry 5)

General procedure A was followed using 1-chloronaphthalene (500  $\mu\text{mol}$ , 68  $\mu\text{L}$ , 90% purity) and *n*-butanol (1.0 mmol, 92  $\mu\text{L}$ ) for 21.5 hours. The crude oil was purified by chromatography on silica gel (gravity) eluting with hexanes to afford 77 mg (85%) of the title compound as a colorless liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.30 (d,  $J_{\text{HH}} = 8$  Hz, 1H), 7.80 (d,  $J_{\text{HH}} = 8$  Hz, 1H), 7.48 (m, 2H), 7.43 (m, 2H), 6.82 (d,  $J_{\text{HH}} = 8$  Hz, 1H), 4.16 (t, 2H), 1.93 (pentet, 2H), 1.62 (sextet, 2H), 1.04 (t, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  155.1, 134.7, 127.6, 126.5, 126.1, 125.9, 125.2, 122.3, 120.1, 104.7, 68.0, 31.6, 19.7, 14.2; IR (neat,  $\text{cm}^{-1}$ ) 3052, 2957, 2932, 2871, 1581, 1460, 1405, 1389, 1271, 1240, 1100, 790, 770. Anal. Calcd for  $\text{C}_{14}\text{H}_{16}\text{O}$ : C, 83.96; H 8.05. Found: C, 83.88; H 8.07.

### **1-butoxy-2-methylnaphthalene** (Table 1, entry 6)

General procedure A was followed with 1-bromo-2-methylnaphthalene (750  $\mu\text{mol}$ , 166 mg, 90% purity) for 24 hours to afford 140 mg (97 %) of the title compound as a colorless liquid.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.08 (d,  $J_{\text{HH}} = 8.7$  Hz, 1H), 7.80 (d,  $J_{\text{HH}} = 8.7$  Hz, 1H), 7.45 (m, 3H), 7.29 (d,  $J_{\text{HH}} = 8.4$  Hz, 1H), 3.96 (t, 2H), 2.45 (s, 3H), 1.92 (pentet, 2H), 1.63 (sextet, 2H), 1.04 (t, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  152.7, 133.7, 129.5, 128.5, 127.9, 126.3, 125.8, 125.3, 123.6, 122.0, 73.8, 32.9, 19.8, 16.4, 14.4; IR (neat,  $\text{cm}^{-1}$ ) 3051, 2957, 2931, 2870, 1598, 1574, 1466, 1356, 1239, 1186, 1087, 807. Anal. Calcd for  $\text{C}_{15}\text{H}_{18}\text{O}$ : C, 84.07; H 8.47. Found: C, 84.21; H 8.58.

### **2-Butoxy-1,4-dimethylbenzene** (Table 1, entry 7)

General procedure B was followed for 14 hours to afford 80 mg (89%) of the title compound as a colorless liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.01 (d,  $J_{\text{HH}} = 7.5$  Hz, 2H), 6.66 (m, 2H), 3.96

(t, 2H), 2.32 (s, 3H), 2.19 (s, 3H), 1.79 (pentet, 2H), 1.55 (sextet, 2H), 0.99 (t, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  157.3, 136.6, 130.4, 123.8, 120.7, 112.2, 67.7, 31.7, 21.6, 19.6, 16.0, 14.1; IR (neat,  $\text{cm}^{-1}$ ) 2958, 2933, 2871, 1614, 1586, 1509, 1265, 1158, 1132, 1029, 802. Anal. Calcd for  $\text{C}_{12}\text{H}_{18}\text{O}$ : C, 80.85; H 10.18. Found: C, 80.59; H 10.20.

### **2-Butoxy-1,4-dimethylbenzene** (Table 1, entry 8)

General procedure B was followed for 15.5 hours to afford 80 mg (89%) of the title compound as a colorless liquid. Data as above.

### **1-Butoxy-2,4-dimethylbenzene** (Table 1, entry 9)

General procedure B was followed for 18 hours. The crude material was purified by column chromatography on silica gel eluting with 95:5 hexanes/toluene to afford 76 mg (85%) of the title compound as a colorless liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.94 (m, 2H), 6.72 (d,  $J_{\text{HH}} = 8$  Hz, 1H), 3.95 (t, 2H), 2.26 (s, 3H), 2.21 (s, 3H), 1.78 (pentet, 2H), 1.52 (sextet, 2H), 0.99 (t, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  155.3, 131.6, 129.4, 127.0, 126.8, 111.2, 68.0, 31.7, 20.6, 19.6, 16.4, 14.2; IR (neat,  $\text{cm}^{-1}$ ) 2958, 2932, 2870, 1504, 1470, 1254, 1227, 1135, 800. Anal. Calcd for  $\text{C}_{12}\text{H}_{18}\text{O}$ : C, 80.85; H 10.18. Found: C, 80.90; H 10.27.

### **1-Butoxy-2,3-dimethylbenzene** (Table 1, entry 10)

General procedure B was followed for 15 hours. The crude material was purified by column chromatography on silica gel eluting with 95:5 hexanes/toluene to afford 82 mg (92%) of the title compound as a colorless liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.04 (d,  $J_{\text{HH}} = 8$  Hz, 1H), 6.77 (d,  $J_{\text{HH}} = 7.5$  Hz, 1H), 6.71 (d,  $J_{\text{HH}} = 8.5$  Hz, 1H), 3.95 (t, 2H), 2.28 (s, 3H), 2.16 (s, 3H), 1.79 (pentet, 2H), 1.54 (sextet, 2H), 0.99 (t, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  157.2, 138.0, 125.9, 125.5, 122.2, 109.1, 68.07, 31.8; 20.3, 19.6, 14.1, 11.8; IR (neat,  $\text{cm}^{-1}$ ) 2958, 2934, 2870, 1585, 1466, 1259, 1104, 767, 711. Anal. Calcd for  $\text{C}_{12}\text{H}_{18}\text{O}$ : C, 80.85; H 10.18. Found: C, 80.63; H 10.32.

**1-[2-(2,3-Dimethylphenoxy)-ethyl]piperidine** (Table 1, entry 11)

General procedure B was followed using 1-bromo-2,3-dimethylbenzene (68  $\mu\text{L}$ , 500  $\mu\text{mol}$ ) and 1-piperidineethanol (100  $\mu\text{L}$ , 750  $\mu\text{mol}$ ) at 100  $^{\circ}\text{C}$  for 22 hours. The crude material was purified by column chromatography on silica gel eluting with 4:1 hexanes/ethyl acetate with 0.5 % triethyl amine to afford 87 mg (74 %) of the title compound as a pale orange oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.04 (t,  $J_{\text{HH}} = 8$  Hz, 1H), 6.78 (d,  $J_{\text{HH}} = 7.5$  Hz, 1H), 6.72 (d,  $J_{\text{HH}} = 8$  Hz, 1H), 4.10 (t, 2H), 2.82 (t, 2H), 2.55 (br s, 4H), 2.28 (s, 3H), 2.16 (s, 3H), 1.61 (pentet, 4H), 1.46 (br s, 2H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  157.0, 138.1, 126.0, 125.5, 122.4, 109.2, 66.8, 58.3, 55.3, 26.3, 24.4, 20.3, 11.9; IR (neat,  $\text{cm}^{-1}$ ) 2933, 2852, 2782, 1585, 1467, 1304, 1259, 1106, 767, 711. Anal. Calcd for  $\text{C}_{15}\text{H}_{23}\text{NO}$ : C, 77.21; H 9.93. Found: C, 77.12; H 10.08.

**1-Butoxy-2-methylbenzene** (Table 1, entry 12)

General procedure B was followed for 15 hours. The crude material was purified by chromatography on silica gel (gravity) eluting with hexanes to afford 67 mg (86 %) of the title compound as a colorless liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.15 (m, 2H), 6.84 (m, 2H), 3.98 (t, 2H), 2.24 (s, 3H), 1.79 (pentet, 2H), 1.54 (sextet, 2H), 1.00 (t, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  157.4, 130.7, 127.0, 126.9, 120.2, 111.1, 67.7, 31.7, 19.6, 16.4, 14.1; IR (neat,  $\text{cm}^{-1}$ ) 2958, 2870, 1602, 1495, 1244, 1124, 749, 713. Anal. Calcd for  $\text{C}_{11}\text{H}_{16}\text{O}$ : C, 80.44; H 9.82. Found: C, 80.15; H 9.94.

**1-Butoxy-2-isopropylbenzene** (Table 1, entry 13)

General procedure B was followed for 14 hours to afford 95 mg (99 %) of the title compound as a colorless liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.23 (d,  $J_{\text{HH}} = 7.5$  Hz, 1H), 7.15 (t,  $J_{\text{HH}} = 7.5$  Hz, 1H), 6.92 (t,  $J_{\text{HH}} = 7.5$  Hz, 1H), 6.85 (d,  $J_{\text{HH}} = 8$  Hz, 1H), 3.98 (t, 2H), 3.35 (septet, 1H), 1.81 (pentet, 2H), 1.55 (sextet, 2H), 1.23 (d, 6H), 1.00 (t, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  156.5, 137.2, 126.7, 126.2, 120.5, 111.3, 67.7, 31.8, 27.1, 22.8, 19.7, 14.1; IR (neat,  $\text{cm}^{-1}$ )

2958, 2934, 2870, 1600, 1492, 1449, 1288, 1240, 1088, 751. Anal. Calcd for C<sub>13</sub>H<sub>20</sub>O: C, 81.20; H 10.48. Found: C, 80.93; H 10.54.

**1-Butoxy-2-(methylphenyl)benzene** (Table 1, entry 14)

General procedure B was followed for 15 hours. The crude material was purified by column chromatography on silica gel eluting with 95:5 hexanes/toluene to afford 116 mg (97%) of the title compound as a colorless liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.27 (m, 5H), 7.20 (d, *J*<sub>HH</sub> = 8 Hz, 1H), 7.11 (d, *J*<sub>HH</sub> = 7.5 Hz, 1H), 6.88 (m, 2H), 4.00 (s, 2H), 3.97 (t, 2H), 1.77 (pentet, 2H), 1.47 (sextet, 2H), 0.97 (t, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 157.0, 141.4, 130.5, 130.0, 129.2, 128.4, 127.5, 125.9, 120.4, 111.3, 67.7, 36.3, 31.6, 19.5, 14.1; IR (neat, cm<sup>-1</sup>) 3026, 2957, 2870, 1599, 1493, 1452, 1244, 1110, 751, 729, 697. Anal. Calcd for C<sub>17</sub>H<sub>20</sub>O: C, 84.95; H 8.39. Found: C, 84.92; H 8.43.

**2-Butoxybiphenyl** (Table 1, entry 15)

General procedure B was followed for 4 hours. The crude material was purified by column chromatography on silica gel eluting with hexanes to 9:1 hexanes/toluene to afford 86 mg (76%) of the title compound as a colorless liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.56 (d, *J*<sub>HH</sub> = 7 Hz, 2H), 7.41 (t, *J*<sub>HH</sub> = 6 Hz, 2H), 7.33 (m, 3H), 7.03 (t, *J*<sub>HH</sub> = 7.5 Hz, 1H), 6.99 (d, *J*<sub>HH</sub> = 8 Hz, 1H), 6.88 (m, 2H), 3.98 (t, 2H), 1.72 (pentet, 2H), 1.43 (sextet, 2H), 0.92 (t, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 156.2, 138.8, 131.1, 129.8, 128.7, 128.0, 126.9, 120.9, 112.6, 68.3, 31.4, 19.5, 14.0; IR (neat, cm<sup>-1</sup>) 3061, 3030, 2961, 2934, 2872, 1598, 1505, 1482, 1432, 1258, 1235, 1127, 1007, 749, 699. Anal. Calcd for C<sub>16</sub>H<sub>18</sub>O: C, 84.91; H 8.02. Found: C, 85.07; H 8.04.

**1-Butoxy-2-methoxybenzene** (Table 1, entry 16)

General procedure B was followed with 2-bromoanisole (750 μmol, 93 μL) and *n*-butanol (1.5 mmol, 140 μL) for 23 hours. The crude material was purified by column chromatography on

silica gel eluting with 4:1 hexane/toluene to afford 13 mg (10%) of the title compound as a colorless liquid. The spectral data is in agreement with those reported in the literature.<sup>9</sup>

**1-Butoxy-2-triisopropylsiloxybenzene** (Table 1, entry 17)

General procedure B was followed for 21 hours. The crude material was purified by column chromatography on silica gel eluting with 8:1 hexanes/toluene to afford 32 mg (20 %) of the title compound as a colorless liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 6.87 (m, 3H), 6.80 (m, 1H), 3.95 (t, 2H), 1.79 (pentet, 2H), 1.51 (sextet, 2H), 1.28 (septet, 3H), 1.10 (d, 18H), 0.98 (t, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 159.8, 145.7, 121.6, 120.7, 120.6, 113.2, 68.3, 31.7, 19.5, 18.1, 14.1, 13.0; IR (neat, cm<sup>-1</sup>) 3062, 2942, 2866, 1593, 1504, 1266, 1221, 1114, 1045, 920, 883, 742, 680. Anal. Calcd for C<sub>19</sub>H<sub>34</sub>SiO<sub>2</sub>: C, 70.75; H 10.62. Found: C, 70.99; H 10.87.

**1-Butoxy-3-ethylbenzene** (Table 2, entry 1)

General procedure B was followed at 70 °C for 16.5 hours. The crude material was purified by column chromatography on silica gel eluting with 95:5 hexanes/toluene to afford 56 mg (63 %) of the title compound as a colorless liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.20 (t, *J*<sub>HH</sub> = 8 Hz, 1H), 6.77 (m, 3H), 3.97 (t, 2H), 2.64 (q, 2H), 1.76 (pentet, 2H), 1.52 (sextet, 2H), 1.25 (t, 2H), 0.99 (t, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 159.4, 146.1, 129.4, 120.3, 114.5, 111.6, 67.7, 31.6, 29.1, 19.5, 15.7, 14.1; IR (neat, cm<sup>-1</sup>) 2961, 2932, 2872, 1601, 1584, 1451, 1263, 1158, 775, 694. Anal. Calcd for C<sub>12</sub>H<sub>18</sub>O: C, 80.85; H 10.18. Found: C, 80.61; H 10.26.

**1-Butoxy-3,5-dimethylbenzene** (Table 2, entry 2)

General procedure B was followed for 16.5 hours to afford 50 mg (56 %) of the title compound as a colorless liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 6.60 (s, 1H), 6.55 (s, 2H), 3.94 (t, 2H), 2.30 (s, 6H), 1.76 (pentet, 2H), 1.50 (sextet, 2H), 0.99 (t, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 159.4, 139.3, 122.4, 112.4, 67.6, 31.6, 21.7, 19.5, 14.1; IR (neat, cm<sup>-1</sup>) 2958, 2930, 2871,

1612, 1596, 1466, 1324, 1295, 1169, 1156, 1074, 829, 688. Anal. Calcd for C<sub>12</sub>H<sub>18</sub>O: C, 80.85; H 10.18. Found: C, 80.66; H 10.27.

### **3-Butoxy-*N,N*-dimethylaniline** (Table 2, entry 3)

General procedure B was followed for 18 hours. The crude material was purified by column chromatography on silica gel eluting with 99:1 hexanes/diethyl ether to afford 62 mg (64 %) of the title compound as a colorless liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 7.15 (t, *J*<sub>HH</sub> = 8.5 Hz, 1H), 6.38 (d, *J*<sub>HH</sub> = 7.5 Hz, 1H), 6.31 (m, 2H), 3.98 (t, 2H), 2.95 (s, 6H), 1.78 (pentet, 2H), 1.51 (sextet, 2H), 0.99 (t, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 160.4, 152.2, 129.9, 102.2, 100.0, 67.7, 40.8, 31.7, 19.5, 14.1; IR (neat, cm<sup>-1</sup>) 2958, 2870, 1612, 1576, 1501, 1450, 1352, 1241, 1152, 827, 750, 686. Anal. Calcd for C<sub>12</sub>H<sub>19</sub>NO: C, 74.57; H 9.91. Found: C, 74.59; H 10.12.

### **1-Butoxy-3-methoxybenzene** (Table 2, entry 4)

General procedure B was followed for 16.5 hours. The crude material was purified by column chromatography on silica gel eluting with 4:1 hexanes/toluene to afford 71 mg (79 %) of the title compound as a colorless liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 7.18 (t, *J*<sub>HH</sub> = 8.5 Hz, 1H), 6.50 (m, 3H), 3.96 (t, 2H), 3.80 (s, 3H), 1.78 (pentet, 2H), 1.50 (sextet, 2H), 0.99 (t, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 161.0, 160.6, 130.0, 106.9, 106.3, 101.1, 67.9, 55.4, 31.5, 19.5, 14.1; IR (neat, cm<sup>-1</sup>) 2958, 2872, 1595, 1493, 1454, 1288, 1265, 1201, 1153, 1045, 835, 762, 687. Anal. Calcd for C<sub>11</sub>H<sub>16</sub>O<sub>2</sub>: C, 73.30; H 8.95. Found: C, 73.04; H 9.00.

### **Benzyl-3-methoxyphenyl ether** (Table 2, entry 5)

General procedure B was followed for 4.5 hours. The crude material was purified by column chromatography on silica gel using 98:2 hexanes/diethyl ether as the eluent to afford 86 mg (80 %) of the title compound as a colorless liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 7.46 (d, *J*<sub>HH</sub> = 7 Hz, 2H), 7.40 (t, *J*<sub>HH</sub> = 7 Hz, 1H), 7.34 (t, *J*<sub>HH</sub> = 7.5 Hz, 1H), 7.21 (t, *J*<sub>HH</sub> = 8.5 Hz, 1H), 6.60 (d, *J*<sub>HH</sub> = 9 Hz, 2H), 6.57 (t, *J*<sub>HH</sub> = 2.5 Hz, 1H), 6.55 (d, *J*<sub>HH</sub> = 8.5 Hz, 1H), 5.06 (s,

2H), 3.80 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  161.0, 160.2, 137.1, 130.1, 128.8, 128.2, 127.7, 107.1, 106.8, 101.5, 70.2, 55.5; IR (neat,  $\text{cm}^{-1}$ ) 3034, 2941, 2837, 1590, 1490, 1451, 1285, 1197, 1150, 1042, 834, 760, 733, 687. Anal. Calcd for  $\text{C}_{14}\text{H}_{14}\text{O}_2$ : C, 78.48; H 6.59. Found: C, 78.18; H 6.50.

### **3-Butoxybiphenyl** (Table 2, entry 6)

General procedure B was followed for 16.5 hours. The crude material was purified by column chromatography on silica gel eluting with 95:5 hexanes/toluene to afford 90 mg (80 %) of the title compound as a colorless liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 (d,  $J_{\text{HH}} = 8$  Hz, 2H), 7.44 (t,  $J_{\text{HH}} = 8$  Hz, 2H), 7.35 (t,  $J_{\text{HH}} = 8$  Hz, 2H), 7.18 (d,  $J_{\text{HH}} = 7.5$  Hz, 1H), 7.14 (t,  $J_{\text{HH}} = 1$  Hz, 1H), 6.90 (d,  $J_{\text{HH}} = 8$  Hz, 1H), 4.04 (t, 2H), 1.81 (pentet, 2H), 1.54 (sextet, 2H), 1.00 (t, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  159.7, 142.9, 141.4, 129.9, 128.9, 127.6, 127.4, 119.7, 113.7, 113.4, 67.9, 31.6, 19.5, 14.1; IR (neat,  $\text{cm}^{-1}$ ) 3031, 2957, 2932, 2871, 1597, 1570, 1472, 1421, 1296, 1205, 757, 698. Anal. Calcd for  $\text{C}_{16}\text{H}_{18}\text{O}$ : C, 84.91; H 8.02. Found: C, 85.04; H 8.13.

### **3-Butoxy-benzoic acid-*tert*-butyl ester** (Table 2, entry 7)

General procedure B was followed for 15 hours. The crude material was purified by column chromatography on silica gel eluting with 9:1 hexanes/methylene chloride to afford 103 mg (82 %) of the title compound as a colorless liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57 (d,  $J_{\text{HH}} = 8$  Hz, 1H), 7.52 (m, 1H), 7.31 (t,  $J_{\text{HH}} = 8$  Hz, 1H), 7.07 (d,  $J_{\text{HH}} = 8.5$  Hz, 1H), 4.01 (t, 2H), 1.79 (pentet, 2H), 1.60 (s, 9H), 1.50 (sextet, 2H), 0.99 (t, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  165.9, 159.2, 133.5, 129.3, 121.8, 119.4, 114.9, 81.2, 68.0, 31.5, 28.4, 19.4, 14.1; IR (neat,  $\text{cm}^{-1}$ ) 2964, 2934, 2876, 1714, 1602, 1478, 1444, 1366, 1293, 1235, 1166, 1104, 1031, 849, 757, 683. Anal. Calcd for  $\text{C}_{15}\text{H}_{22}\text{O}_3$ : C, 71.97; H 8.86. Found: C, 71.72; H 8.89.

### **Benzyl- (3-benzoic acid-*tert*-butyl ester)-ether** (Table 2, entry 8)

General procedure B was followed for 4.5 hours. The crude material was purified by column chromatography on silica gel eluting with 3:1 hexane/toluene to afford 110 mg (77 %) of the title compound as a colorless liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 (m, 1H), 7.60 (t,  $J_{\text{HH}} = 1.5$  Hz, 1H), 7.46 (d,  $J_{\text{HH}} = 7.5$  Hz, 2H), 7.41 (t,  $J_{\text{HH}} = 7.5$  Hz, 2H), 7.33 (m, 2H), 7.15 (ddd,  $J_{\text{HH}} = 1, 2.5, 8.5$  Hz, 1H), 5.11 (s, 2H), 1.60 (s, 9H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  165.8, 158.8, 136.8, 133.6, 128.8, 128.3, 127.8, 122.3, 119.7, 115.3, 81.3, 70.3, 28.4; IR (neat,  $\text{cm}^{-1}$ ) 2980, 2934, 1710, 1586, 1440, 1370, 1293, 1162, 1104, 1027, 849, 757, 699. Anal. Calcd for  $\text{C}_{18}\text{H}_{20}\text{O}_3$ : C, 76.03; H 7.09. Found: C, 75.76; H 7.02.

### **3-But-3-enyloxy-benzoic acid-*tert*-butyl ester** (Table 2, entry 9)

General procedure B was followed at 50 °C using 3-bromo-benzoic acid-*tert*-butyl ester (129 mg, 500  $\mu\text{mol}$ ) and 3-buten-1-ol (64  $\mu\text{L}$ , 750  $\mu\text{mol}$ ) for 46 hours. The crude material was purified by column chromatography on silica gel eluting with 4:1 to 2:1 hexanes/toluene to afford 95 mg (77 %) of the title compound as a colorless liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 (d,  $J_{\text{HH}} = 8$  Hz, 1H), 7.52 (m, 1H), 7.32 (t,  $J_{\text{HH}} = 8$  Hz, 1H), 7.07 (dd,  $J_{\text{HH}} = 3, 8.5$  Hz, 1H), 5.92 (m, 1H), 5.19 (d,  $J_{\text{HH}} = 17.5$  Hz, 1H), 5.12 (d,  $J_{\text{HH}} = 10.5$  Hz, 1H), 4.07 (t, 2H), 2.57 (q, 2H), 1.60 (s, 9H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  165.8, 158.9, 134.5, 133.5, 129.4, 122.0, 119.5, 117.3, 114.9, 81.3, 67.5, 33.8, 28.4; IR (neat,  $\text{cm}^{-1}$ ) 3080, 2979, 2875, 1713, 1602, 1584, 1441, 1368, 1293, 1164, 1102, 1038, 916, 851, 756, 683. Anal. Calcd for  $\text{C}_{15}\text{H}_{20}\text{O}_3$ : C, 72.55; H 8.12. Found: C, 72.30; H 8.03.

### **1-Butoxy-3-trifluoromethylbenzene** (Table 2, entry 10)

General procedure B was followed for 7 hours. The crude material was purified by column chromatography on silica gel eluting with 95:5 hexanes/toluene to afford 95 mg (87 %) of the title compound as a colorless liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34 (t,  $J_{\text{HH}} = 8$  Hz, 1H), 7.16 (d,  $J_{\text{HH}} = 7.5$  Hz, 1H), 7.09 (s, 1H), 7.02 (d,  $J_{\text{HH}} = 8$  Hz, 1H), 3.96 (t, 2H), 1.75 (pentet, 2H), 1.49 (sextet, 2H), 0.96 (t, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  159.5, 132.0 (q,  $J_{\text{CF}} = 32$

(Hz), 130.1, 124.2 (q,  $J_{CF} = 272$  Hz), 118.2, 117.3 (q,  $J_{CF} = 3$  Hz), 111.4 (q,  $J_{CF} = 3$  Hz), 68.2, 31.4, 19.4, 14.0; IR (neat,  $\text{cm}^{-1}$ ) 2964, 2876, 1608, 1592, 1455, 1328, 1241, 1167, 1124, 1066, 784, 698, 658. Anal. Calcd for  $\text{C}_{11}\text{H}_{13}\text{F}_3\text{O}$ : C, 60.54; H 6.00. Found: C, 60.26; H 5.93.

### **3'-Butoxyacetophenone** (Table 2, entry 11)

General procedure B was followed for 17 hours to afford 89 mg (93 %) of the title compound as a colorless liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53 (d,  $J_{HH} = 8$  Hz, 1H), 7.49 (d,  $J_{HH} = 2.5$  Hz, 1H), 7.36 (t,  $J_{HH} = 8$  Hz, 1H), 7.10 (d,  $J_{HH} = 8$  Hz, 1H), 4.02 (t, 2H), 2.60 (s, 3H), 1.79 (pentet, 2H), 1.51 (sextet, 2H), 0.99 (t, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  198.3, 159.5, 138.6, 129.7, 121.1, 120.2, 113.2, 68.1, 31.4, 27.0, 19.4, 14.0; IR (neat,  $\text{cm}^{-1}$ ) 2958, 2934, 2872, 1686, 1595, 1582, 1438, 1356, 1273, 1218, 787, 688. Anal. Calcd for  $\text{C}_{12}\text{H}_{16}\text{O}_2$ : C, 74.97; H 8.39. Found: C, 75.06; H 8.42.

### **1-Butoxy-3-nitrobenzene** (Table 2, entry 12)

General procedure B was followed for 14 hours to afford 95 mg (96 %) of the title compound as a pale yellow liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 (d,  $J_{HH} = 8$  Hz, 1H), 7.73 (t,  $J_{HH} = 2$  Hz, 1H), 7.42 (t,  $J_{HH} = 8.5$  Hz, 1H), 7.22 (d,  $J_{HH} = 8$  Hz, 1H), 4.04 (t, 2H), 1.81 (pentet, 2H), 1.53 (sextet, 2H), 1.00 (t, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  159.9, 149.4, 130.0, 121.9, 115.7, 108.8, 68.6, 31.2, 19.4, 14.0; IR (neat,  $\text{cm}^{-1}$ ) 2959, 2935, 1530, 1470, 1350, 1286, 1249, 1028, 809, 737, 672. Anal. Calcd for  $\text{C}_{10}\text{H}_{13}\text{NO}_3$ : C, 61.50; H 6.70. Found: C, 61.45; H 6.69.

### **1-Butoxy-3-nitrobenzene** (Table 2, entry 13)

General procedure B was followed for 14 hours to afford 93 mg (95 %) of the title compound as a pale yellow liquid. Data as above.

### **1-Methoxy-3-nitrobenzene** (Table 2, entry 14)

General procedure B was followed for 20.5 hours. The crude material was purified by column chromatography on silica gel eluting with 90:10 hexanes/toluene to afford 48 mg (62 %) of the title compound as a pale yellow solid (mp 38-39 °C; lit.<sup>10</sup>, 39 °C). Spectral data is in agreement with those reported in the literature.<sup>10</sup>

**1-Pent-4-enyloxy-3-nitrobenzene** (Table 2, entry 15)

General procedure B was followed at 50 °C using 1-bromo-3-nitrobenzene (101 mg, 500 μmol) and 4-penten-1-ol (62 μL, 600 μmol) for 20.5 hours. The crude material was purified by column chromatography on silica gel eluting with 9:1 hexanes/toluene to afford 99 mg (95 %) of the title compound as a pale yellow liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.81 (d, *J*<sub>HH</sub> = 7.5 Hz, 1H), 7.72 (t, *J*<sub>HH</sub> = 2.5 Hz, 1H), 7.42 (t, *J*<sub>HH</sub> = 8 Hz, 1H), 7.23 (dd, *J*<sub>HH</sub> = 8, 2.5 Hz, 1H), 5.85 (m, 1H), 5.06 (m, 2H), 4.05 (t, 2H), 2.26 (q, 2H), 1.94 (pentet, 2H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 159.8, 149.4, 137.6, 130.1, 121.9, 115.8, 115.7, 108.8, 68.0, 30.2, 28.3; IR (neat, cm<sup>-1</sup>) 3079, 2942, 2877, 1641, 1620, 1580, 1530, 1470, 1350, 1287, 1249, 1096, 1021, 915, 816, 738, 672. Anal. Calcd for C<sub>11</sub>H<sub>13</sub>NO<sub>3</sub>: C, 63.76; H 6.32. Found: C, 63.99; H 6.42.

**6-Butoxyindole-1-carboxylic acid *tert*-butyl ester** (Table 2, entry 16)

General procedure B was followed for 6.5 hours. The crude material was purified by column chromatography on silica gel eluting with 4:1 hexanes/toluene to afford 101 mg (70%) of the title compound as colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.76 (br s, 1H), 7.47 (br s, 1H), 7.41 (d, *J*<sub>HH</sub> = 9 Hz, 1H), 6.87 (dd, *J*<sub>HH</sub> = 2.5, 8.5 Hz, 1H), 6.49 (d, *J*<sub>HH</sub> = 3.5 Hz, 1H), 4.05 (t, 2H), 1.81 (pentet, 2H), 1.68 (s, 9H), 1.53 (sextet, 2H), 1.00 (t, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 157.4, 150.1, 131.4, 124.6, 124.3, 121.4, 112.8, 107.3, 100.2, 83.6, 68.2, 31.6, 28.4, 19.5, 14.1; IR (neat, cm<sup>-1</sup>) 2961, 2937, 2876, 1733, 1617, 1471, 1444, 1378, 1343, 1254, 1220, 1150, 1077, 1023, 942, 853, 811, 768, 718. Anal. Calcd for C<sub>17</sub>H<sub>23</sub>NO<sub>3</sub>: C, 70.56; H 8.01. Found: C, 70.86; H 8.07.

### 3-Chloro-4-butoxyacetophenone (Figure 1)

General procedure A was followed using 3,4-dichloroacetophenone as substrate for 23.5 hours to afford 120 mg (71 %) of the title compound as a white solid (mp 54-55 °C). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.98 (d, *J*<sub>HH</sub> = 2.5 Hz, 1H), 7.84 (dd, *J*<sub>HH</sub> = 8.5, 2 Hz, 1H), 6.94 (d, *J*<sub>HH</sub> = 8.5 Hz, 1H), 4.10 (t, 2H), 2.55 (s, 3H), 1.85 (pentet, 2H), 1.54 (sextet, 2H), 1.00 (t, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 196.0, 158.6, 130.8, 130.6, 128.9, 123.2, 112.2, 69.2, 31.1, 26.5, 19.3, 14.0; IR (neat, cm<sup>-1</sup>) 2958, 2930, 2865, 1671, 1594, 1498, 1410, 1313, 1271, 1056, 910, 821, 807, 748. Anal. Calcd for C<sub>12</sub>H<sub>15</sub>ClO<sub>2</sub>: C, 63.58; H 6.67. Found: C, 63.75; H 6.63.

### 4-Butoxy-benzoic acid methyl ester (Figure 1)

General procedure A was followed using methyl-4-chlorobenzoate as substrate for 15.5 hours to afford 77 mg (74 %) of the title compound as a colorless liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.99 (d, *J*<sub>HH</sub> = 9 Hz, 2H), 6.91 (d, *J*<sub>HH</sub> = 9 Hz, 2H), 4.01 (t, 2H), 3.89 (t, *J*<sub>HH</sub> = 2.5 Hz, 3H), 1.79 (pentet, 2H), 1.50 (sextet, 2H), 0.99 (t, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 167.1, 163.2, 131.8, 122.5, 114.3, 68.1, 52.0, 31.3, 19.4, 14.0; IR (neat, cm<sup>-1</sup>) 2957, 2873, 1716, 1606, 1511, 1434, 1314, 1277, 1252, 1169, 1105, 848, 771, 697. Anal. Calcd for C<sub>12</sub>H<sub>16</sub>O<sub>3</sub>: C, 69.21; H 7.74. Found: C, 69.38; H 7.83.

### 4-Butoxy-benzoic acid-*tert*-butyl ester (Figure 1)

General procedure B was followed using *tert*-butyl-4-bromobenzoate as substrate for 15 hours. The crude material was purified by column chromatography on silica gel eluting with hexanes to 99:1 hexanes/diethyl ether to afford 124 mg (99 %) of the title compound as a colorless liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.93 (d, *J*<sub>HH</sub> = 9 Hz, 2H), 6.89 (d, *J*<sub>HH</sub> = 9 Hz, 2H), 4.01 (t, 2H), 2.30 (s, 6H), 1.79 (pentet, 2H), 1.59 (s, 9H), 1.50 (sextet, 2H), 0.99 (t, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 165.9, 162.8, 131.5, 124.4, 114.0, 80.6, 68.0, 31.4, 28.5, 19.4, 14.0; IR (neat, cm<sup>-1</sup>) 2964, 2934, 1708, 1606, 1292, 1253, 1159, 1115, 849, 772. Anal. Calcd for C<sub>15</sub>H<sub>22</sub>O<sub>3</sub>: C, 71.97; H 8.86. Found: C, 72.10; H 8.91.

#### **4'-Butoxyacetophenone** (Figure 1)

General procedure A was followed using 4-bromoacetophenone as substrate for 23 hours to afford 130 mg (90 %) of the title compound as a colorless liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 (d,  $J_{\text{HH}} = 8.5$  Hz, 2H), 6.92 (d,  $J_{\text{HH}} = 8.5$  Hz, 2H), 4.03 (t,  $J_{\text{HH}} = 6.5$  Hz, 2H), 2.56 (s, 3H), 1.79 (pentet,  $J_{\text{HH}} = 7.0$  Hz, 2H), 1.51 (sextet,  $J_{\text{HH}} = 7.5$  Hz, 2H), 0.99 (t,  $J_{\text{HH}} = 7.5$  Hz, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  197.0, 163.3, 130.8, 130.3, 114.3, 68.1, 31.3, 26.6, 19.4, 14.0; IR (neat,  $\text{cm}^{-1}$ ) 2958, 2873, 1677, 1601, 1509, 1420, 1358, 1307, 1256, 1172, 956, 835. Anal. Calcd for  $\text{C}_{12}\text{H}_{16}\text{O}_2$ : C, 74.97; H 8.39. Found: C, 74.85; H 8.51.

#### **2-Butoxypyridine** (Figure 1)

General procedure A was followed using 2-chloropyridine as substrate for 15.5 hours to afford 90 mg (80 %) of the title compound as a colorless liquid. This compound is commercially available from Aldrich and its identity was confirmed by comparison of  $^1\text{H}$  NMR data to an authentic sample; its purity was determined by GC analysis.

#### **4-Butoxybenzotrile** (Figure 1)

General procedure A was followed using 4-bromobenzotrile as substrate for 25 hours to afford 119 mg (91 %) of the title compound as a pale yellow liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 (d,  $J_{\text{HH}} = 7$  Hz, 2H), 6.94 (d,  $J_{\text{HH}} = 7$  Hz, 2H), 4.01 (t, 2H), 2.56 (s, 3H), 1.79 (pentet, 2H), 1.50 (sextet, 2H), 0.99 (t, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  162.6, 134.1, 119.6, 115.4, 103.8, 68.3, 31.2, 19.3, 14.1; IR (neat,  $\text{cm}^{-1}$ ) 2959, 3873, 2224, 1606, 1508, 1303, 1259, 1172, 835. Anal. Calcd for  $\text{C}_{11}\text{H}_{13}\text{NO}$ : C, 75.33; H 7.48. Found: C, 75.33; H 7.50.

#### **5-(2-Pyridin-2-yl-ethoxy)-indan-1-one** (Figure 1)

General procedure B was followed using 5-bromo-indan-1-one (84 mg, 400  $\mu\text{mol}$ ) and 2-(2-hydroxyethyl)-pyridine (90  $\mu\text{L}$ , 800  $\mu\text{mol}$ ) for 7 hours. The crude material was purified by

column chromatography on silica gel eluting with 1:1 to 4:1 ethyl acetate/hexanes to afford 91 mg (90 %) of the title compound as pale yellow solid (mp = 82-83 °C). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.57 (d, *J*<sub>HH</sub> = 4 Hz, 1H), 7.65 (m, 2H), 7.28 (d, *J*<sub>HH</sub> = 8 Hz, 1H), 7.18 (m, 1H), 6.90 (m, 2H), 4.47 (t, 2H), 3.31 (t, 2H), 3.07 (t, 2H), 2.67 (m, 2H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 205.5, 164.7, 158.3, 158.2, 149.7, 136.7, 130.6, 125.5, 124.0, 121.9, 115.9, 110.5, 67.7, 38.0, 36.2, 26.0; IR (neat, cm<sup>-1</sup>) 2926, 1701, 1599, 1474, 1437, 1303, 1257, 1089, 1018, 752. Anal. Calcd for C<sub>16</sub>H<sub>15</sub>NO<sub>2</sub>: C, 75.87; H 5.97. Found: C, 75.60; H 6.08.

### **5-Butoxy-indan-1-one** (Figure 1)

General procedure B was followed using 5-bromo-indan-1-one (400 μmol, 84 mg) and *n*-butanol (800 μmol, 73 μL) for 6 hours to afford 75 mg (91 %) of the title compound as a pale yellow solid (mp 54-55° C). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.68 (d, *J*<sub>HH</sub> = 9.5 Hz, 1H), 6.89 (m, 2H), 4.04 (t, 2H), 3.09 (t, 2H), 2.67 (t, 2H), 1.81 (pentet, 2H), 1.51 (sextet, 2H), 0.99 (t, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 205.5, 165.1, 158.4, 130.4, 125.5, 115.8, 110.4, 68.3, 36.6, 31.3, 26.1, 19.4, 14.0; IR (neat, cm<sup>-1</sup>) 3067, 2937, 2868, 1701, 1601, 1304, 1269, 1253, 1092, 1039. Anal. Calcd for C<sub>13</sub>H<sub>16</sub>O<sub>2</sub>: C, 76.44; H 7.89. Found: C, 76.41; H 8.05.

### **1-Butoxy-4-methoxybenzene** (Table 3, entry 1)

General procedure B was followed for 23 hours. The crude material was purified by column chromatography on silica gel eluting with 4:1 hexanes/toluene to afford 13 mg (10 %) of the title compound as a colorless liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 6.84 (s, 4H), 3.92 (t, 2H), 3.78 (s, 3H), 1.75 (pentet, 2H), 1.49 (sextet, 2H), 0.98 (t, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 153.8, 153.5, 115.6, 114.8, 68.5, 55.9, 31.7, 19.5, 14.1; IR (neat, cm<sup>-1</sup>) 2958, 2935, 2873, 1509, 1466, 1233, 1042, 824. HRMS (EI) calcd for C<sub>11</sub>H<sub>16</sub>O<sub>2</sub> (M<sup>+</sup>) 180.1145, found 180.1151.

### **1-Butoxy-2-methyl-4-methoxybenzene** (Table 3, entry 2)

General procedure B was followed for 6 hours. The crude material was purified by column chromatography on silica gel eluting with 9:1 hexanes/methylene chloride to afford 61 mg (63 %) of the title compound as a colorless liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.74 (m, 2H), 6.67 (d,  $J_{\text{HH}} = 9$  Hz, 1H), 3.92 (t, 2H), 3.77 (s, 3H), 2.23 (s, 3H), 1.77 (pentet, 2H), 1.52 (sextet, 2H), 0.99 (t, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  153.4, 151.7, 128.4, 117.1, 112.4, 110.9, 68.7, 55.9, 31.8, 19.6, 16.6, 14.1; IR (neat,  $\text{cm}^{-1}$ ) 2957, 2933, 2871, 1504, 1467, 1280, 1221, 1053, 866, 794, 717. Anal. Calcd for  $\text{C}_{12}\text{H}_{18}\text{O}_2$ : C, 74.19; H 9.34. Found: C, 73.93; H 9.28.

### **1-Butoxy-2-ethyl-4-methoxybenzene** (Table 3, entry 3)

General procedure B was followed for 8.5 hours. The crude material was purified by column chromatography on silica gel eluting with hexanes to 6:1 hexanes/toluene to afford 72 mg (69 %) of the title compound as a colorless liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.76 (m, 2H), 6.67 (dd,  $J_{\text{HH}} = 3, 8.5$  Hz, 1H), 3.92 (t, 2H), 3.77 (s, 3H), 2.63 (q, 2H), 1.77 (pentet, 2H), 1.51 (sextet, 2H), 1.20 (t, 3H), 0.99 (t, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  153.6, 151.3, 134.4, 115.6, 112.3, 110.6, 68.5, 55.9, 31.8, 23.6, 19.6, 14.4, 14.1; IR (neat,  $\text{cm}^{-1}$ ) 2961, 2934, 2872, 1590, 1502, 1467, 1212, 1061, 1038, 869, 795, 710. Anal. Calcd for  $\text{C}_{13}\text{H}_{20}\text{O}_2$ : C, 74.96; H 9.68. Found: C, 74.77; H 9.69.

### **1-Butoxy-2-*n*-propyl-4-methoxybenzene** (Table 3, entry 4)

General procedure B was followed for 15 hours. The crude material was purified by column chromatography on silica gel eluting with hexanes to 6:1 hexanes/toluene to afford 58 mg (52 %) of the title compound as a colorless liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.75 (t,  $J_{\text{HH}} = 9.5$  Hz, 1H), 6.73 (s, 1H), 6.67 (dd,  $J_{\text{HH}} = 9, 3$  Hz, 1H), 3.91 (t, 2H), 3.77 (s, 3H), 2.57 (t, 2H), 1.76 (pentet, 2H), 1.61 (sextet, 2H), 1.51 (sextet, 2H), 0.97 (m, 6H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  153.4, 151.5, 132.9, 116.4, 112.4, 110.8, 68.6, 55.8, 32.7, 31.8, 23.3, 19.6, 14.3, 14.1; IR (neat,  $\text{cm}^{-1}$ ) 2957, 2934, 2872, 1590, 1498, 1467, 1212, 1162, 1069, 1042, 865, 795, 710. Anal. Calcd for  $\text{C}_{14}\text{H}_{22}\text{O}_2$ : C, 75.63; H 9.97. Found: C, 75.50; H 9.89.

### **1-Butoxy-2-*i*-propyl-4-methoxybenzene** (Table 3, entry 5)

General procedure B was followed for 22.5 hours. The crude material was purified by column chromatography on silica gel eluting with hexanes to 6:1 hexanes/toluene to afford 76 mg (68 %) of the title compound as a colorless liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.81 (d,  $J_{\text{HH}} = 3$  Hz, 1H), 6.77 (d,  $J_{\text{HH}} = 9$  Hz, 1H), 6.66 (dd,  $J_{\text{HH}} = 8.5$ , 3 Hz, 1H), 3.92 (t, 2H), 3.78 (s, 3H), 3.32 (septet, 1H), 1.77 (pentet, 2H), 1.52 (sextet, 2H), 1.21 (d, 6H), 0.99 (t, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  153.8, 150.8, 138.9, 113.2, 112.4, 110.1, 68.6, 55.8, 31.9, 27.2, 22.9, 19.6, 14.1; IR (neat,  $\text{cm}^{-1}$ ) 2960, 2935, 2871, 2833, 1590, 1499, 1468, 1281, 1210, 1077, 1042, 872, 795. Anal. Calcd for  $\text{C}_{14}\text{H}_{22}\text{O}_2$ : C, 75.63; H 9.97. Found: C, 75.36; H 10.03.

### **1-Butoxy-2-phenyl-4-methoxybenzene** (Table 3, entry 6)

General procedure B was followed for 8.5 hours. The crude material was purified by column chromatography on silica gel eluting with 4:1 hexanes/toluene to afford 11 mg (17 %) of the title compound as a colorless liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (d,  $J_{\text{HH}} = 7$  Hz, 2H), 7.41 (t,  $J_{\text{HH}} = 8$  Hz, 2H), 7.33 (t,  $J_{\text{HH}} = 7$  Hz, 1H), 6.93 (m, 2H), 6.84 (dd,  $J_{\text{HH}} = 9$ , 3.5 Hz, 1H), 3.88 (t, 2H), 3.82 (s, 3H), 1.65 (pentet, 2H), 1.39 (sextet, 2H), 0.90 (t, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  153.9, 150.5, 138.7, 132.3, 129.7, 128.0, 127.1, 116.7, 114.7, 113.3, 69.4, 56.0, 31.6, 19.5, 14.0; IR (neat,  $\text{cm}^{-1}$ ) 2957, 2934, 2872, 1602, 1575, 1505, 1471, 1212, 1046, 764, 699. Anal. Calcd for  $\text{C}_{17}\text{H}_{20}\text{O}_2$ : C, 79.65; H 7.86. Found: C, 79.89; H 7.92.

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