Supporting Information

**Palladium-Catalyzed Intermolecular Hydroamination of Alkynes:
The Rate Acceleration Effect of *ortho*-Aminophenols**

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Experimental

General Information. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM LA-300 (300 MHz) and JEOL JNM α -500 (500 MHz) spectrometers. ^1H NMR spectra are reported as follows: chemical shift in ppm (δ) relative to the chemical shift of CHCl_3 at 7.24 ppm, integration, multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br = broadened), and coupling constants (Hz). ^{13}C NMR spectra reported in ppm (δ) relative to the central line of triplet for CDCl_3 at 77 ppm. IR spectra were recorded on a SHIMADZU FTIR-8200A spectrometer, absorptions are reported in cm^{-1} . High resolution mass spectra were obtained on a JEOL JMS-DX303 and JEOL JMS-AX500 spectrometers. Column chromatography was carried out employing Silica gel 60 N (spherical, neutral, 40~100 μm , KANTO Chemical Co.). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm precoated plate Kieselgel 60 F₂₅₄ (Merck).

Materials. Anhydrous 1,4-dioxane (WAKO), 2-aminophenol (TCI), alkynes (**1a**, **1b**, **1c**, **1d**, **1e** and **1f**) (TCI), $\text{Pd}(\text{NO}_3)_2$ were purchased and used as received. Alkynes (**1g**, **1h**, **1i**, **1j**, **1k**, **1l**, **1m** and **1n**) are prepared according to the literature procedure.ⁱ All other compounds used were commercially available.

Typical procedure for the palladium-catalyzed hydroamination reaction

To a 1,4-dioxane suspension (0.05 mL) of 2-aminophenol **2a** (54.6 mg, 0.5 mmol) and $\text{Pd}(\text{NO}_3)_2$ (17.3 mg, 0.075 mmol) in the reaction vial was added 6-dodecyne **1a** (124.7 mg, 0.75 mmol) under an argon atmosphere. The suspension was heated at 120 °C for 10 hour. The reaction mixture was cooled to room temperature, filtered through a short Al_2O_3 pad using diethyl ether as an eluent, and the resulting filtrate was concentrated. The residue was purified by column chromatography (silica gel, hexane-ethyl acetate 50/1~10/1) to afford 6-dodecanone **3a** in 93 % yield (86.0 mg).

Isolation of the amine (6)ⁱⁱ

To a 1,4-dioxane suspension (0.05 mL) of 2-aminophenol **2a** (54.6 mg, 0.5 mmol) and $\text{Pd}(\text{NO}_3)_2$ (17.3 mg, 0.075 mmol) in the reaction vial was added 6-dodecyne **1a** (124.7 mg, 0.75 mmol) under an argon atmosphere. The suspension was heated at 120 °C for 10 hour. Then the mixture was cooled to room temperature, and suspension of NaBH_3CN (62.8 mg, 1.0 mmol) and ZnCl_2 (68.1 mg, 0.5 mmol) in methanol (2 mL) was added. After being stirred for 5 days at 35 to 50 °C, the mixture was filtered. The solid residue was washed with CH_2Cl_2 (10 mL), and saturated Na_2CO_3 solution was added to the filtrate. After extraction, the organic layer was separated. The aqueous layer was neutralized and extracted with CH_2Cl_2 (6x10 mL). The combined organic layers were dried over Na_2SO_4 . Evaporation of the solvent under reduced pressure and column chromatography (silica gel, hexane-toluene 1/1~1/20) to afford the amine **6** in 62 % yield (85.7mg).

Analytical Data

6-Dodecanone (3a): orange oil; ^1H NMR (300.40 MHz, CDCl_3) δ 0.80-0.92 (6H, m), 1.15-1.37 (10 H, m), 1.47-1.61 (4H, m), 2.36 (4H, t*2, $J=7.4$, 7.4 Hz); ^{13}C NMR (75.45 MHz, CDCl_3) δ 13.90, 14.01, 22.44, 22.48, 23.55, 23.83, 28.92, 31.42, 31.59, 42.76, 42.81, 211.77 (CO); IR (neat) 2957, 2930, 2858, 1717 (CO), 1466, 1412, 1377 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{12}\text{H}_{24}\text{O}$ (M^+) 184.1827. Found 184.1821.

1,2-Diphenylethanone (3b): colorless solid; ^1H NMR (300.40 MHz, CDCl_3) δ 4.27 (2H, s), 7.20-7.38 (5H, m), 7.43 (2H, dd, $J = 7.4$, 7.4 Hz), 7.54 (1H, t, $J = 7.4$ Hz), 8.01 (2H, d, $J = 7.4$ Hz); ^{13}C NMR (75.45 MHz, CDCl_3) δ 45.39, 126.80, 128.52, 128.55, 128.58, 129.39, 133.08, 134.46, 136.50, 197.52 (CO); IR (KBr) 3059, 3038, 2907, 1686 (CO), 1448, 1337, 1076, 993, 752, 729, 700, 687 cm^{-1} .

1-Phenyl-1-propanone (3c): colorless oil; ^1H NMR (300.40 MHz, CDCl_3) δ 1.21 (3H, t, $J = 7.1$ Hz), 2.99 (2H, q, $J = 7.1$ Hz), 7.44 (2H, dd, $J = 7.7$, 7.7 Hz), 7.58 (1H, t, $J = 7.7$ Hz), 7.96 (2H, d, $J = 7.7$ Hz); ^{13}C NMR (75.45 MHz, CDCl_3) δ 8.21, 31.75, 127.94, 128.52, 132.84, 136.89, 200.81 (CO); IR (neat) 2978, 2937, 1688 (CO), 1221, 953, 746, 691 cm^{-1} .

1-Phenyl-2-propanone (4c)ⁱⁱⁱ: colorless oil; ^1H NMR (300.40 MHz, CDCl_3) δ 2.14 (3H, s), 3.68 (2H, s), 7.15-7.37 (5H, m); ^{13}C NMR (75.45 MHz, CDCl_3) δ 29.25, 51.01, 127.04, 128.74, 129.37, 134.21, 206.41 (CO); IR (neat) 2924, 1713 (CO), 1497, 1454, 1358, 740, 698 cm^{-1} .

1-Phenyl-1-hexanone (3d): colorless oil; ^1H NMR (300.40 MHz, CDCl_3) δ 0.89 (3H, t, $J = 7.1$ Hz), 1.28-1.42 (4H, m), 1.72 (2H, t, $J = 7.1$ Hz), 2.94 (2H, t, $J = 7.1$ Hz), 7.44 (2H, dd, $J = 7.6$, 7.6 Hz), 7.53 (1H, t, $J = 7.6$ Hz), 7.94 (2H, d, $J = 7.6$ Hz); ^{13}C NMR (75.45 MHz, CDCl_3) δ 13.92, 22.49, 24.02, 31.51, 38.54, 128.00, 128.49, 132.80, 137.04, 200.56 (CO); IR (neat) 2957, 2932, 2872, 1688 (CO), 1448, 1205, 746, 691 cm^{-1} .

1-Phenyl-2-hexanone (4d)^{iv}: colorless oil; ^1H NMR (300.40 MHz, CDCl_3) δ 0.83 (3H, t, $J = 7.3$ Hz), 1.24 (2H, tq, $J = 7.3$, 7.3 Hz), 2.43 (2H, t, $J = 7.3$ Hz), 3.67 (2H, s), 7.15-7.36 (5H, m); ^{13}C NMR (75.45 MHz, CDCl_3) δ 13.78, 22.19, 25.79, 41.67, 50.09, 126.90, 128.64, 129.35, 134.36, 208.58 (CO); IR (neat) 2959, 2932, 2872, 1715 (CO), 1497, 1456, 698 cm^{-1} .

2-Dodecanone (3e)^v: colorless oil; ^1H NMR (300.40 MHz, CDCl_3) δ 0.85 (3H, t, $J = 6.5$ Hz), 1.20-1.33 (14 H, br s), 1.47-1.62 (2H, m), 2.11 (3H, s), 2.39 (2H, t, $J = 7.5$ Hz); ^{13}C NMR (75.45 MHz, CDCl_3) δ 14.09, 22.66, 23.86, 29.17, 29.29, 29.38, 29.45, 29.55, 29.83, 31.87, 43.81, 209.41 (CO); IR (neat) 2926, 2855, 1720 (CO), 1456, 1360, 1240, 1161 cm^{-1} .

Acetophenone (3f): colorless oil; ^1H NMR (300.40 MHz, CDCl_3) δ 2.59 (3H, s), 7.44 (2H, dd, $J = 7.8$,

7.8 Hz), 7.54 (1H, t, $J = 7.8$ Hz), 7.94 (2H, d, $J = 7.8$ Hz); ^{13}C NMR (75.45 MHz, CDCl_3) δ 26.55, 128.24, 128.50, 133.04, 137.05, 198.09 (CO); IR (neat) 3063, 1682 (CO), 1599, 1360, 1267, 957, 760, 691 cm^{-1} .

6-Methoxy-1-phenyl-1-hexyne (1g): colorless oil; ^1H NMR (300.40 MHz, CDCl_3) δ 1.60-1.80 (4H, m), 2.43 (2H, t, $J = 6.8$ Hz), 3.33 (3H, s), 3.41 (2H, t, $J = 6.5$ Hz), 7.21-7.28 (3H, m), 7.35-7.39 (2H, m); ^{13}C NMR (75.45 MHz, CDCl_3) δ 19.21, 25.38, 28.80, 58.56, 72.26, 80.83, 89.92, 123.95, 127.50, 128.16, 131.16; IR (neat) 2932, 2866, 2230 (alkyne), 1599, 1491, 1443, 1387, 1121 (C-O), 756, 692 cm^{-1} ; Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{O}$: C, 82.93; H, 8.57. Found: C, 82.76; H, 8.68; HRMS (EI) Calcd for $\text{C}_{13}\text{H}_{16}\text{O}$ (M^+) 188.1201. Found 188.1186.

6-Methoxy-1-phenyl-1-hexanone (3g): yellow oil; ^1H NMR (300.40 MHz, CDCl_3) δ 1.35-1.50 (2H, m), 1.60 (2H, tt, $J = 7.9, 7.6$ Hz), 1.74 (2H, tt, $J = 7.9, 7.9$ Hz), 2.95 (2H, t, $J = 7.6$ Hz), 3.30 (3H, s), 3.36 (2H, t, $J = 6.5$ Hz), 7.43 (2H, dd, $J = 7.5, 7.5$ Hz), 7.52 (1H, t, $J = 7.5$ Hz), 7.93 (2H, d, $J = 7.5$ Hz); ^{13}C NMR (75.45 MHz, CDCl_3) δ 24.06, 25.87, 29.45, 38.45, 58.52, 72.56, 127.98, 128.50, 132.85, 136.97, 200.29 (CO); IR (neat) 2934, 2864, 1688 (CO), 1448, 1119 (C-O), 750, 691 cm^{-1} ; Anal. Calcd for $\text{C}_{13}\text{H}_{18}\text{O}_2$: C, 75.68; H, 8.80. Found: C, 75.84; H, 9.00; HRMS (EI) Calcd for $\text{C}_{13}\text{H}_{18}\text{O}_2$ (M^+) 206.1307. Found 206.1339.

6-Methoxy-1-phenyl-2-hexanone (4g): yellow oil; ^1H NMR (300.40 MHz, CDCl_3) δ 1.43-1.68 (4H, m), 2.46 (2H, t, $J = 7.2$ Hz), 3.27 (3H, s), 3.30 (2H, t, $J = 6.5$ Hz), 3.66 (2H, s), 7.14-7.34 (5H, m); ^{13}C NMR (75.45 MHz, CDCl_3) δ 20.36, 28.89, 41.55, 50.09, 58.48, 72.34, 126.94, 128.67, 129.35, 134.28, 208.17 (CO); IR (neat) 2930, 2870, 1713 (CO), 1497, 1454, 1119 (C-O), 731, 700 cm^{-1} ; Anal. Calcd for $\text{C}_{13}\text{H}_{18}\text{O}_2$: C, 75.68; H, 8.80. Found: C, 75.87; H, 9.01; HRMS (EI) Calcd for $\text{C}_{13}\text{H}_{18}\text{O}_2$ (M^+) 206.1307. Found 206.1317.

6-Benzyloxy-1-phenyl-1-hexyne (1h): colorless oil; ^1H NMR (300.40 MHz, CDCl_3) δ 1.63-1.84 (4H, m), 2.42 (2H, t, $J = 7.0$ Hz), 3.52 (2H, t, $J = 6.1$ Hz), 4.51 (2H, s), 7.21-7.40 (5H, m); ^{13}C NMR (75.45 MHz, CDCl_3) δ 19.08, 25.36, 28.82, 69.67, 72.70, 80.78, 89.88, 123.88, 127.34, 127.36, 127.42, 128.03, 128.20, 131.39, 138.46; IR (neat) 2937, 2860, 2230 (alkyne), 1726, 1599, 1491, 1454, 1362, 1109 (C-O), 756, 737, 692 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{19}\text{H}_{20}\text{O}$ (M^+) 264.1514. Found 265.1515.

6-Benzyloxy-1-phenyl-1-hexanone (3h): yellow oil; ^1H NMR (300.40 MHz, CDCl_3) δ 1.39-1.55 (2H, m), 1.66 (2H, tt, $J = 7.2, 7.2$ Hz), 1.74 (2H, tt, $J = 7.8, 7.8$ Hz), 2.96 (2H, t, $J = 7.8$ Hz), 3.47 (2H, t, $J = 7.2$ Hz), 4.48 (2H, s), 7.22-7.34 (5H, m), 7.43 (2H, dd, $J = 7.5$ Hz), 7.53 (1H, t, $J = 7.5$ Hz), 7.94 (2H, d, $J = 7.5$ Hz); ^{13}C NMR (75.45 MHz, CDCl_3) δ 24.06, 25.92, 29.57, 38.43, 70.14, 72.85, 127.42, 127.55, 127.97, 128.28, 128.49, 132.82, 136.97, 138.55, 200.25 (CO); IR (neat) 2936, 2858, 1684 (CO), 1448,

1101 (C-O), 737, 696 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{19}\text{H}_{22}\text{O}_2$ (M^+) 282.1620. Found 282.1611.

6-Benzyloxy-1-phenyl-2-hexanone (4h): yellow oil; ^1H NMR (300.40 MHz, CDCl_3) δ 1.49-1.70 (4H, m), 2.46 (2H, t, $J = 6.7$ Hz), 3.41 (2H, t, $J = 6.0$ Hz), 3.65 (2H, s), 4.45 (2H, s), 7.14-7.36 (10 H, m); ^{13}C NMR (75.45 MHz, CDCl_3) δ 20.43, 28.99, 41.53, 50.07, 69.88, 72.81, 126.90, 127.46, 127.56, 128.30, 128.63, 129.32, 134.27, 138.47, 208.17 (CO); IR (neat) 2934, 2858, 1713 (CO), 1497, 1454, 1101 (C-O), 737, 698 cm^{-1} ; Anal. Calcd for $\text{C}_{19}\text{H}_{22}\text{O}_2$: C, 80.80; H, 7.86. Found: C, 80.75; H, 8.04; HRMS (EI) Calcd for $\text{C}_{19}\text{H}_{22}\text{O}_2$ (M^+) 282.1620. Found 282.1622.

6-Acetoxy-1-phenyl-1-hexyne (1i): colorless oil; ^1H NMR (300.40 MHz, CDCl_3) δ 1.66 (2H, tt, $J = 6.8$, 6.8 Hz), 1.79 (2H, tt, $J = 6.8$, 6.3 Hz), 2.04 (3H, s), 2.43 (2H, t, $J = 6.8$ Hz), 4.10 (2H, t, $J = 6.3$ Hz), 7.21-7.30 (3H, m), 7.32-7.40 (2H, m); ^{13}C NMR (75.45 MHz, CDCl_3) δ 19.07, 20.99, 25.19, 27.81, 64.04, 81.07, 89.44, 123.80, 127.60, 128.19, 131.52, 171.19 (CO); IR (neat) 2953, 2233 (alkyne), 1740 (CO), 1491, 1240 (C-O), 1045 (C-O), 758, 692 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{14}\text{H}_{16}\text{O}_2$ (M^+) 216.1151. Found 216.1132.

6-Acetoxy-1-phenyl-1-hexanone (3i): yellow oil; ^1H NMR (300.40 MHz, CDCl_3) δ 1.37-1.50 (2H, m), 1.67 (2H, tt, $J = 7.5$, 7.1 Hz), 1.76 (2H, tt, $J = 6.9$, 6.9 Hz), 2.02 (3H, s), 2.97 (2H, t, $J = 7.1$ Hz), 4.06 (2H, t, $J = 6.9$ Hz), 7.44 (2H, dd, $J = 7.5$, 7.5 Hz), 7.54 (1H, t, $J = 7.5$ Hz), 7.94 (2H, d, $J = 7.5$ Hz); ^{13}C NMR (75.45 MHz, CDCl_3) δ 20.98, 23.84, 25.70, 28.51, 38.32, 64.33, 127.99, 128.56, 132.95, 136.95, 171.18 (CO, ester), 200.06 (CO, ketone); IR (neat) 2941, 1738 (CO, ester), 1688 (CO, ketone), 1448, 1367, 1242 (C-O), 1047 (C-O), 750, 692 cm^{-1} ; Anal. Calcd for $\text{C}_{14}\text{H}_{18}\text{O}_3$: C, 71.76; H, 7.75. Found: C, 71.54; H, 7.77; HRMS (EI) Calcd for $\text{C}_{14}\text{H}_{18}\text{O}_3$ (M^+) 234.1256. Found 234.1236.

6-Acetoxy-1-phenyl-2-hexanone (4i): yellow oil; ^1H NMR (300.40 MHz, CDCl_3) δ 1.49-1.66 (4H, m), 2.00 (3H, s), 2.46 (2H, t, $J = 6.6$ Hz), 3.66 (2H, s), 3.98 (2H, t, $J = 6.4$ Hz), 7.15-7.35 (5H, m); ^{13}C NMR (75.45 MHz, CDCl_3) δ 20.00, 20.91, 27.86, 41.16, 50.18, 63.98, 127.00, 128.71, 129.31, 134.15, 171.07 (CO, ester), 207.82 (CO, ketone); IR (neat) 2955, 1732 (CO, ester), 1710 (CO, ketone), 1367, 1242 (C-O), 1040 (C-O), 700 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{14}\text{H}_{18}\text{O}_3$ (M^+) 234.1256. Found 234.1249.

6-tert-Butyldimethylsilyloxy-1-phenyl-1-hexyne (1j): colorless oil; ^1H NMR (300.40 MHz, CDCl_3) δ 0.04 (6H, s), 0.88 (9H, s), 1.59-1.74 (4H, m), 2.38-2.46 (2H, m), 3.61-3.69 (2H, m), 7.21-7.30 (3H, m), 7.32-7.40 (2H, m); ^{13}C NMR (75.45 MHz, CDCl_3) δ -5.28, 18.35, 19.22, 25.21, 25.97, 32.01, 62.71, 80.72, 90.18, 124.02, 127.46, 128.16, 131.53; IR (neat) 2953, 2930, 2856, 1256, 1107 (C-O), 837, 775, 756, 691 cm^{-1} ; Anal. Calcd for $\text{C}_{18}\text{H}_{28}\text{OSi}$: C, 74.95; H, 9.79. Found: C, 74.73; H, 9.95; HRMS (EI) Calcd for $\text{C}_{18}\text{H}_{28}\text{OSi}$ (M^+) 288.1910. Found 288.1891.

6-tert-Butyldimethylsilyloxy-1-phenyl-1-hexanone (3j): pale orange oil; ^1H NMR (300.40 MHz, CDCl_3) δ 0.03 (6H, s), 0.87 (9H, s), 1.41 (2H, tt, $J = 7.6, 6.4$ Hz), 1.56 (2H, tt, $J = 7.6, 7.6$ Hz), 1.74 (2H, tt, $J = 7.6, 7.6$ Hz), 2.96 (2H, t, $J = 7.6$ Hz), 3.61 (2H, t, $J = 6.4$ Hz), 7.44 (2H, dd, $J = 7.0, 7.0$ Hz), 7.54 (1H, t, $J = 7.0$ Hz), 7.93 (2H, d, $J = 7.0$ Hz); ^{13}C NMR (75.45 MHz, CDCl_3) δ -5.30, 18.34, 24.13, 25.61, 25.95, 32.66, 38.58, 62.99, 128.02, 128.52, 132.85, 137.04, 200.40 (CO); IR (neat) 2930, 2856, 1690 (CO), 1256, 1099 (C-O), 835, 775, 691 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{18}\text{H}_{30}\text{O}_2\text{Si}$ (M^+) 306.2015. Found 306.1992.

6-tert-Butyldimethylsilyloxy-1-phenyl-2-hexanone (4j): pale orange oil; ^1H NMR (300.40 MHz,

CDCl_3) δ 0.00 (6H, s), 0.86 (9H, s), 1.43 (2H, tt, $J = 7.2, 6.3$ Hz), 1.59 (2H, tt, $J = 7.2, 7.2$ Hz), 2.46 (2H, t, $J = 7.2$ Hz), 3.55 (2H, t, $J = 6.3$ Hz), 3.66 (2H, s), 7.15-7.35 (5H, m); ^{13}C NMR (75.45 MHz, CDCl_3) δ -5.34, 18.30, 20.17, 25.93, 32.08, 41.69, 50.08, 62.74, 126.94, 128.68, 129.36, 134.33, 208.34 (CO); IR (neat) 2955, 2930, 2856, 1715 (CO), 1256, 1099 (C-O), 835, 775, 698 cm^{-1} ; Anal. Calcd for $\text{C}_{18}\text{H}_{30}\text{O}_2\text{Si}$: C, 70.54; H, 9.87. Found: C, 70.63; H, 9.61; HRMS (EI) Calcd for $\text{C}_{18}\text{H}_{30}\text{O}_2\text{Si}$ (M^+) 306.2015. Found 306.2049.

6-Chloro-1-phenyl-1-hexyne (1k): colorless oil; ^1H NMR (300.40 MHz, CDCl_3) δ 1.75 (2H, tt, $J = 7.2, 7.2$ Hz), 1.96 (2H, tt, $J = 7.2, 6.9$ Hz), 2.45 (2H, t, $J = 7.2$ Hz), 3.59 (2H, t, $J = 6.9$ Hz), 7.22-7.31 (3H,

m), 7.32-7.41 (2H, m); ^{13}C NMR (75.45 MHz, CDCl_3) δ 18.7, 25.9, 31.6, 44.6, 81.2, 89.2, 123.7, 127.6, 128.2, 131.5; IR (neat) 2953, 2866, 2232 (alkyne), 1599, 1489, 1443, 756, 692 cm^{-1} ; Anal. Calcd for $\text{C}_{12}\text{H}_{13}\text{Cl}$: C, 74.97; H, 6.82; Cl, 18.21. Found: C, 74.73; H, 7.07; Cl, 18.24. HRMS (EI) Calcd for $\text{C}_{12}\text{H}_{13}\text{Cl}$ (M^+) 192.0706. Found 192.0715.

6-Chloro-1-phenyl-1-hexanone (3k): colorless oil; ^1H NMR (300.40 MHz, CDCl_3) δ 1.51 (2H, tt, $J = 7.3, 6.9$ Hz), 1.76 (2H, tt, $J = 6.9, 6.9$ Hz), 1.82 (2H, tt, $J = 6.9, 6.9$ Hz), 2.98 (2H, t, $J = 7.3$ Hz), 3.54 (2H, t, $J = 6.9$ Hz), 7.44 (2H, dd, $J = 7.3, 7.3$ Hz), 7.54 (1H, t, $J = 7.3$ Hz), 7.94 (2H, d, $J = 7.3$ Hz); ^{13}C NMR (75.45 MHz, CDCl_3) δ 23.40, 26.55, 32.42, 38.25, 44.83, 127.96, 128.54, 132.95, 136.91, 199.97 (CO); IR (neat) 2939, 2866, 1682 (alkyne), 1596, 1448, 1213, 752, 729, 691 cm^{-1} ; Anal. Calcd for $\text{C}_{12}\text{H}_{15}\text{OCl}$: C, 68.54; H, 7.20; Cl, 16.64. Found: C, 68.50; H, 7.19; Cl, 16.51; HRMS (EI) Calcd for $\text{C}_{12}\text{H}_{13}\text{Cl}$ (M^+) 210.0811. Found 210.0832.

9a-Benzyl-1,3,4,9a-tetrahydro-2H-9-oxa-4a-aza-fluorene (5): pale orange oil; ^1H NMR (500.00 MHz, CDCl_3) δ 1.50-1.84 (6H, m), 3.22 (1H, ddd, $J = 14.5, 12.1, 4.0$ Hz), 3.27 (1H, d, $J = 14.4$ Hz), 3.33 (1H, d, $J = 14.4$ Hz), 3.61 (1H, d, $J = 14.5$ Hz), 6.34 (1H, dd, $J = 7.5, 1.0$ Hz), 6.55 (1H, ddd, $J = 7.5, 7.5, 1.0$ Hz), 6.64 (1H, dd, $J = 7.5, 1.0$ Hz), 6.73 (1H, ddd, $J = 7.5, 7.5, 1.0$ Hz), 7.23 (1H, dddd, $J = 7.5, 6.1, 1.1, 1.1$ Hz), 7.27-7.32 (2H, m), 7.33-7.31 (2H, m); ^{13}C NMR (125.65 MHz, CDCl_3) δ 21.27, 22.35, 30.41, 40.75, 42.73, 102.41, 105.52, 107.90, 117.73, 120.95, 126.52, 128.07, 130.49, 136.11, 139.47, 149.34; IR (neat) 3061, 3030, 2941, 2862, 1599, 1487, 1456, 1238, 1194, 1016, 901, 731, 700 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{18}\text{H}_{19}\text{NO}$ (M^+) 265.1467. Found 265.1472.

1-(4-Methoxyphenyl)-1-hexyne (1l): pale orange oil; ^1H NMR (300.40 MHz, CDCl_3) δ 0.92 (3H, t, $J = 7.1$ Hz), 1.46 (2H, tq, $J = 7.1, 7.1$ Hz), 1.57 (2H, tt, $J = 7.1, 7.1$ Hz), 2.37 (2H, t, $J = 7.1$ Hz), 3.78 (3H,

s), 6.79 (2H, d, $J = 8.9$ Hz), 7.31 (2H, d, $J = 8.9$ Hz); ^{13}C NMR (75.45 MHz, CDCl_3) δ 13.64, 19.08, 22.01, 30.95, 55.20, 80.19, 88.71, 113.76, 116.25, 132.82, 158.94; IR (neat) 2957, 2932, 1607, 1510, 1464, 1288, 1246 (C-O), 1173, 1036 (C-O), 831 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{13}\text{H}_{16}\text{O}$ (M^+) 188.1201. Found 188.1170.

1-(4-Methoxyphenyl)-1-hexanone (3l): colorless solid; ^1H NMR (300.40 MHz, CDCl_3) δ 0.87 (3H, t, $J = 6.9$ Hz), 1.27-1.39 (4H, m), 1.69 (2H, tt, $J = 7.1, 7.1$ Hz), 2.86 (2H, t, $J = 7.1$ Hz), 6.89 (2H, d, $J = 8.9$ Hz), 7.91 (2H, d, $J = 8.9$ Hz); ^{13}C NMR (75.45 MHz, CDCl_3) δ 13.89, 22.47, 24.25, 31.54, 38.17, 55.34, 113.57, 130.11, 130.22, 163.22, 199.13 (CO); IR (KBr) 2934, 2855, 1672 (CO), 1605, 1254 (C-O), 1175, 1034 (C-O), 829, 818, 731 cm^{-1} ; Anal. Calcd for $\text{C}_{13}\text{H}_{18}\text{O}_2$: C, 75.68; H, 8.80. Found: C, 75.52; H, 8.67;

HRMS (EI) Calcd for $\text{C}_{13}\text{H}_{18}\text{O}_2$ (M^+) 206.1307. Found 206.1296.

1-(4-Methoxyphenyl)-2-hexanone (4l): pale orange oil; ^1H NMR (300.40 MHz, CDCl_3) δ 0.85 (3H, t, $J = 7.2$ Hz), 1.24 (2H, tq, $J = 7.2, 7.2$ Hz), 1.51 (2H, tt, $J = 7.2, 7.2$ Hz), 2.41 (2H, t, $J = 7.2$ Hz), 3.59 (2H, s), 3.77 (2H, s), 6.84 (2H, d, $J = 8.9$ Hz), 7.09 (2H, d, $J = 8.9$ Hz); ^{13}C NMR (75.45 MHz, CDCl_3) δ 13.80, 22.22, 25.83, 41.51, 49.19, 55.22, 114.08, 126.42, 130.35, 158.56, 209.02 (CO); IR (neat) 2597, 2934, 1713 (CO), 1612, 1512, 1248 (C-O), 1178, 1036 (C-O), 812 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{13}\text{H}_{18}\text{O}_2$ (M^+) 206.1307. Found 206.1343.

1-(4-Tolyl)-1-hexyne (1m): colorless oil; ^1H NMR (300.40 MHz, CDCl_3) δ 0.93 (3H, t, $J = 7.2$ Hz), 1.46

(2H, tq, $J = 7.2, 7.2$ Hz), 1.57 (2H, tt, $J = 7.2, 7.2$ Hz), 2.31 (3H, s), 2.38 (2H, t, $J = 7.2$ Hz), 7.06 (2H, d, $J = 8.3$ Hz), 7.27 (2H, d, $J = 8.3$ Hz); ^{13}C NMR (75.45 MHz, CDCl_3) δ 13.64, 19.09, 21.37, 22.00, 30.90, 80.51, 89.55, 120.98, 128.91, 131.37, 137.37; IR (neat) 2959, 2932, 2872, 1510, 816 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{13}\text{H}_{16}$ (M^+) 172.1252. Found 172.1244.

1-(4-Tolyl)-1-hexanone (3m): pale yellow solid; ^1H NMR (300.40 MHz, CDCl_3) δ 0.89 (3H, t, $J = 7.1$ Hz), 1.27-1.40 (4H, m), 1.71 (2H, tt, $J = 7.1, 7.1$ Hz), 2.39 (3H, s), 2.91 (2H, t, $J = 7.1$ Hz), 7.23 (2H, d, $J = 8.1$ Hz), 7.84 (2H, d, $J = 8.1$ Hz); ^{13}C NMR (75.45 MHz, CDCl_3) δ 13.92, 21.55, 22.50, 24.16, 31.54, 38.44, 128.14, 129.17, 134.59, 143.52, 200.25 (CO); IR (KBr) 2953, 2930, 2858, 1674 (CO), 1609, 1183, 814, 762, 727 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{13}\text{H}_{18}\text{O}$ (M^+) 190.1357. Found 190.1376.

1-(4-Tolyl)-2-hexanone (4m): pale yellow oil; ^1H NMR (300.40 MHz, CDCl_3) δ 0.85 (3H, t, $J = 7.1$ Hz), 1.25 (2H, tq, $J = 7.1, 7.1$ Hz), 1.51 (2H, tt, $J = 7.1, 7.1$ Hz), 2.32 (3H, s), 2.42 (2H, t, $J = 7.1$ Hz), 3.62 (2H, s), 7.06 (2H, d, $J = 8.1$ Hz), 7.12 (2H, d, $J = 8.1$ Hz); ^{13}C NMR (75.45 MHz, CDCl_3) δ 13.80, 21.03, 22.21, 25.83, 41.58, 49.71, 129.21, 129.35, 131.30, 136.51, 208.90 (CO); IR (neat) 2959, 2932, 2872, 1713 (CO), 1514, 1124, 1053, 804 cm^{-1} ; Anal. Calcd for $\text{C}_{13}\text{H}_{18}\text{O}$: C, 82.05; H, 9.54. Found: C, 81.66; H, 9.46; HRMS (EI) Calcd for $\text{C}_{13}\text{H}_{18}\text{O}$ (M^+) 190.1357. Found 190.1347.

1-(4-Fluorophenyl)-1-hexyne (1n): colorless oil; ^1H NMR (300.40 MHz, CDCl_3) δ 0.93 (3H, t, $J = 7.1$ Hz), 1.46 (2H, tq, $J = 7.1, 7.1$ Hz), 1.57 (2H, tt, $J = 7.1, 7.1$ Hz), 2.37 (2H, t, $J = 7.1$ Hz), 6.95 (2H, dd, $^3J(\text{H}, \text{H}) = 8.9$ Hz, $^3J(\text{H}, \text{F}) = 9.1$ Hz), 7.34 (2H, dd, $^3J(\text{H}, \text{H}) = 8.9$ Hz, $^4J(\text{H}, \text{F}) = 5.6$ Hz); ^{13}C NMR (75.45 MHz, CDCl_3) δ 13.59, 19.00, 22.00, 30.79, 79.46, 89.96, 115.31 (d, $^2J(\text{C}, \text{F}) = 21.3$ Hz), 120.15 (d, $^4J(\text{C}, \text{F}) = 3.8$ Hz), 133.25 (d, $^3J(\text{C}, \text{F}) = 8.1$ Hz), 161.99 (d, $^1J(\text{C}, \text{F}) = 248.1$ Hz); IR (neat) 2959, 2932,

2872, 1510, 816 cm^{-1} ; Anal. Calcd for $\text{C}_{12}\text{H}_{13}\text{F}$: C, 81.77; H, 7.44. Found: C, 81.80; H, 7.74; HRMS (EI) Calcd for $\text{C}_{12}\text{H}_{13}\text{F}$ (M^+) 176.1002. Found 176.0988.

1-(4-Fluorophenyl)-1-hexanone (3n): colorless solid; ^1H NMR (300.40 MHz, CDCl_3) δ 0.89 (3H, t, $J = 6.5$ Hz), 1.26-1.42 (4H, m), 1.71 (2H, tt, $J = 7.3, 7.0$ Hz), 2.91 (2H, t, $J = 7.3$ Hz), 7.10 (2H, dd, $^3J(\text{H}, \text{H}) = 8.4$ Hz, $^3J(\text{H}, \text{F}) = 8.4$ Hz), 7.96 (2H, dd, $^3J(\text{H}, \text{H}) = 8.4$ Hz, $^4J(\text{H}, \text{F}) = 5.6$ Hz); ^{13}C NMR (75.45 MHz, CDCl_3) δ 13.91, 22.49, 24.00, 31.48, 38.46, 115.56 (d, $^2J(\text{C}, \text{F}) = 21.8$ Hz), 130.61 (d, $^3J(\text{C}, \text{F}) = 9.4$ Hz), 133.48 (d, $^4J(\text{C}, \text{F}) = 3.1$ Hz), 165.58 (d, $^1J(\text{C}, \text{F}) = 253.7$ Hz), 198.90 (CO); IR (KBr) 2934, 2862, 1676 (CO), 1599, 1232 (C-F), 1202, 1157, 831, 731 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{12}\text{H}_{15}\text{OF}$ (M^+) 194.1107. Found 194.1111.

1-(4-Fluorophenyl)-2-hexanone (4n): colorless oil; ^1H NMR (300.40 MHz, CDCl_3) δ 0.85 (3H, t, $J = 7.2$ Hz), 1.25 (2H, tq, $J = 7.2, 7.2$ Hz), 1.58 (2H, tt, $J = 7.2, 7.2$ Hz), 2.43 (2H, t, $J = 7.2, 7.2$ Hz), 3.64 (2H, s), 6.99 (2H, dd, $^3J(\text{H}, \text{H}) = 8.2$ Hz, $^3J(\text{H}, \text{F}) = 8.2$ Hz), 7.13 (2H, dd, $^3J(\text{H}, \text{H}) = 8.2$ Hz, $^4J(\text{H}, \text{F}) = 5.8$

Hz); ^{13}C NMR (75.45 MHz, CDCl_3) δ 13.78, 22.21, 25.80, 41.80, 49.00, 115.49 (d, $^2J(\text{C}, \text{F}) = 21.2$ Hz), 130.01 (d, $^4J(\text{C}, \text{F}) = 3.8$ Hz), 130.89 (d, $^3J(\text{C}, \text{F}) = 8.1$ Hz), 161.91 (d, $^1J(\text{C}, \text{F}) = 245.0$ Hz), 208.27 (CO); IR (neat) 2961, 2934, 1715 (CO), 1609, 1510, 1223 (C-F), 1159, 1053, 841, 818 cm^{-1} ; Anal. Calcd for $\text{C}_{12}\text{H}_{15}\text{OF}$: C, 74.18; H, 7.79. Found: C, 73.76; H, 8.02; HRMS (EI) Calcd for $\text{C}_{12}\text{H}_{15}\text{OF}$ (M^+) 194.1107. Found 194.1098.

1-(4-Trifluoromethylphenyl)-1-hexyne (1o): colorless oil; ^1H NMR (300.40 MHz, CDCl_3) δ 0.94 (3H, t, $J = 7.3$ Hz), 1.47 (2H, tq, $J = 7.3, 7.3$ Hz), 1.58 (2H, tt, $J = 7.3, 7.3$ Hz), 2.41 (2H, t, $J = 7.3$ Hz), 7.46 (2H, d, $J = 8.3$ Hz), 7.51 (2H, d, $J = 8.3$ Hz); ^{13}C NMR (75.45 MHz, CDCl_3) δ 13.59, 19.10, 22.02, 30.62, 79.48, 93.29, 124.04 (q, $^1J(\text{C}, \text{F}) = 271.1$ Hz), 125.08 (q, $^3J(\text{C}, \text{F}) = 3.9$ Hz), 127.99 (br s), 129.22 (q, $^2J(\text{C}, \text{F}) = 33.0$ Hz), 131.75; IR (neat) 2961, 2936, 2233 (alkyne), 1616, 1323 (C-F), 1167, 1128, 1069, 1018, 843 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{13}\text{H}_{13}\text{F}_3$ (M^+) 226.0970. Found 226.0942.

1-(4-Trifluoromethylphenyl)-1-hexanone (3o): colorless solid; ^1H NMR (300.40 MHz, CDCl_3) δ 0.90 (2H, t, $J = 7.1$ Hz), 1.27-1.43 (4H, m), 1.73 (2H, tt, $J = 7.1, 7.1$ Hz), 2.96 (2H, t, $J = 7.1$ Hz), 7.71 (2H, d,

8.6 Hz), 8.03 (2H, d, $J = 8.6$ Hz); ^{13}C NMR (75.45 MHz, CDCl_3) δ 13.92, 22.49, 23.80, 31.42, 38.87, 123.62 (q, $^1J(\text{C}, \text{F}) = 271.8$ Hz), 125.63 (q, $^3J(\text{C}, \text{F}) = 3.8$ Hz), 128.35, 134.19 (q, $^2J(\text{C}, \text{F}) = 32.4$ Hz), 139.70 (br s), 199.49 (CO); IR (KBr) 2934, 2882, 1682 (CO), 1410, 1329 (C-F), 1167, 1130, 1069, 831 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{13}\text{H}_{15}\text{OF}_3$ (M^+) 244.1075. Found 244.1035.

1-(4-Trifluoromethylphenyl)-2-hexanone (4o): colorless oil; ^1H NMR (300.40 MHz, CDCl_3) δ 0.87 (3H, t, $J = 7.3$ Hz), 1.27 (2H, tq, $J = 7.3, 7.3$ Hz), 1.55 (2H, tt, $J = 7.3, 7.3$ Hz), 2.46 (2H, t, $J = 7.3$ Hz), 3.74 (2H, s), 7.29 (2H, d, $J = 8.1$ Hz), 7.56 (2H, d, $J = 8.1$ Hz); ^{13}C NMR (75.45 MHz, CDCl_3) δ 13.75,

22.19, 42.19, 49.42, 124.13 (q, $^1J(\text{C}, \text{F}) = 271.8$ Hz), 125.49 (q, $^3J(\text{C}, \text{F}) = 3.7$ Hz), 129.25 (q, $^2J(\text{C}, \text{F}) = 32.4$ Hz), 129.79, 138.25 (q, $^4J(\text{C}, \text{F}) = 1.2$ Hz), 207.34 (CO); IR (neat) 2961, 2934, 2876, 1717 (CO),

1620, 1325, 1165, 1124, 1069, 1020, 816 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{13}\text{H}_{15}\text{OF}_3$ (M^+) 244.1075. Found 244.1062.

2-*N*-(1-Pentyl-1-heptyl)aminophenol (6): **; ^1H NMR (300.40 MHz, CDCl_3) δ (6H, t*2, $J = 6.5$ Hz), 1.16-1.58 (18H, m), 3.25 (br tt, $J = 6.0, 6.0$ Hz), 6.58 (1H, br dd, $J = 7.8, 7.8$ Hz), 6.64 (1H, br d, $J = 7.8$ Hz), 6.69 (1H, br d, $J = 7.8$ Hz), 6.82 (1H, br d, $J = 7.8$ Hz); ^{13}C NMR (125.65 MHz, CDCl_3) δ 14.04, 14.06, 22.62, 25.52, 25.82, 29.49, 29.69, 31.83, 32.03, 34.71 (br), 53.49 (br), 114.50 (br), 117.15 (br); IR (neat) 3418 (br), 2955, 2928, 2856, 1609, 1520, 1456, 1255, 735 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{18}\text{H}_{31}\text{NO}$ (M^+) 277.2406. Found 277.2419.

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