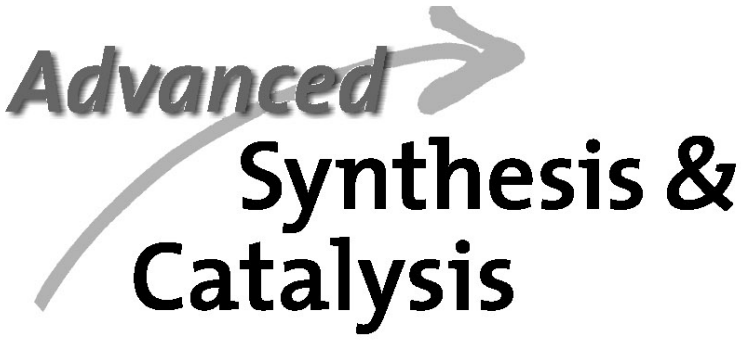

Supporting Information

Cascade reactions: sequential homobimetallic catalysis leading to benzofurans and b,g-unsaturated esters

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Supporting Information

General Remarks. Melting points were determined with a Reichert Thermovar apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded at 25 °C on a Bruker DPX Avance 300 spectrometer in $CDCl_3$ solutions at 300 MHz and 75 MHz, respectively, with Me_4Si as internal standard. Chemical shifts (δ) and coupling constants (*J*) are given in ppm and in Hz, respectively. IR spectra were taken with a Perkin-Elmer Paragon 1000 PC FT-IR spectrometer. Mass spectra were obtained using a Shimadzu QP-2010 GC-MS apparatus at 70 eV ionization voltage. Microanalyses were carried out with a Carlo Erba Elemental Analyzer Mod. 1106. All reactions were analyzed by TLC on silica gel 60 F_{254} and by GLC using a Shimadzu GC-2010 gas chromatograph and capillary columns with polymethylsilicone + 5% phenylsilicone as the stationary phase (HP-5). Column chromatography was performed on silica gel 60 (Merck, 70-230 mesh). Evaporation refers to the removal of solvent under reduced pressure.

Preparation of 1-(2-Allyloxyphenyl)-2-yn-1-ols 1a, 1a', 1c-1r and 2-(1-Hydroxy-3-phenylprop-2-ynyl)phenol 3d

Preparation of alkynylmagnesium bromide. The whole procedure was carried out under nitrogen. To a suspension of Mg turnings (940 mg, 38.7 mmol) in anhydrous THF (8.0 mL), maintained under reflux, was added pure EtBr (0.7 mL) to start the formation of the Grignard reagent. The remaining bromide was added dropwise (ca. 20 min) in THF solution (2.0 mL of EtBr in 22.0 mL of THF; total amount of EtBr added: 3.94 g, 36.1 mmol). The mixture was then allowed to reflux for additional 20 min. After cooling, the solution of EtMgBr thus obtained was transferred under nitrogen to a dropping funnel and added dropwise to a solution of the 1-alkyne (36.0 mmol) in anhydrous THF (5.4 mL) at 0 °C with stirring. After additional stirring at 0 °C for 15 min, the mixture was allowed to warm up to room temperature and then maintained at 50 °C for 2 h, and used as such for the next step.

Allylation of 1-(2-hydroxyphenyl) aldehydes or ketones followed by addition of alkynylmagnesium bromide. K_2CO_3 (11.6 g, 83.9 mmol) was added to a solution of the 1-(2-hydroxyphenyl)aldehyde (30.0 mmol) or the 1-(2-hydroxyphenyl)ketone (30.0 mmol) in acetonitrile (ca. 150 mL), followed by the addition of allyl bromide (4.3 g, 35.5 mmol) or cinnamyl chloride (5.4 g, 35.4 mmol). The resulting mixture was heated under reflux for 5-15 h (allyl bromide and 2-hydroxybenzaldehyde, 2-hydroxyacetophenone, 2-hydroxybenzophenone: 15 h; allyl bromide and 2-hydroxy-3-methoxybenzaldehyde, 2-hydroxy-4-methoxybenzaldehyde, 2-hydroxy-5-methoxybenzaldehyde, 2-hydroxy-5-chlorobenzaldehyde: 8 h; cinnamyl chloride and 2-hydroxybenzaldehyde: 5 h). After cooling to room temperature, the mixture was filtered, and the solvent removed under vacuum. The crude product thus obtained was dissolved in anhydrous THF (22.0 mL) and then added dropwise to a solution of the alkynylmagnesium bromide (prepared as described above) at 50 °C under nitrogen. After stirring at 50 °C for 1.5 h, the mixture was cooled to room temperature and saturated NH_4Cl was added with stirring. After additional stirring at room temperature for 15 min., AcOEt (ca. 20 mL) was added and phases were separated. The aqueous phase was extracted with AcOEt (3 × 50 mL), and the collected organic layers were washed with brine and eventually dried over Na_2SO_4. After filtration and removal of the solvent in vacuo, products were purified by elution through a short SiO_2 column using hexane-acetone or hexane-AcOEt mixtures as the eluent: **1a** (7:3 hexane-acetone, yellow oil, 6.58 g, 90% based on 2-hydroxybenzaldehyde); **1a'** (hexane-AcOEt 9:1, yellow oil, 8.90 g, 93% based on 2-hydroxybenzaldehyde); **1c** (hexane-acetone 8:2, yellow oil, 6.71 g, 92% based on 2-hydroxybenzaldehyde); **1d** (7:3 hexane-acetone, yellow oil, 7.05 g, 89% based on 2-

hydroxybenzaldehyde); **1e** (7:3 hexane-acetone, yellow oil, 7.04 g, 91% based on 2-hydroxybenzaldehyde); **1f** (hexane-acetone 9:1, yellow oil, 7.20 g, 93% based on 2-hydroxyacetophenone); **1g** (hexane-acetone 6:4, pale yellow oil, 7.29 g, 87% based on 2-hydroxyacetophenone); **1h** (7:3 hexane-acetone, pale yellow oil, 8.16 g, 85% based on 2-hydroxybenzophenone); **1i** (7:3 hexane-acetone, yellow oil, 8.40 g, 82% based on 2-hydroxybenzophenone); **1k** (7:3 hexane-acetone, yellow oil, 7.40 g, 90% based on 2-hydroxy-3-methoxybenzaldehyde); **1l** (7:3 hexane-acetone, yellow oil, 7.90 g, 90% based on 2-hydroxy-3-methoxybenzaldehyde); **1m** (hexane-acetone 8:2, yellow oil, 7.30 g, 89% based on 2-hydroxy-4-methoxybenzaldehyde), **1n** (hexane-acetone 6:4, yellow oil, 8.02 g, 91% based on 2-hydroxy-4-methoxybenzaldehyde); **1o** (hexane-acetone 8:2, yellow oil, 7.10 g, 86% based on 2-hydroxy-5-methoxybenzaldehyde); **1p** (hexane-acetone 6:4, yellow oil, 7.81 g, 89% based on 2-hydroxy-5-methoxybenzaldehyde); **1q** (7:3 hexane-acetone, yellow oil, 7.80 g, 92% based on 5-chloro-2-hydroxybenzaldehyde); **1r** (7:3 hexane-acetone, yellow oil, 8.30 g, 93% based on 5-chloro-2-hydroxybenzaldehyde).

Allylation of methyl 2-hydroxybenzoate followed by addition of hexynylmagnesium bromide. K_2CO_3 (2.08 g, 15.05 mmol) was added to a solution of methyl 2-hydroxybenzoate (2.28 g, 14.99 mmol) in acetone (ca. 15 mL), followed by the addition of allyl bromide (1.83 g, 15.13 mmol). The resulting mixture was heated under reflux for 24 h. After cooling to room temperature, the mixture was filtered, and the solvent removed under vacuum. The crude product thus obtained was dissolved in anhydrous THF (10.0 mL) and then added dropwise to a solution of the hexynylmagnesium bromide (prepared as described above) at 50 °C under nitrogen. After stirring at 50 °C for 1.5 h, the mixture was cooled to room temperature and saturated NH_4Cl was added with stirring. After additional stirring at room temperature for 15 min., AcOEt (ca. 20 mL) was added and phases were separated. The aqueous phase was extracted with AcOEt (3 × 50 mL), and the collected organic layers were washed with brine and eventually dried over Na_2SO_4. After filtration and removal of the solvent in vacuo, product **1j** was purified by elution through a short SiO_2 column using 8:2 hexane-acetone as the eluent (yellow oil, 3.78 g, 78% based on methyl 2-hydroxybenzoate).

Addition of phenylethynylmagnesium bromide to 2-hydroxybenzaldehyde. 2-Hydroxybenzaldehyde (1.83 g, 15.0 mmol) was dissolved in anhydrous THF (22.0 mL) and then added dropwise to a solution of the phenylethynylmagnesium bromide (prepared as described above) at 50 °C under nitrogen. After stirring at 50 °C for 1.5 h, the mixture was cooled to room temperature and saturated NH_4Cl was added with stirring. After additional stirring at room

temperature for 15 min., AcOEt (ca. 20 mL) was added and phases were separated. The aqueous phase was extracted with AcOEt (3 × 50 mL), and the collected organic layers were washed with brine and eventually dried over Na_2SO_4. After filtration and removal of the solvent in vacuo, product **3d** was purified by elution through a short SiO_2 column using 9:1 hexane-AcOEt as the eluent (pale yellow solid, mp 84-85 °C, [lit.[1] 85 °C], 2.19 g, 65% based on 2-hydroxybenzaldehyde).

Preparation of 2-(2-Allyloxyphenyl)-prop-2-yn-1-ol 1b and 2-(1-Hydroxyprop-2-ynyl)phenol 3b

Preparation of ethynylmagnesium bromide. The whole procedure was carried out under nitrogen. To a suspension of Mg turnings (3.7 g, 152.2 mmol) in anhydrous THF (10.0 mL) maintained under reflux was added pure EtBr (2.0 mL) to start the formation of the Grignard reagent. The remaining bromide was added dropwise (ca. 45 min) in THF solution (8.9 mL of EtBr in 80 mL of THF; total amount of EtBr added: 15.9 g, 145.9 mmol). The mixture was then allowed to reflux for additional 20 min. After cooling, the solution of EtMgBr thus obtained was transferred under nitrogen to a dropping funnel and added dropwise at room temperature to saturated solution of acetylene in anhydrous THF (200 mL), while maintaining a constant flow of acetylene through the mixture (ca. 2 h). After stirring at room temperature for additional 1.5 h, the solution containing the ethynylmagnesium bromide (ca. 145.9 mmol) was used as such for the next step.

Allylation of 2-hydroxybenzaldehyde followed by addition of ethynylmagnesium bromide. K_2CO_3 (33.3 g, 240.9 mmol) was added to a solution of 2-hydroxybenzaldehyde (10.50 g, 86.0 mmol) in acetonitrile (450 mL), followed by the addition of allyl bromide (12.4 g, 102.5 mmol). The resulting mixture was heated under reflux for 15 h. After cooling to room temperature, the mixture was filtered, and the solvent removed under vacuum. The crude product thus obtained was dissolved in anhydrous THF (40 mL) and then added dropwise to a solution of ethynylmagnesium bromide (prepared as described above) at 0 °C. After stirring at the same temperature for 1 h and at room temperature for 15 h, saturated NH_4Cl (ca. 150 mL) was added with cooling (0 °C) followed by Et_2O (ca. 120 mL). 1 M HCl (150 mL) was then added at room temperature. Phases were separated and the aqueous phase was extracted three times with Et_2O. The collected organic layers were washed with H_2O to neutral pH and then with brine. After drying over Na_2SO_4 and filtration, the solvent was removed in vacuo and the crude product were purified by column chromatography

(SiO_2) using 1:1 hexane-Et_2O as the eluent to give 14.60 g of pure **1b** (yellow oil, 90% based on 2-hydroxybenzaldehyde).

Addition of ethynylmagnesium bromide to 2-hydroxybenzaldehyde. 2-Hydroxybenzaldehyde (6.1 g, 50.0 mmol) was dissolved in anhydrous THF (40 mL) and then added dropwise to a solution of ethynylmagnesium bromide (prepared as described above) at 0 °C. After stirring at the same temperature for 1 h and at room temperature for 15 h, saturated NH_4Cl (ca. 150 mL) was added with cooling (0 °C) followed by Et_2O (ca. 120 mL). 1 M HCl was then added in portions (3 × 50 mL) at room temperature. Phases were separated and the aqueous phase was extracted three times with Et_2O. The collected organic layers were washed with H_2O to neutral pH and then with brine. After drying over Na_2SO_4 and filtration, the solvent was removed in vacuo and the crude product were purified by column chromatography (SiO_2) using 1:1 hexane-Et_2O as the eluent to give pure **3b** as a colorless solid (mp 91-92 °C, lit.[2] 92.1-93.5 °C) (6.68 g, 90% based on 2-hydroxybenzaldehyde).

Characterization of Substrates

1-(2-Allyloxyphenyl)hept-2-yn-1-ol (1a). Yield: 6.58 g, starting from 3.66 g of 2-hydroxybenzaldehyde (90%). Yellow oil. IR (film): ν = 3421 (m, br), 2957 (s), 2929 (s), 2870 (m), 2222 (vw), 1601 (w), 1489 (m), 1455 (m), 1240 (s), 998 (m), 929 (w), 753 (m) cm^{-1}; ^1H NMR: *d* = 7.58 (dd, *J* = 7.3, 2.0, 1 H, H-6), 7.28-7.21 (m, 1 H, H-4), 6.96 (td, *J* = 7.3, 1.0, 1 H, H-5), 6.87 (dd, *J* = 8.3, 1.0, 1 H, H-3), 6.12-5.98 (m, 1 H, C*H*=CH_2), 5.73 (s, br, 1 H, C*H*OH), 5.43 (dq, *J* = 17.1, 1.5, 1 H, CH=C*H*H), 5.28 (dq, *J* = 10.7, 1.5, 1 H, CH=CH*H*), 4.66-4.53 (m, 2 H, OCH_2), 3.18 (d, br, *J* = 4.4, 1 H, OH), 2.26 (td, *J* = 6.8, 2.0, 2 H, ≡CCH_2), 1.58-1.34 (m, 4 H, CH_2C$H_2$$CH_3$), 0.90 (t, *J* = 7.3, 3 H, Me); ^{13}C NMR: *d* = 155.8, 133.0, 130.0, 129.3, 128.0, 121.0, 117.5, 112.1, 86.8, 79.6, 69.0, 61.1, 30.8, 22.0, 18.6, 13.6; GC-MS: *m/z* = 244 (28) [M^+], 203 (84), 197 (10), 187 (28), 173 (15), 169 (15), 161 (16), 160 (18), 159 (18), 158 (18), 157 (59), 147 (31), 145 (26), 144 (60), 135 (22), 134 (20), 133 (24), 131 (48), 129 (22), 128 (28), 122 (33), 121 (100), 115 (44), 109 (19), 107 (29), 105 (21), 91 (28), 79 (22), 77 (32), 55 (16); anal. calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25; found C, 78.78; H, 8.23.

(*E*)-1-[2-(3-Phenylallyloxy)phenyl)hept-2-yn-1-ol (1a'). Yield: 8.90 g, starting from 3.66 g of 2-hydroxybenzaldehyde (93%). Yellow oil. IR (film): ν = 3339 (m, br), 2951 (m), 2926 (m), 2854 (m), 2217 (vw), 1599 (m), 1490 (m), 1451 (m), 1375 (m), 1238 (s), 1016 (s), 961 (m), 745 (m) cm^{-1}; ^1H NMR: *d* = 7.60 (dd, *J* = 7.7, 1.7, 1 H, H-6), 7.42-7.21 (m, 6 H, Ph + H-4), 6.98 (td, *J* = 7.7, 0.9,

1 H, H-5), 6.92 (dd, *J* = 8.1, 0.9, 1 H, H-3), 6.73 (dt, *J* = 16.2, 1.7, 1 H, =CHPh), 6.39 (dt, *J* = 16.2, 5.6, 1 H, C*H*=CHPh), 5.76 (s, br, 1 H, C*H*OH), 4.81-4.68 (m, 2 H, OCH_2), 3.05 (d, br, *J* = 3.9, 1 H, OH), 2.26 (td, *J* = 7.0, 2.1, 2 H, ≡CCH_2), 1.57-1.33 (m, 4 H, $CH_2CH_2CH_3$), 0.88 (t, *J* = 7.3, 3 H, Me); ^{13}C NMR: *d* = 155.9, 136.4, 133.1, 130.1, 129.4, 128.6, 128.0, 126.6, 124.2, 121.1, 112.3, 87.0, 79.6, 69.1, 61.3, 30.8, 22.0, 18.6, 13.5; MS (direct injection): *m/z* = 320 (0.5) [M^+], 198 (9), 186 (3), 157 (5), 156 (4), 155 (2), 142 (4), 141 (4), 118 (12), 117 (100), 116 (9), 115 (22), 91 (12), 77 (3); anal. calcd for $C_{22}H_{24}O_2$: C, 82.46; H, 7.55; found C, 82.34; H, 7.56.

1-(2-Allyloxyphenyl)prop-2-yn-1-ol (1b). Yield: 14.60 g, starting from 3.66 g of 2-hydroxybenzaldehyde (90%). Yellow oil. IR (film): ν = 3419 (m, br), 3289 (s), 2113 (vw), 1600 (w), 1489 (m), 1453 (m), 1287 (w), 1242 (s), 1019 (s), 934 (m), 754 (m), 654 (m) cm^{-1}; ^{1}H NMR: *d* = 7.54 (ddt, *J* = 7.5, 1.8, 0.4, 1 H, H-6), 7.26 (ddd, *J* = 8.2, 7.5, 1.8, 1 H, H-4), 6.96 (td, *J* = 7.5, 1.1, 1 H, H-5), 6.87 (dd, *J* = 8.2, 1.1, 1 H, H-3), 6.11-5.97 (m, 1 H, C*H*=CH_2), 5.70 (d, br, *J* = 2.3, 1 H, C*H*OH), 5.42 (dq, *J* = 17.3, 1.6, 1 H, CH=C*H*H), 5.28 (dq, *J* = 10.6, 1.6, 1 H, CH=CH*H*), 4.65-4.52 (m, 2 H, OCH_2), 3.19 (s, br, 1 H, OH), 2.57 (d, *J* = 2.3, 1 H, ≡CH); ^{13}C NMR: *d* = 155.7, 132.8, 129.6, 128.7, 127.9, 121.1, 117.7, 112.2, 83.3, 73.9, 69.0, 60.9; GC-MS: *m/z* = 188 (35) [M^+], 169 (14), 147 (38), 134 (14), 131 (25), 130 (100), 121 (21), 103 (16), 102 (88), 91 (24), 77 (20), 76 (14), 65 (22), 53 (26), 51 (14); anal. calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43; found C, 76.45; H, 6.44.

1-(2-Allyloxyphenyl)-4,4-dimethylpent-2-yn-1-ol (1c). Yield: 6.71 g, starting from 3.66 g of 2-hydroxybenzaldehyde (92%). Yellow oil. IR (film): ν = 3439 (m, br), 2969 (s), 2926 (m), 2867 (m), 2235 (vw), 1597 (m), 1489 (s), 1455 (m), 1285 (m), 1238 (s), 993 (s), 930 (m), 753 (m) cm^{-1}; ^{1}H NMR: *d* = 7.58 (ddt, *J* = 7.5, 1.8, 0.3, 1 H, H-6), 7.25 (ddd, *J* = 8.2, 7.5, 1.8, 1 H, H-4), 6.97 (td, *J* = 7.5, 1.1, 1 H, H-5), 6.87 (dd, *J* = 8.2, 1.1, 1 H, H-3), 6.12-5.99 (m, 1 H, C*H*=CH_2), 5.74 (s, br, 1 H, C*H*OH), 5.44 (dq, *J* = 17.3, 1.6, 1 H, CH=C*H*H), 5.28 (dq, *J* = 10.6, 1.6, 1 H, CH=CH*H*), 4.67-4.53 (m, 2 H, OCH_2), 3.06 (s, br, 1 H, OH), 1.25 (s, 9 H, *t*-Bu); ^{13}C NMR: *d* = 155.9, 133.0, 130.0, 129.3, 128.0, 121.0, 117.5, 112.1, 95.0, 77.9, 69.0, 61.1, 31.0, 27.5; GC-MS: *m/z* = 244 (30) [M^+], 203 (52), 188 (20), 187 (47), 173 (23), 171 (68), 169 (17), 161 (19), 159 (23), 145 (54), 143 (17), 141 (18), 135 (23), 134 (20), 133 (30), 131 (36), 128 (41), 122 (20), 121 (71), 115 (32), 109 (21), 107 (34), 105 (22), 93 (19), 91 (35), 81 (25), 79 (23), 77 (30), 65 (27), 57 (32); anal. calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25; found C, 78.58; H, 8.25.

1-(2-Allyloxyphenyl)-3-phenylprop-2-yn-1-ol (1d). Yield: 7.05 g, starting from 3.66 g of 2-hydroxybenzaldehyde (89%). Yellow oil. IR (film): ν = 3417 (m, br), 2230 (vw), 1599 (m), 1489

(s), 1453 (m), 1286 (w), 1238 (s), 1017 (m), 997 (m), 755 (s) cm^{-1}; ^{1}H NMR: *d* = 7.61 (dd, *J* = 7.3, 2.0, 1 H, H-6), 7.50-7.41 (m, 2 H on phenyl ring), 7.32-7.22 (m, 3 H on phenyl ring + H-4), 6.98 (td, *J* = 7.3, 1.0, 1 H, H-5), 6.88 (dd, *J* = 8.3, 1.0, 1 H, H-3), 6.12-5.98 (m, 1 H, C*H*=CH_2), 5.93 (s, br, 1 H, C*H*OH), 5.45 (dq, *J* = 17.1, 1.5, 1 H, CH=C*H*H), 5.28 (dq, *J* = 10.7, 1.5, 1 H, CH=CH*H*), 4.63-4.58 (m, 2 H, OCH_2), 3.17 (s, br, 1 H, OH); ^{13}C NMR: *d* = 155.8, 132.9, 131.7, 129.6, 129.3, 128.3, 128.2, 128.1, 122.8, 121.1, 117.7, 112.3, 88.7, 85.8, 69.1, 61.8; GC-MS: *m/z* = 264 (3) [M^+], 247 (20), 224 (17), 223 (100), 207 (21), 205 (22), 178 (22), 176 (19), 167 (25), 165 (38), 152 (27), 142 (21), 141 (19), 129 (30), 121 (46), 115 (18), 102 (16), 77 (21); anal. calcd for $C_{18}H_{20}O_2$: C, 81.79; H, 6.10; found C, 81.85; H, 6.09.

1-(2-Allyloxyphenyl)oct-3-yn-2-ol (1e). Yield: 7.04 g, starting from 3.66 g of 2-hydroxybenzaldehyde (91%). Yellow oil. IR (film): ν = 3420 (m, br), 2957 (m), 2931 (s), 2871 (m), 2244 (vw), 1599 (w), 1585 (w), 1487 (m), 1454 (m), 1383 (m), 1287 (m), 1234 (s), 997 (m), 913 (m), 753 (m) cm^{-1}; ^{1}H NMR: *d* = 7.58 (dd, *J* = 7.8, 2.0, 1 H, H-6), 7.27-7.19 (m, 1 H, H-4), 6.95 (td, *J* = 7.8, 1.0, 1 H, H-5), 6.90 (dd, *J* = 8.3, 1.0, 1 H, H-3), 6.14-6.00 (m, 1 H, C*H*=CH_2), 5.47 (dq, *J* = 17.1, 1.5, 1 H, CH=C*H*H), 5.51 (dq, *J* = 10.7, 1.5, 1 H, CH=CH*H*), 4.64 (dt, *J* = 4.9, 1.5, 2 H, OCH_2), 4.47 (s, br, 1 H, OH), 2.24 (t, *J* = 6.8, 2 H, ≡CCH_2), 1.87 (s, 3 H, C*H*$_3$COH), 1.57-1.34 (m, 4 H, C*H*$_2$C*H*$_2$$CH_3$), 0.89 (t, *J* = 7.3, 3 H, CH_2CH_2C*H*$_3$); ^{13}C NMR: *d* = 155.8, 133.4, 132.7, 128.7, 126.7, 121.1, 117.9, 112.8, 84.3, 83.6, 69.5, 69.2, 30.8, 30.3, 22.0, 18.5, 13.6; GC-MS: *m/z* = 258 (3) [M^+], 244 (10), 243 (54), 201 (15), 171 (6), 161 (7), 159 (8), 145 (7), 131 (8), 128 (8), 121 (50), 115 (8), 110 (8), 109 (100), 91 (7), 79 (10), 77 (8); anal. calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58.; found C, 79.14; H, 8.57.

1-(2-Allyloxyphenyl)-5,5-dimethylhex-3-yn-2-ol (1f). Yield: 7.20 g, starting from 4.08 g of 2-hydroxyacetophenone (93%). Yellow oil. IR (film): ν = 3425 (m, br), 2967 (s), 2927 (m), 2865 (m), 2255 (vw), 1599 (w), 1583 (w), 1487 (m), 1449 (m), 1361 (m), 1285 (m), 1265 (m), 1231 (s), 997 (m), 923 (w), 905 (w), 753 (m) cm^{-1}; ^{1}H NMR: *d* = 7.59 (dd, *J* = 7.6, 1.8, 1 H, H-6), 7.23 (ddd, *J* = 8.2, 7.6, 1.8, 1 H, H-4), 6.95 (td, *J* = 7.6, 1.1, 1 H, H-5), 6.90 (dd, *J* = 8.2, 1.1, 1 H, H-3), 6.15-6.00 (m, 1 H, C*H*=CH_2), 5.48 (dq, *J* = 17.3, 1.5, 1 H, CH=C*H*H), 5.31 (dq, *J* = 10.6, 1.5, 1 H, CH=CH*H*), 4.64 (dt, *J* = 5.0, 1.5, 2 H, OCH_2), 4.42 (s, br, 1 H, OH), 1.85 (s, 3 H, 3 H, C*H*$_3$COH), 1.23 (s, 9 H, CMe_3); ^{13}C NMR: *d* = 155.8, 133.5, 132.6, 128.7, 126.7, 121.0, 117.9, 112.7, 92.5, 82.0, 69.5, 69.2, 31.0, 30.5, 27.3; GC-MS: *m/z* = 258 (3) [M^+], 244 (15), 243 (80), 201 (24), 161 (12), 159 (21), 145 (13), 131 (10), 121 (55), 115 (12), 109 (100), 91 (14), 81 (27), 79 (12), 57 (11); anal. calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58; found C, 79.14; H, 8.57.

2-(2-Allyloxyphenyl)-4-phenylbut-3-yn-2-ol (1g). Yield: 7.29 g, starting from 4.08 g of 2-hydroxyacetophenone (87%). Pale yellow oil. IR (film): ν = 3530 (m, br), 2233 (vw), 1598 (m), 1584 (w), 1489 (s), 1444 (m), 1287 (m), 1233 (s), 1129 (m), 1071 (m), 1048 (m), 996 (m), 893 (w), 754 (s), 691 (m) cm^{-1}; ^{1}H NMR: *d* = 7.60 (dd, *J* = 7.6, 1.8, 1 H, H-6), 7.50-7.38 (m, 2 H on phenyl ring), 7.31-7.21 (m, 4 H, H-4 + 3 H on phenyl ring), 6.97 (td, *J* = 7.5, 1.1, 1 H, H-5), 6.92 (dd, *J* = 8.1, 1.1, 1 H, H-3), 6.15-5.99 (m, 1 H, C*H*=CH_2), 5.49 (dq, *J* = 17.3, 1.5, 1 H, =C*H*H), 5.28 (dq, *J* = 10.6, 1.5, 1 H, =CH*H*), 4.65 (dt, *J* = 5.0, 1.5, 2 H, OCH_2), 4.58 (s, br, 1 H, OH), 1.99 (s, 3 H, Me); ^{13}C NMR: *d* = 155.9, 132.6, 131.6, 129.0, 128.3, 128.2, 128.1, 126.3, 123.1, 121.2, 118.0, 112.9, 92.9, 83.2, 77.2, 69.3, 29.6; MS (direct injection): *m/z* = 278 (4) [M^+], 263 (31), 261 (30), 237 (46), 235 (19), 221 (45), 195 (15), 194 (14), 165 (39), 145 (19), 141 (15), 129 (100), 121 (62), 115 (17), 105 (9), 91 (11), 77 (10), 65 (8); anal. calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52.; found C, 82.12; H, 6.51.

1-(2-Allyloxyphenyl)-1-phenylhept-2-yn-1-ol (1h). Yield: 8.16 g, starting from 5.95 g of 2-hydroxybenzophenone (85%). Pale yellow oil. IR (film): ν = 3518 (m, br), 2957 (s), 2932 (s), 2863 (m), 2236 (vw), 1593 (w), 1580 (w), 1486 (m), 1451 (m), 1285 (w), 1230 (s), 1004 (s), 926 (w), 905 (w), 756 (m), 699 (m) cm^{-1}; ^{1}H NMR: *d* = 7.55 (dd, *J* = 7.7, 1.7, 1 H, H-6), 7.52-7.47 (m, 2 H on phenyl ring), 7.32-7.18 (m, 4 H, H-4 + 3 H on phenyl ring), 6.99-6.92 (m, 1 H, H-5), 6.87-6.82 (m, 1 H, H-3), 5.80-5.65 (m, 1 H, C*H*=CH_2), 5.22-5.11 (m, 2 H, =CH_2), 4.80 (s, br, 1 H, OH), 4.50-4.28 (m, 2 H, OCH_2), 2.28 (t, *J* = 7.0, 2 H, ≡CCH_2), 1.59-1.32 (m, 4 H, $CH_2CH_2CH_3$), 0.88 (t, *J* = 7.3, 3 H, Me); ^{13}C NMR: *d* = 155.8, 145.7, 133.5, 132.5, 129.1, 128.6, 127.8, 127.1, 126.1, 120.9, 117.8, 113.3, 88.1, 82.2, 74.6, 69.5, 30.7, 22.0, 18.7, 13.5; MS (direct injection): *m/z* = 320 (23) [M^+], 303 (31), 279 (100), 263 (23), 243 (16), 237 (20), 223 (20), 219 (22), 205 (15), 191 (17), 189 (15), 187 (16), 173 (14), 165 (19), 159 (20), 147 (23), 131 (30), 121 (37), 109 (40), 105 (39), 91 (21), 77 (27); anal. calcd for $C_{22}H_{24}O_2$: C, 82.46; H, 7.55; found C, 82.37; H, 7.56.

1-(2-Allyloxyphenyl)-1,3-diphenylprop-2-yn-1-ol (1i). Yield: 8.40 g, starting from 5.95 g of 2-hydroxybenzophenone (82%). Yellow oil. IR (film): ν = 3499 (m, br), 2229 (vw), 1597 (w), 1585 (w), 1488 (s), 1449 (m), 1284 (w), 1231 (m), 1165 (w), 1117 (w), 1041 (m), 998 (m), 921 (m), 755 (s), 691 (m) cm^{-1}; ^{1}H NMR: *d* = 7.61-7.56 (m, 2 H aromatic), 7.49-7.40 (m, 3 H aromatic), 7.36-7.18 (m, 7 H aromatic), 6.94 (td, *J* = 7.6, 1.1, 1 H, H-5), 6.87 (dd, *J* = 8.2, 1.1, 1 H, H-3), 5.85-5.70 (m, 1 H, C*H*=CH_2), 5.22 (dq, *J* = 17.3, 1.5, 1 H, =C*H*H), 5.15 (dq, *J* = 10.6, 1.5, 1 H, CH*H*), 4.90 (s, br, 1 H, OH), 4.48 (distorted ddt, *J* = 12.8, 5.2, 1.5, 1 H, OC*H*H), 4.39 (distorted ddt, *J* = 12.8, 5.1,

1.5, 1 H, OCH*H*); ^{13}C NMR: *d* = 155.7, 144.5, 132.9, 132.3, 131.7, 129.4, 128.4, 128.3, 128.2, 128.0, 127.5, 126.3, 122.8, 121.0, 118.0, 113.2, 91.1, 86.9, 74.7, 69.4; MS (direct injection): *m/z* = 340 (4) [M^+], 323 (3), 300 (22), 299 (100), 283 (9), 282 (7), 281 (22), 271 (18), 253 (10), 252 (13), 243 (8), 221 (11), 205 (5), 194 (6), 178 (10), 165 (19), 152 (6), 129 (26), 121 (22), 105 (59), 91 (5), 77 (29); anal. calcd for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92; found C, 84.75; H, 5.91.

7-(2-Allyloxyphenyl)-trideca-5,8-diyn-7-ol (1j). Yield: 3.78 g, starting from 2.28 g of methyl 2-hydroxybenzoate (78%). Yellow oil. IR (film): ν = 3519 (m, br), 2957 (s), 2931 (s), 2870 (m), 2229 (vw), 1599 (w), 1586 (w), 1486 (m), 1452 (m), 1283 (w), 1233 (m), 996 (m), 754 (m) cm^{-1}; ^{1}H NMR: *d* = 7.82 (dd, *J* = 7.6, 1.7, 1 H, H-6), 7.26 (ddd, *J* = 8.3, 7.6, 1.7, 1 H, H-4), 6.97 (td, *J* = 7.6, 0.8, 1 H, H-5), 6.92 (dd, *J* = 8.3, 0.8, 1 H, H-3), 6.15-6.00 (m, 1 H, C*H*=CH_2), 5.50 (dq, *J* = 17.3, 1.5, 1 H =C*H*H), 5.31 (dq, *J* = 10.6, 1.5, 1 H =CH*H*), 4.77 (s, br, 1 H, OH), 4.67 (dt, *J* = 4.8, 1.5, 2 H, OCH_2), 2.27 (t, *J* = 7.0, 4 H, 2 ≡CCH_2), 1.59-1.34 (m, 8 H, 2 CH_2C$H_2$$CH_3$), 0.90 (t, *J* = 7.2, 6 H, 2 Me); ^{13}C NMR: *d* = 155.7, 132.6, 131.2, 129.4, 127.5, 121.0, 117.8, 113.0, 85.0, 80.4, 69.4, 65.2, 30.5, 22.0, 18.6, 13.6; GC-MS: *m/z* = 324 (absent) [M^+], 307 (4), 306 (17), 278 (21), 277 (100), 207 (10), 194 (4), 178 (5), 165 (4), 152 (3), 73 (5); anal. calcd for $C_{22}H_{28}O_2$: C, 81.44; H, 8.70; found C, 81.36; H, 8.69.

1-(2-Allyloxy-3-methoxyphenyl)hept-2-yn-1-ol (1k). Yield: 7.40 g, starting from 4.56 g of 2-hydroxy-3-methoxybenzaldehyde (90%). Yellow oil. IR (film): ν = 3425 (m, br), 2957 (s), 2933 (s), 2871 (m), 2228 (vw), 1587 (w), 1479 (m), 1271 (s), 1207 (m), 993 (s), 927 (m), 749 (m) cm^{-1}; ^{1}H NMR: *d* = 7.15 (dd, *J* = 8.0, 1.7, 1 H, H-6), 7.06 (t, *J* = 8.0, 1 H, H-5), 6.88 (dd, *J* = 8.0, 1.7, 1 H, H-4), 6.21-6.06 (m, 1 H, C*H*=CH_2), 5.66 (t, *J* = 2.1, 1 H, C*H*OH), 5.39 (dq, *J* = 17.1, 1.5, 1 H, CH=C*H*H), 5.25 (dq, *J* = 10.3, 1.5, 1 H, CH=CH*H*), 4.68-4.56 (m, 2 H, OCH_2), 3.84 (s, 3 H, OMe), 3.12 (s, br, 1 H, OH), 2.24 (td, *J* = 6.8, 2.1, 2 H, ≡CCH_2), 1.57-1.33 (m, 4 H, CH_2C$H_2$$CH_3$), 0.89 (t, *J* = 7.3, 3 H, Me); ^{13}C NMR: *d* = 152.7, 145.5, 135.6, 134.3, 124.2, 119.7, 117.7, 112.7, 86.8, 80.2, 74.2, 61.2, 55.9, 30.7, 22.0, 18.6, 13.6; GC-MS: *m/z* = 274 (67) [M^+], 257 (8), 233 (32), 216 (52), 205 (17), 201 (18), 199 (15), 187 (80), 174 (83), 164 (57), 161 (41), 152 (100), 151 (94), 147 (27), 131 (84), 121 (54), 115 (50), 109 (54), 103 (67), 91 (74), 81 (53), 79 (82), 77 (66), 67 (32), 65 (37), 55 (55); anal. calcd for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08; found C, 74.35; H, 8.09.

1-(2-Allyloxy-3-methoxyphenyl)-3-phenylprop-2-yn-1-ol (1l). Yield: 7.90 g, starting from 4.56 g of 2-hydroxy-3-methoxybenzaldehyde (90%). Yellow oil. IR (film): ν = 3424 (m, br), 2226 (vw), 1587 (w), 1479 (s), 1273 (s), 1207 (m), 1081 (m), 1031 (m), 987 (s), 794 (w), 757 (s), 691 (m) cm^{-1};

^{1}H NMR: *d* = 7.46-7.38 (m, 2 H on phenyl ring), 7.32-7.24 (m, 3 H on phenyl ring), 7.19 (dd, *J* = 8.0, 1.7, 1 H, H-6), 7.07 (t, *J* = 8.0, 1.0, 1 H, H-5), 6.89 (dd, *J* = 8.0, 1.7, 1 H, H-4), 6.23-6.08 (m, 1 H, C*H*=CH_2), 5.87 (d, br, *J* = 6.0, 1 H, C*H*OH), 5.39 (dq, *J* = 17.1, 1.5, 1 H, CH=C*H*H), 5.24 (dq, *J* = 10.3, 1.5, 1 H, CH=CH*H*), 4.70-4.65 (m, 2 H, OCH_2), 3.84 (s, 3 H, OMe), 3.32 (d, br, *J* = 6.0, 1 H, OH); ^{13}C NMR: *d* = 152.7, 145.6, 135.0, 134.2, 131.7, 128.4, 128.2, 124.3, 122.8, 119.8, 117.9, 112.9, 89.3, 85.8, 74.2, 61.7, 55.9; MS (direct injection): *m/z* = 294 (49) [M^+], 277 (15), 253 (56), 235 (36), 210 (40), 182 (20), 181 (17), 166 (20), 165 (79), 153 (35), 152 (100), 151 (64), 129 (53), 115 (17), 106 (17), 77 (20); anal. calcd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16; found C, 77.61; H, 6.14.

1-(2-Allyloxy-4-methoxyphenyl)-hept-2-yn-1-ol (1m). Yield: 7.30 g, starting from 4.56 g of 2-hydroxy-4-methoxybenzaldehyde (89%). Yellow oil. IR (film): ν = 3424 (m, br), 2956 (s), 2932 (s), 2837 (m), 2221 (vw), 1611 (m), 1589 (m), 1507 (m), 1291 (m), 1260 (m), 1200 (m), 1165 (m), 1111 (m), 1044 (m), 1021 (m), 1000 (m), 930 (m), 832 (m) cm^{-1}; ^{1}H NMR: *d* = 7.49 (d, *J* = 8.3, 1 H, H-6), 6.48 (dd, *J* = 8.3, 2.3, 1 H, H-5), 6.43 (d, *J* = 2.3, 1 H, H-3), 6.11-5.96 (m, 1 H, C*H*=CH_2), 5.68 (t, br, *J* = 2.0, 1 H, C*H*OH), 5.43 (dq, *J* = 17.3, 1.6, 1 H, CH=C*H*H), 5.28 (dq, *J* = 10.6, 1.6, 1 H, CH=CH*H*), 4.62-4.49 (m, 2 H, OCH_2), 3.77 (s, 3 H, OMe), 2.94 (s, br, 1 H, OH), 2.26 (td, *J* = 7.0, 2.0, 2 H, ≡CCH_2), 1.58-1.35 (m, 4 H, $CH_2CH_2CH_3$), 0.90 (t, *J* = 7.1, 3 H, Me); ^{13}C NMR: *d* = 160.8, 156.8, 132.8, 128.7, 122.7, 117.6, 104.5, 99.9, 86.6, 79.7, 69.0, 60.7, 55.4, 30.8, 22.0, 18.6, 13.6; GC-MS: *m/z* = 274 (16) [M^+], 257 (12), 256 (22), 233 (20), 228 (17), 227 (100), 197 (15), 187 (12), 175 (10), 164 (35), 161 (18), 151 (23), 137 (13), 115 (10), 109 (13), 91 (8), 79 (11), 77 (10); anal. calcd for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08; found C, 74.48; H, 8.08.

1-(2-Allyloxy-4-methoxyphenyl)-3-phenylprop-2-yn-1-ol (1n). Yield: 8.02 g, starting from 4.56 g of 2-hydroxy-4-methoxybenzaldehyde (91%). Yellow oil. IR (film): ν = 3433 (m, br), 2227 (vw), 1611 (s), 1588 (m), 1503 (m), 1291 (m), 1261 (m), 1199 (m), 1164 (m), 1116 (m), 1029 (m), 997 (m), 932 (m), 832 (m), 757 (m), 692 (m); ^{1}H NMR: *d* = 7.53 (d, *J* = 8.1, 1 H, H-6), 7.48-7.41 (m, 2 H on phenyl ring), 7.31-7.24 (m, 3 H on phenyl ring), 6.47 (distorted dd, *J* = 8.1, 2.3, 1 H, H-5), 6.49 (d, *J* = 2.3, 1 H, H-3), 6.12-5.97 (m, 1 H, C*H*=CH_2), 5.88 (d, br, *J* = 5.9, 1 H, C*H*OH), 5.45 (dq, *J* = 17.2, 1.6, 1 H, CH=C*H*H), 5.28 (dq, *J* = 10.6, 1.6, 1 H, CH=CH*H*), 4.64-4.51 (m, 2 H, OCH_2), 3.76 (s, 3 H, OMe), 3.10 (d, br, *J* = 5.9, 1 H, OH); ^{13}C NMR ($CDCl_3$): *d* = 161.0, 156.9, 132.8, 131.8, 128.9, 128.34, 128.28, 123.0, 122.1, 117.8, 104.7, 100.1, 89.0, 85.7, 69.1, 61.3, 55.4; MS (direct injection): *m/z* = 294 (100) [M^+], 277 (32), 253 (21), 236 (18), 225 (16), 197 (33), 182 (25), 166 (17), 165 (49), 153 (15), 152 (28), 151 (12), 129 (60), 91 (11); anal. calcd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16; found C, 77.46; H, 6.18.

1-(2-Allyloxy-5-methoxyphenyl)-hept-2-yn-1-ol (1o). Yield: 7.10 g, starting from 4.56 g of 2-hydroxy-5-methoxybenzaldehyde (86%). Yellow oil. IR (film): ν = 3439 (m, br), 2955 (m), 2931 (m), 2870 (m), 2223 (vw), 1497 (s), 1463 (m), 1426 (m), 1277 (m), 1209 (s), 1159 (w), 1043 (m), 998 (m), 927 (m), 809 (m) cm^{-1}; ^{1}H NMR: *d* = 7.18 (dt, *J* = 2.8, 0.7, 1 H, H-6), 6.81 (distorted dd, *J* = 8.9, 0.7, 1 H, H-3), 6.77 (distorted dd, *J* = 8.9, 2.8, 1 H, H-4), 6.11-5.97 (m, 1 H, C*H*=CH_2), 5.73-5.67 (m, 1 H, C*H*OH), 5.41 (dq, *J* = 17.2, 1.6, 1 H, CH=C*H*H), 5.26 (dq, *J* = 10.5, 1.6, 1 H, CH=CH*H*), 4.61-4.48 (m, 2 H, OCH_2), 3.76 (s, 3 H, OMe), 3.11 (s, br, 1 H, OH), 2.26 (td, *J* = 7.0, 2.1, 2 H, ≡CCH_2), 1.58-1.35 (m, 4 H, CH_2C$H_2$$CH_3$), 0.90 (t, *J* = 7.2, 3 H, Me); ^{13}C NMR: *d* = 153.9, 149.9, 133.3, 131.0, 117.5, 113.9, 113.8, 113.6, 87.0, 79.3, 69.8, 61.2, 55.7, 30.7, 22.0, 18.6, 13.6; GC-MS: *m/z* = 274 (27) [M^+], 256 (25), 228 (17), 227 (100), 205 (10), 187 (10), 161 (9), 152 (10), 151 (10), 137 (20), 121 (14), 115 (11), 109 (63), 91 (12), 81 (22), 79 (27), 77 (13); anal. calcd for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08; found C, 74.51; H, 8.06.

1-(2-Allyloxy-5-methoxyphenyl)-3-phenylprop-2-yn-1-ol (1p). Yield: 7.81 g, starting from 4.56 g of 2-hydroxy-5-methoxybenzaldehyde (89%). Yellow oil. IR (film): ν = 3440 (m, br), 2229 (vw), 1496 (s), 1424 (w), 1278 (m), 1209 (s), 1157 (w), 1037 (m), 758 (m), 691 (m); ^{1}H NMR: *d* = 7.48-7.41 (m, 2 H on phenyl ring), 7.31-7.25 (m, 3 H on phenyl ring), 7.21 (d, *J* = 2.7, 1 H, H-6), 6.83 (distorted d, *J* = 8.8, 1 H, H-3), 6.79 (distorted dd, *J* = 8.8, 2.7, 1 H, H-4), 6.12-5.98 (m, 1 H, C*H*=CH_2), 5.90 (s, br, 1 H, C*H*OH), 5.43 (dq, *J* = 17.3, 1.5, 1 H, CH=C*H*H), 5.27 (dq, *J* = 10.6, 1.5, 1 H, CH=CH*H*), 4.65-4.48 (m, 2 H, OCH_2), 3.76 (s, 3 H, OMe), 3.38 (s, br, 1 H, OH); ^{13}C NMR: *d* = 153.8, 149.9, 133.1, 131.7, 130.3, 128.4, 128.2, 122.7, 117.6, 114.0, 113.9, 113.6, 88.4, 85.9, 69.8, 61.7, 55.7; MS (direct injection): *m/z* = 294 (100) [M^+], 277 (21), 253 (20), 236 (19), 225 (19), 210 (13), 197 (43), 193 (12), 182 (34), 181 (14), 166 (21), 165 (60), 153 (16), 152 (29), 151 (12), 129 (45), 91 (10), 77 (12); anal. calcd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16; found C, 77.61; H, 6.16.

1-(2-Allyloxy-5-chlorophenyl)-hept-2-yn-1-ol (1q). Yield: 7.70 g, starting from 4.70 g of 5-chloro-2-hydroxybenzaldehyde (92%). Yellow oil. IR (film): ν = 3405 (m, br), 2957 (m), 2932 (m), 2871 (m), 2224 (vw), 1485 (s), 1463 (m), 1412 (w), 1249 (s), 1176 (w), 1123 (m), 1018 (m), 997 (m), 929 (w), 809 (m), 681 (w) cm^{-1}; ^{1}H NMR: *d* = 7.57 (d, *J* = 2.7, 1 H, H-6), 7.19 (dd, *J* = 8.8, 2.7, 1 H, H-4), 6.78 (d, *J* = 8.8, 1 H, H-3), 6.10-5.95 (m, 1 H, C*H*=CH_2), 5.68 (t, br, *J* = 2.0, 1 H, C*H*OH), 5.42 (dq, *J* = 17.3, 1.5, 1 H, CH=C*H*H), 5.29 (dq, *J* = 10.6, 1.5, 1 H, CH=CH*H*), 4.63-4.50 (m, 2 H, OCH_2), 3.01 (s, br, 1 H, OH), 2.26 (td, *J* = 7.0, 2.0, 2 H, ≡CCH_2), 1.58-1.35 (m, 4 H, CH_2C$H_2$$CH_3$), 0.91 (t, *J* = 7.2, 3 H, Me); ^{13}C NMR: *d* = 154.3, 132.5, 131.6, 128.9, 128.0, 126.0, 117.9, 113.3, 87.5, 78.8, 69.4, 60.5, 30.6, 22.0, 18.5, 13.6; GC-MS: *m/z* = 280 (20) [M^++2], 278

(57) [M^+], 237 (40), 231 (29), 221 (21), 207 (17), 193 (44), 191 (100), 178 (93), 165 (47), 156 (87), 155 (92), 141 (29), 128 (41), 127 (40), 115 (40), 109 (18), 91 (10), 79 (30), 77 (28), 67 (24); anal. calcd for $C_{16}H_{19}ClO_2$: C, 68.93; H, 6.87; Cl, 12.72.; found C, 70.03; H, 6.88; Cl, 12.67.

1-(2-Allyloxy-5-chlorophenyl)-3-phenylprop-2-yn-1-ol (1r). Yield: 8.30 g, starting from 4.70 g of 5-chloro-2-hydroxybenzaldehyde (93%). Yellow oil. IR (film): ν = 3417 (m, br), 2233 (vw), 1487 (s), 1249 (s), 1175 (w), 1128 (w), 1018 (m), 808 (w), 757 (m), 691 (m) cm^{-1}; ^{1}H NMR: *d* = 7.60 (d, *J* = 2.7, 1 H, H-6), 7.50-7.41 (m, 2 H on phenyl ring), 7.34-7.25 (m, 3 H on phenyl ring), 7.21 (dd, *J* = 8.8, 2.7, 1 H, H-4), 6.79 (d, *J* = 8.8, 1 H, H-3), 6.09-5.95 (m, 1 H, C*H*=CH_2), 5.89 (s, br, 1 H, C*H*OH), 5.43 (dq, *J* = 17.3, 1.5, 1 H, CH=C*H*H), 5.28 (dq, *J* = 10.6, 1.5, 1 H, CH=CH*H*), 4.84-4.51 (m, 2 H, OCH_2), 3.20 (s, br, 1 H, OH); ^{13}C NMR: *d* = 154.3, 132.5, 132.1, 131.8, 129.1, 128.5, 128.3, 128.0, 126.0, 122.5, 118.0, 113.5, 87.9, 86.2, 69.4, 61.0; MS (direct injection): *m/z* = 300 (11) [M^++2], 298 (34) [M^+], 281 (17), 259 (34), 257 (100), 241 (22), 239 (18), 205 (45), 194 (24), 176 (38), 166 (43), 165 (82), 155 (45), 143 (22), 142 (53), 141 (38), 129 (42), 115 (21), 77 (22); anal. calcd for $C_{18}H_{15}ClO_2$: C, 72.36; H, 5.06; Cl, 11.87; found C, 72.03; H, 5.05; Cl, 11.88.

2-(1-Hydroxyprop-2-ynyl)phenol 3b. Yield: 6.68 g, starting from 6.10 g of 2-hydroxybenzaldehyde (90%). Colorless solid, mp 91-92 °C, lit.[2] 92.1-93.5 °C. IR (film): ν = 3315 (m, br), 3288 (s), 2119 (vw), 1599 (m), 1459 (m), 1371 (w), 1281 (w), 1237 (m), 1011 (m), 949 (m), 755 (m), 651 (m) cm^{-1}; ^{1}H NMR: *d* = 7.54 (s, br, ArOH), 7.35 (dd, *J* = 7.7, 1.6, 1 H, H-6), 7.17 (td, *J* = 7.7, 1.6, 1 H, H-4), 6.90-6.80 (m, 2 H, H-3 + H-5), 5.64 (d, br, *J* = 2.1, 1 H, C*H*OH), 4.03 (s, br, 1 H, CHO*H*), 2.68 (d, *J* = 2.1, 1 H, ≡CH); ^{13}C NMR: *d* = 154.6, 130.1, 127.7, 124.6, 120.4, 116.8, 81.9, 75.9, 62.9; GC-MS: *m/z* = 148 (46) [M^+], 147 (100), 131 (32), 121 (36), 111 (11), 105 (14), 91 (17), 77 (28), 65 (10); anal. calcd for $C_9H_8O_2$: C, 72.96; H, 5.44; found C, 72.85; H, 5.45.

2-(1-Hydroxy-3-phenylprop-2-ynyl)phenol 3d. Yield: 2.19 g, starting from 1.83 g of 2-hydroxybenzaldehyde (65%). Yellow solid, mp 84-85 °C, lit.[1] 85°C. IR (film): ν = 3360 (m, br), 2230 (vw), 1600 (m), 1490 (m), 1458 (s), 1381 (m), 1287 (m), 1221 (m), 1007 (m), 1001 (m), 932 (m), 843 (m), 753 (s), 691 (m) cm^{-1}; ^{1}H NMR: *d* = 7.57 (s, br, 1 H, ArO*H*), 7.48-7.38 (m, 3 H aromatic), 7.33-7.14 (m, 4 H aromatic), 6.92-6.84 (m, 2 H aromatic), 5.87 (s, 1 H, C*H*OH), 3.75 (s, br, 1 H, CHO*H*); ^{13}C NMR: *d* = 154.9, 131.8, 130.1, 128.8, 128.3, 127.8, 124.8, 122.0, 120.4, 117.0, 88.0, 86.8, 64.0; MS (direct injection): *m/z* = 224 (M^+, 4), 223 (7), 207 (31), 206 (100), 205 (56), 178 (38), 177 (19), 176 (21), 165 (9), 152 (20), 151 (10), 121 (9), 102 (9), 89 (8) 77 (11), 76 (16); anal. calcd for $C_{15}H_{12}O_2$: C, 80.34; H, 3.39; found C, 80.46; H, 5.37.

Characterization of Products

2-Benzofuran-2-ylhexanoic acid methyl ester (2a). Yield: 449.5 mg, starting from 490.0 mg of **1a** (91%, Table 1, entry 33). Colorless oil. IR (film): ν = 1743 (s), 1600 (w), 1585 (w), 1454 (m), 1252 (m), 1160 (m), 751 (m) cm^{-1}; ^1H NMR: *d* = 7.53-7.49 (m, 1 H, H-4 or H-7), 7.47-7.42 (m, 1 H, H-7 or H-4), 7.27-7.15 (m, 2 H, H-5 + H-6), 6.59-6.58 (m, 1 H, H-3), 3.82 (t, *J* = 7.3, 1 H, C*H*CH_2), 3.72 (s, 3 H, CO_2Me), 2.18-1.93 (m, 2 H, CHC*H*$_2$), 1.43-1.24 (m, 4 H, C*H*$_2$C*H*$_2$$CH_3$), 0.89 (t, *J* = 6.8, 3 H, CH_2C*H*$_3$); ^{13}C NMR: *d* = 172.1, 155.3, 154.8, 128.4, 123.9, 122.7, 120.7, 111.1, 103.8, 52.3, 45.7, 30.6, 29.5, 22.4, 13.8; GC-MS: *m/z* = 246 (33) [M^+], 190 (13), 189 (8), 187 (36), 145 (7), 144 (10), 132 (11), 131 (100), 115 (12); anal. calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37; found: C, 73.41; H, 7.35.

Benzofuran-2-ylacetic acid methyl ester (2b). Yield: 265.8 mg, starting from 375.0 mg of **1b** (70%, Table 2, entry 36). Yellow oil. IR (film): ν = 1745 (s), 1454 (m), 1435 (w), 1251 (m), 1156 (m), 1010 (m), 958 (w), 750 (m) cm^{-1}; ^1H NMR: *d* = 7.53-7.47 (m, 1 H, H-4 or H-7), 7.45-7.40 (m, 1 H, H-7 or H-4), 7.26-7.15 (m, 2 H, H-5 + H-6), 6.61 (q, *J* = 0.8, 1 H, H-3), 3.81 (d, *J* = 0.8, 1 H, C*H*$_2$$CO_2Me$), 3.72 (s, 3 H, CO_2Me); ^{13}C NMR: *d* = 169.3, 154.9, 150.6, 128.5, 124.0, 122.8, 120.8, 111.1, 105.1, 52.4, 34.4; GC-MS: *m/z* = 190 (30) [M^+], 132 (11), 131 (100), 103 (6), 102 (7), 77 (18), 51 (7); anal. calcd for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30; found C, 69.58; H, 5.29.

2-Benzofuran-2-yl-3,3-dimethylbutanoic acid methyl ester (2c). Yield: 395.4 mg, starting from 489.0 mg of **1c** (80%, Table 2, entry 38). Pale yellow solid, mp 60-61 °C. IR (KBr): ν = 1733 (s), 1577 (w), 1474 (w), 1456 (m), 1435 (m), 1371 (m), 1321 (m), 1243 (m), 1205 (m), 1150 (s), 1043 (m), 1007 (m), 827 (m), 755 (m), 747 (m) cm^{-1}; ^1H NMR: *d* = 7.54-7.49 (m, 1 H, H-4 or H-7), 7.46-7.41 (m, 1 H, H-7 or H-4), 7.25-7.14 (m, 2 H, H-5 + H-6), 6.74 (dd, *J* = 1.0, 0.3, 1 H, H-3), 3.73 (d, *J* = 0.3, 1 H, C*H*CMe_3), 3.69 (s, 3 H, CO_2Me), 1.08 (s, 9 H, CMe_3); ^{13}C NMR: *d* = 171.2, 154.5, 153.9, 128.5, 123.7, 122.7, 120.7, 111.0, 105.5, 55.9, 51.7, 35.1, 28.0. GC-MS: *m/z* = 246 (11) [M^+], 191 (12), 190 (100), 187 (8), 175 (22), 158 (35), 131 (27), 130 (9), 102 (8), 57 (30); anal. calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37; found C, 73.02; H, 7.38.

Benzofuran-2-ylphenylacetic acid methyl ester (2d). Yield: 438.1 mg, starting from 528.5 mg of **1d** (82%, Table 2, entry 39). Yellow oil. IR (film): ν = 1739 (s), 1600 (w), 1584 (w), 1453 (m), 1253 (m), 1199 (m), 1156 (s), 1010 (m), 751 (s), 723 (m), 699 (m), cm^{-1}; ^1H NMR: *d* = 7.50-7.26 (m, 7 H, Ph + H-4 + H-7), 7.25-7.12 (m, 2 H, H-5 + H-6), 6.57 (t, *J* = 1.0, 1 H, H-3), 5.14 (s, br, 1

H, C*H*Ph), 3.74 (s, 3 H, CO_2Me); ^{13}C NMR: *d* = 170.5, 155.0, 154.6, 128.8, 128.7, 128.2, 128.0, 124.1, 123.6, 122.7, 120.9, 111.1, 105.2, 52.6, 51.7; GC-MS: *m/z* = 266 (20) [M^+], 208 (17), 207 (100), 179 (8), 178 (31), 176 (6), 152 (6), 89 (5); anal. calcd for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30; found C, 76.81; H, 5.29.

(3-Methylbenzofuran-2-yl)hexanoic acid methyl ester (2e). Yield: 431.2 mg, starting from 516.5 mg of **1e** (83%, Table 2, entry 41). Pale yellow oil. IR (film): ν = 1743 (s), 1643 (w), 1613 (w), 1589 (w), 1455 (m), 1255 (m), 1246 (m), 1185 (m), 1167 (m), 747 (s) cm^{-1}; ^1H NMR: *d* = 7.47-7.40 (m, 2 H, H-4 + H-7), 7.27-7.17 (m, 2 H, H-5 + H-6), 3.84 (dd, *J* = 9.1, 6.6, 1 H, C*H*CH_2), 3.68 (s, 3 H, CO_2Me), 2.21 (s, 3 H, =CCH_3), 2.23-1.96 (m, 2 H, CHC*H*$_2$) 1.41-1.17 (m, 4 H, C*H*$_2$C*H*$_2$$CH_3$), 0.87 (t, *J* = 7.1, 3 H, CH_2C*H*$_3$); ^{13}C NMR: *d* = 172.1, 154.1, 149.6, 130.0, 123.8, 122.2, 119.0, 112.2, 111.1, 52.2, 43.6, 29.7, 29.5, 22.4, 13.9, 7.9; GC-MS: *m/z* = 260 (23) [M^+], 203 (5), 202 (8), 201 (53), 171 (10), 158 (5), 157 (5), 146 (11), 145 (100), 131 (5), 128 (5), 115 (9); anal. calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74; found C, 73.76; H, 7.75.

3,3-Dimethyl-2-(3-methylbenzofuran-2-yl)butyric acid methyl ester (2f). Yield: 416.8 mg, starting from 516.6 mg of **1f** (80%, Table 2, entry 45). Yellow oil. IR (KBr): ν = 1746 (s), 1477 (w), 1454 (m), 1433 (w), 1365 (w), 1331 (m), 1255 (w), 1203 (m), 1145 (s), 745 (s) cm^{-1}; ^1H NMR: *d* = 7.48-7.46 (m, 1 H, H-4 or H-7), 7.45-7.43 (m, 1 H, H-7 or H-4), 7.27-7.17 (m, 2 H, H-5 + H-6), 3.73 (d, *J* = 0.3, 1 H, C*H*CMe_3), 3.65 (s, 3 H, CO_2Me), 2.21 (s, 3 H, =CCH_3), 1.13 (s, 9 H, CMe_3); ^{13}C NMR: *d* = 170.6, 154.1, 149.0, 129.6, 123.9, 122.1, 119.0, 113.4, 111.2, 53.4, 51.6, 35.7, 28.3, 8.4; GC-MS: *m/z* = 260 (19) [M^+], 205 (14), 204 (100), 189 (25), 172 (23), 171 (22), 145 (35), 144 (8), 115 (13), 57 (11); anal. calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74; found C, 73.91; H, 7.72.

(3-Methylbenzofuran-2-yl)phenylacetic acid methyl ester (2g). Yield: 453.4 mg, starting from 556.5 mg of **1g** (81%, Table 2, entry 49). Yellow oil. IR (film): ν = 1745 (s), 1454 (m), 1434 (w), 1247 (m), 1199 (m), 1156 (m), 1089 (w), 1007 (m), 747 (m), 724 (w), 700 (w), cm^{-1}; ^1H NMR: *d* = 7.47-7.15 (m, 9 H aromatic), 5.23 (s, 1 H, C*H*Ph), 3.74 (s, 3 H, CO_2Me), 2.16 (s, 3 H, =CCH_3); ^{13}C NMR: *d* = 170.6, 154.1, 148.6, 135.8, 129.9, 128.8, 128.6, 127.7, 124.1, 122.3, 119.2, 112.6, 111.2, 52.6, 49.6, 8.0; GC-MS: *m/z* = 280 (17) [M^+], 222 (18), 221 (100), 202 (8), 178 (7), 115 (5); anal. calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75; found C, 77.31; H, 5.73.

(3-Phenylbenzofuran-2-yl)hexanoic acid methyl ester (2h). Yield: 478.1 mg, starting from 641.0 mg of **1h** (74%, Table 2, entry 50). Pale yellow oil. IR (film): ν = 1745 (s), 1611 (w), 1496 (w), 1454 (m), 1256 (m), 1215 (m), 1190 (m), 1167 (m), 1013 (w), 968 (w), 749 (m), 702 (m) cm^{-1}; ^1H

NMR: *d* = 7.59-7.36 (m, 7 H, Ph + H-4 + H-7), 7.34-7.20 (m, 2 H, H-5 + H-6), 3.97 (dd, *J* = 9.0, 6.8, 1 H, C*H*CH_2), 3.72 (s, 3 H, CO_2Me), 2.20-1.98 (m, 2 H, CHC*H*$_2$), 1.28-1.08 (m, 4 H, C*H*$_2$C*H*$_2$$CH_3$), 0.79 (t, *J* = 6.8, 3 H, CH_2C*H*$_3$); ^{13}C NMR: *d* = 172.1, 154.3, 150.3, 132.0, 129.3, 128.9, 128.6, 127.6, 124.3, 122.8, 119.9, 119.6, 111.4, 52.3, 43.7, 30.0, 29.4, 22.3, 13.7; GC-MS: *m/z* = 322 (70) [M^+], 264 (26), 263 (99), 219 (11), 208 (20), 207 (100), 205 (35), 179 (35), 178 (25), 165 (8); anal. calcd for $C_{21}H_{22}O_3$: C, 78.23; H, 6.88; found C, 78.45; H, 6.86.

Phenyl-(3-phenylbenzofuran-2-yl)acetic acid methyl ester (2i). Yield: 555.8 mg, starting from 681.0 mg of **1i** (81%, Table 2, entry 53). Yellow oil. IR (film): ν = 1751 (s), 1493 (w), 1450 (m), 1285 (m), 1200 (m), 1145 (s), 973 (w), 750 (s), 702 (s), 700 (s) cm^{-1}; ^{1}H NMR: *d* = 7.59-7.17 (m, 14 H aromatic), 5.31 (s, 1 H, C*H*Ph), 3.69 (s, 3 H, CO_2Me); ^{13}C NMR: *d* = 170.5, 154.5, 149.0, 136.0, 132.8, 131.7, 129.3, 128.93, 128.90, 128.7, 128.3, 127.7, 124.6, 123.0, 120.1, 119.7, 111.5, 52.7, 49.5; GC-MS: *m/z* = 342 (23) [M^+], 284 (24), 283 (100), 253 (6), 252 (8), 239 (6), 205 (29); anal. calcd for $C_{23}H_{18}O_3$: C, 80.68; H, 5.30; found C, 80.56; H, 5.31.

2-(3-Hex-1-ynylbenzofuran-2-yl)hexanoic acid methyl ester (2j). Yield: 520.6 mg, starting from 649.0 mg of **1j** (80%, Table 2, entry 54). Yellow oil. IR (film): ν = 2956 (s), 2930 (s), 2871 (m), 1745 (s), 1681 (w), 1454 (m), 1251 (m), 1215 (m), 1193 (m), 1157 (w), 1009 (w), 749 (m) cm^{-1}; ^{1}H NMR: *d* = 7.61-7.55 (m, 1 H, H-4 or H-7), 7.47-7.38 (m, 1 H, H-7 or H-4), 7.30-7.20 (m, 2 H, H-5 + H-6), 4.08 (dd, *J* = 9.0, 6.5, 1 H, C*H*Bu), 3.69 (s, 3 H, CO_2Me), 2.49 (t, *J* = 6.8, 2 H, ≡CCH_2), 2.24-2.01 (m, 2 H, CHC*H*$_2$), 1.70-1.21 (m, 8 H, ≡CCH_2C*H*$_2$C*H*$_2$ + $CHCH_2$C*H*$_2$C*H*$_2$), 0.97 (t, *J* = 7.2, 3 H, CH_2C*H*$_3$), 0.88 (t, *J* = 7.1, 3 H, CH_2C*H*$_3$); ^{13}C NMR: *d* = 171.6, 156.7, 153.9, 128.9, 124.6, 123.0, 120.1, 111.3, 102.9, 96.6, 69.9, 52.3, 44.4, 30.9, 29.8, 29.4, 22.3, 22.0, 19.4, 13.9, 13.6; GC-MS: *m/z* = 326 (60) [M^+], 269 (12), 268 (25), 267 (100), 212 (16), 211 (86), 197 (12), 183 (12), 181 (29), 169 (19), 168 (12), 155 (13), 152 (16), 131 (14); anal. calcd for $C_{21}H_{26}O_3$: C, 77.27; H, 8.03; found C, 77.15; H, 8.05.

2-(7-Methoxybenzofuran-2-yl)hexanoic acid methyl ester (2k). Yield: 463.7 mg, starting from 548.0 mg of **1k** (84%, Table 2, entry 55). Yellow oil. IR (film): ν = 1741 (s), 1621 (w), 1599 (w), 1493 (m), 1436 (m), 1271 (m), 1209 (m), 1181 (m), 1163 (m), 1096 (m), 976 (w), 731 (m) cm^{-1}; ^{1}H NMR: *d* = 7.15-7.07 (m, 2 H aromatic), 6.79-6.71 (m, 1 H aromatic), 6.59 (s, br, 1 H, H-3), 3.98 (s, 3 H, ArOC*H*$_3$), 3.86 (t, *J* = 7.7, 1 H, C*H*Bu), 3.70 (s, 3 H, CO_2Me), 2.17-1.94 (m, 2 H, CHC*H*$_2$), 1.40-1.25 (m, 4 H, C*H*$_2$C*H*$_2$$CH_3$), 0.88 (t, *J* = 6.8, 3 H, CH_2C*H*$_3$); ^{13}C NMR: *d* = 172.1, 155.7, 145.3, 144.1, 130.3, 123.4, 113.2, 106.5, 104.0, 56.1, 52.2, 45.7, 31.0, 29.6, 22.4, 13.8; GC-MS: *m/z*

= 276 (44) [M^+], 220 (11), 219 (8), 218 (6), 217 (36), 191 (6), 175 (4), 174 (5), 162 (12), 161 (100), 137 (5), 131 (4), 115 (4), 103 (4), 81 (4), 77 (4); anal. calcd for $C_{16}H_{20}O_4$: C, 69.54; H, 7.30; found C, 69.63; H, 7.29.

2-(7-Methoxybenzofuran-2-yl)phenylacetic acid methyl ester (2l). Yield: 486.6 mg, starting from 589.0 mg of **1l** (82%, Table 2, entry 56). Yellow oil. IR (film): ν = 1741 (s), 1621 (w), 1599 (w), 1493 (m) 1455 (w), 1435 (m), 1273 (m), 1207 (m), 1155 (m), 1095 (m), 733 (m), 701 (m) cm^{-1}; ^1H NMR: δ = 7.45-7.26 (m, 5 H aromatic), 7.13-7.06 (m, 2 H aromatic), 6.78-6.70 (m, 1 H aromatic), 6.58-6.57 (m, 1 H, H-3), 5.18 (s, br, 1 H, CHPh), 3.94 (s, 3 H, $ArOCH_3$), 3.74 (s, 3 H, CO_2Me); ^{13}C NMR: δ = 170.5, 154.9, 145.2, 144.3, 135.6, 130.1, 128.8, 128.7, 128.0, 123.5, 113.4, 106.7, 105.7, 56.0, 52.6, 51.7; GC-MS: *m/z* = 296 (27) [M^+], 238 (18), 237 (100), 222 (5), 194 (15), 178 (7), 166 (6), 165 (20); anal. calcd for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44; found C, 72.85; H, 5.43.

2-(6-Methoxybenzofuran-2-yl)hexanoic acid methyl ester (2m). Yield: 440.9 mg, starting from 548.5 mg of **1m** (80%, Table 2, entry 57). Yellow oil. IR (film): ν = 1741 (s), 1624 (m), 1587 (w), 1492 (m), 1438 (m), 1293 (m), 1274 (m), 1195 (m), 1149 (m), 1107 (m), 1027 (m), 961 (w), 823 (m) cm^{-1}; ^1H NMR: *d* = 7.35 (d, *J* = 8.6, 1 H, H-4), 6.99 (d, *J* = 2.2, 1 H, H-7), 6.83 (dd, *J* = 8.6, 2.2, 1 H, H-5), 6.50 (s, 1 H, H-3), 3.83-3.75 (m, 1 H, C*H*Bu), 3.81 (s, 3 H, $ArOCH_3$), 3.71 (s, 3 H, CO_2Me), 2.15-1.90 (m, 2 H, $CHCH_2$), 1.43-1.25 (m, 4 H, $CH_2CH_2CH_3$), 0.89 (t, *J* = 6.9, 3 H, CH_2CH_3); ^{13}C NMR: *d* = 172.3, 157.8, 155.7, 154.3, 121.7, 120.8, 111.7, 103.5, 96.0, 55.7, 52.2, 45.7, 30.5, 29.5, 22.4, 13.9; GC-MS: *m/z* = 276 (54) [M^+], 219 (33), 218 (15), 217 (95), 174 (8), 162 (12), 161 (100), 159 (16); anal. calcd for $C_{16}H_{20}O_4$: C, 69.54; H, 7.30; found C, 69.45; H, 7.30.

2-(6-Methoxybenzofuran-2-yl)phenylacetic acid methyl ester (2n). Yield: 368.3 mg, starting from 588.5 mg of **1n** (62%, Table 2, entry 58). Yellow oil. IR (film): ν = 1745 (s), 1622 (m), 1587 (w), 1493 (m), 1435 (m), 1295 (m), 1276 (m), 1199 (m), 1148 (m), 1107 (m), 1027 (m), 963 (w), 941 (w), 824 (m) cm^{-1}; ^1H NMR: *d* = 7.45-7.26 (m, 6 H, Ph + H-4), 6.95 (d, *J* = 2.2, 1 H, H-7), 6.81 (dd, *J* = 8.6, 2.2, 1 H, H-5), 6.49-6.48 (m, 1 H, H-3), 5.11 (s, br, 1 H, C*H*Ph), 3.77 (s, 3 H, $ArOCH_3$), 3.74 (s, 3 H, CO_2Me); ^{13}C NMR: *d* = 170.7, 157.9, 156.0, 153.6, 135.6, 128.8, 128.7, 128.0, 121.5, 121.0, 111.8, 105.0, 95.9, 55.6, 52.6, 51.7; GC-MS: *m/z* 296 (30) [M^+], 238 (20), 237 (100), 222 (8), 194 (8), 165 (12); anal. calcd for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44; found C, 73.05; H, 5.43.

2-(5-Methoxybenzofuran-2-yl)hexanoic acid methyl ester (2o). Yield: 481.5 mg, starting from 549.0 mg of **1o** (87%, Table 2, entry 59). Yellow oil. IR (film): ν = 1741 (s), 1615 (w), 1602 (w),

1477 (m), 1447 (m), 1435 (m), 1205 (m), 1167 (m), 1031 (w) cm^{-1}; ^1H NMR: *d* = 7.32 (dt, *J* = 8.8, 0.7, 1 H, H-7), 6.98-6.96 (m, 1 H, H-4), 6.84 (dd, *J* = 8.8, 2.7, 1 H, H-6), 6.52 (t, *J* = 0.7, 1 H, H-3), 3.82-3.76 (m, 1 H, C*H*Bu), 3.80 (s, 3 H, ArOCH_3), 3.71 (s, 3 H, CO_2Me), 2.16-1.91 (m, 2 H, CHCH_2), 1.43-1.24 (m, 4 H, CH_2CH_2CH_3), 0.89 (t, *J* = 6.9, 3 H, CH_2CH_3); ^{13}C NMR: *d* = 172.1, 156.1, 156.0, 149.8, 129.0, 112.5, 111.5, 103.9, 103.4, 55.9, 52.3, 45.8, 30.6, 29.5, 22.4, 13.9; GC-MS: *m/z* = 276 (33) [M^+], 220 (12), 219 (10), 218 (7), 217 (43), 216 (6), 191 (6), 162 (12), 161 (100); anal. calcd for $C_{16}H_{20}O_4$: C, 69.54; H, 7.30; found C, 69.69; H, 7.29.

(5-Methoxybenzofuran-2-yl)phenylacetic acid methyl ester (2p). Yield: 419.3 mg, starting from 585.5 mg of **1p** (71%, Table 2, entry 60). Yellow oil. IR (film): ν = 1746 (s), 1613 (w), 1477 (m), 1454 (m), 1434 (m), 1302 (w), 1277 (w), 1207 (s), 1167 (m), 1142 (m), 1031 (m), 813 (m), 720 (m) cm^{-1}; ^1H NMR: *d* = 7.45-7.25 (m, 6 H, Ph + H-7), 6.94 (d, *J* = 2.7, 1 H, H-4), 6.82 (dd, *J* = 8.8, 2.7, 1 H, H-6), 6.52 (s, 1 H, H-3), 5.11 (s, 1 H, C*H*Ph), 3.77 (s, 3 H, ArOCH_3), 3.73 (s, 3 H, CO_2Me); ^{13}C NMR: *d* = 170.5, 156.0, 155.4, 150.0, 135.4, 128.8, 128.7, 128.2, 128.0, 112.7, 111.6, 105.4, 103.5, 55.8, 52.6, 51.7; GC-MS: *m/z* = 296 (28) [M^+], 238 (18), 237 (100), 194 (18), 178 (5), 166 (4), 165 (16), 139 (5); anal. calcd for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44; found C, 73.12; H, 5.43.

2-(5-Chlorobenzofuran-2-yl)hexanoic acid methyl ester (2q). Yield: 493.2 mg, starting from 557.5 mg of **1q** (88%, Table 2, entry 61). Yellow oil. IR (film): ν = 1742 (s), 1594 (w), 1447 (m), 1259 (m), 1159 (m), 1061 (w), 801 (m), 696 (w) cm^{-1}; ^1H NMR: *d* = 7.46 (dt, *J* = 2.0, 0.7, 1 H, H-4), 7.34 (dt, *J* = 8.6, 0.7, 1 H, H-7), 7.18 (dd, *J* = 8.6, 2.0, 1 H, H-6), 6.54 (t, *J* = 0.7, 1 H, H-3), 3.81 (t, *J* = 7.6, 1 H, C*H*Bu), 3.72 (s, 3 H, CO_2Me), 2.17-1.91 (m, 2 H, CHCH_2), 1.43-1.24 (m, 4 H, CH_2CH_2CH_3), 0.89 (t, *J* = 7.0, 3 H, CH_2CH_3); ^{13}C NMR: *d* = 171.8, 157.0, 153.1, 129.8, 128.3, 124.1, 120.3, 112.1, 103.5, 52.4, 45.7, 30.5, 29.5, 22.4, 13.8; GC-MS: *m/z* 282 (7) [M^+ + 2], 280 (22) [M^+], 224 (17), 223 (15), 221 (34), 167 (33), 166 (11), 165 (100), 115 (12); anal. calcd for $C_{15}H_{17}ClO_3$: C, 64.17; H, 6.10; Cl, 12.63; found C, 64.26; H, 6.08; Cl, 12.61.

(5-Chlorobenzofuran-2-yl)phenylacetic acid methyl ester (2r). Yield: 476.8 mg, starting from 597.5 mg of **1r** (79%, Table 2, entry 62). Yellow oil. IR (film): ν = 1743 (s), 1593 (m), 1446 (m), 1259 (m), 1199 (m), 1153 (s), 1060 (w), 1010 (m), 801 (m), 723 (m), 695 (m), cm^{-1}; ^1H NMR: *d* = 7.45-7.26 (m, 7 H, Ph + H-4 + H-7), 7.16 (dd, *J* = 8.8, 2.2, 1 H, H-6), 6.52 (t, *J* = 1.0, 1 H, H-3), 5.11 (s, br, 1 H, C*H*Ph), 3.74 (s, 3 H, CO_2Me); ^{13}C NMR: *d* = 170.3, 156.2, 153.3, 135.1, 129.6, 128.9, 128.6, 128.3, 128.2, 124.3, 120.5, 112.1, 104.9, 52.7, 51.6; GC-MS: *m/z* = 302 (9) [M^+ + 2], 300 (26) [M^+], 243 (43), 242 (21), 241 (100), 206 (10), 205 (13), 178 (38), 176 (14); anal. calcd for $C_{17}H_{13}ClO_3$: C, 67.89; H, 4.36, Cl, 11.79; found C, 67.95; H, 4.35; Cl, 11.77.

1-Allyloxy-2-(1-methoxyhept-2-ynyl)benzene (4a). Yield: 367.2 mg, starting from 489.0 mg of **1a** (71%, Table 1, entry 7). Pale yellow oil. IR (film): ν = 2957 (m), 2931 (s), 2871 (m), 1601 (w), 1491 (m), 1453 (m), 1245 (s), 1079 (s), 753 (m) cm^{-1}; ^1H NMR: *d* = 7.65 (dd, *J* = 7.6, 2.0, 1 H aromatic), 7.29-7.22 (m, 1 H aromatic), 6.99 (td, *J* = 7.6, 1.0, 1 H aromatic), 6.89-6.84 (m, 1 H aromatic), 6.12-5.98 (m, 1 H, CH_2CH=CH_2), 5.50 (t, *J* = 2.0, 1 H, C*H*OMe), 5.43 (dq, *J* = 17.1, 2.3, 1 H, CH_2CH=C*H*H), 5.27 (dq, *J* = 10.8, 2.3, 1 H CH_2CH=CH*H*), 4.64-4.50 (m, CH_2CH=CH_2), 3.43 (s, 3 H, OMe), 2.27 (td, *J* = 6.8, 2.0, 2 H, ≡CCH_2), 1.58-1.34 (m, 4 H, $CH_2CH_2CH_3$), 0.91 (t, *J* = 7.3, 3 H, CH_2CH_3); ^{13}C NMR: *d* = 155.7, 133.3, 129.4, 128.6, 128.0, 120.9, 117.0, 112.1, 87.3, 78.0, 69.1, 67.2, 56.1, 30.8, 22.0, 18.6, 13.6; GC-MS: *m/z* = 258 (10) [M^+], 227 (21), 218 (15), 217 (100), 201 (14), 183 (11), 171 (10), 169 (20), 161 (11), 159 (11), 157 (28), 145 (13), 144 (21), 131 (28), 129 (13), 128 (20), 115 (29), 107 (15), 91 (11), 77 (10); anal. calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58; found C, 79.18; H, 8.59.

4-(2-Allyloxyphenyl)-2-butylbuta-2,3-dienoic acid methyl ester (5a). Yield: 45.8 mg, starting from 489.0 mg of **1a** (8%, Table 1, entry 7). Pale yellow oil. IR (film): ν = 1942 (m), 1715 (s), 1493 (m), 1454 (m), 1435 (w), 1266 (s), 1244 (s), 1119 (m), 1019 (m), 930 (m), 751 (s) cm^{-1}; ^1H NMR: *d* = 7.30 (dd, *J* = 7.3, 2.0, 1 H aromatic), 7.22-7.15 (m, 1 H aromatic), 6.97-6.89 (m, 2 H, 1 H aromatic + =C=C*H*CH_2), 6.88-6.83 (m, 1 H aromatic), 6.12-5.97 (m, 1 H, CH_2CH=CH_2), 5.41 (dq, *J* = 17.1, 1.5, 1 H, CH_2CH=C*H*H), 5.28 (dq, *J* = 10.7, 1.5, 1 H CH_2CH=CH*H*), 4.65-4.47 (m, CH_2CH=CH_2), 3.72 (s, 3 H, CO_2Me), 2.44-2.26 (m, 2 H, =C=CHCH_2), 1.56-1.28 (m, 4 H, $CH_2CH_2CH_3$), 0.89 (t, *J* = 7.3, 3 H, CH_2CH_3); ^{13}C NMR: *d* = 213.0, 167.6, 155.3, 133.2, 128.8, 128.4, 121.3, 121.1, 117.5, 112.5, 103.3, 92.6, 69.2, 52.1, 30.2, 28.7, 22.4, 13.9; GC-MS: *m/z* = 286 (3) [M^+], 246 (14), 245 (83), 189 (51), 186 (15), 185 (100), 171 (13), 161 (26), 157 (23), 144 (24), 143 (44), 131 (32), 129 (15), 128 (22), 127 (19), 115 (37); anal. calcd for $C_{18}H_{22}O_3$: C, 75.50; H, 7.74; found C, 75.43; H, 7.75.

2-(1-Methylenehept-2-ynyl)phenol (6e). Yield: 80.5 mg, starting from 516.5 mg of **1e** (20%, Table 2, entry 40). Yellow oil. IR (film): ν = 3415 (m, br), 2957 (s), 2931 (s), 2870 (m), 2219 (w), 1593 (m), 1485 (m), 1453 (s), 1281 (w), 1234 (m), 1211 (m), 903 (w), 752 (s) cm^{-1}; ^1H NMR: *d* = 7.28 (dd, *J* = 7.8, 2.0, 1 H, H-6), 7.24-7.16 (m, 1 H, H-4 or H-5), 6.92-6.83 (m, 2 H, H-3 + H-5 or H-4), 5.72-5.65 (m, 2 H, =CH_2), 2.38 (t, *J* = 7.1, 2 H, ≡CCH_2), 1.63-1.36 (m, 4 H, $CH_2CH_2CH_3$), 0.92 (t, *J* = 7.3, 3 H, CH_2CH_3); ^{13}C NMR: *d* = 153.6, 129.8, 128.4, 127.1, 124.8, 124.4, 120.5, 116.9, 94.3, 79.5, 30.5, 22.0, 19.0, 13.5; GC-MS: *m/z* = 200 (27) [M^+], 185 (17), 172 (18), 171

(100), 158 (74), 157 (53), 145 (16), 131 (22), 129 (42), 128 (82), 127 (35), 115 (50), 91 (16), 89 (16), 77 (28), 63 (15); anal. calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05; found C, 84.12; H, 8.03.

2-(4,4-Dimethyl-1-Methylenepent-2-ynyl)phenol (6f). Yield: 67.4 mg, starting from 516.5 mg of **1f** (17%, Table 2, entry 42). Yellow oil. IR (film): ν = 3450 (m, br), 2966 (s), 2209 (w), 1592 (m), 1484 (m), 1454 (s), 1362 (w), 1321 (w), 1247 (w), 1205 (m), 903 (m), 751 (m) cm^{-1}; ^1H NMR: *d* = 7.32-7.14 (m, 2 H, H-6 + H-4 or H-5), 6.93-6.82 (m, 2 H, H-3 + H-5 or H-4), 6.81 (s, 1 H, OH), 5.70 (d, *J* = 1.5, 1 H, =C*H*H), 5.64 (d, *J* = 1.5, 1 H, =CH*H*), 1.30 (s, 9 H, t-Bu); ^{13}C NMR: *d* = 153.7, 129.9, 128.2, 126.9, 124.7, 124.3, 120.5, 117.0, 102.3, 78.1, 30.7, 28.2; GC-MS: *m/z* 200 (57) [M^+], 185 (100), 170 (21), 169 (18), 159 (37), 157 (26), 152 (22), 142 (29), 141 (20), 131 (24), 115 (34), 91 (19), 77 (21); anal. calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05; found C, 83.83; H, 8.04.

2-(Methoxyphenylmethyl)-3-methylbenzofuran (7g). Yield: 132.3 mg, starting from 556.5 mg of **1g** (26%, Table 2, entry 46). Yellow oil. IR (film): ν = 2924 (m), 1493 (m), 1453 (s), 1251 (m), 1189 (w), 1179 (w), 1092 (s), 873 (m), 747 (s), 699 (m) cm^{-1}; ^1H NMR: *d* = 7.49-7.17 (m, 9 H aromatic), 5.50 (s, 1 H, C*H*Ph), 3.41 (s, 3 H, OMe), 2.27 (s, 3 H, =CCH_3); ^{13}C NMR: *d* = 154.3, 150.5, 139.1, 128.4, 128.2, 127.8, 126.8, 124.3, 122.2, 119.3, 113.5, 111.3, 77.6, 56.9, 7.9; GC-MS: *m/z* = 252 (20) [M^+], 222 (18), 221 (100), 202 (7), 178 (7), 175 (14), 115 (5), 103 (5), 91 (4), 77 (11); anal. calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39; found C, 81.02; H, 6.38.

2-(Methoxyphenylmethyl)-3-phenylbenzofuran (7i). Yield: 132.6 mg, starting from 680.5 mg of **1i** (21%, Table 2, entry 51). Yellow oil. IR (film): ν = 2926 (m), 1493 (m), 1453 (s), 1253 (m), 1180 (m), 1087 (s), 964 (m), 873 (m), 749 (s), 701 (s), cm^{-1}; ^1H NMR: *d* = 7.57-7.13 (m, 14 H aromatic), 5.52 (s, 1 H, C*H*Ph), 3.33 (s, 3 H, OMe); GC-MS: *m/z* = 314 (21) [M^+], 284 (23), 283 (100), 253 (4), 252 (6), 239 (5), 237 (12), 221 (5), 205 (24), 165 (7); anal. calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77; found C, 84.17; H, 5.76.

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