2,2-Dimethoxy-2-(4-fluorophenyl)-1-phenylethanone and 2,2-Dimethoxy-2-phenyl-1-(4-fluorophenyl)ethanone (2j): ^{1}H NMR δ 8.25–7.95 (m, 2 H), 7.7–6.95 (m, 7 H), 3.25 (s, 6 H); ^{13}C NMR δ 194.7, 193.3, 165.35 (d, $^{1}J_{CF}$ = 256 Hz), 162.9 (d, $^{1}J_{CF}$ = 249 Hz), 136.7, 134.2, 133.0, 132.65 (d, $^{3}J_{CCCF}$ = 9 Hz), 129.8, 128.9, 128.9 (d, $^{3}J_{CCCF}$ = 9 Hz), 128.5, 128.1, 126.8, 115.45 (d, $^{2}J_{CCF}$ = 21 Hz), 115.15 (d, $^{2}J_{CCF}$ = 21 Hz), 103.5, 103.3, 49.9.

(4-Fluorophenyl)phenylethanedione (3j): mp 64–65 °C (lit.[42] mp 64–65 °C); ^{1}H NMR δ 8.15–7.85 (m, 4 H), 7.7–7.35 (m, 3 H), 7.35–7.0 (m, 2 H); ^{13}C NMR δ 193.9, 192.6, 166.8 (d, $^{1}J_{CF}$ = 258 Hz), 134.9, 132.7 (d, $^{3}J_{CCCF}$ = 10 Hz), 129.9, 129.0, 116.35 (d, $^{2}J_{CCF}$ = 22 Hz); MS *m/e* (rel intensity) 228 (6), 123 (65), 105 (100), 95 (40), 77 (51).

From the reactions carried out in acetonitrile/ethylene glycol (5:1) the following products were obtained.

2-Phenyl-2,2′-bi-1,3-dioxolane (9a): mp 77–79 °C; ^{1}H NMR δ 7.6–7.4 (m, 2 H), 7.4–7.2 (m, 3 H), 5.15 (s, 1 H), 4.2–3.7 (m, 4 H), 3.75 (br s, 4 H); ^{13}C NMR δ 138.4, 128.3, 127.7, 126.9, 108.2, 105.1, 65.7, 65.6; MS *m/e* (rel intensity) 162 (1), 149 (100), 105 (70), 91 (4), 77 (37), 73 (18). Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.86; H, 6.35. Found: C, 65.00; H, 6.48.

2-Phenylhexahydro-1,4-dioxino[2,3-*b*]-1,4-dioxin (10a): mp 114–116 °C; ^{1}H NMR δ 7.75–7.55 (m, 2 H), 7.45–7.2 (m, 3 H), 5.3 (s, 1 H), 4.25–3.9 (m, 4 H), 3.75–3.45 (m, 4 H); ^{13}C NMR δ 138.6, 128.9, 128.3, 126.8, 92.8, 62.3, 61.7; MS *m/e* (rel intensity) 222 (2), 149 (11), 123 (44), 105 (100), 77 (54), 73 (12). Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.86; H, 6.35. Found: C, 64.71; H, 6.24.

2-*n*-Hexyl-2,2′-bi-1,3-dioxolane (9d): oil; ^{1}H NMR δ 4.8 (s, 1 H), 4.2–3.75 (m, 8 H), 1.8–1.5 (m, 2 H), 1.5–1.1 (m, 8 H), 0.9 (t, 3 H, J = 7.5 Hz); ^{13}C NMR δ 109.7, 104.8, 66.1, 65.2, 33.5, 31.6, 29.4, 22.3, 22.0, 13.8; MS *m/e* (rel intensity) 229 (1), 187 (1), 157 (100), 99 (17), 73 (29), 45 (17), 43 (30). Anal. Calcd for $C_{12}H_{22}O_4$: C, 62.59; H, 9.63. Found: C, 62.28; H, 9.50.

2-*n*-Hexylhexahydro-1,4-dioxino[2,3-*b*]-1,4-dioxin (10d): mp 40–42 °C; ^{1}H NMR δ 4.4 (s, 1 H), 4.2–3.8 (m, 4 H), 3.8–3.4 (m, 4 H), 1.9–1.5 (m, 2 H), 1.5–1.1 (m, 8 H), 0.9 (t, 3 H, J = 7.5 Hz); ^{13}C NMR δ 94.0, 93.5, 61.8, 61.0, 32.1, 31.7, 29.4, 22.5, 21.1, 13.9; MS *m/e* (rel intensity) 230 (2), 157 (27), 131 (6), 113 (18), 99 (10), 86 (16), 73 (100). Anal. Calcd for $C_{12}H_{22}O_4$: C, 62.59; H, 9.63. Found: C, 62.70, H, 9.74.

2,2′-Diphenyl-2,2′-bi-1,3-dioxolane (12f): oil;[7] ^{1}H NMR δ 7.5–7.3 (m, 2 H), 7.3–7.15 (m, 3 H), 3.8 (s, 4 H); ^{13}C NMR δ 139.2, 128.0, 127.9, 127.0, 110.3, 65.8; MS *m/e* (rel intensity) 149 (100), 105 (39), 77 (21).

5-(1,3-Dioxolan-2-yl)-4-octanone (11g): oil; ^{1}H NMR δ 4.2–3.85 (m, 2 H), 2.55 (t, 1 H, J = 7.5 Hz), 1.9–1.2 (m, 3 H), 0.95 (t, 3 H, J = 7.5 Hz); ^{13}C NMR δ 207.8, 109.6, 63.4, 38.8, 36.3, 16.6, 16.0, 14.0, 13.6; MS *m/e* (rel intensity) 127 (3), 115 (100), 71 (33). Anal. Calcd for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74. Found: C, 64.61; H, 9.89.

2,2′-Di-*n*-propyl-2,2′-bi-1,3-dioxolane (12g): oil; ^{1}H NMR δ 4.2–3.8 (m, 4 H), 1.9–1.55 (m, 2 H), 1.55–1.15 (m, 2 H), 0.95 (t, 3 H, J = 7.5 Hz); ^{13}C NMR δ 113.3, 66.5, 36.4, 15.7, 14.3; MS *m/e* (rel intensity) 170 (1), 115 (100), 99 (3), 71 (19). Anal. Calcd for $C_{12}H_{22}O_4$: C, 62.59; H, 9.63. Found: C, 62.48; H, 9.54.

Reactions of Phenylacetylene 1a with PhSeCl. A mixture of **1a** (2 mmol), phenylselenenyl chloride (2 mmol), and $AgNO_3$ (2 mmol) in MeOH (15 mL) was stirred at rt for 1 h. The reaction mixture was poured into a NH_4OH solution and extracted with CH_2Cl_2. Pure **7a** and **20** were obtained after column chromatography on alumina with mixtures of petroleum ether and ether (from 97:3 to 90:10) as eluants.

In a second reaction phenylselenenyl chloride (2 mmol) and $AgNO_3$ (2.4 mmol) in MeOH (10 mL) were stirred for 1 h at rt. The resulting mixture was added to a solution of **1a** (4.4 mmol) in MeOH (5 mL), cooled with an ice bath, and stirred for 7 h. After the usual workup and column chromatography pure **7a** and **16a** were obtained.

Physical and spectral data of **16a** and **20** are given below.

1,1-Dimethoxy-1-phenyl-2,2-bis(phenylseleno)ethane (16a): oil; ^{1}H NMR δ 7.75–7.65 (m, 2 H), 7.45–7.00 (m, 13 H), 4.85 (s, 1 H), 3.28 (s, 6 H); ^{13}C NMR δ 138.7, 134.8, 131.4, 128.7, 128.6, 128.4, 128.2, 128.0, 127.6, 103.5, 55.4, 50.1; MS *m/e* (rel intensity) 478 (1), 444 (1), 321 (1), 290 (2), 167 (7), 164 (31), 151 (100), 121 (12), 105 (18), 77 (17). Anal. Calcd for $C_{22}H_{22}O_2Se_2$: C, 55.48; H, 4.66. Found: C, 55.57; H, 4.58.

2-Chloro-1,1-dimethoxy-1-phenyl-2-(phenylseleno)ethane (20): oil; ^{1}H NMR δ 7.85–7.6 (m, 4 H), 7.6–7.25 (m, 6 H), 5.55 (s, 1 H), 3.45 (s, 3 H), 3.35 (s, 3 H); ^{13}C NMR δ 135.1, 129.2, 128.9, 128.5, 128.4, 127.8, 102.9, 66.4, 50.3, 49.9; MS *m/e* (rel intensity) 356 (1), 325 (2), 289 (1), 234 (1), 210 (1), 151 (100), 105 (24), 77 (30). Anal. Calcd for $C_{16}H_{17}ClO_2Se$: C, 54.03; H, 4.82. Found: C, 54.12; H, 4.90.

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[42] Denney, D. B.; Denney, D. Z.; Pastor, S. D. *Phosphorus Sulfur* **1985**, *22*, 191.

Stereospecific Palladium(II)-Catalyzed Cyclocarbonylation of 3-Aryl-1-propynes and Iodoarenes or Acid Chlorides To Form (*E*)-3-Arylidenebutenolides

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Iodoarenes react with 3-aryl-1-propynes and carbon monoxide, in the presence of palladium acetate and triphenylphosphine, to form (*E*)-arylidenebutenolides in 33–88% isolated yields. The same product is formed by substitution of acid chloride for a iodoarene.

Cyclocarbonylation reactions catalyzed by transition-metal complexes are useful for the synthesis of lactones and lactams, amongst other heterocyclic compounds. Recent examples include the cobalt carbonyl catalyzed conversion of β-epoxy alcohols to 2-*C*-(2,5-dihydro-2-oxo-3-phenylfur-5-yl)lactic acids,[1] the formation of 3(2*H*)-

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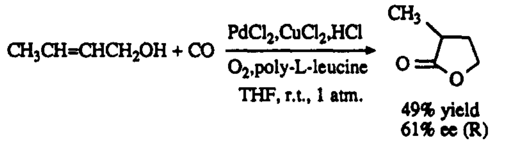
Table I. Palladium(II)-Catalyzed Cyclocarbonylation of Iodoarenes and Alkynes[a]

1, Ar	2, R	reaction time (h)	pressure (psi)	yield of 3 (%)
Ph	H	24	1200	40
	OCH_3	24	300	65
p-$CH_3C_6H_4$	H	18	1200	33
	OCH_3	24	300	85
p-ClC_6H_4	H	18	1200	72
	OCH_3	14	300	68
p-$CH_3OC_6H_4$	H	24	600	57
	OCH_3	24	300	75
p-$CH_3OCOC_6H_4$	H	12	300	69
	OCH_3	12	300	88
o-$CH_3C_6H_4$	H	28	300	40
	OCH_3	24	300	35

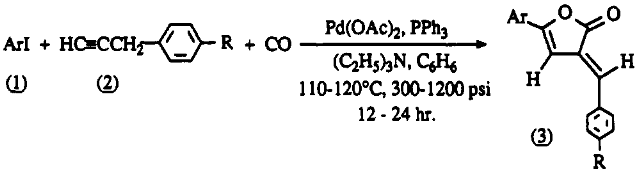
[a] Reaction conditions: 1 (1.0 mmol), 2 (1.2 mmol), Et_3N (2.0 mmol), $Pd(OAc)_2$ (0.05 mmol), PPh_3 (0.10 mmol), C_6H_6 (1-2 mL), CO, 110 °C.

furanones by palladium-catalyzed reaction of iodobenzene with alkynols and carbon monoxide,[2] and lactone generation by palladium-catalyzed intramolecular cyclization of allylic alcohols (eq 1).[3] We now describe a simple, stereospecific synthesis of (*E*)-3-arylidenebutenolides from 3-aryl-1-propynes (benzylacetylenes), iodoarenes, and carbon monoxide catalyzed by palladium acetate.



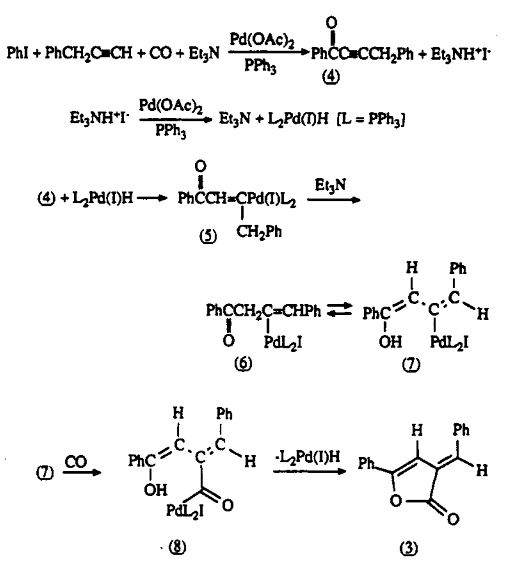
(1)

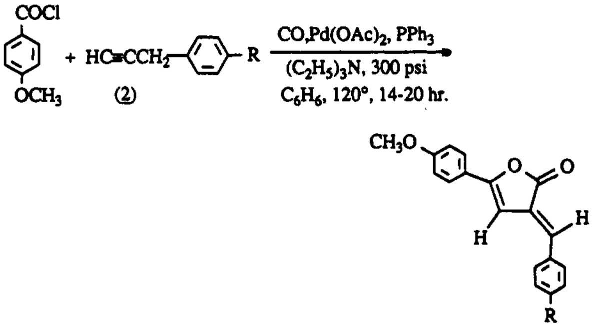
Treatment of iodobenzene (1, Ar = Ph) with 3-phenyl-1-propyne (2, R = H) and carbon monoxide in benzene with palladium acetate as the catalyst and added triphenylphosphine and triethylamine affords the 3-arylidenebutenolide 3 (Ar = Ph, R = H) in 40% isolated yield; this reaction is applicable to iodoarenes containing electron-donating (e.g., CH_3, OCH_3) or -withdrawing substituents ($COOCH_3$) giving the butenolide in 33–88% yields (see Table I for data). All of the reactions were effected for 12–24 h at 110–120 °C using a 20:1 ratio of $1/Pd(OAc)_2$ and 300–1200 psi of carbon monoxide. The process is stereospecific leading to the (*E*)-3-arylidenebutenolide, which was identified by NMR and other spectral data as well as by comparison with literature results.[4-6]



The initial step in this process may involve generation of an acetylenic ketone.[7] In the event, acid chlorides could, in principle, be used instead of iodoarenes for the reaction.[8] Indeed, treatment of an acid chloride such as *p*-methoxybenzoyl chloride with 3-aryl-1-propyne, under the same reaction conditions, does form 3 in reasonable yields (eq 2). A possible mechanism for the production of 3 from 1 and 2 is outlined in Scheme I (illustrated for 1, Ar = Ph, and 2, R = H). Reaction of iodobenzene with 3-phenyl-1-propyne, carbon monoxide, and triethylamine, in the presence of palladium acetate and triphenylphosphine, would afford the alkynone 4 and triethylammonium iodide. The latter can serve as a source of palladium hydride by reversible dehydroiodination. Addition of the palladium hydride to 4 may give the vinylpalladium complex 6 (via base-catalyzed isomerization of 5). Enolization of the latter would generate 7 in which the palladium and phenyl substituents are trans to each other (for steric reasons). Carbonyl insertion to 8 followed by ring closure would give 3 and regenerate the key catalytic species. It should be noted that rearrangement of 4 does not take place, under carbon monoxide, to give a furan.[9]

Scheme I





(2)

3, R=H, 55%
3, R = OCH_3, 57%

In conclusion, (*E*)-3-arylidenebutenolides are isolated in fair to very good yields by the cyclocarbonylation of 3-aryl-1-propynes with iodoarenes or acid chlorides.

Experimental Section

General Considerations. Melting point determinations are corrected, while NMR spectra were recorded on a Varian XL-300 or Gemini-200 spectrometer.

General Procedure for the Reaction of Iodoarenes and 3-Aryl-1-propynes with Carbon Monoxide. Into a 45-mL autoclave were placed the iodoarene (1.0 mmol), 3-aryl-1-propyne (1.2 mmol), triethylamine (2.0 mmol), $Pd(OAc)_2$ (0.05 mmol), PPh_3

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(1) Alper, H.; Eisenstat, A.; Satyanarayana, N. *J. Am. Chem. Soc.* **1990**, *112*, 7060.

(2) Inoue, Y.; Ohuchi, K.; Yen, I. F.; Imaizumi, A. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 3518.

(3) Alper, H.; Hamel, N. *J. Chem. Soc., Chem. Commun.* **1990**, 135.

(4) Maquestiau, A.; van Heverbeke, Y.; Muller, R. N. *Bull. Soc. Chim. Belg.* **1974**, *83*, 259.

(5) Eweiss, N. F.; Hussain, S. G. *J. Univ. Kuwait Sci.* **1981**, *8*, 185.

(6) Berstermann, H. M.; Harder, R.; Winter, H. W.; Wentrup, C. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 564.

(7) Kobayashi, T.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1981**, 333.

(8) Tohda, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1977**, 777.

(9) Sheng, H.; Lin, S.; Huang, Y. *Tetrahedron Lett.* **1986**, *27*, 4893.

(0.10 mmol), and benzene (1–2 mL). After removal of air from the autoclave, the latter was pressurized with CO and the reaction mixture was heated to 110–120 °C (see Table I for pressure and reaction times). Following completion of the reaction, the solvent was removed by rotary evaporation. The residue was washed with 10 mL of hexane and then with cold water (10 mL). The crude product was then dissolved in ethyl acetate (30 mL), and the organic solution was washed with water (10 mL), dried ($MgSO_4$), and concentrated. Recrystallization from CH_2Cl_2/hexane afforded the (*E*)-3-arylidenebutenolide (**3**). Further purification, if necessary, was effected by preparative thin-layer chromatography (silica gel) using hexane–ethyl acetate.

The following butenolides were prepared according to this procedure using the reactants and solvents specified.

3 (Ar = Ph, R = H). Iodobenzene (0.204 g, 1.0 mmol), 3-phenyl-1-propyne (0.160 g, 1.37 mmol), Et_3N (0.200 g, 2.0 mmol), Pd(OAc) (11 mg, 0.049 mmol), PPh_3 (26 mg, 0.1 mmol), CO, and benzene (1.0 mL): yield 0.099 g (40%) of **3**; mp 153–154 °C (lit.[6] mp 154–155 °C); IR ν(CO) 1762 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.92 (d, 1 H, *J* = 0.8 Hz), 7.41 (s (br), 1 H), 7.35–7.80 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 99.81, 125.36, 128.06, 128.92, 129.15, 130.14, 130.32, 130.56, 130.77, 135.18, 135.53, 157.04, 169.45; MS *m/e* 248 (M^+).

3 (Ar = Ph, R = OCH_3). Iodobenzene (0.204 g, 1.0 mmol), alkyne (0.175 g, 1.20 mmol), Et_3N (0.200 g, 2.0 mmol), $Pd(OAc)_2$ (11 mg, 0.049 mmol), PPh_3 (26 mg, 0.1 mmol), CO, and benzene (1.0 mL): yield 0.180 g (65%) of **3**; mp 171–172 °C (lit.[6] mp 171–172.5 °C); IR ν(CO) 1766 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.86 (s, 3 H), 6.90 (d, 1 H, *J* = 0.9 Hz), 6.97 (d, 2 H, *J* = 87 Hz), 7.38 (s (br), 1 H), 7.39–7.70 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 55.34, 99.84, 114.68, 122.90, 125.17, 127.95, 128.28, 128.87, 130.23, 132.16, 135.57, 156.00, 161.53, 170.00; MS *m/e* 278 (M^+).

3 (Ar = *p*-$CH_3C_6H_4$, R = H). *p*-Iodotoluene (0.436 g, 2.0 mmol), 3-phenyl-1-propyne (0.600 g, 5.20 mmol), Et_3N (1.0 g, 10 mmol), $Pd(OAc)_2$ (23 mg, 0.10 mmol), PPh_3 (0.52 mg, 0.20 mmol), CO, and benzene (2 mL): yield 0.173 g (33%) of **3** (Ar = *p*-$CH_3C_6H_4$, R = H); mp 151–152 °C (lit.[5] mp 150 °C); IR ν(CO) 1773 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.38 (s, 3 H), 6.85 (d, 1 H, *J* = 0.8 Hz), 7.23 (d, 2 H, *J* = 8.1 Hz), 7.38 (s (br), 1 H), 7.39–7.62 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 25.51, 98.98, 125.26, 125.50, 129.01, 129.56, 129.96, 130.03, 134.62, 135.20, 140.96, 157.14, 169.43; MS *m/e* 262 (M^+). Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.48; H, 5.42.

3 (Ar = *p*-$CH_3C_6H_4$, *R* = OCH_3). *p*-Iodotoluene (0.218 g, 1.0 mmol), 3-(*p*-methoxyphenyl)-1-propyne (0.178 g, 1.22 mmol), Et_3N (0.25 g, 2.5 mmol), $Pd(OAc)_2$ (11 mg, 0.049 mmol), PPh_3 (25 mg, 0.095 mmol), CO, and benzene (1.0 mL); yield 0.248 g (85%) of **3** (Ar = *p*-$CH_3C_6H_4$, R = OCH_3); mp 163–164 °C; IR ν(CO) 1754 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.37 (s, 3 H), 3.86 (s, 3 H), 6.83 (d, 1 H, *J* = 0.8 Hz), 6.95 (d, 2 H, *J* = 8.8 Hz), 7.33 (s (br), 1 H), 7.40–7.62 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 21.34, 55.32, 99.01, 114.64, 123.08, 125.15, 125.53, 128.68, 129.60, 132.05, 134.84, 140.70, 156.26, 161.38, 170.13; MS *m/e* 292 (M^+). Anal. Calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52. Found: C, 77.81, H, 5.60.

3 (Ar = *p*-ClC_6H_4, R = H). *p*-Chloroiodobenzene (0.238 g, 1.0 mmol), 3-phenyl-1-propyne (0.150 g, 1.3 mmol), Et_3N (0.200 g, 2.0 mmol), $Pd(OAc)_2$ (11 mg, 0.049 mmol), PPh_3 (26 mg, 0.10 mmol), CO, and benzene (1.0 mL): yield 0.204 g (72%) of **3** (Ar = *p*-ClC_6H_4, R = H); mp 208–210 °C (lit.[5] mp 211 °C); IR ν(CO) 1756 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.91 (d, 1 H, *J* = 0.9 Hz), 7.40 (d, 2 H, *J* = 8.8 Hz), 7.42 (s (br), 1 H), 7.38–7.67 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 100.22, 125.19, 126.56, 129.18, 129.26, 130.16, 130.48, 135.05, 136.13, 136.49, 155.91, 169.21; MS *m/e* 284, 282 (M^+).

3 (Ar = *p*-ClC_6H_4, R = CH_3O). *p*-Chloroiodobenzene (0.238 g, 1.0 mmol), 3-(*p*-methoxyphenyl)-1-propyne (0.175 g, 1.2 mmol), Et_3N (0.200 g, 2.0 mmol), $Pd(OAc)_2$ (11 mg, 0.049 mmol), PPh_3 (26 mg, 0.10 mmol), CO, and benzene (1.0 mL): yield 0.212 g (68%) of **3** (Ar = *p*-ClC_6H_4, R = OCH_3); mp 220–222 °C; IR ν(CO) 1754 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.82 (s, 3 H), 6.89 (d, 1 H, *J* = 1.0 Hz), 6.97 (d, 2 H, *J* = 8.8 Hz), 7.40 (s (br), 1 H), 7.39–7.66 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 55.34, 100.27, 114.72, 122.64, 126.36, 126.80, 127.84, 129.20, 132.21, 135.29, 136.13, 154.86, 161.61, 169.86; MS *m/e* 312, 314 (M^+). Anal. Calcd for $C_{18}H_{13}ClO_3$: C, 69.13; H, 4.19. Found: C, 69.34, H, 3.89.

3 (Ar = *p*-$CH_3OC_6H_4$, R = 1). *p*-Iodoanisole (0.234 g, 1.0 mmol), 3-phenyl-1-propyne (0.160 g, 1.40 mmol), Et_3N (0.20 g, 2.0 mmol), $Pd(OAc)_2$ (11 mg, 0.049 mmol), PPh_3 (26 mg, 0.10 mmol), CO, and benzene (1 mL): yield 0.158 g (57%) of **3** (Ar = *p*-$CH_3OC_6H_4$, R = H); mp 174–175 °C; IR ν(CO) 1767 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.84 (s, 3 H), 6.78 (d, 1 H, *J* = 0.9 Hz), 6.93 (d, 2 H, *J* = 9.0 Hz), 7.35 (s (br), 1 H), 7.38–7.69 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 55.30, 97.95, 114.39, 120.68, 125.01, 127.08, 129.08, 129.59, 133.99, 135.40, 157.02, 161.59, 169.80; MS *m/e* 278 (M^+). Anal. Calcd for $C_{18}H_{14}O_3$: C, 77.68; H, 6.01. Found: C, 77.91; H, 6.22.

3 (Ar = *p*-$CH_3OC_6H_4$, R = CH_3O). *p*-Iodoanisole (0.234 g, 1.0 mmol), 3-(*p*-methoxyphenyl)-1-propyne (0.180 g, 1.23 mmol), Et_3N (0.20 g, 2.0 mmol), $Pd(OAc)_2$ (11 mg, 0.049 mmol), PPh_3 (26 mg, 0.10 mmol), CO, and benzene (1.0 mL): yield 0.231 g (75%) of **3** (Ar = *p*-$CH_3OC_6H_4$, R = CH_3O); mp 175–177 °C; IR ν(CO) 1765 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.84 (s, 3 H), 3.86 (s, 3 H), 6.77 (d, 1 H, *J* = 1.0 Hz), 6.93 (d, 2 H, *J* = 9.1 Hz), 6.96 (d, 2 H, *J* = 8.9 Hz), 7.31 (s (br), 1 H), 7.58–7.68 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 55.16, 55.30, 97.98, 114.34, 114.61, 120.93, 123.15, 126.87, 128.16, 131.96, 134.09, 156.01, 161.25, 161.73, 170.23; MS *m/e* 308 (M^+). Anal. Calcd for $C_{19}H_{16}O_4$: C, 74.01; H, 5.23. Found: C, 74.34, H, 5.30.

3 (Ar = *p*-$CH_3OCOC_6H_4$, R = H). Methyl *p*-iodobenzoate (0.262 g, 1.0 mmol), 3-phenyl-1-propyne (0.14 g, 1.20 mmol), Et_3N (0.20 g, 2.0 mmol), $Pd(OAc)_2$ (11 mg, 0.049 mmol), PPh_3 (26 mg, 0.10 mmol), CO, and benzene (2.0 mL): yield 0.211 g (69%) of **3** Ar = *p*-$CH_3OCOC_6H_4$, R = H_3; mp 240.5–241.5 °C; IR ν(CO) 1758 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.92 (s, 3 H), 7.04 (d, 1 H, *J* = 0.9 Hz), 7.40–8.05 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 52.24, 101.92, 125.10, 125.18, 129.24, 130.13, 130.27, 130.71, 131.46, 131.99, 134.95, 137.18, 155.84, 166.42, 169.04; MS *m/e* 306 (M^+). Anal. Calcd for $C_{19}H_{14}O_4$: C, 74.50; H, 4.61. Found: C, 74.81; H, 4.54.

3 (Ar = *p*-$CH_3OCOC_6H_4$, R = OCH_3). Methyl *p*-iodobenzoate (0.262 g, 1.07 mmol), 3-(*p*-methoxyphenyl)-1-propyne (0.180 g, 1.23 mmol), Et_3N (0.200 g, 2.0 mmol), $Pd(OAc)_2$ (11 mg, 0.049 mmol), PPh_3 (26 mg, 0.10 mmol), CO, and benzene (2.0 mL): yield 0.298 g (88%) of **3** (Ar = *p*-$CH_3OCOC_6H_4$, R = OCH_3); mp 258–260 °C; IR ν(CO) 1758 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.87 (s, 3 H), 3.92 (s, 3 H), 6.92 (d, 1 H, *J* = 0.9 Hz), 6.97 (d, 2 H, *J* = 8.6 Hz), 7.45 (s (br), 1 H), 7.61–8.08 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 52.20, 55.38, 102.00, 114.78, 122.48, 124.96, 127.74, 130.09, 131.11, 132.23, 132.39, 137.19, 154.77, 161.87, 166.48, 169.54; MS *m/e* 336 (M^+). Anal. Calcd for $C_{20}H_{16}O_5$: C, 71.42; H, 4.80. Found: C, 71.60; H, 5.02.

3 (Ar = *o*-$CH_3C_6H_4$, R = H). *o*-Iodotoluene (0.436 g, 2.0 mmol), 3-phenyl-1-propyne (0.290 g, 2.5 mmol), Et_3N (0.30 g, 3.0 mmol), $Pd(OAc)_2$ (22 mg, 0.096 mmol), PPh_3 (0.050 g, 0.19 mmol), CO, and benzene (2.0 mL): yield 0.210 g (40%) of **3** (Ar = *o*-$CH_3C_6H_4$, R = H); mp 86–87 °C; IR ν(CO) 1763 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.54 (s, 3 H), 6.74 (d, 1 H, *J* = 0.9 Hz), 7.20–7.68 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 21.98, 101.83, 125.54, 126.27, 127.64, 128.07, 129.17, 130.10, 130.30, 131.64, 135.18, 136.85, 157.33, 169.28; MS *m/e* 262 (M^+). Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.56; H, 5.21.

3 (Ar = *o*-$CH_3C_6H_4$, R = OCH_3). *o*-Iodotoluene (0.436 g, 2.0 mmol), 3-(*p*-methoxyphenyl)-1-propyne (0.365 g, 2.5 mmol), Et_3N (0.30 g, 3.0 mmol), $Pd(OAc)_2$ (22 mg, 0.98 mmol), PPh_3 (0.050 g, 0.19 mmol), CO, and benzene (2.0 mL): yield 0.202 g (35%) of **3** (Ar = *o*-$CH_3C_6H_4$, R = OCH_3); mp 99–100 °C; IR ν(CO) 1765 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.55 (s, 3 H), 3.86 (s, 3 H), 6.72 (d, 1 H, *J* = 1.0 Hz), 6.96 (d, 2 H, *J* = 8.6 Hz), 7.20–7.75 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 21.98, 55.30, 103.87, 114.72, 123.03, 126.22, 127.84, 127.94, 129.84, 131.56, 132.09, 135.68, 136.63, 156.25, 161.54, 169.70; MS *m/e* 292 (M^+). Anal. Calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52. Found: C, 78.12; H, 5.85.

Reaction of *p*-Anisoyl Chloride with 3-Phenyl-1-propyne. Replacement of *p*-iodoanisole by *p*-anisoyl chloride in reaction with 3-phenyl-1-propyne gave **3** (Ar = *p*-$CH_3OC_6H_4$, R = H) in 55% yield.

Reaction of *p*-Anisoyl Chloride with 3-(*p*-Methoxyphenyl)-1-propyne. Replacement of *p*-iodoanisole by p-anisoyl chloride in reaction with 3-(*p*-methoxyphenyl)-1-propyne gave **3** (Ar = *p*-$CH_3CC_6H_4$, R = CH_3) in 57% yield.

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