One-Step Synthesis of α-Pyrones from Acyl Chlorides by the Stille Reaction

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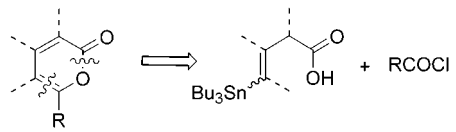
Abstract: Palladium-catalyzed stereoselective annulation of a functional vinylstannane by acyl chlorides gives the corresponding α-pyran-2-ones in good yields. This annulation most probably proceeds through a Stille reaction/cyclization sequence.

The α-pyrones constitute an important class of biologically active compounds, and their synthesis has been a focus of considerable attention in synthetic organic chemistry[1] as well as in medicinal chemistry.[2] In the past decade, numerous methods reported for the synthesis of these structures utilize halolactonization or transition metals (Ag, Hg, Rh, Pd) to promote intramolecular addition of carboxylic acid to alkynes.[3] In general, these reactions of 4-alkynoic acids occur with poor regioselectivity and in many cases mixtures of γ-alkylidenebutenolides and α-pyrones are obtained. The problem of regioselectivity was recently solved by Larock et al., who demonstrated that substituted isocoumarins or α-pyrones could be prepared by treating β-halogeno α,β-unsaturated esters with internal alkynes in the presence of a palladium catalyst.[4] Nevertheless, although these methods are efficient, they use β-halogeno acid or ester precursors which are not commercially available. In addition, we have previously described the synthesis of **2** and demonstrated its efficiency in transferring but-3-enoic-d_4 acid synthons onto miscellaneous substrates.[5] To broaden the use of **2** in synthesis, we planned to prepare α-pyrones from acyl chlorides using tandem Stille and lactonization reactions (Scheme 1).

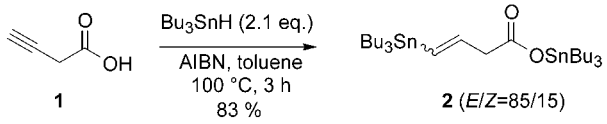
Scheme 1



We report the stereoselective synthesis of α-pyrones under palladium complex catalysis from the functional vinyltin **2**.

The required organotin precursor **2** is easily obtained by radical hydrostannation[6] of but-3-ynoic acid **1** (prepared via carboxylation of the corresponding allenylmagnesium bromide[7]) with 83% yield as a thermodynamic mixture (E/Z = 85/15). It should be noted that radical hydrostannation conducted at a lower temperature (e.g. in benzene) led to a 50/50 mixture of **2** and its internal isomer. Our investigation began with the coupling of **2**

Scheme 2



with benzoyl chloride acid under standard Stille conditions. To obtain good yields of **3a**, we examined the reaction under various conditions (solvent, catalyst). The influence of the solvent on conversion rates was examined in the first step. The cross-coupling reaction failed in the presence of a palladium(II) complex, and numerous tin byproducts were obtained in addition to butenoic acid. Chloroform, DMF, and toluene were found to be ineffective while dioxane afforded low yields of phenylpyrone **3a**. Switching Pd^{II} to phosphine-liganded Pd^0 and using chloroform as solvent also yielded very small quantities of phenylpyrone **3a** and a mixture of *Z* and *E* isomers as major products of the enone resulting from the Stille reaction. Fortunately, vinyltin reagent **2** yielded the desired heterocycle **3a** in 1,4-dioxane and in the presence of 5% of tetrakis(triphenylphosphine)palladium. Attempts conducted at lower temperature (ca 40−50 °C) led to lower yields. Nevertheless, we found that the use of a strongly degassed medium gave better yield in **3a** even at 50 °C. It should be noted that tributyltin carboxylate was found to be inert toward acyl chloride function.

Other acyl chlorides were engaged under similar conditions to determine the scope of the reaction. Reaction of vinyl stannane **2** with a range of acyl chlorides proceeded to give fair to good yields of α-pyrones **3a**−**o** (Table 1). A plausible explanation for the heteroannula-

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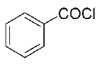
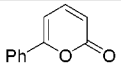
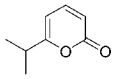
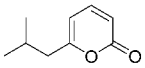
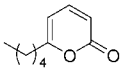
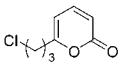
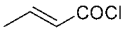
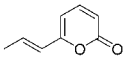
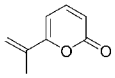
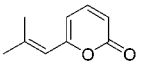
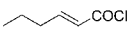
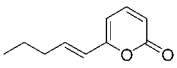
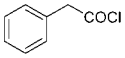
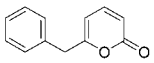
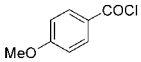
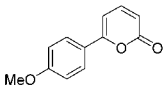
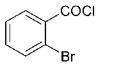
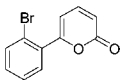
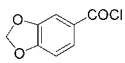
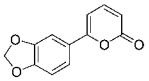
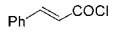
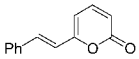
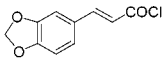
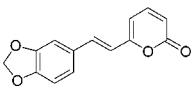
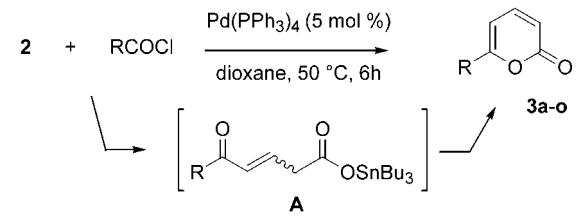
Table 1. Synthesis of α-Pyrones 3

entry	Acyl chloride	α-Pyrone		yield (%)
1			**3a**	84
2			**3b**	66
3			**3c**	62
4			**3d**	55
5			**3e**	48
6			**3f**	61
7			**3g**	51
8			**3h**	43
9			**3i**	52
10			**3j**	53
11			**3k**	70
12			**3l**	56
13			**3m**	83
14			**3n**	85
15			**3o**	68

Scheme 3



tion reaction would be the following mechanism. The first step, according to the Stille mechanism,[8] would yield the tributylstannyl 5-substituted 5-oxopent-3-enoate **A** by oxidative addition, transmetalation, and reductive elimination. Cyclization would then occur via a lactonization reaction on the dienol derived from **A** and with the concomitant formation of bis(tributyltin) oxide. At this stage, the determining role of 1,4-dioxane is difficult to rationalize.

Finally, the synthesis of sibirinone **3f** isolated from a culture of *Hypomyces semitranslucens* G. Arnold,[9] (*E*)-6-pent-1-enyl-pyran-2-one **3i** extracted from *Solenopsis invicta*,[10] 6-pentylpyranone **3d** found in a number of plants and as a pheromone of ant[11,12] and Paracotoin **3m**, an intermediate in the biosynthesis of shikimic acid,[13] was realized by this procedure.

In conclusion, a method was developed for the rapid synthesis of α-pyrones using a functional vinyltin reagent and acyl chloride. This was then applied to the synthesis of natural pyrones isolated from different sources. Stille cross-coupling followed by cyclization of the dienol form resulted in the formation of fair to good yields of the desired product in one step.

Experimental Section

General Methods. ^{1}H NMR spectra were recorded at 200 MHz or at 300 MHz using $CDCl_3$ as the solvent. Data, reported using the residual proton resonance of $CDCl_3$ ($\delta_H = 7.25$ ppm) as the internal reference, are as follows in the order chemical shift (δ in ppm relative to Me_4Si), multiplicity (s, d, t, m, b for singlet, doublet, triplet, quartet, broad), coupling constants (J in Hz). ^{13}C NMR was recorded at 50.5 or 75 MHz using $CDCl_3$ solvent peak at $\delta_C = 77.0$ ppm as the reference. Electron impact mass spectra were measured at 70 eV by GC-MS. Melting points are uncorrected. Standard column chromatography was performed on Merck silica gel (60 Å, 230−400 mesh silica gel) by use of flash column chromatography techniques. Analytical thin-layer chromatography (TLC) was conducted on Merck precoated silica gel 60 F_{254} plates. All reactions were performed in oven-dried glassware under positive argon pressure, unless otherwise noted. Reaction mixtures were stirred magnetically. Toluene and 1,4-dioxane were distilled from sodium and benzophenone prior to use. All reagents were purchased from Aldrich and used without further purification.

Tributylstannyl-4-(tributylstannyl)but-3-enoate (2). Under N_2 atmosphere, a toluene solution (20 mL) of but-3-ynoic acid (1 g, 0.012 mol), tributyltin hydride (8.6 g, 0.029 mol), and azobis(isobutyronitrile) (10 mg) was stirred at 100 °C. After 3

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h, toluene was eliminated under vacuum and then carbon tetrachloride (15 mL) was added to react with the excess tributyltin hydride. After the solution was stirring for 1 h, potassium fluoride solution (0.5 M, 15 mL) and acetone (15 mL) were added. The solution was extracted with diethyl ether after filtration and then dried over magnesium sulfate. After elimination of the solvents, tributylstannyl-4-(tributylstannyl)but-3-enoate (6.56 g) (**2**) was obtained as a 85/15 mixture of *Z* and *E* (83% yield): IR (neat) 2957, 2924, 2872, 2854, 1655, 1580−1550, 1461, 1377, 1074 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ *E* isomer 0.8−1.65 (m, 54H), 3.18 (d, $J = 5.0$ Hz, $J_{Sn-H} = 12$ Hz, 2H), 6.05 (d, $J = 18.9$ Hz, $J_{Sn-H} = 70-73$ Hz, 1H), 6.15 (dt, $J = 18.9$ Hz, 5.0 Hz, $J_{Sn-H} = 61-64$ Hz, 1H), *Z* isomer 3.08 (dd, $J = 7.1$ Hz, 1.3 Hz, 2H), 6.00 (dt, $J = 12.6$ Hz, 1.3 Hz, 1H), 6.69 (dt, $J = 12.6$ Hz, 7.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50.5 MHz) δ *E* isomer 9.3 ($J_{Sn-C} = 340-346$ Hz, 3C), 13.5 (6C), 16.6 ($J_{Sn-C} = 345-355$ Hz, 3C), 26.9 ($J_{Sn-C} = 64$ Hz, 3C), 27.1 ($J_{Sn-C} = 53.5$ Hz, 3C), 27.8 ($J_{Sn-C} = 21$ Hz, 3C), 28.8 ($J_{Sn-C} = 20$ Hz, 3C), 44 ($J_{Sn-C} = 65$ Hz, 1C), 130.7 ($J_{Sn-C} = 369-386$ Hz, 1C), 141.7 ($J_{Sn-C} = 21$ Hz, 1C), 176.7 (1C), *Z* isomer 42.3 (1C), 130.9 (1C), 141.9 (1C); MS (70 eV, EI) *m*/*z* 609 (M^+, 55), 507 (29), 319 (21), 291 (100), 269 (36), 267 (45), 235 (60), 57 (51), 56 (48), 49 (29), 43 (34), 42 (46), 41 (90).

Typical Procedure. In a Schlenk tube, to a degassed solution of 2.11 g (15 mmol) of benzoyl chloride in 50 mL of distilled dioxane was added dropwise 6.64 g (10 mmol) of tributylstannyl-4-(tributylstannyl)but-3-enoate (*E*/*Z* = 91/9), and then 570 mg (5% mol) of tetrakis(triphenylphosphine)palladium(0) was added. After being stirred 6 h at room temperature, the mixture was hydrolyzed with a saturated solution of ammonium chloride and extracted with diethyl ether (3 × 50 mL). The organic phase was washed with a saturated solution of sodium chloride and dried with magnesium sulfate. A 1.24 g (7.20 mmol) yield of 6-phenylpyran-2-one was obtained after purification by column chromatography on silica gel (95/5 hexane/diethyl ether).

6-Phenylpyran-2-one (3a): isolated in 72% yield as a yellow solid; mp 62−63 °C; IR (KBr) 3070, 1722, 1689, 1603, 1580, 1329, 1292 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.29 (dd, $J = 9.3$ Hz, 0.9 Hz, 1H), 6.67 (dd, $J = 6.9$ Hz, 0.9 Hz, 1H), 7.41−7.48 (m, 5H), 7.83 (dd, $J = 9.3$ Hz, 6.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 101.4, 114.4, 126.0, 129.3, 131.3, 131.7, 144.1, 161.5, 162.4; MS (70 eV, EI) *m*/*z* 172 (M^+, 56), 145 (11), 144 (100), 115 (40), 95 (15), 77 (26), 51 (12). Anal. Calcd for $C_{11}H_8O_2$: C, 76.73; H, 4.68. Found: C, 76.79; H, 4.75.

6-Isopropylpyran-2-one (3b): isolated in 66% yield as a colorless liquid; IR (neat) 3096, 2983, 2897, 1738, 1641, 1570, 1098 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.18 (d, $J = 7.1$ Hz, 6H), 2.68 (m, $J = 7.1$ Hz, 1H), 5.96 (d, $J = 6.0$ Hz, 1H), 6.10 (d, $J = 9.3$ Hz, 1H), 7.26 (dd, $J = 9.3$ Hz, 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50.5 MHz) δ 18.4 (2C), 33.6, 100.6, 112.8, 144.3, 163.1, 170.9; MS (70 eV, EI) 138 (M^+, 12), 83 (13), 75 (100), 73 (26), 59 (79), 49 (69), 47 (25), 45 (17), 31 (35), 29 (25), 27 (10). Anal. Calcd for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.59; H, 7.28.

6-Isobutylpyran-2-one (3c): isolated in 62% yield as a colorless liquid; IR (neat) 3100, 2980, 2895, 1740, 1640, 1570, 1095, 805 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 0.83 (d, $J = 8.0$ Hz, 6H), 1.96 (m, 1H), 2.23 (d, $J = 7.2$ Hz, 2H), 5.90 (d, $J = 6.5$ Hz, 1H), 6.04 (d, $J = 9.4$ Hz, 1H), 7.20 (dd, $J = 9.4$, 6.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50.5 MHz) δ 21.8, 22, 26.5, 42.5, 103.5, 112.6, 143.6, 162.7, 165.4; MS (70 eV, EI) *m*/*z* 152 (M^+,19), 124 (12), 110 (58), 95 (65), 82 (33), 81 (40), 68 (12), 53 (14), 43 (28), 39 (100), 38 (11). Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 71.10; H, 7.90.

6-Pentylpyran-2-one (3d): isolated in 55% yield as a colorless liquid; IR (neat) 3087, 2957, 2932, 2862, 1732, 1635, 1558, 1466, 1084 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.83 (t, $J = 7.2$ Hz, 3H), 1.22−1.29 (m, 4H), 1.55−1.61 (m, 2H), 2.40 (t, $J = 7.2$ Hz, 2H), 5.93 (dd, $J = 6.6$ Hz, $J = 0.6$ Hz, 1H), 6.06 (bd, $J = 9.3$ Hz, 1H), 7.21 (dd, $J = 9.3$ Hz, $J = 6.6$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.2, 22.6, 26.9, 31.4, 34.1, 103.0, 113.3, 144.2, 163.2, 167.1; MS (70 eV, EI) *m*/*z* 166 (M^+, 30), 110 (34), 95 (100), 82 (36), 81 (41), 68 (18), 53 (11), 41 (11), 39 (56); HRMS (EI) calcd for $C_{10}H_{14}O_2$, 166.0994, found 166.0988. Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.31; H, 8.41.

6-(3-Chloropropyl)pyran-2-one (3e): isolated in 48% yield as a colorless liquid; IR (neat) 3086, 2957, 2930, 2861, 1730, 1634, 1559, 1082, 723, 654 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.12−2.14 (m, 2H), 2.66 (t, $J = 7.2$ Hz, 2H), 3.56 (t, $J = 7.2$ Hz, 2H), 6.03 (d, $J = 6.6$ Hz, 1H), 6.16 (d, $J = 9.3$ Hz, 1H), 7.26 (dd, $J = 9.3$, 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 29.8, 31.3, 44.0, 103.8, 114.0, 144.0, 162.9, 164.9; MS (70 eV, EI) *m*/*z* 174 (M^+, 10), 172 (31), 144 (34), 95 (100), 82 (12), 81 (33), 39 (19). Anal. Calcd for $C_8H_9ClO_2$: C, 55.67; H, 5.26. Found: C, 55.60; H, 5.23.

6-Prop-1-enylpyran-2-one (3f): isolated in 61% yield as white solid; mp 49.5−50.5 °C; IR (KBr) 3100, 2961, 2938, 2915, 1739, 1653, 1536, 1092 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.87 (dd, $J = 7.2$ Hz, 1.8 Hz, 3H), 5.95 (d, $J = 6.6$ Hz, 1H), 5.99 (dq, $J = 15.6$ Hz, 1.8 Hz, 1H), 6.12 (d, $J = 9.4$ Hz, 1H), 6.65 (dq, $J = 15.6$, 7.2 Hz, 1H), 7.26 (dd, $J = 9.4$, 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.7, 103.2, 114.0, 123.3, 134.8, 144.3, 160.0, 162.3; MS (70 eV, EI) *m*/*z* 136 (M^+, 19), 108 (86), 107 (16), 95 (40), 79 (39), 69 (15), 44 (42), 39 (31). Anal. Calcd for $C_8H_8O_2$: C, 70.57; H, 5.92. Found: C, 70.62; H, 5.90.

6-Isopropenylpyran-2-one (3g): isolated in 51% yield; IR (KBr) 1718, 1605, 1505, 1489, 1236, 1030 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.97 (s, 3H), 5.32 (bs, 1H), 5.96 (bs, 1H), 6.20 (d, $J = 6.8$ Hz, 1H), 6.22 (q, $J = 9.3$ Hz, 1H), 7.34 (dd, $J = 9.3$ Hz, $J = 6.8$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 50.5 MHz) δ 18.5, 101.7, 114.8, 118.8, 134.0, 143.3, 160.6, 161.7; MS (70 eV, EI) *m*/*z* 136 (M^+, 88), 108 (100), 95 (73), 79 (18), 39 (34). Anal. Calcd for $C_8H_8O_2$: C, 70.57; H, 5.92. Found: C, 70.68; H, 5.85.

6-(2-Methylpropenyl)pyran-2-one (3h): isolated in 43% yield; IR (KBr) 3100, 1730, 1650, 1540, 1450, 1370, 1180 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.88 (s, 3H), 2.09 (s, 3H), 5.77 (bs, 1H), 5.94 (d, $J = 6.9$ Hz, 1H), 6.05 (d, $J = 9.3$ Hz, 1H), 7.27 (dd, $J = 9.3$ Hz, 6.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50.5 MHz) δ 20.6, 28.0, 104.2, 111.9, 117.1, 143.9, 146.2, 161.2, 162.1; MS (70 eV, EI) *m*/*z* 150 (M^+, 100), 122 (58), 107 (42), 95 (17), 93 (10), 79 (32), 55 (10), 39 (18). Anal. Calcd for $C_9H_{10}O_2$: C, 71.98; H, 6.71. Found: C, 71.91; H, 6.74.

(*E*)-6-Pent-1-enylpyran-2-one (3i): isolated in 52% yield as a colorless liquid; IR (neat) 1734, 1630, 1555, 1243, 1080 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.90 (t, $J = 7.5$ Hz, 3H), 1.46 (bm, $J \cong 7.5$ Hz, 2H), 2.17 (tdd, $J = 7.5$ Hz, 7.2 Hz, 1.5 Hz, 2H), 5.94 (d, $J = 6.6$ Hz, 1H), 5.97 (dt, $J = 15.6$ Hz, $J = 1.5$ Hz, 1H), 6.13 (d, $J = 9.3$ Hz, 1H), 6.66 (dt, $J = 15.6$ Hz, $J = 7.2$ Hz, 1H), 7.26 (dd, $J = 9.3$ Hz, $J = 6.6$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.0, 22.2, 35.2, 103.4, 114.0, 122.1, 139.9, 144.3, 160.1, 162.4; MS (70 eV, EI) *m*/*z* 164 (M^++1, 100), 136 (18), 123 (21), 122 (68), 121 (10), 110 (37), 107 (96), 95 (83), 94 (95), 79 (41), 77 (38), 55 (17), 39 (86). Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 73.26; H, 7.33.

6-Benzylpyran-2-one (3j): isolated in 53% yield as a colorless liquid; IR (KBr) 3063, 3030, 1732, 1634, 1603, 1556, 1496, 1455, 1089, 699; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.78 (s, 2H), 5.88 (dd, $J = 6.6$ Hz, 0.9 Hz, 1H), 6.13 (d, $J = 9.3$ Hz, 1H), 7.19−7.36 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 28.6, 103.8, 113.8, 127.7, 129.2, 129.6, 135.5, 144.1, 162.8, 165.5; MS (70 eV, EI) *m*/*z* 186 (M^+, 30), 95 (100), 65 (10), 39 (10); HRMS (EI) calcd for $C_{12}H_{10}O_2$ 186.0681, found 186.0674. Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.47; H, 5.46.

6-(4-Methoxyphenyl)pyran-2-one (3k): isolated in 70% yield as white solid; mp 96−98 °C; IR (KBr) 3075, 2936, 1720, 1625, 1544, 1511, 1252, 1186; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.87 (s, 3H), 6.22 (dd, $J = 9.3$ Hz, 0.9 Hz, 1H), 6.56 (d, $J = 6.9$ Hz, 0.9 Hz, 1H), 6.97 (d, $J = 9.0$ Hz, 2H), 7.40 (dd, $J = 9.3$ Hz, 6.9 Hz, 1H), 7.78 (d, $J = 9.0$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 55.8, 100.0, 113.0, 114.7 (2C), 124.3, 127.7 (2C), 144.4, 161.7, 162.2, 162.6, 162.6; MS (70 eV, EI) *m*/*z* 202 (M^+, 82), 175 (11), 174 (100), 159 (53), 131 (20), 77 (18), 39 (14); HRMS (EI) calcd for $C_{12}H_{10}O_3$ 202.0630, found 202.0620. Anal. Calcd for $C_{12}H_{10}O_3$: C, 71.28; H, 4.98. Found: C, 71.17; H, 4.92.

6-(2-Bromophenyl)pyran-2-one (3l): isolated in 56% yield as white solid; mp 57−58 °C; IR (KBr) 3064, 1734, 1628, 1550, 1471, 1079; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.35 (dd, $J = 9.3$ Hz, 0.9 Hz, 1H), 6.63 (dd, $J = 6.9$ Hz, 0.9 Hz, 1H), 7.29−7.33 (m, 1H), 7.38−7.46 (m, 2H), 7.59 (d, $J = 7.8$ Hz, 1H), 7.67 (d, $J = 7.8$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 106.9, 115.4, 121.8, 128.0, 131.2, 131.2, 131.8, 133.6, 134.4, 143.6, 160.6, 162.3; MS (70 eV, EI) *m*/*z* 252 (M^+, 51), 250 (52), 224 (98), 222 (100), 195

(10), 185 (10), 155 (13), 115 (59), 95 (32), 75 (14); HRMS (EI) calcd for $C_{11}H_7O_2Br$: 249.9629, found 249.9624. Anal. Calcd for $C_{11}H_7BrO_2$: C, 52.62; H, 2.81. Found: C, 52.65; H, 2.85.

6-Benzo[1,3]dioxol-5-ylpyran-2-one (3m): isolated in 83% yield as a yellow solid; mp 146−148 °C; IR (KBr) 1718, 1605, 1505, 1489, 1264, 1110; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 6.00 (s, 2H), 6.19 (d, J = 9.3 Hz, 1H), 6.48 (d, J = 6.9 Hz, 1H), 6.83 (d, J = 8.2 Hz, 1H), 7.23 (s, 1H), 7.32−7.41 (m, 2H); ^{13}C NMR ($CDCl_3$, 50.5 MHz) δ 100.6, 102.4, 106.3, 109.2, 113.6, 121.2, 126.1, 144.4, 149.0, 150.6, 161.5, 162.5; MS (70 eV, EI) m/z 216 (M^+, 26), 188 (48), 102 (30), 91 (10), 65 (24), 63 (34), 51 (17), 50 (12), 39 (100). Anal. Calcd for $C_{12}H_8O_2$: C, 66.67; H, 3.73. Found: C, 66.75; H, 3.76.

(*E*)-6-Styrylpyran-2-one (3n): isolated in 85% yield as a yellow solid; mp 115−116 °C; IR (KBr) 3047, 1733, 1686, 1637, 1528, 1359, 1094; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 6.10 (d, J = 6.7 Hz, 1H), 6.16 (d, J = 9.3 Hz, 1H), 6.57 (d, J = 16.0 Hz, 1H), 7.23−7.35 (m, 4H), 7.38−7.47 (m, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 104.9, 114.1, 118.6, 127.3 (2C), 128.8 (2C), 135.1, 135.2, 143.6, 159.5, 161.7; MS (70 eV, EI) m/z 198 (M^+, 29), 170 (23), 142 (23), 141 (36), 115 (17), 95 (10), 77 (30), 51 (34), 39 (100). Anal. Calcd for $C_{13}H_{10}O_2$: C, 78.77; H, 5.09. Found: C, 78.82; H, 5.06.

(*E*)-6-(2-Benzo[1,3]dioxol-5-vinyl)pyran-2-one (3o): isolated in 68% yield as a yellow solid; mp 173−174 °C; IR (KBr) 1728, 1714, 1629, 1531, 1262, 1037; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 6.03 (s, 1H), 6.14 (d, J = 6.7 Hz, 1H), 6.23 (d, J = 9.1 Hz, 1H), 6.48 (d, J = 15.9 Hz, 1H), 6.84 (d, J = 6.7 Hz, 1H), 7.01 (d, J = 7.6 Hz, 1H), 7.05 (s, 1H), 7.37 (dd, J = 9.1 Hz, J = 6.7 Hz, 1H), 7.43 (d, J = 15.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50.5 MHz) δ 102.1, 105.1, 106.4, 109.3, 114.4, 117.5, 124.3, 130.4, 135.6, 144.4, 148.9, 149.5, 160.5, 162.5; MS (70 eV, EI) m/z 242 (M^+, 29), 214 (15), 186 (25), 128 (31), 95 (11), 89 (24), 78 (10), 63 (36), 51 (20), 39 (100). Anal. Calcd for $C_{14}H_{10}O_4$: C, 69.42; H, 4.16. Found: C, 69.55; H, 4.19.

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Supporting Information Available: An ^{1}H NMR spectrum of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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