

NMR δ 6.14 (1 H, td, $J = 7.0$ and 1.1 Hz), 4.21 (2 H, d, $J = 7.0$ Hz), 2.43 (1 H, septet, $J = 6.8$ Hz), 0.99 (6 H, d, $J = 6.8$ Hz), 0.15 (9 H, s); ^{13}C NMR δ 150.54, 136.33, 62.34, 32.59, 23.08, 0.62.

Oxidation of 12. Oxidation of 12 (4.2 mmol) afforded 0.39 g (50% of 4,4-dimethyl-3-(trimethylsilyl)-2-penten-1-ol (22) ($E:Z = 42:58$) as a colorless liquid: IR (neat) 3300 (OH, br), 1590 (w), 1460 (m), 1410 (m), 1390 (m), 1360 (s), 1250 (s), 1220 (m), 1200 (m), 1030 (s), 980 (m), 930 (m), 830 (s), 760 (m), 680 (m). *E* isomer (minor): ^1H NMR δ 5.76 (1 H, t, $J = 5.2$ Hz), 4.36 (2 H, d, $J = 5.0$ Hz), 2.93 (1 H, br, OH), 1.10 (9 H, s), 0.11 (9 H, s); ^{13}C NMR δ 150.76, 140.89, 61.59, 36.68, 31.55, 1.89. *Z* isomer (major): ^1H NMR δ 6.08 (1 H, t, $J = 6.7$ Hz), 4.22 (2 H, d, $J = 6.4$ Hz), 2.59 (1 H, br, OH), 1.05 (9 H, s), 0.19 (9 H, s); ^{13}C NMR δ 151.93, 136.50, 61.91, 37.75, 30.22, 3.34. The ^1H and ^{13}C NMR spectra of the major isomer were found to be identical with those of (*Z*)-4,4-di-

methyl-3-(trimethylsilyl)-2-penten-1-ol (crystalline solid, mp 68.5–69.5 °C, overall yield 25%) independently synthesized from 4,4-dimethyl-2-pentyn-1-ol by a procedure reported previously.^{3b}

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Supplementary Material Available: ^1H NMR and ^{13}C NMR spectra of 16a, 15b, 16b, and all new compounds (78 pages). Ordering information is given on any current masthead page.

Palladium-Catalyzed Cyclocarbonylation of 3-(Heteroaryl)allyl Acetates¹

Masakazu Iwasaki, Yoshihiro Kobayashi, Ji-Ping Li, Hiroyuki Matsuzaka, Youichi Ishii, and Masanobu Hidai*

Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan

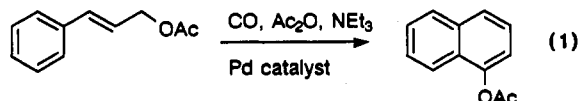
Received April 4, 1990

Acetoxybenzofurans, acetoxybenzothiophenes, acetoxyindoles, and acetoxycarbazoles were obtained in high yields by cyclocarbonylation of 3-furyl-, 3-thienyl-, 3-pyrrolyl-, and 3-indolylallyl acetates, respectively, in the presence of Ac_2O , NEt_3 , and a catalytic amount of $\text{PdCl}_2(\text{PPh}_3)_2$ at 130–170 °C under 50–70 atm of CO. 3-(3-Furyl)allyl and 3-(3-thienyl)allyl acetates cyclized selectively at the 2-position of the heterocyclic nucleus to give 7-acetoxybenzofuran and 7-acetoxybenzothiophene, respectively. The synthetic utility of the reaction was demonstrated by the synthesis of cannabifuran from isothymol.

Introduction

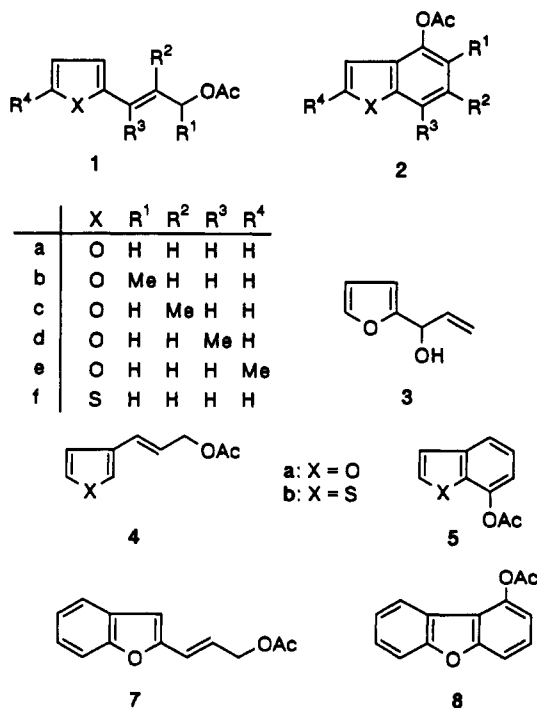
Fused heteroaromatic systems, such as benzofurans, indoles, and carbazoles, are among the most attractive targets of organic synthesis because of their wide occurrence in natural products. Especially desirable is a synthetic route to fused-ring heteroaromatics with functional groups at specific positions. The catalytic cyclocarbonylation of monocyclic aromatic heterocycles shows promise as a useful reaction for the synthesis of such functionalized fused-ring heteroaromatics.

Although there are reports of cyclocarbonylations leading to anthraquinone,² indenones,³ and indanones,⁴ no examples of the cyclocarbonylation of aromatic heterocycles have appeared in the literature. Earlier, we reported⁵ a novel palladium-catalyzed cyclocarbonylation of cinnamyl acetates, which involved an intramolecular carbonylation of the phenyl ring, to give naphthyl acetates (eq 1). We



have also applied cyclocarbonylation to the selective synthesis of 1- and 4-acetoxyphenanthrenes.⁶ The reaction

Chart I



(1) Construction of Polycyclic Compounds by Cyclocarbonylation. 6. Part 5: See ref 7.

(2) Arzoumanidis, G. G.; Rauch, F. C. *J. Mol. Catal.* 1980, 9, 335.
(3) (a) Kim, P. J.; Hagihara, N. *Bull. Chem. Soc. Jpn.* 1965, 38, 2022.
(b) Hong, P.; Cho, B.; Yamazaki, H. *Chem. Lett.* 1979, 339.

(4) (a) Bruson, H. A.; Plant, H. L. *J. Org. Chem.* 1967, 32, 3356. (b) Doyama, K.; Fujiwara, K.; Joh, T.; Maeshima, K.; Takahashi, S. *Chem. Lett.* 1988, 901.

(5) (a) Matsuzaka, H.; Hiroe, Y.; Iwasaki, M.; Ishii, Y.; Koyasu, Y.; Hidai, M. *Chem. Lett.* 1988, 377. (b) Matsuzaka, H.; Hiroe, Y.; Iwasaki, M.; Ishii, Y.; Koyasu, Y.; Hidai, M. *J. Org. Chem.* 1988, 53, 3832. (c) Koyasu, Y.; Matsuzaka, H.; Hiroe, Y.; Uchida, Y.; Hidai, M. *J. Chem. Soc., Chem. Commun.* 1987, 575.

is synthetically valuable because easily accessible 3-arylallyl acetates are used as starting materials. Extensive investigation of the reaction has led to a novel synthetic method for fused-ring heteroaromatic compounds with acetoxy

(6) Iwasaki, M.; Matsuzaka, H.; Hiroe, Y.; Ishii, Y.; Hidai, M. *Chem. Lett.* 1988, 1159.

Table I. Synthesis of Benzofurans and Benzothiophenes

run	substrate	reactn conditns ^a	product	isolated yield, ^b %
1	1a	A	2a	85
2	1a	A ^c	2a	83 (98 ^d)
3	1a	A ^e	2a	45 (48 ^d)
4	1a	A/	2a	(5 ^d)
5	1b	A	—	—
6	1c	A	2c	78
7	1d	B	2d	56
8	1e	A	2e	76
9	1f	B	2f	79
10	3	C	2a	56
11	4a	A	5a	89
12	4b	B	5b	86
13	7	B	8	70

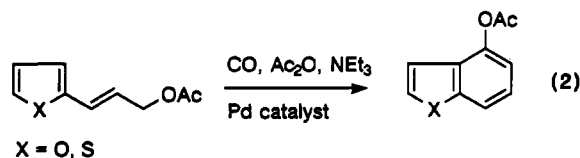
^aA: Substrate, 10 mmol; PdCl₂(PPh₃)₂, 0.5 mmol; Ac₂O, 20 mmol; NEt₃, 20 mmol; benzene, 10 mL; CO, 70 kg/cm² at room temperature; 170 °C (unless otherwise noted); 1.5 h. B: Substrate, 3 mmol; PdCl₂(PPh₃)₂, 0.15 mmol; Ac₂O, 6 mmol; NEt₃, 6 mmol; benzene, 2 mL; CO, 70 kg/cm² at room temperature; 170 °C; 1.5 h. C: Substrate, 3 mmol; PdCl₂(PPh₃)₂, 0.15 mmol; Ac₂O, 12 mmol; NEt₃, 12 mmol; benzene, 4 mL; CO, 70 kg/cm² at room temperature; 170 °C; 1.5 h. ^bBased on substrate. ^cReaction temperature: 130 °C. ^dDetermined by GLC. ^eReaction temperature: 100 °C. ^fReaction temperature: 70 °C.

groups at specific positions. Preliminary results were reported earlier.⁷ Here we report in detail the cyclocarbonylation of 3-(heteroaryl)allyl acetates.

Results and Discussion

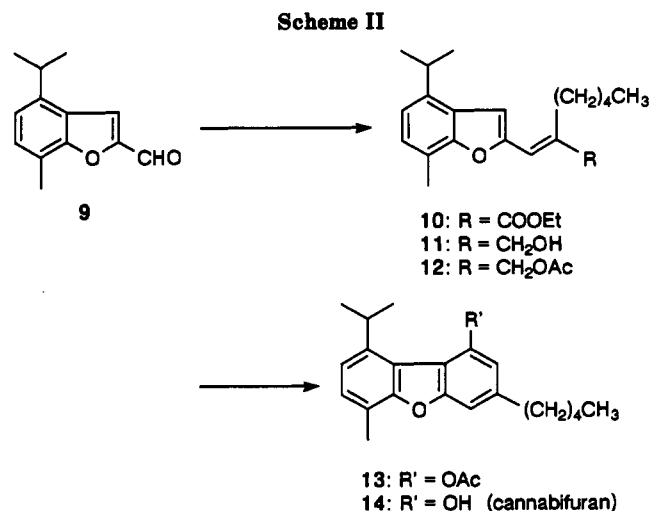
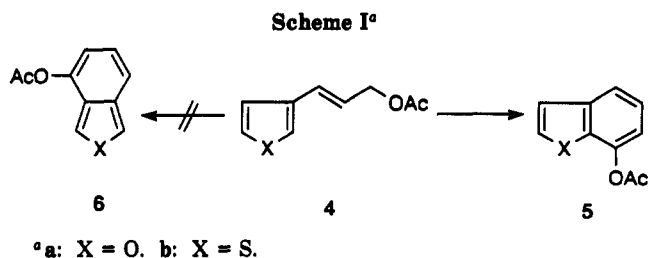
The cyclocarbonylation of various 3-(heteroaryl)allyl acetates was catalyzed by PdCl₂(PPh₃)₂. Triethylamine and acetic anhydride were used to esterify, in situ, the phenols initially produced. Reaction temperatures above 130 °C were necessary to obtain high (>80%) yields. Therefore, most reactions were performed at 170 °C. At lower temperatures, lower yields were obtained. Side reactions at lower temperatures afforded unidentifiable high-boiling byproducts. For example, at 100 °C, 1a gave 2a (Chart I) in only 48% yield, although 1a was completely consumed (Table I, run 3).

Synthesis of Benzofurans and Benzothiophenes. As shown in Table I, cyclocarbonylation of 3-(furyl)allyl acetates and 3-(thienyl)allyl acetates (eq 2) gave acetoxybenzofurans and acetoxybenzothiophenes, respectively, in high yields. Only with 1b, a secondary allylic acetate, was



no cyclocarbonylation product isolated. In this case, elimination of acetic acid and polymerization of the resulting diene were, possibly, competing reactions.⁸ The γ -substituted allyl acetate 1d gave acetoxybenzofuran 2d, but the yield was relatively low. Here also, diene formation and subsequent polymerization probably occurred. The secondary allylic alcohol 3 also gave 2a, in moderate yield. Here, acetylation apparently preceded carbonylation.

The dibenzofuran skeleton was also constructed, from 3-(2-benzofuranyl)allyl acetate (7). It was of great interest that 3-(3-furyl)allyl acetate (4a) and 3-(3-thienyl)allyl acetate (4b) selectively cyclized at the 2-position of the

Table II. Synthesis of Indoles and Carbazoles^a

run	substrate	product (yield, ^b %)
1	15a	16a (52), 17 (28)
2 ^c	15a	16a (57), 17 (trace ^e)
3 ^d	15a	16a (52, 69 ^e), 17 (6)
4	15b	16b (36)
5	18a	19a (53), 20 (6)
6	18b	19b (36)

^aSubstrate, 3 mmol; PdCl₂(PPh₃)₂, 0.15 mmol; Ac₂O, 6 mmol; NEt₃, 6 mmol; benzene, 2 mL; CO, 70 kg/cm² at room temperature; 130 °C; 1.5 h. ^bIsolated yield based on substrate. ^cReaction temperature: 170 °C. ^dAc₂O, 12 mmol; NEt₃, 12 mmol; benzene, 4 mL. ^eDetermined by GLC.

heterocyclic nucleus to give 7-acetoxybenzofuran (5a) and 7-acetoxybenzothiophene (5b), respectively, as the only products. No 3-acetoxyisobenzofuran (6a), 3-acetoxyisobenzothiophene (6b), or related compounds formed by cyclization at the 4-position of the heterocyclic nucleus were detected (Scheme I).

The synthetic utility of the reaction was demonstrated in a facile synthesis of cannabifuran (14), a naturally occurring dibenzofuran derived from *Cannabis sativa* L.⁹ Benzofuran 12 was easily obtained by reduction and subsequent acetylation of the condensation product of aldehyde 9 (prepared from isothymol¹⁰) and ethyl heptanoate. Cyclocarbonylation of 12 proceeded smoothly, and acetoxydibenzofuran 13 was obtained in 74% yield. Hydrolysis of 13 afforded 14 in 94% yield (Scheme II).

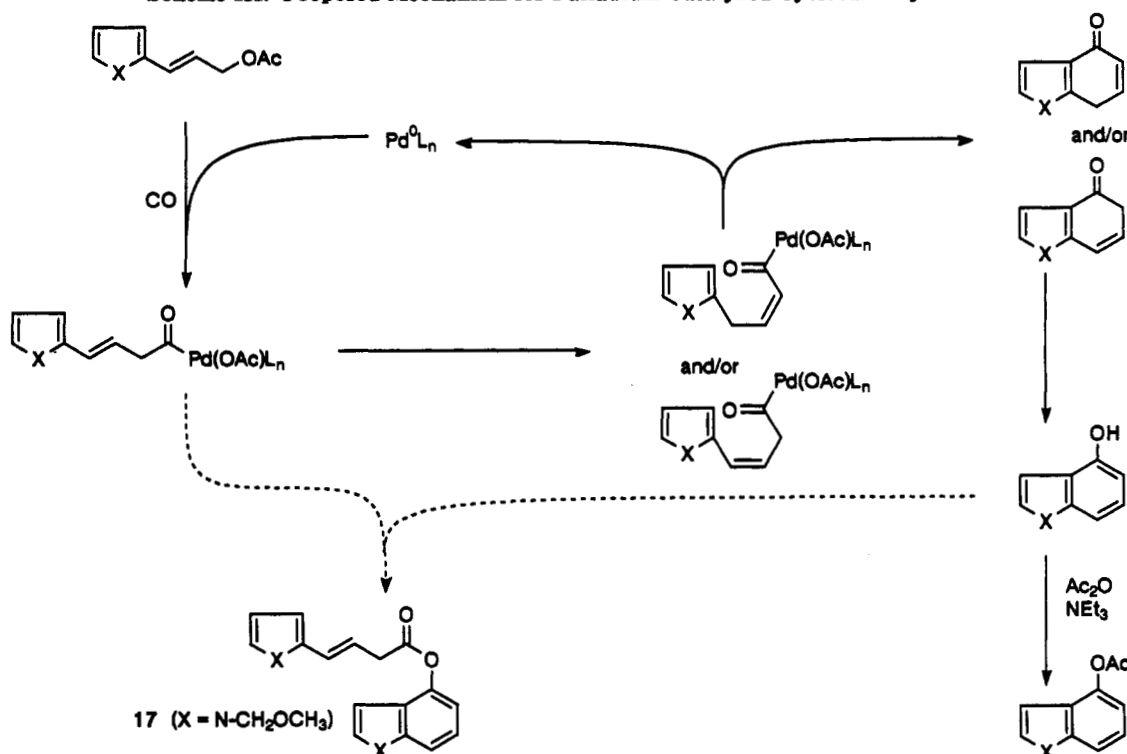
Synthesis of Indoles and Carbazoles. Allyl acetates substituted with a pyrrole or indole ring underwent cyclocarbonylation at 130 °C. Thus, 3-(2-pyrrolyl)- and 3-(3-indolyl)allyl acetates gave 4-acetoxyindoles and 1-acetoxycarbazoles, respectively (Table II). However, the yields were somewhat lower than those obtained from furan or thiophene systems, probably because of the rel-

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(9) Friedrich-Friehtl, J.; Spiteller, G. *Tetrahedron* 1975, 31, 479.

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Scheme III. Proposed Mechanism for Palladium-Catalyzed Cyclocarbonylation^a

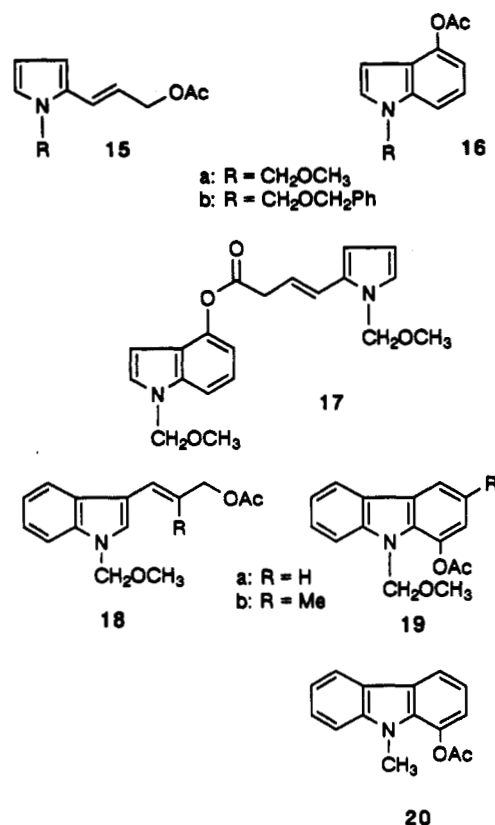
^aX = O, S, NCH₂OCH₃, NCH₂OCH₂Ph; L = CO, PPh₃; n = 1, 2.

ative instability of five-membered nitrogen heterocycles.¹¹ On the other hand, 3-(2-pyridyl)- and 3-(3-pyridyl)allyl acetates gave *no* cyclocarbonylation products, even at 170 °C.

Compound 15a gave not only 16a but also dimeric 17 (Chart II). Compound 17 was possibly formed from the reaction of 4-hydroxy-1-(methoxymethyl)indole and an intermediate acylpalladium complex (*vide infra*). The formation of 17 was suppressed either by performing the reaction at a higher temperature (Table II, run 2) or by using a large excess of Ac₂O and NEt₃ (Table II, run 3). In both cases, there was no significant change in the yield of 16a. In the cyclocarbonylation of 18a, in addition to the expected product 19a, a small amount of the *N*-methylcarbazole 20 was obtained. The mechanism of formation of this byproduct is not clear.

Mechanism of Cyclocarbonylation. On the basis of the results of stoichiometric model cyclocarbonylations of the cinnamyl acetates, it was proposed^{5a,b} that intermediate unsaturated acylpalladium complexes, such as [(*Z*)-ArCH=CHCH₂CO]Pd(OAc)(PPh₃)_n or [(*Z*)-ArCH₂CH=CHCO]Pd(OAc)(PPh₃)_n (n = 1 or 2), could be formed by successive oxidative addition of allylic acetate, CO insertion, and C=C double bond *E-Z* isomerization. It is reasonable to assume that similar intermediates are involved in the cyclocarbonylation of 3-(heteroaryl)allyl acetates. In the latter case, intramolecular cyclization of the intermediate would produce bicyclic ketones. Isomerization of the ketones to phenols, followed by acetylation,

Chart II

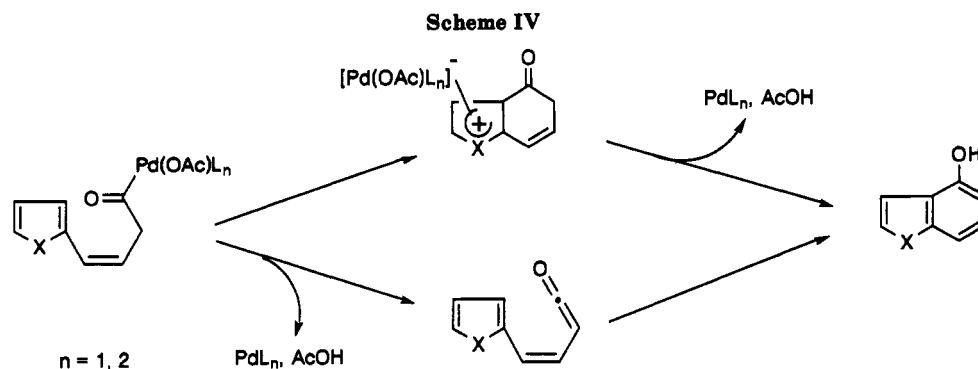


(11) Although the byproducts were not identified, polymerization¹² of 15a might have been caused by trace acidic impurities. Alternatively, thermal decomposition might have occurred. Attempted distillation in vacuo of 15a at temperatures above 150 °C gave a dark blue viscous oil. Attempted purification of 15a by silica gel column chromatography (ether/hexane, 2:1) at room temperature produced a similar color change, which also suggested decomposition.

(12) Livingstone, L. In *Rodd's Chemistry of Carbon Compounds*, 2nd ed.; Coffey, S., Ed.; Elsevier: Amsterdam, 1973; Vol. 4, Part A, Chapter 4, pp 329, 335.

would yield the final products (Scheme III). Reaction between an unsaturated acylpalladium complex and a phenol would explain the formation of 17 in the carbonylation of 15a (*vide supra*).

The detailed mechanism of the ring closure of the acyl complexes is still unknown. However, several facts useful



in elaborating the mechanism were obtained. It was observed⁶ that cyclization of 3-(2-naphthyl)allyl acetate occurred selectively at the 1-position of the aromatic nucleus, despite greater steric hindrance, to give 4-phenanthryl acetate. In the reaction of 3-(heteroaryl)allyl acetates described above, 5a and 5b were similarly selectively formed, in good yield, from 4a and 4b, respectively. Furthermore, cinnamyl acetate gave 1-naphthyl acetate in only 2% yield (98% conversion) at 100 °C. Finally, 3-(2-pyridyl)- and 3-(3-pyridyl)allyl acetate gave no cyclocarbonylation products, even at 170 °C, whereas 1a at 100 °C afforded 2a in moderate yield (vide supra). These facts indicate that the order of reactivity of aromatic rings in the cyclocarbonylation is furan > benzene > pyridine ring.⁷ Furthermore, the findings strongly suggest that the ring closure step is an electrophilic addition, which may involve either direct electrophilic attack of the acyl moiety on the aromatic ring or, alternatively, cyclization of a vinylketene intermediate formed from the acylpalladium complex (Scheme IV). A reaction mechanism involving a vinylketene intermediate has been proposed¹³ for the benzannulation of chromium-arylcabene complexes.

In conclusion, palladium-catalyzed cyclocarbonylation was successfully applied to the construction of fused-ring heteroaromatic compounds. The utility of the reaction as a synthetic tool was demonstrated by its use in a synthesis of cannabifuran. Elucidation of the reaction mechanism is still under way.

Experimental Section

¹H and ¹³C NMR spectra were recorded as CDCl₃ solutions. Fast atom bombardment mass spectra (FABMS) were recorded by using a *m*-nitrobenzyl alcohol matrix. GLC analyses were performed with a flame ionization detector and a 25-m Hicap-CBP1 capillary column. Helium was the carrier gas.

PdCl₂(PPh₃)₂ was prepared by a published method.¹⁴ All solvents were dried and then were distilled under nitrogen. With the exception of compounds 1a, 1b, and 3, the 3-substituted allyl acetates were prepared from the appropriate aromatic aldehyde in a manner similar to that used for the preparation of compound 7. Unless indicated otherwise, solid products were purified by recrystallization and oils were purified by Kugelrohr distillation.

3-(2-Furyl)allyl Acetate (1a). To an ice-cooled solution of 3-(2-furyl)acrolein (5.01 g, 41 mmol) in MeOH (120 mL) was added NaBH₄ (2.3 g, 60 mmol) in small portions under N₂. The mixture was warmed to room temperature and stirred for 1 h. Evaporation of solvent gave a white slurry, which was dissolved in water (100 mL). The solution was extracted with ether. The extract was dried (MgSO₄). The solvent was evaporated to give crude 3-(2-furyl)allyl alcohol (5.08 g, 100%) as a pale yellow oil. The crude alcohol was stirred with Ac₂O (5.7 mL), NEt₃ (11.2 mL), and

4-(*N,N*-dimethylamino)pyridine (DMAP) (50 mg) in ether (100 mL) for 12 h at room temperature. The mixture was then washed (1 N aqueous HCl, saturated aqueous NaHCO₃, and water) and dried (MgSO₄). Solvent was evaporated to give crude 1a as yellow oil. Kugelrohr distillation gave a colorless oil (5.58 g, 33.6 mmol): ¹H NMR δ 2.08 (s, 3 H), 4.67 (dd, *J* = 1.4, 6.4 Hz, 2 H), 6.20 (dt, *J* = 16.0, 6.4 Hz, 1 H), 6.28 (d, *J* = 3.1 Hz, 1 H), 6.36 (dt, *J* = 1.8, 3.1 Hz, 1 H), 6.45 (dt, *J* = 16.0, 1.4 Hz, 1 H), 7.35 (d, *J* = 1.8 Hz, 1 H); IR (neat) 1745 cm⁻¹ (C=O). Anal. Calcd for C₉H₁₀O₃: C, 65.05; H, 6.07. Found: C, 64.88; H, 6.25.

3-(2-Furyl)-1-methylallyl Acetate (1b). To a suspension of LiAlH₄ (4.0 g, 105 mmol) in THF (40 mL) at -20 °C was added, dropwise, a solution of furfuralacetone (13.01 g, 96 mmol) and THF (40 mL). The mixture was stirred at -20 to -10 °C for 3 h. Then the mixture was carefully hydrolyzed with 1 N aqueous HCl (100 mL). The aqueous layer was extracted with ether several times. The combined organic layers were washed (saturated aqueous NaHCO₃ and water) and dried (MgSO₄). Evaporation of solvent gave 3-(2-furyl)-1-methylallyl alcohol as a pale yellow oil. The crude product was acetylated as described for 1a. Distillation gave 1b as a colorless oil (12.97 g, 68% from furfuralacetone): bp 71–74 °C (0.5 mmHg); ¹H NMR δ 1.39 (d, *J* = 6.4 Hz, 3 H), 2.07 (s, 3 H), 5.48 (quintet of d, *J* = 6.6, 0.9 Hz, 1 H), 6.12 (dd, *J* = 6.6, 15.9 Hz, 1 H), 6.26 (d, *J* = 3.2 Hz, 1 H), 6.37 (dd, *J* = 1.8, 3.2 Hz, 1 H), 6.42 (dd, *J* = 0.9, 15.9 Hz, 1 H), 7.35 (d, *J* = 1.8 Hz, 1 H); IR (neat) 1735 cm⁻¹ (C=O). Anal. Calcd for C₁₀H₁₂O₃: C, 66.65; H, 6.71. Found: C, 66.52; H, 6.91.

3-(2-Furyl)-2-methylallyl acetate (1c): colorless oil (24% from furfural); ¹H NMR δ 2.02 (d, *J* = 0.6 Hz, 3 H), 2.11 (s, 3 H), 4.60 (s, 2 H), 6.30–6.31 (m, 2 H), 6.41 (dd, *J* = 1.8, 3.3 Hz, 1 H), 7.39 (d, *J* = 1.8 Hz, 1 H); IR (neat) 1739 cm⁻¹ (C=O). Anal. Calcd for C₁₀H₁₂O₃: C, 66.65; H, 6.71. Found: C, 66.17; H, 6.58.

3-(2-Furyl)-3-methylallyl acetate (1d): colorless oil (42% from acetylfuran); ¹H NMR δ 2.00 (s, 3 H), 2.07 (s, 3 H), 4.77 (d, *J* = 7.3 Hz, 2 H), 6.16 (t, *J* = 7.3 Hz, 1 H), 6.32 (d, *J* = 3.4 Hz, 1 H), 6.37 (dd, *J* = 1.8, 3.4 Hz, 1 H), 7.35 (d, *J* = 1.8 Hz, 1 H); IR (neat) 1740 cm⁻¹ (C=O). Anal. Calcd for C₁₀H₁₂O₃: C, 66.65; H, 6.71. Found: C, 66.28; H, 6.87.

3-(5-Methyl-2-furyl)allyl acetate (1e): colorless oil (39% from 5-methylfurfural); ¹H NMR δ 2.08 (s, 3 H), 2.29 (s, 3 H), 4.68 (dd, *J* = 1.2, 6.7 Hz, 2 H), 5.96 (dq, *J* = 3.2, 0.9 Hz, 1 H), 6.13 (dt, *J* = 15.7, 6.7 Hz, 1 H), 6.16 (d, *J* = 3.2 Hz, 1 H), 6.39 (dt, *J* = 15.7, 1.2 Hz, 1 H); IR (neat) 1740 cm⁻¹ (C=O). Anal. Calcd for C₁₀H₁₂O₃: C, 66.65; H, 6.71. Found: C, 65.99; H, 6.72.

3-(2-Thienyl)allyl acetate (1f): colorless oil (9% from 2-thiophenecarboxaldehyde); ¹H NMR δ 2.07 (s, 3 H), 4.66 (d, *J* = 6.6 Hz, 2 H), 6.09 (dt, *J* = 15.5, 6.6 Hz, 1 H), 6.75 (d, *J* = 15.5 Hz, 1 H), 6.93–6.97 (m, 2 H), 7.15 (d, *J* = 5.2 Hz, 1 H); IR (neat) 1743 cm⁻¹ (C=O). Anal. Calcd for C₉H₁₀O₂S: C, 59.32; H, 5.53. Found: C, 59.05; H, 5.71.

1-(2-Furyl)allyl Alcohol (3). A 1 M solution of vinylmagnesium bromide in THF (37 mL) was added dropwise to a solution of furfural (3.16 g) in ether (10 mL) at room temperature. The mixture was stirred for 3 h and then was hydrolyzed with saturated aqueous NH₄Cl (100 mL). The layers were separated, and the aqueous layer was extracted with ether. The combined organic layers were dried (MgSO₄), and solvent was evaporated to give an orange oil. Purification by Kugelrohr distillation gave 3 (3.21 g) as a colorless oil: ¹H NMR δ 4.55 (d, *J* = 5.5 Hz, 1 H, D₂O-exchangeable), 5.06–5.09 (m, 2 H), 5.27 (dt, *J* = 17.2 Hz, 1 H), 6.00 (ddd, *J* = 17.2, 10.1, 5.9 Hz, 1 H), 6.14 (dt, *J* = 3.1, 0.9

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H_z, 1 H), 6.25 (dd, *J* = 3.1, 1.8 Hz, 1 H), 7.35 (dd, *J* = 1.8, 0.9 Hz, 1 H); IR (neat) 3320 cm⁻¹ (OH). Anal. Calcd for C₇H₈O₂: C, 67.73; H, 6.50. Found: C, 67.50; H, 6.72.

3-(3-Furyl)allyl acetate (4a): colorless oil (46% from 3-furancarboxaldehyde); ¹H NMR δ 2.09 (s, 3 H), 4.67 (dd, *J* = 1.2, 6.7 Hz, 2 H), 6.02 (dt, *J* = 15.9, 6.7 Hz, 1 H), 6.53 (m, 1 H), 6.53 (dt, *J* = 15.6, 1.2 Hz, 1 H), 7.37 (m, 1 H), 7.44 (s, 1 H); IR (neat) 1742 cm⁻¹ (C=O). Anal. Calcd for C₇H₈O₂: C, 67.73; H, 6.50. Found: C, 67.50; H, 6.72.

3-(3-Thienyl)allyl acetate (4b): colorless oil (28% from 3-thiophenecarboxaldehyde); ¹H NMR δ 2.09 (s, 3 H), 4.69 (dd, *J* = 1.2, 6.4 Hz, 2 H), 6.14 (dt, *J* = 15.6, 6.4 Hz, 1 H), 6.66 (br d, *J* = 15.6 Hz, 1 H), 7.19–7.22 (m, 2 H), 7.28 (m, 1 H); IR (neat) 1735 cm⁻¹ (C=O). Anal. Calcd for C₉H₁₀O₂S: C, 59.32; H, 5.53. Found: C, 59.63; H, 5.35.

3-(2-Benzofuranyl)allyl Acetate (7). A solution of 2-benzofurancarboxaldehyde (3.8 g, 26 mmol) in EtOAc (10 mL) was added dropwise to a suspension of Na sand (0.80 g, 35 mmol) and absolute EtOH (0.1 mL) in EtOAc (10 mL) at -15 °C. The mixture was stirred for 2 h at -15 to -5 °C. AcOH (15 mL) and water (30 mL) were then carefully added, and the aqueous layer was extracted with EtOAc. The combined organic layers were washed (saturated aqueous NaHCO₃ and water) and dried (MgSO₄). Solvent was evaporated to give crude ethyl 3-(2-benzofuranyl)acrylate as orange crystals (2.33 g, 10.7 mmol). The ester (2.33 g) was dissolved in toluene (30 mL), and diisobutylaluminum hydride (24 mmol) in toluene (24 mL) was added dropwise at 0 °C. The mixture was warmed to room temperature, stirred for 15 h, and hydrolyzed with 1 N aqueous HCl (50 mL). The aqueous layer was extracted with ether. The combined organic layers were washed (saturated aqueous NaHCO₃ and water) and dried (MgSO₄). The solvent was evaporated to give crude 3-(2-benzofuranyl)allyl alcohol as a yellow solid (1.76 g, 10.1 mmol). Acetylation as described above for **1a** gave **7** as a colorless solid (1.79 g, 8.3 mmol). Recrystallization (hexane/Et₂O, 95:5) gave colorless needles: mp 53–54 °C; ¹H NMR δ 2.12 (s, 3 H), 4.77 (d, *J* = 5.7 Hz, 2 H), 6.50 (dt, *J* = 15.6, 5.7 Hz, 1 H), 6.58 (d, *J* = 15.6 Hz, 1 H), 6.61 (s, 1 H), 7.19 (td, *J* = 7.6, 1.2 Hz, 1 H), 7.27 (td, *J* = 7.6, 1.2 Hz, 1 H), 7.43 (br d, *J* = 7.6 Hz, 1 H), 7.52 (br d, *J* = 7.6 Hz, 1 H); IR (KBr) 1738 cm⁻¹ (C=O). Anal. Calcd for C₁₃H₁₂O₃: C, 72.21; H, 5.59. Found: C, 72.10; H, 5.71.

3-[1-(Methoxymethyl)-2-pyrrolyl]allyl acetate (15a): slightly red oil after purification by ice-cooled silica gel chromatography (ether/hexane, 1:2) (71% from *N*-(methoxymethyl)-2-pyrrolicarboxaldehyde); ¹H NMR δ 2.07 (s, 3 H), 3.23 (s, 3 H), 4.68 (dd, *J* = 1.2, 6.7 Hz, 2 H), 5.19 (s, 2 H), 6.09 (dt, *J* = 15.8, 6.7 Hz, 1 H), 6.13 (dd, *J* = 3.9, 2.7 Hz, 1 H), 6.43 (dd, *J* = 3.9, 1.7 Hz, 1 H), 6.63 (br d, *J* = 15.8 Hz, 1 H), 6.73 (dd, *J* = 2.7, 1.7 Hz, 1 H); IR (neat) 1735 cm⁻¹ (C=O). Anal. Calcd for C₁₁H₁₅NO₃: C, 63.14; H, 7.23; N, 6.69. Found: C, 63.17; H, 7.35; N, 6.95.

3-[1-(Benzyloxy)methyl]-2-pyrrolyl]allyl acetate (15b): pale yellow oil after purification by ice-cooled silica gel chromatography (ether/hexane, 1:2) (80% from *N*-(benzyloxy)methyl)-2-pyrrolicarboxaldehyde); ¹H NMR (acetone-*d*₆) δ 2.06 (s, 3 H), 4.40 (s, 2 H), 5.26 (s, 2 H), 4.66 (d, *J* = 6.7 Hz, 2 H), 6.12 (dt, *J* = 15.7, 6.7 Hz, 1 H), 6.14 (dd, *J* = 3.7, 2.8 Hz, 1 H), 6.45 (dd, *J* = 1.5, 3.7 Hz, 1 H), 6.64 (d, *J* = 15.7 Hz, 1 H), 6.71 (dd, *J* = 1.5, 2.8 Hz, 1 H), 7.27–7.36 (m, 5 H); ¹³C NMR (acetone-*d*₆) δ 21.3, 66.2, 70.6, 76.8, 109.7, 109.9, 122.2, 124.5, 125.1, 128.9, 129.0, 129.6, 132.0, 139.1, 171.2; IR (neat) 1738 cm⁻¹ (C=O); HREIMS calcd for C₁₇H₁₉NO₃ 285.137, found 285.138.

3-[1-(Methoxymethyl)-3-indolyl]allyl acetate (18a): pale yellow oil after purification by ice-cooled silica gel chromatography (ether/hexane/benzene, 1:3:3) [12% from *N*-(methoxymethyl)-3-indolecarboxaldehyde]; ¹H NMR δ 2.08 (s, 3 H), 3.19 (s, 3 H), 4.74 (d, *J* = 7.0 Hz, 2 H), 5.35 (s, 2 H), 6.29 (dt, *J* = 16.0, 7.0 Hz, 1 H), 6.80 (d, *J* = 16.0 Hz, 1 H), 7.16–7.27 (m, 3 H), 7.44 (d, *J* = 8.2 Hz, 1 H), 7.84 (d, *J* = 8.5 Hz, 1 H); IR (neat) 1732 cm⁻¹ (C=O). Anal. Calcd for C₁₅H₁₇NO₃: C, 69.48; H, 6.61; N, 5.40. Found: C, 69.59; H, 6.57; N, 5.02.

3-[1-(Methoxymethyl)-3-indolyl]-2-methylallyl acetate (18b): pale yellow oil after purification by ice-cooled silica gel chromatography (ether/hexane/benzene, 1:3:3) [53% from *N*-(methoxymethyl)-3-indolecarboxaldehyde]; ¹H NMR δ 1.99 (s, 3 H), 2.13 (s, 3 H), 3.25 (s, 3 H), 4.72 (s, 2 H), 5.46 (s, 2 H), 6.71

(s, 1 H), 7.14–7.29 (m, 3 H), 7.47 (d, *J* = 8.2 Hz, 1 H), 7.66 (d, *J* = 7.9 Hz, 1 H); IR (neat) 1734 cm⁻¹ (C=O). Anal. Calcd for C₁₆H₁₉NO₃: C, 70.31; H, 7.01; N, 5.12. Found: C, 70.53; H, 6.99; N, 5.11.

3-(2-Pyridyl)allyl acetate: pale yellow oil after purification by silica gel chromatography (EtOAc/hexane/benzene, 2:2:1) (10% from 2-pyridinecarboxaldehyde); ¹H NMR (acetone-*d*₆) δ 1.99 (s, 3 H), 4.69 (dd, *J* = 1.5, 5.8 Hz, 2 H), 6.69 (dt, *J* = 15.7, 1.5 Hz, 1 H), 6.80 (dt, *J* = 15.7, 5.8 Hz, 1 H), 7.14 (dd, *J* = 4.6, 7.6 Hz, 1 H), 7.31 (d, *J* = 7.6 Hz, 1 H), 7.64 (t, *J* = 7.6 Hz, 1 H), 8.47 (d, *J* = 4.6 Hz, 1 H); ¹³C NMR (acetone-*d*₆) δ 21.2, 65.1, 123.1, 123.8, 129.5, 133.6, 137.8, 150.9, 156.0, 171.1; HREIMS calcd for C₁₀H₁₁NO₂ 177.079, found 177.080.

3-(3-Pyridyl)allyl acetate: pale yellow oil after purification by silica gel chromatography (EtOAc/hexane/benzene, 2:2:1) (18% from 3-pyridinecarboxaldehyde); ¹H NMR (acetone-*d*₆) δ 1.99 (s, 3 H), 4.66 (d, *J* = 6.1 Hz, 2 H), 6.41 (dt, *J* = 16.0, 6.1 Hz, 1 H), 6.65 (d, *J* = 16.0, 1 H), 7.25 (dd, *J* = 4.9, 8.1 Hz, 1 H), 7.79 (dt, *J* = 1.8, 8.1 Hz, 1 H), 8.40 (dd, *J* = 1.8, 4.9 Hz, 1 H), 8.58 (d, *J* = 1.8 Hz, 1 H); ¹³C NMR (acetone-*d*₆) δ 21.2, 65.4, 124.7, 127.5, 130.8, 133.3, 134.0, 149.7, 150.2, 171.2; HREIMS calcd for C₁₀H₁₁NO₂ 177.079, found 177.078.

Palladium-Catalyzed Cyclocarbonylation of 3-(Heteroaryl)allyl Acetates. The following procedure is representative. A mixture of **1a** (10 mmol), PdCl₂(PPh₃)₂ (0.5 mmol), Ac₂O (20 mmol), NEt₃ (20 mmol), and benzene (10 mL) in a stainless steel autoclave was pressurized with CO (70 kg/cm² at room temperature) and was heated at 170 °C for 1.5 h, with stirring. The autoclave was cooled, and CO was discharged. The mixture was diluted with ether, washed (dilute aqueous HCl, saturated aqueous NaHCO₃, and water), and dried (MgSO₄). Solvent was evaporated, and the crude product was purified by silica gel column chromatography (1,2-dichloroethane/hexane, 1:2) to give 4-acetoxybenzofuran (**2a**) (85%) as a colorless oil: ¹H NMR δ 2.34 (s, 3 H), 6.65 (dd, *J* = 0.9, 2.1 Hz, 1 H), 6.99 (d, *J* = 8.2 Hz, 1 H), 7.26 (t, *J* = 8.1 Hz, 1 H), 7.38 (dd, *J* = 0.9, 8.2 Hz, 1 H), 7.57 (d, *J* = 2.1 Hz, 1 H); IR (neat) 1769 cm⁻¹ (C=O). Anal. Calcd for C₁₀H₈O₃: C, 68.18; H, 4.58. Found: C, 67.87; H, 4.56.

4-Acetoxy-6-methylbenzofuran (2c): colorless oil; ¹H NMR δ 2.37 (s, 3 H), 2.46 (s, 3 H), 6.61 (dd, *J* = 0.9, 2.1 Hz, 1 H), 6.83 (s, 1 H), 7.20 (d, *J* = 0.9 Hz, 1 H), 7.53 (d, *J* = 2.1 Hz, 1 H); IR (neat) 1764 cm⁻¹ (C=O). Anal. Calcd for C₁₁H₁₀O₃: C, 69.46; H, 5.30. Found: C, 69.91; H, 5.29.

4-Acetoxy-7-methylbenzofuran (2d): colorless prisms (hexane); mp 49–50 °C; ¹H NMR δ 2.37 (s, 3 H), 2.50 (s, 3 H), 6.66 (d, *J* = 2.1 Hz, 1 H), 6.89 (d, *J* = 8.0 Hz, 1 H), 7.07 (d, *J* = 8.0 Hz, 1 H), 7.60 (d, *J* = 2.1 Hz, 1 H); IR (KBr) 1766 cm⁻¹ (C=O); ¹³C NMR δ 14.7, 20.9, 104.1, 115.1, 119.6, 120.4, 125.0, 141.8, 144.7, 154.9, 169.1; HREIMS calcd for C₁₁H₁₀O₃ 190.063, found 190.061.

4-Acetoxy-2-methylbenzofuran (2e): colorless prisms (hexane); mp 50–51 °C; ¹H NMR δ 2.36 (s, 3 H), 2.44 (d, *J* = 0.9 Hz, 3 H), 6.28 (m, 1 H), 6.92 (dd, *J* = 0.9, 8.1 Hz, 1 H), 7.18 (t, *J* = 8.1 Hz, 1 H), 7.29 (d, *J* = 8.1 Hz, 1 H); IR (KBr) 1764 cm⁻¹ (C=O). Anal. Calcd for C₁₁H₁₀O₃: C, 69.46; H, 5.30. Found: C, 69.37; H, 5.22.

4-Acetoxybenzothiophene (2f): colorless needles (petroleum ether); mp 33–34 °C (lit.¹⁵ mp 38.5–40.0 °C); ¹H NMR δ 2.41 (s, 3 H), 7.12 (dd, *J* = 0.9, 7.9 Hz, 1 H), 7.25 (dd, *J* = 0.9, 5.2 Hz, 1 H), 7.35 (t, *J* = 7.9 Hz, 1 H), 7.44 (d, *J* = 5.2 Hz, 1 H), 7.75 (dt, *J* = 0.9, 7.9 Hz, 1 H); IR (KBr) 1769 cm⁻¹ (C=O). Anal. Calcd for C₁₀H₈O₂S: C, 62.48; H, 4.20. Found: C, 62.84; H, 4.16.

7-Acetoxybenzofuran (5a): colorless oil; ¹H NMR δ 2.41 (s, 3 H), 6.80 (d, *J* = 2.1 Hz, 1 H), 7.05 (dd, *J* = 7.9, 0.9 Hz, 1 H), 7.21 (t, *J* = 7.9 Hz, 1 H), 7.47 (dd, *J* = 0.9, 7.9 Hz, 1 H), 7.61 (d, *J* = 2.1, 1 H); IR (neat) 1771 cm⁻¹ (C=O). Anal. Calcd for C₁₀H₈O₃: C, 68.18; H, 4.58. Found: C, 68.53; H, 4.43.

7-Acetoxybenzothiophene (5b): colorless oil; ¹H NMR δ 2.42 (s, 3 H), 7.15 (d, *J* = 7.9 Hz, 1 H), 7.35 (d, *J* = 5.4 Hz, 1 H), 7.37 (t, *J* = 7.9 Hz, 1 H), 7.43 (d, *J* = 5.4 Hz, 1 H), 7.69 (d, *J* = 7.9 Hz, 1 H); IR (neat) 1768 cm⁻¹ (C=O). Anal. Calcd for C₁₀H₈O₂S: C, 62.48; H, 4.20. Found: C, 62.65; H, 4.16.

1-Acetoxydibenzofuran (8): colorless prisms (hexane); mp 77–78 °C; ¹H NMR δ 2.50 (s, 3 H), 7.16 (dd, *J* = 6.1, 2.8 Hz, 1

H), 7.35 (ddd, $J = 7.7, 7.3, 1.1$ Hz, 1 H), 7.46 (d, $J = 6.1$ Hz, 1 H), 7.47 (d, $J = 2.8$ Hz, 2 H), 7.48 (ddd, $J = 8.3, 7.3, 1.3$ Hz, 1 H), 7.58 (ddd, $J = 8.3, 1.1, 0.7$ Hz, 1 H), 7.85 (ddd, $J = 0.7, 1.3, 7.7$ Hz, 1 H); IR (KBr) 1746 cm^{-1} (C=O). Anal. Calcd for $\text{C}_{14}\text{H}_{10}\text{O}_3$: C, 74.43; H, 4.46. Found: C, 74.17; H, 4.52.

4-Acetoxy-1-(methoxymethyl)indole (16a): colorless prisms (hexane); mp $60\text{--}61\text{ }^\circ\text{C}$; $^1\text{H NMR } \delta$ 2.83 (s, 3 H), 3.23 (s, 3 H), 5.42 (s, 2 H), 6.43 (d, $J = 3.4$ Hz, 1 H), 6.90 (d, $J = 7.9$ Hz, 1 H), 7.15 (d, $J = 3.4$ Hz, 1 H), 7.21 (t, $J = 7.9$ Hz, 1 H), 7.36 (d, $J = 7.9$ Hz, 1 H); IR (neat) 1764 cm^{-1} (C=O); FABMS m/e 219 (M^+). Anal. Calcd for $\text{C}_{12}\text{H}_{13}\text{NO}_3$: C, 65.74; H, 5.98; N, 6.39. Found: C, 65.99; H, 6.00; N, 6.37.

4-Acetoxy-1-[(benzyloxy)methyl]indole (16b): colorless prisms (hexane); mp $73\text{--}75\text{ }^\circ\text{C}$; $^1\text{H NMR } \delta$ 2.39 (s, 3 H), 4.41 (s, 2 H), 5.52 (s, 2 H), 6.44 (d, $J = 3.2$ Hz, 1 H), 6.91 (d, $J = 6.6$ Hz, 1 H), 7.15 (d, $J = 3.2$ Hz, 1 H), 7.20–7.38 (m, 7 H); IR (KBr) 1759 cm^{-1} (C=O). Anal. Calcd for $\text{C}_{18}\text{H}_{17}\text{NO}_3$: C, 73.20; H, 5.80; N, 4.74. Found: C, 73.46; H, 5.77; N, 4.60.

1-(Methoxymethyl)-4-[(E)-4-[1-(methoxymethyl)-2-pyrrolyl]-3-butenoyl]oxyindole (17): orange oil after purification by ice-cooled silica gel column chromatography (ether/hexane, 1:2); $^1\text{H NMR } \delta$ 3.23 (s, 3 H), 3.25 (s, 3 H), 3.55 (dd, $J = 1.5, 7.3$ Hz, 2 H), 5.21 (s, 2 H), 5.42 (s, 2 H), 6.15 (t, $J = 3.0$ Hz, 2 H), 6.28 (dt, $J = 15.9, 7.3$ Hz, 1 H), 6.42 (d, $J = 3.2$ Hz, 1 H), 6.44 (dd, $J = 3.0, 1.5$ Hz, 1 H), 6.63 (br d, $J = 15.9$ Hz, 1 H), 6.73 (dd, $J = 3.0, 1.5$ Hz, 1 H), 6.92 (d, $J = 8.1$ Hz, 1 H), 7.14 (d, $J = 3.2$ Hz, 1 H), 7.21 (t, $J = 8.1$ Hz, 1 H), 7.36 (d, $J = 8.1$ Hz, 1 H); IR (neat) 1756 cm^{-1} (C=O); HREIMS calcd for $\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_4$ 354.158, found 354.159.

1-Acetoxy-9-(methoxymethyl)carbazole (19a): colorless needles (benzene/hexane); mp $105\text{--}107\text{ }^\circ\text{C}$; $^1\text{H NMR } \delta$ 2.41 (s, 3 H), 3.21 (s, 3 H), 5.77 (s, 2 H), 7.16 (dd, $J = 1.0, 7.9$ Hz, 1 H), 7.25 (t, $J = 7.9$ Hz, 1 H), 7.27 (ddd, $J = 7.8, 6.7, 1.2$ Hz, 1 H), 7.48 (ddd, $J = 8.2, 6.7, 1.2$ Hz, 1 H), 7.52 (br d, $J = 8.2$ Hz, 1 H), 7.95 (dd, $J = 7.9, 1.0$ Hz, 1 H), 8.06 (d, $J = 7.6$ Hz, 1 H); IR (KBr) 1765 cm^{-1} (C=O); FABMS m/e 269 (M^+). Anal. Calcd for $\text{C}_{18}\text{H}_{15}\text{NO}_3$: C, 71.36; H, 5.61; N, 5.20. Found: C, 71.47; H, 5.71; N, 5.18.

1-Acetoxy-3-methyl-9-(methoxymethyl)carbazole (19b): colorless needles (ether/hexane); mp $111\text{--}114\text{ }^\circ\text{C}$; $^1\text{H NMR } \delta$ 2.41 (s, 3 H), 2.52 (s, 3 H), 3.19 (s, 3 H), 5.73 (s, 2 H), 6.99 (s, 1 H), 7.25 (t, $J = 7.9$ Hz, 1 H), 7.45 (t, $J = 7.9$ Hz, 1 H), 7.49 (d, $J = 7.9$ Hz, 1 H), 7.74 (s, 1 H), 8.02 (d, $J = 7.9$ Hz, 1 H); IR (KBr) 1769 cm^{-1} (C=O). Anal. Calcd for $\text{C}_{17}\text{H}_{17}\text{NO}_3$: C, 72.07; H, 6.05; N, 4.94. Found: C, 72.11; H, 6.11; N, 4.95.

1-Acetoxy-9-methylcarbazole (20): colorless needles (ether/hexane); mp $123\text{--}125\text{ }^\circ\text{C}$; $^1\text{H NMR } \delta$ 2.44 (s, 3 H), 3.98 (s, 3 H), 7.14 (dd, $J = 7.7, 1.4$ Hz, 1 H), 7.18 (t, $J = 7.7$ Hz, 1 H), 7.24 (br t, $J = 7.6$ Hz, 1 H), 7.37 (br d, $J = 8.9$ Hz, 1 H), 7.47 (ddd, $J = 8.9, 7.6, 1.2$ Hz, 1 H), 7.96 (dd, $J = 7.7, 1.4$ Hz, 1 H), 8.07 (br d, $J = 7.6$ Hz, 1 H); IR (KBr) 1764 cm^{-1} (C=O); FABMS m/e 239 (M^+). Anal. Calcd for $\text{C}_{15}\text{H}_{13}\text{NO}_2$: C, 75.30; H, 5.48; N, 5.85. Found: C, 75.01; H, 5.45; N, 5.71.

Synthesis of Cannabifuran. To a solution of lithium diisopropylamide (47 mmol) in toluene (30 mL) at $-78\text{ }^\circ\text{C}$ were successively added ethyl heptanoate (7.33 g) and a toluene solution (40 mL) of 4-isopropyl-7-methyl-2-benzofurancarboxaldehyde¹⁰ (9, 6.06 g). The mixture was warmed to $-10\text{ }^\circ\text{C}$ and stirred for 2 h. The mixture was then hydrolyzed with a solution of AcOH (3.5 g) and water (50 mL) and was extracted with ether. The extract was dried (MgSO_4), and solvent was evaporated to give a β -hydroxy ester as an orange oil: IR (neat) 3450 cm^{-1} (br, OH).

A benzene solution (150 mL) of the ester and *p*-toluenesulfonic acid (0.5 g) was heated under reflux for 1 h to effect dehydration. Silica gel column chromatography (ether/hexane, 1:19) of the crude product afforded unsaturated ester **10** as a pale yellow oil (5.1 g): IR (neat) $1709\text{ (C=O)}, 1632\text{ cm}^{-1}$ (C=C). Compound

10 was stirred with diisobutylaluminum hydride (36 mmol) in toluene (50 mL) for 4 h at room temperature. The mixture was then treated with 1 N aqueous HCl (100 mL) and extracted with ether, and the extract was dried (MgSO_4). Evaporation of solvent gave allylic alcohol **11** (4.3 g). The alcohol was stirred with Ac_2O (2.0 g), NEt_3 (2.5 g), DMAP (4 mg), and ether (20 mL) for 2 h at room temperature. The mixture was then diluted with ether, washed (dilute aqueous HCl, saturated aqueous NaHCO_3 , and water), and dried (MgSO_4). Evaporation of solvent gave crude acetate ester **12**, which upon purification by column chromatography on silica gel (ether/hexane, 1:19) gave pure (*E*)-3-(4-isopropyl-7-methyl-2-benzofuranyl)-2-pentylallyl acetate (**12**) as a colorless oil (3.88 g, 38% from **9**): $^1\text{H NMR } \delta$ 0.91 (t, $J = 7.2$ Hz, 3 H), 1.33 (d, $J = 7.0$ Hz, 6 H), 1.26–1.46 (m, 4 H), 1.61 (m, 2 H), 2.13 (s, 3 H), 2.48 (s, 3 H), 2.61 (t, $J = 8.1$ Hz, 2 H), 3.18 (septet, $J = 7.0, 1$ H), 4.68 (d, $J = 1.2$ Hz, 2 H), 6.39 (s, 1 H), 6.68 (s, 1 H), 6.96 (d, $J = 7.8$ Hz, 1 H), 7.01 (d, $J = 7.8$ Hz, 1 H). Anal. Calcd for $\text{C}_{29}\text{H}_{36}\text{O}_3$: C, 77.16; H, 8.83. Found: C, 77.38; H, 8.77. The *E* configuration of **12** was established by an NOE experiment. Irradiation at δ 4.68 (AcOCH_2) increased the intensity of the signal at δ 6.39 (vinyl H) by 20%.

Ester **12** (1.027 g, 3 mmol) was cyclocarbonylated as described above. The reaction mixture was washed (dilute aqueous HCl, saturated aqueous NaHCO_3 , and water) and dried (MgSO_4). Solvent was evaporated to give a brown oil, which was purified by column chromatography on silica gel (ether/hexane, 1:30) to give 1-acetoxy-9-isopropyl-6-methyl-3-pentylidibenzofuran (**13**, 0.784 g, 74%) as a pale yellow oil: $^1\text{H NMR } \delta$ 0.90 (t, $J = 7.0$ Hz, 3 H), 1.35 (d, $J = 6.8$ Hz, 6 H), 1.30–1.40 (m, 4 H), 1.70 (m, 2 H), 2.42 (s, 3 H), 2.53 (s, 3 H), 2.75 (t, $J = 7.8$ Hz, 2 H), 3.97 (septet, $J = 6.8$ Hz, 1 H), 6.89 (d, $J = 1.2$ Hz, 1 H), 7.15 (d, $J = 7.6$ Hz, 1 H), 7.22 (d, $J = 7.6$ Hz, 1 H), 7.31 (d, $J = 1.2$ Hz, 1 H); IR (neat) 1778 cm^{-1} (C=O). Anal. Calcd for $\text{C}_{23}\text{H}_{28}\text{O}_3$: C, 78.38; H, 8.01. Found: C, 78.51; H, 7.85.

Acetate **13** (336 mg), KOH (440 mg), and MeOH (10 mL) were stirred for 1 h at room temperature. The mixture was acidified with 6 N aqueous HCl (5 mL) and extracted with ether, and the extract was dried (MgSO_4). Evaporation of solvent gave crude 9-isopropyl-6-methyl-3-pentylidibenzofuran-1-ol (**14**, 277 mg, 94%) as a pale yellow solid. Recrystallization (hexane) gave colorless prisms: mp $80\text{--}81\text{ }^\circ\text{C}$ (lit.¹⁰ mp $78\text{--}79\text{ }^\circ\text{C}$, lit.¹⁶ mp $80\text{--}81\text{ }^\circ\text{C}$); $^1\text{H NMR}^9,10\text{ } \delta$ 0.89 (t, $J = 7.0, 3$ H), 1.28–1.30 (m, 4 H), 1.34 (d, $J = 7.0, 6$ H), 1.65 (m, 2 H), 2.53 (s, 3 H), 2.65 (t, $J = 7.6$ Hz, 2 H), 4.39 (septet, $J = 7.0$ Hz, 1 H), 5.23 (s, 1 H), 6.43 (s, 1 H), 7.01 (s, 1 H), 7.16 (d, $J = 7.9$ Hz, 1 H), 7.17 (d, $J = 7.9$ Hz, 1 H); IR (KBr) 3500 cm^{-1} (OH); $^{13}\text{C NMR}^{16}\text{ } \delta$ 14.0, 15.0, 22.6, 24.3 (2 C), 30.5, 31.0, 31.4, 35.8, 104.1, 109.8, 110.7, 118.4, 118.9, 121.3, 127.4, 142.0, 143.2, 149.7, 154.4, 158.3.

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Supplementary Material Available: $^1\text{H NMR}$ spectra of compounds **2d**, **14**, **15b**, **17**, 3-(2-pyridyl)allyl acetate, and 3-(3-pyridyl)allyl acetate, $^{13}\text{C NMR}$ spectra of compounds **2d**, **14**, **15b**, 3-(2-pyridyl)allyl acetate, and 3-(3-pyridyl)allyl acetate, and IR spectra of compounds **10**, **14**, and ethyl 2-[[4-(2-propyl)-7-methyl-2-benzofuranyl]hydroxymethyl]heptanoate (16 pages). Ordering information is given on any current masthead page.

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