

Synthesis of Spiro[furan-2(3*H*),1'-(1',2',3',4'-tetrahydronaphthalene)] and 3a,4,5,9b-Tetrahydronaphtho[1,2-*b*]furan Derivatives Using Manganese(III) Acetate

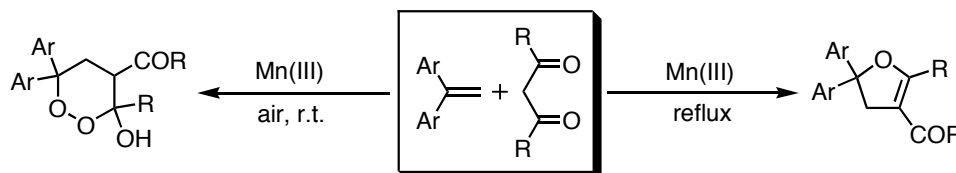
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Introduction

Construction of furans and tetrahydrofurans is interesting since there are many natural products which consist of furan rings and tetrahydrofuran rings.¹ 4,5-Dihydrofurans are convenient synthetic starting materials since the dihydrofurans can be transformed by dehydrogenation or reduction into the corresponding furans or tetrahydrofurans. The authors reported that the oxidation of 1,1-diarylethenes with tris(2,4-pentanedionato)manganese(III) or manganese(III) acetate in the presence of active methylene compounds in boiling acetic acid gave 5,5-diaryl-4,5-dihydrofurans in good yields.^{2,3} On the other hand, a similar reaction at ambient temperature in air quantitatively yielded 6,6-diaryl-1,2-dioxan-3-ols (Scheme 1).^{2,4} Here we report the synthesis of new type of spiro[furan-2(3*H*),1'-(1',2',3',4'-tetrahydronaphthalene)] derivatives and 3a,4,5,9b-tetrahydronaphtho[1,2-*b*]furan derivatives using the manganese(III)-based oxidation of *exo*- and *endo*-methylene compounds in the presence of various 1,3-dicarbonyl compounds.

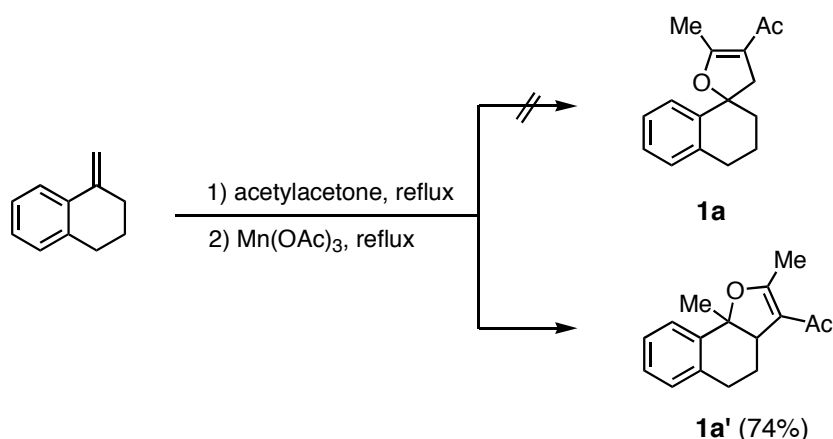


Scheme 1

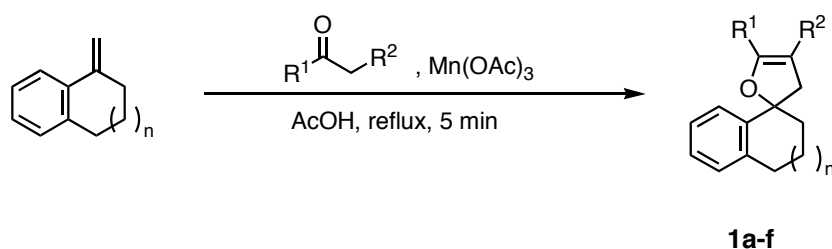
Results and Discussion

Reaction of 1-Methylenetetralin with Acetylacetone in the Presence of Manganese(III) Acetate. A mixture of 1-methylenetetralin and acetylacetone was heated in acetic acid, and then manganese(III) acetate dihydrate was added to the mixture just before boiling. After work-up, however, 3-acetyl-2,9b-dimethyl-3a,4,5,9b-tetrahydronaphtho[1,2-*b*]furan (**1a'**) was obtained instead of desired 4-acetyl-5-methylspiro[furan-2(3*H*),1'-(1',2',3',4'-tetrahydronaphthalene)] (**1a**) (Scheme 2). It was considered that the *exo-endo* isomerization of 1-methylenetetralin under the acidic conditions caused the formation of **1a'**. Therefore, the desired spiro[furan-2(3*H*),1'-(1',2',3',4'-tetrahydronaphthalene)] derivatives were synthesized by heating a mixture of *exo*-alkenes, 1,3-dicarbonyl compounds, and manganese(III) acetate before the *exo-endo* isomerization.

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Synthesis of Spiro[furan-2(3*H*),1'-(1',2',3',4'-tetrahydronaphthalene)] Derivatives. 1-Methylenetetralin or 1-methylenebenzo[2.3]cycloheptane reacted with acetylacetone, methyl acetoacetate, ethyl acetoacetate, or benzoylacetone in the presence of manganese(III) acetate dihydrate in acetic acid at the reflux temperature to give the corresponding dihydrofurans **1a-f** (Scheme 3). The product yields are summarized in Table 1. Single crystals of **1a** and **1f** were successfully grown from diethyl ether-hexane and analyzed by X-ray crystallography. The crystal structures were shown in Figure 1.



- 1a** : R¹ = Me, R² = Ac, n = 1
1b : R¹ = Me, R² = COOMe, n = 1
1c : R¹ = Me, R² = COOEt, n = 1
1d : R¹ = Ph, R² = Ac, n = 1
1e : R¹ = Me, R² = Bz, n = 1
1f : R¹ = Me, R² = Ac, n = 2

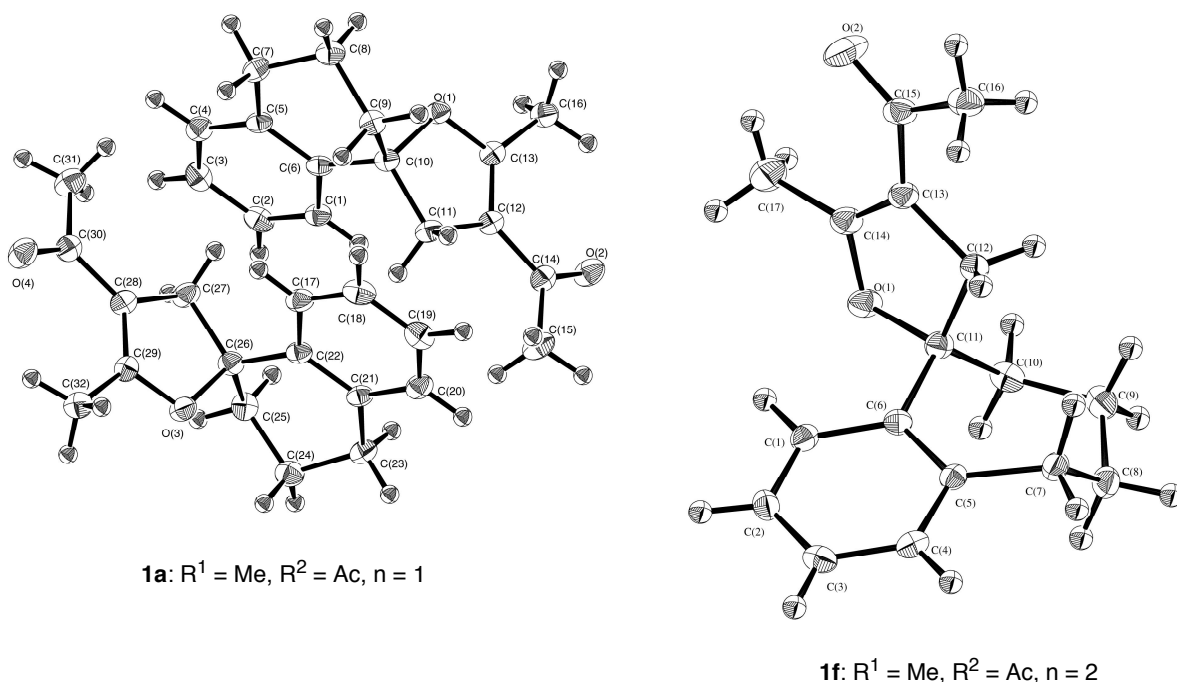
Scheme 3

Table 1. Reaction of *exo*-Alkenes with Various 1,3-Dicarbonyl Compounds in the Presence of Manganese(III) Acetate Dihydrate^a

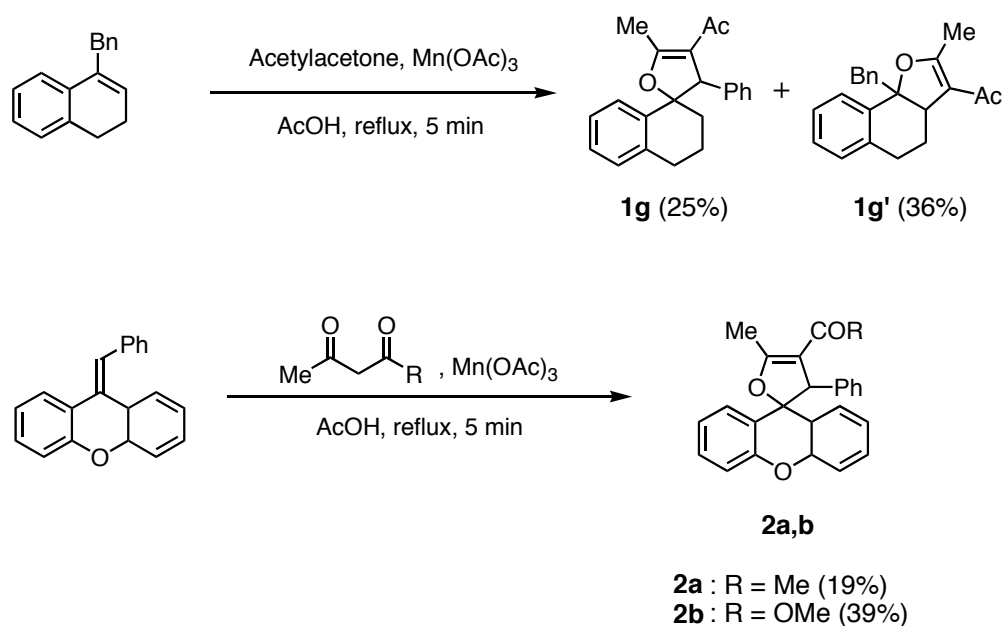
Entry	<i>exo</i> -Alkene	1,3-Dicarbonyl Compound	Product (Yield/%) ^b
1	n = 1	acetylacetone	1a (68)
2	n = 1	methyl acetoacetate	1b (70)
3	n = 1	ethyl acetoacetate	1c (71)
4	n = 1	benzoylacetone	1d (39) 1e (18)
5	n = 2	acetylacetone	1f (75)

^a The reaction was carried out in boiling acetic acid (50 mL) at the molar ratio of alkene:1,3-dicarbonyl compound:Mn(III) = 1:3.5:3.

^b Isolated yield based on the alkene used.

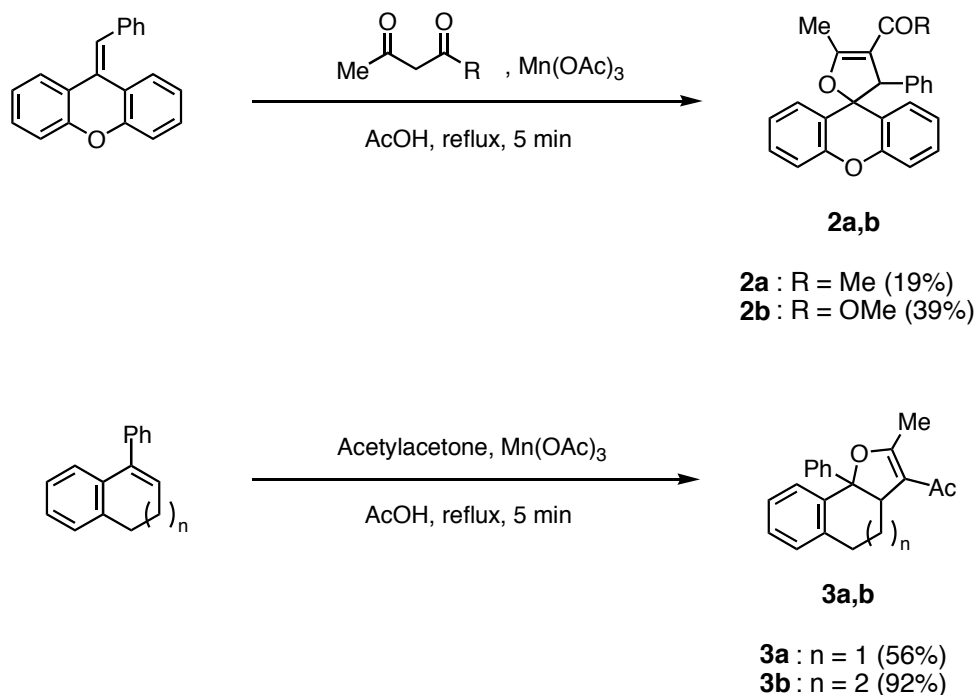
Figure 1. ORTEP Drawings of **1a** and **1f**

A similar reaction of 1-benzyl-3,4-dihydronaphthalene with acetylacetone in the presence of manganese(III) acetate afforded 4-acetyl-5-methyl-3-phenylspiro[furan-2(3*H*),1'-(1',2',3',4'-tetrahydronaphthalene)] (**1g**) together with 3-acetyl-9b-benzyl-2-methyl-3a,4,5,9b-tetrahydronaphtho[1,2-*b*]furan (**1g'**) in 25% and 36% yields, respectively (Scheme 4). It was supposed that the *exo-endo* isomerization of 1-benzyl-3,4-dihydronaphthalene occurred during the reaction. Benzylidenexanthene was oxidized with manganese(III) acetate in the presence of acetylacetone in boiling acetic acid to give 4-acetyl-5-methyl-3-phenylspiro[furan-2(3*H*),9'-xanthene] (**2a**). 4-Methoxycarbonyl-5-methyl-3-phenylspiro[furan-2(3*H*),9'-xanthene] (**2b**) was obtained in a similar oxidation in the presence of methyl acetoacetate (Scheme 4).



Scheme 4

Synthesis of 3a,4,5,9b-Tetrahydronaphtho[1,2-*b*]furan Derivatives. 1-Phenyl-3,4-dihydronaphthalene reacted with acetylacetone in the presence of manganese(III) acetate to give 3-acetyl-2-methyl-9b-phenyl-3a,4,5,9b-tetrahydronaphtho[1,2-*b*]furan (**3a**) in 56% yield. 9-Phenyl-6,7-dihydro-5*H*-benzocycloheptene was also converted into 3-acetyl-2-methyl-10b-phenyl-3a*H*-benzo[6.7]cyclohepta[1,2-*b*]furan (**3b**) in 92% yield (Scheme 5). In order to corroborate the product structures, single crystals of **2a** and **3a** were subjected to X-ray analyses, and we obtained the corresponding ORTEP drawings as shown in Figure 2. In addition, it was confirmed that the stereochemistry of the ring junction for **3a** was *cis*-fused configuration (Figure 2).

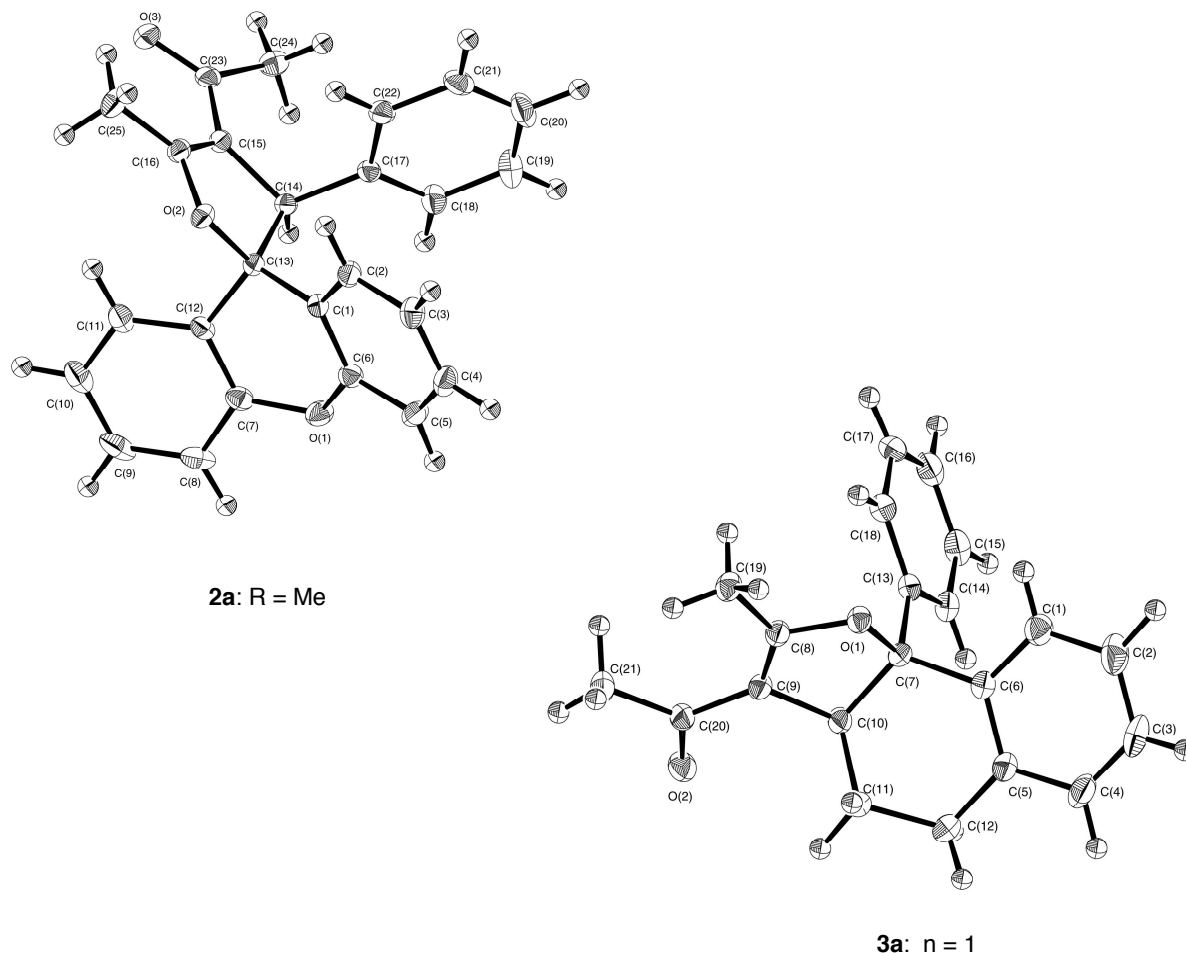


Scheme 5

Experimental

Measurements. All the melting points were determined by a Yanaco micromeltingpoint apparatus MP-J3 and were uncorrected. All of the NMR spectra were recorded on a JNM-AL 300 FT NMR spectrometer (300 MHz for ^1H and 75 MHz for ^{13}C) with tetramethylsilane as the internal standard. The chemical shifts are shown in \square (ppm) and coupling constants in Hz. The IR spectra were measured on a Paragon 1000 FT IR spectrometer or SHIMADZU FTIR-8400. The IR spectral data are expressed in cm^{-1} . The mass spectra were measured on a SHIMADZU GCMS-QP5050A at an ionizing voltage of 70 eV. High resolution mass spectra were recorded on a JMS-HX110A mass spectrometer. Elemental analyses were performed at the Center of Instrumental Analysis Center, Kumamoto University, Kumamoto, Japan.

Materials. Manganese(III) acetate dihydrate, $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$, was prepared according to the literature method.⁵ Alkenes were prepared by Wittig reaction of the corresponding carbonyl compounds with methyltriphenyl phosphonium bromide. Acetylacetone, methyl acetoacetate, and ethyl acetoacetate were purchased from Wako Pure Chemical Ind., Ltd., and were used as received. Benzoylacetone was purchased from Tokyo-Kasei Co., Ltd., and was used as received.

Figure 2. ORTEP Drawings of **2a** and **3a**

Manganese(III)-Based Radical Cyclization of Alkenes with 1,3-Dicarbonyl Compounds. A mixture of alkene (1 mmol), 1,3-dicarbonyl compound (3.5 mmol), and manganese(III) acetate dihydrate (3 mmol) was heated under reflux in acetic acid (50 ml) with stirring until the dark-brown color of Mn(III) disappeared (normally within 5 min). The solvent was removed *in vacuo* and the residue was triturated with 2 M hydrochloric acid (50 mL), followed by extraction with dichloromethane (20 x 3 mL). The extract was washed with water, followed by a saturated aqueous solution of sodium hydrogencarbonate, and dried over anhydrous magnesium sulfate. The products were separated by silica gel TLC (Wakogel B-10) using chloroform or diethyl ether-hexane (4:6-8:2 v/v) as a developing solvent. The yields are summarized in Table 1 and Schemes 4, 5. Analytical samples were further purified by recrystallization from an appropriate solvent mentioned below except for liquid products.

4-Acetyl-5-methylspiro[furan-2(3H),1'-(1',2',3',4'-tetrahydronaphthalene)] (1a): R_f = 0.70 (8:2 diethyl ether-hexane); colorless plates (from diethyl ether), mp 62.0-64.0 °C; IR (CHCl₃) $\bar{\nu}$ 1663 (C=O); ¹H NMR (CDCl₃) δ 7.39-7.04 (4H, m, arom H), 3.13 (2H, ddq, J = 54.8, 14.3, 1.47 Hz, CH₂), 2.92-2.72 (2H, m, CH₂), 2.30 (3H, t, J = 1.47 Hz, CH₃), 2.22 (3H, s, COCH₃), 2.16-1.77 (4H, m, CH₂ x 2); ¹³C NMR (CDCl₃) δ 194.5 (C=O), 166.8 (C-5), 139.5, 136.4 (arom C), 128.8, 127.9, 126.7, 126.2 (arom CH), 111.2 (C-4), 87.2 (C-2(1')), 45.7 (C-3), 36.7 (C-2'), 29.5 (COCH₃), 29.3 (C-4'), 19.8 (C-3'), 15.3 (CH₃); MS m/z (rel intensity), 242 (M⁺, 24), 224 (12), 199 (14), 182 (33), 181 (59), 167 (15), 141 (11), 128 (23), 115 (18), 43

(100). Anal. Calcd for C₁₆H₁₈O₂: C, 79.31; H, 7.49. Found: C, 79.38; H, 7.50.

3-Acetyl-2,9b-dimethyl-3a,4,5,9b-tetrahydronaphtho[1,2-*b*]furan (1a'): $R_f = 0.28$ (5:5 diethyl ether-hexane); colorless plates (from diethyl ether), mp 61.0-62.5 °C; IR (CHCl₃) $\bar{\nu}$ 1612 (C=O); ¹H NMR (CDCl₃) δ 7.59-7.50 (1H, m, arom H), 7.33-7.07 (3H, m, arom H), 3.12 (1H, dd, $J = 10.84, 5.14$ Hz, CH), 2.77-2.48 (2H, m, CH₂), 2.37-2.15 (1H, m, CH_aH_b), 2.33 (3H, s, COCH₃), 2.30 (3H, s, CH₃), 1.55 (3H, s, CH₃), 1.44-1.24 (1H, m, CH_aH_b); ¹³C NMR (CDCl₃) δ 194.4 (C=O), 166.5 (C-2), 137.7, 137.4 (arom C), 128.1, 127.6, 127.3, 126.7 (arom CH), 117.6 (C-3), 85.9 (C-9b), 49.4 (C-3a), 29.6 (COCH₃), 29.3 (CH₃), 28.4 (C-5), 27.9 (C-4), 15.8 (CH₃); MS m/z (rel intensity), 242 (M⁺, 24), 227 (9), 209 (15), 181 (27), 165 (12), 142 (86), 128 (18), 115 (17), 43 (100). Anal. Calcd for C₁₆H₁₈O₂: C, 79.31; H, 7.49. Found: C, 79.24; H, 7.48.

4-Methoxycarbonyl-5-methylspiro[furan-2(3*H*),1'-(1',2',3',4-tetrahydro-naphthalene)] (1b): $R_f = 0.64$ (5:5 diethyl ether-hexane); colorless plates (from hexane), mp 74.0-76.0 °C; IR (CHCl₃) $\bar{\nu}$ 1687 (C=O); ¹H NMR (CDCl₃) δ 7.38-7.01 (4H, m, arom H), 3.70 (3H, s, COOCH₃), 3.06 (2H, ddq, $J = 55.9, 14.7, 1.47$ Hz, CH₂), 2.87-2.68 (2H, m, CH₂), 2.26 (3H, t, $J = 1.47$ Hz, CH₃), 2.15-1.72 (4H, m, CH₂ x 2); ¹³C NMR (CDCl₃) δ 167.2 (C=O), 166.5 (C-5), 139.7, 136.4 (arom C), 128.8, 127.8, 126.7, 126.3 (arom CH), 100.5 (C-4), 87.1 (C-2(1')), 50.7 (COOCH₃), 44.9 (C-3), 36.7 (C-2'), 29.3 (C-4'), 19.8 (C-3'), 14.3 (CH₃); MS m/z (rel intensity), 258 (M⁺, 34), 226 (89), 211 (69), 208 (19), 183 (66), 155 (74), 153 (27), 128 (55), 115 (37), 43 (100). Anal. Calcd for C₁₆H₁₈O₃: C, 74.39; H, 7.02. Found: C, 74.25; H, 7.10.

4-Ethoxycarbonyl-5-methylspiro[furan-2(3*H*),1'-(1',2',3',4'-tetrahydro-naphthalene)] (1c): $R_f = 0.63$ (5:5 diethyl ether-hexane); colorless liquid; IR (CHCl₃) $\bar{\nu}$ 1682 (C=O); ¹H NMR (CDCl₃) δ 7.39-7.02 (4H, m, arom H), 4.18 (2H, q, $J = 7.17$ Hz, COOCH₂CH₃), 3.07 (2H, ddq, $J = 54.0, 14.7, 1.47$ Hz, CH₂), 2.89-2.66 (2H, m, CH₂), 2.26 (3H, t, $J = 1.47$ Hz, CH₃), 2.12-1.74 (4H, m, CH₂ x 2), 1.28 (3H, t, $J = 7.17$ Hz, COOCH₂CH₃); ¹³C NMR (CDCl₃) δ 166.9 (C=O), 166.1 (C-5), 139.8, 136.3 (arom C), 128.7, 127.8, 126.6, 126.3 (arom CH), 100.7 (C-4), 86.9 (C-2(1')), 59.4 (COOCH₂CH₃), 45.0 (C-3), 36.7 (C-2'), 29.3 (C-4'), 19.8 (C-3'), 14.5 (CH₃), 14.3 (COOCH₂CH₃); MS m/z (rel intensity), 272 (M⁺, 22), 226 (72), 211 (51), 183 (50), 155 (53), 153 (19), 128 (40), 115 (29), 43 (100); FAB HRMS found m/z 273.1513, calcd for C₁₇H₂₁O₃ M⁺, 273.1491.

4-Acetyl-5-phenylspiro[furan-2(3*H*),1'-(1',2',3',4'-tetrahydronaphthalene)] (1d): $R_f = 0.30$ (2:8 diethyl ether-hexane); light yellow liquid, IR (CHCl₃) $\bar{\nu}$ 1618 (C=O); ¹H NMR (CDCl₃) δ 7.64-7.06 (9H, m, arom H), 3.33 (2H, dd, $J = 55.4, 15.2$ Hz, CH₂), 2.92-2.73 (2H, m, CH₂), 2.29-1.78 (4H, m, CH₂ x 2), 2.01 (3H, s, COCH₃); ¹³C NMR (CDCl₃) δ 194.4 (C=O), 165.2 (C-5), 139.4, 136.5, 131.1 (arom C), 130.5, 129.2 (2C), 128.8, 128.2 (2C), 127.9, 126.7, 126.3 (arom CH), 113.7 (C-4), 87.1 (C-2(1')), 46.4 (C-3), 36.6 (C-2'), 29.3 (C-4'), 29.0 (COCH₃), 19.6 (C-3'); MS m/z (rel intensity), 304 (M⁺, 12), 286 (14), 244 (26), 128 (15), 115 (22), 105 (100), 77 (41), 43 (37); FAB HRMS found m/z 305.1543, calcd for C₂₁H₂₁O₂ M⁺, 305.1542.

4-Benzoyl-5-methylspiro[furan-2(3*H*),1'-(1',2',3',4'-tetrahydronaphthalene)] (1e): $R_f = 0.45$ (2:8 diethyl ether-hexane); colorless liquid; IR (CHCl₃) $\bar{\nu}$ 1599 (C=O); ¹H NMR (CDCl₃) δ 7.64-7.05 (9H, m, arom H), 3.28 (2H, ddq, $J = 65.7, 14.7, 1.47$ Hz, CH₂), 2.94-2.69 (2H, m, CH₂), 2.20-1.75 (4H, m, CH₂ x 2), 1.91 (3H, t, $J = 1.47$ Hz, CH₃); ¹³C NMR (CDCl₃)

\square 193.0 (C=O), 168.0 (C-5), 141.1, 139.4, 136.5 (arom C), 130.8, 128.8, 128.2 (2C), 127.9, 127.7 (2C), 126.7, 126.3 (arom CH), 111.5 (C-4), 87.4 (C-2(1')), 46.1 (C-3), 36.5 (C-2'), 29.2 (C-4'), 19.8 (C-3'), 15.8 (CH₃); MS *m/z* (rel intensity), 304 (M⁺, 12), 286 (14), 244 (32), 128 (18), 115 (14), 105 (100), 91 (14), 77 (44), 43 (23); FAB HRMS found *m/z* 305.1543, calcd for C₂₁H₂₁O₂ M⁺, 305.1542.

4'-Acetyl-5'-methylspiro[5H-benzocycloheptene-5,2'(3'H)-furan] (1f): *R_f* = 0.32 (5:5 diethyl ether-hexane); colorless prisms (from hexane), mp 74.0-75.5 °C; IR (CHCl₃) \square 1669 (C=O); ¹H NMR (CDCl₃) \square 7.42-7.35 (1H, m, arom H), 7.22-7.08 (3H, m, arom H), 3.48 (1H, dq, *J* = 14.13, 1.47 Hz, CH_{a1}H_{b1}), 2.95-2.72 (3H, m, CH₂, CH_{a1}H_{b1}), 2.37 (3H, t, *J* = 1.47 Hz, CH₃), 2.19 (3H, s, COCH₃), 2.10-1.89 (5H, m, CH₂ x 2, CH_{a2}H_{b2}), 1.50-1.29 (1H, m, CH_{a2}H_{b2}); ¹³C NMR (CDCl₃) \square 194.1 (C=O), 165.2 (C-5'), 145.1, 139.0 (arom C), 130.8, 127.3, 126.1, 123.8 (arom CH), 111.9 (C-4'), 92.1 (C-5(2')), 40.2 (C-3'), 38.3 (C-4), 36.3 (C-2), 29.2 (COCH₃), 27.5 (C-1), 25.8 (C-3), 15.0 (CH₃); MS *m/z* (rel intensity), 256 (M⁺, 6), 238 (10), 214 (26), 196 (21), 195 (32), 169 (23), 167 (10), 141 (21), 128 (24), 115 (20), 91 (10), 43 (100). Anal. Calcd for C₁₇H₂₀O₂: C, 79.65; H, 7.86. Found: C, 79.63; H, 8.01.

4-Acetyl-5-methyl-3-phenylspiro[furan-2(3H),1'-(1',2',3',4'-tetrahydronaphthalene)] (1g): *R_f* = 0.33 (2:8 diethyl ether-hexane); colorless needles (from ethanol), mp 111.0-112.0 °C; IR (CHCl₃) \square 1665 (C=O); ¹H NMR (CDCl₃) \square 7.64-7.57 (1H, m, arom H), 7.41-7.00 (8H, m, arom H), 4.68 (1H, q, *J* = 1.10 Hz, CH), 2.79-2.56 (2H, m, CH₂), 2.41 (3H, d, *J* = 1.10 Hz, CH₃), 1.85 (3H, s, COCH₃), 1.77-1.60 (2H, m, CH₂), 1.57-1.42 (2H, m, CH₂); ¹³C NMR (CDCl₃) \square 195.1 (C=O), 168.4 (C-5), 140.5, 139.8, 136.7 (arom C), 130.2 129.1, 128.4 (2C), 128.3 (2C), 127.3, 127.0, 125.5 (arom) CH, 115.8 (C-4), 89.5 (C-2(1')), 60.3 (C-3), 33.3 (C-4'), 29.6 (COCH₃), 29.3 (C-2'), 19.4 (C-3'), 15.3 (CH₃); MS *m/z* (rel intensity), 318 (M⁺, 20), 300 (17), 275 (22), 258 (48), 147 (16), 129 (47), 115 (14), 91 (23), 43 (100). Anal. Calcd for C₂₂H₂₂O₂: C, 82.99; H, 6.96. Found: C, 83.23; H, 7.08.

3-Acetyl-9b-benzyl-2-methyl-3a,4,5,9b-tetrahydronaphtho[1,2-b]furan (1g'): *R_f* = 0.25 (2:8 diethyl ether-hexane); colorless needles (from hexane), mp 79.0-81.0 °C; IR (CHCl₃) \square 1614 (C=O); ¹H NMR (CDCl₃) \square 7.60 (1H, dd, *J* = 7.72, 1.10 Hz, arom H), 7.34-6.97 (6H, m, arom H), 6.84-6.78 (2H, m, arom H), 3.35 (1H, ddd, *J* = 11.76, 5.33, 0.92 Hz, CH), 3.06 (2H, dd, *J* = 23.33, 13.05 Hz, CH₂), 2.46 (1H, dt, *J* = 15.25, 3.31 Hz, CH_{a1}H_{b1}), 2.30-2.19 (1H, m, CH_{a1}H_{b1}), 2.18 (3H, d, *J* = 0.92 Hz, CH₃), 2.16 (3H, s, COCH₃), 2.02-1.88 (1H, m, CH_{a2}H_{b2}), 1.12 (1H, ddd, *J* = 24.80, 12.68, 3.12 Hz, CH_{a2}H_{b2}); ¹³C NMR (CDCl₃) \square 193.9 (C=O), 166.1 (C-2), 138.9, 136.5, 135.0 (arom C), 130.3 (2C), 127.8, 127.7 (2C), 127.7, 127.5, 126.7, 126.5 (arom CH), 117.9 (C-3), 88.2 (C-9b), 48.7 (CH₂), 46.0 (C-3a), 29.2 (COCH₃), 28.4 (C-5), 27.8 (C-4), 15.6 (CH₃); MS *m/z* (rel intensity), 227 (100), 91 (25), 43 (92). Anal. Calcd for C₂₂H₂₂O₂: C, 82.99; H, 6.96. Found: C, 83.10; H, 7.04.

4-Acetyl-5-methyl-3-phenylspiro[furan-2(3H),9'-xanthene] (2a)^{3a}: *R_f* = 0.51 (5:5 diethyl ether-hexane); colorless prisms (from ethanol), mp 142.5-143.5 °C (lit.^{3a} mp 141 °C); IR (CHCl₃) \square 1669 (C=O); ¹H NMR (CDCl₃) \square 7.51-6.67 (13H, m, arom H), 4.43 (1H, q, *J* = 1.47 Hz, CH), 2.69 (3H, d, *J* = 1.47 Hz, CH₃), 1.78 (3H, s, COCH₃); ¹³C NMR (CDCl₃) \square 196.0 (C=O), 169.1 (C-5), 150.2, 149.3, 138.3 (2C), 121.4 (arom C), 129.2, 128.8, 128.3, 128.0 (2C), 127.1, 126.8 (2C), 124.1, 123.9, 122.5, 116.9, 115.7 (arom CH), 112.1 (C-4), 86.3 (C-2(9')), 65.2 (C-3), 29.6 (COCH₃), 14.8 (CH₃); MS *m/z* (rel intensity), 368 (M⁺, 9), 350 (7), 325 (100), 310 (17), 281 (33), 197 (24), 181 (43), 152 (9), 129 (27), 77 (10), 43 (44).

4-Methoxycarbonyl-5-methyl-3-phenylspiro[furan-2(3H),9'-xanthene] (2b): $R_f = 0.61$ (5:5 diethyl ether-hexane); colorless microcrystals (from ethanol), mp 151.0-152.5 °C; IR (CHCl₃) $\bar{\nu}$ 1697 (C=O); ¹H NMR (CDCl₃) δ 7.50-6.64 (13H, m, arom H), 4.41 (1H, q, $J = 1.47$ Hz, CH), 3.48 (3H, s, COOCH₃), 2.66 (3H, d, $J = 1.47$ Hz, CH₃); ¹³C NMR (CDCl₃) δ 169.2 (C=O), 166.1 (C-5), 150.2, 149.2, 138.5, 126.8, 121.5 (arom C), 129.1, 128.6, 127.9 (2C), 127.6 (2C), 126.9, 126.5, 124.2, 123.8, 122.4, 116.7, 115.6 (arom CH), 103.0 (C-4), 86.1 (C-2(9')), 64.2 (C-3), 50.9 (COOCH₃), 14.2 (CH₃); MS m/z (rel intensity), 384 (M⁺, 17), 366 (12), 341 (24), 309 (13), 281 (100), 205 (12), 180 (15), 152 (14), 128 (18), 43 (13).

3-Acetyl-2-methyl-9b-phenyl-3a,4,5,9b-tetrahydronaphtho[1,2-b]furan (3a): $R_f = 0.33$ (5:5 diethyl ether-hexane); colorless prisms (from ethanol), mp 160.0-160.5 °C; IR (CHCl₃) $\bar{\nu}$ 1619 (C=O); ¹H NMR (CDCl₃) δ 7.32-7.05 (9H, m, arom H), 3.50 (1H, ddd, $J = 10.09, 5.32, 0.92$ Hz, CH), 2.87-2.80 (2H, m, CH₂), 2.43-2.32 (1H, m, CH_aH_b), 2.40 (3H, d, $J = 0.92$ Hz, CH₃), 2.24 (3H, s, COCH₃), 1.72-1.57 (1H, m, CH_aH_b); ¹³C NMR (CDCl₃) δ 194.2 (C=O), 166.8 (C-2), 146.9, 138.2, 137.3 (arom C), 129.9, 128.2 (2C), 128.1, 127.8, 127.1, 126.8, 124.8 (2C) (arom CH), 117.3 (C-3), 89.2 (C-9b), 52.0 (C-3a), 29.4 (COCH₃), 28.2 (C-5), 27.9 (C-4), 15.5 (CH₃); MS m/z (rel intensity), 304 (M⁺, 46), 262 (12), 243 (19), 228 (18), 217 (18), 204 (65), 91 (12), 43 (100). Anal. Calcd for C₂₁H₂₀O₂: C, 82.86; H, 6.62. Found: C, 82.82; H, 6.65.

3-Acetyl-2-methyl-10b-phenyl-3aH-benzo[6.7]cyclohepta[1,2-b]furan (3b): $R_f = 0.35$ (5:5 diethyl ether-hexane); light yellow prisms (from hexane), mp 123.5-125.0 °C; IR (CHCl₃) $\bar{\nu}$ 1627 (C=O); ¹H NMR (CDCl₃) δ 7.69-7.61 (1H, m, arom H), 7.35-7.08 (8H, m, arom H), 3.70 (1H, dt, $J = 11.21, 1.10$ Hz, CH), 2.62-2.43 (2H, m, CH₂), 2.34 (3H, d, $J = 1.10$ Hz, CH₃), 2.32 (3H, s, COCH₃), 1.93-1.73 (2H, m, CH₂), 1.65-1.48 (1H, m, CH_aH_b), 1.36-1.17 (1H, m, CH_aH_b); ¹³C NMR (CDCl₃) δ 193.6 (C=O), 165.1 (C-2), 144.8, 139.4, 136.7 (arom C), 129.1, 128.4 (2C), 128.3, 128.3, 126.9, 126.6, 125.7 (2C) (arom CH), 118.4 (C-3), 95.0 (C-10b), 51.8 (C-3a), 31.6 (C-6), 29.3 (COCH₃), 27.8 (C-4), 25.0 (C-5), 15.7 (CH₃); MS m/z (rel intensity), 318 (M⁺, 4), 276 (12), 218 (100), 203 (23), 165 (10), 115 (15), 91 (13), 77 (10), 43 (88). Anal. Calcd for C₂₂H₂₂O₂: C, 82.99; H, 6.96. Found: C, 82.89; H, 6.99.

X-Ray Crystallography of 1a, 1f, 2a, and 3a. All measurements were made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71069$ Å). Indexing was performed from 2 oscillations which were exposed for 3.3 minutes. The camera radius was 127.40 mm. Readout was performed in the 0.100 mm pixel mode. The data were collected at a temperature of -180 ± 1 °C and anode power 50 kV x 32 mA. Crystallographic data and details of data collections and refinements are given in Table 2-4. Data reduction was carried out by the PROCESS-AUTO program package, and Lorentz and polarization corrections were performed. A correction for secondary extinction was applied. The structures were solved by direct method and were refined on SIR-92.⁶ The refinements were followed by least-squares full matrix method, with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were included but not refined. All calculations were performed using the teXsan⁷ crystallographic software package of Molecular Structure Corporation.

Table 2. Crystal Data and Structure Refinement of Compound 1a

1a	
Empirical Formula	C ₃₂ H ₃₆ O ₄
Formula Weight	484.63
Crystal Color, Habit	colorless, platelet
Crystal Dimensions	0.30 x 0.40 x 0.10 mm
Crystal System	monoclinic
Lattice Parameters	$a = 9.2579(4) \text{ \AA}$ $b = 17.3043(9) \text{ \AA}$ $c = 16.2643(8) \text{ \AA}$ $V = 2555.6(2) \text{ \AA}^3$
Space Group	$P2_1/c$ (# 14)
Formula Units per Cell	$Z = 4$
Density (calculated)	$\rho = 1.259 \text{ g cm}^{-3}$
$F(000)$	1040.00
Absorption Coefficient	0.81 cm^{-1}
2θ Range for Data Collection	$5.1\text{--}55.0^\circ$
Data Images	74 exposure at 2.5 minutes per degree
Oscillation Range	θ $130.0\text{--}190.0^\circ$ with 3.0° step ϕ $0.0\text{--}162.0^\circ$ with 3.0° step
No. of Reflection Measured	Total: 17591 Unique: 5768 ($R_{int} = 0.057$)
No. Observations ($I > 3.00\sigma(I)$)	3297
No. Variables	470
Reflection/Parameter Ratio	7.01
Residuals: R ; R_w	0.040; 0.047
Goodness of Fit Indicator	1.14
Max/Min Residual Density	$+0.32/-0.19 \text{ e}^- \text{ \AA}^{-3}$

Table 3. Crystal Data and Structure Refinement of Compound 1f

1f	
Empirical Formula	C ₁₆ H ₁₈ O ₂
Formula Weight	242.32
Crystal Color, Habit	colorless, prism
Crystal Dimensions	0.50 x 0.40 x 0.03 mm
Crystal System	orthorhombic
Lattice Parameters	$a = 8.4382(2) \text{ \AA}$ $b = 16.0661(5) \text{ \AA}$ $c = 20.4929(4) \text{ \AA}$ $V = 2778.2(1) \text{ \AA}^3$
Space Group	$Pbca$ (# 61)
Formula Units per Cell	$Z = 8$
Density (calculated)	$\rho = 1.159 \text{ g cm}^{-3}$
$F(000)$	1040.00
Absorption Coefficient	0.75 cm^{-1}
2θ Range for Data Collection	$2.5\text{--}54.7^\circ$
Data Images	74 exposure at 3.3 minutes per degree
Oscillation Range	θ $130.0\text{--}190.0^\circ$ with 3.0° step ϕ $0.0\text{--}162.0^\circ$ with 3.0° step
No. of Reflection Measured	Total: 25293 Unique: 3134 ($R_{int} = 0.040$)
No. Observations ($I > 3.00\sigma(I)$)	2152
No. Variables	252
Reflection/Parameter Ratio	8.54
Residuals: R ; R_w	0.035; 0.046
Goodness of Fit Indicator	0.88
Max/Min Residual Density	$+0.22/-0.23 \text{ e}^- \text{ \AA}^{-3}$

Table 4. Crystal Data and Structure Refinement of Compound 2a

2a	
Empirical Formula	C ₂₅ H ₂₀ O ₃
Formula Weight	368.43
Crystal Color, Habit	colorless, prism
Crystal Dimensions	0.30 x 0.40 x 0.10 mm
Crystal System	monoclinic
Lattice Parameters	$a = 11.0904(4) \text{ \AA}$ $b = 10.9721(4) \text{ \AA}$ $c = 15.6705(5) \text{ \AA}$ $V = 1904.1(1) \text{ \AA}^3$
Space Group	$P2_1/c$ (# 14)
Formula Units per Cell	$Z = 4$
Density (calculated)	$\rho = 1.285 \text{ g cm}^{-3}$
$F(000)$	776.00
Absorption Coefficient	0.83 cm^{-1}
2θ Range for Data Collection	$4.5\text{--}55.0^\circ$
Data Images	74 exposure at 1.7 minutes per degree
Oscillation Range	θ $130.0\text{--}190.0^\circ$ with 3.0° step ϕ $0.0\text{--}162.0^\circ$ with 3.0° step
No. of Reflection Measured	Total: 16107 Unique: 4357 ($R_{int} = 0.030$)
No. Observations ($I > 3.00\sigma(I)$)	3627
No. Variables	334
Reflection/Parameter Ratio	10.86
Residuals: R ; R_w	0.042; 0.065
Goodness of Fit Indicator	0.83
Max/Min Residual Density	$+0.39/-0.27 \text{ e}^- \text{ \AA}^{-3}$

Table 5. Crystal Data and Structure Refinement of Compound 3a

3a	
Empirical Formula	C ₂₁ H ₂₀ O ₂
Formula Weight	304.39
Crystal Color, Habit	colorless, prism
Crystal Dimensions	0.15 x 0.40 x 0.40 mm
Crystal System	orthorhombic
Lattice Parameters	$a = 13.9736(3) \text{ \AA}$ $b = 28.6550(8) \text{ \AA}$ $c = 8.0136(2) \text{ \AA}$ $V = 3208(1) \text{ \AA}^3$
Space Group	$Pbca$ (# 61)
Formula Units per Cell	$Z = 8$
Density (calculated)	$\rho = 1.260 \text{ g cm}^{-3}$
$F(000)$	1296.00
Absorption Coefficient	0.79 cm^{-1}
2θ Range for Data Collection	$3.2\text{--}55.0^\circ$
Data Images	110 exposure at 5.0 minutes per degree
Oscillation Range	θ $130.0\text{--}190.0^\circ$ with 2.0° step ϕ $0.0\text{--}162.0^\circ$ with 2.0° step
No. of Reflection Measured	Total: 23073 Unique: 3630 ($R_{int} = 0.041$)
No. Observations ($I > 3.00\sigma(I)$)	2884
No. Variables	289
Reflection/Parameter Ratio	9.98
Residuals: R ; R_w	0.066; 0.188
Goodness of Fit Indicator	1.06
Max/Min Residual Density	$+0.88/-0.28 \text{ e}^- \text{ \AA}^{-3}$

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