Synthesis of Thienyl-Substituted Dihydrofuran Compounds Promoted by Manganese(III) Acetate

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Radical cyclization reactions of both aliphatic 1,3-diones **1a** and **1b** and of cyclic 1,3-diones **1c**–**1e** with 2-thienyl- and 3-thienyl-substituted alkenes **2a**–**2d** in the presence of manganese(III) acetate were investigated. Thienyl-substituted dihydrofurans **3** were obtained with moderate to high yields (*Table 1–3*). Also, the favorable effect of the thienyl substituent on the intermediate carbocation stability was evaluated by comparison with a phenyl substituent.

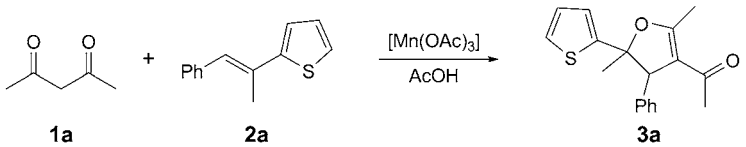
Introduction. – Previously, we have reported the formation of furan [1] and dihydrofuran [2] derivatives resulting from radical cyclizations with various alkenes and alkynes. Moreover, the cyclization reactions of 4-hydroxycoumarins (=4-hydroxy-2*H*-1-benzopyran-2-ones), 2-hydroxy-1,4-naphthoquinones [3] and 3-oxopropanenitriles [4] with alkenes have been studied, and 4,5-dihydrofurans-3-carbonitriles have shown antibacterial and antifungal activities [5].

In the course of our studies, we found that the radical cyclization reactions are possible with 1,3-diones **1** and thienyl-substituted alkenes **2a**–**2d** mediated by $[Mn(OAc)_3]$. Thienyl-substituted dihydrofuran compounds were achieved as a result of these reactions. We conceive the effect of heteroaromatic substituents in radical cyclization reactions. The impact of this effect on the yields is also demonstrated in this article.

Results and Discussion. – At first, we attempted to opimize the radical cyclization reaction of acetylacetone (=pentane-1,3-dione; **1a**) and 2-[(1*E*)-1-methyl-2-phenylethenyl]thiophene (**2a**). For this purpose, we varied the reaction temperature and the amounts of the reagents along with that of $[Mn(OAc)_3]$. When we modified the amount the alkene **2a** and $[Mn(OAc)_3]$, the yields of **3a** differed with the amount of each reagent (*Table 1*). Also the reaction temperature influenced the yield of the product **3a**. Finally, the highest yield of **3a** was obtained with 2.0 equiv. of **1a** and 1.0 equiv. of **2a** in the presence of 3.0 equiv. of $[Mn(OAc)_3]$ in AcOH at 60° (*Table 1*, *Entry 3*).

The mechanism we propose for the formation of 4,5-dihydrofurans involves the interaction of $[Mn(OAc)_3]$ with 1,3-diones **1a**–**1e** resulting in a $[Mn^{III}(enolato)]$ complex **A** (*Scheme*). Radical **B** is formed while Mn^{III} is reduced to Mn^{II}. Addition of **B** to alkene **2b** might take place by the two *Pathways i* and *ii*. If the reaction follows

Table 1. *Manganese(III)-Mediated Reaction of Acetylacetone* (**1a**) *with [(1*E*)-1-Methyl-2-phenylethenyl]thiophene* (**2a**) *under Various Conditions*

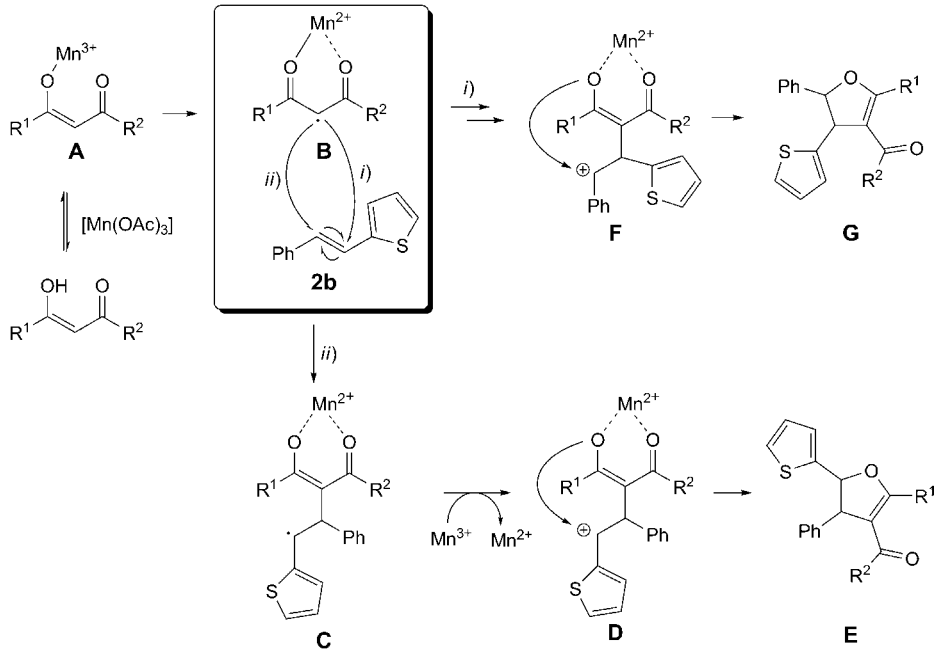


1a **2a** **3a**

Entry	Reaction Conditions [mmol]			Temperature [°]	Yield of **3a** [%]
	1a	**2a**	$[Mn(OAc)_3]$		
1	1.0	1.2	2.0	60	43
2	1.0	1.2	2.0	80	33
3	2.0	1.0	3.0	60	55
4	2.0	1.0	3.0	80	33

Pathway i, radical intermediate **F** is generated and finally product **G** is obtained. On the other hand, if *Pathway ii* is followed, radical intermediate **C** is generated, which is then oxidized to carbocation **D** with 1 equiv. of Mn^{III}. Thereafter, the intramolecular ring closure leads to dihydrofuran **E**.

Scheme. *Mechanism of the Formation of 4,5-Dihydrofurans*



Thus, according to the mechanism, dihydrofurans **E** and **G** might be observed depending on the addition to the alkene. However, only dihydrofuran product **E** was obtained. Other cyclization products were not found in isolable amounts. Differ-

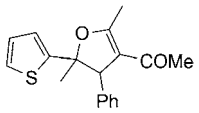
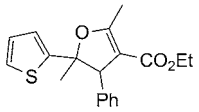
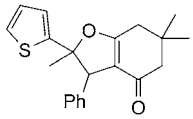
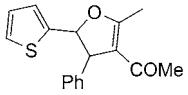
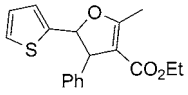
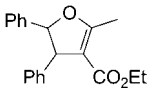
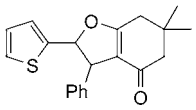
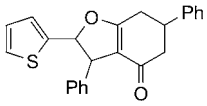
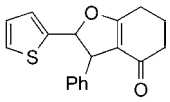
entiation of structures **E** and **G** was realized by ^{1}H-NMR and HMBC measurement of 4,5-dihydro-5-(2-thienyl)furan derivative **3e** (*Table 2*, *Entry 5*). The signal of H–C(5) of **3e** was observed at lower field than that of H–C(4), because H–C(5) is next to the ether O-atom. Moreover, C(4) correlated with the H_{ortho} atoms of the phenyl group of **3e**. This indicated that the phenyl group was attached to C(4) and the 2-thienyl group to C(5) of the dihydrofuran moiety. These results showed unambiguously that the isolated compound possessed structure **E** and that the addition of **B** to alkene **2b** followed *Pathway ii*.

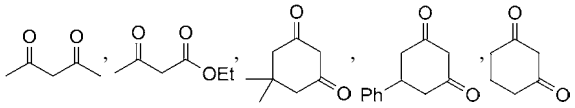
Treatment of **1a**–**1c** with **2a** gave 4,5-dihydrofuran derivatives **3a**–**3c**, while 2-[(1*E*)-phenylethenyl]thiophene (**2b**) gave **3d**, **3e**, and **3g** in slightly lower yields (*Table 2*, *Entries 1–3 vs. Entries 4*, *5*, and *7*). The higher efficiency of **2a** as compared to **2b** is due to the additional Me group of **2a**, which increases the stability of the intermediate carbocation of type **D**. Moreover, to determine the effect of the thienyl substituent on the carbocation stability, ethyl acetoacetate (=ethyl 3-oxobutanoate; **1b**) was treated with **2b** and (*E*)-stilbene (=1,1′-[(1*E*)-ethene-1,2-diylbis[benzene]; **2c**) leading to the formation of **3e** and **3f** in yields of 62 and 45%, respectively (*Table 2*, *Entry 5 vs. Entry 6*). Thus, the 2-thienyl group was stabilizing the intermediate carbocation **D** more efficiently than the phenyl group. On the other hand, although the phenyl and 2-thienyl substituents are in *trans*-position in alkene **2b**, the phenyl and 2-thienyl moieties turned in *cis*-position in 4,5-dihydro-4-phenyl-5-(2-thienyl)furans **3d**, **3e**, and **3g**–**3i**. Also in the case of **3f**, the two phenyl groups were *cis*-positioned. These results were established by the NOESY spectra.

The 3-[(1*E*)-1-methyl-2-phenylthenyl]thiophene (**2d**) used additionally in this study resembles **2a**, the main difference being that **2d** is a 3-substituted instead of a 2-substituted thiophene. The effect of the position of the S-atom on the stability of the intermediate carbocation (see *Scheme*) was thereby investigated. Radical cyclization reaction of **1a** with **2d** gave **3j** in 42% yield (*Table 3*). Similarly, treatment of **2d** with ethyl acetoacetate (**1b**) and dimedone (**1c**) produced 4,5-dihyro-4-phenyl-5-(3-thienyl)furans **3k** (58%) and **3l** (70%), respectively. The less electron-releasing nature of the 3-thienyl than of the 2-thienyl group [6] causes the decrease in the yields of **3j**–**3l** compared with those of **3a**–**3c**.

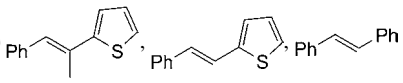
Conclusions. – Electron-rich thienyl-substituted alkenes **2a**–**2d** were used in the cyclization reactions with 1,3-diones **1a**–**1e** promoted by [$Mn(OAc)_3$]. Consequently, we established that the thienyl substituent of the alkenes affects the stability of the intermediate carbocation of type **D** *via* the vicinal heteroatom of the thiophene moiety thus increasing the yields of the products **3**. In other words, carbocations were formed adjacent to the electron-rich heteroaromatic subtituent (see **D** in *Scheme*). Also, (2-thienyl)- and (3-thienyl)-substituted alkenes **2a** and **2d** were compared to understand the involvement of the position of the S-atom on carbocation stability. Hence, the position of the substitution at the thiophene moiety of alkenes **2** influences the yields of the products **3**.

Table 2. *Reaction of 2-[(1*E*)-1-Methyl-2-phenylethenyl]thiophene* (**2a**)*, 2-[(1*E*)-2-Phenylethenyl)thiophene* (**2b**)*, and (*E*)-Stilbene* (**2c**) *with 1,3-Diones* **1**

Entry	1,3-Diones[a])	Alkene[b])	Product	Yield [%]
1	**1a**	**2a**	**3a** 	55
2	**1b**	**2a**	**3b** 	64
3	**1c**	**2a**	**3c** 	76
4	**1a**	**2b**	**3d** 	53
5	**1b**	**2b**	**3e** 	62
6	**1b**	**2c**	**3f** 	45
7	**1c**	**2b**	**3g** 	71
8	**1d**	**2b**	**3h** 	56
9	**1e**	**2b**	**3i** 	66

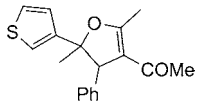
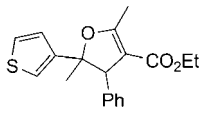
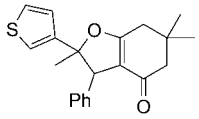
a) 

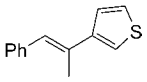
1a **1b** **1c** **1d** **1e**

b) 

2a **2b** **2c**

Table 3. *Reaction of 3-[(1E)-1-Methyl-2-phenylethenyl]thiophene* (**2d**) *with 1,3-Diones*

1,3-Dione[a])	Alkene[b])	Product	Yield [%]
1a	**2d**	**3j** 	42
1b	**2d**	**3k** 	58
1c	**2d**	**3l** 	70

[a]) See *Footnote a* of *Table 2*. [b])  **2d**

Experimental Part

General. Acetylacetone (= pentane-2,4-dione; **1a**), ethyl acetoacetate (= ethyl 3-oxobutanoate; **1b**), dimedone (= 5,5-dimethylcyclohexane-1,3-dione; **1c**), 5-phenylcyclohexane-1,3-dione (**1d**), and cyclohexane-1,3-dione (**1e**) are commercially available and were purchased from *Merck*. The 2-[(1*E*)-1-methyl-2-phenylethenyl]thiophene (**2a**) [7], 2-[(1*E*)-1-phenylethenyl)thiophene (**2b**) [8], (*E*)-stilbene (**2c**), and 3-[(1*E*)-1-methyl-2-phenylethenyl]thiophene (**2d**) were prepared as described in [9] (see below). All conjugated alkenes were freshly prepared before being used in the radical cyclizations. Column chromatography (CC): silica gel *60* (SiO_2, 40–60 μm; *Merck*). Prep. TLC: silica gel $PF_{254-366}$ (SiO_2; *Merck*), 2 mm thickness on 20 × 20 cm plates. TLC: aluminium-packed silica gel plates (SiO_2; *Merck*). M.p.: *Gallenkamp* capillary melting point apparatus. IR Spectra (KBr disc): *Matson-1000* FT-IR spectrometer; 400–4000 cm^{-1} range with 4 cm^{-1} resolution; $\tilde{\nu}$ in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *Bruker-DPX-400* MHz high performance digital FT-NMR spectrometer; at 400 (^1H) and 100 MHz (^{13}C); in $CDCl_3$; δ in ppm rel. to Me_4Si as internal standard, J in Hz; Tph = thienyl. MS: *Micromass-UK-Platform-II* spectrophotometer; in *m/z* (rel. %). Elemental analyses: *Leco 932 CHNS-O* instrument.

Substituted Alkenes **2a**–**2d**: *General Procedure*. NaH (22 mmol, in 60% mineral oil) was added to a soln. of benzyltriphenylphosphonium bromide (21 mmol) in anh. THF. This mixture was kept at 60° for 1 h, and then the corresponding ketone or aldehyde (20 mmol) was added dropwise under stirring and cooling in ice maintaining the temp. between 5° and 10°. The temp. was then rapidly raised to reflux temp. for 2 h and the mixture kept overnight at r.t. The precipitated NaBr was then removed by filtering through a funnel. The filtrate was concentrated, and the residue was extracted with hexane (5 × 20 ml). The org. phase was dried (Na_2SO_4), and concentrated, and the crude product purified by CC (hexane).

Dihydrofurans: General Procedure. Oxidative cyclization reactions were carried out with **1**/**2**/$[Mn(OAc)_3]\cdot 2\,H_2O$ in a molar ratio of 2:1:3. $[Mn(OAc)_3]\cdot 2\,H_2O$ (98%) was prepared electrochemically according to [10].

Thus, $[Mn(OAc)_3]\cdot 2\,H_2O$ (0.83 g, 3 mmol) in AcOH (20 ml) was heated under N_2 to 80° until it dissolved. Thereafter, the soln. was cooled to 60°, and a soln. of **1** (2 mmol) and **2** (1 mmol) in AcOH (5 ml) was added. The reaction was completed when the initial dark brown soln. had changed to red. H_2O (20 ml) was added and the mixture extracted with $CHCl_3$ (3 × 20 ml). The combined org. phase was neutralized with sat. $NaHCO_3$ soln., dried (Na_2SO_4) and concentrated and the crude product purified by CC or prep. TLC (SiO_2, hexane/AcOEt).

1-[4,5-Dihydro-2,5-dimethyl-4-phenyl-5-(2-thienyl)furan-3-yl]ethanone (**3a**): Yield 164 mg (55%). Yellow oil. IR: 3063, 3027 (arom. C–H), 2981, 2932 (aliph. C–H), 1699 (C=O), 1649 (C=C). ^{1}H-NMR: 7.26 – 7.41 (*m*, 5 arom. H, H–C(5) of Tph); 7.07 (*d*, *J* = 3.6, H–C(3) of Tph); 7.02 (*dd*, *J* = 5.0, 3.6, H–C(4) of Tph); 4.56 (*s*, H–C(4)); 2.47 (*d*, *J* = 1.3, Me–C(2)); 1.88 (*s*, MeCO–C(3)); 1.30 (*s*, Me–C(5)). ^{13}C-NMR: 195.6 (C=O); 168.3 (C(2)); 151.9; 139.3; 129.0; 127.9; 127.0; 124.4; 122.7; 115.4 (C(3)); 90.4 (C(5)); 61.2 (C(4)); 29.7; 26.1; 15.4. MS: 299 (9, $[M+H]^+$), 298 (23, M^+), 280 (6, $[M-H_2O]^+$), 255 (10, $[M-C_2H_3O]^+$), 172 (9, $[M-C_4H_3S-C_2H_3O]^+$), 111 (17, $C_5H_3OS^+$), 91 (6, $C_6H_5CH_2^+$), 83 (3, $C_4H_3S^+$), 77 (13, $C_6H_5^+$). Anal. calc. for $C_{18}H_{18}O_2S$ (298.40): C 72.5, H 6.1, S 10.8; found: C 72.3, H 6.0, S 10.6.

Ethyl 4,5-Dihydro-2,5-dimethyl-4-phenyl-5-(2-thienyl)furan-3-carboxylate (**3b**): Yield 210 mg (64%). Yellow oil. IR: 3063 (arom. C–H), 2988, 2928 (aliph. C–H), 1670 (C=C), 1598 (C=O). ^{1}H-NMR: 7.25 – 7.37 (*m*, 5 arom. H, H–C(5) of Tph); 7.08 (*d*, *J* = 3.6, H–C(3) of Tph); 7.02 (*dd*, *J* = 5.0, 3.6, H–C(4) of Tph); 4.54 (*s*, H–C(4)); 3.93 – 4.08 (*m*, MeC*H*$_2$O); 2.45 (*d*, *J* = 1.3, Me–C(2)); 1.31 (*s*, Me–C(5)); 1.02 (*t*, *J* = 7.1, *Me*CH$_2$O). ^{13}C-NMR: 167.9 (C=O); 165.8 (C(2)); 152.2; 139.7; 128.8; 128.5; 127.4; 127.0; 124.3; 122.6; 106.5 (C(3)); 90.1 (C(5)); 60.4; 59.6; 46.3; 26.2; 14.6; 14.3. MS: 329 (7, $[M+H]^+$), 328 (22, M^+), 313 (2, $[M-Me]^+$), 285 (8, $[M-C_3H_5O_2]^+$), 239 (12, $[M-C_7H_5]^+$), 128 (19, $C_{13}H_{12}S^+$), 111 (12, $C_5H_3OS^+$), 77 (13, $C_6H_5^+$), 43 (100, $C_3H_5O_2^+$). Anal. calc. for $C_{19}H_{20}O_3S$ (328.42): C 69.5, H 6.1, S 9.7; found: C 69.3, H 6.0, S 9.6.

*3,5,6,7-Tetrahydro-2,6,6-trimethyl-3-phenyl-2-(2-thienyl)benzofuran-4(2*H*)-one* (**3c**): Yield 257 mg (76%). Yellow oil. IR: 3022 (arom. C–H), 2955, 2922 (aliph. C–H), 1641 (C=O). ^{1}H-NMR: 7.28 – 7.35 (*m*, 4 arom. H); 7.13 – 7.15 (*m*, 1 arom. H, H–C(5) of Tph); 7.07 (*d*, *J* = 3.6, H–C(3) of Tph); 7.02 (*dd*, *J* = 5.0, 3.6, H–C(4) of Tph); 4.60 (*s*, H–C(3)); 2.57 (*dd*, *J* = 16.5, 2.0, H–C(7)); 2.32 (*s*, 2 H); 1.35 (*s*, Me–C(2)); 1.28 (*s*, Me–C(6)); 1.19 (*s*, Me–C(6)). MS: 339 (26, $[M+H]^+$), 338 (100, M^+), 323 (20, $[M-Me]^+$), 320 (6, $[M-H_2O]^+$), 254 (14, $[M-C_4H_4S]^+$), 212 (5, $[M-C_6H_6O]^+$), 178 (10, $[M-C_4H_3S-C_6H_5]^+$), 152 (12, $[M-C_{12}H_{10}S]^+$), 91 (18, $C_6H_5CH_2^+$), 83 (60, $C_4H_3S^+$), 77 (25, $C_6H_5^+$). Anal. calc. for $C_{21}H_{22}O_2S$ (338.46): C 74.5, H 6.6, S 9.5; found: C 74.4, H 6.7, S 9.4.

1-[4,5-Dihydro-2-methyl-4-phenyl-5-(2-thienyl)furan-3-yl]ethanone (**3d**): Yield 151 mg (53%). Yellow oil. IR: 3082, 3028 (arom. C–H), 2922 (aliph. C–H), 1754, 1716, 1670 (C=O). ^{1}H-NMR: 7.12 – 7.27 (*m*, 5 arom. H, H–C(5) of Tph); 6.92 (*d*, *J* = 3.1, H–C(3) of Tph); 6.89 (*dd*, *J* = 4.8, 3.6, H–C(4) of Tph); 5.42 (*d*, *J* = 5.3, H–C(5)); 4.36 (*d*, *J* = 5.3, H–C(4)); 2.33 (*s*, Me–C(2)); 1.81 (*s*, MeCO–C(3)). ^{13}C-NMR: 194.9 (C=O); 168.1 (C(2)); 143.4; 142.5; 129.1; 127.5; 127.3; 125.8; 125.2; 115.2 (C(3)); 87.7 (C(5)); 58.1 (C(4)); 29.6; 15.1. MS: 285 (1, $[M+H]^+$), 284 (2, M^+), 241 (2, $[M-C_2H_3O]^+$), 184 (1, $[M-C_5H_8O_2]^+$), 139 (0.5, $[M-C_{10}H_4O^+]$), 91 (1, $C_6H_5CH_2^+$), 83 (1, $C_4H_3S^+$), 77 (3, $C_6H_5^+$), 43 (100, $C_2H_3O^+$). Anal. calc. for $C_{17}H_{16}O_2S$ (284.37): C 71.8, H 5.7, S 11.3; found: C 71.7, H 5.6, S 11.2.

Ethyl 4,5-Dihydro-2-methyl-4-phenyl-5-(2-thienyl)furan-3-carboxylate (**3e**): Yield 195 mg (62%). Yellow oil. IR: 3055, 3022 (arom. C–H), 2922, 2853 (aliph. C–H), 1741 (C=O), 1702, 1648 (C=C). ^{1}H-NMR: 7.16 – 7.29 (*m*, 5 arom. H, H–C(5) of Tph); 6.98 (*d*, *J* = 3.3, H–C(3) of Tph); 6.93 (*dd*, *J* = 4.9, 3.3, H–C(4) of Tph); 5.54 (*d*, *J* = 5.5, H–C(5)); 4.36 (*d*, *J* = 5.5, H–C(4)); 3.90 – 4.00 (*m*, MeC*H*$_2$O); 2.33 (*s*, Me–C(2)); 0.99 (*t*, *J* = 7.1, *Me*CH$_2$O). MS: 315 (8, $[M+H]^+$), 314 (3, M^+), 268 (11, $[M-C_2H_5OH]^+$), 128 (7, $[M-C_6H_8O_3]^+$), 91 (4, $C_6H_5CH_2^+$), 83 (4, $C_4H_3S^+$), 77 (10, $C_6H_5^+$). Anal. calc. for $C_{18}H_{18}O_3S$ (314.40): C 68.8, H 5.8, S 10.2; found: C 68.7, H 5.7, S 10.1.

Ethyl 4,5-Dihydro-2-methyl-4,5-diphenylfuran-3-carboxylate (**3f**): Yield 139 mg (45%). Yellow oil. ^{1}H-NMR: 7.20 – 7.40 (*m*, 10 arom. H); 5.40 (*d*, *J* = 5.6, H–C(5)); 4.20 (*dd*, *J* = 5.6, 1.6, H–C(4)); 3.90 – 4.00 (*m*, MeC*H*$_2$O); 2.40 (*s*, Me–C(2)); 1.00 (*t*, *J* = 7.2, *Me*CH$_2$O). MS: 309 (100, $[M+H]^+$). Anal. calc. for $C_{20}H_{20}O_3$ (308.37): C 77.9, H 6.5; found: C 78.0, H 6.6.

*3,5,6,7-Tetrahydro-6,6-dimethyl-3-phenyl-2-(2-thienyl)benzofuran-4(2*H*)-one* (**3g**): Yield 230 mg (71%). Yellow oil. IR: 3053, 3020 (arom. C–H), 2953, 2872 (aliph. C–H), 1655 (C=O), 1631 (C=C). ^{1}H-NMR: 7.14 – 7.29 (*m*, 5 arom. H, H–C(5) of Tph); 7.01 (*d*, *J* = 3.4, H–C(3) of Tph); 6.95 (*dd*, *J* = 5.0, 3.5, H–C(4) of Tph); 5.68 (*d*, *J* = 5.4, H–C(2)); 4.43 (*d*, *J* = 5.4, H–C(3)); 2.41 (*dd*, *J* = 12.0, 2.0, H–C(7)); 2.23 (*s*, 2 H); 1.14 (*s*, Me–C(6)); 1.11 (s, Me–C(6)). ^{13}C-NMR: 193.6 (C=O); 175.6 (C(7a)); 143.1; 141.8; 129.1; 127.5; 127.3; 127.2; 126.5; 125.9; 114.9 (C(3a)); 90.6 (C(2)); 54.1; 51.5; 46.3; 38.3; 34.5; 29.0; 28.9. MS: 325 (1, $[M+H]^+$), 324 (3, M^+), 306 (2, $[M-H_2O]^+$), 291 (1, $[M-H_2O-CH_3]^+$), 233 (7, $[M-C_6H_5CH_2]^+$), 164 (3, $[M-C_6H_5-C_4H_3S]^+$), 111 (14, $C_5H_3OS^+$), 91 (11, $C_6H_5CH_2^+$), 83 (100, $C_4H_3S^+$). Anal. calc. for $C_{20}H_{20}O_2S$ (324.44): C 74.0, H 6.2, S 9.8; found: C 73.9, H 6.1, S 9.7.

*3,5,6,7-Tetrahydro-3,6-diphenyl-2-(2-thienyl)benzofuran-4(2*H*)-one* (**3h**): Yield 209 mg (56%). Pale yellow oil. IR: 3082, 3053 (arom. C–H), 2914, 2822 (aliph. C–H), 1635 (C=O). ^{1}H-NMR: 7.36 – 7.40 (*m*, 5 arom. H); 7.29 – 7.33 (*m*, 5 arom. H); 7.21 (*d*, *J* = 7.2, H–C(5) of Tph); 7.13 (*d*, *J* = 3.2, H–C(4) of Tph); 7.06 (*dd*, *J* = 3.2, 1.5, H–C(3) of Tph); 5.80 (*d*, *J* = 5.5, H–C(2)); 4.59 (*d*, *J* = 5.5, H–C(3)); 3.58 – 3.63 (*m*, H–C(6)); 2.69 – 2.90 (*m*, 4 H). ^{13}C-NMR: 193.2 (C=O); 175.6 (C(7a)); 142.7; 141.6; 141.3; 129.1; 127.6; 127.4; 127.3; 127.2; 127.0; 126.6; 126.3; 126.1; 116.3 (C(3a)); 90.8 (C(2)); 53.9; 44.5; 40.6; 32.0. MS: 373 (31, $[M+H]^+$), 372 (100, M^+), 354 (2, $[M-H_2O]^+$), 281 (6, $[M-C_6H_5CH_2]^+$), 226 (13, $[M-C_{10}H_{10}O]^+$), 186 (2, $C_{12}H_{10}S^+$), 91 (21, $C_6H_5CH_2^+$), 83 (2, $C_4H_3S^+$), 77 (32, $C_6H_5^+$). Anal. calc. for $C_{24}H_{20}O_2S$ (372.48): C 77.4, H 5.4, S 8.6; found: C 77.3, H 5.3, S 8.5.

*3,5,6,7-Tetrahydro-3-phenyl-2-(2-thienyl)benzofuran-4(2*H*)-one* (**3i**): Yield 196 mg (66%). Pale yellow oil. IR: 3026 (arom. C–H), 2945, 2888 (aliph. C–H), 1652 (C=C), 1633 (C=O). ^{1}H-NMR: 7.10 – 7.25 (*m*, 5 arom. H, H–C(5) of Tph); 6.98 (*d*, *J* = 3.4, H–C(3) of Tph); 6.92 (*dd*, *J* = 4.9, 3.4, H–C(4) of Tph); 5.61 (*d*, *J* = 5.7, H–C(2)); 4.40 (*d*, *J* = 5.7, H–C(3)); 2.40 – 2.60 (*m*, 2 H); 2.24 – 2.37 (*m*, 2 H); 2.07 – 2.01 (*m*, 2 H). MS: 297 (22, $[M+H]^+$), 296 (100, M^+), 278 (5, $[M-H_2O]^+$), 213 (8, $[M-C_4H_3S]^+$), 184 (17, $[M-C_5H_4OS]^+$), 110 (22, $C_{12}H_{10}S^+$), 91 (14, $C_6H_5CH_2^+$), 77 (28, $C_6H_5^+$). Anal. calc. for $C_{18}H_{16}O_2S$ (296.38): C 72.9, H 5.4, S 10.8; found: C 72.8, H 5.3, S 10.7.

1-[4,5-Dihydro-2,5-dimethyl-4-phenyl-5-(3-thienyl)furan-3-yl]ethanone (**3j**): Yield 125 mg (42%). Yellow oil. ^{1}H-NMR: 7.30 – 7.34 (*m*, 5 arom. H, H–C(5) of Tph); 7.18 (*dd*, *J* = 3.1, 1.5, H–C(2) of Tph); 7.11 (*dd*, *J* = 5.1, 1.5, H–C(4) of Tph); 4.40 (*s*, H–C(4)); 2.47 (*d*, *J* = 1.2, Me–C(2)); 1.81 (*s*, MeCO–C(3)); 1.19 (*s*, Me–C(5)). ^{13}C-NMR: 195.6 (C=O); 168.5 (C(2)); 149.0; 139.7; 129.0; 127.8; 127.0; 125.4; 124.9; 119.5 (C(3)); 92.1; 90.6; 60.2 (C(4)); 29.7; 25.4; 15.4. Anal. calc. for $C_{18}H_{18}O_2S$ (296.38): C 72.5, H 6.1, S 10.7; found: C 72.4, H 6.2, S 10.6.

Ethyl 4,5-Dihydro-2,5-dimethyl-4-phenyl-5-(3-thienyl)furan-3-carboxylate (**3k**): Yield 190 mg (58%). Pale yellow oil. ^{1}H-NMR: 7.15 – 7.36 (*m*, 5 arom. H, 2 H of Tph); 7.10 (*d*, *J* = 4.8, H–C(4)); 4.38 (*s*, H–C(4)); 3.85 – 4.03 (*m*, MeC*H*$_2$O); 2.44 (*s*, Me–C(2)); 1.20 (*s*, Me–C(5)); 0.96 (*t*, *J* = 7.2, *Me*CH$_2$O). Anal. calc. for $C_{19}H_{20}O_3S$ (328.42): C 69.5, H 6.1, S 9.8; found: C 69.4, H 6.2, S 9.7.

*3,5,6,7-Tetrahydro-2,6,6-trimethyl-3-phenyl-2-(3-thienyl)benzofuran-4(2*H*)-one* (**3l**). Yield 237 mg (70%). Yellow oil. ^{1}H-NMR: 7.16 – 7.39 (*m*, 5 arom. H, H–C(5) of Tph); 7.11 (*d*, *J* = 3.8, H–C(2) of Tph); 7.08 (*dd*, *J* = 5.2, 1.6, H–C(4) of Tph); 4.44 (*s*, H–C(3)); 2.55 (*d*, *J* = 17.6, H_b–C(7)); 2.46 (*dd*, *J* = 17.6, 2.4, H_a–C(7)); 2.27 (*s*, 2 H); 1.25 (*s*, Me–C(2)); 1.24 (*s*, Me–C(6)); 1.15 (*s*, Me–C(6)). ^{13}C-NMR: 194.1 (C=O); 175.8 (C(7a)); 148.3; 138.4; 128.7; 128.6; 127.5; 127.1; 124.9; 119.6 (C(3a)); 95.0 (C(2)); 94.1 (C(3)); 56.2; 51.5; 38.4; 34.3; 29.2; 29.1; 25.2. Anal. calc. for $C_{21}H_{22}O_2S$ (338.46): C 74.5, H 6.6, S 9.5; found: C 74.4, H 6.7, S 9.4.

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Received February 28, 2012