Radical Cyclization Reactions *via* Manganese(III) Acetate Leading to 2-Thienyl-Substituted Dihydrofuran Compounds

by **Emre Biçer***[a]), **Mehmet Yılmaz***[b]), **Melih Karataş**[a]), and **Ahmet Tarık Pekel**[a])

[a]) Department of Chemistry, Faculty of Science, Ankara University, TR-06100 Tandogan/Ankara (phone: +90-312-2126720/1428; e-mail: emre.bicer@mam.gov.tr)

[b]) Department of Chemistry, Faculty of Arts and Sciences, Kocaeli University, TR-41380 Umuttepe, Kocaeli (phone: +90-262-3032058; e-mail: mehmet.yilmaz@kocaeli.edu.tr)

The 2-thienyl-substituted 4,5-dihydrofuran derivatives **3**–**8** were obtained by the radical cyclization reaction of 1,3-dicarbonyl compounds **1a**–**1f** with 2-thienyl-substituted conjugated alkenes **2a**–**2e** by using $[Mn(OAc)_3]$ (*Tables 1–5*). In this study, reactions of 1,3-dicarbonyl compounds **1a**–**1e** with alkenes **2a**–**2c** gave 4,5-dihydrofuran derivatives **3**–**5** in high yields (*Tables 1–3*). Also the cyclic alkenes **2d** and **2e** gave the dihydrobenzofuran compounds, *i.e.*, **6** and **7** in good yields (*Table 4*). Interestingly, the reaction of benzoylacetone (=1-phenylbutane-1,3-dione; **1f**) with some alkenes gave two products due to generation of two stable carbocation intermediates (*Table 5*).

Introduction. – In the last three decades, oxidative cyclization reactions *via* transition metal salts (Mn^{3+}, Co^{3+} Cu^{2+}, Ce^{4+}) have been very popular in synthetic organic chemistry [1]. The distinctive properties of radical cyclization reactions have always been attractive to organic chemists. Therefore, cyclization reactions of enolizable 1,3-dicarbonyl compounds with unsaturated hydrocarbons leading to the formations of functionalized products such as furans [2], dihydrofurans [3], lactones [4], and lactams [5] in high yields have aroused much interest because of their potential to open ways to natural products [6].

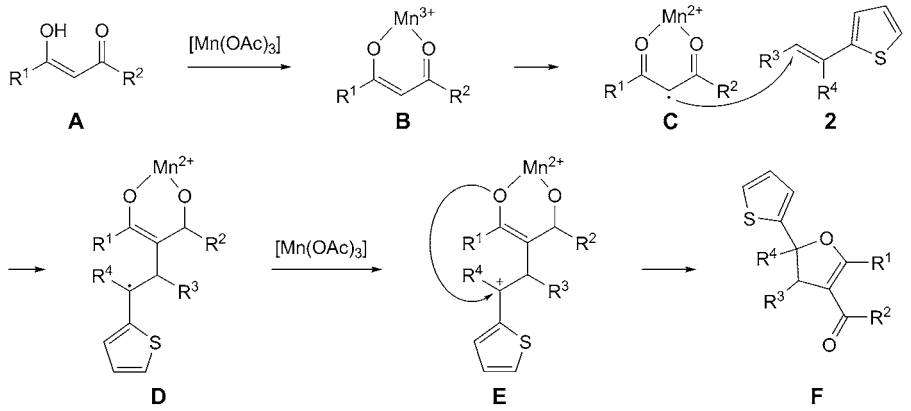
Recently, we have reported the formation of dihydrofuran and furan derivatives resulting from radical cyclizations of 1,3-dicarbonyl compounds with alkenes [7] and alkynes [8] by using $[Mn(OAc)_3]$. The radical cyclization reactions of 3-oxopropanenitriles with conjugated alkenes, substituted with phenyl and 2-thienyl groups [9], and with α,β-unsaturated amides [10] have been studied as well. And, in addition, 4,5-dihydrofuran-3-carbonitrile compounds have shown antifungal and antibacterial activity [11]. A study focused on the reactions of 3-oxopropanenitriles with 2-thienyl-substituted alkenes has been published [12]. Also, the reaction of 4-hydroxycoumarin (=4-hydroxy-2*H*-1-benzopyran-2-one) and 2-hydroxy-1,4-naphthoquinones with electron-rich alkenes has been reported [13].

Reactions of 1,3-dicarbonyl compounds with 2-thienyl-substituted conjugated alkenes have not been investigated so far. In this study, we describe the radical cyclization reactions of conjugated 2-thienyl-substituted alkenes **2a**–**2e** with various acyclic and cyclic 1,3-dicarbonyl compounds, mediated by $[Mn(OAc)_3]$. As a result of these reactions, 2-thienyl-substituted 4,5-dihydrofuran derivatives were obtained in high yields.

Results and Discussion. – In this study, 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**), cyclohexane-1,3-dione (**1e**), and benzoylacetone (= 1-phenylbutane-1,3-dione; **1f**) were used as 1,3-dicarbonyl compounds, and 2-(1-phenylethenyl)thiophene (**2a**), 2-[1-(4-methylphenyl)ethenyl]-thiophene (**2b**), 2-[1-(4-fluorophenyl)ethenyl]thiophene (**2c**), 2-(cyclohex-1-en-1-yl)thiophene (**2d**), and 2-(cyclopent-1-en-1-yl)thiophene (**2e**) were used as 2-thienyl-substituted alkenes (for formulas, see below, *Tables 1–5*). The thiophenes **2a**–**2e** were synthesized by elimination of H_2O from the corresponding alcohols, which, in turn, were prepared by *Grignard* reaction of the respective carbonyl compounds [9].

The mechanism of the cyclization reactions of 1,3-dicarbonyl compounds with 2-thienyl-substituted alkenes **2** is depicted in *Scheme 1*. First, [Mn^{III}-(enolato)] complex **B** is generated by the reaction of [$Mn(OAc)_3$] and enolizable 1,3-dicarbonyl compound **A**. Mn^{III} is then reduced to Mn^{II} by the uptake of an electron within **B**, whereby radical **C** is generated. After the addition of **C** to alkene **2**, radical intermediate **D** is oxidized by Mn^{III} to yield the carbocation **E**. Dihydrofuran **F** is then formed by cyclization.

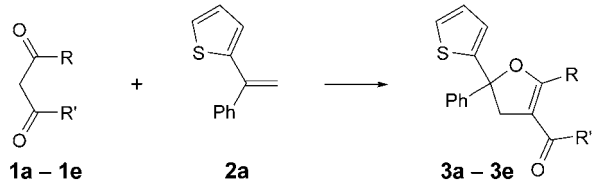
Scheme 1. *Mechanism of the Radical Cyclization Reaction* of *1,3-Dicarbonyl Compounds* **1a**–**1e** *with Alkenes* **2** *Mediated by* Mn^{III}



The reaction of 1,3-dicarbonyl compounds **1a**–**1e** with the 2-(1-arylethenyl)thiophenes **2a**–**2c** gave 2-thienyl-substituted dihydrofuran derivatives **3**–**5** in high yields (*Tables 1–3*). The characterization of these products was performed by ^{1}H-NMR spectroscopy. An *AB* system with $^2J = 14.4–14.8$ Hz was found for $CH_2(4)$ of the 4,5-dihydrofuran compounds **3a**, **3b**, **4a**, **5a**, and **5b**; the *AB* system was further split into a *q* by a ^5J coupling of 1.2–1.6 Hz with Me–C(2). This long-range coupling constant was confirmed by a COSY experiment with **3b**. Most of the 2-(2-thienyl)-substituted 3,5,6,7-tetrahydrobenzofuran-4(2*H*)-ones **3c**–**3e**, **4c**, **4d**, and **5c**–**5e**, obtained with the cyclic 1,3-dicarbonyl compounds **1c**–**1e**, showed similar patterns in the ^{1}H-NMR spectra.

For instance, the diastereotopic $CH_2(3)$ protons of **4c** at δ(H) 3.46 and 3.66 ($^2J_{AB} =$ 14.8 Hz) showed also a ^5J coupling of 2.0 Hz with $CH_2(7)$, and the signal of the diastereotopic $CH_2(7)$ protons appeared at δ(H) 2.41 as a *t* ($^5J = 2$ Hz). This ^5J was confirmed by a COSY experiment with **4b**. The yields of **5a**–**5e** in *Table 3* shows that a

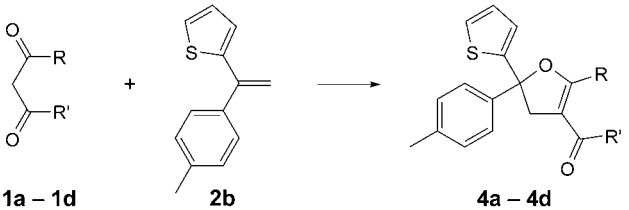
Table 1. *Reaction of 2-(1-Phenylethenyl)thiophene* (**2a**) *with 1,3-Dicarbonyl Compounds*



1a – 1e **2a** **3a – 3e**

1,3-Dione	R	R′	Product	Yield [%]
1a	Me	Me	**3a**	86
1b	Me	EtO	**3b**	89
1c		$–CH_2C(Me_2)CH_2–$	**3c**	91
1d		$–CH_2CH(Ph)CH_2–$	**3d**	81
1e		$–(CH_2)_3–$	**3e**	84

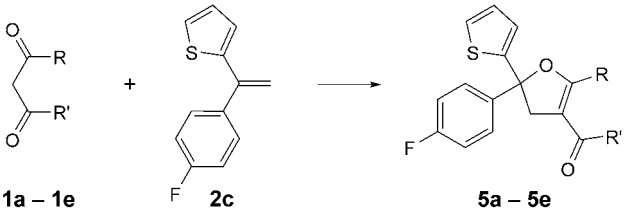
Table 2. *Reaction of 2-[1-(4-Methylphenyl)ethenyl]thiophene* (**2b**) *with 1,3-Dicarbonyl Compounds*



1a – 1d **2b** **4a – 4d**

1,3-Dione	R	R′	Product	Yield [%]
1a	Me	Me	**4a**	87
1b	Me	EtO	**4b**	89
1c		$–CH_2C(Me_2)CH_2–$	**4c**	96
1d		$–CH_2CH(Ph)CH_2–$	**4d**	93

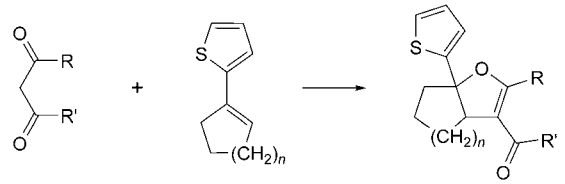
Table 3. *Reaction of 2-[1-(4-Fluorophenyl)ethenyl]thiophene* (**2c**) *with 1,3-Dicarbonyl Compounds*



1a – 1e **2c** **5a – 5e**

1,3-Dione	R	R′	Product	Yield [%]
1a	Me	Me	**5a**	100
1b	Me	EtO	**5b**	96
1c		$–CH_2C(Me_2)CH_2–$	**5c**	100
1d		$–CH_2CH(Ph)CH_2–$	**5d**	98
1e		$–(CH_2)_3–$	**5e**	100

Table 4. *Reaction of 2-(Cyclohex-1-en-1-yl)- and 2-(Cyclopent-1-en-1-yl)thiophene* (**2d** and **2e**, resp.) *with 1,3-Dicarbonyl Compounds*



1a – 1c, **1e** **2d** *n* = 2 **2e** *n* = 1 **6a – 6c** *n* = 2 **7a – 7c** *n* = 1

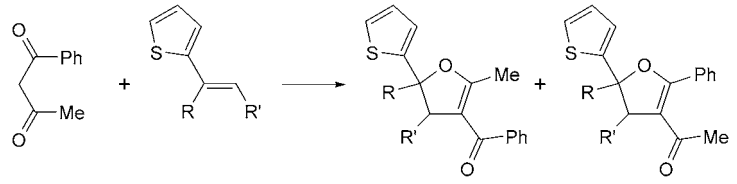
1,3-Dione	R	R′	Alkene	*n*	Product	Yield [%]
1a	Me	Me	**2d**	2	**6a**	61
1c	$-CH_2C(Me_2)CH_2-$		**2d**	2	**6b**	70
1e	$-(CH_2)_3-$		**2d**	2	**6c**	73
1a	Me	Me	**2e**	1	**7a**	80
1b	Me	EtO	**2e**	1	**7b**	86
1e	$-(CH_2)_3-$		**2e**	1	**7c**	89

p-fluoro substituent influences positively the Mn^{III}-promoted cyclization reactions, *i.e.*, the carbocation character of intermediate **E** (*Scheme 1*) is stabilized by the 4-fluoro substituent at the Ar ring (R^4), resulting in almost quantitative yields for the reaction of alkene **2c** with the 1,3-dicarbonyl compounds **1a** – **1e**.

Good yields were also realized with the cyclic alkenes **2d** and **2e** yielding **6a** – **6c** and **7a** – **7c**, respectively (*Table 4*). But the reactions with five-membered cycloalkene **2e** were more efficient than with the six-membered cycloalkene **2d**, which can be explained by the higher ring strain of **2e**.

Interestingly, treatment of benzoylacetone (**1f**) with $[Mn(OAc)_3]$ in the presence of an alkene **2** provided two products **8** (*Table 5*). A proposed mechanism for this reaction is displayed in *Scheme 2*. Thus, after addition of the radical form of the enolate to alkene **2**, an adduct radical intermediate is generated and then oxidized with 1 equiv. of

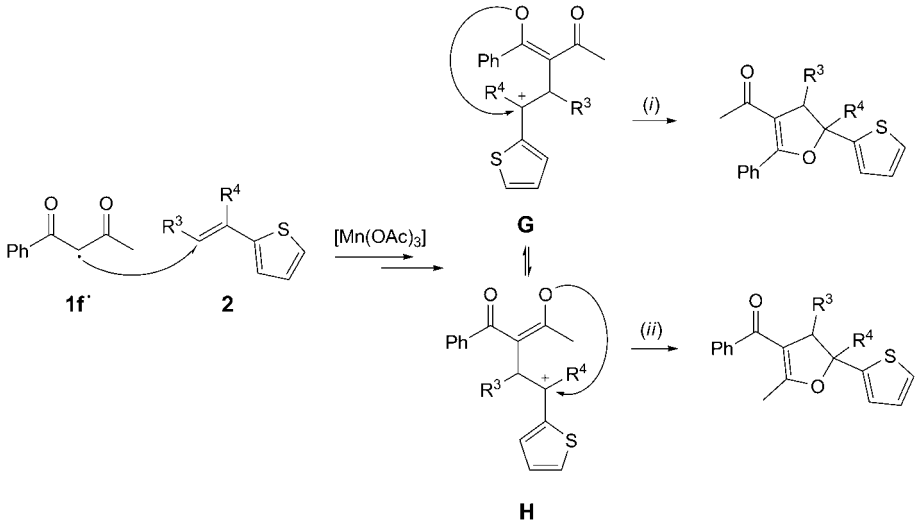
Table 5. *Reaction of 1-Phenylbutane-1,3-dione* (**1f**) *with Alkenes* **2**



1f **2a – 2d** **8a**, **8c**, **8e**, **8g** **8b**, **8d**, **8f**, **8h**

Alkene	R	R′	Product	Yield [%]	Product	Yield [%]
2a	Ph	H	**8a**	30	**8b**	54
2b	4-Me–C_6H_4	H	**8c**	33	**8d**	56
2c	4-F–C_6H_4	H	**8e**	38	**8f**	56
2d	$-(CH_2)_4-$		**8g**	34	**8h**	40

Scheme 2. *Mechanism of the Radical Cyclization Reaction of Benzoylacetone* (**1f**) *with Alkenes* **2**



Mn^{III} to the corresponding carbocation (*cf. Scheme 1*). Due to the fact that benzoylacetone has two enolic forms, two carbocations **G** and **H** are generated. After the ring closure, two dihydrofuran products are obtained, *i.e.*, a 2-phenyl-substituted dihydrofuran by pathway *i*, and a 2-methyl-substituted dihydrofuran by pathway *ii*.

The structures of the two products **8** obtained from each alkene **2** with **1f** were determined by the ^{1}H-NMR spectra. For instance, the difference of the coupling pattern of the diastereotopic CH_2(4) protons of **8a** and **8b** established their structures: **8a** exhibited 2 *dq* with $^2J_{AB} = 14.8$ Hz and $^5J = 1.6$ Hz, and **8b** just an *AB* system with $^2J_{AB} = 14.8$ Hz.

In conclusion, $[Mn(OAc)]_3$-mediated, radical cyclization reactions of acyclic and cyclic 1,3-dicarbonyl compounds **1** with 2-thienyl-subtituted alkenes **2** gave corresponding dihydrofuran compounds in good to excellent yields. Moreover, unexpected products were obtained in the reaction of alkenes **2** with benzoylacetone **1f**, *i.e.*, two different structures were formed due to two enolic forms of **1f**.

Experimental Part

General. All 1,3-dicarbonyl compounds and other reagents were purchased from *Merck*. Column chromatography (CC): silica gel (SiO_2 *60*, 40–60 μm; *Merck*). Prep. TLC: silica gel (SiO_2 $PF_{254-366}$ nm; *Merck*), 2 mm thickness on 20 × 20 cm plates. TLC: aluminium-packed silica gel plates (*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; in cm^{-1}. ^{1}H- (400 MHz) and ^{13}C-NMR (100 MHz) Spectra: *Bruker-DPX-400* high-performance digital FT-NMR spectrometer; in $CDCl_3$; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz; Tph = 2-thienyl. MS: *Waters-2695-Alliance* HPLC/*Waters-Micromass-2Q* (ESI method) and *Micromass-UK-Platform II* (EI-MS method) spectrometers; in *m*/*z* (rel. %). Elemental analyses: *Leco-932-CHNS-O* instrument.

Dihydrofurans by Oxidative Cyclization Reactions. Oxidative cyclization reactions were carried out with **1**/**2**/$[Mn(OAc)_3]$ in a molar ratio 2 : 1 : 3. $[Mn(OAc)_3] \cdot 2\ H_2O$ (98%) was prepared electrochemically according to [14].

Thus, $[Mn(OAc)_3]\cdot 2\,H_2O$ (0.83 g, 3 mmol) in AcOH (20 ml) was heated under N_2 at 80° until it dissolved. Then, the soln. was cooled to 50°, and a soln. of **1** (2 mmol) and **2** (1 mmol) in AcOH (3 ml) was added. The reaction was completed when the dark brown color of the 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 by washing 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-methyl-5-phenyl-5-(2-thienyl)furan-3-yl]ethanone (**3a**): Yield 244.2 mg (86%). Yellow oil. IR: 3065, 3028 (arom. C–H), 2920, 2864 (aliph. C–H), 1674 (C=O), 1623 (C=C). ^{1}H-NMR: 7.48–7.28 (*m*, Ph, H–C(5) of Tph); 6.96 (*dd*, $J=5.0, 3.6$, H–C(4) of Tph); 6.92 (*dd*, $J=3.6, 1.2$, H–C(3) of Tph); 3.82 (*dq*, $J=14.5, 1.5$, H_a–C(4)); 3.62 (*dq*, $J=14.5, 1.5$, H_b–C(4)); 2.39 (*t*, $J=1.5$, Me–C(2)); 2.27 (*s*, MeCO–C(3)). ^{13}C-NMR: 194.0 (C=O); 165.5 (C(2)); 149.2; 144.6; 128.4; 127.9; 126.6; 125.8; 125.8; 125.4; 112.1 (C(3)); 89.3 (C(5)); 46.4; 29.4; 15.1. MS: 285 (1.5, $[M+H]^+$), 284 (6, M^+), 266 (2, $[M-H_2O]^+$), 241 (14, $[M-C_2H_3O]^+$), 201 (1, $[M-C_4H_3O]^+$), 184 (1, $[C_5H_8O_2]^+$), 91 (1, $[C_6H_5CH_2]^+$), 83 (0.5, $[C_4H_3S]^+$). Anal. calc. for $C_{17}H_{16}O_2S$: C 71.8, H 5.7, S 11.3; found: C 71.9, H 5.6, S 11.4.

Ethyl 4,5-Dihydro-2-methyl-5-phenyl-5-(2-thienyl)furan-3-carboxylate (**3b**): Yield 279.5 mg (89%). Yellow oil. IR: 3063, 3029 (arom. C–H), 2979, 2928 (aliph. C–H), 1698 (C=O), 1654 (C=C). ^{1}H-NMR: 7.41–7.20 (*m*, Ph, H–C(5) of Tph); 6.89 (*dd*, $J=5.0, 3.6$, H–C(4) of Tph); 6.86 (*dd*, $J=3.6, 1.2$, H–C(3) of Tph); 4.12 (*q*, $J=7.1$, MeCH_2O); 3.69 (*dq*, $J=14.7, 1.5$, H_a–C(4)); 3.48 (*dq*, $J=14.7, 1.5$, H_b–C(4)); 2.29 (*t*, $J=1.5$, Me–C(2)); 1.23 (*t*, $J=7.1$, *Me*CH_2O). ^{13}C-NMR: 166.2 (C=O); 165.9 (C(2)); 149.8; 145.1; 128.5; 128.0; 126.8; 125.9; 125.5; 102.0 (C(3)); 89.5 (C(5)); 59.9; 46.0; 14.7; 14.5. MS: 314 (4, M^+), 313 (14, $[M-H]^+$), 187 (5, $[M-C_4H_3S-C_2H_3O-H]^+$). Anal. calc. for $C_{18}H_{18}O_3S$: C 68.8, H 5.8, S 10.2; found: C 68.9, H 5.7, S 10.1.

*3,5,6,7-Tetrahydro-6,6-dimethyl-2-phenyl-2-(2-thienyl)benzofuran-4(2*H*)-one* (**3c**): Yield 294.8 mg (91%). Yellow oil. IR: 3096, 3063 (arom. C–H), 2955, 2930 (aliph. C–H), 1641 (C=O). ^{1}H-NMR: 7.40–7.21 (*m*, Ph, H–C(5) of Tph); 6.87 (*dd*, $J=5.0, 3.6$, H–C(4) of Tph); 6.81 (*dd*, $J=3.6, 1.2$, H–C(3) of Tph); 3.64 (*dt*, $J=14.7, 1.8$, H_a–C(3)); 3.41 (*dt*, $J=14.7, 1.8$, H_b–C(3)); 2.37 (*s*, 2 H); 2.20 (*s*, 2 H); 1.08 (*s*, Me–C(6)); 1.06 (*s*, Me–C(6)). MS: 325 (100, $[M+H]^+$), 306 (1, $[M-H_2O]^+$), 241 (27, $[M-C_4H_3S]^+$), 211 (1, $[M-C_4H_4S-C_2H_5]^+$). Anal. calc. for $C_{20}H_{20}O_2S$: C 74.0, H 6.2, S 9.9; found: C 73.8, H 6.3, S 9.8.

*3,5,6,7-Tetrahydro-2,6-diphenyl-2-(2-thienyl)benzofuran-4(2*H*)-one* (**3d**): Yield 301.3 mg (81%). Light yellow oil. IR: 3061, 3029 (arom. C–H), 2948, 2902 (aliph. C–H), 1770 (C=C), 1641 (C=O). ^{1}H-NMR: 7.48–7.27 (*m*, 2 Ph, H–C(5) of Tph); 6.99–6.93 (*m*, 2 H of Tph); 3.76 (*d*, $J=13.7$, H_a–C(3)); 3.57–3.51 (*m*, 2 H); 2.91–2.84 (*m*, 2 H); 2.75–2.67 (*m*, 2 H). ^{13}C-NMR: 198.8 (C=O); 167.6 (C(7a)); 146.7; 144.3; 128.7; 128.4; 127.5; 127.4; 127.0; 126.9; 126.6; 126.5; 126.2; 126.0; 125.6; 113.0 (C(3a)); 93.8 (C(2)); 40.1; 31.8. MS: 372 (10, M^+), 354 (14, $[M-H_2O]^+$), 267 (2, $[M-C_8H_9]^+$), 226 (7, $[M-C_{10}H_{10}O]^+$), 186 (7, $[M-C_{12}H_{12}S]^+$), 104 (18, $[C_8H_8]^+$), 84 (22, $[C_4H_4S]^+$), 69 (13, $[C_4H_3O]^+$), 43 (100, $[C_3H_7]^+$). Anal. calc. for $C_{24}H_{20}O_2S$: C 77.4, H 5.4, S 8.6; found: C 77.5, H 5.4, S 8.5.

*3,5,6,7-Tetrahydro-2-phenyl-2-(2-thienyl)benzofuran-4(2*H*)-one* (**3e**): Yield 248.6 mg (84%). Light yellow oil. IR: 3067 (arom. C–H), 2946, 2869 (aliph. C–H), 1673 (C=C), 1605 (C=O). ^{1}H-NMR: 7.46–7.29 (*m*, Ph, H–C(5) of Tph); 6.96 (*dd*, $J=5.0, 3.6$, H–C(4) of Tph); 6.92 (*dd*, $J=3.6, 1.2$, H–C(3) of Tph); 3.73 (*dt*, $J=14.8, 1.7$, H_a–C(3)); 3.50 (*dt*, $J=14.8, 1.7$, H_b–C(3)); 2.61–2.55 (*m*, 2 H); 2.45–2.39 (*m*, 2 H); 2.15–2.07 (*m*, 2 H). ^{13}C-NMR: 196.0 (C=O); 175.5 (C(7a)); 148.9; 144.4; 128.6; 128.3; 126.9; 126.4; 125.9; 125.5; 117.8; 112.9 (C(3a)); 93.2 (C(2)); 42.3; 36.7; 24.2; 21.9. MS: 297 (8, $[M+H]^+$), 296 (28, M^+), 278 (75, $[M-H_2O]^+$), 268 (19, $[M-C_2H_4]^+$), 212 (17, $[M-C_4H_4S]^+$), 184 (16, $[C_{12}H_8S]^+$), 171 (40, $[C_7H_9O_2]^+$), 84 (5, $[C_4H_4S]^+$), 77 (28, $[C_6H_5]^+$). Anal. calc. for $C_{18}H_{16}O_2S$: C 72.9, H 5.4, S 10.8; found: C 72.8, H 5.3, S 10.9.

4,5-Dihydro-1-[2-methyl-5-(4-methylphenyl)-5-(2-thienyl)furan-3-yl]ethanone (**4a**): Yield 259.3 mg (87%). Brownish yellow oil. IR: 3090, 3015 (arom. C–H), 2924, 2866 (aliph. C–H), 1673 (C=O), 1621 (C=C). ^{1}H-NMR: 7.32 (*d*, $J=8.4$, 2 arom. H); 7.25 (*dd*, $J=5.2, 1.2$, H–C(5) of Tph); 7.17 (*d*, $J=8.4$, 2 arom. H); 6.92 (*dd*, $J=5.2, 3.6$, H–C(4) of Tph); 6.88 (*dd*, $J=3.6, 1.2$, H–C(3) of Tph); 3.76 (*dq*, $J=14.4, 1.6$, H_a–C(4)); 3.57 (*dq*, $J=14.4, 1.6$, H_b–C(4)); 2.35 (*s*, 6 H); 2,22 (*d*, $J=1.6$, Me–C(2)). LC/ESI-MS: 299 (100, $[M+H]^+$). Anal. calc. for $C_{18}H_{18}O_2S$: C 72.5, H 6.1, S 10.7; found: C 72.4, H 6.2, S 10.8.

Ethyl 4,5-Dihydro-2-methyl-5-(4-methylphenyl)-5-(2-thienyl)furan-3-carboxylate (**4b**): Yield 291.9 mg (89%). Yellow oil. IR: 2972, 2924 (aliph. C–H), 1697 (C=O), 1652 (C=C). ^{1}H-NMR: 7.33 (*d*, *J* = 8.4, 2 arom. H); 7.25 (*dd*, *J* = 5.6, 1.6, H–C(5) of Tph); 7.17 (*d*, *J* = 8.4, 2 arom. H); 6.92 (*dd*, *J* = 5.6, 3.2, H–C(4) of Tph); 6.90 (*dd*, *J* = 3.2, 1.6, H–C(3) of Tph); 4.16 (*q*, *J* = 7.2, MeC*H*$_2$O); 3.70 (*dq*, *J* = 14.4, 1.2, H$_a$–C(4)); 3.51 (*dq*, *J* = 14.4, 1.2, H$_b$–C(4)); 2.35 (*s*, *Me*C$_6$H$_4$); 2.33 (*t*, *J* = 1.2, Me–C(2)); 1.27 (*t*, *J* = 7.2, *Me*CH$_2$O). LC/ESI-MS: 329 (100, $[M+H]^+$). Anal. calc. for $C_{19}H_{20}O_3S$: C 69.5, H 6.1, S 9.8; found: C 69.6, H 6.0, S 9.7.

*3,5,6,7-Tetrahydro-6,6-dimethyl-2-(4-methylphenyl)-2-(2-thienyl)benzofuran-4(2*H*)-one* (**4c**): Yield 324.5 mg (96%). Yellow oil. IR: 3029 (arom. C–H), 2949, 2874 (aliph. C–H), 1641 (C=O). ^{1}H-NMR: 7.28–7.30 (*m*, 2 arom. H); 7.26 (*dd*, *J* = 4.8, 1.6, H–C(5) of Tph); 7.16–7.18 (*m*, 2 arom. H); 6.92 (*dd*, *J* = 4.8, 3.6, H–C(4) of Tph); 6.86 (*dd*, *J* = 3.6, 1.6, H–C(3) of Tph); 3.66 (*dt*, *J* = 14.8, 2.0, H$_a$–C(3)); 3.46 (*dt*, *J* = 14.8, 2.0, H$_b$–C(3)); 2.41 (*t*, *J* = 2.0, 2 H); 2.35 (*s*, *Me*C$_6$H$_4$); 2.25 (*s*, 2 H); 1.13 (*s*, Me–C(6)); 1.11 (*s*, Me–C(6)). ^{13}C-NMR: 194.8 (C=O); 174.4 (C(7a)); 149.2; 141.4; 138.1; 129.3; 126.8; 126.2; 125.8; 125.5; 111.5 (C(3a)); 93.5 (C(2)); 51.2; 42.2; 38.1; 34.5; 29.0; 28.9; 21.3. LC/ESI-MS: 339 (100, $[M+H]^+$). Anal. calc. for $C_{21}H_{22}O_2S$: C 74.5, H 6.6, S 9.5; found: C 74.4, H 6.5, S 9.6.

*3,5,6,7-Tetrahydro-2-(4-methylphenyl)-6-phenyl-2-(2-thienyl)benzofuran-4(2*H*)-one* (**4d**): Yield 358.9 mg (93%). Yellow oil. IR: 3026 (arom. C–H), 2936, 2870 (aliph. C–H), 1629 (C=O). ^{1}H-NMR: 7.25–7.36 (*m*, 8 arom. H); 7.18–7.20 (*m*, 2 arom. H); 6.89–6.96 (*m*, 2 H of Tph); 3.67–3.74 (*m*, H$_a$–C(3)); 3.46–3.53 (*m*, 2 H); 2.77–2.83 (*m*, 2 H); 2.61–2.66 (*m*, 2 H); 2.36 (*Me*C$_6$H$_4$). LC/ESI-MS: 387 (100, $[M+H]^+$). Anal. calc. for $C_{25}H_{22}O_2S$: C 77.7, H 5.7, S 8.3; found: C 77.8, H 5.6, S 8.3.

1-[5-(4-Fluorophenyl)-4,5-dihydro-2-methyl-5-(2-thienyl)furan-3-yl]ethanone (**5a**): Yield 302 mg (100%). Yellow oil. IR: 3071 (arom. C–H), 1675 (C=O), 1614 (C=C). ^{1}H-NMR: 7.37–7.40 (*m*, 2 arom. H); 7.24–7.26 (*m*, H–C(5) of Tph); 7.00–7.04 (*m*, 2 arom. H); 6.91 (*dd*, *J* = 5.2, 4.0, H–C(4) of Tph); 6.86 (*dd*, *J* = 4.0, 1.2, H–C(3) of Tph); 3.78 (*dq*, *J* = 14.4, 1.2, H$_a$–C(4)); 3.52 (*dq*, *J* = 14.4, 1.2, H$_b$–C(4)); 2.33 (*d*, *J* = 1.2, Me–C(2)); 2.22 (*s*, MeCO–C(3)). ^{13}C-NMR: 194.2 (C=O); 165.6 (C(2)); 163.7; 149.2; 140.7; 140.6; 127.4; 127.3; 126.9; 126.2; 125.6; 115.6; 115.3; 112.4 (C(3)); 89.1 (C(5)); 46.6; 29.6; 15.3. LC/ESI-MS: 303 (100, $[M+H]^+$). Anal. calc. for $C_{17}H_{15}FO_2S$: C 67.5, H 5.0, F 6.3, S 10.6; found: C 67.6, H 5.1, F 6.2, S 10.5.

Ethyl 5-(4-Fluorophenyl)-4,5-dihydro-2-methyl-5-(2-thienyl)furan-3-carboxylate (**5b**): Yield 318.7 mg (96%). Yellow oil. IR: 3098 (arom. C–H), 2974, 2916, 2857 (aliph. C–H), 1693 (C=O), 1644 (C=C). ^{1}H-NMR: 7.39–7.42 (*m*, 2 arom. H); 7.25 (*dd*, *J* = 4.8, 1.6, H–C(5) of Tph); 7.03–7.00 (*m*, 2 arom. H); 6.92 (*dd*, *J* = 4.8, 3.6, H–C(4) of Tph); 6.89 (*dd*, *J* = 3.6, 1.6, H–C(3) of Tph); 4.18 (*q*, *J* = 7.2, MeC*H*$_2$O); 3.74 (*dq*, *J* = 14.4, 1.6, H$_a$–C(4)); 3.48 (*dq*, *J* = 14.8, 1.6, H$_b$–C(4)); 2.33 (*d*, *J* = 1.6, Me–C(2)); 1.28 (*t*, *J* = 7.2, *Me*CH$_2$O). ^{13}C-NMR: 166.1 (C=O); 165.7 (C(2)); 163.7; 161.2; 149.5; 127.5; 126.9; 126.1; 125.5; 115.5; 102.0 (C(3)); 89.1 (C(5)); 59.9; 46.0; 29.9; 14.4. LC/ESI-MS: 333 (100, $[M+H]^+$). Anal. calc. for $C_{18}H_{17}FO_3S$: C 65.0, H 5.2, F 5.7, S 9.6; found: C 65.1, H 5.1, F 5.7, S 9.5.

*2-(4-Fluorophenyl)-3,5,6,7-tetrahydro-6,6-dimethyl-2-(2-thienyl)benzofuran-4(2*H*)-one* (**5c**): Yield 342 mg (100%). Yellow oil. IR: 3111, 3071 (arom. C–H), 2943 (aliph. C–H), 1641 (C=O). ^{1}H-NMR: 7.37–7.41 (*m*, 2 arom. H); 7.30 (*dd*, *J* = 5.2, 1.2, H–C(5) of Tph); 7.03–7.08 (*m*, 2 arom. H); 6.94 (*dd*, *J* = 5.2, 3.6, H–C(4) of Tph); 6.86 (*dd*, *J* = 3.6, 1.2, H–C(3) of Tph); 3.69 (*dt*, *J* = 14.4, 2.0, H$_a$–C(3)); 3.43 (*dt*, *J* = 14.4, 2.0, H$_b$–C(3)); 2.42 (*t*, *J* = 2.0, 2 H); 2.27 (*d*, *J* = 2.0, 2 H); 1.14 (*s*, Me–C(6)); 1.12 (*s*, Me–C(6)). LC/ESI-MS: 343 (100, $[M+H]^+$). Anal. calc. for $C_{20}H_{19}FO_2S$: C 70.2, H 5.6, F 5.5, S 9.4; found: C 70.3, H 5.5, F 5.5, S 9.5.

*2-(4-Fluorophenyl)-3,5,6,7-tetrahydro-6-phenyl-2-(2-thienyl)benzofuran-4(2*H*)-one* (**5d**): Yield 383.2 mg (98%). Light yellow oil. IR: 3065, 3028 (arom. C–H), 2943 (aliph. C–H), 1639 (C=O). ^{1}H-NMR: 7.35–7.42 (*m*, 2 arom. H); 7.30–7.33 (*m*, 3 arom. H); 7.28–7.20 (*m*, 3 arom. H); 7.00–7.06 (*m*, 2 arom. H); 6.89–6.93 (*m*, 2 H of Tph); 3.71 (*dt*, *J* = 14.2, 1.4, H$_a$–C(3)); 3.44–3.49 (*m*, 2 H); 2.76 (*m*, 2 H); 2.62 (*m*, 2 H). ^{13}C-NMR: 193.9 (C=O); 174.4 (C(7a)); 163.8; 161.4; 148.5; 142.7; 140.2; 129.1; 127.6; 127.4; 127.0; 126.8; 126.0; 115.6; 112.8 (C(3a)); 93.2 (C(2)); 44.2; 42.4; 40.6; 31.7; 21.2; 14.5. LC/ESI-MS: 391 (100, $[M+H]^+$). Anal. calc. for $C_{24}H_{20}FO_2S$: C 73.6, H 5.1, F 4.9, S 8.2; found: C 73.5, H 5.2, F 4.8, S 8.1.

*2-(4-Fluorophenyl)-3,5,6,7-tetrahydro-2-(2-thienyl)benzofuran-4(2*H*)-one* (**5e**): Yield 314 mg (100%). Yellow oil. IR: 3105, 3080 (arom. C–H), 2951, 2866 (aliph. C–H), 1637 C=O. ^{1}H-NMR:

7.35 – 7.40 (*m*, 2 arom. H); 7.23 (*dd*, *J* = 4.8, 1.2, H–C(5) of Tph); 7.00 (*dd*, *J* = 8.4, 2.0, 2 arom. H); 6.88 (*dd*, *J* = 4.8, 3.4, H–C(4) of Tph); 6.85 (*dd*, *J* = 3.4, 1.2, H–C(3) of Tph); 3.65 (*dt*, *J* = 14.8, 2.0, H_a–C(3)); 3.38 (*dt*, *J* = 14.8, 2.0, H_b–C(3)); 2.49 – 2.52 (*m*, 2 H), 2.30 – 2.35 (*m*, 2 H), 2.03 – 2.10 (*m*, 2 H). ^{13}C-NMR: 195.4 (C=O); 175.2 (C(7a)); 163.7; 161.3; 148.6; 140.3; 127.5; 127.4; 127.0; 126.6; 125.9; 115.6; 115.4; 112.8 (C(3a)); 92.7 (C(2)); 42.4; 36.7; 24.2; 21.9. LC/ESI-MS: 315 (100, $[M+H]^+$). Anal. calc. for $C_{18}H_{15}FO_2S$: C 68.8, H 4.8, F 6.0, S 10.2; found: C 68.9, H 4.9, F 6.1, S 10.1.

1-[3a,4,5,6,7,7a-Hexahydro-2-methyl-7a-(2-thienyl)benzofuran-3-yl]ethanone (**6a**): Yield 159.8 mg (61%). Light yellow oil. IR: 2936, 2862 (aliph. C–H), 1616 (C=O). ^{1}H-NMR: 7.13 (*dd*, *J* = 4.8, 1.2, H–C(5) of Tph); 6.95 (*dd*, *J* = 4.6, 3.6, H–C(4) of Tph); 6.89 (*dd*, *J* = 3.6, 1.2, H–C(3) of Tph); 3.33 (*t*, *J* = 6.4, H–C(3a)); 2.22 (*s*, MeCO–C(3)); 2.19 (*s*, Me–C(2)); 2.00 – 2.07 (*m*, 2 H); 1.88 – 1.96 (*m*, 2 H); 1.51 – 1.60 (*m*, 2 H); 1.36 – 1.46 (*m*, 2 H). LC/ESI-MS: 263 (100, $[M+H]^+$). Anal. calc. for $C_{15}H_{18}O_2S$: C 68.7, H 6.9, S 12.2; found: C 68.6, H 6.8, S 12.3.

*3,4,5a,6,7,8,9,9a-Octahydro-3,3-dimethyl-5a-(2-thienyl)dibenzofuran-1(2*H*)-one* (**6b**): Yield 211.4 mg (70%). Yellow oil. IR: 2934 (aliph. C–H), 1637 (C=O). ^{1}H-NMR: 7.24 (*dd*, *J* = 5.2, 1.2, H–C(5) of Tph); 7.04 (*dd*, *J* = 3.6, 1.2, H–C(3) of Tph); 6.97 (*dd*, *J* = 5.0, 3.2, H–C(4) of Tph); 3.52 (*t*, *J* = 6.0, H–C(9a)); 2.32 (*d*, *J* = 1.6, 2 H); 2.23 (*s*, 2 H); 2.11 – 2.20 (*m*, 2 H); 1.88 – 1.93 (*m*, 2 H); 1.55 – 1.58 (*m*, 2 H); 1.45 – 1.49 (*m*, 2 H); 1.13 (*s*, Me–C(3)); 1.10 (*s*, Me–C(3)). ^{13}C-NMR: 195.2 (C=O); 175.3 (C(4a)); 149.5; 127.0; 124.9; 123.5; 115.4 (C(9b)); 92.4 (C(5a)); 51.5; 45.7; 38.3; 34.4; 34.0; 29.2; 28.6; 24.1; 18.7; 18.6. LC/ESI-MS: 303 (100, $[M+H]^+$). Anal. calc. for $C_{18}H_{22}O_2S$: C 71.2, H 7.3, S 10.6; found: C 71.3, H 7.2, S 10.7.

*3,4,5a,6,7,8,9,9a-Octahydro-5a-(2-thienyl)dibenzofuran-1(2*H*)-one* (**6c**): Yield 200.0 mg (73%). Yellow oil. IR: 3098, 3074 (arom. C–H), 2940, 2864 (aliph. C–H), 1635 (C=O). ^{1}H-NMR: 7.40 (*dd*, *J* = 5.2, 1.2, H–C(5) of Tph); 7.04 (*dd*, *J* = 3.8, 1.2, H–C(3) of Tph); 6.97 (*dd*, *J* = 5.0, 3.8, H–C(4) of Tph); 3.51 (*tt*, *J* = 6.0, 1.2, H–C(9a)); 2.45 – 2.52 (*m*, 2 H); 2.31 – 2.37 (*m*, 2 H); 2.11 – 2.15 (*m*, 2 H); 2.02 – 2.07 (*m*, 2 H); 1.85 – 1.98 (*m*, 2 H); 1.50 – 1.65 (*m*, 2 H); 1.40 – 1.48 (*m*, 2 H). LC/ESI-MS: 274 (100, $[M+H]^+$). Anal. calc. for: $C_{16}H_{18}O_2S$: C 70.0, H 6.6, S 11.7; found: C 70.1, H 6.5, S 11.8.

*1-[3a,5,6,6a-Tetrahydro-2-methyl-6a-(2-thienyl)-4*H*-cyclopenta[*b*]furan-3-yl]ethanone* (**7a**): Yield 198.4 mg (80%). Light yellow oil. IR: 2953 (aliph. C–H), 1666 (C=O), 1598 (C=C). ^{1}H-NMR: 7.23 (*dd*, *J* = 4.8, 1.6, H–C(5) of Tph); 6.95 – 6.99 (*m*, 2 H of Tph); 3.67 (*d*, *J* = 8.8, H–C(3a)); 2.40 (*dd*, *J* = 13.4, 8.6, H–C(4)); 2.79 (*d*, *J* = 1.6, Me–C(2)); 2.22 (*s*, MeCO–C(3)); 2.01 – 2.17 (*m*, 2 H); 1.80 – 1.85 (*m*, 2 H); 1.67 – 1.71 (*m*, 1 H). LC/ESI-MS: 249 (100, $[M+H]^+$). Anal. calc. for $C_{14}H_{16}O_2S$: C 67.7, H 6.5, S 12.9; found: C 67.6, H 6.4, S 13.0.

*Ethyl 3a,5,6,6a-Tetrahydro-2-methyl-6a-(2-thienyl)-4*H*-cyclopenta[*b*]furan-3-carboxylate* (**7b**): Yield 239.1 mg (86%). Yellow oil. IR: 2961, 2870 (aliph. C–H), 1695 (C=O), 1644 (C=C). ^{1}H-NMR: 7.21 (*dd*, *J* = 5.0, 1.6, H–C(5) of Tph); 6.98 (*dd*, *J* = 5.0, 3.6, H–C(4) of Tph); 6.94 (*dd*, *J* = 3.4, 1.6, H–C(3) of Tph); 4.10 – 4.21 (*m*, MeCH_2O); 3.63 (*d*, *J* = 8.0, H–C(3a)); 2,40 (*dd*, *J* = 13.6, 7.8, H–C(4)); 2.25 (*d*, *J* = 1.4, Me–C(2)); 2.05 – 2.15 (*m*, 1 H); 1.85 – 2.00 (*m*, 2 H); 1.75 – 1.81 (*m*, 1 H); 1.63 – 1.73 (*m*, 1 H); 1.30 (*t*, *J* = 6.8, *Me*CH_2O). ^{13}C-NMR: 167.5 (C=O); 166.2 (C(2)); 148.4; 122.8; 124.7; 127.1; 105.5 (C(3)); 97.0 (C(6a)); 59.6; 55.5; 43.0; 34.2; 24.6; 14.7; 14.4. LC/ESI-MS: 279 (100, $[M+H]^+$). Anal. calc. for $C_{15}H_{18}O_3S$: C 64.7, H 6.5, S 11.5; found: C 64.6, H 6.6, S 11.6.

*1,2,3,3a,5,6,7,8b-Octahydro-3a-(2-thienyl)-8*H*-cyclopenta[*b*]benzofuran-8-one* (**7c**): Yield 243.9 mg (89%). Yellow oil. IR: 3101 (arom. C–H), 2938, 2868 (aliph. C–H), 1631 (C=O). ^{1}H-NMR: 7.26 (*dd*, *J* = 4.0, 1.2, H–C(5) of Tph); 6.96 – 7.01 (*m*, 2 H of Tph); 3.71 (*t*, *J* = 3.2, H–C(8b)); 2.44 – 2.49 (*m*, 2 H); 2.34 – 2.40 (*m*, 2 H); 2.00 – 2.14 (*m*, 2 H); 1.92 – 1.96 (*m*, 2 H); 1.81 – 1.86 (*m*, 2 H); 1.61 – 1.69 (*m*, 2 H). LC/ESI-MS: 261 (100, $[M+H]^+$). Anal. calc. for $C_{16}H_{18}O_2S$: C 70.0, H 6.6, S 11.7; found: C 69.9, H 6.5, S 11.8.

[4,5-Dihydro-2-methyl-5-phenyl-5-(2-thienyl)furan-3-yl]phenylmethanone (**8a**): Yield 103.8 mg (30%). Yellow oil. IR: 3065 (arom. C–H), 2926 (aliph. C–H), 1610 (C=O). ^{1}H-NMR: 7.55 (*m*, 2 arom. H); 7.24 – 7.47 (*m*, Ph, H–C(5) of Tph); 6.91 (*dd*, *J* = 5.2, 3.6, H–C(4) of Tph); 6.88 (*dd*, *J* = 3.6, 1.2, H–C(3) of Tph); 3.90 (*dq*, *J* = 14.8, 1.6, H_a–C(4)); 3.72 (*dq*, *J* = 14.8, 1.6, H_b–C(4)); 1.93 (*t*, *J* = 1.6, Me–C(2)). ^{13}C-NMR: 193.0 (C=O); 171.3 (C(2)); 149.3; 144.6; 140.9; 131.4; 128.6; 128.5; 128.1; 126.8; 126.0; 125.8; 125.5; 112.6 (C(3)); 89.7 (C(5)); 47.1; 15.8. LC/ESI-MS: 347 (100, $[M+H]^+$). Anal. calc. for $C_{22}H_{18}O_2S$: C 76.3, H 5.2, S 9.3; found: C 76.2, H 5.3, S 9.2.

1-[4,5-Dihydro-2,5-diphenyl-5-(2-thienyl)furan-3-yl]ethanone (**8b**): Yield 186.9 mg (54%). Yellow oil. IR: 3100, 3073 (arom. C–H), 2947, 2928, 2864 (aliph. C–H), 1621 (C=O). ^{1}H-NMR: 7.63 – 7.65 (*m*, 2 arom. H); 7.26 – 7.54 (*m*, Ph, H–C(5) of Tph); 6.90 – 6.94 (*m*, 2 H of Tph); 3.97 (*d*, *J* = 15.0, H_a–C(4)); 3.80 (*d*, *J* = 14.8, H_b–C(4)); 1.97 (*s*, MeCO–C(3)). ^{13}C-NMR: 194.6 (C=O); 171.3 (C(2)); 149.4; 144.6; 131.0; 130.9; 129.6; 128.6; 128.2; 126.8; 126.0; 125.7; 125.6; 114.9 (C(5)); 89.7 (C(3)); 47.2; 29.1. LC/ESI-MS: 347 (100, $[M+H]^+$). Anal. calc. for $C_{22}H_{18}O_2S$: C 76.3, H 5.2, S 9.3; found: C 76.4, H 5.3, S 9.3.

[4,5-Dihydro-2-methyl-5-(4-methylphenyl)-5-(2-thienyl)furan-3-yl]phenylmethanone (**8c**): Yield 118.8 mg (33%). Light yellow oil. IR: 3057, 3024 (arom. C–H), 2920, 2866 (aliph. C–H), 1612 (C=O). ^{1}H-NMR: 7.56 – 7.59 (*m*, 2 arom. H); 7.36 – 7.48 (*m*, 5 arom. H); 7.27 (*dd*, *J* = 5.2, 1.2, H–C(5) of Tph); 7.19 – 7.20 (*m*, 2 arom. H); 6.93 (*dd*, *J* = 5.0, 4.0, H–C(4) of Tph); 6.91 (*dd*, *J* = 4.0, 1.2, H–C(3) of Tph); 3.91 (*dq*, *J* = 14.8, 1.6, H_a–C(4)); 3.74 (*dq*, *J* = 14.8, 1.6, H_b–C(4)); 2.37 (*s*, *Me*C_6H_4); 1.95 (*t*, *J* = 1.6, Me–C(2)). LC/ESI-MS: 361 (100, $[M+H]^+$). Anal. calc. for $C_{23}H_{20}O_2S$: C 76.6, H 5.6, S 8.9; found: C 76.5, H 5.7, S 8.9.

1-[4,5-Dihydro-5-(4-methylphenyl)-2-phenyl-5-(2-thienyl)furan-3-yl]ethanone (**8d**): Yield 201.6 mg (56%). Light yellow oil. IR: 3047 (arom. C–H), 2922 (aliph. C–H), 1623 (C=O). ^{1}H-NMR: 7.64 (*dd*, *J* = 8.0, 1.2, 2 arom. H); 7.45 – 7.52 (*m*, Ph, H–C(5) of Tph); 7.42 (*d*, *J* = 8.0, 2 arom. H); 7.25 – 7.30 (*m*, 1 arom. H); 7.19 (*d*, *J* = 8.0, 2 arom. H); 6.94 (*dd*, *J* = 4.0, 1.2, 2 H of Tph); 3.95 (*d*, *J* = 14.8, H_a–C(4)); 3.80 (*d*, *J* = 14.8, H_b–C(4)); 2.36 (*s*, *Me*C_6H_4); 1.97 (*s*, Me–C(2)). LC/ESI-MS: 361 (100, $[M+H]^+$). Anal. calc. for $C_{23}H_{20}O_2S$: C 76.6, H 5.6, S 8.9; found: C 76.5, H 5.5, S 9.0.

[5-(4-Fluorophenyl)-4,5-dihydro-2-methyl-5-(2-thienyl)furan-3-yl]phenylmethanone (**8e**): Yield 138.3 mg (38%). Yellow oil. IR: 3069 (arom. C–H), 2924 (aliph. C–H), 1610 (C=C). ^{1}H-NMR: 7.57 – 7.61 (*m*, 2 arom. H); 7.40 – 7.48 (*m*, 5 arom. H); 7.28 (*dd*, *J* = 5.2, 1.2, H–C(5) of Tph); 7.07 (*m*, 2 arom. H); 6.95 (*dd*, *J* = 5.2, 4.0, H–C(4) of Tph); 6.91 (*dd*, *J* = 4.0, 1.2, H–C(3) of Tph); 3.93 (*dq*, *J* = 14.4, 1.2, H_a–C(4)); 3.72 (*dd*, *J* = 14.4, 1.2, H_b–C(4)); 1.95 (*t*, *J* = 1.2, Me–C(2)). ^{13}C-NMR: 193.0 (C=O); 166.6 (C(2)); 163.7; 161.3; 149.1; 140.8; 140.5; 140.4; 131.5; 128.6; 128.2; 127.5; 127.4; 126.9; 126.2; 125.9; 115.6; 115.4; 112.6 (C(3)); 89.3 (C(5)); 47.1; 15.8. LC/ESI-MS: 365 (100, $[M+H]^+$). Anal. calc. for $C_{22}H_{17}FO_2S$: C 72.5, H 4.7, F 5.2, S 8.8; found: C 72.4, H 4.8, F 5.2 S 8.7.

1-[5-(4-Fluorophenyl)-4,5-dihydro-2-phenyl-5-(2-thienyl)furan-3-yl]ethanone (**8f**): Yield 203.8 mg (56%). Yellow oil. IR: 3098, 3073 (arom. C–H), 2947, 2926, 2862 (aliph. C–H), 1623 (C=O). ^{1}H-NMR: 7.60 – 7.65 (*m*, 2 arom. H); 7.47 – 7.51 (*m*, 5 arom. H); 7.28 – 7.30 (*m*, 1 arom. H); 7.06 – 7.10 (*m*, 2 arom. H); 6.93 – 6.96 (*m*, 2 H of Tph); 3.97 (*d*, *J* = 15.2, H_a–C(4)); 3.77 (*d*, *J* = 15.2, H_b–C(4)); 1.99 (*s*, MeCO–C(3)). ^{13}C-NMR: 194.5 (C=O); 164.3 (C(2)); 163.8; 161.3; 149.2; 140.5; 131.1; 130.7; 129.6; 128.7; 127.6; 127.5; 127.0; 126.2; 125.7; 115.6; 115.4; 114.9 (C(3)); 89.3 (C(5)); 47.2; 29.1. LC/ESI-MS: 365 (100, $[M+H]^+$). Anal. calc. for $C_{22}H_{17}FO_2S$: C 72.5, H 4.7, F 5.2, S 8.8; found: C 72.5, H 4.8, F 5.1, S 8.7.

[3a,4,5,6,7,7a-Hexahydro-2-methyl-7a-(2-thienyl)benzofuran-3-yl]phenylmethanone (**8g**): Yield 110.2 mg (34%). Yellow oil. IR: 3067, 3028 (arom. C–H), 2938, 2864 (aliph. C–H), 1635 (C=O). ^{1}H-NMR: 7.55 – 7.59 (*m*, 2 arom. H); 7.47 – 7.50 (*m*, 1 arom. H); 7.40 – 7.42 (*m*, 2 arom. H); 7.26 (*dd*, *J* = 5.0, 1.2, H–C(5) of Tph); 7.11 (*dd*, *J* = 3.6, 1.2, H–C(3) of Tph); 6.90 (*dd*, *J* = 5.0, 3.6, H–C(4) of Tph); 3.71 (*tq*, *J* = 6.0, 1.2, H–C(3a)); 2.11 – 2.25 (*m*, 2 H); 1.79 – 1.93 (*m*, 2 H); 1.74 (*d*, *J* = 1.2, Me–C(2)); 1.56 – 1.69 (*m*, 2 H); 1.44 – 1.54 (*m*, 2 H). LC/ESI-MS: 325 (100, $[M+H]^+$). Anal calc. for $C_{20}H_{20}O_2S$: C 74.0, H 6.2, S 9.9; found: C 74.0, H 6.3, S 9.8.

1-[3a,4,5,6,7,7a-Hexahydro-2-phenyl-7a-(2-thienyl)benzofuran-3-yl]ethanone (**8h**): Yield 129.6 mg (40%). Yellow oil. IR: 3076 (arom. C–H), 2934, 2861 (aliph. C–H), 1617 (C=O). ^{1}H-NMR: 7.54 – 7.56 (*m*, 2 arom. H); 7.41 – 7.47 (*m*, 3 arom. H); 7.22 (*dd*, *J* = 5.2, 1.2, H–C(5) of Tph); 7.07 (*dd*, *J* = 3.6, 1.2, H–C(3) of Tph); 6.97 (*dd*, *J* = 5.2, 3.6, H–C(4) of Tph); 3.57 (*t*, *J* = 6,8, H–C(3a)); 2.38 (*dt*, *J* = 14.8, 4.4, H_a–C(4)); 2.18 – 2.22 (*m*, 1 H); 1.94 – 2.04 (*m*, 1 H); 1.89 (*s*, MeCO–C(3)); 1.59 – 1.67 (*m*, 4 H); 1.38 – 1.44 (*m*, 1 H). LC/ESI-MS: 325 (100, $[M+H]^+$). Anal. calc. for $C_{20}H_{20}O_2S$: C 74.0, H 6.2, S 9.9; found: C 74.1, H 6.4, S 9.7.

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