Tetrahedron 64 (2008) 10331–10338

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Highly stereoselective synthesis of β,γ-disubstituted and α,β,γ-trisubstituted butyrolactones

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ARTICLE INFO

Article history:
Received 16 June 2008
Received in revised form 28 August 2008
Accepted 29 August 2008
Available online 4 September 2008

ABSTRACT

β,γ-Disubstituted butyrolactones were produced effectively and steroeselectively from arsonium ylides generated in situ and substituted olefins. The transformation could be realized in one-pot or in two steps, which depended on the electronic properties of the olefins. With the adjustment of the solvent and in the presence of EtOH, α,β,γ-trisubstituted butyrolactones were also obtained in high yield from arsonium ylides and substituted olefins.

1. Introduction

Substituted γ-butyrolactones are ubiquitous in many natural products[1] and medicinal compounds possessing interesting biological properties.[2] Additionally γ-butyrolactones contain great synthetic utility as versatile intermediates in organic synthesis.[3] Considerable efforts have been made for the development of approaches to di or trisubstituted γ-butyrolactone products.[4] Nevertheless, highly stereoselective and practical useful protocols for the synthesis of contiguous stereogenic γ-butyrolactones are still desired. Furthermore, few results concerning the efficient and practical synthesis of trisubstituted γ-butyrolactones could be found in the literature.[5]

In our previous results, as depicted in Figure 1, it was discovered that substituted cyclopropanes or γ-butyrolactones were obtained from the reactions between in situ generated arsonium ylides and substituted electron deficient olefins with moderate to good yield and high stereoselectivity.[6] Transformation of substituted cyclopropanes into corresponding γ-butyrolactones was also described previously.

As part of our research in the preparation of cyclopropane derivatives and corresponding transformations into lactones, herein we would like to report the results concerning reactions between arsonium ylides containing furoyl or thienoyl functional group **1** and 2,2-dimethyl-1,3-dioxa-5-substituted benzylidene-4,6-dione **2**. One-pot synthesis of α,β,γ-trisubstituted butyrolactones from **1** and **2**, which was discovered serendipitously would also be addressed in this paper.

2. Results and discussion

2.1. Synthesis of β,γ-disubstituted butyrolactones

The in situ generated arsonium ylides were derived form 2-furoylmethyl triphenylarsonium bromide **1a** or 2-thienoylmethyl triphenylarsonium bromide **1b**. According to the previous results, olefins with substituents of different electronic property would result in totally discrepant products.[6] Therefore, olefins **2a** with a strong electron donating methoxyl on the aryl ring and **2f** with an electron withdrawing Cl on the aryl ring were picked out together with ylide precursor **1a** as the model substrates for the initial screening of the reaction conditions. Polar aprotic solvent DME, which proved previously to be highly beneficial for the reactions between the ylides and substituted olefins was employed at the beginning. Olefins **2a** and **1a** were stirred together with $KF\cdot 2H_2O$ in DME for 12 h, *trans*-β,γ-disubstituted butyrolactone **3aa** was obtained totally regioselectively in excellent yield (Scheme 1). In contrast, with olefin **2f** as the substrate the same reaction condition resulted in trans substituted cyclopropane **4af** exclusively in 91% yield (Scheme 1). These interesting results, which coincided with the previous results employing other ylide precursors,[6] prompted us to investigate more systematically aiming to define experimental procedures, which could lead to γ-butyrolactones or product with cyclopropane moiety effectively and selectively. Furthermore effective transformation of cyclopropane derivatives into corresponding lactones was also one of our goals.

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doi:10.1016/j.tet.2008.08.094

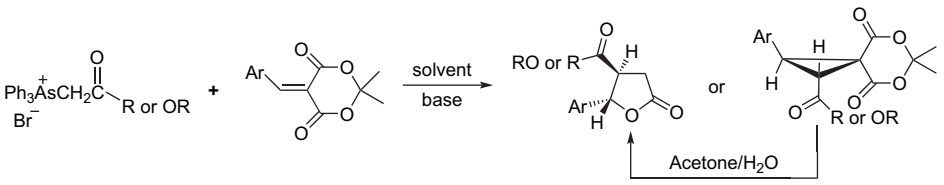
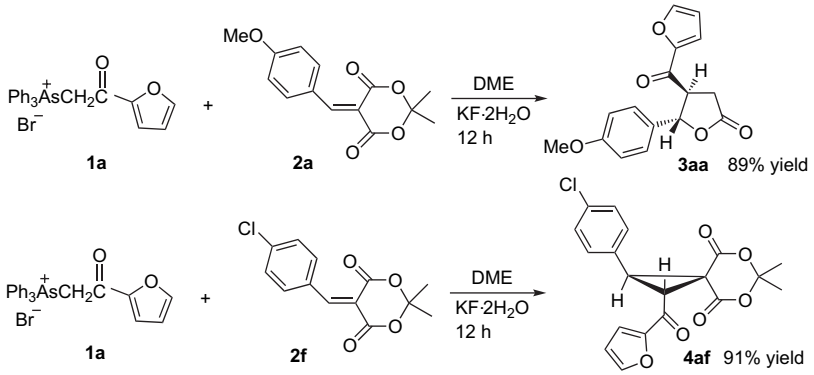


Figure 1.



Scheme 1.

In the optimization of the conditions for the formation of γ-butyrolactones, various bases for the in situ generation of ylide and solvents with different polarity were screened. The results were listed in Table 1. As expected, among the solvents screened, polar aprotic solvent DME afforded the best results in terms of reaction time and yield, 89% yield in 12 h (Table 1, entry 4). With benzene as the solvent resulted in a sluggish reaction, 33% yield in 48 h (Table 1, entry 1). With THF or $CHCl_3$ as the solvent, the yields were comparable to that of DME (Table 1, entries 2 and 3), 70% and 82%, respectively, and longer reaction time was required for complete consumption of the start material. As for the bases examined in this reaction, inorganic base $KF{\cdot}2H_2O$ seemed to be most effective in promoting the in situ formation of ylide from **1a** (Table 1, entry 4). With Na_2CO_3, K_2CO_3, or NaOH as base, the yield was slightly lower than that of $KF{\cdot}2H_2O$ (Table 1, entries 5–7). However, organic base such as TEA only resulted in a moderate yield (Table 1, entry 8) and using NaOAc almost no desired product isolated with the start material intact (Table 1, entry 9).

Then the reactions between ylide precursors **1a**, **b** and with olefins containing electron rich aryl substituents **2a**–**2c** were examined. As shown in Table 2, the reaction between **1** and olefins with electron rich aryl ring **2a**–**2c** proceeded smoothly to afford the *trans*-β,γ-disubstituted butyrolactones **3** in good to excellent yield. We were pleased that γ-butyrolactones produced selectively with almost no cyclopropanes detected in the products. The X-ray crystallographic and ^1H NMR analyses revealed that the stereochemistry of **3aa** as trans, Figure 2. The other lactone products were also suggested to have a similar configuration by comparison of the coupling constants on ^1H NMR spectral data.[7]

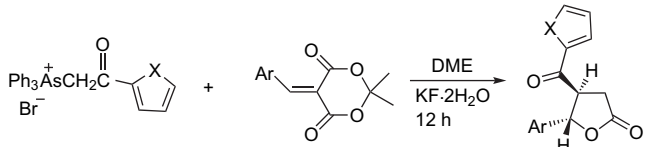
As for the olefins with electron withdrawing or weak electron donating groups on aryl ring, the reactions were conducted using DME as a solvent and $KF{\cdot}2H_2O$ as a base.[8] The cyclopropane products were transformed into the corresponding γ-disubstituted butyrolactones by treating the isolated cyclopropane products with acetone and water at elevated temperature. As shown in Scheme 2 and Table 3, substituted cyclopropanes **4** were generated smoothly with high stereoselectivity in good to excellent yield without the occurrence of disubstituted γ-butyrolactones **3** when olefins **2d**–**2g**

Table 1
Screening of the reaction conditions for one-pot synthesis of γ-butyrolactones[a]

Entry	Solvent	Base	Time (h)	Yield[b] % of **3aa**
1	Benzene	$KF{\cdot}2H_2O$	48	33
2	THF	$KF{\cdot}2H_2O$	18	70
3[c]	$CHCl_3$	$KF{\cdot}2H_2O$	18	82
4	DME	$KF{\cdot}2H_2O$	12	89
5	DME	Na_2CO_3	12	85
6	DME	K_2CO_3	12	88
7	DME	NaOH	12	80
8	DME	NEt_3	12	54
9	DME	NaOAc	12	—[d]

[a] Compounds **1a** and **2a** as the substrates, 1.5 equiv base used, room temperature.
[b] Chromatography yield.
[c] Trace amount trisubstituted butyrolactones **5aa** detected.
[d] Almost no formation of the desired product.

Table 2
One-pot synthesis of γ-butyrolactones **3** from **2a**–**2c**[a]



1a X = O
1b X = S
2a Ar = 4-$CH_3OC_6H_4$
2b Ar = 4-$(CH_3)_2NC_6H_4$
2c Ar = 3,4-$CH_2O_2C_6H_3$

Entry	X	Ar	Product	Yield[b] % of **3**
1	O	4-$CH_3OC_6H_4$	**3aa**	89
2	O	4-$(CH_3)_2NC_6H_4$	**3ab**	80
3	O	3,4-$CH_2O_2C_6H_3$	**3ac**	86
4	S	4-$CH_3OC_6H_4$	**3ba**	90
5	S	4-$(CH_3)_2NC_6H_4$	**3bb**	74
6	S	3,4-$CH_2O_2C_6H_3$	**3bc**	80

[a] DME as the solvent, 1.5 equiv $KF{\cdot}2H_2O$ used, stirring for 12 h at room temperature.
[b] Isolated yield.

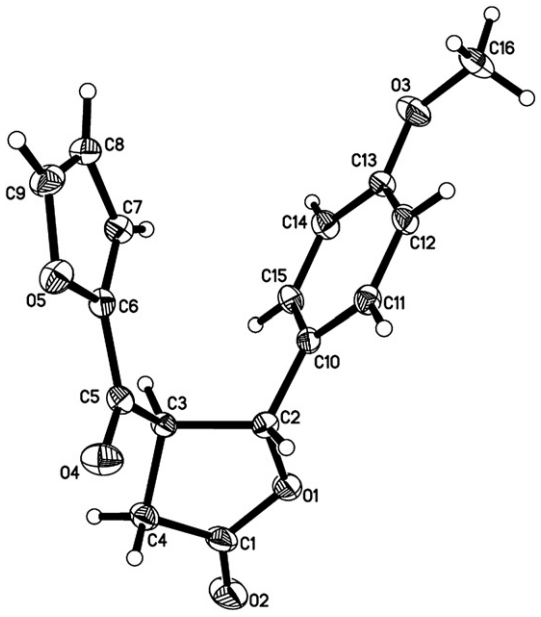


Figure 2. The ORTEP view of **3aa**.

were employed. The configuration of cyclopropanes **4** turned out to be trans, which was indicated by X-ray of **4af** and the comparison of coupling constant on ^{1}H NMR spectral.[7] Treating compound **4** with acetone and H_2O at 60 °C for 24 h, compound **3** with trans stereochemistry formed with the yield ranged from 55% to 80%. Numerous efforts had been tried to prepare compound **3** in one-pot from olefins **2d**–**2g**. Prolonging the reaction time or conducting the reaction in elevated temperature only resulted in the formation of compound **4** or decomposition of starting materials (Fig. 3).

As mentioned above, with slight difference of electronic property in olefins, γ-butyrolactones **3** or cyclopropanes **4** were produced. Both of them the major isomers were trans isomers in all the cases. For this discrepancy, a mechanism was speculated, which was depicted in Figure 4. The stereochemistry outcome of cyclopropanes **4** was determined through **TS 1**, which was assumed to have less important steric interaction. The newly formed cyclopropanes **4** were quite stable with electron withdrawing or poor electron donating groups on aryl ring. When with electron donating groups on Ar, the benzyl cation was stabilized. **TS 2** was generated through **TS 1**. Followed by an intramolecular enolate nucleophilic addition of the cation furnished **TS 3**, which was susceptible to nucleophilic addition. After the elimination of acetone and decarboxylation γ-disubstituted butyrolactones **3** was obtained. For cyclopropanes, which were stable under standard reaction condition, when treated with acetone and water at elevated temperature also produced γ-butyrolactones **3** through intermediates similar to **TS 2** and **TS 3**.

Table 3
Two-step synthesis of γ-butyrolactones from **2d**–**2g**[a]

Entry	X	Ar	Product **4**	Yield[b] % of **4**	Product **3**	Yield[b] % of **3**
1	O	C_6H_5	**4ad**	82	**3ad**	68
2	O	4-$CH_3C_6H_4$	**4ae**	77	**3ae**	63
3	O	4-ClC_6H_4	**4af**	91	**3af**	64
4	O	4-$NO_2C_6H_4$	**4ag**	84	**3ag**	80
5	S	C_6H_5	**4bd**	79	**3bd**	74
6	S	4-$CH_3C_6H_4$	**4be**	81	**3be**	55
7	S	4-ClC_6H_4	**4bf**	86	**3bf**	65
8	S	4-$NO_2C_6H_4$	**4bg**	85	**3bg**	80

[a] Step 1: DME as the solvent, 1.5 equiv KF·2H_2O used, stirring for 12 h at room temperature; Step 2: acetone–H_2O=2:1, conducted at 60 °C for 24 h.
[b] Isolated yield.

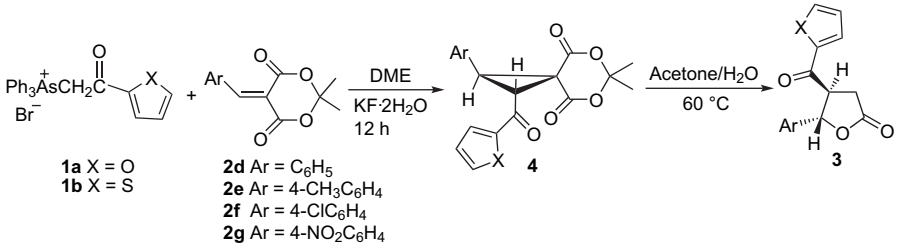
2.2. Synthesis of α,β,γ-trisubstituted butyrolactones

During the optimization of reaction conditions as shown in Table 1, we observed that trace amount of *trans*,*trans*-α,β,γ-trisubstituted butyrolactones **5aa** was formed. It's believed that the ethoxyl group came from the ethanol in commercial $CHCl_3$ as a stabilizer. When the reaction was carried out in ethanol free $CHCl_3$ no formation of **5aa** was detected. DME, THF, and DCM were also screened in the presence of ethanol for this transformation (Table 4, entries 1–3), however, resulted in a mixture of disubstituted and trisubstituted lactones. Using $CHCl_3$ as the solvent in the presence of 1 equiv ethanol trisubstituted lactones were obtained in high yield. Only olefins with electron donating substituted aryl groups worked in this reaction to produce the trisubstituted products. The synthesis of trisubstituted γ-butyrolactones has attracted considerable attention in recent years because of the wide range of their biological activities.[2b,5,9] Preparation of lactones **5** in one-pot would be very useful in synthesis of this moiety. The trans,trans stereochemistry of **5** was confirmed by X-ray and ^{1}H NMR spectral data,[7] Figure 5 (Scheme 3).

As discussed above, intermediate **TS 3** played an important role in the trisubstitution chemistry outcome. Since ethanol is more nucleophilic than water, in this case, ethanol instead of water added to **TS 3**. Followed by elimination of acetone and protonation at α position, *trans*,*trans*-α,β,γ-trisubstituted butyrolactones **5** was generated.

3. Conclusions

In summary, we have thus demonstrated that disubstituted and trisubstituted γ-butyrolactones could be produced in high stereoselectivity and good yield from the reactions between arsonium ylides and substituted olefins. When olefins with strong electron donating substituents on aryl ring were used, *trans*-β,γ-disubstituted γ-butyrolactones were obtained in one-pot under mild reaction conditions. As for olefins with weak electron donating or electron deficient groups on aryl ring, the same reaction conditions resulted in the formation of *trans* cyclopropane products, which could be further transformed into the corresponding



Scheme 2.

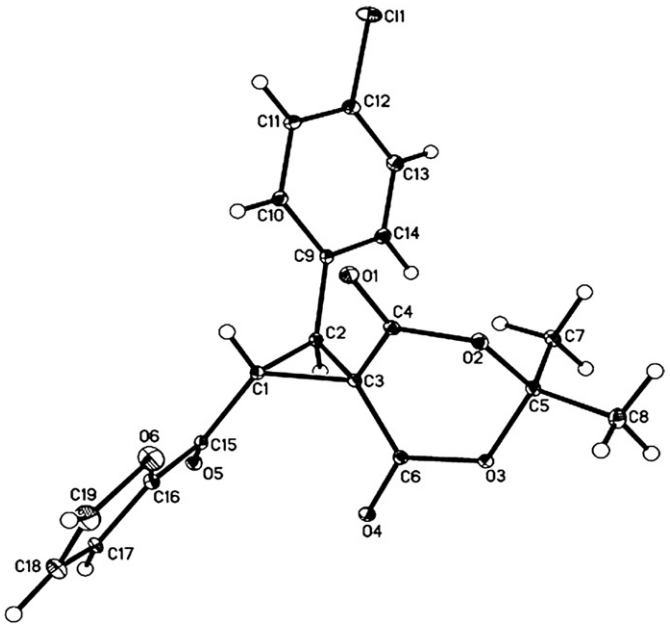


Figure 3. The ORTEP view of **4af**.

γ-butyrolactones when treated with acetone and water at elevated temperature. By adjustment of the solvent, $CHCl_3$ instead of DME, and in the presence of EtOH, *trans*,*trans*-α,β,γ-trisubstituted butyrolactones formed exclusively in high yield and high selectivity for the olefins with electron donating substituents on aryl ring. Provided that high stereoselectivity and synthetic practical yield were achieved, the using of toxic arsonium species could be compensated to some extend. Further research in the construction of γ-butyrolactones via cyclopropane intermediates from ylides other than arsonium salts and the application of this method in the synthesis of biological interest compounds is currently under way in our group.

Table 4
One-pot synthesis of α,β,γ-trisubstituted butyrolactones **5**[a]

Entry	X	Ar	Solvent	Product **5**	Yield[b] % of **5**
1	O	4-$CH_3OC_6H_4$	DME	**5aa**	59(26)
2	O	4-$CH_3OC_6H_4$	THF	**5aa**	40(40)
3	O	4-$CH_3OC_6H_4$	DCM	**5aa**	57(31)
4	O	4-$CH_3OC_6H_4$	$CHCl_3$	**5aa**	88
5	O	4-$(CH_3)_2NC_6H_4$	$CHCl_3$	**5ab**	80
6	O	3,4-$CH_2O_2C_6H_3$	$CHCl_3$	**5ac**	86
7	S	4-$CH_3OC_6H_4$	$CHCl_3$	**5ba**	83
8	S	4-$(CH_3)_2NC_6H_4$	$CHCl_3$	**5bb**	74
9	S	3,4-$CH_2O_2C_6H_3$	$CHCl_3$	**5bc**	85

[a] 1.5 equiv $KF\cdot 2H_2O$, 1 equiv EtOH used, stirring for 12 h at room temperature.
[b] Isolated yield, the yield in parentheses refers to the yield of **3**.

4. Experimental

4.1. General information

All reagents and solvents were obtained from commercial sources and used without further purification. All melting points were uncorrected. Melting points were determined on a WRS-1 digital melting point apparatus made by Shanghai Physical Optical Instrument Factory (SPOIF), China. IR spectra were measured on an AVATAR370 FT spectrometer and expressed in cm^{-1} (KBr disc). All ^1H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker AM-500, using $CDCl_3$ as solvent. Mass spectra were recorded on an HP5989A mass spectrometer. Elemental analyses were measured on the elementar vario EL III. X-ray crystal data were collected with a Bruker Smart Apex2 CCD. Flash chromatography was performed on columns of silica gel (20–30 μ).

Arsonium bromide **1**[10] and electron deficient trisubstituted olefins **2**[11] were prepared as described in the reference and the references therein.

4.2. General procedure for the synthesis of compounds 3aa–3ac, 3ba–3bc and 4ad–4ag, 4bd–4bg

To a mixture of fur-α-oylmethyltriphenylarsonium bromide **1a** or thien-α-oylmethyltriphenylarsonium bromide **1b** (1.1 mmol) and 2,2-dialkyl-1,3-dioxa-5-substituted-benzylidene-4,6-dione **2**

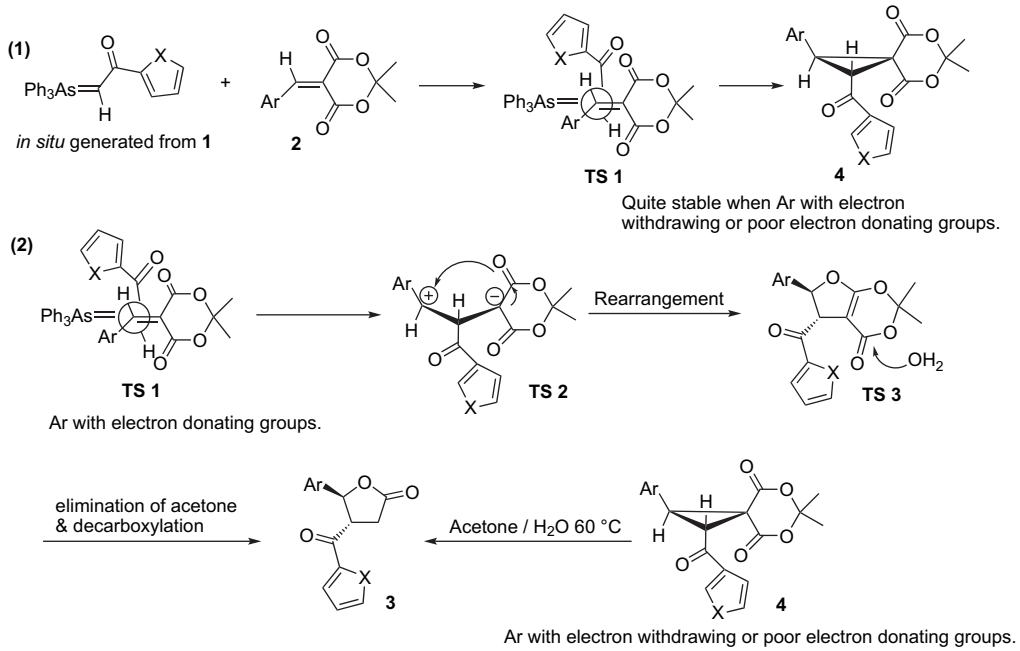


Figure 4. Proposed transitions for stereochemistry of the addition and rearrangement.

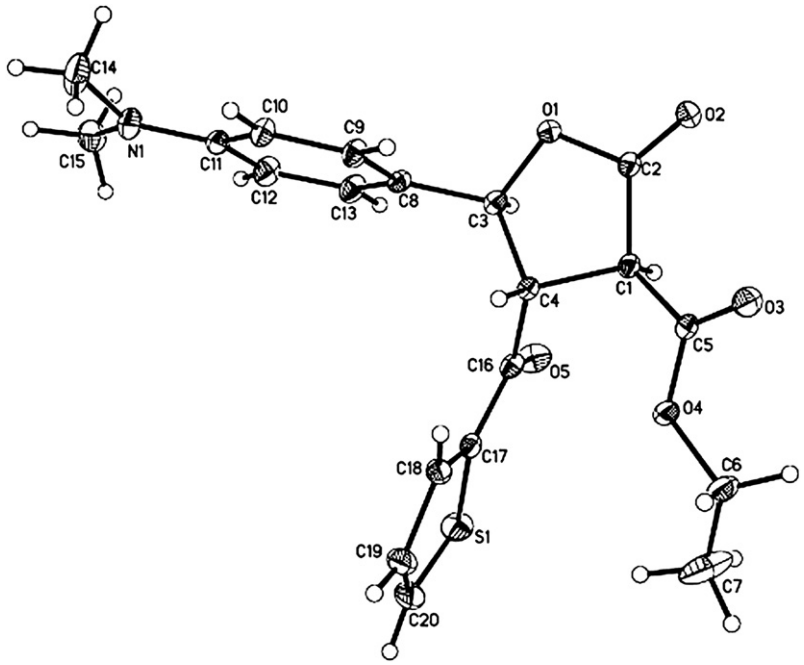


Figure 5. The ORTEP view of **5ab**.

(1 mmol) in 10 mL DME, $KF{\cdot}2H_2O$ (1.5 mmol) was added in one portion while stirring at room temperature. The reaction was followed by TLC. After the completion of the reaction, the insoluble solid was discarded by filtration and the solvent was removed by evaporated under reduced pressure. The crude products were purified by column chromatography over silica gel flushed with petroleum ether–ethyl acetate (V:V=4:1) for **3aa–3ac**, **3ba–3bc** and petroleum ether–ethyl acetate (V:V=6:1) for **4ad–4ag**, **4bd–4bg**.

*4.2.1. trans-β-(Fur-α-oyl)-γ-(4-methoxylphenyl) -γ-butyrolactone **3aa***

White solid; yield: 89%; mp 108.8–109.1 °C; ^{1}H NMR ($CDCl_3$) δ: 3.00 (ABX, J_{Ax}=9.5 Hz, J_{Bx}=9.5 Hz, J_{AB}=17.5 Hz, 2H), 3.81 (s, 3H), 4.08–4.15 (m, 1H), 5.68 (d, J=7.8 Hz, 1H), 6.52 (dd, J=4.0, 1.5 Hz, 1H), 6.88 (d, J=9.0 Hz, 2H), 7.12 (d, J=4.0 Hz, 1H), 7.28 (d, J=9.0 Hz, 2H), 7.59 (d, J=1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ: 33.00, 51.59, 55.54, 82.24, 113.08, 114.35, 119.43, 127.30, 130.03, 147.82, 151.76, 160.14, 174.42, 185.13; IR (KBr, cm^{-1}) ν_{max}: 1785, 1663, 1612, 1516, 1462, 1256, 1196, 1141, 1031, 989, 781; MS m/z (EI): 286 (M^+). Anal. Calcd for $C_{16}H_{14}O_5$: C, 67.13; H, 4.93; found: C, 67.03; H, 5.12.

*4.2.2. trans-β-(Fur-α-oyl)-γ-(4-N,N-dimethylaminophenyl) -γ-butyrolactone **3ab***

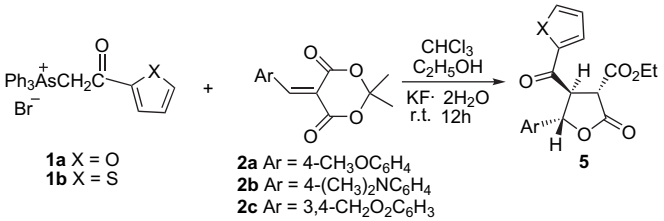
Red solid; yield: 80%; mp 132.1–133.5 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.90–3.10 (m, 8H), 4.10–4.15 (m, 1H), 5.62 (d, J=8.0 Hz, 1H), 6.52 (dd, J=3.5, =1.5 Hz, 1H), 6.68 (d, J=8.5 Hz, 2H), 7.07 (d, J=3.5 Hz, 1H), 7.22 (d, J=8.5 Hz, 2H), 7.58 (d, J=1.5 Hz, 1H); IR (KBr, cm^{-1}) ν_{max}: 3132, 2889, 2806, 1773, 1666, 1467; MS m/z: 299 ($[M]^+$). Anal. Calcd for $C_{17}H_{17}NO_4$: C, 68.21; H, 5.72; N, 4.68; found: C, 67.96; H, 6.04; N, 4.53.

*4.2.3. trans-β-(Fur-α-oyl)-γ-(3,4-dioxomethlenephenyl) -γ-butyrolactone **3ac***

Yellow liquid; yield: 86%; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 3.02 (ABX, J_{Ax}=9.2 Hz, J_{Bx}=9.2 Hz, J_{AB}=17.5 Hz, 2H), 4.05–4.12 (m, 1H), 5.67 (d, J=7.5 Hz, 1H), 5.90 (s, 2H), 6.56 (dd, J=3.5, =1.5 Hz, 1H), 6.70–6.88 (m, 3H), 7.16 (d, J=3.5 Hz, 1H), 7.60 (d, J=1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 33.06, 51.66, 82.16, 101.56, 106.16, 108.56, 113.18, 119.43, 119.78, 131.91, 147.85, 148.26, 148.38, 151.82, 174.22, 185.10; IR (KBr, cm^{-1}) ν_{max}: 1756, 1672, 1466, 1264, 1238, 1210, 1143, 1040, 965, 935; MS m/z (%) (EI): 300 ($[M]^+$). Anal. Calcd for $C_{16}H_{12}O_6$: C, 64.00; H, 4.03; found: C, 63.24; H, 4.28.

*4.2.4. trans-β-(Thien-α-oyl)-γ-(4-methoxylphenyl) -γ-butyrolactone **3ba***

Yellow liquid; yield: 90%; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 3.05 (ABX, J_{Ax}=6.7 Hz, J_{Bx}=6.7 Hz, J_{AB}=17.5 Hz, 2H), 3.78 (s, 3H), 4.17 (dt, J=8.0, =6.7 Hz, 1H), 5.61 (d, J=8.0 Hz, 1H), 6.87 (d, J=8.5 Hz, 2H), 7.05 (dd, J=3.5, 5 Hz, 1H), 7.24 (d, J=8.5 Hz, 2H), 7.42 (d, J=3.5 Hz, 1H), 7.70 (d, J=5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 33.68, 52.33, 52.39, 82.76, 114.29, 127.37, 129.80, 133.47, 135.47, 135.87, 142.83, 160.11, 174.33, 189.23; IR (KBr, cm^{-1}) ν_{max}: 1782, 1657, 1177, 1612, 1516, 1413, 1357; MS m/z (%) (EI): 302 ($[M]^+$). Anal. Calcd for $C_{16}H_{14}O_4S$: C, 63.56; H, 4.67; found: C, 63.37; H, 4.81.



Scheme 3.

4.2.5. trans-β-(Thien-α-oyl)-γ-(4-N,N-dimethylaminophenyl) -γ-butyrolactone ***3bb***

Red solid; yield: 74%; mp 87.8–88.2 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.90–3.25 (m, 8H), 4.13–4.20 (m, 1H), 5.60 (d, *J*=8.0 Hz, 1H), 6.68 (d, *J*=8.5 Hz, 2H), 7.07 (dd, *J*=4.5, =4.0 Hz, 1H), 7.18 (d, *J*=8.5 Hz, 2H), 7.40 (dd, *J*=4.0, 1.0 Hz, 1H), 7.69 (dd, *J*=4.5, 1.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 33.88, 50.31, 82.57, 111.96, 124.39, 127.92, 128.94, 134.55, 136.55, 142.73, 15.72, 174.37, 190.11; IR (KBr, cm^{-1}) ν_{max}: 3431, 3135, 1776, 1661, 1218, 1620, 1534, 1415, 1363; MS *m*/*z* (%) (EI): 315 ($[M]^+$). Anal. Calcd for $C_{17}H_{17}NO_3S$: C, 64.74; H, 5.43; N, 4.44; found: C, 64.39; H, 5.68; N, 4.68.

4.2.6. trans-β-(Thien-α-oyl)-γ-(3,4-dioxomethlenephenyl) -γ-butyrolactone ***3bc***

White solid; yield: 80%; mp 146.3–146.8 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 3.05 (ABX, J_{Ax}=6.7 Hz, J_{Bx}=6.7 Hz, J_{AB}=17.5 Hz, 2H), 4.10–4.19 (m, 1H), 5.59 (d, *J*=8.0 Hz, 1H), 5.96 (s, 2H), 6.70–6.80 (m, 2H), 6.80–6.85 (m, 1H), 7.08 (dd, *J*=5, =3.5 Hz, 1H), 7.48 (d, *J*=3.5 Hz, 1H), 7.71 (d, *J*=5.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 33.71, 52.36, 82.71, 101.47, 106.09, 108.41, 119.94, 128.69, 131.59, 133.49, 135.96, 142.79, 148.20, 148.27, 174.15, 189.16; IR (KBr, cm^{-1}) ν_{max}: 1783, 1657, 1503, 1448, 1414, 1252, 1037, 931, 731; MS *m*/*z* (%) (EI): 316 ($[M]^+$). Anal. Calcd for $C_{16}H_{12}O_5S$: C, 60.75; H, 3.82; found: C, 61.13; H, 4.74.

4.2.7. trans-1-Fur-α-oyl-2-phenyl-6,6-dimethyl-5,7-dioxaspiro[2,5]-4,8-octadione ***4ad***

White solid; yield: 82%; mp 172.4–173.0 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.72 (s, 3H), 1.77 (s, 3H), 4.11 (d, *J*=9.6 Hz, 1H), 4.28 (d, *J*=9.6 Hz, 1H), 6.58 (dd, *J*=3.6, =1.6 Hz, 1H), 7.32 (dd, *J*=3.6, 0.6 Hz, 1H), 7.32–7.44 (m, 5H), 7.61 (dd, *J*=0.6, 1.6 Hz, 1H); IR (KBr, cm^{-1}) ν_{max}: 1746, 1768, 1677, 1314; MS *m*/*z* (%) (EI): 282 ($[M-C_3H_6O]^+$). Anal. Calcd for $C_{19}H_{16}O_6$: C, 67.05; H, 4.74; found: C, 67.03; H, 4.59.

4.2.8. trans-1-Fur-α-oyl-2-(4-methylphenyl)-6,6-dimethyl-5,7-dioxaspiro[2,5]-4,8-octadione ***4ae***

White solid; yield: 77%; mp 136.8–137.2 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.71 (s, 3H), 1.76 (s, 3H), 2.35 (s, 3H), 4.08 (d, *J*=9.7 Hz, 1H), 4.27 (d, *J*=9.7 Hz, 1H), 6.58 (dd, *J*=3.6, =1.7 Hz, 1H), 7.16–7.34 (m, 5H), 7.62 (dd, *J*=0.6, 1.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 21.18, 27.58, 28.01, 38.74, 39.83, 45.10, 105.37, 112.68, 118.15, 127.04, 129.33, 139.10, 147.12, 152.25, 162.47, 164.86, 179.00; IR (KBr, cm^{-1}) ν_{max}: 1746, 1768, 1677, 1314; MS *m*/*z* (%) (EI): 296 ($[M-C_3H_6O]^+$). Anal. Calcd for $C_{20}H_{18}O_6$: C, 67.79; H, 5.12; found: C, 67.56; H, 5.36.

4.2.9. trans-1-Fur-α-oyl-2-(4-chlorophenyl)-6,6-dimethyl-5,7-dioxaspiro[2,5]-4,8-octadione ***4af***

White solid; yield: 91%; mp 177.4–177.9 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.71 (s, 3H), 1.78 (s, 3H), 4.08 (d, *J*=10.0 Hz, 1H), 4.23 (d, *J*=10.0 Hz, 1H), 6.58 (dd, *J*=3.6, =1.6 Hz, 1H), 7.30–7.38 (m, 5H), 7.61 (dd, *J*=3.6, 0.6 Hz, 1H); IR (KBr, cm^{-1}) ν_{max}: 1741, 1762, 1683, 1313; MS *m*/*z* (%) (EI): 316 ($[M-C_3H_6O]^+$). Anal. Calcd for $C_{19}H_{15}ClO_6$: C, 60.89; H, 4.03; found: C, 60.64; H, 4.56.

4.2.10. trans-1-Fur-α-oyl-2-(4-nitrophenyl)-6,6-dimethyl-5,7-dioxaspiro[2,5]-4,8-octadione ***4ag***

White solid; yield: 84%; mp 186.7–187.3 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.74 (s, 3H), 1.82 (s, 3H), 4.19 (d, *J*=9.8 Hz, 1H), 4.25 (d, *J*=9.8 Hz, 1H), 6.61 (dd, *J*=1.6, =3.6 Hz, 1H), 7.37 (dd, *J*=3.6, 0.6 Hz, 1H), 7.57 (d, *J*=6.8 Hz, 2H), 7.61 (dd, *J*=0.6, 3.6 Hz, 1H), 8.26 (d, *J*=6.8 Hz, 2H); IR (KBr, cm^{-1}) ν_{max}: 1736, 1768, 1697, 1517, 1314; MS *m*/*z* (%) (EI): 327 ($[M-C_3H_6O]^+$). Anal. Calcd for $C_{19}H_{15}NO_8$: C, 59.22; H, 3.64; N, 3.64; found: C, 58.97; H, 3.84; N, 3.47.

4.2.11. trans-1-Thien-α-oyl-2-phenyl-6,6-dimethyl-5,7-dioxaspiro[2,5]-4,8-octadione ***4bd***

White solid; yield: 79%; mp 178.9–180.6 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.72 (s, 3H), 1.78 (s, 3H), 4.14 (d, *J*=9.5 Hz, 1H), 4.37 (d, *J*=9.5 Hz, 1H), 7.15 (dd, *J*=4.9, =3.9 Hz, 1H), 7.38–7.42 (m, 5H), 7.72 (dd, *J*=4.9, 1.1 Hz, 1H), 7.78 (dd, *J*=3.9, 1.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 27.63, 28.24, 38.81, 40.87, 45.78, 105.90, 128.13, 128.83, 129.54, 133.33, 135.13, 136.12, 136.74, 142.37, 162.27, 164.83, 182.76; IR (KBr, cm^{-1}) ν_{max}: 1746, 1665, 1517, 1411, 1383, 1308; MS *m*/*z* (%) (EI): 298 ($[M-C_3H_6O]^+$). Anal. Calcd for $C_{19}H_{16}O_5S$: C, 64.03; H, 4.53; found: C, 64.12; H, 4.78.

4.2.12. trans-1-Thien-α-oyl-2-(4-methylphenyl)-6,6-dimethyl-5,7-dioxaspiro[2,5]-4,8-octadione ***4be***

White solid; yield: 81%; mp 148.8–149.2 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.66 (s, 3H), 1.68 (s, 3H), 2.38 (s, 3H), 4.10 (d, *J*=9.6 Hz, 1H), 4.38 (d, *J*=9.6 Hz, 1H), 7.15–7.80 (m, 7H); IR (KBr, cm^{-1}) ν_{max}: 1776, 1738, 1677, 1516, 1458, 1413, 1396, 1310; MS *m*/*z* (%) (EI): 312 ($[M-C_3H_6O]^+$). Anal. Calcd for $C_{20}H_{18}O_5S$: C, 64.85; H, 4.90; found: C, 64.49; H, 5.04.

4.2.13. trans-1-Thien-α-oyl-2-(4-chlorophenyl)-6,6-dimethyl-5,7-dioxaspiro[2,5]-4,8-octadione ***4bf***

White solid; yield: 86%; mp 183.3–183.5 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.70 (s, 3H), 1.78 (s, 3H), 4.12 (d, *J*=10.0 Hz, 1H), 4.32 (d, *J*=10.0 Hz, 1H), 7.15 (dd, *J*=5.0, =3.9 Hz, 1H), 7.30–7.38 (m, 4H), 7.71 (dd, *J*=5.0, 1.1 Hz, 1H), 7.76 (dd, *J*=3.9, 1.1 Hz, 1H); IR (KBr, cm^{-1}) ν_{max}: 1779, 1733, 1671, 1512, 1497, 1452, 1410; MS *m*/*z* (%) (EI): 332 ($[M-C_3H_6O]^+$). Anal. Calcd for $C_{19}H_{15}ClO_5S$: C, 58.39; H, 3.87; found: C, 58.03; H, 4.02.

4.2.14. trans-1-Thien-α-oyl-2-(4-nitrophenyl)-6,6-dimethyl-5,7-dioxaspiro[2,5]-4,8-octadione ***4bg***

White solid; yield: 85%; mp 210.6–211.1 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.68 (s, 3H), 1.72 (s, 3H), 4.22 (d, *J*=9.8 Hz, 1H), 4.31 (d, *J*=9.8 Hz, 1H), 7.18 (dd, *J*=5.0, =4.0 Hz, 1H), 7.61 (d, *J*=8.5 Hz, 2H), 7.73 (d, *J*=5.0 Hz, 1H), 7.86 (d, *J*=4.0 Hz, 1H), 8.25 (d, *J*=8.5 Hz, 2H); IR (KBr, cm^{-1}) ν_{max}: 1735, 1769, 1605, 1518, 1455, 1416, 1351, 1309; MS *m*/*z* (%) (EI): 343 ($[M-C_3H_6O]^+$). Anal. Calcd for $C_{19}H_{15}NO_7S$: C, 56.85; H, 3.77; N, 3.49; found: C, 56.39; H, 3.96; N, 3.04.

4.3. General procedure for the synthesis of compounds 3ad–3ag and 3bd–3bg

Cyclopropane derivatives **4ad**–**4ag** and **4bd**–**4bg** (1 mmol) were dissolved in 8 mL acetone–water (V:V=2:1). The mixture was stirred at 60 °C. After the completion of the reaction, the mixture was extracted with ethyl acetate (3×15 mL). Then the combined organic layer was washed with brine. The organic layer was dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the crude product was purified by column chromatography with petroleum–ethyl acetate (V:V=3:1) as eluent to afford compounds **3ad**–**3ag** and **3ad**–**3bg**.

4.3.1. trans-β-(Fur-α-oyl)-γ-phenyl-γ-butyrolactone ***3ad***

White solid; yield: 68%; mp 109.7–110.2 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 3.05 (ABX, J_{Ax}=9.0 Hz, J_{Bx}=9.0 Hz, J_{AB}=17.5 Hz, 2H), 4.11 (td, *J*=9.0, 7.5 Hz, 1H), 5.76 (d, *J*=7.5 Hz, 1H), 6.55 (dd, *J*=1.0, 3.5 Hz, 1H), 7.14 (d, *J*=3.5 Hz, 1H), 7.37–7.40 (m, 5H), 7.58 (d, *J*=1.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 32.87, 51.65, 82.09, 113.15, 119.44, 125.65, 129.06, 135.19, 138.32, 147.82, 151.78, 174.43, 185.15; IR (KBr, cm^{-1}) ν_{max}: 1787, 1664, 1559, 1460, 1391, 1273, 1200, 998, 783; MS *m*/*z* (%) (EI): 256 ($[M]^+$). Anal. Calcd for $C_{15}H_{12}O_4$: C, 70.31; H, 4.72; found: C, 70.16; H, 5.17.

4.3.2. trans-β-(Fur-α-oyl)-γ-(4-methylphenyl)-γ-butyrolactone ***3ae***

White solid; yield: 63%; mp 120.3–121.0 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.35 (s, 3H), 3.04 (ABX, J_{Ax}=9.0 Hz, J_{Bx}=9.0 Hz, J_{AB}=17.5 Hz, 2H), 4.10 (td, J=9.0, =7.5 Hz, 1H), 5.72 (d, J=7.5 Hz, 1H), 6.54 (dd, J=3.5, 1.5 Hz, 1H), 7.13 (d, J=3.5 Hz, 1H), 7.13–7.23 (m, 4H), 7.50–7.60 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 21.36, 32.94, 51.63, 82.21, 113.13, 119.41, 125.70, 129.71, 135.29, 138.99, 147.79, 151.82, 174.51, 185.26; IR (KBr, cm^{-1}) ν_{max}: 1788, 1757, 1665, 1560, 1461, 1273, 1199, 1141, 994, 777; MS *m*/*z* (%) (EI): 270 ([M]$^+$). Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22; found: C, 69.92; H, 5.34.

4.3.3. trans-β-(Fur-α-oyl)-γ-(4-chlorophenyl)-γ-butyrolactone ***3af***

White solid; yield: 64%; mp 138.7–139.2 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 3.02 (ABX, J_{Ax}=9.4 Hz, J_{Bx}=9.4 Hz, J_{AB}=16.0 Hz, 2H), 4.07 (td, J=9.4, =8.0 Hz, 1H), 5.76 (d, J=8.0 Hz, 1H), 6.58 (dd, J=3.5, 1.5 Hz, 1H), 7.19 (d, J=3.5 Hz, 1H), 7.28 (d, J=6.5 Hz, 2H), 7.34 (d, J=6.5 Hz, 2H), 7.59 (d, J=1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 33.01, 51.66, 82.26, 113.29, 119.48, 127.07, 129.28, 134.91, 136.82, 147.89, 151.74, 174.02, 184.89; IR (KBr, cm^{-1}) ν_{max}: 1786, 1750, 1663, 1540, 1465, 1274, 1200, 1130, 990, 779; MS *m*/*z* (%) (EI): 291 ([M]$^+$). Anal. Calcd for $C_{15}H_{11}ClO_4$: C, 61.98; H, 3.81; found: C, 61.73; H, 4.03.

4.3.4. trans-β-(Fur-α-oyl)-γ-(4-nitrophenyl)-γ-butyrolactone ***3ag***

White solid; yield: 80%; mp 168.1–168.5 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.85 (dd, J=4.0, =18 Hz, 1H), 3.25 (dd, J=5.5, 18 Hz, 1H), 4.65–4.73 (m, 1H), 5.99 (d, J=8 Hz, 1H), 6.48 (dd, J=1.5, 3.5 Hz, 1H), 6.97 (d, J=3.5 Hz, 1H), 7.27 (d, J=9 Hz, 2H), 7.53 (d, J=1.5 Hz, 1H), 8.04 (d, J=9.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 30.49, 47.46, 80.51, 113.69, 118.46, 123.65, 126.91, 142.32, 147.02, 148.07, 151.96, 174.70, 184.68; IR (KBr, cm^{-1}) ν_{max}: 1785, 1657, 1513, 1464, 1350, 1158, 1006, 881, 781; MS *m*/*z* (%) (EI): 301 ([M]$^+$). Anal. Calcd for $C_{15}H_{11}NO_6$: C, 59.80; H, 3.68; N, 4.65; found: C, 59.59; H, 3.71; N, 4.49.

4.3.5. trans-β-(Thien-α-oyl)-γ-phenyl-γ-butyrolactone ***3bd***

White solid; yield: 74%; mp 119.3–120.8 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.81 (dd, J=8.4, =17.5 Hz, 1H), 3.30 (dd, J=6, 17.5 Hz, 1H), 4.54–4.60 (m, 1H), 5.89 (d, J=8.1 Hz, 1H), 7.04–7.08 (m, 3H), 7.10–7.18 (m, 3H), 7.52 (dd, J=0.75, 4.8 Hz, 1H), 7.58 (dd, J=0.75, 3.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 31.20, 49.13, 82.32, 126.19, 128.32, 128.24, 129.00, 132.75, 134.77, 135.21, 143.75, 175.57, 188.71; IR (KBr, cm^{-1}) ν_{max}: 1784, 1644, 1522, 1418, 1240, 1148, 1030, 990, 733; MS *m*/*z* (%) (EI): 272 ([M]$^+$). Anal. Calcd for $C_{15}H_{12}O_3S$: C, 66.16; H, 4.44; found: C, 65.94; H, 4.77.

4.3.6. trans-β-(Thien-α-oyl)-γ-(4-methylphenyl)-γ-butyrolactone ***3be***

Yellow oil; yield: 55%; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.35 (s, 3H), 2.97 (dd, J=9.0, =17.5 Hz, 1H), 3.14 (dd, J=10, 17.5 Hz, 1H), 4.07–4.14 (m, 1H), 5.68 (d, J=8.0 Hz, 1H), 7.11 (dd, J=5.0, 4.0 Hz, 1H), 7.16–7.21 (m, 4H), 7.41 (dd, J=1.0, 4 Hz, 1H), 7.71 (dd, J=1.0, 5.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 21.29, 32.72, 52.54, 82.79, 125.73, 128.67, 129.69, 133.41, 135.10, 135.91, 139.07, 142.91, 174.35, 189.59; IR (KBr, cm^{-1}) ν_{max}: 1787, 1654, 1515, 1413, 1262, 1000, 815, 726; MS *m*/*z* (%) (EI): 287 ([M]$^+$). Anal. Calcd for $C_{16}H_{14}O_3S$: C, 67.11; H, 4.93; found: C, 66.93; H, 5.06.

4.3.7. trans-β-(Thien-α-oyl)-γ-(4-chlorophenyl)-γ-butyrolactone ***3bf***

White solid; yield: 65%; mp 183.3–183.5 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.99 (dd, J=9, =17.5 Hz, 1H), 3.13 (dd, J=10, 18.0 Hz, 1H), 4.04–4.09 (m, 1H), 5.72 (d, J=8.0 Hz, 1H), 7.10 (dd, J=4.0, 5.0 Hz, 1H), 7.11–7.27 (m, 2H), 7.33–7.35 (m, 2H), 7.44 (d, J=4.0 Hz, 1H), 7.73 (d, J=5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 34.07, 52.78, 81.92, 127.13, 128.86, 129.36, 133.46, 135.09, 136.25, 136.70, 142.85, 173.84, 188.90; IR (KBr, cm^{-1}) ν_{max}: 1786, 1656, 1412, 1260, 1147, 1089, 1007, 820, 728; MS *m*/*z* (%) (EI): 307 ([M]$^+$). Anal. Calcd for $C_{15}H_{11}ClO_3S$: C, 58.73; H, 3.61; found: C, 58.87; H, 3.86.

4.3.8. trans-β-(Thien-α-oyl)-γ-(4-nitrophenyl)-γ-butyrolactone ***3bg***

White solid; yield: 80%; mp 143.2–144.3 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.99 (dd, J=8.5, =18 Hz, 1H), 3.13 (dd, J=5, 18.0 Hz, 1H), 4.59–4.65 (m, 1H), 5.94 (d, J=8.0 Hz, 1H), 7.07 (dd, J=4.0, 5.0 Hz, 1H), 7.27–7.30 (m, 2H), 7.56 (dd, J=1.0, 4.0 Hz, 1H), 7.65 (d, J=1.0, 5.0 Hz, 1H), 8.03–8.05 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 31.55, 48.67, 80.84, 123.70, 127.21, 128.68, 132.94, 136.17, 142.12, 143.35, 148.12, 174.52, 188.39; IR (KBr, cm^{-1}) ν_{max}: 1787, 1637, 1516, 1414, 1244, 1151, 1004, 835, 741; MS *m*/*z* (%) (EI): 317 ([M]$^+$). Anal. Calcd for $C_{15}H_{11}NO_5S$: C, 56.78; H, 3.49; N, 4.41; found: C, 56.53; H, 3.53; N, 4.06.

4.4. General procedure for the synthesis of compounds 5aa–5cc and 5ba–5bc

To a mixture of fur-α-oylmethyltriphenylarsonium bromide **1a** or thien-α-oylmethyltriphenylarsonium bromide **1b** (1.1 mmol) and 2,2-dialkyl-1,3-dioxa-5-substituted-benzylidene-4,6-dione **2** (1 mmol) in 10 mL $CHCl_3$, $KF{\cdot}2H_2O$ (1.5 mmol) and ethanol (1 mmol) were added in one portion while stirring at room temperature. After the completion of the reaction, the insoluble solid was discarded by filtration and the solvent was removed by evaporated under reduced pressure. The crude products were purified by column chromatography over silica gel flushed with petroleum ether–ethyl acetate (V:V=3:1) afford compounds **5aa**–**5cc** and **5ba**–**5bc**.

4.4.1. trans,trans-α-Carboethoxy-β-(fur-α-oyl)-γ-(4-methoxyphenyl)-γ-butyrolactone ***5aa***

White solid; yield: 88%; mp 90.7–91.1 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.29 (t, J=7.0 Hz, 3H), 3.81 (s, 3H), 4.20–4.30 (m, 3H), 4.58 (dd, J=11, 9 Hz, 1H), 5.53 (d, J=9.0 Hz, 1H), 6.48 (dd, J=3.5, 1.5 Hz, 1H), 6.89 (dd, J=2.0, 6.5 Hz, 2H), 7.05 (dd, J=3.5, 0.5 Hz, 1H), 7.28 (dd, J=2.0, 6.5 Hz, 2H), 7.57 (dd, J=1.5, 0.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 14.15, 51.23, 54.93, 55.47, 62.81, 81.56, 113.06, 114.40, 120.88, 127.94, 128.69, 148.51, 151.59, 160.49, 166.74, 169.37, 183.36; IR (KBr, cm^{-1}) ν_{max}: 1787, 1736, 1667, 1611, 1516, 1461, 1381, 1261, 1173; MS *m*/*z* (%) (EI): 358 ([M]$^+$). Anal. Calcd for $C_{19}H_{18}O_7$: C, 63.68; H, 5.06; found: C, 63.42; H, 5.26.

4.4.2. trans,trans-α-Carboethoxy-β-(fur-α-oyl)-γ-(4-N,N-dimethylaminophenyl)-γ-butyrolactone ***5ab***

Red solid; yield: 80%; mp 82.5–83.2 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.29 (t, J=7.0 Hz, 3H), 2.95 (s, 6H), 4.20–4.30 (m, 3H), 4.62 (dd, J=9.0, =10.5 Hz, 1H), 5.48 (d, J=9.0 Hz, 1H), 6.46 (dd, J=1.5, 3.5 Hz, 1H), 6.67–6.70 (m, 2H), 7.03 (d, J=3.5 Hz, 1H), 7.20–7.23 (m, 2H), 7.56 (d, J=1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 14.14, 40.41, 51.71, 55.47, 62.73, 82.77, 112.29, 123.30, 127.93, 128.71, 134.58, 136.49, 143.13, 151.31, 166.91, 169.57, 188.35; IR (KBr, cm^{-1}) ν_{max}: 3433, 3131, 1775, 1746, 1667, 1613, 1532, 1381, 1322, 1271, 1163, 1108, 1062, 961, 785, 691; MS *m*/*z* (%) (EI): 371 ([M]$^+$). Anal. Calcd for $C_{20}H_{21}NO_6$: C, 64.68; H, 5.70; N, 3.77; found: C, 64.83; H, 5.68; N, 4.01.

4.4.3. trans,trans-α-Carboethoxy-β-(fur-α-oyl)-γ-(3,4-dioxomethlenephenyl)-γ-butyrolactone ***5ac***

White solid; yield: 86%; mp 92.5–93.7 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.28 (t, J=7.0 Hz, 3H), 4.27–4.35 (m, 3H), 4.58 (dd, J=9.0, =10.5 Hz, 1H), 5.53 (d, J=9.0 Hz, 1H), 5.98–5.60 (m, 2H), 6.51 (dd, J=3.5, 2 Hz, 1H), 6.73–6.78 (m, 2H), 6.88–6.90 (m, 1H), 7.10–7.13 (m, 1H), 7.58–7.61 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 14.12,

51.21, 54.86, 62.84, 81.50, 101.60, 106.50, 108.48, 113.11, 120.56, 120.90, 130.49, 148.47, 148.56, 148.60, 151.57, 166.64, 169.22, 183.29; IR (KBr, cm^{-1}) ν_{max}: 1786, 1734, 1669, 1567, 1504, 1464, 1399, 1253, 1158, 1105, 1036, 928, 770; MS *m*/*z* (%) (EI): 372 ($[M]^+$). Anal. Calcd for $C_{19}H_{16}O_8$: C, 61.29; H, 4.33; found: C, 61.04; H, 4.79.

4.4.4. *trans,trans-α-Carboethoxy-β-(thien-α-oyl)-γ-(4-methoxyphenyl)-γ-butyrolactone* ***5ba***

White solid; yield: 83%; mp 96.8–97.0 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ: 1.29 (t, *J*=7.0 Hz, 3H), 3.80 (s, 3H), 4.20–4.33 (m, 3H), 4.65 (dd, *J*=10.5, =9.5 Hz, 1H), 5.51 (d, *J*=9.5 Hz, 1H), 6.88 (dd, *J*=6.5, 2.0 Hz, 2H), 7.01 (dd, *J*=5.0, 4.0 Hz, 1H), 7.25–7.28 (m, 2H), 7.37 (dd, *J*=1.0, 4.0 Hz, 1H), 7.70 (d, *J*=5, 1.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 14.11, 51.64, 55.45, 55.72, 62.84, 82.00, 114.45, 127.95, 128.60, 128.74, 134.50, 136.69, 143.03, 140.53, 166.73, 169.34, 188.08; IR (KBr, cm^{-1}) ν_{max}: 1807, 1733, 1650, 1613, 1517, 1415, 1382, 1331, 1254, 1170, 1146, 1061, 1029, 1001, 928, 849, 727; MS *m*/*z* (%) (EI): 374 ($[M]^+$). Anal. Calcd for $C_{19}H_{18}O_6S$: C, 60.95; H, 4.85; found: C, 60.63; H, 5.06.

4.4.5. *trans,trans-α-Carboethoxy-β-(thien-α-oyl)-γ-(4-N,N-dimethylaminophenyl)-γ-butyrolactone* ***5bb***

Red solid; yield: 74%; mp 97.7–98.6 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ: 1.29 (t, *J*=7.0 Hz, 3H), 2.90–3.00 (m, 6H), 4.20–4.32 (m, 3H), 4.72 (dd, *J*=10.5, =9.0 Hz, 1H), 5.45 (d, *J*=9.0 Hz, 1H), 6.66 (d, *J*=9.0 Hz, 2H), 6.98–7.02 (m, 1H), 7.21 (d, *J*=9.0 Hz, 2H), 7.39 (d, *J*=4 Hz, 1H), 7.69 (d, *J*=5.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 13.94, 40.19, 51.51, 62.52, 82.59, 112.09, 123.09, 123.08, 127.74, 128.54, 134.39, 136.32, 142.91, 151.12, 166.71, 169.40, 188.14; IR (KBr, cm^{-1}) ν_{max}: 1800, 1730, 1655, 1611, 1507, 1411, 1383, 1334, 1255, 1170, 1140, 1060, 1023, 1008, 925, 848, 725; MS *m*/*z* (%) (EI): 378 ($[M]^+$). Anal. Calcd for $C_{20}H_{21}NO_3S$: C, 62.00; H, 5.46; N, 3.62; found: C, 61.84; H, 5.63; N, 4.00.

4.4.6. *trans,trans-α-Carboethoxy-β-(thien-α-oyl)-γ-(3,4-dioxomethlenephenyl)-γ-butyrolactone* ***5bc***

White solid; yield: 85%; mp 109.8–110.1 °C; ^1H NMR ($CDCl_3$, 500 MHz, ppm) δ: 1.29 (t, *J*=7.0 Hz, 3H), 4.20–4.32 (m, 3H), 4.62 (dd, *J*=9.0, =11.0 Hz, 1H), 5.47 (d, *J*=9.0 Hz, 1H), 5.98–6.00 (m, 2H), 6.70–6.75 (m, 2H), 6.87–6.90 (m, 1H), 7.05 (dd, *J*=4, 5 Hz, 1H), 7.45 (dd, *J*=4, 1.5 Hz, 1H), 7.73 (dd, *J*=5, 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 14.08, 51.62, 55.61, 62.86, 81.96, 101.60, 106.43, 108.49, 120.65, 128.76, 130.35, 134.50, 136.79, 142.98, 148.45, 148.64, 166.62, 169.16, 187.97; IR (KBr, cm^{-1}) ν_{max}: 1809, 1730, 1654, 1504, 1451, 1416, 1328, 1251, 1177, 1152, 1035, 1015, 923, 727; MS *m*/*z* (%) (EI): 388 ($[M]^+$). Anal. Calcd for $C_{19}H_{16}O_7S$: C, 58.76; H, 4.15; found: C, 58.74; H, 4.37.

4.5. X-ray crystal structure data of compounds 3aa, 4af, and 5ab

Intensity data were collected at 293(2) K on Bruker P4 diffract meter with graphite monochromatized and Mo Kα radiation (λ=0.71073 Å). The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically, hydrogen atoms were included but not refined. The final cycle of full matrix least-squares refinement was based on F^2, respectively. All calculations were performed using SHELXS-97 and SHELXL-97 programs.

Crystallographic data have been deposited to the Cambridge Crystallographic Data Center, CCDC 651152 for **3aa**, 682953 for **4af**, and 661008 for **5ab**. Copies of the information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.ac.uk), upon request.

Acknowledgements

Financial support from the National Natural Science Foundation of China (NNSFC) and the Foundation of Education Commission of Shanghai Municipality (Grant Nos. 08ZZ44 and J50102) are acknowledged.

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