Tetrahedron 66 (2010) 7384–7388

Contents lists available at ScienceDirect

Tetrahedron

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

A new odorless one-pot synthesis of thioesters and selenoesters promoted by Rongalite®

Weixing Dan [a], Hongjuan Deng [a], Jiuxi Chen [a,*], Miaochang Liu [a], Jinchang Ding [a,b], Huayue Wu [a,*]

[a] College of Chemistry and Materials Engineering, Wenzhou University, Xueyuan Rd. 276, Wenzhou 325035, PR China
[b] Wenzhou Vocational and Technical College, Wenzhou 325035, PR China

ARTICLE INFO

Article history:
Received 11 May 2010
Received in revised form 8 July 2010
Accepted 13 July 2010
Available online 21 July 2010

Keywords:
Rongalite®
Acylation
Disulfides
Anhydrides
Thioesters
Selenoesters

ABSTRACT

Rongalite® promotes cleavage of diaryl disulfides generating chalcogenolate anions that then undergo facile acylation with anhydrides in the presence of CsF to afford thioesters (**3**) with good to excellent yields. By using the present protocol, 5-arylthio-5-oxopentanoic acid (**4**) can be facilely prepared. The important features of the methodology are broad substrate scope, simple operation, and no requirement for metal catalysts. It is noteworthy that acylations of diphenyl diselane with anhydrides are also conducted smoothly to afford selenoesters (**5**) in good yields under the standard conditions.

1. Introduction

Thioesters are versatile intermediates in natural product synthesis, which have been widespread applications in synthetic chemistry as precursors to aldehydes, ketones, acids, esters, lactones, amides, lactams, and heterocycles, etc.[1] Due to the importance of these compounds, a number of methods for the synthesis of thioesters have been described in the past few years. One of the most common methods involves the acylation reaction of acyl derivatives, such as acids, anhydrides, aldehydes, acyl chlorides, *N*-acylphthalimides, and *N*-acylbenzotriazoles with thiols.[2] Recently, Alper and co-workers introduced a new procedure for preparation of thioesters utilizing palladium-catalyzed thiocarbonylation of iodoarenes with thiols in ionic liquid.[3] However, the use of highly volatile and unpleasant smelling free thiols leads to serious environmental, safety problems and also limits the use of these methods for large-scale operations in all the reported methods. Besides the drawback of these methodologies are associated with undesirable side reactions owing to the oxidation of thiols. In order to minimize or eliminate the encountered problems, the method has been developed in recent years for the synthesis of thioesters by the reaction of anhydrides or acyl halides with disulfides in the presence of various promoting agents, such as In or InI,[4] Sm/$CoCl_2$,[5] SmI_2,[6] Sm/Cp_2TiCl_2,[7] Sm/$NiCl_2$,[8] Zn/$AlCl_3$,[9] Zn/$ZrCl_4$,[10] and $RhCl(PPh_3)_3/H_2$ (1 atm).[11] In 2005, Kim and co-workers developed a new method for the synthesis of thioesters through tin-free radical carbonylation of alkyl allyl sulfone with arylsulfonyl derivatives at the higher pressure of CO in the presence of V-40 (1,1′-azobis(cyclohexane-1-carbonitrile)).[12] Recently, Yamaguchi and co-workers reported rhodium-catalyzed alkylthio exchange reaction of thioester with disulfide.[13]

However, these methods usually suffer from one or more limitations, such as the use of unpleasant odor substrates[2,3] and expensive, toxic or metallic catalysts,[3–11,13] long reaction times,[11,12] unsatisfactory yields,[5] as well as elevated temperature.[12,13] On the other hand, only a few of them have been studied with more complete anhydride scope, and substrates bearing sensitive groups, such as furanyl and thienyl, might not be fully compatible. In this context, developing versatile approaches to achieve thioesters from anhydrides with disulfides still remain in great demand.

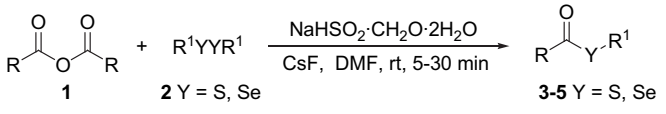
Selenoesters are also important intermediate in organic synthesis[14] and the field of molecular materials.[15] Various approaches toward the synthesis of selenoesters have been explored during the past years. Selenoesters are usually available by the reaction of acyl chlorides and selenides (RSeX, X=H, MgBr, $SnMe_3$, $(n\text{-}Bu)_3Sn$, $SiMe_3$ or SeR) in the presence of metallic catalysts.[16] Recently, Braga and co-workers reported synthesis of selenoesters from acid chlorides mediated by indium metal.[17]

Very recently, we reported Rongalite® (sodium formaldehyde sulfoxylate, $NaHSO_2\cdot CH_2O\cdot 2H_2O$ as an inexpensive reagent)-promoted ring opening of epoxides with disulfides[18] and thia-Michael addition of

* Corresponding authors. Tel./fax: +86 577 8836 8280; e-mail addresses: jiuxichen@wzu.edu.cn (J. Chen), huayuewu@wzu.edu.cn (H. Wu).

0040-4020/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2010.07.023

disulfides to α,β-unsaturated carbonyl compounds[19] in the presence of base. As a continuing interest in the synthesis of sulfur-contained compounds,[18–20] we expected to apply the Rongalite/base system in the acylation of anhydrides with diaryl disulfides. Herein, we wish to report a highly practical method to access thioesters by Rongalite-promoted cleavage of disulfides and subsequent acylation reaction under mild reaction conditions. Moreover, acylation of anhydrides with diphenyl diselenide was also successful to afford selenoesters in good yields under the same conditions (Scheme 1).



1a: R = CH_3
1b: R = Ph
1c: R = CH_3CH_2
1d: R = *p*-$OCH_3C_6H_4$
1e: R = *p*-$CH_3C_6H_4$
1f: R = *o*-$CH_3C_6H_4$
1g: R = *m*-$CH_3C_6H_4$
1h: R = *p*-ClC_6H_4
1i: R = *p*-$NO_2C_6H_4$
1j: R = 2-thienyl
1k: R = 2-furanyl
1l:R = -$(CH_2)_3$-

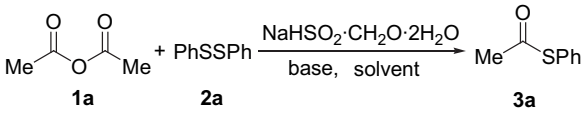
2a: R = Ph; Y = S
2b: R = *p*-ClC_6H_4; Y = S
2c: R = *p*-BrC_6H_4; Y = S
2d: R = *p*-$NO_2C_6H_4$; Y = S
2e: R = *p*-$CH_3C_6H_4$; Y = S
2f: R = *p*-$OCH_3C_6H_4$; Y = S
2g: R = 2-thienyl; Y = S
2h: R = 2-methylfuran-3-yl; Y = S
2i: R = *o*-$NH_2C_6H_4$; Y= S
2j: R = Ph; Y = Se

Scheme 1. Rongalite®-promoted one-pot synthesis of thioesters and selenoesters.

2. Results and discussion

The model reaction of acetic anhydride (**1a**) with diphenyl disulfide (**2a**) was conducted to screen the optimal reaction conditions and the results were listed in Table 1. Initially, the effect of solvents was tested. Among all the solvents screened, trace target product was detected in the presence of a series of solvents, such as CH_2Cl_2, CH_3CN, CH_3CH_2OH, and 1,4-dioxane. However, we were delighted to find that the yield of the desired product **3a** could be improved to 78% when the combination of K_2CO_3 and DMF was employed at room temperature (Table 1, entries 1–5). Encouraged by these promising results, we further optimized the reaction conditions, such as bases, the amount of Rongalite loading, and bases (Table 1, entries 6–17).

Table 1
Screening conditions for the acylation of diphenyl disulfide with acetic anhydride[a]



Entry	Rongalite® (equiv)	Solvent	Base	Yield[b] (%)
1	3	CH_2Cl_2	K_2CO_3	Trace
2	3	CH_3CN	K_2CO_3	Trace
3	3	CH_3CH_2OH	K_2CO_3	Trace
4	3	DMF	K_2CO_3	78
5	3	1,4-Dioxane	K_2CO_3	Trace
6	3	DMF	CsF	83
7	3	DMF	Cs_2CO_3	79
8	3	DMF	Na_2CO_3	75
9	3	DMF	$NaHCO_3$	70
10	2	DMF	CsF	73
11	1	DMF	CsF	58
12	3	DMF	CsF	85[c]
13	3	DMF	CsF	81[d]
14	3	DMF	CsF	91[e]
15	—	DMF	CsF	NR
16	3	DMF	—	45
17	3	DMF	CsF	82[f]

NR=No reaction.
[a] All reactions were run with **1a** (0.4 mmol), **2a** (0.2 mmol), and base (1.5 equiv) in solvent (2 mL) at room temperature for 20 min.
[b] Isolated yields.
[c] CsF (1.0 equiv).
[d] CsF (0.5 equiv).
[e] CsF (0.75 equiv).
[f] At 50 °C.

Among the screened bases ($NaHCO_3$, Na_2CO_3, K_2CO_3, Cs_2CO_3, and CsF), CsF is the best results (Table 1, entries 4, 6–9). Moreover, the results indicated that the yield was decreased to some extent when 2 equiv of Rongalite was added (Table 1, entry 10), and no reaction was observed even for longer time in the absence of Rongalite (Table 1, entry 15). We also examined the effect of the amount of CsF (Table 1, entries 12–14), the target product was obtained in 45% yield without CsF (Table 1, entry 16). With 0.75 equiv of CsF we obtained the best yield of the product. The yield was decreased to some extent when the reaction was carried out at the elevated temperature (Table 1, entry 17). As a result, the model reaction was carried out under optimized conditions with 3 equiv of Rongalite and 0.75 equiv CsF at room temperature in DMF, which led to **3a** in 91% yield.

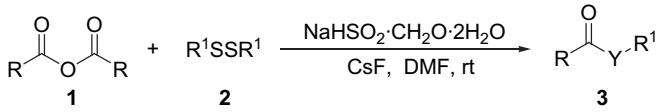
With the optimal conditions in hand, the scope and limitations of this new methodology were examined as shown in Table 2. A variety of diaryl disulfides, both electron-donating and electron-withdrawing groups on the aromatic ring, were reacted with acetic anhydride (**1a**) to generate the thioesters (**3**) in good to excellent yields. Electronic effects on the aromatic ring associated with disulfides had little effect on the yields. It is observed that the corresponding products were obtained in excellent yields by the acylation of electron-deficient disulfides, such as *p*-chlorophenyl disulfide (**2b**), *p*-bromophenyl disulfide (**2c**), and *p*-nitrophenyl disulfide (**2d**) (Table 2, entries 2–4) under optimal conditions. In contrast, the yields were decreased slightly when electron-rich disulfides, such as *p*-methylphenyl disulfide (**2e**) and *p*-methoxyphenyl disulfide (**2f**) were used (Table 2, entries 5–6). Moreover, we examined the reactivity of heterocyclic disulfides, such as 2-thienyl disulfide (**2g**) and 2-methylfuran-3-yl disulfide (**2h**) with **1a**, the corresponding thioesters **3g** and **3h** in good yields under the standard conditions (Table 2, entries 7–8).

On the other hand, the combination of a wide range of anhydrides **1b**–**1k** with diphenyl disulfide (**2a**) was also checked in our reaction system (Table 2, entries 9–18). Various anhydrides bearing either electron-donating or electron-withdrawing groups on the aromatic ring were investigated. It is observed that the substitution group on the phenyl ring did not make any difference in this reaction.

We further examined the steric effect in our system. A mono-substitution group on the *para*-, *ortho*-, and *meta*-position for anhydrides (Table 2, entries 12–14) had little effect on the yields in the reaction. For example, **2a** reacted with anhydrides, such as *p*-methylbenzoic anhydride (**1e**), *o*-methylbenzoic anhydride (**1f**), and *m*-methylbenzoic anhydride (**1g**) efficiently and afforded **3l**, **3m**, and **3n** in 85%, 82%, and 83% yields, respectively. Moreover, we also examined the reactivity of heterocyclic anhydrides with **2a** in the presence of Rogalite and CsF (Table 2, entries 17–18). The results indicated that heterocyclic anhydrides exhibited analogous behavior to that of aromatic anhydrides and aliphatic anhydrides. Unfortunately, attempt to acylation of dibenzyl disulfide, a dialkyl disulfide, with acetic anhydride failed.

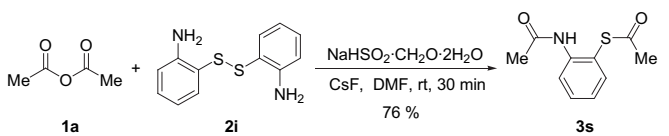
It is noteworthy that we examined acylation of *o*-aminophenyl disulfide (**2i**) with acetic anhydride (**1a**) under the standard conditions (Scheme 2). The corresponding diacylated product **3s** was obtained in 28% yield. Increasing the amount of **1a** to 4 equiv resulted in 76% yield of **3s**.

Table 2
Synthesis of thioesters from anhydride and disulfides in the presence of Rogalite and CsF[a]



Entry	R (**1**)	R^1 (**2**)	Time (min)	Product	Yield[b] (%)
1	CH_3 **1a**	C_6H_5 **2a**	15	**3a**	91, 92[c]
2	**1a**	*p*-(Cl)C_6H_5 **2b**	5	**3b**	98
3	**1a**	*p*-(Br)C_6H_5 **2c**	5	**3c**	95
4	**1a**	*p*-(NO_2)C_6H_5 **2d**	5	**3d**	96
5	**1a**	*p*-(CH_3)C_6H_5 **2e**	20	**3e**	87
6	**1a**	*p*-(OCH_3)C_6H_5 **2f**	25	**3f**	85
7	**1a**	2-Thienyl **2g**	10	**3g**	96
8	**1a**	2-Methylfuran-3-yl **2h**	20	**3h**	90
9	C_6H_5 **1b**	**2a**	30	**3i**	87
10	CH_3CH_2 **1c**	**2a**	30	**3j**	87
11	*p*-(OCH_3)C_6H_5 **1d**	**2a**	30	**3k**	82
12	*p*-(CH_3)C_6H_5 **1e**	**2a**	30	**3l**	85
13	*o*-(CH_3)C_6H_5 **1f**	**2a**	30	**3m**	82
14	*m*-(CH_3)C_6H_5 **1g**	**2a**	30	**3n**	83
15	*p*-(Cl)C_6H_5 **1h**	**2a**	30	**3o**	87
16	*p*-(NO_2)C_6H_5 **1i**	**2a**	30	**3p**	73
17	2-Furanyl **1j**	**2a**	30	**3q**	89
18	2-Thienyl **1k**	**2a**	30	**3r**	91

[a] All reactions were run with anhydrides **1** (0.44 mmol), disulfides **2** (0.2 mmol), $NaHSO_2 \cdot CH_2O \cdot 2H_2O$ (0.6 mmol), CsF (0.15 mmol), and DMF (2 mL) at room temperature.
[b] Isolated yields.
[c] The reaction was run with acetic anhydride **1a** (22 mmol, 2.24 g), diphenyl disulfide **2a** (10 mmol, 2.18 g), $NaHSO_2 \cdot CH_2O \cdot 2H_2O$ (30 mmol) and CsF (7.5 mmol) in 10 mL of DMF at room temperature for 25 min.

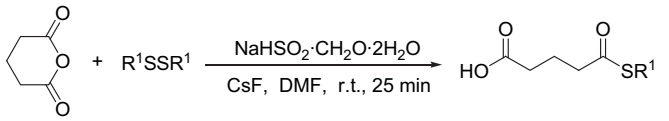


Scheme 2. Rongalite®-promoted acylation of *o*-aminophenyl disulfide with acetic anhydride.

As listed in Table 3, the acylation of cyclic anhydride, such as glutaricanhydride (**1l**) with different diaryl disulfides was also investigated using the present protocol. In all cases, Rongalite and base-promoted reactions proceeded smoothly and the corresponding 5-arylthio-5-oxopentanoic acids (**4a**–**4f**) were achieved in good yields.

Next, to extend the scope of this reaction, the acylation of various anhydrides (**1**) with diphenyl diselenide (**2j**) were also tested under the standard conditions. The yield was decreased to some extent when aliphatic anhydride, such as acetic anhydride (**1a**) was used (Table 4, entry 1). Aryl anhydrides with electron-donating groups gave a high yield (Table 4, entries 3 and 4), whereas aryl anhydrides with strongly electron-withdrawing group (NO_2) afforded in slight lower yield (81%, Table 4, entry 6). However, heterocyclic anhydrides (**1j** and **1k**) could afford the corresponding selenoestes **5g** and **5h** in excellent yields.

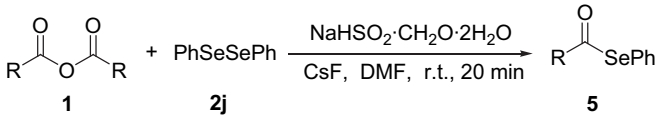
Table 3
Synthesis of 5-arylthio-5-oxopentanoic acid from glutaricanhydride and disulfides in the presence of Rogalite and CsF[a]



Entry	R^1 (**2**)	Product	Yield[b] (%)
1	C_6H_5 **2a**	**4a**	80
2	*p*-(Cl)C_6H_5 **2b**	**4b**	82
3	*p*-(CH_3)C_6H_5 **2e**	**4c**	78
4	*p*-(OCH_3)C_6H_5 **2f**	**4d**	74
5	2-thienyl **2g**	**4e**	85
6	2-methylfuran-3-yl **2h**	**4f**	80

[a] All reactions were run with **1l** (0.44 mmol), disulfides **2** (0.2 mmol), $NaHSO_2 \cdot CH_2O \cdot 2H_2O$ (0.6 mmol), CsF (0.15 mmol), and DMF (2 mL) at room temperature.
[b] Isolated yields.

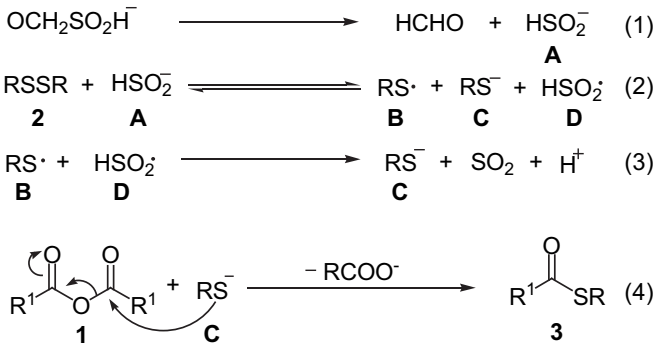
Table 4
Synthesis of thioesters from anhydride and disulfides in the presence of Rogalite and CsF[a]



Entry	R	Product	Yield[b] (%)
1	CH_3 **1a**	**5a**	78
2	C_6H_5 **1b**	**5b**	93
3	*p*-(OCH_3)C_6H_5 **1d**	**5c**	94
4	*p*-(CH_3)C_6H_5 **1e**	**5d**	96
5	*p*-(Cl)C_6H_5 **1h**	**5e**	91
6	*p*-(NO_2)C_6H_5 **1i**	**5f**	81
7	2-Furanyl **1j**	**5g**	95
8	2-Thienyl **1k**	**5h**	97

[a] All reactions were run with **1** (0.44 mmol), diphenyl diselenide (0.2 mmol), CsF (0.15 mmol), and DMF (2 mL) at room temperature.
[b] Isolated yields.

According to the previous proposed mechanism,[14] a tentative mechanism for the formation of thioesters was proposed in Scheme 3. Rongalite® can be readily decomposed into HCHO and HSO_2^- anion (**A**). Intermediate (**A**) then reacts with RSSR (**2**) to generate two radical intermediates (**B** and **D**) and an anion (**C**). The radical (**B**) can also be converted into thiolate anion (**C**) by reacting with intermediate (**D**). Finally, the acylation of the thiolate anion (**C**) with anhydrides (**1**) affords the target product.



Scheme 3. A tentative mechanism for the formation of thioesters.

Finally, the present route to thioesters was successfully applied to a large-scale reaction. For instance, the acylation of acetic anhydride **1a** (2.24 g) with diphenyl disulfide **2a** (2.18 g) promoted by Rongalite provided the desired product **3a** in 92% yield (Table 2, entry 1).

3. Conclusion

In summary, a simple, efficient and broadly applicable general method for the synthesis of thioesters and selenoesters promoted by inexpensive Rongalite has been developed. Compare to reported methodologies, the important features of this methodology are broad substrates scope, high yield, no requirement of metal catalysts, reasonably rapid reaction rate and especially in a scaled-up synthesis, which provides a better and practical alternative to the existing procedures. Efforts to explore the detailed mechanism and further applications of the present system in other transformations using disulfide as a reaction partner are ongoing in our group.

4. Experimental section

4.1. General

Chemicals and solvents were either purchased or purified by standard techniques. Melting points were uncorrected and recorded on Digital Melting Point Apparatus WRS-1B. IR spectra were recorded on an AVATAR 370 FI-Infrared Spectrophotometer. NMR spectroscopy was performed on both a Bruck-300 spectrometer operating at 300 MHz (^{1}H NMR) and 125 MHz (^{13}C NMR). TMS (tetramethylsilane) was used as an internal standard and $CDCl_3$ was used as the solvent. Mass spectra were measured with Thermo Finnigan LCQ-Advantage. Elemental analysis was determined on a Carlo-Erba 1108 instrument.

4.2. General procedure for synthesis of synthesis of thioesters

A mixture of anhydride **1** (0.44 mmol), disulfide **2** (0.2 mmol), Rongalite (3 equiv), and CsF (0.75 equiv) in DMF (2 mL) was stirred at room temperature for respective min in Table 2 under air. The reaction mixture washed with brine and extracted with ethyl acetate (3×10 mL). The organic phase was separated and dried over anhydrous magnesium sulfate, filtered, and the solvent was evaporated under vacuum. The residue was purified by flash column chromatography (ethyl acetate or hexane/ethyl acetate) to afford the desired product **3** and **4**.

*4.2.1. S-2-Acetamidophenyl ethanethioate (**3s**) (Scheme 2).* White solid, mp 110–112 °C (lit.[21] 113–114 °C); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.17 (s, 3H), 2.46 (s, 3H), 7.12–7.17 (m, 1H), 7.38–7.48 (m, 2H), 7.70 (br s, 1H), 8.28–8.30 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 24.7, 30.3, 117.0, 122.3, 124.7, 131.5, 136.0, 139.5, 168.1, 193.4.

*4.2.2. 5-(Phenylthio)-5-oxo-pentanoic acid (**4a**) (Table 3, entry 1).* White solid, mp 58–60 °C (not reported); IR (liquid film) 1699.0 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.99–2.09 (m, 2H), 2.47 (t, J=7.3 Hz, 2H), 2.76 (t, J=7.3 Hz, 2H), 7.42 (m, 5H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 20.3, 32.8, 42.3, 127.6, 129.2, 129.5, 134.5, 178.8, 196.9. MS (ESI) m/z (%): 225 ([M+1]$^+$, 100). Anal. Calcd for $C_{11}H_{12}O_3S$: C, 58.91; H, 5.39. Found: C 58.88; H 5.43.

*4.2.3. 5-(p-Chlorophenylthio)-5-oxopentanoic acid (**4b**) (Table 3, entry 2).* Colorless crystal, mp 56–58 °C (not reported); IR (liquid film) 1698.4 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.01–2.06 (m, 2H), 2.48 (t, J=7.2 Hz, 2H), 2.77 (t, J=7.2 Hz, 2H), 7.31–7.41 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 20.2, 32.5, 42.3, 125.9, 129.5, 135.7, 135.9, 178.1, 196.3. MS (ESI) m/z (%): 261 ([M+3]$^+$, 35), 259 ([M+1]$^+$, 100). Anal. Calcd for $C_{11}H_{11}ClO_3S$: C, 51.07; H, 4.29. Found: C 51.12; H 4.25.

*4.2.4. 5-(p-Tolylthio)-5-oxo-pentanoic acid (**4c**) (Table 3, entry 3).* White crystal, mp 78–79 °C (not reported); IR (liquid film) 1702.9 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.00–2.07 (m, 2H), 2.37 (s, 3H), 2.47 (t, J=7.2 Hz, 2H), 2.74 (t, J=7.2 Hz, 2H), 7.21–7.30 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 20.2, 21.3, 32.7, 42.1, 123.9, 130.0, 134.4, 139.7, 178.7, 197.4. MS (ESI) m/z (%): 239 ([M+1]$^+$, 100). Anal. Calcd for $C_{12}H_{14}O_3S$: C, 60.48; H, 5.92. Found: C 60.53; H 5.95.

*4.2.5. 5-(p-Methoxyphenylthio)-5-oxopentanoic acid (**4d**) (Table 3, entry 4).* White crystal, mp 72–74 °C (not reported); IR (liquid film) 1708.4 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.00–2.07 (m, 2H), 2.46 (t, J=7.2 Hz, 2H), 2.74 (t, J=7.2 Hz, 2H), 3.82 (s, 3H), 6.94 (d, J=8.6 Hz, 2H), 7.31 (d, J=8.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 20.2, 32.7, 42.0, 55.3, 114.9, 118.2, 136.1, 160.7, 178.8, 197.9. MS (ESI) m/z (%): 255 ([M+1]$^+$, 100). Anal. Calcd for $C_{12}H_{14}O_4S$: C, 56.68; H, 5.55. Found: C 56.73; H 5.58.

*4.2.6. 5-(Thiophen-2-ylthio)-5-oxo-pentanoic acid (**4e**) (Table 3, entry 5).* Colorless oil; IR (liquid film) 1704.9 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.00–2.07 (m, 2H), 2.47 (t, J=7.2 Hz, 2H), 2.76 (t, J=7.2 Hz, 2H), 7.10–7.17 (m, 2H), 7.55–7.57(m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 20.0, 32.6, 41.6, 124.4, 127.9, 131.9, 135.8, 178.8, 196.9. MS (ESI) m/z (%): 231 ([M+1]$^+$, 100). Anal. Calcd for $C_9H_{10}O_3S_2$: C, 46.94; H, 4.38. Found: C 46.99; H 4.45.

*4.2.7. 5-Oxo-5-(2-methylfuran-3-ylthio)pentanoic acid (**4f**) (Table 3, entry 6).* Pale oil; IR (liquid film) 1701.4 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.95–2.04 (m, 2H), 2.23 (s, 3H), 2.42 (t, J=7.2 Hz, 2H), 2.70 (t, J=7.2 Hz, 2H), 6.30 (s, 1H), 7.34 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.8, 20.2, 32.6, 41.8, 103.9, 114.7, 141.0, 156.1, 177.6, 196.7. MS (ESI) m/z (%): 229 ([M+1]$^+$, 100). Anal. Calcd for $C_{10}H_{12}O_4S$: C, 52.62; H, 5.30. Found: C 52.57; H 5.35.

4.3. General procedure for synthesis of synthesis of selenoesters

A mixture of anhydride **1** (0.44 mmol), diphenyl diselenide (0.2 mmol), Rongalite (3 equiv), and CsF (0.75 equiv) in DMF (2 mL) was stirred at room temperature for 25 min under air. The reaction mixture washed with brine and extracted with ethyl acetate (3×10 mL). The organic phase was separated and dried over anhydrous magnesium sulfate, filtered, and the solvent was evaporated under vacuum. The residue was purified by flash column chromatography (ethyl acetate or hexane/ethyl acetate) to afford the desired product **5**.

*4.3.1. Se-Phenyl benzoselenoate (**5b**) (Table 4, entry 2).* Yellow solid, mp 40–41 °C (lit.[4a] 37–38 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43–7.52 (m, 5H), 7.60–7.63 (m, 3H), 7.93–7.96 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 125.8, 127.3, 128.9, 129.0, 129.3, 133.8, 136.3, 138.5, 192.3.

*4.3.2. Se-Phenyl 4-methoxybenzoselenoate (**5c**) (Table 4, entry 3).* Colorless crystal, mp 59–61 °C (lit.[22] 61–62 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.88 (s, 3H), 6.95–6.98 (m, 2H), 7.42–7.44 (m, 3H), 7.59–7.63 (m, 2H), 7.91–7.94 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.5, 114.1, 125.8, 128.8, 129.2, 129.6, 131.3, 136.4, 164.4, 191.2.

*4.3.3. Se-Phenyl thiophene-2-carboselenoate (**5h**) (Table 4, entry 6).* Pale yellow solid, mp 57–59 °C (lit.[23] 60–61); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.16–7.19 (m, 1H), 7.42–7.44 (m, 3H), 7.60–7.63 (m, 2H), 7.70–7.72 (m, 1H), 7.88–7.90 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 125.5, 128.0, 129.1, 129.3, 132.0, 133.6, 136.2, 143.0, 183.5.

Acknowledgements

We thank the National Key Technology R&D Program (No. 2007BAI34B00), the Technology Program of Zhejiang Province (No. 2009C31159) and the Natural Science Foundation of Zhejiang Province (No. Y4080107) for financial support.

Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2010.07.023.

References and notes

1. (a) Evans, D. A.; Dart, M. J.; Duffy, J. L.; Yang, M. G. *J. Am. Chem. Soc.* **1996**, *118*, 4322; (b) Paz, M. M.; Corrca, J. F.; Cabcza, M. I.; Sardina, F. J. *Tetrahedron Lett.* **1996**, *37*, 9259; (c) Um, P. J.; Drucckhammer, D. G. *J. Am. Chem. Soc.* **1998**, *120*, 5605; (d) Agarwal, V. K.; Thomas, A.; Schade, S. *Tetrahedron* **1997**, *53*, 16213; (e) Yang, W. I.; Romo, D. *Tetrahedron* **1997**, *53*, 16471; (f) Mizumo, M.; Muramuto, I.; Kawakami, T.; Soike, M.; Aimoto, S.; Hanoda, K.; Inazu, T. *Tetrahedron Lett.* **1998**, *39*, 55; (g) White, J. D.; Kim, T. S.; Nambu, M. *J. Am. Chem. Soc.* **1997**, *119*, 103.
2. (a) Bandgar, B. P.; More, P. E.; Kamble, V. T.; Sawant, S. S. *Aust. J. Chem.* **2008**, *61*, 1006; (b) Chen, C. T.; Kuo, J. H.; Li, C. H.; Barhate, N. B.; Hon, S. W.; Li, T. W.; Chao, S. D.; Liu, C. C.; Li, Y. C.; Chang, I. H.; Lin, J. S.; Liu, C. J.; Chou, Y. C. *Org. Lett.* **2001**, *3*, 3729; (c) Katritzky, A. R.; Shestopalov, A. A.; Suzuki, K. *Synthesis* **2004**, 1806; (d) Yamada, S. I.; Yokoyama, Y.; Shioiri, T. *J. Org. Chem.* **1974**, *39*, 3302; (e) Kadam, S. T.; Kim, S. S. *Synthesis* **2008**, 3307; (f) Zhang, L.; Luo, Y.; Fan, R. H.; Wu, J. *Green Chem.* **2007**, *9*, 1022; (g) Jeyakumar, K.; Chand, D. K. *J. Mol. Catal. A: Chem.* **2006**, *255*, 275; (h) Chakraborti, A.; Shivani, K. *J. Org. Chem.* **2006**, *71*, 5785; (i) Firouzabadi, H.; Iranpoor, N.; Farahi, S. *J. Mol. Catal. A: Chem.* **2008**, *289*, 61; (j) Ranu, B. C.; Jana, R. *Adv. Synth. Catal.* **2005**, *347*, 1811; (k) Bandgar, S. B.; Bandgar, B. P.; Korbad, B. L.; Sawant, S. S. *Tetrahedron Lett.* **2007**, *48*, 1287; (l) Qiu, R.; Zhang, G.; Ren, X.; Xu, X.; Yang, R.; Luo, S.; Yin, S. *J. Organomet. Chem.* **2010**, *695*, 1182.
3. Cao, H.; McNamee, L.; Alper, H. *J. Org. Chem.* **2008**, *73*, 3530.
4. (a) Peppe, C.; Castro, L. B. D. *Can. J. Chem.* **2009**, *87*, 678; (b) Ranu, B. C.; Mandal, T. *J. Org. Chem.* **2004**, *69*, 5793.
5. (a) Chen, R. E.; Zhang, Y. M. *Synth. Commun.* **1999**, *29*, 3699; (b) Chowdhury, S.; Roy, S. *Tetrahedron Lett.* **1997**, *38*, 2149.
6. (a) Wang, X. X.; Zou, X. F.; Du, J. X. *J. Chem. Res., Synop.* **2006**, 64; (b) Patra, P. K.; Shanmugasundaram, K.; Matoba, M.; Nishide, K.; Kajimoto, T.; Node, M. *Synthesis* **2005**, 447; (c) Bao, W. L.; Zhang, Y. M. *Synth. Commun.* **1995**, *25*, 143.
7. Jia, X. S.; Zhang, Y. M. *J. Chem. Res., Synop.* **2003**, *9*, 540.
8. Wu, H. Y.; Chen, R. E.; Zhang, Y. M. *Chin. Chem. Lett.* **1999**, *10*, 899.
9. (a) Lakouraj, M. M.; Movassagh, B.; Fadaei, Z. *Monatsh. Chem.* **2002**, *133*, 1085; (b) Movassagh, B.; Lakouraj, M. M.; Fadaei, Z. *J. Chem. Res., Synop.* **2001**, 22.
10. Tian, F. S.; Zhu, Y. M.; Zhang, S. L.; Wang, Y. L. *J. Chem. Res., Synop.* **2002**, *11*, 582.
11. Ajiki, K.; Hirano, M.; Tanaka, K. *Org. Lett.* **2005**, *7*, 4193.
12. Kim, S.; Kim, S.; Otsuka, N.; Ryu, I. *Angew. Chem., Int. Ed.* **2005**, *44*, 6183.
13. Arisawa, M.; Kubota, T.; Yamaguchi, M. *Tetrahedron Lett.* **2008**, *49*, 1975.
14. (a) Keck, G.; Grier, M. C. *Synlett* **1999**, 1657; (b) Boger, D. L.; Mathvink, R. J. *J. Org. Chem.* **1992**, *57*, 1429; (c) Chen, C.; Crich, D.; Papadatos, A. *J. Am. Chem. Soc.* **1992**, *114*, 8313; (d) Hiiro, T.; Morita, Y.; Inoue, T.; Kambe, N.; Ogawa, A.; Ryu, I.; Sonoda, N. *J. Am. Chem. Soc.* **1990**, *112*, 455; (e) Kobayashi, S.; Uchiro, H.; Fujishita, Y.; Shiina, I.; Mukaiyama, T. *J. Am. Chem. Soc.* **1991**, *113*, 4247.
15. (a) Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 3348; (b) Yamada, J.; Akutsu, H.; Nishikawa, H.; Kikuchi, K. *Chem. Rev.* **2004**, *104*, 5057; (c) Woon, K. L.; Aldred, M. P.; Vlachos, P.; Mehl, G. H.; Stirner, T.; Kelly, S. M.; O'Neill, M. *Chem. Mater.* **2006**, *18*, 2311; (d) Cristiano, R.; Vieira, A. A.; Ely, F.; Gallardo, H. *Liq. Cryst.* **2006**, *33*, 381.
16. (a) Munbunjong, W.; Lee, E. H.; Ngernmaneerat, P.; Kim, S. J.; Singh, G.; Chavasiri, W.; Jang, D. O. *Tetrahedron* **2009**, *65*, 2467; (b) Yamamoto, T.; Moriura, E.; Sawa, A.; Yoshimatsu, M. *Chem. Lett.* **2008**, *37*, 1046; (c) Toyofuku, M.; Murase, E.; Fujiwara, S. I.; Shin-ike, T.; Kuniyasu, H.; Kambe, N. *Org. Lett.* **2008**, *10*, 3957; (d) Wallner, O. A.; Szabo, K. J. *J. Org. Chem.* **2005**, *70*, 9215; (e) Movassagh, B.; Mirshojaei, F. *Monatsh. Chem.* **2003**, *134*, 831; (f) Nishiyama, Y.; Kawamatsu, H.; Funato, S.; Tokunaga, K.; Sonoda, N. *J. Org. Chem.* **2003**, *68*, 3599; (g) Nishino, T.; Okada, M.; Kuroki, T.; Watanabe, T.; Nishiyama, Y.; Sonoda, N. *J. Org. Chem.* **2002**, *67*, 8696; (h) Beletskaya, I. P.; Sigeev, A. S.; Peregudov, A. S.; Petrovskii, P. V. *Russ. J. Org. Chem.* **2001**, *37*, 1703; (i) Silveira, C. C.; Braga, A. L.; Larghi, E. L. *Organometallics* **1999**, *18*, 5183.
17. Marin, G.; Braga, A. L.; Rosa, A. S.; Galetto, F. Z.; Burrow, R. A.; Gallardo, H.; Paixao, M. W. *Tetrahedron* **2009**, *65*, 4614 and reference therein.
18. Guo, W. X.; Chen, J. X.; Wu, D. Z.; Ding, J. C.; Chen, F.; Wu, H. Y. *Tetrahedron* **2009**, *65*, 5240.
19. Guo, W. X.; Lv, G. S.; Chen, J. X.; Gao, W. X.; Ding, J. C.; Wu, H. Y. *Tetrahedron* **2010**, *66*, 2297.
20. (a) Chen, J. X.; Wu, H. Y.; Jin, C.; Zhang, X. X.; Xie, Y. Y.; Su, W. K. *Green Chem.* **2006**, *8*, 330; (b) Su, W. K.; Chen, J. X.; Wu, H. Y.; Jin, C. *J. Org. Chem.* **2007**, *72*, 4524; (c) Xiao, H. L.; Chen, J. X.; Liu, M. C.; Zhu, D. J.; Ding, J. C.; Wu, H. Y. *Chem. Lett.* **2009**, *38*, 170; (d) Cai, M. T.; Lv, G. S.; Chen, J. X.; Gao, W. X.; Ding, J. C.; Wu, H. Y. *Chem. Lett.* **2010**, *39*, 368.
21. Collings, A. J.; Morgan, K. J. *Tetrahedron* **1964**, *20*, 2167.
22. Kato, S.; Kabuto, H.; Ishihara, H.; Murai, T. *Synthesis* **1985**, 520.
23. Back, T. G.; Collins, S.; Kerr, R. G. *J. Org. Chem.* **1981**, *46*, 1564.