Peer-reviewed version available at *Molecules* **2018**, *23*, 1339; doi:10.3390/molecules23061339

*Article*

# Indium-Catalyzed Direct Conversion of Lactones into Thiolactones Using a Disilathiane as a Sulfur Source

**Yohei Ogiwara, Ken Takano, Shuhei Horikawa and Norio Sakai***

Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan; yoheiogiwara@rs.tus.ac.jp (Y.O.); 7218534@ed.tus.ac.jp (K.T.); 7216665@alumni.tus.ac.jp (S.H.)

* Correspondence: sakachem@rs.noda.tus.ac.jp; Tel.: +81-4-7123-9890

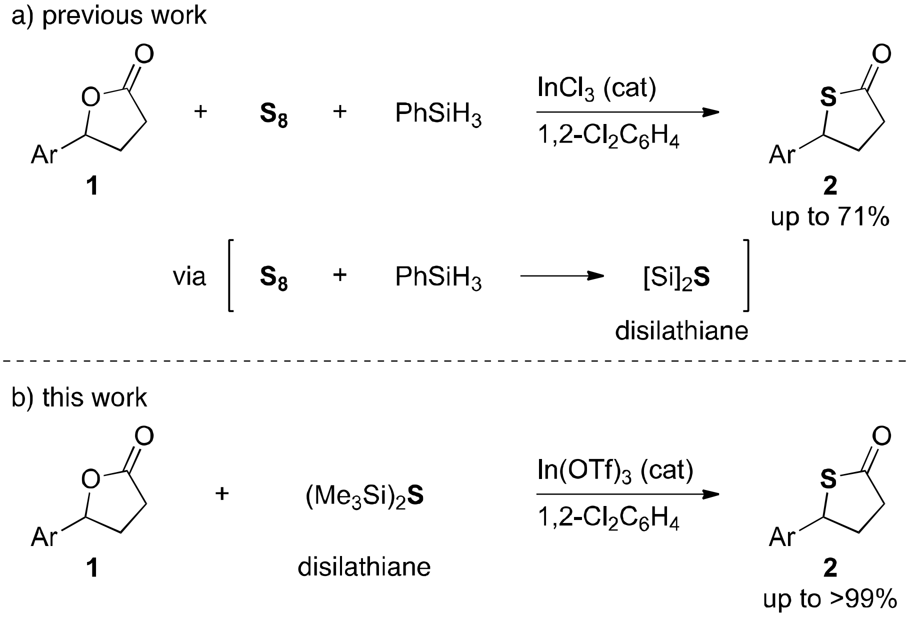
**Abstract:** Indium-catalyzed reaction of lactones and a disilathiane leading to thiolactones is described. The direct synthesis of thiolactones from lactones with an appropriate sulfur source is one of the most attractive approaches in organic and pharmaceutical chemistry. In this context, we found an indium-catalyzed direct conversion of lactones into thiolactones in the presence of elemental sulfur and a hydrosilane via formation of the disilathiane *in-situ*. On the basis of the previous reaction, the application utilizing the disilathiane as a sulfur source was performed herein for the efficient synthesis of a variety of thiolactone derivatives from lactones by an indium-catalyst.

**Keywords:** indium-catalyst; disilathiane; lactones; thiolactones.

## 1. Introduction

The introduction of sulfur atom to organic molecules is a significant topic in synthetic chemistry because it potentially provides the complex and important sulfur-containing compounds directly. Therefore, a search for undiscovered sulfur source that could be applicable to organic sulfur chemistry is imperative, and extensive efforts have been devoted for development of molecular transformations utilizing a novel sulfur source by many research groups thus far [1–6]. In this context, our group have demonstrated that the copper-catalyzed construction of diaryl sulfides from aryl iodides and hexamethyldisilathiane, $(Me_3Si)_2S$ [7]. In the reaction, the disilathiane functioned as a novel and effective S1 source of sulfides, and the results encouraged us that the strategy employing the disilathiane could be acceptable for any other sulfur-introduction reactions [8–12].

Recently, we also reported the indium-catalyzed reductive conversion of lactones **1** into thiolactones **2** using a combination of elemental sulfur ($S_8$) and a hydrosilane, wherein the generation of a disilathiane ($[Si]_2S$) from $S_8$ and a hydrosilane is a key process for the formation of thiolactones **2** (Scheme 1a) [13]. Although the *in-situ* formation strategy of the disilathiane is useful and easily-handling procedure, the yields of thiolactones **2** obtained by the method remained in low to moderate levels. We envisioned that the problem could be overcome by utilizing the activated disilathiane, which can be easily prepared from $S_8$ and a hydrosilane in advance. Herein, we describe the indium-catalyzed direct formation of thiolactones **2** from lactones **1** using hexamethyldisilathiane as an effective S1 source (Scheme 1b).

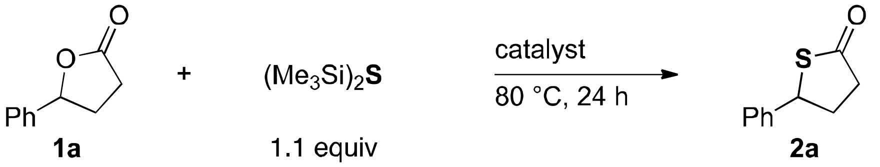


**Scheme 1.** Indium-catalyzed conversion of lactones **1** to thiolactones **2**.

## 2. Results and Discussion

On the bases of our previous study on the $InCl_3$-catalyzed transformation of lactones **1** to thiolactones **2** employing elemental sulfur ($S_8$) and a hydrosilane, the optimization studies utilizing a disilathiane as a sulfur source were initially conducted (Table 1). When γ-phenyl-γ-butyrolactone (**1a**) was treated with 1.1 equiv of hexamethyldisilathiane, $(Me_3Si)_2S$, in the presence of 5 mol % of $InCl_3$ in 1,2-dichlorobenzene at 80 °C for 24 h, the corresponding γ-butyrothiolactone **2a** was obtained in a 77% GC yield (entry 1). The formation of **2a** was also observed in the cases with other indium(III) catalysts, such as $InBr_3$, $InI_3$, $In(OAc)_3$, and $In(OTf)_3$, in good yields (entries 2–5). Especially, $In(OTf)_3$ proved to be the most effective catalyst for the reaction, shown in entry 5, which provided **2a** in a 99% GC yield with a 94% isolated yield. In contrast, in the absence of the catalyst, the thiolactone was not generated (entry 6). Although several solvents (chlorobenzene, 1,2-dichloroethane, and toluene) were acceptable to the reaction, these yields were not higher than that using 1,2-$Cl_2C_6H_4$ as a solvent (entries 7–9 vs entry 5). The reaction with lower catalyst loading (1 mol % of $In(OTf)_3$) was also possible to form **2a** in a 97% GC yield, then the product was isolated in an 83% yield (entry 10). Employing a stoichiometric amount of TfOH instead of $In(OTf)_3$ catalyst provided the thiolactone quantitatively (entry 11), whereas its application to the TfOH-catalyzed reaction did not proceed well (entry 12).

**Table 1.** Screening of the reaction conditions for the catalytic conversion of **1a** to **2a**.[a]



| Entry | Catalyst | Solvent | GC yield of 2a |
|---|---|---|---|
| 1 | $InCl_3$ (5 mol %) | 1,2-$Cl_2C_6H_4$ | 77 |
| 2 | $InBr_3$ (5 mol %) | 1,2-$Cl_2C_6H_4$ | 62 |
| 3 | $InI_3$ (5 mol %) | 1,2-$Cl_2C_6H_4$ | 69 |
| 4 | $In(OAc)_3$ (5 mol %) | 1,2-$Cl_2C_6H_4$ | 78 |
| 5 | $In(OTf)_3$ (5 mol %) | 1,2-$Cl_2C_6H_4$ | 99 (94)[b] |
| 6 | none | 1,2-$Cl_2C_6H_4$ | 0 |
| 7 | $In(OTf)_3$ (5 mol %) | $ClC_6H_5$ | 76 |

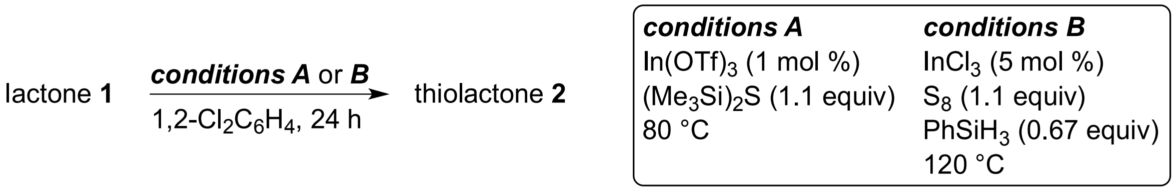
Peer-reviewed version available at *Molecules* **2018**, *23*, 1339; doi:10.3390/molecules23061339

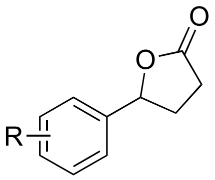
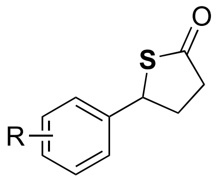
| | | | |
|---|---|---|---|
| 8 | $\text{In(OTf)}_3$ (5 mol %) | $\text{ClCH}_2\text{CH}_2\text{Cl}$ | 95 |
| 9 | $\text{In(OTf)}_3$ (5 mol %) | $\text{CH}_3\text{C}_6\text{H}_5$ | 59 |
| 10 | $\text{In(OTf)}_3$ (1 mol %) | 1,2-$\text{Cl}_2\text{C}_6\text{H}_4$ | 97 (83)[b] |
| 11 | TfOH (100 mol %) | 1,2-$\text{Cl}_2\text{C}_6\text{H}_4$ | 99 |
| 12 | TfOH (15 mol %) | 1,2-$\text{Cl}_2\text{C}_6\text{H}_4$ | 23 |

[a] Reaction conditions: **1a** (0.5 mmol), $(\text{Me}_3\text{Si})_2\text{S}$ (0.55 mmol), catalyst (0.005–0.025 mmol), solvent (0.5 mL) at 80 °C for 24 h. [b] Isolated yield.

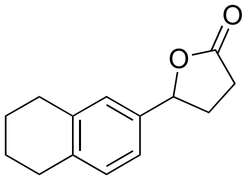
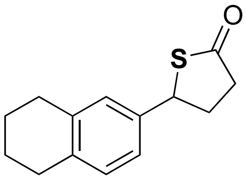
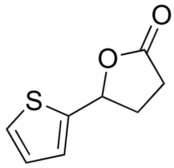
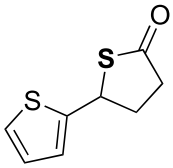
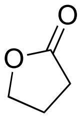
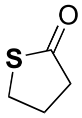
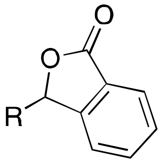
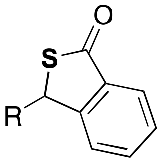
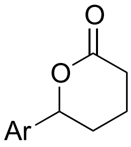
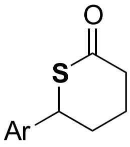
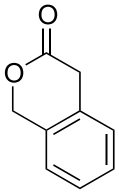
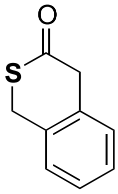
Examination of the $\text{In(OTf)}_3$-catalyzed direct transformation of several lactones **1** was then conducted under the conditions described for entry 10 in Table 1. The results of the present reaction utilizing $\text{In(OTf)}_3/(\text{Me}_3\text{Si})_2\text{S}$ system (conditions A) and our previous yields of thiolactones **2** by $\text{InCl}_3$-catalyzed reaction using $\text{S}_8/\text{PhSiH}_3$ (conditions B) [13] are summarized in Table 2. In most of the substrates, the conditions A showed a better reactivity for the conversion of **1** into **2** than that of conditions B. Reactions of γ-aryl-γ-butyrolactons **1b–1k** bearing various functional groups at the aryl ring, such as methyl, phenyl, methoxy, and halogen afforded the corresponding γ-aryl-γ-butyrothiolactones **2b–2k** (entries 1–10). A tetralin and a thiophene ring were also acceptable to γ-aryl substituents of the butyrolactons, **1l** and **1m**, forming **2l** and **2m** (entries 11 and 12). Simple unsubstituted γ-butyrolactons **1n**, phthalide (**1o**) and its derivative **1p**, were converted into the products **2n–2p**, respectively (entries 13–15). When δ-lactones, **1q–1t**, were used as starting substrates, the formation of the expected 6-membered thioactones, **2q–2t**, were observed (entries 16–19).

**Table 2.** Indium-catalyzed conversion of lactones **1** to the thiolactones **2**.



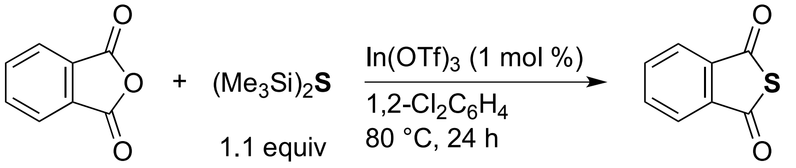
| Entry | Lactone 1 | Thiolactone 2 | Isolated yield of 2 (%) | |
|---|---|---|---|---|
| | | | Conditions A[a] | Conditions B[b] |
| |  |  | | |
| 1 | **1b** (R = 2-Me) | **2b** | 73 | 71 |
| 2 | **1c** (R = 3-Me) | **2c** | 82 | 55 |
| 3 | **1d** (R = 4-Me) | **2d** | 64 | 66 |
| 4 | **1e** (R = 2,5-$\text{Me}_2$) | **2e** | 65 | 49 |
| 5 | **1f** (R = 4-Ph) | **2f** | 61 | n/a |
| 6 | **1g** (R = 3-MeO) | **2g** | 79 | 16 |
| 7 | **1h** (R = 4-MeO) | **2h** | 22 | 8 |
| 8 | **1i** (R = 4-F) | **2i** | 79 | 61 |
| 9 | **1j** (R = 4-Cl) | **2j** | 87 | 60 |
| 10 | **1k** (R = 4-Br) | **2k** | 74 | 60 |

Peer-reviewed version available at *Molecules* **2018**, *23*, 1339; doi:10.3390/molecules23061339

| | | | | |
|---|---|---|---|---|
| 11 | <br>**1l** | <br>**2l** | 36 | 34 |
| 12 | <br>**1m** | <br>**2m** | 23 | 0 |
| 13 | <br>**1n** | <br>**2n** | 66[c] | n/a |
| 14 | <br>**1o** (R = H) | <br>**2o** | 18[d] | 0 |
| 15 | **1p** (R = Ph) | **2p** | 85 | 10 |
| 16 | <br>**1q** (Ar = Ph) | <br>**2q** | 10[e] | 14 |
| 17 | **1r** (Ar = 4-MeC$_6$H$_4$) | **2r** | 9 | n/a |
| 18 | **1s** (Ar = 4-ClC$_6$H$_4$) | **2s** | 4 | n/a |
| 19 | <br>**1t** | <br>**2t** | 88[f] | 23 |

[a] This work: **1** (0.5 mmol), (Me$_3$Si)$_2$S (0.55 mmol), In(OTf)$_3$ (0.005 mmol), 1,2-Cl$_2$C$_6$H$_4$ (0.5 mL) at 80 °C for 24 h. [b] Previous work: **1** (0.5 mmol), S$_8$ (0.55 mmol of S atom), PhSiH$_3$ (0.33 mmol), InCl$_3$ (0.025 mmol), 1,2-Cl$_2$C$_6$H$_4$ (0.5 mL) at 120 °C for 24 h. [c] NMR yield. [d] 7 d. [e] 120 °C, 3 d. [f] InCl$_3$ (0.025 mmol, 5 mol %), 120 °C, 20 h.

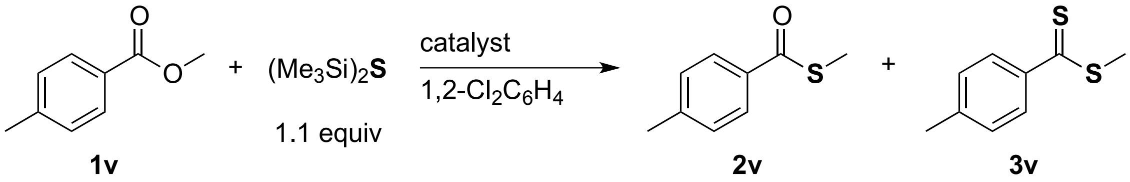
Finally, the present procedure was evaluated using substrates involving an ester moiety, but not lactones. When phthalic anhydride (**1u**) was treated with a disilathiane, the corresponding reaction proceeded to give thiophthalic anhydride (**2u**) in a 74% isolated yield (eq 1).



**1u** **2u**, 74%

(1)

Although an acyclic ester, methyl benzoate derivative **1v**, was not acceptable to the transformation under the optimal conditions, the use of 5 mol % of $InI_3$ catalyst at 120 °C for 20 h improve the reactivity for the reaction, leading to the expected thioester **2v** in a 38% isolated yield. Along with the formation of thioester **2v** in that conditions, the unexpected dithioester **3v** was also isolated in an 18% yield (Scheme 2).



| | 2v | 3v |
|---|---|---|
| $In(OTf)_3$ (1 mol %), 80 °C, 24 h | 0% | 0% |
| $InI_3$ (5 mol %), 120 °C, 20 h | 38% | 18% |

**Scheme 2.** Reaction of an acyclic ester.

## 3. Materials and Methods

### 3.1. General Information

$^1H$ and $^{13}C$ NMR spectra were recorded on a 300 or 500 MHz spectrometer. Chemical shifts in the $^1H$ and $^{13}C$ NMR spectra were reported in ppm relative to the residual solvent peaks such as those of chloroform (δ 7.26 for $^1H$, and δ 77.0 for $^{13}C$) or of the internal reference tetramethylsilane (δ 0.00 for both $^1H$ and $^{13}C$). High-resolution mass spectra (HRMS) were measured using NBA (3-nitrobenzylalcohol) as a matrix. GC analyses were performed using a DB-5 capillary column (30 m × 0.25 mm, film thickness = 0.25 μm). Reactions were monitored by TLC analysis of the reaction aliquots. Column chromatography was performed using a silica gel. All indium compounds and hexamethyldisilathiane were commercially available and were used without further purification. 1,2-Dichlorobenzene was distilled from $CaH_2$. Lactones **1a**, **1f**, **1n**, **1o**, **1q**, **1t** and phthalic anhydride (**1u**), and an ester **1v** were purchased and used without further purification. Lactones **1b** and **1l** were prepared by the gallium-catalyzed reductive cyclization of keto acids [14]. Lactones **1c**, **1d**, **1e**, **1g**, **1h**, **1i**, **1j**, **1k**, **1m**, **1p**, **1r**, and **1s** were prepared via modified literature method [15].

### 3.2. General Procedure A for the Indium-Catalyzed Conversion of Lactones or Its Derivatives **1** into Thiolactones **2** Using a Disilathiane (In the case of **1** in solid state at room temperature)

To a screw-capped tube, lactone or the derivative **1** (0.50 mmol) was added. The tube was sealed and moved into a glovebox, then $In(OTf)_3$ (2.8 mg, 0.0050 mmol) was added. The tube was sealed again and removed from the glovebox. 1,2-Dichlorobenzene (0.5 mL) and hexamethyldisilathiane (98.1 mg, 0.550 mmol) were successively added, and after the tube was sealed, the mixture was heated at 80 °C for 24 h. The resulting mixture was cooled to room temperature, and chloroform was added. The mixture was transferred into a round-bottom flask, which was then evaporated under the reduced pressure. The crude material was purified by a silica gel column chromatography (hexane/EtOAc), followed by a gel permeation chromatography (GPC) in some cases.

### 3.3. General Procedure B for the Indium-Catalyzed Conversion of Lactones **1** into Thiolactones **2** Using a Disilathiane (In the case of **1** in liquid state at room temperature)

Peer-reviewed version available at *Molecules* **2018**, *23*, 1339; doi:10.3390/molecules23061339

To a screw-capped tube, In(OTf)$_3$ (2.8 mg, 0.0050 mmol) was added in a glovebox. The tube was then sealed and removed from the glovebox, 1,2-dichlorobenzene (0.5 mL), lactone **1** (0.50 mmol), and hexamethyldisilathiane (98.1 mg, 0.550 mmol) were added in this order. After the tube was sealed, the mixture was heated at 80 °C for 24 h. The resulting mixture was cooled to room temperature, and chloroform was added. The mixture was transferred into a round-bottom flask, which was then evaporated under the reduced pressure. The crude material was purified by a silica gel column chromatography (hexane/EtOAc), followed by a gel permeation chromatography (GPC) in some cases.

### *3.4. Product Characterization*

**Dihydro-5-phenyl-2(3*H*)-thiophenone** (**2a**) [13]. General procedure A was followed with 5-phenyldihydrofuran-2-one (**1a**, 80.2 mg). Column chromatography (10/1 hexane/EtOAc) afforded **2a** as a colorless oil (73.4 mg, 83%): $^1$H NMR ($CDCl_3$, 500 MHz) δ 2.22–2.30 (m, 1 H, $CH_2$), 2.57–2.79 (m, 3 H, $CH_2$, $CH_2$), 4.99 (dd, *J* = 10.0, 5.5 Hz, 1 H, $CH$), 7.25–7.43 (m, 5 H, Ar*H*); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 34.9, 42.8, 54.2, 127.3, 128.1, 128.8, 139.4, 207.8; MS (EI) *m/z* (%) 178 ($M^+$, 78), 117 (100).

**Dihydro-5-(2-methylphenyl)-2(3*H*)-thiophenone** (**2b**) [13]. General procedure B was followed with 5-(2-methylphenyl)dihydrofuran-2-one (**1b**, 89.9 mg). Column chromatography (10/1 hexane/EtOAc) afforded **2b** as a colorless oil (69.7 mg, 73%): $^1$H NMR ($CDCl_3$, 500 MHz) δ 2.26–2.34 (m, 1 H, $CH_2$), 2.42 (s, 3 H, $CH_3$), 2.55–2.60 (m, 1 H, $CH_2$), 2.67–2.74 (m, 1 H, $CH_2$), 2.77–2.83 (m, 1 H, $CH_2$), 5.25 (dd, *J* = 9.5, 5.5 Hz, 1 H, $CH$), 7.20–7.21 (m, 3 H, Ar*H*), 7.55 (d, *J* = 8.0 Hz, 1 H, Ar*H*); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 19.5, 33.4, 42.7, 50.3, 126.5, 126.7, 127.8, 130.7, 135.7, 137.2, 208.0; MS (EI) *m/z* (%) 192 ($M^+$, 82), 117 (100).

**Dihydro-5-(3-methylphenyl)-2(3*H*)-thiophenone** (**2c**) [13]. General procedure B was followed with 5-(3-methylphenyl)dihydrofuran-2-one (**1c**, 92.3 mg). Column chromatography (10/1 hexane/EtOAc) afforded **2c** as a dark yellow oil (81.9 mg, 82%): $^1$H NMR ($CDCl_3$, 500 MHz) δ 2.25–2.29 (m, 1 H, $CH_2$), 2.37 (s, 3 H, $CH_3$), 2.58–2.80 (m, 3 H, $CH_2$, $CH_2$), 4.96 (dd, *J* = 10.0, 5.5 Hz, 1 H, $CH$), 7.13 (d, *J* = 7.0 Hz, 1 H, Ar*H*), 7.21–7.27 (m, 3 H, Ar*H*); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 21.4, 35.0, 42.9, 54.3, 124.4, 128.1, 128.7, 128.9, 138.6, 139.3, 208.0; MS (EI) *m/z* (%) 192 ($M^+$, 100).

**Dihydro-5-(4-methylphenyl)-2(3*H*)-thiophenone** (**2d**) [13]. General procedure A was followed with 5-(4-methylphenyl)dihydrofuran-2-one (**1d**, 87.5 mg). Column chromatography (10/1 hexane/EtOAc) afforded **2d** as a colorless oil (61.3 mg, 64%): $^1$H NMR ($CDCl_3$, 500 MHz) δ 2.21–2.29 (m, 1 H, $CH_2$), 2.35 (s, 3 H, $CH_3$), 2.56–2.78 (m, 3 H, $CH_2$, $CH_2$), 4.96 (dd, *J* = 10.0, 5.5 Hz, 1 H, $CH$), 7.17 (d, *J* = 8.0 Hz, 2 H, Ar*H*), 7.30 (d, *J* = 8.0 Hz, 2 H, Ar*H*); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 21.0, 35.0, 42.9, 54.1, 127.2, 129.5, 136.4, 137.9, 208.0; MS (EI) *m/z* (%) 192 ($M^+$, 82), 117 (100).

**Dihydro-5-(2,5-dimethylphenyl)-2(3*H*)-thiophenone** (**2e**) [13]. General procedure A was followed with 5-(2,5-dimethylphenyl)dihydrofuran-2-one (**1e**, 94.5 mg). Column chromatography (10/1 hexane/EtOAc) afforded **2e** as a yellow oil (66.6 mg, 65%): $^1$H NMR ($CDCl_3$, 500 MHz) δ 2.24–2.31 (m, 1 H, $CH_2$), 2.33 (s, 3 H, $CH_3$), 2.36 (s, 3 H, $CH_3$), 2.53–2.58 (m, 1 H, $CH_2$), 2.65–2.73 (m, 1 H, $CH_2$), 2.76–2.82 (m, 1 H, $CH_2$), 5.22 (dd, *J* = 10.0, 5.5 Hz, 1 H, $CH$), 7.01 (d, *J* = 7.5 Hz, 1 H, Ar*H*), 7.07 (d, *J* = 7.5 Hz, 1 H, Ar*H*), 7.36 (s, 1 H, Ar*H*); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 19.0, 21.0, 33.4, 42.7, 50.3, 127.1, 128.5, 130.6, 132.5, 136.2, 136.9, 208.1; MS (EI) *m/z* (%) 206 ($M^+$, 85), 131 (100).

**Dihydro-5-([1,1'-biphenyl]-4-yl)-2(3*H*)-thiophenone** (**2f**). General procedure A was followed with 5-[1,1'-Biphenyl]-4-yldihydro-2(3*H*)-furanone (**1f**, 96.2 mg). Column chromatography (10/1 hexane/EtOAc) and GPC afforded **2f** as a colorless solid (61.6 mg, 61%): mp 120–121 °C; $^1$H NMR ($CDCl_3$, 500 MHz) δ 2.78–2.36 (m, 1 H, $CH_2$), 2.63–2.83 (m, 3 H, $CH_2$, $CH_2$), 5.05 (dd, *J* = 10.0, 5.5 Hz, 1 H, $CH$), 7.35–7.61 (m, 9 H, Ar*H*); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 35.0, 42.9, 54.1, 127.0, 127.5, 127.6, 127.9, 128.8, 138.4, 140.4, 141.1, 207.8; MS (EI) *m/z* (%) 254 ($M^+$, 100); HRMS (EI) calcd for $[M]^+$ ($C_{16}H_{14}OS$) *m/z* 254.0765, found 254.0771.

Peer-reviewed version available at *Molecules* **2018**, *23*, 1339; doi:10.3390/molecules23061339

**Dihydro-5-(3-methoxyphenyl)-2(3*H*)-thiophenone** (**2g**) [13]. General procedure B was followed with 5-(3-methoxyphenyl)dihydrofuran-2-one (**1g**, 100.9 mg). Column chromatography (10/1 hexane/EtOAc) afforded **2g** as a yellow oil (86.4 mg, 79%): $^1$H NMR ($\text{CDCl}_3$, 500 MHz) δ 2.21–2.30 (m, 1 H, $CH_2$), 2.59–2.78 (m, 3 H, $CH_2$, $CH_2$), 3.81 (s, 3 H, $CH_3$), 4.96 (dd, *J* = 10.0, 5.5 Hz, 1 H, C*H*), 6.85 (dd, *J* = 8.0, 3.0 Hz, 1 H, Ar*H*), 6.97 (s, 1 H, Ar*H*), 7.00 (d, *J* = 8.0 Hz, 1 H, Ar*H*), 7.28 (dd, *J* = 8.0, 8.0 Hz, 1 H, Ar*H*); $^{13}$C NMR ($\text{CDCl}_3$, 125 MHz) δ 34.8, 42.7, 54.2, 55.2, 113.1, 113.3, 119.6, 129.8, 140.9, 159.8, 207.8; MS (EI) *m*/*z* (%) 208 (M$^+$, 100).

**Dihydro-5-(4-methoxyphenyl)-2(3*H*)-thiophenone** (**2h**) [13]. General procedure B was followed with 5-(4-methoxyphenyl)dihydrofuran-2-one (**1h**, 97.7 mg). Column chromatography (10/1 hexane/EtOAc) afforded **2h** as a colorless solid (23.2 mg, 22%): mp 74–75 °C; $^1$H NMR ($\text{CDCl}_3$, 500 MHz) δ 2.21–2.29 (m, 1 H, $CH_2$), 2.56–2.59 (m, 1 H, $CH_2$), 2.65–2.80 (m, 2 H, $CH_2$, $CH_2$), 3.81 (s, 3 H, $CH_3$), 4.97 (dd, *J* = 10.5, 5.5 Hz, 1 H, C*H*), 6.90 (d, *J* = 8.0 Hz, 2 H, Ar*H*), 7.35 (d, *J* = 8.0 Hz, 2 H, Ar*H*); $^{13}$C NMR ($\text{CDCl}_3$, 125 MHz) δ 35.2, 43.1, 54.0, 55.3, 114.2, 128.6, 131.3, 159.4, 208.1; MS (EI) *m*/*z* (%) 208 (M$^+$, 79), 147 (100).

**Dihydro-5-(4-fluorophenyl)-2(3*H*)-thiophenone** (**2i**) [13]. General procedure B was followed with 5-(4-fluorophenyl)dihydrofuran-2-one (**1i**, 96.3 mg). Column chromatography (10/1 hexane/EtOAc) afforded **2i** as a pale green oil (82.3 mg, 79%): $^1$H NMR ($\text{CDCl}_3$, 297 MHz) δ 2.17–2.29 (m, 1 H, $CH_2$), 2.56–2.82 (m, 3 H, $CH_2$, $CH_2$), 4.99 (dd, *J* = 9.8, 5.0 Hz, 1 H, C*H*), 7.03–7.08 (m, 2 H, Ar*H*), 7.38–7.42 (m, 2 H, Ar*H*); $^{13}$C NMR ($\text{CDCl}_3$, 74.8 MHz) δ 35.1, 42.8, 53.5, 115.7 (d, $J_{\text{C–F}}$ = 20.9 Hz), 129.0 (d, $J_{\text{C–F}}$ = 9.0 Hz), 135.2 (d, $J_{\text{C–F}}$ = 3.7 Hz), 162.3 (d, $J_{\text{C–F}}$ = 246.8 Hz), 207.4; MS (EI) *m*/*z* (%) 196 (M$^+$, 72), 135 (100).

**Dihydro-5-(4-chlorophenyl)-2(3*H*)-thiophenone** (**2j**) [13]. General procedure A was followed with 5-(4-chlorophenyl)dihydrofuran-2-one (**1j**, 98.1 mg). Column chromatography (10/1 hexane/EtOAc) afforded **2j** as a colorless solid (85.5 mg, 87%): mp 45–48 °C; $^1$H NMR ($\text{CDCl}_3$, 500 MHz) δ 2.18–2.26 (m, 1 H, $CH_2$), 2.59–2.80 (m, 3 H, $CH_2$, $CH_2$), 4.97 (dd, *J* = 10.0, 5.5 Hz, 1 H, C*H*), 7.34–7.35 (m, 4 H, Ar*H*); $^{13}$C NMR ($\text{CDCl}_3$, 125 MHz) δ 34.9, 42.7, 53.5, 128.7, 129.0, 133.8, 138.0, 207.2; MS (EI) *m*/*z* (%) 214 (M$^+$+2, 23), 212 (M$^+$, 63), 117 (100).

**Dihydro-5-(4-bromophenyl)-2(3*H*)-thiophenone** (**2k**) [13]. General procedure A was followed with 5-(4-bromophenyl)dihydrofuran-2-one (**1k**, 120.1 mg). Column chromatography (10/1 hexane/EtOAc) afforded **2k** as a colorless solid (96.1 mg, 74%): mp 58–60 °C; $^1$H NMR ($\text{CDCl}_3$, 500 MHz) δ 2.18–2.26 (m, 1 H, $CH_2$), 2.58–2.80 (m, 3 H, $CH_2$, $CH_2$), 4.95 (dd, *J* = 10.0, 5.5 Hz, 1 H, C*H*), 7.30 (d, *J* = 7.0 Hz, 2 H, Ar*H*), 7.50 (d, *J* = 7.0 Hz, 2 H, Ar*H*); $^{13}$C NMR ($\text{CDCl}_3$, 125 MHz) δ 34.9, 42.7, 53.6, 122.0, 129.1, 132.0, 138.6, 207.2; MS (EI) *m*/*z* (%) 258 (M$^+$+2, 59), 256 (M$^+$, 58), 117 (100).

**Dihydro-5-(5,6,7,8-tetrahydronaphthalen-2-yl)-2(3*H*)-thiophenone** (**2l**) [13]. General procedure B was followed with 5-(5,6,7,8-Tetrahydronaphthalen-2-yl)dihydrofuran-2(3*H*)-one (**1l**, 96.8 mg). Column chromatography (10/1 hexane/EtOAc) and GPC afforded **2l** as a colorless oil (37.4 mg, 36%): $^1$H NMR ($\text{CDCl}_3$, 500 MHz) δ 1.78–1.81 (m, 4 H, $CH_2$), 2.23–2.31 (m, 1 H, $CH_2$), 2.55–2.80 (m, 7 H, $CH_2$, $CH_2$), 4.94 (dd, *J* = 10.5, 5.5 Hz, 1 H, C*H*), 7.07 (d, *J* = 8.0 Hz 1 H, Ar*H*) 7.12–7.15 (m, 2 H, Ar*H*); $^{13}$C NMR ($\text{CDCl}_3$, 125 MHz) δ 23.0, 23.1, 29.1, 29.4, 35.0, 43.0, 54.3, 124.4, 128.1, 129.6, 136.4, 137.3, 137.7, 208.3; MS (EI) *m*/*z* (%) 232 (M$^+$, 100).

**Dihydro-5-(thiophen-2-yl)-2(3*H*)-thiophenone** (**2m**). General procedure B was followed with dihydro-5-(3-thienyl)-2(3*H*)-furanone (**1m**, 89.0 mg). Column chromatography (10/1 hexane/EtOAc) afforded **2m** as a light green oil (22.3 mg, 23%): $^1$H NMR ($\text{CDCl}_3$, 500 MHz) δ 2.34–2.42 (m, 1 H, $CH_2$), 2.65–2.85 (m, 3 H, $CH_2$, $CH_2$), 5.29 (dd, *J* = 7.5, 5.5 Hz, 1 H, C*H*), 6.97 (dd, *J* = 5.0, 3.5 Hz, 1 H, Ar*H*), 7.07 (d, *J* = 3.5 Hz, 1 H, Ar*H*), 7.27 (dd, *J* = 5.0, 3.5 Hz, 1 H, Ar*H*); $^{13}$C NMR ($\text{CDCl}_3$, 125 MHz) δ 35.6, 42.3, 49.1, 125.3, 125.6, 126.9, 143.7, 207.0; MS (EI) *m*/*z* (%) 184 (M$^+$, 64), 123 (100); HRMS (EI) calcd for [M]$^+$ ($C_8H_8OS_2$) *m*/*z* 184.0017, found 184.0011.

**Thiophthalide** (**2o**) [16]. General procedure A was followed with phthalide (**1o**, 67.6 mg). Column chromatography (10/1 hexane/EtOAc) afforded **2o** as a colorless solid (26.8 mg, 18%): mp 68–70 °C; $^1$H NMR ($CDCl_3$, 500 MHz) δ 4.48 (s, 2 H, C*H*$_2$), 7.48 (dd, *J* = 7.5, 7.5 Hz, 1 H, Ar*H*), 7.55 (d, *J* = 7.0 Hz, 1 H, Ar*H*), 7.63 (dd, *J* = 7.5, 7.5 Hz, 1 H, Ar*H*), 7.85 (d, *J* = 7.5 Hz, 1 H, Ar*H*); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 34.6, 123.9, 126.3, 128.0, 133.1, 135.8, 147.0, 198.0; MS (EI) *m*/*z* (%) 150 ($M^+$, 89), 121 (100).

**3-Phenyl-benzo[*c*]thiophen-1(3*H*)-one** (**2p**) [13]. General procedure A was followed with 3-phenylisobenzofuran-1-one (**1p**, 105.9 mg). Column chromatography (10/1 hexane/EtOAc) afforded **2p** as a pale yellow solid (7.5 mg, 85%): mp 87–88 °C; $^1$H NMR ($CDCl_3$, 500 MHz) δ 5.91 (s, 1 H, C*H*), 7.25–7.36 (m, 6 H, Ar*H*), 7.48 (dd, *J* = 7.5, 7.5 Hz, 1 H, Ar*H*), 7.56 (dd, *J* = 7.5, 7.5 Hz, 1 H, Ar*H*), 7.86 (d, *J* = 7.5 Hz, 1 H, Ar*H*); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 54.6, 123.6, 126.6, 128.29, 128.33, 128.4, 129.1, 133.6, 135.7, 138.8, 151.2, 197.2; MS (EI) *m*/*z* (%) 226 ($M^+$, 100).

**Tetrahydro-6-phenyl-2*H*-benzothiopyran-2-one** (**2q**) [13]. General procedure A was followed with tetrahydro-6-phenyl-2*H*-pyran-2-one (**1q**, 89.3 mg). Colum chromatography (10/1 hexane/EtOAc) afforded **2q** as an orange oil (9.7 mg, 10%): $^1$H NMR ($CDCl_3$, 500 MHz) δ 1.94–2.10 (m, 2 H, C*H*$_2$), 2.14–2.19 (m, 1 H, C*H*$_2$), 2.37–2.41 (m, 1 H, C*H*$_2$), 2.57–2.43 (m, 1 H, C*H*$_2$), 2.59–2.78 (m, 1 H, C*H*$_2$), 4.65 (dd, *J* = 11.0, 4.0 Hz, 1 H, C*H*), 7.29–7.32 (m, 1 H, Ar*H*), 7.35–7.39 (m, 4 H, Ar*H*); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 22.7, 32.4, 40.5, 50.5, 127.7, 128.1, 128.9, 140.4, 201.3; MS (EI) *m*/*z* (%) 192 ($M^+$, 59), 104 (100).

**Tetrahydro-6-(4-methylphenyl)-2*H*-thiopyran-2-one** (**2r**). General procedure A was followed with tetrahydro-6-(4-methylphenyl)-2*H*-Pyran-2-one (**1r**, 92.3 mg). Column chromatography (10/1 hexane/EtOAc) and GPC afforded **2r** as a colorless oil (9.5 mg, 9%): $^1$H NMR ($CDCl_3$, 500 MHz) δ 1.93–2.07 (m, 2 H, C*H*$_2$), 2.15–2.17 (m, 1 H, C*H*$_2$), 2.35 (s, 3 H, C*H*$_3$), 2.37–2.44 (m, 1 H, C*H*$_2$), 2.72–2.76 (m, 1 H, C*H*$_2$), 4.61 (dd, *J* = 11.0, 3.5 Hz, 1 H, C*H*), 7.17 (d, *J* = 7.5 Hz, 2 H, Ar*H*), 7.26 (d, *J* = 7.5 Hz, 2 H, Ar*H*); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 21.1, 22.7, 32.4, 40.5, 50.2, 127.5, 129.5, 137.4, 137.9, 201.6; MS (EI) *m*/*z* (%) 206 ($M^+$, 62), 118 (100); HRMS (EI) calcd for $[M]^+$ ($C_{12}H_{14}OS$) *m*/*z* 206.0765, found 206.0766.

**6-(4-Chlorophenyl)tetrahydro-2*H*-thiopyran-2-one** (**2s**). General procedure A was followed with 6-(4-chlorophenyl)tetrahydro-2*H*-pyran-2-one (**1s**, 107.5 mg). Column chromatography (10/1 hexane/EtOAc) and GPC afforded **2s** as a colorless oil (4.8 mg, 4%): $^1$H NMR ($CDCl_3$, 500 MHz) δ 1.93–2.02 (m, 2 H, C*H*$_2$), 2.04–2.19 (m, 1 H, C*H*$_2$), 2.34–2.39 (m, 1 H, C*H*$_2$), 2.56–2.63 (m, 1 H, C*H*$_2$), 2.73–2.78 (m, 1 H, C*H*$_2$), 4.62 (dd, *J* = 11.0, 4.5 Hz, 1 H, C*H*), 7.30–7.35 (m, 4 H, Ar*H*); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 22.6, 32.4, 40.5, 49.7, 129.0, 129.1, 133.9, 139.0, 200.8; MS (EI) *m*/*z* (%) 226 ($M^+$+2, 20), 210 ($M^+$, 23), 138 (100); HRMS (EI) calcd for $[M]^+$ ($C_{11}H_{11}OSCl$) *m*/*z* 226.0219, found 226.0241.

**1,4-Dihydro-3*H*-2-benzothiopyran-3-one** (**2t**) [13]. General procedure A was followed with 1,4-dihydro-3*H*-2-benzopyran-3-one (**1t**, 74.3 mg). Column chromatography (10/1 hexane/EtOAc) afforded **2t** as a pale yellow solid (40.9 mg, 50%): mp 90–93 °C; $^1$H NMR ($CDCl_3$, 500 MHz) δ 3.79 (s, 2 H, C*H*$_2$), 4.22 (s, 2 H, C*H*$_2$), 7.21–7.32 (m, 4 H, Ar*H*); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 34.2, 49.2, 126.6, 127.4, 128.0, 128.7, 133.7, 134.2, 202.9; MS (EI) *m*/*z* (%) 164 ($M^+$, 14), 104 (100).

**Phthalic thioanhydride** (**2u**) [17]. General procedure A was followed with phthalic anhydride (**1u**, 77.3 mg). Column chromatography (10/1 hexane/EtOAc) afforded **2u** as a yellow solid (56.1 mg, 74%): mp 68–70 °C; $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.81–7.83 (m, 2 H, Ar*H*), 7.97–7.99 (m, 2 H, Ar*H*); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 123.8, 135.0, 138.7, 189.8; MS (EI) *m*/*z* (%) 164 ($M^+$, 100).

***S*-Methyl 4-methylbenzothioate** (**2v**). General procedure A was followed with methyl 4-methylbenzoate (**1v**, 75.0 mg). Column chromatography (100/1 hexane/EtOAc) afforded **2v** as a red oil (31.8 mg, 38%): $^1$H NMR ($CDCl_3$, 500 MHz) δ 2.40 (s, 3 H, C*H*$_3$), 2.46 (s, 3 H, C*H*$_3$), 7.24 (d, *J* = 14.5

Peer-reviewed version available at *Molecules* **2018**, *23*, 1339; doi:10.3390/molecules23061339

Hz, 2 H, Ar*H*), 7.87 (d, *J* = 14.5 Hz, 2 H, Ar*H*); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 11.6, 21.7, 127.2, 129.2, 134.5, 144.1, 192.1; MS (EI) *m*/*z* (%) 166 ($M^+$, 5), 119 (100).

**Methyl 4-methylbenzodithioate** (**3v**) [18]. General procedure A was followed with methyl 4-methylbenzoate (**1v**, 75.0 mg). Column chromatography (100/1 hexane/EtOAc) afforded **3v** as an orange oil (15.9 mg, 18%): $^1$H NMR ($CDCl_3$, 500 MHz) δ 2.38 (s, 3 H, C*H*$_3$), 2.77 (s, 3 H, C*H*$_3$), 7.18 (d, *J* = 13.5 Hz, 2 H, Ar*H*), 7.94 (d, *J* = 13.5 Hz, 2 H, Ar*H*); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 20.5, 21.5, 126.8, 129.0, 142.6, 143.2, 228.8; MS (EI) *m*/*z* (%) 182 ($M^+$, 22), 135(100).

**5-[1,1'-Biphenyl]-4-yldihydro-2(3*H*)-furanone** (**1f**). A colorless solid: mp 100–102 °C; $^1$H NMR ($CDCl_3$, 500 MHz) δ 2.19–2.29 (m, 1 H, C*H*$_2$), 2.66–2.72 (m, 3 H, C*H*$_2$), 5.54–5.57 (m, 1 H, C*H*), 7.35–7.46 (m, 5 H, Ar*H*), 7.58–7.62 (m, 4 H, Ar*H*); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 29.0, 30.9, 81.0, 125.8, 127.1, 127.45, 127.53, 128.8, 138.3, 140.4, 141.4, 176.9; MS (EI) *m*/*z* (%) 238 ($M^+$, 100); HRMS (EI) calcd for $[M]^+$ ($C_{16}H_{14}O_2$) *m*/*z* 238.0994, found 238.1002.

**Tetrahydro-6-(4-methylphenyl)-2*H*-pyran-2-one** (**1r**). A colorless solid: mp 81–83 °C; $^1$H NMR ($CDCl_3$, 500 MHz) δ 1.80–1.88 (m, 1 H, C*H*$_2$), 1.92–1.98 (m, 2 H, C*H*$_2$), 2.09–2.14 (m, 1 H, C*H*$_2$), 2.34 (s, 3 H, C*H*$_3$), 2.51–2.56 (m, 1 H, C*H*$_2$), 2.57–2.71 (m, 1 H, C*H*$_2$), 5.30 (dd, *J* = 10.5, 3.5 Hz, 1 H, C*H*), 7.17 (d, *J* = 7.5 Hz, 2 H, Ar*H*), 7.22 (d, *J* = 7.5 Hz, 2 H, Ar*H*); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 18.4, 21.0, 29.3, 30.3, 81.5, 125.5, 129.1, 136.6, 137.8, 171.4; MS (EI) *m*/*z* (%) 190 ($M^+$, 42), 118 (100); HRMS (EI) calcd for $[M]^+$ ($C_{12}H_{14}O_2$) *m*/*z* 190.0994, found 190.0995.

**Tetrahydro-6-(4-chlorophenyl)-2*H*-pyran-2-one** (**1s**). An orange solid: mp 91–98 °C; $^1$H NMR ($CDCl_3$, 500 MHz) δ 1.77–1.85 (m, 1 H, C*H*$_2$), 1.96–2.01 (m, 2 H, C*H*$_2$), 2.12–2.16 (m, 1 H, C*H*$_2$), 2.53–2.60 (m, 1 H, C*H*$_2$), 2.67–2.73 (m, 1 H, C*H*$_2$), 5.32 (dd, *J* = 10.5, 3.0 Hz, 1 H, C*H*), 7.28 (d, *J* = 8.5 Hz, 2 H, Ar*H*), 7.34 (d, *J* = 8.5 Hz, 2 H, Ar*H*); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 18.4, 29.3, 30.4, 80.8, 127.0, 128.6, 133.9, 138.2, 171.0; MS (EI) *m*/*z* (%) 212 ($M^+$+2, 7), 210 ($M^+$, 23), 70 (100); HRMS (EI) calcd for $[M]^+$ ($C_{11}H_{11}O_2Cl$) *m*/*z* 210.0448, found 210.0449.

## 4. Conclusions

An indium-catalyzed formation of thiolactones from lactones and a disilathiane was developed. A disilathiane was found to be a novel and an effective sulfur source for this type of conversion, and a wide range of lactone derivatives were successfully converted into the corresponding thiolactones.

**Supplementary Materials:** The following are available online at www.mdpi.com/link, $^1$H and $^{13}$C NMR spectra.

**Acknowledgments:** The authors deeply thank Shin-Etsu Chemical Co., Ltd., for the gift of hydrosilanes and chlorosilanes.

**Author Contributions:** N.S. conceived and designed the experiments; K.T. and S.H. performed the experiments; Y.O., K.T. and S.H. analyzed the data; Y.O. and N.S. wrote the paper.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Jones, B. A.; Bradshaw, J. S. Synthesis and Reduction of Thiocarboxylic *O*-Esters. *Chem. Rev.* **1984**, *84*, 17–30, doi: 10.1021/cr00059a002.
2. Beletskaya, I. P.; Ananikov, V. P. Transition-Metal-Catalyzed C–S, C–Se, and C–Te Bond Formation via Cross-Coupling and Atom-Economic Addition Reactions. *Chem. Rev.* **2011**, *111*, 1596–1636, doi: 10.1021/cr100347k.
3. Liu, H.; Jiang, X. Transfer of Sulfur: From Simple to Diverse. *Chem. Asian J.* **2013**, *8*, 2546–2563, doi: 10.1002/asia.201300636.
4. Shen, C.; Zhang, P.; Sun, Q.; Bai, S.; Hor, T. S. A.; Liu, X. Recent advances in C–S bond formation *via* C–H bond functionalization and decarboxylation. *Chem. Soc. Rev.* **2015**, *44*, 291–314, doi: 10.1039/c4cs00239c.

5. Ghaderi, A. Advances in transition-metal catalyzed thioetherification reactions of aromatic compounds. *Tetrahedron* **2016**, *72*, 4758–4782, doi: 10.1016/j.tet.2016.06.067.
6. Nguyen, T. B. Recent Advances in Organic Reactions Involving Elemental Sulfur. *Adv. Synth. Catal.* **2017**, *359*, 1066–1130, doi: 10.1002/adsc.201601329.
7. Ogiwara, Y.; Maeda, H.; Sakai, N. Copper-Catalyzed Production of Diaryl Sulfides Using Aryl Iodides and a Disilathiane. *Synlett* **2018**, *29*, 655–657, doi: 10.1055/s-0036-1591723.
8. Capozzi, F.; Capozzi, G.; Menichetti, S. Thiiranes: One-pot Synthesis from Alkenes, and Catalytic Desulphurization. *Tetrahedron Lett.* **1988**, *29*, 4177–4180, doi: 10.1016/S0040-4039(00)80449-9.
9. Lin, P.-Y.; Ku, W.-S.; Shiao, M.-J. A New Method for Converting Nitriles into Primary Thioamides by Sodium Trimethylsilanethiolate. *Synthesis* **1992**, 1219–1220, doi: 10.1055/s-1992-26341.
10. Tsay, S.-C.; Yep, G. L.; Chen, B.-L.; Lin, L. C.; Hwu, J. R. DIRECT SYNTHESIS OF DIALLYL SULFIDES FROM ALLYL ALCOHOLS AND HEXAMETHYLDISILATHIANE. *Tetrahedron* **1993**, *49*, 8969–8976, doi: 10.1016/S0040-4020(01)91216-5.
11. Degl'Innocenti, A.; Capperucci, A. Organosilane-Induced Synthesis and Functionalization of Sulfur-Containing Compounds. *Eur. J. Org. Chem.* **2000**, 2171–2186, doi: 10.1002/1099-0690(200006)2000:12<2171::AID-EJOC2171>3.0.CO;2-3.
12. Dávila, M. F. C.; Schneider, J. P.; Godard A.; Hazelard, D.; Compain, P. One-Pot, Highly Stereoselective Synthesis of Dithioacetal-$\alpha$,$\alpha$-Diglycosides. *Molecules* **2018**, *23*, 914–924, doi:10.3390/molecules23040914.
13. Sakai, N.; Horikawa, S.; Ogiwara, Y. Indium-Catalyzed Direct Conversion of Lactones into Thiolactones and Selenolactones in the Presence of Elemental Sulfur and Selenium. *Synthesis* **2018**, *50*, 565–574, doi: 10.1055/s-0036-1591849.
14. Sakai, N.; Horikawa, S.; Ogiwara, Y. Gallium-catalyzed reductive lactonization of $\gamma$-keto acids with a hydrosilane. *RSC Adv.* **2016**, *6*, 81763–81766, doi: 10.1039/c6ra19286f.
15. Grover, H. K.; Emmett, M. R.; Kerr, M. A. $\gamma$-Substituted Butanolides from Cyclopropane Hemimalonates: An Expedient Synthesis of Natural (*R*)-Dodecan-4-olide. *Org. Lett.* **2013**, *15*, 4838–4841, doi: 10.1021/ol402252u.
16. Dowd, P.; Weber, W. 3-Thiolen-2-one. A Useful Dienophile. *J. Org. Chem.* **1982**, *47*, 4777–4779, doi: 10.1021/jo00145a036.
17. Murai, T.; Asai, F. Three-Component Coupling Reactions of Thioformamides with Organolithium and Grignard Reagents Leading to Formation of Tertiary Amines and a Thiolating Agent. *J. Am. Chem. Soc.* **2007**, *129*, 780–781, doi: 10.1021/ja068523f.
18. Kato, S.; Hori, A.; Mizuta, M.; Katada, T.; Ishihara, H.; Fujieda, K.; Ikebe, Y. On carbon-13 spectra of thio- and dithiocarboxylic acids triorgano group 14 metal esters. *J. Organomet. Chem.* **1991**, *420*, 13–22, doi: 10.1016/0022-328X(91)86440-2.

**Sample Availability:** Samples of the compounds are not available from the authors.