Efficient Synthesis of Thioesters and Amides from Aldehydes by Using an Intermolecular Radical Reaction in Water

Hisanori Nambu, Kayoko Hata, Masato Matsugi, and Yasuyuki Kita*[a]

Abstract: The combination of the water-soluble radical initiator, 2,2′-azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride (VA-044) and the surfactant, cetyltrimethyl-ammonium bromide (CTAB), was found to be the most suitable condition for the effective and direct synthesis of useful active thioesters (pentafluorophenyl thioesters) in water. In addition, the direct amidation of aldehydes was achieved by the addition of the amines to the thioesterification reaction mixture in water.

Keywords: aldehydes · amidation · radical reactions · surfactants · thioesters

Introduction

Thioesters are synthetically as well as biologically important compounds.[1] Their "active" esters are highly reactive toward various nucleophiles so that they can be utilized in a wide range of synthetic transformations. They have been used as useful intermediates in the synthesis of amides[2] (peptides,[3] β-lactams[4]), esters[5] (β-lactones[6]), ketones[7] and carboxylic acids.[8] The reduction of thioesters to aldehydes[9] and sulfides[10] can be accomplished with various reductive agents. In addition, they have been employed as substrates in stereoselective aldol reactions[11] and as building blocks of heterocyclic compounds.[12]

Furthermore, thioesters have been frequently utilized as useful intermediates for the syntheses of various natural products.[13] Accordingly, many thioesterification procedures have been reported. The general synthetic method is the direct coupling of a thiol with the parent carboxylic acid and an activating agent,[14] or the coupling of a heavy metal thiolate with an acid chloride or an acid anhydrate.[15] A disulfide[16] or a thiocyanate[17] can be used as a source of the thiol moiety to prepare the thioesters. If the thioester is used as the intermediate for the synthesis of thiols or of their sulfur-containing derivatives, the approach will consist of the coupling of the alkali metal thiocarboxylates with arenediazonium salts[18] or diaryliodonium salts.[19] Under these circumstances, the direct synthesis of thioesters from aldehydes using thioanions or thiyl radicals would be a useful method.[20] Especially, no one has reported the thioesterification with aldehydes using thiyl radicals except for Takagi's report.[21] This method is concise, but has some disadvantages from the viewpoint of reagent efficiency. Namely, a large amount of the aldehyde is required, since the aldehyde must be used not only as the reagent, but also as the solvent. We now wish to report the effective intermolecular radical reaction of C–S bond formation in a micellar system using the combination of a water-soluble radical initiator (Figure 1)[22]

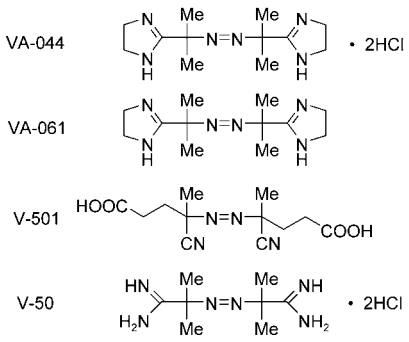


Figure 1. Water-soluble radical initiators.

and surfactant[23] in water.[24] Our present method readily produced useful pentafluorophenyl thioesters, which has already been successfully utilized by Davis et al.,[2a] in high yields, and the reaction was carried out under mild conditions.[25] Therefore, much attention is being devoted to this reaction from the viewpoint of green chemistry.[26]

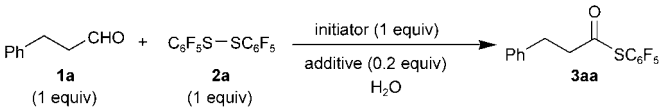
[a] Dr. H. Nambu, K. Hata, Dr. M. Matsugi, Prof. Dr. Y. Kita
Graduate School of Pharmaceutical Sciences, Osaka University
1-6, Yamada-oka, Suita, Osaka 565-0871 (Japan)
Fax: (+81) 6-6879-8229
E-mail: kita@phs.osaka-u.ac.jp

 DOI: 10.1002/chem.200400754

Results and Discussion

First, we examined the possibility of thioesterifications in water using 3-phenylpropionaldehyde (**1a**) and dipentafluorophenyl disulfide (**2a**) with various water-soluble azo-type initiators and a catalytic amount of CTAB as the first chosen surfactant (Table 1). As a result, we could confirm the formation of thioesters in these systems. Especially, VA-044 was found to be the most effective initiator among the initiators listed in Table 1 (entry 1). A side-reaction occurred when the typical radical initiator AIBN was used (entry 6); when Et_3B, a known radical initiator for low reaction temperatures, was used the reaction hardly proceeded (entry 7). In the presence of the galvinoxyl free radical as a radical scavenger, the thioesterification did not occur at all (entry 2), and hence this reaction would proceed via a radical mechanism. Next, we investigated the effect of surfactants on the reaction using VA-044 as the initiator. The cationic surfactants (CTAC, $CTAHSO_4$) gave the thioesters in good yields (entries 9 and 10). On the contrary, the anionic surfactant (SDS), the nonionic surfactant (Triton X-100) and phase-transfer catalyst ($Et_4N^+Br^-$) did not give satisfactory results (entries 11–13). In the absence of the surfactant, the reaction did not proceed at all (entry 8). These results clearly show that the addition of cationic surfactants is effective for this thioesterification.[27]

Table 1. Effect of various initiators and additives.



Entry	Initiator	Additive	T [°C]	t [h]	Yield [%]
1	VA-044	CTAB	50	18	73
2[a]	VA-044	CTAB	50	24	NR[f]
3	VA-061	CTAB	80	2	decomposition
4	V-501	CTAB	70	24	32
5	V-50	CTAB	60	24	45
6	AIBN	CTAB	80	12	37
7	Et_3B	CTAB	RT to 50	24	trace
8	VA-044	none	50	24	NR[f]
9	VA-044	CTAC[b]	50	24	67
10	VA-044	$CTAHSO_4$[c]	50	24	63
11	VA-044	SDS[d]	50	24	18
12	VA-044	Triton X-100[e]	50	24	16
13	VA-044	$Et_4N^+Br^-$	50	24	trace

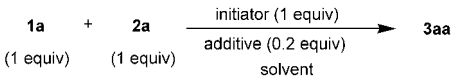
[a] Reaction was carried out with galvinoxyl free radical (2 equiv). [b] CTAC: cetyltrimethylammonium chloride. [c] $CTAHSO_4$: cetyltrimethylammonium hydrogen sulfate. [d] SDS: sodium dodecyl sulfate. [e] Triton X-100: polyoxyethylene(10) isooctylphenylether. [f] NR: no reaction.

The solvent effect on this reaction by using **1a**, **2a**, VA-044 and CTAB is shown in Table 2. From these results, water was found to be the best solvent for the thioesterification. The reaction did not proceed in benzene or under neat conditions (entries 1–3). In addition, when the radical initiators AIBN, V-70 L[28] and Et_3B were used in benzene, the yields of the thioester were lower than the former case (entries 4–6).

The utility of the pentafluorophenyl thioester have been already reported by Davis et al. The amidation of the pentafluorophenyl thioester occurred more effectively than that of the phenyl thioester.[2a] Therefore, we tried to develop a novel synthetic methodology for the active and useful pentafluorophenyl thioesters. We investigated this thioesterification using the various disulfides **2a**–**c**, and pentafluorophenyl thiol (**2a′**) as the sulfur source (Table 3). The thioesterifications with pentafluorophenyl disulfide (**2a**) gave the corresponding thioesters in good yields. On the other hand, the reaction with diphenyl disulfide (**2b**), dibenzyl disulfide (**2c**) or pentafluorophenyl thiol (**2a′**) gave the thioesters in lower yields. We clarified that the most effective sulfur source for this thioesterification is the pentafluorophenyl disulfide. These results indicated that the yields of the thioesters might be affected by the difference in the S–S bond dissociation energies with these disulfides.

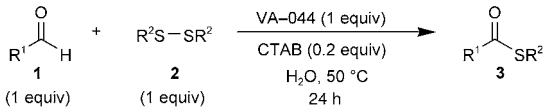
We then investigated the generality of this thioesterification with various aldehydes using pentafluorophenyl disulfide (**2a**), VA-044 and CTAB in water, which was the most effective condition. These results are summarized in Table 4. Under these conditions, the aliphatic aldehydes **1a**–**d** smoothly reacted and gave the corresponding thioesters **3aa**–**da** in good yields (Table 4, entries 1–4). Similarly, we investigated this thioesterification using various aromatic aldehydes **1e**–**k**. These aldehydes with electron-releasing functional groups **1g**–**i** smoothly reacted and gave the corresponding thioesters **3ga**–**ia** in good yields (Table 4, entries 7–9). When benzaldehyde (**1e**) and *p*-anisaldehyde (**1f**)

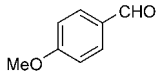
Table 2. Effect of various solvents and initiators.



Entry	Initiator	Solvent	Additive	T [°C]	t [h]	Yield [%]
1	VA-044	H_2O	CTAB	50	18	73
2	VA-044	neat	CTAB	50	24	trace
3	VA-044	benzene	CTAB	50	24	NR
4	AIBN	benzene	none	80	24	32
5	V-70L	benzene	none	50	24	29
6	Et_3B	benzene	none	RT	24	trace

Table 3. Thioesterification by using some disulfides.



Entry	Aldehyde R^1-CHO	Sulfur source $R^2=C_6F_5$	$R^2=Ph$	$R^2=Bn$	C_6F_5SH
1	Ph(CH$_2$)$_2$CHO **1a**	73[a] (**3aa**)	44 (**3ab**)	41 (**3ac**)	29 (**3aa**)
2	CH$_3$(CH$_2$)$_9$CHO **1b**	88[b] (**3ba**)	26 (**3bb**)	24 (**3bc**)	
3	 **1f**	56 (**3ca**)	47 (**3cb**)	38 (**3cc**)	

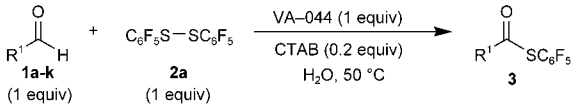
[a] Reaction time: 18 h. [b] Reaction time: 8 h.

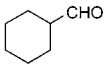
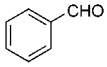
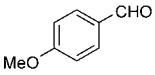
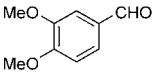
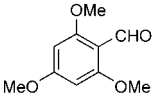
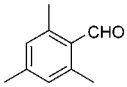
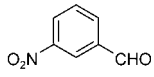
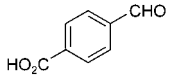
were treated under the same conditions, the corresponding thioesters (**3ea**, **3fa**) were obtained in moderate yields (Table 4, entries 5 and 6). The addition of 1.5 equivalents of VA-044 brought about an improvement in the yields of the thioesters (**3ea**, **3fa**). On the other hand, the thioesterification of the aromatic aldehydes with an electron-withdrawing substituent (**1j**, **1k**) did not proceed at all (entries 10, 11). These results of the thioesterifications might be affected by the stabilities of the acyl radical[29] intermediates formed from the aldehydes.[30]

A plausible reaction mechanism of this thioesterification is shown in Scheme 1. First, the disulfide **2** dissociates with the initiator (VA-044) to give the thiyl radical **A**. Secondly, the hydrogen in the aldehyde **1** is trapped by the thiyl radical **A**, and then the acyl radical **B** is formed. The acyl radical reacts with the disulfide **2** or thiyl radical **A**, and the thioesterification **3** is achieved.[31] The thiol **2′**, produced by the reaction of the thiyl radical **A** and aldehyde **1**, regenerates the thiyl radical with the initiator, and this thiyl radical **A** takes part in the reaction cycle again, whereas, the nucleophilic alkyl radicals prepared by the initiator did not trap the hydrogen of the aldehyde as reported by Chatgilialoglu et al.[29] The experimental results supporting this radical cycle mechanism are shown in Scheme 2. Disulfide **2a** reacted with the olefin compound to give the addition product under this reaction condition [Eq. (1)]; and this reaction did not proceed at all without the radical initiator, VA-044. These results clearly show that disulfide is dissociated with the initiator (VA-044) and the thiyl radical is generated. Disulfide **2a** was prepared from thiol **2a′** under the same conditions [Eq. (2)], and the thioesterification with **1a** and thiol **2a′** instead of disulfide **2a** under the same conditions proceeded to give the corresponding thioester **3aa** in 29% yield [Eq. (3)]. These results clearly show that the thiyl radicals are prepared from the thiols.

Since the mechanism showed that the amount of disulfide to aldehyde was theoretically 0.5 equivalents, we examined the thioesterification with a decreased equivalent of disulfide. These results are summarized in Table 5. When some aldehydes (**1b**, **1h**, **1i**) were treated with 0.5–0.6 equivalents disulfide **2a**, the corresponding thioesters (**3ba**, **3ha**, **3ia**) were obtained in good yields (entries 2b, 2c, 4b, 5b). However, the thioesterification with **1a** and **1g** with 0.5–0.6 equivalents of **2a** produced only in moderate yields (entries 1b, 3b).

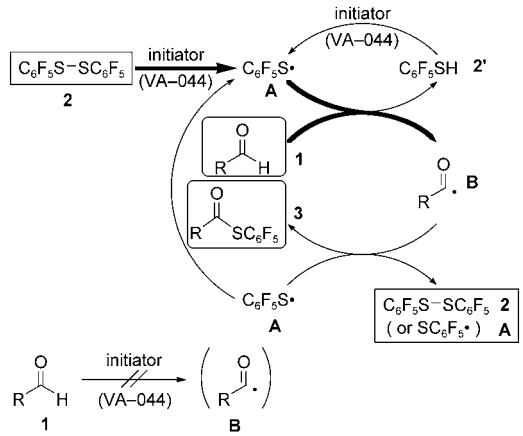
Table 4. Thioesterification using various aromatic aldehydes and disulfides.



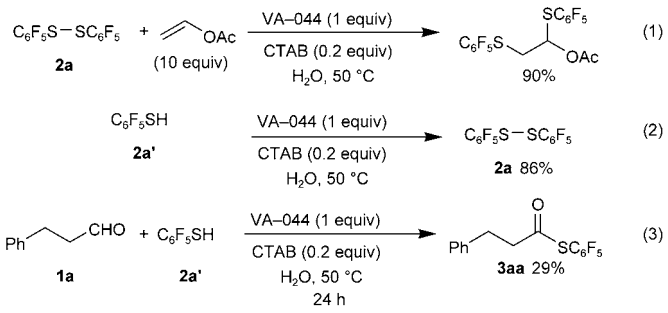
Entry	Aldehyde		Product	t [h]	Yield [%]
1	Ph(CH$_2$)$_2$CHO	**1a**	**3aa**	18	73
2	CH$_3$(CH$_2$)$_9$CHO	**1b**	**3ba**	8	88
3		**1c**	**3ca**	3	75
4	EtO$_2$C(CH$_2$)$_5$CHO	**1d**	**3da**	12	86
5		**1e**	**3ea**	24	47 [54][a]
6		**1f**	**3fa**	24	56 [68][a]
7		**1g**	**3ga**	24	72
8		**1h**	**3ha**	8	95
9		**1i**	**3ia**	24	90
10		**1j**		24	NR
11		**1k**		24	NR

[a] 1.5 Equivalents of VA-044 were used.

Pentafluorophenyl thioesters produced by our method are relatively stable and highly active carbonyl compounds. We then investigated the synthesis of various useful compounds

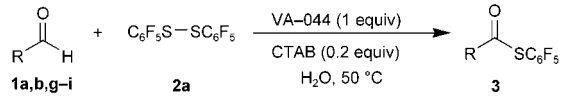


Scheme 1. The plausible thioesterification reaction mechanism.



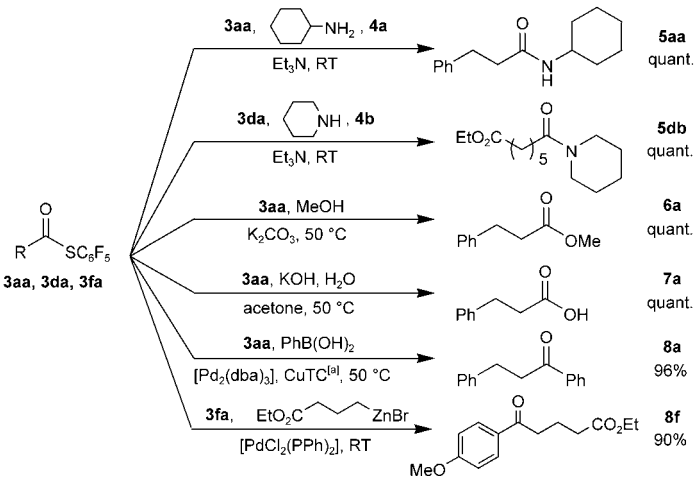
Scheme 2. The experimental results supporting the mechanism.

Table 5. Thioesterification with decreased equivalent of disulfide **2a**.



Entry	Aldehyde		Disulfide (equiv)	t [h]	Yield [%]
1a	Ph CHO	**1a**	1	18	73
b			0.6	24	48
2a	$CH_3(CH_2)_9CHO$	**1b**	1	8	88
b			0.6	8	85
c			0.5	18	78
3a	MeO, MeO, CHO	**1g**	1	24	72
b			0.5	24	51
4a	OMe, MeO, OMe, CHO	**1h**	1	8	95
b			0.5	24	81
5a	CHO	**1i**	1	24	90
b			0.5	24	87

from active pentafluorophenyl thioesters (Scheme 3). Primary and secondary amines **4a**, **4b** smoothly reacted with thioesters **3aa**, **3da** to give the corresponding amides **5aa**, **5db** in quantitative yields. In particular, the amidation of the thioester group of **3da** bearing an ester group proceeded in a chemoselective manner. Moreover, methyl ester **6a** was quantitatively obtained when the alcohol (MeOH) was used as a nucleophile, and the hydrolysis of **3aa** smoothly proceeded to give the corresponding carboxylic acid **7a** in quantitative yield. In addition, the other reaction to a ketone from the pentafluorophenyl thioesters **3aa**, **3fa** was similarly achieved by the coupling reactions reported by Liebeskind[7h] or Fukuyama.[7f] The treatment of thioester **3aa** and **3fa** with a Pd catalyst furnished the corresponding phenyl ketone **8a** in 96% yield, and the corresponding *p*-methoxyphenyl ketone **8f** in 90% yield. Thus, we clarified that pentafluorophenyl thioesters were useful intermediates in organic synthesis.

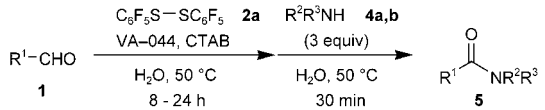


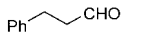
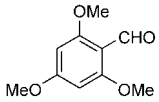
Scheme 3. The synthesis of various useful compounds from pentafluorophenyl thioesters; [a] CuTC: copper(I) thiophene-2-carboxylate.

Finally, we investigated the direct amidation of aldehydes via the pentafluorophenyl thioester intermediates. The general synthetic method of amides is the direct coupling of amines with the parent carboxylic acid and an activating agent.[32] In contrast, a few methods involving the direct synthesis of amides from aldehydes have been reported. In these reports, metal oxidative amidations with aldehydes and amines using Ni, Pd, Ru or Rh catalysts have been achieved.[33] Especially, no one has reported the direct synthesis of amides from aldehydes using a radical initiator except for Markó's report.[34] Their method is convenient, but highly toxic CCl_4 was used as the reaction solvent. On the other hand, the reaction solvent used in our method is water, therefore, our method has the advantage of cost, safety and environmental concern.

We have also examined the direct amidation of aldehydes using a one-pot synthetic methodology (Table 6). The addition of three equivalents of amines **4a**, **4b** to the mixture of

Table 6. Direct amidation of aldehydes in one-pot synthesis.



Entry	Aldehyde		Thioester yield [%]	Amine[a]	Product	Amide yield [%]
1a		**1a**	(73)	**4a**	**5aa**	71
b				**4b**	**5ab**	70
2a	$CH_3(CH_2)_9CHO$	**1b**	(88)	**4a**	**5ba**	82
b				**4b**	**5bb**	76
3a	$EtO_2C(CH_2)_5CHO$	**1d**	(86)	**4a**	**5da**	84
b				**4b**	**5db**	75
4a		**1h**	(95)	**4a**	**5ha**	83 [93][b]
b				**4b**	**5hb**	87 [91][b]

[a] Amine **4a**: cyclohexylamine. **4b**: piperidine. [b] Five equivalents of amine were used.

the thioesterification reaction (**2a**, VA-044 and CTAB) afforded the corresponding amides **5** in good yields. As these yields of amide compounds **5** reflect the thioesterification ones, the amidation yields are efficiently quantitative.

Conclusion

In summary, we found that the combination of a water-soluble radical initiator, VA-044, and cationic surfactant, CTAB, is an ideal reaction system to accomplish C–S bond formation in water. This method is effective for the synthesis of active thioesters under mild conditions, and could be applied to the thioesterification of various aldehydes. In addition, the pentafluorophenyl thioester, which was prepared by our method, has valuable properties, since we have clarified that it has a high activity toward various nucleophiles. We also have achieved the direct amidation of aldehydes using a one-pot synthetic methodology. These reactions occur under mild conditions in water, therefore, our procedure may find widespread use in organic chemistry.

Experimental Section

General methods: All melting points were measured by using a Büchi 545 apparatus and are uncorrected. The IR absorption spectra were recorded using a Shimadzu FT/IR-8400 spectrometer with KBr pellets. The ^{1}H and ^{13}C NMR spectra were measured in $CDCl_3$ by using JEOL JNM-AL 300 spectrometers with TMS or $CHCl_3$ as the internal standard. The ^{19}F NMR spectra were measured in $CDCl_3$ by using VARIAN VXR-200 spectrometers with hexafluorobenzene (−162.9 ppm) as the internal standard. Merck silica gel 60 (70–230 mesh ASTM) and Fuji Silysia Chemical silica gel BW-300 were used for the column chromatography and flash column chromatography. Anhydrous CH_2Cl_2 was distilled from P_2O_5. Anhydrous THF was distilled from sodium/benzophenone under nitrogen.

Compound **1a** was purified by flash chromatography on silica gel (hexane/EtOAc 10:1). Compound **1d** was prepared according to the literature procedure.[35] All other commercially available compounds were used without further purification.

Bis(2,3,4,5,6-pentafluorophenyl) disulfide (2a):[36] Pentafluorobenzenethiol (5.0 g, 25.0 mmol) was added to a solution of sodium perborate monohydrate (5.0 g, 50.0 mmol) in HOAc/H_2O (62.5 mL HOAc + 25 mL H_2O) at room temperature. After the reaction mixture was stirred for 2 h, HOAc and water were evaporated off, and to the residue was added EtOAc and water. The organic layer was washed with water, saturated aqueous $NaHCO_3$ and brine. The organic layer was dried with $MgSO_4$ and concentrated. The residue was purified by column chromatography on silica gel (hexane only) to afford **2a** (5.0 g, 12.5 mmol, quant.) as pale yellow crystals. M.p. 52.6–52.7 °C (lit.[36a] m.p. 50–51 °C); IR (KBr): $\tilde{\nu}$ = 1638, 1514, 1489, 1094, 982 cm^{-1}; ^{19}F NMR (188 MHz, $CDCl_3$): δ = −160.42 (dt, J=21.5, 4.5 Hz, 4F), −148.78 (t, J=21.5 Hz, 2F), −132.34 (dt, J=21.5, 4.5 Hz, 4F).

General procedure for the preparation of pentafluorophenyl thioester (3aa–ia), phenyl thioester (3ab, bb, eb, fb) and benzyl thioester (3ac, bc, ec, fc): VA-044 (48.5 mg, 0.15 mmol) was added to a solution of aldehydes (**1a–i**) (0.30 mmol), disulfide (**2a–c**) (0.30 mmol) and CTAB (21.9 mg, 0.060 mmol) in H_2O (3 mL) at room temperature. The reaction mixture was then stirred and heated to 50 °C. After 3 h, an additional amount of the initiator VA-044 (48.5 mg, 0.15 mmol) was added to the reaction mixture. The progress of the reaction was monitored by TLC. The reaction mixture was then extracted with EtOAc, and the organic layer was washed with brine, dried with Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc 50:1→4:1) to afford the pure thioesters **3**.

***(S)*-(2,3,4,5,6-Pentafluorophenyl) 3-phenylpropanethioate (3aa)**: obtained in 73% as colorless crystals; m.p. 68.7–68.8 °C; IR (KBr): $\tilde{\nu}$ = 1736, 1514, 1495 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.05 (s, 4H), 7.19–7.34 (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 31.2, 45.2, 102.8 (dt, J=21.5, 4.4 Hz), 126.7, 128.4 (2C), 128.8 (2C), 137.9 (dm, J=257 Hz, 2C), 139.2, 142.9 (dm, J=258 Hz), 147.0 (ddd, J=250, 10.6, 4.4 Hz, 2C), 191.6; ^{19}F NMR (188 MHz, $CDCl_3$): δ = −161.55 (t, J=21.3 Hz, 2F), −150.40 (t, J=21.3 Hz, 1F), −131.55 (d, J=21.3 Hz, 2F); HRMS (FAB): m/z: calcd for $C_{15}H_9F_5OSNa$: 355.0192, found: 355.0206 [M+Na]$^+$; elemental analysis calcd (%) for $C_{15}H_9F_5OS$: C 54.22, H 2.73; found: C 54.06, H 2.91.

***(S)*-(2,3,4,5,6-Pentafluorophenyl) undecanethioate (3ba)**: obtained in 88% as colorless oil; IR (KBr): $\tilde{\nu}$ = 2926, 2856, 1732, 1514, 1493 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, J=6.5 Hz, 3H), 1.27 (brs, 14H), 1.74 (quint, J=7.3 Hz, 2H), 2.73 (t, J=7.3 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.1, 22.7, 25.5, 28.8, 29.2, 29.3, 29.4, 29.6, 31.9, 43.8, 103.2 (dt, J=21.5, 4.4 Hz), 137.9 (dm, J=256 Hz, 2C), 142.7 (dm, J=257 Hz), 147.0 (ddd, J=249, 11.2, 4.4 Hz, 2C), 192.5; ^{19}F NMR (188 MHz, $CDCl_3$): δ = −161.67 (t, J=21.3 Hz, 2F), −150.60 (t, J=21.3 Hz, 1F), −132.06 (d, J=21.3 Hz, 2F); elemental analysis calcd (%) for $C_{17}H_{21}F_5OS$: C 55.42, H 5.75; found: C 55.50, H 5.64.

***(S)*-(2,3,4,5,6-Pentafluorophenyl) cyclohexanecarbothioate (3ca)**: obtained in 75% as colorless crystals; m.p. 41.7–41.8 °C; IR (KBr): $\tilde{\nu}$ = 2936, 2858, 1730, 1514, 1493 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.22–1.41 (m, 3H), 1.49–1.62 (m, 2H), 1.67–1.71 (m, 1H), 1.81–1.87 (m, 2H), 2.02–2.07 (m, 2H), 2.68 (tt, J=11.1, 3.6 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 25.4 (2C), 25.6, 29.4 (2C), 52.7, 103.4 (dt, J=21.5, 4.4 Hz), 137.9 (dm, J=255 Hz, 2C), 142.7 (dtt, J=257, 13.7, 5.0 Hz), 147.1 (ddd, J=249, 10.6, 4.4 Hz, 2C), 195.8; ^{19}F NMR (188 MHz, $CDCl_3$): δ = −161.82 (dt, J=21.3, 4.6 Hz, 2F), −150.90 (t, J=21.3 Hz, 1F),

−132.18 (d, J=21.3 Hz, 2F); elemental analysis calcd (%) for $C_{13}H_{11}F_5OS$: C 50.32, H 3.57; found: C 50.43, H 3.67.

Ethyl 7-oxo-7-[(2,3,4,5,6-pentafluorophenyl)sulfanyl]heptanoate (3da): obtained in 86% as colorless oil; IR (KBr): $\tilde{\nu}$ = 2937, 2866, 1734, 1732, 1514, 1493 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.26 (t, J=7.2 Hz, 3H), 1.37–1.47 (m, 2H), 1.67 (quint, J=7.3 Hz, 2H), 1.77 (quint, J=7.3 Hz, 2H), 2.32 (t, J=7.3 Hz, 2H), 2.75 (t, J=7.3 Hz, 2H), 4.13 (q, J=7.2 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.3, 24.5, 25.1, 28.3, 34.0, 43.5, 60.4, 103.1 (dt, J=21.2, 4.4 Hz), 137.9 (dm, J=255 Hz, 2C), 142.8 (dtt, J=257, 13.4, 5.0 Hz), 147.0 (ddd, J=249, 11.2, 4.4 Hz, 2C), 173.5, 192.2; ^{19}F NMR (188 MHz, $CDCl_3$): δ = −161.58 (dt, J=21.5, 4.5 Hz, 2F), −150.43 (t, J=21.5 Hz, 1F), −132.10 (d, J=21.5 Hz, 2F); elemental analysis calcd (%) for $C_{15}H_{15}F_5O_3S$: C 48.65, H 4.08; found: C 48.91, H 4.16.

(*S*)-(2,3,4,5,6-Pentafluorophenyl) benzenecarbothioate (3ea): obtained in 47% as colorless crystals; m.p. 40.7–40.8°C; IR (KBr): $\tilde{\nu}$ = 1697, 1514, 1495 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53 (t, J=7.4 Hz, 2H), 7.68 (t, J=7.4 Hz, 1H), 8.03 (d, J=7.4 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 102.7 (dt, J=21.2, 4.4 Hz), 127.9 (2C), 129.0 (2C), 134.6, 135.1, 137.9 (dm, J=256 Hz, 2C), 142.9 (dtt, J=258, 13.4, 5.0 Hz), 147.4 (ddd, J=250, 11.2, 4.4 Hz, 2C), 185.0; ^{19}F NMR (188 MHz, $CDCl_3$): δ = −161.52 (t, J=21.5 Hz, 2F), −150.18 (t, J=21.5 Hz, 1F), −131.59 (d, J=21.5 Hz, 2F); elemental analysis calcd (%) for $C_{13}H_5F_5OS$: C 51.32, H 1.66; found: C 51.23, H 1.85.

(*S*)-(2,3,4,5,6-Pentafluorophenyl) 4-methoxybenzenecarbothioate (3fa): obtained in 56% as colorless crystals; m.p. 54.5–54.6°C; IR (KBr): $\tilde{\nu}$ = 1697, 1601, 1514, 1495 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.90 (s, 3H), 6.97 (d, J=9.0 Hz, 2H), 7.98 (d, J=9.0 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 55.7, 103.2 (dt, J=21.2, 4.4 Hz), 114.3 (2C), 127.9, 130.4 (2C), 137.9 (dm, J=256 Hz, 2C), 142.8 (dt, J=257, 13.7 Hz), 147.5 (ddd, J=249, 10.6, 4.4 Hz, 2C), 164.9, 183.4; ^{19}F NMR (188 MHz, $CDCl_3$): δ = −161.75 (dt, J=21.5, 6.0 Hz, 2F), −150.56 (t, J=21.5 Hz, 1F), −131.68 (dt, J=21.5, 4.5 Hz, 2F); elemental analysis calcd (%) for $C_{14}H_7F_5O_2S$: C 50.30, H 2.11; found: C 50.29, H 2.24.

(*S*)-(2,3,4,5,6-Pentafluorophenyl) 3,4-dimethoxybenzenecarbothioate (3ga): obtained in 72% as colorless crystals; m.p. 116.0–116.1°C; IR (KBr): $\tilde{\nu}$ = 1692, 1593, 1514, 1493 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.95 (s, 3H), 3.98 (s, 3H), 6.95 (d, J=8.5 Hz, 1H), 7.44 (d, J=2.0 Hz, 1H), 7.74 (dd, J=8.5, 2.0 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 56.0, 56.2, 103.0 (t, J=21.5 Hz), 109.7, 110.4, 122.9, 127.9, 137.8 (dm, J=256 Hz, 2C), 142.7 (dm, J=257 Hz), 147.4 (ddd, J=249, 11.2, 4.4 Hz, 2C), 149.2, 154.5, 183.5; ^{19}F NMR (188 MHz, $CDCl_3$): δ = −161.70 (t, J=20.0 Hz, 2F), −150.44 (t, J=20.0 Hz, 1F), −131.69 (d, J=20.0 Hz, 2F); elemental analysis calcd (%) for $C_{15}H_9F_5O_3S$: C 49.46, H 2.49; found: C 49.46, H 2.55.

(*S*)-(2,3,4,5,6-Pentafluorophenyl) 2,4,6-trimethoxybenzenecarbothioate (3ha): obtained in 95% as colorless crystals; m.p. 154.3–154.4°C; IR (KBr): $\tilde{\nu}$ = 1663, 1612, 1578, 1510, 1487, 1475 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.85 (s, 3H), 3.87 (s, 6H), 6.11 (s, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 55.6, 56.1 (2C), 90.7 (2C), 104.7 (dt, J=21.2, 4.4 Hz), 109.1, 137.7 (dm, J=255 Hz, 2C), 142.5 (dtt, J=257, 13.7, 5.0 Hz), 147.2 (ddd, J=249, 10.6, 4.4 Hz, 2C), 159.8 (2C), 164.3, 183.5; ^{19}F NMR (188 MHz, $CDCl_3$): δ = −162.31 (t, J=21.5 Hz, 2F), −151.66 (t, J=21.5 Hz, 1F), −131.79 (d, J=21.5 Hz, 2F); elemental analysis calcd (%) for $C_{16}H_{11}F_5O_4S$: C 48.74, H 2.81; found: C 48.66, H 2.84.

(*S*)-(2,3,4,5,6-Pentafluorophenyl) 2,4,6-trimethylbenzenecarbothioate (3ia): obtained in 90% as colorless crystals; m.p. 160.5–160.6°C; IR (KBr): $\tilde{\nu}$ = 1692, 1514, 1497 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.31 (s, 3H), 2.38 (s, 6H), 6.90 (s, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 18.9 (2C), 21.2, 103.1 (t, J=21.8 Hz), 128.7 (2C), 134.2 (2C), 135.7, 138.0 (dm, J=257 Hz, 2C), 140.7, 143.0 (dm, J=258 Hz), 147.2 (ddd, J=250, 11.0, 4.4 Hz, 2C), 191.1; ^{19}F NMR (188 MHz, $CDCl_3$): δ = −161.38 (t, J=20.5 Hz, 2F), −150.21 (t, J=20.5 Hz, 1F), −131.97 (d, J=20.5 Hz, 2F); elemental analysis calcd (%) for $C_{16}H_{11}F_5OS$: C 55.49, H 3.20; found: C 55.33, H 3.20.

(*S*)-Phenyl 3-phenylpropanethioate (3ab):[37] obtained in 44% as colorless crystals; m.p. 48.4–48.5°C (lit.[37] m.p. 49–50°C); IR (KBr): $\tilde{\nu}$ = 1707, 1477, 1441 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.93–3.06 (m, 4H), 7.19–7.33 (m, 5H), 7.35–7.42 (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 31.4, 45.1, 126.4, 127.6, 128.4 (2C), 128.6 (2C), 129.2 (2C), 129.4, 134.5 (2C), 139.9, 196.7.

(*S*)-Phenyl undecanethioate (3bb): obtained in 26% as colorless oil; IR (KBr): $\tilde{\nu}$ = 2924, 2853, 1711, 1477, 1466, 1441 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, J=6.6 Hz, 3H), 1.27 (br s, 14H), 1.71 (quint, J=7.5 Hz, 2H), 2.64 (t, J=7.5 Hz, 2H), 7.40 (s, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.1, 22.7, 25.6, 29.0, 29.2, 29.3, 29.4, 29.5, 31.9, 43.7, 128.0, 129.1 (2C), 129.3, 134.5 (2C), 197.6; elemental analysis calcd (%) for $C_{17}H_{26}OS$: C 73.33, H 9.41, S 11.52; found: C 73.59, H 9.37, S 11.24.

(*S*)-Phenyl benzenecarbothioate (3eb):[17a,18b,19,20] obtained in 35% as colorless crystals; m.p. 55.6–55.7°C (lit.[18b,19] m.p. 54–55°C, lit.[17a] m.p. 55–56°C); IR (KBr): $\tilde{\nu}$ = 1680, 1580, 1477, 1441 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.44–7.54 (m, 7H), 7.61 (t, J=7.3 Hz, 1H), 8.03 (d, J=7.3 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 127.3, 127.5 (2C), 128.8 (2C), 129.3 (2C), 129.5, 133.7, 135.1 (2C), 136.6, 190.2.

(*S*)-Phenyl 4-methoxybenzenecarbothioate (3fb):[17a,38] obtained in 47% as colorless crystals; m.p. 93.6–93.7°C (lit.[38] m.p. 93–95°C, lit.[17a] m.p. 94–95°C); IR (KBr): $\tilde{\nu}$ = 1666, 1599, 1506, 1477, 1439 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.87 (s, 3H), 6.95 (d, J=8.7 Hz, 2H), 7.43–7.52 (m, 5H), 8.00 (d, J=8.7 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 55.5, 113.9 (2C), 127.6, 129.2 (2C), 129.3, 129.4, 129.7 (2C), 135.2 (2C), 164.0, 188.6; elemental analysis calcd (%) for $C_{14}H_{12}O_2S$: C 68.83, H 4.95, S 13.13; found: C 68.94, H 5.07, S 12.92.

(*S*)-Benzyl 3-phenylpropanethioate (3ac): obtained in 41% as pale yellow oil; IR (KBr): $\tilde{\nu}$ = 1688, 1495, 1454 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.84–2.90 (m, 2H), 2.96–3.02 (m, 2H), 4.12 (s, 2H), 7.15–7.31 (m, 10H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 31.4, 33.2, 45.2, 126.4, 127.2, 128.3 (2C), 128.5 (2C), 128.6 (2C), 128.8 (2C), 137.6, 139.9, 197.8; elemental analysis calcd (%) for $C_{16}H_{16}OS$: C 74.96, H 6.29, S 12.51; found: C 75.23, H 6.55, S 12.34.

(*S*)-Benzyl undecanethioate (3bc): obtained in 24% as colorless oil; IR (KBr): $\tilde{\nu}$ = 2924, 2853, 1693, 1495, 1454 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, J=6.7 Hz, 3H), 1.25 (br s, 14H), 1.66 (quint, J=7.5 Hz, 2H), 2.56 (t, J=7.5 Hz, 2H), 4.11 (s, 2H), 7.21–7.32 (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.1, 22.7, 25.6, 28.9, 29.2, 29.3, 29.4, 29.5, 31.9, 33.1, 43.8, 127.2, 128.6 (2C), 128.8 (2C), 137.7, 198.9; elemental analysis calcd (%) for $C_{18}H_{28}OS$: C 73.92, H 9.65, S 10.96; found: C 74.22, H 9.66, S 10.74.

(*S*)-Benzyl benzenecarbothioate (3ec):[20,39] obtained in 32% as colorless crystals; m.p. 36.6–36.7°C (lit.[39b] m.p. 34.5–35.5°C, lit.[39c] m.p. 38–39°C); IR (KBr): $\tilde{\nu}$ = 1661, 1580, 1495, 1448 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.32 (s, 2H), 7.25–7.47 (m, 7H), 7.56 (t, J=7.3 Hz, 1H), 7.97 (d, J=7.1 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 33.3, 127.3 (2C), 127.3, 128.6 (2C), 128.7 (2C), 129.0 (2C), 133.5, 136.7, 137.5, 191.3.

(*S*)-Benzyl 4-methoxybenzenecarbothioate (3fc):[40] obtained in 38% as colorless crystals; mp 51.0–51.1°C (lit.[40] m.p. 51–52°C); IR (KBr): $\tilde{\nu}$ = 1657, 1601, 1508, 1495, 1454 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.86 (s, 3H), 4.30 (s, 2H), 6.91 (d, J=8.9 Hz, 2H), 7.24–7.39 (m, 5H), 7.94 (d, J=8.9 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 33.2, 55.5, 113.8 (2C), 127.2, 128.6 (2C), 129.0 (2C), 129.5 (2C), 129.6, 137.7, 163.8, 189.8.

1,2-Bis-pentafluorophenylsulfanylethyl acetate: VA-044 (24.4 mg, 0.075 mmol) was added to a solution of **2a** (60.0 mg, 0.151 mmol), vinyl acetate (139 μL, 1.51 mmol) and CTAB (11.0 mg, 0.030 mmol) in H_2O (3.0 mL) at room temperature. The reaction mixture was then stirred and heated to 50°C. After 6 h, the reaction mixture was extracted with EtOAc, and the organic layer was washed with brine, dried with Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc 20:1) to afford the title compound as colorless crystals (65.6 mg, 0.135 mmol, 90%). M.p. 74.3–74.4°C; IR (KBr): $\tilde{\nu}$ = 1759, 1639, 1485, 1371 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.03 (s, 3H), 3.08 (dd, J=14.4, 9.5 Hz, 1H), 3.78 (dd, J=14.4, 3.7 Hz, 1H), 5.91 (dd, J=9.5, 3.7 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.3, 29.7 (2C), 39.0, 77.3, 104.1–108.0 (2C), 135.5–140.5 (4C), 144.3–150.0 (4C), 169.0; ^{19}F NMR (188 MHz, $CDCl_3$): δ = −161.31 (br, 2F), −160.92 (br, 2F), −152.00 (br, 1F), −149.69 (br, 1F), −132.76 (d, J=24.4 Hz, 2F), −131.29 (d, 22.9 Hz, 2F).

Preparation of bis(2,3,4,5,6-pentafluorophenyl) disulfide (2a) by using pentafluorobenzenethiol (2a′), VA-044 and CTAB: VA-044 (65.0 mg, 0.20 mmol) was added to a solution of **2a′** (80.0 mg, 0.40 mmol) and CTAB (29.3 mg, 0.080 mmol) in H_2O (4 mL) at room temperature. The reaction mixture was then stirred and heated to 50 °C. After 20 min, the reaction mixture was extracted with EtOAc, and the organic layer was washed with brine, dried with Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (hexane only) to afford **2a** (68.5 mg, 0.17 mmol, 86 %) as pale yellow crystals.

Preparation of pentafluorophenyl thioester (3aa) by using pentafluorobenzenethiol (2a′): VA-044 (48.5 mg, 0.15 mmol) was added to a solution of **1a** (40.3 mg, 0.30 mmol), **2a′** (120 mg, 0.60 mmol) and CTAB (21.9 mg, 0.060 mmol) in H_2O (3 mL) at room temperature. The reaction mixture was then stirred and heated to 50 °C. After 3 h, an additional amount of VA-044 (48.5 mg, 0.15 mmol) was added to the reaction mixture. After 24 h, the reaction mixture was extracted with EtOAc, and the organic layer was washed with brine, dried with Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc 50:1) to afford **3aa** (28.9 mg, 0.087 mmol, 29 %) as colorless crystals.

***N*-Cyclohexyl-3-phenylpropanamide (5aa)**:[41] Cyclohexylamine (**4a**) (18.9 μL, 0.165 mmol) and Et_3N (23.0 μL, 0.165 mmol) were added to a solution of **3aa** (49.8 mg, 0.150 mmol) in dry CH_2Cl_2 (1.5 mL) at room temperature under a nitrogen atmosphere. The reaction mixture was then stirred for 5 min and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc 2:1) to afford **5aa** (34.7 mg, 0.15 mmol, quant.) as colorless crystals. M.p. 111.9–112.0 °C (lit.[41] m.p. 110–111 °C); IR (KBr): $\tilde{\nu}$ = 3302, 2934, 2853, 1636, 1543 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 0.94–1.18 (m, 3H), 1.23–1.40 (m, 2H), 1.55–1.68 (m, 3H), 1.80–1.85 (m, 2H), 2.43 (t, J = 7.6 Hz, 2H), 2.95 (t, J = 7.6 Hz, 2H), 3.67–3.79 (m, 1H), 5.19 (br d, 1H), 7.17–7.30 (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 24.8 (2C), 25.5, 31.9, 33.1 (2C), 38.8, 48.0, 126.2, 128.4 (2C), 128.5 (2C), 140.9, 171.0; elemental analysis calcd (%) for $C_{15}H_{21}NO$: C 77.88, H 9.15, N 6.05; found: C 77.59, H 9.05, N 5.96.

Ethyl 7-oxo-7-tetrahydropyridin-1(2*H*)-ylheptanoate (5db): Piperidine (**4b**) (16.3 μL, 0.165 mmol) and Et_3N (23.0 μL, 0.165 mmol) were added to a solution of **3da** (55.6 mg, 0.150 mmol) in dry CH_2Cl_2 (1.5 mL) at room temperature under a nitrogen atmosphere. The reaction mixture was then stirred for 5 min and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc 1:1) to afford **5db** (38.3 mg, 0.15 mmol, quant.) as colorless oil. IR (KBr): $\tilde{\nu}$ = 2936, 2856, 1732, 1643, 1443 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.25 (t, J = 7.2 Hz, 3H), 1.33–1.43 (m, 2H), 1.49–1.71 (m, 10H), 2.28–2.34 (m, 4H), 3.39 (t, J = 5.4 Hz, 2H), 3.54 (t, J = 5.4 Hz, 2H), 4.12 (q, J = 7.2 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.2, 24.6, 24.8, 25.1, 25.6, 26.6, 29.0, 33.2, 34.2, 42.7, 46.7, 60.2, 171.3, 173.8; elemental analysis calcd (%) for $C_{14}H_{25}NO_3$: C 65.85, H 9.87, N 5.49; found: C 65.42, H 9.71, N 5.22.

Methyl 3-phenylpropionate (6a):[42] K_2CO_3 (27.6 mg, 0.20 mmol) was added to a solution of **3aa** (66.5 mg, 0.20 mmol) in dry MeOH (1 mL) under a nitrogen atmosphere. The reaction mixture was stirred at 50 °C for 30 min. To the reaction mixture, a saturated aqueous NH_4Cl and EtOAc were added, and the organic layer was separated and the aqueous layer extracted with EtOAc. The organic layer was washed with brine, dried with Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc 2:1) to afford **6a** (32.8 mg, 0.20 mmol, quant.) as colorless oil. IR (KBr): $\tilde{\nu}$ = 3028, 2952, 2928, 2858, 1740, 1497, 1437 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 2.63 (t, J = 7.8 Hz, 2H), 2.95 (t, J = 7.8 Hz, 2H), 3.66 (s, 3H), 7.18–7.21 (m, 3H), 7.24–7.31 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 31.0, 35.7, 51.6, 126.3, 128.3 (2C), 128.5 (2C), 140.5, 173.3.

3-Phenyl-1-propionic acid (7a):[43] KOH (16.8 mg, 0.30 mmol) was added to a solution of **3aa** (66.5 mg, 0.20 mmol) in acetone/H_2O (1 mL acetone + 1 mL H_2O). The reaction mixture was stirred at 50 °C for 1 h. To the reaction mixture was extracted with EtOAc. The organic layer was washed with 1 N aqueous HCl and brine. The organic layer was dried with Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc/HOAc 75:25:1) to afford **7a** (30.0 mg, 0.20 mmol, quant.) as colorless crystals. M.p. 47.6–47.7 °C (lit.[43a] m.p. 47–48 °C, lit.[43b] m.p. 47–49 °C); IR (KBr): $\tilde{\nu}$ = 3028, 2932, 1709, 1454, 1413, 1219 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 2.69 (t, J = 7.8 Hz, 2H), 2.96 (t, J = 7.8 Hz, 2H), 7.20–7.32 (m, 5H), 11.6 (br s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 30.6, 35.6, 126.4, 128.3 (2C), 128.6 (2C), 140.1, 179.1.

1,3-Diphenylpropan-1-one (8a):[44] According to the reported prcedure,[7h] **8a** can be obtained in 96 % yield as colorless crystals. M.p. 66.6–66.7 °C (lit.[44a] m.p. 67–69 °C, lit.[44b] mp 70–71 °C); IR (KBr): $\tilde{\nu}$ = 2927, 1686, 1597, 1495, 1448, 1205 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 3.07 (t, J = 7.7 Hz, 2H), 3.30 (t, J = 7.7 Hz, 2H), 7.18–7.32 (m, 5H), 7.41–7.57 (m, 3H), 7.95 (d, J = 7.3 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 30.1, 40.4, 126.1, 128.0 (2C), 128.4 (2C), 128.5 (2C), 128.5 (2C), 128.6 (2C), 133.0, 136.8, 141.3, 199.2.

Ethyl 4-(4-methoxybenzoyl)butanoate (8f):[45] According to the reported prcedure,[7f] **8f** can be obtained in 90 % yield as colorless crystals. M.p. 56.5–56.6 °C (lit.[45b] m.p. 56–58 °C, lit.[45a] m.p. 58.5–59 °C); IR (KBr): $\tilde{\nu}$ = 2982, 2960, 1734, 1668, 1602, 1281, 1259, 1186, 1175 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.25 (t, J = 7.2 Hz, 3H), 2.06 (quint, J = 7.2 Hz, 2H), 2.42 (t, J = 7.2 Hz, 2H), 3.00 (t, J = 7.2 Hz, 2H), 3.87 (s, 3H), 4.14 (q, J = 7.2 Hz, 2H), 6.93 (d, J = 8.9 Hz, 2H), 7.95 (d, J = 8.9 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.2, 19.6, 33.4, 37.1, 55.4, 60.3, 113.6 (2C), 129.9, 130.2 (2C), 163.4, 173.3, 198.0.

General procedure for the preparation of amide (5) from aldehyde (1a, b, d, h): VA-044 (48.5 mg, 0.15 mmol) was added to a solution of aldehydes (**1a**, **b**, **d**, **h**) (0.30 mmol), **2a** (119 mg, 0.30 mmol) and CTAB (21.9 mg, 0.060 mmol) in H_2O (3 mL) at room temperature. The reaction mixture was then stirred and heated to 50 °C. After 3 h, an additional amount of the initiator VA-044 (48.5 mg, 0.15 mmol) was added to the reaction mixture. The progress of the reaction was monitored by TLC. After the completion of the thioesterification, amine (**4a** or **4b**) (0.90 mmol) was added to the thioesterification mixture, and the reaction mixture was stirred at 50 °C for 30 min. The reaction mixture was then extracted with EtOAc, and the organic layer was washed with brine, dried with Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc 3:1→100 % EtOAc) to afford the pure amides **5**.

3-Phenyl-1-tetrahydropyridin-1(2*H*)-ylpropan-1-one (5ab):[46] obtained in 70 % as pale yellow oil; IR (KBr): $\tilde{\nu}$ = 2936, 2855, 1643, 1441 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.40–1.65 (m, 6H), 2.61 (t, J = 8.0 Hz, 2H), 2.96 (t, J = 8.0 Hz, 2H), 3.33 (t, J = 5.5 Hz, 2H), 3.55 (t, J = 5.5 Hz, 2H), 7.16–7.31 (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 24.5, 25.5, 26.4, 31.6, 35.2, 42.8, 46.7, 126.1, 128.4 (2C), 128.5 (2C), 141.4, 170.6.

***N*-Cyclohexylundecanamide (5ba)**: obtained in 82 % as colorless crystals; m.p. 81.2–81.3 °C; IR (KBr): $\tilde{\nu}$ = 3298, 2920, 2851, 1638, 1551 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.6 Hz, 3H), 1.03–1.44 (m, 19H), 1.58–1.73 (m, 5H), 1.88–1.94 (m, 2H), 2.13 (t, J = 7.6 Hz, 2H), 3.71–3.83 (m, 1H), 5.26 (br d, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.1, 22.7, 24.9 (2C), 25.6, 25.9, 29.3, 29.3, 29.4, 29.5, 29.6, 31.9, 33.3 (2C), 37.2, 48.0, 172.2; elemental analysis calcd (%) for $C_{17}H_{33}NO$: C 76.34; H 12.44; N 5.24; found: C 76.05; H 12.25; N 5.17.

1-Tetrahydropyridin-1(2*H*)-ylundecan-1-one (5bb): obtained in 76 % as colorless oil; IR (KBr): $\tilde{\nu}$ = 2924, 2853, 1649, 1433 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.5 Hz, 3H), 1.26 (br s, 14H), 1.53–1.64 (m, 8H), 2.31 (t, J = 7.7 Hz, 2H), 3.39 (t, J = 5.3 Hz, 2H), 3.54 (t, J = 5.3 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.1, 22.7, 24.6, 25.5, 25.6, 26.6, 29.3, 29.4, 29.5, 29.6, 29.6, 31.9, 33.5, 42.6, 46.8, 171.6; elemental analysis calcd (%) for $C_{16}H_{31}NO$: C 75.83; H 12.33; N 5.53; found: C 75.34; H 12.15; N 5.25.

Ethyl 7-(cyclohexylamino)-7-oxoheptanoate (5da): obtained in 84 % as colorless crystals; m.p. 69.9–70.0 °C; IR (KBr): $\tilde{\nu}$ = 3296, 2932, 2855, 1736, 1638, 1541 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.04–1.43 (m, 7H), 1.25 (t, J = 7.2 Hz, 3H), 1.57–1.74 (m, 7H), 1.88–1.93 (m, 2H), 2.14 (t, J = 7.4 Hz, 2H), 2.30 (t, J = 7.4 Hz, 2H), 3.69–3.82 (m, 1H), 4.12 (q, J = 7.2 Hz, 2H), 5.46 (br d, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.2, 24.5, 24.8 (2C), 25.4, 25.5, 28.6, 33.2 (2C), 34.0, 36.6, 48.0, 60.2, 171.8, 173.6; elemental analysis calcd (%) for $C_{15}H_{27}NO_3$: C 66.88; H 10.10; N 5.20; found: C 66.71 H, 9.98; N 5.15.

***N*-Cyclohexyl-2,4,6-trimethoxybenzamide (5ha)**: obtained in 83% as colorless crystals; m.p. 147.1–147.2°C; IR (KBr): $\tilde{\nu}$ = 3287, 2932, 2851, 1649, 1607, 1589, 1454 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.15–1.26 (m, 3H), 1.35–1.48 (m, 2H), 1.59–1.75 (m, 3H), 1.99–2.04 (m, 2H), 3.79 (s, 6H), 3.80 (s, 3H), 3.93–4.05 (m, 1H), 5.63 (br d, 1H), 6.09 (s, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 24.8 (2C), 25.7, 33.0 (2C), 48.2, 55.4, 56.0 (2C), 90.8 (2C), 109.5, 158.5 (2C), 161.9, 164.7; elemental analysis calcd (%) for $C_{16}H_{23}NO_4$: C 65.51; H 7.90; N 4.77; found: C 65.35; H 7.77; N 4.76.

Tetrahydropyridin-1(2*H*)-yl(2,4,6-trimethoxyphenyl)methanone (5hb): obtained in 87% as colorless crystals; m.p. 122.3–122.4°C; IR (KBr): $\tilde{\nu}$ = 2936, 2853, 1632, 1607, 1589, 1435 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.47 (br s, 2H), 1.61–1.64 (m, 4H), 3.19 (t, J = 5.5 Hz, 2H), 3.74 (br s, 2H), 3.78 (s, 6H), 3.81 (s, 3H), 6.11 (s, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 24.8, 25.7, 26.4, 42.4, 47.7, 55.4, 55.8 (2C), 90.6 (2C), 108.0, 157.4 (2C), 161.7, 165.2; elemental analysis calcd (%) for $C_{15}H_{21}NO_4$: C 64.50; H 7.58; N 5.01; found: C 64.36; H 7.57; N 4.94.

Acknowledgement

We thank Wako Pure Chemical Industries, Ltd., for the generous supply of several water-soluble azo-type initiators. This work was supported by a Grant-in-Aid for Scientific Research (S) (No.7690) from the Ministry of Education, Culture, Sports, Science and Technology, Japan. H.N. acknowledges the JSPS Research Fellowship for Young Scientists.

[1] a) L. Field, *Synthesis* **1972**, 101–133; b) E. Haslam, *Tetrahedron* **1980**, *36*, 2409–2433; and references therein.
[2] a) A. P. Davis, J. J. Walsh, *Tetrahedron Lett.* **1994**, *35*, 4865–4868; b) A. P. Davis, J. J. Walsh, *Chem. Commun.* **1996**, 449–451; c) A. P. Davis, S. Menzer, J. J. Walsh, D. J. Williams, *Chem. Commun.* **1996**, 453–455.
[3] a) Z.-H. Huang, J. Wu, K. D. W. Roth, Y. Yang, D. A. Gage, J. T. Watson, *Anal. Chem.* **1997**, *69*, 137–144; b) M. Kurosu, *Tetrahedron Lett.* **2000**, *41*, 591–594.
[4] a) R. Annunziata, M. Benaglia, M. Cinquini, F. Cozzi, *Tetrahedron Lett.* **1995**, *36*, 613–616; b) M. Benaglia, M. Cinquini, F. Cozzi, *Eur. J. Org. Chem.* **2000**, 563–572.
[5] S. Masamune, Y. Hayase, W. Schilling, W. K. Chan, G. S. Bates, *J. Am. Chem. Soc.* **1977**, *99*, 6756–6758.
[6] R. L. Danheiser, J. S. Nowick, *J. Org. Chem.* **1991**, *56*, 1176–1185.
[7] a) T. Mukaiyama, M. Araki, H. Takei, *J. Am. Chem. Soc.* **1973**, *95*, 4763–4765; b) R. J. Anderson, C. A. Henrick, L. D. Rosenblum, *J. Am. Chem. Soc.* **1974**, *96*, 3654–3655; c) Y. Kawanami, T. Katsuki, M. Yamaguchi, *Tetrahedron Lett.* **1983**, *24*, 5131–5132; d) R. Conrow, P. S. Portoghese, *J. Org. Chem.* **1986**, *51*, 938–940; e) G. J. McGarvey, J. M. Williams, R. N. Hiner, Y. Matsubara, T. Oh, *J. Am. Chem. Soc.* **1986**, *108*, 4943–4952; f) H. Tokuyama, S. Yokoshima, T. Yamashita, T. Fukuyama, *Tetrahedron Lett.* **1998**, *39*, 3189–3192; g) C. Savarin, J. Srogl, L. S. Liebeskind, *Org. Lett.* **2000**, *2*, 3229–3231; h) L. S. Liebeskind, J. Srogl, *J. Am. Chem. Soc.* **2000**, *122*, 11260–11261; i) T. Shimizu, M. Seki, *Tetrahedron Lett.* **2001**, *42*, 429–432; j) T. Shimizu, M. Seki, *Tetrahedron Lett.* **2002**, *43*, 1039–1042.
[8] S. Iimura, K. Manabe, S. Kobayashi, *Org. Lett.* **2003**, *5*, 101–103; and references therein.
[9] a) T. Fukuyama, S.-C. Lin, L. Li, *J. Am. Chem. Soc.* **1990**, *112*, 7050–7051; b) T. Tokuyama, S. Yokoshima, S.-C. Lin, L. Li, T. Fukuyama, *Synthesis* **2002**, 1121–1123.
[10] a) E. L. Eliel, R. A. Daignault, *J. Org. Chem.* **1964**, *29*, 1630–1631; b) D. E. Bublitz, *J. Org. Chem.* **1967**, *32*, 1630–1631.
[11] Diastereoselective aldol reaction: a) R. Annunziata, M. Cinquini, F. Cozzi, P. G. Cozzi, E. Consolandi, *Tetrahedron* **1991**, *47*, 7897–7910; b) K.-H. Suh, D.-J. Choo, *Tetrahedron Lett.* **1995**, *36*, 6109–6112; c) G. Lalic, A. D. Aloise, M. D. Shair, *J. Am. Chem. Soc.* **2003**, *125*, 2852–2853; Asymmetric aldol reaction.
[12] C. Alvarez-Ibarra, M. Mendoza, G. Orellana, M. L. Quiroga, *Synthesis* **1989**, 560–562.
[13] Some recent reports: a) R. K. Jr., Boeckman, T. J. Clark, B. C. Shook, *Org. Lett.* **2002**, *4*, 2109–2112; b) D. A. Longbottom, A. J. Morrison, D. J. Dixon, S. V. Ley, *Angew. Chem.* **2002**, *114*, 2910–2914; *Angew. Chem. Int. Ed.* **2002**, *41*, 2786–2790; c) X. Bu, X. Wu, G. Xie, Z. Guo, *Org. Lett.* **2002**, *4*, 2893–2895; d) D. A. Evans, H. A. Rajapakse, A. Chiu, D. Stenkamp, *Angew. Chem.* **2002**, *114*, 4755–4758; *Angew. Chem. Int. Ed.* **2002**, *41*, 4573–4576; e) A. Endo, A. Yanagisawa, M. Abe, S. Tohma, T. Kan, T. Fukuyama, *J. Am. Chem. Soc.* **2002**, *124*, 6552–6554; f) V. K. Aggarwal, B. N. Esquivel-Zamora, *J. Org. Chem.* **2002**, *67*, 8618–8621; g) K. Agapiou, M. J. Krische, *Org. Lett.* **2003**, *5*, 1737–1740; h) R. Ingenito, H. Wenschuh, *Org. Lett.* **2003**, *5*, 4587–4590; i) J. A. Camarero, B. J. Hackel, J. J. de Yoreo, A. R. Mitchell, *J. Org. Chem.* **2004**, *69*, 4145–4151.
[14] a) J. R. Grunwell, D. L. Foerst, *Synth. Commun.* **1976**, *6*, 453–455; b) H.-J. Liu, S. I. Sabesan, *Can. J. Chem.* **1980**, *58*, 2645–2648; c) T. Imamoto, M. Kodera, M. Yokoyama, *Synthesis* **1982**, 134–136; d) K. Sucheta, G. S. R. Reddy, D. Ravi, N. R. Rao, *Tetrahedron Lett.* **1994**, *35*, 4415–4416; e) M. H. Kim, D. V. Patel, *Tetrahedron Lett.* **1994**, *35*, 5603–5606; f) M. Seki, K. Kondo, T. Iwasaki, *Synlett* **1995**, 315–316; g) M. Adamczyk, J. R. Fishpaugh, *Tetrahedron Lett.* **1996**, *37*, 4305–4308; h) S. Iimura, K. Manabe, S. Kobayashi, *Chem. Commun.* **2002**, 94–95.
[15] a) G. O. Spessard, W. K. Chan, S. Masamune, *Org. Synth.* **1982**, *61*, 134–141; b) S. Ahmad, J. Iqbal, *Tetrahedron Lett.* **1986**, *27*, 3791–3794; c) H. M. Meshram, G. S. Reddy, K. H. Bindu, J. S. Yadav, *Synlett* **1998**, 877–878; d) C. C. Silveira, A. L. Braga, E. L. Larghi, *Organometallics* **1999**, *18*, 5183–5186.
[16] a) T. Endo, S. Ikenaga, T. Mukaiyama, *Bull. Chem. Soc. Jpn.* **1970**, *43*, 2632–2633; b) M. M. Lakouraj, B. Movassagh, Z. Fadaei, *Monatsh. Chem.* **2002**, *133*, 1085–1088.
[17] a) P. A. Grieco, Y. Yokoyama, E. Williams, *J. Org. Chem.* **1978**, *43*, 1283–1285; b) M. Kurauchi, T. Imamoto, M. Yokoyama, *Tetrahedron Lett.* **1981**, *22*, 4985–4986; c) X. Jia, Y. Zhang, X. Zhou, *Tetrahedron Lett.* **1994**, *35*, 8833–8834.
[18] a) G. Petrillo, M. Novi, G. Garbariono, M. Filiberti, *Tetrahedron* **1989**, *45*, 7411–7420; b) M. Barbero, I. Degani, S. Dughera, R. Fochi, *Synthesis* **2003**, 1225–1230.
[19] J.-Z. You, Z.-C. Chen, *Synthesis* **1992**, 521–522.
[20] T. Inoue, T. Takeda, N. Kambe, A. Ogawa, I. Ryu, N. Sonoda, *J. Org. Chem.* **1994**, *59*, 5824–5827.
[21] a) M. Takagi, S. Goto, T. Matsuda, *J. Chem. Soc. Chem. Commun.* **1976**, 92–93; b) M. Takagi, S. Goto, M. Tazaki, T. Matsuda, *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1982–1987.
[22] Y. Kita, M. Matsugi, Radical Initiators in *Radicals in Organic Synthesis, Vol. 1* (Eds.: P. Renaud, M. P. Sibi), Wiley-VCH, Weinheim, **2001**, pp. 1–10; the water-soluble azo type radical initiators used in our studies are available from Wako Pure Chemical Industries, Ltd. Osaka (Japan).
[23] a) J. H. Fendler, "Catalysis in Micellar and Macromolecular Systems", Academic Press, New York, **1975**; b) M. J. Rosen, "Surfactants and Interfacial Phenomena", 2nd ed., Wiley, New York, **1989**; c) S. Tascioglu, *Tetrahedron* **1996**, *52*, 11113–11152; d) H. Tohma, S. Takizawa, H. Watanabe, Y. Kita, *Tetrahedron Lett.* **1998**, *39*, 4547–4550; e) H. Tohma, S. Takizawa, H. Watanabe, Y. Fukuoka, T. Maegawa, Y. Kita, *J. Org. Chem.* **1999**, *64*, 3519–3523.
[24] H. Nambu, K. Hata, M. Matsugi, Y. Kita, *Chem. Commun.* **2002**, 1082–1083.
[25] Radical reaction under micellar conditions in water: a) Y. Kita, H. Nambu, N. G. Ramesh, G. Anilkumar, M. Matsugi, *Org. Lett.* **2001**, *3*, 1157–1160; b) H. Nambu, G. Anilkumar, M. Matsugi, Y. Kita, *Tetrahedron* **2003**, *59*, 77–85.
[26] a) C.-J. Li, T.-H. Chan, "Organic Reactions in Aqueous Media", Wiley, New York, **1997**; b) *Organic Synthesis in Water* (Ed. P. A. Grieco), Blackie Academic, London, **1998**; c) B. Cornils, W. A.

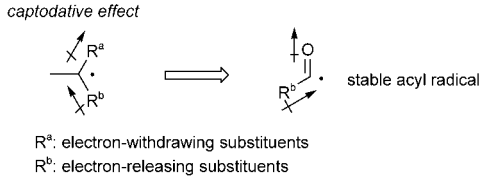
Herrmann, "Aqueous-Phase Organometallic Catalysis", Wiley-VCH, Weinheim, **1998**.

[27] This thioesterification was accelerated by the addition of a cationic surfactant (CTAB). It is reasonable to postulate that this surfactant activates the carbonyl group of the aldehyde. Namely, the aldehyde in the cationic micellar system formed by the cationic surfactant would be activated by the cationic effect.

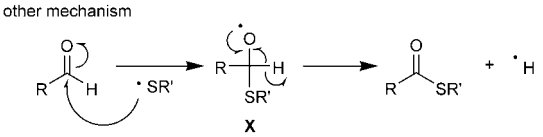
[28] a) Y. Kita, A. Sano, T. Yamaguchi, M. Oka, K. Gotanda, M. Matsugi, *J. Org. Chem.* **1999**, *64*, 675–678; b) M. Matsugi, K. Gotanda, C. Ohira, M. Suemura, A. Sano, Y. Kita, *J. Org. Chem.* **1999**, *64*, 6928–6930; c) K. Gotanda, M. Matsugi, M. Suemura, C. Ohira, A. Sano, M. Oka, Y. Kita, *Tetrahedron* **1999**, *55*, 10315–10324; and references therein.

[29] C. Chatgilialoglu, D. Crich, M. Komatsu, I. Ryu, *Chem. Rev.* **1999**, *99*, 1991–2069; and references therein.

[30] The yields of these thioesterifications were affected by the electron density of the functional groups of aldehydes. It is reasonable to suppose that the acyl radical intermediate of the thioesterification is stabilized by electrical effects. That is, the acyl radical formed from the aliphatic aldehyde or aromatic aldehyde with an electron-releasing substituent would be stabilized by the captodative effect. On the other hand, the acyl radical formed from the aromatic aldehyde with an electron-withdrawing substituent would not be stabilized, therefore, the thioesterification with **1j** and **1k** did not proceed at all; cf. captodative effect: L. Stella, J. N. Harvey, in *Radicals in Organic Synthesis, Vol. 1* (Eds.: P. Renaud, M. P. Sibi), Wiley-VCH, Weinheim, **2001**, pp. 360–380.



[31] It is possible that this thioesterification proceeds via the nucleophilic addition of the thiyl radical to the aldehyde. Namely, the thiyl radical produced by the disulfide nucleophilically attacks the carbonyl group of the aldehyde, and then the alkoxyl radical (**X**) is formed. Next, the hydride radical is eliminated from the alkoxyl radical intermediate (**X**), and the thioesterification is achieved. If this thioesterification will proceed via this plausible reaction mechanism, the aldehydes with an electron-withdrawing substitute (**1j**, **1k**) should be nucleophilically attacked by the thiyl radical. However, these thioesterification with **1j** and **1k** did not proceed at all (Table 4, entries 10, 11). In addition, the alkyl or aryl radical is more stable than the hydride radical, therefore, it is difficult that the hydride radical eliminates from the alkoxyl radical intermediate (**X**). Accordingly, it might be inferred from this reactivity that this thioesterification is achieved via the acyl radical intermediate (Scheme 1).



[32] Some recent reports: a) I. Shiina, Y. Kawakita, *Tetrahedron Lett.* **2003**, *44*, 1951–1955; b) K. Wakasugi, A. Nakamura, A. Iida, Y. Nishii, N. Nakatani, S. Fukushima, Y. Tanabe, *Tetrahedron* **2003**, *59*, 5337–5345; and references therein.

[33] a) K. Nakagawa, H. Onoue, K. Minami, *J. Chem. Soc. Chem. Commun.* **1966**, 17–18; b) Y. Tamaru, Y. Yamada, Z. Yoshida, *Synthesis* **1983**, 474–476; c) T. Naota, S.-I. Murahashi, *Synlett* **1991**, 693–694; d) A. Tillack, I. Rudloff, M. Beller, *Eur. J. Org. Chem.* **2001**, 523–528.

[34] I. E. Markó, A. Mekhalfia, *Tetrahedron Lett.* **1990**, *31*, 7237–7240.

[35] R. Ballini, E. Marcantoni, M. Petrini, *Synth. Commun.* **1991**, *21*, 1075–1081.

[36] a) T. Kitazume, J. M. Shreeve, *J. Am. Chem. Soc.* **1978**, *100*, 492–496; b) A. Mckillop, D. Koyuncu, *Tetrahedron Lett.* **1990**, *31*, 5007–5010.

[37] S. E. Tomas, G. J. Tustin, *Tetrahedron* **1992**, *48*, 7629–7640.

[38] G. Cilento, *J. Am. Chem. Soc.* **1953**, *75*, 3748–3750.

[39] a) T. Nowicki, A. Markowska, P. Kielbasinski, M. Mikolajczyk, *Synthesis* **1986**, 305–308; b) H. Ohmori, H. Maeda, K. Konomoto, K. Sakai, M. Masui, *Chem. Pharm. Bull.* **1987**, *35*, 4473–4481; c) T. Takido, M. Toriyama, K. Itabashi, *Synthesis* **1988**, 404–406.

[40] D. H. R. Barton, D. P. Manly, D. A. Widdowson, *J. Chem. Soc. Perkin Trans. 1* **1975**, 1568–1574.

[41] T. Kametani, O. Umezawa, *Chem. Pharm. Bull.* **1966**, *14*, 369–375.

[42] a) M. Kunishima, C. Kawachi, J. Morita, K. Terao, F. Iwasaki, S. Tani, *Tetrahedron* **1999**, *55*, 13159–13170; b) S. Oi, M. Moro, H. Ito, Y. Honma, S. Miyano, Y. Inoue, *Tetrahedron* **2002**, *58*, 91–97.

[43] a) C. N. Robinson, P. K. Li, J. F. Addison, *J. Org. Chem.* **1972**, *37*, 2939–2941; b) H. Kawabata, M. Hayashi, *Tetrahedron Lett.* **2002**, *43*, 5645–5647.

[44] a) S. Fukuzawa, K. Mutoh, T. Tsuchimoto, T. Hiyama, *J. Org. Chem.* **1996**, *61*, 5400–5405; b) M. R. Pitts, J. R. Harrison, C. J. Moody, *J. Chem. Soc. Perkin Trans. 1* **2001**, 955–977; c) L. J. Gooßen, K. Ghosh, *Eur. J. Org. Chem.* **2002**, 3254–3267.

[45] a) H. Sakuragi, K. Tokumaru, H. Itoh, K. Terakawa, K. Kikuchi, R. A. Caldwell, C.-C. Hsu, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1049–1057; b) Y. Senda, H. Kanto, H. Itoh, *J. Chem. Soc. Perkin Trans. 2* **1997**, 1143–1146.

[46] A. Banerji, S. Jana, K. R. Sur, *J. Indian Chem. Soc.* **1989**, *66*, 664–672.

Received: July 22, 2004
Published online: December 3, 2004

