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Cyclization of Aryl Acyl Radicals Generated from *S*-(4-Cyano)phenyl Thiolesters by a Nickel Complex Catalyzed Electroreduction

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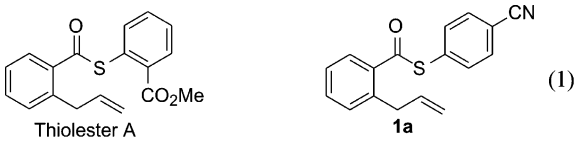
Abstract: Aromatic acyl radicals generated from *S*-(4-cyano)phenyl 2-alkenylthiobenzoate by a nickel complex catalyzed electroreduction undergo 5- and 6-exo cyclization to give 1-indanone and dihydro-1-naphthalenone derivatives, respectively.

The generation of acyl radicals and their intra- and intermolecular carbon−carbon bond-forming reactions has long been recognized as a useful tool for homolytic synthesis. The majority of the above reactions have been achieved by employing acyl selenides,[1] aryl acyl tellurides,[2] and *S*-acylxanthates[3] as the acyl radical precursors by means of organostannane-mediated chain reactions. In the tin hydride method, the use of *S*-phenyl thiolesters which are more stable under oxidizing conditions and attractive as acyl radical precursors is known not to be practical, since the reactions of stannyl radical with simple *S*-phenyl thiolesters are too sluggish to set the chain propagation viable.[4] The tin-free methods such as the photochemical method where the acylgermanes[5] or acylcobalt(III)[6] was used as acyl radical precursors have also been developed and found useful applications in synthesis of cyclic ketones and lactams, respectively.

We have developed a nickel complex catalyzed electroreductive method as an organotin-free tool available to conduct radical reactions.[7] In our previous paper, we demonstrated that the *S*-(2-methoxycarbonyl)phenyl thiolesters are a comvenient acyl radical precursor and that cyclic ketones are isolated in modest to good yield on subjecting the thiolesters to this electroreductive method.[8]

Herein, we report a study of the generation of aryl acyl radicals from the *S*-(4-cyano)phenyl thiolesters and their intramolecular additions reactions, which would proceed according to the reaction path as shown in Scheme 1.

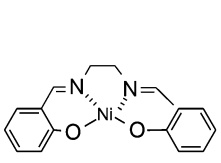
In the search for a precursors suitable to generation of aryl acyl radicals, a thiolester **A**, composed of methyl 2-mercaptobenzoate and 2-(prop-2-enyl)benzoic acid, was subjected to Ni(salen)-catalyzed electroreduction.[10]



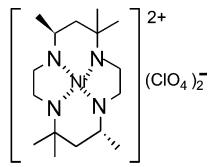
(1)

The electrolysis of **A** provided 30% of 2-(prop-2-enyl)-benzyl alcohol as a major product and cyclized products 2-methylindanone and 3,4-dihydro-1(2*H*)-naphthalenone in 13% and 4% yield, respectively. The yield of a significant amount of the benzyl alcohol seemed to indicate that the generated acyl radical would suffer from further electroreductions, followed by attack with residual water in DMF (Scheme 1). When thiolester **1a**, a counterpart of **A** bearing an *S*-(4-cyano)phenyl group instead of an *S*-(2-methoxycarbony)phenyl group, which exhibits reductive peak of voltammetric measurement at ca. 0.3 V less negative potential than **A**, was reductively electrolyzed at 60 °C using Ni(*tet* a)$^{2+}$ [9] as a catalyst, 5-exo and 6-exo cyclizations of the generated acy radicals were shown to be major reactions as shown in Table 1.

The comparison of results of the electrolysis in entry 1 with those of entries 3 and 4 suggests that cyclization of aryl acyl radical onto an alkene proceeds more smoothly at elevated temperature (60 °C) than at ambient temperature. In previous papers, we have reported that alkyl and vinyl radicals generated by similar catalytic electroreduction undergo efficient inter- and intramolecular carbon−carbon bond-forming reactions even at ambient temperature.[7] The present observation that the intramolecular cyclizations of acyl radicals require heating seems to indicate that the addition rates of acyl radicals onto alkenes are significantly smaller than those of alkyl and



Ni(salen)



Ni(*tet* a)$(ClO_4)_2$

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(9) Thiolester **A** and **1a** show reduction peak of voltammogram at −2.08 and −1.78 V vs SCE, respectively. Ni(salen) exhibits its Ni(I)/Ni(II) redox wave at −1.70/−1.60 V vs SCE and was found to catalyze electroreduction of thiolester **A** , while Ni(tet *a*)$(ClO_4)_2$ exhibits its Ni(I)/Ni(II) redox wave at −1.36/−1.28 V vs SCE and was found to catalyze electroreduction of **1a**. For details, see ref 7b.

(10) Product **2c** was accompanied by formation of compound **1cH** (5%), which was derived from reduction of the acceptor double bond in **1c**.

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SCHEME 1

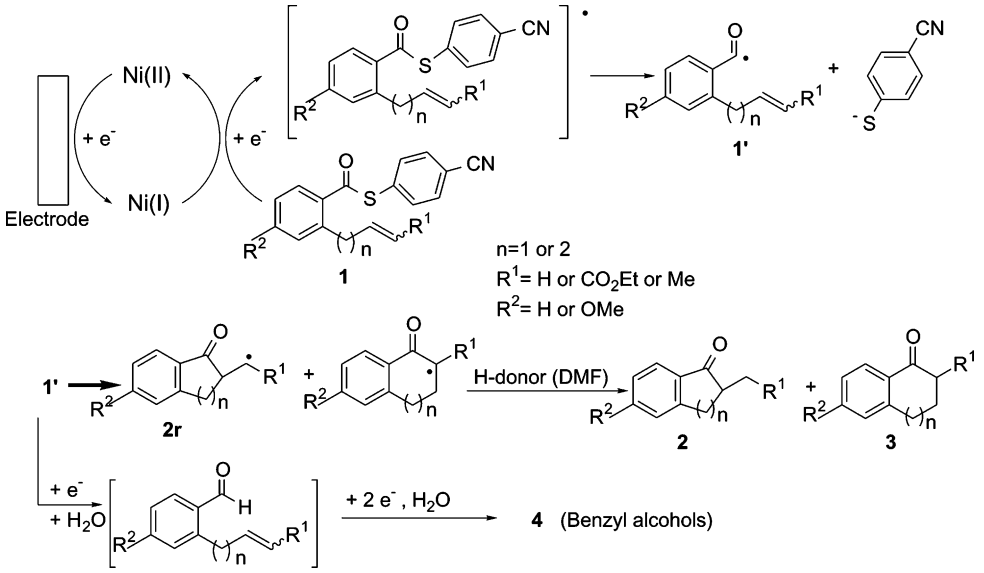
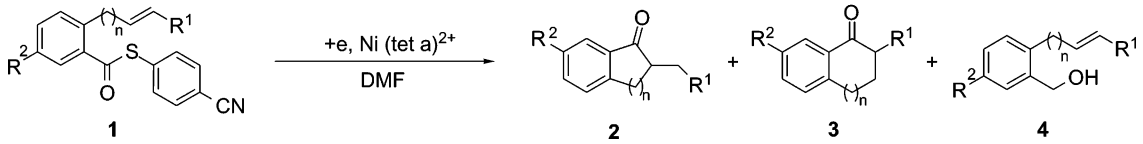


TABLE 1. Electroreductive Intramolecular Cyclization of *S*-(4-Cyano)phenyl Thiolester[a]



	substrate				product, yield (%)		
entry	**1**	R^1	R^2	*n*	**2**	**3**	**4**
1[b]	**1a**	H	H	1	**2a**, 22	**3a**, trace	**4a**, 42
2[c]	**1a**	H	H	1	4	trace	80
3	**1a**	H	H	1	8 (42)[d]	2	0
4[e]	**1a**	H	H	1	46	trace	11
5	**1b**	CH_3	H	1	**2b**, 40	**3b**,[f] trace	**4b**, 19
6	**1c**	CO2Et	H	1	**2c**, 59	0	0
7[e]	**1c**	CO_2Et	H	1	54[g]	0	0
8[e]	**1d**	H	OMe	1	**2d**, 63	**3d**,[f] trace	**4d**, 14
9[e]	**1e**	CO_2Et	H	2	**2e**, 44	0	0
10[e]	**1f**	H	H	2	**2f**, 41	0	**4f**, 6

[a] Electrolysis was conducted in DMF (20 mL) using a thiolester **1** (1 mmol), Ni(tet *a*)$^{2+}$ (0.2 mmol), and tetraethylammonium *p*-toluenesulfonate (2 mmol) at 60 °C. [b] Electrolysis at room temperature. [c] Electrolysis without Ni(tet *a*)$^{2+}$. [d] Obtained as dimer of **2a**. [e] Electrolysis with 2 equiv of Ph_2PH. [f] The existences of **3b** and **3d** are recognized by ^{1}H NMR of the mixture with **2b** and **2d**, respectively. [g] Accompanied with a byproduct (5%) derived from reduction of the acceptor double bond in **1c**.

vinyl radicals. Under the present reaction conditions, the acyl radicals **1′** were also shown to provide products resulting from 5-exo cyclization in much better yields than those from 6-endo cyclization. Electroreduction of **1a** without a catalyst Ni(*tet* a)$^{2+}$ afforded a benzyl alcohol **4a** in 80% yield and a trace amount of a cyclic ketone **2a**. Electrolysis in entry 3 shows that a large part of the cyclized radical was isolated as dimer **2a′**; i.e., the trapping rate of the cyclized radical **2r** (Scheme 1) by hydrogen from the solvent DMF could not be fast enough to prevent the coupling of the cyclized radical **2r** derived from **1a**. The formation of the dimer **2a′** was suppressed, and 2-methylindanone **2a** was provided in 46% yield on addition of 2 equiv of diphenylphosphine as a hydrogen donor (entry 4).[7d] As shown in entry 5, introduction of a methyl group at the terminal of the acceptor also suppressed the formation of the product from coupling of the corresponding radicals **2r**, however, it decreased yield of **2b** to 40% and increased the yield of the corresponding benzyl alcohol instead. These observations may suggest that the decreased yield of **2b** results from the decrease in the rate of cyclization of the corresponding acyl radical onto alkene. On the other hand, the introduction of an electron-withdrawing group $-CO_2Et$ facilitated the 5-exo cyclization of the acyl radical regardless of the presence or absence of diphenylphosphine. The results in entries 5−7 seem to be consistent with the explanation that acyl radicals exhibit nucleophilic character.[11] Electrolysis of a thiolester **1d** prepared with 3-methoxybenzoic acid provided a methylindanone **2d** most effectively, probably because the nucleophilic character of the acyl radical derived from **1d** is somewhat enhanced by the methoxy group. [11b] The thiolesters **1e** and **1f** afforded dihydro-1-naphthalenones **2e** and **2f**, respectively, via 6-exo cyclization in modest yield. 6-Exo cyclizations are slower

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than the related 5-exo cyclizations, and the intramolecular allylic hydrogen transfer to give hydrogenated products of the initial radicals usually becomes a serious concern.[12] However, the results of entries 9 and 10 suggest that 6-exo cyclization of the aryl acyl radicals can compete with the intramolecular allylic hydrogen transfer even with a thiolester **1f** bearing unactivated alkene under the present reaction conditions.[1b,13] Definite explanations for the observations in entries 9 and 10 seem to be unobtainable until mechanistic behaviors of alk-6-enoyl radicals are fully investigated like the related alk-5-enoyl radicals.[11a,14] Under the present reaction conditions, the rate of competitive decarbonylation of aryl acyl radicals **1′** could be presumed to be significantly smaller than those for 5-exo and 6-exo cyclizations of the corresponding acyl radicals **1′** onto alkene acceptors judging from the observation that the products derived from the decarbonylation of acyl radical **1′** were not detected.[14]

In summary, modification of the structure of radical precursors, *S*-phenylthiolesters, was found to allow aryl acyl radicals which are generated by nickel complex catalyzed electroreductive methods to undergo 5- and 6-exo cyclization reactions similarly to alkyl acyl radicals.[8] This organotin-free methodology could be a useful alternative to other methods available to conduct reactions of acyl radicals due to the merits that reactions could be driven by the use of stable starting materials and harmless reagents with no need for desiccation of the solvent.

Experimental Section

General Methods. ^{1}H and ^{13}C NMR spectra were recorded as $CDCl_3$ solutions at 300 and 75 MHz, respectively, using TMS as internal reference. The *J* values are given in hertz (Hz). Column chromatography was carried out on SiO_2 (silica gel 60, 0.063−0.2 mm). Melting points are uncorrected. Cyclic voltammetry was performed with a three-elecrode system employing a linear scanning unit (Huso Electronical System HECS 321B) equipped with a potentiostat (Hokuto Denko PS-55B). Constant current electrolysis was carried out with a potentio-galvanostat (Hokuto Denko HA105S), and the quantity of electricity was recorded with a coulometer (Hokuto Denko HF-201). All chemicals used were commercially available.

General Procedure for the Preparation of *S*-(4-Cyano)-phenyl Thiolesters 1. *S*-(4-Cyano)phenyl thiolesters were prepared by condensation reaction of 4-cyanobenzenethiol with the corresponding benzoic acids which were synthesized by one of the three different methods A, B, and C. 4-Cyanobenzenethiol was prepared from 4-cyanophenol according to the known method for synthesis of 2-(prop-2-enyl)benzenethiol.[15]

Method A: 2-(Prop-2-enyl)benzoic Acid. To a solution of 4,4-dimethyl-2-phenyl-2-oxazoline (7.71 g, 44 mmol) in dry THF (130 mL) was added BuLi (37 mL of 1.6 M in hexane, 59 mmol) dropwise at 0 °C, and the mixture was stirred for 3.5 h. The solution was transferred to a suspension of cuprous bromide (6.24 g, 43.5 mmol) in dry THF using a cannula (2 mm in diameter) and nitrogen gas. The green mixture was stirred at 0 °C for 1.5 h, and then allyl bromide (4.84 g, 40 mmol) was added and stirred overnight. To the mixture was added 45 mL of water followed by 28% NH_3 in water. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. Purification of the crude product by column chromatography provided 4,4-dimethyl-2-[2(prop-2-enyl)]phenyl-2-oxazoline (5.47 g, 58%) as an oil. The oxazoline was converted to the methiodide salt by stirring in excess MeI and DMSO overnight at room temperature, and the volatiles were evaporated under reduced pressure. The crude oxazoline methiodide was added to 80 mL of 2 N NaOH and the mixture heated under reflux for 8 h. The solution was washed with CH_2Cl_2 (35 mL × 2), acidified to pH 1−2 with 10 N HCl, and extracted with CH_2Cl_2 (40 mL × 2). The extracts were washed with brine, dried ($MgSO_4$), and concentrated to leave 2-(prop-2-enyl)benzoic acid as a yellow oil (2.54 g, 62%).

Method B: 5-Methoxy-2-(prop-2-enyl)benzoic Acid. To a solution of 2-bromo-5-methoxybenzoic acid (2.9 g, 12.6 mmol) in MeOH (10 mL) was added 1.5 mL of concentrated H_2SO_4 dropwise at 0 °C, and the mixture was heated for 3 h. The mixture was transferred into ice-cold water (25 mL), extracted with AcOEt, washed successively with water (15 mL × 2), 5% $NaHCO_3$ (25 mL × 2), and 10 mL of brine, dried, and concentrated under reduced pressure. Purification of the crude product by column chromatography afforded methyl 2-bromo-5-methoxybenzoate (3.06 g, 99%). Methyl 2-bromo-5-methoxybenzoate (3.06 g, 12.5 mmol), allyltributyltin (4.55 g, 13.75 mmol), and $Pd(PPh_3)_4$ (0.144 g, 0.125 mmol) were added to 10 mL of benzene in a sealed tube and the mixture heated at 120 °C for 20 h. The mixture was transferred into 10 mL of water and extracted with benzene. The extract was washed with water and dried. The crude product obtained after concentration of the solution was purified by column chromatography to provide methyl 5-methoxy-2-(prop-2-enyl)benzoate (1.25 g, 57%) as a yellow oil. The methyl benzoate (1.25 g, 6.1 mmol) was refluxed with 6 mL of EtOH and 6 mL of 10% aqueous NaOH for 1 h. To the mixture was added 10 mL of water, and the mixture washed with CH_2Cl_2 (15 mL × 2) and extracted with AcOEt (30 mL × 3) after the pH was adjusted to pH 1−2 with 10 N HCl. The organic layer was dried and concentrated under reduced pressure to provide 5-methoxy-2-(prop-2-enyl)benzoic acid (0.92 g, 79%) as a yellow oil.

Method C: 2-(Ethylbut-2-enoyl)benzoic Acid. This benzoic acid and the related benzoic acid 2-(ethyl pent-2-enoyl)-benzoic acid were prepared according to the literature method.[1b]

Condensation of 4-Cyanobenzenethiol with 2-(Prop-2-enyl)benzoic Acid To Provide *S*-(4-Cyano)phenyl 2-(Prop-2-enyl)benzenethioate (1a). Diethyl cyanophosphonate (1.47 g, 9 mmol) was added dropwise to the 2-(prop-2-enyl)benzoic acid in DMF dry (15 mL) at 0 °C and the mixture stirred for 30 min. To the mixture were succesively added dropwise 4-cyanobenzenethiol in 4 mL of DMF and Et_3N (0.90 g, 8.9 mmol) and the mixture stirred for 2 h at 0 °C. The mixture was transferred to 150 mL of benzene and washed successively with 60 mL of 5% citric acid, saturated $NaHCO_3$, and brine. The crude product obtained after concentration of the solvent was purified by recrystallization from AcOEt−hexane to afford *S*-(4-cyano)-phenyl 2-(prop-2-enyl)benzenethioate **1a** (0.95 g, 39%) as a white solid: mp 87−91 °C; ^{1}H NMR δ 3.60 (2H, d, J = 6.4), 4.98 (1H, dd, J = 1.6, 16.8), 5.05 (1H, dd, J = 1.4, 10.0), 5.90−5.99 (1H, m), 7.29−7.38 (2H, m), 7.51 (1H, td, J = 1.1, 7.5), 7.63 (2H, d, J = 8.4), 7.73 (2H, d, J = 8.4), 7.89 (1H, d, J = 7.7); ^{13}C NMR δ 37.5, 113.0, 116.1, 126.4, 126.5, 128.6, 131.2, 132.5, 132.6, 132.7, 134.6, 139.2, 190.2; IR (Nujol) ν_{max} 767, 915, 1004, 1205, 1220, 1635 (C═C), 1680 (SC═O), 2230 (CN) cm^{-1}; FABMS *m/e* 280 (M^+ + H); FABHRMS *m/e* 280.0777 ($C_{14}H_{17}NOS$ requires 280.0796). Characterization based on the analytical and spectral data of the benzoic acids prepared by one of the three different methods A, B, and C and thiolesters **1b**−**f** are given in the Supporting Information.

Procedure for the Electroreduction of the Thiolesters 1. The electroreduction was performed in DMF (10 or 20 mL) using 0.5 or 1.0 mmol of a thiolester **1**, 0.1 or 0.2 mmol of Ni(*tet* a)$(ClO_4)_2$, 1 or 2 mmol of tetraethylammonium tosylate (TEATs) as a supporting electrolyte, a graphite plate as a cathode, and an aluminum rod as an anode in an undivided cell at 60 °C under an atmosphere of nitrogen. A constant current (3 mA) was

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passed until the substrate was consumed (determined by TLC). The electricity passed was 3 F/mol of the substrate **1**. The solution from the electrolysis was transferred to a brine solution (100 mL) and extracted with ether (40 mL × 3). The crude product obtained after concentration under vacuum was purified by silica gel column chromatography. Yields of products are given in Table 1; their characterization data based on the analytical and spectral data are given below.

2,3-Dihydro-2-methyl-1*H*-inden-1-one (2a): colorless oil; ^{1}H NMR δ 1.21 (3H, d, J = 7.1), 2.57−2.62 (1H, m), 2.63−2.67 (1H, m), 3.25−3.34 (1H, m), 7.23−7.30 (1H, m), 7.33−7.36 (1H, m), 7.44−7.50 (1H, m), 7.63−7.67 (1H, m); ^{13}C NMR δ 16.2, 34.9, 41.9, 123.9, 126.4, 127.3, 134.6, 136.3, 153.4, 209.4; IR (neat) ν max 765, 1203, 1274, 1464, 1611, 1710 (C═O), 2950 (CH_3) cm^{-1}; EIMS *m/e* 146 (M^+), 131 ($M^+ - CH_3$); EIHRMS *m/e* 146.0744 ($C_{10}H_{10}O$ requires 146.0732).

1,2-Di(1-indanoyl)ethane (2a′): colorless oil; ^{1}H NMR δ 2.95−3.01 (4H, m, CH_2CH_2), 3.04−3.05 (1H × 2, m), 3.36−3.44 (1H × 2, dd, J = 6.8, 16.7), 3.68 (1H × 2, d, J = 9.1), 7.35−7.42 (3H, m), 7.44−7.47 (1H, m), 7.51−7.57 (2H, m), 7.58−7.63 (1H, m), 7.73−7.75 (1H, m); ^{13}C NMR δ 32.4, 33.7, 46.2, 124.1, 126.5, 127.3, 127.7, 132.3, 135.2, 205.5; EIMS *m/e* 290 (M^+), 145 ($^1/_2$ M^+).

2,3-Dihydro-2-ethyl-1*H*-inden-1-one (2b): colorless oil; ^{1}H NMR δ 1.02 (3H, t, J = 7.4), 1.23−1.34 (1H, m), 1.94−2.02 (1H, m), 2.58−2.66 (1H, m), 2.83 (1H, dd, J = 3.8, 17.1), 3.32 (1H, dd, J = 8.1, 17.1), 7.36 (1H, td, J = 0.7, 7.3), 7.46 (1H, dt, J = 0.9, 8.6), 7.58 (1H, td, J = 1.2, 7.4), 7.75 (1H, d, J = 7.5); EIMS *m/e* 160 (M^+), 145 ($M^+ - CH_3$), 132, 131 ($M^+ - C_2H_5$); EIHRMS *m/e* 160.0918 ($C_{11}H_{12}O$ requires 160.0888).

Ethyl 2-[2-(2,3-dihydro-1-oxo-1*H*-indenyl)]acetate (2c): white solid; mp 40−41 °C; ^{1}H NMR δ 1.21 (3H, t, J = 7.1), 2.58−2.67 (1H, m), 2.85−3.06 (3H, m), 3.46 (1H, dd, J = 7.8, 16.9), 4.14 (2H, q, J = 7.1), 7.38 (1H, t, J = 7.4), 7.46 (1H, d, J = 7.7), 7.56−7.62 (1H, m), 7.77 (1H, d, J = 7.7); ^{13}C NMR δ 14.0, 32.8, 35.1, 43.4, 60.6, 123.8, 126.4, 127.3, 134.7, 136.2, 153.2, 171.8, 206.7; IR (Nujol) ν_{max} 770, 1183, 1228, 1410, 1607, 1710 (ketone C═O), 1725 (ester C═O) cm^{-1}; EIMS *m/e* 218 (M^+), 172, 145 ($M^+ - CO_2Et$); EIHRMS *m/e* 218.0954 ($C_{13}H_{14}O$ requires 218.0943).

2,3-Dihydro-6-methoxy-2-methyl-1*H*-inden-1-one (2d): colorless oil; ^{1}H NMR δ 1.31 (3H, J = 7.3), 2.61−2.68 (1H, m,), 2.70−2.77 (1H, m), 3.32 (1H, dd, J = 7.3, 16.2), 3.83 (3H, s), 7.16−7.19 (2H, m), 7.32−7.35 (1H, m); ^{13}C NMR δ 16.3, 34.2, 42.7, 55.5, 105.1, 124.0, 127.1, 137.4, 146.2, 159.3, 209.4; IR (neat) ν_{max} 1027, 1245, 1280, 1490, 1617, 1710 (C═O), 2930, 2960 cm^{-1}; FABMS *m/e* 177 ($M^+ + H$), 149 ($M^+ + H - CO$); FABHRMS *m/e* 177.0919 ($C_{11}H_{12}O_2$ requires 177.0916).

Ethyl 2-[2-(1,2,3,4-tetrahydro-1-oxonaphthalenyl)]acetate (2e): white solid; mp 53−55 °C; ^{1}H NMR δ 1.28 (3H, t, J = 7.1), 1.98 (1H, ddd, J = 4.5, 12.9, 25.5), 2.20−2.29 (1H, m), 2.38−2.51 (1H, m), 2.93−3.19 (4H, m), 4.19 (2H, q, J = 7.1), 7.23 (1H, d, J = 7.5), 7.30 (1H, t, J = 7.5), 7.47 (1H, td, J = 1.4, 7.3), 8.03 (1H, dd, J = 1.2, 7.8); ^{13}C NMR δ 14.1, 29.1, 35.0, 44.6, 53.3, 60.4, 126.5, 127.3, 128.6, 132.4, 133.2, 143.9, 172.4, 198.3; IR (Nujol) ν_{max} 760, 900, 1176, 1200, 1290, 1320, 1600, 1674 (ketone C═O), 1730 (ester C═O) cm^{-1}; EIMS *m/e* 232 (M^+), 144 ($M^+ - CH_3CO_2Et$); EIHRMS *m/e* 232.1107 ($C_{14}H_{16}O$ requires 232.1099).

3,4-Dihydro-2-methyl-1(2*H*)-naphthalenone (2f): colorless oil; ^{1}H NMR δ 1.27 (3H, d, J = 6.7), 1.89 (1H, ddd, J = 5.1, 12.9, 24.9), 2.20 (1H, dq, J = 4.4, 13.2), 2.53−2.75 (1H, m,), 2.94−3.11 (2H, m,), 7.23 (1H, d, J = 7.7), 7.30 (1H, t, J = 7.5), 7.47 (1H, td, J = 1.4, 7.3), 8.03 (1H, dd, J = 1.2); ^{13}C NMR δ 15.3, 28.7, 31.2, 42.5, 126.4, 127.2, 128.6, 132.3, 132.9, 144.0, 200.6; IR (Nujol) ν_{max} 740, 968, 1230, 1456, 1600, 1683 (ketone C═O), 2930 cm^{-1}; EIMS *m/e* 160 (M^+), 145 ($M^+ - CH_3$), 118 ($M^+ - C_3H_6$); EIHRMS *m/e* 160.0913 ($C_{11}H_{12}O$ requires 160.0888).

3,4-Dihydro-1(2*H*)-naphthalenone (3a): colorless oil; ^{1}H NMR δ 2.05−2.11 (2H, m), 2.57−2.61 (2H, m), 2.88−2.95 (2H, m), 7.19−7.39 (2H,m), 7.50 (1H, t, J = 7.5), 7.96 (1H, d, J = 7.5).

2-(But-2-enyl)benzyl alcohol (4a): colorless oil; ^{1}H NMR δ 3.39 (2H, d, J = 6.2), 4.63 (2H, s), 4.91 (1H, dd, J = 1.2, 16.7), 4.98 (1H, dd, J = 1.2, 10.0), 5.90−5.93 (1H, m), 7.12−7.21 (4H, m).

5-Methoxy-2-(prop-2-enyl)benzyl alcohol (4d): yellow oil; ^{1}H NMR δ 1.58 (1H, t, J = 6.0), 3.39 (2H, d, J = 6.0), 3.80 (3H, s), 4.67 (2H, d, J = 5.8), 4.93−5.07 (2H, m), 5.91−6.04 (1H, m), 6.79 (1H, dd, J = 2.7, 8.2), 6.98 (1H, d, J = 2.5), 7.10 (1H, d, J = 8.4,); ^{13}C NMR δ 36.0, 55.2, 63.0, 113.1, 113.5, 115.5, 129.4, 130.9, 137.8, 140.0, 158.3; IR (neat) ν_{max} 920, 1038, 1160, 1193, 1260, 1498, 1576, 1610, 1637, 2940 cm^{-1}; EIMS *m/e* 178 (M^+); EIHRMS *m/e* 178.1000 ($C_{11}H_{14}O_2$ requires 178.0994).

2-(But-3-enyl)benzyl alcohol (4f): colorless oil; ^{1}H NMR δ 1.26 (1H, t, J = 7.1), 2.22 (2H, q, J = 7.7), 2.79 (2H, t, J = 7.9), 4.73 (2H, d, J = 4.5), 4.97−5.09 (2H, m), 5.81−5.92 (1H, m), 7.25−7.35 (2H, m), 7.37−7.39 (1H, m), 7.48−7.53 (1H, m); EIMS *m/e* 162 (M^+); EIHRMS *m/e* 162.1056 ($C_{11}H_{14}O$ requires 162.1045).

Ethyl 4-[2-[(4-cyanophenyl)thiocarbonyl]phenyl]-butanoate (1cH): white solid; mp 76−79 °C; ^{1}H NMR δ 1.23 (3H, t, J = 7.1), 1.92 (2H, q, J = 7.5), 2.32 (2H, t, J = 7.5), 2.84 (2H, t, J = 7.7), 4.10 (2H, q, J = 7.1), 7.30−7.37 (1H, m), 7.47−7.61 (2H, m), 7.65 (2H, d, J = 8.0), 7.75 (2H, d, J = 8.0), 7.90 (1H, d, J = 7.7); IR (Nujol) ν_{max} 907, 1200, 1263, 1638, 1657, 1683 (SC═O), 1730 (OC═O), 2225 (CN) cm^{-1}; FABMS *m/e* 354 (M^++H), 219 ($M^+ - SAr$); FABHRMS *m/e* 354.1167 ($C_{20}H_{20}NO_3S$ requires 354.1164).

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Supporting Information Available: Characterization data (^{1}H NMR, ^{13}C NMR, MS) for thiolesters **1b**−**f** and three benzoic acids. Copies of ^{1}H and ^{13}C NMR spectra for compounds **1a**−**f**, **2a**−**f**, and ^{1}H NMR spectra of **4a**,**b**,**f** and **1cH**. This material is available free of charge via the Internet at http://pubs.acs.org.

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