N-Thioaroylmorpholines in Silica Gel–Water: An Efficient System to Access Functionalized Allylic Thioesters from Baylis–Hillman Bromides

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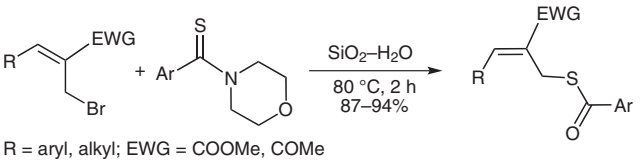
Abstract: A facile, one-pot synthesis of allylic thioesters starting from Baylis–Hillman (BH) bromides and *N*-thioaroylmorpholines is described. The synthesis is performed in a silica gel–water system without any additional catalyst or co-catalyst. The reaction pathway involves selective S-alkylation of *N*-thioaroylmorpholines via nucleophilic displacement (S_N2) with BH bromides, followed by hydrolysis to afford the corresponding thioesters. The present synthetic protocol avoids the application of malodorous sulfur compounds of limited accessibility such as thiols, and thioacids and their salts as reactants.

Key words: Baylis–Hillman adducts, aqueous medium, allylic thioesters, nucleophilic displacement, green chemistry, regioselectivity

The development of new synthetic methodologies has had to undergo a paradigmatic shift due to increasingly tight restrictions on the release of waste and toxic emissions, in order to control environmental pollution. Thus, besides the usual requisites of mildness and selectivity, the issue of environmentally friendly reaction conditions has become increasingly important in the design of alternate synthetic routes for fine chemicals. In this context, the use of micelles, microemulsions, surfactants, and other microheterogeneous liquids as media for organic reactions in water has gained considerable interest among synthetic chemists. Silica gel is easily available, low cost, nontoxic, and is of general use for chromatographic separation of organic compounds. It plays an important role as a heterogeneous catalyst in organic synthesis[1] and can be viewed as being analogous to microheterogeneous liquids. Thus, the combination of silica gel and water, originally established by Minakata and Komatsu,[2] constitutes a powerful organic reaction media that offers several advantages, such as easy isolation of crude products, potential reuse of the silica gel, and minimization of waste production.

The synthesis of organosulfur compounds, essentially routes involving the carbon–sulfur bond formation, has attracted much attention due to their occurrence in many molecules that are of biological, pharmaceutical, and material interest.[3,4] Thioesters are protected thiols and represent a unique class of organosulfur compounds with widespread application in drug discovery,[5] industry,[6] and as key intermediates in various synthetic organic transformations; such compounds have distinct chemical properties compared to their oxo-analogues.[7–9] Unsaturated thoiesters are well-known as interesting synthetic building blocks, and their utilization in asymmetric cycloaddition, in peptide synthesis, and in natural product synthesis are well-documented.[10,11] Moreover, allylic thioesters serve as useful starting materials for the synthesis of allylic sulfides and their S-derivatized products, owing to the ease of hydrolysis of the former to the corresponding allylic thiols followed by facile alkylation, arylation, or heteroarylation.[12]

Most preparations of thioesters employ either activated acyl derivatives, such as acyl halides or anhydrides, with thiols in the presence of a base, or the reaction of thioacids and their salts with electrophilic reagents such as alkyl halides or Michael acceptors.[13] Recently, some elegant approaches have been introduced to access thioesters that avoids the application of unpleasant and noxious compounds of limited accessibility such as thiols, thioacids and their salts, as reactants.[14] However, malodorous sulfur compound free methodologies with which to access allylic thioesters has been rarely reported until now.[14b] Thus, given the importance of allylic sulfur compounds,[15] it is highly desirable to develop an environmentally benign protocol that provides efficient access to such a highly useful family of organosulfur compounds. Herein, Baylis–Hillman (BH) chemistry has been applied to accomplish this goal (Scheme 1).



R = aryl, alkyl; EWG = COOMe, COMe

Scheme 1 One-pot synthesis of allylic thioesters using BH chemistry

Among the leading 'name' reactions in organic synthesis, the BH reaction[16] has become a popular atom-economical carbon–carbon bond-forming reaction that yields functionalized allylic alcohols. Multifunctional allylic alcohols (BH adducts) could be readily transformed into suitable leaving groups, such as acetate or bromide (commonly known as BH acetate or BH bromide), through acetylation and bromination, respectively. The BH acetates and bromides have been used as nucleophilic acceptors in many useful organic transformations, leading to the

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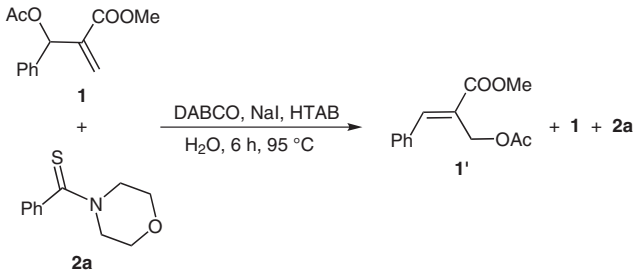
synthesis of trisubstituted alkenes and to a range of multifunctional molecules en route to heterocycles through a nucleophilic displacement (S_N2 or S_N2') with various C-, N-, and O-centered nucleophiles.[17] However, their exploitation for generating sulfur-containing products with S-centered nucleophiles has been limited and includes only arenesulfinates,[18] thiolates,[19] thiocyanate anions,[20] and thiol acetic acid.[21] Recently, we have reported a one-pot, stereoselective synthesis of allyl dithiocarbamates involving nucleophilic displacement (S_N2') of BH acetates by dithiocarbamate anions in water.[22d]

In a continuation of our recent interest in synthetic applications of BH adducts,[22] we report herein a regioselective, one-pot synthesis of hitherto unknown functionalized *Z*-allylic thioesters from BH bromides using *N*-thioaroylmorpholines in a silica gel–water system without any additional catalyst or co-catalyst (Scheme 1). We initiated our experiment with BH acetate **1** as an electrophilic substrate, which is known to undergo nucleophilic displacement (S_N2') with S-centered nucleophiles.[18–21,22d] However, we could not obtain any product from the reaction of BH acetate **1** and *N*-thioaroylmorpholine **2a** under the reaction conditions reported for S-alkylation of *N*-thioaroylmorpholines with benzyl/alkyl halides[14c] (Scheme 2). Instead of an S-alkylated product, isomerized BH acetate **1′** was obtained in 20% yield, along with starting materials **1** and **2a**.

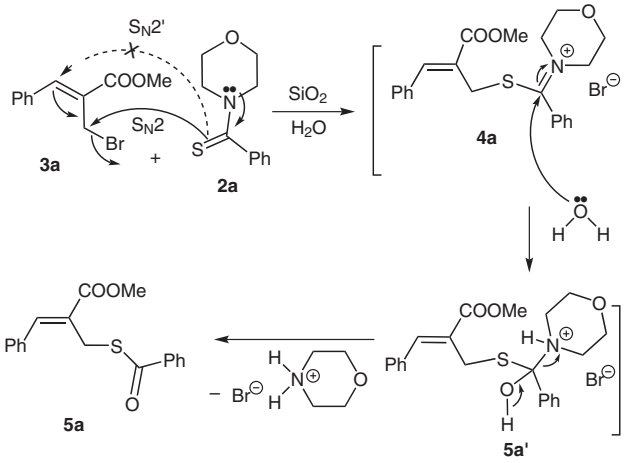


Scheme 2 Reaction of BH acetate **1** with *N*-thioaroylmorpholine **2a** in the presence of DABCO

This is consistent with the earlier observations that BH acetate **1** isomerizes in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO),[23] and that it fails to undergo a nucleophilic displacement reaction with potassium thiocyanate (KSCN).[24] Boeini and Kashan reported that the hydrolysis of thiouronium salt **4a** was catalyzed by DABCO.[14c] We proposed the hypothesis that thiouronium salt **4a** would be hydrolyzed even in the absence of DABCO and, indeed, this was found to be the case (Scheme 3).

The above points led us to develop a new, environmentally benign system that would be a more economical and viable approach that is able to facilitate S-alkylation of *N*-thioaroylmorpholines with BH acetate **1**. In this regard, we chose to use a silica gel–water system to access the target allylic thioester **5a** by treating BH acetate **1** with *N*-thioaroylmorpholine **2a**, in the absence of any additional catalyst or co-catalyst, at 80 °C. Unfortunately, no reaction took place even after prolonged stirring at 80–95 °C.

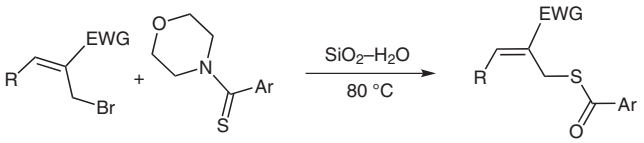
We then turned our attention towards activated allylic halides known as BH bromides **3**, which are distinct from benzyl halides both in structure and reactivity. The BH bromides **3** are more prone to nucleophilic displacement (S_N2 and S_N2') than the corresponding acetates **1** and these were thus chosen as electrophilic substrates for the present study. At the outset, it was unclear whether S-alkylation of *N*-thioaroylmorpholines **2** with BH bromides **3** would be effective in a silica gel–water system and whether it would follow the S_N2 or S_N2' pathway.



Scheme 3 One-pot synthesis of allylic thioesters **5a** in a silica gel–water system

Gratifyingly, we observed rapid S-alkylation of *N*-thioaroylmorpholine **2a** through only S_N2 type nucleophilic displacement with BH bromide **3a** in the silica gel–water system. Thus, on stirring **2a** (1 mmol) and **3a** (1 mmol) in the silica gel–water system at 80 °C for two hours, the corresponding allylic thioester **5a** (94% isolated yield) was obtained in the absence of any additional catalyst or co-catalyst (Scheme 3). The temperature appears crucial, because the reaction did not take place appreciably even after stirring for 20 hours at room temperature. The effectiveness of the reaction in the absence of silica gel was also investigated; under these conditions, the reaction proceeded sluggishly to give a poor yield (30%) of allylic thioester **5a** after stirring the reaction mixture for three hours at 95 °C. Thus, the use of silica gel in water facilitates the reaction, presumably by enlargement of the surface area available for reaction compared with that of the interface in a conventional liquid–liquid biphasic system. This is because the organic substrate is adsorbed onto the silica through hydrophobic interactions between the surface of the silica and the organic molecule.[2] Encouraged by this result, various other BH bromides **3** were treated with a variety of *N*-thioaroyl morpholines **2** following the same protocol. Table 1 summarizes our results, which demonstrate the generality of the method by the successful synthesis of variously functionalized allylic thioesters **5** in good to excellent yields (87–94%) with high regioselectivity.

Table 1 Synthesis of Functionalized Allylic Thioesters **5**[a]



(*Z*)-**3** **2** (*Z*)-**5**

Compound	R	Ar	EWG	Yield (%)[b,c]
5a	Ph	Ph	CO_2Me	94
5b	Ph	2-naphthyl	CO_2Me	89
5c	Ph	4-ClC_6H_4	CO_2Me	92
5d	2-ClC_6H_4	4-MeC_6H_4	CO_2Me	90
5e	Ph	4-biphenyl	CO_2Me	93
5f	4-$MeOC_6H_4$	Ph	CO_2Me	94
5g	4-$O_2NC_6H_4$	Ph	CO_2Me	87
5h	Ph	Ph	COMe	91
5i	4-ClC_6H_4	4-ClC_6H_4	COMe	89
5j	4-MeC_6H_4	4-MeC_6H_4	COMe	90
5k	2-$MeOC_6H_4$	Ph	COMe	94
5l	4-*i*-PrC_6H_4	Ph	COMe	88
5m	*n*-Pr	2-naphthyl	COMe	90
5n	*n*-Hept	Ph	COMe	92

[a] Reaction conditions: BH bromide **3** (1 mmol), *N*-thioaroylmorpholine **2** (1 mmol), silica gel–water (1 g in 5 mL) at 80 °C for 2 h. For experimental procedure, see experimental section.
[b] Pure product after column chromatography.
[c] All compounds gave C, H and N analysis within ±0.35% and satisfactory spectral (IR, ^{1}H NMR, ^{13}C NMR and EIMS) data.

In summary, we have described an expedient, green synthetic protocol for the synthesis of densely functionalized *Z*-allylic thioesters via selective S-alkylation of *N*-thioaroylmorpholines with BH bromides, followed by hydrolysis in a silica gel–water system. The present methodology avoids the need to handle unpleasant and noxious thiols as well as corrosive acid chlorides. The approach requires no added catalyst or co-catalyst, and needs only the use of distilled water in combination with easily available, inexpensive, and nontoxic silica gel. The method offers several advantages, such as the ease of crude product separation, potential catalyst reuse (SiO_2), and minimization of waste production.

All starting materials, unless otherwise stated, were purchased as reagent grade and used without further purification. The requisite *N*-thioaroylmorpholines **2**, BH bromides **3**, and BH acetate **1** were prepared by a known method.[25] Dry silica gel (Merck 60–100 mesh) was used in the reaction. Column chromatography was carried out over silica gel (Merck 100–200 mesh) and TLC was performed using silica gel GF254 (Merck) plates. Melting points were determined by the open glass capillary method and are uncorrected. IR spectra were recorded with a Perkin–Elmer 993 IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AVII 400 spectrometer in $CDCl_3$ using TMS as internal reference. Mass (EI) spectra were recorded with a JEOL D-300 mass spectrometer. Elemental analyses were performed with a Carlo Erba 1108 microanalyzer or Elementar's Vario EL III microanalyzer.

Synthesis of Allylic Thioesters 5; General Procedure

A mixture of *N*-thioaroylmorpholine **2** (1 mmol), BH bromide **3** (1 mmol), and silica gel 60–100 mesh (1 g) in H_2O (5 mL) was stirred at 80 °C for 2 h. After completion of the reaction (as indicated by TLC), the reaction mixture was cooled to r.t. and filtered through Celite. The filter cake was washed with EtOAc (3 × 5 mL) and the organic phase was retained. The aqueous phase was extracted with EtOAc (2 × 5 mL), and the combined organic extracts were dried over $MgSO_4$, filtered, and evaporated to afford the crude allylic thioester **5**, which was purified by silica gel column chromatography (hexane–EtOAc, 8:2) to give the desired pure allylic thioester **5**.

(*Z*)-Methyl 2-(Benzoylthiomethyl)-3-phenylacrylate (5a)

IR (neat): 1711, 1668, 1628, 1578, 1422, 1240, 1030, 760, 692 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.85 (s, 3 H, OCH_3), 4.26 (s, 2 H, CH_2S), 7.37–7.47 (m, 7 H, ArH), 7.58–7.60 (m, 1 H, ArH), 7.88 (s, 1 H, =CH), 7.97–8.00 (m, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.6, 52.2, 127.2, 128.4, 128.7, 129.1, 129.8, 130.2, 133.4, 134.9, 136.8, 141.4, 167.5, 191.9.

MS (EI): *m*/*z* = 312 [M]$^+$.

Anal. Calcd for $C_{18}H_{16}O_3S$: C, 69.21; H, 5.16. Found: C, 69.49; H, 5.04.

(*Z*)-Methyl 2-[(2-Naphthoylthio)methyl]-3-phenylacrylate (5b)

IR (KBr): 1709, 1664, 1621, 1582, 1418, 1398, 1246, 1028, 884, 815, 730, 690 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.82 (s, 3 H, OCH_3), 4.21 (s, 2 H, CH_2S), 7.35–7.43 (m, 5 H, ArH), 7.56–7.59 (m, 2 H, ArH), 7.86 (s, 1 H, =CH), 7.91 (t, *J* = 8.3 Hz, 2 H, ArH), 7.98 (d, *J* = 8.0 Hz, 1 H, ArH), 8.03 (dd, *J* = 8.6, 1.5 Hz, 1 H, ArH), 8.56 (s, 1 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.9, 52.1, 123.4, 125.8, 127.1, 128.0, 128.4, 128.7, 129.0, 129.3, 129.7, 130.0, 130.6, 132.3, 134.1, 134.7, 135.8, 141.1, 167.7, 191.2.

MS (EI): *m*/*z* = 362 [M]$^+$.

Anal. Calcd for $C_{22}H_{18}O_3S$: C, 72.90; H, 5.01. Found: C, 72.14; H, 5.23.

(*Z*)-Methyl 2-[(4-Chlorobenzoylthio)methyl]-3-phenylacrylate (5c)

IR (neat): 1713, 1670, 1630, 1578, 1426, 1240, 1028, 820, 764, 710 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.84 (s, 3 H, OCH_3), 4.28 (s, 2 H, CH_2S), 7.31–7.36 (m, 5 H, ArH), 7.41–7.46 (m, 2 H, ArH), 7.88 (s, 1 H, =CH), 7.95–7.98 (m, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.7, 52.2, 128.4, 128.8, 129.2, 129.8, 130.2, 134.3, 134.7, 133.1, 140.3, 141.2, 167.4, 189.6.

MS (EI): *m*/*z* = 346 [M]$^+$, 348 [M + 2]$^+$.

Anal. Calcd for $C_{18}H_{15}ClO_3S$: C, 62.33; H, 4.36. Found: C, 61.98; H, 4.39.

(*Z*)-Methyl 3-(4-Chlorophenyl)-2-[(4-methylbenzoylthio)methyl]acrylate (5d)

IR (KBr): 2968, 2922, 1710, 1662, 1621, 1580, 1428, 1237, 1094, 1028, 840 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.39 (s, 3 H, CH_3), 3.81 (s, 3 H, OCH_3), 4.26 (s, 2 H, CH_2S), 7.23 (d, *J* = 8.2 Hz, 2 H, ArH), 7.41 (d,

J = 8.0 Hz, 2 H, ArH), 7.54 (d, *J* = 8.0 Hz, 2 H, ArH), 7.88 (s, 1 H, =CH), 7.94 (d, *J* = 8.2 Hz, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6, 28.7, 53.4, 127.2, 128.7, 129.2, 129.6, 130.1, 133.2, 134.3, 135.1, 141.4, 144.3, 167.1, 191.2.

MS (EI): *m*/*z* = 360 $[M]^+$, 362 $[M + 2]^+$.

Anal. Calcd for $C_{19}H_{17}ClO_3S$: C, 63.24; H, 4.75. Found: C, 63.19; H, 4.81.

(*Z*)-Methyl 2-(Biphenylcarbonylthiomethyl)-3-phenylacrylate (5e)

IR (KBr): 1714, 1671, 1629, 1580, 1430, 1240, 1098, 1024, 824, 760, 710 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.81 (s, 3 H, OCH_3), 4.26 (s, 2 H, CH_2S), 7.31–7.43 (m, 6 H, ArH), 7.50 (d, *J* = 7.4 Hz, 2 H, ArH), 7.64 (d, *J* = 7.4 Hz, 2 H, ArH), 7.71 (d, *J* = 8.3 Hz, 2 H, ArH), 7.88 (s, 1 H, =CH), 8.05 (d, *J* = 8.3 Hz, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.7, 52.4, 127.3, 127.8, 128.2, 128.6, 128.8, 129.1, 129.4, 129.7, 130.0, 130.3, 134.8, 139.8, 141.1, 146.2, 167.8, 191.8.

MS (EI): *m*/*z* = 388 $[M]^+$.

Anal. Calcd for $C_{24}H_{20}O_3S$: C, 74.20; H, 5.19. Found: C, 74.29; H, 5.11.

(*Z*)-Methyl 2-(Benzoylthiomethyl)-3-(4-methoxyphenyl)acrylate (5f)

IR (neat): 1710, 1670, 1631, 1580, 1424, 1260, 1238, 1031, 831, 760, 714 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.82 (s, 3 H, OCH_3), 3.88 (s, 3 H, OCH_3), 4.30 (s, 2 H, CH_2S), 6.94 (d, *J* = 8.8 Hz, 2 H, ArH), 7.36 (d, *J* = 8.8 Hz, 2 H, ArH), 7.42–7.48 (m, 2 H, ArH), 7.56–7.59 (m, 1 H, ArH), 7.87 (s, 1 H, =CH), 7.97–8.01 (m, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.9, 52.1, 53.6, 114.1, 126.4, 127.6, 128.5, 129.0, 129.8, 130.4, 136.8, 141.6, 160.3, 167.9, 191.4.

MS (EI): *m*/*z* = 342 $[M]^+$.

Anal. Calcd for $C_{19}H_{18}O_4S$: C, 66.65; H, 5.30. Found: C, 66.80; H, 5.12.

(*Z*)-Methyl 2-(Benzoylthiomethyl)-3-(4-nitrophenyl)acrylate (5g)

IR (KBr): 1718, 1672, 1624, 1576, 1520, 1424, 1342, 1264, 1232, 1036, 830, 756, 712 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.86 (s, 3 H, OCH_3), 4.30 (s, 2 H, CH_2S), 7.41–7.46 (m, 2 H, ArH), 7.54–7.58 (m, 3 H, ArH), 7.91 (s, 1 H, =CH), 7.97–8.01 (m, 2 H, ArH), 8.20 (d, *J* = 8.7 Hz, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.9, 52.7, 124.0, 127.3, 128.2, 129.8, 130.8, 133.6, 136.8, 139.9, 141.7, 147.6, 165.6, 190.8.

MS (EI): *m*/*z* = 357 $[M]^+$.

Anal. Calcd for $C_{18}H_{15}NO_5S$: C, 60.49; H, 4.23; N, 3.92. Found: C, 60.30; H, 4.78; N, 3.81.

(*Z*)-*S*-2-Benzylidene-3-oxobutyl Benzothioate (5h)

IR (neat): 1676, 1666, 1625, 1580, 1424, 1240, 1032, 760, 680 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.50 (s, 3 H, CH_3CO), 4.20 (s, 2 H, CH_2S), 7.34–7.45 (m, 7 H, ArH), 7.56–7.59 (m, 1 H, ArH), 7.76 (s, 1 H, =CH), 7.95–7.99 (m, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.2, 30.2, 127.3, 128.1, 128.8, 129.4, 129.8, 133.6, 134.2, 135.2, 136.8, 140.6, 191.5, 197.1.

MS (EI): *m*/*z* = 296 $[M]^+$.

Anal. Calcd for $C_{18}H_{16}O_2S$: C, 72.94; H, 5.44. Found: C, 72.69; H, 5.29.

(*Z*)-*S*-2-(4-Chlorobenzylidene)-3-oxobutyl 4-Chlorobenzothioate (5i)

IR (KBr): 1678, 1664, 1628, 1590, 1420, 1242, 1094, 1036, 840 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.49 (s, 3 H, CH_3CO), 4.21 (s, 2 H, CH_2S), 7.32–7.46 (m, 6 H, ArH), 7.79 (s, 1 H, =CH), 7.95–7.98 (m, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.1, 30.2, 128.4, 128.8, 129.2, 130.9, 132.6, 135.1, 135.4, 135.8, 139.6, 140.8, 192.0, 197.3.

MS (EI): *m*/*z* = 364 $[M]^+$, 366 $[M + 2]^+$.

Anal. Calcd for $C_{18}H_{14}Cl_2O_2S$: C, 59.19; H, 3.86. Found: C, 59.41; H, 3.78.

(*Z*)-*S*-2-(4-Methylbenzylidene)-3-oxobutyl 4-Methylbenzothioate (5j)

IR (neat): 2964, 2928, 1674, 1668, 1620, 1578, 1424, 1246, 1032, 856 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.36 (s, 3 H, CH_3), 2.40 (s, 3 H, CH_3), 2.47 (s, 3 H, CH_3CO), 4.20 (s, 2 H, CH_2S), 7.23–7.26 (m, 4 H, ArH), 7.50–7.52 (d, *J* = 7.7 Hz, 2 H, ArH), 7.80 (s, 1 H, =CH), 7.92–7.94 (d, *J* = 8.2 Hz, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4, 21.6, 26.2, 30.4, 127.4, 129.2, 129.7, 129.9, 131.5, 134.1, 135.3, 140.2, 140.5, 144.2, 191.5, 196.7.

MS (EI): *m*/*z* = 324 $[M]^+$.

Anal. Calcd for $C_{20}H_{20}O_2S$: C, 74.04; H, 6.21. Found: C, 73.71; H, 6.14.

(*Z*)-*S*-2-(2-Methoxybenzylidene)-3-oxobutyl Benzothioate (5k)

IR (KBr): 1672, 1664, 1620, 1582, 1420, 1236, 1028, 930, 860, 760 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.51 (s, 3 H, CH_3CO), 3.88 (s, 3 H, OCH_3), 4.16 (s, 2 H, CH_2S), 6.94 (d, *J* = 8.3 Hz, 1 H, ArH), 7.06 (m, 1 H, ArH), 7.42–7.48 (m, 3 H, ArH), 7.59–7.61 (m, 1 H, ArH), 7.72 (d, *J* = 7.9 Hz, 1 H, ArH), 7.81 (s, 1 H, =CH), 7.94–7.98 (m, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.3, 30.1, 55.6, 110.7, 120.8, 123.3, 128.4, 128.8, 129.6, 131.4, 135.2, 135.6, 139.5, 140.4, 157.8, 191.4, 197.1.

MS (EI): *m*/*z* = 326 $[M]^+$.

Anal. Calcd for $C_{19}H_{18}O_3S$: C, 69.91; H, 5.56. Found: C, 70.09; H, 5.43.

(*Z*)-*S*-2-(4-Isopropylbenzylidene)-3-oxobutyl Benzothioate (5l)

IR (neat): 2960, 2927, 1672, 1669, 1626, 1576, 1430, 1248, 1040, 860, 730, 710 cm^{-1}.

H NMR (400 MHz, $CDCl_3$): δ = 1.30 (d, *J* = 7.0 Hz, 6 H), 2.48 (s, 3 H, CH_3CO), 2.97 (sept, *J* = 7.0 Hz, 1 H), 4.16 (s, 2 H, CH_2S), 7.35–7.48 (m, 4 H, ArH), 7.54–7.59 (m, 3 H, ArH), 7.78 (s, 1 H, =CH), 7.96–8.00 (m, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.7, 26.2, 30.1, 34.0, 127.2, 128.3, 128.8, 130.0, 131.6, 135.1, 135.4, 139.5, 140.6, 151.2, 191.8, 197.1.

MS (EI): *m*/*z* = 338 $[M]^+$.

Anal. Calcd for $C_{21}H_{22}O_2S$: C, 74.52; H, 6.55. Found: C, 74.79; H, 6.49.

(*Z*)-*S*-2-Acetylhex-2-enyl Naphthalene-2-carbothioate (5m)
IR (KBr): 2973, 2928, 2854, 1686, 1664, 1621, 1588, 1416, 1242, 1032, 890, 820, 760, 714 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.98 (t, *J* = 7.5 Hz, 3 H), 1.52 (m, 2 H), 2.24–2.40 (m, 5 H), 3.89 (s, 2 H, CH_2S), 6.89 (t, *J* = 7.6 Hz, 1 H, =CH), 7.53–7.56 (m, 2 H, ArH), 7.89 (t, *J* = 8.3 Hz, 2 H, ArH), 7.96 (d, *J* = 8.0 Hz, 1 H, ArH), 8.01 (dd, *J* = 8.6, 1.5 Hz, 1 H, ArH), 8.54 (s, 1 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 22.6, 25.7, 30.6, 31.3, 123.2, 125.9, 127.1, 128.6, 128.9, 129.2, 129.6, 132.4, 134.1, 135.4, 135.8, 146.2, 191.4, 196.9.

MS (EI): *m*/*z* = 312 $[M]^+$.

Anal. Calcd for $C_{19}H_{20}O_2S$: 73.04; H, 6.45. Found: 72.88; H, 6.71.

(*Z*)-*S*-2-Acetyldec-2-enyl Benzothioate (5n)
IR (neat): 2980, 2926, 2852, 1686, 1669, 1626, 1590, 1420, 1240, 1034, 760, 714 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.83 (t, *J* = 6.8 Hz, 3 H), 1.19–1.51 (m, 10 H), 2.21–2.39 (m, 5 H), 3.91 (s, 2 H, CH_2S), 6.87 (t, *J* = 7.5 Hz, 1 H, =CH), 7.26–7.35 (m, 2 H, ArH), 7.54–7.58 (m, 1 H, ArH), 7.99–8.02 (m, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 22.5, 25.4, 28.6, 28.9, 29.2, 29.4, 30.8, 31.6, 127.1, 128.6, 132.4, 135.6, 136.8, 146.6, 191.1, 196.7.

MS (EI): *m*/*z* = 318 $[M]^+$.

Anal. Calcd for $C_{19}H_{26}O_2S$: C, 71.66; H, 8.23. Found: C, 71.41; H, 8.36.

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