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ARTICLE

One-Pot Synthesis of Thioesters with Sodium Thiosulfate as Sulfur Surrogate under Transition Metal-Free Conditions

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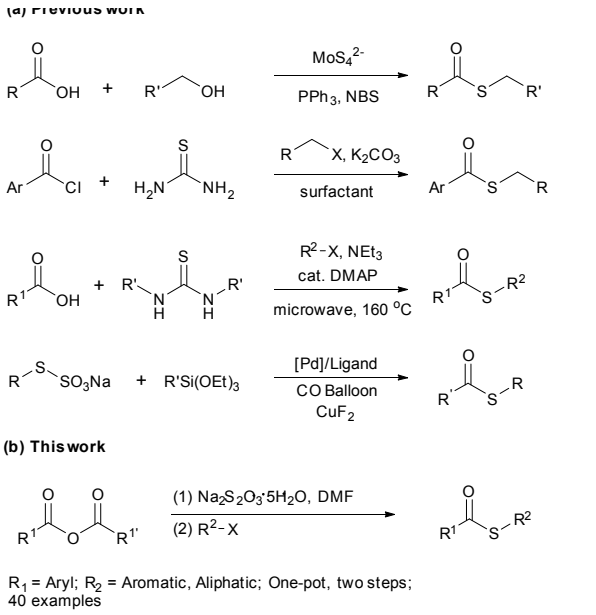
In this paper, we report an efficient synthetic method for thioester formation from sodium thiosulfate pentahydrate, organic halides, and aryl anhydrides. In the one-pot two-step reactions developed in this study, sodium thiosulfate was used as the sulfur surrogate for acylation with anhydrides, followed by substitution with organic halides through the *in situ* generation of thioaroylate. Furthermore, two important organic compounds could be successfully synthesized using our developed method. The advantages of the one-pot two-step reactions are operational simplicity, structurally diverse products with 42%–90% yields, use of relatively low toxic and odourless reagents, and easy applicability to large-scale operation.

Introduction

Carbon–sulfur bond formation is valuable in organic chemistry,[1] and these bonds have received much attention due to their wide application in natural products,[2] materials,[3] and chemical biology.[4] Hence, developing mild and new synthetic methods for carbon–sulfur bond formation is still highly desirable. Moreover, thioesters are one of the carbon–sulfur bond derivatives and are useful and important building blocks due to their acyl transfer ability in organic synthesis[5] and chemical biology.[6] Conventional synthetic methods for thioesters involve the substitution of thiol groups with acid chloride or acid anhydride in the presence of strong bases, such as triethylamine, pyridine, and 4-dimethylaminopyridine,[7] or the condensation of thiol groups with carboxylic acid in the presence of an activating agent, such as diethyl phosphorochloridate or dicyclohexylcarbodiimide.[8] More recently, numerous synthetic methods have been developed for thioesters in organic synthesis, including the use of *N*-acylbenzotriazoles as mild *S*-acylating agents;[9] the substitution of alkyl halides with thiocarboxylic acid;[10] metal-catalyzed thiocarbonylations with carbon monoxide;[11] new activating agents for condensation reactions of carboxylic acids with thiols, such as azopyridines, chlorodiphenylphosphine/iodine/imidazole, and trifluoroacetic acid;[12] oxidative coupling of thioesterification between aldehydes and thiols;[13] thioester formation by the functionalization of the C(sp^3)-H bond;[14] and other synthetic methods [(triflates, cesium fluoride, zeolites, zinc, *N*-bromosuccinimide, ionic liquids, and phase transfer agent);[12a] microwave/SiO_2;[15] and rongalite[16]]. Although thioesters can be efficiently synthesized using numerous existing methods, one disadvantage of most of the aforementioned methods is that the thiol group has a foul smell. Moreover, the thiol group has a propensity to undergo slow oxidation to form disulfide bonds. Therefore, for thioester formation, new synthetic methods that are more feasible and environmentally friendly are still in strong demand. To solve the aforementioned problems, recent studies have developed new sulfur surrogates, such as tetrathiomolybdate[17] and thiourea,[18] through the *in situ* generation of the sulfur atom during the reaction process (Scheme 1a). Moreover, Jiang and co-workers recently



Scheme 1. Synthetic methods for thioester formation

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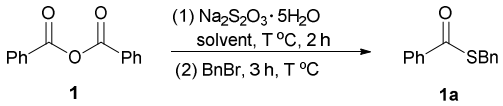
exploited palladium-catalyzed the cross-coupling reaction involving organosilicon reagent and Bunte salt for thioester formation (Scheme 1a).[11d] These sulfur surrogates are highly desirable for developing new and interesting synthetic methods for thioesters in chemistry. Hence, our research continuously focuses on developing synthetic methods for carbon–sulfur bond formation in which environmentally friendly agents are used under transition metal-free conditions. In this paper, we report the successful preparation of thioesters in a one-pot two-step reaction under transition metal-free conditions, in which anhydrides were directly coupled with sodium thiosulfate pentahydrate ($Na_2S_2O_3{\cdot}5H_2O$), which was used as the sulfur source (Scheme 1b).

Results and Discussion

The model study of the one-pot two-step reaction of thioester formation was optimized using benzoic anhydride **1** and sodium thiosulfate pentahydrate with benzyl bromide (Table 1). Initially, to investigate the reactivities of sodium thiosulfate in different solvents, the reactions were performed with dimethylformamide (DMF), acetonitrile (ACN), methanol (MeOH), and water (H_2O) under mild heating conditions (Table 1, entries 1–5). The results revealed that the reaction proceeded more favorably with sodium thiosulfate in DMF than with sodium thiosulfate in ACN, MeOH, or H_2O. Therefore, DMF was selected as the reaction solvent for further study. To determine the accurate amount of sodium thiosulfate required, the amount utilized was 1 equivalent (Table 1, entry 6) and 1.5 equivalent (Table 1, entry 7). When the amount of sodium thiosulfate was increased, a reaction yield of only 61% was found (Table 1, entry 7). Hence, entry 1 was found to be the minimum amount of sodium thiosulfate required for optimum activity. After optimizing the amount of sodium thiosulfate, the reaction temperature was also optimized. The results revealed that a low temperature resulted in a low reaction yield (Table 1, entries 8–9). Unexpectedly, when anhydrous sodium thiosulfate was utilized under the optimized condition, the desired product **1a** was obtained in a reaction yield of only 10% (Table 1, entry 10). According to similar previous reports,[19] we assumed that hydrates in sodium thiosulfate can be recognized as a hydrogen-bonding donor and can be used as a general acid catalyst for the activation of carbonyl groups. In addition, we found that this optimized condition is suitable for large-scale procedures, which provided the desired product **1a** in good yields (Table 1, entry 11). The benzoyl chloride was applied to optimized condition, and the result revealed that the desired product was not obtained (Table 1, entry 12). The reaction of aliphatic anhydrides including acetic, hexanoic and phenylacetic anhydrides with sodium thiosulfate under optimized conditions did not lead to the desired products.

To extend the scope of this study, the aforementioned optimized conditions for the one-pot two-step protocol were employed to synthesize a series of functionalized thioesters by using prepared aryl anhydrides, sodium thiosulfate pentahydrate, and organic halides. Under these optimized

Table 1. Optimization of the reaction conditions

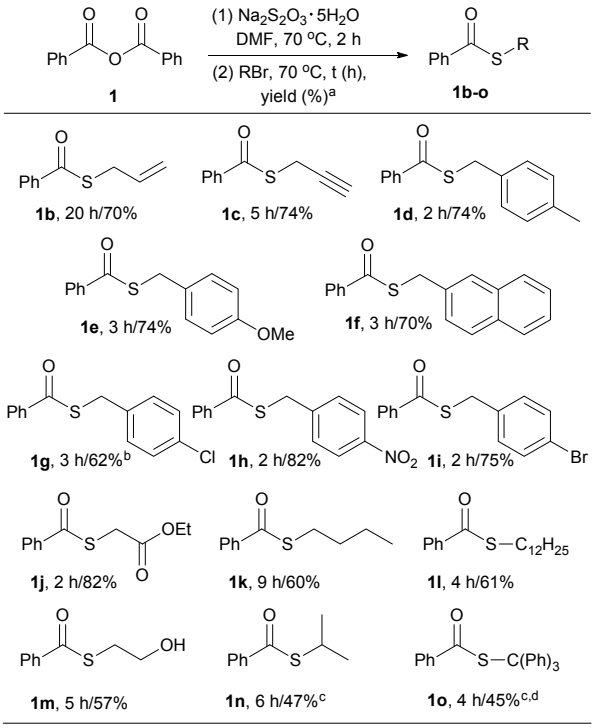


1 **1a**

Entry[a]	T (°C)	Solvent	Yield (%)[b]
1	70	DMF	73
2	70	ACN	8
3	70	MeOH	24
4	70	H_2O	n.d.[c]
5	70	H_2O	n.d.[d]
6	70	DMF	66[e]
7	70	DMF	61[f]
8	r.t.	DMF	36
9	50	DMF	47
10	70	DMF	10[g]
11	70	DMF	75[h]
12[i]	70	DMF	n.d.[j]

[a] Reaction conditions: 1 equiv. anhydride, 1.1 equiv. $Na_2S_2O_3{\cdot}5H_2O$, 1.5 equiv. benzyl bromide, and DMF (0.067M) under nitrogen atmosphere. [b] Isolated yield. [c] Added 2wt % TX-100 (PTC)/H_2O to the reaction mixture, n.d. = not detected. [d] Added 2wt % SDS (PTC)/H_2O to the reaction mixture. [e] Use 1 equiv. $Na_2S_2O_3{\cdot}5H_2O$. [f] Use 1.5 equiv. $Na_2S_2O_3{\cdot}5H_2O$. [g] Use anhydrous $Na_2S_2O_3$. [h] Gram scale (1g of **1**). [i] Using benzoyl chloride. [j] Got benzoic acid and benzylthiol. PTC: Phase transfer catalyst.

Table 2. Thioesterification with various organic halides



Reaction conditions: 1 equiv. anhydride, 1.1 equiv. $Na_2S_2O_3{\cdot}5H_2O$, 1.5 equiv. R-Br, and DMF (0.067 M). [a] One-pot two steps yield. [b] Use 4-chlorobenzyl chloride [c] Use 3 equiv. organic halides.[d] Use trityl chloride.

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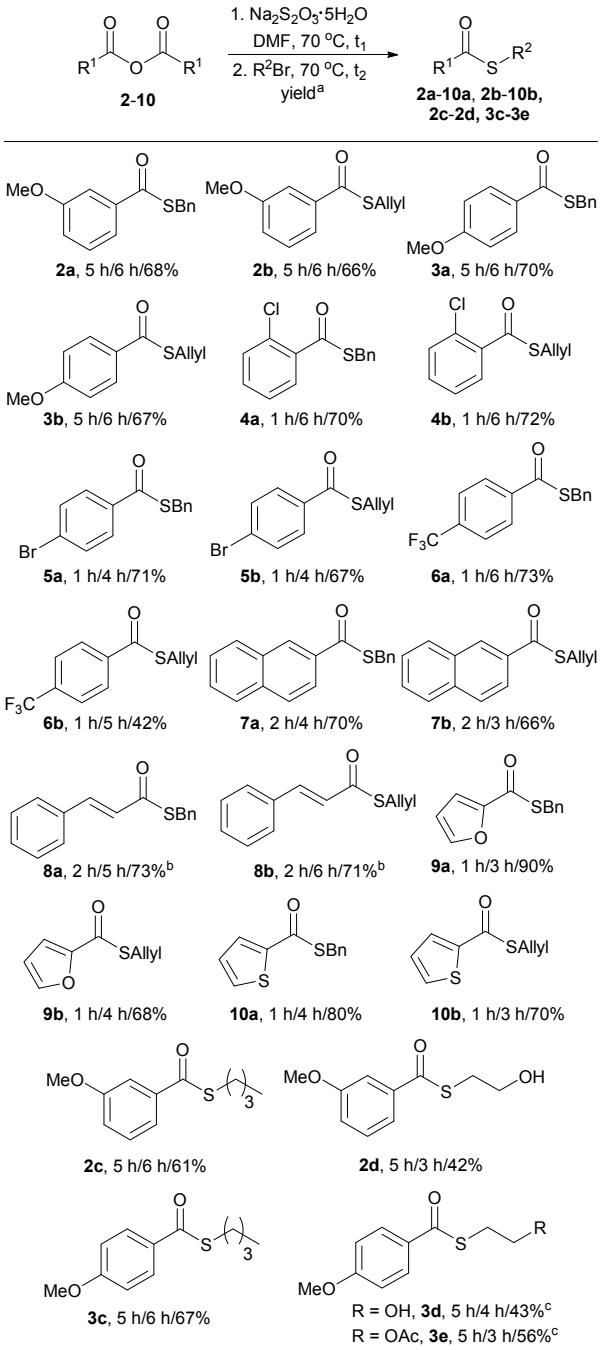
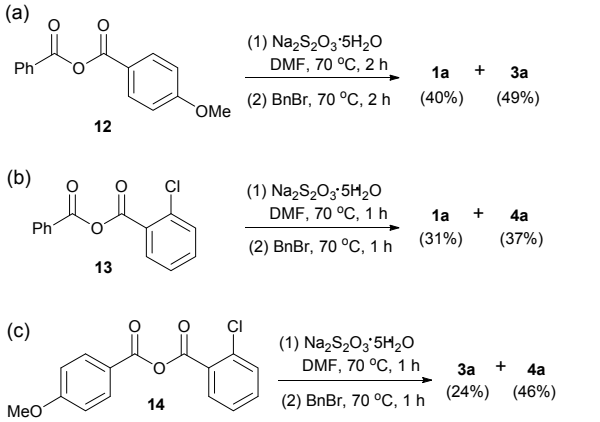
Table 3. Thioesterification with various aryl anhydrides.



Reaction conditions: 1 equiv. anhydride, 1.1 equiv. $Na_2S_2O_3·5H_2O$, 1.5 equiv. R^2Br, [a] One-pot two steps yield, [b] Use 3 equiv. R^2Br. [c] Byproduct 4-methoxybenzoic dithioperoxyanhydride **11** was obtained with 23% and 36% in **3d** and **3e** conditions, respectively.

conditions, various structurally and electronically tuned organic halides with benzoic anhydride were investigated (Table 2). The results revealed that under the reaction conditions, different organic halides were easily converted to thioester adducts (**1b**–**1o**) within appropriate reaction times, with moderate to high isolated yields (45%–82%). Higher yields were obtained for more reactive primary bromide compounds (**1b**–**1j**), such as aryl benzylic bromide and allyl- and propargyl bromide, than for those with a medium-length alkyl chain, such as *n*-butyl (**1k**) and *n*-dodecyl bromide (**1l**). According to previous study,[18b,20] the reactivity of alkyl halides toward nucleophilic addition is known to be reduced as the alkyl chain is lengthened. Moreover, under our reaction conditions, the reactions involving secondary and tertiary organic halides provided favorable results, and the corresponding products **1n** and **1o** were obtained in 47% and 45% isolated yields, respectively. The steric hindrance from secondary and tertiary alky halides hindered the substitution reaction. We also applied these aforementioned optimized conditions to various prepared anhydrides with benzyl- and allyl bromides (Table 3). A wide range of aryl anhydrides[21] were smoothly converted to corresponding thioester adducts (**2a**–**10a**, **2b**–**10b**, **2c**–**2d**, and **3c**–**3e**), with moderate to high reaction yields (42%–90%). Aryl anhydrides bearing electron-donating groups (EDGs) and electron-withdrawing groups (EWGs) were successfully reacted with sodium thiosulfate pentahydrate. Importantly, this aryl system showed high functional group tolerance. Moreover, methoxyl (Table 3, entries **2a**–**2d** and **3a**–**3b**), chloro (Table 3, entries **4a**–**4b**), bromo (Table 3, entries **5a**–**5b**), trifluoromethyl (Table 3, entries **6a**-**6b**), naphtha (Table 3, entries **7a**-**7b**), furan (Table 3, **9a**–**9b**), and thiophene (Table 3, **10a**–**10b**) products were all obtained in high yields under the reaction conditions. In addition, the less reactive primary bromide compounds of 1-bromobutane and 2-bromoethanol were reacted with substituted aryl anhydrides; this reaction provided favorable results (**2c**–**2d** and **3c**–**3d**). We found that when 2-bromoethanol was replaced with 2-bromoethyl acetate, the reaction yield of thioester formation increased to 56% (Table 3, **3e**).

To further determine the applicability of this one-pot two-step reaction, we explored the possibility of performing this reaction with unsymmetric aryl anhydrides.[21] Hence, we performed the reaction with benzyl bromide, sodium thiosulfate pentahydrate, and three unsymmetric aryl anhydrides. The results are summarized in Scheme 2. Benzoic 4-methoxybenzoic- (**12**) and benzoic 2-chlorobenzoic (**13**)



Scheme 2. Thioesterification with unsymmetric aryl anhydrides

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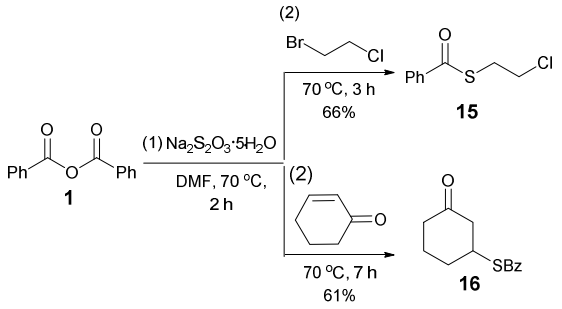
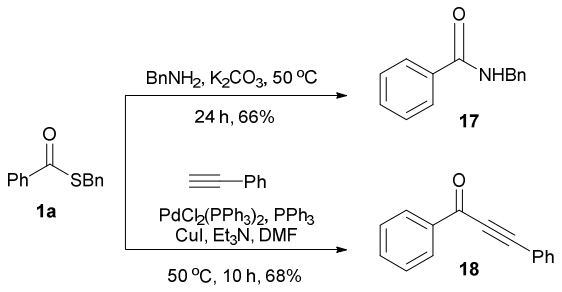
anhydrides were successfully utilized in this method (Scheme 2a–2b). The results revealed that two thioester adducts were obtained, and the reaction yields did not show a considerable difference. Notably, when 2-chlorobenzoic 4-methoxybenzoic anhydride (**14**) was used, the reaction yield of aryl thioester bearing EWGs (**4a**, 46%) was higher than that of those bearing EDGs (**3a**, 24%), as shown in Scheme 2c. We assumed that EWGs on unsymmetric anhydride may induce a more electronic effect, which resulted in high reactivity.

Finally, to further demonstrate the synthetic utility of our developed method in comparison with that of other reported protocols, using the sequential one-pot two-step strategy, benzoic anhydride **1** was transformed into the fungicide of chloroethylbenzoyl sulfide **15**[17] and the thia-Michael adduct **16** (Scheme 3).[22] The results revealed that the substitution addition



Scheme 3. Synthetic applications by one-pot two-step method

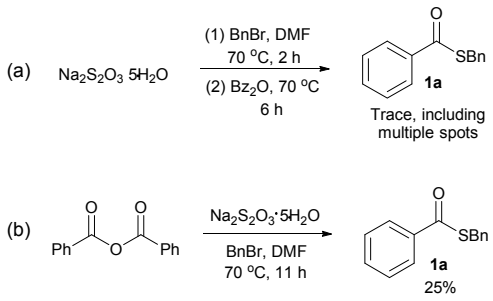
product **15** was obtained in 66% yield from reaction with 1-bromo-2-chloroethane. Moreover, this reaction did not produce a dimer byproduct, which had been formed through intermolecular double substitution addition.[17] In addition, according to a previous study,[22] the thia-Michael addition adduct **16** has been obtained in 52% yield through intermolecular thia-Michael addition with benzoic acid, triphenylphosphine, *N*-bromosuccinimide, tetrathiomolybdate, and cyclohexenone. By contrast, using our developed method, the corresponding thioester was readily produced from the benzoic anhydride through the *in situ* generation of thioaroylate, which produced the desired product **16** with 61% yield. Moreover, applications of thioesters for preparing important organic compounds are illustrated with two efficient transformations (Scheme 4). Amide **17** and alkynone **18** were



Scheme 4. Thioester transformations

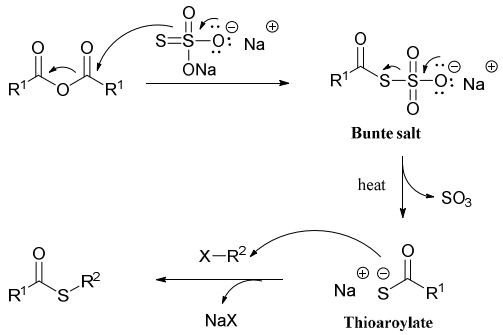
highly efficiently synthesized through acylation and Sonogashira coupling.[11d,23]

To understand the mechanism of this reaction, we conducted control experiments (Scheme 5). As shown in Scheme 5a, the reaction was first performed with sodium thiosulfate pentahydrate and benzyl bromide, and benzoic anhydride was then added. However, the result revealed that multiple spots were obtained through thin-layer chromatography. For comparison with the result in Scheme 5a,



Scheme 5. Control experiments for the one-pot thioester formation

sodium thiosulfate pentahydrate, benzyl bromide, and the benzoic anhydride were stirred under the same reaction conditions, which produced the desired product **1a** in 25% yield, as well as multiple spots, including those for the benzyl disulfide byproduct, through thin-layer chromatography (Scheme 5b). Based on these results, we proposed a plausible mechanism for this reaction (Scheme 6). An aryl anhydride proceeds to undergo a nucleophilic acyl substitution reaction with sodium thiosulfate to produce the corresponding Bunte salt as an intermediate. After the addition of organic halide to the reaction mixture, the salt spontaneously forms a thioaroylate anion. Finally, the thioaroylate reacts with organic halide to obtain the thioester product.



Scheme 6. A proposed mechanism for one-pot two-step thioester formation

Conclusions

In this study, we presented an efficient, versatile, and odorless method for the one-pot synthesis of thioester compounds from sodium thiosulfate pentahydrate, organic halides, and aryl anhydrides under transition metal-free conditions. In this reaction, we demonstrated that sodium thiosulfate served as the sulfur source for the formation of the Bunte salt with anhydride,

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which was spontaneously formed through the *in situ* generation of thioaroylate for substitution with organic halides. Furthermore, we effectively synthesized two important organic compounds by using our developed method and illustrated two applications from the thioester product. Hence, we believe that this one-pot two-step synthetic method for thioester formation can find wide application for the generation of organosulfur compounds.

Experimental Section

General Information

All reactions were performed under nitrogen atmosphere. Solvents were purified following standard literature procedures. ^{1}H NMR and ^{13}C NMR spectra were reported on a Varian 400 MHz NMR spectrometer with $CDCl_3$ as the solvent. Chemical shifts were reported in parts per million (ppm) relative to residual solvent peak ($CDCl_3$ δ H = 7.26 ppm, δ C = 77.0 ppm). The IR spectra were measured on a Thermo Scientific Nicolet iS5 FT-IR spectrophotometer. TLC was performed on pre-coated glass plates of Silica Gel 60 F254 (0.25 mm, E. Merck); detection was performed by spraying with using a UV light and a solution of phosphomolybdic acid (PMA) with heating. Flash column chromatography was carried out on Silica Gel 60 (230–400 mesh, E. Merck). High resolution mass spectrometry data were recorded on ESI and EI source. Melting points were measured by Thermo Scientific "Mel-Temp" type melting point apparatus and are uncorrected. The following abbreviations were used to indicate multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quin. = quintet, sex. = sextet, sep. = septet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, tt = triplet of triplets, br = broad, m = multiplet.

General procedure for synthesis of thioesters 1a-1o, 2a-10a, 2b-10b, 2c-2d, 3c-3e

To a solution of the organic anhydride (1.0 equiv.) in DMF (0.1 M) was added $Na_2S_2O_3{\cdot}5H_2O$ (1.1 equiv.) stirred at 70 °C under nitrogen atmosphere for several hours, then the organic halide (1.5 or 3.0 equiv.) in DMF was added to the reaction mixture (overall, 0.067 M) and stirred at 70 °C under nitrogen atmosphere. The resulting reaction mixture was stirred for several hours until the reaction was completed as indicated by TLC. The mixture was extracted with ether for three times and the combined organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated. The crude products were purified by flash column chromatography to afford the desired product.

S-benzyl benzothioate (1a)[13i]

Following general procedure, using benzoic anhydride (50.0 mg, 0.221 mmol), $Na_2S_2O_3{\cdot}5H_2O$ (60.3 mg, 0.243 mmol), and benzyl bromide (56.7 mg, 0.332 mmol). The crude product was then purified by column chromatography (hexane/CH_2Cl_2, 8:1) to afford **1a** (36.8 mg, 73% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (dd, *J* = 8.4, 1.2 Hz, 2H), δ 7.57 (tt, *J* = 7.5, 1.4 Hz, 1H), δ 7.47-7.42 (m, 2H), δ 7.39-7.37 (m, 2H), δ 7.34-7.30 (m, 2H), δ 7.28-7.24 (m, 1H), δ 4.32 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.3, 137.4, 136.8, 133.4, 129.0, 128.61, 128.59, 127.29, 127.26, 33.3.

S-allyl benzothioate (1b)[13i]

Following general procedure, using benzoic anhydride (50.0 mg, 0.221 mmol), $Na_2S_2O_3{\cdot}5H_2O$ (60.3 mg, 0.243 mmol), and allyl bromide (40.1 mg, 0.332 mmol). The crude product was then purified by column chromatography (hexane/CH_2Cl_2, 8:1) to afford **1b** (27.7 mg, 70% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (dd, *J* = 8.5, 1.3 Hz, 2H), δ 7.58 (tt, *J* = 7.4, 1.3 Hz, 1H), δ 7.48-7.43 (m, 2H), δ 5.95-5.85 (m, 1H), δ 5.35-5.30 (m, 1H), δ 5.17-5.14 (m, 1H), δ 3.74 (dt, *J* = 6.9, 1.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.2, 136.9, 133.4, 133.0, 128.6, 127.2, 118.1, 31.8.

S-(prop-2-yn-1-yl) benzothioate (1c)[18c]

Following general procedure, using benzoic anhydride (100.0 mg, 0.442 mmol), $Na_2S_2O_3{\cdot}5H_2O$ (120.7 mg, 0.486 mmol), and propargyl bromide (78.88 mg, 0.663 mmol). The crude product was then purified by column chromatography (hexane/CH_2Cl_2, 8:1) to afford **1c** (57.3 mg, 74% yield) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (dd, *J* = 8.4, 1.2 Hz, 2H), δ 7.60 (tt, *J* = 7.5, 1.2 Hz, 1H), δ 7.49-7.45 (m, 2H), δ 3.84 (d, *J* = 2.7 Hz, 2H), δ 2.22 (t, *J* = 2.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.9, 136.1, 133.7, 128.6, 127.2, 78.8, 71.0, 17.4.

S-(4-methylbenzyl) benzothioate (1d)[24]

Following general procedure, using benzoic anhydride (100.0 mg, 0.442 mmol), $Na_2S_2O_3{\cdot}5H_2O$ (120.7 mg, 0.486 mmol), and 4-methylbenzyl bromide (143.2 mg, 0.663 mmol). The crude product was then purified by column chromatography (hexane/CH_2Cl_2, 10:1) to afford **1d** (79.1 mg, 74% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.4 Hz, 2H), δ 7.56 (tt, *J* = 7.5, 1.3 Hz, 1H), δ 7.46-7.42 (m, 2H), δ 7.28 (d, *J* = 7.9 Hz, 2H), δ 7.13 (d, *J* = 7.9 Hz, 2H), δ 4.30 (s, 2H) δ 2.33 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.4, 137.0, 136.8, 134.3, 133.3, 129.3, 128.8, 128.5, 127.2, 33.1, 21.1.

S-(4-methoxybenzyl) benzothioate (1e)[13i]

Following general procedure, using benzoic anhydride (100.0 mg, 0.442 mmol), $Na_2S_2O_3{\cdot}5H_2O$ (120.7 mg, 0.486 mmol), and 4-methoxybenzyl bromide (103.5 mg, 0.663 mmol). The crude product was then purified by column chromatography (hexane/CH_2Cl_2, 8:1) to afford **1e** (83.9 mg, 74% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 7.3 Hz, 2H), δ 7.56 (t, *J* = 7.4 Hz, 1H), δ 7.44 (t, *J* = 7.6 Hz, 2H), δ 7.30 (d, *J* = 8.6 Hz, 2H), δ 6.85 (d, *J* = 8.6 Hz, 2H), δ 4.28 (s, 2H), δ 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.5, 158.8, 136.8, 133.3, 130.1, 129.4, 128.6, 127.2, 114.0, 55.2, 32.8.

S-(naphthalen-2-ylmethyl) benzothioate (1f)[25]

Following general procedure, using benzoic anhydride (100.0 mg, 0.442 mmol), $Na_2S_2O_3{\cdot}5H_2O$ (120.7 mg, 0.486 mmol), and 2-(bromomethyl)naphthalene (146.6 mg, 0.663 mmol). The crude product was then purified by column chromatography

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(hexane/CH_2Cl_2, 8:1) to afford **1f** (86.3 mg, 70% yield) as a white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00-7.97 (m, 2H), δ 7.85 (s, 1H), δ 7.82-7.80 (m, 3H), δ 7.57 (tt, *J* = 7.4, 1.3 Hz, 1H), δ 7.50-7.43 (m, 5H), δ 4.49 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.1, 136.7, 134.8, 133.4, 133.3, 132.5, 128.5, 128.4, 127.7, 127.6, 127.2, 126.9, 126.2, 125.8, 33.5.

S-(4-chlorobenzyl) benzothioate (1g)

Following general procedure, using benzoic anhydride (100.0 mg, 0.442 mmol), $Na_2S_2O_3{\cdot}5H_2O$ (120.7 mg, 0.486 mmol), and 4-chlorobenzyl chloride (106.8 mg, 0.663 mmol). The crude product was then purified by column chromatography (hexane/CH_2Cl_2, 8:1) to afford **1g** (71.7 mg, 62% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (dd, *J* = 8.4, 1.3 Hz, 2H), δ 7.58 (tt, *J* = 7.4, 1.3 Hz, 1H), δ 7.47-7.43 (m, 2H), δ 7.34-7.27 (m, 4H), δ 4.27 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.9, 136.5, 136.1, 133.5, 133.1, 130.3, 128.7, 128.6, 127.2, 32.5; IR (KBr): *v* = 3060, 2929, 1662, 1490, 1447, 912, 687 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{14}H_{11}ClNaOS$: 285.0117, found: 285.0121.

S-(4-nitrobenzyl) benzothioate (1h)[18a]

Following general procedure, using benzoic anhydride (100.0 mg, 0.442 mmol), $Na_2S_2O_3{\cdot}5H_2O$ (120.7 mg, 0.486 mmol), and 4-nitrobenzyl bromide (143.2 mg, 0.663 mmol). The crude product was then purified by column chromatography (hexane/EtOAc, 20:1) to afford **1h** (99.5 mg, 82% yield) as a white solid; m. p. 92-94 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19-8.16 (m, 2H), δ 7.96 (dd, *J* = 8.4, 1.3 Hz, 2H), δ 7.62-7.54 (m, 3H), δ 7.49-7.44 (m, 2H), δ 4.37 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.3, 147.0, 145.5, 136.2, 133.8, 129.7, 128.7, 127.3, 123.7, 32.4.

S-(4-bromobenzyl) benzothioate (1i)[18a]

Following general procedure, using benzoic anhydride (100.0 mg, 0.442 mmol), $Na_2S_2O_3{\cdot}5H_2O$ (120.7 mg, 0.486 mmol), and 4-bromobenzyl bromide (165.7 mg, 0.663 mmol). The crude product was then purified by column chromatography (hexane/CH_2Cl_2, 8:1) to afford **1i** (101.0 mg, 75% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (dd, *J* = 8.4, 1.3 Hz, 2H), δ 7.58 (tt, *J* = 7.4, 1.3 Hz, 1H), δ 7.47-7.42 (m, 4H), δ 7.27-7.25 (m, 2H), 4.26 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.8, 136.6, 136.5, 133.5, 131.6, 130.6, 128.6, 127.2, 121.1, 32.5.

Ethyl 2-(benzoylthio)acetate (1j)[24]

Following general procedure, using benzoic anhydride (100.0 mg, 0.442 mmol), $Na_2S_2O_3{\cdot}5H_2O$ (120.7 mg, 0.486 mmol), and ethyl 2-bromoacetate (110.7 mg, 0.663 mmol). The crude product was then purified by column chromatography (hexane/EtOAc, 8:1) to afford **1j** (81.4 mg, 82% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 7.7 Hz, 2H), δ 7.60 (t, *J* = 7.6 Hz, 1H), δ 7.47 (t, *J* = 7.6 Hz, 2H), δ 4.23 (q, *J* = 7.1 Hz, 2H), δ 3.89 (s, 2H), δ 1.30 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.0, 168.7, 136.1, 133.7, 128.6, 127.3, 61.8, 31.3, 14.0.

S-butyl benzothioate (1k)[26]

Following general procedure, using benzoic anhydride (50.0 mg, 0.221 mmol), $Na_2S_2O_3{\cdot}5H_2O$ (60.3 mg, 0.243 mmol), and 1-bromobutane (45.4 mg, 0.332 mmol). The crude product was then purified by column chromatography (hexane/CH_2Cl_2, 8:1) to afford **1k** (25.6 mg, 60% yield) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (dd, *J* = 8.4, 1.3 Hz, 2H), δ 7.60 (tt, *J* = 7.4, 1.3 Hz, 1H), δ 7.47-7.43 (m, 2H), δ 3.08 (t, *J* = 7.3 Hz, 2H), δ 1.70-1.62 (m, 2H), δ 1.50-1.41 (m, 2H), δ 0.95 (t, *J* = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.1, 137.2, 133.1, 128.5, 127.1, 31.6, 28.7, 22.0, 13.6.

S-dodecyl benzothioate (1l)[13g]

Following general procedure, using benzoic anhydride (100.0 mg, 0.442 mmol), $Na_2S_2O_3{\cdot}5H_2O$ (120.7 mg, 0.486 mmol), and 1-bromododecane (165.3 mg, 0.663 mmol). The crude product was then purified by column chromatography (hexane/CH_2Cl_2, 30:1) to afford **1l** (82.7 mg, 61% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99-7.96 (m, 2H), δ 7.56 (t, *J* = 7.4 Hz, 1H), δ 7.44 (t, *J* = 7.7 Hz, 2H), δ 3.07 (t, *J* = 7.3 Hz, 2H), δ 1.67 (quin., *J* = 7.2 Hz, 2H), δ 1.46-1.39 (m, 2H), δ 1.32-1.26 (m, 16H), δ 0.88 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.1, 137.3, 133.2, 128.5, 127.1, 31.9, 29.62 (CH_2*2), 29.57, 29.55, 29.49, 29.3, 29.2, 29.1, 29.0, 22.7, 14.1.

S-(2-hydroxyethyl) benzothioate (1m)[27]

Following general procedure, using benzoic anhydride (50.0 mg, 0.221 mmol), $Na_2S_2O_3{\cdot}5H_2O$ (60.3 mg, 0.243 mmol), and 2-bromoethanol (41.4 mg, 0.332 mmol). The crude product was then purified by column chromatography (hexane/EtOAc, 3:1) to afford **1m** (22.9 mg, 57% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (dd, *J*= 8.4, 1.3 Hz, 2H), δ 7.59 (tt, *J* = 7.4, 1.2 Hz, 1H), δ 7.48-7.44 (m, 2H), δ 3.87 (q, *J* = 5.5 Hz, 2H), δ 3.30 (t, *J* = 6.0 Hz, 2H), δ 2.03 (t, *J* = 4.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.2, 136.7, 133.5, 128.6, 127.2, 61.7, 31.8.

S-isopropyl benzothioate (1n)[28]

Following general procedure, using benzoic anhydride (100.0 mg, 0.442 mmol), $Na_2S_2O_3{\cdot}5H_2O$ (120.7 mg, 0.486 mmol), and 2-bromopropane (163.1 mg, 1.326 mmol). The crude product was then purified by column chromatography (hexane/CH_2Cl_2, 8:1) to afford **1n** (37.1 mg, 47% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (dd, *J* = 8.3, 1.3 Hz, 2H), δ 7.55 (tt, *J* = 7.4, 1.2 Hz, 1H), δ 7.46-7.42 (m, 2H), δ 3.86 (sep., *J* = 6.9 Hz, 1H), δ 1.41 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.1, 137.3, 133.1, 128.5, 127.1, 34.9, 23.1.

S-trityl benzothioate (1o)

Following general procedure, using benzoic anhydride (100.0 mg, 0.442 mmol), $Na_2S_2O_3{\cdot}5H_2O$ (120.7 mg, 0.486 mmol), and trityl chloride (369.7 mg, 1.326 mmol). The crude product was then purified by column chromatography (hexane/CH_2Cl_2, 8:1) to afford **1o** (75 mg, 45% yield) as a white solid; m. p. 178-180 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.0 Hz, 2H), δ 7.53 (t, *J* = 7.6 Hz, 1H), δ 7.39 (t, *J* = 7.6 Hz, 2H), δ 7.34-7.23 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.7, 143.8, 137.4,

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133.2, 129.9, 128.5, 127.8, 127.4, 127.1, 70.4; IR (KBr): ν = 3052, 3029, 2923, 1667, 1483, 1441 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{26}H_{20}NaOS$: 403.1127, found: 403.1118.

_S_-benzyl 3-methoxybenzothioate (2a)[13e]
Following general procedure, using 3-methoxybenzoic anhydride (50.0 mg, 0.175 mmol), $Na_2S_2O_3{\cdot}5H_2O$ (47.7 mg, 0.192 mmol), and benzyl bromide (44.8 mg, 0.262 mmol). The crude product was then purified by column chromatography (hexane/EtOAc, 30:1) to afford **2a** (30.9 mg, 68% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.56 (m, 1H), δ 7.47 (t, J = 2.0 Hz, 1H), δ 7.39-7.30 (m, 5H), δ 7.27-7.24 (m, 1H), δ 7.12-7.10 (m, 1H), δ 4.32 (s, 2H), δ 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.2, 159.7, 138.1, 137.4, 129.6, 128.9, 128.6, 127.3, 119.93, 119.86, 111.4, 55.4, 33.4.

_S_-allyl 3-methoxybenzothioate (2b)
Following general procedure, using 3-methoxybenzoic anhydride (50.0 mg, 0.175 mmol), $Na_2S_2O_3{\cdot}5H_2O$ (47.7 mg, 0.192 mmol), and allyl bromide (31.7 mg, 0.262 mmol). The crude product was then purified by column chromatography (hexane/CH_2Cl_2, 8:1) to afford **2b** (23.8 mg, 66% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.56 (m, 1H), δ 7.47 (t, J = 2.2 Hz, 1H), δ 7.35 (t, J = 8.0 Hz, 1H), δ 7.12 (dd, J = 8.2, 2.4 Hz, 1H), δ 5.95-5.85 (m, 1H), δ 5.33 (d, J = 16.9 Hz, 1H), δ 5.16 (d, J = 10.0 Hz, 1H), δ 3.85 (s, 3H), δ 3.73 (d, J = 6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.2, 159.7, 138.2, 133.0, 129.6, 119.9, 118.1, 111.4, 55.4, 31.9; IR (KBr): ν = 3081, 3005, 2937, 2835, 1663, 1596, 1484, 1427, 1262, 1041 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{11}H_{12}NaO_2S$: 231.0456, found: 231.0448.

_S_-butyl 3-methoxybenzothioate (2c)[13e]
Following general procedure, using 3-methoxybenzoic anhydride (50.0 mg, 0.175 mmol), $Na_2S_2O_3{\cdot}5H_2O$ (47.7 mg, 0.192 mmol), and 1-bromobutane (35.9 mg, 0.262 mmol). The crude product was then purified by column chromatography (hexane/CH_2Cl_2, 8:1) to afford **2c** (23.9 mg, 61% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.57 (m, 1H), δ 7.47 (t, J = 2.2 Hz, 1H), δ 7.35 (t, J = 8.1 Hz, 1H), δ 7.11 (dd, J = 8.2, 2.6 Hz, 1H), δ 3.85 (s, 3H), δ 3.07 (t, J = 7.4 Hz, 2H), δ 1.66 (quin., J = 7.6 Hz, 2H), δ 1.46 (sex., J = 7.4 Hz, 2H), δ 0.95 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.0, 159.7, 138.6, 129.5, 119.8, 119.6, 111.4, 55.4, 31.6, 28.8, 22.0, 13.6.

_S_-(2-hydroxyethyl) 3-methoxybenzothioate (2d)
Following general procedure, using 3-methoxybenzoic anhydride (50.0 mg, 0.175 mmol), $Na_2S_2O_3{\cdot}5H_2O$ (47.7 mg, 0.192 mmol), and 2-bromoethanol (32.8 mg, 0.262 mmol). The crude product was then purified by column chromatography (hexane/EtOAc, 3:1) to afford **2d** (15.6 mg, 42% yield) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, J = 7.7 Hz, 1H), δ 7.47 (t, J = 2.4 Hz, 1H), δ 7.36 (t, J = 8.0 Hz, 1H), δ 7.14-7.11 (m, 1H), δ 3.88-3.86 (m, 5H), δ 3.29 (t, J = 6.0 Hz, 2H), δ 1.97 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.0, 159.6, 138.0, 129.6, 119.9, 119.9, 111.5, 61.7, 55.4, 31.8; IR (KBr): ν = 3391, 3072, 2938, 2835, 1664, 1596, 1483, 1263, 1042 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{10}H_{12}NaO_3S$: 235.0405, found: 235.0404.

_S_-benzyl 4-methoxybenzothioate (3a)[14a]
Following general procedure, using 4-methoxybenzoic anhydride (50.0 mg, 0.175 mmol), $Na_2S_2O_3{\cdot}5H_2O$ (47.7 mg, 0.192 mmol), and benzyl bromide (44.8 mg, 0.262 mmol). The crude product was then purified by column chromatography (hexane/EtOAc, 30:1) to afford **3a** (31.7 mg, 70% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 8.8 Hz, 2H), δ 7.37 (d, J = 7.3 Hz, 2H), δ 7.31 (t, J = 7.1 Hz, 2H), δ 7.25-7.22 (m, 1H), δ 6.91 (d, J = 8.8 Hz, 2H), δ 4.30 (s, 2H), δ 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.7, 163.8, 137.7, 129.6, 129.4, 128.9, 128.6, 127.2, 113.8, 55.5, 33.2.

_S_-allyl 4-methoxybenzothioate (3b)[29]
Following general procedure, using 4-methoxybenzoic anhydride (50.0 mg, 0.175 mmol), $Na_2S_2O_3{\cdot}5H_2O$ (47.7 mg, 0.192 mmol), and allyl bromide (31.7 mg, 0.262 mmol). The crude product was then purified by column chromatography (hexane/CH_2Cl_2, 8:1) to afford **3b** (24.3 mg, 67% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 8.8 Hz, 2H), δ 6.92 (d, J = 8.8 Hz, 2H), δ 5.95-5.85 (m, 2H), δ 5.31 (d, J = 17.0 Hz, 1H), δ 5.14 (d, J = 10.0 Hz, 1H), δ 3.87 (s, 3H), δ 3.72 (d, J = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.7, 163.7, 133.3, 129.8, 129.4, 117.8, 113.7, 55.5, 31.7.

_S_-butyl 4-methoxybenzothioate (3c)[13h]
Following general procedure, using 4-methoxybenzoic anhydride (50.0 mg, 0.175 mmol), $Na_2S_2O_3{\cdot}5H_2O$ (47.7 mg, 0.192 mmol), and 1-bromobutane (35.9 mg, 0.262 mmol). The crude product was then purified by column chromatography (hexane/EtOAc, 30:1) to afford **3c** (26.4 mg, 67% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 8.8 Hz, 2H), δ 6.92 (d, J = 8.8 Hz, 2H), δ 3.86 (s, 3H), δ 3.05 (t, J = 7.3 Hz, 2H), δ 1.65 (quin., J = 7.2 Hz, 2H), δ 1.45 (sex., J = 7.4 Hz, 2H), δ 0.95 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.7, 163.6, 130.1, 129.3, 113.7, 55.5, 31.7, 28.6, 22.0, 13.6.

_S_-(2-hydroxyethyl) 4-methoxybenzothioate (3d)[30]
Following general procedure, using 4-methoxybenzoic anhydride (60.0 mg, 0.208 mmol), $Na_2S_2O_3{\cdot}5H_2O$ (57.3 mg, 0.231 mmol), and 2-bromoethanol (39.3 mg, 0.315 mmol). The crude product was then purified by column chromatography (hexane/EtOAc, 3:1) to afford **3d** (19.2 mg, 43% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, J = 9.0 Hz, 2H), δ 6.93 (d, J = 9.0 Hz, 2H), δ 3.87-3.85 (m, 5H), δ 3.27 (t, J = 6.0 Hz, 2H), δ 2.08 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.7, 163.9, 129.5, 113.7, 61.9, 55.5, 31.7.

2-((4-methoxybenzoyl)thio)ethyl acetate (3e)
Following general procedure, using 4-methoxybenzoic anhydride (78.4 mg, 0.274 mmol), $Na_2S_2O_3{\cdot}5H_2O$ (74.8 mg, 0.301 mmol), and 2-bromoethyl acetate (68.7 mg, 0.411 mmol). The crude product was then purified by column

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chromatography (hexane/EtOAc, 3:1) to afford **3e** (39.1 mg, 56% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 9.0 Hz, 2H), δ 6.93 (d, J = 9.0 Hz, 2H), δ 4.26 (t, J = 6.5 Hz, 2H), δ 3.87 (s, 3H), δ 3.31 (t, J = 6.5 Hz, 2H), δ 2.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.3, 170.7, 163.9, 129.52, 129.46, 113.8, 63.0, 55.5, 27.5, 20.8; IR (KBr): ν = 30056, 2958, 2937, 2841, 1741, 1659, 1601, 1508, 1260, 1028 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{10}H_{12}NaO_3S$: 277.0511, found: 277.0502.

***S*-benzyl 2-chlorobenzothioate (4a)**[13c]
Following general procedure, using 2-chlorobenzoic anhydride (90.0 mg, 0.306 mmol), $Na_2S_2O_3{\cdot}5H_2O$ (83.6 mg, 0.337 mmol), and benzyl bromide (78.5 mg, 0.459 mmol). The crude product was then purified by column chromatography (hexane/CH_2Cl_2, 8:1) to afford **4a** (55.8 mg, 70% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (dd, J = 7.7, 1.4 Hz, 1H), δ 7.46-7.25 (m, 8H), δ 4.33 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.2, 137.1, 136.9, 132.2, 130.8, 129.2, 128.9, 128.7, 127.4, 126.6, 34.2.

***S*-allyl 2-chlorobenzothioate (4b)**
Following general procedure, using 2-chlorobenzoic anhydride (134.0 mg, 0.456 mmol), $Na_2S_2O_3{\cdot}5H_2O$ (124.4 mg, 0.501 mmol), and allyl bromide (82.7 mg, 0.684 mmol). The crude product was then purified by column chromatography (hexane/CH_2Cl_2, 8:1) to afford **4b** (69.9 mg, 72% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (dd, J = 7.6, 1.5 Hz, 1H), δ 7.46-7.39 (m, 2H), δ 7.32 (td, J = 7.4, 1.5 Hz, 1H), δ 5.96-5.86 (m, 1H), δ 5.34 (dd, J = 16.9, 1.2 Hz, 1H), δ 5.18 (d, J = 10.0 Hz, 1H), δ 3.74 (d, J = 7.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.2, 137.3, 132.5, 132.2, 130.8, 129.2, 126.7, 118.5, 32.8; IR (KBr): ν = 3084, 3013, 2924, 1678, 1587, 1466, 1432, 912, 647 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{10}H_9ClNaOS$: 234.9960, found: 234.9962.

***S*-benzyl 4-bromobenzothioate (5a)**[31]
Following general procedure, using 4-bromobenzoic anhydride (81.9 mg, 0.214 mmol), $Na_2S_2O_3{\cdot}5H_2O$ (58.5 mg, 0.236 mmol), and benzyl bromide (55.0 mg, 0.322 mmol). The crude product was then purified by column chromatography (hexane/CH_2Cl_2, 8:1) to afford **5a** (46.9 mg, 71% yield) as a white solid; m. p. 68-70 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 8.8 Hz, 2H), δ 7.59 (d, J = 8.8 Hz, 2H), δ 7.38-7.24 (m, 5H), δ 4.32 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.3, 137.1, 135.5, 131.9, 128.9, 128.7, 128.7, 128.5, 127.4, 33.5.

***S*-allyl 4-bromobenzothioate (5b)**
Following general procedure, using 4-bromobenzoic anhydride (74.0 mg, 0.194 mmol), $Na_2S_2O_3{\cdot}5H_2O$ (52.9 mg, 0.213 mmol), and allyl bromide (35.2 mg, 0.291 mmol). The crude product was then purified by column chromatography (hexane/CH_2Cl_2, 10:1) to afford **5b** (33.4 mg, 67% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 8.7 Hz, 2H), δ 7.59 (d, J = 8.6 Hz, 2H), δ 5.94-5.84 (m, 1H), δ 5.33 (dd, J = 16.9, 1.4 Hz, 1H), δ 5.18-5.14 (m, 1H), δ 3.73 (dt, J = 6.9, 1.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.2, 135.6, 132.7, 131.8, 128.6, 128.4, 118.3, 31.9; IR (KBr): ν = 3084, 3102, 2924, 1667, 1583, 1482, 1420, 640 cm^{-1}; HRMS (EI) m/z: $[M]^+$ calcd. for $C_{10}H_9BrOS$: 255.9557, found: 255.9550.

***S*-benzyl 4-(trifluoromethyl)benzothioate (6a)**[32]
Following general procedure, using 4-(trifluoromethyl)benzoic anhydride (58.0 mg, 0.160 mmol), $Na_2S_2O_3{\cdot}5H_2O$ (43.7 mg, 0.176 mmol), and benzyl bromide (41.1 mg, 0.240 mmol). The crude product was then purified by column chromatography (hexane/CH_2Cl_2, 8:1) to afford **6a** (34.4 mg, 73% yield) as a white solid; m. p. 44-45 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, J = 8.1 Hz, 2H), δ 7.70 (d , J = 8.2 Hz, 2H), δ 7.34 (d, J = 7.4 Hz, 2H), δ 7.32 (t, J = 7.3 Hz, 2H), δ 7.28-7.24 (m, 1H), δ 4.34 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.4, 139.5, 136.9, 134.7 (q, J = 33.0 Hz), 129.0, 128.7, 127.6, 127.5, 125.7 (q, J = 3.5 Hz), 123.5 (q, J = 271.0 Hz), 33.6.

***S*-allyl 4-(trifluoromethyl)benzothioate (6b)**
Following general procedure, using 4-(trifluoromethyl)benzoic anhydride (44.0 mg, 0.122 mmol), $Na_2S_2O_3{\cdot}5H_2O$ (33.2 mg, 0.134 mmol), and allyl bromide (22.1 mg, 0.183 mmol). The crude product was then purified by column chromatography (hexane/CH_2Cl_2, 8:1) to afford **6b** (12.6 mg, 42% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 8.1 Hz, 2H), δ 7.72 (d, J = 8.2 Hz, 2H), δ 5.95-5.85 (m, 1H), δ 5.35 (dd, J = 17.0, 1.3 Hz, 1H), δ 5.18 (dd, J = 10.0, 1.1 Hz, 1H), δ 3.76 (dt, J = 6.9, 1.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.4, 139.7, 134.7 (q, J = 28.0 Hz), 132.5, 127.6, 125.7 (q, J = 3.5 Hz), 123.5 (q, J = 272.0 Hz), 118.6, 32.1; IR (KBr): ν = 3087, 2927, 1667, 1583, 1510, 1409, 1323 cm^{-1}; HRMS (EI) m/z: $[M]^+$ calcd. for $C_{11}H_9F_3OS$: 246.0326, found: 246.0332.

***S*-benzyl naphthalene-2-carbothioate (7a)**[33]
Following general procedure, using 2-naphthoic anhydride (125.0 mg, 0.383 mmol), $Na_2S_2O_3{\cdot}5H_2O$ (104.7 mg, 0.422 mmol), and benzyl bromide (98.3 mg, 0.575 mmol). The crude product was then purified by column chromatography (hexane/EtOAc, 30:1) to afford **7a** (75.0 mg, 70% yield) as a white solid; m. p. 73-74 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (s, 1H), δ 8.00 (dd, J = 8.6, 1.8 Hz, 1H), δ 7.95 (d, J = 8.3 Hz, 1H), δ 7.90-7.86 (m, 2H), δ 7.62-7.53 (m, 2H), δ 7.42 (d, J = 7.2 Hz, 2H), δ 7.34 (t, J = 7.4 Hz, 2H), δ 7.29-7.24 (m, 1H), δ 4.38 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.1, 137.4, 135.7, 134.0, 132.3, 129.4, 128.9, 128.64, 128.59, 128.4, 127.7, 127.3, 126.8, 123.1, 33.4.

***S*-allyl naphthalene-2-carbothioate (7b)**[34]
Following general procedure, using 2-naphthoic anhydride (150.0 mg, 0.460 mmol), $Na_2S_2O_3{\cdot}5H_2O$ (125.6 mg, 0.506 mmol), and allyl bromide (83.5 mg, 0.690 mmol). The crude product was then purified by column chromatography (hexane/CH_2Cl_2, 8:1) to afford **7b** (69.1 mg, 66% yield) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (s, 1H), δ 8.01-7.96 (m, 2H), δ 7.90-7.86 (m, 2H), δ 7.62-7.54 (m, 2H), δ 6.00-5.90 (m, 1H), δ 5.37 (dd, J = 16.9, 1.0 Hz, 1H), δ 5.18 (dd, J = 10.0, 1.0 Hz, 1H), δ 3.80 (dt, J = 6.9, 1.1 Hz, 2H); ^{13}C NMR

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(100 MHz, $CDCl_3$): δ 191.1, 135.7, 134.1, 133.1, 132.4, 129.5, 128.6, 128.4, 127.7, 126.8, 123.1, 118.1, 32.0.

_S_-benzyl (E)-3-phenylprop-2-enethioate (8a)[35]

Following general procedure, using cinnamic anhydride (50.0 mg, 0.180 mmol), $Na_2S_2O_3{\cdot}5H_2O$ (49.1 mg, 0.198 mmol), and benzyl bromide (92.3 mg, 0.540 mmol). The crude product was then purified by column chromatography (hexane/CH_2Cl_2, 8:1) to afford **8a** (33.5 mg, 73% yield) as a white solid; m. p. 66-67 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65(d, *J* = 15.8 Hz, 1H), δ 7.54 (dd, *J* = 6.6, 3.1 Hz, 2H), δ 7.40-7.24 (m, 8H), δ 6.73 (d, *J* = 15.8 Hz, 1H), δ 4.28 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.1, 140.9, 137.6, 134.0, 130.6, 128.92, 128.87, 128.6, 128.4, 127.3, 124.6, 33.2.

_S_-allyl (E)-3-phenylprop-2-enethioate (8b)[36]

Following general procedure, using cinnamic anhydride (80.0 mg, 0.288 mmol), $Na_2S_2O_3{\cdot}5H_2O$ (78.5 mg, 0.316 mmol), and allyl bromide (104.4 mg, 0.863 mmol). The crude product was then purified by column chromatography (hexane/CH_2Cl_2, 8:1) to afford **8b** (41.8 mg, 71% yield) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 15.8 Hz, 1H), δ 7.55 (dd, *J* = 6.7, 2.8 Hz, 2H), δ 7.41-7.38 (m, 3H), δ 6.72 (d, *J* = 15.8 Hz, 1H), δ 5.92-5.82 (m, 1H), δ 5.30 (dd, *J* = 16.9, 1.3 Hz, 1H), δ 5.14 (d, *J* = 10.0 Hz, 1H), δ 3.68 (d, *J* = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.0, 140.7, 134.0, 133.0, 130.5, 128.9, 128.3, 124.7, 117.9, 31.7.

_S_-benzyl furan-2-carbothioate (9a)[37]

Following general procedure, using furan-2-carboxylic anhydride (125.0 mg, 0.607 mmol), $Na_2S_2O_3{\cdot}5H_2O$ (165.6 mg, 0.667 mmol), and benzyl bromide (155.7 mg, 0.910 mmol). The crude product was then purified by column chromatography (hexane/CH_2Cl_2, 8:1) to afford **9a** (119 mg, 90% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (dd, *J* = 1.5, 0.6 Hz, 1H), δ 7.36 (d, *J* = 7.7 Hz, 2H), δ 7.31 (t, *J* = 7.4 Hz, 2H), δ 7.27-7.23 (m, 1H), δ 7.20 (dd, *J* = 3.5, 0.6 Hz, 1H), δ 6.53 (dd, *J* = 3.6, 1.7 Hz, 1H), δ 4.30 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.8, 150.5, 146.1, 137.2, 128.9, 128.6, 127.3, 115.7, 112.2, 32.3.

_S_-allyl furan-2-carbothioate (9b)

Following general procedure, using furan-2-carboxylic anhydride (50.1 mg, 0.243 mmol), $Na_2S_2O_3{\cdot}5H_2O$ (66.4 mg, 0.268 mmol), and allyl bromide (44.1 mg, 0.364 mmol). The crude product was then purified by column chromatography (hexane/CH_2Cl_2, 8:1) to afford **9b** (27.9 mg, 68% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (dd, *J* = 1.6, 0.7 Hz, 1H), δ 7.20 (d, *J* = 3.6 Hz, 1H), δ 6.54 (dd, *J* = 3.6, 1.7 Hz, 1H), δ 5.93-5.83 (m, 1H), δ 5.31 (dd, *J* = 16.9, 1.3 Hz, 1H), δ 5.15 (dd, *J* = 10, 1.0 Hz, 1H), δ 3.71 (dt, *J* = 6.9, 1.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.8, 150.7, 146.1, 132.8, 118.2, 115.6, 112.2, 30.9; IR (KBr): *ν* = 3135, 3085, 2924, 1652, 1567, 1467, 1385, 1150 cm^{-1}; HRMS (EI) m/z: $[M]^+$ calcd. for $C_8H_8O_2S$: 168.0245, found: 168.0249.

_S_-benzyl thiophene-2-carbothioate (10a)[37]

Following general procedure, using thiophene-2-carboxylic anhydride (125.0 mg, 0.525 mmol), $Na_2S_2O_3{\cdot}5H_2O$ (143.4 mg, 0.578 mmol), and benzyl bromide (134.8 mg, 0.788 mmol). The crude product was then purified by column chromatography (hexane/CH_2Cl_2, 8:1) to afford **10a** (98.0 mg, 80% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (dd, *J* = 3.8, 1.1 Hz, 1H), δ 7.62 (dd, *J* = 4.9, 1.2 Hz, 1H), δ 7.38-7.36 (m, 2H), δ 7.34-7.30 (m, 2H), δ 7.27-7.24 (m, 1H), δ 7.11 (dd, *J* = 3.8, 4.9 Hz, 1H), δ 4.32 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.3, 141.7, 137.3, 132.7, 131.1, 128.9, 128.6, 127.9, 127.4, 33.4.

_S_-allyl thiophene-2-carbothioate (10b)

Following general procedure, using thiophene-2-carboxylic anhydride (150.0 mg, 0.630 mmol), $Na_2S_2O_3{\cdot}5H_2O$ (172.1 mg, 0.693 mmol), and allyl bromide (114.4 mg, 0.946 mmol). The crude product was then purified by column chromatography (hexane/CH_2Cl_2, 8:1) to afford **10b** (81.2 mg, 70% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (dd, *J* = 3.8, 0.9 Hz, 1H), δ 7.62 (dd, *J* = 4.9, 0.8 Hz, 1H), δ 7.11 (dd, *J* = 4.8 4.0 Hz, 1H), δ 5.95-5.84 (m, 1H), δ 5.32 (dd, *J* = 16.9, 1.2 Hz, 1H), δ 5.15 (d, *J* = 10.0 Hz, 1H), δ 3.73 (d, *J* = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.2, 141.9, 132.9, 132.6, 131.1, 127.8, 118.2, 32.0; IR (KBr): *ν* = 3085, 3011, 2923, 1686, 1651, 1514, 1411, 1205 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_8H_8NaOS_2$: 206.9914, found: 206.9898.

4-methoxybenzoic dithioperoxyanhydride (11)[38]

White solid; m. p. 118-119 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.9 Hz, 4H), δ 6.98 (d, *J* = 8.9 Hz, 4H), δ 3.89 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.7, 164.5, 130.5, 128.0, 114.1, 55.6.

_S_-(2-chloroethyl) benzothioate (15)[17]

To a solution of the benzoic anhydride (100.0 mg, 0.442 mmol, 1.0 equiv.) in DMF (0.1 M) was added $Na_2S_2O_3{\cdot}5H_2O$ (120.7 mg, 0.486 mmol, 1.1 equiv.) stirred at 70 °C under nitrogen atmosphere for 2 hours, then the 1-bromo-2-chloroethane (627.3 mg, 4.420 mmol, 10 equiv.) in DMF was added to the reaction mixture (overall, 0.067 M) and stirred at 70 °C under nitrogen atmosphere. The resulting reaction mixture was stirred for 3 hours until the reaction was complete as indicated by TLC. After the reaction was completed, the mixture was extracted with ether for three times and the combined organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated. The crude product was then purified by column chromatography (hexane/CH_2Cl_2, 8:1) to afford **15** (58.4 mg, 66% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 7.3 Hz, 2H), δ 7.60 (t, *J* = 7.4 Hz, 1H), δ 7.47 (t, *J* = 7.6 Hz, 2H), δ 3.71 (t, *J* = 7.1 Hz, 2H), δ 3.43 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.7, 136.5, 133.7, 128.7, 127.3, 42.7, 31.2.

_S_-(3-oxocyclohexyl) benzothioate (16)[22]

To a solution of the benzoic anhydride (100.0 mg, 0.442 mmol, 1.0 equiv.) in DMF (0.1 M) was added $Na_2S_2O_3{\cdot}5H_2O$ (120.7 mg, 0.486 mmol, 1.1 equiv.) stirred at 70 °C under nitrogen

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atmosphere for 2 hours, then added 2-cyclohexen-1-one (212.5 mg, 2.211 mmol, 5 equiv.) in DMF (0.067 M) to the solution and still stirred at 70 °C under nitrogen atmosphere. The resulting reaction mixture was stirred for 7 hours until the reaction was complete as indicated by TLC. After the reaction was completed, the mixture was extracted with ether for three times and the combined organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated. The crude product was then purified by column chromatography (hexane/EtOAc, 5:1) to afford **16** (62.9 mg, 61% yield) as a white solid; m. p. 82-83 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J = 8.0 Hz, 2H), δ 7.58 (t, J = 8.0 Hz, 1H), δ 7.45 (t, J = 7.8 Hz, 2H), δ 4.12-4.05 (m, 1H), δ 2.85-2.80 (m, 1H), δ 2.56-2.50 (m, 1H), δ 2.48-2.34 (m, 2H), δ 2.29-2.24 (m, 1H), δ 2.15-2.08 (m, 1H), δ 1.95-1.86 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.0, 190.5, 136.7, 133.6, 128.6, 127.2, 47.3, 41.6, 40.9, 31.2, 24.4.

_N_-benzylbenzamide (17)[39]

To a solution of S-benzyl benzothioate (**1a**; 63.3 mg, 0.278 mmol, 1.0 equiv.) in DMF (0.3 M) was added benzylamine (59.5 mg, 0.555 mmol, 2.0 equiv.) and K_2CO_3 (76.7 mg, 0.555 mmol, 2.0 equiv.) stirred at 50 °C under nitrogen atmosphere for 24 hours. After the reaction was completed, the mixture was extracted with EtOAc for three times and the combined organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated. The crude product was then purified by column chromatography (hexane/EtOAc, 3:1) to afford **17** (38.5 mg, 66% yield) as a white solid; m. p. 104-105 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, J = 7.2 Hz, 2H), δ 7.51 (t, J = 7.4 Hz, 1H), δ 7.43 (t, J = 7.5 Hz, 2H), δ 7.37-7.28 (m, 5H), δ 6.38 (br, 1H), δ 4.66 (d, J = 5.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4, 138.2, 134.3, 131.5, 128.7, 128.5, 127.8, 127.5, 126.9, 44.0.

1,3-diphenylprop-2-yn-1-one (18)[40]

A solution of the _S_-benzyl benzothioate (**1a**; 60.5 mg, 0.265 mmol, 1.0 equiv.), $PdCl_2(PPh_3)_2$ (18.6 mg, 0.0265 mmol, 10 mol%), CuI (101.1 mg, 0.531 mmol, 2.0 equiv.) triphenylphosphine (17.4 mg, 0.0663 mmol, 25 mol%), Et_3N (95.7 μL) and phenylacetylene (54.2 mg, 0.531 mmol, 2.0 equiv.) in DMF (0.55 M) was stirred at 50 °C for 10 hours. After the reaction was completed, the mixture was diluted with EtOAc, and quenched with H_2O. The mixture was filtered through a pad of Celite and the filtrate was partitioned. The aqueous layer was extracted with EtOAc for 3 times. The combined organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated. The crude product was then purified by column chromatography (hexane/EtOAc, 30:1) to afford **18** (37.3 mg, 68% yield) as a brown oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, J = 7.2 Hz, 2H), δ 7.71-7.68 (m, 2H), δ 7.64 (t, J = 7.4 Hz, 1H), δ 7.55-7.47 (m, 3H), δ 7.45-7.41 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.0, 136.8, 134.1, 133.0, 130.8, 129.5, 128.63, 128.57, 120.1, 93.1, 86.9.

Conflicts of interest

There are no conflicts of interest to declare

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We have developed one-pot reaction to provide thioester derivatives via sodium thiosulfate as sulfur source under transition metal-free condition.