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REGULAR ARTICLE

Methanesulfonic anhydride-promoted sustainable synthesis of thioesters from feedstock acids and thiols

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Abstract. An unprecedented metal-, halogen- and solvent-free, MSAA-promoted *S*-carbonylation of thiols with feedstock acids has been developed. This new transformation provides an efficient and atom-economic strategy for the synthesis of thioesters in a single operation from readily available and inexpensive starting materials. The reaction avoids the use of expensive and hazardous coupling reagents, bases and generates water as the only by-product, thus making this chemical synthetic process more viable, environment-friendly and contributing towards sustainable chemistry.

Keywords. Dehydrative thioesterification; *S*-carbonylation; MSA; MSAA; Mixed anhydride.

1. Introduction

In the modern era of chemistry, undisputed attention has been placed towards solvent-less technology due to the poisonous, expensive and volatile nature of many organic solvents, particularly chlorinated hydrocarbons.[1–3] With the emergence of the concept of novelty, selectivity, and effectiveness, the synthetic chemists have been very attentive in rendering the required reactions in metal-, halogen-, and solvent-free conditions to lead the goal of triple bottom-line benefits of environmental, economic, and social improvements.[4] Recently, the desire of greener, hazard-free, waste-free, and energy-efficient sustainable synthetic routes has increased for bond-forming steps which are fundamental to the pharmaceutical industries.

Among the widespread category of reactions, thioesterification has seen as a significant example of such fundamental transformation. There exists and continues to be a significant amount of progress in this reaction because thioesters represent excellent building blocks for chemical biology and organic synthesis.[5–8] Thioesters act as an important class of acyl donors and are protagonists in the biosynthesis of many natural polyketide antibiotics, including erythromycin, enterobactin, vancomycin, penicillin, and bacitracin biochemistry.[5,9,10] These air-stable acyl donors are tolerant to column purification on silica gel and therefore easier to handle than the corresponding acyl halides. Examples of applications of thioesters in organic synthesis are illustrated in Scheme 1. Fukuyama *et al.,* established a chemoselective protocol to access the ketones from thioesters using Pd-catalysis and a zinc aryl or alkyl species.[11] Different procedures have also been developed for the synthesis of acetylene ketones, esters, amides, and acylsilanes from thiol esters.[12–14] Furthermore, it is possible to reduce this carboxylic acid derivative selectively to either alcohol or aldehyde depending on the conditions used while leaving other functional groups such as esters and amides intact.[15,16] Sekiya and Lawesson demonstrated the successful replacement of the oxygen atom of thioester by sulfur or CCl_2 group.[17,18] In addition, benzodithioate products can be exploited as an attractive source for the synthesis of different sulfur containing heterocycles. Furthermore, it is possible to synthesize 2-methylthio-1,3-oxazoles from both aryl and alkyl thioesters using *N*-(ethoxycarbonylmethyl)-iminodithiocarbonate.[19]

In consideration of their relevant role in biological systems and their synthetic versatility, preparation of

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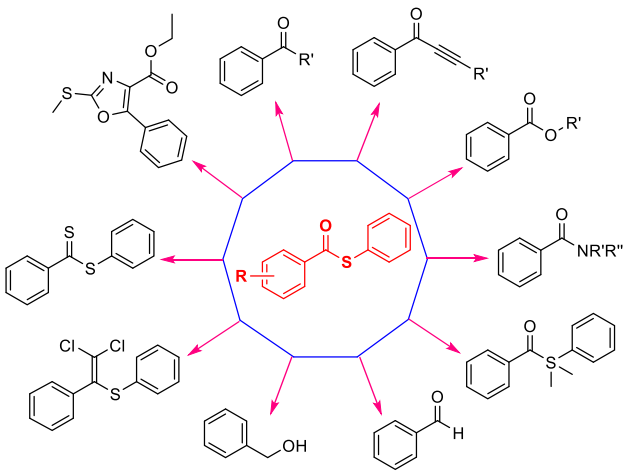


Scheme 1. Thioesters as precursors in organic synthesis.

thioesters is still an urgent need. Despite the broad range of described methods reported for their synthesis, the acylation of thiols or thiolate anions by reaction with carboxylic acid derivatives, namely acid anhydrides and acyl halides in organic solvent[20–36] is probably the most widely used. Moreover, thioesters have been synthesized by direct reaction of carboxylic acids with thiols and in the presence of diverse reaction conditions and catalysts.[37–41] Although most of these approaches provide efficient access to thioesters, they suffer from the use of corrosive reagents, harsh reaction conditions, expensive catalysts or reagents which could have detrimental environmental effects, unfriendly organic solvents and long reaction time. There are many drawbacks associated with the use of moisture sensitive acyl chlorides and anhydrides for *S*-acylation, e.g. reaction of thiols with acyl chlorides can be highly exothermic and this transformation produces an equal amount of non-eco-friendly halide ion when acyl halides were used.[42–46] Therefore, to address the aforementioned challenging issues, we were eager to develop an environmentally benign reaction course, based on readily available inexpensive and eco-friendly precursors and organic reagents for the synthesis of diverse thioesters.

Methanesulfonic acid (MSA) is a low molecular weight compound, derived from biomass and commonly used as a strong acid.[47–49] MSA is considered to be attractive from a sustainability point of view and it has been used to catalyse a wide variety of transformations and as a solvent for rearrangement and condensation reactions. Suitable industrial processes have already been disclosed for the biodegradation of MSA, would be beneficial for waste steam processing.[50] Eaton's reagent (P_2O_5/MSA) has been used in intermolecular acylation reaction.[51–55] The use of MSA as a solvent for similar reactions promoted by alumina or graphite has also been detailed.[56–58] Methanesulfonic anhydride (MSAA), the anhydride of MSA, has been used as an excellent reagent for the improvement in Friedel-Crafts acylation reaction.[59] MSAA is readily available, inexpensive, eco-friendly, bench stable, non-hygroscopic reagent and easy to handle. However, to the best of our knowledge, MSAA has never been explored for *S*-carbonylation of thiols leading to thioesters. Intrigued by the aforementioned attractive assets of MSAA and our ongoing work on metal-free catalysis,[60–65] in the present paper, we report a MSAA-promoted direct thioester formation from feedstock acids and thiols under solvent-free conditions.

2. Experimental

2.1 *General information*

All chemicals were purchased at the highest purity grade and used for solvent-free protocol without further purification. All syntheses were performed in standard glassware without any special precautions taken for the removal of moisture or air. Merck precoated 0.25 mm silica gel plates (60F-254) were used to perform the analytical TLC. Visualization was achieved with shortwave UV light. Column chromatography was carried out with silica gel (100–200 mesh) using EtOAc/hexanes. NMR spectra were recorded in $CDCl_3$ and using TMS as internal standard on JEOL ECX-400-II. Chemical shifts of ^{1}H NMR spectra were given in parts per million with respect to TMS and the coupling constant *J* was measured in Hz. The signals from solvent $CDCl_3$, 7.26 and 77.0 ppm, are set as the reference peaks in ^{1}H NMR and ^{13}C NMR spectra, respectively. Melting points were recorded on a Perfit melting point instrument and are uncorrected. The following abbreviations were used to describe the multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet.

2.2 *General procedure for the synthesis of thioesters* ***3***

To a mixture of carboxylic acid **1** (0.5 mmol) and thiol **2** (0.6 mmol), was added methanesulfonic anhydride (0.65 mmol, 1.3 equiv.) The reaction was heated to 80 °C for 4 h, after which the mixture was placed under high vacuum at room temperature. The reaction

mixture was diluted with ether (10 mL) and the slurry was kept at 0 °C for 20 min. The ether solution was concentrated and the residue was subjected to silica gel column chromatography, using ethyl acetate and hexanes (5:95) as eluent to afford the pure product **3**.

2.3 *Characterization data*

2.3a *S-p-Tolyl 4-nitrobenzothiolate (3aa):*[66]: Yield: 131 mg (96%) as light yellow solid; M.p.: 101–103 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, J = 8.4 Hz, 2H), 8.17 (d, J = 8.8 Hz, 2H), 7.46 (s, 1H), 7.39 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 2.42 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.4, 150.7, 141.3, 140.6, 134.91, 130.5, 128.6, 124.1, 122.6, 21.5 ppm.

2.3b *S-Phenyl 4-nitrobenzothiolate (3ab):*[67]: Yield: 124 mg (96%) as light yellow solid; MP: 141–143 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (d, J = 8.8 Hz, 2H), 8.18 (d, J = 8.8 Hz, 2H), 7.54–7.44 (m, 5H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.0, 150.7, 141.3, 135.0, 130.2, 129.6, 128.6, 126.2, 124.1 ppm.

2.3c *S-4-Chlorophenyl 4-nitrobenzothiolate (3ac):*[68]: Yield: 136 mg (93%) as light yellow solid; M.p.: 75–77 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (d, J = 8.8 Hz, 2H), 8.17 (d, J = 8.4 Hz, 2H), 7.46 (t, J = 11.2 Hz, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.5, 150.8, 141.1, 136.7, 136.2, 129.9, 128.6, 124.6, 124.2 ppm.

2.3d *S-4-Bromophenyl 4-nitrobenzothiolate (3ad):*[65]: Yield: 150 mg (89%) as light yellow solid; M.p.: 74–76 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (d, J = 8.0 Hz, 2H), 8.17 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.3, 150.9, 141.0, 136.4, 132.8, 128.6, 125.3, 125.0, 124.2 ppm.

2.3e *S-p-Tolylbenzothiolate (3ba):*[69]: Yield: 105 mg (92%) as white solid; M.p.: 73–75 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.0 (d, J = 7.6 Hz, 2H), 7.58 (t, J = 7.6 Hz, 1H), 7.48–7.37 (m, 4H), 7.25 (d, J = 8.4 Hz, 2H), 2.38 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.8, 139.9, 136.9, 135.1, 133.7, 130.2, 128.8, 127.6, 123.8, 29.5 ppm.

2.3f *S-Phenyl benzothiolate (3bb):*[70]: Yield: 96 mg (90%) as white solid; M.p.: 51–53 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, J = 7.6 Hz, 1H), 8.01 (d, J = 7.6 Hz, 1H), 7.64–7.57 (m, 1H), 7.51–7.42 (m, 6H), 7.28–7.19 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.3, 136.7, 135.2, 133.8, 129.6, 129.3, 128.8, 127.6, 127.4 ppm.

2.3g *S-4-Chlorophenyl benzothiolate (3bc):*[71]: Yield: 106 mg (85%) as white solid; MP: 73–75 °C; ^{1}HNMR (400 MHz, $CDCl_3$): δ 8.02 (d, J = 8.0 Hz, 2H), 7.62 (t, J = 7.2 Hz, 1H), 7.52–7.44 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.7, 136.4, 136.1, 134.0, 129.6, 128.9, 127.6, 125.9 ppm.

2.3h *S-4-Bromophenyl benzothiolate (3bd):*[72]: Yield: 125 mg (85%) as white solid; M.p.: 70–71 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, J = 7.6 Hz, 2H), 7.64–7.58 (m, 3H), 7.50 (t, J = 7.6 Hz, 2H), 7.38 (d, J = 7.6 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.6, 136.6, 136.4, 134.0, 132.6, 128.9, 127.6, 126.5, 124.4 ppm.

2.3i *S-Napthalen-2-yl benzothiolate (3be):*[73]: Yield: 116 mg (88%) as white solid; M.p.: 101–103 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, J = 7.2 Hz, 2H), 7.93–7.85 (m, 3H), 7.65–7.49 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.6, 136.7, 135.1, 133.8, 133.7, 133.5, 131.5, 128.9, 128.9, 128.1, 127.9, 127.6, 127.3, 126.6, 124.8 ppm.

2.3j *S-p-Tolyl 3-methylbenzothiolate (3ca):*[74]: Yield: 108 mg (89%) as light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84–7.81 (m, 2H), 7.44–7.34 (m, 4H), 7.28–7.26 (m, 2H), 2.43 (s, 3H), 2.41 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.8, 139.8, 138.7, 136.8, 135.1, 134.4, 130.2, 128.7, 128.0, 124.8, 124.0, 21.5, 21.4 ppm.

2.3k *S-Phenyl 3-methylbenzothiolate (3cb):*[71]: Yield: 101 mg (89%) as white solid; M.p.: 95–97 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83–7.81 (m, 1H), 7.52–7.34 (m, 6H), 7.28–7.19 (m, 1H), 2.42 (s, 3H), 2.41 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.3, 138.8 136.8, 135.2, 134.5, 129.6, 129.3, 128.7, 128.0, 128.0, 124.8, 21.4 ppm.

2.3l *S-4-Chlorophenyl 3-methylbenzothiolate (3cc):*[65]: Yield: 105 mg (83%) as light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83–7.81 (m, 2H), 7.44–7.36 (m, 6H), 2.44 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.8, 138.8, 136.5, 136.4, 136.0, 134.7, 129.6, 128.8, 128.0, 126.1, 124.8, 21.4 ppm.

2.3m *S-Naphthalen-2-yl 3-methylbenzothiolate (3ce):*[65]: Yield: 115 mg (83%) as white solid; M.p.: 95–97 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (s, 1H), 7.94–7.85 (m, 5H), 7.58–7.38 (m, 5H), 2.45 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.6, 141.6, 138.8, 136.8, 135.1, 134.6, 133.7, 133.5, 131.5, 128.9, 128.1, 127.9, 127.3, 126.6, 126.6, 124.9, 124.9, 21.5 ppm.

2.3n *S-p-Tolyl 4-methoxybenzothiolate (3da):*[71]: Yield: 107 mg (91%) as light yellow solid; M.p.: 61–63 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.0 (d, J = 9.2 Hz, 2H), 7.39 (d, J = 10.0 Hz, 2H), 7.27–7.25 (m, 2H), 6.95 (d, J = 9.2 Hz, 2H), 3.88 (s, 3H), 2.40 (s, 3H) ppm; ^{13}CNMR (100 MHz, $CDCl_3$): δ 189.1, 164.0, 139.7, 135.2, 130.13, 129.8, 129.6, 124.1, 114.0, 55.6, 21.5 ppm.

2.3o *S-Phenyl 4-methoxybenzothiolate (3db):*[70]: Yield: 110 mg (90%) as white solid; M.p.: 92–94 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, J = 8.8 Hz, 1H), 8.01 (d, J = 8.8 Hz, 1H), 7.52–7.40 (m, 3H), 7.28–7.19 (m, 2H), 6.97 (t, J = 10.0 Hz, 2H), 3.90 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.7, 135.3, 132.4, 129.8, 129.52, 129.3, 125.8, 121.9, 113.9, 55.6 ppm.

2.3p *S-4-Chlorophenyl 4-methoxybenzothiolate (3dc):*[71]: Yield: 121 mg (87%) as white solid; M.p.: 93–95 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 8.8 Hz, 2H), 7.43 (t, J = 9.6 Hz, 4H), 6.96 (d, J= 8.8 Hz, 2H), 3.89 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.1, 164.2, 136.5, 135.9, 129.8, 129.5, 129.2, 126.2, 114.1, 55.7 ppm.

2.3q *S-4-Bromophenyl 4-methoxybenzothiolate (3dd):*[71]: Yield: 126 mg (78%) as white solid; M.p.: 102–104 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 8.8 Hz, 2H), 7.57 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 6.96 (d, J= 8.4 Hz, 2H), 3.89 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.9, 164.2, 136.7, 132.4, 129.9, 129.2, 126.9, 124.2, 114.1, 55.7 ppm.

2.3r *S-Naphthalen-2-yl 4-methoxybenzothiolate (3de):*[65]: Yield: 93 mg (75%) as white solid; M.p.: 123–125 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (s, 1H), 7.94–7.85 (m, 4H), 7.58–7.38 (m, 5H), 7.23–7.17 (m, 1H), 2.45 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.9, 164.1, 135.1, 133.7, 133.5, 131.7, 129.8, 129.5, 128.8, 128.1, 127.9, 127.2, 126.6, 125.1, 114.0, 55.7 ppm.

2.3s *S-p-Tolylethanethiolate (3ea):*[75]: Yield: 69 mg (83%) as yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 2.40 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.8, 139.8, 134.5, 130.1, 124.5, 30.2, 21.4 ppm.

2.3t *S-Phenyl ethanethiolate (3eb):*[76]: Yield: 61 mg (80%) as yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (m, 5H), 2.43 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.2, 134.5, 129.5, 129.3, 128.0, 30.3 ppm.

2.3u *S-4-Chlorophenyl ethanethiolate (3ec):*[76]: Yield: 73 mg (78%) as light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42–7.26 (m, 4H), 2.42 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.5, 135.9, 135.7, 129.5, 126.4, 30.3 ppm.

2.3v *S-4-Bromophenyl ethanethiolate (3ed):*[75]: Yield: 90 mg (78%) as light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, J= 8.0 Hz, 2H), 7.26–7.24 (m, 2H), 2.41 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.4, 136.0, 132.5, 127.0, 124.2, 30.3 ppm.

2.3w *S-Naphthalen-2-yl ethanethiolate (3ee):*[75]: Yield: 81 mg (80%) as white solid; M.p.: 105–107 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98–7.95 (m, 1H), 7.88–7.73 (m, 4H), 7.53–7.51 (m, 1H), 7.46–7.44 (m, 1H), 2.46 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.5, 134.4, 133.6, 133.4, 130.98, 128.9, 128.1, 127.9, 127.3, 126.7, 125.3, 30.4 ppm.

2.3x *S-Benzyl 4-nitrobenzothiolate (3af):*[77]: Yield: 132 mg (97%) as light yellow solid; M.p.: 80–82 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, J = 8.8 Hz, 2H), 8.09 (d, J = 8.8 Hz, 2H), 7.37–7.24 (m, 5H) 4.34 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.9, 150.5, 141.4, 136.6, 129.1, 128.8, 128.3, 127.7, 124.0, 34.0 ppm.

2.3y *S-Benzyl benzothiolate (3bf):*[71]: Yield: 108 mg (95%) as white solid; M.p.: 36–38 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, J = 7.6 Hz, 2H), 7.56 (t, J = 7.6 Hz, 1H), 7.45–7.38 (m, 4H), 7.34–7.24 (m, 3H) 4.34 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.4, 137.6, 136.9, 133.6, 129.1, 128.8, 128.8, 127.5, 127.4, 33.5 ppm.

2.3z *S-Benzyl 3-methylbenzothiolate (3cf):*[77]: Yield: 109 mg (90%) as white solid; M.p.: 81–83 °C; ^{1}H

NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 6.8 Hz, 2H), 7.38–7.22 (m, 7H), 4.31 (s, 2H), 2.39 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.5, 138.6, 137.6, 136.9, 134.3, 129.1, 128.7, 128.6, 127.9, 127.4, 124.6, 33.4, 21.4 ppm.

2.3aa *S-Benzyl 4-methoxybenzothiolate (3df)*:[78]: Yield: 107 mg (92%) as white solid; M.p.: 53–55 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 8.8 Hz, 2H), 7.38–7.22 (m, 5H), 6.91 (d, J = 8.8 Hz, 2H), 4.30 (s, 2H), 3.84 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.9, 163.9, 137.9, 129.7, 129.6, 129.1, 128.7, 127.3, 113.9, 55.6, 33.3 ppm.

2.3ab *S-Benzyl ethanethiolate (3ef)*:[75]: Yield: 73 mg (88%) as light yellow oil; ^1H NMR (400 MHz, $CDCl_3$): δ 7.31–7.20 (m, 5H), 4.10 (s, 2H), 2.33 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.3, 137.7, 128.9, 128.7, 127.4, 35.5, 30.4 ppm.

2.3ac *S-Cyclohexyl 4-nitrobenzothiolate (3ag)*:[79]: Yield: 125 mg (94%) as light yellow oil; ^1H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, J = 8.4 Hz, 2H), 8.09 (d, J = 8.4 Hz, 2H), 3.81–3.71 (m, 1H), 2.04–1.96 (m, 2H), 1.77–1.74 (m, 2H), 1.65–1.59 (m, 2H), 1.53–1.45 (m, 2H), 1.37–1.30 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.4, 150.4, 142.1, 128.2, 123.9, 43.5, 33.0, 26.0, 25.6 ppm.

2.3ad *S-Cyclohexylbenzothiolate (3bg)*:[78]: Yield: 102 mg (93%) as yellow oil; ^1H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 7.2 Hz, 2H), 7.53 (t, J = 7.6 Hz, 1H), 7.42 (t, J = 8.0 Hz, 2H), 3.76–3.70 (m, 1H), 2.04–2.01 (m, 2H), 1.76–1.73 (m, 3H), 1.63–1.60 (m, 2H), 1.56–1.43 (m, 2H), 1.35–1.28 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.9, 137.5, 133.2, 128.6, 127.2, 42.6, 33.2, 26.1, 25.7 ppm.

2.3ae *S-Cyclohexyl3-methylbenzothiolate (3cg)*:[65]: Yield: 104 mg (89%) as light yellow oil; ^1H NMR (400 MHz, $CDCl_3$): δ 7.77–7.73 (m, 2H), 7.36–7.19 (m, 2H), 3.78–3.70 (m, 1H), 2.46–2.38 (m, 3H), 2.07–2.00 (m, 2H), 1.82–1.73 (m, 2H), 1.68–1.56 (m, 2H), 1.40–1.30 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.1, 138.4, 137.6, 133.9, 128.5, 127.7, 124.4, 42.5, 33.3, 26.1, 25.7, 21.4 ppm.

2.3af *S-Cyclohexyl 4-methoxybenzothiolate (3dg)*:[41]: Yield: 113 mg (90%) as light yellow oil; ^1H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 3.82 (s, 3H), 3.71–3.64 (m, 1H), 2.02–1.99 (m, 2H), 1.80–1.71 (m, 2H), 1.62–1.46 (m, 5H), 1.44–1.28 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.4, 163.6, 130.4, 129.3, 113.7, 55.5, 42.4, 33.4, 26.1, 25.7 ppm.

2.3ag *Methyl 3-(4-nitrobenzoylthio)propanoate (3ah)*:[65]: Yield: 121 mg (90%) as light yellow oil; ^1H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, J = 8.4 Hz, 2H), 8.09 (d, J = 8.4 Hz, 2H), 3.71 (s, 3H), 3.35 (t, J = 6.8 Hz, 2H), 2.75 (t, J = 6.8 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.1, 172.0, 150.6, 141.4, 128.3, 124.0, 52.1, 33.9, 24.6 ppm.

2.3ah *Methyl 3-(benzoylthio)propanoate (3bh)*:[65]: Yield: 106 mg (95%) as colourless oil; ^1H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J = 7.2 Hz, 2H), 7.55 (t, J = 7.6 Hz, 1H), 7.42 (t, J = 7.6 Hz, 2H), 3.69 (s, 3H), 3.30 (t, J = 6.8 Hz, 2H), 2.72 (t, J = 7.2 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.52, 172.22, 136.87, 133.57, 128.70, 127.29, 51.93, 34.33, 24.09 ppm.

2.3ai *Methyl 3-(3-methylbenzoylthio)propanoate (3ch)*:[65]: Yield: 105 mg (88%) as light yellow oil; ^1H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 6.4 Hz, 2H), 7.34–7.13 (m, 2H), 3.67 (s, 3H), 3.26 (t, J = 7.2 Hz, 2H), 2.69 (t, J= 7.2 Hz, 2H), 2.36 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.7, 172.3, 138.6, 136.9, 134.4, 128.6, 127.8, 124.5, 52.0, 34.4, 24.1, 21.4 ppm.

2.3aj *Methyl 3-(4-methoxybenzoylthio)propanoate (3dh)*:[80]: Yield: 95 mg (85%) as light yellow oil; ^1H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, J = 8.8 Hz, 2H), 6.89 (d, J= 8.8 Hz, 2H), 3.83 (s, 3H), 3.68 (s, 3H), 3.27 (t, J = 7.2 Hz, 2H), 2.70 (t, J = 6.8 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.9, 173.2, 163.9, 129.8, 129.5, 113.8, 55.6, 51.9, 34.5, 24.0 ppm.

2.3ak *S-o-Tolylbenzothiolate (3ib)*:[66]: Yield: 106 mg (93%) as colorless oil; ^1H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, J = 7.6 Hz, 2H), 7.61 (t, J = 7.2 Hz, 1H), 7.49 (t, J = 7.2 Hz, 4H), 7.40 –7.36 (m, 2H), 2.40 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.5, 139.2, 136.8, 135.8, 133.7, 132.2, 130.5, 129.2, 128.8, 127.6, 127.1, 21.4 ppm.

2.3al *S-o-Tolylethanethiolate (3ie)*:[81]: Yield: 70 mg (84%) as colorless oil; ^1H NMR (400 MHz, $CDCl_3$): δ 7.30–7.26 (m, 1H), 7.22–7.19 (m, 3H), 2.38 (s, 3H), 2.34 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.5, 139.2, 136.2, 131.6, 130.4, 129.1, 127.7, 30.3, 21.4 ppm.

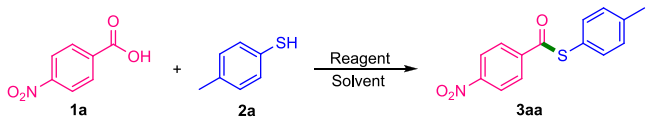
2.3am *S-m-Tolylbenzothiolate (3jb):*[66]: Yield: 102 mg (90%) as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, J = 7.6 Hz, 2H), 7.62 (t, J = 7.6 Hz, 1H), 7.50 (t, J = 7.6 Hz, 3H), 7.42–7.38 (m, 2H), 7.30–7.26 (m, 1H), 2.43 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.7, 142.8, 136.9, 136.5, 133.7, 130.9, 130.3, 128.8, 127.6, 126.9, 126.8, 20.9 ppm.

2.3an *S-m-Tolylethanethiolate (3je):*[82]: Yield: 72 mg (87%) as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, J = 8.0 Hz, 1H), 7.36–7.31 (m, 2H), 7.24–7.20 (m, 1H), 2.42 (s, 3H), 2.36 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.9, 142.0, 137.0, 130.8, 130.2, 127.5, 126.7, 30.3, 20.8 ppm.

3. Results and Discussion

Initially, 4-nitrobenzoic acid (**1a**) and 4-methylthiophenol (**2a**) were chosen as model substrates to screen the optimal conditions, and the results are summarized in Table 1. In our first attempt, trifluoroacetic anhydride (TFAA) was used for the preparation of thioester. Delightedly, 90% yield of the desired thiol ester **3aa** was obtained, when the reaction was carried out in acetonitrile at 80 °C (entry 1). While this fluorinated reagent was beneficial, it suffered from a few drawbacks such as the mass of waste associated with stoichiometric reagent and the process for the disposal of fluorinated waste streams found to be difficult. The reaction was sensitive to solvent: it appeared limited to aprotic solvents in a model scheme (entries 2 and 3), and very low yield of product was observed with the use of tetrahydrofuran (THF) under otherwise identical conditions (entry 3) but there was no formation of even traces of thiolate in solvent-free case (entry 4). Afterwards, we began to consider how to improve this reaction by avoiding the use of halogenated reagents. We reasoned that a stronger acid than TFAA may extend the reaction in a green and economic fashion. Thus, we sought a strong acid, with a low molecular weight, and preferably not halogenated to aid waste

Table 1. Optimization of reaction conditions[a].



Entry	Reagent (equiv)	Solvent (mL)	Temperature	Time (h)	Yield[b] (%)
1	TFAA (1.3)	MeCN (5)	80 °C	6	90
2	TFAA (1.3)	CH_2Cl_2 (5)	Reflux	6	90
3	TFAA (1.3)	THF (5)	Reflux	12	25
4[c]	TFAA (1.3)	Neat	80 °C	24	ND
5	MSAA (1.3)	CH_2Cl_2 (5)	80 °C	4	96
6	MSAA (1.3	MeCN (5)	Reflux	4	96
7	MSAA (1.3)	Neat	80 °C	4	96
8	MSAA (1.2)	Neat	80 °C	6	90
9	MSAA (1.0)	Neat	80 °C	15	85
10	MSAA (1.3)	Neat	60 °C	8	85
11	MSAA (1.3)	Neat	40 °C	15	85
12	MSAA (1.3)	Neat	100 °C	4	96
13[d]	–	–	80 °C	24	NR

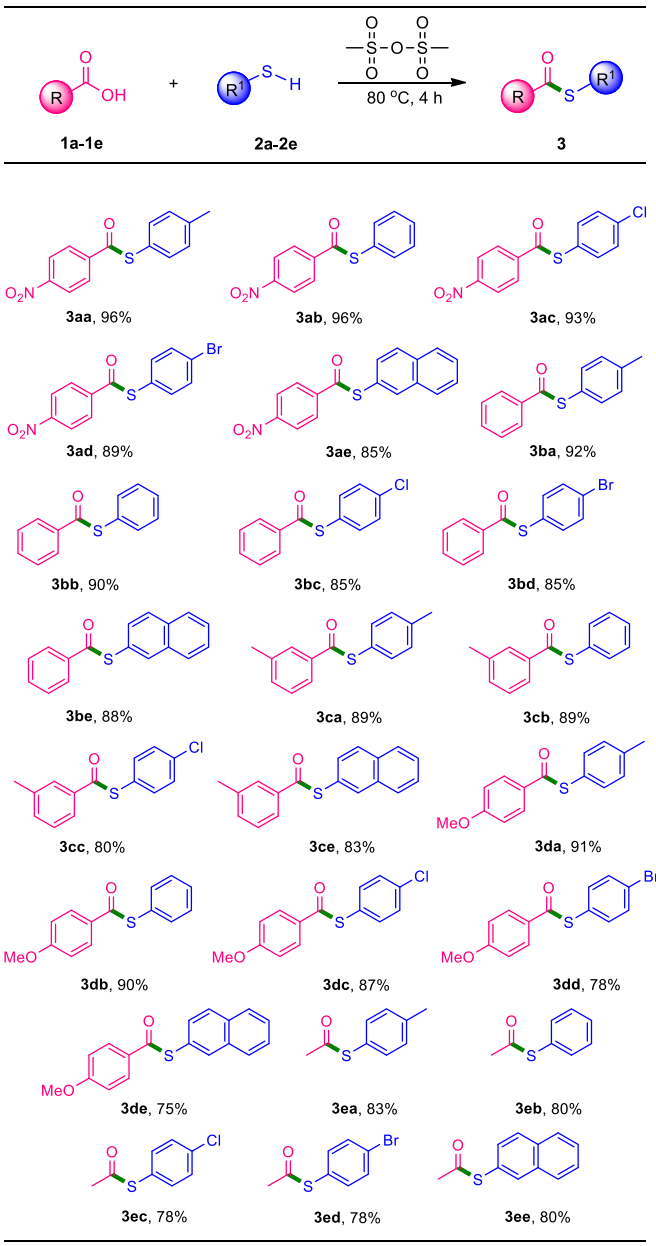
[a]Conditions: **1a** (0.5 mmol) **2a** (0.6 mmol).

[b]Yield of isolated product.

[c]ND = Not determined.

[d]NR = No reaction.

Table 2. MSAA-promoted *S*-carbonylation of aryl thiols with carboxylic acids[ab].

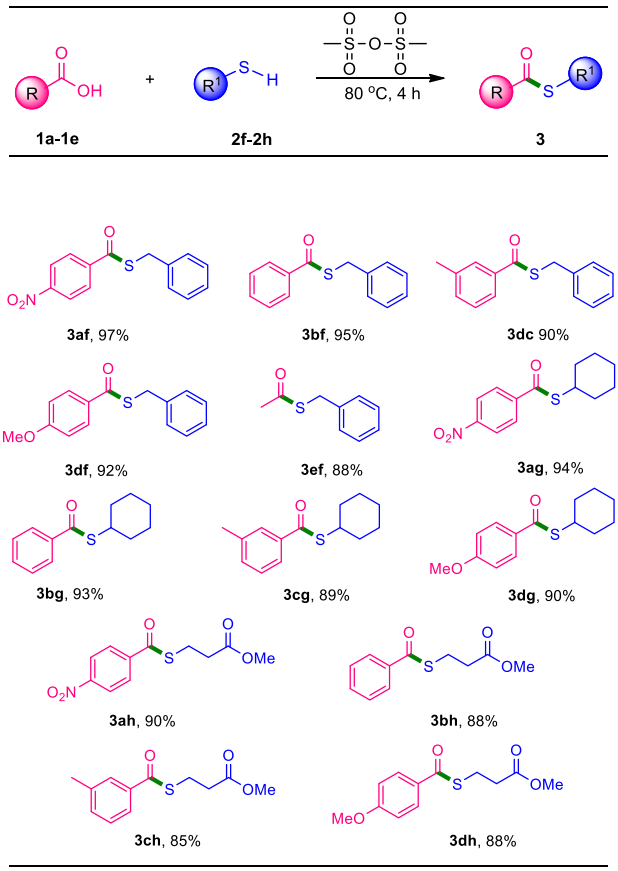


[a]Reaction conditions: feedstock acid **1** (0.5 mmol), alryl thiol **2** (0.6 mmol), MSAA (0.65 mmol), 80 °C, 4 h.

[b]Yield of pure product.

treatment. This consideration led us to use methanesulfonic anhydride (MSAA). We began the work by screening conditions similar to those used with TFAA. Gratifyingly, the desired product **3aa** was obtained in excellent yield when the reaction was carried out under the influence of MSAA in dichloromethane (entry 5). Switching the solvent to acetonitrile did not affect the rate of reaction and the yield of the product (entry 6). The reaction worked well under neat conditions and the reactivity of precursors **1a** and **2a** was

Table 3. MSAA-promoted S-carbonylation of alkylthiols with carboxylic acids[ab].



[a]Reaction conditions: feedstock acid **1** (0.5 mmol), alkyl thiol **2** (0.6 mmol), MSAA (0.65 mmol), 80 °C, 4 h.
[b]Yield of pure product.

preserved (entry 7). Probably, the reaction of MSAA with thiol under the influence of MSAA may be proceeding *via* the *in situ* generation of mixed anhydride species which releases methanesulfonic acid. This acid could be strong enough to facilitate the subsequent reaction with thiol leading to thioester. Then this process was examined to check the impact on reaction time and yield by varying the quantity of MSAA. Decreasing the loading of MSAA from 1.3 to 1.0 equiv., resulted in a somewhat diminished rate of the reaction and the yield of **3aa** (entries 8 and 9). This screening led to the identification that stoichiometric amount of MSAA is necessary to furnish the product **3aa** in excellent yield. It is noteworthy that variation in the yield of product was observed while changing the reaction temperature. Excellent amount of product was formed at 80 °C (entry 4); lowering the reaction temperature up to 40 °C gave the product in reduced yield (entry 10). Even longer reaction time could not improve the yield of the product (entry 11), yet the reaction at 100 °C did not exhibit obvious promotion in the rate of reaction and the yield of **3aa** (entry 12) with respect to the results of entry 7. The reaction failed to promote the carbonylation of **1a** in the absence of MSAA, indicating the important role of this anhydride in the direct synthesis of thioester (entry 13). Thus the exclusive tuning of **1a** and **2a** with MSAA at 80 °C provided the best conditions for further studies.

After optimizing the reaction conditions (Table 1, entry 7), we investigated the substrate scope and generality for this novel thioester-forming protocol. For this purpose, the reactions of acids **1** with aryl thiols **2a–2e** were first studied, and the results are collected in Table 2. Thiophenol and its derivatives with electron-donating and withdrawing substituents at the *para*-position of the phenyl group, when treated with **1a**, were transformed into the corresponding products **3aa–3ad** with very good to excellent yields. The reaction of **1a** with bulky substrate 2-naphthol (**2e**) furnished the thiolate **3ae** in 85% yield. Similarly, benzoic acid (**1b**) reacted smoothly with **2a–2e**, and afforded the target products **3ba–3be** in high yields. Encouraged by these results, benzoic acids bearing electron-donating substituents **1c** and **1d** were next investigated to check the efficacy of the present reaction system. These substrates responded nicely in the current protocol to furnish the target compounds **3ca, 3cb, 3cc, 3ce** and **3da–3de** in good to excellent yields. Remarkably, aliphatic acid **1e** could also provide the aryl alkyl thioesters **3ea–3ee** in good yields ranging from 78–83%.

With the promising results obtained in the case of aryl thiols, we turned our attention towards alkyl thiols to broaden the substrate scope of this elegant methodology. As revealed in Table 3, the developed process once again showed good functional group compatibility. Carboxylic acids possessing electron-withdrawing groups displayed high reactivity with benzylmercaptan (**2f**) under the optimized conditions and generated the product **3af** in excellent yield. Benzoic acid and its derivatives bearing *m*-Me and *p*-OMe substituents (**1b**, **1c** and **1d**) served as powerful aroyl surrogates when treated with thiol **2f** and furnished the *S*-aroylated products **3bf**, **3cf** and **3df** in high yields. Moreover, it was possible to expand the scope of this carbonylation process to acetic acid and the product **3ef** was seen in a very good yield. As expected, benzoic acids **1a–1d** worked well with cyclohexanethiol (**2g**) and afforded their corresponding products **3ag–3dg** in 90–94% isolated yields.

Further, synthetically attractive ester functionalized thiol **2h**, acts as an ideal substrate with **1a–1d** in this

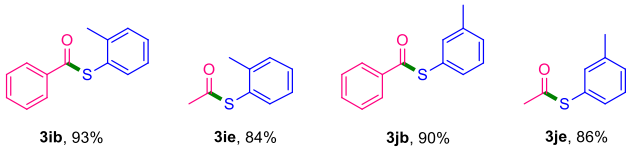


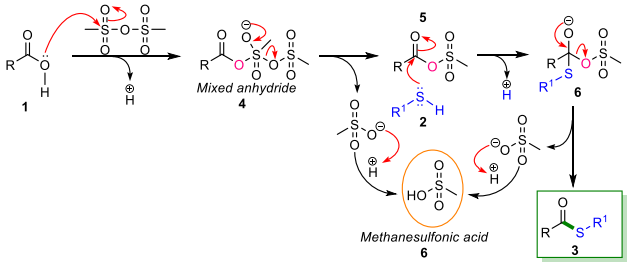
Figure 1. Scope of thiocresols: Reaction conditions: feedstock acid **1** (0.5 mmol), thiocresol **2i/2j** (0.6 mmol), MSAA (0.65 mmol), 80 °C, 4 h.

protocol and furnished the alkyl thioesters **3ah–3dh** in very good yields.

With the above positive results, structurally diverse thiocresols were explored as well to examine their substituent effect at different positions of phenyl ring on product outcome, and the representative results are presented in Figure 1. Thiocresols such as *ortho*-thiocresol (**2i**) and *meta*-thiocresol (**2j**) were found to be ideal reaction partners with benzoic acid (**2b**) and acetic acid (**2e**) under similar reaction conditions affording the corresponding products **3ib**, **3ie**, **3jb** as well as **3je** in good to excellent yields. The above observations explicate that thiophenols with the methyl group in *ortho*-, *meta*- or *para*-position showed no significant difference in the yields. Compared to the 92% yield of **3ib** might be due to the steric effect of the methyl group on the *ortho*-position and similarly in the case of **3ea** and **3ie**.

Finally, in order to demonstrate the synthetic utility of developed process; the reaction of 4-nitrobenzoic acid (**1a**) and 4-methylthiophenol (**2f**) as starting materials was conducted on a 5 mmol scale under similar reaction conditions. The product *S*-benzyl 4-nitrobenzothiolate (**3af**) was isolated in a quite good amount. This confirmed the efficacy of the present solvent-free track for the gram-scale preparation of thioesters (Scheme 2).

All these results described above indicated that *in situ* generated mixed anhydride mediates the coupling with thiols which is the key step for the success of this dehydrative thioesterification process. Thus, the present methodology for the carbonylation of thiols under neat conditions is highly versatile and holds the potential for the synthesis of a large variety of thioesters.

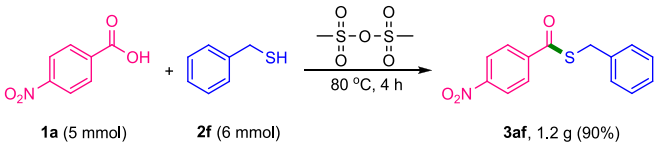


Scheme 3. Plausible reaction mechanism.

On the basis of the above experimental results and the previous literature report,[59] a plausible mechanism for this transformation is proposed in Scheme 3. The *in situ* generation of mixed anhydride intermediate **4** from carboxylic acid **1** and MSAA triggers the reaction by the release of methanesulfonate and activated complex **5** of carboxylic acid **1**. The ensuing intermolecular attack of thiol **2** toward **5** and subsequent elimination of methanesulfonate liberates the thioester product **3**. The methanesulfonate combines with proton to give the by-product methanesulfonic acid (**6**).

4. Conclusions

In summary, we have established an efficient and novel strategy for dehydrative nucleophilic substitution reaction of feedstock acids with thiols, which systematically unravels the feasibility and practicality of thioester formation in a step- and atom-economical fashion. The successful implementation of this C–S bond-forming strategy relies on the *in situ* generation of mixed anhydride intermediate from carboxylic acid and cheap and easily handled MSAA which was an initial starting point to drive this reaction. The reaction can be run at gram-scale. Moreover, the power of this sustainable paradigm for the synthesis of thioesters has been fully exemplified by the tolerance of various functionalities that can serve as useful synthetic handles for subsequent chemical manipulation. We believe that this metal-, halogen- and solvent-free approach for the synthesis of thioesters will generate broad applications among practitioners of synthetic,



Scheme 2. Gram-scale synthesis of thioester **3af**.

pharmaceutical and industrial chemistry. Exploring the utility of MSAA to construct other useful products is currently underway in our laboratory.

Supplementary Information (SI)

Copies of NMR spectra of the products are available in Supplementary Information.

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