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An Odorless, One-Pot Synthesis of Thioesters from Organic Halides, Thiourea and Benzoyl Chlorides in Water

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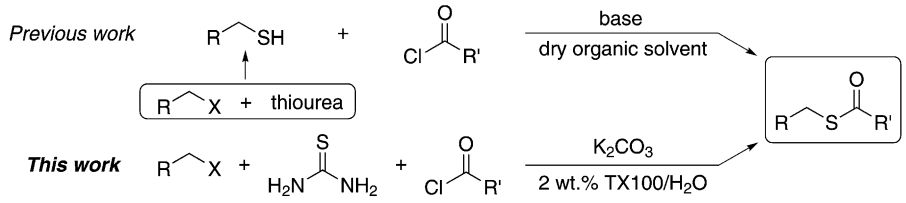
Abstract: Thioesterification can be realized *via* an odorless, one-pot reaction through the *in situ* generation of *S*-alkylisothiouronium salts from organic halides and thiourea in aqueous Triton X-100 (TX100) micelles. The protocol is free of foul-smell thiols and organic solvents, and operates under mild conditions, thereby offering considerable potential for applications in organic synthesis.

Keywords: *S*-alkylisothiouronium salts; green chemistry; micelles; multicomponent reactions; thioesterification; water chemistry

Thioesters are a class of important synthetic intermediates in organic synthesis, that are applied for peptide coupling,[1] acyl transfer,[2] protecting groups for thiols,[3] and also as coupling partners in organometallic reactions.[4] They are also key intermediates in various biological systems,[5] and are widely present in a number of biologically active and medicinal agents.[6] Traditionally, thiols[7] or thiocarboxylates[8] are required for the synthesis of such versatile compounds. These methodologies, however, suffer from limitations such as difficulties encountered in handling the foul-smelling thiols and thioacids. In order to eliminate these problems, several odorless protocols have been reported. Disulfides as the thiol equivalent precursors can react with aldehydes by radical-mediated couplings,[9] and thioesters can also be synthesized *via* thioaroylate ions generated *in situ* from acyloxyphosphonium salts and benzyltriethylammonium tetrathiomolybdate.[10] Nevertheless, these odorless procedures also encounter disadvantages, such as pre-preparation of disulfides from thiols, use of non-commercial or high-cost reagents.

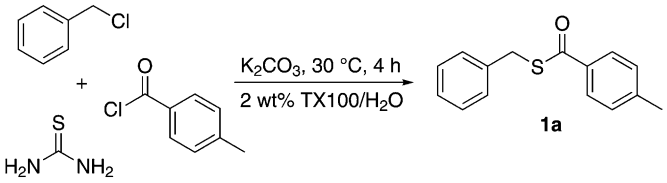
Recently, several attempts have also been made for the formation of thioethers through the *in situ* generation of *S*-alkylisothiouronium salts in place of thiols which are, in turn, formed from organic halides and thiourea.[11] Ideally, the thioesterification reaction would be carried out in water as the only medium by an odorless method.[12] Along this line, we describe here an odorless, one-pot process for the synthesis of thioesters using thiourea as the sulfur source in water, avoiding the pre-generation of thiols with thiourea and organic halides and the use of organic solvents as in the previous literature[13] (Scheme 1).

It is common knowledge that carboxylic acid halides are quite water-sensitive (leading to rapid hydrolysis), so it seems virtually impossible to perform the reactions of carboxylic acid halides in water. Adding surfactants in water to form micelles may decrease the kinetics of hydrolysis by preventing and/or hindering acyl halides from encountering the water molecules.[14] As a starting point, we performed a test reaction of thiourea, benzyl chloride and 4-toluoyl chloride using K_2CO_3 as the base in 2 wt% SDS aqueous



Scheme 1. The synthesis of thioesters using thiourea as the sulfur source.

Table 1. Optimization of the reaction conditions.[a]



Entry	Surfactant	Base	Yield [%][b]
1	SDS[c]	K_2CO_3	98[d]
2	SDS	K_2CO_3	82
3	–	K_2CO_3	63
4	TX100[e]	K_2CO_3	87 (78)[f]
5	CTAB[g]	K_2CO_3	79
6	Tween60[h]	K_2CO_3	71
7	Span80[i]	K_2CO_3	75
8	TPGS-750-M[j]	K_2CO_3	80
9	TX100	NaOH	74
10	TX100	NEt_3	78
11	TX100	–	n.r.
12	TX100	K_2CO_3	82[f,k]

[a] *Reaction conditions:* 4-toluoyl chloride 0.5 mmol, thiourea 1.0 mmol, benzyl chloride 1.0 mmol, K_2CO_3 1.5 mmol, 2 wt% solution of aqueous surfactant 1.0 mL, 4 h, 30 °C.
[b] The yield is determined by GC.
[c] Sodium dodecyl sulfate.
[d] The reaction is carried out at 60 °C for 8 h.
[e] *t*-Octylphenoxypolyethoxyethanol.
[f] Isolated yield.
[g] Cetyltrimethylammonium bromide.
[h] Polyoxyethylene (20) sorbitan monostearate.
[i] Sorbitane monooleate.
[j] Polyethanyl-α-tocopherylsuccinate.
[k] *Reaction conditions:* 4-toluoyl chloride 10 mmol, thiourea 20 mmol, 4-tolyl chloride 20 mmol, K_2CO_3 30 mmol, reaction medium 10 mL, 8 h, 30 °C.

solution at 60 °C for 8 h. The reaction proceeded well and the desired thioester **1a** was obtained in 98% yield (Table 1, entry 1). The yield is also satisfactory (82%) when the reaction is conducted at 30 °C for 4 h (entry 2). The use of surfactant is crucial for the reaction, and the yield dropped from 82% to 63% in the absence of a surfactant (entry 2 *vs.* entry 3). After screening the different surfactants and bases, the combination of K_2CO_3 and 2 wt% TX100 aqueous solution emerged as the best selection (entry 4). No reaction took place without a base (entry 11). In order to show the possibility for large-scale operation, we also scaled up the reaction to 10 mmol, and the reaction proceeded well with 82% yield of the desired product (entry 12).

With the optimized conditions in hand, a series of benzoyl chlorides and different benzyl chlorides were chosen to establish the scope and generality of the method (Table 2). The reactions of 4-methylbenzyl chloride or benzyl chloride could go to completion at 30 °C to provide the desire products (**1a–d**). A slight heating (60 °C) was required when benzyl halides with electron-withdrawing groups were used (**1e–h**). Primary alkyl halides could also be applied to the reaction successfully (**1i–k**). Ethyl bromoacetate and (*E*)-1,3-dichloroprop-1-ene proved to be more efficient reactants than primary alkyl halides, so the final products (**1l–n**) could be formed at 30 °C.

2-Bromo-1,1-diethoxyethane could react with thiourea and benzoyl chloride to provide **1o** with a moderate yield under mild heating conditions. Likewise, the reactions of thiourea, benzoyl chloride and dibromides occurred to afford the corresponding dibenzothioates (**1p**, **1q**) under identical conditions. However, more steric hindered alkyl bromides (such as cyclohexyl bromide, *tert*-butyl bromide) failed to afford the desired products. The hydrolysis rate of other acyl chlorides (such as propionyl chloride, 2-chloroacetyl chloride) in water is too fast for them to react with the *S*-benzylisothiouronium salts formed *in situ* from thiourea and benzyl chloride.

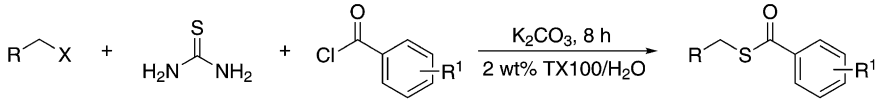
S-Prop-2-ynyl benzothioate **1r** generated through a one-pot process from 3-bromoprop-1-yne, thiourea and benzoyl chloride, could be attached to a peptidomimetic by copper-catalyzed "click" reaction (Scheme 2).[15] Furthermore, the thioester **3** could be readily transformed into a more versatile SH group under mild reaction conditions for the further structure modification.

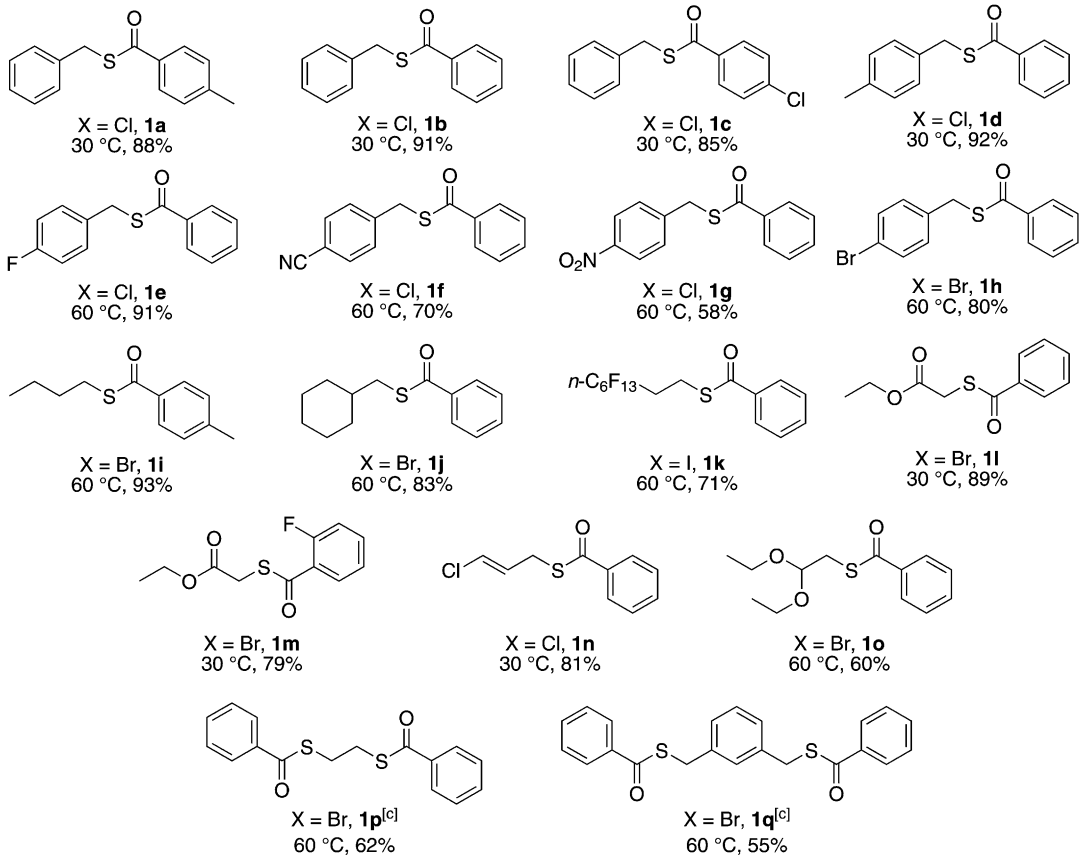
To further highlight the potential of this methodology, thioester **1t**, a crucial intermediate *en route* to **4** which displays potent anti-HIV properties in human macrophages, was synthesized by the one-pot, odorless procedure in water (Scheme 3), rather than by use of the foul-smelling thiol and an organic solvent as in the previous reports.[5c,d]

An initial attempt was also made to employ benzoic anhydride in the protocol. Although the desired thioesters were provided by the reaction of a variety of benzyl halides, thiourea and benzoic anhydride in 2 wt% TX100/H_2O at 80 °C for 8 h, low yields and undesired symmetrical thioethers were noted owing to the lower reactivity of benzoic anhydride compared to benzoyl chloride. The reactions of benzyl chlorides, thiourea and benzenesulfonyl chloride were carried out under likewise identical conditions. Although two *S*-benzyl benzenesulfonothioates (**5a**, **5b**) were synthesized successfully (Scheme 4), no desired product was obtained using benzyl chlorides with electron-withdrawing groups as the reactants.

Finally, a proposed mechanism for the reaction was also illustrated in Scheme 5. We believe that this reaction proceeds by the *in situ* generation of an *S*-alkylisothiouronium salt (not *S*-benzoylisothiouronium salts[16]) which is hydrolyzed in the reaction mixture to produce a thiolate moiety and urea.[11] Then the

Table 2. The reactions of various organic halides, thiourea and benzoyl chlorides in water.[a,b]

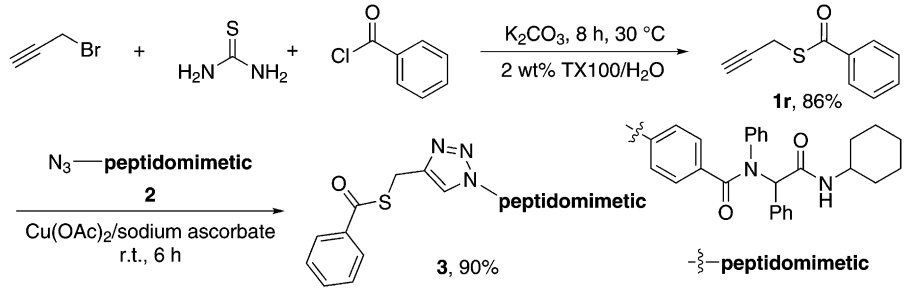




[a] *Reaction conditions:* organic halide 0.5 mmol, thiourea 1.0 mmol, benzoyl chloride 1.0 mmol, K_2CO_3 1.5 mmol, 2 wt% TX100 aqueous solution 1.0 mL, 8 h.

[b] Isolated yield.

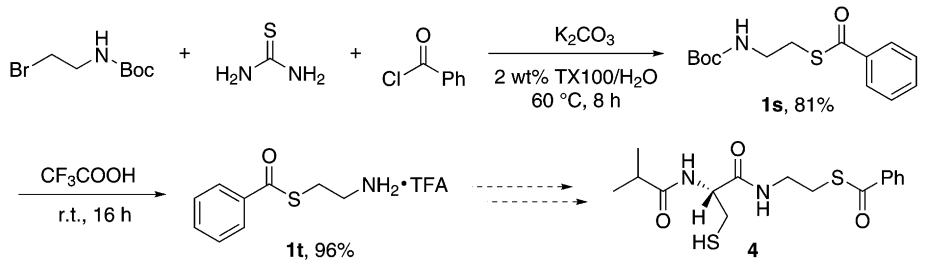
[c] *Reaction conditions:* dibromide compound 0.5 mmol, thiourea 2.0 mmol, benzoyl chloride 2.0 mmol, K_2CO_3 3.0 mmol, 2 wt% TX100 aqueous solution 1.5 mL, 8 h.



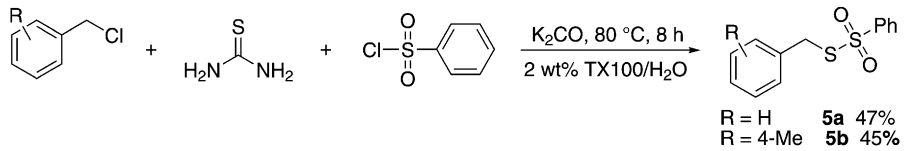
Scheme 2. The thioester **1r** is attached to a peptidomimetic by a "click" reaction.

generated thiolate ion which is a synthetic equivalent of thiol and an odorless moiety may react with benzoyl chloride to form the final product.

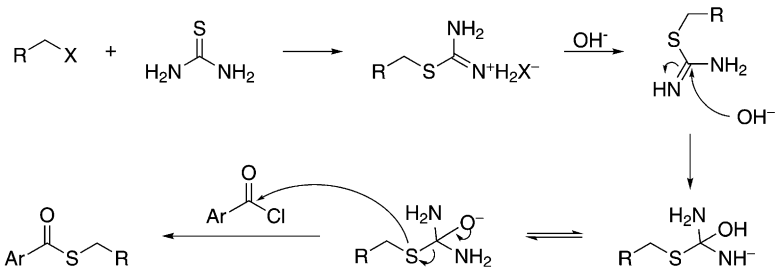
In summary, the preparation of thioesters can be performed in water through the one-pot, three-component reaction of organic halides, thiourea and ben-



Scheme 3. A potential application of the protocol in organic synthesis.



Scheme 4. The reactions of benzyl chlorides, thiourea and benzenesulfonyl chloride in water.



Scheme 5. A proposed mechanism for the thioesterification resaction of organic halides, thiourea and benzoyl chlorides.

zoyl chlorides. The non-ionic surfactant Triton X-100 that self-assembles in water to form micelles proves to diminish the hydrolysis of benzoyl chlorides. The newly developed procedure is free of organic solvents and foul-smelling thiols during these reactions, and work-up entails only an in-flask extraction with a minimal amount of a single, recoverable organic solvent, making it more environmentally friendly and suitable for large-scale operations. In addition, benzenesulfonyl chloride and benzoic anhydride in place of benzoyl chlorides can also be applied in the protocol.

Experimental Section

General Procedure for the Synthesis of Thioesters from Organic Halides, Thiourea and Benzoyl Chlorides in Water

A mixture of organic halide (0.5 mmol), thiourea (1.0 mmol), benzoyl chloride (1.0 mmol) and K_2CO_3 (1.5 mmol) in 2 wt% aqueous Triton X-100 solution (1.0 mL) was stirred at 30 °C or 60 °C for 8 h. Upon completion, the reaction mixture was diluted with EtOAc (4.0 mL), filtered through a bed of silica gel layered over Celite, The volatiles were removed under vacuum to afford the crude product. The extent of conversion was determined by GC. Further column chromatography on silica gel afforded the desired pure product.

General Procedure for the Synthesis of Thioesters from Benzyl Halides, Thiourea and Benzoic Anhydride or Benzenesulfonyl Chloride in Water

A mixture of benzyl halide (0.5 mmol), thiourea (1.0 mmol), benzoic anhydride or benzenesulfonyl chloride (1.0 mmol) and K_2CO_3 (1.5 mmol) in 2 wt% aqueous Triton X-100 solution (1.0 mL) was stirred at 80 °C for 8 h. Upon completion, the reaction mixture was diluted with EtOAc (4.0 mL), filtered through a bed of silica gel layered over Celite, The volatiles were removed under vacuum to afford the crude product. The extent of conversion was determined by GC. Further column chromatography on silica gel afforded the desired pure products.

Characterization Data of New Compounds

***S*-4-Fluorobenzyl benzothioate (1e):** ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 4.31$ (s, 2H), 7.00–7.04 (m, 2H), 7.36–7.39 (dd, $J = 8.5$, 5.5 Hz, 2H), 7.46–7.49 (m, 2H), 7.58–7.61 (m, 1H), 7.98–8.00 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 31.6$, 114.4, 114.6, 126.3, 127.7, 129.6, 129.7, 132.4, 132.6, 135.7,

160.1, 162.0, 190.2; MS (ESI): $m/z=246$; anal. calcd. for $C_{14}H_{11}FOS$: C 68.27, H 4.50%; found: C 68.51, H 4.73%.

***S*-4-Cyanobenzyl benzothioate (1f):** ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=4.34$ (s, 2H), 7.46–7.52 (m, 4H), 7.59–7.63 (m, 3H), 7.61–7.98 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=$ 31.8, 110.2, 117.7, 126.4, 127.8, 128.7, 131.4, 132.8, 135.4, 142.5, 189.5; MS (ESI): $m/z=253$; anal. calcd. for $C_{15}H_{11}NOS$: C 71.12, H 4.38, N 5.53%; found: C 70.91, H 4.73, N 5.23%.

***S*-Cyclohexylmethyl benzothioate (1j):** ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=1.01$–1.09 (m, 2H), 1.16–1.31 (m, 3H), 1.54–1.61 (m, 1H), 1.66–1.69 (m, 1H), 1.73–1.77 (m, 2H), 1.87–1.90 (m, 2H), 3.01 (d, $J=6.5$ Hz, 2H), 7.56–7.59 (t, $J=7.5$ Hz, 1H), 8.00 (dd, $J=8.0$, 1.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=25.0$, 25.3, 31.6, 34.9, 37.1, 126.2, 127.6, 132.2, 136.3, 191.2; MS (ESI): $m/z=234$; anal. calcd. for $C_{14}H_{18}OS$: C 71.75, H 7.74%; found: C 71.56, H 7.43%.

***S*-1*H*,1*H*,2*H*,2*H*-perfluorooctyl benzothioate (1k):** ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=2.47$–2.57 (m, 2H), 3.30–3.33 (m, 2H), 7.48–7.51 (t, $J=7.5$ Hz, 2H), 7.60–7.64 (t, $J=$ 7.5 Hz, 1H), 7.97–7.99 (dd, $J=8.0$, 1.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=19.1$, 30.8, 126.3, 127.8, 132.8, 135.5, 189.8; ^{19}F NMR (470 MHz, $CDCl_3$): $\delta=-126.2$, -123.4, -122.9, -121.9, -114.5, -80.9; MS (ESI): $m/z=484$; anal. calcd. for $C_{15}H_9F_{13}OS$: C 37.20, H 1.87%; found: C 36.98, H 1.78%.

Ethyl 2-(2-fluorobenzoylthio)acetate (1m): ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=1.31$–1.34 (t, $J=7.0$ Hz, 3H), 3.90 (s, 2H), 4.23–4.28 (q, $J=7.0$ Hz, 2H), 7.18–7.22 (m, 1H), 7.25–7.28 (m, 1H), 7.91–7.95 (td, $J=7.5$, 1.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=13.1$, 30.8, 68.9, 116.1, 123.4, 128.9, 133.9, 158.7, 160.8, 167.6, 180.6; ^{19}F NMR (470 MHz, $CDCl_3$): $\delta=-109.7$; MS (ESI): $m/z=242$; anal. calcd. for $C_{11}H_{11}FO_3S$: C 54.53, H 4.58%; found: C 54.76, H 4.69%.

(*E*)-*S*-3-Chloroallyl benzothioate (1n): ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=3.73$–3.75 (dd, $J=7.5$, 1.5 Hz, 2H), 5.99–6.04 (dt, $J=13.0$, 8.0 Hz, 1H), 6.31–6.34 (dt, $J=13.5$, 1.0 Hz, 1H), 7.46–7.50 (t, $J=7.0$ Hz, 2H), 7.59–7.62 (t, $J=$ 7.5 Hz), 7.97 (d, $J=7.5$ Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=28.0$, 120.6, 126.3, 127.5, 127.7, 132.6, 135.7, 189.8; MS (ESI): $m/z=212$; anal. calcd. for $C_{10}H_9ClOS$: C 56.47, H 4.26%; found: C 56.72, H 4.04%.

***S*-2,2-Diethoxyethyl benzothioate (1o):** ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=1.25$–1.27 (t, $J=7.0$ Hz, 6H), 3.33 (d, $J=5.5$ Hz, 2H), 3.61–3.65 (m, 2H), 3.72–3.78 (m, 2H), 4.62 (t, $J=5.5$ Hz, 1H), 7.48–7.49 (t, $J=7.5$ Hz, 2H), 7.58–7.61 (t, $J=7.5$ Hz, 1H), 8.01 (d, $J=7.5$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=14.2$, 31.3, 81.6, 100.5, 126.3, 127.6, 128.0, 132.5, 135.9, 190.6; MS (ESI): $m/z=254$; anal. calcd. for $C_{13}H_{18}FO_3S$: C 61.39, H 7.13%; found: C 61.07, H 7.39%.

***S*-(1-{4-[(2-{cyclohexylamino}-2-oxo-1-phenylethyl)-(phenyl)carbamoyl]phenyl}-1*H*-1,2,3-triazol-4-yl) methyl benzothioate (3):** ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=1.06$–1.17 (m, 3H), 1.32–1.41 (m, 2H), 1.58–1.71 (m, 3H), 1.91–1.99 (m, 2H), 3.86–3.93 (m, 1H), 4.41 (s, 2H), 5.72 (br, 1H), 6.20 (s, 1H), 7.02 (br, 5H), 7.26 (br, 5H), 7.44–7.52 (m, 6H), 7.57–7.60 (t, $J=7.0$ Hz, 1H), 7.93–7.95 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=22.7$, 23.7, 23.8, 24.5, 31.8, 47.9, 65.7, 118.3, 119.6, 126.3, 126.5, 127.6, 127.7, 129.1, 129.3, 129.4, 132.7, 133.6, 135.5, 136.1, 139.9, 144.4, 167.4, 168.8, 170.1, 190.4; MS (ESI): $m/z=628$ $(M-H)^-$; anal. calcd. for $C_{37}H_{35}N_5O_3S$: C 70.56, H 5.60, N 11.12%; found: C 70.37, H 5.81, N 11.38%.

***S*-4-Methylbenzyl benzenesulfonothioate (5b):** ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=2.31$ (s, 3H), 4.17 (s, 2H), 7.01 (d, $J=8.0$ Hz, 2H), 7.07 (d, $J=8.0$ Hz, 2H), 7.48–7.51 (m, 2H), 7.57–7.61 (m, 1H), 7.90–7.92 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=20.1$, 34.4, 125.4, 127.8, 128.3, 131.4, 132.0, 136.4, 140.9, 167.3; MS (ESI): $m/z=278$; anal. calcd. for $C_{14}H_{14}O_2S_2$: C 60.40, H 5.07%; Found: C 60.63, H 4.85%.

Acknowledgements

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COMMUNICATIONS