Green Chemistry

Accepted Manuscript

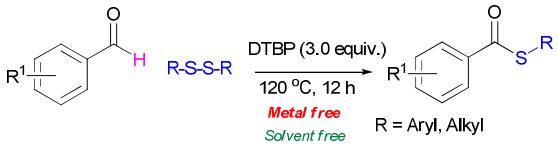
ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/greenchem

Metal-Free Cross-Coupling Reaction of Aldehydes with Disulfides By Using DTBP as an Oxidant in Solvent-Free Conditions

Jing-Wen Zeng, Yi-Chen Liu, Bing-An Xie, Yu-Ting Huang, Chih-Lun Yi, Satpal Singh Badsara and Chin-Fa Lee*

Abstract



A DTBP-promoted C-H thiolation of aldehydes with disulfides under metal-free and solvent-free conditions is described. The system shows good functional group tolerance to afford thioesters and amides in moderate to excellent yields.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Metal-Free Cross-Coupling Reaction of Aldehydes with Disulfides By Using DTBP as an Oxidant in Solvent-Free Conditions

Jing-Wen Zeng, Yi-Chen Liu, Bing-An Xie, Yu-Ting Huang, Chih-Lun Yi, Satpal Singh Badsara and Chin-Fa Lee*

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

A DTBP-promoted C-H thiolation of aldehydes with disulfides under metal-free and solvent-free conditions is described. The system shows good functional group tolerance to afford thioesters in moderate to excellent yields.

Introduction

Metal-catalyzed C-H functionalization has emerged as an effective and fascinating area of organic research owing to it's highly desirable atom-economy and environment friendly synthetic methodologies.[1] More recently, organo-catalysis[2] has been employed as an alternative approach to these transition metal mediated transformations; however, the direct C-H bond thiolation of aldehydes with disulfides[3] has received less attention. For this reason, we have elected to focus on the development of reliable metal-free and solvent-free, methods for the synthesis of thioethers.

The thioester functionality has gained considerable attention due to it's importance as an acyl transfer reagent in organic synthesis,[4] and in chemical biology.[5] Traditional method for synthesis of thioesters from carboxylic acids has poor atom economy. For example, the starting materials, acyl chlorides are moisture-sensitive, and this approach will produce an equal amount of halide anion when acyl halides were used. Furthermore, the traditional method used in preparation of thioesters also suffers from significant drawbacks.[6] Therefore, the direct coupling of aldehydes with thiol surrogates can serve as an alternative and ideal route to the preparation of thioesters.

It is known that thioesters can be prepared under photo-irradiation of disulfides with aldehydes in the year of 1976;[3a,b] however, there are several synthetic limitations. First, only low concentrations are permissible in this system, and it is difficult to scale-up the process using this protocol. Second, the substrates are limited to phenyl aldehydes, and substituted aryl aldehydes are not tolerated. Third, a photo reactor is required, and this limits the practical synthesis in an organic laboratory. Recently, Bandgar *et al.* reported the synthesis of thioesters *via* Dess-Martin periodinane-promoted coupling of aldehydes with aryl thiols. However, there are still some limitations in this system. First, 6 equiv of Dess-Martin periodinane and 6 equiv of NaN_3 were required to give the desired thioesters in reasonable yields. Second, the scope of the substrate is limited to aryl thiols.[3c] Takemoto and co-workers have recently described the carbene-catalyzed coupling of aldehydes with thiols, however, carbenes used in this work are expensive. Moreover, alkyl aldehydes are less reactive when compared to aryl aldehydes and as a result, an electron-rich carbene is required for the coupling of thiols with alkyl aldehydes.[3d] Kita *et al.* reported a protocol to afford thioesters through the coupling of aldehydes with dipentafluorophenyl disulfide;[3e,f] again, limitations are observed in this system. First, the reaction conditions are limited to dipentafluorophenyl disulfide, and other aryl disulfides and alkyl disulfides are not suitable. Second, quaternary ammonium salts are used as surfactants. Third, one equivalent of a radical initiator is necessary for promoting the reaction. Very recently, we have also reported the copper-catalyzed direct coupling of thiols with aldehydes in the presence of TBHP as an oxidant.[3g] As part of our ongoing progress in C-S bond cross-coupling reactions[3g,7] we herein, report a metal and solvent-free direct C-H thiolation of aldehydes promoted by DTBP. This system shows good functional group compatibility with electron donating and electron withdrawing groups and also with halo-groups as they are all tolerated by the reaction conditions employed.

Results and discussion

Initially, 4-methoxybenzaldehyde and diphenyl disulfide were chosen as the coupling partners to determine the optimal reaction conditions. The results are summarized in Table 1. TBHP[8] was used for the preparation of thioesters under copper catalysis.[3g] Interestingly, a 15% yield of the target was obtained when the reaction was carried out in the absence of copper salt (Table 1, entry 1). Based on this result, we screened other oxidants (Table1, entries 2-7), and DTBP was found to be the best, giving **3a** in almost quantitative yield (Table 1, entry 7).[9] Lower volumes as a

Department of Chemistry, National Chung Hsing University, Taichung, Taiwan 402, R.O.C

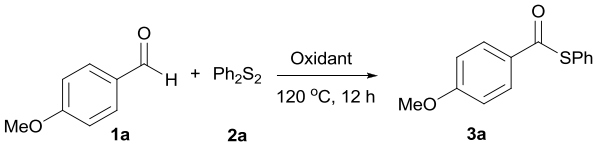
Fax: (+886) 4-2286-2547;; Tel: +886 4 2284-0411 ext. 810

E-mail: cfalee@dragon.nchu.edu.tw

† Electronic Supplementary Information (ESI) available: NMR spectra (^1H and ^{13}C) for compounds **3** and **4** See DOI: 10.1039/b000000x//

result of decreasing the amount of 4-methoxybenzaldehyde reduced the yield (91%) (Table 1, entry 8). It was also found that lower reaction temperatures (Table 1, entry 9) and lower DTBP amounts[8,9] (Table 1, entries 10 and 11, 92% and 77% yields were obtained when 2 equiv and 1 equiv of TBHP were used, respectively) diminished the yield of the product. To our delight, lower reaction times (10 h) gave the product in a 99% yield (Table 1, entry 12).

Table 1. Optimization of reaction conditions



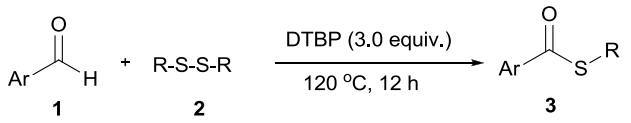
Entry	Oxidant (equiv.)	Yield (%)[b]
1	TBHP (3)	15
2	PCC (3)	trace
3	H_2O_2 (3)	N.R.
4	BPO (3)	32
5	$K_2S_2O_8$ (3)	2
6	AcOOH (3)	trace
7	DTBP (3)	99
8[c]	DTBP (3)	91
9[d]	DTBP (3)	90
10	DTBP (2)	92
11	DTBP (1)	77
12[e]	DTBP (3)	99

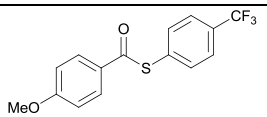
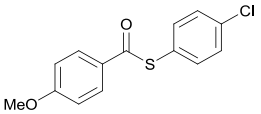
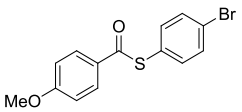
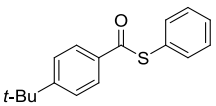
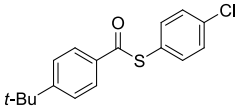
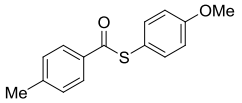
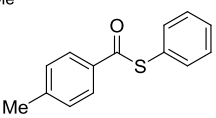
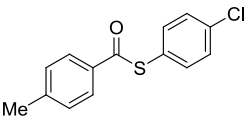
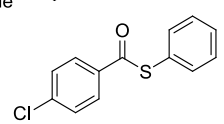
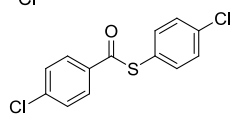
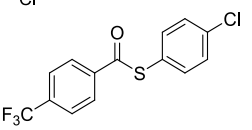
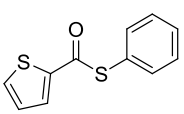
[a] Reaction conditions: 4-methoxybenzaldehyde (1.0 mL), diphenyl disulfide (0.5 mmol) and oxidant (3.0 mmol) were reacted at 120 °C for 12 h. [b] Isolated yield. [c] 0.5 mL of 4-methoxybenzaldehyde was used. [d] 110 °C. [e]10 h. (TBHP = *tert*-butyl hydroperoxide, PCC = pyridinium chlorochromate, BPO = benzoyl peroxide, AcOOH = peracetic acid, DTBP = di-*tert*-butyl peroxide)

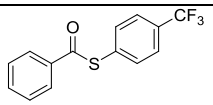
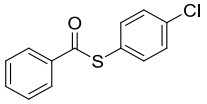
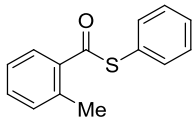
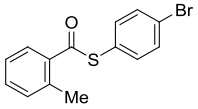
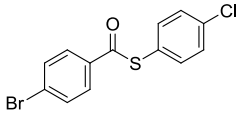
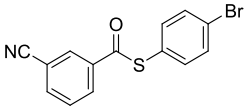
Based on the optimized reaction conditions, we then studied the scope of this novel system for a variety of substrates. As shown in Table 2, a wide range of diaryl disulfides were smoothly coupled with aldehydes, giving the corresponding thioesters in good to excellent yields. Aryl aldehydes bearing electron-donating and electron-withdrawing groups were successfully reacted with substituted aryl disulfides. Importantly, this system shows good functional group tolerance; trifluoromethyl (Table 2, entries 1, 11 and 13), chloro (Table 2, entries 2, 5, 8-11, 14 and 17), bromo (Table 2, entries 3, 16 and 18), thiophene (Table 2, entry 12) and nitrile (Table 2, entry 18) were all tolerated by the reaction conditions employed. Moreover, sterically demanding *ortho*-substituted aryl aldehydes underwent the C-S bond formation with thiols to provide the targets in good yields (Table 2, entries 15 and 16).

With the promising results in the coupling of aldehydes with diaryl disulfides, we next turned our attention to the use of dialkyl disulfides as coupling partners in our DTBP-promoted coupling reaction with aldehydes; the results are summarized in Table 3. A variety of aryl aldhydes bearing electron-withdrawing and electron-donating groups were successfully coupled with various dialkyl disulfides, providing the resulting thioesters in moderate to excellent yields. Functional groups including chloro (Table 3,

Table 2. DTBP-promoted synthesis of thioesters from diaryl disulfides and aldehydes.[a]



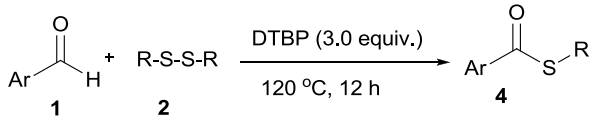
Entry	Product		Yield (%)[b]
1		**3b**	95
2		**3c**	99
3		**3d**	65
4		**3e**	63
5		**3f**	76
6		**3g**	90
7		**3h**	82
8		**3i**	68
9		**3j**	63
10		**3k**	89
11		**3l**	84
12		**3m**	53

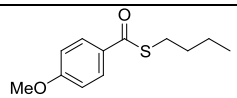
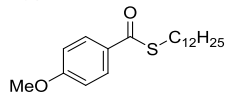
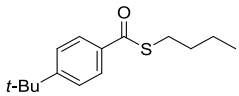
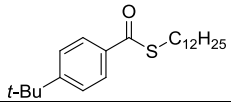
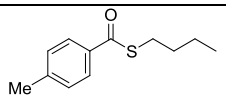
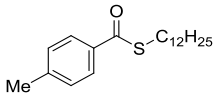
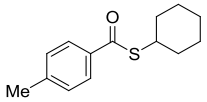
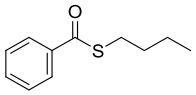
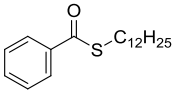
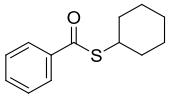
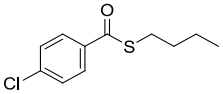
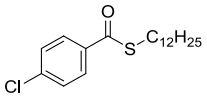
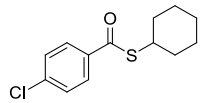
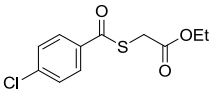
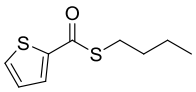
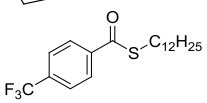
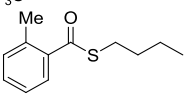
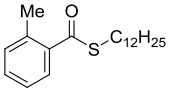
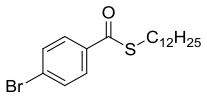
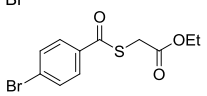
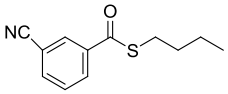
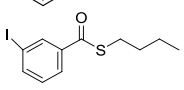
13		**3n**	88
14		**3o**	93
15		**3p**	90
16		**3q**	92
17		**3r**	91
18		**3s**	55

[a] Reaction conditions unless otherwise stated: aldehyde (1.0 mL), diaryl disulfide (0.5 mmol) and DTBP (3.0 mmol) were reacted at 120 °C for 12 h. [b] Isolated yield.

entries 11-14), ester (Table 3, entries 14 and 20), trifluoromethyl (Table 3, entry 16), bromo (Table 3, entries 19 and 20), nitrile (Table 3, entry 21) and iodo (Table 3, entry 22) were tolerated by the reaction conditions. The sterically demanding *ortho*-substituted aldehydes smoothly coupled with dialkyl disulfides to provide products in good yields (Table 3, entries 17 and 18). Importantly, thiophene-containing alkyl thioester could not be prepared in previous method,[3g] to our delight; the target could be formed in a 66% yield when the reaction was carried out by using 2-thiophenecarboxaldehyde as the coupling partner (Table 3, entry 15).

Table 3. DTBP-promoted coupling reaction of dialkyl disulfides with aldehydes.[a]

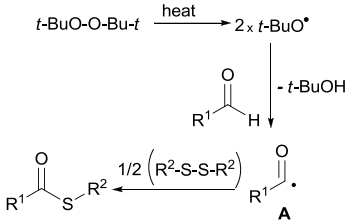


Entry	Product		Yield (%)[b]
1		**4a**	80
2		**4b**	78
3		**4c**	90
4		**4d**	90
5		**4e**	77
6		**4f**	77
7[c]		**4g**	47
8		**4h**	88
9		**4i**	71
10[c]		**4j**	44
11		**4k**	88
12		**4l**	67
13[c]		**4m**	42
14		**4n**	46
15[d]		**4o**	66
16		**4p**	78
17		**4q**	67
18		**4r**	73
19		**4s**	70
20		**4t**	50
21		**4u**	89
22		**4v**	40

[a] Reaction conditions unless otherwise stated: aldehyde (1.0 mL), dialkyl disulfide (0.5 mmol) and DTBP (3.0 mmol) were reacted at 120 °C for 12 h. [b] Isolated yield. [c] 24 h. [d] 16 h.

A potential mechanism for DTBP-promoted C-S coupling reactions of aldehydes with disulfides is depicted in Scheme 1. The aldehydic radical **A** is generated by treating aldehyde with DTBP.[9] The aldehydic radical then further reacts with disulfides to give the thioester.

Scheme 1. Plausible mechanism.



Conclusions

In conclusion, we have developed a general and efficient approach for the preparation of thioesters using DTBP as an oxidant under metal-free and solvent-free conditions. This system shows good functional group compatibility, giving thioesters in moderate to excellent yields. Although good results are obtained by the reactions of disulfides with aryl aldehydes, however, the alkyl aldehydes are not suitable as the coupling partners under these reaction conditions. Therefore, to develop a general procedure for the coupling of disulfides with aryl- and alkyl aldehydes in metal-free conditions, and to apply DTBP as an oxidant for other metal-free cross-coupling reactions are underway in our laboratory.

Experimental

General information

All chemicals were purchased from commercial suppliers and used without further purification. All reactions were carried out under an inert atmosphere. Flash chromatography was performed on Merck silica gel 60 (230-400 mesh). NMR spectra were recorded on a Varian Unity Inova-600 or a Varian Mercury-400 instrument using $CDCl_3$ as solvent. Chemical shifts are reported in parts per million (ppm) and referenced to the residual solvent resonance. Coupling constant (J) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s = singlet, d = doublet, t = triplet, dd = double of doublet, q = quartet, m = multiplet, b = broad. Melting points (m.p.) were determined using a Büchi 535 apparatus and are reported uncorrected. GC-MS analyses were performed on a GC-MS analysis on HP 5890 GC equipped with HP 5972 MS. High-resolution mass spectra were carried out on a Jeol JMS-HX 110 spectrometer by the services at the National Chung Hsing University.

General procedure for Table 1.

A Schlenk tube equipped with a magnetic stirrer bar was charged with diphenyl disulfide (0.109 g, 0.5 mmol), 4-methoxybenzaldehyde (1.0 mL) and oxidant (3 mmol) under a nitrogen-filled balloon and heated at 120 °C for 12 h in an oil bath. After the reaction was completed (monitored by TLC), the reaction mixture was cooled to ambient temperature, poured into 20 mL of brine, and extracted with ethyl acetate (3 × 20 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and filtered, and all of the volatiles were removed under reduced pressure. The resulting residue was purified by column chromatography (SiO_2, hexane) to provide **3a.**

Representative example of Table 1. *S*-phenyl 4-methoxybenzothioate (3a).[3c] The title compound was prepared following the general procedure for Table 1, using diphenyl disulfide (0.109 g, 0.5 mmol), 4-methoxybenzaldehyde (1.0 mL), DTBP (0.56 mL, 3 mmol), provided **3a** as a white solid (0.243 g, 99% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.81 (s, 3 H), 6.95 (d, J = 8.4 Hz, 2 H), 7.46-7.56 (m, 5 H), 8.04 (d, J = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.5, 114.0, 127.7, 129.2, 129.3, 129.4, 129.7, 135.2, 164.0, 188.4.

General procedure for Table 2:

A Schlenk tube equipped with a magnetic stirrer bar was charged with diaryl disulfide (0.5 mmol), aldehyde (1.0 mL) and DTBP (0.56 mL, 3.0 mmol) under a nitrogen-filled balloon and heated at 120 °C for 12 h in an oil bath. After the reaction was completed (monitored by TLC), the reaction mixture was cooled to ambient temperature, poured into 20 mL of brine, and extracted with ethyl acetate (3 × 20 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and filtered, and all of the volatiles were removed under reduced pressure. The resulting residue was purified by column chromatography (SiO_2, hexane) to yield **3**.

***S*-(4-(Trifluoromethyl)phenyl) 4-methoxybenzothioate (3b).**[3g] The title compound was prepared following the general procedure for Table 2, using 1,2-bis(4-(trifluoromethyl)phenyl)disulfane (0.177g, 0.5 mmol), 4-methoxybenzalde- hyde (1.0 mL) and DTBP (0.56 mL, 3 mmol), provided **3b** as a white solid (0.296 g, 95% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.86 (s, 3 H), 6.96 (d, J = 8.4 Hz, 2 H), 7.63 (d, J = 8.4 Hz, 2 H), 7.68 (d, J = 8.4 Hz, 2 H), 7.99 (d, J = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.5, 114.0, 123.9 (d, J = 270.4 Hz), 125.8, 125.8, 128.9, 129.8, 131.2 (d, J = 32.8 Hz), 132.5, 135.2, 164.3, 187.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ -64.3 (s).

***S*-(4-Chlorophenyl) 4-methoxybenzothioate (3c).**[3g] The title compound was prepared following the general procedure for Table 2, using 1,2-bis(4-chlorophenyl)disulfane (0.144 g, 0.5 mmol), 4-methoxybenzaldehyde (1.0 mL) and DTBP (0.56 mL, 3 mmol), provided **3c** as a white solid (0.276 g, 99% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.84 (s, 3 H), 6.93 (d, J = 8.8 Hz, 2 H), 7.40 (s, 4 H), 7.97 (d, J = 8.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.4, 113.9, 126.0, 128.9, 129.3, 129.6, 135.6, 136.3, 164.0, 187.9.

***S*-(4-Bromophenyl) 4-methoxybenzothioate (3d).**[3g] The title compound was prepared following the general procedure for Table 2, using 1,2-bis(4-bromophenyl)disulfane (0.188 g, 0.5 mmol), 4-methoxybenzaldehyde (1.0 mL) and DTBP (0.56 mL, 3 mmol), provided **3d** as a white solid (0.209 g, 65% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.83 (s, 3 H), 6.92 (d, J = 9.2 Hz, 2 H), 7.33 (d, J = 8.4 Hz, 2 H), 7.54 (d, J = 8.4 Hz, 2 H), 7.96 (d, J = 8.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.4, 113.8, 123.9, 126.7, 128.8, 129.6, 132.2, 136.5, 164.0, 187.7.

***S*-Phenyl 4-(*t*-butyl)benzothioate (3e).**[10b] The title compound was prepared following the general procedure for Table 2, using diphenyl disulfide (0.109 g, 0.5 mmol), 4-(*t*-butyl)benzaldehyde (1.0 mL), DTBP

(0.56 mL, 3 mmol), provided **3e** as a yellow oil (0.170 g, 63% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26-1.35 (m, 9 H), 7.40-7.52 (m, 7 H), 7.95-7.98 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.0, 35.1, 125.6, 127.3, 127.5, 129.1, 129.3, 133.9, 135.0, 157.4, 189.5.

***S*-(4-Chlorophenyl) 4-(*t*-butyl)benzothioate (3f).** The title compound was prepared following the general procedure for Table 2, using 1,2-bis(4-chlorophenyl)disulfane (0.144 g, 0.5 mmol), 4-(*t*-butyl)benzaldehyde (1.0 mL) and DTBP (0.56 mL, 3 mmol), provided **3f** as a yellow solid (0.231 g, 76% yield); M.P. = 120-121 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.29-1.35 (m, 9 H), 7.38-7.50 (m, 6 H), 7.95 (dd, J = 1.2 & 6.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.0, 35.1, 125.7, 126.0, 127.4, 129.4, 133.6, 135.7, 136.3, 157.7, 189.0; HRMS-ESI calcd. for $C_{17}H_{17}ClOS$: 304.0689, found: 305.0771.

***S*-(4-Methoxyphenyl) 4-methylbenzothioate (3g).[10c]** The title compound was prepared following the general procedure for Table 2, using 1,2-bis(4-methoxyphenyl)disulfane (0.109 g, 0.5 mmol), 4-methylbenzaldehyde (1.0 mL) and DTBP (0.56 mL, 3 mmol), provided **3g** as a white solid (0.232 g, 90% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.40 (s, 3 H), 3.81 (s, 3 H), 6.96 (dd, J = 2.4, & 6.8 Hz, 2 H), 7.25 (d, J = 7.6 Hz, 2 H), 7.40 (dd, J = 2.0 & 6.8 Hz, 2 H), 7.90 (d, J = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6, 55.2, 114.8, 117.9, 127.4, 129.3, 133.9, 136.6, 144.4, 160.6, 190.5.

***S*-Phenyl 4-methylbenzothioate (3h).[3c]** The title compound was prepared following the general procedure for Table 2, using diphenyl disulfide (0.109 g, 0.5 mmol), 4-methylbenzaldehyde (1.0 mL) and DTBP (0.56 ml, 3 mmol), provided **3h** as a white solid (0.187 g, 82% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.34 (s, 3 H), 7.17-7.24 (m, 2 H), 7.37-7.51 (m, 5 H), 7.86-7.92 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6, 127.4, 128.9, 129.1, 129.3, 129.6, 133.9, 135.0, 144.4, 189.5.

***S*-(4-Chlorophenyl) 4-methylbenzothioate (3i).[10d]** The title compound was prepared following the general procedure for Table 2, using 1,2-bis(4-chlorophenyl)disulfane (0.144 g, 0.5 mmol), 4-methylbenzaldehyde (1.0 mL) and DTBP (0.56 mL, 3 mmol), provided **3i** as a white solid (0.179 g, 68% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.41 (s, 3 H), 7.25 (d, J = 8.0 Hz, 2 H), 7.41 (s, 4 H), 7.89 (d, J = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.7, 126.0, 127.5, 129.3, 133.7, 135.7, 136.3, 144.8, 189.0.

***S*-Phenyl 4-chlorobenzothioate (3j).[3c]** The title compound was prepared following the general procedure for Table 2, using 1,2-diphenyldisulfane (0.109 g, 0.5 mmol), 4-chlorobenzaldehyde (1.0 mL) and DTBP (0.56 mL, 3 mmol), provided **3j** as a yellow solid (0.156 g, 63% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45-7.52 (m, 7 H), 7.96 (dd, J = 1.6, 6.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 126.8, 128.8, 129.0, 129.3, 129.7, 134.9, 135.0, 140.0, 189.1.

***S*-(4-Chlorophenyl) 4-chlorobenzothioate (3k).[3g]** The title compound was prepared following the general procedure for Table 2, using 1,2-bis(4-chlorophenyl)disulfane (0.144 g, 0.5 mmol), 4-chlorobenzaldehyde (1.0 mL) and DTBP (0.56 mL, 3 mmol), provided **3k** as a yellow solid (0.252 g, 89% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25-7.52 (m, 6 H), 7.94 (d, J = 8.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 125.3, 128.8, 129.1, 129.5, 134.6, 136.1, 136.2, 140.3, 188.5.

***S*-(4-Chlorophenyl) 4-(trifluoromethyl)benzothioate (3l).** The title compound was prepared following the general procedure for Table 2, using 1,2-bis(4-chlorophenyl)disulfane (0.144 g, 0.5 mmol), 4-(trifluoromethyl)benzaldeh- yde (1.0 mL) and DTBP (0.56 mL, 3 mmol), provided **3l** as a white solid (0.266 g, 84% yield); M.P. 100-101 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (s, 4 H), 7.75 (d, J = 8.0 Hz, 2 H), 8.10 (d, J = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 123.4 (d, J = 271.3 Hz), 124.9, 125.8, 127.4, 129.6, 135.0 (d, J = 32.8 Hz), 136.1, 136.3, 139.0, 188.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -64.7 (s); HRMS-EI calcd. for $C_{14}H_8ClF_3OS$: 315.9936, found: 315.9927.

***S*-Phenyl thiophene-2-carbothioate (3m).[10b]** The title compound was prepared following the general procedure for Table 2, using 1,2-diphenyldisulfane (0.109 g, 0.5 mmol), thiophene-2-carbaldehyde (1.0 mL) and DTBP (0.56 ml, 3 mmol), provided **3m** as a yellow oil (0.117 g, 53% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.15 (t, J = 4.4 Hz, 1 H), 7.44-7.65 (m, 5 H), 7.71 (d, J = 5.2 Hz, 1 H), 7.91 (d, J = 3.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 126.9, 128.0, 129.2, 129.6, 131.6, 133.2, 135.0, 141.4, 182.0.

***S*-(4-(Trifluoromethyl)phenyl) benzothioate (3n).** The title compound was prepared following the general procedure for Table 2, using 1,2-bis{4-(trifluoromethyl)phenyl}disulfane (0.177 g, 0.5 mmol), benzaldehyde (1.0 mL) and DTBP (0.56 mL, 3 mmol), provided **3n** as a white solid (0.249 g, 88% yield); M.P. 105-106 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45-7.49 (m, 2 H), 7.58-7.69 (m, 5 H), 8.00 (dd, J = 1.2 & 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 123.8 (d, J = 270.4 Hz), 125.9, 127.5, 128.8, 131.3 (d, J = 32.7 Hz), 132.2, 134.0, 135.1, 136.2, 188.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -64.3 (s); HRMS-ESI calcd. for $C_{14}H_9F_3OS$: 282.0326, found: 283.0408.

***S*-(4-Chlorophenyl) benzothioate (3o).[10e]** The title compound was prepared following the general procedure for Table 2, using 1,2-bis(4-chlorophenyl)disulfane (0.144 g, 0.5 mmol), benzaldehyde (1.0 mL) and DTBP (0.56 mL, 3 mmol), provided **3o** as a white solid (0.231 g, 93% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41-7.50 (m, 6 H), 7.59-7.63 (m, 1 H), 7.99-8.02 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 114.7, 125.8, 127.5, 128.8, 129.5, 133.8, 135.9, 136.3, 189.6.

***S*-Phenyl 2-methylbenzothioate (3p).[10b]** The title compound was prepared following the general procedure for Table 2, using diphenyl disulfide (0.109 g, 0.5 mmol), 2-methylbenzaldehyde (1.0 mL) and DTBP (0.56 mL, 3 mmol), provided **3p** as a yellow oil (0.206 g, 90% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.47 (s, 3 H), 7.21-7.28 (m, 2 H), 7.35-7.51 (m, 6 H), 7.92 (d, J = 7.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.7, 125.7, 128.0, 128.5, 129.1, 129.3, 131.6, 131.9, 134.8, 136.5, 137.3, 191.9; HRMS-EI calcd. for $C_{14}H_{12}OS$: 228.0609, found: 228.0603.

***S*-(4-Bromophenyl) 2-methylbenzothioate (3q).** The title compound was prepared following the general procedure for Table 2, using 1,2-bis(4-bromophenyl)disulfane (0.188 g, 0.5 mmol), 2-methylbenzaldehyde (1.0 mL) and DTBP (0.56 mL, 3 mmol), provided **3q** as a yellow solid (0.283 g, 92% yield); M.P. 91-92 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ =

2.47 (s, 3 H), 7.23-7.30 (m, 1 H), 7.34-7.41 (m, 3 H), 7.56 (dd, *J* = 2.0 & 6.4 Hz, 2 H), 7.91 (dd, *J* = 0.8 & 7.6 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.8, 124.1, 125.8, 127.2, 128.6, 131.8, 132.2, 132.3, 136.1, 136.3, 137.5, 191.2; HRMS-EI calcd. for $C_{14}H_{11}BrOS$: 305.9714, found: 305.9723.

***S*-(4-Chlorophenyl) 4-bromobenzothioate (3r).**[10d] The title compound was prepared following the general procedure for Table 2, using 1,2-bis(4-chlorophenyl)disulfane (0.144 g, 0.5 mmol), 4-bromobenzaldehyde (1.0 mL) and DTBP (0.56 mL, 3 mmol), provided **3r** as a white solid (0.298 g, 91% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (s, 4 H), 7.63 (d, *J* = 4.8 Hz, 2 H), 7.87 (d, *J* = 4.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 125.3, 128.9, 129.0, 129.6, 132.1, 135.1, 136.2, 136.2, 188.7.

***S*-(4-Bromophenyl) 3-cyanobenzothioate (3s).**[3g] The title compound was prepared following the general procedure for Table 2, using 1,2-bis(4-bromophenyl)disulfane (0.188 g, 0.5 mmol), 3-formylbenzonitrile (1.0 mL) and DTBP (0.56 mL, 3 mmol), provided **3s** as a white solid (0.175 g, 55% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25-7.42 (m, 2 H), 7.52-7.66 (m, 3 H), 7.89 (d, *J* = 8.0 Hz, 1 H), 8.22 (dd, *J* = 1.2 & 8.0 Hz, 1 H), 8.28 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 113.4, 117.5, 124.8, 125.2, 129.9, 131.0, 131.3, 132.7, 136.3, 136.6, 137.2, 187.8.

4. General procedure for Table 3:

A Schlenk tube equipped with a magnetic stirrer bar was charged with dialkyl disulfide (0.5 mmol), aldehyde (1.0 mL) and DTBP (0.56 mL, 3.0 mmol) under a nitrogen-filled balloon and heated at 120 °C for 12 h in an oil bath. After the reaction was completed (monitored by TLC), the reaction mixture was cooled to ambient temperature, poured into 20 mL of brine, and extracted with ethyl acetate (3 x 20 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and filtered, and all of the volatiles were removed under reduced pressure. The resulting residue was purified by column chromatography (SiO_2, hexane) to provide **4**.

***S*-(*n*-Butyl) 4-methoxybenzothioate (4a).** The title compound was prepared following the general procedure for Table 3, using 1,2-dibutyldisulfane (0.106 ml, 0.5 mmol), 4-methoxybenzaldehyde (1.0 mL) and DTBP (0.56 mL, 3 mmol), provided **4a** as a white solid (0.179 g, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94 (t, *J* = 7.2 Hz, 3 H), 1.40-1.49 (m, 2 H), 1.60-1.68 (m, 2 H), 3.05 (t, *J* = 7.2 Hz, 2 H), 3.83 (s, 3 H), 6.90 (d, *J* = 8.8 Hz, 2 H), 7.94 (d, *J* = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.5, 22.0, 28.5, 31.7, 55.3, 113.6, 129.2, 130.0, 163.5, 190.4; HRMS-EI calcd. for $C_{16}H_{12}O_2S$: 224.0871, found: 224.0865.

***S*-(*n*-Dodecyl) 4-methoxybenzothioate (4b).**[3g] The title compound was prepared following the general procedure for Table 3, using 1,2-didodecyldisulfane (0.270 g, 0.5 mmol), 4-methoxybenzaldehyde (1.0 mL) and DTBP (0.56 ml, 3 mmol), provided **4b** as a white solid (0.263 g, 78% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.82 (t, *J* = 6.6 Hz, 3 H), 1.20-1.37 (m, 18 H), 1.56-1.63 (m, 2 H), 2.98 (t, *J* = 7.4 Hz, 2 H), 3.80 (s, 3 H), 6.85 (d, *J* = 8.8 Hz, 2 H), 7.89 (d, *J* = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.6, 28.8, 28.9, 29.1, 29.3, 29.5, 29.5, 29.6, 29.6, 29.6, 31.9, 55.3, 113.6, 129.2, 130.0, 163.5, 190.5.

***S*-(*n*-Butyl) 4-(*t*-butyl)benzothioate (4c).** The title compound was prepared following the general procedure for Table 3, using 1,2-dibutyldisulfane (0.106 ml, 0.5 mmol), 4-(*t*-butyl)benzaldehyde (1.0 mL) and DTBP (0.56 mL, 3 mmol), provided **4c** as a yellow oil (0.226 g, 90% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94 (t, *J* = 7.4 Hz, 3 H), 1.22-1.50 (m, 11 H), 1.61-1.68 (m, 2 H), 3.06 (t, *J* = 7.2 Hz, 2 H), 7.44 (d, *J* = 8.4 Hz, 2 H), 7.92 (d, *J* = 7.6 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.5, 21.9, 28.4, 30.9, 31.6, 34.9, 125.3, 126.9, 134.5, 156.7, 191.4; HRMS-EI calcd. for $C_{15}H_{22}OS$: 250.1391, found: 250.1399.

***S*-(*n*-Dodecyl) 4-(*t*-butyl)benzothioate (4d).** The title compound was prepared following the general procedure for Table 3, using 1,2-didodecyldisulfane (0.270 g, 0.5 mmol), 4-(*t*-butyl)benzaldehyde (1.0 mL) and DTBP (0.56 mL, 3 mmol), provided **4d** as a white solid (0.326 g, 90% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.4 Hz, 3 H), 1.26-1.44 (m, 27 H), 1.63-1.70 (m, 2 H), 3.06 (t, *J* = 7.0 Hz, 2 H), 7.45 (d, *J* = 6.8 Hz, 2 H), 7.90-7.93 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.7, 28.9, 28.9, 29.1, 29.3, 29.5, 29.6, 29.6, 31.0, 31.9, 35.0, 125.4, 127.0, 134.6, 156.8, 191.6; HRMS-EI calcd. for $C_{23}H_{38}OS$: 362.2643, found: 362.2645.

***S*-(*n*-Butyl) 4-methylbenzothioate (4e).** The title compound was prepared following the general procedure for Table 3, using 1,2-dibutyldisulfane (0.106 mL, 0.5 mmol), 4-methylbenzaldehyde (1.0 mL) and DTBP (0.56 mL, 3 mmol), provided **4e** as a yellow oil (0.160 g, 77% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94 (t, *J* = 7.4 Hz, 3 H), 1.42-1.49 (m, 2 H), 1.61-1.68 (m, 2 H), 2.38 (s, 3 H), 3.05 (t, *J* = 7.2 Hz, 2 H), 7.21 (d, *J* = 8.0 Hz, 2 H), 7.86 (d, *J* = 7.6 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.6, 21.5, 22.0, 28.5, 31.6, 127.1, 129.1, 134.6, 143.9, 191.6; HRMS-EI calcd. for $C_{12}H_{16}OS$: 208.0922, found: 208.0924.

***S*-(*n*-Dodecyl) 4-methylbenzothioate (4f).** The title compound was prepared following the general procedure for Table 3, using 1,2-didodecyldisulfane (0.270 g, 0.5 mmol), 4-methylbenzaldehyde (1.0 mL) and DTBP (0.56 mL, 3 mmol), provided **4f** as a white solid (0.247 g, 77% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 7.0 Hz, 3 H), 1.25-1.42 (m, 18 H), 1.61-1.69 (m, 2 H), 2.37 (s, 3 H), 3.04 (t, *J* = 7.4 Hz, 2 H), 7.21 (d, *J* = 8.0 Hz, 2 H), 7.86 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 21.5, 22.6, 28.9, 28.9, 29.1, 29.3, 29.5, 29.6, 29.6, 31.9, 127.2, 129.1, 134.7, 143.8, 191.5; HRMS-EI calcd. for $C_{20}H_{32}OS$: 320.2174, found: 320.2163.

***S*-Cyclohexyl 4-methylbenzothioate (4g).**[10f] The title compound was prepared following the general procedure for Table 3, using 1,2-dicyclohexyldisulfane (0.115 g, 0.5 mmol), 4-methylbenzaldehyde (1.0 mL) and DTBP (0.56 mL, 3 mmol), provided **4g** as a yellow oil (0.110 g, 47% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26-1.36 (m, 1 H), 1.43-1.64 (m, 5 H), 1.74-1.79 (m, 2 H), 2.00-2.23 (m, 2 H), 2.40 (s, 3 H), 3.69-3.72 (m, 1 H), 7.22 (d, *J* = 8.4 Hz, 2 H), 7.85 (d, *J* = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6, 25.6, 26.0, 33.2, 42.4, 127.2, 129.1, 134.9, 143.9, 191.4

***S*-(*n*-Butyl) benzothioate (4h).** The title compound was prepared following the general procedure for Table 3, using 1,2-dibutyldisulfane (0.106 mL, 0.5 mmol), benzaldehyde (1.0 mL) and DTBP (0.56 mL, 3 mmol), provided **4h** as a white solid (0.171 g, 88% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95 (t, *J* = 7.4 Hz, 3 H), 1.43-1.49 (m, 2 H), 1.62-1.70 (m, 2 H), 3.08 (t, *J* = 7.4 Hz, 2 H), 7.44 (t, *J* = 7.4 Hz, 2 H), 7.56 (t, *J* =

7.2 Hz, 1 H), 7.97 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 22.3, 29.0, 31.9, 127.5, 128.8, 133.5, 137.6, 192.4; HRMS-EI calcd. for $C_{11}H_{14}OS$: 194.0765, found: 194.0760.

***S*-(*n*-Dodecyl) benzothioate (4i).**[6c] The title compound was prepared following the general procedure for Table 3, using 1,2-didodecyldisulfane (0.270 g, 0.5 mmol), benzaldehyde (1.0 ml) and DTBP (0.56 mL, 3 mmol), provided **4i** as a white solid (0.218 g, 71% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.6 Hz, 3 H), 1.26-1.45 (m, 18 H), 1.63-1.70 (m, 2 H), 3.06 (t, *J* = 7.4 Hz, 2 H), 7.42 (t, *J* = 7.6 Hz, 2 H), 7.54 (d, *J* = 7.6 Hz, 2 H), 7.97 (d, *J* = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.6, 28.9, 29.0, 29.1, 29.3, 29.5, 29.5, 29.5, 29.6, 31.9, 127.1, 128.4, 133.1, 137.2, 191.9.

***S*-Cyclohexyl benzothioate (4j)**[10a] The title compound was prepared following the general procedure for Table 3, using 1,2-dicyclohexyldisulfane (0.115 g, 0.5 mmol), benzaldehyde (1.0 mL) and DTBP (0.56 mL, 3 mmol), provided **4j** as a yellow oil (0.097 g, 44% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26-1.36 (m, 1 H), 1.44-1.65 (m, 5 H), 1.74-1.79 (m, 2 H), 2.01-2.17 (m, 2 H), 3.71-3.76 (m, 1 H), 7.42-7.45 (m, 2 H), 7.53-7.57 (m, 1 H), 7.94-7.97 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.9, 26.3, 33.4, 40.9, 42.8, 127.4, 128.8, 133.4, 137.8, 196.4.

***S*-(*n*-Butyl) 4-chlorobenzothioate (4k).** The title compound was prepared following the general procedure for Table 3, using 1,2-dibutyldisulfane (0.106 mL, 0.5 mmol), 4-chlorobenzaldehyde (1.0 mL) and DTBP (0.56 mL, 3 mmol), provided **4k** as a yellow oil (0.201 g, 88% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94 (t, *J* = 7.2 Hz, 3 H), 1.41-1.49 (m, 2 H), 1.61-1.68 (m, 2 H), 3.07 (t, *J* = 7.4 Hz, 2 H), 7.40 (d, *J* = 7.6 Hz, 2 H), 7.90 (d, *J* = 7.6 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.5, 21.9, 28.8, 31.4, 128.4, 128.7, 135.4, 139.4, 1910.7; HRMS-EI calcd. for $C_{11}H_{13}ClOS$: 228.0376, found: 228.0375.

***S*-(*n*-Dodecyl) 4-chlorobenzothioate (4l).**[3g] The title compound was prepared following the general procedure for Table 3, using 1,2-didodecyldisulfane (0.270 g, 0.5 mmol), 4-chlorobenzaldehyde (1.0 mL) and DTBP (0.56 mL, 3 mmol), provided **4l** as a yellow oil (0.228 g, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 3 H), 1.26-1.43 (m, 18 H), 1.62-1.69 (m, 2 H), 3.06 (t, *J* = 7.2 Hz, 2 H), 7.39 (d, *J* = 8.4 Hz, 2 H), 7.89 (d, *J* = 8.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 22.6, 28.9, 29.1, 29.3, 29.4, 29.5, 29.6, 31.4, 128.4, 128.7, 135.5, 139.4, 190.6.

***S*-Cyclohexyl 4-chlorobenzothioat*e* (4m).**[10a] The title compound was prepared following the general procedure for Table 3, using 1,2-dicyclohexyldisulfane (0.115 g, 0.5 mmol), 4-chlorobenzaldehyde (1.0 mL) and DTBP (0.56 mL, 3 mmol), provided **4m** as a colorless oil (0.107 g, 42% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.31-1.37 (m, 1 H), 1.43-1.64 (m, 5 H), 1.73-1.78 (m, 2 H), 2.00-2.03 (m, 2 H), 3.70-3.75 (m, 1 H), 7.38-7.42 (m, 2 H), 7.87-7.90 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.5, 25.9, 33.0, 42.7, 128.4, 128.7, 135.7, 139.4, 190.6.

Ethyl 2-{(4-chlorobenzoyl)thio}acetate (4n).[3g] The title compound was prepared following the general procedure for Table 3, using diethyl 2,2'-disulfanediyldiacetate (0.119 g, 0.5 mmol), 4-chlorobenzaldehyde (1.0 mL) and DTBP (0.56 mL, 3 mmol), provided **4n** as a white solid (0.119 g, 46% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.21 (t, *J* = 7.0 Hz, 3 H), 3.80 (s, 2 H), 4.14 (q, *J* = 7.2 Hz, 2 H), 7.35 (dd, *J* = 2.0 & 6.8 Hz, 2 H), 7.83 (dd, *J* = 2.0 & 6.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 31.4, 61.9, 128.6, 128.9, 134.3, 140.1, 168.4, 188.8.

***S*-(*n*-Butyl) thiophene-2-carbothioate (4o).** The title compound was prepared following the general procedure for Table 3, using 1,2-dibutyldisulfane (0.106 mL, 0.5 mmol), thiophene-2-carbaldehyde (1.0 mL)and DTBP (0.56 mL, 3 mmol), provided **4o** as a yellow oil (0.132 g, 66% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94 (t, *J* = 7.6 Hz, 3 H), 1.41-1.49 (m, 2 H), 1.63-1.69 (m, 2 H), 3.07 (t, *J* = 7.2 Hz, 2 H), 7.09 (t, *J* = 4.4 Hz, 1 H), 7.59 (dd, *J* = 1.2 & 4.8 Hz, 1 H), 7.78 (dd, *J* = 1.2 & 4.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.5, 21.9, 28.8, 31.6, 127.7, 130.7, 132.3, 142.2, 184.0; HRMS-EI calcd. for $C_9H_{12}OS_2$: 200.0330, found: 200.0336.

***S*-(*n*-Dodecyl) 4-(trifluoromethyl)benzothioate (4p).** The title compound was prepared following the general procedure for Table 3, using 1,2-didodecyldisulfane (0.270 g, 0.5 mmol), 4-(trifluoromethyl) benzaldehyde (1.0 mL) and DTBP (0.56 mL, 3 mmol), provided **4p** as a yellow oil (0.292 g, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.6 Hz, 3 H), 1.26-1.44 (m, 18 H), 1.64-1.72 (m, 2 H), 3.10 (t, *J* = 7.4 Hz, 2 H), 7.70 (d, *J* = 8.0 Hz, 2 H), 8.06 (d, *J* = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.7, 28.9, 29.1, 29.3, 29.4, 29.4, 29.6, 29.6, 31.9, 123.5 (d, *J* = 271.2 Hz), 125.6, 127.5, 134.5 (d, *J* = 32.8 Hz), 140.0, 191.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -64.7 (s); HRMS-EI calcd. for $C_{20}H_{29}F_3OS$: 374.1891, found: 374.1887.

***S*-(*n*-Butyl) 2-methylbenzothioate (4q).** The title compound was prepared following the general procedure for Table 3, using 1,2-dibutyldisulfane (0.106 mL, 0.5 mmol), 2-methylbenzaldehyde (1.0 mL) and DTBP (0.56 mL, 3 mmol), provided **4q** as a colorless oil (0.140 g, 67% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94 (t, *J* = 7.2 Hz, 3 H), 1.40-1.49 (m, 2 H), 1.61-1.68 (m, 2 H), 2.47 (s, 3 H), 3.02 (t, *J* = 7.4 Hz, 2 H), 7.19-7.24 (m, 2 H), 7.34 (t, *J* = 7.6 Hz, 1 H), 7.76 (d, *J* = 7.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.5, 20.4, 22.0, 29.2, 31.6, 125.6, 128.2, 131.3, 131.4, 136.5, 137.7, 194.4; HRMS-EI calcd. for $C_{12}H_{16}OS$: 208.0922, found: 208.0921.

***S*-Dodecyl 2-methylbenzothioate (4r).**[3g] The title compound was prepared following the general procedure for Table 3, using 1,2-didodecyldisulfane (0.270 g, 0.5 mmol), 2-methylbenzaldehyde (1.0 mL) and DTBP (0.56 mL, 3 mmol), provided **4r** as a colorless oil (0.234 g,73% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.6 Hz, 3 H), 1.26-1.43 (m, 18 H), 1.62-1.69 (m, 2 H), 2.47 (s, 3 H), 3.01 (t, *J* = 7.4 Hz, 2 H), 7.18-7.23 (m, 2 H), 7.33 (t, *J* = 7.2 Hz, 1 H), 7.75 (d, *J* = 7.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 20.5, 22.6, 28.9, 29.1, 29.3, 29.5, 29.6, 29.6, 31.9, 125.6, 128.3, 131.3, 131.4, 136.5, 137.7, 194.3.

***S*-Dodecyl 4-bromobenzothioate (4s).**[3g] The title compound was prepared following the general procedure for Table 3, using 1,2-didodecyldisulfane (0.270 g, 0.5 mmol), 4-bromobenzaldehyde (1.0 mL) and DTBP (0.56 mL, 3 mmol), provided **4s** as a white solid (0.270 g, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 3 H), 1.26-1.43 (m, 18 H), 1.62-1.69 (m, 2 H), 3.06 (t, *J* = 7.4 Hz, 2 H), 7.55 (d, *J* =

8.0 Hz, 2 H), 7.81 (d, J = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.6, 28.9, 29.1, 29.3, 29.4, 29.4, 29.5, 29.6, 31.9, 128.1, 128.5, 131.7, 135.9, 190.8.

Ethyl 2-{(4-bromobenzoyl)thio} acetate (4t).[3g] The title compound was prepared following the general procedure for Table 3, using diethyl 2,2'-disulfanediyldiacetate (0.119 g, 0.5 mmol), 4-bromobenzaldehyde (1.0 mL) and DTBP (0.56 mL, 3 mmol), provided **4t** as a yellow solid (0.152 g, 50% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.30 (t, J = 7.2 Hz, 3 H), 3.89 (s, 2 H), 4.23 (q, J = 7.2 Hz, 2 H), 7.60 (dd, J = 2.0 & 7.2 Hz, 2 H), 7.84 (dd, J = 1.6 & 6.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 31.4, 61.9, 128.7, 128.8, 131.9, 134.8, 168.4, 189.1.

***S*-(*n*-Butyl) 3-cyanobenzothioate (4u).** The title compound was prepared following the general procedure for Table 3, using 1,2-dibutyldisulfane (0.106 mL, 0.5 mmol), 3-formylbenzonitrile (1.0 mL) and DTBP (0.56 mL, 3 mmol), provided **4u** as a white solid (0.195 g, 89% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.96 (t, J = 7.2 Hz, 3 H), 1.41-1.50 (m, 2 H), 1.62-1.70 (m, 2 H), 3.11 (t, J = 7.4 Hz, 2 H), 7.62 (t, J = 7.8 Hz, 1 H), 7.86 (d, J = 7.2 Hz, 1 H), 8.17-8.23 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.6, 22.0, 28.9, 29.1, 31.4, 94.1, 126.3, 130.1, 135.9, 138.9, 141.9, 190.7; HRMS-EI calcd. for $C_{12}H_{13}NOS$: 219.0718, found: 219.0710.

***S*-Butyl 3-iodobenzothioate (4v).** The title compound was prepared following the general procedure for Table 3, using 1,2-dibutyldisulfane (0.106 mL, 0.5 mmol), 3-iodobenzaldehyde (1.0 mL) and DTBP (0.56 mL, 3 mmol), provided **4v** as a yellow oil (0.128 g, 40% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95 (t, J = 7.4 Hz, 3 H), 1.42-1.50 (m, 2 H), 1.62-1.69 (m, 2 H), 3.08 (t, J = 7.2 Hz, 2 H), 7.18 (t, J = 7.8 Hz, 1 H), 7.87-7.94 (m, 2 H), 8.28 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.6, 22.0, 28.9, 29.1, 31.4, 94.1, 126.3, 130.1, 135.9, 138.9, 141.9, 190.7; HRMS-EI calcd. for $C_{11}H_{13}IOS$: 319.9732, found: 319.9734.

Acknowledgements

The National Science Council, Taiwan (NSC 101-2113-M-005-008-MY3), the National Chung Hsing University and the Centre of Nanoscience and Nanotechnology (NCHU) are gratefully acknowledged for financial support. We also thank Prof. Fung-E Hong (NCHU) for sharing his GC-MS instruments. C.F.L. is a Golden-Jade Fellow of Kenda Foundation, Taiwan.

References

1 For selected reviews, please see: (a) S. Murai, *Activation of Unreactive Bonds and Organic Synthesis*, Springer, Berlin, Germany, 1999**,** p. 48; (b) G. Dyker, *Handbook of C–H Transformations. Applications in Organic Synthesis*, Wiley-VCH, Weinheim, Germany, 2005; (c) C.-L. Sun, B.-J. Li and Z.-J. Shi, *Chem. Rev.* 2011, **111**, 1293-1314; (d) C. S. Yeung and V. M. Dong, *Chem. Rev.* 2011, **111**, 1215-1292; (e) C. Liu, H. Zhang, W. Shi and A. Lei, *Chem. Rev.* 2011, **111**, 1780-1824; (f) I. A. Mkhalid, J. H. Barnard, T. B. Marder, J. M. Murphy and J. F. Hartwig, *Chem. Rev*., 2010, **110**, 890-931; (g) T. W. Lyons and M. S. Sanford, *Chem. Rev*., 2010, **110**, 1147-1169; (h) J. C. Lewis, R. G. Bergman and J. A. Ellman, *Acc. Chem. Res.*, 2008, **41**, 1013-1025; (i) Y. J. Park, J. W. Park and C. H. Jun, *Acc. Chem. Res.*, 2008, **41**, 222-234; (j) M. M. D. Requejo and P. J. Pérez, *Chem. Rev.*, 2008, **108**, 3379-3394; (k) D. A. Colby, R. G. Bergman and J. A. Ellman, *Chem. Rev.*, 2010, **110**, 624-655; (l) N. Shi, C. Liu and A. Lei, *Chem. Soc. Rev.*, 2011, **40**, 2761-2776.

2 (a) E. Shirakawa, K.-i. Itoh, T. Higashino and T. Hayashi, *J. Am. Chem. Soc.* 2010, **132**, 15537-15539; (b) C.-L. Sun, H. Li, D.-G. Yu, M. Yu, X. Zhou, X.-Y. Lu, K. Huang, S-F. Zheng, B.-J. Li and Z.-J. Shi, *Nature Chem.*, 2010, **2**, 1044-1049; (c) W. Liu, H. Cao, H. Zhang, H. Zhang, K. H. Chung, C. He, H. Wang, F. Y. Kwong and A. Lei, *J. Am. Chem. Soc*. 2010, **132**, 16737-16740.

3 (a) M. Takagi, S. Goto and T. Matsuda, *J. Chem. Soc. Chem. Commun.* 1976, 92-93; (b) M. Takagi, S. Goto, M. Tazaki and T. Matsuda, *Bull. Chem. Soc. Jpn.* 1980, **53**, 1982-1987; (c) S. B. Bandgar, B. P. Bandgar, B. L. Korbad and S. S. Sawant, *Tetrahedron Lett.* 2007, **48**, 1287-1290; (d) T. Uno, T. Inokuma and Y. Takemoto, *Chem. Commun.* 2012, **48**, 1901-1903; (e) H. Nambu, K. Hata, M. Matsugi and Y. Kita, *Chem. Commun.* 2002, 1082-1083; (f) H. Nambu, K. Hata, M. Matsugi and Y. Kita, *Chem. Eur. J.* 2005, **11**, 719-727; (g) C.-L. Yi, Y.-T. Huang and C.-F. Lee, *Green Chem.* 2013, **15**, 2476-2484; (h) M. Tingoli, A. Temperini, L. Testaferri and M. Tiecco, *Synlett* 1995, 1129-1130; (i) S. Singh and L. D. S. Yadav, *Tetrahedron Lett.* 2012, **53**, 5136-5140.

4 (a) S. Rossi, M. Benaglia, F. Cozzi, A. Genoni and T. Benincori, *Adv. Synth. Catal.* 2011, **353**, 848-854; (b) D. Crich and I. Sharma, *Angew. Chem. Int. Ed.* 2009, 48, 2355-2358; (c) D. Crich and K. Sasaki, *Org. Lett.* 2009, **11**, 3514-3517; (d) M. Benaglia, M. Cinquini and F. Cozzi, *Eur. J. Org. Chem.* 2000, 563-572; (e) K. Matsuo and M. Sindo, *Org. Lett.* 2010, **12**, 5346-5349; (f) S. Iimura, K. Manabe and S. Kobayashi, *Org. Lett.* 2003, **5**, 101-103; (g) T. Fukuyama and H. Tokuyama, *Aldrichimica Acta* 2004, **37**, 87-96; (h) H. Yang, H. Li, R. Wittenberg, M. Egi, W. Huang and L. S. Liebeskind, *J. Am. Chem. Soc.* 2007, **129**, 1132-1140; (i) H. Li, H. Yang and L. S. Liebeskind, *Org. Lett.* 2008, **10**, 4375-4378; (j) K. Kunchithapatham, C. C. Eichman and J. P. Stambuli, *Chem. Commun.* 2011, **47**, 12679-12681; (k) J. M. Yost, G. Zhou and D. M. Coltart, *Org. Lett.* 2006, **8**, 1503-1506; (l) N. Utsumi, S. Kitagaki and C. F. Barbas III, *Org. Lett.* 2008, **10**, 3405-3408; (m) D. A. Alonso, S. Kitagaki, N. Utsumi and C. F. Barbas III, *Angew. Chem., Int. Ed.* 2008, **47**, 4588-4591; (n) A. Iida, J. Osada,R. Nagase, T. Misaki and Y. Tanabe, *Org. Lett.* 2007, **9**, 1859-1862.

5 J. Staunton and K. J. Weissman, *Nat. Prod. Rep*. 2001, **18**, 380-416.

6 (a) S. Magens and B. Plietker, *Chem.–Eur. J.* 2011, **17**, 8807-8809; (b) A. R. Katritzky, A. A. Shestopalov and K. Suzuki, *Synthesis* 2004, 1806-1813; (c) S. limura, K. Manabe and S. Kobayashi, *Chem. Commun.* 2002, 94-95; (d) S. Ahmad and J. Iqbal, *Tetrahedron Lett.* 1986, **27**, 3791-3794; (e) G. O. Spessard, W. K. Chan and S. Masamune, *Org. Synth.* 1982, **61**, 134-141; (f) C. C. Silveira, A. L. Braga and E. L. Larghi, *Organometallics* 1999, **18**, 5183-5186; (g) H. M. Meshram G. S. Reddy, K. H. Mindu and J. S. Yadav, *Synlett*, 1998, 877-878.

7 (a) Y.-C. Liu and C.-F. Lee, *Synlett* 2013, **24**, 2320-2326; (b) C.-L. Yi, T.-J. Liu, J.-H. Cheng and C.-F. Lee, *Eur. J. Org. Chem.* 2013, 3910-3918; (c) T.-J. Liu, C.-L. Yi, C.-C. Chan and C.-F. Lee, *Chem. Asian. J.* 2013, **8**, 1029-1034; (d) C.-H. Cheng, C. Ramesh, H.-L. Kao, Y.-J. Wang, C.-C. Chan and C.-F. Lee, *J. Org. Chem.* 2012, **77**, 10369-10374; (e) J.-H. Cheng, C.-L. Yi, T.-J. Liu and C.-F. Lee, *Chem. Commun.* 2012, **48**, 8440-8442; (f) Y.-Y. Lin, Y.-J. Wang, C.-H. Lin, J.-H. Cheng and C.-F. Lee, *J. Org. Chem.* 2012, **77**, 6100-6106; (g) C.-S. Lai, H.-L. Kao, Y.-J. Wang and C.-F. Lee, *Tetrahedron Lett.* 2012, **53**, 4365-4367; (h) H.-L. Kao and C.-F. Lee, *Org. Lett*. 2011, **13**, 5204-5207; (i) H.-L. Kao, C.-K. Chen, Y.-J. Wang and C.-F. Lee, *Eur. J. Org. Chem.* 2011, 1776-1781; (j) C.-K. Chen, Y.-W. Chen, C.-H. Lin, H.-P. Lin and C.-F. Lee, *Chem. Commun.* 2010, **46**, 282-284; (k) J.-R. Wu, C.-H. Lin and C.-F. Lee, *Chem. Commun.* 2009, 4450-4452.

8 M.-B. Zhou, R.-J. Song, X.-H. Ouyang, Y. Liu, W.-T. Wei, G.-B. Deng and J.-H. Li, *Chem. Sci*. 2013, **4**, 2690-2694.

9 S.-R. Guo, Y.-Q. Yuan and J.-N. Xiang, *Org. Lett.*, 2013, **15**, 4654-4657.

10 (a) A. S. El-Azab and A. A.-M. Abdel-Aziz1, *Phosphorus, Sulfur, and Silicon*, 2012, **187**, 1046-1055; (b) M. N. Burhardt, R. H.

Taaning and T. Skrydstrup, *Org. Lett.* 2013, **15**, 948-951; (c) Y. Minami, H. Kuniyasu, K. Miyafuji and N. Kambe, *Chem. Commun.*2009, 3080- 3082; (d) B. W. Fausett and L. S. Liebeskind, *J. Org. Chem.* 2005, **70**, 4851-4853; (e) B. Basu, S. Paul and A. K. Nanda, *Green Chem.*, 2010, **12**, 767-771; (f) N. Iranpoor, H. Firouzabadi, D. Khalili and S. Motevalli, *J. Org. Chem.* 2008, **73**, 4882-4887.