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P_4S_{10}/dimethicone tandem: efficient reagent for thionation of various aromatic amides and esters

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ABSTRACT

Organosulfur compounds are valuable because of their rich and varied chemistry especially in biological field. We report a new and efficient way for thionation of various aromatic amides and esters using P_4S_{10}/dimethicone tandem. The ease of handling and higher yield makes this protocol economical.

1. Introduction

Sulfur containing compounds especially thiocarbonyls are highly versatile intermediate or precursor, which find many applications both in synthetic and biological chemistry.[1] This growing repertoire of applications draw significant attention to develop new and efficient methods for thionation, the widely applied method for the synthesis of organosulfur compounds. There have been gargantuan ways and modifications made on this method. Few of the most recent and popular methods employed Lawesson's reagent with and without modifications,[2] P_4S_{10} in combination with other reagents or materials, such as hexamethyldisiloxane (HMDO)[3] or Al_2O_3,[4] $PSCl_3$ with H_2O and Et_3N,[5] thiourea,[6] and aqueous ammonium sulfide.[7] Some of these methods offer various advantages and drawbacks one way or another. To quote a few drawbacks are difficulty in separation, longer reaction time, expensive reagent, and low yield. Herein we report dimethicone, commonly known as silicon oil, as a new additive for P_4S_{10} that efficiently thionates aromatic amide and esters.

2. Results and discussion

Dimethicone (Fig. 1) has been explored in our laboratory for various applications in organic synthesis. Since it is an oligomer of

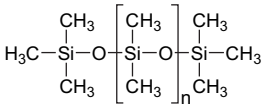
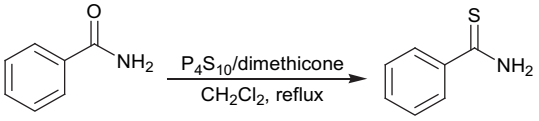


Figure 1. Structure of dimethicone.

HMDO, we hypothesized that perhaps it could also function as such in the thionation reaction. Furthermore, dimethicone is immiscible in methanol thus; dissolving the product in this solvent could separate the dimethicone and possibly recycle it. Consequently, we check this possibility using benzamide (Scheme 1).



Scheme 1. Thionation of benzamide.

Our optimization studies showed that 0.2 equiv of P_4S_{10} in 5 mL of dimethicone (Dow Corning Corporation 200® fluid, viscosity 50 cSt) using CH_2Cl_2 solvent is the appropriate condition. It is necessary to use CH_2Cl_2 solvent to dissolve the starting benzamide. Since dimethicone is immiscible in methanol (Fig. 2) it is possible to extract the product to methanol layer by simple decantation[8] and

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recovered the dimethicone for possible reuse. Test tube A shows the crude reaction mixture containing dimethicone after the removal of CH_2Cl_2 solvent. First extraction was tried by shaking the mixture with methanol (test tube B) and standing it for a while clearly separated the methanol layer (upper) and the dimethicone layer (lower) as shown in test tube C. Further extractions were done to ensure that no more product remained in the dimethicone layer (test tubes E–G). It was noticeable that further extractions led to the recovery of dimethicone as a viscous transparent liquid (test tube G lower layer), that is, ready for reuse.

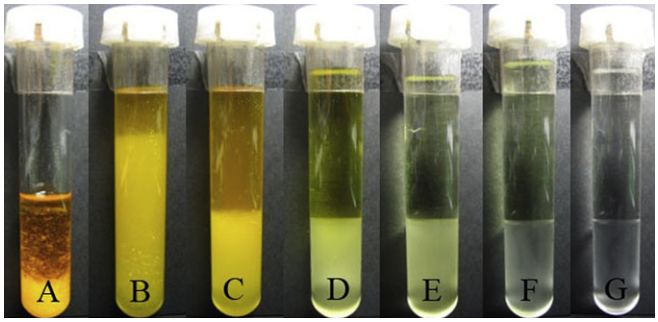


Figure 2. Reaction mixture (A) and extraction (B and C: first, D: second, E: third, F: fourth, G: fifth extraction) of product using methanol (upper layer).

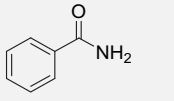
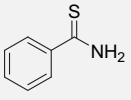
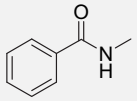
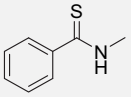
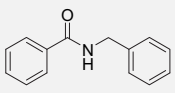
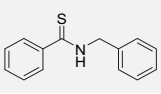
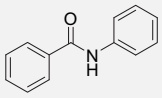
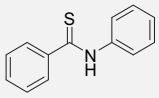
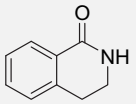
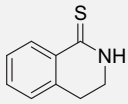
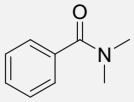
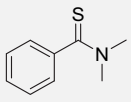
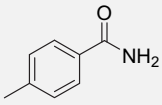
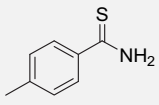
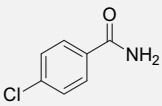
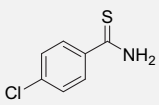
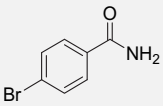
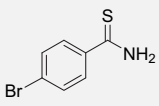
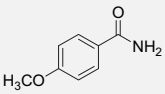
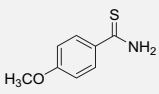
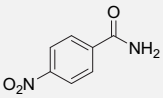
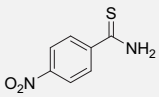
Recycle test (Table 1) showed that certain volume of dimethicone was consumed during the reaction. These results demonstrated that it acts in the same manner as HMDO as previously studied by some group.[3b] Even though dimethicone was consumed (0.60–1.2 mL in every run) during the reaction it can still be reuse up to four times without considerable loss of reactivity. Furthermore its immiscibility in methanol was an advantage because it makes the separation easy. To further validate this observation several amides were tested for thionation (Table 2) with and without dimethicone.

Table 1
Dimethicone recovery test for thionation of benzamide[a]

Run	Volume (mL)	Yield (%)
First	5.0	87
Second	4.4	85
Third	3.6	90
Fourth	2.4	89

[a] Reaction conditions: Reflux benzamide (3.0 mmol), P_4S_{10} (0.6 mmol), and dimethicone (5 mL) in CH_2Cl_2 solvent (10 mL) for 1.5 h. Reuse the dimethicone for the succeeding trials. Independently, using 0.6 mL of dimethicone gave 83% yield.

Table 2
Thionation of various aromatic amides[a]

Entry	Starting material	Product	Time	Isolated yield (%)	
				Dimethicone	
				With	Without
1			1.5 h	87	67
2			2 h	94	87
3			10 min	93	82
4			1.5 h	96	74
5			5 h	91	71
6			15 min	99	90
7			6 h	96	62
8			3 h	90	40
9			8 h	84	67
10			2.5 h	68	56
11[b]			12 h	89	41

[a] Procedure: Reflux starting material (3.0 mmol), P_4S_{10} (0.6 mmol), and dimethicone (5 mL) in CH_2Cl_2 solvent (10 mL).
[b] Used 45 mL solvent.

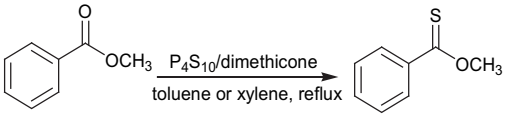
Table 2 revealed that thionation yield is much higher using P_4S_{10} with dimethicone compared to that of without. Previous study[3] described that during the thionation with P_4S_{10}, the reaction environment becomes more electrophilic due to the successive replacement of sulfur by oxygen on the phosphorus atom. It produces highly electrophilic species that may act as potent electrophile capable of promoting undesirable side reactions with the carbonyl and thiocarbonyl compounds present in the reaction mixture thereby giving lower yield.

We presumed that dimethicone acted as scavenger of these electrophilic species by simply entrapping them perhaps via encapsulation and also via reaction like HMDO. This is probably the reason for the good to excellent yield of thionated product. In addition, the short reaction time probably makes some of the dimethicone to simply act as adsorbent of the produced electrophilic species that intervenes in the reaction progress.

Moreover, our results showed that an increase in the electron density on the oxygen atom of the amido group favors thionation such that tertiary amide (entry 6) reacts faster than secondary (entry 2) and primary (entry 1). Furthermore, the presence of electron withdrawing group on the ring, such as nitro group (entry 11) also supports this observation. However, the presence of methoxy substituent gave lower yield presumably because of the competition between the carbonyl oxygen and the more basic oxygen for electrophilic phosphorus in the active thionating species.

Significantly, we obtained higher thionation yield at a shorter reaction time for most of the common substrate also tested with other thionating agents aforementioned especially P_4S_{10}/HMDO tandem.[3b]

To further expound on the validity of this protocol, we also considered the thionation reaction of esters by testing methylbenzoate (Scheme 2). Thionation of esters are usually difficult and gave lower yield due to the generally lower reactivity of carbonyl ester toward the electrophilic thionating agents. Several groups have demonstrated this. For instance, thionation of esters with Lawesson's reagent[9a] and P_4S_{10}/HMDO required refluxing condition with either toluene or *p*-xylene at a prolong time while thionation of amides required shorter time and lower temperature.[3] Furthermore, thionation of esters sometimes gave mixtures[9b] substantiating its lower reactivity.



Scheme 2. Thionation of methylbenzoate.

At first, we considered exactly the same conditions however; using CH_2Cl_2 solvent gave lower yield due to reaction temperature. Thus, we opted to change the solvent to a higher boiling point one, such as toluene and *p*-xylene. *p*-Xylene gave much better results for every cases.

Dimethicone recovery test was also done using methyl 4-methoxybenzoate (Table 3).[10] The yield is almost the same all throughout however; it is visible that the volume of dimethicone quickly decreases. Presumably at longer reaction time (12 h) and higher temperature some of the dimethicone reacts with the electrophilic species produced during the thionation reaction leading to the decrease in the volume of dimethicone recovered.

Table 3
Dimethicone recovery test for thionation of methyl 4-methoxybenzoate[a]

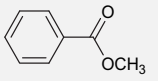
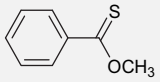
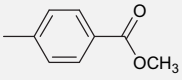
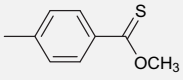
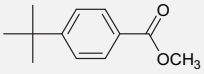
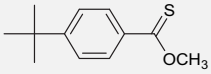
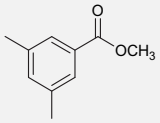
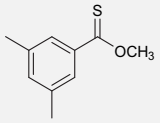
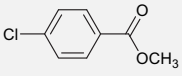
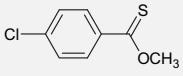
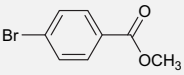
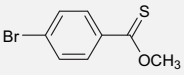
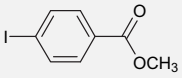
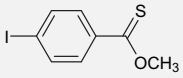
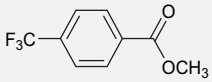
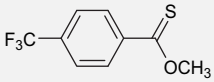
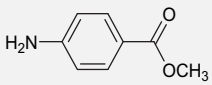
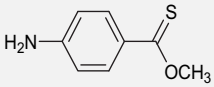
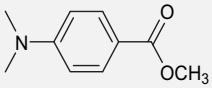
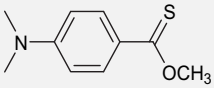
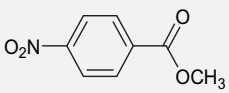
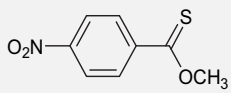
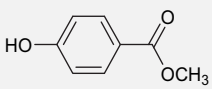
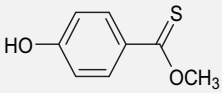
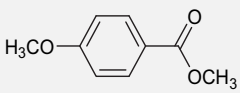
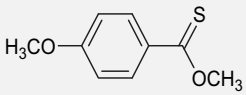
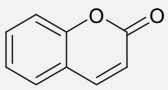
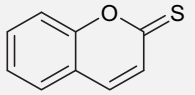
Run	Volume (mL)	Yield (%)
First	5.0	95
Second	4.4	95
Third	2.8	94

[a] Reaction Conditions: Reflux methyl 4-methoxybenzoate (3.0 mmol), P_4S_{10} (0.75 mmol), and dimethicone (5 mL) in *p*-xylene solvent (10 mL) for 12 h. Reuse the dimethicone for the succeeding trials.

As depicted in Table 4, thionation of esters using our protocol gave fairly good results. The presence of electron donating substituents on the ring (entries 2–4, 10, and 13) gave higher yield compared to those with electron withdrawing substituents (entries 5, 8, and 11). Noticeably substituents on the ring having free hydroxyl and amino group (entries 9, 12) likewise gave lower yield. In the case of halogen substituents on the ring (entries 5–7), the yield of reaction was descending from chloro to iodo substituent. It is presumed that the lone pair of halogen atom may interact with the electrophilic phosphorus and iodine atom can coordinate better than chlorine and bromine atom toward the electrophilic phosphorus species. The α,β-unsaturated carbonyl group (entry 14) increases the rate of reaction.

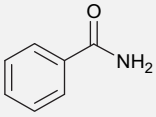
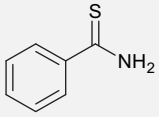
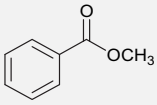
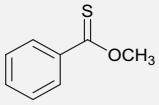
Microwave irradiation has been considered as well. There have been reports on the efficiency of microwave irradiation on thionation such that it enhanced the yield at a shorter reaction time.[11] To check the effect of microwave irradiation in our protocol we considered checking the thionation of representative sample of amide and ester. As shown in Table 5, the yield was almost the same but the reaction time was dramatically decreased. Indeed, this protocol could also be applied under microwave condition leading to the same reaction yield but shorter reaction time.

Table 4
Thionation of various aromatic esters[a]

Entry	Starting material	Product	Yield (%) toluene/xylene
1			15/81
2			55/82
3			63/81
4			29/71
5			6/70
6			8/39
7			8/25
8			23/51
9			8/9
10			23/86
11			4/28
12			10/15
13			52/95
14			94/quant

[a] Reaction Conditions: Reflux starting material (3.0 mmol), P_4S_{10} (0.75 mmol), and dimethicone (5 mL) in toluene or *p*-xylene solvent (10 mL) for 12 h.

Table 5
Microwave (MW) reaction versus thermal reaction of selected compounds[a]

Entry	Starting material	Product	Time		Isolated yield (%)	
			MW (min)	Thermal (h)	MW	Thermal
1			5 min	1.5 h	92	87
2			40 min	12 h	81	81

[a] Reaction Conditions: Reflux starting material (3.0 mmol), P_4S_{10} (0.75 mmol), and dimethicone (5 mL) in CH_2Cl_2 (entry 1) and *p*-xylene (entry 2) solvent (10 mL) for specified time using MW and thermal condition.

3. Conclusion

In summary, we have investigated and presented a valuable alternative for thionation. This protocol necessitate only minimum amount of P_4S_{10} to facilitate thionation. The use of dimethicone as scavenger of electrophilic species that hinders the reaction and as facilitator for reaction rate is very economical. Thus, this new protocol for thionation is facile and practical.

4. Experimental section

4.1. General procedure for thionation of amides

The amide starting material (3.0 mmol), P_4S_{10} (0.6 mmol), and dimethicone (5 mL; Dow Corning Corporation 200® fluid, viscosity 50 cSt) were reflux in 10 mL of CH_2Cl_2 solvent. The reaction mixture was continuously stirred until completion based on TLC monitoring. If the starting spot never disappeared we varied the reaction time to find the maximum yield possible. Upon completion, CH_2Cl_2 solvent was evaporated using rotary evaporator. Methanol was added to the residue several times necessary to extract the product from dimethicone. The methanol was evaporated and the crude mixture was purified by silica gel column chromatography using *n*-hexane/EtOAc (either 3:1 or 20:1 v/v) as eluent system. The same procedure was applied for trials without dimethicone. The dimethicone was simply omitted so as the methanol addition during work-up.

4.1.1. Thiobenzamide (Table 2, entry 1)[12]. Pale yellow solid purified using *n*-hexane/EtOAc (3:1 v/v; R_f=0.23) as eluent system in silica gel column chromatography. ^{1}H NMR ($CDCl_3$): δ 7.89 (d, J=7.8 Hz, 2H, ArH), 7.64 (br s, 1H, NH), 7.53 (t, J=7.4 Hz, 1H, ArH), 7.42 (t, J=7.7 Hz, 2H, ArH), 7.22 (br s, 1H, NH).

4.1.2. N-Methylthiobenzamide (Table 2, entry 2)[7]. Pale yellow solid purified using *n*-hexane/EtOAc (3:1 v/v; R_f=0.30) as eluent system in silica gel column chromatography. ^{1}H NMR ($CDCl_3$): δ 7.76 (d, J=7.5 Hz, 2H, ArH), 7.77 (br s, 1H, NH), 7.39–7.47 (m, 3H, ArH), 3.37 (d, J=4.8 Hz, 3H, CH_3).

4.1.3. N-Benzylthiobenzamide (Table 2, entry 3)[7]. Pale yellow solid purified using *n*-hexane/EtOAc (20:1 v/v; R_f=0.10) as eluent system in silica gel column chromatography. ^{1}H NMR ($CDCl_3$): δ 7.77 (d, J=7.2 Hz, 2H, ArH), 7.69 (br s, 1H, NH), 7.36–7.48 (m, 8H, ArH), 5.01 (d, J=5.1 Hz, 2H, CH_2).

4.1.4. Thiobenzanilide (Table 2, entry 4)[13]. Pale yellow solid purified using *n*-hexane/EtOAc (3:1 v/v; R_f=0.45) as eluent system in silica gel column chromatography. ^{1}H NMR ($CDCl_3$): δ 9.01 (br s, 1H, NH), 7.87 (d, J=6.9 Hz, 2H, ArH), 7.79 (d, J=7.8 Hz, 2H, ArH), 7.32–7.52 (m, 7H, ArH).

4.1.5. 3,4-Dihydroquinoline-2(1H)-thione (Table 2, entry 5)[14]. Pale yellow solid purified using *n*-hexane/EtOAc (3:1 v/v; R_f=0.50) as eluent system in silica gel column chromatography. ^{1}H NMR ($CDCl_3$): δ 9.72 (br s, 1H, NH), 7.07–7.20 (m, 2H, ArH), 7.09 (t, J=7.4 Hz, 1H, ArH), 6.86 (d, J=7.8 Hz, 1H, ArH), 3.12 (dd, J=8.4, 6.3 Hz, 2H, CH_2), 2.90 (t, J=7.5 Hz, 2H, CH_2).

4.1.6. N,N-Dimethylthiobenzamide (Table 2, entry 6)[15]. Pale yellow solid purified using *n*-hexane/EtOAc (20:1 v/v; R_f=0.10) as eluent system in silica gel column chromatography. ^{1}H NMR ($CDCl_3$): δ 7.31–7.35 (m, 5H, ArH), 3.62 (s, 3H, CH_3), 3.18 (s, 3H, CH_3).

4.1.7. 4-Methylthiobenzamide (Table 2, entry 7)[12]. Pale yellow solid purified using *n*-hexane/EtOAc (3:1 v/v; R_f=0.18) as eluent system in silica gel column chromatography. ^{1}H NMR ($CDCl_3$): δ 7.80 (d, J=8.4 Hz, 2H, ArH), 7.65 (br s, 1H, NH), 7.22 (d, J=8.1 Hz, 2H, ArH), 7.18 (br s, 1H, NH), 2.40 (s, 3H, CH_3).

4.1.8. 4-Chlorothiobenzamide (Table 2, entry 8)[16]. Pale yellow solid purified using *n*-hexane/EtOAc (3:1 v/v; R_f=0.23) as eluent system in silica gel column chromatography. ^{1}H NMR ($CDCl_3$): δ 7.83 (dt, J=8.7, 2.3 Hz, 2H, ArH), 7.69 (br s, 1H, NH), 7.39 (dt, J=8.7, 2.2 Hz, 2H, ArH), 7.17 (br s, 1H, NH).

4.1.9. 4-Bromothiobenzamide (Table 2, entry 9)[17]. Pale yellow solid purified using *n*-hexane/EtOAc (3:1 v/v; R_f=0.18) as eluent system in silica gel column chromatography. ^{1}H NMR ($CDCl_3$): δ 7.75 (dt, J=8.7, 2.3 Hz, 2H, ArH), 7.69 (br s, 1H, NH), 7.55 (dt, J=8.1,2.2 Hz, 2H, ArH), 7.16 (br s, 1H, NH).

4.1.10. 4-Methoxythiobenzamide (Table 2, entry 10)[16]. Pale yellow solid purified using *n*-hexane/EtOAc (3:1 v/v; R_f=0.13) as eluent system in silica gel column chromatography. ^{1}H NMR ($CDCl_3$): δ 7.91 (dt, J=9.3, 2.7 Hz, 2H, ArH), 7.54 (br s, 1H, NH), 7.12 (br s, 1H, NH), 6.91 (dt, J=9.3, 2.7 Hz, 2H, ArH), 3.87 (s, 3H, OCH_3).

4.1.11. 4-Nitrothiobenzamide (Table 2, entry 11)[16]. Pale yellow solid purified using *n*-hexane/EtOAc (3:1 v/v; R_f=0.14) as eluent system in silica gel column chromatography. ^{1}H NMR ($CDCl_3$): δ 8.28 (dt, J=8.7, 2.1 Hz, 2H, ArH), 8.00 (dt, J=9.3, 2.1 Hz, 2H, ArH), 7.71 (br s, 1H, NH), 7.22 (br s, 1H, NH).

4.2. General procedure for thionation of esters

The ester starting material (3.0 mmol), P_4S_{10} (0.75 mmol), and dimethicone (5 mL; Dow Corning Corporation 200® fluid, viscosity

50 cSt) were reflux in toluene and *p*-xylene solvent (10 mL) in different trials. The reaction mixture was continuously stirred for 12 h. Upon completion, all solvent was evaporated using rotary evaporator. Methanol was added to the residue several times necessary to extract the product from dimethicone. All methanol was evaporated and the crude mixture was purified by silica gel column chromatography using *n*-hexane/EtOAc (either of the following ratio: 60:1, 30:1, 20:1, 10:1 or 5:1 v/v) as eluent system.

4.2.1. Methyl thiobenzoate (Table 4, entry 1)[18]. Orange liquid purified using *n*-hexane/EtOAc (60:1 v/v; R_f=0.50) as eluent system in silica gel column chromatography. ^{1}H NMR ($CDCl_3$): δ 8.20 (d, *J*=8.1 Hz, 2H, ArH), 7.55 (t, *J*=7.2 Hz, 1H, ArH), 7.40 (t, *J*=6.9 Hz, 2H, ArH), 4.31 (s, 3H, OCH_3).

4.2.2. Methyl 4-methylbenzenecarbothioate (Table 4, entry 2)[18]. Orange liquid purified using *n*-hexane/EtOAc (60:1 v/v; R_f=0.38) as eluent system in silica gel column chromatography. ^{1}H NMR ($CDCl_3$): δ 8.11 (d, *J*=8.1 Hz, 2H, ArH), 7.20 (d, *J*=7.8 Hz, 2H, ArH), 4.30 (s, 3H, OCH_3), 2.40 (s, 3H, $ArCH_3$).

4.2.3. Methyl 4-tert-butylbenzenecarbothioate (Table 4, entry 3)[19]. Orange liquid purified using *n*-hexane/EtOAc (30:1 v/v; R_f=0.43) as eluent system in silica gel column chromatography. ^{1}H NMR ($CDCl_3$): δ 8.13 (d, *J*=9.0 Hz, 2H, Ar–H), 7.41 (d, *J*=8.4 Hz, 2H, ArH), 4.30 (s, 3H, OCH_3), 1.34 (s, 9H, $C(CH_3)_3$).

4.2.4. Methyl 3,5-dimethylbenzenecarbothioate (Table 4, entry 4). Orange liquid purified using *n*-hexane/EtOAc (60:1 v/v; R_f=0.38) as eluent system in silica gel column chromatography. ^{1}H NMR ($CDCl_3$): δ 7.82 (s, 2H, ArH), 7.19 (s, 1H, ArH), 4.29 (s, 3H, OCH_3), 2.37 (s, 6H, $ArCH_3$); ^{13}C NMR ($CDCl_3$): δ 213.2, 138.5, 137.9, 134.8, 126.8, 59.5, 21.5; IR (neat): 2938, 1448, 1223, 1200 cm^{-1}; HRMS *m*/*z* calcd for $C_{10}H_{12}OS$ 180.0609, found 180.0610.

4.2.5. Methyl 4-chlorobenzenecarbothioate (Table 4, entry 5)[18]. Yellow solid purified using *n*-hexane/EtOAc (60:1 v/v; R_f=0.40) as eluent system in silica gel column chromatography. ^{1}H NMR ($CDCl_3$): δ 8.14 (dt, *J*=8.7, 2.1 Hz, 2H, ArH), 7.37 (dt, *J*=8.7, 2.2 Hz, 2H, ArH), 4.30 (s, 3H, OCH_3).

4.2.6. Methyl 4-bromobenzenecarbothioate (Table 4, entry 6)[20]. Orange solid purified using *n*-hexane/EtOAc (60:1 v/v; R_f=0.50) as eluent system in silica gel column chromatography. ^{1}H NMR ($CDCl_3$): δ 8.06 (dt, *J*=8.4, 2.1 Hz, 2H, ArH), 7.54 (dt, *J*=8.7, 2.0 Hz, 2H, ArH), 4.30 (s, 3H, OCH_3).

4.2.7. Methyl 4-iodobenzenecarbothioate (Table 4, entry 7). Orange solid purified using *n*-hexane/EtOAc (60:1 v/v; R_f=0.50) as eluent system in silica gel column chromatography. Mp: 63–64 °C; ^{1}H NMR ($CDCl_3$): δ 7.91 (d, *J*=8.4 Hz, 2H, ArH), 7.76 (d, *J*=8.4 Hz, 2H, ArH), 4.29 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$): δ 211.1, 137.7, 137.6, 130.4, 101.3, 59.7; IR (neat): 2930, 1577, 1220, 821 cm^{-1}; HRMS *m*/*z* calcd for C_8H_7OSI 277.9262, found 277.9259.

4.2.8. Methyl 4-trifluoromethylbenzenecarbothioate (Table 4, entry 8)[20]. Orange liquid purified using *n*-hexane/EtOAc (60:1 v/v; R_f=0.50) as eluent system in silica gel column chromatography. ^{1}H NMR ($CDCl_3$): δ 8.29 (d, *J*=8.1 Hz, 2H, ArH), 7.66 (d, *J*=8.4 Hz, 2H, ArH), 4.34 (s, 3H, OCH_3).

4.2.9. Methyl 4-aminobenzenecarbothioate (Table 4, entry 9)[21]. Orange solid purified using *n*-hexane/EtOAc (5:1 v/v; R_f=0.23) as eluent system in silica gel column chromatography. ^{1}H NMR ($CDCl_3$): δ 8.09 (d, *J*=8.7 Hz, 2H, ArH), 6.59 (d, *J*=8.7 Hz, 2H, ArH), 4.26 (s, 3H, OCH_3), 4.13 (br s, 2H, NH).

4.2.10. Methyl 4-(N,N-dimethyl)aminobenzene-carbothioate (Table 4, entry 10)[22]. Orange liquid purified using *n*-hexane/EtOAc (7:1 v/v; R_f=0.48) as eluent system in silica gel column chromatography. ^{1}H NMR ($CDCl_3$): δ 8.15 (d, *J*=9.3 Hz, 2H, ArH), 6.60 (d, *J*=9.0 Hz, 2H, ArH), 4.26 (s, 3H, OCH_3), 3.07 (s, 6H, NMe_2).

4.2.11. Methyl 4-nitrobenzenecarbothioate (Table 4, entry 11)[18]. Orange solid purified using *n*-hexane/EtOAc (10:1 v/v; R_f=0.50) as eluent system in silica gel column chromatography. ^{1}H NMR ($CDCl_3$): δ 8.34 (dt, *J*=9.3, 2.2 Hz, 2H, ArH), 8.24 (dt, *J*=8.7, 2.1 Hz, 2H, ArH), 4.35 (s, 3H, OCH_3).

4.2.12. Methyl 4-hydroxybenzenecarbothioate (Table 4, entry 12)[23]. Orange liquid purified using *n*-hexane/EtOAc (10:1 v/v; R_f=0.18) as eluent system in silica gel column chromatography. ^{1}H NMR ($CDCl_3$): δ 8.17 (d, *J*=9.0 Hz, 2H, ArH), 7.81 (d, *J*=9.0 Hz, 2H, ArH), 5.39 (br s, 1H, OH), 4.28 (s, 3H, OCH_3).

4.2.13. Methyl 4-methoxybenzenecarbothioate (Table 4, entry 13)[18]. Orange liquid purified using *n*-hexane/EtOAc (60:1 v/v; R_f=0.23) as eluent system in silica gel column chromatography. ^{1}H NMR ($CDCl_3$): δ 8.20 (d, *J*=8.7 Hz, 2H, ArH), 6.88 (d, *J*=8.7 Hz, 2H, ArH), 4.28 (s, 3H, S=C–OCH_3), 3.87 (s, 3H, $ArOCH_3$).

4.2.14. 2H-Chromene-2-thione (Table 4, entry 14)[2b]. Orange liquid purified using *n*-hexane/EtOAc (60:1 v/v; R_f=0.15) as eluent system in silica gel column chromatography. ^{1}H NMR ($CDCl_3$): δ 7.63–7.50 (m, 3H, ArH), 7.46 (d, *J*=9.3 Hz, 1H, C-2), 7.34 (t, *J*=7.5 Hz, 1H, ArH), 7.24 (d, *J*=9.0 Hz, 1H, C-1).

4.3. General procedure for thionation using Microwave

The starting material (3.0 mmol), P_4S_{10} (0.6 mmol), dimethicone (5 mL; Dow Corning Corporation 200® fluid, viscosity 50 cSt), and 10 mL of solvent (CH_2Cl_2 for amide and *p*-xylene for ester) were put together in a long neck round bottom flask attached to a reflux condenser. The condenser was attached to a balloon filled with Ar. This set-up was placed on the microwave reactor (CEM Discover System, Model 908005). The temperature was set to the boiling point of the solvent used plus 20 °C at 300 W power. The reaction mixture was continuously stirred until completion based on TLC monitoring. Upon completion, all solvent was evaporated using rotary evaporator. Methanol was added to the residue several times necessary to extract the product from dimethicone. The methanol was evaporated and the crude mixture was purified by silica gel column chromatography using *n*-hexane/EtOAc (either 3:1 or 60:1 v/v) as eluent system.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2010.05.100.

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