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An efficient synthesis of benzothiazole using tetrabromomethane as a halogen bond donor catalyst†

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An efficient and mild protocol has been developed for the synthesis of 2-substituted benzothiazole under solvent- and metal-free conditions using CBr_4 as the catalyst. This process involves the activation of a thioamide through halogen bond formation between the sulphur atom of the thioamide and bromine atom of the CBr_4 molecule. The presence of halogen-bonding interaction between *N*-methylthioamides and tetrabromomethane has been demonstrated with several control experiments, spectroscopic analysis and density functional theory (DFT). This methodology has a wide substrate scope for the synthesis of both 2-alkyl and 2-aryl substituted benzothiazoles.

Introduction

Noncovalent interactions such as halogen and chalcogen bonds play a major role in different fields in organic synthesis.[1] Halogen-bonding (XB) is an important noncovalent interaction in the emerging field of organocatalysis that allows the activation of functional groups towards nucleophilic addition.[2] The interaction between a terminal halogen atom (X) in compounds of the type R–X (X = I, Br, Cl, F; R = electron withdrawing group) and Lewis bases (XB acceptor) is known as the halogen bond.[1c,d,3] In 1950s, Hassel reported this noncovalent interaction through X-ray crystallographic studies of dihalogens with electron donor molecules.[4] At the beginning, most studies of XB were applied in solid state chemistry[5a] and crystal engineering.[5b] But in the past few years, its applications have grown in organocatalysis,[1c] medicinal chemistry[5c] and supramolecular chemistry.[5d]

Of late, XB catalyzed reactions have gained considerable attention in organic synthesis. In 2008, Bolm *et al.* for the first time showed that perfluorinated iodoalkanes can be used as a catalyst for the reduction of quinoline derivatives with a Hantzsch ester.[6] Since then, several halogen-bond-based catalysts have been reported for the halide abstraction,[1a,7a] Michael reaction,[7b] heteroarene reduction,[7c] and Diels–Alder[7d] reaction. Over the past few years, our group has been exploring the application of halogen bond catalysts in the field of organic synthesis.[8] Recently, we have shown that CBr_4 functions as the XB donor for the selective activation of benzaldehyde to synthesize α,β-unsaturated ketones.[9] Thus, we envisioned that this XB donor catalyst can be used as an efficient tool to activate several other functional groups through halogen-bonding.

In recent years, the application of CBr_4 has gained more importance due to its transition-metal-like reactivities, commercial availability, easy recoverability and reusability.[9,10] Moreover, CBr_4 has been employed for the tandem cyclization of amidines with ketones,[11a] oxidative C–N bond formation of *ortho*-aminopyridine with ketones,[11b] cross-dehydrogenative coupling reaction of amines,[11c] oxidative dehydrogenative coupling of isochromans with ketones,[11d] double oxidative dehydrogenative cyclization of glycine derivatives with dioxane,[11e] and acylation of alcohols and thiols.[11f]

Substituted benzothiazoles are an important class of heterocyclic compounds that exhibit notable biological and therapeutic activities. These structural frameworks show antitumor (LPAAT-β inhibitor and PMX-610), antidiabetic (zopolrestat), anticonvulsant (riluzole), aldose reductase (IDD552) and amyloid inhibitor (Schiff base) type activity (Fig. 1A).[12] In general, 2-substituted benzothiazoles are synthesized directly from *ortho*-amino thiophenols on their reaction with different electrophiles,[13a–k] copper-catalyzed intramolecular cyclization of *ortho*-haloanilides,[13l] Lewis acid catalyzed cyclization of 2-aminothiophenol with orthoesters,[13m] and H_3PO_4 catalyzed cyclocondensation of 2-aminothiophenol with β-ketoesters.[13n] However, most of the reported procedures have several limitations like harsh reaction conditions, use of toxic organic solvents and requirement of hazardous metal salts as catalysts.

Thioamides are very useful building blocks in organic synthesis. Here, thioamides were chosen as the XB acceptors,

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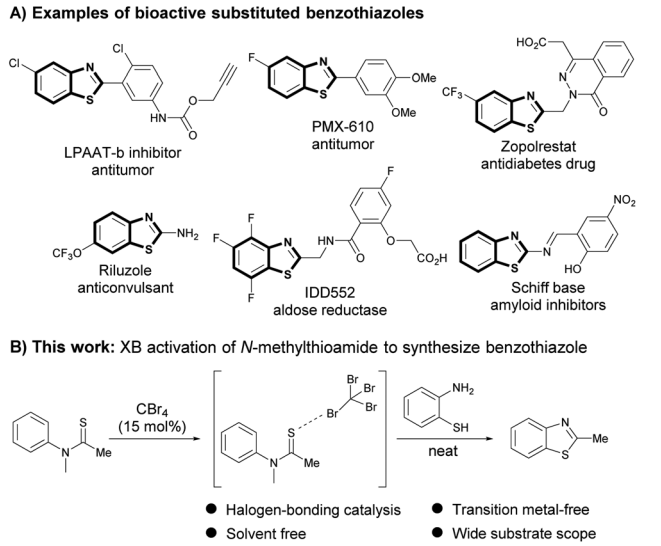


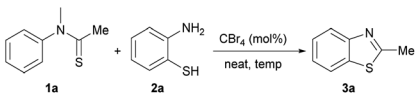
Fig. 1 (A) Biologically active compounds containing a benzothiazole scaffold. (B) Metal- and solvent-free synthesis of benzothiazole using the halogen bond catalyst CBr_4.

which can be activated *via* interaction with the XB donor.[14] In continuation of our research in developing metal-free organic transformations,[15] herein, we demonstrate how CBr_4 has been employed as a XB donor catalyst for the synthesis of 2-substituted benzothiazoles from 2-aminothiophenols and *N*-methylthioamides under solvent- and metal-free conditions (Fig. 1B). The advantages of the present methodology can be summarized as follows: (1) the current protocol is simple and is a greener approach to synthesize 2-substituted benzothiazoles. CBr_4 is economic and readily available and has emerged as an efficient catalyst. Here, only 15 mol% of CBr_4 is adequate to drive the reaction to completion. (2) It eludes the use of a transition-metal catalyst which is often expensive, toxic and requires complete removal from products particularly in the synthesis of pharmaceutical drugs.[16] (3) The reaction takes place smoothly under solvent-free conditions. The solvent-free organic transformations are easy to handle, reduce the waste produced from reactions and occur more selectively and efficiently compared to the reactions accomplished with solvents.

Results and discussion

Initially, we had chosen *N*-methylthioamide (XB acceptor) **1a** and 2-aminothiophenol **2a** as the model substrates with tetrabromomethane as the catalyst. The reaction of 1 equiv. of *N*-methylthioamide **1a** with 2 equiv. of 2-aminothiophenol **2a** in the presence of 20 mol% of tetrabromomethane under solvent free conditions yielded 96% of 2-methylbenzothiazole **3a** at 80 °C in 19 h (Table 1, entry 1). We did not observe any reduction in the yield of the product on decreasing the reaction temperature from 80 °C to 70 °C (entry 2). Later, it was

Table 1 Optimization of the reaction conditions[a]



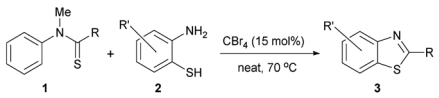
Entry	**2a** (equiv.)	Catalyst (mol%)	Temp (°C)	Time (h)	Yield[b] (%)
1	2.0	CBr_4 (20)	80	19	96
2	2.0	CBr_4 (20)	70	22	96
3	1.5	CBr_4 (20)	70	24	95
4	1.2	CBr_4 (20)	70	27	85
5	1.0	CBr_4 (20)	70	27	80
6	1.5	CBr_4 (20)	60	30	86
7	1.5	CBr_4 (20)	50	40	76
8	1.5	CBr_4 (20)	rt	48	47
9[c]	**1.5**	**CBr_4 (15)**	**70**	**25**	**95(93)**
10	1.5	CBr_4 (10)	70	30	81
11	1.5	CBr_4 (5)	70	30	67
12	1.5	CBr_4 (2)	70	30	45
13[d]	1.5	MeBr (15)	70	26	58
14	1.5	CH_2Br_2 (15)	70	26	53
15	1.5	$CHBr_3$ (15)	70	26	48
16[e]	1.5	HBr (15)	70	25	45
17	1.5	CI_4 (15)	70	30	55
18	1.5	—	70	25	27

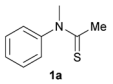
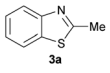
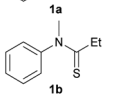
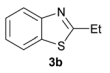
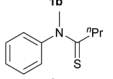
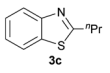
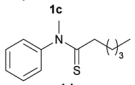
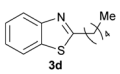
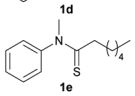
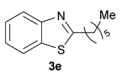
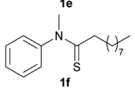
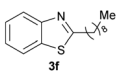
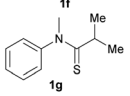
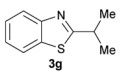
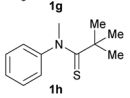
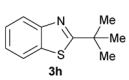
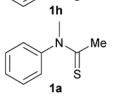
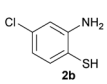
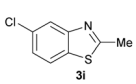
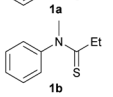
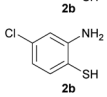
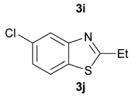
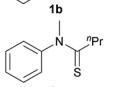
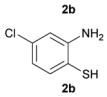
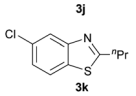
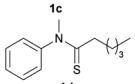
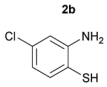
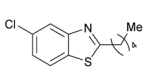
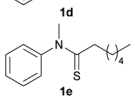
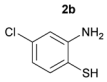
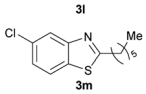
[a] All the reactions are conducted on a 0.25 mmol scale. [b] ^{1}H NMR yield using 1,3,5-trimethoxybenzene as an internal standard. [c] Isolated yield (yield in parenthesis). [d] Reaction conducted in a pressure tube. [e] Aqueous solution of HBr was used.

discerned that 1.5 equiv. of **2a** was adequate to push the reaction towards completion (entries 3–5). On varying the temperature, it was observed that, the yield of the desired product was substantially reduced by a decrease in the reaction temperature (entries 6–8). Next, the amount of catalyst loading was reduced to 15 mol% and it yielded 95% of product **3a** in 25 h (entry 9). Further decreasing the amount of catalyst loading from 10 mol% to 5 and 2 mol% was not fruitful (entries 11 and 12). Later, a range of catalysts were screened to improve the efficiency of this synthetic transformation (entries 13–17) and the results are summarized in Table 1. Finally, when the reaction was carried out in the absence of CBr_4, it yielded only 27% of the desired product (entry 18).

To explore the efficiency of the CBr_4-catalyzed reactions, various *N*-methylthioamides and 2-aminothiophenols were studied under the standard reaction conditions (Table 1, entry 9) and the results are shown in Table 2. A variety of α-non-branched aliphatic thioamides with 2-aminothiophenol underwent the reaction smoothly and provided the corresponding 2-substituted benzothiazole products **3b–3f** in good to excellent yields. Substrates with α-branched aliphatic thioamides were less reactive and generated the desired benzothiazole products **3g** and **3h** in moderate to good yields. Notably, the presence of an electron withdrawing group like chloro in 2-aminothiophenol was well tolerated under the standard reaction conditions. Several aliphatic thioamides reacted with 2-amino-4-chlorothiophenol and were found to provide very good yields (**3i–3o**). However, product **3o** was obtained in less yield, due to the steric hindrance of the *tert*-butyl group.

Table 2 Substrate scope of 2-substituted benzothiazole[a]



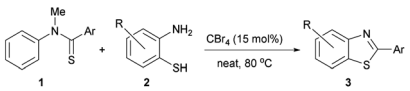
Entry	Substrate (**1**)	Substrate (**2**)	Product	Time (h)	Yield[b] (%)
1	 **1a**	 **2a**	 **3a**	25	93
2	 **1b**	 **2a**	 **3b**	28	89
3	 **1c**	 **2a**	 **3c**	26	82
4	 **1d**	 **2a**	 **3d**	24	82
5	 **1e**	 **2a**	 **3e**	25	81
6	 **1f**	 **2a**	 **3f**	29	83
7	 **1g**	 **2a**	 **3g**	36	70
8	 **1h**	 **2a**	 **3h**	35	72
9	 **1a**	 **2b**	 **3i**	29	84
10	 **1b**	 **2b**	 **3j**	26	78
11	 **1c**	 **2b**	 **3k**	25	75
12	 **1d**	 **2b**	 **3l**	24	82
13	 **1e**	 **2b**	 **3m**	25	73
14	**1f**	**2b**	**3n**	26	76
15	**1h**	**2b**	**3o**	27	68

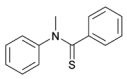
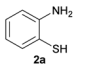
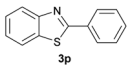
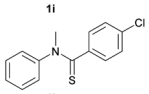
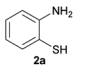
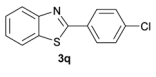
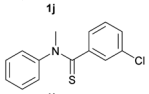
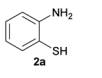
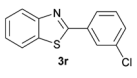
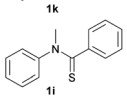
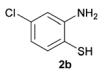
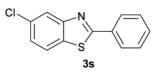
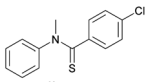
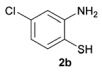
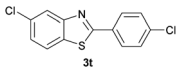
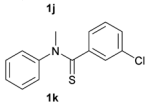
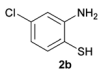
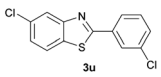
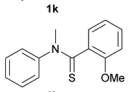
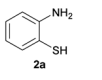
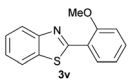
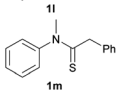
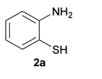
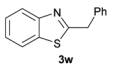
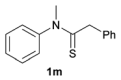
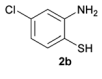
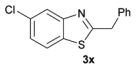
[a] Reaction conditions: 0.5 mmol of **1**, 0.75 mmol of **2** under solvent free conditions. [b] Isolated yield.

It is worth mentioning that substrates with α-branched aromatic thioamides were less reactive and required slightly higher temperatures (80 °C) and provided moderate to good yields of the corresponding 2-substituted benzothiazole products (Table 3). The electron withdrawing chloro substituents on aromatic thioamides in different positions such as *meta* and *para* were well tolerated and found to provide good yields (**3q–3u**). However, a decrease in the yield was observed, probably due to the steric hindrance of the *ortho*-methoxy group (**3v**). Finally, benzyl substituted groups containing *N*-methylthioamides were evaluated under standard reaction conditions and the corresponding products **3w** and **3x** were obtained in 78% and 81% yields, respectively.

To showcase the practical utility and efficacy of the CBr_4 catalyzed benzothiazole synthesis, a scale-up reaction was performed by employing 1.65 g (10 mmol) of *N*-methylthioamide

Table 3 Substrate scope of 2-substituted benzothiazole[a]



Entry	Substrate (1)	Substrate (2)	Product	Time (h)	Yield[b] (%)
1	 1i	 2a	 3p	30	81
2	 1j	 2a	 3q	25	76
3	 1k	 2a	 3r	28	77
4	 1i	 2b	 3s	29	75
5	 1j	 2b	 3t	28	67
6	 1k	 2b	 3u	28	71
7	 1l	 2a	 3v	32	62
8	 1m	 2a	 3w	25	78
9	 1m	 2b	 3x	25	81

[a] Reaction conditions: 0.5 mmol of **1**, 0.75 mmol of **2** under solvent free conditions. [b] Isolated yield.

under optimized reaction conditions. Convincingly, this methodology proceeded readily to provide 86% of **3a** within 24 h (Scheme 1).

The formation of a halogen bond between *N*-methylthioamide and tetrabromomethane was supported by DFT calculations. The distance between the sulfur atom of *N*-methylthioamide **1a** and the bromine atom of CBr_4 is 3.36 Å, which is higher than the sum of the covalent radii of S and Br (2.25 Å) and lower than the sum of the van der Waals radii of S and Br (3.65 Å) (Fig. 2A). The C–Br–S bond angle of the XB complex between **1a** and CBr_4 is 178° which is close to the expected value of 180° (Fig. 2A). Fig. 2B shows the halogen bond between *N*-methylthioamide **1a** and CBr_4 with their

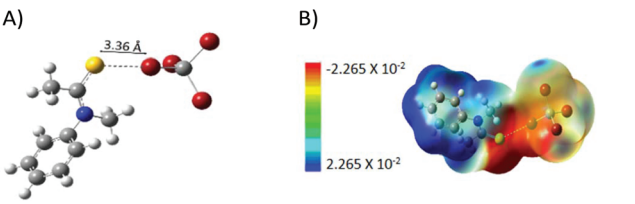
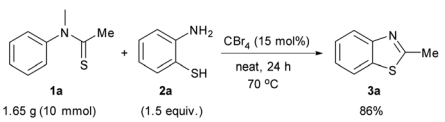


Fig. 2 (A) Optimized structure with DFT using the ωB97X-D functional and 6-311G(d,p) for C,H; 6-311+G(d,p) for N,S; Def2TZV for Br under vacuum. (B) Calculated electrostatic potential of *N*-methylthioamide and tetrabromomethane (red = negative electrostatic potential, blue = positive electrostatic potential) on the 0.0004 au isodensity surface (ωB97X-D/Def2TZV).

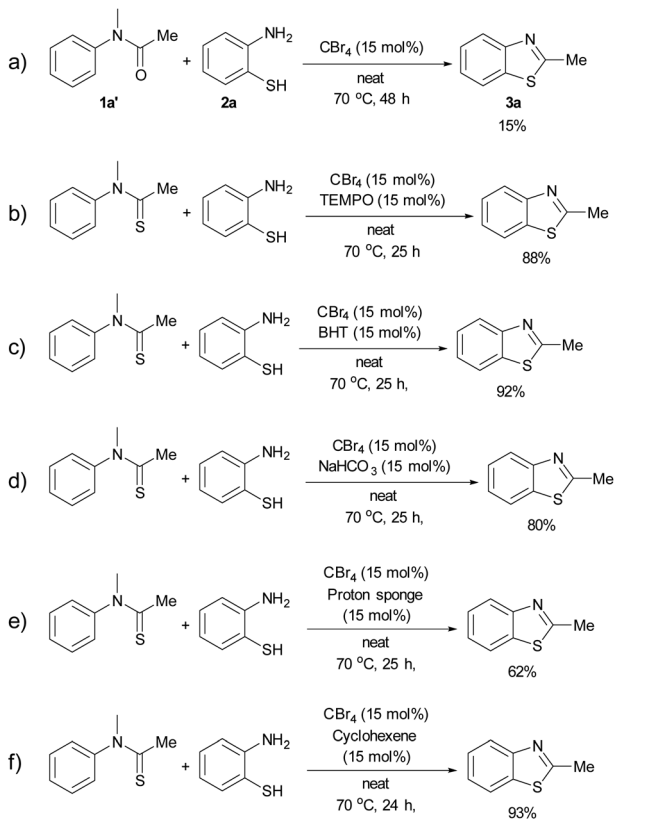


Scheme 1 Scalability of CBr_4 catalyzed 2-methylbenzo[*d*]thiazole synthesis.

mapped electrostatic potential. The blue region indicates high electrostatic potential and the red region indicates low electrostatic potential (Fig. 2B).

In order to have a better understanding of the mechanism of this CBr_4 catalyzed benzothiazole synthesis, a series of control experiments were conducted. At the beginning, *N*-methylamide (**1a′**) was taken as a starting material to investi-

gate the role of XB in this reaction. It is expected that *N*-methylamide **1a′** will weakly coordinate with the XB donor (CBr_4) compared to *N*-methylthioamide **1a** in the reaction with tetrabromomethane. This is due to the fact that polarizable Lewis bases act as excellent halogen bond acceptors with the XB donor atom.[17] As a result, sulphur tends to act as a better halogen bond acceptor in comparison to oxygen. The reaction of compound **1a′** with 2-aminothiophenol in the presence of 15 mol% CBr_4 gave the desired 2-methylbenzothiazole **3a** in 15% yield (Scheme 2a), whereas the corresponding reaction of *N*-methylthioamide **1a** gave a 95% yield of **3a** (Table 1, entry 9).[18] On performing DFT calculations, it was found that the C–Br bond length in the *N*-methylthioamide···CBr_4 complex is 1.94 Å and for the *N*-methylamide···CBr_4 complex it is 1.93 Å. The increased bond length in the case of *N*-methylthioamide in comparison to *N*-methylamide indicates that *N*-methylthioamide acts as a better halogen bond acceptor than *N*-methylamide (Fig. S1 in the ESI†). Radical trapping experiments were performed by employing TEMPO (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl and BHT (2,6-di-*tert*-butyl-4-methylphenol) under the optimized reaction conditions as radical scavengers. In the presence of TEMPO and BHT, the reactions were unaffected and afforded the product in 88% and 92% yields, respectively (Scheme 2, entries b and c). These observations implied that the reaction proceeds *via* a non-radical pathway.



Scheme 2 Control experiments.

It is expected that HBr might be generated by the decomposition of CBr_4.[19] Next, to rule out the possibility of hidden Brønsted acid (HBr) catalysis, control experiments were carried out by the addition of 15 mol% $NaHCO_3$ and 15 mol% proton sponge respectively (Scheme 2, entries d and e) and in both cases, significantly higher yields have been obtained.[7a,20] These results may be attributed to the halogen bond activation of thioamide (XB acceptor) by tetrabromomethane. The reaction was performed in the presence of 15 mol% cyclohexene under optimized conditions and gave a 93% yield of **3a** (Scheme 2, entry f). This control experiment rules out the possible formation of dibromocarbene in the reaction medium.

Furthermore, an array of NMR experiments were conducted to examine the decomposition of CBr_4 to $CHBr_3$, CH_2Br_2 and CH_3Br, which are the probable by-products during the decomposition of CBr_4.[2b,9] However, no peaks for $CHBr_3$, CH_2Br_2 and CH_3Br were observed in ^{1}H NMR and ^{13}C NMR spectra (Fig. S2 and S3 in the ESI†). When the ^{13}C NMR spectrum of the crude reaction mixture was recorded after the completion of the reaction, a peak at −29.5 ppm was detected which confirmed the presence of CBr_4 (Fig. S3 in the ESI†). Also, 60% of CBr_4 was recovered from the reaction mixture (Table 1, entry 9) which shows that CBr_4 remains intact during the reaction.

To prove the presence of halogen-bonding interaction between the XB acceptor **1a** and tetrabromomethane (XB donor), several ^{13}C NMR experiments were performed in $CDCl_3$.[21] The ^{13}C NMR spectrum of CBr_4 was recorded and the peak of the carbon atom of CBr_4 was detected at δ = −29.5 ppm (Fig. 3, spectrum b). When 4 equiv. of *N*-methylthioamide was added to CBr_4, the peak of the carbon atom of CBr_4 shifted downfield from δ = −29.5 to δ = −28.5 ppm (Fig. 3, spectrum c). These ^{13}C NMR experiments are consistent with the previous reports and clearly proved that there is an interaction between the bromine atom of CBr_4 and the sulfur atom of **1a**.[1b,7d,14a] On forming the halogen bond, the electrons of the sulfur atom of *N*-methylthioamide enter

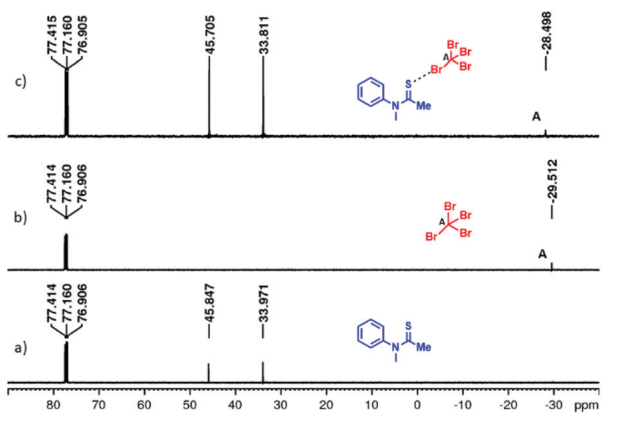
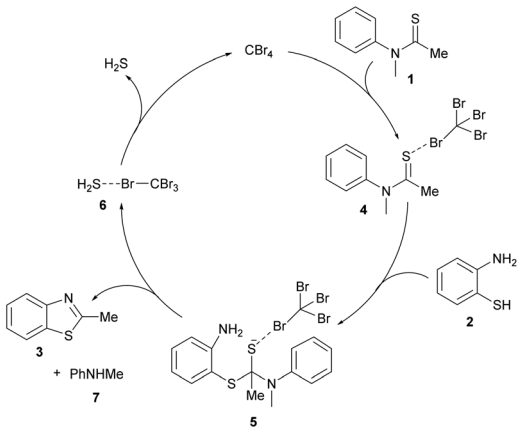


Fig. 3 Cutouts of the ^{13}C NMR spectra of *N*-methylthioamide (bottom), CBr_4 (middle) and thioamide : CBr_4 (4 : 1) (top) in $CDCl_3$.



Scheme 3 A plausible mechanistic pathway for benzothiazole synthesis.

the antibonding orbital of the bromine atom of CBr_4. This downfield shift of CBr_4 (*ca.* 1 ppm) points towards the increased electrophilicity of the thiocarbonyl group of **1a**.

On the basis of the above experimental evidence and literature reports, a plausible catalytic cycle for the activation of the thioamide has been depicted in Scheme 3. Initially, the interaction between the sulfur atom of **1** and the tetrabromomethane (XB donor) activates the thioamide to form **4**. 2-Aminothiophenol reacts with the activated thioamide and results in the formation of intermediate **5**. Furthermore, the interaction of tetrabromomethane with the thiol group of **5** leads to the generation of **6** along with 2-methylbenzothiazole **3** and *N*-methylaniline **7**, which was isolated with 82% yield. Finally, the dissociation of H_2S from **6** regenerates the catalyst CBr_4 in the reaction mixture for the next catalytic cycle.[22]

Conclusions

In conclusion, we have developed a CBr_4 catalyzed simple, mild, and efficient protocol for the preparation of 2-substituted benzothiazole from 2-aminothiophenols and *N*-methylthioamides under solvent free conditions. This methodology avoids the use of a metal catalyst and shows a broad substrate scope. Controlled experiments, NMR studies and DFT calculations supported the formation of halogen bond interactions between *N*-methylthioamide and tetrabromomethane in the catalytic system.

Experimental section

General considerations

All reactions were carried out in oven dried reaction tubes. CBr_4, CI_4, CH_2Br_2 and a proton sponge were purchased from the Sigma-Aldrich chemical company. MeBr, $CHBr_3$, *N*-methylaniline and HBr ~47% in water were purchased from Spectrochem Pvt. Ltd. Various 2-aminothiophenol and acyl chloride were purchased from Alfa Aesar, Sigma-Aldrich, TCI, Avra synthesis, Spectrochem Pvt. Ltd and used directly as received. The reactions were monitored by thin layer chromatography (TLC) using Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized by UV fluorescence quenching using an appropriate mixture of ethyl acetate and hexanes as the eluting solvent mixture. Silica gel for column chromatography (particle size 100–200 mesh) was purchased from Avra Synthesis Pvt. Ltd and used for column chromatography using the hexanes and ethyl acetate mixture as the eluent. All the reactions were carried out in temperature controlled IKA magnetic stirrers. Melting points were recorded on a Guna capillary melting point apparatus and are corrected with benzoic acid as the reference. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz instrument. ^{1}H NMR spectra are reported relative to residual $CDCl_3$ (δ 7.26 ppm). $^{13}C\{^1H\}$ NMR spectra are reported relative to residual $CDCl_3$ (δ 77.16 ppm). Chemical shifts were recorded in parts per million (ppm) and multiplicities are as indicated: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), m (multiplet), and quin (quintet). The coupling constant, *J*, is reported in hertz. FTIR spectra were recorded on a JASCO spectrometer and are reported in frequency of absorption (cm^{-1}) using dry KBr pellets. High resolution mass spectra (HRMS) were recorded on a Q-Tof Micro mass spectrometer.

Experimental procedure for synthesis of 2-substituted benzothiazole from 2-aminothiophenols and *N*-methylthioamides

An oven-dried reaction tube equipped with a magnetic stir bar was charged with *N*-methylthioamides (83 mg, 0.5 mmol) and tetrabromomethane (25 mg, 0.075 mmol). 2-Aminothiophenol (94 mg, 0.75 mmol) was added to the reaction tube and the reaction mixture was stirred at 70 °C under neat conditions. After completion of the reaction, the mixture was extracted with ethyl acetate (10 mL). The combined organic layer was washed with water (2 × 10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* to obtain the crude product. The crude product was then purified by silica gel column chromatography using hexane/ethyl acetate to give 2-methylbenzo[*d*]thiazole **3a** (69 mg, 93%).

2-Methylbenzo[*d*]thiazole (3a)

69 mg, 93% yield; yellow liquid; R_f = 0.30 (5% ethyl acetate in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.83 (s, 3H), 7.30–7.36 (m, 1H), 7.40–7.47 (m, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 20.2, 121.5, 122.5, 124.8, 126.0, 135.7, 153.5, 167.0; FTIR (KBr): 750, 1174, 1265, 1303, 1432, 1526, 2982, 3056 cm^{-1}; HRMS (*m*/*z*): $[M + H]^+$ calculated for C_8H_8NS: 150.0377; found: 150.0368.

2-Ethylbenzo[*d*]thiazole (3b)

73 mg, 89% yield; colourless liquid; R_f = 0.23 (2% ethyl acetate in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.47 (d, *J* = 7.6 Hz, 3H), 3.15 (q, *J* = 7.6 Hz, 2H), 7.31–7.37 (m, 1H), 7.41–7.48 (m, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H); $^{13}C\{^1H\}$

NMR (100 MHz, $CDCl_3$) δ 13.9, 27.9, 121.6, 122.6, 124.7, 126.0, 135.2, 153.4, 173.7; FTIR (KBr): 753, 1268, 1429, 1641, 2984, 3056 cm^{-1}; HRMS (*m*/*z*): $[M + H]^+$ calculated for $C_9H_{10}NS$: 164.0534; found: 164.0547.

2-Propylbenzo[*d*]thiazole (3c)

73 mg, 82% yield; pale yellow liquid; R_f = 0.16 (2% ethyl acetate in hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 1.06 (t, *J* = 7.2 Hz, 3H), 1.86–1.97 (m, 2H), 3.09 (t, *J* = 7.2 Hz, 2H), 7.31–7.37 (m, 1H), 7.41–7.47 (m, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 13.8, 23.2, 36.4, 121.6, 122.6, 124.7, 125.9, 135.3, 153.4, 172.3; FTIR (KBr): 756, 1268, 1430, 1636, 2983, 3056 cm^{-1}; HRMS (*m*/*z*): $[M + H]^+$ calculated for $C_{10}H_{12}NS$: 178.0690; found: 178.0690.

2-Pentylbenzo[*d*]thiazole (3d)

84 mg, 82% yield; yellow liquid; R_f = 0.38 (2% ethyl acetate in hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, *J* = 7.2 Hz, 3H), 1.33–1.47 (m, 4H), 1.88 (quin, *J* = 7.6 Hz, 2H), 3.11 (t, *J* = 7.6 Hz, 2H), 7.31–7.37 (m, 1H), 7.41–7.47 (m, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 14.1, 22.5, 29.6, 31.5, 34.5, 121.6, 122.6, 124.7, 126.0, 135.3, 153.4, 172.6; FTIR (KBr): 756, 1268, 1446, 1518, 2953 cm^{-1}; HRMS (*m*/*z*): $[M + H]^+$ calculated for $C_{12}H_{16}NS$: 206.1003; found: 206.1009.

2-Hexylbenzo[*d*]thiazole (3e)

89 mg, 81% yield; yellow liquid; R_f = 0.44 (5% ethyl acetate in hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 0.85–0.93 (m, 3H), 1.27–1.39 (m, 4H), 1.39–1.48 (m, 2H), 1.87 (quint, *J* = 7.6 Hz, 2H), 3.11 (t, *J* = 8.0 Hz, 2H), 7.31–7.37 (m, 1H), 7.41–7.47 (m, 1H), 7.81–7.85 (m, 1H), 7.97 (d, *J* = 8.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 14.2, 22.6, 29.0, 29.8, 31.6, 34.5, 121.6, 122.6, 124.7, 126.0, 135.3, 153.4, 172.6; FTIR (KBr): 751, 894, 1266, 1439, 1519, 2933, 3057 cm^{-1}; HRMS (*m*/*z*): $[M + H]^+$ calculated for $C_{13}H_{18}NS$: 220.1159; found: 220.1168.

2-Nonylbenzo[*d*]thiazole (3f)

108 mg, 83% yield; pale yellow liquid; R_f = 0.42 (2% ethyl acetate in hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, *J* = 6.4 Hz, 3H), 1.21–1.38 (m, 10H), 1.39–1.48 (m, 2H), 1.88 (quin, *J* = 7.2 Hz, 2H), 3.11 (t, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 14.2, 22.8, 29.3, 29.4, 29.5, 29.6, 29.9, 32.0, 34.5, 121.6, 122.6, 124.7, 126.0, 135.3, 153.4, 172.6; FTIR (KBr): 754, 1267, 1430, 1518, 2985, 3056 cm^{-1}; HRMS (*m*/*z*): $[M + H]^+$ calculated for $C_{16}H_{24}NS$: 262.1629; found: 262.1634.

2-Isopropylbenzo[*d*]thiazole (3g)

62 mg, 70% yield; pale yellow liquid; R_f = 0.44 (5% ethyl acetate in hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 1.48 (d, *J* = 6.8 Hz, 6H), 3.37–3.48 (m, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 23.0, 34.2, 121.7, 122.7, 124.7, 125.9, 134.8, 153.3, 178.7; FTIR (KBr): 743, 1007, 1265, 1310, 1447, 1516, 2975, 3056 cm^{-1}; HRMS (*m*/*z*): $[M + H]^+$ calculated for $C_{10}H_{12}NS$: 178.0690; found: 178.0679.

2-(*tert*-Butyl)benzo[*d*]thiazole (3h)

69 mg, 72% yield; yellow liquid; R_f = 0.25 (2% ethyl acetate in hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 1.53 (s, 9H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 30.9, 38.4, 121.6, 122.8, 124.6, 125.9, 135.1, 153.4, 182.0; FTIR (KBr): 747, 1267, 1430, 1509, 1724, 2980, 3056 cm^{-1}; HRMS (*m*/*z*): $[M + H]^+$ calculated for $C_{11}H_{14}NS$: 192.0847; found: 192.0852.

5-Chloro-2-methylbenzo[*d*]thiazole (3i)

77 mg, 84% yield; light yellow solid; mp 68–70 °C [68–69 °C, lit];[23] R_f = 0.39 (5% ethyl acetate in hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 2.82 (s, 3H), 7.28–7.34 (m, 1H), 7.68–7.74 (m, 1H), 7.92 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 20.3, 122.2, 122.4, 125.3, 132.1, 134.0, 154.4, 169.1; FTIR (KBr): 748, 1171, 1267, 1431, 1522, 2983, 3055 cm^{-1}; HRMS (*m*/*z*): $[M + H]^+$ calculated for C_8H_7ClNS: 183.9988; found: 183.9984.

5-Chloro-2-ethylbenzo[*d*]thiazole (3j)

77 mg, 78% yield; light yellow solid; mp 58–60 °C [54–56 °C, lit];[24] R_f = 0.33 (5% ethyl acetate in hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 1.46 (t, *J* = 7.6 Hz, 3H), 3.14 (q, *J* = 7.6 Hz, 2H), 7.29–7.34 (m, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 2.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 13.8, 28.0, 122.3, 122.6, 125.2, 132.0, 133.5, 154.3, 175.7; FTIR (KBr): 752, 903, 1267, 1431, 1517, 2981, 3055 cm^{-1}; HRMS (*m*/*z*): $[M + H]^+$ calculated for C_9H_9ClNS: 198.0144; found: 198.0145.

5-Chloro-2-propylbenzo[*d*]thiazole (3k)

79 mg, 75% yield; brown solid; mp 58–60 °C; R_f = 0.26 (2% ethyl acetate in hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 1.05 (t, *J* = 7.2 Hz, 3H), 1.84–1.96 (m, 2H), 3.08 (t, *J* = 7.2 Hz, 2H), 7.29–7.34 (m, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.94 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 13.8, 23.1, 36.4, 122.3, 122.6, 125.2, 132.0, 133.6, 154.3, 174.4; FTIR (KBr): 735, 884, 1151, 1265, 1432, 1516, 2970, 3054 cm^{-1}; HRMS (*m*/*z*): $[M + H]^+$ calculated for $C_{10}H_{11}ClNS$: 212.0300; found: 212.0300.

5-Chloro-2-pentylbenzo[*d*]thiazole (3l)

98 mg, 82% yield; pale yellow liquid; R_f = 0.32 (2% ethyl acetate in hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, *J* = 6.8 Hz, 3H), 1.32–1.46 (m, 4H), 1.87 (quin, *J* = 7.6 Hz, 2H), 3.09 (t, *J* = 7.6 Hz, 2H), 7.31 (dd, J_1 = 2.0 Hz, J_2 = 8.4 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 2.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 14.1, 22.5, 29.4, 31.4, 34.5, 122.3, 122.5, 125.2, 132.0, 133.5, 154.3, 174.6; FTIR (KBr): 751, 904, 1266, 1431, 1516, 2959, 3055 cm^{-1}; HRMS (*m*/*z*): $[M + H]^+$ calculated for $C_{12}H_{15}ClNS$: 240.0613; found: 240.0622.

5-Chloro-2-hexylbenzo[*d*]thiazole (3m)

93 mg, 73% yield; pale yellow liquid; R_f = 0.32 (2% ethyl acetate in hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 0.85–0.91 (m, 3H), 1.26–1.38 (m, 4H), 1.38–1.47 (m, 2H), 1.86 (quin, *J* =

7.6 Hz, 2H), 3.09 (t, J = 7.6 Hz, 2H), 7.31 (dd, J_1 = 2.0 Hz, J_2 = 8.4 Hz, 1H), 7.73 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 2.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 14.2, 22.6, 28.9, 29.7, 31.6, 34.6, 122.3, 122.5, 125.2, 132.0, 133.5, 154.3, 174.6; FTIR (KBr): 754, 904, 1267, 1431, 1517, 2955, 3055 cm^{-1}; HRMS (m/z): $[M + H]^+$ calculated for $C_{13}H_{17}ClNS$: 254.0770; found: 254.0777.

5-Chloro-2-nonylbenzo[*d*]thiazole (3n)

112 mg, 76% yield; pale yellow liquid; R_f = 0.32 (2% ethyl acetate in hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, J = 6.4 Hz, 3H), 1.22–1.37 (m, 10H), 1.38–1.47 (m, 2H), 1.86 (quin, J = 7.2 Hz, 2H), 3.09 (t, J = 7.6 Hz, 2H), 7.31 (dd, J_1 = 1.6 Hz, J_2 = 8.4 Hz, 1H), 7.73 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 2.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 14.2, 22.8, 29.2, 29.3, 29.4, 29.5, 29.8, 32.0, 34.6, 122.3, 122.6, 125.2, 132.0, 133.5, 154.3, 174.7; FTIR (KBr): 749, 903, 1266, 1431, 1551, 2929, 3055 cm^{-1}; HRMS (m/z): $[M + H]^+$ calculated for $C_{16}H_{23}ClNS$: 296.1239; found: 296.1243.

2-(*tert*-Butyl)-5-chlorobenzo[*d*]thiazole (3o)

77 mg, 68% yield; pale yellow liquid; R_f = 0.44 (2% ethyl acetate in hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 1.51 (s, 9H), 7.28–7.33 (m, 1H), 7.74 (d, J = 8.8 Hz, 1H), 7.97 (d, J = 1.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 30.8, 38.6, 122.3, 122.7, 125.1, 131.9, 133.4, 154.3, 184.1; FTIR (KBr): 752, 1077, 1267, 1365, 1429, 1509, 2972, 3053 cm^{-1}; HRMS (m/z): $[M + H]^+$ calculated for $C_{11}H_{13}ClNS$: 226.0457; found: 226.0461.

2-Phenylbenzo[*d*]thiazole (3p)

86 mg, 81% yield; light yellow solid; mp 108–110 °C [110–112 °C, lit];[25] R_f = 0.25 (2% ethyl acetate in hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 (t, J = 8.0 Hz, 1H), 7.47–7.54 (m, 4H), 7.91 (d, J = 8.0 Hz, 1H), 8.06–8.14 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 121.8, 123.4, 125.3, 126.5, 127.7, 129.2, 131.1, 133.7, 135.2, 154.3, 168.2; FTIR (KBr): 958, 1156, 1268, 1309, 1442, 1506, 3012 cm^{-1}; HRMS (m/z): $[M + H]^+$ calculated for $C_{13}H_{10}NS$: 212.0534; found: 212.0528.

2-(4-Chlorophenyl)benzo[*d*]thiazole (3q)

93 mg, 76% yield; light yellow solid; mp 108–110 °C [112 °C, lit];[26] R_f = 0.42 (2% ethyl acetate in hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 (t, J = 7.6 Hz, 1H), 7.44–7.53 (m, 3H), 7.90 (d, J = 8.0 Hz, 1H), 8.00–8.05 (m, 2H), 8.06 (d, J = 8.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 121.8, 123.4, 125.6, 126.6, 128.8, 129.4, 132.2, 135.2, 137.2, 154.2, 166.8; FTIR (KBr): 756, 1166, 1253, 1310, 1469, 1507, 3055 cm^{-1}; HRMS (m/z): $[M + H]^+$ calculated for $C_{13}H_9ClNS$: 246.0144; found: 246.0145.

2-(3-Chlorophenyl)benzo[*d*]thiazole (3r)

95 mg, 77% yield; light yellow solid; mp 92–94 °C [97–99 °C, lit];[26] R_f = 0.28 (2% ethyl acetate in hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 7.38–7.48 (m, 3H), 7.48–7.54 (m, 1H), 7.88–7.97 (m, 2H), 8.09 (d, J = 8.0 Hz, 1H), 8.11–8.14 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 121.8, 123.6, 125.7, 125.8, 126.7, 127.5, 130.4, 131.0, 135.2, 135.3, 135.4, 154.1, 166.4; FTIR (KBr): 756, 1268, 1429, 1464, 1638 cm^{-1}; HRMS (m/z): $[M + H]^+$ calculated for $C_{13}H_9ClNS$: 246.0144; found: 246.0153.

5-Chloro-2-phenylbenzo[*d*]thiazole (3s)

92 mg, 75% yield; orange solid; mp 138–140 °C [139–141 °C, lit];[26] R_f = 0.34 (2% ethyl acetate in hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 7.34–7.38 (m, 1H), 7.48–7.53 (m, 3H), 7.80 (d, J = 8.8 Hz, 1H), 8.04–8.10 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 122.4, 123.2, 125.8, 127.8, 129.2, 131.4, 132.4, 133.4, 135.5, 155.1, 170.1; FTIR (KBr): 755, 1153, 1268, 1427, 1548, 3056 cm^{-1}; HRMS (m/z): $[M + H]^+$ calculated for $C_{13}H_9ClNS$: 246.0144; found: 246.0145.

5-Chloro-2-(4-chlorophenyl)benzo[*d*]thiazole (3t)

94 mg, 67% yield; light yellow solid; mp 144–146 °C [140–142 °C, lit];[25] R_f = 0.44 (2% ethyl acetate in hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.8 Hz, 1H), 7.42–7.48 (m, 2H), 7.75–7.80 (m, 1H), 7.95–8.00 (m, 2H), 8.02 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 122.4, 123.2, 126.0, 128.9, 129.5, 131.9, 132.6, 133.4, 137.6, 155.0, 168.6; FTIR (KBr): 753, 898, 1267, 1429, 1466, 2984, 3056 cm^{-1}; HRMS (m/z): $[M + H]^+$ calculated for $C_{13}H_8Cl_2NS$: 279.9754; found: 279.9757.

5-Chloro-2-(3-chlorophenyl)benzo[*d*]thiazole (3u)

99 mg, 71% yield; light yellow solid; mp 142–144 °C [141–143 °C, lit];[25] R_f = 0.44 (2% ethyl acetate in hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 7.37–7.43 (m, 1H), 7.42–7.51 (m, 2H), 7.81 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 7.2 Hz, 1H), 8.06–8.11 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 122.5, 123.4, 125.9, 126.2, 127.6, 130.5, 131.4, 132.7, 133.4, 135.0, 135.4, 154.9, 168.2; FTIR (KBr): 755, 1268, 1426, 1514, 1638, 3057 cm^{-1}; HRMS (m/z): $[M + H]^+$ calculated for $C_{13}H_8Cl_2NS$: 279.9754; found: 279.9755.

2-(2-Methoxyphenyl)benzo[*d*]thiazole (3v)

75 mg, 62% yield; white solid; mp 114–116 °C [120–121 °C, lit];[27] R_f = 0.24 (2% ethyl acetate in hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 4.06 (s, 3H), 7.07 (d, J = 8.4 Hz, 1H), 7.14 (t, J = 7.6 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 7.43–7.53 (m, 2H), 7.93 (d, J = 7.6 Hz, 1H), 8.10 (d, J = 8.4 Hz, 1H), 8.54 (d, J = 8.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 55.9, 111.8, 121.3, 121.4, 122.4, 122.9, 124.7, 126.0, 129.7, 131.9, 136.2, 152.3, 157.4, 163.3; FTIR (KBr): 755, 1167, 1248, 1311, 1459, 1591, 2959, 3060 cm^{-1}; HRMS (m/z): $[M + H]^+$ calculated for $C_{14}H_{12}NOS$: 242.0640; found: 242.0638.

2-Benzylbenzo[*d*]thiazole (3w)

88 mg, 78% yield; pale yellow liquid; R_f = 0.13 (2% ethyl acetate in hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 4.45 (s, 2H), 7.27–7.33 (m, 1H), 7.34 (m, 1H), 7.35–7.41 (m, 4H), 7.46 (t, J = 7.6 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 8.01 (d, J = 8.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 40.7, 121.6, 122.9, 124.9, 126.0, 127.4, 129.0, 129.3, 135.8, 137.3, 153.4, 171.3; FTIR (KBr): 754, 896, 1267, 1430, 1507, 2983, 3057 cm^{-1}; HRMS

(m/z): $[M + H]^+$ calculated for $C_{14}H_{11}NS$: 226.0690; found: 226.0693.

2-Benzyl-5-chlorobenzo[*d*]thiazole (3x)

105 mg, 81% yield; light yellow solid; mp 78–80 °C [78–79 °C, lit];[28] R_f = 0.25 (2% ethyl acetate in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.43 (s, 2H), 7.28–7.33 (m, 2H), 7.33–7.38 (m, 4H), 7.69 (d, J = 9.6 Hz, 1H), 7.98 (d, J = 1.6 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 40.8, 122.3, 122.8, 125.5, 127.6, 129.1, 129.3, 132.1, 134.1, 137.0, 154.3, 173.4; FTIR (KBr): 755, 899, 1268, 1429, 1506, 2984, 3056 cm^{-1}; HRMS (m/z): $[M + H]^+$ calculated for $C_{14}H_{10}ClNS$: 260.0301; found: 260.0300.

***N*-Methylaniline (7)**

25 mg, 82% yield; brown liquid; R_f = 0.39 (2% ethyl acetate in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.85 (s, 3H), 6.31 (d, J = 8.0 Hz, 2H), 6.73 (t, J = 7.2 Hz, 1H), 7.17–7.24 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 30.9, 112.5, 117.4, 129.3, 149.5.

Experimental procedure for synthesis of *N*-methyl-*N*-phenylacetamide (1a′) from *N*-methylaniline and acetic anhydride[29]

N-Methylaniline (5 mmol) was added *via* a syringe into an oven-dried 50 mL RB flask fitted with a rubber septum. The flask was purged with nitrogen and dry dichloromethane (DCM, 10 mL) was added. Acetic anhydride (6 mmol) was added dropwise and the resulting mixture was stirred at room temperature for 1 hour. After completion of the reaction, the reaction mixture was quenched with aqueous saturated $NaHCO_3$ and extracted with dichloromethane. The combined organic layer was washed with water (2 × 25 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* to obtain the crude product. The crude product was then purified by silica gel column chromatography using hexane/ethyl acetate.

***N*-Methyl-*N*-phenylacetamide (1a′)**

589 mg, 79% yield; white solid; R_f = 0.21 (15% ethyl acetate in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.86 (s, 3H), 3.26 (s, 3H), 7.18 (d, J = 7.6 Hz, 2H), 7.33 (t, J = 7.2 Hz, 1H), 7.41 (t, J = 7.2 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 22.6, 37.3, 127.2, 127.8, 129.9, 144.7, 170.7.

Experimental procedure for synthesis of *N*-methyl-*N*-phenylpropionamide (1b′) from *N*-methylaniline and propionyl chloride[30]

A 100 mL RB flask containing a solution of *N*-methylaniline (5 mmol) and triethylamine (6 mmol) in 25 mL dry dichloromethane was immersed in a cooling bath at 0 °C. Propionyl chloride (6 mmol) was added dropwise at 0 °C and the resulting mixture was stirred at room temperature for 4 hours. After completion of the reaction, the reaction mixture was quenched with aqueous saturated $NaHCO_3$ and extracted with dichloromethane. The combined organic layer was washed with water (2 × 25 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* to obtain the crude product. The crude product was then purified by silica gel column chromatography using hexane/ethyl acetate.

***N*-Methyl-*N*-phenylpropionamide (1b′)**

674 mg, 76% yield; pale yellow liquid; R_f = 0.22 (15% ethyl acetate in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98–1.10 (m, 3H), 2.01–2.13 (m, 2H), 3.26 (s, 3H), 7.14–7.20 (m, 2H), 7.28–7.36 (m, 1H), 7.37–7.44 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 9.7, 27.5, 37.3, 127.3, 127.7, 129.7, 144.3, 173.9.

Experimental procedure for synthesis of *N*-methyl-*N*-phenylbutyramide (1c′) from *N*-methylaniline and butyryl chloride[30]

A 100 mL RB flask containing a solution of *N*-methylaniline (5 mmol) and triethylamine (6 mmol) in 25 mL dry dichloromethane was immersed in a cooling bath at 0 °C. Butyryl chloride (6 mmol) was added dropwise at 0 °C and the resulting mixture was stirred at room temperature for 6 hours. After completion of the reaction, the reaction mixture was quenched with aqueous saturated $NaHCO_3$ and extracted with dichloromethane. The combined organic layer was washed with water (2 × 25 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* to obtain the crude product. The crude product was then purified by silica gel column chromatography using hexane/ethyl acetate.

***N*-Methyl-*N*-phenylbutyramide (1c′)**

638 mg, 72% yield; pale yellow liquid; R_f = 0.19 (15% ethyl acetate in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.79 (t, J = 7.2 Hz, 3H), 1.57 (sext, J = 7.2 Hz, 2H), 1.98–2.06 (m, 2H), 3.24 (s, 3H), 7.15 (d, J = 7.6 Hz, 2H), 7.31 (t, J = 7.2 Hz, 1H), 7.39 (t, J = 7.6 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 13.9, 18.9, 36.1, 37.3, 127.4, 127.7, 129.8, 144.4, 173.2.

Experimental procedure for synthesis of *N*-methyl-*N*-phenylhexanamide (1d′) from *N*-methylaniline and hexanoic acid[13c]

Hexanoic acid (5 mmol) was taken in an oven-dried 100 mL RB flask fitted with a rubber septum and the flask was purged with nitrogen. Thionyl chloride (6 mmol) was added dropwise at 0 °C and the resulting mixture was stirred at 80 °C. After stirring at 80 °C for 1 hour, excess thionyl chloride was distilled off and 20 mL of dichloromethane was added into the reaction mixture at room temperature. To it 5 mmol of *N*-methylaniline was added and the resulting mixture was stirred at room temperature for 1 hour. After completion of the reaction, the reaction mixture was quenched with aqueous saturated $NaHCO_3$ and extracted with dichloromethane. The combined organic layer was washed with water (2 × 25 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* to obtain the crude product. The crude product was then purified by silica gel column chromatography using hexane/ethyl acetate.

***N*-Methyl-*N*-phenylhexanamide (1d′)**

831 mg, 81% yield; pale yellow liquid; R_f = 0.39 (10% ethyl acetate in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80 (t, J = 6.4 Hz, 3H), 1.10–1.25 (m, 4H), 1.55 (quint, J = 7.6 Hz, 2H),

2.04 (t, J = 7.6 Hz, 2H), 3.24 (s, 3H), 7.16 (d, J = 7.6 Hz, 2H), 7.32 (t, J = 7.2 Hz, 1H), 7.40 (t, J = 7.6 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 13.9, 22.5, 25.3, 31.6, 34.1, 37.4, 127.4, 127.8, 129.8, 144.4, 173.5.

Experimental procedure for synthesis of *N*-methyl-*N*-phenylheptanamide (1e′) from *N*-methylaniline and heptanoic acid[13c]

Heptanoic acid (5 mmol) was taken in an oven-dried 100 mL RB flask fitted with a rubber septum and the flask was purged with nitrogen. Thionyl chloride (6 mmol) was added dropwise at 0 °C and the resulting mixture was stirred at 80 °C. After stirring at 80 °C for 1 hour, excess thionyl chloride was distilled off and 20 mL of dichloromethane was added into the reaction mixture at room temperature. To it 5 mmol of *N*-methylaniline was added and the resulting mixture was stirred at room temperature for 1 hour. After completion of the reaction, the reaction mixture was quenched with aqueous saturated $NaHCO_3$ and extracted with dichloromethane. The combined organic layer was washed with water (2 × 25 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* to obtain the crude product. The crude was then purified by silica gel column chromatography using hexane/ethyl acetate.

N-Methyl-*N*-phenylheptanamide (1e′)

724 mg, 66% yield; pale yellow liquid; R_f = 0.31 (10% ethyl acetate in hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 0.81 (t, J = 6.8 Hz, 3H), 1.10–1.26 (m, 6H), 1.48–1.60 (m, 2H), 2.04 (t, J = 7.6 Hz, 2H), 3.25 (s, 3H), 7.16 (d, J = 7.6 Hz, 2H), 7.32 (t, J = 7.2 Hz, 1H), 7.40 (t, J = 7.2 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 14.1, 22.6, 25.6, 29.1, 31.6, 34.2, 37.4, 127.4, 127.8, 129.8, 144.4, 173.4; FTIR (KBr): 774, 1384, 1496, 1595, 1659, 2955, 3061 cm^{-1}; HRMS (m/z): $[M + H]^+$ calculated for $C_{14}H_{22}NO$: 220.1701; found: 220.1716.

Experimental procedure for synthesis of *N*-methyl-*N*-phenyldecanamide (1f′) from *N*-methylaniline and decanoic acid[13c]

Decanoic acid (5 mmol) was taken in an oven-dried 100 mL RB flask fitted with a rubber septum and the flask was purged with nitrogen. Thionyl chloride (6 mmol) was added dropwise at 0 °C and the resulting mixture was stirred at 80 °C. After stirring at 80 °C for 1 hour, excess thionyl chloride was distilled off and 20 mL of dichloromethane was added into the reaction mixture at room temperature. To it 5 mmol of *N*-methylaniline was added and the resulting mixture was stirred at room temperature for 3 hours. After completion of the reaction, the reaction mixture was quenched with aqueous saturated $NaHCO_3$ and extracted with dichloromethane. The combined organic layer was washed with water (2 × 25 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* to obtain the crude product. The crude product was then purified by silica gel column chromatography using hexane/ethyl acetate.

N-Methyl-*N*-phenyldecanamide (1f′)

1098 mg, 84% yield; pale yellow liquid; R_f = 0.38 (10% ethyl acetate in hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 0.85 (t, J = 6.8 Hz, 3H), 1.12–1.28 (m, 12H), 1.49–1.60 (m, 2H), 2.05 (t, J = 7.2 Hz, 2H), 3.25 (s, 3H), 7.16 (d, J = 7.6 Hz, 2H), 7.32 (t, J = 7.2 Hz, 1H), 7.40 (t, J = 7.6 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 14.2, 22.8, 25.7, 29.4 (2C), 29.5, 32.0, 34.2, 37.4, 127.5, 127.8, 129.8, 144.5, 173.5.

Experimental procedure for synthesis of *N*-methyl-*N*-phenylisobutyramide (1g′) from *N*-methylaniline and isobutyryl chloride[29]

A 100 mL RB flask containing a solution of *N*-methylaniline (5 mmol) and triethylamine (6 mmol) in 25 mL dry dichloromethane was immersed in a cooling bath at 0 °C. Isobutyryl chloride (6 mmol) was added dropwise at 0 °C and the resulting mixture was stirred at room temperature for 6 hours. After completion of the reaction, the reaction mixture was quenched with aqueous saturated $NaHCO_3$ and extracted with dichloromethane. The combined organic layer was washed with water (2 × 25 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* to obtain the crude product. The crude product was then purified by silica gel column chromatography using hexane/ethyl acetate.

N-Methyl-*N*-phenylisobutyramide (1g′)

629 mg, 71% yield; cream colour solid; R_f = 0.24 (15% ethyl acetate in hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 1.02 (d, J = 6.8 Hz, 6H), 2.43–2.56 (m, 1H), 3.24 (s, 3H), 7.18 (d, J = 7.6 Hz, 2H), 7.34 (t, J = 7.2 Hz, 1H), 7.41 (t, J = 7.2 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 19.8, 31.1, 37.6, 127.4, 127.8, 129.9, 144.4, 177.6.

Experimental procedure for synthesis of *N*-methyl-*N*-phenylpivalamide (1h′) from *N*-methylaniline and pivaloylchloride[30]

A 100 mL RB flask containing a solution of *N*-methylaniline (5 mmol) and triethylamine (6 mmol) in 25 mL dry dichloromethane was immersed in a cooling bath at 0 °C. Pivaloyl chloride (6 mmol) was added dropwise at 0 °C and the resulting mixture was stirred at room temperature for 3 hours. After completion of the reaction, the reaction mixture was quenched with aqueous saturated $NaHCO_3$ and extracted with dichloromethane. The combined organic layer was washed with water (2 × 25 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* to obtain the crude product. The crude product was then purified by silica gel column chromatography using hexane/ethyl acetate.

N-Methyl-*N*-phenylpivalamide (1h′)

736 mg, 77% yield; white solid; R_f = 0.30 (10% ethyl acetate in hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 1.03 (s, 9H), 3.21 (s, 3H), 7.21 (d, J = 7.2 Hz, 2H), 7.29–7.35 (m, 1H), 7.38 (t, J = 7.2 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 29.6, 40.9, 41.5, 127.9, 128.9, 129.3, 145.4, 178.3.

Experimental procedure for synthesis of *N*-methyl-*N*-phenylbenzamide (1i′) from *N*-methylaniline and benzoyl chloride[30]

A 100 mL RB flask containing a solution of *N*-methylaniline (5 mmol) and triethylamine (6 mmol) in 25 mL dry dichloromethane was immersed in a cooling bath at 0 °C. Benzoyl

chloride (6 mmol) was added dropwise at 0 °C and the resulting mixture was stirred at room temperature for 5 hours. After completion of the reaction, the reaction mixture was quenched with aqueous saturated $NaHCO_3$ and extracted with dichloromethane. The combined organic layer was washed with water (2 × 25 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* to obtain the crude product. The crude product was then purified by silica gel column chromatography using hexane/ethyl acetate.

N-Methyl-*N*-phenylbenzamide (1i′)

1034 mg, 91% yield; yellow solid; R_f = 0.21 (10% ethyl acetate in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.50 (s, 3H), 7.03 (d, J = 7.6 Hz, 2H), 7.10–7.18 (m, 3H), 7.18–7.25 (m, 3H), 7.27–7.32 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 38.5, 126.6, 127.0, 127.8, 128.8, 129.3, 129.7, 136.0, 145.0, 170.8.

Experimental procedure for synthesis of 4-chloro-*N*-methyl-*N*-phenylbenzamide (1j′) from *N*-methylaniline and 4-chlorobenzoyl chloride[30]

A 100 mL RB flask containing a solution of *N*-methylaniline (5 mmol) and triethylamine (6 mmol) in 25 mL dry dichloromethane was immersed in a cooling bath at 0 °C. 4-Chlorobenzoyl chloride (6 mmol) was added dropwise at 0 °C and the resulting mixture was stirred at room temperature for 7 hours. After completion of the reaction, the reaction mixture was quenched with aqueous saturated $NaHCO_3$ and extracted with dichloromethane. The combined organic layer was washed with water (2 × 25 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* to obtain the crude product. The crude product was then purified by silica gel column chromatography using hexane/ethyl acetate.

4-Chloro-*N*-methyl-*N*-phenylbenzamide (1j′)

1143 mg, 93% yield; colourless liquid; R_f = 0.28 (10% ethyl acetate in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.48 (s, 3H), 7.02 (d, J = 7.6 Hz, 2H), 7.10–7.19 (m, 3H), 7.20–7.25 (m, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 38.6, 126.9, 127.0, 128.1, 129.5, 130.4, 134.4, 135.8, 144.8, 169.6.

Experimental procedure for synthesis of 3-chloro-*N*-methyl-*N*-phenylbenzamide (1k′) from *N*-methylaniline and 3-chlorobenzoyl chloride[30]

A 100 mL RB flask containing a solution of *N*-methylaniline (5 mmol) and triethylamine (6 mmol) in 25 mL dry dichloromethane was immersed in a cooling bath at 0 °C. 3-Chlorobenzoyl chloride (6 mmol) was added dropwise at 0 °C and the resulting mixture was stirred at room temperature for 4 hours. After completion of the reaction, the reaction mixture was quenched with aqueous saturated $NaHCO_3$ and extracted with dichloromethane. The combined organic layer was washed with water (2 × 25 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* to obtain the crude product. The crude product was then purified by silica gel column chromatography using hexane/ethyl acetate.

3-Chloro-*N*-methyl-*N*-phenylbenzamide (1k′)

1093 mg, 89% yield; white solid; R_f = 0.17 (10% ethyl acetate in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.49 (s, 3H), 7.01–7.12 (m, 4H), 7.14–7.22 (m, 2H), 7.25 (t, J = 7.2 Hz, 2H), 7.33–7.36 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 38.5, 126.8, 127.0, 129.0, 129.1, 129.4, 129.8, 133.9, 137.7, 144.5, 169.2.

Experimental procedure for synthesis of 2-methoxy-*N*-methyl-*N*-phenylbenzamide (1l′) from *N*-methylaniline and 2-methoxybenzoyl chloride[29]

A 100 mL RB flask containing a solution of *N*-methylaniline (5 mmol) and triethylamine (6 mmol) in 25 mL dry dichloromethane was immersed in a cooling bath at 0 °C. 2-Methoxybenzoyl chloride (6 mmol) was added dropwise at 0 °C and the resulting mixture was stirred at room temperature for 6 hours. After completion of the reaction, the reaction mixture was quenched with aqueous saturated $NaHCO_3$ and extracted with dichloromethane. The combined organic layer was washed with water (2 × 25 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* to obtain the crude product. The crude product was then purified by silica gel column chromatography using hexane/ethyl acetate.

2-Methoxy-*N*-methyl-*N*-phenylbenzamide (1l′)

893 mg, 74% yield; yellow solid; R_f = 0.25 (2% ethyl acetate in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.48 (s, 3H), 3.61 (s, 3H), 6.61 (d, J = 8.0 Hz, 1H), 6.73–6.83 (m, 1H), 7.00–7.09 (m, 3H), 7.10–7.19 (m, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 37.2, 55.2, 110.6, 120.3, 126.6, 126.7 (2C), 128.5, 128.8, 130.4, 144.1, 155.2.

Experimental procedure for synthesis of *N*-methyl-*N*,2-diphenylacetamide (1m′) from *N*-methylaniline and phenylacetic acid[13c]

Phenylacetic acid (5 mmol) was taken in an oven-dried 100 mL RB flask fitted with a rubber septum and the flask was purged with nitrogen. Thionyl chloride (6 mmol) was added dropwise at 0 °C and the resulting mixture was stirred at 80 °C. After stirring at 80 °C for 1 hour, excess thionyl chloride was distilled off and 20 mL of dichloromethane was added into the reaction mixture at room temperature. To it 5 mmol of *N*-methylaniline was added and the resulting mixture was stirred at room temperature for 3 hours. After completion of the reaction, the reaction mixture was quenched with aqueous saturated $NaHCO_3$ and extracted with dichloromethane. The combined organic layer was washed with water (2 × 25 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* to obtain the crude product. The crude product was then purified by silica gel column chromatography using hexane/ethyl acetate.

N-Methyl-*N*,2-diphenylacetamide (1m′)

969 mg, 86% yield; pale yellow liquid; R_f = 0.21 (10% ethyl acetate in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.28 (s, 3H), 3.46 (s, 2H), 7.05 (d, J = 6.8 Hz, 2H), 7.12 (d, J = 7.2 Hz, 2H), 7.16–7.25 (m, 3H), 7.32–7.43 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz,

$CDCl_3$) δ 37.7, 41.0, 126.7, 127.7, 128.0, 128.4, 129.2, 129.8, 135.5, 144.1, 171.1.

Experimental procedure for synthesis of *N*-methylthioamides (1a–1m) from *N*-methylamides (1a′–1m′)[31]

To a solution of *N*-methylamide (2 mmol) in dry dichloromethane (DCM, 10 mL) was added 1 mmol of Lawesson's reagent and the resulting mixture was stirred at room temperature for a specific period of time. After completion of the reaction, the reaction mixture was concentrated under vacuum and purified by silica gel column chromatography (hexane/ethyl acetate).

N-Methyl-*N*-phenylethanethioamide (1a)

268 mg, 81% yield; 3 h; cream colour solid; R_f = 0.25 (5% ethyl acetate in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 3.73 (s, 3H), 7.14–7.19 (m, 2H), 7.35–7.41 (m, 1H), 7.42–7.48 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 34.0, 45.8, 125.4, 128.6, 130.1, 145.9, 201.4.

N-Methyl-*N*-phenylpropanethioamide (1b)

255 mg, 71% yield; 4 h; yellow liquid; R_f = 0.16 (2% ethyl acetate in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18 (t, J = 7.6 Hz, 3H), 2.48 (q, J = 7.6 Hz, 2H), 3.72 (s, 3H), 7.14–7.19 (m, 2H), 7.36–7.42 (m, 1H), 7.42–7.48 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 14.6, 37.2, 45.9, 125.6, 128.6, 130.1, 145.7, 207.8; FTIR (KBr): 701, 773, 1121, 1278, 1493, 1594, 2978, 3061 cm^{-1}; HRMS (m/z): $[M + H]^+$ calculated for $C_{10}H_{14}NS$: 180.0847; found: 180.0863.

N-Methyl-*N*-phenylbutanethioamide (1c)

340 mg, 88% yield; 6 h; pale yellow liquid; R_f = 0.42 (10% ethyl acetate in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.77 (t, J = 7.6 Hz, 3H), 1.72 (sext, J = 7.2 Hz, 2H), 2.45 (t, J = 7.6 Hz, 2H), 3.72 (s, 3H), 7.15 (d, J = 8.0 Hz, 2H), 7.39 (t, J = 7.2 Hz, 1H), 7.45 (t, J = 7.2 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 13.8, 23.8, 45.7, 125.7, 128.6, 130.0, 145.8, 206.3; FTIR (KBr): 773, 1289, 1492, 1593, 2965, 3061 cm^{-1}; HRMS (m/z): $[M + H]^+$ calculated for $C_{11}H_{16}NS$: 194.1003; found: 194.1002.

N-Methyl-*N*-phenylhexanethioamide (1d)

385 mg, 87% yield; 24 h; pale yellow liquid; R_f = 0.21 (2% ethyl acetate in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.78 (t, J = 6.4 Hz, 3H), 1.05–1.19 (m, 4H), 1.69 (quint, J = 7.6 Hz, 2H), 2.48 (t, J = 7.6 Hz, 2H), 3.72 (s, 3H), 7.16 (d, J = 7.6 Hz, 2H), 7.36–7.42 (m, 1H), 7.42–7.48 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 14.0, 22.3, 30.1, 31.4, 44.0, 46.0, 125.7, 128.6, 130.0, 145.8, 206.6; FTIR (KBr): 702, 773, 1073, 1276, 1494, 1593, 2957, 3062; HRMS (m/z): $[M + H]^+$ calculated for $C_{13}H_{20}NS$: 222.1316; found: 222.1333.

N-Methyl-*N*-phenylheptanethioamide (1e)

320 mg, 68% yield; 9 h; pale yellow liquid; R_f = 0.22 (2% ethyl acetate in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.79 (t, J = 6.8 Hz, 3H), 1.00–1.22 (m, 6H), 1.68 (quint, J = 7.2 Hz, 2H), 2.48 (t, J = 7.6 Hz, 2H), 3.72 (s, 3H), 7.16 (d, J = 7.6 Hz, 2H), 7.39 (t, J = 7.2 Hz, 1H), 7.45 (t, J = 7.2 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 14.1, 22.5, 28.9, 30.4, 31.4, 44.0, 46.0, 125.7, 128.6, 130.0, 145.8, 206.6; FTIR (KBr): 702, 772, 1075, 1283, 1493, 1593, 2956, 3061; HRMS (m/z): $[M + H]^+$ calculated for $C_{14}H_{22}NS$: 236.1473; found: 236.1495.

N-Methyl-*N*-phenyldecanethioamide (1f)

504 mg, 91% yield; 12 h; pale yellow liquid; R_f = 0.25 (2% ethyl acetate in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (t, J = 6.8 Hz, 3H), 1.13–1.21 (m, 10H), 1.21–1.28 (m, 2H), 1.63–1.72 (m, 2H), 2.45–2.52 (m, 2H), 3.72 (s, 3H), 7.16 (d, J = 8.0 Hz, 2H), 7.39 (t, J = 7.2 Hz, 1H), 7.45 (t, J = 7.2 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 14.2, 22.8, 29.2 (2C), 29.3, 29.4, 30.4, 31.9, 44.0, 46.0, 125.7, 128.6, 130.0, 145.8, 206.7; FTIR (KBr): 701, 772, 1078, 1280, 1498, 1593, 2926, 3062; HRMS (m/z): $[M + H]^+$ calculated for $C_{17}H_{28}NS$: 278.1942; found: 278.1960.

N,2-Dimethyl-*N*-phenylpropanethioamide (1g)

236 mg, 61% yield; 24 h; white solid; R_f = 0.38 (5% ethyl acetate in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.13 (d, J = 6.4 Hz, 6H), 2.81–2.93 (m, 1H), 3.71 (s, 3H), 7.15 (d, J = 7.2 Hz, 2H), 7.37–7.43 (m, 1H), 7.43–7.50 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 23.7, 38.4, 45.7, 125.6, 128.6, 130.2, 145.9, 213.2.

N,2,2-Trimethyl-*N*-phenylpropanethioamide (1h)

261 mg, 63% yield; 24 h; white solid; R_f = 0.24 (2% ethyl acetate in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (s, 9H), 3.70 (s, 3H), 7.20 (d, J = 7.2 Hz, 2H), 7.32–7.44 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 33.2, 46.5, 51.5, 127.1, 128.3, 129.4, 148.3, 216.1.

N-Methyl-*N*-phenylbenzothioamide (1i)

291 mg, 64% yield; 5 h; yellow solid; R_f = 0.19 (2% ethyl acetate in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.94 (s, 3H), 6.98–7.04 (m, 2H), 7.05–7.15 (m, 4H), 7.16–7.24 (m, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 46.4, 126.3, 127.3, 127.6, 127.8, 128.5, 129.2, 143.6, 146.7, 202.5.

4-Chloro-*N*-methyl-*N*-phenylbenzothioamide (1j)

471 mg, 90% yield; 10 h; yellow liquid; R_f = 0.34 (5% ethyl acetate in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.92 (s, 3H), 6.98–7.08 (m, 4H), 7.13–7.19 (m, 3H), 7.20–7.26 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 46.5, 126.3, 127.6, 127.9, 129.2, 129.5, 134.5, 142.0, 146.5; FTIR (KBr): 832, 1092, 1299, 1492, 1592, 3061 cm^{-1}; HRMS (m/z): $[M + H]^+$ calculated for $C_{14}H_{12}NSCl$: 262.0457; found: 262.0476.

3-Chloro-*N*-methyl-*N*-phenylbenzothioamide (1k)

361 mg, 69% yield; 3 h; yellow solid; mp 94–96 °C; R_f = 0.35 (5% ethyl acetate in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.93 (s, 3H), 6.94–7.10 (m, 5H), 7.13–7.19 (m, 1H), 7.20–7.29 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 46.3, 125.7, 126.2, 127.7, 128.1, 128.5, 128.8, 129.5, 133.6, 145.0, 146.3, 200.3; FTIR (KBr): 768, 1114, 1262, 1492, 1591, 3062; HRMS (m/z):

$[M + H]^+$ calculated for $C_{14}H_{12}NClS$: 262.0457; found: 262.0480.

2-Methoxy-*N*-methyl-*N*-phenylbenzothioamide (1l)

443 mg, 86% yield; 4 h; yellow solid; mp 90–92 °C; R_f = 0.31 (10% ethyl acetate in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.57 (s, 3H), 3.91 (s, 3H), 6.48 (d, J = 8.4 Hz, 1H), 6.80 (t, J = 7.6 Hz, 1H), 7.01–7.07 (m, 3H), 7.07–7.12 (m, 1H), 7.12–7.17 (m, 2H), 7.31 (d, J = 7.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 45.2, 55.1, 110.5, 120.3, 125.9, 127.4, 128.3, 129.4, 129.8, 133.3, 146.0, 152.4, 199.3; FTIR (KBr): 753, 1106, 1249, 1492, 1595, 2960, 3062; HRMS (m/z): $[M + H]^+$ calculated for $C_{15}H_{16}NOS$: 258.0952; found: 258.0971.

***N*-Methyl-*N*,2-diphenylethanethioamide (1m)**

280 mg, 58% yield; 36 h; pale yellow liquid; R_f = 0.45 (10% ethyl acetate in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.73 (s, 3H), 4.02 (s, 2H), 6.96–7.02 (m, 4H), 7.14–7.19 (m, 3H), 7.33–7.37 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 46.4, 50.9, 126.1, 126.8, 128.3, 128.6, 128.8, 129.8, 136.8, 145.5, 202.9; FTIR (KBr): 699, 769, 1098, 1277, 1493, 1597, 2955, 3060 cm^{-1}; HRMS (m/z): $[M + H]^+$ calculated for $C_{15}H_{16}NS$: 242.1003; found: 242.1021.

Conflicts of interest

There are no conflicts to declare.

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