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Decomposition of benzoylthioureas into benzamides and thiobenzamides under solvent-free conditions using iodine–alumina as the catalyst and its mechanistic study by density functional theory†

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The breaking down of benzoylthioureas to benzamides and thiobenzamides in a single route using iodine–alumina as the catalyst under solvent-free conditions is highlighted. Results show that when an electron donating group, such as the methyl or methoxy group, is at the *para*-position of the aryl group of **1**, benzamide (**2**) is the favoured product. When an electron withdrawing group, such as the chlorine or nitro group, is at the *para*-position of the aryl group of **1**, thiobenzamide (**3**) is the favoured product. From the study of the reaction mechanism, it may be postulated that the formation of benzamide is due to the migration of the aryl group, whereas the formation of thiobenzamide may be due to the migration of the phenyl group. Thus, a new method for the formation of benzamides and thiobenzamides was developed.

Introduction

Amides and thioamides are important for the synthesis of various natural products as well as intermediates for the synthesis of organic compounds.[1] In general, amides can be prepared from their corresponding ketoximes by the Beckmann rearrangement[2,3] and by the coupling of carboxylic acids with amines.[4,5] In most cases, thioamides are prepared by the thionation of the corresponding amide analogues by Lawesson's reagent.[1b,c,6] The thionation of benzamides with Lawesson's reagent was accomplished in refluxing chlorobenzene, which is a toxic chemical.[1b] The Beckmann rearrangement generally requires a strong acid, high reaction temperatures, harsh reaction conditions and results in the production of unwanted by-products.[7] Several methodologies to check the reaction conditions, such as in a liquid phase,[8] in a vapor phase,[9] in supercritical water,[10] and in ionic liquids,[11] have been developed. However, the drawbacks in such methods are the use of toxic solvents, expensive reagents, long reaction times, low yields and the production of considerable amounts of by-products. In recent years, molecular iodine (I_2) has emerged as a useful catalyst for various organic transformations because of its inexpensive, non-toxic, ready availability and eco-friendly nature.[12] It has high tolerance to air and moisture that can be removed from reaction systems easily, and thus has also been explored as a useful reagent in organic synthesis.[13] Molecular iodine is known to form electron donor–acceptor addition complexes on reacting with organo-sulfur compounds[14] and it is thiophilic in nature.[15] Recently, solvent-free organic synthesis using inorganic supports has become a popular method[16] and attracted immense interest as an environmentally benign methodology, because it often leads to high yields, clean reactions, and shorter reaction times. In continuation of our work on the clean conversion of thioureas into 2-(*N*-arylamino) benzothiazoles under solvent free conditions,[17] we herein report a simple and efficient process for the conversion of benzoylthioureas to benzamides and thiobenzamides using iodine–alumina as the catalyst without any solvent. The method (Scheme 1) is simple with high yields and easy for isolation of the products from the reaction mixture.

Results and discussion

To optimize the reaction conditions, *N*-2-pyridinyl-*N*′-benzoylthiourea (**1a**) was used as a model substrate for the reaction with iodine–alumina (I_2–Al_2O_3). A few experiments were carried out with different solvents at varied reaction temperatures and mol% of catalyst, as illustrated in Table 1. The reaction was first

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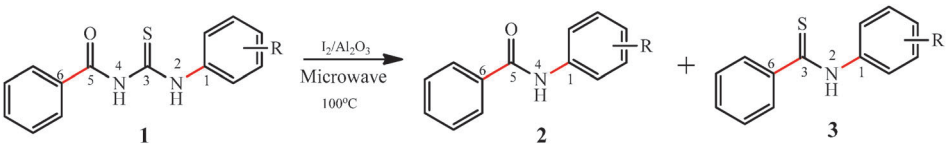
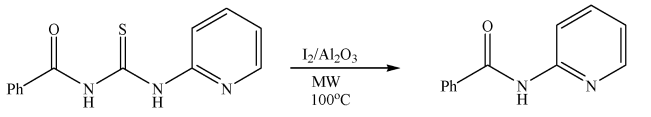
† Electronic supplementary information (ESI) available. See DOI: 10.1039/c4nj02021a



Scheme 1 Decomposition of benzoyl thioureas, **1**, into benzamides, **2**, and thiobenzamides, **3**.

Table 1 Optimization of the reaction conditions for the preparation of **2a**[a]



Entry	Catalyst (mol%)	Temperature (°C)	Solvent	Yield[b] (%)
1	10	30	H_2O	No reaction
2	10	30	H_2O : CH_3CN (1 : 1)	No reaction
3	10	80	H_2O	No reaction
4	10	80	H_2O : CH_3CN (1 : 1)	Trace
5	10	Reflux	CH_3CN	63
6	10	180	DMF	42
7	10	100	DMSO	45
8	10	Reflux	Toluene	28
9	20	Reflux	CH_3CN	74
10	30	Reflux	CH_3CN	65
11	20	180	DMF	58
12	20	110	No solvent	82
13	20	100 (MW)	No solvent	96

[a] *N*-2-Pyridinyl-*N*′-benzoylthiourea (1 mmol), solvent (10 mL). [b] Isolated yield.

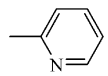
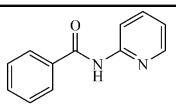
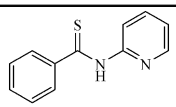
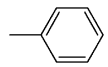
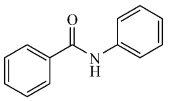
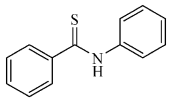
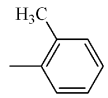
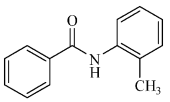
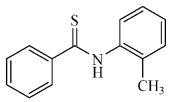
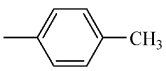
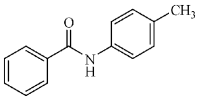
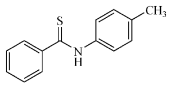
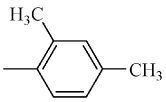
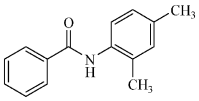
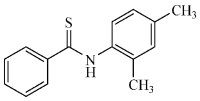
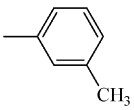
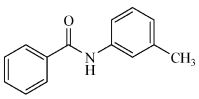
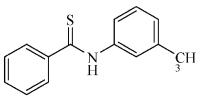
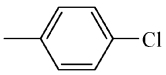
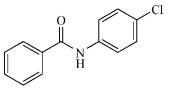
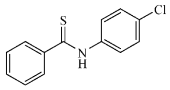
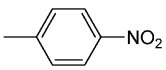
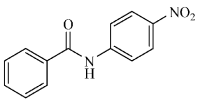
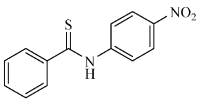
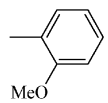
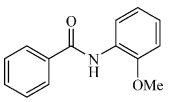
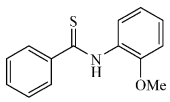
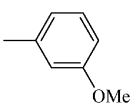
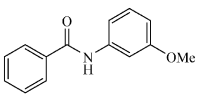
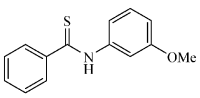
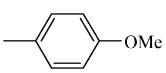
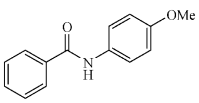
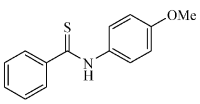
carried out in water by stirring **1a** with iodine–alumina (10 mol%) as the catalyst at room temperature. The reaction failed to give the desired product even when the reaction time was extended up to 48 h (Table 1, entry 1). The desired product could not be obtained when water : acetonitrile (1 : 1) was used as the solvent by keeping the same reaction conditions (Table 1, entry 2). Therefore, the same reaction was tried under reflux conditions with different solvents (Table 1, entries 3–8). Only traces of the target product could be obtained (Table 1, entry 4) when water : acetonitrile (1 : 1) was used. It was found that the yield obtained was increased (63% yield) when acetonitrile was used alone (Table 1, entry 5) but the yield decreased when the reaction was carried out in other solvents (Table 1, entries 6–8). To increase the yield, we looked for different reaction conditions. Increasing the catalytic amount from 10 to 20 mol% resulted in the increase of the yield. To our delight, the starting materials disappeared and desired product, *N*-(pyridin-2-yl)benzamide **2a**, was formed in good yield (74% yield) (Table 1, entry 9), and there was little difference in the yield on increasing the catalytic amount from 20 to 30 mol% (Table 1, entry 10). When the reaction was performed under solvent-free conditions at 110 °C with 20 mol% of the catalyst, the yield was found to be 82% (entry 12). We carried out the reaction under microwave irradiation (10 min, 100 W) without any solvent and it was found that the product was obtained in good yield (96%) (entry 13). Thus, the reaction of benzoylthioureas with iodine–alumina (20 mol%) under microwave (MW) irradiation without any solvent was found to be the optimized reaction conditions.

As the optimal condition was established, the scope and limitations of the reaction scheme were investigated on different substituted benzoylthioureas. In a typical procedure, iodine–alumina (20 mol%) was added to benzoylthiourea **1** (1 mmol) whereby the reaction mixture was grounded using a motor and pestle, stirred for 30 seconds and irradiated in a microwave, MW (10–20 min, 100 W) without any solvent to give products **2** and **3**. Various substituted benzoylthioureas were reacted with iodine–alumina (20 mol%) under MW irradiation without any solvent, and all the reactions proceeded smoothly and gave the corresponding *N*-substituted benzamides **2a–k** and thiobenzamides **3b–k** in good to excellent isolated yields (Table 2). When *N*-2-pyridinyl-*N*′-benzoylthiourea was used as the substrate, the benzamide derivative was found to be the only product (Table 2, entry 1). However, when *N*-phenyl-*N*′-benzoylthiourea was reacted under the same reaction conditions, a mixture of benzamide **2b** and thiobenzamide **3b** (Table 2, entry 2) was obtained with an overall yield of 94%. Similarly, mixtures of *N*-substituted benzamides (**2c–k**) with an overall yield of 30–96% and thiobenzamides (**3c–k**) with an overall yield of 17–53% were obtained from the corresponding thioureas (Table 2, entries 3–11).

Density functional calculations were also performed to study the reactions. All the structures were optimized by the hybrid density functional B3LYP using the segmented all-electron relativistically contracted Def2-TZVP(-df) basis set with the help of ORCA. The calculations show that the formations of both benzamide and the thiobenzamide products with the byproducts as isothiocyanate and isocyanate, respectively, are endothermic. The formation of benzamide and isothiocyanate involves lower energy (Table 3). This indicates that out of the two reactions, the formation of the benzamide product is the thermodynamically favoured reaction although it is observed from the experimental results that both products are formed except in the *o*-pyridinated starting molecule where only the energetically favoured benzamide product is formed.

The plausible mechanism for the formation of benzamides and thiobenzamides is shown in Scheme 2. To understand the mechanistic pathway, the two most probable iodide intermediates **A** and **B**, formed after the reaction with molecular iodine (I_2) molecule, were considered (Scheme 2 and Table 4). The I–I bond in molecular iodine is often known to be perturbed by thiones and form iodides.[14a] The formation of the iodide intermediate through the oxygen atom is ruled out because of its relatively high energy compared to those of intermediates **A** and **B** (ESI†). To the best of our knowledge, examples of the O–I bond formation of molecular iodine with ketones are not found in the previous reports. The results show that the intermediate (**A**) has the lowest energy, which indicates that it is the most probable intermediate. The results further show that for all the reactions theoretically considered, the

Table 2 Synthesis of *N*-substituted benzamides–thiobenzamides from *N*-aryl-*N*′-benzoylthioureas[a]

Entry	Ar	Product (%) 2	3	Time (min)	Yield[b] (%)
1		 **2a** (96%)	 **3a** (0%)	10	96[c]
2		 **2b** (59%)	 **3b** (35%)	10	94
3		 **2c** (32%)	 **3c** (53%)	20	85
4		 **2d** (63%)	 **3d** (19%)	18	82
5		 **2e** (55%)	 **3e** (33%)	15	88
6		 **2f** (56%)	 **3f** (22%)	18	78
7		 **2g** (30%)	 **3g** (50%)	20	80
8		 **2h** (35%)	 **3h** (49%)	15	84
9		 **2i** (52%)	 **3i** (26%)	20	78
10		 **2j** (59%)	 **3j** (17%)	20	76
11		 **2k** (51%)	 **3k** (31%)	16	82

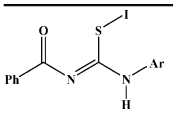
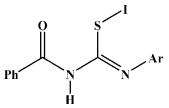
[a] Aryl substituent. [b] Overall yield of the mixture. [c] Absolute yield of **2a**.

intermediate (**A**) has the lowest energy, except for the *p*-chlorinated molecule, which indicates that it is the most probable intermediate. To study the possibility of breaking the molecular backbone, the strength of different bonds were considered based on the Mayer bond order,[18] which indicates the number of electron pairs that constitute a bond. When considering the backbone structure,

Table 3 Relative energy and energy of reaction of the products

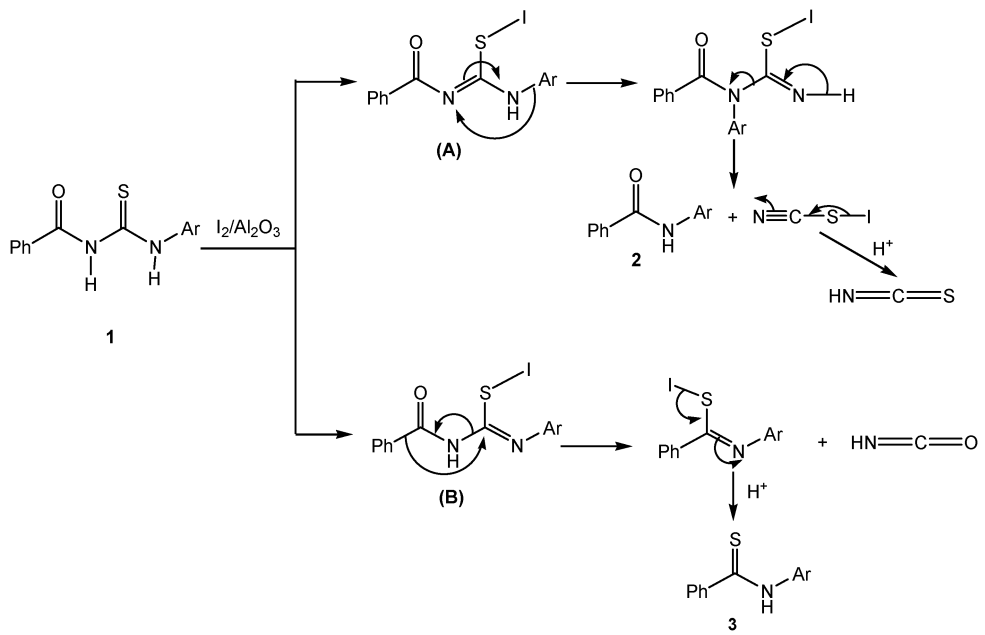
Product	Relative energy (kcal)	Energy of reaction (kcal)
o-Pyridine		
2a	0	9.25
3a	2.16	11.42
Unsubstituted benzoylthiourea		
2b	0	5.17
3b	1.56	6.73
o-Methyl		
2c	0	5.56
3c	1.90	7.46
p-Methyl		
2d	0	5.27
3d	1.45	6.72
p-Chloro		
2g	0	5.21
3g	1.68	6.89

Table 4 Relative energies of different intermediates for the parent and *p*-chlorinated molecules

	Unsubstituted benzoylthiourea		*p*-Chlorinated benzoylthiourea	
Structure	Intermediate	Relative energy (kcal)	Intermediate	Relative energy (kcal)
	**A**	0.0	**A_*p*-Cl**	0.2
	**B**	0.5	**B_*p*-Cl**	0.0

C1–N2 has the least Mayer bond order in intermediate **A** while C5–C6 has the least bond order in the intermediate **B** (Table 5). In case of the *p*-chlorinated molecule, which has an electron withdrawing substituent at the *para*-position of the aryl group, the intermediate **B** is the energetically most favored intermediate. This indicates that the migration of the phenyl group in *p*-chlorinated molecule to attack the thiocarbonyl carbon is the favored step, as shown in Scheme 2, which on further rearrangement gives the product thiobenzamide (**3g**). The proposed steps are supported by the experimental results where the thiobenzamide is the major product (Table 2). The probable reason for the formation of an appreciable amount of the benzamide product (**2g**), although it is not the favored step mechanistically, could be that the benzamide product is thermodynamically more stable than the thiobenzamide product (Table 3). The formation of benzamide occurs through the intermediate **A** by the migration of the aryl group as the C1–N2 bond order is the least in intermediate **A** (Scheme 2).

For other substituted molecules also, C5–C6 has the least bond order in the intermediate **B**, as mentioned earlier. This explains that the formation of the thiobenzamide product is due to the migration of the phenyl group following similar steps as in the *p*-chlorinated molecule. However, when the electron withdrawing *p*-chlorinated aryl group is replaced by the *p*-methylated aryl group, the benzamide product (**2d**) is the major one. The reason for the reaction in this case could be that the formation of the benzamide product is preferred by breaking the C1–N2 bond in intermediate **A** than the mechanistically favored step by breaking the C5–C6 bond in intermediate **B** (as in the *p*-chlorinated molecule). This is so because the intermediate **A** has lower energy than **B**. It is also interesting to note that when the electron donating group methyl is at the *ortho*-position in the



Scheme 2 Proposed mechanism for the formation of benzamides and thiobenzamides.

Table 5 Mayer bond order for selected bonds for the parent and the *p*-chlorinated molecules

	Mayer bond order				
Intermediates	C1–N2	N2–C3	C3–N4	N4–C5	C5–C6
Unsubstituted benzoylthiourea					
A	0.9092	1.1663	1.5143	1.3996	0.9238
B	1.1027	1.8061	0.9953	1.1750	0.9085
p-Chlorinated benzoylthiourea					
A_*p*-Cl	0.9138	1.1550	1.5238	1.3918	0.9254
B_*p*-Cl	1.1197	1.7945	1.0017	1.1714	0.9103

aryl group, the intermediate **A**, which has lowest energy, has the lowest bond order at C5–C6 bond. This makes the breaking of the C1–N2 bond in intermediate **A** less probable, thus rendering the formation of the thiobenzamide product (**3c**) the major product. A similar result is obtained in the *o*-pyridinated molecule.

Conclusion

In conclusion, we have developed a new process for the preparation of amides and thioamides from benzoyl thioureas under solvent free conditions precluding the use of any additional Lewis or Brønsted acids as a cocatalyst, toxic organic solvents, and without producing any significant corrosive waste. This versatile synthetic method is expected to find valuable applications in various areas, particularly as intermediates for the synthesis of heterocyclic compounds. The DFT studies showed that the formation of benzamide was due to the migration of the aryl group (in intermediate **A**), whereas the formation of thiobenzamide may be due to the migration of the phenyl group (in intermediate **B**). It was found that the formation of the benzamide product is the thermodynamically favoured reaction, although it is observed from the experimental results that both products are formed, except in *N*-2-pyridinyl-*N*′-benzoylthiourea where only the energetically favoured benzamide product is formed. We have developed a new method for the formation of benzamides and thiobenzamides, which were generally derived by the thionation of benzamides with Lawesson's reagent.

Experimental section

General information

All of the reagents were of commercial grade and purified according to the established procedures. NMR spectra were recorded using 300 MHz and 400 MHz spectrometers using $CDCl_3$ as the solvent. ^{1}H NMR and ^{13}C NMR chemical shifts are given in δ (parts per million) relative to tetramethylsilane (0 ppm). IR spectra were recorded in KBr discs using a Shimadzu FT-IR-8400 spectrometer. Elemental analyses (C, H and N) were carried out using a Perkin-Elmer 2400 analytical instrument. All microwave (MW) irradiation reactions were carried out using a Microwave synthesis system (Monowave 300 Anton Paar) instrument at 100 W output power. Silica gel (60–120 mesh size) was used for column chromatography. The completion of the reactions was monitored by TLC using silica gel 60 F_{254} (0.25 mm). The melting points were recorded using a Buchi M-560 melting point apparatus and are uncorrected.

General procedure for the synthesis of *N*-substituted benzamides (2) and thiobenzamides (3) from benzoylthioureas (1)

Iodine–alumina (0.71 mmol of iodine adsorbed using 1.8 g of neutral alumina, *i.e.* 20 mol%) was added to *N*-substituted-*N*′-benzoylthioureas (1 mmol) and the mixture was ground thoroughly using a motor and pestle. The mixture was stirred for 30 s until they were mixed thoroughly. The reaction mixture was then irradiated without any solvent in a microwave for 10–20 min at 100 °C using the irradiation power of 100 W. The reaction progress was monitored by TLC. After the reaction was complete, the mixture was allowed to cool to room temperature and then poured into cold water. The product was purified by silica gel column chromatography (EtOAc–hexane) to give the corresponding amide. The structures of the products **2b**,[19a–d,21] **2c**,[19e,22] **2d**,[19f,22] **2f**,[19g] **2g**,[19f] **2h**,[19h,23] **2i**,[19i] **2j**,[19e] **2k**,[19j,24] **3b**,[25] **3d**,[26] **3f**,[27] **3g**,[28] **3h**,[29] **3i**,[1b] **3j** [1b] and **3k** [1b] were confirmed by comparison of their mps, TLC, IR, ^{1}H NMR and ^{13}C NMR data with authentic samples obtained commercially or prepared by previously reported methods. The residue of the catalyst was washed with water and dried under vacuum to afford the catalyst, which was used in subsequent runs.

N-(Pyridin-2-yl)benzamide (2a)

White solid (190 mg, 96%); mp 79–81 °C (lit.[20] 80–83 °C); IR (ν_{max}, KBr) 3217, 3022, 1674, 1527, 1435, 1308, 777 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 9.06 (br s, 1H), 8.41 (1H, d, J = 8.4 Hz), 8.17 (1H, d, J = 4.5 Hz), 7.94–7.92 (2H, m), 7.78–7.73 (1H, m), 7.59–7.46 (3H, m), 7.06–7.02 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 165.9, 151.6, 147.8, 138.5, 134.3, 128.8, 127.2, 119.9, 114.2. Mass (m/z) 198, anal. calcd for $C_{12}H_{10}N_2O$: C, 72.71%, H 5.08%, N, 14.13%. Found: C, 72.76%, H, 5.16%, N, 14.39%.

N-Phenylbenzamide (2b)

White solid (115 mg, 59%); mp 162–164 °C (lit.[19] 163–164 °C); IR (ν_{max}, KBr) 3344, 3053, 1656, 1535, 1323, 752, 690 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.88–7.86 (3H, m), 7.66–7.55 (3H, m), 7.53–7.27 (3H, m), 7.18–7.14 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 165.9, 137.9, 135.0, 129.0, 128.7, 127.1, 124.5, 120.3. Mass (m/z) 197, anal. calcd for $C_{13}H_{11}NO$: C, 79.19%, H 5.58%, N, 7.12%. Found: C, 79.27%, H, 5.47%, N, 7.23%.

N-(*o*-Tolyl)benzamide (2c)

White solid (67.5 mg, 32%); mp 140–142 °C (lit.[19] 143–144 °C); IR (ν_{max}, KBr) 3247, 3058, 1651, 1487, 1310, 747 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 9.81 (br s, 1H), 8.09 (2H, d, J = 7.2 Hz), 7.64 (1H, t, J = 7.5 Hz), 7.52 (2H, t, J = 7.8 Hz), 7.28–7.23 (3H, m), 7.12 (1H, t, J = 6.9 Hz), 2.42 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 168.7, 135.7, 133.4, 132.1, 130.4, 128.9, 128.3, 127.9, 126.6,

124.5, 18.1. Mass (*m*/*z*) 211. Anal. calcd for $C_{14}H_{13}NO$: C, 79.62%, H 6.16%, N, 6.64%. Found: C, 79.85%, H, 6.28%, N, 6.51%.

N-(*p*-Tolyl)benzamide (2d)

White solid (132 mg, 63%); mp 153–155 °C (lit.[19] 156–157 °C); IR (ν_{max}, KBr) 3266, 3054, 1658, 1345, 688 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ_H 8.06 (3H, d, J = 7.2 Hz), 7.72 (1H, d, J = 8.1 Hz), 7.60–7.44 (4H, m), 7.15 (1H, t, J = 7.8 Hz), 7.02 (1H, s), 2.32 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 166.2, 136.0, 133.0, 132.2, 131.6, 128.9, 128.4, 128.2, 126.2, 125.5, 124.4, 21.3. Mass (*m*/*z*) 211. Anal. calcd for $C_{14}H_{13}NO$: C, 79.62%, H 6.16%, N, 6.64%. Found: C, 79.85%, H, 6.28%, N, 6.51%.

N-(2,4-Dimethylphenyl)benzamide (2e)

White solid (124 mg, 55%); mp 170–173 °C; IR (ν_{max}, KBr) 3268, 3024, 1647, 1520, 1310, 818 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 7.92 (br s, 1H), 7.88–7.58 (2H, m), 7.57–7.52 (3H, m), 7.50 (1H, s), 7.27–7.06 (2H, m), 2.33 (3H, s), 2.31 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 165.2, 142.9, 133.8, 131.8, 131.2, 128.9, 127.6, 127.0, 21.8, 17.6. Mass (*m*/*z*) 225. Anal. calcd for $C_{15}H_{15}NO$: C, 79.97%, H 6.71%, N, 6.22%. Found: C, 79.99%, H, 6.67%, N, 6.29%.

N-(*m*-Tolyl)benzamide (2f)

White solid (118 mg, 56%); mp 124–125 °C (lit.[19] 117–118 °C); IR (ν_{max}, KBr) 3270, 3059, 2915, 1650, 1537, 1308, 781 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ_H 7.87 (2H, d, J = 6.7 Hz), 7.79 (1H, br s), 7.58–7.49 (4H, m), 7.46–7.23 (2H, m), 6.98 (1H, d, J = 7.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 165.8, 136.4, 135.2, 133.7, 131.7, 131.3, 129.8, 128.8, 126.6, 124.3, 21.6. Mass (*m*/*z*) 211. Anal. calcd for $C_{14}H_{13}NO$: C, 79.62%, H 6.16%, N, 6.64%. Found: C, 79.85%, H, 6.28%, N, 6.51%.

N-(4-Chlorophenyl)benzamide (2g)

White solid (69 mg, 30%); mp 202–204 °C (lit.[19] 199–200 °C); IR (ν_{max}, KBr) 3248, 3055, 1665, 1532, 1317, 798 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ_H 10.61 (br s, 1H), 7.93–7.88 (2H, m), 7.70–7.64 (3H, m), 7.58–7.53 (2H, m), 7.38 (2H, d, J = 8.94 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 167.0, 136.2, 133.9, 132.3, 131.5, 129.3, 129.1, 127.5, 125.5, 124.6. Mass (*m*/*z*) 231. Anal. calcd for $C_{13}H_{10}ClNO$: C, 67.53%, H 4.33%, N, 6.06%. Found: C, 67.49%, H, 4.38%, N, 6.13%.

N-(4-Nitrophenyl)benzamide (2h)

Yellow solid (85 mg, 35%); mp 200–202 °C (lit.[20] 198–199 °C); IR (ν_{max}, KBr) 3338, 3024, 1656, 1573, 1517, 1306, 1253, 845, 790 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 9.46 (br s, 1H), 8.05–8.02 (2H, m), 7.67–7.64 (3H, m), 7.63–7.51 (2H, m), 7.39–7.26 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 165.4, 151.6, 137.2, 133.4, 132.1, 129.0, 128.9, 127.8, 124.4, 120.5. Mass (*m*/*z*) 242. Anal. calcd for $C_{13}H_{10}N_2O_3$: C, 64.46%, H 4.13%, N, 11.57%. Found: C, 64.57%, H, 4.20%, N, 11.43%.

N-(4-Methoxyphenyl)benzamide (2k)

White solid (116 mg, 51%); mp 152–155 °C (lit.[21] 147–157 °C); IR (ν_{max}, KBr) 3328, 3055, 2835, 1665, 1523, 1276, 850, 798 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ_H 7.72–6.90 (9H, m), 3.94 (3H, s, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 165.2, 157.6, 138.2, 129.1, 128.9, 124.4, 121.6, 116.4, 55.8. Mass (*m*/*z*) 227. Anal. calcd for $C_{14}H_{13}NO_2$: C, 74.00%, H 5.73%, N, 6.17%. Found: C, 74.13%, H, 5.68%, N, 6.10%.

N-Phenylbenzothioamide (3b)

Yellow solid (74 mg, 35%); mp 101–104 °C (lit.[22] 102 °C); IR (ν_{max}, KBr) 3210, 3034, 1551, 1238, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 7.86 (br s, 1H), 7.42–7.10 (10H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 179.8, 136.9, 129.6, 128.9, 127.1, 125.3, 119.9. Mass (*m*/*z*) 213. Anal. calcd for $C_{13}H_{11}NS$: C, 73.20%, H 5.20%, N, 6.57%. Found: C, 73.58%, H, 5.46%, N, 6.82%.

N-(*o*-Tolyl)benzothioamide (3c)

White solid (121.5 mg, 53%); mp 150–152 °C; IR (ν_{max}, KBr) 3331, 3148, 1526, 1236, 766 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 7.96 (br s, 1H), 7.90–7.69 (2H, m), 7.55–7.50 (2H, m), 7.28–7.11 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 182.5, 135.2, 131.2, 128.4, 127.8, 127.0, 17.8. Mass (*m*/*z*) 227. Anal. calcd for $C_{14}H_{13}NS$: C, 73.97%, H 5.76%, N, 6.16%. Found: C, 73.76%, H, 5.57%, N, 6.02%.

N-(2,4-Dimethylphenyl)benzothioamide (3e)

White solid (80 mg, 33%); mp 142–144 °C; IR (ν_{max}, KBr) 3198, 3023, 1553, 1219, 1146, 808 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 8.08 (br s, 1H), 7.43–7.21 (4H, m), 7.08–7.03 (4H, m), 2.47 (3H, s), 2.26 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 181.3, 138.0, 135.2, 131.9, 127.9, 127.7, 21.1, 17.9. Mass (*m*/*z*) 241. Anal. calcd for $C_{15}H_{15}NS$: C, 74.65%, H 6.26%, N, 5.80%. Found: C, 74.43%, H, 6.06%, N, 5.66%.

N-(4-Chlorophenyl)benzothioamide (3g)

Yellow solid (124 mg, 50%); mp 160–162 °C (lit.[23] 149 °C); IR (ν_{max}, KBr) 3211, 3020, 1593, 1537, 1249, 823 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ_H 9.12 (br s, 1H), 7.89 (2H, d, J = 7.35 Hz), 7.70–7.64 (3H, m), 7.58–7.53 (2H, m), 7.38 (2H, d, J = 8.73 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 178.5, 133.9, 132.2, 131.5, 129.3, 129.0, 127.5, 125.3. Mass (*m*/*z*) 247. Anal. calcd for $C_{13}H_{10}ClNS$: C, 63.02%, H 4.07%, N, 5.65%. Found: C, 63.16%, H, 4.13%, N, 5.83%.

N-(4-Methoxyphenyl)benzothioamide (3k)

Yellow solid (75 mg, 31%); mp 127–129 °C (lit.[24] 131–133 °C); IR (ν_{max}, KBr) 3335, 3064, 2845, 1573, 1242, 750 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ_H 7.67 (br s, 1H), 7.54–7.52 (2H, m), 7.37–7.27 (2H, m), 7.22–7.14 (2H, m), 7.11–6.94 (3H, m), 3.94 (3H, s, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 184.6, 157.6, 147.2, 142.9, 127.4, 124.1, 122.5, 121.9, 121.3, 117.4, 117.3, 55.8. Mass (*m*/*z*) 243. Anal. calcd for $C_{14}H_{13}NOS$: C, 69.14%, H 5.35%, N, 5.76%. Found: C, 69.19%, H, 5.28%, N, 5.83%.

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