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

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† Electronic supplementary information (ESI) available.

Abstract

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

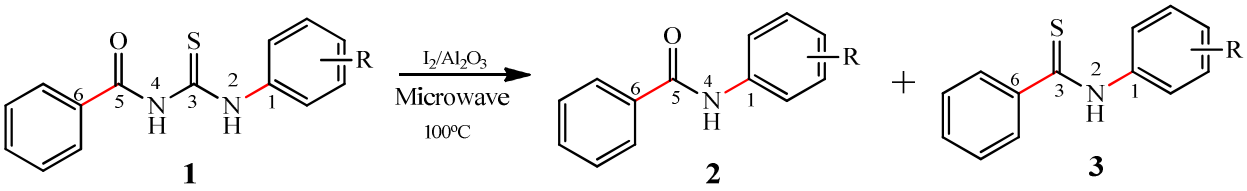
Keywords:

Iodine-alumina, Benzoylthioureas, Benzamide, Thiobenzamide, Solvent-free

Introduction

Amides and thioamides are important for the synthesis of various natural products as well as intermediates for synthesis of organic compounds.[1] In general, amides can be prepared from their corresponding ketoximes by Beckmann rearrangement[2,3] and by coupling of carboxylic acids with amines.[4,5] In most cases, thioamides are prepared by thionation of the corresponding amide analogues by Lawesson's reagent.[1b,1c,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 temperature, harsh reaction conditions and production of unwanted by-products.[7] Several methodologies to check the reaction conditions, such as, in liquid phase,[8] in 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, readily available and eco-friendly nature.[12] It has high tolerance to air and moisture that can be removed from the reaction systems easily, and so 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 catalyst without any solvent. The method (Scheme 1) is simple with high yields and easy for isolation of the products from the reaction mixture.



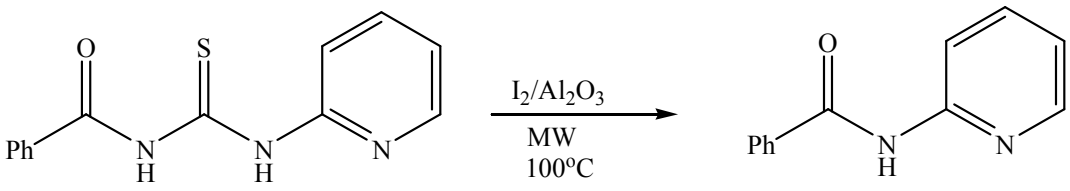
Scheme 1. Decomposition of benzoyl thioureas, 1 into benzamides, 2 and thiobenzamides, 3

Results and Discussion

To optimize the reaction conditions, *N*-2-pyridinyl-*N*'-benzoylthiourea (**1a**) was used as a model substrate for reaction with iodine-alumina (I_2-Al_2O_3). Few experiments were carried out with different solvents at varied reaction temperature and mol % of catalyst as illustrated in Table 1. The reaction was first 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 hr (Table1, entry 1). The desired product could not be obtained when water: acetonitrile (1:1) was used as solvent by keeping the same reaction conditions (Table1, entry 2). So the same reaction was tried under reflux condition with different solvents (Table 1, entries 3-8). Only traces of the target product could be obtained (Table1, 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 (Table1, entry 5) but the yield decreased when the reaction was carried out in other solvents (Table1, entries 6-8). To increase the yield, we looked for different reaction conditions. Increasing the catalytic amount from 10 to 20 mol%, it 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) (Table1, entry 9)

and there was little difference in the yield on increasing from 20 to 30 mol% (Table1, entry 10). When the reaction was performed under solvent-free condition 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 condition.

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



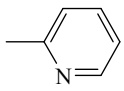
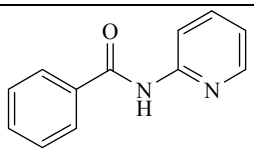
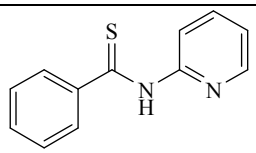
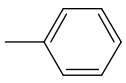
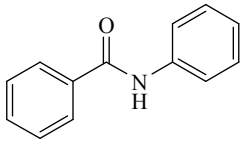
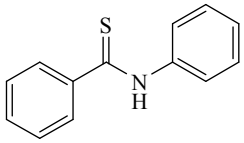
1a **2a**

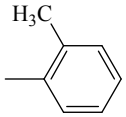
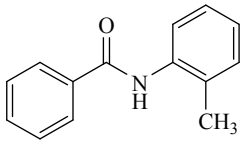
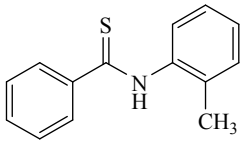
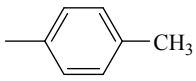
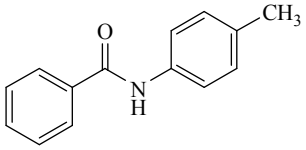
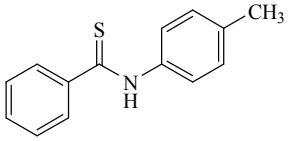
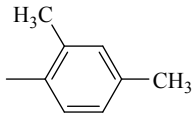
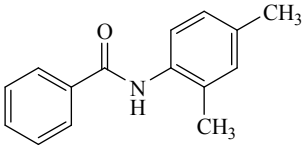
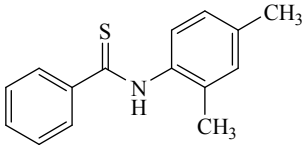
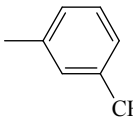
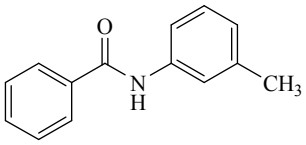
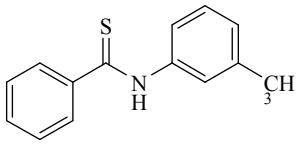
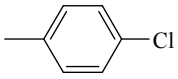
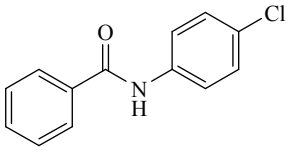
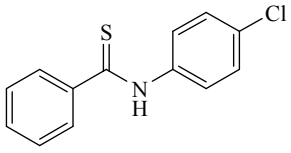
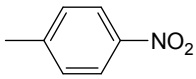
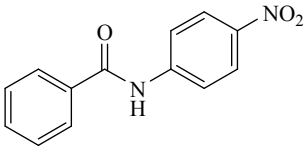
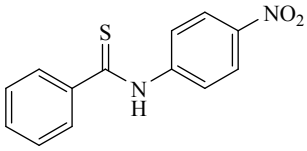
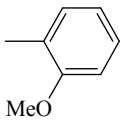
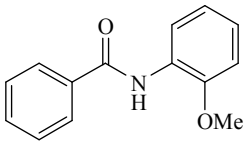
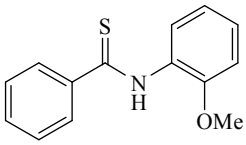
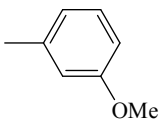
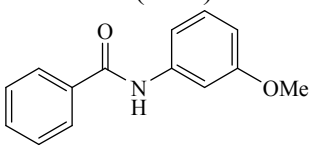
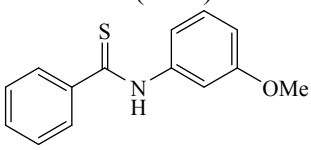
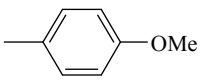
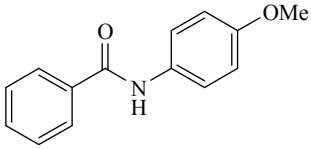
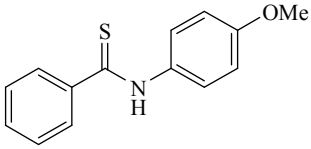
Entry	Catalyst (mol %)	Temperature (°C)	Solvent	Yield (%)[b]
1	10	30	H_2O	No reaction
2	10	30	H_2O:CH_3CN (1:1)	No reaction
3	10	80	H_2O	No reaction
4	10	80	H_2O:CH_3CN (1:1)	Trace
5	10	Reflux	CH_3CN	63
6	10	180	DMF	42
7	10	100	DMSO	45
8	10	Reflux	Toluene	28
9	20	Reflux	CH_3CN	74
10	30	Reflux	CH_3CN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

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 pestle, stirred for 30 seconds and was irradiated in microwave, MW (10-20 min, 100 W) without any solvent to give the 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 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 94% yield. Similarly, mixtures of *N*-substituted benzamides (**2c-k**) with an overall yield 30-96% and thiobenzamides (**3c-k**) with an overall yield 17-53% were obtained from the corresponding thioureas (Table 2, entries 3-11).

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

Entry	Ar	Product (%)		Time (min)	Yield (%)[b]
		2	3		
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**

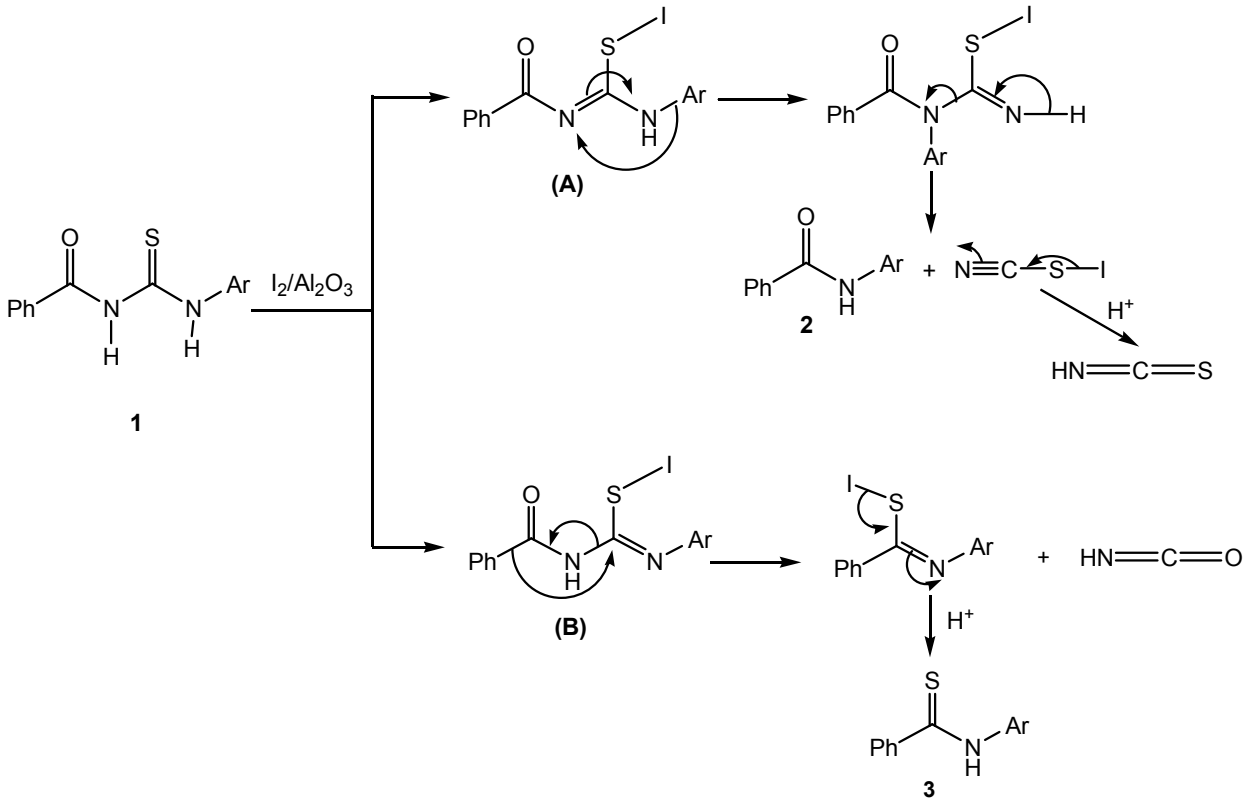
Density functional calculations were also performed to study the reactions. All the structures were optimized by hybrid density functional B3LYP using the segmented all-electron relativistically contracted Def2-TZVP(-df) basis set with the help of ORCA. The calculations show that the formations of both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

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

The plausible mechanism for the formation of benzamides and thiobenzamides is shown in scheme 2. To understand the mechanistic pathway, two most probable iodide intermediates **A** and **B** formed after 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 iodide intermediate through oxygen atom is being ruled out because of its relatively high energy compared to those of intermediates **A** and **B** (supplementary information). To the best of our knowledge, examples of O—I bond formation of molecular iodine with ketones are not found in the literature. 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 intermediate (**A**) has the lowest energy, except for *p*-chlorinated molecule, which indicates that it is the most probable intermediate. In order to study the possibility of breaking molecular backbone, the strength of different bonds were considered based on Mayer bond order[18] which indicates the number of electron pairs that constitute the bond. When considering the backbone structure, 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, 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 appreciable amount of the benzamide product (**2g**), although 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).



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

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 the similar steps as in *p*-chlorinated molecule. However, when the electron withdrawing *p*-chlorinated aryl group is replaced by *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 benzamide product is preferred by breaking the C1-N2 bond in intermediate **A** than the mechanistically favored step by breaking C5-C6 bond in intermediate **B**

(as in *p*-chlorinated moleclule). This is so because the intermediate **A** has lower energy than **B**. It is also interesting to note that when an electron donating group methyl is at the *ortho*-position in the aryl group, the intermediate **A** which has lowest energy has the least bond order at C5-C6 bond. This makes the breaking of C1-N2 bond in intermediate **A** less probable, thus rendering the formation of thiobenzamide product (**3c**) as the major product. Similar result is obtained in *o*-pyridinated molecule.

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

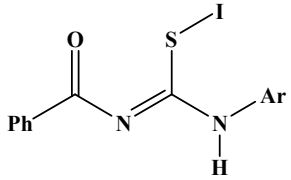
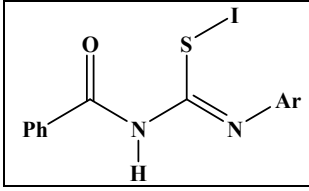
Structure	Unsubstituted benzoylthiourea		*p*-Chlorinated benzoylthiourea	
	Intermediate	Relative Energy (kcal)	Intermediate	Relative Energy (kcal)
	**A**	0.0	**A_p-Cl**	0.2
	**B**	0.5	**B_p-Cl**	0.0

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

Intermediates	Mayer Bond Order				
	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

Conclusion

In conclusion, we have developed a new process for preparation of amides and thioamides from benzoyl thioureas under solvent free conditions precluding the use of any additional Lewis or Bronsted acids as a cocatalyst, toxic organic solvents, and without producing any significant corrosive waste. This versatile synthetic method is expected to find valuable application in various areas, especially as intermediates for 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**) while the formation of thiobenzamide may be due to the migration of the phenyl group (in intermediate **B**). It was found that the formation of benzamide product is the thermodynamically favoured reaction although it is observed from the experimental results that both the 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 thionation of benzamides with Lawesson's reagent.

Experimental Section

General information: All the reagents were commercial grade and purified according to the established procedures. NMR spectra were recorded on 300 MHz and 400 MHz Spectrometers using $CDCl_3$ as a 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 on a Shimadzu FT-IR-8400 spectrometer. Elemental analyses (C, H and N) were carried out on a Perkin-Elmer 2400 analytical instrument. All microwave (MW) irradiation reactions were carried out on 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 on silica gel 60 F_{254} (0.25 mm). The melting points were recorded on 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 on 1.8g 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 pestle. The mixture was stirred for 30 sec until they were mixed thoroughly. The reaction mixture was then irradiated without any solvent in microwave for 10-20 min at 100°C using 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 literature method. 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%); m.p. 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. Cald. 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}; ^1H 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. Cald. 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}; ^1H 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. Cald. 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. Cald. 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. Cald. 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. Cald. 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. Cald. 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, 790cm^{-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. Cald. 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. Cald. 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. Cald. 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 (121.5mg, 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. Cald. 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. Cald. 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. Cald. 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. Cald. 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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