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Samarium diiodide promoted formation of 1,2-diketones and 1-acylamido-2-substituted benzimidazoles from *N*-acylbenzotriazoles

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Abstract—*N*-Acylbenzotriazoles, when treated with samarium diiodide in THF, undergo self-coupling reaction to afford 1,2-diketones in good to excellent yields; while when treated with samarium diiodide in CH_3CN, they undergo ring-opening reaction to afford 1-acylamido-2-alkyl (or aryl) benzimidazoles in reasonable to good yields. A plausible mechanism was suggested.

1. Introduction

Benzotriazole is a very useful synthetic auxiliary[1] and its application in organic chemistry has been extensively investigated. After the introduction of benzotriazole group into a molecule, the resulting benzotriazole derivatives can usually undergo three types of transformation:[1e] (i) transformation in which the benzotriazole group is retained; (ii) transformation involving the removal of the benzotriazole group; and (iii) transformation involving the cleavage of the benzotriazole ring. Whilst engaging in the research of the application of samarium reagents, we are especially interested in the reactions between benzotriazole derivatives and samarium reagents. SmI_2 as an one-electron reducing agent can remove the benzotriazolyl moiety from α-benzotriazolyl ketones to afford the corresponding ketones.[2] Also, the elimination of benzotriazolyl radical ($Bt^{\cdot}$) from *N*-[(*N*,*N*-dialkylamino)alkyl]benzotriazoles is realized by the reduction of SmI_2 with the generation of α-amino radicals, which undergo dimerization to form vicinal diamines.[3] Besides, SmI_2 can eliminate the $Bt^{\cdot}$ from the appropriately designed benzotriazole adducts with an activated double bond to produce an α-amino radical, which undergo intramolecular addition to the double bond to afford *N*-cycloalkylamines.[4] Organosamarium reagent allylsamarium bromide could substitute the benzotriazolyl group, thus providing a new method for the preparation of a variety of secondary and tertiary homoallylamines.[5] All the above reactions involve the removal of benzotriazole group and no report concerning the benzotriazole ring-opening reaction by samarium reagents has been available so far. Herein we wish to describe the reaction type (ii) and type (iii) of the benzotriazole derivatives *N*-acylbenzotriazoles promoted by SmI_2.

We have noted that promoted by SmI_2 in THF, benzoyl chlorides underwent reductive coupling reaction to give α-diketones[6] while they, when treated with SmI_2 in CH_3CN, could afford α,α′-stilbenediol dibenzoate compounds in high yields.[7] Keeping in view that benzotriazole group in many ways is comparable to a halogen substituent because of its leaving abilities,[1] we began to focus on the present study on the reactivity of the benzoyl chlorides analogues *N*-acylbenzotriazoles promoted by SmI_2. The reactions conducted in THF and in CH_3CN are investigated, respectively.

2. Results and discussion

2.1. With THF as the solvent

As shown in Scheme 1 and Table 1, *N*-acylbenzotriazoles (**1**) when treated with samarium diiodide in THF at room temperature could afford α-diketones (**2**) in reasonable to excellent yields.

Acid chlorides and keto cyanides[8] were both reported to be coupled by samarium diiodide into 1,2-diketones. In both

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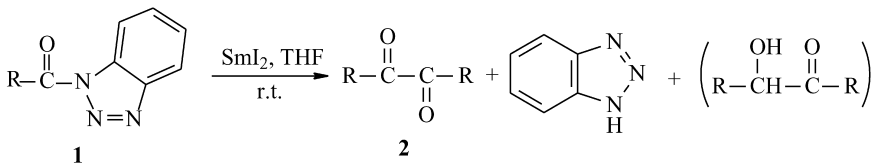


Scheme 1.

Table 1. SmI_2 promoted coupling of *N*-acylbenzotriazoles giving 1,2-diketones

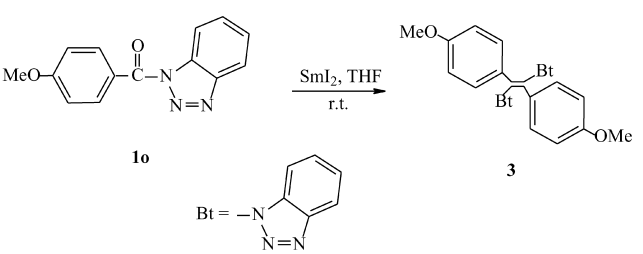
Entry	R	Substrate	SmI_2 equivalents	Product	Reaction time (min)	Yield (%)[a]
1	C_6H_5	**1a**	2.2	**2a**	10	68 (26)
2	C_6H_5	**1a**	3.3	**2a**	180[b]	60 (29)
3	*m*-ClC_6H_4	**1b**	2.2	**2b**	5	95 (0)
4	*m*-ClC_6H_4	**1b**	3.3	**2b**	180[b]	92[c] (0)
5	*m*-ClC_6H_4	**1b**	2.2[d]	**2b**	5	96[c] (0)
6	*m*-ClC_6H_4	**1b**	2.2[e]	**2b**	180	83 (12)
7	*p*-ClC_6H_4	**1c**	2.2	**2c**	5	93 (0)
8	*p*-BrC_6H_4	**1d**	2.2	**2d**	5	95 (0)
9	*p*-IC_6H_4	**1e**	2.2	**2e**	5	92 (0)
10	*p*-$CH_3C_6H_4$	**1f**	2.2	**2f**	5	68 (trace)
11	*o*-$CH_3OC_6H_4$	**1g**	2.2	**2g**	5	52 (trace)
12	*p*-$Et_2NC_6H_4$	**1h**	2.2	**2h**	5	65 (trace)
13	2-furyl	**1i**	2.2	**2i**	5	53 (trace)
14	*p*-$NO_2C_6H_4$	**1j**	2.2	**2j**	5	0 (0)
15	3-Pyridyl	**1k**	2.2	**2k**	5	0 (0)
16	4-Pyridyl	**1l**	2.2	**2l**	5	0 (0)
17	*n*-C_4H_9	**1m**	2.2	**2m**	10	11 (35)
18	*n*-C_6H_{12}	**1n**	2.2	**2n**	10	16 (30)

The reaction was conducted at room temperature unless specified otherwise.
[a] The yield of α-hydroxy ketones obtained is shown in parentheses.
[b] The characteristic blue color of SmI_2 still persisted.
[c] No obvious decrease in the yield of 1,2-diketone.
[d] The run was carried out with 2.2 equivalents of SmI_2 and l.1 equivalents of samarium powder at room temperature.
[e] This run was carried out with 2.2 equiv. of SmI_2 and 1.1 equiv. of samarium powder under reflux conditions.

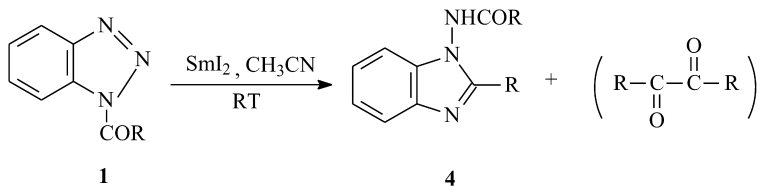
cases, acyl anion species and RCO· radicals were deduced or even verified[9] to be the intermediates and a leaving group (Cl^- or CN^-) was involved. In our investigation here, acyl anion species and RCO· radicals may also be involved with benzotriazoles acting as a leaving group. Despite the similarity in the reaction mechanism, the present study is a very useful method for the synthesis of α-diketones. Unlike acyl chlorides and keto cyanides (the preparation of them[10] is tedious, needs high temperature and requires the use of toxic cyanides), *N*-acylbenzotriazoles are stable crystals and readily available from carboxylic acids and *N*-(1-methanesulfonyl)benzotriazole.[11] What's more, benzotriazole as an auxiliary group can be recovered almost quantitatively after the reaction and therefore the method has the potential of recycling the starting material. These characteristics coupled with the short reaction time and mild reaction conditions may make the method an attractive one for the preparation of 1,2-diketones.

As for aromatic *N*-acylbenzotriazoles, the reaction is strongly influenced by the substituents on the aromatic ring. With an electron-withdrawing group present, the reaction is very clean and affords 1,2-diketones exclusively in high yields. While *N*-acylbenzotriazoles with an electron-donating group attached on the aromatic ring gave relatively lower yields. Though an iodo group on the aromatic ring is potentially reactive towards SmI_2,[12] we were surprised to find that the reaction can tolerate the iodo group (entry 9) and afford the 1,2-bis(4-iodophenyl)ethanedione in excellent yield. However, substrates **1j** (entry 14), **1k** (entry 15) and **1l** (entry 16) failed to give any desirable products besides benzotriazole. It is probable that the corresponding radicals produced undergo decarbonylation[13] before their dimerization or electron transfer from SmI_2 to form an acyl anion species. Aliphatic *N*-acylbenzotriazoles mainly afford with low yields α-ketol compounds instead of the corresponding 1,2-diketones (entries 17 and 18). Finally, when R is a *p*-methoxyphenyl group (substrate **1o**), *vic*-di(1*H*-1,2,3-benzotriazol-1-yl)alkene (**3**) was obtained in 68% yield under the same SmI_2–THF conditions (Scheme 2).

N-Acylbenzotriazoles may be seen as a special type of amide and *vic*-di(1*H*-1,2,3-benzotriazol-1-yl)alkene **3** may be looked on as a product formed from the deoxygenative coupling reaction of amides. Bearing in mind that the deoxygenative coupling reaction of amides could be effectively realized under SmI_2/Sm system,[14] we treated substrate **1b** with SmI_2/Sm system (entry 5 and 6).



Scheme 2.



Scheme 3.

Table 2. Preparation of 1-acylamido-2-substituted benzimidazoles

Substrate[a]	R	Product[a]	Reaction time	Yield (%)[b]
1a	C_6H_5	**4a**	5 h	60 (10)
1b	*m*-ClC_6H_4	**4c**	5 h	50 (15)
1c	*p*-ClC_6H_4	**4d**	5 h	43 (26)
1f	*p*-$CH_3C_6H_4$	**4b**	5 h	62 (–)[c]
1p	*o*-ClC_6H_4	**4p**	5 h	59 (–)[c]
1m	$CH_3(CH_2)_2CH_2$	**4m**	30 min	63
1n	$CH_3(CH_2)_4CH_2$	**4n**	30 min	75
1o	*p*-$CH_3OC_6H_4$	**4o**	30 min	0 (72)
1q	$CH_3(CH_2)_6CH_2$	**4q**	30 min	60
1r	$CH_3(CH_2)_7CH_2$	**4r**	30 min	63
1s	*c*-C_6H_{11}	**4s**	30 min	82
1t	CH_3CH_2	**4t**	30 min	79
1u	CH_3	**4u**	30 min	73

[a] The products were identified by mp, ^{1}H NMR, MS, IR spectra, and elemental analysis.
[b] The yield of 1,2-diketones obtained is shown in parentheses.
[c] No attempts were made to isolate the by-products since the amount of by-products was minute according to the TLC.

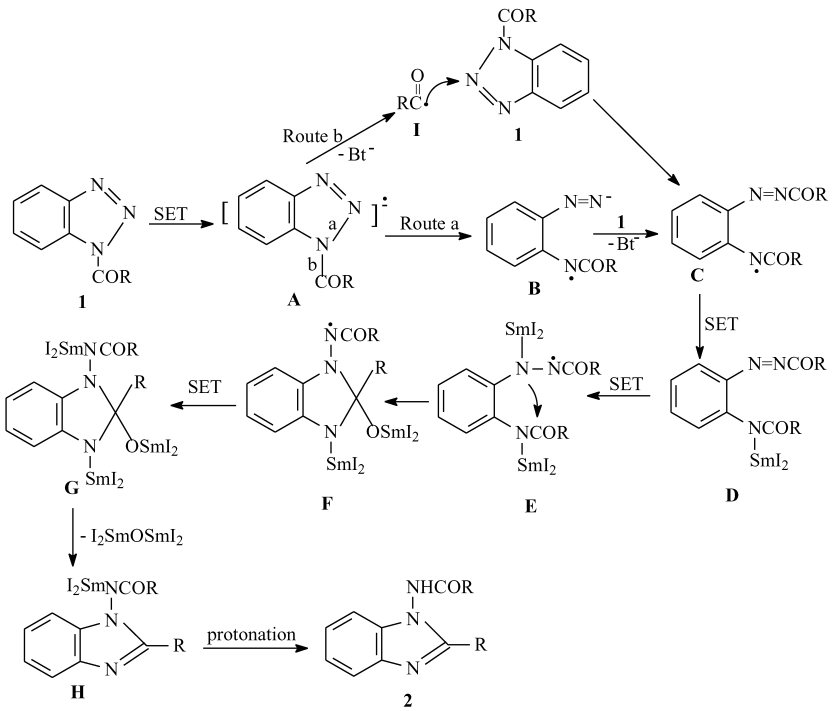
However, the expected deoxygenative coupling product was not obtained and 1,2-diketone remains to be the main product with the α-ketol type compound as by-product.

2.2. With CH_3CN as the solvent

As mentioned previously, benzoyl chlorides when treated with samarium diiodide in acetonitrile give α,α′-stilbenediol dibenzoate compounds in high yields, which is in contrast to the report that benzoyl chlorides when treated by samarium diiodide in tetrahydrofuran afford α-diketones or α-hydroxy ketones. This may indicate that SmI_2 in THF and in CH_3CN show very different reactivity. Therefore, we treated *N*-acylbezotriazoles with SmI_2 in CH_3CN. Interestingly, a drastically different kind of products is obtained, which is characterized as 1-acylamido-2-alkyl (or aryl) benzimidazoles (**4**) by IR, ^{1}H NMR, MS and elemental analysis (Scheme 3 and Table 2).

The formation of 1-acylamido-2-alkyl (or aryl) benzotriazoles indicates that the benzotriazole ring is opened by the reduction of SmI_2 in acetonitrile.

Benzotriazole ring is usually highly stable to acids and bases, to oxidation and reduction and to heat.[1] However, more and more reports are available concerning the benzotriazole ring opening. For example,[15] 1-aryl-benzotrizoles can be converted into carbazoles with loss of nitrogen at 360°C.[16] 1-Butyl-, 1-allyl-, 1-benzyl-, and 1-phenethylbenzonitriles ring open and lose nitrogen at 400°C.[17] Substituted benzotriazoles exclude nitrogen to form diradicals which then cyclize to form carbazoles on photolysis.[18] The opening of the benzotriazole ring in benzotriazol-1-yl alkyl carbanions α to the benzotriazol-1-yl group tend to loss of nitrogen, thus affording *o*-lithiated



Scheme 4.

aniline imines.[19] 1-(α-Alkoxyalkyl)benzotriazoles, when treated with Grignard reagents, can also undergo the benzotriazole ring opening.[20] On standing, lithiated *N*-(α-alkoxyalkyl)-benzotriazoles extrude nitrogen, which presents a synthetically useful method for the preparation of *o*-substituted anilines and benzannelated heterocycles.[21] 2-(Benzotriazol-1-yl)enamines undergo rearrangement, and loss of nitrogen in refluxing toluene to give 2,4-diarylquinazolines.[15] Treatment of α-benzotriazol-1-yl hydrazones with *n*-butyllithium in the presence of TMEDA gave benzotriazines or indoles by the corresponding ring scission.[22]

The formation of 1-acylamido-2-alkyl (or aryl) benzotriazoles in this investigation is an addition to the examples of benzotriazole ring opening. Besides, it is one of the few cases where there is no nitrogen releasing during the ring opening and the three N atoms are retained altogether in the products.

Though the detailed mechanism is not clarified yet, a plausible reaction pathway is proposed as in Scheme 4.

In Scheme 4, the intermediate **C** may be produced by Route a where the N–N bond (a) in **A** is broken to form an intermediate **B**, which was acylated[23] by another molecule of compound **1**. **C** can also be formed through Route b where the N–C bond (b) in **A** cleaves to give an acyl radical **I**, which attacks the N–N bond in another molecule of compound **1**. **C** gets another electron from SmI_2 to form the intermediate **D**. The N=N bond in compound **D** is further reduced[24] by an equivalent of SmI_2 to give **E**. The amino anion attached to the aromatic ring attacks the carbonyl carbon intramolecularly in such a way that it can preferentially form a five-membered ring (see **F**). After another electron transfer from SmI_2 to the N atom (see **F** to **G**), an elimination of $I_2SmOSmI_2$ from intermediate **G** constructs the benzimidazole skeleton (see **H**). Subsequent protonation gives the final product **2**.

Notably, when R is an alkyl group in compound **1**, the reaction for the formation of **2** is clean and the yield is high. However, when R is an aryl group, the yield of **2** is relatively low and α-diketones can be obtained as a by-product. For such substrate **1o**, the corresponding α-diketone even becomes the main product and product **4** is not obtained.

In summary, here describes the first example of benzotrizole ring opening promoted by SmI_2. The unique reductivity of SmI_2 in CH_3CN makes the benzotriazole ring susceptible to ring opening. By cyclization again, it affords a synthetically useful way for the preparation of 1-acylamido 2-alkyl (or aryl) benzimidazoles.

The benzimidazole ring system is part of the vitamin B-12 structure and several benzimidazole derivatives are of commercial importance as pharmaceuticals, veterinary anthelmintics and fungicides.[25] Development of new benzimidazole derivatives and research into their potential uses are always of interest. As far as we know, 1-acylamido-2-alkyl (or aryl) benzimidazoles remain less investigated. The ring opening of benzotriazole ring in *N*-acylbenzotriazoles promoted by SmI_2 in CH_3CN provides a novel and short way for the syntheses of 1-acylamido-2-alkyl (or aryl) benzimidazoles and may be superior to the previously reported method starting from *o*-nitrophenylhydrazine.[26]

3. Conclusions

With THF and CH_3CN as the reaction media, the benzotriazole derivatives *N*-acylbezotriazoles can undergo, respectively, transformation where the benzotriazolyl group leaves and transformation where the benzotriazole ring cleaves promoted by SmI_2, thus providing synthetically useful methods for both 1,2-diketones and 1-acylamido-2-substituted benzimidazoles. Further studies concerning the reactivity of samarium reagents towards heteroatom compounds are still in progress in our laboratory.

4. Experimental

4.1. General

Tetrahydrofuran was distilled from sodium-benzophenone and acetonitrile was distilled in the presence of phosphorus pentoxide immediately prior to use. All reactions were conducted under a nitrogen atmosphere. Melting points are uncorrected. ^{1}H NMR spectra were recorded on a Bruker AC-400 instrument as $CDCl_3$ or d^6-DMSO solutions using TMS as internal standard. Chemical shifts (δ) are reported in ppm and coupling constants *J* are given in Hz. IR spectra were recorded using KBr disks with a Bruker Vector-22 infrared spectrometer. Elemental analyses were performed on a EA-1110 instrument. Metallic samarium and other reagents were purchased from commercial sources, without further purification before use. Substrates **1a–1m** were synthesized according to reported procedure with compounds **1d**,**e**,**m** being new compounds.[11]

4.2. General procedure for the preparation of substrates 1[11]

*Typical procedure for the synthesis of compounds **2** and **3***: under nitrogen atmosphere, 1H-1,2,3-benzotriazole-1-yl(4-chlorophenyl)methanone (**1c**, 0.258 g, 1 mmol) dissolved in dry THF (3 mL) was added at room temperature to 2.2 mmol of SmI_2 dissolved in THF (20 mL). The resulting solution turned yellow in 5 min. Dilute hydrochloric acid (2 M, 5 mL) was added and the resulting mixture extracted with diethyl ether (3×20 mL). The combined organic layer was washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was separated on preparative TLC on silica gel with ethyl acetate and cyclohexane (1:3) as eluent to afford the 1,2-bis(4-chlorophenyl) ethanedione 0.259 g in 93% yield.

*General procedure for the synthesis of compounds **4***: Samarium powder (0.33 g, 2.2 mmol) was placed in a well-dried three-necked round bottom flask containing a magnetic stirrer bar. The flask was evacuated and flushed with nitrogen several times. Acetonitrile (15 mL) was added through a rubber septum by a syringe. Iodine (0.54 g, 2.13 mmol) was added to the flask and the mixture was

stirred at room temperature until the solution became deep brown (2 h). To the solution of SmI_2 thus prepared was added *N*-acylbenzotriazole **1** (1 mmol) in acetonitrile (3 mL) by syringe. After being stirred for a given time (Table 1), most of the solvent was removed under reduced pressure. Hydrochloric acid (0.2N, 3 mL) was added and the mixture was extracted with diethyl ether (3×30 mL). The combined organic extract was washed with brine, dried over anhydrous sodium sulfate and concentrated. The residue was separated by preparative TLC on silica gel with ethyl acetate and cyclohexane (1:3) as eluent to afford product **4**.

4.2.1. 1H-1,2,3-Benzotriazole-1-yl(4-bromophenyl)-methanone (1d). White plates, yield: 66%, mp: 142–143°C. δ_H: 8.39 (1H, d, *J*=8.0 Hz), 8.16 (3H, dd, *J*=8.4, 8.0 Hz), 7.71–7.75 (3H, m), 7.55–7.59 (1H, m). ν_{max}(KBr)/cm^{-1}: 1707, 1588, 1482, 1377, 943, 751. *m/z* (%): 303 (M$^+$, 8.57), 301 (M$^+$, 9.24), 273 (76.52), 275 (74.11), 183 (100), 185 (92.48). Anal. $C_{13}H_8BrN_3O$. Calcd C, 51.68; H, 2.67; N, 13.91. Found C, 51.61; H, 2.77; N, 13.86%.

4.2.2. 1H-1,2,3-Benzotriazole-1-yl(4-iodophenyl)methanone (1e). Golden plates, yield: 58%, mp: 153–155°C. δ_H: 8.38 (1H, d, *J*=8.4 Hz), 8.17 (1H, d, *J*=8.0 Hz), 7.96 (4H, s), 7.73 (1H, t, *J*=7.6 Hz), 7.57 (1H, t, *J*=7.6 Hz). ν_{max}(KBr)/cm^{-1}: 1710, 1596, 1391, 937, 747. *m/z* (%): 349 (M$^+$, 17.31), 321 (100), 231 (81.44). Anal. $C_{13}H_8IN_3O$. Calcd C, 44.72; H, 2.31; N, 12.04. Found C, 44.76; H, 2.37; N, 11.99%.

4.2.3. 1H-1,2,3-Benzotriazole-1-yl(4-methoxyphenyl)-methanone (1o). White needles, yield: 73%, mp: 113–114°C. δ_H: 8.38 (1H, d, *J*=8.4 Hz), 8.30 (2H, d, *J*=8.8 Hz), 8.17 (1H, d, *J*=8.4 Hz), 7.70 (1H, t, *J*=7.6 Hz), 7.54 (1H, t, *J*=7.6 Hz), 7.07 (2H, d, *J*=8.8 Hz), 3.94 (3H, s). ν_{max}(KBr)/cm^{-1}: 1710, 1607, 1578. *m/z* (%): 253 (M$^+$, 6.87), 135 (100). Anal. $C_{14}H_{11}N_3O_2$. Calcd C, 66.40; H, 4.38; N, 16.59. Found C, 66.45; H, 4.42; N, 16.55%.

4.2.4. 1H-1,2,3-Benzotriazole-1-yl(2-chlorophenyl)methanone (1p). White crystals, yield: 70%, mp: 84–86°C. δ_H: 8.42 (1H, d, *J*=8.0 Hz), 8.17 (1H, d, *J*=8.4 Hz), 7.44–7.77 (6H, m). ν_{max}(KBr)/cm^{-1}: 1724, 1589, 1484. *m/z* (%): 257 (M$^+$, 12.57), 139 (100). Anal. $C_{13}H_8ClN_3O$. Calcd C, 60.60; H, 3.13; N, 16.31. Found C, 60.61; H, 3.20; N, 16.28%.

4.2.5. 1H-1,2,3-Benzotriazole-1-yl(*n*-hexyl)methanone (1n). White crystals, yield: 70%, mp: 50–52°C. δ_H: 8.29 (1H, d, *J*=8.4 Hz), 8.12 (1H, d, *J*=8.4 Hz), 7.63–7.67 (1H, m), 7.48–7.52 (1H, m), 3.42 (2H, t, *J*=7.2 Hz), 1.87–1.94 (2H, m), 1.32–1.50 (6H, m), 0.90 (3H, t, *J*=6.8 Hz). ν_{max}(KBr)/cm^{-1}: 2946, 2919, 2867, 1746, 1589, 1484. *m/z* (%): 231 (M$^+$, 3.29). Anal. $C_{13}H_{17}N_3O$. Calcd C, 67.57; H, 7.41; N, 18.17. Found C, 67.61; H, 7.47; N, 18.14%.

4.2.6. 1H-1,2,3-Benzotriazole-1-yl(*n*-octyl)methanone (1q). White crystals, yield: 82%, mp: 48–49°C. δ_H: 8.29 (1H, d, *J*=7.6 Hz), 8.12 (1H, d, *J*=8.4 Hz), 7.63–7.67 (1H, m), 7.48–7.52 (1H, m), 3.42 (2H, t, *J*=7.2 Hz), 1.87–1.94 (2H, m), 1.29–1.51 (10H, m), 0.89 (3H, t, *J*=6.8 Hz). ν_{max}(KBr)/cm^{-1}: 2946, 2919, 2858, 1742, 1589, 1484. *m/z* (%): 259 (M$^+$, 2.10). Anal. $C_{15}H_{21}N_3O$. Calcd C, 69.47; H, 8.16; N, 16.20. Found C, 69.45; H, 8.23; N, 16.17%.

4.2.7. 1H-1,2,3-Benzotriazole-1-yl(*n*-nonyl)methanone (1r). White crystals, yield: 82%, mp: 38–40°C. δ_H: 8.29 (1H, d, *J*=7.6 Hz), 8.12 (1H, d, *J*=8.0 Hz), 7.63–7.67 (1H, m), 7.48–7.52 (1H, m), 3.42 (2H, t, *J*=7.2 Hz), 1.87–1.94 (2H,m), 1.27–1.51 (12H, m), 0.87 (3H, t, *J*=6.8 Hz). ν_{max}(KBr)/cm^{-1}: 2946, 2919, 2851, 1740, 1595, 1485. *m/z* (%): 273 (M$^+$, 1.89). Anal. $C_{16}H_{23}N_3O$. Calcd C, 70.30; H, 8.48; N, 15.37. Found C, 70.27; H, 8.55; N, 15.33%.

4.2.8. 1H-1,2,3-Benzotriazole-1-yl(*c*-hexyl)methanone (1s). White crystals, yield: 65%, mp: 94–96°C. δ_H: 8.30 (1H, d, *J*=8.4 Hz), 8.12 (1H, d, *J*=8.4 Hz), 7.63–7.67 (1H, m), 7.48–7.52 (1H, m), 3.88–3.95 (1H, m), 2.12–2.15 (2H, m), 1.88–1.92 (2H, m), 1.69–1.78 (3H, m), 1.48–1.51 (2H, m), 1.30–1.35 (1H, m). ν_{max}(KBr)/cm^{-1}: 3106, 2950, 2934, 2853, 1730, 1594, 1482. *m/z* (%): 229 (M$^+$, 5.52), 146 (100). Anal. $C_{13}H_{15}N_3O$. Calcd C, 68.10; H, 6.59; N, 18.33. Found C, 68.12; H, 6.63; N, 18.30%.

4.2.9. 1,2-Diphenyl-1,2-ethanedione (2a). Yellow crystals, yield: 68%, mp: 95–97°C (lit.,[27] 95–97°C). δ_H: 7.99–7.97 (4H, m), 7.69–7.64 (2H, m), 7.53–7.50 (4H, m). ν_{max}(KBr)/cm^{-1}: 3064, 1660, 1594, 1450, 1211, 719, 643.

4.2.10. 1,2-Di(3-chlorophenyl)-1,2-ethanedione (2b). Yellow crystals, yield: 96%, mp:116–117°C (lit.,[29] 115°C). δ_H: 7.97 (2H, s), 7.83–7.85 (2H, m), 7.64–7.66 (2H, m), 7.46–7.49 (2H, m). ν_{max}(KBr)/cm^{-1}: 3076, 3059, 1673, 1588, 1570, 1198.

4.2.11. 1,2-Di(4-chlorophenyl)-1,2-ethanedione (2c). Yellow crystals, yield: 93%, mp:195–198°C (lit.,[27] 195–196°C). δ_H: 7.91 (4H, d, *J*=8.4 Hz), 7.50 (4H, d, *J*=8.4 Hz). ν_{max}(KBr)/cm^{-1}: 3010, 1659, 1586, 1571, 1404, 1209.

4.2.12. 1,2-Di(4-bromophenyl)-1,2-ethanedione (2d). Yellow crystals, yield: 95%, mp: 227–229°C (lit.,[29] 228–229°C). δ_H: 7.83 (4H, d, *J*=8.4 Hz), 7.67 (4H, d, *J*=8.4 Hz). ν_{max}(KBr)/cm^{-1}: 3150, 1664, 1586.

4.2.13. 1,2-Di(4-iodophenyl)-1,2-ethanedione (2e). Golden crystals, yield: 92%, mp: 243–245°C(lit.,[28b] 255°C). δ_H: 8.03 (4H, d, *J*=8.4 Hz), 7.67 (4H, d, *J*=8.4 Hz). ν_{max}(KBr)/cm^{-1}: 3066, 1664, 1579.

4.2.14. 1,2-Di(4-methylphenyl)-1,2-ethanedione (2f). White crystals, yield: 68%, mp: 103–105°C (lit.,[27] 104–105°C). δ_H: 7.86 (4H, d, *J*=8.0 Hz), 7.30 (4H, d, *J*=8.0 Hz), 2.43 (6H, s). ν_{max}(KBr)/cm^{-1}: 2919, 1661, 1605, 1172.

4.2.15. 1,2-Di(2-methoxyphenyl)-1,2-ethanedione (2g). Orange crystals, yield: 52%, mp: 123–125°C (lit.,[28a] 127°C). δ_H: 8.08 (2H, d, *J*=8.0 Hz), 7.59–7.55 (2H, m), 7.14–7.10 (2H, m), 6.95 (2H, d, *J*=8.0 Hz), 3.60 (6H, s). ν_{max}(KBr)/cm^{-1}: 2945, 1657, 1595, 1321. *m/z* (%): 270 (M$^+$, 3.74), 135 (M$^+$/2, 100).

4.2.16. 1,2-Di(4-diethylaminophenyl)-1,2-ethanedione (2h). Light yellow crystals, yield: 65%, mp: 85–87°C; δ_H: 7.85 (4H, d, *J*=8.4 Hz), 6.70 (4H, d, *J*=7.2 Hz), 3.43 (8H, q, *J*=7.0 Hz), 1.20 (12H, t, *J*=7.0 Hz). ν_{max}(KBr)/cm^{-1}: 2972, 2933, 2902, 2871, 1645, 1585, 1546, 1527. *m/z* (%): 352 (M$^+$, 6.51), 176 (M$^+$/2, 100). Anal. $C_{22}H_{28}N_2O_2$.

Calcd C, 74.97; H, 8.01; N, 7.95. Found C, 74.93; H, 8.10; N, 7.86%.

4.2.17. 1,2-Di(2-furyl)-1,2-ethanedione (2i). Yellow crystals, yield: 53%, mp: 160–162°C (lit.,[27] 163–165°C). δ_H: 7.78–7.79 (2H, m), 7.65–7.66 (2H, m), 6.64–6.65 (2H, m). ν_{max}(KBr)/cm^{-1}: 3150, 3125, 1647, 1551, 1454.

4.2.18. *vic*-Di(1H-1,2,3-benzotriazol-1-yl)alkene (3). Yellow needles, yield: 68%, mp 138–140°C. ^{1}H NMR (400 MHz, $CDCl_3$): 8.72–8.74 (2H, d, J=8.4 Hz), 8.50 (2H, d, J=8.4 Hz). 8.05 (2H, d, J=8.0 Hz), 7.93–7.95 (2H, m), 7.78–7.80 (2H, m), 7.10 (4H, d, J=8.8 Hz), 3.93 (6H, s). ^{13}C NMR (100 MHz, $CDCl_3$): 162.54, 159.74, 146.15, 141.21, 135.40, 130.55, 129.32, 128.98, 128.25, 114.40, 55.48. ν_{max}: 1605 (C=C), 1504 cm^{-1}. *m/z* (%): 237 (M$^+$/2, 1.88), 209 (100), 166 (38.38). Anal. $C_{28}H_{22}N_6O_2$. Calcd C, 70.89; H, 4.64; N, 17.72. Found C, 70.80; H, 4.59; N, 17.65%.

4.2.19. 1-Benzoylamido-2-phenyl benzimidazole (4a). Yellow crystals, mp: 184–186°C. δ_H: 8.06 (1H, br), 7.78–7.80 (2H, m), 7.35–7.55 (8H, m), 7.01–7.06 (2H, m), 6.61–6.69 (2H, m). ν_{max}(KBr)/cm^{-1}: 3262, 3056, 1621, 1575, 1521. *m/z* (%): 313 (M$^+$, 30.94), 208 (100), 105 (32.50). Anal. $C_{20}H_{15}N_3O$. Calcd C, 76.66; H, 4.83; N, 13.41. Found C, 76.58; H, 4.88; N, 13.31.

4.2.20. 1-(3-Chloro-benzoylamido)-2-(3-chlorophenyl) benzimidazole (4b). Yellow crystals, mp: 182–185°C. δ_H: 8.07 (1H, m), 7.84 (1H, d, J=8.1 Hz), 7.65 (1H, d, J=7.6 Hz), 7.53 (1H, s), 7.33–7.46 (5H, m), 7.05–7.06 (2H, m), 6.68–6.69 (1H, m), 6.50 (1H, s). ν_{max}(KBr)/cm^{-1}: 3337, 3062, 1622, 1588, 1569, 1497. *m/z* (%): 383 (M$^+$, 9.47), 381 (M$^+$, 14.18), 242 (100), 244 (33.63), 139 (29.90). Anal. $C_{20}H_{13}N_3Cl_2O$. Calcd C, 62.84; H, 3.43; N, 10.99. Found C, 62.92; H, 3.58; N, 10.83.

4.2.21. 1-(4-Chloro-benzoylamido)-2-(4-chlorophenyl) benzimidazole (4c). Yellow crystals, mp: 250–252°C. δ_H (DMSO): 9.70 (1H, s), 7.91 (1H, d, J=8.0 Hz), 7.73 (2H, d, J=8.6 Hz), 7.66 (2H, d, J=8.8 Hz), 7.50–7.60 (2H, m), 7.08–7.10 (1H, m), 6.95–7.00 (2H, m). ν_{max}(KBr)/cm^{-1}: 3358, 1653, 1619, 1589, 1568, 1559. *m/z* (%): 383 (M$^+$, 7.88), 381 (M$^+$, 11.57), 242 (100), 244 (33.36), 139 (30.75). Anal. $C_{20}H_{13}N_3Cl_2O$. Calcd C, 62.84; H, 3.43; N, 10.99; Found C, 62.72; H, 3.57; N, 10.84.

4.2.22. 1-(4-Methyl-benzoylamido)-2-(4-methylphenyl) benzimidazole (4f). Yellow crystals, mp: 197–199°C. δ_H: 8.07 (1H, br), 7.71 (2H, d, J=8.1 Hz), 7.46 (2H, d, J=8.2 Hz), 7.16–7.26 (4H, m), 6.99–7.02 (2H, m), 6.75 (1H, s), 6.65–6.68 (1H, m), 2.40 (3H, s), 2.36 (3H, s). ν_{max}(KBr)/cm^{-1}: 3245, 3198, 2967, 2919, 1610, 1586, 1532. *m/z* (%): 341 (M$^+$, 35.92), 222 (100), 119 (46.96). Anal. $C_{22}H_{19}N_3O$. Calcd C, 77.40; H, 5.61; N, 12.31. Found C, 77.31; H, 5.70; N, 12.19.

4.2.23. 1-(2-Chloro-benzoylamido)-2-(2-chlorophenyl) benzimidazole (4p). Light yellow crystals, mp: 214–216°C. δ_H ($CDCl_3$): 8.16 (1H, s), 7.22–7.48 (8H, m), 7.10 (2H, s), 6.66 (1H, s), 6.55 (1H, s). ν_{max}(KBr)/cm^{-1}: 3206, 3123, 3065, 3000, 1629, 1586, 1518, 1491. *m/z* (%): 383 (M$^+$, 11.84), 381 (M$^+$, 18.22), 242 (100), 244 (32.71), 139 (23.03). Anal. $C_{20}H_{13}N_3Cl_2O$. Calcd C, 62.84; H, 3.43; N, 10.99; Found C, 62.93; H, 3.56; N, 10.85%.

4.2.24. 1-(*n*-Pentanoylamido)-2-(2-*n*-butyl) benzimidazole (4m). Oily compound. δ_H ($CDCl_3$): 7.86 (1H, br), 6.89–6.91 (2H, m), 6.44–6.50 (2H, m), 2.68 (2H, t, J=7.6 Hz), 2.22 (2H, t, J=7.6 Hz), 1.60–1.70 (4H, m), 1.37–1.44 (4H, m), 0.92–0.96 (6H, m). ν_{max}(KBr)/cm^{-1}: 3260, 3128, 2958, 2931, 2872, 1627, 1588, 1492. *m/z* (%): 274 (M$^+$+1, 27.83), 273 (M$^+$, 17.94), 189 (100). Anal. $C_{16}H_{23}N_3O$. Calcd C, 70.30; H, 8.48; N, 15.37. Found C, 70.45; H, 8.62; N, 15.29%.

4.2.25. 1-(*n*-Heptanoylamido)-2-(2-*n*-hexyl) benzimidazole (4n). White crystals, mp: 70–72°C. δ_H ($CDCl_3$): 7.89 (1H, br), 6.91–6.94 (2H, m), 6.46–6.48 (1H, m), 5.90 (1H, s), 2.66 (2H, t, J=7.6 Hz), 2.23 (2H, t, J=7.6 Hz), 1.60–1.70 (4H, m), 1.25–1.40 (12H, m), 0.88–0.90 (6H, m). ν_{max}(KBr)/cm^{-1}: 3259, 2920, 2926, 2855, 1628, 1589, 1492. *m/z* (%): 330 (M$^+$+1, 15.04), 329 (M$^+$, 12.43), 217 (100). Anal. $C_{20}H_{31}N_3O$. Calcd C, 72.91; H, 9.48; N, 12.75. Found C, 72.78; H, 9.62; N, 12.66%.

4.2.26. 1-(*n*-Octanoylamido)-2-(2-*n*-octyl) benzimidazole (4q). Oily compound. δ_H ($CDCl_3$): 7.85 (1H, br), 6.88–6.90 (2H, m), 6.48–6.59 (2H, m), 2.67 (2H, t, J=7.6 Hz), 2.21 (2H, t, J=7.6 Hz), 1.60–1.70 (4H, m), 1.27–1.38 (20H, m), 0.86–0.89 (6H, m). ν_{max}(KBr)/cm^{-1}: 3261, 2955, 2926, 2855, 1628, 1589, 1492. *m/z* (%): 386 (M$^+$+1, 6.21), 245 (100). Anal. $C_{24}H_{39}N_3O$. Calcd C, 74.76; H, 10.20; N, 10.90. Found C, 74.68; H, 10.32; N, 10.76%.

4.2.27. 1-(*n*-Nonanoylamido)-2-(2-nonyl) benzimidazole (4r). White crystals, mp: 42–43°C. δ_H ($CDCl_3$): 7.89 (1H, br), 6.91–6.94 (2H, m), 6.46–6.48 (1H, m), 5.86 (1H, s), 2.66 (2H, t, J=7.6 Hz), 2.23 (2H, t, J=7.6 Hz), 1.63–1.70 (4H, m), 1.27–1.38 (24H, m), 0.86–0.89 (6H, m). ν_{max}(KBr)/cm^{-1}: 3256, 2924, 2853, 1627, 1588, 1492. *m/z* (%): 414 (M$^+$+1, 1.92), 413 (M$^+$, 5.68), 259 (100). Anal. $C_{26}H_{43}N_3O$. Calcd C, 75.50; H, 10.48; N, 10.16. Found C, 75.59; H, 10.56; N, 10.08%.

4.2.28. 1-(*c*-Hexylacetamido)-2-(2-*c*-hexyl) benzimidazole (4s). White crystals, mp: 229–231°C. δ_H ($CDCl_3$): 7.88 (1H, br), 6.89–6.92 (2H, m), 6.45–6.47 (1H, m), 5.81 (1H, s), 3.14–3.20 (1H, m), 2.11–2.17 (2H, m), 1.70–1.94 (10H, m), 1.26–1.37 (10H, m). ν_{max}(KBr)/cm^{-1}: 3243, 3210, 3125, 2929, 2850, 1620, 1586, 1492. *m/z* (%): 326 (M$^+$+1, 2.12), 325 (M$^+$, 7.76), 215 (100). Anal. $C_{20}H_{27}N_3O$. Calcd C, 73.81; H, 8.36; N, 12.91. Found C, 73.90; H, 8.45; N, 12.83%.

4.2.29. 1-(Propionylamido)-2-(2-ethyl) benzimidazole (4t). White crystals, mp: 164–166°C (lit.,[26] 142–148°C). δ_H ($CDCl_3$): 7.91 (1H, br), 6.90–6.94 (2H, m), 6.46–6.48 (1H, m), 5.94 (1H, s), 2.69 (2H, q, J=7.6 Hz), 2.26 (2H, q, J=7.6 Hz), 1.15–1.23 (6H, m). ^{13}C NMR: 172.14, 152.66, 132.04, 125.13, 124.97, 122.98, 121.03, 112.47, 27.02, 25.36, 9.63, 8.48. ν_{max} (KBr)/cm^{-1}: 3356, 3129, 2972, 2937, 1625, 1586, 1530, 1492.

4.2.30. 1-(Acetamido)-2-(2-methyl) benzimidazole (4u). White crystals, mp: 210–212°C (lit.,[26] 203–204°C). δ_H ($CDCl_3$): 7.88 (1H, br), 6.93–6.95 (2H, m), 6.46–6.48 (1H,

m), 5.99 (1H, s), 2.30 (3H, s), 2.00 (3H, s). ^{13}C NMR: 168.79, 148.89, 131.86, 125.29, 124.51, 123.15, 121.17, 112.49, 22.50, 18.19. ν_{max}(KBr)/cm^{-1}: 3257, 3127, 2972, 1633, 1583, 1492.

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