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# Divergent synthesis of 1,5-benzodiazepines and benzimidazoles *via* a $BiCl_3$-catalyzed one-pot condensation–cyclization process

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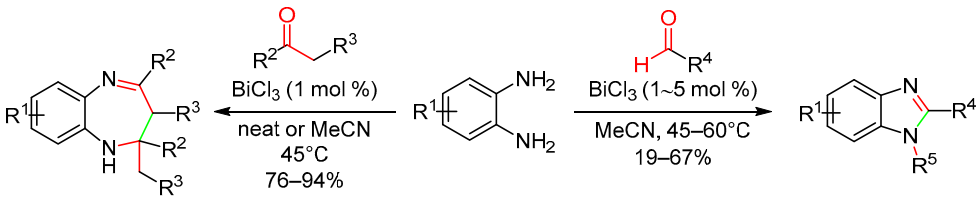



$R^1$ = H, Me, Cl, $NO_2$; $R^2$, $R^3$ = Alk, Ar; $R^4$ = Alk, Ar, HetAr; $R^5$ = H, $CH_2$Alk, $CH_2$Ar, $CH_2$HetAr

Catalyzed by $BiCl_3$, aromatic *o*-diamines reacted with ketones efficiently to produce 1,5-benzodiazepines in good to excellent yields by condensation–cyclization reaction. Using aldehydes as substrates, mono- or disubstituted benzimidazoles were obtained as the final products. All reactions were carried out under mild reaction conditions and showed good functional group compatibility.

**Keywords**: aldehyde, benzimidazoles, 1,5-benzodiazepines, bismuth(III) chloride, ketone, condensation–cyclization.

Nitrogen-containing heterocyclic compounds are extensively presented in pharmaceuticals, agrochemicals, functional materials, and other chemical products. Among them, 1,5-benzodiazepines received growing attention for their remarkable pharmacological and biological activities,[1] such as being anti-inflammatory, antipyretic, anticonvulsant, antianxiety, and antipsychosis agents.[2] In recent decades, researches on the biological activity of 1,5-benzodiazepines and its derivatives have been extended to various diseases, such as cancer,[3] HIV,[4] and neurological disorders.[5] Moreover, these compounds are widely applied as building blocks or intermediates in synthesis of various kinds of aza-fused-ring compounds.[6,7]

The outstanding performance of 1,5-benzodiazepines in pharmacological activity, organic synthesis, and industrial applications has stimulated design of practical strategies for the construction of 1,5-benzodiazepine skeleton.[8] Typically, the condensation–cyclization of aromatic *o*-diamines with carbonyl derivatives was considered to be the most straightforward and effective method. To increase the reaction efficiency, many catalytic systems have been successfully developed, including molecular iodine catalysis,[9] Lewis acidic catalysts,[10] heteropoly acidic catalysts,[11] ionic liquid[12] and microwave-assisted synthesis.[13] Metal-organic frameworks (MOFs),[14] such as MOF-235(Fe),[15] also demonstrated catalytic properties in the synthesis of 1,5-benzodiazepines. Although great success has been achieved, harsh reaction conditions, complex purification process, toxic catalysts and reagents, and large amounts of byproducts are limitations for a large-scale synthesis. Therefore, it is still necessary to develop alternative approaches for the synthesis of 1,5-benzodiazepines with wide substrate scope, fine functional group tolerance, and environmentally friendly conditions.

In the course of investigating the bismuth-catalyzed coupling reaction of propargyl amidines and aromatic *o*-diamines,[16] we found that 1,5-benzodiazepines were formed in excellent yield when acetone was used as solvent. As nontoxic and practical catalysts, bismuth salts[17] had been reported to catalyze the synthesis of 1,5-benzodiazepines, however, high loading of catalyst and expensive ionic liquid was needed.[18] With the aim to develop a simple and

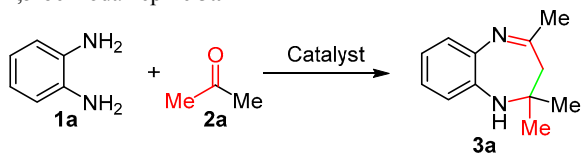
efficient method to construct heterocyclic compounds in terms of high yield, low cost, and simple purification process, further investigation was then carried out (Table 1). In the presence of 0.1 equiv of $BiCl_3$, the condensation–cyclization of *o*-phenylenediamine (**1a**) and acetone (**2a**) at 45°C proceeded smoothly to give 2,2,4-trimethyl-2,3-dihydro-1*H*-1,5-benzodiazepine (**3a**) in 91% yield, in which acetone worked as reactant and solvent (Table 1, entry 1). The yield increased to 94% when the loading of $BiCl_3$ was decreased to 0.01 equiv (Table 1, entry 2). Screening other bismuth catalysts showed that $BiCl_3$ was the most effective (Table 1, entries 3–8). Lowering the temperature would lead to a lower yield and longer reaction time (Table 1, entry 9). Control experiment indicated that no target product was generated in the absence of $BiCl_3$ (Table 1, entry 10). Additionally, this reaction proceeded well in other solvents, and MeCN facilitated the formation of desired product **3a** (Table 1, entries 11–14). Compared with $BiCl_3$, this transformation was less efficiently catalyzed by other common Lewis acidic catalysts at the same loading (Table 1, entries 15–18). Finally, the optimal reaction conditions were identified as follows: $BiCl_3$ (1 mol %) used as catalyst, *o*-phenylenediamine **1a** (1.0 mmol) reacted with acetone **2a** (5.0 ml) under air at 45°C for 4 h to give the target product **3a** in 94% yield.

Then, the optimized reaction conditions were applied to examine the scope of this transformation (Table 2). Aliphatic ketones, including linear and cyclic, reacted with *o*-phenylenediamine **1a** efficiently to afford the corresponding products **3a–e** in good to excellent yields. The increased steric hindrance of alkyl substituent in the proximity of carbonyl group slightly decreased the yields of target products **3a–c**. The standard reaction conditions were not suitable for aromatic ketones because no evidence for the formation of 1,5-benzodiazepine products was attained. We were pleased to observe that the condensation–cyclization reaction underwent smoothly in MeCN and delivered the desired products **3f–j** in satisfactory yields. Aromatic ketone substances bearing a functional group with a weak electronic effect on benzene ring usually gave products with better yields (products **3h**, **i**). The presence of an electron-donating or an electron-withdrawing group on *o*-phenylenediamines **1** had an insignificant effect on this transformation, as target products **3k–q** were isolated in excellent yields. Regrettably, products from mono-substituted *o*-phenylenediamines were obtained as mixtures of two regioisomers. For example, the regioselectivity of these reactions involving *o*-phenylenediamines substituted with a weak-electronic effect group was 1:1 (products **3k**,**l**,**n**,**o**). A better regioselectivity of 14:1 was obtained in the case of 4-nitro-substituted *o*-phenylenediamines (product **3m**).

The structure of compound **3a** was determined by X-ray structural analysis (Fig. 1).

Based on the experimental results mentioned above, further investigations were undertaken to examine the feasibility of the reaction between aromatic *o*-diamines **1** and aldehydes **4** (Table 3).[19] In this attempt, *o*-phenylenediamines **1a** reacted with aliphatic aldehydes with a larger steric hindrance, such as *n*-pentanal and *i*-butanal, in

**Table 1**. Optimization of the bismuth-catalyzed synthesis of 1,5-benzodaizepine **3a***




| Entry | Catalyst (mol %) | Solvent | Time, h | Yield,** % |
|---|---|---|---|---|
| 1 | $BiCl_3$ (10) | $Me_2CO$ | 4 | 91 |
| 2 | $BiCl_3$ (1) | $Me_2CO$ | 4 | 94 |
| 3 | $BiI_3$ (1) | $Me_2CO$ | 4 | 90 |
| 4 | $Bi(NO_3)_3$ (1) | $Me_2CO$ | 4 | 87 |
| 5 | $BiPh_3$ (1) | $Me_2CO$ | 4 | 83 |
| 6 | $Bi(OTf)_3$ (1) | $Me_2CO$ | 4 | 89 |
| 7 | $Bi_2O_3$ (1) | $Me_2CO$ | 4 | 32 |
| 8 | $NaBiO_3$ (1) | $Me_2CO$ | 4 | –*** |
| 9 | $BiCl_3$ (1) | $Me_2CO$ | 20 | 82*[4] |
| 10 | – | $Me_2CO$ | 20 | –*** |
| 11 | $BiCl_3$ (1) | PhMe | 6 | 41*[5] |
| 12 | $BiCl_3$ (1) | THF | 6 | 77*[5] |
| 13 | $BiCl_3$ (1) | MeCN | 4 | 89*[5] |
| 14 | $BiCl_3$ (1) | DMF | 4 | 81*[5] |
| 15 | $InCl_3$ (1) | $Me_2CO$ | 4 | 76*[6] |
| 16 | $CuCl_2$ (1) | $Me_2CO$ | 3 | 56 |
| 17 | $Sc(OTf)_3$ (1) | $Me_2CO$ | 4 | 71 |
| 18 | $AgNO_3$ (1) | $Me_2CO$ | 4 | 63 |

* Reaction conditions: compound **1a** (1.0 mmol), compound **2a** (5.0 ml), 45°C.
** Isolated yields.
*** No product.
*[4] 25°C.
*[5] Reaction conditions: compound **1a** (1.0 mmol, 0.2 N), compound **2a** (3.0 mmol).
*[6] 89% yield with 10 mol % $InCl_3$.

MeCN to afford 1,2-disubstituted benzimidazoles **5a**,**b** in moderate yields. Benzimidazoles are another important class of azaheterocyclic compounds, which is used as core-structure in drug design for various enzymes and protein receptors, widely being applied in therapeutics, such as anticancer, antiallergic, antiHIV, and other medicinal agents.[20] The reaction of *o*-phenylenediamines **1a** with aromatic aldehydes also occurred, albeit it generally required harsher conditions and gave lower yields (products **5c–e**).

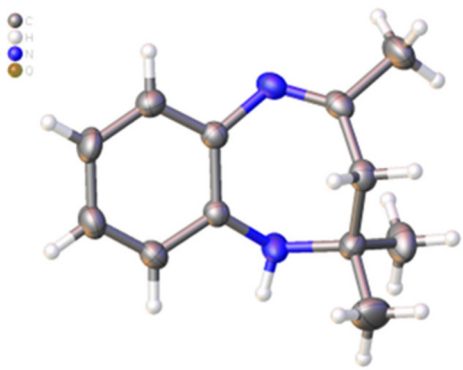
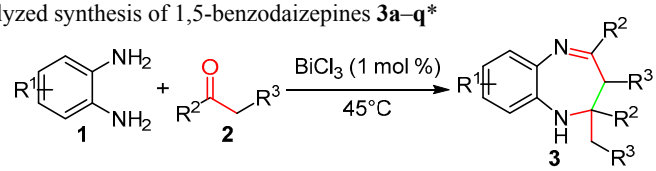
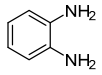
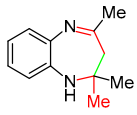
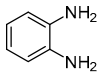
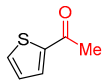
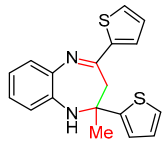
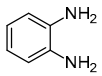
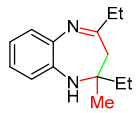
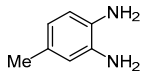
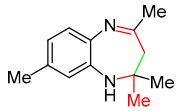
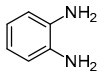
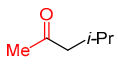
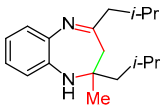
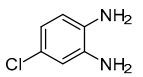
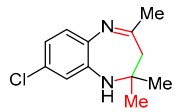
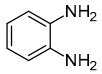
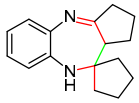
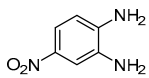
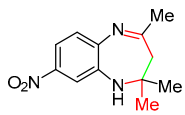
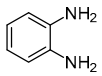
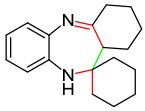
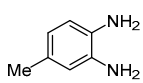
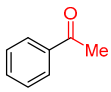
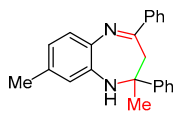
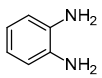
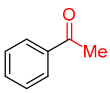
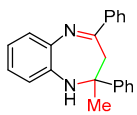
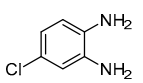
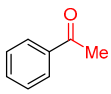
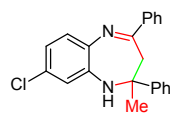
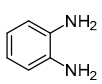
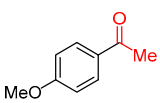
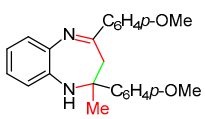


**Figure 1**. The molecular structure of compound **3a** with atoms represented by thermal vibration ellipsoids of 50% probability.

**Table 2**. Generality of $BiCl_3$-catalyzed synthesis of 1,5-benzodaizepines **3a–q***




| *o*-Diamine | Ketone | Product | Product (yield,** %) | *o*-Diamine | Ketone | Product | Product (yield,** %) |
|---|---|---|---|---|---|---|---|
|  |  |  | **3a** (94) |  |  |  | **3j** (87) |
|  |  |  | **3b** (90) |  |  |  | **3k** (92)*** |
|  |  |  | **3c** (85) |  |  |  | **3l** (93)*** |
|  |  |  | **3d** (89) |  |  |  | **3m** (84)*[4] |
|  |  |  | **3e** (91) |  |  |  | **3n** (91)*** |
|  |  |  | **3f** (91) |  |  |  | **3o**(88)*** |
|  |  |  | **3g** (76) |  |  |  | |
|  |  |  | **3h** (87) |  |  |  | **3p** (92) |
|  |  |  | **3i** (83) |  |  |  | **3q** (90) |

* Conditions A for synthesis of 1,5-benzodaizepines **3a–e**,**k–m**,**p**,**q**: *o*-diamine **1** (1.0 mmol), aliphatic ketone **2** (5.0 ml), $BiCl_3$ (1 mol %), 45°C, 4 h. Conditions B for synthesis of 1,5-benzodaizepines **3f–j**,**n**,**o**: *o*-diamine **1** (1.0 mmol), aromatic ketone **2** (3.0 mmol), $BiCl_3$ (1 mol %), MeCN (5.0 ml), 45°C, 4–6 h.

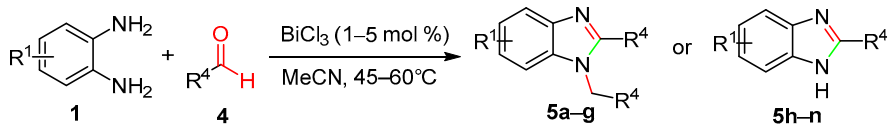
** Isolated yields.

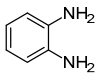
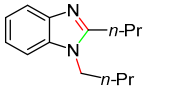
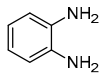
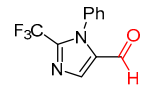
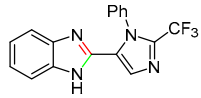
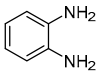
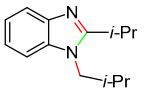
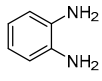
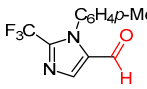
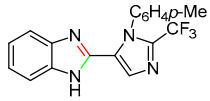
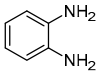
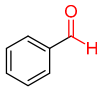
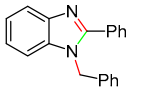
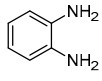
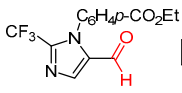
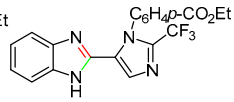
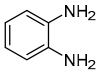
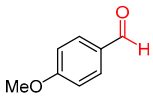
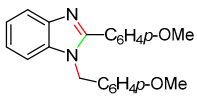
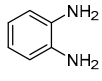
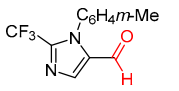
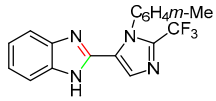
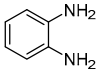
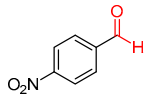
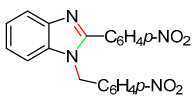
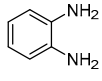
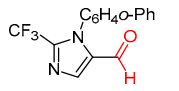
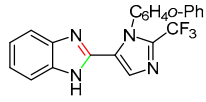
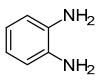
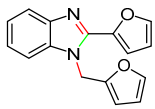
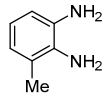
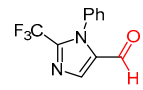
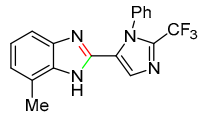
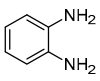
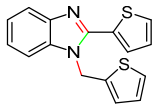
*** 1:1 mixture of two regioisomers.

*[4] 14:1 mixture of two regioisomers.

Electron-rich aldehyde, as well as heterocyclic aromatic aldehydes, reacted very well to give the desired products **5d** and **5f**,**g**, respectively, in a higher yield than electron-deficient aldehyde (product **5e**). In addition, 1,2-disubstituted benzimidazole **5c** was detected as the sole product even the loading of the aldehyde was decreased to 0.3 equiv. Surprisingly, unexpected products of monosubstituted 2-[2-(fluoroalkyl)imidazol-5-yl]benzimidazoles **5h–n** were obtained as the final products in moderate yields when a fluorinated imidazole-5-carbaldehyde[16] was used as substrate. In these reactions, substrates bearing electron-donating groups at *para*, or *meta* position of benzene ring afforded the desired products **5i**,**k** in higher yields. Electron-withdrawing group would lead to a low yield (product **5j**). When a phenyl group was attached at the *ortho* position of the benzene ring, only 33% yield was obtained (product **5l**).

**Table 3**. The scope of $BiCl_3$-catalyzed synthesis of benzimidazoles **5a–n***




| *o*-Diamine | Aldehyde | Product | Product (yield,** %) | *o*-Diamine | Aldehyde | Product | Product (yield,** %) |
|---|---|---|---|---|---|---|---|
|  |  |  | **5a** (63)*** |  |  |  | **5h** (49) |
|  |  |  | **5b** (59)*** |  |  |  | **5i** (62) |
|  |  |  | **5c** (38)*[4] |  |  |  | **5j** (40) |
|  |  |  | **5d** (54) |  |  |  | **5k** (56) |
|  |  |  | **5e** (19) |  |  |  | **5l** (33) |
|  |  |  | **5f** (59) |  |  |  | **5m** (61) |
|  |  |  | **5g** (67) |  |  |  | **5n** (47) |

* Conditions: *o*-diamine **1** (1.0 mmol), aldehyde **4** (3.0 mmol), $BiCl_3$ (1–5 mol %), MeCN (5.0 ml), 45–60°C, 4–6 h.
** Isolated yields.
*** $BiCl_3$ (1 mol %), 45°C.
*[4] Aldehyde **4** (0.3 mmol).

The examination on the effect of substituted aromatic *o*-diamines **1** suggested the *ortho*-substituted phenylenediamine generally delivered target product in a higher yield and shorter time compared with the *meta*-substituted substrate (compounds **5m**,**n**).

The proposed mechanisms described in Scheme 1 showed that these transformations proceeded in two steps. The initial step was likely to be the formation of diimine **7** by condensation of *o*-phenylenediamines **1** and carbonyl compounds **2**. In the case when ketones were used as

**Scheme 1**. A possible reaction mechanism

substrates, one of the imine groups isomerized to enamine **N**, and then intramolecular nucleophilic attack occurred on another imine group activated by bismuth catalyst to afford 1,5-benzodiazepine **3** (Scheme 1, pathway 1). When aldehydes were used as substrates, the activated imine underwent an intramolecular nucleophilic attacked by a nitrogen atom of another imine group to afford intermediate **M** which would convert to 1,2-substituted benzimidazole **5** by a proton shift (Scheme 1, pathway 2). From the sterically hindred 2-(trifluoromethyl)imidazole-5-carbaldehydes, monoimine **8** was generated, which was followed by the formation of intermediate **O** by intramolecular nucleophilic addition. Upon oxidation of intermediate **O** in air, benzo-fused bisimidazoles **6** formed (pathway 3).[21]

In summary, an efficient, easily operable and environmentally friendly protocol for the synthesis of 1,5-benzodiazepines and benzimidazoles catalyzed by $BiCl_3$ was developed. In these reactions, aliphatic ketones efficiently reacted with aromatic *o*-diamines to produce 1,5-benzodiazepines in good to excellent yields under solvent-free conditions. Satisfactory yields could be obtained when reactions involving aromatic ketones were carried out in MeCN. Using unfluorinated aldehydes as substrates, 1,2-disubstituted benzimidazoles were afforded in moderate yields. Benzo-fused bisimidazoles would be generated as the final products when 2-trifluoromethyl imidazole-5-carbaldehydes were used as substrates. All the reactions were carried out under mild reaction conditions and showed good functional group compatibility. Further studies on the regioselective synthesis of 1,5-benzodiazepines and the optimization of the reaction conditions for the synthesis of benzimidazoles are still ongoing in our laboratory.

## Experimental

$^1$H and $^{13}$C NMR spectra were recorded on a Bruker AM-300 spectrometer (300 and 75 MHz, respectively) in $CDCl_3$ or $CD_3OD$ with TMS as internal standard. Assignments in $^{13}$C NMR spectra are made in analogy to the known compounds. High-resolution mass spectra were recorded at the Guangxi Normal University on a LTQ FT spectrometer in the electron ionization (EI) mode for benzodiazepines **3**, 1,2-disubstituted benzoimidazoles **5** and in the electrospray ionization (ESI) mode for 2-substituted benzimidazoles **6**. Melting points were determined on a Melt-Temp apparatus and were uncorrected. TLC analysis was performed on silica gel plates. Column chromatography was performed by packing glass column with silica gel (mesh 300–400), using the combination of petroleum ether – EtOAc as eluent.

All reagents were purchased from commercial sources and purified before used by standard procedures. Unless otherwise specified, all reactions were carried out in a Schlenk tube equipped with a magnetic stirrer under appropriate conditions.

**Synthesis of 1,5-benzodiazepines 3** (General procedure). Method A. Into a Schlenk tube, $BiCl_3$ (3 mg, 0.01 mmol) and aliphatic ketone **2** (5.0 ml) were added, followed by addition of aromatic *o*-diamine **1** (1.0 mmol), with stirring. The reaction mixture was heated at 45°C and monitored by TLC. After completion of the reaction, the excess ketone **2** was removed under vacuum and the residue was purified by column chromatography on silica gel with petroleum ether – ethyl acetate, 4:1 as the eluent to give the desired products **3a**–**e**,**k**–**m**,**p**,**q**.

Method B. Into a Schlenk tube, $BiCl_3$ (3 mg, 0.01 mmol), MeCN (5.0 ml), aromatic ketone **2** (3.0 mmol), and aromatic *o*-diamine **1** (1.0 mmol) were added subsequently. The system was heated at 45°C and monitored by TLC. After completion of a reaction, the solvent was removed under vacuum and the residue was purified by column chromatography on silica gel with petroleum ether – ethyl acetate, 4:1 as the eluent to give the desired products **3f**–**j**,**n**,**o**.

**2,2,4-Trimethyl-2,3-dihydro-1*H*-1,5-benzodiazepine (3a)**. Yield 176 mg (94%), yellow flakes, mp 135–137°C (mp 136–138°C[10b]). $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 1.31 (6H, s, $CH_3$); 2.19 (2H, s, $CH_2$); 2.35 (3H, s, $CH_3$); 2.94 (1H, br. s, NH); 6.68–6.71 (1H, m, H Ph); 6.94–6.96 (2H, m, H Ph); 7.08–7.10 (1H, m, H Ph). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 29.9 ($CH_3$); 30.5 ($CH_3$); 45.1 ($CH_2$); 68.5 (C–N); 121.8 (C Ph); 122.2 (C Ph); 125.6 (C Ph); 126.9 (C Ph); 137.9 (C Ph); 140.8 (C Ph); 172.6 (C=N).

**2,4-Diethyl-2-methyl-2,3-dihydro-1*H*-1,5-benzodiazepine (3b)**. Yield 194 mg (90%), yellow solid, mp 138–139°C (mp 137–139°C[10b]). $^1$H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.99 (3H, t, *J* = 8.0, $CH_3$); 1.25 (3H, t, *J* = 7.0, $CH_3$); 1.72 (2H, q, *J* = 8.0, $C\underline{H}_2CH_3$); 2.15–2.16 (2H, m, $CH_2$); 2.35 (3H, s, $CH_3$); 2.69 (2H, q, *J* = 8.6, $C\underline{H}_2CH_3$); 3.25 (1H, br. s, NH); 6.71–6.72 (1H, m, H Ph); 6.90–6.95 (2H, m, H Ph); 7.15–7.18 (1H, m, H Ph). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 8.9 ($CH_3$); 10.6 ($CH_3$); 10.7 ($CH_3$); 26.8 ($\underline{C}H_2CH_3$); 35.5 ($\underline{C}H_2CH_3$); 42.2 ($CH_2$); 70.5 (C-N); 121.6 (C Ph); 121.7 (C Ph); 125.4 (C Ph); 127.1 (C Ph); 137.8 (C Ph); 140.8 (C Ph); 175.9 (C=N). Found, *m*/*z*: 216.1628 $[M]^+$. $C_{14}H_{20}N_2$. Calculated, *m*/*z*: 216.1626.

**2,4-Diisobutyl-2-methyl-2,3-dihydro-1*H*-1,5-benzodiazepine (3c)**. Yield 231 mg (85%), yellow solid, mp 123–124°C (mp 118–120°C[10b]). $^1$H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.95–1.03 (12H, m, $CH(C\underline{H}_3)_2$); 1.32 (3H, s, $CH_3$); 1.48–1.51 (2H, m, $CH_2$); 1.65–1.73 (1H, m, CH); 2.06–2.13 (3H, m, $C\underline{H}_2C\underline{H}$); 2.24 (2H, d, *J* = 12.8, $C\underline{H}_2CH$); 3.36 (1H, br. s, NH); 6.60–6.64 (1H, m, H Ph); 6.88–6.97 (2H, m, H Ph); 7.05–7.11 (1H, m, H Ph). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 22.8 ($CH_3$); 22.9 ($CH_3$); 24.4 (CH); 25.1 ($CH_3$); 25.2 ($CH_3$); 26.4 (CH); 28.2 ($CH_2$); 43.5 ($CH_3$); 51.8 ($CH_2$); 52.0 ($CH_2$); 70.8 (C–N); 121.4 (C Ph); 121.6 (C Ph); 125.2 (C Ph); 127.2 (C Ph); 137.8 (C Ph); 140.4 (C Ph), 173.8 (C=N). Found, *m*/*z*: 272.2250 $[M]^+$. $C_{18}H_{28}N_2$. Calculated, *m*/*z*: 272.2252.

**2,3,9,10a-Tetrahydro-1*H*-spiro[cyclopenta[*b*][1,5]benzodiazepine-10,1'-cyclopentane] (3d)**. Yield 214 mg (89%), yellow solid, mp 137–139°C (mp 137–138°C[10b]). $^1$H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.45–1.84 (10H, m, $CH_2$); 1.92–2.06 (2H, m, $CH_2$); 2.59–2.64 (2H, m, $CH_2$); 2.71 (1H, t, *J* = 7.8, CH); 4.55 (1H, br. s, NH); 6.68–6.73 (1H, m, H Ph); 7.07–7.13 (2H, m, H Ph); 7.28–7.33 (1H, m, H Ph). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 23.4 ($CH_2$); 24.2 ($CH_2$); 24.3 ($CH_2$); 29.0 ($CH_2$); 33.6 ($CH_2$); 38.6 ($CH_2$); 39.5 ($CH_2$); 54.5 (CH); 67.8 (C); 119.0 (C Ph);

119.6 (C Ph); 127.2 (C Ph); 132.5 (C Ph); 134.2 (C Ph); 139.5 (C Ph); 178.0 (C=N). Found, *m/z*: 240.1626 $[M]^+$. $C_{16}H_{20}N_2$. Calculated, *m/z*: 240.1626.

**1',2',3',4',10',11a'-Hexahydrospiro[cyclohexane-1,11'-dibenzo[*b*,*e*][1,4]diazepine] (3e)**. Yield 244 mg (91%), yellow solid, mp 133–134°C (mp 136–137°C[10b]). $^1$H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.19–1.80 (16H, m, $CH_2$); 2.36–2.40 (1H, m, N=CC<u>H</u>); 2.55 (2H, t, *J* = 6.6, N=CC<u>H</u>$_2$); 4.41 (1H, br. s, NH); 6.60–6.64 (1H, m, H Ph); 7.03–7.09 (2H, m, H Ph); 7.18–7.22 (1H, m, H Ph). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 21.8 ($CH_2$); 24.4 ($CH_2$); 25.2 ($CH_2$); 26.8 ($CH_2$); 27.1 ($CH_2$); 33.3 ($CH_2$); 34.1 ($CH_2$); 40.6 ($CH_2$); 41.0 ($CH_2$); 41.8 (CH); 51.8 (C–N); 121.2 ($CH_2$); 121.4 ($CH_2$); 126.0 (C Ph); 129.4 (C Ph); 138.4 (C Ph); 138.6 (C Ph); 176.3 (C=N). Found, *m/z*: 268.1944 $[M]^+$. $C_{18}H_{24}N_2$. Calculated, *m/z*: 268.1940.

**2-Methyl-2,4-diphenyl-2,3-dihydro-1*H*-1,5-benzodiazepine (3f)**. Yield 284 mg (91%), yellow solid, mp 150–152°C (mp 150–152°C[10b]). $^1$H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.75 (3H, s, $CH_3$); 2.97 (1H, d, *J* = 13.4, $CH_2$); 3.13 (1H, d, *J* = 13.0, $CH_2$); 3.52 (1H, br. s, NH); 6.83 (1H, d, *J* = 7.6, H Ph); 7.03–7.07 (2H, m, H Ph); 7.14–7.33 (7H, m, H Ph); 7.58–7.60 (4H, m, H Ph). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 29.9 ($CH_3$); 42.7 ($CH_2$); 73.5 (C–N); 121.1 (C Ph); 121.9 (C Ph); 125.4 (C Ph); 126.1 (C Ph); 127.0 (C Ph); 127.1 (C Ph); 127.7 (C Ph); 128.2 (C Ph); 128.8 (C Ph); 129.8 (C Ph); 138.0 (C Ph); 140.0 (C Ph); 140.1 (C Ph); 147.5 (C Ph); 167.4 (C=N). Found, *m/z*: 312.1628 $[M]^+$. $C_{22}H_{20}N_2$. Calculated, *m/z*: 312.1626.

**2,4-Bis(4-methoxyphenyl)-2-methyl-2,3-dihydro-1*H*-1,5-benzodiazepine (3g)**. Yield 283 mg (76%), yellow solid, mp 122–125°C (mp 118–120°C[22]). $^1$H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.75 (3H, s, $CH_3$); 2.94 (1H, d, *J* = 13.4, $CH_2$); 3.07 (1H, d, *J* = 13.4, $CH_2$); 3.44 (1H, br. s, NH); 3.78 (3H, s, $OCH_3$); 3.82 (3H, s, $OCH_3$); 6.79–6.85 (5H, m, H Ph); 7.06–7.08 (2H, m, H Ph); 7.30–7.32 (1H, m, H Ph); 7.56 (2H, d, *J* = 7.8, H Ph); 7.62 (2H, d, *J* = 7.8, H Ph). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 29.8 ($CH_3$); 43.0 ($CH_2$); 55.4 ($OCH_3$); 55.5 ($OCH_3$); 73.5 (C–N); 113.5 (C Ph); 113.6 (C Ph); 121.5 (C Ph); 121.8 (C Ph); 126.1 (C Ph); 126.6 (C Ph); 128.1 (C Ph); 129.0 (C Ph); 132.2 (C Ph); 139.0 (C Ph); 139.8 (C Ph); 140.5 (C Ph); 158.7 (C=N); 161.2 (C Ph); 167.3 (C Ph). Found, *m/z*: 372.1837 $[M]^+$. $C_{24}H_{24}N_2O_2$. Calculated, *m/z*: 372.1838.

**2,4-Bis(4-chlorophenyl)-2-methyl-2,3-dihydro-1*H*-1,5-benzodiazepine (3h)**. Yield 331 mg (87%), yellow solid, mp 145–147°C (mp 144–146°C[22]). $^1$H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.76 (3H, s, $CH_3$); 2.90 (1H, d, *J* = 13.4, $CH_2$); 3.07 (1H, d, *J* = 13.4, $CH_2$); 3.40 (1H, br. s, NH); 6.82 (1H, d, *J* = 7.6, H Ph); 7.04–7.09 (2H, m, H Ph); 7.21–7.30 (5H, m, H Ph); 7.49–7.55 (4H, m, H Ph). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 30.0 ($CH_3$); 42.8 ($CH_2$); 73.3 (C–N); 121.2 (C Ph); 122.2 (C Ph); 126.5 (C Ph); 126.9 (C Ph); 128.1 (C Ph); 128.3 (C Ph); 128.4 (C Ph); 133.3 (C Ph); 136.4 (C Ph); 137.5 (C Ph); 137.7 (C Ph); 140.4 (C Ph); 145.9 (C Ph); 165.9 (C=N). Found, *m/z*: 380.0845 $[M]^+$. $C_{22}H_{18}Cl_2N_2$. Calculated, *m/z*: 380.0847.

**2-Methyl-2,4-bis(4-nitrophenyl)-2,3-dihydro-1*H*-1,5-benzodiazepine (3i)**. Yield 334 mg (83%), orange solid, mp 156–158°C (mp 152–154°C[10i]). $^1$H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.83 (3H, s, $CH_3$); 2.96 (1H, d, *J* = 13.4, $CH_2$); 3.29 (1H, d, *J* = 13.4, $CH_2$); 3.57 (1H, br. s, NH); 6.93 (1H, d, *J* = 6.8, H Ph); 7.09–7.13 (1H, m, H Ph); 7.15–7.18 (1H, m, H Ph); 7.34–7.36 (1H, m, H Ph); 7.68 (2H, d, *J* = 7.4, H Ph); 7.77 (2H, d, *J* = 7.4, H Ph); 8.04–8.07 (4H, m, H Ph). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 30.1 ($CH_3$); 43.0 ($CH_2$); 73.5 (C–N); 121.2 (C Ph); 122.3 (C Ph); 123.3 (C Ph); 123.5 (C Ph); 126.8 (C Ph); 127.7 (C Ph); 127.8 (C Ph); 129.6 (C Ph); 137.2 (C Ph); 138.8 (C Ph); 144.5 (C Ph); 147.1 (C Ph); 148.5 (C Ph); 154.0 (C Ph); 163.9 (C=N). Found, *m/z*: 402.1326 $[M]^+$. $C_{22}H_{18}N_4O_4$. Calculated, *m/z*: 402.1328.

**2-Methyl-2,4-di(thiophen-2-yl)-2,3-dihydro-1*H*-1,5-benzodiazepine (3j)**. Yield 283 mg (87%), pale-brown solid, mp 90–91°C (mp 90–91°C[22]). $^1$H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.86 (3H, s, $CH_3$); 3.01 (1H, d, *J* = 13.5, $CH_2$); 3.08 (1H, d, *J* = 13.5, $CH_2$); 3.64 (1H, br. s, NH); 6.81–6.83 (1H, m, H Ar); 6.91–6.94 (2H, m, H Ar); 7.02–7.08 (4H, m, H Ar); 7.11–7.12 (1H, m, H Ar); 7.27–7.29 (1H, m, H Ar); 7.39–7.41 (1H, m, H Ar). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 30.5 ($CH_3$); 44.4 ($CH_2$); 72.4 (C–N); 122.2 (C Ar); 122.7 (C Ar); 122.9 (C Ar); 124.2 (C Ar); 126.4 (C Ar); 126.8 (C Ar); 127.6 (C Ar); 128.0 (C Ar); 128.5 (C Ar); 130.5 (C Ar); 137.2 (C Ar); 153.2 (C Ar); 162.7 (C=N). Found, *m/z*: 324.0758 $[M]^+$. $C_{18}H_{16}N_2S_2$. Calculated, *m/z*: 324.0755.

**2,2,4,8-Tetramethyl-2,3-dihydro-1*H*-1,5-benzodiazepine (3k), a 1:1 mixture with 2,2,4,7-tetramethyl-2,3-dihydro-1*H*-1,5-benzodiazepine (3k')**.[10i] Yield 186 mg (92%), yellow semisolid. $^1$H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.28 (6H, s, $CH_3$); 1.29 (6H, s, $CH_3$); 2.16 (2H, s, $CH_2$); 2.18 (2H, s, $CH_2$); 2.24 (3H, s, $CH_3$); 2.26 (3H, s, $CH_3$); 2.32 (3H, s, $CH_3$); 2.33 (3H, s, $CH_3$); 3.44 (2H, br. s, NH); 6.50 (1H, d, *J* = 0.9, H Ph); 6.62 (1H, d, *J* = 7.8, H Ph); 6.74–6.75 (2H, m, H Ph); 6.94 (1H, d, *J* = 1.6, H Ph); 7.02 (1H, d, *J* = 7.8, H Ph). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 20.4 ($CH_3$); 20.6 ($CH_3$); 29.6 ($CH_3$); 30.0 ($CH_3$); 30.3 ($CH_3$); 45.0 ($CH_2$); 45.2 ($CH_2$); 67.6 (C–N); 68.4 (C–N); 121.8 (C Ph); 122.0 (C Ph); 122.6 (C Ph); 126.2 (C Ph); 126.9 (C Ph); 131.6 (C Ph); 135.2 (C Ph); 135.3 (C Ph); 137.7 (C Ph); 137.9 (C Ph); 140.8 (C Ph); 171.4 (C=N); 172.3 (C=N). Found, *m/z*: 202.1473 $[M]^+$. $C_{13}H_{18}N_2$. Calculated, *m/z*: 202.1470.

**8-Chloro-2,2,4-trimethyl-2,3-dihydro-1*H*-1,5-benzodiazepine (3l), a 1:1 mixture with 7-chloro-2,2,4-trimethyl-2,3-dihydro-1*H*-1,5-benzodiazepine (3l')**.[10i] Yield 206 mg (93%), yellow solid. $^1$H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.30 (12H, s, $CH_3$); 2.18–2.21 (4H, m, $CH_2$); 2.30–2.33 (6H, m, $CH_3$); 3.35 (2H, br. s, NH); 6.61–6.62 (1H, m, H Ph); 6.67–6.68 (1H, m, H Ph); 6.84–6.87 (2H, m, H Ph); 7.02–7.04 (1H, m, H Ph); 7.10–7.11 (1H, m, H Ph). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 29.5 ($CH_3$); 29.6 ($CH_3$); 30.3 ($CH_3$); 30.4 ($CH_3$); 45.0 ($CH_2$); 45.1 ($CH_2$); 67.5 (C–N); 68.1 (C–N); 120.8 (C Ph); 121.4 (C Ph); 122.5 (C Ph); 125.2 (C Ph); 126.4 (C Ph); 126.5 (C Ph); 128.1 (C Ph); 130.0 (C Ph); 136.5 (C Ph); 138.4 (C Ph); 139.1 (C Ph); 141.4 (C Ph); 172.6 (C=N); 173.6 (C=N). Found, *m/z*: 222.0922 $[M]^+$. $C_{12}H_{15}ClN_2$. Calculated, *m/z*: 222.0924.

**2,2,4-Trimethyl-8-nitro-2,3-dihydro-1*H*-1,5-benzodiazepine (3m)**.[10b] Yield 196 mg (84%), yellow solid, mp 155–157°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 1.90 (6H, s, $CH_3$); 2.95 (3H, s, $CH_3$); 3.20 (2H, s, $CH_2$); 7.15–7.17 (1H, m, H Ph); 8.10–8.13 (1H, m, H Ph); 8.76 (1H, s, H Ph). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 30.0 ($CH_3$); 30.2 ($CH_3$); 30.3 ($CH_3$); 45.7 ($CH_2$); 60.8 (C–N); 118.4 (C Ph); 121.2 (C Ph); 126.4 (C Ph); 132.3 (C Ph); 138.0 (C Ph); 145.4 (C Ph); 170.5 (C=N). Found, *m*/*z*: 233.1160 $[M]^+$. $C_{12}H_{15}N_3O_2$. Calculated, *m*/*z*: 233.1164,

**2,8-Dimethyl-2,4-diphenyl-2,3-dihydro-1*H*-1,5-benzodiazepine (3n), a 1:1 mixture with 2,7-dimethyl-2,4-diphenyl-2,3-dihydro-1*H*-1,5-benzodiazepine (3n')**.[22] Yield 293 mg (91%), yellow solid. $^1$H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.77 (3H, s, $CH_3$); 1.78 (3H, s, $CH_3$); 2.36 (3H, s, Ar $CH_3$); 2.38 (3H, s, Ar $CH_3$); 2.98–3.01 (2H, m, $CH_2$); 3.12–3.16 (2H, m, $CH_2$); 3.51 (2H, br. s, NH); 6.68 (1H, m, H Ph); 6.77 (1H, d, *J* = 8.0, H Ph); 6.90 (1H, d, *J* = 8.0, H Ph); 6.92 (1H, d, *J* = 8.0, H Ph); 7.16–7.31 (14H, m, H Ph); 7.59–7.67 (8H, m, H Ph). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 20.4 ($CH_3$); 21.0 ($CH_3$); 29.6 ($CH_3$); 30.0 ($CH_3$); 42.8 ($CH_2$); 43.3 ($CH_2$); 72.8 (C–N); 73.8 (C–N); 121.4 (C Ph); 121.5 (C Ph); 122.2 (C Ph); 125.3 (C Ph); 125.4 (C Ph); 125.5 (C Ph); 126.9 (C Ph); 127.1 (C Ph); 127.9 (C Ph); 128.0 (C Ph); 128.1 (C Ph); 128.6 (C Ph); 128.8 (C Ph); 129.4 (C Ph); 129.8 (C Ph); 131.2 (C Ph); 136.1 (C Ph); 137.2 (C Ph); 137.9 (C Ph); 139.5 (C Ph); 139.8 (C Ph); 140.4 (C Ph); 147.9 (C Ph); 166.5 (C=N) 167.8 (C=N). Found, *m*/*z*: 326.1779 $[M]^+$. $C_{23}H_{22}N_2$. Calculated, *m*/*z*: 326.1783.

**8-Chloro-2-methyl-2,4-diphenyl-2,3-dihydro-1*H*-1,5-benzodiazepine (3o), a 1:1 mixture with 7-chloro-2-methyl-2,4-diphenyl-2,3-dihydro-1*H*-1,5-benzodiazepine (3o')**.[22] Yield 304 mg (88%), yellow solid. $^1$H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.77 (3H, s, $CH_3$); 1.79 (3H, s, $CH_3$); 2.97–3.00 (2H, m, $CH_2$); 3.15–3.18 (2H, m, $CH_2$); 3.55 (1H, br. s, NH); 3.62 (1H, br. s, NH); 6.77 (1H, d, *J* = 8.4, H Ph); 6.83 (1H, d, *J* = 2.4, H Ph); 6.88–7.01 (1H, m, H Ph); 7.03–7.05 (1H, m, H Ph); 7.16–7.34 (14H, m, H Ph); 7.56–7.61 (8H, m, H Ph). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 29.6 ($CH_3$); 29.9 ($CH_3$); 43.0 ($CH_2$); 43.1 ($CH_2$); 72.8 (C–N); 73.7 (C–N); 120.4 (C Ph); 121.1 (C Ph); 122.2 (C Ph); 125.2 (C Ph); 126.1 (C Ph); 127.1 (C Ph); 127.2 (C Ph); 127.4 (C Ph); 128.0 (C Ph); 128.2 (C Ph); 128.4 (C Ph); 128.5 (C Ph); 129.9 (C Ph); 130.1 (C Ph); 130.2 (C Ph); 131.1 (C Ph); 138.2 (C Ph); 139.1 (C Ph); 139.5 (C Ph); 147.3 (C Ph); 167.7 (C=N); 168.6 (C=N). Found, *m*/*z*: 346.1233 $[M]^+$. $C_{22}H_{19}ClN_2$. Calculated, *m*/*z*: 346.1237.

**2,2,4,7,8-Pentamethyl-2,3-dihydro-1*H*-1,5-benzodiazepine (3p)**. Yield 199 mg (92%), yellow solid, mp 118–120°C (mp 112–114°C[10b]). $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 1.31 (6H, s, $CH_3$); 2.16 (3H, s, $CH_3$); 2.17 (3H, s, $CH_3$); 2.19 (2H, s, $CH_2$); 2.33 (3H, s, $CH_3$); 3.38 (1H, br. s, NH); 6.52 (1H, s, H Ph); 6.91 (1H, s, H Ph). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 18.8 ($CH_3$); 19.2 ($CH_3$); 29.8 ($CH_3$); 30.3 ($CH_3$); 45.4 ($CH_2$); 67.9 (C–N); 122.8 (C Ph); 127.9 (C Ph); 130.1 (C Ph); 133.9 (C Ph); 135.4 (C Ph); 138.4 (C Ph); 171.5 (C=N). Found, *m*/*z*: 216.1622 $[M]^+$. $C_{14}H_{20}N_2$. Calculated, *m*/*z*: 216.1626.

**7,8-Dichloro-2,2,4-trimethyl-2,3-dihydro-1*H*-1,5-benzodiazepine (3q)**.[10i] Yield 230 mg (90%), yellow solid, mp 141–143°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 1.33 (6H, s, $CH_2$); 2.22 (2H, s, $CH_2$); 2.34 (3H, s, $CH_3$); 3.17 (1H, br. s, NH); 6.84 (1H, s, H Ph); 7.22 (1H, s, H Ph). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 30.0 ($CH_3$); 30.6 ($CH_3$); 45.4 ($CH_2$); 67.8 (C–N); 122.4 (C Ph); 124.5 (C Ph); 128.2 (C Ph); 128.3 (C Ph); 137.8 (C Ph); 139.8 (C Ph); 174.1 (C=N). Found, *m*/*z*: 256.0533 $[M]^+$. $C_{12}H_{14}Cl_2N_2$. Calculated, *m*/*z*: 256.0534.

**Synthesis of benzimidazoles 5** (General method). Into a Schlenk tube, $BiCl_3$ (1–5 mol %), MeCN (5.0 ml), aldehydes (3.0 mmol), and *o*-phenylenediamines (1.0 mmol) were added subsequently. The system was stirred at 45–60°C for appropriate time. After completion of a reaction, the solvent was removed under vacuum and the residue was purified by column chromatography on silica gel with petroleum ether – ethyl acetate as the eluent to give the desired products **5a**–**g** and **5h**–**n**.

**1-Butyl-2-propyl-1*H*-benzimidazole (5a)**.[19g] Yield 136 mg (63%), yellow oil. $^1$H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.98 (3H, t, *J* = 6.8, $CH_3$); 1.07 (3H, t, *J* = 6.8, $CH_3$); 1.38–1.44 (2H, m, $C\underline{H}_2CH_3$); 1.76–1.83 (2H, m, $C\underline{H}_2CH_3$); 1.85–1.88 (2H, m, $NCH_2C\underline{H}_2CH_2$); 2.86 (2H, t, *J* = 7.8, Ar–$C\underline{H}_2CH_2$); 4.10 (2H, t, *J* = 7.6, $NC\underline{H}_2CH_2$); 7.21–7.25 (2H, m, H Ph); 7.30–7.32 (1H, m, H Ph); 7.72–7.73 (1H, m, H Ph). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 13.8 ($CH_3$); 14.1 ($CH_3$); 20.2 ($\underline{C}H_2CH_3$); 21.3 ($\underline{C}H_2CH_3$); 29.3 (Ar–$\underline{C}H_2$); 31.8 (N–$CH_2\underline{C}H_2$); 43.4 (N–$\underline{C}H_2CH_2$); 109.5 (C Ph); 119.0 (C Ph); 122.1 (C Ph); 122.2 (C Ph); 134.8 (C Ph); 142.0 (C Ph); 154.8 (C Ar). Found, *m*/*z*: 216.1622 $[M]^+$. $C_{14}H_{20}N_2$. Calculated, *m*/*z*: 216.1626.

**1-Isobutyl-2-isopropyl-1*H*-benzimidazole (5b)**.[19g] Yield 127 mg (59%), yellow oil. $^1$H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.02 (6H, d, *J* = 8.0, $CH_3$); 1.48 (6H, d, *J* = 8.0, $CH_3$); 2.18–2.24 (1H, m, $NCH_2C\underline{H}$); 3.17–3.22 (1H, m, Ar–C$\underline{H}$); 3.92 (2H, d, *J* = 8.0, $NC\underline{H}_2$); 7.21–7.24 (2H, m, H Ph); 7.27–7.30 (1H, m, H Ph); 7.77–7.79 (1H, m, H Ph). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 20.4 ($CH_3$); 21.6 ($CH_3$); 26.1 ($NCH_2\underline{C}H$); 29.2 (Ar–CH); 50.5 (N–$CH_2$); 109.9 (C Ph); 118.8 (C Ph); 121.5 (C Ph); 121.7 (C Ph); 134.8 (C Ph); 142.5 (C Ph); 160.2 (C Ar). Found, *m*/*z*: 216.1625 $[M]^+$. $C_{14}H_{20}N_2$. Calculated, *m*/*z*: 216.1626.

**1-Benzyl-2-phenyl-1*H*-benzimidazole (5c)**. Yield 108 mg (38%), light-yellow solid, mp 127–129°C (mp 130–132°C[19f]). $^1$H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 5.49 (2H, s, $CH_2$); 7.15 (2H, d, *J* = 6.8, H Ph); 7.24–7.27 (2H, m, H Ph); 7.33–7.37 (4H, m, H Ph); 7.47–7.49 (3H, m, H Ph); 7.74 (2H, d, *J* = 7.2, H Ph); 7.91 (1H, d, *J* = 7.8, H Ph). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 48.6 ($CH_2$); 110.5 (C Ph); 120.0 (C Ph); 122.9 (C Ph); 123.2 (C Ph); 126.1 (C Ph); 127.8 (C Ph); 128.6 (C Ph); 129.1 (C Ph); 129.2 (C Ph); 130.0 (C Ph); 130.1 (C Ph); 136.1 (C Ph); 136.4 (C Ph); 143.2 (C Ph); 154.2 (C Ar). Found, *m*/*z*: 284.1314 $[M]^+$. $C_{20}H_{16}N_2$. Calculated, *m*/*z*: 284.1313.

**1-(4-Methoxybenzyl)-2-(4-methoxyphenyl)-1*H*-benzimidazole (5d)**. Yield 186 mg (54%), light-yellow solid, mp 131–133°C (mp 130–131°C[19f]) $^1$H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 3.78 (3H, s, $OCH_3$); 3.85 (3H, s,

$OCH_3$); 5.51 (2H, s, $CH_2$); 6.86 (2H, d, $J$ = 7.6, H Ph); 7.01 (2H, d, $J$ = 8.0, H Ph); 7.12 (2H, d, $J$ = 8.0, H Ph); 7.20–7.26 (3H, m, H Ph); 7.60–7.65 (2H, m, H Ph); 7.83–7.86 (1H, m, H Ph). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 48.4 ($CH_2$); 56.4 ($OCH_3$); 56.7 ($OCH_3$); 112.4 (C Ph); 115.5 (C Ph); 115.6 (C Ph); 120.2 (C Ph); 123.4 (C Ph); 123.6 (C Ph); 123.8 (C Ph); 128.8 (C Ph); 130.1 (C Ph); 131.8 (C Ph); 137.1 (C Ph); 144.0 (C Ph); 154.5 (C Ar); 159.9 (C Ph); 161.8 (C Ph). Found, *m*/*z*: 344.1528 $[M]^+$. $C_{22}H_{20}N_2O_2$. Calculated, *m*/*z*: 344.1525.

**1-(4-Nitrobenzyl)-2-(4-nitrophenyl)-1*H*-benzimidazole (5e)**. Yield 71 mg (19%), yellow solid, mp 296–299°C (mp 302–304°C[19f]). $^1$H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 5.64 (2H, s, $CH_2$); 7.25 (1H, d, $J$ = 7.6, H Ph); 7.29–7.31 (2H, m, H Ph); 7.37–7.39 (1H, m, H Ph); 7.42–7.44 (1H, m, H Ph); 7.88 (2H, d, $J$ = 8.8, H Ph); 7.99 (1H, d, $J$ = 7.2, H Ph); 8.29 (2H, d, $J$ = 8.0, H Ph); 8.36 (2H, d, $J$ = 8.2, H Ph). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 48.5 ($CH_2$); 112.5 (C Ph); 121.2 (C Ph); 124.2 (C Ph); 125.0 (C Ph); 125.1 (C Ph); 125.2 (C Ph); 128.8 (C Ph); 131.6 (C Ph); 137.2 (C Ph); 137.3 (C Ph); 143.8 (C Ph); 145.6 (C Ph); 148.1 (C Ph); 149.8 (C Ph); 152.4 (C Ar). Found, *m*/*z*: 374.1010 $[M]^+$. $C_{20}H_{14}N_4O_4$. Calculated, *m*/*z*: 374.1015.

**2-(Furan-2-yl)-1-(furan-2-ylmethyl)-1*H*-benzimidazole (5f)**. Yield 156 mg (59%), white solid, mp 97–99°C (mp 94–95°C[19f]). $^1$H NMR specturm ($CDCl_3$) δ, ppm (*J*, Hz): 5.54 (2H, s, $CH_2$); 6.14–6.22 (2H, m, H Ar); 6.52–6.55 (1H, m, H Ar); 7.15 (1H, d, $J$ = 3.3, H Ar); 7.20–7.25 (3H, m, H Ar); 7.40–7.43 (1H, m, H Ar); 7.59 (1H, d, $J$ = 1.2, H Ar); 7.68–7.73 (1H, m, H Ar). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 41.6 ($CH_2$); 108.4 (C Ar); 109.9 (C Ar); 110.5 (C Ar); 112.2 (C Ar); 112.9 (C Ar); 119.7 (C Ar); 122.6 (C Ar); 123.2 (C Ar); 135.4 (C Ar); 142.5 (C Ar); 142.9 (C Ar); 143.8 (C Ar); 143.9 (C Ar); 145.4 (C Ar); 149.5 (C Ar). Found, *m*/*z*: 264.0895 $[M]^+$. $C_{16}H_{12}N_2O_2$. Calculated, *m*/*z*: 264.0899.

**2-(Thiophen-2-yl)-1-(thiophen-2-ylmethyl)-1*H*-benzimidazole (5g)**. Yield 198 mg (67%), light-yellow solid, mp 150–152°C (mp 146–147°C[19f]). $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 5.69 (2H, s, $CH_2$); 6.70–6.85 (2H, m, H Ar); 7.13–7.16 (1H, m, H Ar); 7.23–7.41 (4H, m, H Ar); 7.45–7.51 (2H, m, H Ar); 7.82–7.85 (1H, m, H Ar). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 44.6 ($CH_2$); 110.0 (C Ar); 119.8 (C Ar); 121.5 (C Ar); 122.7 (C Ar); 123.2 (C Ar); 125.6 (C Ar); 126.4 (C Ar); 126.5 (C Ar); 127.4 (C Ar); 128.2 (C Ar); 130.9 (C Ar); 135.8 (C Ar); 137.6 (C Ar); 143.0 (C Ar); 149.5 (C Ar). Found, *m*/*z*: 296.0447 $[M]^+$. $C_{16}H_{12}N_2S_2$. Calculated, *m*/*z*: 296.0442.

**2-[1-Phenyl-2-(trifluoromethyl)-1*H*-imidazol-5-yl]-1*H*-benzimidazole (5h)**. Yield 161 mg (49%), white solid, mp 117–120°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 7.21–7.23 (3H, m, H Ph); 7.43–7.45 (2H, m, H Ph); 7.53–7.57 (2H, m, H Ar); 7.59–7.65 (2H, m, H Ar); 7.79 (1H, s, H Ar); 9.52 (1H, s, NH). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 109.9 (C Ph); 118.8 (C Ph); 120.4 (q, $J$ = 306.0, $CF_3$); 121.9 (C Ph); 122.9 (C Ph); 126.7 (C Ph); 127.6 (C Ph); 128.9 (C Ph); 129.4 (C Ph); 129.8 (C Ph); 132.2 (C Ph); 133.3 (C Ar); 137.5 (q, $J$ = 58.1, C–$CF_3$ Ar); 139.9 (C Ar); 142.0 (C Ar). Found, *m*/*z*: 329.1007 $[M+H]^+$. $C_{17}H_{11}F_3N_4$. Calculated, *m*/*z*: 329.1009

**2-[1-(*p*-Tolyl)-2-(trifluoromethyl)-1*H*-imidazol-5-yl]-1*H*-benzimidazole (5i)**. Yield 212 mg (62%), white solid, mp 41–44°C. $^1$H NMR spectrum ($CD_3OD$), δ, ppm: 2.37 (3H, s, $CH_3$); 7.20–7.22 (2H, m, H Ph); 7.25–7.30 (4H, m, H Ph); 7.45–7.52 (3H, m, H Ph); 7.71 (1H, s, H Ar). $^{13}$C NMR spectrum ($CD_3OD$), δ, ppm (*J*, Hz): 21.2 ($CH_3$); 112.7 (C Ph); 119.6 (q, $J$ = 271.0, $CF_3$); 124.4 (C Ph); 128.6 (C Ph); 128.9 (C Ph); 129.9 (C Ph); 130.4 (C Ph); 130.9 (C Ph); 131.1 (C Ph); 131.4 (C Ph); 132.9 (C Ar); 135.6 (C Ph); 139.5 (q, $J$ = 39.3, C Ar); 142.0 (C Ar); 142.1 (C Ar). Found, *m*/*z*: 343.1164 $[M+H]^+$. $C_{18}H_{14}F_3N_4$, Calculated, *m*/*z*: 343.1165.

**Ethyl 4-[5-(1*H*-benzimidazol-2-yl)-2-(trifluoromethyl)-1*H*-imidazol-1-yl]benzoate (5j)**. Yield 160 mg (40%), white solid, mp 134–135°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.42 (3H, t, $J$ = 7.2, $CH_2C\underline{H}_3$); 1.78 (s, $H_2O$); 4.42 (2H, q, $J$ = 7.2, $C\underline{H}_2CH_3$); 7.20–7.24 (2H, m, H Ph); 7.30–7.32 (1H, m, H Ph); 7.50 (2H, d, $J$ = 8.4, H Ph); 7.62 (1H, m, H Ph); 7.73 (1H, s, H Ar); 8.18 (2H, d, $J$ = 12.4, H Ph); 9.77 (1H, s, NH). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 14.3 ($CH_2\underline{C}H_3$); 61.7 ($\underline{C}H_2CH_3$); 111.0 (C Ph); 118.3 (q, $J$ = 271.9, $CF_3$); 120.0 (C Ph); 123.1 (C Ph); 124.2 (C Ph); 127.9 (C Ph); 128.5 (C Ph); 130.2 (C Ph); 130.9 (C Ph); 132.5 (C Ph); 133.3 (C Ar); 138.1 (C Ph); 138.6 (q, $J$ = 39.6, C Ar); 140.4 (C Ar); 143.2 (C Ar); 165.3 (COOEt). Found, *m*/*z*: 401.1221 $[M+H]^+$. $C_{20}H_{16}F_3N_4O_2$. Calculated, *m*/*z*: 401.1220,

**2-[1-(*m*-Tolyl)-2-(trifluoromethyl)-1*H*-imidazol-5-yl]-1*H*-benzimidazole (5k)**. Yield 192 mg (56%), white solid, mp 119–122°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.46 (3H, s, $CH_3$); 7.21–7.26 (3H, m, H Ph); 7.29–7.32 (2H, m, H Ph); 7.47–7.54 (2H, m, H Ph); 7.73 (1H, d, $J$ = 8.8, H Ph); 7.95 (1H, s, H Ar); 8.40 (1H, s, NH). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 21.4 ($CH_3$); 110.7 (C Ph); 118.4 (q, $J$ = 271.9, $CF_3$); 119.9 (C Ph); 123.1 (C Ph); 123.9 (C Ph); 124.8 (C Ph); 128.3 (C Ph); 128.5 (C Ph); 129.9 (C Ph); 130.9 (C Ph); 132.0 (C Ph); 133.0 (C Ar); 134.3 (C Ph); 138.4 (q, $J$ = 39.6, C Ar); 140.8 (C Ar); 141.1; 142.9 (C Ar). Found, *m*/*z*: 343.1164 $[M+H]^+$. $C_{18}H_{14}F_3N_4$. Calculated, *m*/*z*: 343.1165.

**2-{1-[(1,1'-Biphenyl)-2-yl]-2-(trifluoromethyl)-1*H*-imidazol-5-yl}-1*H*-benzimidazole (5l)**. Yield 133 mg (33%), yellow solid, mp 95–97°C. $^1$H NMR spectrum ($CD_3OD$), δ, ppm (*J*, Hz): 6.52–6.55 (2H, m, H Ph); 6.99 (1H, t, $J$ = 7.6, H Ph); 7.17 (1H, t, $J$ = 7.6, H Ph); 7.21 (2H, br. s, H Ph); 7.31–7.36 (1H, m, H Ph); 7.40 (2H, br. s, H Ph); 7.48 (1H, s, H Ar); 7.59–7.65 (2H, m, H Ph); 7.68–7.70 (1H, m, H Ph). $^{13}$C NMR spectrum ($CD_3OD$), δ, ppm (*J*, Hz): 112.5 (C Ph); 119.9 (q, $J$ = 271.1, $CF_3$); 120.0 (C Ph); 124.2 (C Ph); 124.6 (C Ph); 128.7 (C Ph); 128.8 (C Ph); 129.2 (C Ph); 129.7 (C Ph); 129.9 (C Ph); 130.0 (C Ph); 130.3 (C Ph); 130.4 (2C Ph); 131.8 (C Ph); 132.0 (C Ph); 133.6 (C Ar); 138.7 (C Ph); 139.4 (q, $J$ = 38.9, C Ar); 141.0 (C Ar); 142.2 (C Ar). Found, *m*/*z*: 405.1313 $[M+H]^+$. $C_{23}H_{16}F_3N_4$. Calculated, *m*/*z*: 405.1322.

**7-Methyl-2-[1-phenyl-2-(trifluoromethyl)-1*H*-imidazol-5-yl]-1*H*-benzimidazole (5m)**. Yield 208 mg (61%), white solid, mp 111–112°C. $^1$H NMR spectrum ($CD_3OD$), δ, ppm (*J*, Hz): 2.43 (3H, s, $CH_3$); 6.99 (1H, br. s, H Ph); 7.09 (1H,

t, $J$ = 15.2, H Ph); 7.26 (1H, br. s, H Ph); 7.40–7.42 (2H, m, H Ph); 7.44–7.52 (3H, m, H Ph); 7.73 (1H, s, H Ar). $^{13}$C NMR spectrum ($CD_3OD$), δ, ppm ($J$, Hz): 16.7 ($CH_3$); 110.0 (C Ph); 117.5 (C Ph); 119.9 (q, $J$ = 270.9, $CF_3$); 124.0 (C Ph); 124.9 (C Ph); 125.5 (C Ph); 129.0 (C Ph); 130.3 (C Ph); 130.4 (C Ph); 131.3 (C Ph); 134.9 (C Ar); 135.8 (C Ph); 139.3 (q, $J$ = 39.3, C Ar); 141.7 (C Ar); 143.8 (C Ar). Found, $m/z$: 343.1163 $[M+H]^+$. $C_{18}H_{14}F_3N_4$. Calculated, $m/z$: 343.1165.

**6-Methyl-2-[1-phenyl-2-(trifluoromethyl)-1*H*-imidazol-5-yl]-1*H*-benzimidazole (5n)**. Yield 161 mg (47%), white solid, mp 115–118°C. $^1$H NMR spectrum ($CD_3OD$), δ, ppm: 2.39 (3H, s, $CH_3$); 7.03–7.05 (1H, m, H Ph); 7.25 (1H, br. s, H Ph); 7.33–7.35 (1H, m, H Ph); 7.39–7.41 (2H, m, H Ph); 7.45–7.53 (3H, m, H Ph); 7.70 (1H, s, H Ar). $^{13}$C NMR spectrum ($CD_3OD$), δ, ppm ($J$, Hz): 21.7 ($CH_3$); 112.2 (C Ph); 119.5 (C Ph); 119.8 (q, $J$ = 270.9, $CF_3$); 125.7 (C Ph); 128.9 (C Ph); 130.3 (q, $J$ = 1.4, C Ar); 130.4 (C Ph); 130.9 (C Ph); 131.4 (C Ph); 135.6 (C Ph); 136.6 (C Ph); 139.3 (q, $J$ = 39.3, C Ar); 141.6 (C Ar). Found, $m/z$: 343.1161 $[M+H]^+$. $C_{18}H_{14}F_3N_4$. Calculated, $m/z$: 343.1165.

**X-ray structural investigation of compound 3a**. A crystal of compound **3a** was obtained by recrystallization from $CH_2Cl_2$ solution. X-ray single crystal structure data were collected using a Bruker Apex Smart CCDC Venture diffractometer at 293(2)K. The complete crystallographic information on compound **3a** has been deposited at the Cambridge Crystallographic Data Center (deposit CCDC 2052113).

Supplementary information file containing $^1$H and $^{13}$C NMR spectra as well as X-ray data of compound **3a** is is available at the journal website http://link.springer.com/journal/10593.

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