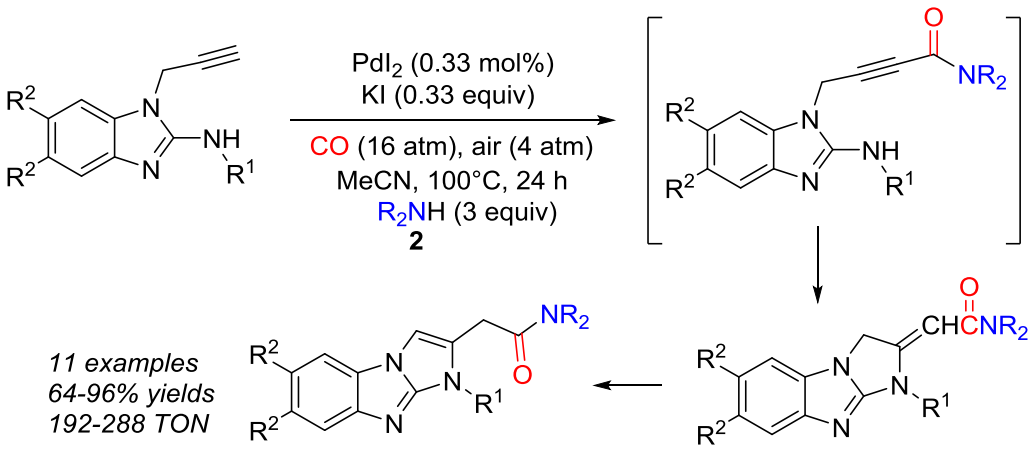
A Palladium Iodide – Catalyzed Oxidative Aminocarbonylation-Heterocyclization Approach to Functionalized Benzimidazoimidazoles

Lucia Veltri,*,† Salvatore V. Giofrè,‡ Perry Devo,§ Roberto Romeo,‡ Adrian P. Dobbs,§ and Bartolo Gabriele

†Laboratory of Industrial and Synthetic Organic Chemistry (LISOC), Department of Chemistry and Chemical Technologies,
University of Calabria, Via P. Bucci 12/C, 87036 Arcavacata di Rende (CS), Italy
‡Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche e Ambientali, University of Messina, Via SS Annunziata, 98168
Messina, Italy
§School of Science, University of Greenwich, Central Avenue, Chatham Maritime, Kent ME4 4TB, U.K.

lucia.veltri@unical.it (L.V.); bartolo.gabriele@unical.it (B.G.)



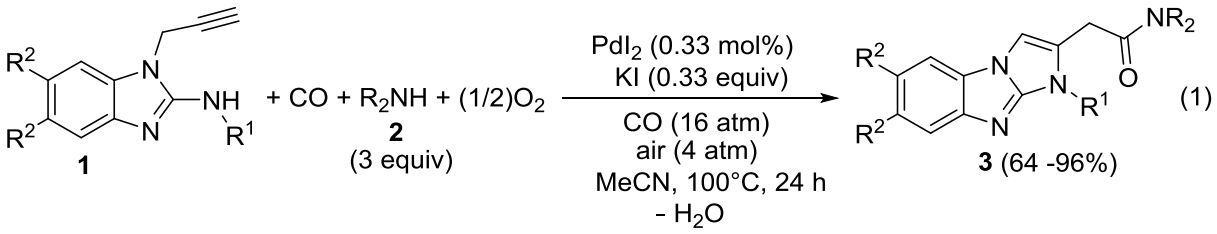
Abstract

A novel carbonylative approach to the synthesis of functionalized 1*H*-benzo[*d*]imidazo[1,2-*a*]imidazoles is presented. The method consists in the oxidative aminocarbonylation of *N*-substituted-1-(prop-2-yn-1-yl)-1*H*-benzo[*d*]imidazol-2-amines, carried out in the presence of secondary nucleophilic amines, to give the corresponding alkynylamide intermediates, followed by in situ conjugated addition and double bond isomerization, to give 2-(1-alkyl-1*H*-benzo[*d*]imidazo[1,2-*a*]imidazol-2-yl)acetamides. Products were obtained in good to excellent yields (64-96%) and high turnover numbers (192-288 mol of product per mol of catalyst) under relatively mild conditions (100 °C under 20 atm of a 4:1 mixture of CO-air), using a simple catalytic system, consisting of PdI_2 (0.33 mol%) in conjunction with KI (0.33 equiv).

Introduction

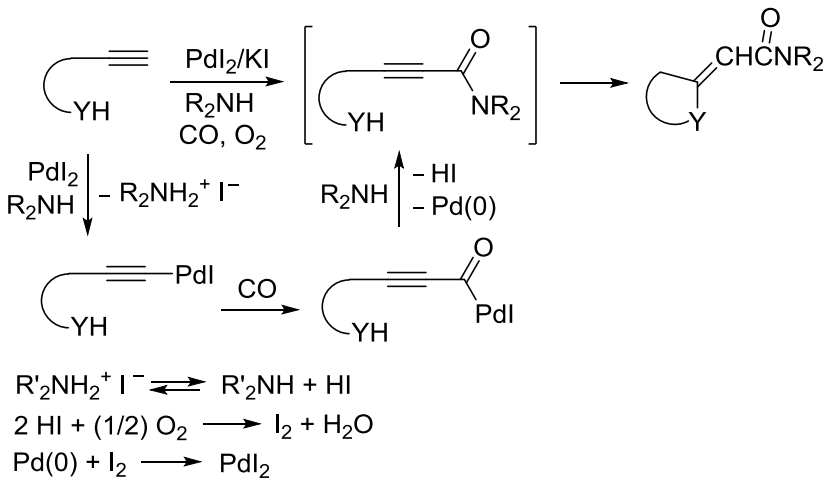
1*H*-benzo[*d*]imidazo[1,2-*a*]imidazoles are an important class of polyheterocyclic derivatives, which display a wide range of pharmacological properties, including analgesic, anti-inflammatory, hypotensive, anti-aggregant, hypoglycemic and anti-cancer activities.[1] Although several methods for the preparation of these compounds are currently known,[2] the possibility to obtain functionalized 1*H*-benzo[*d*]imidazo[1,2-*a*]imidazole derivatives in one step by a catalytic multicomponent approach, starting from simple and/or readily available building blocks, is still of high synthetic interest.

In this Note, we report a novel carbonylative approach[3] to the direct synthesis of functionalized benzimidazoimidazoles, that are, *N*,*N*-dialkyl-2-(1-alkyl-1*H*-benzo[*d*]imidazo[1,2-*a*]imidazol-2-yl)acetamides **3**, starting from *N*-substituted-1-(prop-2-yn-1-yl)-1*H*-benzo[*d*]imidazol-2-amines **1** (Equation 1) Our method is based on PdI_2/KI-catalyzed[4] oxidative monoaminocarbonylation-heterocyclization of **1**, carried out in the presence of a nucleophilic secondary amine **2** as the external nucleophile and oxygen as the oxidant, and allows the direct synthesis of polyheterocyclic derivatives **3** in good to excellent yields in a multicomponent fashion under relatively mild conditions (Equation 1)



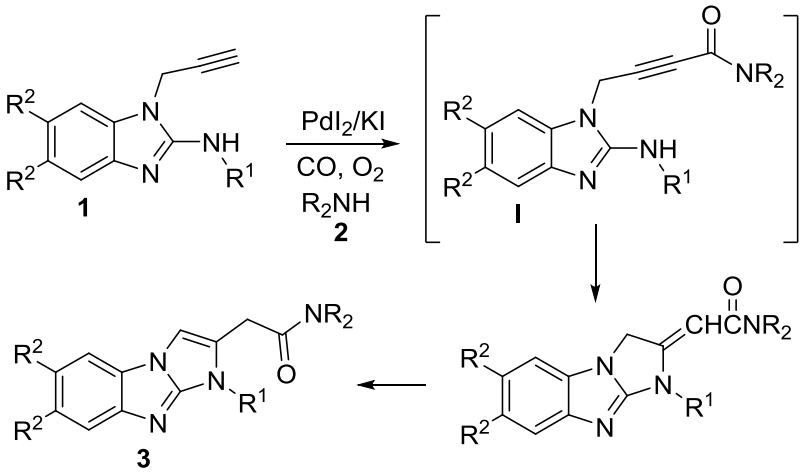
Results and Discussion

PdI_2-KI catalyzed sequential oxidative monoaminocarbomylation of the triple bond followed by heterocyclization has emerged as a powerful method for the direct synthesis of carbonylated hetero- or carbocycles starting from readily acetylenic substrates bearing a suitably placed hetero- or carbo-nucleophile.[4a,5] The process, carried out in the presence of a secondary amine as external nucleophile and oxygen as external oxidant, starts with the formation of an alkynylapalladium species from the reaction between the substrate triple bond and PdI_2, with the amine acting as a base (Scheme 1). After CO insertion and nucleophilic displacement by the amine (now acting as nucleophile), an alkynylamide intermediate is formed, from which the final product is produced by in situ intramolecular conjugate addition (Scheme 1; in this and in the following Schemes anionic palladium ligands are omitted for clarity)



Scheme 1. PdI_2/KI-catalyzed sequential oxidative aminocarbonylation of terminal trible bond followed by intramolecular conjugate addition leading to heter- or carbocyclic derivatives (YH = nucleophilic group)

In this paper, this kind of chemistry has been applied to the direct carbonylative synthesis of *N*,*N*-dialkyl-2-(1-alkyl-1*H*-benzo[*d*]imidazo[1,2-*a*]imidazol-2-yl)acetamides **3**, starting from *N*-substituted-1-(prop-2-yn-1-yl)-1*H*-benzo[*d*]imidazol-2-amines **1** (readily available by propargylation of 1*H*-benzo[*d*]imidazole-2-amines)[6] and amines **2**. According to Scheme 2, heterocyclization of the 2-alkynylamide intermediate **I** by intramolecular conjugate addition of the amino group at C-2 to the triple bond followed by double bond isomerization would afford the desired products **3**.

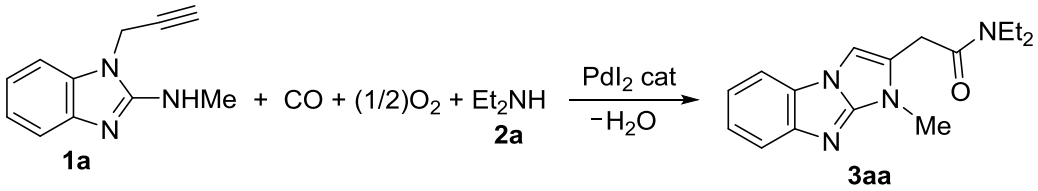


Scheme 2. *Work hypothesis:* PdI_2/KI-catalyzed sequential oxidative aminocarbonylation-conjugate addition-isomerization leading to *N*,*N*-dialkyl-2-(1-alkyl-1*H*-benzo[*d*]imidazo[1,2-*a*]imidazol-2-yl)acetamides **3**, starting from *N*-substituted-1-(prop-2-yn-1-yl)-1*H*-benzo[*d*]imidazol-2-amines **1**

Initial studies were focused on the reaction of *N*-methyl-1-(prop-2-yn-1-yl)-1*H*-benzo[*d*]imidazol-2-amine **1a**, carried out in the presence of PdI_2 (0.33 mol %), KI (0.33 equiv), Et_2NH **2a** (5 equiv), CO (16 atm) and air (4 atm).[7] After 6 h, according to our work hypothesis, analysis of the reaction mixture revealed the formation of *N*,*N*-diethyl-2-(1-methyl-1*H*-benzo[*d*]imidazo[1,2-*a*]imidazol-2-yl)acetamide **3aa**, which was isolated in

75% yield based on starting **1a**, at 85% substrate conversion (Table 1, entry 1). Although this yield was already quite satisfactory, an optimization study on reactions conditions was carried out; the results obtained are shown in Table 1. As can be seen from Table 1, the best conditions with respect to **3aa** yield corresponded to those reported in entry 14, that are: PdI_2:KI:**1a**:**2a** molar ratio = 1:100:300:900, MeCN as the solvent at 100 °C for 24 h under 20 atm (at 25 °C) of a 4:1 CO-air mixture. In fact, under these optimized conditions, the **3aa** yield was practically quantitative (97% by GLC, 95% isolated).

Table 1. PdI_2-Catalyzed Oxidative Aminocarbonylation-Heterocyclization-Isomerization of *N*-methyl-1-(Prop-2-yn-1-yl)-1*H*-benzo[*d*]imidazol-2-amine 1a Under Different Conditions[a].



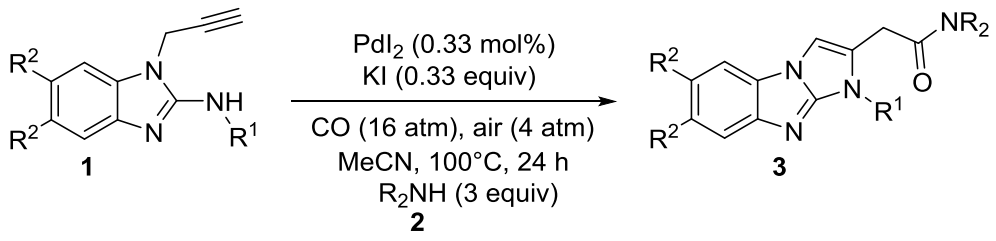
Entry	Solvent	PdI_2:KI:**1a**:**2a** molar ratio	T (°C)	t (h)	Conversion of **1a**[b] (%)	Yield of **3a**a[c] (%)
1	MeCN	1:100:300:1500	100	6	85 (76)	78 (75)
2	DME	1:100:300:1500	100	6	69	67
3	dioxane	1:100:300:1500	100	6	63	60
4	MeOH	1:100:300:1500	100	6	55	52
5	MeCN	1:50:300:1500	100	6	72	36
6	MeCN	1:300:300:15000	100	6	81	74
7	MeCN	1:100:300:300	100	6	65	39
8	CH_3CN	1:100:300:600	100	6	84	76
9	MeCN	1:100:300:900	100	6	86	83
10	MeCN	1:100:300:1500	80	6	60	56
11	MeCN	1:100:500:2500	100	6	64	58
12	MeCN	1:100:300:900	100	6	86	82

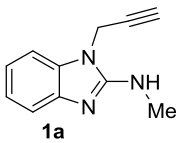
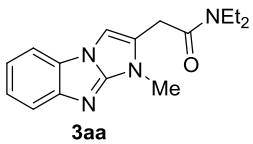
13	MeCN	1:100:300:900	100	15	95	93
14	MeCN	1:100:300:900	100	24	100	97 (95)

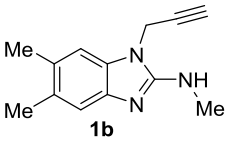
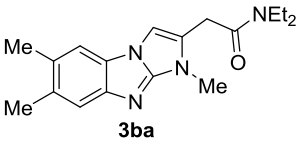
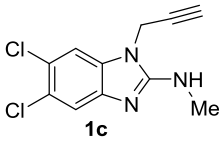
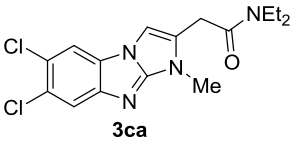
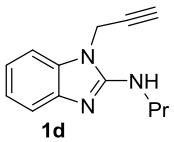
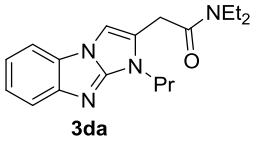
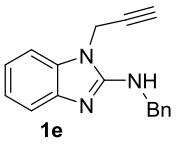
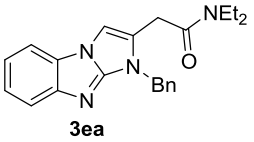
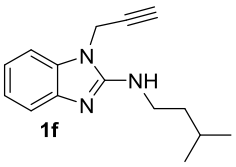
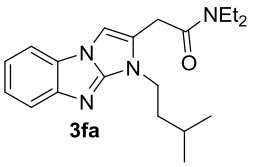
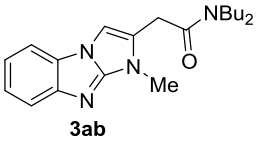
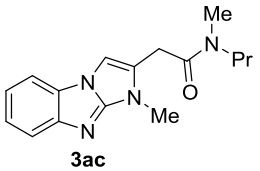
[a] Unless otherwise noted, all reactions were carried out with a substrate concentration of 0.1 mmol of **1a** per mL of solvent under 20 atm (at 25 °C) of a 4:1 mixture of CO-air. [b] GLC conversion (isolated conversio) *b*ased on starting **1a**. [c] GLC yields (isolated yield) *b*ased on starting **1a**.

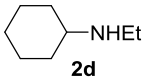
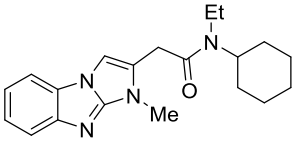
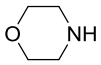
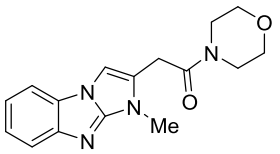
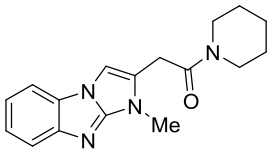
Under the optimized conditions, other differently substituted substrates, bearing electron-releasing or electron-withdrawing groups on the benzene ring, were smoothly converted into the corresponding benzimidazoimidazole derivatives , as shown by the results reported in Table 2, entries 2 (**1b**, R^2 = Me; **3ba** yield 78%) and 3 (**1c**, R^2 = Cl; **3ca** yield 79%). Good product yields were also observed in the case of *N*-substituted-1-(prop-2-yn-1-yl)-1*H*-benzo[*d*]imidazol-2-amines bearing an alkyl substituent on the amino group at C-2 different from methyl, as shown in Table 2, entries 4 (**1d**, R^1 = propyl; **3da** yield 78%), 5 (**1e**, R^1 = benzyl, **3ea** yield 64%), and 6 (**1f**, R^1 = isopentyl, **3fa** yield 94%). On the other hand, the use of different nucleophilic secondary amines, such as dibutylamine **2b** (Table 2, entry 7; **3ab** yield 74%), *N*-methylpropylamine **2c** (Table 2, entry 8; **3ac** yield 96%), *N*-ethylcyclohexylamine (Table 2, entry 9; **3ad** yield 86%), morpholine (Table 2, entry 10; **3ae** yield 76%), and piperidine (Table 2, entry 11; 3af yield 93%), also led to excellent results.

Table 2. Synthesis of *N*,*N*-dialkyl-2-(1-alkyl-1*H*-benzo[*d*]imidazo[1,2-*a*]imidazol-2-yl)acetamides 3 by PdI_2-Catalyzed Oxidative Aminocarbonylation-Heterocyclization-Isomerization of (1-Prop-2-ynyl-1*H*-benzimidazol-2-yl)amines 1[a]



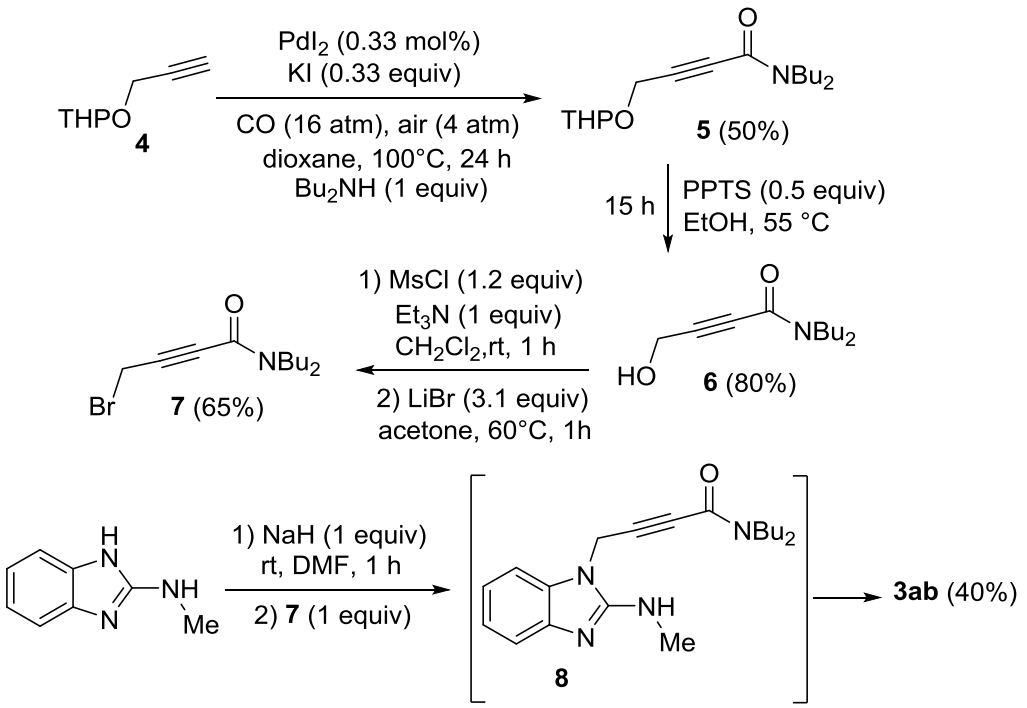
Entry	**1**	**2**	**3**	Yield of **3**[b] (%)	TON[c]
1	 **1a**	Et_2NH **2a**	 **3aa**	95	285

2	 **1b**	**2a**	 **3ba**	78	234
3	 **1c**	**2a**	 **3ca**	79	237
4	 **1d**	**2a**	 **3da**	78	234
5	 **1e**	**2a**	 **3ea**	64	192
6	 **1f**	**2a**	 **3fa**	94	282
7[d]	**1a**	Bu_2NH **2b**	 **3ab**	74	222
8	**1a**	PrNHMe **2c**	 **3ac**	96	288

9	**1a**	 **2d**	 **3ad**	96	288
10	**1a**	 **2e**	 **3ae**	76	228
11	**1a**	 **2f**	 **3af**	93	279

[a]Unless otherwise noted, all reactions were carried out in MeCN (0.1 mmol of **1** per mmol of solvent) at 100 °C for 24 h under 20 atm (at 25 °C) of a 4:1 mixture of CO-air, in the presence of the amine **2** (3 equiv), PdI_2 (0.33 mol%), and KI (0.33 equiv). [b] Isolated yield based on starting **1**. [d] TON = turnover number (mol of product 3 per mole of palladium) [d] Reaction time was 39 h.

As shown in Scheme 2, the key step in the formation of **3** are the PdI_2-catalyzed oxidative monoaminocarbonylation of the terminal triple bond to give 2-ynamide intermediate **I** and the subsequent cyclization by intramolecular conjugate addition. Accordingly, a substrate bearing an internal triple bond, such as 1-(but-2-yn-1-yl)-*N*-methyl-1*H*-benzo[*d*]imidazol-2-amine **1g**, was unreactive under the reaction conditions. To further corroborate the mechanistic hypothesis shown in Scheme 2, we tried to synthesize the 2-ynamide compound **8** in order to assess its possible conversion into the corresponding benzimidazoimidazole **3ab**. Thus, THP-protected propargyl alcohol **4** was subjected to oxidative monoaminocarbonylation conditions[8] to give the corresponding *N*,*N*-dibutyl-4-hydroxybut-2-ynamide **5**, which was easily converted into 4-bromo-N,N-dibutylbut-2-ynamide **7** by deprotection to give **6**, mesylation, and nucleophilic substitution with LiBr (Scheme 3). When **7** was allowed to react with *N*-methyl-1*H*-benzo[*d*]imidazol-2-amine, **3ab** was directly obtained by in situ cyclization of the *N*,*N*-dibutyl-4-(2-(methylamino)-1*H*-benzo[d]imidazol-1-yl)but-2-ynamide intermediate **8**, in perfect agreement with our mechanistic hypothesis.



Scheme 3. Formation of benzimidazoimidazoles **3ab** by the reaction between *N*-methyl-1*H*-benzo[*d*]imidazol-2-amine and 4-bromo-*N*,*N*-dibutylbut-2-ynamide **7**.

In conclusion, we have reported a multicomponent approach to the direct synthesis of functionalized benzimidazoimidazole derivatives, that are, *N*,*N*-dialkyl-2-(1-alkyl-1*H*-benzo[*d*]imidazo[1,2-*a*]imidazol-2-yl)acetamides **3**, starting from readily available *N*-substituted-1-(prop-2-yn-1-yl)-1*H*-benzo[*d*]imidazol-2-amines **1** and nucleophilic secondary amines **2**, by a sequential PdI_2/KI-catalyzed oxidative aminocarbonylation-intramolecular conjugate addition-isomerization process. Reactions were carried out under relatively mild conditions (100 °C under 20 atm of a 4:1 mixture of CO-air), and led to the selective formation of polyheterocycles **3** starting from differently substituted substrates **1** and different amines **2**, with good to excellent isolated yields (64-96%) and high turnover numbers (192-288 mol of product per mol of palladium employed). Our method provides a new convenient entry to an important class of polyheterocycles, with important potential pharmacological properties.

Experimental Section

General Experimental Methods. Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded at 25 °C in $CDCl_3$ or DMSO-d_6 or CD_3OD at 300 or 500 MHz and 75 or 125 MHz, respectively, with Me_4Si as internal standard. Chemical shifts (δ) and coupling constants (J) are given in ppm and in Hz, respectively. IR spectra were taken with an FT-IR spectrometer. Mass spectra were obtained using a GC-MS apparatus at 70 eV ionization voltage Microanalyses were carried out at our analytical laboratory. All reactions were analyzed by TLC on silica gel 60 F_{254} or on neutral alumina and by GLC using a gas chromatograph and capillary columns with polymethylsilicone + 5% phenylsilicone as the stationary phase or

using a gas chromatograph and a capillary columns with diethyl tertbutylsilyl-β-cyclodextrine as the stationary phase. Column chromatography was performed on silica gel 60 (70-230 mesh). Evaporation refers to the removal of solvent under reduced pressure.

Substrates **1a-f** were prepared as we already reported.[6] Substrate **1g** was prepared in as similar way, as described below. All other materials were commercially available and were used without further purification.

Preparation of 1-(But-2-yn-1-yl)-*N*-methyl-1*H*-benzo[*d*]imidazol-2-amine 1g

To a cooled (0°C) solution of *N*-methyl-1*H*-benzo[*d*]imidazol-2-amine[6] (2.00 g, 13.6 mmol) in anhydrous DMF (24 mL), was added portionwise, under nitrogen, sodium hydride (95%, 13.6 mmol, 344 mg). The mixture was then stirred at room temperature for 1 h. 1-Bromo-2-butyne (2.0 g, 15.0 mmol) was added and stirring continued for 15 h. Water (100 mL) and chloroform (100 mL) were added, and phases were separated. The aqueous phase was washed with chloroform (2×50 mL). The collected organic phases were finally washed with brine (50 mL) and dried over sodium sulfate. After filtration and evaporation of the solvent, the crude product was purified by column chromatography on silica gel using 7:3 $CHCl_3$-acetone as eluent. Yield: 1.73 g, starting from 2.00 g *N*-methyl-1*H*-benzo[*d*]imidazol-2-amine (64%); colorless solid; mp = 173-176 °C. IR (KBr): ν = 2226 (vw), 1620 (m), 1603 (m), 1574 (s), 1466 (m), 1454 (m), 1416 (m), 1386 (w), 1344 (w), 1283 (w), 1260 (w), 1238 (m), 1084 (w), 1015 (w), 731 (s) cm^{-1}. ^{1}H NMR (300 MHz, CD_3OD): δ = 7.32-7.25 (m, 1 H, aromatic), 7.17-7.10 (m, 1 H, aromatic), 7.08-6.95 (m, 2 H, aromatic), 4.64 (q, *J* = 2.3, 2 H, $CH_2C{\equiv}$), 3.02 (s, 3 H, NCH_3), 1.74 (t, *J* = 2.3, 3 H, $\equiv CCH_3$). (*Note:* the NH signal was too broad to be detected). ^{13}C NMR (75 MHz, CD_3OD): δ = 156.7, 143.2, 135.3, 122.4, 120.8, 116.3, 108.9, 81.8, 73.5, 32.7, 30.0, 2.9. GC-MS: *m/z* = 199 (M^+, 100), 198 (36), 184 (16), 169 (3), 157 (3), 146 (93), 129 (12), 119 (45), 118 (41), 102 (4), 92 (16), 90 (17), 77 (12). Anal. calcd for $C_{12}H_{13}N_3$ (199.26): C, 72.33; H, 6.58; N, 21.09; found C, 72.48; H, 6.56; N, 21.02.

General Procedure for the Synthesis of 2-(1-Alkyl-1*H*-benzo[*d*]imidazo[1,2-*a*]imidazol-2-yl)acetamides 3

A 250 mL stainless steel autoclave was charged in the presence of air with PdI_2 (1.1 mg, 3.05×10^{-3} mmol), KI (50.0 mg, 0.301 mmol), anhydrous CH_3CN (9.2 mL), (1-prop-2-ynyl-1*H*-benzoimidazol-2-yl)amine **1** (0.92 mmol) [**1a**: 170 mg; 1**b**: 196 mg; **1c**: 234 mg; 1**d**: 196 mg; **1e**: 240 mg; **1f**: 222 mg], and amine **2** (2.76 mmol) [**2a**: 202 mg; **2b**: 356 mg; **2c**: 240 mg; **2d**: 235 mg; **2e**: 351 mg; **2f**: 202mg]. The autoclave was sealed and, while the mixture was stirred, the autoclave was pressurized with CO (16 atm) and air (up to 20 atm). After being stirred at 100 °C for 24-39 h (see Table 2), the autoclave was cooled, degassed and opened. After evaporation of the solvent, products **3** were purified by column chromatography on silica gel using 7:3 $CHCl_3$-acetone (**3aa**, **3ca**, **3da**, **3ea**, **3fa**, **3ac**, **3ad**, **3ae**, **3af**) or 9:1 $CHCl_3$-acetone (**3ba**) or 8:2 hexane - acetone (**3ab**) as eluent.

*N,N-diethyl-2-(1-methyl-1H-benzo[d]imidazo[1,2-a]imidazol-2-yl)acetamide (**3aa**).* Yield: 249 mg, starting from 170 mg of **1a** (95%). Colorless solid, mp: 137 – 139°C; IR (KBr): ν = 1638 (s), 1587 (s), 1563 (s), 1444 (s), 980 (m), 949 (m), 926 (m), 910 (m), 847 (m), 793 (m), 706 (s), 652 (m) cm^{-1}; ^{1}H-NMR (300 MHz, CD_3OD): δ =7.59-7.51 (m, 2 H, aromatic), 7.27 (s, br, 1 H, =CH), 7.26-7.20 (m, 1 H, aromatic), 7.11-7.04 (m, 1 H, aromatic), 3.64 (d, br, *J* = 0.5, 2 H, CH_2CO), 3.47 (s, 3 H, NCH_3), 3.46-3.33 (m, 4 H, 2 CH_2CH_3), 1.24 (t, *J* = 7.2, 3 H, CH_2CH_3), 1.11 (t, *J* = 7.1, 3 H, CH_2CH_3); ^{13}C NMR (75 MHz, CD_3OD): δ = 169.7, 153.0, 147.2, 128.8, 128.5, 123.8, 119.6, 118.0, 111.3, 105.2, 43.6, 42.0, 30.4, 29.8, 14.5, 13.2; GC/MS = 284 (M^+, 99), 211 (26), 184 (93), 169 (7), 129 (12), 100 (100), 72 (59); anal. calcd for $C_{16}H_{20}N_4O$ (284.36): C , 67.58; H, 7.09, N, 19.70; found C, 67.44, H, 7.11, N, 19.76.

*N,N-diethyl-2-(1,6,7-trimethyl-1H-benzo[d]imidazo[1,2-a]imidazol-2-yl)acetamide (**3ba**).* Yield: 224 mg, starting from 196 mg of **1b** (78%). Yellow solid, mp: 140-142°C; IR (KBr): ν = 1636 (s), 1589 (s), 1558 (s), 1385

(m), 1323 (m), 1217 (m), 1155 (m), 1088 (w), 1001 (w), 853 (s), 845 (m), 729 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.37 (s, 1 H, aromatic), 7.27 (s, 1 H, aromatic), 7.20 (s, 1 H, =CH), 3.77 (s, br, 2 H, CH_2CO), 3.65 (s, 3 H, NCH_3), 3.47-3.38 (m, 4 H, 2 CH_2CH$_3$), 2.343 (s, 3 H, CH_3 on aromatic ring), 2.337 (s, 3 H, CH_3 on aromatic ring), 1.27 (t, *J* = 7.3, 3 H, CH$_2$CH_3), 1.15 (t, *J* = 7.3, 3 H, CH_2CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.9, 149.3, 141.3, 132.3, 128.4, 127.3, 124.8, 117.0, 110.8, 104.5, 42.6, 40.9, 30.7, 30.3, 20.4, 20.2, 14.5, 13.0; GC/MS = 312 (M^+, 62), 297 (2), 239 (18), 212 (100), 197 (6), 157 (5), 142 (2), 100 (37), 91 (2); anal. calcd for $C_{18}H_{24}N_4O$ (312.42): C, 69.20; H, 7.74; N 17.93; found C, 69.10; H, 7.75; N 17.94.

*2-(6,7-Dichloro-1-methyl-1H-benzo[d]imidazo[1,2-a]imidazol-2-yl)-N,N-diethylacetamide (**3ca**).* Yield: 257 mg, starting from 234 mg of **1c** (79%). Yellow solid, mp: 155 - 160°C; IR (KBr): v = 1655 (s), 1618 (s), 1591 (s), 1555 (s), 1460 (s), 1406 (m), 1267 (m), 1088 (m), 851 (m), 826 (w) cm^{-1}; ^1H NMR (300 MHz, CD_3OD) δ = 7.78 (s, 1 H, aromatic), 7.55 (s, 1 H, aromatic), 7.39 (s, 1 H, =CH), 3.91 (s, 2 H, CH_2CO), 3.55 (s, 3 H, NCH_3), 3.54 (q, *J* = 7.1, 2 H, NCH_2CH$_3$), 3.43 (q, *J* = 7.1, 2 H, NCH_2CH$_3$), 1.31 (t, *J* = 7.2, 3 H, CH$_2$CH_3), 1.16 (t, *J* = 7.1, 3 H, CH$_2$CH_3); ^{13}C NMR (75 MHz, CD_3OD) δ = 169.6, 154.0, 146.5, 129.9, 127.6, 127.2, 122.5, 118.8, 113.0, 105.8, 43.8, 42.0, 30.6, 30.1, 14.5, 13.3; GC/MS = 354 [(M +2)$^+$, 9], 353 [(M+1)$^+$, 3], 352 (M^+, 17), 252 (13), 217 (5), 189 (3), 100 (100); anal. calcd for $C_{16}H_{18}Cl_2N_4O$ (353.25): C, 54.40; H, 5.14; Cl, 20.07; N, 15.86; found C 54.45, H, 5.13; Cl, 20.09; N, 15.84; S, 9.59.

*N,N-diethyl-2-(1-propyl-1H-benzo[d]imidazo[1,2-a]imidazol-2-yl)acetamide (**3da**).* Yield: 225 mg, starting from 196 mg of **1d** (78%). Yellow solid, mp: 98-99°C. IR (KBr): v = 1636 (s), 1586 (w), 1560 (m), 1431 (m), 1396 (m), 1358 (w), 1256 (m), 1233 (m), 1132 (m), 760 (m), 745 (w) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.72-7.64 (m, 1 H, aromatic), 7.53-7.46 (m, 1 H, aromatic), 7.31-7.20 (m, 1 H, aromatic), 7.15-7.04 (m, 2 H, 1 H aromatic + =CH), 4.05-3.95 (m, 2 H, NCH_2CH$_2$CH$_3$), 3.69 (d, *J* = 1.0, 2 H, CH_2CO), 3.50-3.35 (m, 4 H, 2 NCH_2CH$_3$), 1.92 (hexuplet, *J* = 7.5, 2 H, NCH$_2$CH_2CH$_3$), 1.23 (t, *J* = 7.2, 3 H, Me), 1.17 (t, *J* = 7.1, 3 H, Me), 0,98 (t, *J* = 7.5, 3 H, Me); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.9, 151.9, 146.9, 127.3, 126.2, 122.5, 118.1, 118.0, 109.7, 103.4, 45.4, 42.6, 40.9, 30.6, 22.6, 14.5, 13.0, 11.2; GC/MS = 312 (M^+, 65), 297 (6), 283 (5), 269 (4), 255 (2), 240 (14), 212 (48), 198 (30), 185 (18), 171 (56), 157 (3), 144 (15), 129 (21), 100 (87), 72 (100); anal. calcd for $C_{18}H_{24}N_4O$ (312.42): C, 69.20; H, 7.74; N 17.93; found C, 69.35; H, 7.72; N 17.90.

*2-(1-Benzyl-1H-benzo[d]imidazo[1,2-a]imidazol-2-yl)-N,N-diethylacetamide (**3ea**).* Yield: 212 mg, starting from 240 mg of **1e** (64%). Yellow solid, mp: 57-59°C; IR (film): v = 1643 (s), 1589 (m), 1566 (m), 1470 (w), 1454 (m), 1238 (m), 1136 (m), 743 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.69 (d, br, *J* = 8.1, 1 H, aromatic), 7.51 (d, br, *J* = 7.9, 1 H, aromatic), 7.32–7.15 (m, 7 H, 6 H aromatic + =CH), 7.13-7.05 (m, 1 H, aromatic), 5.36 (s, 2 H, CH_2Ph), 3.45 (s, br, 2 H, CH_2CO), 3.36 (q, *J* = 7.1, 2 H, NCH_2), 3.09 (q, *J* = 7.2, 2 H, NCH_2), 1.13 (t, *J* = 7.1, 3 H, Me), 0.99 (t, *J* = 7.1, 3 H, Me); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.8, 152.5, 146.8, 136.5, 128.9, 127.9, 127.4, 126.9, 126.4, 122.5, 118.2, 118.0, 109.8, 104.1, 47.1, 42.4, 40.7, 30.5, 14.1, 13.0; GC/MS = 360 (M^+, 55), 287 (27), 260 (39), 246 (3), 198 (13), 170 (32), 129 (19), 100 (44), 91 (100), 72 (59); anal. calcd for $C_{22}H_{24}N_4O$ (360.46): C, 73.31; H, 6.71; N 15.54; found C, 73.45; H, 6.70; N 15.51.

N,N-diethyl-2-(1-isopentyl-1H-benzo[d]imidazo[1,2-a]imidazol-2-yl)acetamide (***3fa***). Yield: 294 mg, starting from 222 mg of **1f** (94%). Colorless solid, mp: 52-54°C; IR (film): v = 1634 (s), 1586 (m), 1562 (m), 1557 (m), 1454 (m), 1435 (m), 1381 (m), 1365 (w), 1256 (m), 1229 (m), 1136 (m), 1098 (w), 797 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.65 (d, br, *J* = 7.9, 1 H, aromatic), 7.45 (d, br, *J* = 7.9, 1 H, aromatic), 7.25-7.17 (m, 1 H, aromatic), 7.07-6.99 (m, 1 H, aromatic), 7.05 (s, 1 H, =CH), 4.03-3.94 (m, 2 H, NCH_2), 3.61 (s, br, 2 H CH_2CO), 3.45-3.29 (m, 4 H, 2 NCH_2CH$_3$), 1.78-1.57 (m, 3 H, NCH$_2$CH_2CH), 1.19 (t, *J* = 7.1, 3 H, NCH$_2$CH_3), 1.13 (t, *J* = 7.1, 3 H, NCH$_2$CH_3), 0.94 [d, *J* = 6.4, 6 H, CH(CH_3)$_2$]; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.8, 151.9, 147.0, 127.3, 126.0, 122.4, 118.0, 117.9, 109.7, 103.4, 42.5, 42.3, 40.8, 37.9, 30.5, 26.1, 22.5, 14.5, 13.0; GC/MS = 340 (M^+, 100), 325 (56), 311 (5), 297 (5), 284 (9), 269 (26), 255 (11), 241 (25), 240 (28), 226 (20), 212 (13), 198 (18), 197 (17), 185 (97), 184 (46), 170 (44), 138 (18), 137 (18), 129 (10), 100 (24), 72 (34); anal. calcd for

$C_{20}H_{28}N_4O$ (340.47): C, 70.56; H, 8.29; N 16.46; found C, 70.49; H, 8.31; N 16.47.

*N,N-dibutyl-2-(1-methyl-1H-benzo[d]imidazo[1,2-a]imidazol-2-yl)acetamide (**3ab**).*Yield: 232 mg, starting from 170 mg of **1a** (74%). Yellow solid, mp: 60-62°C; IR (KBr): v = 1649 (s), 1591 (m), 1566 (m), 1344 (m), 1321 (m), 1281 (w), 1238 (m), 1140 (m), 924 (w), 858 (m), 827 (m), 738 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 7.68-7.62 (m, 1 H, aromatic), 7.48-7.43 (m, 1 H, aromatic), 7.28-7.21 (m, 1 H, aromatic), 7.11-7.02 (m, 1 H, aromatic), 7.03 (s, br, 1 H, =CH), 3.58 (s, 3 H, NCH_3), 3.53 (d, br, *J* = 0.6, 2 H, CH_2CO), 3.37-3.23 (m, 4 H, 2 NCH_2), 1.65-1.45 (m, 4 H, 2 NCH_2CH_2), 1.45-1.24 (m, 4 H, 2 CH_2CH_3), 0.98 (t, *J* = 7.3, 3 H, Me), 0.92 (t, *J* = 7.3, 3 H, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 167.2, 152.1, 146.7, 127.4, 126.6, 122.4, 118.0, 117.8, 109.7, 103.3, 48.1, 46.2, 31.2, 30.1, 29.8, 29.69, 29.58, 20.2, 20.1, 13.8; GC/MS = 340 (M^+, 67), 297 (2), 211 (25), 184 (48), 156 (30), 129 (7), 100 (33), 90 (3), 57 (100); anal. calcd for $C_{20}H_{28}N_4O$ (340.47): C, 70.56; H, 8.29; N 16.46; found C, 70.63; H, 8.30; N 16.41.

*N-methyl-2-(1-methyl-1H-benzo[d]imidazo[1,2-a]imidazol-2-yl)-N-propylacetamide (**3ac**).* (Mixture of diastereoisomers A+B, deriving from hindered rotation around the (CO)-N amide bond; A/B ca. 1.5, by ^1H NMR). Yield: 251 mg, starting from 170 mg of **1a** (96%). Colorless solid, mp: 67-70°C; IR (KBr): v = 1643 (s), 1589 (w), 1566 (w), 1470 (m), 1454 (m), 1402 (w), 1238 (m), 1136 (m), 800 (m) cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ = 7.77-7.66 [m, 1 H (A) + 1 H (B), aromatic], 7.56 [s, br, 1 H (A) + 1 H (B), =CH], 7.52-7.43 [m, 1 H (A) + 1 H (B), aromatic], 7.23-7.12 [m, 1 H (A) + 1 H (B), aromatic], 7.08-6.96 [m, 1 H (A) + 1 H (B), aromatic], 3.93 [s, br, 2 H (A) + 2 H (B), CH_2CO], 3.60–3.22 [m, 2 H (A) + 2 H (B), NCH_2], 3.51 [s, br, 3 H (A) + 3 H (B), NCH_3], 3.08 [s, 3 H (A), $CH_3N(CO)$], 2.86 [s, 3 H (B), $CH_3N(CO)$], 1.69–1.56 [m, 2 H (B), $NCH_2CH_2CH_3$), 1.56–1.43 [m, 2 H (A), $NCH_2CH_2CH_3$], 0.92 [t, *J* = 7.1, 3 H (B), $NCH_2CH_2CH_3$], 0.83 [t, *J* = 7.1, 3 H (A), $NCH_2CH_2CH_3$]; ^{13}C NMR (125 MHz, DMSO-d_6): δ = 167.8 (A), 167.7 (B), 151.4 (A+B), 145.9 (A+B), 127.80 (B), 127.76 (A), 126.9 (A+B), 121.9 (A+B), 117.4 (B), 116.8 (A), 110.3 (A+B), 103.8 (A+B), 50.7 (B), 48.6 (A), 35.0 (A), 33.0 (B), 29.7 (B), 29.2 (A), 20.9 (B), 19.9 (A), 11.0 (A), 10.8 (B); GC/MS = 284 (M^+, 97), 212 (16), 211 (15), 184 (100), 169 (8), 155 (4), 143 (6), 129 (10), 116 (4), 100 (39), 90 (5), 77 (2); anal. calcd for $C_{16}H_{20}N_4O$ (284.36): C, 67.58; H, 7.09; N 19.70; found C, 67.69; H, 7.10; N 19.66.

*N-cyclohexyl-N-ethyl-2-(1-methyl-1H-benzo[d]imidazo[1,2-a]imidazol-2-yl)acetamide (**3ad**).* (Mixture of diastereoisomers A+B, deriving from hindered rotation around the (CO)-N amide bond; A/B ca. 1.1, by ^1H NMR). Yield: 299 mg, starting from 170 mg of **1a** (96%). Colorless solid, mp: 68-71°C; IR (film): v = 1643 (s), 1589 (w), 1564 (m), 1452 (m), 1381 (w), 1240 (m), 1132 (w), 741 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ =7.64 [d, br, *J* = 8.1, 1 H (A) + 1 H (B), aromatic], 7.44 [d, br, *J* = 7.8, 1 H (A) + 1 H (B), aromatic), 7.23 [t, br, *J* = 7.5, 1 H (A) + 1 H (B), aromatic), 7.05 [t, br, *J* = 7.5, 1 H (A) + 1 H (B), aromatic], 6.99 [s, br, 1 H (A), =CH], 6.97 [s, br, 1 H (B), =CH], 3.52 [s, br, 3 H (B), NCH_3], 3.50 [s, br, 3 H (A), NCH_3], 3.45 [s, br, 2 H (A)], 3.42 [s, br, 2 H (B), CH_2CO], 3.34–3.20 [m, 2 H (A) + 2 H (B), NCH_2CH_3], 1.94–1.04 [m, 14 H (A) + 14 H (B), cyclohexyl + NCH_2CH_3]; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.4 (B), 166.8 (A), 152.0 (A+B), 146.7 (A+B), 127.3 (A+B), 126.8 (A), 126.7 (B), 122.3 (A+B), 117.9 (A+B), 117.6 (A+B), 109.8 (A+B), 103.2 (A), 103.1 (B), 57.6 (A+B), 54.5 (A+B), 38.4 (B), 37.0 (A), 31.7 (A+B), 30.8 (A+B), 30.5 (A), 30.3 (B), 29.5 (A+B), 25.9 (A), 25.8 (B), 25.4 (B), 25.1 (A), 16.8 (A), 14.8 (B); GC/MS = 338 (M^+, 32), 211 (9), 184 (47), 169 (7), 154 (20), 129 (7), 116 (3), 102 (8), 83 (100), 72 (13); anal. calcd for $C_{20}H_{26}N_4O$ (338.46): C, 70.98; H, 7.74; N 16.55; found C, 70.81; H, 7.75; N 16.59.

*2-(1-Methyl-1H-benzo[d]imidazo[1,2-a]imidazol-2-yl)-1-morpholinoethan-1-one (**3ae**).* Yield: 209 mg, starting from 170 mg of **1a** (76%). Colorless solid, mp: 189-192°C; . IR (KBr): v = 1647 (s), 1587 (w), 1562 (m), 1420 (m), 1271 (w), 1242 (m), 1115 (m), 1038 (w), 854 (w), 741 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 7.67 (d, br, *J* = 8.0, 1 H, aromatic), 7.48 (d, *J* = 7.8, 1 H, aromatic), 7.32-7.22 (m, 1 H, aromatic), 7.13 - 7.03 (m, 1 H, 1 H aromatic), 7.04 (s, br, 1 H, =CH), 3.75–3.43 (m, 8 H, morpholine ring), 3.58 (s, 3 H, NCH_3), 3.51 (s, br, 2 H, CH_2CO); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.4, 152.2, 146.8, 127.3, 125.8, 122.6, 118.1, 117.9, 109.7, 103.3, 66.7, 66.4, 46.2, 42.3, 29.9, 29.6; GC/MS = 298 (M^+, 75), 212 (18), 211 (15), 184 (100), 169 (7), 155 (3), 143

(5), 129 (7), 114 (11), 102 (6), 70 (13); anal. calcd for $C_{16}H_{18}N_4O_2$ (298.35): C, 64.41; H, 6.08; N 18.78; found C, 64.30; H, 6.06; N 18.74.

*2-(1-Methyl-1H-benzo[d]imidazo[1,2-a]imidazol-2-yl)-1-(piperidin-1-yl)ethan-1-one (**3af**).* Yield: 254 mg, starting from 170 mg of **1a** (93%). Yellow solid, mp: 148-150°C; IR (KBr): ν = 1630 (s), 1589 (m), 1566 (m), 1456 (s), 1395 (m), 1352 (w), 1130 (s), 1016 (m), 851 (m), 820 (w), 733 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 7.67 (d, br, *J* = 8.1, 1 H, aromatic), 7.48 (d, br, *J* = 7.7, 1 H, aromatic), 7.31-7.22 (m, 1 H, aromatic), 7.13-7.04 (m, 1 H, aromatic), 7.08 (s, br, 1 H, =CH), 3.64 (s, 3 H, NCH_3), 3.63 (s, br, 2 H CH_2CO), 3.62-3.56 (m, 2 H, NCH_2), 3.49-3.44 (m, 2 H, NCH_2), 1.74-1.53 (m, 6 H, $CH_2CH_2CH_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 165.9, 152.1, 146.7, 127.3, 126.5, 122.5, 118.1, 117.9, 109.7, 103.3, 47.1, 43.3, 30.4, 29.7, 26.5, 25.5, 24.3; GC/MS = 296 (M^+, 100), 267 (1), 211 (17), 184 (98), 169 (11), 143 (8), 129 (13), 112 (97), 102 (13), 90 (7), 69 (76); anal. calcd for $C_{17}H_{20}N_4O$ (296.37): C, 68.90; H, 6.80; N 18.90; found C, 68.81; H, 6.82; N 18.96.

Preparation of *N*,*N*-dibutyl-4-[(tetrahydro-2*H*-pyran-2-yl)oxy]but-2-ynamide 5.[8]

A 250 mL stainless steel autoclave was charged in the presence of air with PdI_2 (14.9 mg, 41.4 × 10^{-3} mmol), KI (686.3 mg, 4.14 mmol), and a solution of 2-(prop-2-yn-1-yloxy)tetrahydro-2*H*-pyran (1.74 g, 12.4 mmol) and dibutylamine (1.60 g, 12.4 mmol) in anhydrous dioxane (25 mL). The autoclave was sealed and, while the mixture was stirred, the autoclave was pressurized with CO (16 atm) and air (up to 20 atm). After being stirred at 100 °C for 24 h, the autoclave was cooled, degassed and opened. After evaporation of the solvent, the crude mixture was purified by column chromatography on silica gel using as eluent 9:1 hexane- AcOEt to give *N*,*N*-dibutyl-4-[(tetrahydro-2*H*-pyran-2-yl)oxy]but-2-ynamide as a colorless oil. Yield: 1.85 g, starting from 1.74 g 2-(prop-2-yn-1-yloxy)tetrahydro-2*H*-pyran (50%). IR (film): ν = 2957 (m), 2934 (m), 2872 (w), 2241 (vw), 1630 (s), 1466 (m), 1458 (m), 1427 (w), 1377 (w), 1294 (w), 1227 (w), 1202 (w), 1121 (m), 1028 (m), 903 (w) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 4.82 (t, *J* = 3.0, 1 H, OCH), 4.41 (s, 2 H, $CH_2C{\equiv}$), 3.89-3.78 (m, 1 H, OC*H*H), 3.56-3.47 (m, 2 H, NCH_2), 3.40-3.30 (m, 2 H, NCH_2), 3.22-3.12 (m, 2 H, OCH*H*), 1.88 – 1.23 (m, 14 H, $OCH_2CH_2CH_2CH_2$ + 2 $NCH_2CH_2CH_2$), 0.96 (t, *J* = 7.3, 3 H, Me), 0.93 (t, *J* = 7.3, 3 H, Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.7, 97.0, 86.6, 79.0, 62.0, 53.9, 48.8, 44.5, 31.0, 30.2, 29.5, 25.3, 20.2, 19.9, 18.9, 13.9, 13.8. GC-MS: *m/z* = 295 (M^+, absent), 252 (10), 212 (5), 194 (10), 180 (7), 168 (15), 151 (19), 140 (13), 128 (25), 124 (12), 109 (65), 94 (13), 85 (100), 81 (26), 67 (54), 57 (49), 55 (46). Anal. calcd for $C_{17}H_{29}NO_3$ (295.42): C, 69.12; H, 9.89; N, 4.74; found C, 69.25; H, 9.88; N, 4.75.

Preparation of *N*,*N*-dibutyl-4-hydroxybut-2-ynamide 6

A mixture of *N*,*N*-dibutyl-4-[(tetrahydro-2*H*-pyran-2-yl)oxy]but-2-ynamide (1.5 g, 5.08 mmol) and PPTS (0.65 g, 2.59 mmol) in anhydrous EtOH (16 mL) was stirred under nitrogen for 15 h at 55°C. Ethanol was removed, then water (20 mL) and $CHCl_3$ (20 mL) were added and the phases were separated. The aqueous phase was extracted with $CHCl_3$ (10 mL), and the collected organic phases were dried on Na_2SO_4. After filtration and evaporation of the solvent, the crude product was purified by column chromatography on silica gel using as eluent 1:1 hexane-acetone. Yield: 0.86 g, starting from 1.5 g 2-(prop-2-yn-1-yloxy)tetrahydro-2H-pyran (80%); colorless oil. IR (KBr): ν = 3381 (m, br), 2959 (m), 2932 (m), 2872 (m), 2245 (w), 2226 (w), 1620 (s), 1464 (m), 1454 (m), 1433 (m), 1377 (w), 1296 (w), 1229 (m), 1159 (w), 1034 (m), 737 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 4.42 (s, 2 H, CH_2OH), 3.52 (t, *J* = 7.3, 2 H, NCH_2), 3.34 (t, *J* = 7.4, 2 H, NCH_2), 1.65-1.45 (m, 4 H, 2 NCH_2CH_2), 1.42-1.23 (m, 4 H, 2 CH_2CH_3), 0.95 (t, *J* = 7.6, 3 H, Me), 0.92 (t, *J* = 7.6, 3 H, Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.4, 89.8, 78.6, 50.8, 49.1, 44.8, 31.2, 29.8, 20.3, 20.0, 13.7. GC-MS: *m/z* = 211 (M^+, 1), 196 (5), 180 (3), 168 (36), 154 (4), 151 (8), 150 (8), 136 (8), 126 (65), 114 (15), 109 (6), 94 (8), 86 (51), 83 (100), 79 (12). Anal. calcd for $C_{12}H_{21}NO_2$ (211.31): C, 68.21; H, 10.02; N, 6.63; found C, 68.33; H, 10.00; N, 6.64.

Preparation of 4-Bromo-*N*,*N*-dibutylbut-2-ynamide 7

To a solution of *N*,*N*-dibutyl-4-hydroxybut-2-ynamide (0.76 g, 3.6 mmol) and NEt_3 (0.37 g, 3.66 mmol) in anhydrous CH_2Cl_2 (20 mL), mantained under nitrogen and cooled in ice, was added dropwise MsCl (0.5 g, 4.36 mmol). The solution was stirred for 1 h at room temperature and then water was added (15 mL). The phases were separated, and the organic layer was washed with HCl (2M, 10 ml) followed by brine (10 mL) and saturated $NaHCO_3$ (10 mL). After drying over Na_2SO_4 and filtration, the solvent was removed and the crude mesylate was introduced under nitrogen in a flask containing anhydrous acetone (23 mL) and LiBr (1 g, 11.5 mmol). After refluxing for 1 h, the mixture was cooled, and the precipitate was filtered off. Acetone was removed by evaporation, and water was added to the residue (20 mL). The mixture was then extracted with light petroleum (b.p. 40-60) (2 × 10 mL) and dried over Na_2SO_4. After filtration and evaporation of the solvent, the crude product was purified by column chromatography on silica gel using as eluent 9:1 hexane-AcOEt. Yield: 0.47 g, starting from 0.76 g *N*,*N*-dibutyl-4-hydroxybut-2-ynamide (65%); colorless oil. IR (KBr): ν = 2959 (m), 2932 (m), 2872 (w), 2226 (vw), 1628 (s), 1466 (m), 1427 (m), 1377 (w), 1294 (w), 1227 (m), 733 (w) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 4.03 (s, 2 H, CH_2Br), 3.53-3.46 (m, 2 H, NCH_2), 3.38-3.31 (m, 2 H, NCH_2), 1.66-1.46 (m, 4 H, 2 NCH_2CH_2), 1.44-1.24 (m, 4 H, 2 CH_2CH_3), 0.97 (t, *J* = 7.3, 3 H, CH_3), 0.92 (t, *J* = 7.3, 3 H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.2, 84.7, 79.3, 48.8, 44.6, 31.0, 29.5, 20.2, 19.9, 13.8, 12.9. GC-MS: *m/z* = 275 [$(M+2)^+$, 1], 273 (M^+, 1), 232 (32), 230 (34), 194 (69), 190 (29), 188 (29), 176 (3), 166 (5), 152 (44), 147 (36), 145 (36), 138 (8), 128 (8), 110 (7), 95 (17), 86 (100), 81 (12). Anal. calcd for $C_{12}H_{20}BrNO$ (274.20): C, 52.56; H, 7.35;Br, 29.14; N, 5.11; found C, 52.40; H, 7.36; Br, 29.17 N, 5.09.

Reaction Between 4-Bromo-*N*,*N*-dibutylbut-2-ynamide 4 and *N*-methyl-1*H*-benzo[d]imidazol-2-amine Leading to Benzimidazimidazole 3ab

To a cooled (0°C) solution of *N*-methyl-1*H*-benzo[*d*]imidazol-2-amine[6] (0.27 g, 1.83 mmol) in anhydrous DMF (2.1 mL), was added portionwise, under nitrogen, sodium hydride (95%, 1.83 mmol, 46 mg). The mixture was then stirred at room temperature for 1 h. 4-Bromo-*N*,*N*-dibutylbut-2-ynamide (0.5 g, 1.83 mmol) was added, and stirring continued for 15 h. Water (10 mL) and chloroform (10 mL) were added, and phases were separated. The aqueous phase was washed with chloroform (2×10 mL). The collected organic phases were finally washed with brine (10 mL) and dried over Na_2SO_4. After filtration, evaporation of the solvent and column chromatography on silica gel (8:2 $CHCl_3$-acetone), *N*,*N*-dibutyl-2-(1-methyl-1H-benzo[d]imidazo[1,2-a]imidazol-2-yl)acetamide **3ab** was obtained in 40 % yield (0.249 g).

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