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Aryliminophosphoranes as Key Intermediates in the One-Pot Synthesis of 1-Aryl-1,3-dihydro-2*H*-benzimidazol-2-ones from *N*-Aryl-2-nitrosoanilines and Carbon Dioxide under Mild Metal-Free Conditions

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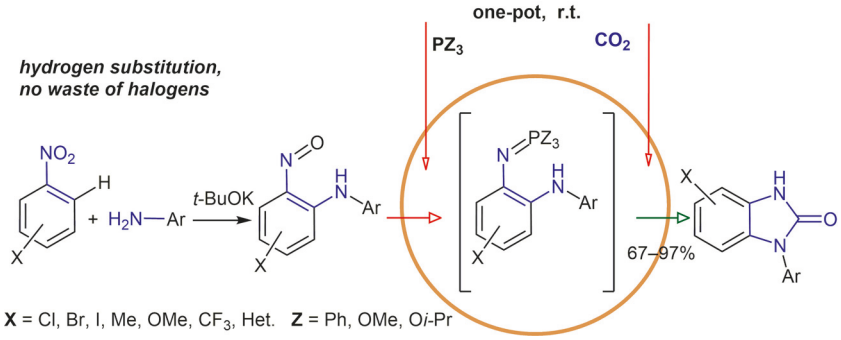

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Abstract A new and convenient protocol is presented for the synthesis of 1-arylbenzimidazol-2-ones by a one-pot reaction of *N*-aryl-2-nitrosoanilines using solid carbon dioxide as a source of the key carbonyl moiety. The metal-free process is carried out under mild conditions and is compatible with a variety of substituents. The atom economy of the synthesis of the starting nitrosoanilines, accomplished by substitution of hydrogen, makes the entire synthesis of the target compounds environmentally friendly.

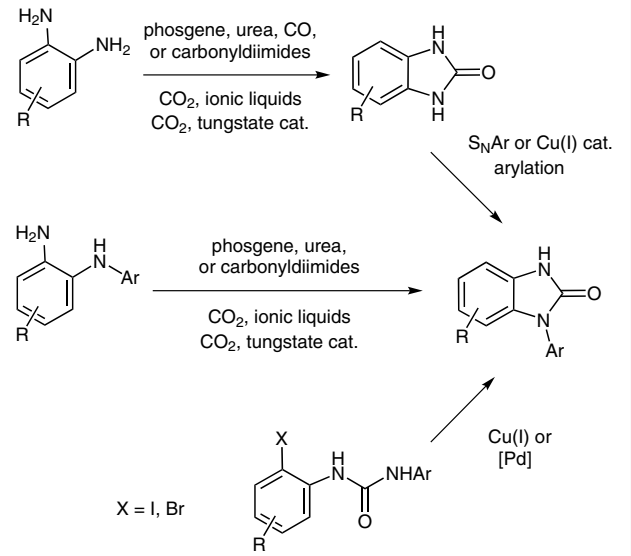
Key words annulations, heterocycles, cyclizations, nitroso compounds, fused-ring systems

In 2014, we described a simple synthesis of 2-(arylamino)aryliminophosphoranes from *N*-aryl-2-nitrosoanilines by a Cadogan-type reaction with triphenylphosphine,[1a] and we subsequently demonstrated the versatility of the products as 1,2-arylenediamine equivalents in reactions with isocyanates, nitrous acid, or carbon disulfide, leading efficiently to 2-aminobenzimidazoles,[1a] benzotriazoles[1b] and 2-thiobenzimidazoles,[2] respectively. Because *N*-aryl-2-nitrosoanilines can be obtained through substitution of hydrogen in nitroarenes by arylamines,[3] the synthesis of 2-(arylamino)aryliminophosphoranes does not require S_NAr substitution of halogens (mainly fluorine) in *o*-haloni-troarenes. When not commercially available, the latter substrates can be difficult to synthesize. Therefore, an approach that omits the introduction and subsequent wastage of halogen substituents can be considered as environmentally friendly chemistry.

The above uses of aryliminophosphoranes do not exhaust their synthetic potential. The compounds appear to be perfect reagents for the upgrading of carbon dioxide by incorporation into heterocyclic systems. Because of the low cost and lack of toxicity of the compound, the conversion of carbon dioxide into important chemicals has recently received increasing attention.[4] Incorporation of carbon dioxide into heteronucleophiles opens a door to the synthesis of five- or six-membered heterocyclic compounds, which is of vital importance from the viewpoint of the production of biologically and pharmacologically significant structures. The so-called chemical fixation of carbon dioxide has been successfully applied in the synthesis of cyclic carbonates,[5] ureas,[6] quinazoline-2,4(1*H*,3*H*)-diones,[7] 2-benzothiazolones, benzimidazoles,[8] and 2-benzimidazolones.[9,10] The last compounds were obtained from suitable *o*-arylenediamines by reaction with carbon dioxide in a 1,8-diazabicyclo[5.4.0]undec-7-ene-based ionic liquid[10] or in *N*-methylpyrrolidin-2-one promoted by a tungstate catalyst.[9] Although both processes were performed at high temperatures (120 and 140 °C, respectively), the former needed 9 MPa of carbon dioxide to be effective. Although these two methods represent a promising synthetic approach, superior to earlier procedures,[11] they have some obvious inconveniences related to the rather harsh reaction conditions and the availability of the starting materials.

Among the general methods available for the synthesis of 2-benzimidazolones, only a few have been used for the preparation of 1-aryl derivatives (Scheme 1). Intramolecular copper(I)-mediated arylation of the appropriate 1,3-diarylureas[12] or cyclization of *o*-arylenediamines with phos-

gene,[13] triphosgene (bistrichloromethyl carbonate),[14] urea,[15a,b] carbonyldiimide,[15c–e] or carbon monoxide[15f] are frequently adopted approaches.



Scheme 1 Common synthetic routes to 1-arylbenzimidazol-2-ones

Reported occasionally are nonregioselective arylation of 1,3-dihydro-2-benzimidazolones through aromatic nucleophilic substitution with activated arenes[16] and copper(I)-mediated arylation with bromo- or iodoarenes[17a] or with boronic acids.[17b,c] All these methods suffer from various inconveniences. Some require elevated temperatures and/or high pressures, whereas others use expensive or toxic and dangerous reagents.

The target 1-arylbenzimidazol-2-ones are important compounds because of their biological activity. For example, the simple structures shown in Figure 1, such as 1-phenyl-1,3-dihydro-2*H*-benzimidazol-2-one (**A**) and 6-chloro-1-phenyl-1,3-dihydro-2*H*-benzimidazol-2-one (**B**) exhibit antisecretory and antiulcer activities.[18] The trifluoromethyl derivatives **C** and **D** have well-documented BK channel-opening activity.[19] Compound **E** has not been prepared, but its bioactivity has been predicted on the basis of molecular modelling.[20] Compound **F** demonstrates evidence of ATPase inhibition.[13b]

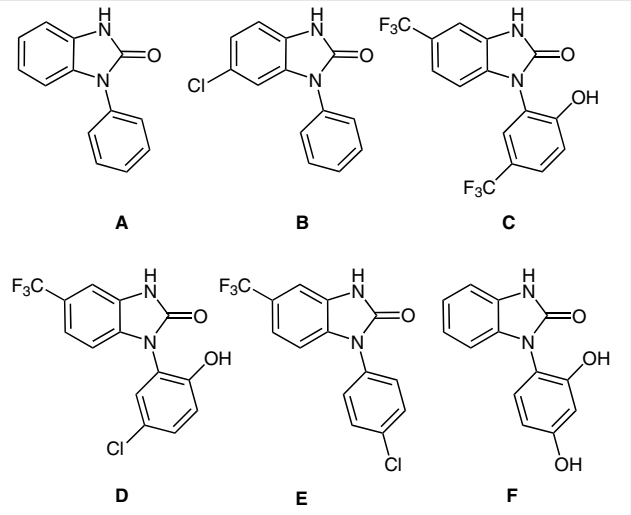
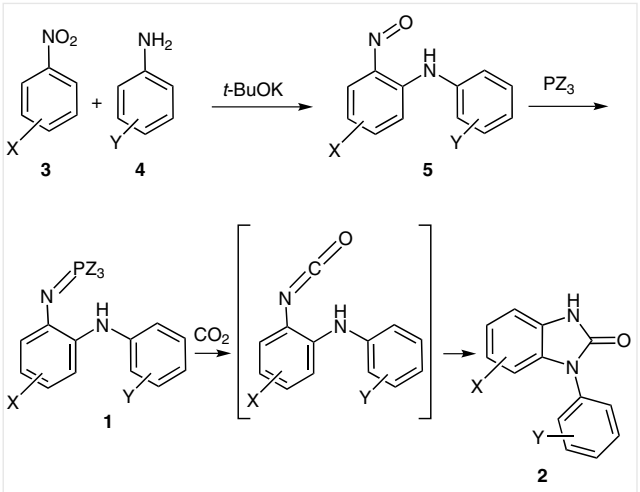


Figure 1 Biologically active 1,3-dihydro-2*H*-benzimidazol-2-ones

Here, we present a reaction of 2-(arylamino)aryliminophosphoranes with carbon dioxide to give 1-aryl-1,3-dihydro-2*H*-benzimidazol-2-ones. The process involves condensation of carbon dioxide with the iminophosphorane function,[21] followed by cyclization of the nonisolable intermediate by reaction of the isocyanate group with the arylamino group.



Scheme 2 Three-step synthetic route from nitroarenes to 1-arylbenzimidazol-2-ones through iminophosphorane intermediates

The transformation of the iminophosphoranes **1** into 1-aryl-1,3-dihydro-2*H*-benzimidazol-2-ones **2** concludes a reaction sequence (Scheme 2) in which nucleophilic substitution of hydrogen in a nitroarene **3** with arylamine **4** provides a 2-nitrosoaniline **5** that is transformed into the appropriate iminophosphorane **1**. The idea was to provide a safe and environmentally friendly protocol for the synthesis of the title compounds from simple reagents, such as nitroarenes, without wastage of halogen atoms in substitution processes, and which eliminates the need for any reduction step and avoids the use of metallic, toxic, or dangerous reagents.

To determine the optimal conditions for the reaction, we examined the reactions of iminophosphoranes **1** (Z = Ph) obtained according to the reported procedures from the corresponding 2-nitrosoanilines and triphenylphosphine. In the initial experiments, the iminophosphoranes were stirred under a balloon filled with gaseous carbon dioxide at near-atmospheric pressure. The reaction was slow and

needed several weeks to achieve completion. However, when a solution of iminophosphorane **1** was treated with solid carbon dioxide at low temperature in a sealed glass ampoule and then stirred at ambient temperature, the reaction time was significantly reduced to a few days. The pressure in the vessel, measured on one occasion during the reaction, did not exceed 2 bar (~0.2 MPa). We examined the reaction of iminophosphorane **1a** under these conditions in various solvents (Table 1).

Table 1 Solvent Effect on the Synthesis of Benzimidazolone **2a** by the Reaction of Carbon Dioxide with Iminophosphorane **1a** (X = Cl; Y = 2-I-4-Cl; Z = Ph)

Entry	Solvent	Time (d)	Yield[a] (%) of **2a**
1	THF	7	85
2	CH_2Cl_2	2	83
3	acetone	7	91
4	EtOAc	16	95
5	DMF	5	91
6	MeCN	12	63[b]
7	MeOH	3	traces
8	toluene	2	87
9	THF–H_2O[c]	15	34[d]

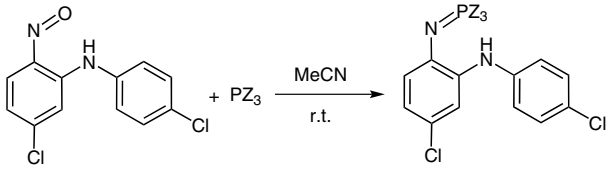
[a] Isolated yield.
[b] 30% of the substrate was recovered.
[c] NH_4HCO_3 was used instead of CO_2.
[d] Partial conversion.

The highest yield was achieved in ethyl acetate (95%), but the reaction time was relatively long (entry 4). The reaction failed to occur in methanol, and all the starting material was recovered after several days. Although the solubility of iminophosphorane **1a** in methanol was much lower than in the other tested solvents (~7 mg/mL), it should have been sufficient for the reaction to proceed; the result can therefore be attributed to the protic character of the solvent. Aprotic solvents (tetrahydrofuran, dichloromethane, acetone, *N*,*N*-dimethylformamide, or toluene), other than acetonitrile, all gave similar results. In an additional experiment (entry 9), we used ammonium bicarbonate instead of solid carbon dioxide. In this case, the reaction was not very effective, and the desired product was accompanied by several unidentified byproducts. Eventually, we chose *N*,*N*-dimethylformamide (entry 5) as the best solvent for the reaction with solid carbon dioxide. Subsequently, we prepared a number of 1-aryl-2-benzimidazolones under our optimized conditions (Figure 2).

The reaction appears to be compatible with either electron-withdrawing (CF_3) or electron-donating (OR) substituents X and Y, as well as with heterocyclic groups (4-pyridyl). All the reactions gave high or excellent yields. The reaction was also insensitive to steric hindrance by substituents, giving high yields even when bulky *ortho* groups were present in the *N*-aryl ring (e.g., **2a** or **2p**). Therefore, the reaction has general character. The results collected in Figure 2 show that it can be successfully applied in syntheses of compounds with known biological activities, as mentioned above and shown in Figure 1 (**2e** = **A**, **2b** = **B**, and **2m** = **E**). The methoxy-substituted benzimidazolones **2k**, **2l**, and **2n** are convenient direct intermediates for the synthesis of the corresponding hydroxybenzimidazolones **C**, **D**, and **F**, respectively.[14a,19]

Triphenylphosphine, used as the phosphorus(III) reagent PZ_3 in the reaction, is convenient on a small laboratory scale and permits the production of crystalline intermediate triphenyliminophosphoranes **1**; however, it suffers from several serious drawbacks. The high molecular mass of the triphenylphosphoranylidene moiety in **1**, which is lost in the subsequent reaction step, markedly reduces the atom economy of the transformation. Furthermore, the formation of large amounts of triphenylphosphine oxide byproduct, which is sparingly soluble in most solvents and difficult to remove, is not easily acceptable on a larger scale and is not environmentally friendly. To overcome these problems, we examined some other trivalent phosphorus compounds as alternatives to triphenylphosphine (Table 2).

Table 2 Formation of Iminophosphoranes **1h**–**w** by Using Selected Phosphorus(III) Reagents



5h **1**

Entry	PZ_3	Iminophosphorane	Yield[a] (%)
1	PPh_3	**1h**	90
2	$P(NMe_2)_3$	**1s**	92
3	PBu_3	**1t**	51
4	$P(OMe)_3$	**1u**	–[b]
5	$P(O\text{-}i\text{-}Pr)_3$	**1w**	–[c]

[a] Isolated yield.
[b] Multicomponent mixture.
[c] A rearrangement of **1** was observed.

In all the reactions, the conversion of the starting material and the formation of products were evident by thin-layer chromatography, but the iminophosphorane **1** could only be isolated in three cases. We assume that iminophosphoranes formed from alkyl phosphites (entries 4 and 5) are unstable and, consequently, cannot be isolated or undergo rapid rearrangement. The idea then arose of combining two steps, the formation of **1** and its reaction with car-

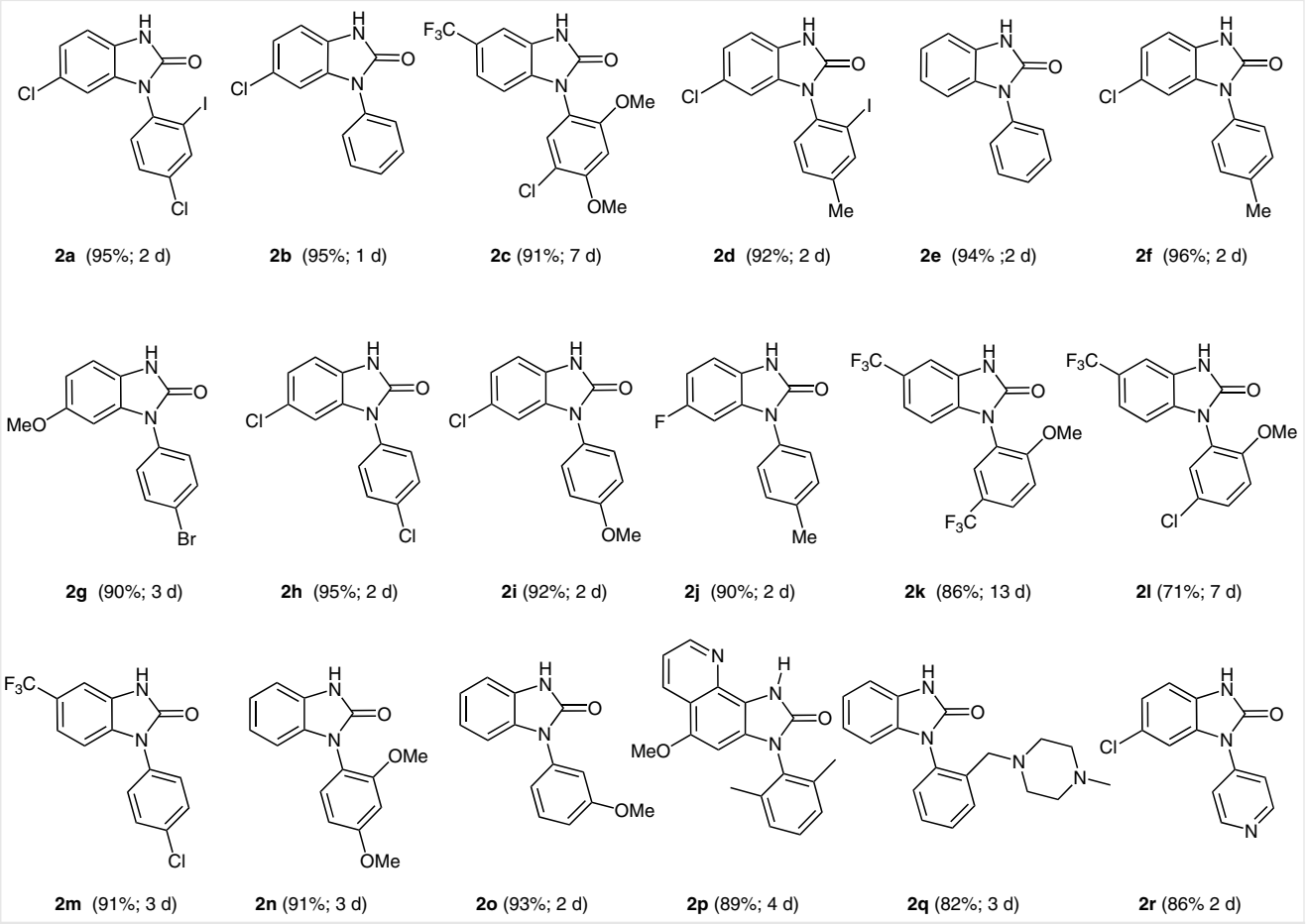


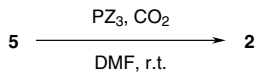
Figure 2 Synthesis of 1-arylbenzimidazol-2-ones **2a–r** by the reactions of iminophosphoranes **1a–r** with carbon dioxide

bon dioxide, in a one-pot system by mixing the phosphite with carbon dioxide and converting the 2-nitrosoaniline directly into the target 2-benzimidazolone **2**.

The high-yielding use of hexamethylphosphorous triamide (HMPT; entry 2) had to be abandoned because of the toxicity of the reagent. Trimethyl phosphite seemed to be particularly suitable because of its low molecular mass, low toxicity, and ready hydrolysis, which permits simple work-up of the reaction mixture. Although trimethyl phosphite was found to promote the reaction, the yields were generally unsatisfactory (Table 3). A significant improvement in the yield was achieved by using triisopropyl phosphite, which is a little more expensive than trimethyl phosphite but retains all its other merits. In this case, the unstable intermediate trialkyliminophosphorane was efficiently trapped by carbon dioxide, protecting the former from possible rearrangement or decomposition.

The yields of the one-pot reaction of *N*-aryl-2-nitrosoanilines with triisopropyl phosphite and carbon dioxide were generally close to the combined yields of the two-step process consisting of independent formation of **1** (Z = Ph)

Table 3 One-Pot Synthesis of 2-Benzimidazolones **2** from *N*-Aryl-2-nitrosoanilines **5**



Entry	Product[a]	Z = OMe		Z = O*i*-Pr	
		Time (d)	Yield[b] (%)	Time (d)	Yield[b] (%)
1	**2c**	–	–	4	67
2	**2d**	2	80	1	94
3	**2e**	7	59	1	95
4	**2f**	7	56	1	80
5	**2g**	7	40	3	75
6	**2h**	7	59	1	86
7	**2l**	–	–	3	87
8	**2m**	–	–	1	96
9	**2r**	8	50	7	71

[a] For structures, see Figure 2.
[b] Isolated yield.

followed by its reaction with carbon dioxide, as presented in Figure 2. However, the one-pot procedure from **5** to **2**, employing cheap lightweight reagents, omitting laborious isolation processes, and eliminating mass wastage, has considerable advantages over the two-step method, particularly in large-scale processing.

In conclusion, we have developed a new and convenient protocol for the synthesis of 1-arylbenzimidazol-2-ones by a one-pot three-component reaction of *N*-aryl-2-nitrosoanilines using solid carbon dioxide as the source of the carbonyl moiety. The high-yielding process is carried out under mild conditions, i.e. ambient temperature and a relatively low positive pressure, and is compatible with a variety of aryl substituents. Furthermore, the atom economy of the synthesis of the starting nitrosoanilines, accomplished by nucleophilic substitution of hydrogen, renders the whole synthesis environmentally friendly, competing strongly with other known procedures.

Melting points of solid compounds are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 298 K on Varian Mercury 400 MHz and 500 MHz instruments and on a Varian VNMRS 600 MHz instrument. Chemical shifts are expressed in ppm relative to TMS (^{1}H NMR at 400, 500, or 600 MHz) or to the solvent used (^{13}C NMR at 100, 125, and 150 MHz). Mass spectra were recorded on a GCT Premier spectrometer (EI, 70 eV) or on a API 365i apparatus (ESI in MeOH). IR spectra were recorded on a FT/IR Jasco 6200 spectrometer in KBr. Silica gel Merck 60 (230–400 mesh) was used for column chromatography. THF was distilled from sodium/benzophenone ketyl before use. DMF was dried over CaH_2, distilled, and stored over MS.

Common reagents and materials were purchased from commercial sources and were used as received.

Known *N*-aryl-2-nitrosoanilines **5**[1–3] and 2-(arylamino)phenyliminophosphoranes **1a**,**d**,**e**,**g**,**q**[2] and **1f**,**h**,**i**,**j**,**p**,**r**[1] were prepared as described previously. Preparations and characterizations of new 2-(arylamino)aryliminophosphoranes **1** and the starting *N*-aryl-2-nitrosoanilines **5** are described in the Supporting Information.

Benzimidazol-2-ones 2 from Iminophosphoranes 1; General Procedure

A solution of the appropriate iminophosphorane **1a**–**r** (1 mmol) in anhyd DMF (10 mL) was placed in a glass ampoule equipped with a Teflon stopcock and cooled to –65 °C. Solid CO_2 (crushed dry ice; 200 mg, 4.5 mmol) was added in one portion. The ampule was sealed and the mixture was stirred at r.t. for the time specified in Figure 2. When the reaction was complete, the mixture was poured into H_2O and extracted with EtOAc. The organic phase was dried (Na_2SO_4) and concentrated, and the residue was purified by column chromatography [silica gel, hexane–EtOAc (9:1 to 2:1)]. The yields are listed in Figure 2.

One-Pot Synthesis of Benzimidazol-2-ones 1 from *N*-Aryl-2-nitrosoarenes 5; General Procedure

A solution of the appropriate *N*-aryl-2-nitrosoaniline **5** (1 mmol) in DMF (10 mL) was placed in a glass ampoule equipped with a Teflon stopcock and cooled to –65 °C. Solid CO_2 (crushed dry ice; 200 mg, 4.5 mmol) was added in one portion, followed by addition of trimethyl or triisopropyl phosphite (3 mmol). The ampoule was sealed, and the mixture was stirred at r.t. for the time specified in Table 3. When the reaction was complete, the mixture was poured into H_2O and extracted with EtOAc. The organic phase was dried (Na_2SO_4) and concentrated, and the residue was purified by column chromatography [silica gel, hexane–EtOAc (9:1 to 2:1)]. The yields are listed in Table 3.

6-Chloro-(4-chloro-2-iodophenyl)-1,3-dihydro-2*H*-benzimidazol-2-one (2a)

White solid; yield: 383 mg (95%); mp 275–277 °C.

IR (KBr): 3169, 3078, 1711, 1573, 1492 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 6.63 (s, 1 H), 7.06–7.12 (m, 2 H), 7.56 (d, J = 8.3 Hz, 1 H), 7.67 (dd, J = 8.3, 2.2 Hz, 1 H), 8.15 (d, J = 2.2 Hz, 1 H), 11.31 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 101.1, 108.3, 110.3, 121.5, 125.1, 127.4, 129.8, 131.2, 131.6, 134.6, 135.7, 138.7, 152.7.

MS (EI): *m/z* (%) = 406 (44), 405 (10), 404 [M$^+$] (69), 279 (65), 278 (22).

HRMS (EI): *m/z* calcd for $C_{13}H_7{}^{35}Cl_2IN_2O$: 403.8980; found: 403.8979.

6-Chloro-1-phenyl-1,3-dihydro-2*H*-benzimidazol-2-one (2b)[18]

White solid; yield: 232 mg (95%); mp 241–244 °C (Lit.[18] 238–240 °C).

IR (KBr): 3182, 1719, 1596, 1505, 1482 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 6.91–6.96 (m, 1 H), 7.04–7.13 (m, 2 H), 7.42–7.62 (m, 5 H), 11.33 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 108.0, 110.3, 121.5, 125.1, 126.0, 127.4, 127.7, 129.5, 131.1, 134.0, 153.3.

MS (EI): *m/z* (%) = 246 (41), 245 (19), 244 [M$^+$] (100), 217 (11), 215 (33).

HRMS (EI): *m/z* calcd for $C_{13}H_9{}^{35}ClN_2O$: 244.0403; found: 244.0401.

1-(5-Chloro-2,4-dimethoxyphenyl)-5-(trifluoromethyl)-1,3-dihydro-2*H*-benzimidazol-2-one (2c)

White solid; yield: 338 mg (91%); mp 250–252 °C.

IR (KBr): 3129, 3043, 2977, 1714, 1605, 1584 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 3.81 (s, 3 H), 4.00 (s, 3 H), 6.77 (d, J = 8.5 Hz, 1 H), 7.00–7.04 (m, 1 H), 7.27–7.34 (m, 2 H), 7.52–7.58 (m, 1 H), 11.40 (s, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 56.3, 56.6, 98.5, 105.4 (d, J_{CF} = 4 Hz), 108.4, 111.8, 114.3, 118.1 (d, J_{CF} = 3.5 Hz), 121.9 (d, J_{CF} = 32 Hz), 124.7 (d, J_{CF} = 270 Hz), 128.6, 130.3, 134.0, 153.6, 155.4, 156.0.

MS (EI): *m/z* (%) = 374 (33), 372 [M$^+$] (100), 353 (11), 329 (10).

HRMS (EI): *m/z* calcd for $C_{16}H_{12}{}^{35}ClF_3N_2O_3$: 372.0489; found: 372.0482.

6-Chloro-1-(2-iodo-4-methylphenyl)-1,3-dihydro-2*H*-benzimidazol-2-one (2d)

White solid; yield: 352 mg (92%); mp 251–253 °C.

IR (KBr): 3145, 1703, 1496, 1477 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.38 (s, 3 H), 6.48–6.51 (m, 1 H), 7.06–7.08 (m, 2 H), 7.36–7.43 (m, 2 H), 7.90 (s, 1 H), 11.24 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 20.1, 99.5, 108.0, 110.2, 121.2, 127.4, 129.9, 130.4, 131.5, 133.8, 139.9, 141.2, 152.9 (one signal missing).

MS (EI): *m/z* (%) = 386 (23), 385 (11), 384 [M$^+$] (69), 259 (34), 257 (100).

HRMS (EI): *m/z* calcd for $C_{14}H_{10}{}^{35}ClIN_2O$: 383.9526; found: 383.9519.

1-Phenyl-1,3-dihydro-2*H*-benzimidazol-2-one (2e)[10,12d]

White solid; yield: 198 mg (94%); mp 207–208 °C [Lit.[18] 200–202 °C (benzene); Lit.[12d] 187–188 °C (hexane)].

IR (KBr): 3127, 3014, 1699, 1591, 1501, 1481 cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6): δ = 7.04–7.06 (m, 2 H), 7.08–7.11 (m, 1 H), 7.15–7.17 (m, 1 H), 7.42–7.45 (m, 1 H), 7.56–7.58 (m, 4 H), 10.68 (s, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 108.8, 110.1, 121.5, 122.3, 126.3, 127.9, 128.1, 129.3, 130.5, 134.4, 155.2.

MS (EI): *m/z* (%) = 210 [M^+] (100), 181 (34).

HRMS (EI): *m/z* calcd for $C_{13}H_{10}N_2O$: 210.0793; found: 210.0797.

6-Chloro-1-(4-tolyl)-1,3-dihydro-2*H*-benzimidazol-2-one (2f).

White solid; yield: 248 mg (96%); mp 226–229 °C.

IR (KBr): 3036, 1700, 1520, 1484 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 2.38 (s, 3 H), 6.87–6.90 (m, 1 H), 7.04–7.10 (m, 2 H), 7.33–7.41 (m, 4 H), 11.26 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 20.7, 107.9, 110.2, 121.3, 125.0, 125.9, 127.3, 129.9, 131.4, 137.2, 153.3 (one signal missing).

MS (EI): *m/z* (%) = 260 (33), 259 (19), 258 [M^+] (100), 215 (10).

HRMS (EI): *m/z* calcd for $C_{14}H_{11}{}^{35}ClN_2O$: 258.0560; found: 258.0565.

1-(4-Bromophenyl)-6-methoxy-1,3-dihydro-2*H*-benzimidazol-2-one (2g).

White solid; yield: 286 mg (90%); mp 202–204 °C.

IR (KBr): 3170, 3070, 1702, 1616, 1492, 1387 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 3.69 (s, 3 H), 6.59 (d, *J* = 2.2 Hz, 1 H), 6.66 (dd, *J* = 8.3, 2.2 Hz, 1 H), 6.97 (d, *J* = 8.3 Hz, 1 H), 7.48–7.55 (m, 2 H), 7.70–7.76 (m, 2 H), 10.97 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 55.6, 95.1, 107.7, 109.6, 119.8, 122.2, 127.8, 130.3, 132.3, 133.9, 153.4, 154.7.

MS (EI): *m/z* (%) = 320 (15), 319 (94), 318 [M^+] (24), 317 (100), 223 (10).

HRMS (EI): *m/z* calcd for $C_{14}H_{11}{}^{79}BrN_2O_2$: 318.0004; found: 318.0015.

6-Chloro-1-(4-chlorophenyl)-1,3-dihydro-2*H*-benzimidazol-2-one (2h)[18]

White solid; yield: 264 mg (95%); mp 243–245 °C [Lit.[18] 235–237 °C (aq. EtOH)].

IR (KBr): 3040, 1746, 1719, 1499, 1482 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 6.91–7.20 (m, 3 H), 7.47–7.75 (m, 4 H), 11.33 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 108.1, 110.3, 121.6, 125.1, 127.4, 127.7, 129.5, 130.8, 131.9, 132.9, 153.1.

MS (EI): *m/z* (%) = 280 (65), 279 (16), 278 [M^+] (100).

HRMS (EI): *m/z* calcd for $C_{13}H_8{}^{35}Cl_2N_2O$: 278.0014; found: 278.0021.

6-Chloro-1-(4-methoxyphenyl)-1,3-dihydro-2*H*-benzimidazol-2-one (2i)[15e,18]

White solid; yield: 252 mg (92%); mp 252–254 °C (Lit.[18] 252–253 °C).

IR (KBr): 3040, 1703, 1519, 1484, 1393 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 3.82 (s, 3 H), 6.82–6.87 (m, 1 H), 7.03–7.15 (m, 4 H), 7.39–7.46 (m, 2 H), 11.22 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 55.4, 107.7, 110.1, 114.7, 121.1, 125.0, 126.5, 127.3, 127.6, 131.7, 153.5, 158.5.

MS (EI): *m/z* (%) = 276 (33), 275 (16), 274 [M^+] (100), 261 (18).

HRMS (EI): *m/z* calcd for $C_{14}H_{11}{}^{35}ClN_2O_2$: 274.0509; found: 274.0518.

6-Fluoro-1-(4-tolyl)-1,3-dihydro-2*H*-benzimidazol-2-one (2j)

White solid; yield: 218 mg (90%); mp 253–255 °C.

IR (KBr): 3039, 3002, 1709, 1621, 1519, 1491 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 2.38 (s, 3 H), 6.74–6.79 (m, 1 H), 6.83–6.91 (m, 1 H), 7.01–7.07 (m, 1 H), 7.33–7.43 (m, 4 H), 11.13 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 20.7, 96.3 (d, J_{CF} = 29 Hz), 107.7 (d, J_{CF} = 24 Hz), 109.5 (d, J_{CF} = 10 Hz), 124.7, 125.7, 129.9, 130.8 (d, J_{CF} = 12 Hz), 131.5, 137.0, 153.7, 157.6 (d, J_{CF} = 233 Hz).

MS (EI): *m/z* (%) = 242 [M^+] (100), 241 (11), 199 (14).

HRMS (EI): *m/z* calcd for $C_{14}H_{11}FN_2O$: 242.0855; found: 242.0852.

1-[2-Methoxy-5-(trifluoromethyl)phenyl]-5-(trifluoromethyl)-1,3-dihydro-2*H*-benzimidazol-2-one (2k)[19]

White solid; yield: 323 mg (86%); mp 229–231 °C (Lit.[19] 226 °C).

IR (KBr): 3138, 1718, 1524, 1448 cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6): δ = 3.86 (s, 3 H), 6.81 (d, *J* = 8.0 Hz, 1 H), 7.29–7.38 (m, 2 H), 7.46–7.53 (m, 1 H), 7.87–7.96 (m, 2 H), 11.52 (s, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 56.8, 106.0 (d, J_{CF} = 3 Hz), 109.2, 114.0, 118.6 (d, J_{CF} = 3 Hz), 121.4 (d, J_{CF} = 39 Hz), 121.9 (J_{CF} = 32 Hz), 122.7, 124.4 (d, J_{CF} = 272 Hz), 124.8 (J_{CF} = 271 Hz), 127.7 (d, J_{CF} = 4 Hz), 128.3 (d, J_{CF} = 3 Hz), 129.2, 133.9, 153.9, 158.5.

MS (EI): *m/z* (%) = 376 [M^+] (100), 359 (22), 346 (26), 319 (38).

HRMS (EI): *m/z* calcd for $C_{16}H_{10}F_6N_2O_2$: 376.0646; found: 376.0662.

1-(5-Chloro-2-methoxyphenyl)-5-(trifluoromethyl)-1,3-dihydro-2*H*-benzimidazol-2-one (2l)[14a]

White solid; yield: 243 mg (71%); mp 225–227 °C (Lit.[14a] 135–138 °C).

IR (KBr): 3139, 3046, 1714, 1634, 1595, 1505, 1483 cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6): δ = 3.76 (s, 3 H), 6.80 (d, *J* = 8.5 Hz, 1 H), 7.29–7.35 (m, 3 H), 7.56–7.62 (m, 2 H), 11.48 (s, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 56.1, 105.5 (d, J_{CF} = 3.5 Hz), 108.7, 114.4, 118.2 (d, J_{CF} = 4 Hz), 122.0 (d, J_{CF} = 32 Hz), 122.8, 124.0, 124.7 (d, J_{CF} = 269 Hz), 128.7, 129.6, 130.1, 133.4, 153.3, 154.2.

MS (EI): *m/z* (%) = 344 (33), 343 (18), 342 [M^+] (100), 325 (19), 323 (17).

HRMS (EI): *m/z* calcd for $C_{15}H_{10}{}^{35}ClF_3N_2O_2$: 342.0383; found: 342.0393.

1-(4-Chlorophenyl)-5-(trifluoromethyl)-1,3-dihydro-2*H*-benzimidazol-2-one (2m)

White solid; yield: 284 mg (91%); mp 212–215 °C.

IR (KBr): 3139, 3038, 1730, 1636, 1498 cm^{-1}.

^1H NMR (600 MHz, DMSO-d_6): δ = 7.16 (d, *J* = 8.3 Hz, 1 H), 7.33–7.39 (m, 2 H), 7.59–7.66 (m, 4 H), 11.58 (s, 1 H).

^{13}C NMR (150 MHz, DMSO-d_6): δ = 105.6, 105.7 (d, J_{CF} = 4 Hz), 108.6, 118.3 (d, J_{CF} = 4 Hz), 122.4 (d, J_{CF} = 32 Hz), 124.6 (d, J_{CF} = 270 Hz), 127.9, 128.7, 129.5, 132.2, 132.8 (d, J_{CF} = 3 Hz), 153.2.

MS (EI): *m/z* (%) = 314 (33), 313 (16), 312 [M^+] (100), 249 (21).

HRMS (EI): *m/z* calcd for $C_{14}H_8{}^{35}ClF_3N_2O$: 312.0277; found: 312.0269.

1-(2,4-Dimethoxyphenyl)-1,3-dihydro-2*H*-benzimidazol-2-one (2n)[13b]

White solid; yield: 246 mg (91%); mp 210–213 °C.

IR (KBr): 3136, 3061, 1712, 1693, 1610, 1519 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 3.71 (s, 3 H), 3.84 (s, 3 H), 6.52 (d, *J* = 7.6 Hz, 1 H), 6.65 (dd, *J* = 8.6, 2.2 Hz, 1 H), 6.78 (d, *J* = 2.2 Hz, 1 H), 6.89–6.95 (m, 1 H), 6.96–7.05 (m, 2 H), 7.26 (d, *J* = 8.6 Hz, 1 H), 10.93 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 55.6, 55.7, 99.6, 105.3, 108.1, 108.8, 115.2, 120.6, 121.1, 128.4, 130.5, 131.5, 153.7, 156.4, 160.7.

MS (EI): *m/z* (%) = 270 [M^+] (100), 255 (21), 253 (22).

HRMS (EI): *m/z* calcd for $C_{15}H_{14}N_2O_3$: 270.1004; found: 270.1000.

1-(3-Methoxyphenyl)-1,3-dihydro-2*H*-benzimidazol-2-one (2o)

White solid; yield: 223 mg (93%); mp 136–139 °C.

IR (KBr): 3010, 1701, 1603, 1582, 1497 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 3.80 (s, 3 H), 6.95–7.15 (m, 7 H), 7.43–7.52 (m, 1 H), 11.14 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 55.4, 108.3, 109.1, 111.7, 113.1, 118.0, 120.9, 121.8, 128.4, 130.0, 130.1, 135.7, 153.1, 159.9.

MS (EI): *m/z* (%) = 240 [M^+] (100), 198 (10), 181 (13).

HRMS (EI): *m/z* calcd for $C_{14}H_{12}N_2O_2$: 240.0899; found: 240.0908.

3-(2,6-Dimethylphenyl)-5-methoxy-1,3-dihydro-2*H*-imidazo[4,5-*h*]quinolin-2-one (2p)

Yellow solid; yield: 284 mg (89%); mp >270 °C.

IR (KBr): 3000, 1694, 1633, 1597, 1523, 1489 cm^{-1}.

^1H NMR (600 MHz, F_3CCO_2D): δ = 2.10 (s, 6 H), 4.08 (s, 3 H), 6.81 (s, 1 H), 7.40 (d, *J* = 7.8 Hz, 2 H), 7.52 (t, *J* = 7.8 Hz, 1 H), 7.90–8.00 (m, 1 H), 9.03 (d, *J* = 5.4 Hz, 1 H), 9.63 (d, *J* = 8.4 Hz, 1 H) (N–H proton was not observed).

^{13}C NMR (150 MHz, F_3CCO_2D): δ = 18.2, 58.6, 95.1, 110.3, 120.5, 122.6, 127.4, 130.6, 131.8, 133.9, 138.5, 139.5, 145.4, 147.3, 157.4, 157.5.

MS (EI): *m/z* (%) = 319 [M^+] (100), 304 (34), 276 (11), 262 (10).

HRMS (EI): *m/z* calcd for $C_{19}H_{17}N_3O_2$: 319.1312; found: 319.1324.

1-{2-[(4-Methylpiperazin-1-yl)methyl]phenyl}-1,3-dihydro-2*H*-benzimidazol-2-one (2q)

White solid; yield: 264 mg (82%); mp 163–166 °C.

IR (KBr): 3062, 2679, 1703, 1619, 1499 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 1.83–2.17 (m, 11 H), 3.23 (d, *J* = 12.0 Hz, 1 H), 3.45 (d, *J* = 12.0 Hz, 1 H), 6.54 (d, *J* = 8.0 Hz, 1 H), 6.92 (t, *J* = 8.0 Hz, 1 H), 6.99–7.09 (m, 2 H), 7.34–7.57 (m, 4 H), 11.01 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 45.6, 52.5, 54.3, 58.6, 107.8, 108.8, 120.5, 121.1, 128.0, 128.6, 128.7, 129.1, 130.5, 131.5, 133.3, 136.9, 153.4.

MS (EI): *m/z* (%) = 322 [M^+] (60), 310 (33), 309 (19), 308 (100), 307 (35).

HRMS (EI): *m/z* calcd for $C_{19}H_{22}N_4O$: 322.1794; found: 322.1809.

6-Chloro-1-pyridin-4-yl-1,3-dihydro-2*H*-benzimidazol-2-one (2r)

White solid; yield: 211 mg (86%); mp 270–272 °C.

IR (KBr): 3185, 1733, 1589, 1507, 1485 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 6.99–7.39 (m, 3 H), 7.55–7.83 (m, 2 H), 8.60–8.88 (m, 2 H), 11.49 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 109.0, 110.6, 119.2, 122.4, 125.3, 127.7, 129.4, 141.7, 151.0, 152.6.

MS (EI): *m/z* (%) = 247 (39), 246 (18), 245 [M^+] (100), 216 (18).

HRMS (EI): *m/z* calcd for $C_{12}H_8{}^{35}ClN_3O$: 245.0356; found: 245.0359.

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Supporting Information

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