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Synthesis of Indolyl Imidazole Derivatives via Base-Promoted Tandem Reaction of *N*-[2-(1-Alkynyl)phenyl]carbodiimides with Isocyanides

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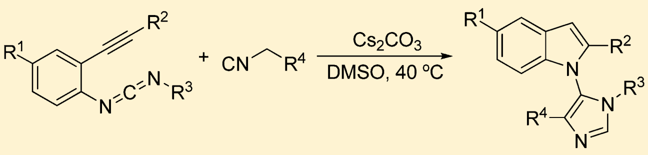
Supporting Information

ABSTRACT: An efficient route to indolyl imidazole derivatives has been developed through a base-promoted tandem reaction of *N*-[2-(1-alkynyl)phenyl]carbodiimides with isocyanides in DMSO at 40 °C. The present tandem process allows the assembly of a variety of indolyl imidazole derivatives in moderate to good yields.



Construction of natural product-like compounds with privileged scaffolds that are prone to display different biological activities are in great demand. Among these privileged scaffolds, the indole unit is abundant in natural heterocycles and acts as the functional core in the structures of various fragrances, dyes, agricultural chemicals, and pharmaceuticals.[1] The synthesis of indoles has been an active research field due to their structural diversity as well as numerous applications of natural and synthetic indole derivatives. Over the past several decades, enormous efforts have been devoted to the development of these heteroaromatic compounds, and a variety of approaches have been successfully developed.[2] For instance, the venerable Fischer indole synthesis was represented as one of the most powerful and versatile routes for the synthesis of indole heterocycles, although this method often suffers from several drawbacks such as using strong acids; certain carcinogenic, unstable, and not readily available hydrazines; and poor regioselectivity with nonsymmetric ketones.[3] The synthesis of indoles catalyzed by transition metals such as palladium,[4] copper,[5] iron,[6] and rhodium[7] has been highlighted by Larock and other researchers. However, there are few methods reported for the preparation of the indolyl imidazole skeletons, especially an imidazole ring on the indole nitrogen.[8] Considering the importance of imidazole derivatives,[9] development of an efficient and practical route for the preparation of indolyl imidazoles is of highly desirable.

Isocyanide addition chemistry has also attracted much attention recently, and the important progress of isocyanide additions for the construction of *N*-heterocyclic compounds has been witnessed.[10−13] For instance, Wu and co-workers reported the synthesis of tetrahydroindeno[2,1-*b*]pyrroles via a base-promoted reaction of (*E*)-2-alkynylphenylchalcone with 2-isocyanoacetate.[10a] Carbodiimide has been widely used in heterocyclic synthesis, cycloaddition reactions, and peptide and nucleotide coupling reactions as a diversity of reagent in the field of organic synthesis because of its special electronic properties.[14] The carbodiimide molecule has two centers of reactivity: the central carbon atom is electrophilic, and the terminal nitrogen atom is electron-rich. By far the most important reactions involve nucleophilic attack of a reagent E−Nu that may add by stepwise or concerted paths.[15] Prompted by the advancement of carbodiimide chemistry, we envision that *N*-[2-(1-alkynyl)phenyl]carbodiimides would be powerful intermediates for the production of *N*-heterocycles with privileged structures. Therefore, we started to study the reactions of *N*-[2-(1-alkynyl)phenyl]carbodiimides **1** with 2-isocyanoacetates **2**, with an aim to enrich our natural product-like libraries of quinazolines **3**. To our surprise, the desired quinazoline **3** was not observed, and an unexpected compound **4** was isolated instead (Scheme 1).

We reasoned that in the presence of a base, the formal [3 + 2] cycloaddition of 2-isocyanoacetate **2** to a carbodiimide moiety in compound **1** would occur first to produce intermediate **A**. Intermediate **A** could then undergo protonolysis and isomerization to afford intermediate **C**. Finally, an intramolecular cyclization of intermediate **C** would happen to give the target product **3** (Scheme 2).

To optimize the transformation, a set of experiments were subsequently carried out using phenyl(2-phenylethynylphenyl)-carbodiimide (**1a**) and ethyl 2-isocyanoacetate (**2a**) as model substrates, and the results are summarized in Table 1. As shown in Table 1, in the presence of DBU as a base, the reaction in acetonitrile at 80 °C gave the desired ethyl 1-phenyl-5-(2-phenyl-1*H*-indol-1-yl)-1*H*-imidazole-4-carboxylate **3a** in 24% yield (Table 1, entry 1). Next, a series of bases were examined. It is evident that Cs_2CO_3 was the best choice, leading to the desired product **3a** in 32% yield (Table 1, entry 2). The structure of **3a** was further confirmed by X-ray diffraction analysis (see Figure 1 in the Supporting Information). Taking into account the activation of the acetylenic bond, different Lewis acids as the catalyst in the presence of Cs_2CO_3 were screened in acetonitrile at 80 °C, but the results were not satisfactory (Table 1, entries 11−14). In the absence of the

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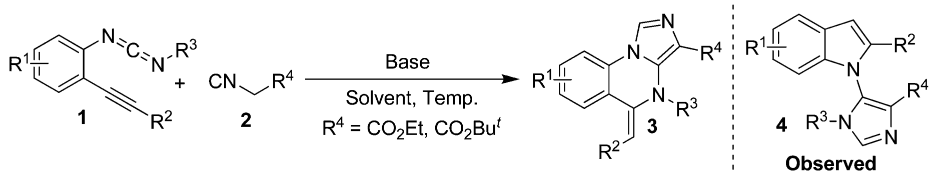
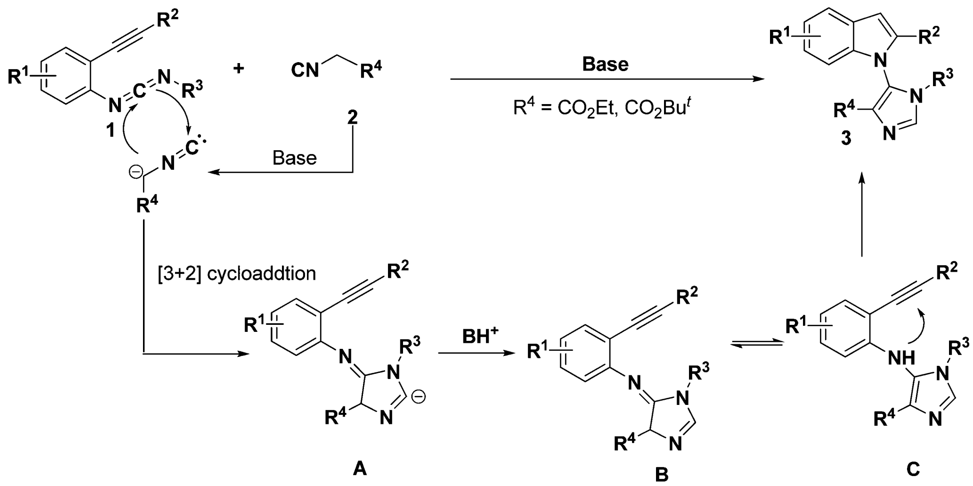
Scheme 1



Scheme 2. Proposed Mechanism for the Generation of Indol-1-yl-1*H*-imidazole-4-carboxylates via Base-Promoted Tandem Reaction of *N*-[2-(1-Alkynyl)phenyl]carbodiimides 1 and 2-Isocyanoacetates 2



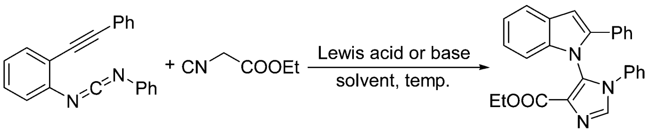
base, the reaction failed when catalytic CuI was added into the reaction (Table 1, entry 15). Switching to other Lewis acids, such as $PdCl_2$, $Pd(OAc)_2$, $FeCl_3$, etc. also did not produce the desired outcome (Table 1, entries 16−19). We next examined the solvent effect (Table 1, entries 20−23). When DMSO was employed as the solvent, the yield increased to 42% (Table 1, entry 23). When the reaction temperature was reduced to 60 °C, the reaction was completed with a yield of 55% (Table 1, entry 26). The highest yield of 62% was obtained when Cs_2CO_3 in DMSO at 40 °C was used (Table 1, entry 25).

Under the optimized reaction conditions [Cs_2CO_3 (2.0 equiv), DMSO, 40 °C], the scope of the reactions was investigated, and the results are shown in Table 2. All reactions proceeded smoothly, leading to the desired indolyl imidazole derivatives in moderate to good yields. For example, when we changed ethyl 2-isocyanoacetate (**2a**) to *tert*-butyl 2-isocyanoacetate (**2b**) or 1-isocyanomethanesulfonyl-4-methylbenzene (TosMIC, **2c**),[16] the corresponding products **3b** and **3c** were obtained in 71% and 76% yield, respectively (Table 2, entries 2 and 3). The reaction worked well when the R^2 group in the substrate *N*-[2-(1-alkynyl)phenyl]carbodiimides **1** was an electron-rich or electron-deficient aryl group (Table 2, entries 4−6). To our surprise, when the R^2 group in the substrate *N*-[2-(1-alkynyl)phenyl]carbodiimides **1** was an alkyl group such as *n*-butyl or *n*-hexyl, the desired products were not obtained. However, when the R^2 group was a cyclopropyl group, the desired product **3g** was obtained in 60% yield (Table 2, entry 7). For the R^3 group in the *N*-[2-(1-alkynyl)phenyl]-carbodiimides **1**, both aryl and alkyl groups were all tolerated. For instance, the reaction of isocyanoacetate **2a** and compound **1** with a tolyl group attached on the position of R^3 gave rise to the corresponding product **3k** in 64% yield (Table 2, entry 11). While the R^3 position was changed to an *n*-butyl group, the expected product **3l** was afforded in 60% yield (Table 2, entry 12). Reactions of ethyl 2-isocyanoacetate **2a** and *N*-[2-(1-alkynyl)phenyl]carbodiimides **1** with different substitutions on the aromatic ring were studied. As expected, all reactions proceeded smoothly to furnish the desired products in good yields (such as **3m** in 60% yield, **3n** in 61% yield). The products **3i** and **3j** were obtained in lower yields due to the formation of byproducts unidentified.

It was found that when TosMIC (**2c**) reacted with *N*-[2-(1-alkynyl)phenyl]carbodiimide **1** under the same conditions, the yield dramatically increased. Therefore, the tandem reactions of TosMIC (**2c**) with various *N*-[2-(1-alkynyl)phenyl]-carbodiimides **1** were investigated. Generally the reactions proceeded successfully under the optimal conditions to afford the corresponding indolyl imidazole derivatives **3o**−**3x** in good yields (Table 2, entries 15−24). For instance, 1-(4-fluorophenyl)-5-(2-phenyl-1*H*-indol-1-yl)-4-(*p*-tolylsulfonyl)-1*H*-imidazole **3r** was obtained in 85% yield, and 5-(5-methyl-2-phenyl-1*H*-indol-1-yl)-1-phenyl-4-(*p*-tolylsulfonyl)-1*H*-imidazole **3w** was obtained in 81% yield. The reaction also proceeded effectively when the R^2 group in the *N*-[2-(1-alkynyl)phenyl]-carbodiimides **1** was an electron-rich or electron-deficient aryl group (Table 2, entries 15−17). For the R^3 group in the substrate **1**, both aryl and alkyl groups were well tolerated.

In conclusion, we have described an efficient route for the construction of indolyl imidazole derivatives via a base-promoted cascade reaction of *N*-[2-(1-alkynyl)phenyl]-carbodiimides with isocyanides. The reaction could be performed under mild conditions with high efficiency. In the reaction, a [3 + 2] cycloaddition of isocyanide to carbodiimide and the intramolecular cyclization are involved. More transformations incorporating carbodiimides and 2-isocyanoacetates to synthesize biologically interesting molecules is ongoing in our laboratory, and the results will be reported in due course.

Table 1. Initial Studies for the Tandem Reaction of Phenyl(2-phenylethynylphenyl)carbodiimide 1a with Ethyl 2-Isocyanoacetate 2a[a]



1a **2a** **3a**

entry	Lewis acid[b]	base	solvent	T (°C)	t (h)	yield (%)[c]
1		DBU	CH_3CN	80	12	24
2		Cs_2CO_3	CH_3CN	80	12	32
3		K_3PO_4	CH_3CN	80	12	25
4		DABCO	CH_3CN	80	24	trace
5		Na_2CO_3	CH_3CN	80	24	trace
6		K_2CO_3	CH_3CN	80	24	trace
7		*n*-BuLi	CH_3CN	80	20	7
8		NaOH	CH_3CN	80	20	10
9		KOH	CH_3CN	80	20	11
10		*t*-BuOK	CH_3CN	80	20	8
11	CuI	Cs_2CO_3	CH_3CN	80	12	32
12	$PdCl_2$	Cs_2CO_3	CH_3CN	80	12	32
13	$Pd(OAc)_2$	Cs_2CO_3	CH_3CN	80	12	32
14	$FeCl_3$	Cs_2CO_3	CH_3CN	80	12	32
15	CuI		CH_3CN	80	24	NR
16	$PdCl_2$		CH_3CN	80	24	trace
17	$Pd(OAc)_2$		CH_3CN	80	24	trace
18	$FeCl_3$		CH_3CN	80	24	trace
19	CuI + $PdCl_2$		CH_3CN	80	24	trace
20		Cs_2CO_3	DMF	80	24	trace
21		Cs_2CO_3	DCE	80	24	trace
22		Cs_2CO_3	Toluene	80	24	trace
23		Cs_2CO_3	DMSO[d]	80	12	42
24		Cs_2CO_3	DMSO	25	24	25
25		Cs_2CO_3	DMSO	40	12	62
26		Cs_2CO_3	DMSO	60	12	55
27		Cs_2CO_3	DMSO	100	3	40

[a]Reaction was performed with **1a** (0.2 mmol), **2a** (0.4 mmol), and base (0.4 mmol) in solvent (2 mL). [b]0.1 equiv of Lewis acid catalyst was used. [c]Isolated yield based on phenyl(2-phenylethynylphenyl)-carbodiimide **1a**. [d]Different bases such as *t*-BuOK, KOH, K_3PO_4, K_2CO_3, and DBU were tested with DMSO as the solvent, and Cs_2CO_3 was also found to be the best choice.

■ EXPERIMENTAL SECTION

General Methods. ^{1}H and ^{13}C NMR spectra were recorded with $CDCl_3$ as the solvent and TMS as an internal standard. The starting *N*-[2-(1-alkynyl)phenyl]carbodiimides were prepared according to the reported literature procedure.[17] The other chemicals were purchased from commercial sources and used as received, unless otherwise noted.

General Procedure for the Synthesis of Indolyl Imidazole Derivatives via a Tandem Reaction of *N*-[2-(1-Alkynyl)phenyl]-carbodiimides 1 with Isocyanides 2. A mixture of *N*-[2-(1-alkynyl)phenyl]carbodiimide **1a** (0.2 mmol), 2-isocyanoacetate **2a** (0.4 mmol), and Cs_2CO_3 (0.4 mmol) in DMSO (2.0 mL) was stirred at 40 °C for 12 h. After completion of reaction as indicated by TLC, the mixture was concentrated and directly purified by flash column chromatography (EtOAc/petroleum ether, 1:2) to give the desired product **3a**.

Ethyl 1-Phenyl-5-(2-phenyl-1*H*-indol-1-yl)-1*H*-imidazole-4-carboxylate (3a). Yellow solid (50.5 mg, 62%). Mp 185−187 °C. IR (KBr): 3052, 1720, 1600, 1577, 1500, 1454, 1154, 760 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (s, 1H), 7.61−7.63 (m, 1H), 7.17−7.29 (m, 5H), 7.10−7.13 (m, 2H), 7.02−7.06 (m, 2H), 6.84−6.86 (m, 2H), 6.58 (s, 1H), 6.31−6.33 (m, 2H), 4.13−4.29 (m, 2H), 1.00 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.6, 140.4, 139.2, 135.9, 133.7, 131.5, 129.3, 129.1, 128.7, 128.6, 128.3, 127.8, 127.7, 123.8, 123.1, 121.5, 120.8, 111.0, 104.4, 60.8, 13.9. MS (EI, 70 eV) *m*/*z*: 407 [M]$^+$. HRMS calcd for $C_{26}H_{22}N_3O_2^+$ (M + H$^+$): 408.1707, found 408.1701. Anal. Calcd for $C_{26}H_{21}N_3O_2$: C, 76.64; H, 5.19; N, 10.31. Found: C, 76.36; H, 5.24; N, 10.18.

***tert*-Butyl 1-Phenyl-5-(2-phenyl-1*H*-indol-1-yl)-1*H*-imidazole-4-carboxylate (3b).** Yellow solid (61.8 mg, 71%). Mp 199−201 °C. IR (KBr): 3052, 2973, 1721, 1598, 1569, 1501, 1457, 1410, 1153, 748 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (s, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.11−7.27 (m, 5H), 7.11−7.14 (m, 2H), 7.01−7.05 (m, 2H), 6.86 (d, *J* = 7.6 Hz, 2H), 6.56 (s, 1H), 6.32 (d, *J* = 8.0 Hz, 2H), 1.13 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.7, 140.0, 139.3, 135.8, 133.7, 131.6, 130.5, 129.8, 129.2, 128.6, 128.5, 128.3, 127.7, 123.9, 122.9, 121.3, 120.7, 111.0, 103.8, 81.1, 27.6. MS (EI, 70 eV) *m*/*z*: 435 [M]$^+$. HRMS calcd for $C_{28}H_{26}N_3O_2^+$ (M + H$^+$): 436.2020, found 436.2009. Anal. Calcd for $C_{28}H_{25}N_3O_2$: C, 77.22; H, 5.79; N, 9.65. Found: C, 76.97; H, 5.64; N, 9.49.

1-Phenyl-5-(2-phenyl-1*H*-indol-1-yl)-4-(*p*-tolylsulfonyl)-1*H*-imidazole (3c). Yellow solid (74.4 mg, 76%). Mp 175−177 °C. IR (KBr): 2920, 1596, 1566, 1502, 1324, 1151, 1082, 761 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78−7.82 (d, *J* = 8.0 Hz, 2H), 7.68 (s, 1H), 7.61 (d, *J* = 6.8 Hz, 1H), 7.16−7.26 (m, 6H), 7.00−7.10 (m, 5H), 6.77 (d, *J* = 7.6 Hz, 2H), 6.60 (s, 1H), 6.26 (d, *J* = 7.6 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.6, 140.9, 140.0, 137.4, 137.3, 136.2, 133.0, 131.1, 129.6, 129.3, 129.1, 128.7, 128.4, 128.2, 127.9, 127.7, 127.1, 124.0, 123.2, 121.8, 120.9, 111.3, 105.1, 21.6. MS (EI, 70 eV) *m*/*z*: 489 [M]$^+$. HRMS calcd for $C_{30}H_{24}N_3O_2S^+$ (M + H$^+$): 490.1584, found 490.1571. Anal. Calcd for $C_{30}H_{23}N_3O_2S$: C, 73.60; H, 4.74; N, 8.58. Found: C, 73.42; H, 4.96; N, 8.39.

Ethyl 5-[2-(4-Chlorophenyl)-1*H*-indol-1-yl]-1-phenyl-1*H*-imidazole-4-carboxylate (3d). Yellow solid (50.4 mg, 57%). Mp 168−169 °C. IR (KBr): 3054, 1721, 1637, 1567, 1500, 1451, 1152, 802, 766 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (s, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.21−7.30 (m, 4H), 7.06−7.12 (m, 4H), 6.79 (d, *J* = 8.8 Hz, 2H), 6.58 (s, 1H), 6.37 (d, *J* = 7.6 Hz, 2H), 4.15−4.30 (m, 2H), 1.03 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.5, 139.3, 139.0, 136.0, 133.9, 133.6, 130.5, 130.0, 129.4, 129.2, 128.9, 128.8, 128.5, 123.8, 123.5, 121.7, 121.0, 111.0, 104.8, 60.8, 13.9. MS (EI, 70 eV) *m*/*z*: 441 [M]$^+$. HRMS calcd for $C_{26}H_{21}ClN_3O_2^+$ (M + H$^+$): 442.1317, found 442.1305. Anal. Calcd for $C_{26}H_{20}ClN_3O_2$: C, 70.66; H, 4.56; N, 9.50. Found: C, 70.44; H, 4.65; N, 9.33.

Ethyl 5-[2-(4-Methoxyphenyl)-1*H*-indol-1-yl]-1-phenyl-1*H*-imidazole-4-carboxylate (3e). Yellow solid (57.7 mg, 66%). Mp 172−174 °C. IR (KBr): 3050, 2977, 1725, 1611, 1598, 1580, 1501, 1455, 1250, 1176, 836, 751 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (s, 1H), 7.58−7.60 (m, 1H), 7.18−7.24 (m, 4H), 7.07 (t, *J* = 8.0 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 6.66 (d, *J* = 8.4 Hz, 2H), 6.50 (s, 1H), 6.38 (d, *J* = 7.6 Hz, 2H), 4.13−4.29 (m, 2H), 3.77 (s, 3H), 1.01 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.6, 159.3, 140.3, 139.1, 135.9, 133.7, 131.0, 129.3, 129.0, 128.8, 128.6, 124.1, 123.9, 122.8, 121.4, 120.6, 113.7, 110.8, 103.6, 60.7, 55.3, 13.9. MS (EI, 70 eV) *m*/*z*: 437 [M]$^+$. HRMS calcd for $C_{27}H_{24}N_3O_3^+$ (M + H$^+$): 438.1812, found 438.1801. Anal. Calcd for $C_{27}H_{23}N_3O_3$: C, 74.13; H, 5.30; N, 9.60. Found: C, 73.89; H, 5.17; N, 9.43.

Ethyl 5-[2-(*p*-Tolyl)-1*H*-indol-1-yl]-1-phenyl-1*H*-imidazole-4-carboxylate (3f). Yellow solid (57.3 mg, 68%). Mp 174−176 °C. IR (KBr): 2952, 2923, 2854, 1727, 1597, 1570, 1500, 1455, 1248, 1171, 803, 752 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (s, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.28−7.35 (m, 4H), 7.15 (t, *J* = 7.6 Hz, 2H), 7.04 (d, *J* = 7.8 Hz, 2H), 6.86 (d, *J* = 7.8 Hz, 2H), 6.65 (s, 1H), 6.48 (d, *J* = 7.6 Hz, 2H), 4.23−4.37 (m, 2H), 2.40 (s, 3H), 1.09 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.6, 140.6, 139.2, 137.7, 136.1, 135.9, 133.7, 131.0, 129.3, 129.0, 128.8, 128.7, 127.6, 123.9, 120.8, 120.7, 111.0, 104.1, 104.0, 60.8, 21.3, 13.9. MS (EI, 70 eV) *m*/*z*: 421 [M]$^+$. HRMS calcd for $C_{27}H_{24}N_3O_2^+$ (M + H$^+$): 422.1863, found 422.1843. Anal. Calcd for $C_{27}H_{23}N_3O_2$: C, 76.94; H, 5.50; N, 9.97. Found: C, 76.69; H, 5.27; N, 9.78.

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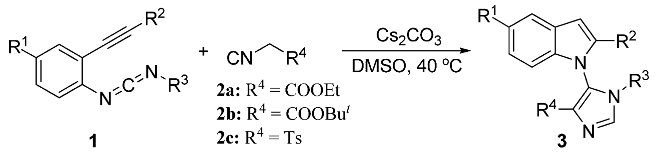
Table 2. Synthesis of Indolyl Imidazole Derivatives via a Tandem Reaction of *N*-[2-(1-Alkynyl)phenyl]carbodiimides 1 with Isocyanides 2[a]



entry	R^1	R^2	R^3	R^4	product	yield (%)[b]
1	H	Ph	Ph	COOEt	**3a**	62
2	H	Ph	Ph	$COOBu^t$	**3b**	71
3	H	Ph	Ph	Ts	**3c**	76
4	H	4-ClC_6H_4	Ph	COOEt	**3d**	57
5	H	4-MeOC_6H_4	Ph	COOEt	**3e**	66
6	H	4-MeC_6H_4	Ph	COOEt	**3f**	68
7	H	cyclopropyl	Ph	COOEt	**3g**	60
8	H	Ph	4-FC_6H_4	COOEt	**3h**	65
9	H	Ph	$4\text{-O}_2NC_6H_4$	COOEt	**3i**	51
10	H	Ph	4-MeOC_6H_4	COOEt	**3j**	47
11	H	Ph	4-MeC_6H_4	COOEt	**3k**	64
12	H	Ph	$n\text{-C}_4H_9$	COOEt	**3l**	60
13	Me	Ph	Ph	COOEt	**3m**	60
14	Cl	Ph	Ph	COOEt	**3n**	61
15	H	4-ClC_6H_4	Ph	Ts	**3o**	76
16	H	4-MeOC_6H_4	Ph	Ts	**3p**	78
17	H	4-MeC_6H_4	Ph	Ts	**3q**	80
18	H	Ph	4-FC_6H_4	Ts	**3r**	85
19	H	Ph	4-MeOC_6H_4	Ts	**3s**	65
20	H	Ph	4-MeC_6H_4	Ts	**3t**	67
21	H	Ph	cyclohexyl	Ts	**3u**	77
22	H	Ph	$n\text{-C}_4H_9$	Ts	**3v**	70
23	Me	Ph	Ph	Ts	**3w**	81
24	Cl	Ph	Ph	Ts	**3x**	79
25	H	4-ClC_6H_4	Ph	$COOBu^t$	**3y**	75

[a]Reaction was performed with N-[2-(1-alkynyl)phenyl]carbodiimide **1** (0.2 mmol), isocyanide **2** (0.4 mmol), Cs_2CO_3 (0.4 mmol) in DMSO (2 mL) at 40 °C for 12 h. [b]Isolated yield.

Ethyl 5-(2-Cyclopropyl-1*H*-indol-1-yl)-1-phenyl-1*H*-imidazole-4-carboxylate (3g). Yellow solid (44.6 mg, 60%). Mp 117−119 °C. IR (KBr): 2980, 1731, 1597, 1583, 1499, 1458, 1249, 1166, 747 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.95 (s, 1H), 7.46−7.48 (m, 1H), 7.26−7.30 (m, 3H), 7.06−7.12 (m, 4H), 6.98−7.00 (m, 1H), 6.10 (s, 1H), 4.00−4.14 (m, 2H), 1.33−1.38 (m, 1H), 0.86−0.89 (t, J = 7.2 Hz, 3H), 0.70−0.75 (m, 1H), 0.62−0.67 (m, 1H), 0.53−0.60 (m, 1H), 0.16−0.22 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.4, 144.1, 139.3, 136.4, 134.3, 129.8, 128.9, 128.6, 123.9, 122.1, 120.9, 120.2, 114.0, 109.7, 99.5, 60.5, 13.7, 7.9, 7.4, 6.4. MS (EI, 70 eV) *m/z*: 371 $[M]^+$. HRMS calcd for $C_{23}H_{22}N_3O_2^+$ (M + H^+): 372.1707, found 372.1690. Anal. Calcd for $C_{23}H_{21}N_3O_2$: C, 74.38; H, 5.70; N, 11.31. Found: C, 74.13; H, 5.48; N, 11.16.

Ethyl 1-(4-Fluorophenyl)-5-(2-phenyl-1*H*-indol-1-yl)-1*H*-imidazole-4-carboxylate (3h). Yellow solid (55.3 mg, 65%). Mp 203−205 °C. IR (KBr): 3051, 2977, 1723, 1601, 1510, 1455, 1222, 1162, 841, 749 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, J = 4.8 Hz, 1H), 7.61 (s, 1H), 7.13−7.28 (m, 6H), 6.90 (d, J = 7.2 Hz, 2H), 6.73 (t, J = 8.6 Hz, 2H), 6.60 (s, 1H), 6.25−6.29 (m, 2H), 4.14−4.30 (m, 2H), 1.00 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.3 (d, $^1J_{CF}$ = 247 Hz), 161.5, 140.1, 139.2, 135.9, 131.5, 130.9, 129.6, 129.1, 128.7, 128.4, 127.9, 127.6, 125.9 (d, $^3J_{CF}$ = 8 Hz), 123.3, 121.7, 120.9, 116.3 (d, $^2J_{CF}$ = 23 Hz), 110.9, 104.5, 60.8, 13.8. MS (EI, 70 eV) *m/z*: 425 $[M]^+$. HRMS calcd for $C_{26}H_{21}FN_3O_2^+$ (M + H^+): 426.1612, found 426.1598. Anal. Calcd for $C_{26}H_{20}FN_3O_2$: C, 73.40; H, 4.74; N, 9.87. Found: C, 73.18; H, 4.51; N, 9.69.

Ethyl 1-(4-Nitrophenyl)-5-(2-phenyl-1*H*-indol-1-yl)-1*H*-imidazole-4-carboxylate (3i). Yellow solid (46.2 mg, 51%). Mp 208−210 °C. IR (KBr): 3053, 2977, 1721, 1599, 1525, 1502, 1347, 1252, 1179, 752 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.62 (s, 1H), 7.61 (d, J = 9.2 Hz, 1H), 7.12−7.27 (m, 6H), 6.90 (d, J = 7.2 Hz, 2H), 6.84 (d, J = 8.0 Hz, 2H), 6.60 (s, 1H), 6.24 (d, J = 8.0 Hz, 2H), 4.10−4.28 (m, 2H), 0.99 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.2, 156.1, 147.2, 139.7, 138.8, 138.7, 135.3, 131.1, 128.7, 128.6, 128.1, 127.5, 124.7, 124.4, 123.6, 122.1, 121.2, 110.9, 105.0, 61.1, 13.8. MS (EI, 70 eV) *m/z*: 452 $[M]^+$. HRMS calcd for $C_{26}H_{21}N_4O_4^+$ (M + H^+): 453.1557, found 453.1536. Anal. Calcd for $C_{26}H_{20}N_4O_4$: C, 69.02; H, 4.46; N, 12.38. Found: C, 68.79; H, 4.27; N, 12.25.

Ethyl 1-(4-Methoxyphenyl)-5-(2-phenyl-1*H*-indol-1-yl)-1*H*-imidazole-4-carboxylate (3j). Yellow solid (41.1 mg, 47%). Mp 157−159 °C. IR (KBr): 2924, 1720, 1593, 1516, 1456, 1251, 1178, 839, 750 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, J = 8.4 Hz, 1H), 7.63 (s, 1H), 7.17−7.29 (m, 6H), 6.96 (d, J = 7.2 Hz, 2H), 6.63 (s, 1H), 6.57 (d, J = 8.4 Hz, 2H), 6.29 (d, J = 8.8 Hz, 2H), 4.16−4.30 (m, 2H), 3.74 (s, 3H), 1.03 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.6, 142.2, 136.1, 131.6, 129.0, 128.7, 128.3, 127.7, 125.3, 123.1, 121.5, 120.8, 114.3, 110.9, 104.3, 60.7, 55.5, 13.8. MS (EI, 70 eV) *m/z*: 437 $[M]^+$. HRMS calcd for $C_{27}H_{24}N_3O_3^+$ (M + H^+): 438.1812, found 438.1796. Anal. Calcd for $C_{27}H_{23}N_3O_3$: C, 74.13; H, 5.30; N, 9.60. Found: C, 73.87; H, 5.08; N, 9.47.

Ethyl 5-(2-Phenyl-1*H*-indol-1-yl)-1-(*p*-tolyl)-1*H*-imidazole-4-carboxylate (3k). Yellow solid (54.0 mg, 64%). Mp 186−188 °C. IR (KBr): 3049, 2977, 1723, 1564, 1516, 1442, 1248, 1161, 762 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.62 (s, 1H), 7.61 (d, J = 9.2 Hz, 1H), 7.12−7.27 (m, 6H), 6.90 (d, J = 7.2 Hz, 2H), 6.84 (d, J = 8.0 Hz, 2H), 6.60 (s, 1H), 6.24 (d, J = 8.0 Hz, 2H), 4.12−4.26 (m, 2H), 2.24 (s, 3H), 0.99 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.6, 140.5, 139.4, 138.8, 136.1, 131.6, 131.1, 130.9, 129.8, 129.1, 128.7, 128.3, 127.7, 123.7, 123.1, 121.5, 120.8, 110.9, 104.3, 60.7, 21.0, 13.8. MS (EI, 70 eV) *m/z*: 421 [M]$^+$. HRMS calcd for $C_{27}H_{24}N_3O_2^+$ (M + H$^+$): 422.1863, found 422.1846. Anal. Calcd for $C_{27}H_{23}N_3O_2$: C, 76.94; H, 5.50; N, 9.97. Found: C, 76.75; H, 5.23; N, 9.79.

Ethyl 1-Butyl-5-(2-phenyl-1*H*-indol-1-yl)-1*H*-imidazole-4-carboxylate (3l). Yellow solid (46.5 mg, 60%). Mp 74−76 °C. IR (KBr): 3059, 2957, 2870, 1700, 1588, 1563, 1420, 1267, 1186, 1073, 765 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.90 (s, 1H), 7.76−7.81 (m, 3H), 7.52−7.54 (m, 2H), 7.46 (t, *J* = 7.8 Hz, 3H), 7.36−7.41 (m, 1H), 7.30−7.32 (m, 1H), 6.57 (s, 1H), 4.46−4.52 (m, 2H), 3.82 (s, 2H), 1.49−1.52 (m, 3H), 1.29−1.32 (m, 2H), 0.94−0.99 (m, 2H), 0.66 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 162.3, 139.6, 135.1, 135.1, 129.2, 128.7, 128.6, 127.4, 127.0, 125.8, 124.2, 115.7, 115.4, 115.1, 60.3, 54.9, 30.2, 19.7, 14.7, 13.6. MS (EI, 70 eV) *m/z*: 387 [M]$^+$. HRMS calcd for $C_{24}H_{26}N_3O_2^+$ (M + H$^+$): 388.2020, found 388.2009. Anal. Calcd for $C_{24}H_{25}N_3O_2$: C, 74.40; H, 6.50; N, 10.84. Found: C, 74.16; H, 6.31; N, 10.69.

Ethyl 5-(5-Methyl-2-phenyl-1*H*-indol-1-yl)-1-phenyl-1*H*-imidazole-4-carboxylate (3m). Yellow solid (50.6 mg, 60%). Mp 182−184 °C. IR (KBr): 3045, 2976, 1727, 1596, 1568, 1501, 1416, 1249, 1170, 806, 758 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.65 (s, 1H), 7.41 (s, 1H), 7.16−7.22 (m, 2H), 7.09−7.13 (m, 4H), 7.03−7.07 (m, 2H), 6.84−6.86 (m, 2H), 6.52 (s, 1H), 6.32−6.34 (m, 2H), 4.19−4.29 (m, 2H), 2.48 (s, 3H), 1.06 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 161.6, 140.4, 137.6, 135.8, 133.7, 131.7, 131.1, 130.8, 129.2, 129.0, 128.6, 128.2, 127.6, 127.6, 124.7, 123.8, 120.6, 110.6, 104.1, 60.7, 21.5, 13.9. MS (EI, 70 eV) *m/z*: 421 [M]$^+$. HRMS calcd for $C_{27}H_{24}N_3O_2^+$ (M + H$^+$): 422.1863, found 422.1841. Anal. Calcd for $C_{27}H_{23}N_3O_2$: C, 76.94; H, 5.50; N, 9.97. Found: C, 76.76; H, 5.71; N, 9.78.

Ethyl 5-(5-Chloro-2-phenyl-1*H*-indol-1-yl)-1-phenyl-1*H*-imidazole-4-carboxylate (3n). Yellow solid (53.9 mg, 61%). Mp 183−185 °C. IR (KBr): 3045, 1721, 1598, 1567, 1499, 1451, 1245, 1172, 1154, 760 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.65 (s, 1H), 7.59 (d, *J* = 2.0 Hz, 1H), 7.20−7.25 (m, 3H), 7.12−7.16 (m, 3H), 7.05−7.09 (m, 2H), 6.83−6.86 (m, 2H), 6.53 (s, 1H), 6.30−6.33 (m, 2H), 4.20−4.30 (m, 2H), 1.08 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 161.4, 141.8, 137.6, 136.0, 133.5, 131.7, 131.0, 130.4, 129.7, 129.4, 128.8, 128.4, 128.1, 127.7, 127.2, 123.8, 123.4, 120.3, 112.0, 103.8, 60.9, 14.0. MS (EI, 70 eV) *m/z*: 441 [M]$^+$. HRMS calcd for $C_{26}H_{21}ClN_3O_2^+$ (M + H$^+$): 442.1317, found 442.1301. Anal. Calcd for $C_{26}H_{20}ClN_3O_2$: C, 70.66; H, 4.56; N, 9.50. Found: C, 70.41; H, 4.32; N, 9.39.

1-Phenyl-5-[2-(4-chlorophenyl)-1*H*-indol-1-yl]-4-(*p*-tolylsulfonyl)-1*H*-imidazole (3o). Yellow solid (79.7 mg, 76%). Mp 176−178 °C. IR (KBr): 2919, 1595, 1498, 1417, 1394, 1185, 892, 714 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.71 (s, 1H), 7.61 (d, *J* = 6.8 Hz, 1H), 7.52−7.54 (m, 1H), 7.18−7.28 (m, 5H), 7.04−7.08 (m, 4H), 6.73 (d, *J* = 8.4 Hz, 2H), 6.60 (s, 1H), 6.33 (d, *J* = 7.6 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 144.8, 140.1, 139.7, 138.4, 137.7, 137.2, 136.4, 134.0, 133.0, 132.3, 129.8, 129.7, 129.0, 128.9, 128.6, 128.5, 128.4, 127.8, 124.0, 121.1, 121.0, 111.2, 105.6, 21.7. MS (EI, 70 eV) *m/z*: 523 [M]$^+$. HRMS calcd for $C_{30}H_{23}ClN_3O_2S^+$ (M + H$^+$): 524.1194, found 524.1193. Anal. Calcd for $C_{30}H_{22}ClN_3O_2S$: C, 68.76; H, 4.23; N, 8.01. Found: C, 68.47; H, 4.46; N, 7.82.

1-Phenyl-5-[2-(4-methoxyphenyl)-1*H*-indol-1-yl]-4-(*p*-tolylsulfonyl)-1*H*-imidazole (3p). Yellow solid (81.1 mg, 78%). Mp 222−224 °C. IR (KBr): 2922, 1647, 1596, 1500, 1438, 1384, 1150, 707, 676 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.80 (d, *J* = 8.0 Hz, 2H), 7.68 (s, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.16−7.28 (m, 5H), 7.00−7.07 (m, 3H), 6.73 (d, *J* = 8.4 Hz, 2H), 6.61 (d, *J* = 8.4 Hz, 2H), 6.52 (s, 1H), 6.32 (d, *J* = 8.4 Hz, 2H), 3.76 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 144.6, 140.8, 139.8, 137.4, 137.2, 133.0, 129.7, 129.6, 129.3, 129.1, 128.7, 128.4, 128.2, 128.1, 124.0, 123.5, 113.7, 113.6, 111.0, 104.2, 104.1, 55.3, 21.6. MS (EI, 70 eV) *m/z*: 519 [M]$^+$. HRMS calcd for $C_{31}H_{26}N_3O_3S^+$ (M + H$^+$): 520.1689, found 520.1685. Anal. Calcd for $C_{31}H_{25}N_3O_3S$: C, 71.66; H, 4.85; N, 8.08. Found: C, 71.37; H, 4.99; N, 7.87.

1-Phenyl-5-[2-(*p*-tolyl)-1*H*-indol-1-yl]-4-(*p*-tolylsulfonyl)-1*H*-imidazole (3q). Yellow solid (80.6 mg, 80%). Mp 173−174 °C. IR (KBr): 2928, 1611, 1599, 1501, 1455, 1320, 1250, 1176, 751 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.67 (s, 1H), 7.58−7.60 (m, 1H), 7.18−7.26 (m, 5H), 7.02−7.07 (m, 3H), 6.88 (d, *J* = 7.6 Hz, 2H), 6.69 (d, *J* = 8.0 Hz, 2H), 6.56 (s, 1H), 6.31−6.33 (m, 2H), 2.40 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 144.5, 141.2, 140.0, 137.8, 137.5, 137.4, 136.2, 133.2, 130.0, 129.6, 129.3, 129.1, 129.0, 128.8, 128.4, 128.3, 127.7, 124.1, 123.1, 121.8, 120.8, 111.2, 104.7, 21.7, 21.2. MS (EI, 70 eV) *m/z*: 503 [M]$^+$. HRMS calcd for $C_{31}H_{26}N_3O_2S^+$ (M + H$^+$): 504.1740, found 504.1718. Anal. Calcd for $C_{31}H_{25}N_3O_2S$: C, 73.93; H, 5.00; N, 8.34. Found: C, 73.77; H, 5.12; N, 8.18.

1-(4-Fluorophenyl)-5-(2-phenyl-1*H*-indol-1-yl)-4-(*p*-tolylsulfonyl)-1*H*-imidazole (3r). Yellow solid (86.3 mg, 85%). Mp 213-215 °C. IR (KBr): 2953, 2924, 2854, 1599, 1580, 1462, 1456, 1377, 1261, 802 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.59 (s, 1H), 7.54 (d, *J* = 7.2 Hz, 1H), 7.44−7.49 (m, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.11−7.17 (m, 3H), 6.99−7.03 (m, 3H), 6.73 (d, *J* = 7.2 Hz, 2H), 6.64 (t, *J* = 8.4 Hz, 2H), 6.55 (s, 1H), 6.12−6.15 (m, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 162.4 (d, $^1J_{CF}$ = 249 Hz), 144.8, 140.6, 139.9, 137.2, 137.0, 136.3 (d, $^2J_{CF}$ = 25 Hz), 130.9, 129.8, 129.5, 128.9, 128.5, 128.3, 128.1 (d, $^3J_{CF}$ = 7 Hz), 127.5, 127.3, 126.0, 121.0, 120.8, 116.3, 111.1, 105.1, 104.9, 21.6. MS (EI, 70 eV) *m/z*: 507 [M]$^+$. HRMS calcd for $C_{30}H_{23}FN_3O_2S^+$ (M + H$^+$): 508.1490, found 508.1478. Anal. Calcd for $C_{30}H_{22}FN_3O_2S$: C, 70.99; H, 4.37; N, 8.28. Found: C, 70.75; H, 4.56; N, 8.09.

1-(4-Methoxyphenyl)-5-(2-phenyl-1*H*-indol-1-yl)-4-(*p*-tolylsulfonyl)-1*H*-imidazole (3s). Yellow solid (67.5 mg, 65%). Mp 162−164 °C. IR (KBr): 2963, 2935, 1595, 1567, 1511, 1454, 1325, 1251, 1147, 808 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.82 (d, *J* =7.2 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.60 (s, 1H), 7.19−7.26 (m, 5H), 7.04−7.11 (m, 3H), 6.87 (d, *J* = 7.2 Hz, 2H), 6.62 (s, 1H), 6.50 (d, *J* = 8.0 Hz, 2H), 6.20 (d, *J* = 8.0 Hz, 2H), 3.66 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 144.6, 141.0, 140.1, 137.4, 137.2, 136.6, 136.4, 131.2, 129.8, 129.6, 128.7, 128.5, 128.3, 128.1, 127.8, 125.8, 125.5, 121.9, 121.7, 121.0, 120.8, 114.4, 105.1, 55.5, 21.7. MS (EI, 70 eV) *m/z*: 519 [M]$^+$. HRMS calcd for $C_{31}H_{26}N_3O_3S^+$ (M + H$^+$): 520.1689, found 520.1688. Anal. Calcd for $C_{31}H_{25}N_3O_3S$: C, 71.66; H, 4.85; N, 8.08. Found: C, 71.42; H, 4.98; N, 7.92.

1-(*p*-Tolyl)-5-(2-phenyl-1*H*-indol-1-yl)-4-(*p*-tolylsulfonyl)-1*H*-imidazole (3t). Yellow solid (67.5 mg, 67%). Mp 191−193 °C. IR (KBr): 2956, 2924, 1596, 1567, 1515, 1455, 1328, 1149, 815, 706 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.62 (s, 1H), 7.18−7.27 (m, 6H), 7.05−7.11 (m, 4H), 6.84 (t, *J* = 7.6 Hz, 3H), 6.62 (s, 1H), 6.19 (d, *J* = 8.0 Hz, 2H), 2.41 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 144.6, 141.0, 140.1, 139.4, 137.4, 136.4, 136.2, 131.2, 130.6, 130.1, 129.9, 129.8, 129.5, 128.7, 128.5, 128.4, 128.2, 127.8, 123.9, 121.0, 120.8, 105.1, 105.0, 21.7, 21.1. MS (EI, 70 eV) *m/z*: 503 [M]$^+$. HRMS calcd for $C_{31}H_{26}N_3O_2S^+$ (M + H$^+$): 504.1740, found 504.1728. Anal. Calcd for $C_{31}H_{25}N_3O_2S$: C, 73.93; H, 5.00; N, 8.34. Found: C, 73.68; H, 4.79; N, 8.15.

1-Cyclohexyl-5-(2-phenyl-1*H*-indol-1-yl)-4-(*p*-tolylsulfonyl)-1*H*-imidazole (3u). Yellow solid (76.3 mg, 77%). Mp 238−239 °C. IR (KBr): 2935, 2852, 1596, 1555, 1492, 1448, 1316, 1145, 749, 700 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.14 (d, *J* = 7.6 Hz, 2H), 8.03 (d, *J* = 8.4 Hz, 2H), 7.88 (s, 1H), 7.66−7.68 (m, 1H), 7.41−7.45 (m, 2H), 7.26−7.39 (m, 6H), 6.74 (s, 1H), 3.81−3.87 (m, 1H), 2.37 (s, 3H), 2.04−2.07 (m, 1H), 1.55−1.57 (m, 1H), 1.37−1.43 (m, 3H), 1.16−1.26 (m, 2H), 0.83−0.98 (m, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 143.7, 139.4, 138.3, 135.2, 132.4, 130.7, 130.0, 129.6, 128.9, 128.7, 128.5, 128.1, 127.9, 127.7, 126.4, 124.5, 115.2, 69.2, 31.5, 30.8, 25.8, 25.7, 25.3, 21.6. MS (EI, 70 eV) *m/z*: 495 [M]$^+$. HRMS calcd for $C_{30}H_{30}N_3O_2S^+$ (M + H$^+$): 496.2053, found 496.2032. Anal. Calcd for $C_{30}H_{29}N_3O_2S$: C, 72.70; H, 5.90; N, 8.48. Found: C, 72.54; H, 5.65; N, 8.29.

1-Butyl-5-(2-phenyl-1*H*-indol-1-yl)-4-(*p*-tolylsulfonyl)-1*H*-imidazole (3v). Yellow solid (65.7 mg, 70%). Mp 131−133 °C. IR (KBr): 2959, 2925, 1626, 1588, 1557, 1493, 1317, 1302, 1142, 1086, 761 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, J = 8.0 Hz, 2H), 7.87 (s, 1H), 7.80−7.82 (m, 2H), 7.75 (d, J = 7.2 Hz, 1H), 7.46−7.50 (m, 2H), 7.31−7.43 (m, 6H), 6.57 (s, 1H), 3.78 (s, 2H), 2.41 (s, 3H), 1.14−1.21 (m, 2H), 0.85−0.95 (m, 2H), 0.57 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.6, 139.5, 137.0, 134.7, 134.3, 129.8, 129.6, 129.3, 129.1, 129.0, 128.7, 127.7, 127.5, 126.5, 125.5, 124.2, 116.8, 115.4, 115.3, 56.5, 30.5, 21.6, 19.6, 13.5. MS (EI, 70 eV) m/z: 469 [M]$^+$. HRMS calcd for $C_{28}H_{28}N_3O_2S^+$ (M + H$^+$): 470.1897, found 470.1876. Anal. Calcd for $C_{28}H_{27}N_3O_2S$: C, 71.62; H, 5.80; N, 8.94. Found: C, 71.38; H, 5.58; N, 8.76.

5-(5-Methyl-2-phenyl-1*H*-indol-1-yl)-1-phenyl-4-(*p*-tolylsulfonyl)-1*H*-imidazole (3w). Yellow solid (81.6 mg, 81%). Mp 240−242 °C. IR (KBr): 3060, 1596, 1570, 1502, 1467, 1330, 1216, 1151, 1086, 810, 760 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 8.4 Hz, 2H), 7.67 (s, 1H), 7.40 (s, 1H), 7.14−7.28 (m, 4H), 7.01−7.06 (m, 6H), 6.71−6.73 (m, 2H), 6.52 (s, 1H), 6.26−6.28 (m, 2H), 2.49 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.6, 140.9, 138.5, 137.4, 136.1, 133.2, 131.3, 131.2, 130.0, 129.6, 129.3, 129.1, 128.9, 128.4, 128.2, 127.7, 127.6, 127.1, 124.8, 123.9, 120.7, 111.0, 104.8, 21.6, 21.5. MS (EI, 70 eV) m/z: 503 [M]$^+$. HRMS calcd for $C_{31}H_{26}N_3O_2S^+$ (M + H$^+$): 504.1740, found 504.1731. Anal. Calcd for $C_{31}H_{25}N_3O_2S$: C, 73.93; H, 5.00; N, 8.34. Found: C, 73.65; H, 5.23; N, 8.16.

5-(5-Chloro-2-phenyl-1*H*-indol-1-yl)-1-phenyl-4-(*p*-tolylsulfonyl)-1*H*-imidazole (3x). Yellow solid (82.8 mg, 79%). Mp 182−184 °C. IR (KBr): 2917, 1652, 1597, 1498, 1437, 1317, 1149, 710, 661 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (s, 1H), 7.64 (d, J = 8.0 Hz, 2H), 7.49 (s, 1H), 7.21 (d, J = 7.8 Hz, 2H), 7.11−7.16 (m, 2H), 7.06 (d, J = 8.4 Hz, 1H), 6.93−7.01 (m, 5H), 6.67 (d, J = 7.6 Hz, 2H), 6.50 (s, 1H), 6.23(d, J = 7.6 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.5, 141.9, 137.9, 136.8, 136.5, 132.4, 131.9, 130.1, 129.4, 129.2, 128.1, 127.8, 127.1, 126.9, 126.8, 123.6, 123.0, 119.9, 112.0, 103.9, 21.3. MS (EI, 70 eV) m/z: 523 [M]$^+$. HRMS calcd for $C_{30}H_{23}ClN_3O_2S^+$ (M + H$^+$): 524.1194, found 524.1179. Anal. Calcd for $C_{30}H_{22}ClN_3O_2S$: C, 68.76; H, 4.23; N, 8.01. Found: C, 68.47; H, 4.51; N, 7.89.

***tert*-Butyl 5-[2-(4-Chlorophenyl)-1*H*-indol-1-yl]-1-phenyl-1*H*-imidazole-4-carboxylate (3y).** Yellow solid (70.5 mg, 75%). Mp 260−262 °C. IR (KBr): 2970, 1724, 1597, 1578, 1500, 1455, 1256, 1154, 840, 797 cm^{-1}.^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (s, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.20−7.31 (m, 4H), 7.05−7.13 (m, 4H), 6.80 (d, J = 8.4 Hz, 2H), 6.56 (s, 1H), 6.37 (d, J = 7.6 Hz, 2H), 1.14 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.6, 139.4, 138.7, 136.0, 133.9, 133.7, 130.7, 130.1, 129.3, 128.9, 128.7, 128.5, 123.8, 123.3, 121.6, 120.9, 111.0, 104.3, 81.3, 27.7. MS (EI, 70 eV) m/z: 469 [M]$^+$. HRMS calcd for $C_{28}H_{25}ClN_3O_2^+$ (M + H$^+$): 470.1630, found 470.1622. Anal. Calcd for $C_{28}H_{24}ClN_3O_2$: C, 71.56; H, 5.15; N, 8.94. Found: C, 71.35; H, 5.34; N, 8.78.

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra for the products and X-ray crystal data of compound **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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