EurJOC European Journal of Organic Chemistry

FULL PAPER

DOI: 10.1002/ejoc.201300369

Leaving Group and Regioselectivity Switches in the Aminoalkylation Reaction of Indoles and Related Heterocycles with α-Amido Sulfones

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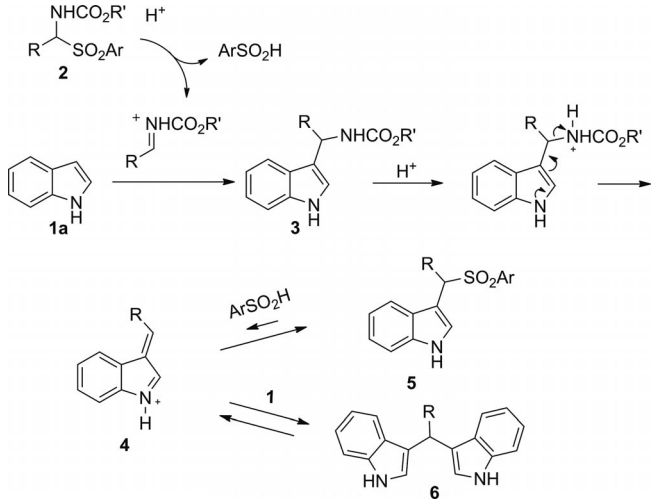
Keywords: Synthetic methods / Nitrogen heterocycles / Regioselectivity / Sulfur / Alkylation

The regioselective aminoalkylation of indoles and related heterocycles with α-amido sulfones under basic conditions has been studied. The reaction that employed the MeMgBr/$MgBr_2$ system provided high yields of 3-(1-carbamoylalkyl)-indoles. On the other hand, the reaction that used Cs_2CO_3 afforded 1-(1-carbamoylalkyl)indoles exclusively in high yields. The first reaction constitutes a switch of the leaving group of the α-amido sulfone in comparison to previously reported reactions between indoles and α-amido sulfones, which provided 3-(1-arylsulfonylalkyl)indoles. The second reaction constitutes a switch in the regioselectivity. The extensions of these *C*- and *N*-aminoalkylations starting from pyrroles and 7-azaindole have also been studied. Structurally diverse aminoalkylated indoles, pyrroles, and 7-azaindoles were obtained with excellent yield in most of the cases.

Introduction

The indole framework represents a key structural motif in a large number of biologically active natural products and pharmaceutical compounds.[1] Therefore, intense efforts have been devoted to the modification of the indole structure, particularly to the introduction of functionalized alkyl frameworks at the C-3 position of the indole system, including the development of enantioselective variants.[2] The majority of available methods to attain this goal use a Friedel–Crafts (F-C) reaction, which exploits the electron-rich nature of the indole nucleus and uses epoxides,[3] α,β-unsaturated carbonyl compounds,[4] and nitroalkenes[5] as electrophilic reagents. However, the use of imines and their derivatives to form 3-indolylalkylamines is challenging because of the poor electrophilicity of the azomethine carbon atom and the trend towards the formation of double addition products through the elimination of the amine moiety (see Scheme 1).[6]

Some general methods to synthesize 3-indolylalkylamines involve the enhancement of the electrophilic character of the carbon–nitrogen double bond by binding electron-withdrawing groups to the nitrogen atom to lead to *N*-protected 3-indolylalkylamines. Thus, *N*-sulfinyl and *N*-sulfonyl imines have been widely used as electrophiles in F-C reactions with indoles to afford *N*-sulfinyl and *N*-sulfonyl 3-indolylalkylamines, respectively.[7] Additionally, *N*-acyl-



Scheme 1. Proposed mechanism for the addition of indoles to α-amido sulfones under acidic conditions (previous work).

imines and *N*-acyliminium cations have also been used as electrophiles.[8] These species are very reactive, but also highly unstable and generally need to be generated in situ from appropriate precursors, such as α-amido sulfones. α-Amido sulfones can be conveniently prepared from aldehydes, sodium arenesulfinates, and carbamates, and most of them are stable solids that can be stored for a prolonged time.[9] α-Amido sulfones **2** react either with acid reagents to give *N*-acyliminium ions or with base to afford the corresponding *N*-acylimines. The acidic approach has been used by several authors who have described the F-C reaction of aromatic compounds with α-amido sulfones to give the corresponding adducts.[10] However, when these reaction conditions were applied to indole (**1a**) as the nucleophilic com-

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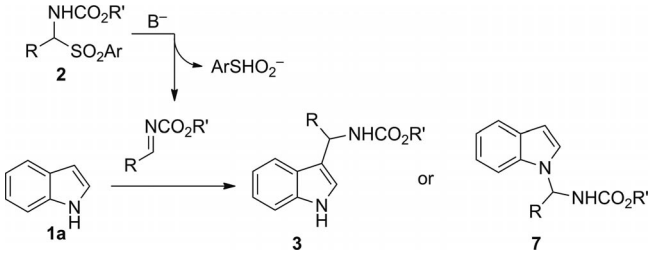
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201300369.

ponent, the reaction did not give the expected 3-aminoalkylated indole **3** with the carbamoyl moiety. Instead, 3-substituted indole **5** that contained an arylsulfonyl group was obtained. The authors rationalized their results through the initial formation of the expected F-C alkylation product **3**, which was unstable under these reaction conditions and rapidly eliminated the carbamoyl moiety to generate an alkylideneindolenium ion **4**. This ion underwent addition with either $ArSO_2H$ or indole to afford product **5** or the double addition product **6**, respectively (see Scheme 1).[11]

We envisaged that these drawbacks could be avoided if the reaction was carried out in a basic medium (see Scheme 2). Under these conditions, deprotonation of the carbamate and elimination of the sulfinate group of α-amido sulfone **2** gives an *N*-carbamoyl imine that undergoes reaction with the indole to lead to the corresponding adduct **3**, which should be stable under the basic conditions, preventing the elimination of the carbamate. This overall process represents a switch of the leaving group with regard to the acidic conditions in the previously published results. Still, we assume that N-H indoles are ambidentate nucleophiles under basic conditions and, therefore, the introduction of an aminoalkyl moiety at the nitrogen atom is also possible to give the corresponding *N*-aminoalkylated product **7**, which involves a switch in the regioselectivity of the reaction. This switch should closely depend upon the reaction conditions.[12]



Scheme 2. Addition of indole to α-amido sulfones under basic conditions and the regioselectivity of the aminoalkylation reaction (this work).

Results and Discussion

Initially, we investigated the use of different bases in the reaction of indole (**1a**) and α-amido sulfone **2a** (R = Ph, R′ = Bn, Ar = 4-MeC_6H_4). We first investigated the suitability of using CsF in dichloromethane for the deprotonation of the α-amido sulfone, as Sato had described for a stannylation reaction.[13] However, low yields (43%) of the *C*-3-aminoalkylated product **3aa** together with 14% of the diindolyl deriative **6aa** were obtained by using this system. Lithium, sodium, and potassium carbonates provided product **3aa** with high selectivity, but there was incomplete conversion (see Table 1, Entries 2–4). Cesium carbonate was also investigated, but this base did not afford compound **3aa**. Instead, *N*-aminoalkylated product **7aa** was obtained in high yield with a complete switch in the regioselectivity (see Table 1, Entry 5). The amount of base could be reduced to 2 equiv. with practically no detriment to the yield (see Table 1, Entry 6), but the use of other halogenated solvents did not improve this result (see Table 1, Entries 8 and 9).

Table 1. Reaction between indole (**1a**) and α-amido sulfone **2a** according to Scheme 2. Optimization of the reaction conditions.[a]

Entry	Base (equiv.)	Solvent	*T* [°C]	*t* [h]	Yield [%][b] **3aa**	**7aa**	**6aa**
1	CsF (3)	CH_2Cl_2	r.t.	48	43	–	14
2	Li_2CO_3 (3)	CH_2Cl_2	r.t.	72	70	–	3
3	Na_2CO_3 (3)	CH_2Cl_2	r.t.	96	60	–	–
4	K_2CO_3 (3)	CH_2Cl_2	r.t.	72	70	–	2
5	Cs_2CO_3 (3)	CH_2Cl_2	r.t.	3	–	88	–
6	Cs_2CO_3 (2)	CH_2Cl_2	r.t.	3	–	87	–
7	Cs_2CO_3 (1)	CH_2Cl_2	r.t.	27	12	–	–
8	Cs_2CO_3 (3)	$CHCl_3$	r.t.	20	–	87	–
9	Cs_2CO_3 (3)	$(ClCH_2)_2$	r.t.	22	–	75	–
10	Et_2Zn (2)	CH_2Cl_2	0	48	49	–	15
11	MeMgBr (1)	CH_2Cl_2	0	1.5	74	–	–
12[c]	MeMgBr (1)	CH_2Cl_2	0	1.5	91	–	–
13[d]	MeMgBr (1)	CH_2Cl_2	0	4	83	–	–
14[c]	MeMgBr (0.5)	CH_2Cl_2	0	1.5	35	–	–
15[c]	MeMgBr (1)	$CHCl_3$	0	0.75	80	–	–
16[c]	MeMgBr (1)	$(ClCH_2)_2$	0	5	85	–	–
17[c]	MeMgBr (1)	THF	r.t.	20	42	–	–
18[c]	MeMgBr (1)	Et_2O	r.t.	4	30	–	–

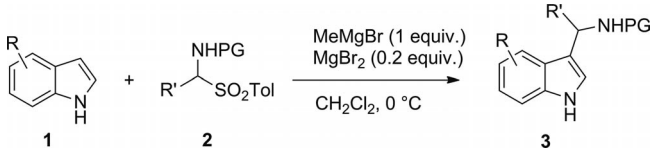
[a] Reagents and conditions: **1a** (0.125 mmol) and **2a** (0.125 mmol) in solvent (1.5 mL). [b] Yield of isolated product. [c] $MgBr_2$ (20 mol-%) was used as additive. [d] $MgBr_2$ (10 mol-%) was used as additive.

Inspired by our previous work with α-amido sulfones,[14] we employed a stronger base such as diethylzinc, which led to a decrease in the yield of **3aa** and to the formation of double addition product **6aa** (see Table 1, Entry 10). On the other hand, the use MeMgBr as a base accelerated the reaction to give product **3aa** in good yield and with high selectivity (see Table 1, Entry 11). Next, we carried out the reaction using MeMgBr in the presence of 20 mol-% of $MgBr_2$, as this salt had been used as a Lewis acid together with MeMgBr to increase the reactivity of an electrophile.[15] To our delight, product **3aa** was obtained in excellent yield (91%) and with total selectivity with regard to both attack position and leaving group (see Table 1, Entry 12). A decrease of either the salt loading or the amount of base resulted in a lower yield (see Table 1, Entries 13 and 14). The use of different chlorinated or ether solvents did not show an improvement over the results that were obtained with CH_2Cl_2 (see Table 1, Entries 15–18). In summary, the optimized reaction conditions were established, that is, the *C*-3-aminoalkylated products **3** were obtained by using the MeMgBr/$MgBr_2$ system in CH_2Cl_2 at 0 °C (see Table 1, Entry 12), and the *N*-1-aminoalkylated products **7** were produced by using Cs_2CO_3 in CH_2Cl_2 at room temperature (see Table 1, Entry 6). Remarkably, in both cases we can use equimolar amounts of the reactants.

Once the optimized conditions for the regioselective aminoalkylations were established, several indoles **1** were treated with different α-amido sulfones **2** by using both methods (see Tables 2 and 3). First, the scope of reaction at C-3 was studied. The reactions between indole (**1a**) and α-

amido sulfones **2a**–**2f**, which contained either electron-donating or -withdrawing groups at different positions of the phenyl group, as well as α-amido sulfones **2g** and **2h**, with heteroaromatic groups, afforded products **3** with excellent selectivity and high yields (see Table 2, Entries 1–8).

Table 2. Regioselective *C*-3-aminoalkylation of indoles with α-amido sulfones. Scope of the reaction.[a]



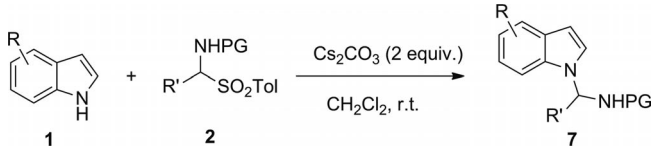
1 2 3

Entry	1	R	2	R′	*t* [h]	3	Yield [%][b]
1	**1a**	H	**2a**	Ph	3	**3aa**	91
2	**1a**	H	**2b**	4-MeC_6H_4	3.5	**3ab**	72
3	**1a**	H	**2c**	4-MeOC_6H_4	1	**3ac**	99
4	**1a**	H	**2d**	4-ClC_6H_4	3	**3ad**	81
5	**1a**	H	**2e**	3-MeC_6H_4	3	**3ae**	99
6	**1a**	H	**2f**	2-ClC_6H_4	3	**3af**	99
7	**1a**	H	**2g**	3-furanyl	1	**3ag**	95
8	**1a**	H	**2h**	2-thienyl	2	**3ah**	90
9[c]	**1a**	H	**2i**	*n*Bu	1	**3ai**	75
10[c]	**1a**	H	**2j**	isobutyl	1	**3aj**	74
11[c]	**1a**	H	**2k**	neopentyl	0.5	**3ak**	86
12[c]	**1a**	H	**2l**	cyclohexyl	1.5	**3al**	88
13[c]	**1a**	H	**2m**	*i*Pr	2	**3am**	85
14[d]	**1a**	H	**2n**	Ph	3.5	**3an**	91
15[d]	**1a**	H	**2o**	4-MeC_6H_4	1.5	**3ao**	79
16	**1b**	1-CH_3	**2a**	Ph	1.5	**3ba**	98
17	**1c**	1-CH_3OC	**2a**	Ph	24	**3ca**	n.r.
18	**1d**	2-$COOCH_3$	**2a**	Ph	24	**3da**	39
19	**1e**	2-CH_3	**2a**	Ph	4	**3ea**	n.d.[e]
20	**1g**	4-CH_3	**2a**	Ph	1	**3ga**	91
21	**1h**	5-CH_3O	**2a**	Ph	3	**3ha**	93
22	**1i**	5-Cl	**2a**	Ph	3	**3ia**	97
23	**1j**	6-F	**2a**	Ph	3	**3ja**	92
24	**1k**	7-CH_3	**2a**	Ph	3	**3ka**	97

[a] Reagents and conditions: **1** (0.125 mmol), **2** (0.125 mmol), MeMgBr (1 equiv.), and $MgBr_2$ (20 mol-%) in CH_2Cl_2 (1.5 mL) at 0 °C, PG = Cbz unless otherwise stated. [b] Isolated product. [c] **1a** (0.375 mmol), **2** (0.125 mmol), MeMgBr (1 equiv.), and $MgBr_2$ (20 mol-%) in $CHCl_3$ (1.5 mL) at room temp. [d] PG = Boc, n.r. = no reaction. [e] A complex mixture was obtained (n.d. = not detected).

The introduction of an alkyl moiety at the C-3 position was problematic because of the lower reactivity of the aliphatic α-amido sulfone. It was possible, however, to find a compromise between the low reactivity of the α-amido sulfone and the formation of the double addition product **6** by performing the reaction in $CHCl_3$ at room temperature with 3 equiv. of indole (**1a**). By using these modified conditions, the reaction also tolerated α-amido sulfones with alkyl groups that were substituted at the α position by a hydrogen atom. Independently, these were primary, secondary, cyclic, or highly branched alkyl substituents on the α-amido sulfone (see Table 2, Entries 9–13) to afford the *C*-3-aminoalkylated products **3** in good yields. This method was also applied to *N*-Boc-protected α-amido sulfones (Boc = *tert*-butoxycarbonyl) with results similar to those obtained with the benzyloxycarbonyl (Cbz) protecting group (see Table 2, Entries 14 and 15).

Table 3. Regioselective *N*-1-aminoalkylation of indoles with α-amido sulfones. Scope of the reaction.[a]



1 2 7

Entry	1	R	2	R′	*t* [h]	7	Yield [%][b]
1	**1a**	H	**2a**	Ph	3	**7aa**	87
2	**1a**	H	**2b**	4-MeC_6H_4	3.5	**7ab**	89
3	**1a**	H	**2c**	4-MeOC_6H_4	12	**7ac**	91
4	**1a**	H	**2d**	4-ClC_6H_4	3	**7ad**	84
5	**1a**	H	**2e**	3-MeC_6H_4	12	**7ae**	96
6	**1a**	H	**2f**	2-ClC_6H_4	6	**7af**	86
7	**1a**	H	**2g**	3-furanyl	1	**7ag**	90
8	**1a**	H	**2h**	2-thienyl	48	**7ah**	86
9	**1a**	H	**2i**	*n*Bu	3	**7ai**	89
10	**1a**	H	**2j**	isobutyl	3	**7aj**	92
11	**1a**	H	**2k**	neopentyl	3	**7ak**	93
12	**1a**	H	**2l**	cyclohexyl	3	**7al**	88
13	**1a**	H	**2m**	*i*Pr	6	**7am**	99
14[c]	**1a**	H	**2n**	Ph	4	**7an**	87
15[c]	**1a**	H	**2o**	4-MeC_6H_4	8	**7ao**	88
16	**1d**	2-$COOCH_3$	**2a**	Ph	5	**7da**	72
17	**1e**	2-CH_3	**2a**	Ph	5	**7ea**	n.d.[d]
18	**1f**	3-CH_3	**2a**	Ph	5	**7fa**	80
19	**1g**	4-CH_3	**2a**	Ph	5	**7ga**	92
20	**1h**	5-CH_3O	**2a**	Ph	5	**7ha**	86
21	**1i**	5-Cl	**2a**	Ph	3.5	**7ia**	91
22	**1j**	6-F	**2a**	Ph	21	**7ja**	94
23	**1k**	7-CH_3	**2a**	Ph	3	**7ka**	51

[a] Reagents and conditions: **1** (0.125 mmol), **2** (0.125 mmol) and Cs_2CO_3 (2 equiv.) in CH_2Cl_2 (1.5 mL) at room temp., PG = Cbz unless otherwise stated. [b] Isolated product. [c] PG = Boc. [d] A complex mixture was obtained (n.d. = not detected).

The scope of the reaction was further studied by employing differently substituted indoles and α-amido sulfone **2a**. Indoles that were substituted on the heterocyclic ring gave variable results (see Table 2, Entries 16–19). 1-Acetylindole (**1c**) did not react, and the starting material was recovered unchanged (see Table 2, Entry 17). The presence of a substituent at the C-2 position of the indole affected the reactivity, but not the regioselectivity. Thus, 2-(methoxycarbonyl)indole (**1d**) slowly underwent a reaction to give the *C*-3-aminoalkylation product **3da** in 39% yield after 24 h (see Table 2, Entry 18), whereas 2-methylindole (**1e**) was very reactive and gave a complex reaction mixture (see Table 2, Entry 19). On the other hand, the presence of substituents on the homocyclic ring did not affect the yield or the reactivity. Regardless of their nature or position, the expected *C*-3-aminoalkylation products were obtained in excellent yields (see Table 2, Entries 20–24).

Moreover, we studied the scope of the *N*-aminoalkylation reaction. Indole (**1a**) was treated under the optimized conditions with several α-amido sulfones **2** that contained different phenyl-substituted moieties (see Table 3, Entries 1–6) or heteroaromatic groups (see Table 3, Entries 7

and 8) to give compounds **7** in very high yields and with total regioselectivity. The reaction also tolerated α-amido sulfones with alkyl moieties (see Table 3, Entries 9–13) to afford again excellent results in terms of yield and selectivity.

In addition, it was possible to perform the reaction with *N*-Boc-protected α-amido sulfones (see Table 3, Entries 14 and 15). Furthermore, α-amido sulfone **2a** was treated with several substituted indoles **1**. The reaction afforded good results when the substituent was located away from the reaction center, and this occurred regardless of the nature or position of the substitutent (see Table 3, Entries 18–22). When the substituent was located close to the reaction center, results were not as good (see Table 3, Entries 16, 17, and 23). Again, the presence of substituents at the C-2 position did not exert any effect on the regioselectivity. 2-(Methoxycarbonyl)indole (**1d**) gave compound **7da** in good yield (72%, see Table 3, Entry 16), whereas 2-methylindole (**1e**) produced a complex mixture (see Table 3, Entry 17), as in the reaction with MeMgBr (Table 2, Entry 19).

Finally, an extension of these regioselective *C*- and *N*-aminoalkylations by starting from pyrroles and 7-azaindole was investigated. After optimizing the experimental conditions (see Supporting Information), we found that pyrroles underwent reaction at the C-2 position to afford the corresponding aminoalkylated products **8** in good yields, even when aliphatic α-amido sulfones were used. Moreover, the less reactive 7-azaindole gave the desired product in a modest yield, which is in agreement with previously reported examples involving the Pictet–Spengler reaction.[16] On the other hand, pyrrole showed a lower reactivity under the reaction conditions for the *N*-substitution, but 7-azaindole afforded the desired products in good yields (see Figure 1).

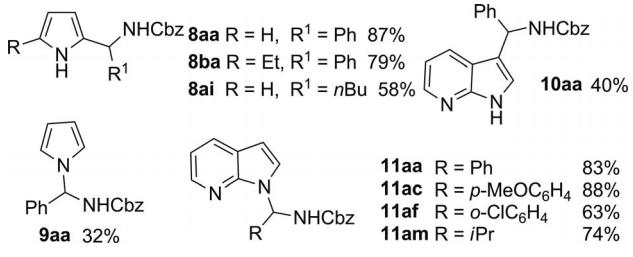
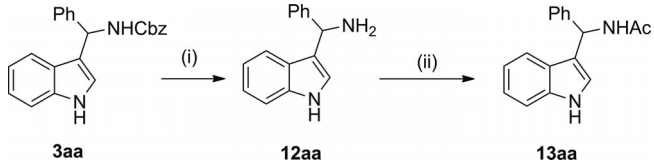


Figure 1. *C*- and *N*-aminoalkylations of pyrroles and 7-azaindole with α-amido sulfones.

Compounds **3** and **7** are gramine and *N*-isogramine derivatives, respectively, which are particularly interesting on account of their biological activities and their use as starting materials in further transformations. The cleavage of the Cbz group in compound **3aa** was carried out under reductive conditions to afford **12aa** in quantitative yield followed by the transformation into monoacetyl derivative **13aa** for comparative purposes (see Scheme 3).[17] However, the deprotection of the *N*-aminoalkylated products **7** was not possible by either reducing or acid methods, possibly because of the instability of the aminal that would be formed.



Scheme 3. Deprotection of the product **3aa** and acetylation of amine **12aa**. Reagents and conditions: (i) Na (20 equiv.), NH_3/tetrahydrofuran (THF), –78 °C, 30 min, 100%; (ii) AcCl (3 equiv.), NaOH (2.2 equiv.), CH_2Cl_2, room temp., 1 h, 70%.

Conclusions

We have developed two methods for the regioselective aminoalkylation of indoles and related heterocycles with α-amido sulfones. Both methods allowed the preparation *C*- and *N*-aminoalkylated indoles, pyrroles, and 7-azaindole with high selectivity, in excellent yields in most of the cases, and with a wide structural diversity by using α-amido sulfones that contained aromatic, heteroaromatic, and even aliphatic groups. The C-3 aminoalkylation (F-C) of indoles involved an unprecedented switch of the leaving group of the α-amido sulfone in comparison to previously reported F-C reactions of indoles and α-amido sulfones, but the *N*-1-aminoalkylation constituted a switch in the regioselectivity of the reaction.

Experimental Section

General Methods: Reactions were carried out under nitrogen in round-bottomed flasks that were oven-dried at 120 °C overnight. Commercial reagents were used as purchased. α-Amido sulfones were synthesized as described in the literature.[9] Dichloromethane was freshly distilled from CaH_2. Chloroform was filtered through basic alumina, distilled from P_2O_5, and stored over molecular sieves (4 Å). Reactions were monitored by TLC analysis using Merck silica gel 60 F-254 thin layer plates. Flash column chromatography was performed on Merck silica gel 60, 0.040–0.063 mm. Melting points were determined with capillary tubes. The NMR spectroscopic data were recorded at 300 MHz for ^{1}H NMR and at 75 MHz for ^{13}C NMR by using the residual nondeuterated solvent as the internal standard ($CDCl_3$: δ = 7.26 ppm for ^{1}H NMR and δ = 77.0 ppm for ^{13}C NMR; [D_6]DMSO: δ = 2.50 ppm for ^{1}H NMR and δ = 39.52 ppm for ^{13}C NMR; [D_6]acetone: δ = 2.05 ppm for ^{1}H NMR and δ = 29.84 ppm for ^{13}C NMR). Chemical shifts are given in ppm. The ^{13}C assignments were determined by using DEPT experiments. High resolution mass spectra (ESI) were recorded with a Q-TOF spectrometer equipped with an electrospray source and a capillary voltage of 3.3 kV.

Procedures for the Synthesis of *C*-3-Aminoalkylated Indoles

(a) With Aromatic α-Amido Sulfones: Table 2. MeMgBr (1 M solution in THF, 125 μL, 0.125 mmol) was added to a cooled (ice bath) solution of indole **1** (0.125 mmol) and $MgBr_2$ (4.6 mg, 0.025 mmol) in CH_2Cl_2 (0.5 mL). The mixture was stirred at 0 °C for 2 h. Then, a suspension of α-amido sulfone (0.125 mmol) in CH_2Cl_2 (1 mL) was added, and the mixture was stirred at 0 °C until the reaction reached completion (TLC). Then, it was quenched with a saturated aqueous solution of NH_4Cl (1 mL), and the resulting mixture was extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were washed with brine (50 mL) and dried with anhydrous Na_2SO_4.

Purification by flash chromatography on silica gel (hexane/EtOAc) afforded compounds **3**.

(b) With Aliphatic α-Amido Sulfones: Table 2. MeMgBr (1 M solution in THF, 125 μL, 0.125 mmol) was added to a cooled (ice bath) solution of indole **1** (0.375 mmol) and $MgBr_2$ (4.6 mg, 0.025 mmol) in $CHCl_3$ (0.5 mL). The mixture was stirred at 0 °C for 2 h. Then, a suspension of α-amido sulfone (0.125 mmol) in $CHCl_3$ (1 mL) was added, and the reaction mixture was stirred at room temperature until it reached completion (TLC). Then, it was quenched with a saturated aqueous solution of NH_4Cl (1 mL), and the resulting solution was extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were washed with brine (50 mL) and dried with anhydrous Na_2SO_4. Purification by flash chromatography on silica gel (hexane/EtOAc) afforded compounds **3**.

Benzyl [(1*H*-Indol-3-yl)(phenyl)methyl]carbamate (3aa): 40.5 mg, 91% yield; m.p. 132–133 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.05 (s, 1 H), 7.48 (d, $J_{H,H}$ = 8.0 Hz, 1 H), 7.44–7.27 (m, 11 H), 7.21 (ddd, $J_{H,H}$ = 8.0, 7.0, 1.0 Hz, 1 H), 7.08 (ddd, $J_{H,H}$ = 8.0, 7.0, 1.0 Hz, 1 H), 6.76 (s, 1 H), 6.28 (d, $J_{H,H}$ = 7.5 Hz, 1 H), 5.45 (d, $J_{H,H}$ = 6.5 Hz, 1 H), 5.17 (d, $J_{H,H}$ = 12.5 Hz, 1 H), 5.12 (d, $J_{H,H}$ = 12.5 Hz, 1 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 155.7 (C), 141.5 (C), 136.6 (C), 136.3 (C), 128.41 (CH), 128.36 (CH), 128.0 (CH), 127.9 (CH), 127.2 (CH), 126.8 (CH), 125.7 (C), 123.4 (CH), 122.3 (CH), 119.7 (CH), 119.2 (CH), 116.9 (C), 111.4 (CH), 66.8 (CH_2), 52.3 (CH) ppm. HRMS (ESI): calcd. for $C_{23}H_{20}N_2NaO_2$ [M + Na]$^+$ 379.1422; found 379.1410.

Benzyl [(1*H*-Indol-3-yl)(*p*-tolyl)methyl]carbamate (3ab): 33.3 mg, 72% yield; m.p. 144–145 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.17 (s, 1 H), 7.53–7.45 (m, 1 H), 7.42–7.13 (m, 11 H), 7.08 (ddd, $J_{H,H}$ = 8.0, 7.0, 1.0 Hz, 1 H), 6.73 (s, 1 H), 6.25 (d, $J_{H,H}$ = 8.0 Hz, 1 H), 5.49 (d, $J_{H,H}$ = 7.5 Hz, 1 H), 5.18 (d, $J_{H,H}$ = 12.5 Hz, 1 H), 5.13 (d, $J_{H,H}$ = 12.5 Hz, 1 H), 2.37 (s, 3 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 155.7 (C), 138.6 (C), 136.8 (C), 136.6 (C), 136.4 (C), 129.1 (CH), 128.5 (CH), 128.4 (CH), 128.0 (CH), 126.8 (CH), 125.7 (C), 123.2 (CH), 122.4 (CH), 119.8 (CH), 119.4 (CH), 117.4 (C), 111.3 (CH), 66.8 (CH_2), 52.1 (CH), 21.1 (CH_3) ppm. HRMS (ESI): calcd. for $C_{24}H_{22}N_2NaO_2$ [M + Na]$^+$ 393.1579; found 393.1586.

Benzyl [(1*H*-Indol-3-yl)(4-methoxyphenyl)methyl]carbamate (3ac): 47.8 mg, 99% yield; m.p. 147–148 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.04 (s, 1 H), 7.45 (d, $J_{H,H}$ = 7.5 Hz, 1 H), 7.40–7.26 (m, 8 H), 7.24–7.14 (m, 1 H), 7.07 (ddd, $J_{H,H}$ = 8.0, 7.0, 1.0 Hz, 1 H), 6.94–6.83 (m, 2 H), 6.80 (s, 1 H), 6.22 (d, $J_{H,H}$ = 8.0 Hz, 1 H), 5.41 (d, $J_{H,H}$ = 5.0 Hz, 1 H), 5.17 (d, $J_{H,H}$ = 12.5 Hz, 1 H), 5.11 (d, $J_{H,H}$ = 12.5 Hz, 1 H), 3.81 (s, 3 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 158.8 (C), 155.7 (C), 136.7 (C), 136.5 (C), 133.4 (C), 128.5 (CH), 128.0 (CH), 128.0 (CH), 125.8 (C), 123.1 (CH), 122.5 (CH), 119.8 (CH), 119.5 (CH), 117.7 (C), 113.8 (CH), 111.3 (CH), 66.8 (CH_2), 55.3 (CH_3), 51.8 (CH) ppm. HRMS (ESI): calcd. for $C_{24}H_{22}NaN_2O_2$ [M + Na]$^+$ 409.1528; found 409.1535.

Benzyl [(4-Chlorophenyl)(1*H*-indol-3-yl)methyl]carbamate (3ad): 39.5 mg, 81% yield; m.p. 152–153 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.18 (s, 1 H), 7.46 (d, $J_{H,H}$ = 8.0 Hz, 1 H), 7.44–7.28 (m, 10 H), 7.25–7.18 (m, 1 H), 7.14–7.05 (m, 1 H), 6.71 (s, 1 H), 6.23 (d, $J_{H,H}$ = 7.5 Hz, 1 H), 5.47 (d, $J_{H,H}$ = 6.5 Hz, 1 H), 5.18 (d, $J_{H,H}$ = 12.5 Hz, 1 H), 5.12 ppm (d, $J_{H,H}$ = 12.5 Hz, 1 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 155.7 (C), 140.2 (C), 136.6 (C), 136.3 (C), 133.0 (C), 128.6 (CH), 128.5 (CH), 128.2 (CH), 128.1 (CH), 128.1 (CH), 128.1 (CH), 125.6 (C), 123.3 (CH), 122.7 (CH), 120.1 (CH), 119.2 (CH), 116.9 (C), 111.4 (CH), 67.0 (CH_2), 51.8 (CH) ppm. HRMS (ESI): calcd. for $C_{23}H_{19}ClN_2NaO_2$ [M + Na]$^+$ 413.1033; found 413.1016.

Benzyl [(1*H*-Indol-3-yl)(*m*-tolyl)methyl]carbamate (3ae): 45.8 mg, 99% yield; m.p. 117–118 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.15 (s, 1 H), 7.51 (d, $J_{H,H}$ = 8.0 Hz, 1 H), 7.44–7.15 (m, 10 H), 7.15–7.05 (m, 2 H), 6.73 (s, 1 H), 6.26 (d, $J_{H,H}$ = 7.5 Hz, 1 H), 5.49 (d, $J_{H,H}$ = 7.5 Hz, 1 H), 5.19 (d, $J_{H,H}$ = 12.5 Hz, 1 H), 5.14 (d, $J_{H,H}$ = 12.5 Hz, 1 H), 2.35 (s, 3 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$). δ = 155.7 (C), 141.5 (C), 138.0 (C), 136.6 (C), 136.5 (C), 128.4 (CH), 128.3 (CH), 128.0 (CH), 127.57 (CH), 125.82 (C), 123.86 (CH), 123.29 (CH), 122.42 (CH), 119.8 (CH), 119.4 (CH), 117.4 (C), 111.3 (CH), 66.8 (CH_2), 52.3 (CH), 21.5 (CH_3) ppm. HRMS (ESI): calcd. for $C_{24}H_{22}KN_2O_2$ [M + K]$^+$ 409.1318; found 409.1329.

Benzyl [(2-Chlorophenyl)(1*H*-indol-3-yl)methyl]carbamate (3af): 48.2 mg, 99% yield; m.p. 57–60 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.11 (s, 1 H), 7.51–7.44 (m, 1 H), 7.37 (dd, $J_{H,H}$ = 7.5, 2.0 Hz, 1 H), 7.31–7.05 (m, 10 H), 7.00 (ddd, $J_{H,H}$ = 8.0, 7.0, 1.0 Hz, 1 H), 6.53–6.43 (m, 2 H), 5.45 (d, $J_{H,H}$ = 6.0 Hz, 1 H), 5.07 (d, $J_{H,H}$ = 12.5 Hz, 1 H), 5.01 (d, $J_{H,H}$ = 12.5 Hz, 1 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 155.5 (C), 139.1 (C), 136.6 (C), 136.4 (C), 133.2 (C), 129.9 (CH), 128.5 (CH), 128.4 (CH), 128.0 (CH), 127.8 (CH), 126.9 (CH), 125.8 (C), 123.4 (CH), 122.5 (CH), 119.9 (CH), 119.1 (CH), 115.5 (C), 111.4 (CH), 66.8 (CH_2), 50.0 (CH) ppm. HRMS (ESI): calcd. for $C_{23}H_{19}ClNaN_2O_2$ [M + Na]$^+$ 413.1033; found 413.1037.

Benzyl [(Fur-3-yl)(1*H*-indol-3-yl)methyl]carbamate (3ag): 41.0 mg, 95% yield; m.p. 100–102 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.20 (s, 1 H), 7.55 (d, $J_{H,H}$ = 8.0 Hz, 1 H), 7.42–7.29 (m, 8 H), 7.25–7.18 (m, 1 H), 7.14–7.05 (m, 1 H), 6.98 (s, 1 H), 6.37 (s, 1 H), 6.24 (d, $J_{H,H}$ = 8.5 Hz, 1 H), 5.39 (d, $J_{H,H}$ = 6.5 Hz, 1 H), 5.16 (s, 2 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$). δ = 155.7 (C), 143.3 (CH), 139.9 (CH), 136.6 (C), 136.4 (C), 128.5 (CH), 128.1 (CH), 128.0 (CH), 126.7 (C), 125.6 (C), 122.8 (CH), 122.5 (CH), 119.8 (CH), 119.4 (CH), 116.3 (C), 111.4 (CH), 109.9 (CH), 66.9 (CH_2), 45.0 (CH) ppm. HRMS (ESI): calcd. for $C_{21}H_{18}NaN_2O_3$ [M + Na]$^+$ 369.1220; found 369.1215.

Benzyl [(1*H*-Indol-3-yl)(thien-2-yl)methyl]carbamate (3ah): 40.7 mg, 90% yield; m.p. 125–126 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.25 (s, 1 H), 7.50 (d, $J_{H,H}$ = 8.0 Hz, 1 H), 7.36 (dd, $J_{H,H}$ = 4.54, 3.0 Hz, 6 H), 7.28–7.17 (m, 2 H), 7.09 (dd, $J_{H,H}$ = 11.0, 4.0 Hz, 1 H), 7.04–6.92 (m, 3 H), 6.55 (d, $J_{H,H}$ = 8.0 Hz, 1 H), 5.60 (d, $J_{H,H}$ = 6.5 Hz, 1 H), 5.18 (s, 2 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 155.5 (C), 146.0 (C), 136.6 (C), 136.3 (C), 128.5 (CH), 128.1 (CH), 128.0 (CH), 126.7 (CH), 125.4 (C), 125.0 (CH), 124.5 (CH), 123.0 (CH), 122.5 (CH), 119.9 (CH), 119.3 (CH), 116.7 (C), 111.4 (CH), 67.0 (CH_2), 48.6 (CH) ppm. HRMS (ESI): calcd. for $C_{21}H_{18}NaN_2O_2S$ [M + Na]$^+$ 385.0987; found 385.09907.

Benzyl [1-(1*H*-Indol-3-yl)pentyl]carbamate (3ai): 31.5 mg, 75% yield; m.p. 55–56 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.11 (s, 1 H), 7.67 (d, $J_{H,H}$ = 7.5 Hz, 1 H), 7.44–6.95 (m, 9 H), 5.23–4.89 (m, 4 H), 2.10–1.85 (m, 2 H), 1.48–1.19 (m, 4 H), 0.89 (t, $J_{H,H}$ = 7.0 Hz, 3 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 155.9 (C), 136.7 (C), 136.5 (C), 128.4 (CH), 128.0 (CH), 125.9 (C), 122.3 (CH), 121.4 (CH), 119.7 (CH), 119.3 (CH), 117.5 (C), 111.3 (CH), 66.6 (CH_2), 48.6 (CH), 35.2 (CH_2), 28.6 (CH_2), 22.5 (CH_2), 14.0 (CH_3) ppm. HRMS (ESI): calcd. for $C_{21}H_{24}NaN_2O_2$ [M + Na]$^+$ 359.1743; found 359.1735.

Benzyl [1-(1*H*-Indol-3-yl)-3-methylbutyl]carbamate (3aj): 31.1 mg, 74% yield; m.p. 68–70 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.02 (s, 1 H), 7.58 (d, $J_{H,H}$ = 8.0 Hz, 1 H), 7.31–7.17 (m, 6 H), 7.11 (ddd, $J_{H,H}$ = 8.0, 7.0, 1.0 Hz, 1 H), 7.06–6.92 (m, 2 H), 5.13–4.82 (m, 4 H), 1.86–1.49 (m, 3 H), 0.92–0.85 (m, 6 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 155.8 (C), 136.6 (C), 136.5 (C), 128.5

(CH), 128.0 (CH), 125.9 (C), 122.3 (CH), 121.4 (CH), 119.7 (CH), 119.4 (CH), 117.7 (C), 111.3 (CH), 66.6 (CH_2), 46.6 (CH), 44.6 (CH_2), 25.1 (CH), 22.6 (CH_3), 22.6 (CH_3) ppm. HRMS (ESI): calcd. for $C_{21}H_{24}NaN_2O_2$ $[M + Na]^+$ 359.1743; found 359.1738.

Benzyl [1-(1*H*-Indol-3-yl)-3,3-dimethylbutyl]carbamate (3ak): 37.6 mg, 86% yield; m.p. 130–132 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.01 (s, 1 H), 7.62 (d, $J_{H,H}$ = 7.0 Hz, 1 H), 7.34–6.87 (m, 9 H), 5.23–4.86 (m, 4 H), 1.96 (dd, $J_{H,H}$ = 14.0, 5.0 Hz, 1 H), 1.79 (dd, $J_{H,H}$ = 14.0, 8.0 Hz, 1 H), 0.92 (s, 9 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$). δ = 155.4 (C), 136.7 (C), 136.6 (C), 129.0 (C), 128.4 (CH), 128.0 (CH), 125.6 (C), 122.3 (CH), 121.1 (CH), 119.6 (CH), 119.4 (CH), 111.3 (CH), 66.5 (CH_2), 49.3 (CH_2), 45.9 (CH), 30.7 (C), 29.9 (CH_3) ppm. HRMS (ESI): calcd. for $C_{22}H_{26}NaN_2O_2$ $[M + Na]^+$ 373.1892; found 373.1895.

Benzyl [Cyclohexyl(1*H*-indol-3-yl)methyl]carbamate (3al): 39.8 mg, 88% yield; m.p. 129–130 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.17 (s, 1 H), 7.64 (d, $J_{H,H}$ = 7.5 Hz, 1 H), 7.41–7.27 (m, 6 H), 7.25–7.16 (m, 1 H), 7.16–7.07 (m, 1 H), 7.02 (s, 1 H), 5.21–4.98 (m, 3 H), 4.83 (t, $J_{H,H}$ = 8.5 Hz, 1 H), 2.03–1.54 (m, 7 H), 1.35–0.86 (m, 4 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 156.2 (C), 136.6 (C), 136.5 (C), 128.4 (CH), 128.1 (CH), 128.0 (CH), 125.9 (C), 122.1 (CH), 121.9 (CH), 119.6 (CH), 119.3 (CH), 116.4 (C), 111.4 (CH), 66.7 (CH_2), 54.0 (CH), 42.5 (CH), 30.4 (CH_2), 29.6 (CH_2), 26.3 (CH_2), 26.1 (CH_2), 26.1 (CH_2) ppm. HRMS (ESI): calcd. for $C_{23}H_{27}N_2O_2$ $[M + H]^+$ 363.2074; found 363.2073.

Benzyl [1-(1*H*-Indol-3-yl)-2-methylpropyl]carbamate (3am): 34.2 mg, 85% yield; m.p. 79–81 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.15 (s, 1 H), 7.64 (d, $J_{H,H}$ = 7.5 Hz, 1 H), 7.43–6.91 (m, 9 H), 5.19–5.02 (m, 3 H), 4.84 (t, $J_{H,H}$ = 9.0 Hz, 1 H), 2.39–2.21 (m, 1 H), 1.03 (d, $J_{H,H}$ = 6.5 Hz, 3 H), 0.94 (d, $J_{H,H}$ = 6.5 Hz, 3 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 156.2 (C), 136.6 (C), 136.4 (C), 128.5 (CH), 128.1 (CH), 128.0 (CH), 125.9 (C), 122.2 (CH), 121.7 (CH), 119.6 (CH), 119.4 (CH), 116.7 (C), 111.3 (CH), 66.7 (CH_2), 54.7 (CH), 32.8 (CH), 20.1 (CH_3), 18.9 (CH_3) ppm. HRMS (ESI): calcd. for $C_{20}H_{22}N_2NaO_2$ $[M + Na]^+$ 345.1579; found 345.1573.

***tert*-Butyl [(1*H*-Indol-3-yl)(phenyl)methyl]carbamate (3an):** 36.6 mg, 91% yield; m.p. 144–146 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.25 (s, 1 H), 7.53 (d, $J_{H,H}$ = 8.0 Hz, 1 H), 7.45–7.24 (m, 6 H), 7.24–7.16 (m, 1 H), 7.10 (ddd, $J_{H,H}$ = 8.0, 7.0, 1.0 Hz, 1 H), 6.68 (s, 1 H), 6.22 (d, $J_{H,H}$ = 6.0 Hz, 1 H), 5.26 (d, $J_{H,H}$ = 4.0 Hz, 1 H), 1.48 (s, 9 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 155.3 (C), 142.0 (C), 136.7 (C), 128.3 (CH), 127.1 (CH), 126.8 (CH), 125.9 (C), 123.3 (CH), 122.3 (CH), 119.7 (CH), 119.3 (CH), 117.7 (C), 111.3 (CH), 79.6 (C), 51.7 (CH), 28.4 (CH_3) ppm. HRMS (ESI): calcd. for $C_{20}H_{22}NaN_2O_2$ $[M + Na]^+$ 345.1579; found 345.1580.

***tert*-Butyl [(1*H*-Indol-3-yl)(*p*-tolyl)methyl]carbamate (3ao):** 33.2 mg, 79% yield; m.p. 137–139 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.23 (s, 1 H), 7.53 (d, $J_{H,H}$ = 8.0 Hz, 1 H), 7.39–7.04 (m, 7 H), 6.73 (d, $J_{H,H}$ = 1.5 Hz, 1 H), 6.19 (d, $J_{H,H}$ = 7.5 Hz, 1 H), 5.24 (d, $J_{H,H}$ = 7.5 Hz, 1 H), 2.36 (s, 3 H), 1.48 (s, 9 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 155.2 (C), 139.0 (C), 136.7 (C), 136.6 (C), 129.0 (CH), 126.7 (CH), 125.9 (C), 123.2 (CH), 122.3 (CH), 119.7 (CH), 119.4 (CH), 117.9 (C), 111.3 (CH), 79.5 (C), 51.4 (CH), 28.4 (CH_3), 21.1 (CH_3) ppm. HRMS (ESI): calcd. for $C_{21}H_{24}N_2NaO_2$ $[M + Na]^+$ 359.1735; found 359.1734.

Benzyl [(1-Methyl-1*H*-indol-3-yl)(phenyl)methyl]carbamate (3ba): 45.3 mg, 98% yield; m.p. 142–143 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.52 (d, $J_{H,H}$ = 8.0 Hz, 1 H), 7.47–7.23 (m, 12 H), 7.11 (ddd, $J_{H,H}$ = 8.0, 6.5, 1.5 Hz, 1 H), 6.64 (s, 1 H), 6.31 (d, $J_{H,H}$ = 7.5 Hz, 1 H), 5.50 (d, $J_{H,H}$ = 7.0 Hz, 1 H), 5.20 (d, $J_{H,H}$ = 12.0 Hz, 1 H), 5.14 (d, $J_{H,H}$ = 12.0 Hz, 1 H), 3.70 (s, 3 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 155.6 (C), 141.7 (C), 137.4 (C), 136.5 (C), 128.5 (CH), 128.4 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 127.2 (CH), 126.8 (CH), 126.2 (C), 122.0 (CH), 119.5 (CH), 119.4 (CH), 115.8 (C), 109.4 (CH), 66.7 (CH_2), 52.2 (CH), 32.6 (CH_3) ppm. HRMS (ESI): calcd. for $C_{24}H_{22}N_2NaO_2$ $[M + Na]^+$ 393.1579; found 393.1580.

Methyl 3-[{[(Benzyloxy)carbonyl]amino}(phenyl)methyl]-1*H*-indole-2-carboxylate (3da): Oil (20.2 mg, 39% yield). ^1H NMR (300 MHz, $CDCl_3$): δ = 9.02 (s, 1 H), 7.75 (d, $J_{H,H}$ = 8.0 Hz, 1 H), 7.46–7.08 (m, 11 H), 6.88 (s, 2 H), 5.18 (d, $J_{H,H}$ = 12.5 Hz, 1 H), 5.15–5.08 (m, 2 H), 4.72 (s, 1 H), 3.82 (s, 3 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 162.0 (C), 156.1 (C), 141.6 (C), 136.5 (C), 136.2 (C), 135.6 (C), 128.5 (CH), 128.4 (CH), 128.3 (CH), 128.1 (CH), 127.0 (CH), 126.3 (CH), 126.1 (CH), 124.2 (C), 122.8 (C), 121.1 (CH), 121.0 (CH), 112.0 (CH), 66.8 (CH_2), 52.1 (CH), 50.2 (CH_3) ppm. HRMS (ESI): calcd. for $C_{25}H_{23}N_2O_4$ $[M + H]^+$ 415.1658; found 415.1651.

Benzyl [(4-Methyl-1*H*-indol-3-yl)(phenyl)methyl]carbamate (3ga): 42.1 mg, 91% yield; m.p. 145–146 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.13 (s, 1 H), 7.55–7.22 (m, 10 H), 7.17 (d, $J_{H,H}$ = 8.0 Hz, 1 H), 7.14–7.04 (m, 1 H), 6.93–6.80 (m, 1 H), 6.53 (s, 1 H), 6.45 (d, $J_{H,H}$ = 7.0 Hz, 1 H), 5.42 (d, $J_{H,H}$ = 6.5 Hz, 1 H), 5.19 (d, $J_{H,H}$ = 12.5 Hz, 1 H), 5.09 (d, $J_{H,H}$ = 12.5 Hz, 1 H), 2.61 (s, 3 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 155.1 (C), 142.2 (C), 137.0 (C), 136.5 (C), 130.7 (C), 128.4 (CH), 128.3 (CH), 128.0 (CH), 127.2 (CH), 126.9 (CH), 124.8 (C), 124.4 (CH), 122.6 (CH), 121.7 (CH), 118.0 (C), 109.2 (CH), 66.7 (CH_2), 52.9 (CH), 19.9 (CH_3) ppm. HRMS (ESI): calcd. for $C_{24}H_{23}N_2O_2$ $[M + H]^+$ 371.1760; found 371.1769.

Benzyl [(5-Methoxy-1*H*-indol-3-yl)(phenyl)methyl]carbamate (3ha): 44.9 mg, 93%; m.p. 121–123 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.06 (s, 1 H), 7.43–7.17 (m, 11 H), 6.94–6.77 (m, 2 H), 6.65 (s, 1 H), 6.24 (d, $J_{H,H}$ = 7.5 Hz, 1 H), 5.48 (d, $J_{H,H}$ = 7.0 Hz, 1 H), 5.19 (d, $J_{H,H}$ = 12.5 Hz, 1 H), 5.10 (d, $J_{H,H}$ = 12.5 Hz, 1 H), 3.72 (s, 3 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 155.7 (C), 154.1 (C), 141.5 (C), 136.5 (C), 131.7 (C), 128.4 (CH), 128.0 (CH), 127.3 (CH), 126.8 (CH), 126.2 (C), 124.0 (CH), 117.1 (C), 112.7 (CH), 112.1 (CH), 100.9 (CH), 66.8 (CH_2), 55.7 (CH), 52.2 (CH_3) ppm. HRMS (ESI): calcd. for $C_{24}H_{22}N_2NaO_3$ $[M + Na]^+$ 409.1530; found 409.1520.

Benzyl [(5-Chloro-1*H*-indol-3-yl)(phenyl)methyl]carbamate (3ia): 47.3 mg, 97% yield; m.p. 127–128 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.32 (s, 1 H), 7.53–7.02 (m, 13 H), 6.70 (s, 1 H), 6.20 (d, $J_{H,H}$ = 8.0 Hz, 1 H), 5.48 (d, $J_{H,H}$ = 6.5 Hz, 1 H), 5.19 (d, $J_{H,H}$ = 12.5 Hz, 1 H), 5.12 (d, $J_{H,H}$ = 12.5 Hz, 1 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 155.7 (C), 141.1 (C), 136.3 (C), 135.0 (C), 128.6 (CH), 128.5 (CH), 128.1 (CH), 128.0 (CH), 127.5 (CH), 126.8 (CH), 125.5 (C), 124.6 (CH), 122.8 (CH), 118.7 (CH), 116.9 (C), 112.4 (CH), 66.9 (CH_2), 52.2 (CH) ppm. HRMS (ESI): calcd. for $C_{23}H_{19}ClN_2NaO_2$ $[M + Na]^+$ 413.1033; found 413.1035.

Benzyl [(6-Fluoro-1*H*-indol-3-yl)(phenyl)methyl]carbamate (3ja): 43.0 mg, 92% yield; m.p. 131–133 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.18 (s, 1 H), 7.46–7.21 (m, 11 H), 6.99 (dd, $J_{H,H}$ = 9.5, 2.0 Hz, 1 H), 6.82 (dt, $J_{H,H}$ = 9.0, 2.0 Hz, 1 H), 6.69 (s, 1 H), 6.23 (d, $J_{H,H}$ = 8.0 Hz, 1 H), 5.47 (d, $J_{H,H}$ = 6.0 Hz, 1 H), 5.18 (d, $J_{H,H}$ = 12.5 Hz, 1 H), 5.12 (d, $J_{H,H}$ = 12.5 Hz, 1 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 160.05 (d, $J_{H,H}$ = 238.5 Hz, C), 155.7 (C), 141.3 (C), 136.6 (d, $J_{H,H}$ = 12.5 Hz, C), 136.4 (C), 128.5 (CH), 128.1 (CH), 128.0 (CH), 127.4 (CH), 126.8 (CH), 123.6 (CH), 123.5 (CH), 122.4 (C), 120.1 (d, $J_{H,H}$ = 10.0 Hz, CH), 117.4 (C), 108.6 (d, $J_{H,H}$ = 24.5 Hz, CH), 97.6 (d, $J_{H,H}$ = 26.0 Hz, CH), 66.9 (CH_2),

52.3 (CH) ppm. HRMS (ESI): calcd. for $C_{23}H_{20}FN_2O_2$ $[M + H]^+$ 375.1509; found 375.1510.

Benzyl [(7-Methyl-1*H*-indol-3-yl)(phenyl)methyl]carbamate (3ka): 44.8 mg, 97% yield; m.p. 158–159 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.12 (s, 1 H), 7.52–7.22 (m, 11 H), 7.08–6.95 (m, 2 H), 6.74 (s, 1 H), 6.29 (d, $J_{H,H}$ = 8.0 Hz, 1 H), 5.52 (d, $J_{H,H}$ = 7.0 Hz, 1 H), 5.19 (d, $J_{H,H}$ = 12.5 Hz, 1 H), 5.13 [d, $J_{H,H}$ = 12.5 Hz, 1 H), 2.46 (s, 3 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 155.7 (C), 141.6 (C), 136.4 (C), 136.2 (C), 128.4 (CH), 128.4 (CH), 128.0 (CH), 127.2 (CH), 126.8 (CH), 125.3 (C), 123.0 (CH), 122.9 (CH), 120.5 (C), 120.1 (CH), 117.7 (C), 117.0 (CH), 66.8 (CH_2), 52.4 (CH), 16.5 (CH_3) ppm. HRMS (ESI): calcd. for $C_{24}H_{23}N_2O_2$ $[M + H]^+$ 371.1760; found 371.1762.

General Procedure for the Synthesis of *N*-1-Aminoalkylated Indoles: Table 3. Cs_2CO_3 (84.4 mg, 0.25 mmol) was dried in a Schlenk tube by using a heat gun under vacuum. α-Amido sulfone (0.125 mmol) was added, and the system was purged with nitrogen. Then, CH_2Cl_2 (0.7 mL) was added, and the mixture was stirred at room temperature for 2 h. A solution of the indole **1** (0.125 mmol) in CH_2Cl_2 (0.5 mL) was added. The mixture was stirred at room temperature until it reached completion (TLC). Then, it was quenched with water (1 mL), and the resulting solution was extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were washed with brine (50 mL) and dried with anhydrous Na_2SO_4. Purification by flash chromatography on silica gel (hexane/EtOAc) afforded compounds **7**.

Benzyl [(1*H*-Indol-1-yl)(phenyl)methyl]carbamate (7aa): 38.7 mg, 87% yield; m.p. 118–120 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.72–7.63 (m, 1 H), 7.47–7.12 (m, 14 H), 7.10 (d, $J_{H,H}$ = 3.5 Hz, 1 H), 6.57 (dd, $J_{H,H}$ = 3.5, 0.5 Hz, 1 H), 5.90 (d, $J_{H,H}$ = 8.5 Hz, 1 H), 5.18 (d, $J_{H,H}$ = 12.0 Hz, 1 H), 5.07 (d, $J_{H,H}$ = 12.0 Hz, 1 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 155.3 (C), 137.4 (C), 135.7 (C), 135.5 (C), 129.2 (C), 128.9 (CH), 128.8 (CH), 128.5 (CH), 128.3 (CH), 128.2 (CH), 126.3 (CH), 125.8 (CH), 122.0 (CH), 121.1 (CH), 120.2 (CH), 110.4 (CH), 102.8 (CH), 67.5 (CH_2), 65.3 (CH) ppm. HRMS (ESI): calcd. for $C_{23}H_{20}N_2NaO_2$ $[M + Na]^+$ 379.1422; found 379.1424.

Benzyl [(1*H*-Indol-1-yl)(*p*-tolyl)methyl]carbamate (7ab): 41.2 mg, 89% yield; m.p. 119–120 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.72–7.60 (m, 1 H), 7.48–6.99 (m, 14 H), 6.56 (dd, $J_{H,H}$ = 3.5, 0.5 Hz, 1 H), 5.87 (d, $J_{H,H}$ = 7.0 Hz, 1 H), 5.18 (d, $J_{H,H}$ = 12.0 Hz, 1 H), 5.07 (d, $J_{H,H}$ = 12.0 Hz, 1 H), 2.37 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.3 (C), 138.6 (C), 135.7 (C), 135.4 (C), 134.4 (C), 129.5 (CH), 129.1 (C), 128.5 (CH), 128.3 (CH), 128.2 (CH), 126.2 (CH), 125.8 (CH), 121.9 (CH), 121.0 (CH), 120.1 (CH), 110.5 (CH), 102.6 (CH), 67.4 (CH_2), 65.2 (CH), 21.0 (CH_3) ppm. HRMS (ESI): calcd. for $C_{24}H_{22}N_2NaO_2$ $[M + Na]^+$ 393.1579; found 393.1573.

Benzyl [(1*H*-Indol-1-yl)(4-methoxyphenyl)methyl]carbamate (7ac): 43.9 mg, 91% yield; m.p. 142–144 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.67–7.63 (m, 1 H), 7.43–7.23 (m, 7 H), 7.22–7.06 (m, 5 H), 6.92–6.80 (m, 2 H), 6.55 (d, $J_{H,H}$ = 3.0 Hz, 1 H), 5.83 (d, $J_{H,H}$ = 8.5 Hz, 1 H), 5.17 (d, $J_{H,H}$ = 12.0 Hz, 1 H), 5.06 (d, $J_{H,H}$ = 12.0 Hz, 1 H), 3.80 (s, 3 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 159.8 (C), 155.3 (C), 135.7 (C), 135.4 (C), 129.3 (C), 129.2 (C), 128.5 (CH), 128.3 (CH), 128.2 (CH), 127.6 (CH), 125.8 (CH), 122.0 (CH), 121.1 (CH), 120.1 (CH), 114.2 (CH), 110.5 (CH), 102.6 (CH), 67.4 (CH_2), 65.0 (CH), 55.2 (CH_3) ppm. HRMS (ESI): calcd. for $C_{24}H_{22}N_2NaO_3$ $[M + Na]^+$ 409.1528; found 409.1535.

Benzyl [(4-Chlorophenyl)(1*H*-indol-1-yl)methyl]carbamate (7ad): 40.9 mg, 84% yield; m.p. 175–177 °C. ^{1}H NMR (300 MHz, [D$_6$]-DMSO): δ = 9.12 (d, $J_{H,H}$ = 9.0 Hz, 1 H), 7.60–7.50 (m, 2 H), 7.45–6.96 (m, 13 H), 6.52 (d, $J_{H,H}$ = 3.0 Hz, 1 H), 5.13 (d, $J_{H,H}$ = 12.5 Hz, 1 H), 5.06 (d, $J_{H,H}$ = 12.5 Hz, 1 H) ppm. ^{13}C NMR (75.5 MHz, [D$_6$]DMSO): δ = 155.6 (C), 137.4 (C), 136.5 (C), 135.0 (C), 133.0 (C), 128.5 (CH), 128.4 (CH), 128.4 (CH), 128.0 (CH), 126.0 (CH), 125.1 (CH), 121.5 (CH), 120.6 (CH), 119.7 (CH), 110.6 (CH), 102.0 (CH), 66.1 (CH_2), 64.3 (CH) ppm. HRMS (ESI): calcd. for $C_{23}H_{19}ClN_2NaO_2$ $[M + Na]^+$ 413.1033; found 413.1032.

Benzyl [(1*H*-Indol-1-yl)(*m*-tolyl)methyl]carbamate (7ae): 44.4 mg, 96% yield; m.p. 123–124 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.75–7.59 (m, 1 H), 7.47–6.93 (m, 14 H), 6.57 (dd, $J_{H,H}$ = 3.5, 0.5 Hz, 1 H), 5.89 (d, $J_{H,H}$ = 8.0 Hz, 1 H), 5.18 (d, $J_{H,H}$ = 12.0 Hz, 1 H), 5.08 (d, $J_{H,H}$ = 12.0 Hz, 1 H), 2.34 (s, 3 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 155.3 (C), 138.7 (C), 137.3 (C), 135.7 (C), 135.5 (C), 129.5 (CH), 129.1 (C), 128.8 (CH), 128.5 (CH), 128.3 (CH), 128.2 (CH), 126.9 (CH), 125.8 (CH), 123.4 (CH), 122.0 (CH), 121.0 (CH), 120.1 (CH), 110.4 (CH), 102.7 (CH), 67.4 (CH_2), 65.2 (CH), 21.4 (CH_3) ppm. HRMS (ESI): calcd. for $C_{24}H_{22}N_2NaO_2$ $[M + Na]^+$ 393.1579; found 393.1577.

Benzyl [(2-Chlorophenyl)(1*H*-indol-1-yl)methyl]carbamate (7af): 41.9 mg, 86% yield; m.p. 108–110 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68–7.60 (m, 1 H), 7.54 (d, $J_{H,H}$ = 7.5 Hz, 1 H), 7.49–7.40 (m, 2 H), 7.40–7.10 (m, 10 H), 7.01 (s, 1 H), 6.54 (d, $J_{H,H}$ = 3.0 Hz, 1 H), 5.72 (s, 1 H), 5.18 (d, $J_{H,H}$ = 12.0 Hz, 1 H), 5.13 (d, $J_{H,H}$ = 12.0 Hz, 1 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 154.9 (C), 135.7 (C), 135.5 (C), 135.2 (C), 133.6 (C), 130.4 (CH), 130.3 (CH), 129.1 (C), 128.5 (CH), 128.3 (CH), 128.1 (CH), 127.4 (CH), 127.2 (CH), 124.4 (CH), 122.2 (CH), 121.1 (CH), 120.3 (CH), 110.2 (CH), 102.8 (CH), 67.5 (CH_2), 63.3 (CH) ppm. HRMS (ESI): calcd. for $C_{23}H_{19}ClKN_2O_2$ $[M + K]^+$ 429.0765; found 429.0775.

Benzyl [(Fur-3-yl)(1*H*-indol-1-yl)methyl]carbamate (7ag): Oil (38.9 mg, 90% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.71–7.61 (m, 1 H), 7.55–7.05 (m, 12 H), 6.55 (dd, $J_{H,H}$ = 3.5, 0.5 Hz, 1 H), 6.24 (s, 1 H), 5.83 (d, $J_{H,H}$ = 9.0 Hz, 1 H), 5.16 (d, $J_{H,H}$ = 12.0 Hz, 1 H), 5.04 (d, $J_{H,H}$ = 12.0 Hz, 1 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 155.2 (C), 144.3 (CH), 140.4 (CH), 135.6 (C), 135.3 (C), 129.2 (C), 128.5 (CH), 128.4 (CH), 128.2 (CH), 125.5 (CH), 124.1 (C), 122.0 (CH), 121.1 (CH), 120.2 (CH), 110.5 (CH), 109.3 (CH), 102.9 (CH), 67.5 (CH_2), 59.8 (CH) ppm. HRMS (ESI): calcd. for $C_{21}H_{18}N_2NaO_3$ $[M + Na]^+$ 369.1215; found 369.1201.

Benzyl [(1*H*-Indol-1-yl)(thien-2-yl)methyl]carbamate (7ah): 38.9 mg, 86% yield; m.p. 86–87 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.72–7.61 (m, 1 H), 7.60–7.06 (m, 11 H), 7.03–6.94 (m, 1 H), 6.90 (s, 1 H), 6.58 (d, $J_{H,H}$ = 3.5 Hz, 1 H), 6.03 (d, $J_{H,H}$ = 7.0 Hz, 1 H), 5.17 (d, $J_{H,H}$ = 12.0 Hz, 1 H), 5.06 (d, $J_{H,H}$ = 12.0 Hz, 1 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 155.0 (C), 141.2 (C), 135.5 (C), 135.3 (C), 129.2 (C), 128.5 (CH), 128.3 (CH), 128.2 (CH), 127.3 (CH), 126.4 (CH), 126.2 (CH), 125.6 (CH), 122.1 (CH), 121.1 (CH), 120.3 (CH), 110.4 (CH), 103.2 (CH), 67.6 (CH_2), 62.5 (CH) ppm. HRMS (ESI): calcd. for $C_{21}H_{19}N_2O_2S$ $[M + H]^+$ 363.1167; found 363.1167.

Benzyl [1-(1*H*-Indol-1-yl)pentyl]carbamate (7ai): Oil (37.4 mg, 89%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53 (m, 2 H), 7.28–6.97 (m, 8 H), 6.45 (d, $J_{H,H}$ = 3.0 Hz, 1 H), 6.01 (d, $J_{H,H}$ = 7.5 Hz, 1 H), 5.35 (d, $J_{H,H}$ = 8.5 Hz, 1 H), 5.02 (d, $J_{H,H}$ = 12.0 Hz, 1 H), 4.88 (d, $J_{H,H}$ = 12.0 Hz, 1 H), 1.80–2.12 (m, 2 H), 1.37–1.05 (m, 4 H), 0.77 (t, $J_{H,H}$ = 7.0 Hz, 3 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 155.3 (C), 135.8 (C), 135.5 (C), 128.7 (CH), 128.5 (CH), 128.2 (CH), 128.1 (C), 123.7 (CH), 121.9 (CH), 120.9 (CH), 119.9 (CH), 110.2 (CH), 102.6 (CH), 67.1 (CH_2), 63.0 (CH), 34.7

(CH_2), 27.6 (CH_2), 22.1 (CH_2), 13.8 (CH_3) ppm. HRMS (ESI): calcd. for $C_{21}H_{24}N_2NaO_2$ $[M + Na]^+$ 359.1735; found 359.1730.

Benzyl [1-(1*H*-Indol-1-yl)-3-methylbutyl]carbamate (7aj): 38.6 mg, 92% yield; m.p. 68–70 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.72–7.59 (m, 2 H), 7.44–7.05 (m, 8 H), 6.56 (d, $J_{H,H}$ = 3.0 Hz, 1 H), 6.33–6.11 (m, 1 H), 5.45 (d, $J_{H,H}$ = 8.5 Hz, 1 H), 5.13 (d, $J_{H,H}$ = 12.0 Hz, 1 H), 4.98 (d, $J_{H,H}$ = 12.0 Hz, 1 H), 2.10–1.84 (m, 2 H), 1.63–1.40 (m, 1 H), 0.97 (d, $J_{H,H}$ = 6.0 Hz, 6 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 155.3 (C), 135.8 (C), 135.5 (C), 128.6 (C), 128.5 (CH), 128.2 (CH), 128.1 (CH), 123.7 (CH), 122.0 (CH), 120.9 (CH), 119.9 (CH), 110.2 (CH), 102.7 (CH), 67.1 (CH_2), 61.3 (CH), 43.8 (CH_2), 24.6 (CH), 22.4 (CH_3), 22.2 (CH_3) ppm. HRMS (ESI): calcd. for $C_{21}H_{24}N_2NaO_2$ $[M + Na]^+$ 359.1735; found 359.1733.

Benzyl [1-(1*H*-Indol-1-yl)-3,3-dimethylbutyl]carbamate (7ak): 40.6 mg, 93% yield; m.p. 97–98 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.75–7.57 (m, 2 H), 7.47–7.00 (m, 8 H), 6.55 (d, $J_{H,H}$ = 3.0 Hz, 1 H), 6.27 (d, $J_{H,H}$ = 6.5 Hz, 1 H), 5.53 (d, $J_{H,H}$ = 8.0 Hz, 1 H), 5.12 (d, $J_{H,H}$ = 12.0 Hz, 1 H), 4.96 (d, $J_{H,H}$ = 12.5 Hz, 1 H), 2.21–1.85 (m, 2 H), 0.94 (s, 9 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 155.0 (C), 135.8 (C), 135.0 (C), 128.7 (C), 128.5 (CH), 128.2 (CH), 128.1 (CH), 124.2 (CH), 121.9 (CH), 121.0 (CH), 119.8 (CH), 110.3 (CH), 102.6 (CH), 67.1 (CH_2), 60.9 (CH), 48.5 (CH_2), 30.3 (C), 29.5 (CH_3) ppm. HRMS (ESI): calcd. for $C_{22}H_{26}N_2NaO_2$ $[M + Na]^+$ 373.1892; found 373.1886.

Benzyl [(Cyclohexyl)(1*H*-indol-1-yl)methyl]carbamate (7al): 39.8 mg, 88% yield; m.p. 55–58 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.65 (dd, $J_{H,H}$ = 9.0, 0.5 Hz, 1 H), 7.58 (d, $J_{H,H}$ = 7.5 Hz, 1 H), 7.44–6.97 (m, 8 H), 6.56 (d, $J_{H,H}$ = 3.0 Hz, 1 H), 5.81 (t, $J_{H,H}$ = 9.0 Hz, 1 H), 5.56 (d, $J_{H,H}$ = 8.5 Hz, 1 H), 5.12 (d, $J_{H,H}$ = 12.5 Hz, 1 H), 4.97 (d, $J_{H,H}$ = 12.5 Hz, 1 H), 2.14–1.91 (m, 2 H), 1.82 (s, 1 H), 1.66 (s, 2 H), 1.43–0.74 (m, 6 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 155.6 (C), 135.8 (C), 135.7 (C), 128.5 (CH), 128.2 (CH), 128.1 (CH), 124.4 (CH), 121.9 (CH), 120.9 (CH), 119.7 (CH), 119.7 (C), 110.1 (CH), 102.5 (CH), 67.8 (CH), 67.1 (CH_2), 42.1 (CH), 29.7 (CH_2), 28.9 (CH_2), 25.9 (CH_2), 25.5 (CH_2), 25.4 (CH_2) ppm. HRMS (ESI): calcd. for $C_{23}H_{27}N_2O_2$ $[M + H]^+$ 363.2073; found 363.2070.

Benzyl [1-(1*H*-Indol-1-yl)-2-methylpropyl]carbamate (7am): Oil (39.8 mg, 99%). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.68–7.50 (m, 2 H), 7.41–6.95 (m, 8 H), 6.55 (d, $J_{H,H}$ = 3.0 Hz, 1 H), 5.90–5.36 (m, 2 H), 5.11 (d, $J_{H,H}$ = 12.5 Hz, 1 H), 4.98 (d, $J_{H,H}$ = 12.5 Hz, 1 H), 2.38 (s, 1 H), 1.15 (d, $J_{H,H}$ = 6.5 Hz, 3 H), 0.77 (d, $J_{H,H}$ = 6.0 Hz, 3 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 155.6 (C), 135.8 (C), 135.7 (C), 128.5 (CH), 128.2 (CH), 128.1 (CH), 124.3 (CH), 121.9 (CH), 120.9 (CH), 119.8 (CH), 119.7 (C), 110.1 (CH), 102.6 (CH), 68.9 (CH), 67.2 (CH_2), 33.2 (CH), 19.3 (CH_3), 18.8 (CH_3) ppm. HRMS (ESI): calcd. for $C_{20}H_{22}N_2NaO_2$ $[M + Na]^+$ 345.1579; found 345.1580.

***tert*-Butyl [(1*H*-Indol-yl)(phenyl)methyl]carbamate (7an):** 35.0 mg, 87% yield; m.p. 127–128 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.71–7.63 (m, 1 H), 7.45–7.06 (m, 11 H), 6.57 (d, $J_{H,H}$ = 3.0 Hz, 1 H), 5.60 (d, $J_{H,H}$ = 8.5 Hz, 1 H), 1.46 (s, 9 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 154.5 (C), 137.9 (C), 135.5 (C), 129.1 (C), 128.8 (CH), 128.6 (CH), 126.3 (CH), 125.7 (CH), 121.9 (CH), 121.0 (CH), 120.0 (CH), 110.5 (CH), 102.4 (CH), 80.7 (C), 64.9 (CH), 28.2 (CH_3) ppm. HRMS (ESI): calcd. for $C_{20}H_{22}N_2NaO_2$ $[M + Na]^+$ 345.1579; found 345.1569.

***tert*-Butyl [(1*H*-Indol-1-yl)(*p*-tolyl)methyl]carbamate (7ao):** 37.0 mg, 88% yield; m.p. 130–131 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.73–7.60 (m, 1 H), 7.43–7.04 (m, 9 H), 6.56 (d, $J_{H,H}$ = 3.0 Hz, 1 H), 5.58 (d, $J_{H,H}$ = 8.5 Hz, 1 H), 2.36 (s, 3 H), 1.46 (s, 9 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 154.5 (C), 138.5 (C), 135.5 (C), 134.9 (CH), 129.5 (CH), 129.1 (C), 126.2 (CH), 125.7 (CH), 121.8 (CH), 121.0 (CH), 119.9 (CH), 110.5 (CH), 102.3 (CH), 80.7 (C), 64.8 (CH), 28.2 (CH_3), 21.1 (CH_3) ppm. HRMS (ESI): calcd. for $C_{21}H_{24}N_2NaO_2$ $[M + Na]^+$ 359.1735; found 359.1737.

Methyl 1-[{[(Benzyloxy)carbonyl]amino}(phenyl)methyl]-1*H*-indole-2-carboxylate (7da): 37.3 mg, 72% yield; m.p. 87–88 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.91–7.68 (m, 3 H), 7.61–7.15 (m, 12 H), 7.05–6.87 (m, 2 H), 5.27 (d, $J_{H,H}$ = 12.0 Hz, 1 H), 5.08 (d, $J_{H,H}$ = 12.0 Hz, 1 H), 3.70 (s, 3 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 162.6 (C), 156.4 (C), 140.0 (C), 138.8 (C), 136.0 (C), 128.5 (CH), 128.4 (CH), 128.2 (CH), 128.2 (CH), 127.8 (CH), 126.7 (C), 126.2 (CH), 125.5 (C), 125.0 (CH), 122.7 (CH), 121.5 (CH), 113.7 (CH), 111.0 (CH), 67.3 (CH_2), 63.7 (CH), 52.0 (CH_3) ppm. HRMS (ESI): calcd. for $C_{25}H_{22}N_2NaO_4$ $[M + Na]^+$ 437.1477; found 437.1477.

Benzyl [(3-Methyl-1*H*-indol-1-yl)(phenyl)methyl]carbamate (7fa): 37.0 mg, 80% yield; m.p. 104–105 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.68–7.54 (m, 1 H), 7.46–7.09 (m, 14 H), 6.84 (d, $J_{H,H}$ = 0.8 Hz, 1 H), 5.81 (d, $J_{H,H}$ = 7.5 Hz, 1 H), 5.18 (d, $J_{H,H}$ = 12.0 Hz, 1 H), 5.07 (d, $J_{H,H}$ = 12.0 Hz, 1 H), 2.32 (d, $J_{H,H}$ = 1.0 Hz, 3 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 155.4 (C), 137.6 (C), 135.9 (C), 135.8 (C), 129.5 (C), 128.8 (CH), 128.7 (CH), 128.5 (CH), 128.3 (CH), 128.2 (CH), 126.4 (CH), 123.2 (CH), 122.0 (CH), 119.5 (CH), 119.1 (CH), 112.0 (C), 110.3 (CH), 67.4 (CH_2), 65.1 (CH), 9.7 (CH_3) ppm. HRMS (ESI): calcd. for $C_{24}H_{22}N_2NaO_2$ $[M + Na]^+$ 393.1579; found 393.1574.

Benzyl [(4-Methyl-1*H*-indol-1-yl)(phenyl)methyl]carbamate (7ga): 42.6 mg, 92% yield; m.p. 108–109 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.49–7.01 (m, 14 H), 6.96 (dd, $J_{H,H}$ = 8.0, 1.0 Hz, 1 H), 6.59 (dd, $J_{H,H}$ = 3.5, 0.5 Hz, 1 H), 5.88 (d, $J_{H,H}$ = 7.0 Hz, 1 H), 5.18 (d, $J_{H,H}$ = 12.0 Hz, 1 H), 5.07 (d, $J_{H,H}$ = 12.0 Hz, 1 H), 2.59 (s, 3 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 155.8 (C), 137.9 (C), 136.2 (C), 135.6 (C), 131.0 (C), 129.5 (C), 129.3 (CH), 129.2 (CH), 129.0 (CH), 128.8 (CH), 128.7 (CH), 126.8 (CH), 125.7 (CH), 122.6 (CH), 120.8 (CH), 108.5 (CH), 101.7 (CH), 67.9 (CH_2), 66.0 (CH), 19.1 (CH_3) ppm. HRMS (ESI): calcd. for $C_{24}H_{22}N_2NaO_2$ $[M + Na]^+$ 393.1579; found 393.1567.

Benzyl [(5-Methoxy-1*H*-indol-1-yl)(phenyl)methyl]carbamate (7ha): 43.2 mg, 86% yield; m.p. 112–114 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.15 (m, 12 H), 7.12 (d, $J_{H,H}$ = 2.5 Hz, 1 H), 7.07 (d, $J_{H,H}$ = 3.0 Hz, 1 H), 6.82 (d, $J_{H,H}$ = 8.0 Hz, 1 H), 6.48 (d, $J_{H,H}$ = 3.0 Hz, 1 H), 5.90 (d, $J_{H,H}$ = 7.5 Hz, 1 H), 5.17 (d, $J_{H,H}$ = 12.0 Hz, 1 H), 5.07 (d, $J_{H,H}$ = 12.0 Hz, 1 H), 3.85 (s, 3 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 155.4 (C), 154.4 (C), 137.4 (C), 135.7 (C), 130.7 (C), 129.7 (C), 128.9 (CH), 128.8 (CH), 128.5 (CH), 128.3 (CH), 128.2 (CH), 126.5 (CH), 126.3 (CH), 112.1 (CH), 111.2 (CH), 102.8 (CH), 102.3 (CH), 67.4 (CH_2), 65.5 (CH), 55.8 (CH_3) ppm. HRMS (ESI): calcd. for $C_{24}H_{22}KN_2O_3$ $[M + K]^+$ 425.1267; found 425.1260.

Benzyl [(5-Chloro-1*H*-indol-1-yl)(phenyl)methyl]carbamate (7ia): 46.2 mg, 91% yield; m.p. 112–113 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.61 (d, $J_{H,H}$ = 2.0 Hz, 1 H), 7.44–7.01 (m, 14 H), 6.49 (d, $J_{H,H}$ = 3.5 Hz, 1 H), 5.91 (d, $J_{H,H}$ = 7.5 Hz, 1 H), 5.16 (d, $J_{H,H}$ = 12.0 Hz, 1 H), 5.06 (d, $J_{H,H}$ = 12.0 Hz, 1 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 155.3 (C), 137.0 (C), 135.6 (C), 133.9 (C), 130.2 (C), 129.0 (CH), 128.6 (CH), 128.4 (CH), 128.2 (CH), 127.0 (CH), 126.2 (CH), 125.9 (C), 122.3 (CH), 120.5 (CH), 111.4 (CH), 102.4 (CH), 67.6 (CH_2), 65.5 (CH) ppm. HRMS (ESI): calcd. for $C_{23}H_{19}ClKN_2O_2$ $[M + K]^+$ 429.0772; found 429.0763.

Benzyl [(6-Fluoro-1*H*-indol-1-yl)(phenyl)methyl]carbamate (7ja): 43.9 mg, 94% yield; m.p. 142–143 °C. ^1H NMR (300 MHz,

$CDCl_3$): δ = 7.55 (dd, $J_{H,H}$ = 8.5, 5.5 Hz, 1 H), 7.44–7.15 (m, 11 H), 7.09 (d, $J_{H,H}$ = 3.5 Hz, 1 H), 7.00 (d, $J_{H,H}$ = 9.5 Hz, 1 H), 6.90 (ddd, $J_{H,H}$ = 9.5, 8.5, 2.5 Hz, 1 H), 6.53 (d, $J_{H,H}$ = 3.5 Hz, 1 H), 5.86 (d, $J_{H,H}$ = 7.5 Hz, 1 H), 5.17 (d, $J_{H,H}$ = 12.0 Hz, 1 H), 5.09 (d, $J_{H,H}$ = 12.0 Hz, 1 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 159.73 (d, $J_{H,H}$ = 238.5 Hz, C), 155.3 (C), 137.0 (C), 135.6 (C), 135.48 (d, $J_{H,H}$ = 12.0 Hz, C), 129.0 (CH), 129.0 (CH), 128.6 (CH), 128.4 (CH), 128.2 (CH), 126.2 (CH), 125.5 (C), 121.76 (d, $J_{H,H}$ = 10.0 Hz, CH), 108.93 (d, $J_{H,H}$ = 24.5 Hz, CH), 102.8 (CH), 97.09 (d, $J_{H,H}$ = 27.0 Hz, CH), 67.6 (CH_2), 65.6 (CH) ppm. HRMS (ESI): calcd. for $C_{23}H_{19}FKN_2O_2$ $[M + K]^+$ 413.1068; found 413.1056.

Benzyl [(7-Methyl-1*H*-indol-1-yl)(phenyl)methyl]carbamate (7ka): Oil (23.8 mg, 51%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.80 (d, $J_{H,H}$ = 7.5 Hz, 1 H), 7.52 (d, $J_{H,H}$ = 7.5 Hz, 1 H), 7.44–7.27 (m, 7 H), 7.17–6.94 (m, 6 H), 6.60 (d, $J_{H,H}$ = 3.5 Hz, 1 H), 5.76 (d, $J_{H,H}$ = 8.0 Hz, 1 H), 5.19 (d, $J_{H,H}$ = 12.5 Hz, 1 H), 5.10 (d, $J_{H,H}$ = 12.0 Hz, 1 H), 2.72 (s, 3 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 155.0 (C), 139.3 (C), 135.7 (C), 135.3 (C), 129.6 (C), 128.9 (CH), 128.7 (CH), 128.6 (CH), 128.4 (CH), 128.2 (CH), 126.0 (CH), 125.5 (CH), 125.0 (CH), 121.2 (C), 120.3 (CH), 119.2 (CH), 104.0 (CH), 67.5 (CH_2), 66.2 (CH), 20.2 (CH_3) ppm. HRMS (ESI): calcd. for $C_{24}H_{22}KN_2O_2$ $[M + K]^+$ 409.1318; found 409.1315.

Procedure for the Synthesis of *C*-2-Aminoalkylated Pyrroles 8: MeMgBr (1 M solution in THF, 125 μL, 0.125 mmol) was added to a solution of pyrrole (26.0 μL, 0.375 mmol) and $MgBr_2$ (4.6 mg, 0.025 mmol) in CH_2Cl_2 (0.5 mL) at 0 °C under nitrogen. The mixture was stirred at 0 °C for 2 h. Then, a suspension of α-amido sulfone (0.125 mmol) in CH_2Cl_2 (1 mL) was added, and the mixture was stirred (0 °C for aromatic α-amido sulfones, room temperature for aliphatic α-amido sulfones) until it reached completion (TLC). The reaction was quenched with NH_4Cl (1 M saturated aqueous solution, 1 mL), and the resulting solution was extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were washed with brine (5 mL) and dried with anhydrous Na_2SO_4. Purification by flash chromatography on silica gel (hexane/EtOAc) afforded compound **8**.

Benzyl [(Phenyl)(1*H*-pyrrol-2-yl)methyl]carbamate (8aa): 33.3 mg, 87% yield; m.p. 93–94 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.58 (s, 1 H), 7.49–7.13 (m, 10 H), 6.71 (s, 1 H), 6.11 (dd, $J_{H,H}$ = 6.0, 3.0 Hz, 1 H), 5.96 (d, $J_{H,H}$ = 8.0 Hz, 1 H), 5.83 (s, 1 H), 5.56 (d, $J_{H,H}$ = 5.5 Hz, 1 H), 5.19–5.05 (m, 2 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 156.2 (C), 139.7 (C), 136.1 (C), 132.2 (C), 128.7 (CH), 128.5 (CH), 128.2 (CH), 128.1 (CH), 127.9 (CH), 127.1 (CH), 118.1 (CH), 108.1 (CH), 107.3 (CH), 67.1 (CH_2), 53.4 (CH) ppm. HRMS (ESI): calcd. for $C_{19}H_{19}N_2O_2$ $[M + H]^+$ 307.1442; found 307.1447.

Benzyl [(5-Ethyl-1*H*-pyrrol-2-yl)(phenyl)methyl]carbamate (8ba): 33.0 mg, 79% yield; m.p. 85–87 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.33 (s, 1 H), 7.50–7.12 (m, 10 H), 5.92 (d, $J_{H,H}$ = 8.0 Hz, 1 H), 5.78 (t, $J_{H,H}$ = 3.0 Hz, 1 H), 5.65 (s, 1 H), 5.51 (d, $J_{H,H}$ = 8.0 Hz, 1 H), 5.24–5.04 (m, 2 H), 2.57 (q, $J_{H,H}$ = 7.5 Hz, 2 H), 1.22 (t, $J_{H,H}$ = 7.5 Hz, 3 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 156.2 (C), 139.8 (C), 136.2 (C), 134.8 (C), 130.7 (C), 128.7 (CH), 128.5 (CH), 128.2 (CH), 128.1 (CH), 127.8 (CH), 127.1 (CH), 107.4 (CH), 103.9 (CH), 67.0 (CH_2), 53.5 (CH), 20.8 (CH_2), 13.4 (CH_3) ppm. HRMS (ESI): calcd. for $C_{21}H_{23}N_2O_2$ $[M + H]^+$ 335.1760; found 335.1758.

Benzyl [1-(1*H*-Pyrrol-2-yl)pentyl]carbamate (8ai): 22.8 mg, 58% yield; m.p. 123–124 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.89 (s, 1 H), 7.44–7.29 (m, 5 H), 6.71 (s, 1 H), 6.12 (dd, $J_{H,H}$ = 6.0, 3.0 Hz, 1 H), 6.05–5.99 (m, 1 H), 5.14 (d, $J_{H,H}$ = 12.0 Hz, 1 H), 5.08 (d, $J_{H,H}$ = 12.0 Hz, 1 H), 4.95 (d, $J_{H,H}$ = 8.0 Hz, 1 H), 4.70 (td, $J_{H,H}$ = 8.0, 6.5 Hz, 1 H), 2.16–1.70 (m, 2 H), 1.54–1.20 (m, 4 H), 0.92 (t, $J_{H,H}$ = 7.0 Hz, 3 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 157.0 (C), 136.2 (C), 133.7 (C), 128.5 (CH), 128.2 (CH), 128.0 (CH), 117.5 (CH), 107.6 (CH), 104.1 (CH), 66.9 (CH_2), 48.6 (CH), 32.7 (CH_2), 28.5 (CH_2), 22.4 (CH_2), 13.9 (CH_3) ppm. HRMS (ESI): calcd. for $C_{19}H_{27}N_2O_2$ $[M + H]^+$ 315.2073; found 315.2077.

Benzyl [(Phenyl)(1*H*-pyrrol-1-yl)methyl]carbamate (9aa): Cs_2CO_3 (84.4 mg, 0.25 mmol) was dried in a Schlenk tube by using a heat gun under vacuum. α-Amido sulfone **2a** (0.125 mmol) was added, and the system was purged with nitrogen. Then, CH_2Cl_2 (0.7 mL) was added, and the mixture was stirred at room temperature for 2 h. A solution of pyrrole (8.7 μL, 0.125 mmol) in CH_2Cl_2 (0.5 mL) was added. The mixture was stirred at room temperature for 3 h and then quenched with water (1 mL). The resulting solution was extracted with CH_2Cl_2 (3 × 25 mL), and the combined organic layers were washed with brine and dried with anhydrous Na_2SO_4. Purification by flash chromatography on silica gel (hexane/EtOAc) afforded compound **9aa** (13.2 mg, 32%); m.p. 114–116 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47–7.27 (m, 8 H), 7.21–7.10 (m, 2 H), 6.90 [d, $J_{H,H}$ = 7.5 Hz, 1 H), 6.77 [t, $J_{H,H}$ = 2.0 Hz, 2 H), 6.22 [t, $J_{H,H}$ = 2.0 Hz, 2 H), 5.73 [d, $J_{H,H}$ = 4.5 Hz, 1 H), 5.19 [d, $J_{H,H}$ = 12.0 Hz, 1 H), 5.11 [d, $J_{H,H}$ = 12.0 Hz, 1 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 155.6 (C), 138.6 (C), 136.2 (C), 129.3 (CH), 129.0 (CH), 128.8 (CH), 128.7 (CH), 126.6 (CH), 119.8 (CH), 109.4 (CH), 67.9 (CH_2), 30.1 (CH) ppm. HRMS (ESI): calcd. for $C_{19}H_{18}N_3NaO_2$ $[M + Na]^+$ 329.1266; found 329.1258.

Benzyl [(Phenyl)(1*H*-pyrrolo[2,3-*b*]pyridin-3-yl)methyl]carbamate (10aa): MeMgBr (1 M solution in THF, 125 μL, 0.125 mmol) was added to a solution of 7-azaindole (14.8 mg, 0.125 mmol) and $MgBr_2$ (4.6 mg, 0.025 mmol) in CH_2Cl_2 (0.5 mL) at 0 °C under nitrogen. The mixture was stirred at 0 °C for 2 h. Then, a suspension of α-amido sulfone **2a** (0.125 mmol) in CH_2Cl_2 (1 mL) was added, and the mixture was stirred at room temp. for 7 h and then quenched with NH_4Cl (1 M saturated aqueous solution, 1 mL). The resulting solution was extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were washed with brine and dried with anhydrous Na_2SO_4. Purification by flash chromatography on silica gel (hexane/EtOAc) afforded compound **10aa** (17.9 mg, 40%); m.p. 210–212 °C. ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 11.47 (s, 1 H), 8.31 (d, $J_{H,H}$ = 9.0 Hz, 1 H), 8.18 (dd, $J_{H,H}$ = 4.5, 1.5 Hz, 1 H), 7.76 (dd, $J_{H,H}$ = 8.0, 1.5 Hz, 1 H), 7.48–7.40 (m, 2 H), 7.40–7.20 (m, 8 H), 7.07 (d, $J_{H,H}$ = 2.0 Hz, 1 H), 6.98 (dd, $J_{H,H}$ = 8.0, 4.5 Hz, 1 H), 6.11 (d, $J_{H,H}$ = 9.0 Hz, 1 H), 5.10 (d, $J_{H,H}$ = 12.5 Hz, 1 H), 5.04 (d, $J_{H,H}$ = 12.5 Hz, 1 H) ppm. ^{13}C NMR (75.5 MHz, [D_6]-DMSO): δ = 155.7 (C), 148.7 (C), 142.7 (CH), 142.6 (C), 137.1 (C), 128.3 (CH), 128.2 (CH), 127.8 (CH), 127.1 (CH), 127.0 (CH), 126.9 (CH), 123.5 (CH), 117.9 (C), 115.4 (C), 115.1 (CH), 65.4 (CH_2), 51.7 (CH) ppm. HRMS (ESI): calcd. for $C_{22}H_{20}N_3O_2$ $[M + H]^+$ 358.1555; found 358.1556.

Procedure for the Synthesis *N*-1-Aminoalkylated Azaindoles 11: Cs_2CO_3 (84.4 mg, 0.25 mmol) was dried in a Schlenk tube by using a heat gun under vacuum. α-Amido sulfone (0.125 mmol) was added, and the system was purged with nitrogen. Then, CH_2Cl_2 (0.7 mL) was added, and the mixture was stirred at room temperature for 2 h. A solution of 7-azaindole (14.8 mg, 0.125 mmol) in CH_2Cl_2 (0.5 mL) was added. The mixture was stirred at room temperature until it reached completion (TLC), and then it was quenched with water (1 mL). The resulting solution was extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were washed with brine and dried with anhydrous Na_2SO_4. Purification by flash chromatography on silica gel (hexane/EtOAc) afforded compounds **11**.

Benzyl [(Phenyl)(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)methyl]carbamate (11aa): 37.0 mg, 83% yield; m.p. 94–96 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.25 (dd, $J_{H,H}$ = 4.5, 1.5 Hz, 1 H), 7.93 (dd, $J_{H,H}$ = 8.0, 1.5 Hz, 1 H), 7.63–6.98 (m, 14 H), 6.52 (d, $J_{H,H}$ = 3.5 Hz, 1 H), 5.20 (d, $J_{H,H}$ = 12.0 Hz, 1 H), 5.08 (d, $J_{H,H}$ = 12.0 Hz, 1 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 155.5 (C), 147.3 (C), 143.0 (CH), 138.6 (C), 135.9 (C), 129.0 (CH), 128.6 (CH), 128.5 (CH), 128.3 (CH), 128.2 (CH), 128.1 (CH), 127.1 (CH), 125.8 (CH), 121.2 (C), 116.3 (CH), 100.4 (CH), 67.2 (CH_2), 66.1 (CH) ppm. HRMS (ESI): calcd. for $C_{22}H_{20}N_3O_2$ [M + H]$^+$ 358.1556; found 358.1548.

Benzyl [(4-Methoxyphenyl)(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)methyl]carbamate (11ac): Oil (42.6 mg, 88% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.24 (dd, $J_{H,H}$ = 4.5, 1.5 Hz, 1 H), 7.92 (dd, $J_{H,H}$ = 8.0, 1.5 Hz, 1 H), 7.45–7.26 (m, 5 H), 7.06 (td, $J_{H,H}$ = 9.0, 4.5 Hz, 4 H), 6.84–6.75 (m, 2 H), 6.50 (d, $J_{H,H}$ = 3.5 Hz, 1 H), 5.18 (d, $J_{H,H}$ = 12.0 Hz, 1 H), 5.06 (d, $J_{H,H}$ = 12.0 Hz, 1 H), 3.75 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.5 (C), 155.6 (C), 147.2 (C), 143.0 (CH), 135.9 (C), 130.7 (C), 129.0 (CH), 128.5 (CH), 128.2 (CH), 128.1 (CH), 127.1 (CH), 127.0 (CH), 121.3 (C), 116.2 (CH), 113.9 (CH), 100.3 (CH), 67.2 (CH_2), 65.9 (CH), 55.2 (CH_3) ppm. HRMS (ESI): calcd. for $C_{23}H_{22}N_3O_3$ [M + H]$^+$ 388.1661; found 388.1664.

Benzyl [(2-Chlorophenyl)(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)methyl]carbamate (11af): Oil (30.8 mg, 63%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.19 (dd, $J_{H,H}$ = 4.7, 1.5 Hz, 1 H), 7.81 (dd, $J_{H,H}$ = 8.0, 1.5 Hz, 1 H), 7.59 (d, $J_{H,H}$ = 9.0 Hz, 1 H), 7.41–6.90 (m, 13 H), 6.38 (d, $J_{H,H}$ = 3.5 Hz, 1 H), 5.08 (d, $J_{H,H}$ = 12.5 Hz, 1 H), 4.99 (d, $J_{H,H}$ = 12.5 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.1 (C), 147.3 (C), 143.0 (CH), 138.6 (C), 136.0 (C), 135.9 (CH), 133.0 (C), 130.1 (CH), 129.9 (CH), 129.85 (CH), 129.0 (CH), 128.5 (CH), 128.1 (CH), 127.9 (CH), 126.9 (CH), 121.3 (C), 116.4 (CH), 100.4 (CH), 67.3 (CH_2), 64.1 (CH) ppm. HRMS (ESI): calcd. for $C_{22}H_{19}ClN_3O_2$ [M + H]$^+$ 392.1166; found 392.1160.

Benzyl [2-Methyl-1-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)propyl]carbamate (11am): Oil (29.9 mg, 74%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.15 (dd, $J_{H,H}$ = 4.5, 1.5 Hz, 1 H), 7.81 (dd, $J_{H,H}$ = 8.0, 1.5 Hz, 1 H), 7.36–7.12 (m, 6 H), 6.97 (dd, $J_{H,H}$ = 8.0, 4.5 Hz, 1 H), 6.66 (d, $J_{H,H}$ = 9.5 Hz, 1 H), 6.31 (d, $J_{H,H}$ = 3.5 Hz, 1 H), 5.53 (t, $J_{H,H}$ = 10.0 Hz, 1 H), 5.05 (d, $J_{H,H}$ = 12.0 Hz, 2 H), 4.90 (d, $J_{H,H}$ = 12.0 Hz, 1 H), 2.74 (qd, $J_{H,H}$ = 13.5, 6.5 Hz, 1 H), 1.05 (d, $J_{H,H}$ = 6.5 Hz, 3 H), 0.57 (d, $J_{H,H}$ = 6.5 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.9 (C), 146.9 (C), 142.4 (CH), 136.1 (C), 128.9 (CH), 128.4 (CH), 128.3 (CH), 128.1 (CH) 128.0 (CH), 121.5 (C), 116.0 (CH), 99.1 (CH), 71.6 (CH), 67.0 (CH_2), 32.7 (CH), 19.3 (CH_3), 19.0 (CH_3) ppm. HRMS (ESI): calcd. for $C_{19}H_{22}N_3O_2$ [M + H]$^+$ 324.1712; found 324.1711.

(1*H*-Indol-3-yl)(phenyl)methanamine (12aa):[7e] Na (46 mg, 2 mmol) was dissolved in liquid NH_3 (approximately 10 mL) under nitrogen at –78 °C. Then, a solution of **3aa** (33 mg, 0.1 mmol) in THF (1 mL) was added dropwise. The mixture was stirred at –78 °C for 30 min. Then, NH_4Cl (150 mg) was added with caution at –78 °C. EtOAc (10 mL) and water (30 mL) were added. The resulting mixture was extracted with EtOAc (50 mL) and dried with Na_2SO_4. The solvent was removed under reduced pressure to afford product **12aa** (23.6 mg, 100%). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 10.85 (s, 1 H), 7.50–7.39 (m, 3 H), 7.35–7.19 (m, 4 H), 7.19–7.11 (m, 1 H), 7.01 (ddd, $J_{H,H}$ = 8.0, 7.0, 1.0 Hz, 1 H), 6.86 (ddd, $J_{H,H}$ = 8.0, 7.0, 1.0 Hz, 1 H), 5.31 (s, 1 H) ppm. ^{13}C NMR (75.5 MHz, [D$_6$]-DMSO): δ = 147.3 (C), 136.5 (C), 127.9 (CH), 126.9 (CH), 126.2 (CH), 125.7 (C), 122.0 (CH), 120.9 (CH), 120.6 (C), 119.3 (CH), 118.1 (CH), 111.4 (CH), 52.7 (CH) ppm.

***N*-[(1*H*-Indol-3-yl)(phenyl)methyl]acetamide (13aa):**[17] Acetyl chloride (21 μL, 0.3 mmol) was added dropwise to a stirred suspension of compound **12aa** (23.6 mg, 0.1 mmol) and NaOH (8.8 mg, 0.22 mmol) in CH_2Cl_2 (10 mL) at room temperature. The reaction progress was monitored by TLC, and H_2O (1 mL) was added when the starting material was consumed. The mixture was extracted with EtOAc (3 × 25 mL). The combined organic layers were dried with Na_2SO_4. Purification by flash chromatography on silica gel (hexane/EtOAc) afforded compound **13aa** (18.5 mg, 70%); m.p. 169–172 °C. ^{1}H NMR (300 MHz, [D$_6$]acetone): δ = 10.13 (s, 1 H), 7.75 (d, $J_{H,H}$ = 8.0 Hz, 1 H), 7.48–7.28 (m, 6 H), 7.28–7.20 (m, 1 H), 7.10 (ddd, $J_{H,H}$ = 8.0, 7.0, 1.0 Hz, 1 H), 6.97 (ddd, $J_{H,H}$ = 8.0, 7.0, 1.0 Hz, 1 H), 6.90 (dd, $J_{H,H}$ = 2.5, 1.0 Hz, 1 H), 6.52 (d, $J_{H,H}$ = 8.5 Hz, 1 H), 1.98 (s, 3 H) ppm. ^{13}C NMR (75.5 MHz, [D$_6$]-acetone): δ = 169.1 (C), 144.0 (C), 138.0 (C), 129.0 (CH), 128.0 (CH), 127.6 (CH), 127.3 (C), 124.4 (CH), 122.5 (CH), 120.0 (CH), 119.8 (CH), 118.2 (C), 112.3 (CH), 50.6 (CH), 22.9 (CH_3) ppm. HRMS (ESI): calcd. for $C_{17}H_{16}N_2NaO$ [M + Na]$^+$ 287.1160; found 287.1162.

Supporting Information (see footnote on the first page of this article): Synthetic procedures and characterization data for α-amido sulfones **2**. Copies of ^{1}H and ^{13}C NMR spectra of compounds **3** and **7**–**13**.

Acknowledgments

Financial support from the MINECO (Gobierno de España) and FEDER (European Union) (CTQ2009-13083) and from Generalitat Valenciana (ACOMP2012-212 and ISIC2012/001) is gratefully acknowledged. M. M. thanks the Universitat de València for a predoctoral grant.

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Received: March 11, 2013
Published Online: May 5, 2013

