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3-(2-Azidoethyl)oxindoles: Advanced Building Blocks for One-Pot Assembly of Spiro[pyrrolidine-3,3′-oxindoles]

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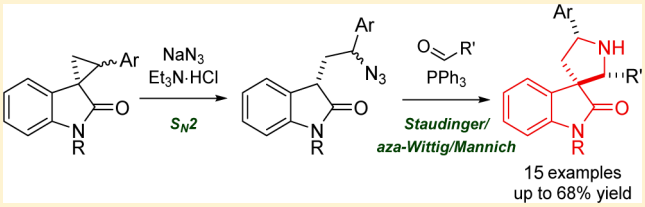
Supporting Information

ABSTRACT: A new synthetic approach to biologically relevant spiro[pyrrolidine-3,3′-oxindoles] was developed on the basis of the cascade transformation of 3-(2-azidoethyl)-oxindoles via Staudinger/*aza*-Wittig/Mannich reactions. The parent azides were readily synthesized through a nucleophilic ring opening of spiro[cyclopropane-1,3′-oxindoles] with the azide ion. A series of new spiro[pyrrolidine-3,3′-oxindoles] with various (het)aryl substituents at the C2 and C5 positions of the pyrrolidine ring were synthesized. In vitro experiments revealed their high cytotoxicity toward LNCaP and PC-3 tumor cell lines.



INTRODUCTION

The tricyclic system of spiro[pyrrolidine-3,3′-oxindole] is a key framework inherent in a subclass of spirooxindole alkaloids that are extremely intriguing because of their important biological properties (Figure 1A).[1] A considerable number of spiro-

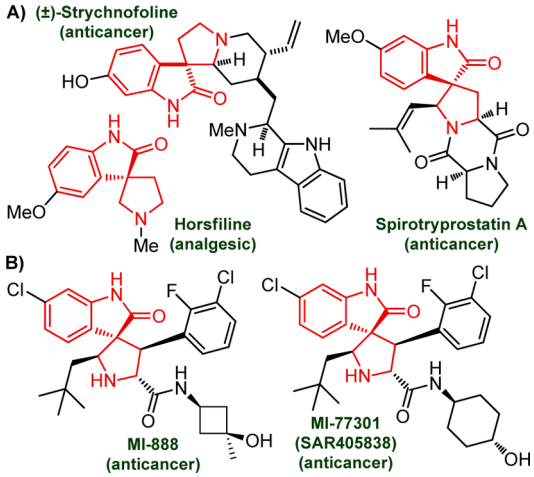


Figure 1. Selected examples of natural (**A**) and artificial (**B**) spiro[pyrrolidine-3,3′-oxindoles].

[pyrrolidine-3,3′-oxindole] alkaloids display anticancer activity that is apparently related to their ability to inhibit p53-MDM2 protein−protein interaction and, consequently, cause the rapid regression of tumor cells.[2] Insight into the origin of the anticancer effect of these spiro-fused natural molecules allowed for the design of their more efficient non-natural analogues. Among them, MI-77301 (SAR405838) is currently under clinical trials as a promising anticancer drug (Figure 1B).[1a,3]

As a result of the high efficiency of artificial spiro[pyrrolidine-3,3′-oxindoles] (especially as anticancer agents), they attract particular attention of synthetic chemists, which leads to considerable advances in the synthesis of these compounds. One of the main concepts in the synthesis of spiro[pyrrolidine-3,3′-oxindole] skeletons is based on the assembly of the pyrrolidine ring.[1] Nowadays, common methods for this include intramolecular Mannich reactions of imines synthesized from oxytryptamines and tryptophans;[4] [3 + 2]-cycloaddition of azomethine ylides to the alkenes derived from isatins;[5] [3 + 2]-cycloaddition of spiro[cyclopropane-1,3′-oxindoles] to aldimines;[6] oxidative rearrangement of tetrahydro-β-carbolines synthesized via Pictet−Spengler or Bishler−Napieralski reactions;[7] and intramolecular nucleophilic substitution[8] (Scheme 1A).

Recently, we have reported[9] original access to pyrrolidine derivatives via a cascade of Staudinger/*aza*-Wittig/Mannich reactions of carbonyl compounds with readily available organic azides,[10] wherein the 1,3-relationship between the azido group and an activated CH-fragment provided desired reactivity (Scheme 1B). In this context, our further efforts were directed toward the development of a new approach to spiro-[pyrrolidine-3,3′-oxindoles] based on our original strategy for pyrrolidine assembly.

Herein, we report the first synthesis of biologically relevant spiro[pyrrolidine-3,3′-oxindoles] via a cascade of Staudinger/*aza*-Wittig/Mannich reactions (Scheme 1C). In this regard, a novel access to the starting 3-(2-azidoethyl)oxindoles through a

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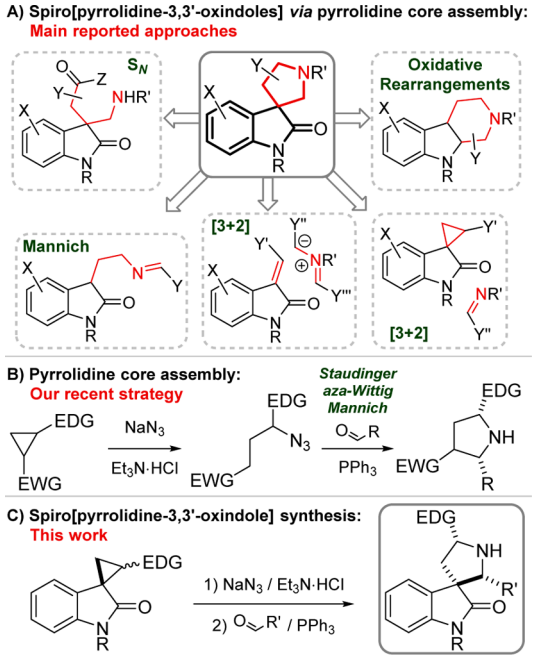
Scheme 1. Pyrrolidine Core Assembly for the Completion of Spiro[Pyrrolidine-3,3′-oxindole] Tricyclic System



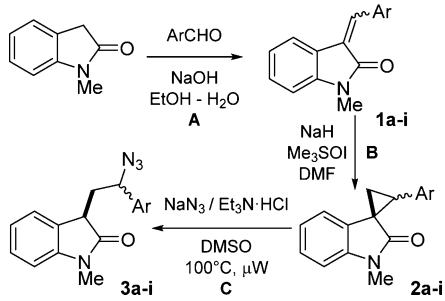
nucleophilic ring opening of spiro[cyclopropane-1,3′-oxindoles] using an azide ion was developed on the basis of our recent results.

RESULTS AND DISCUSSION

We began our research by preparation of initial 3-(2-azidoethyl)oxindoles **3a**–**i** via a three-step procedure starting from *N*-methyloxindole (Table 1). Synthesis of intermediate cyclopropanes **2** was performed through sequential Knoevenagel and Corey-Chaykovsky reactions according to the literature procedures.[11,12] Cyclopropanes **2a**–**i** were obtained in good yields as diastereomeric mixtures. In order to carry out transformation of cyclopropanes **2** into azides **3**, we have modified the reaction conditions, previously reported by us for the nucleophilic ring opening of donor–acceptor cyclopropanes with the azide ion.[10] To achieve complete **2**-to-**3** conversion, this process was thermally activated in a microwave reactor. The reaction proceeds with exceptional regioselectivity as a nucleophilic attack on the benzylic position in the three-membered ring in **2**. Cyclopropanes **2a**–**h** containing phenyl or more electron-abundant aryls give 3-(2-azidoethyl)oxindoles **3a**–**h** as mixtures of two diastereomers in reasonable yields. The presence of the electron-withdrawing 3-pyridinyl group in **2i** significantly deactivates this cyclopropane toward the nucleophilic attack of the azide ion: even after 7 h, we did not observe complete conversion of **2i**. Adding 2 more equivalents of NaN_3-Et_3N·HCl and heating the reaction mixture for 4 more hours did lead to total **2i** conversion; however, the yield of the desired azide **3i** was found to be extremely low. The synthesized azides **3a**–**h** were then examined in a cascade of Staudinger/*aza*-Wittig/Mannich reactions with various aldehydes.

In order to elucidate suitable reaction conditions, we carried out a series of initial experiments using the mixture of azide **3a**, benzaldehyde, and triphenylphosphane as a model system (Table 2). While researching conditions, we looked into our prior results related to the synthesis of pyrrolidine-3,3-diesters.[9]

Table 1. Synthesis of Parent 3-(2-Azidoethyl)oxindoles



1-3	Ar	Yield (%)[b] [dr][c] 1	2	3
a		60[13a] [85:15]	84[14a] [74:26]	70 [53:47]
b		71[13a] [91:9]	98[14b] [62:38]	43 [52:48]
c		55[13a] [85:15]	84[14a] [71:29]	51 [53:47]
d		71[13a] [81:19]	89[14a] [73:27]	57 [52:48]
e		74 [84:16]	86 [74:26]	46 [51:49]
f		82 [89:11]	91 [74:26]	49 [54:46]
g		88[13b] [100:0]	91 [72:28]	45 [56:44]
h		69[13c] [92:8]	87[14a] [75:25]	55 [56:44]
i		61 [58:42]	68 [54:46]	3[d] [52:48]

[a]Reaction conditions: (A) *N*-methyloxindole (1.0 equiv), ArCHO (1.1 equiv), NaOH (2 equiv) in EtOH–H_2O (1:1, 0.25 M); B) **1** (1.0 equiv), NaH (2.2 equiv), Me_3SOI (2.0 equiv) in DMF (0.15 M); C) **2** (1.0 equiv), NaN_3 (2.0 equiv), Et_3N×HCl (2.0 equiv) in DMSO (0.5 M), 100 °C, mW, 3–5 h. [b]Isolated yield. [c]Diastereomeric ratios [dr] were determined by NMR data for reaction mixtures. [d]Complete conversion of **2i** was observed in 11 h.

Maintaining ambient temperature in CH_2Cl_2 for 30 h resulted in the model system yielding a mixture of the desired spiro-compound **4a** and intermediate iminophosphorane **5a** in a 88:12 ratio, albeit the isolated yield of **4a** only amounted to 36% (Table 2, entry 1). An increase in the reaction temperature to 39 °C resulted in the complete conversion of **5a**, but the yield of **4a** decreased (Table 2, entries 2,3). Heating of the reaction mixture in a microwave reactor was found to be more efficient, allowing for a significant increase in the yield of the product **4a**, but also decreasing the reaction time (Table 2, entries 4,5). Performing this reaction for 12 h under microwave heating at 39 °C provided the optimal conditions to convert azide **3a** into spiro-product **4a** in a 68% yield (Table 2, entry 5).

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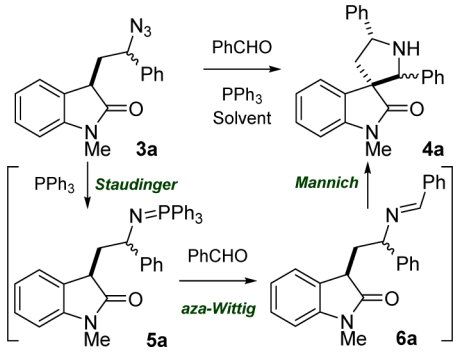
Table 2. Optimization of 3a-into-4a Transformation



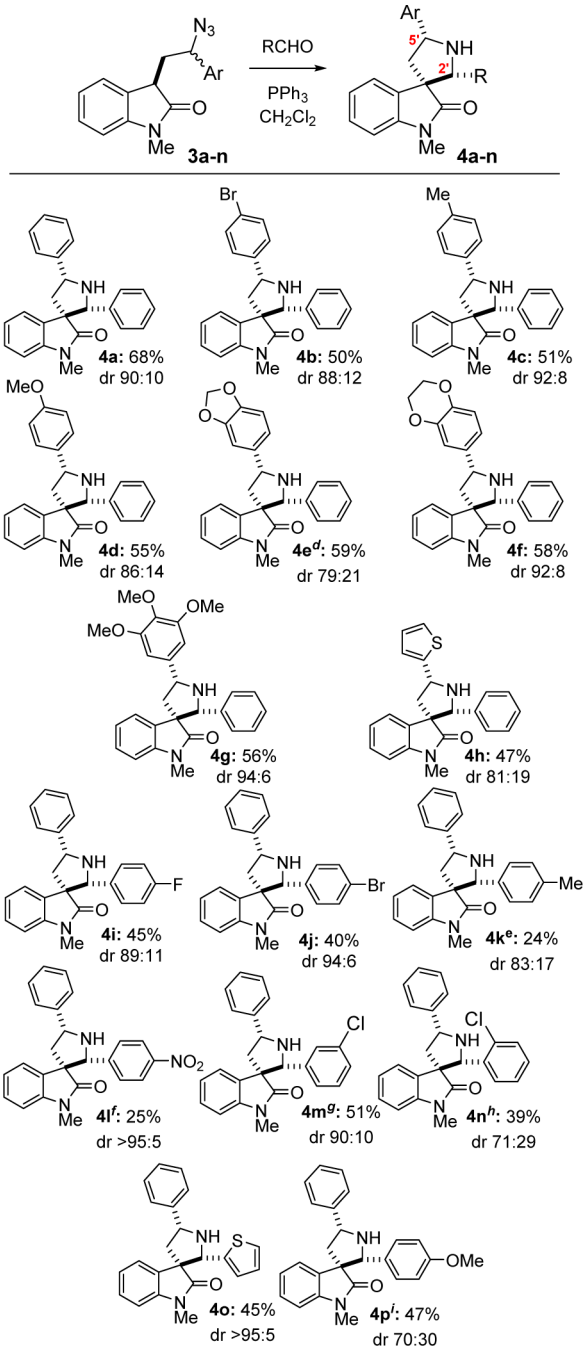
entry	T (°C)	t (h)	solvent	4a:5a[b]	yield 4a (%)[c] [cis:trans][b]
1	25	30	DCM	88:12	36 [88:12]
2	30	40	DCM	91:9	29 [87:13]
3	39	25	DCM	>95:5	25 [91:9]
4	39[d]	22	DCM	>95:5	64 [86:14]
5	39[d]	12	DCM	>95:5	68 [90:10]
6	39[d]	12	toluene	>95:5	43[e] [89:11]
7	39[d]	5	MeCN	>95:5	21[e] [70:30]
8	39[d]	12	DMF	>95:5	[f]

[a]Reaction conditions: **3a** (1 equiv), PhCHO (1.5 equiv), PPh_3 (1.05 equiv) in CH_2Cl_2 (1 M). [b]Ratios were determined by NMR data for reaction mixtures. [c]Isolated yield. [d]Under μW heating. [e]Yields were determined by NMR data for reaction mixtures. [f]Complex mixture of nonidentified products.

Meanwhile, the replacement of DCM by less- (toluene) or more-polar (MeCN, DMF) solvents (entries 6−8) leads to a significant decrease in the yield of **4a**. An increase in reaction temperature intensifies the retro-Mannich reaction (see below Scheme 4) resulting in a considerable loss in diastereoselectivity, as well as the yield of **4**.

Subsequently, this reaction was extended to a series of azides **3b−h** and readily available aromatic and heteroaromatic aldehydes (Scheme 2). We have found that the optimized conditions can be applied for the transformation of azides that contain both acceptor (**3b**) and donor (**3c−h**) (het)aryl substituents into spiro-products **4b−h**. Besides benzaldehyde, their more electrophilic derivatives containing F, Cl, Br, or NO_2 groups in their aromatic ring readily produced spiro-[pyrrolidine-3,3′-oxindoles] **4i−o**. A reaction between **3a** and the most reactive 4-nitrobenzaldehyde could be completed even at ambient temperature in 4 h. High reactivity of 4-nitrobenzaldehyde apparently causes poor chemoselectivity in the process, yielding low amounts of product **4l** (25%) along with a complex mixture of unidentified products. On the contrary, aldehydes with more electron-abundant aryls than phenyl were found to exhibit lower reactivity under studied conditions. Reaction of azide **3a** with 4-methoxybenzaldehyde did not display complete conversion of iminophosphorane **5a**. Moreover, the presence of electron-donating groups in the aromatic ring of an intermediate imine of type **6** prevents pyrrolydine ring closure via the final Mannich reaction, whereas it facilitates retro-Mannich ring opening in the final product **4**. This causes a lower stability of pyrrolidines **4k,p** vs phenyl-derived pyrrolidines **4a−h**. Product **4k** was isolated with 24% yield only, whereas less-stable **4p** was not isolated after column chromatography at all. Summarizing, products **4** were obtained in reasonable yields, taking into account that the studied

Scheme 2. Substrate Scope[a,b,c]



[a]Reaction conditions: **3** (1 equiv), RCHO (1.5 equiv), PPh_3 (1.05 equiv) in CH_2Cl_2 (1 M), 39 °C, μW, 12 h. [b]Isolated yield. [c]Ratios of 2′,5′-cis-**4** and their 2′-epimers (dr) were determined by NMR data for reaction mixtures. [d]Reaction was carried out for 18 h. [e]74% conversion of iminophosphorane was observed. [f]Reaction was carried out at 25 °C for 4 h. [g]Reaction was carried out for 6 h. [h]Reaction was carried out for 13 h. [i]Reaction was carried out for 24 h; NMR yield.

transformation of azides **3** into spiro[pyrrolidine-3,3′-oxindoles] **4** is a complex multiple-stage process.

The transformation of azides **3** into spiro-compounds **4** proceeds diastereoselectively with predominant formation of (2′*RS*,3*SR*,5′*RS*)-isomers of **4** while the corresponding epimers (2′*SR*,3*SR*,5′*RS*)-**4** are formed as minor products. High diastereoselectivity can originate from the intramolecular

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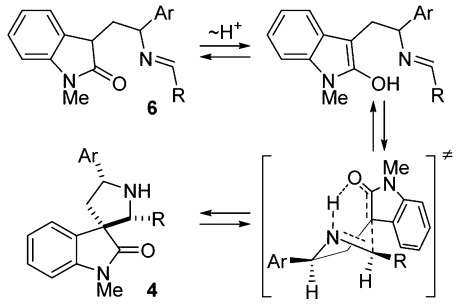
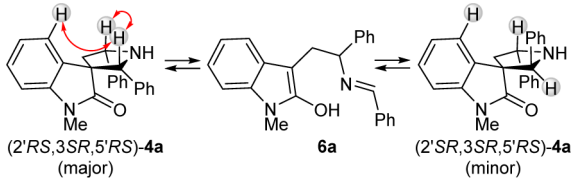
Mannich transition state with a pseudoequatorial location of substituents at C2′ and C5′ of a newly formed pyrrolidine ring (Scheme 3).[9]

Scheme 3. Origin of Diastereoselectivity in the Formation of 4



The relative configurations of the major and minor isomers were determined on the basis of NOE data (Scheme 4). In

Scheme 4. Epimerization of 4a Via Retro-Mannich/Mannich Reaction



NOESY spectra, a cross-peak between the signals of H2′ and H5′ is observed for the major isomer of **4a** that indicates *cis*-location of aryls in the pyrrolidine ring. The relative arrangement of pyrrolidine and oxindole fragments in the spiro-fused system of the major isomer was assigned on the basis of a cross-peak between H2′ and H4. For the minor isomer, the aforementioned cross-peaks are not observed; therefore, this isomer was assigned to the C2′-epimer of the major isomer. In solutions, slow isomerization of (2′*RS*,3*SR*,5′*RS*)-**4** into minor epimers (2′*SR*,3*SR*,5′*RS*)-**4** was observed. This can be explained by the presence of an equilibrium between these isomers that is achieved via retro-Mannich/Mannich reactions.[1e,3b,8b]

In order to estimate antiproliferative activity of spiro[pyrrolidine-3,3′-oxindoles] **4**, we carried out in vitro experiments using LNCaP, PC-3, HCT116 p53−/−, and HCT116 p53+/+ cell lines. Compounds **4a−e, g, j, l** exhibited a high toxic effect toward LNCaP and PC-3 cell lines, whereas HCT116 p53−/− and HCT116 p53+/+ cells were found to be 3−6 times more viable under the same conditions (Table 3). For comparison, nutlin-3a, when using as a positive control, exhibits similar effects toward PC-3 (p53-) and HCT116 (p53+/+ (w.t.)) and also displays high selectivity over all cancer cell lines with mutated or deleted p53. Consequently, prostatic cancer cell lines LNCaP and PC-3 are more sensitive toward **4** than colon carcinoma cell lines HCT116. However, no selectivity was observed for cancer cell lines with mutated or deleted p53. These preliminary results do not allow for the conclusion that the proliferative activity of **4** is related to inhibition of the p53-MDM2 interaction.

CONCLUSIONS

In conclusion, we have developed a new approach to the synthesis of spiro[pyrrolidine-3,3′-oxindoles] via a cascade of Staudinger/*aza*-Wittig/Mannich reactions. The method exhibited good tolerance toward 2-aryl-substituted 3-(2-azidoethyl)oxindoles and various aromatic and heteroaromatic aldehydes, allowing for the diastereoselective synthesis of 2′,5′-aryl-disubstituted spiro[pyrrolidine-3,3′-oxindoles] in reasonable yields. Considerable cytotoxicity against tumor cell lines makes the synthesized compounds promising candidates for research toward their anticancer activity.

EXPERIMENTAL SECTION

General Information. NMR spectra were acquired at room temperature if not specified otherwise; the chemical shifts δ were measured in ppm with respect to solvent (^{1}H: $CDCl_3$, δ = 7.27 ppm; ^{13}C: $CDCl_3$, δ = 77.0 ppm). Splitting patterns are designated as s, singlet; d, doublet; t, triplet; m, multiplet; dd, double doublet. Coupling constants (J) are given in hertz. The structures of all compounds were elucidated with the aid of 1D NMR (^{1}H, ^{13}C) and 2D NMR (COSY ^{1}H−^{1}H, HSQC ^{1}H−^{13}C, HMBC ^{1}H−^{13}C, and NOESY ^{1}H−^{1}H) spectroscopy. In infrared (IR) spectra, wavenumbers are indicated in cm^{-1}. High-resolution mass spectra (HRMS) were performed using ESI and a TOF mass analyzer. Melting points (mp) were determined using a capillary melting point apparatus; the values are uncorrected. Microwave reactions were performed in a microwave reactor in sealed reaction vessels; the temperature was monitored with an installed IR detector. Analytical thin-layer chromatography (TLC) was carried out with silica gel plates (silica gel 60, F_{254}, supported on aluminum) and was visualized with UV lamp (254 nm). Column chromatography was performed on silica gel 60 (230−400 mesh). NaH (60% dispersion in mineral oil) and trimethylsulfoxonium iodide are available commercially. Alkenes **1a−i** and cyclopropanes **2a−i** were prepared by Knoevenagel/Corey−Chaykovsky reactions starting from the corresponding aldehydes.[11,12] Their spectra and physical data are very consistent with earlier published data, except for unreported

Table 3. Results of Cell Assay

	IC_{50} (μM)			
4	PC-3 (p53-)	LNCaP (p53+, w.t.)	HCT116 p53−/−	HCT116 p53+/+ (w.t.)
4a	4.9 ± 1.8	3.2 ± 2.2	18.1 ± 2.2	12.6 ± 3.1
4b	7.9 ± 2.3	4.1 ± 3.1	12.8 ± 0.9	6.4 ± 1.2
4c	6.0 ± 1.4	5.1 ± 2.1	35.1 ± 1.4	25.1 ± 2.6
4d	5.7 ± 2.0	2.4 ± 1.3	9.9 ± 1.6	10.2 ± 1.1
4e	8.6 ± 1.9	5.1 ± 2.2	16.8 ± 2.4	10.2 ± 2.8
4g	4.7 ± 1.6	2.0 ± 1.2	>100	>50
4j	4.0 ± 2.2	4.5 ± 1.7	26.2 ± 2.1	18.9 ± 3.8
4l	7.0 ± 3.0	4.2 ± 1.5	38.6 ± 4.2	32.4 ± 2.9
Nutlin-3a	29.8 ± 1.6	2.8 ± 1.9	40.8 ± 1.2	2.3 ± 1.7

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compounds **1e**, **1f**, **1i**, **2e**−**g**, **2i**. Their spectral and physical data are given below. All the reactions were carried out using freshly distilled and dry solvents.

General Procedure for the Synthesis of Alkenes 1. An aromatic aldehyde (1.1 equiv) was added to a solution of 1-methylindolin-2-one (1.0 equiv) in ethanol (1 M). The resulting solution was added dropwise to a solution of sodium hydroxide (2.0 equiv) in ethanol−water (1:2, 0.67 M) at 0 °C (ice bath). When the addition was completed, the reaction mixture was allowed to warm up to room temperature and was stirred for a specified time. Then, the reaction mixture was diluted with water and extracted with ethyl acetate. The organic layer was washed with water, dried with sodium sulfate, and concentrated under reduced pressure. Alkene **1** was purified by column chromatography on silica gel.

*3-Benzylidene-1-methylindolin-2-one (**1a**).*[13a] 1-Methylindolin-2-one (1.000 g, 6.80 mmol) and benzaldehyde (765 μL, 7.48 mmol) were stirred in ethanol (14 mL) and water (14 mL) in the presence of sodium hydroxide (544 mg, 13.61 mmol) for 2 h, yielding **1a** (956 mg, 60%) as an orange oil. Two isomers **A**:**B** = 85:15. R_f = 0.50, 0.65 (ethyl acetate/petroleum ether; 1:3).

A: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 3.29 (s, 3H, NCH_3), 6.78 (d, ^3J 7.8 Hz, 1H, Ar), 6.85 (ddd, ^3J 7.6, ^3J 7.6, ^4J 1.0 Hz, 1H, Ar), 7.23 (ddd, ^3J 7.6, ^3J 7.8, ^4J 1.1 Hz, 1H, Ar), 7.38−7.41 (m, 1H, Ar), 7.42−7.45 (m, 2H, Ar), 7.60−7.62 (m, 3H, Ar), 7.83 (s, 1H, CH═); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 26.1 (NCH_3), 108.2 (CH, Ar), 121.1 (C, Ar), 121.7 (CH, Ar), 122.7 (CH, Ar), 127.2 (C, Ar), 128.6 (2 × CH, Ar), 129.3 (2 × CH, Ar), 129.5 (CH, Ar), 129.8 (CH, Ar), 135.0 (C, Ar), 137.00 (CH═), 144.3 (C, Ar), 168.4 (C═O).

B: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 3.27 (s, 3H, NCH_3), 6.81 (d, ^3J 7.7 Hz, 1H, Ar), 7.07 (ddd, ^3J 7.6, ^3J 7.6, ^4J 1.0 Hz, 1H, Ar), 7.29 (ddd, ^3J 7.7, ^3J 7.7, ^4J 1.1 Hz, 1H, Ar), 7.41−7.48 (m, 3H, Ar), 7.52−7.53 (m, 2H, Ar), 8.30−8.32 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 25.9 (NCH_3), 107.9 (CH, Ar), 118.9 (CH, Ar), 121.8 (CH, Ar), 124.4 (C, Ar), 126.1 (C, Ar), 128.3 (2 × CH, Ar), 128.9 (CH, Ar), 130.4 (CH, Ar), 132.0 (2 × CH, Ar), 133.9 (C, Ar), 137.03 (CH═), 142.4 (C, Ar), 166.1 (C═O).

*3-(4-Bromobenzylidene)-1-methylindolin-2-one (**1b**).*[13a] 1-Methylindolin-2-one (3.449 g, 23.46 mmol) and 4-bromobenzaldehyde (4.749 g, 25.81 mmol) were stirred in ethanol (47 mL) and water (47 mL) in the presence of sodium hydroxide (1.877 g, 46.93 mmol) for 2.5 h, yielding **1b** (5.197 g, 71%) as an orange oil. Two isomers **A**:**B** = 91:9. R_f = 0.43, 0.73 (ethyl acetate/petroleum ether; 1:3).

A: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 3.28 (s, 3H, NCH_3), 6.83 (d, ^3J 7.8 Hz, 1H, Ar), 6.90 (ddd, ^3J 7.7, ^3J 7.7, ^4J 1.0 Hz, 1H, Ar), 7.29 (ddd, ^3J 7.8, ^3J 7.7, ^4J 1.1 Hz, 1H, Ar), 7.52 (d, ^3J 8.5 Hz, 2H, Ar), 7.56 (d, ^3J 7.7 Hz, 1H, Ar), 7.60 (d, ^3J 8.5 Hz, 2H, Ar), 7.75 (s, 1H, CH═); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 26.2 (NCH_3), 108.3 (CH, Ar), 120.9 (C, Ar), 121.9 (CH, Ar), 122.7 (CH, Ar), 123.7 (C, Ar), 127.8 (C, Ar), 130.1 (CH, Ar), 130.8 (2 × CH, Ar), 131.9 (2 × CH, Ar), 133.9 (C, Ar), 135.5 (CH═), 144.4 (C, Ar), 168.3 (C═O).

*1-Methyl-3-(4-methylbenzylidene)indolin-2-one (**1c**).*[13a] 1-Methylindolin-2-one (3.400 g, 23.13 mmol) and 4-methylbenzaldehyde (3.0 mL, 25.44 mmol) were stirred in ethanol (47 mL) and water (47 mL) in the presence of sodium hydroxide (1.850 g, 46.26 mmol) for 2.5 h, yielding **1c** (3.169 g, 55%) as an orange oil. Two isomers **A**:**B** = 85:15. R_f = 0.52, 0.72 (ethyl acetate/petroleum ether; 1:3).

A: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.44 (s, 3H, CH_3), 3.30 (s, 3H, NCH_3), 6.84 (d, ^3J 7.7 Hz, 1H, Ar), 6.91 (ddd, ^3J 7.7, ^3J 7.7, ^4J 1.1 Hz, 1H, Ar), 7.26−7.31 (m, 3H, Ar), 7.58 (d, ^3J 8.1 Hz, 2H, Ar), 7.71 (br. d, ^3J 7.7 Hz, 1H, Ar), 7.85 (s, 1H, CH═); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 21.5 (CH_3), 26.1 (NCH_3), 108.0 (CH, Ar), 121.4 (C, Ar), 121.7 (CH, Ar), 122.7 (CH, Ar), 126.5 (C, Ar), 129.3 (2 × CH, Ar), 129.45 (2 × CH, Ar), 129.54 (CH, Ar), 132.1 (C, Ar), 137.4 (CH═), 139.9 (C, Ar), 144.2 (C, Ar), 168.6 (C═O).

*3-(4-Methoxybenzylidene)-1-methylindolin-2-one (**1d**).*[13a] 1-Methylindolin-2-one (500 mg, 3.40 mmol) and 4-methoxybenzaldehyde (455 μL, 3.74 mmol) were stirred in ethanol (7.0 mL) and water (7.0 mL) in the presence of sodium hydroxide (272 mg, 6.80 mmol) for 2.5 h, yielding **1d** (638 mg, 71%) as an orange oil. Two isomers **A**:**B** = 81:19. R_f = 0.27, 0.45 (ethyl acetate/petroleum ether; 1:3).

A: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 3.29 (s, 3H, NCH_3), 3.89 (s, 3H, OCH_3), 6.84 (d, ^3J 7.6 Hz, 1H, Ar), 6.92 (ddd, ^3J 7.6, ^3J 7.7, ^4J 1.1 Hz, 1H, Ar), 6.99 (d, ^3J 8.8 Hz, 2H, Ar), 7.27 (ddd, ^3J 7.7, ^3J 7.8, ^4J 1.1 Hz, 1H, Ar), 7.64−7.67 (m, 2H, Ar), 7.76 (br. d, ^3J 7.7 Hz, 1H, Ar), 7.81 (s, 1H, CH═); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 26.2 (NCH_3), 55.4 (OCH_3), 108.1 (CH, Ar), 114.1 (2 × CH, Ar), 121.5 (C, Ar), 121.7 (CH, Ar), 122.4 (CH, Ar), 125.4 (C, Ar), 127.3 (C, Ar), 129.3 (CH, Ar), 131.5 (2 × CH, Ar), 137.4 (CH═), 144.0 (C, Ar), 160.8 (C, Ar), 168.8 (C═O).

B: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 3.29 (s, 3H, NCH_3), 3.88 (s, 3H, OCH_3), 6.81 (d, ^3J 7.8 Hz, 1H, Ar), 6.97 (d, ^3J 9.0 Hz, 2H, Ar), 7.05 (ddd, ^3J 7.5, ^3J 7.6, ^4J 1.0 Hz, 1H, Ar), 7.26 (ddd, ^3J 7.6, ^3J 7.7, ^4J 1.2 Hz, 1H, Ar), 7.49 (s, 1H, CH═), 7.51 (br. d, ^3J 7.5 Hz, 1H, Ar), 8.39−8.41 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 25.9 (NCH_3), 55.4 (OCH_3), 107.8 (CH, Ar), 113.7 (2 × CH, Ar), 118.4 (CH, Ar), 121.5 (CH, Ar), 124.8 (C, Ar), 127.0 (C, Ar), 128.2 (CH, Ar), 131.5 (C, Ar), 134.4 (2 × CH, Ar), 137.1 (CH═), 141.9 (C, Ar), 161.6 (C, Ar), 171.2 (C═O).

*3-(Benzo[d][1,3]dioxol-5-ylmethylene)-1-methylindolin-2-one (**1e**).* 1-Methylindolin-2-one (1.256 g, 8.54 mmol) and benzo[*d*][1,3]-dioxole-5-carbaldehyde (1.410 g, 9.40 mmol) were stirred in ethanol (17 mL) and water (17 mL) in the presence of sodium hydroxide (684 mg, 17.09 mmol) for 3 h, yielding **1e** (1.772 g, 74%) as an orange oil. Two isomers **A**:**B** = 84:16. R_f = 0.45, 0.64 (ethyl acetate/petroleum ether; 1:3).

A: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 3.28 (s, 3H, NCH_3), 6.05 (s, 2H, OCH_2), 6.79 (d, ^3J 7.8 Hz, 1H, Ar), 6.87 (d, ^3J 8.0 Hz, 1H, Ar), 6.89 (dd, ^3J 7.6, ^3J 7.8 Hz, 1H, Ar), 7.13 (s, 1H, Ar), 7.17 (d, ^3J 8.0 Hz, 1H, Ar), 7.24 (dd, ^3J 7.6, ^3J 7.7 Hz, 1H, Ar), 7.70 (s, 1H, CH═), 7.72 (d, ^3J 7.7 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 26.1 (NCH_3), 101.6 (OCH_2), 108.1 (CH, Ar), 108.6 (CH, Ar), 109.4 (CH, Ar), 121.2 (C, Ar), 121.70 (CH, Ar), 122.6 (CH, Ar), 124.73 (CH, Ar), 125.8 (C, Ar), 128.8 (C, Ar), 129.47 (CH, Ar), 137.1 (CH═), 144.1 (C, Ar), 147.9 (C, Ar), 148.9 (C, Ar), 168.6 (C═O).

B: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 3.28 (s, 3H, NCH_3), 6.03 (s, 2H, OCH_2), 6.76 (d, ^3J 7.6 Hz, 1H, Ar), 6.83 (d, ^3J 8.1 Hz, 1H, Ar), 7.01 (dd, ^3J 7.5, ^3J 7.6 Hz, 1H, Ar), 7.21−7.24 (m, 1H, Ar), 7.36 (s, 1H, CH═), 7.43 (d, ^3J 7.4 Hz, 1H, Ar), 7.68 (d, ^3J 8.1 Hz, 1H, Ar), 8.41 (s, 1H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 25.9 (NCH_3), 101.6 (OCH_2), 107.7 (CH, Ar), 108.0 (CH, Ar), 111.6 (CH, Ar), 118.4 (CH, Ar), 121.65 (CH, Ar), 123.8 (C, Ar), 124.68 (C, Ar), 128.3 (CH, Ar), 128.6 (C, Ar), 128.9 (CH, Ar), 137.0 (CH═), 141.9 (C, Ar), 147.7 (C, Ar), 149.8 (C, Ar), 166.2 (C═O);

IR (film, cm^{-1}): 3055, 2920, 2890, 1700, 1635, 1605, 1500, 1485, 1470, 1450, 1420, 1380, 1375, 1340, 1305, 1260, 1200, 1160, 1135, 1120, 1100, 1030, 925, 905, 870, 805, 775, 745, 725, 695;

HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{17}H_{14}NO_3$, 280.0968, found 280.0965.

*3-((2,3-Dihydrobenzo[b][1,4]dioxin-6-yl)methylene)-1-methylindolin-2-one (**1f**).* 1-Methylindolin-2-one (2.363 g, 16.08 mmol) and 2,3-dihydrobenzo[*b*][1,4]dioxine-6-carbaldehyde (2.900 g, 17.68 mmol) were stirred in ethanol (32 mL) and water (32 mL) in the presence of sodium hydroxide (1.286 g, 32.15 mmol) for 2 h, yielding **1f** (3.865 g, 82%) as an orange oil. Two isomers **A**:**B** = 89:11. R_f = 0.33, 0.41 (ethyl acetate/petroleum ether; 1:3).

A: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 3.25 (s, 3H, NCH_3), 4.24−4.33 (m, 4H, OCH_2), 6.80 (d, ^3J 7.7 Hz, 1H, Ar), 6.88−6.94 (m, 2H, Ar), 7.17−7.21 (m, 2H, Ar), 7.24 (ddd, ^3J 7.6, ^3J 7.7, ^4J 1.1 Hz, 1H, Ar), 7.72 (s, 1H, CH═), 7.77 (d, ^3J 7.6 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 26.2 (NCH_3), 64.3 (OCH_2), 64.6 (OCH_2), 108.1 (CH, Ar), 117.5 (CH, Ar), 118.6 (CH, Ar), 121.3 (C, Ar), 121.8 (CH, Ar), 122.6 (CH, Ar), 123.6 (CH, Ar), 125.7 (C, Ar), 128.2 (C, Ar), 129.4 (CH, Ar), 137.1 (CH═), 143.5 (C, Ar), 144.0 (C, Ar), 145.1 (C, Ar), 168.7 (C═O).

B: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 3.25 (s, 3H, NCH_3), 4.24−4.33 (m, 4H, OCH_2), 6.77 (d, ^3J 7.7 Hz, 1H, Ar), 6.88−6.94 (m, 1H, Ar), 7.01 (ddd, ^3J 7.6, ^3J 7.6, ^4J 0.9 Hz, 1H, Ar), 7.17−7.21 (m, 1H, Ar), 7.37 (s, 1H, CH═), 7.46 (d, ^3J 7.5 Hz, 1H, Ar), 7.84 (dd, ^3J 8.5,

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^4J 2.1 Hz, 1H, Ar), 8.12 (d, ^4J 2.1 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 25.9 (NCH_3), 64.1 (OCH_2), 64.8 (OCH_2), 107.7 (CH, Ar), 117.0 (CH, Ar), 118.5 (CH, Ar), 121.2 (C, Ar), 121.6 (CH, Ar), 124.0 (CH, Ar), 124.7 (C, Ar), 126.8 (CH, Ar), 127.8 (C, Ar), 128.3 (CH, Ar), 136.9 (CH═), 141.9 (C, Ar), 143.0 (C, Ar), 146.0 (C, Ar), 166.2 (C═O);

IR (KBr, cm^{-1}): 3055, 2995, 2950, 2885, 1705, 1630, 1605, 1580, 1510, 1485, 1470, 1450, 1425, 1395, 1375, 1360, 1335, 1300, 1265, 1250, 1215, 1165, 1150, 1120, 1095, 1060, 1040, 1030, 970, 950, 910, 885, 865, 850, 815, 785, 770, 760, 740, 715, 690;

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{16}NO_3$, 294.1125, found 294.1120.

*(E)-1-Methyl-3-(3,4,5-trimethoxybenzylidene)indolin-2-one (**1g**).*[13b] 1-Methylindolin-2-one (500 mg, 3.40 mmol) and 3,4,5-trimethoxybenzaldehyde (733 mg, 3.74 mmol) were stirred in ethanol (7.0 mL) and water (7.0 mL) in the presence of sodium hydroxide (272 mg, 6.80 mmol) for 3 h, yielding **1g** (970 mg, 88%) as yellow oil. R_f = 0.75 (ethyl acetate/petroleum ether; 1:1).

^{1}H NMR ($CDCl_3$, 600 MHz): δ = 3.30 (s, 3H, NCH_3), 3.95 (s, 3H, OCH_3), 3.99 (s, 6H, OCH_3), 6.83 (d, ^3J 7.7 Hz, 1H, Ar), 7.07 (ddd, ^3J 7.5, ^3J 7.5, ^4J 0.6 Hz, 1H, Ar), 7.29 (ddd, ^3J 7.6, ^3J 7.6, ^4J 0.9 Hz, 1H, Ar), 7.45 (s, 1H, CH═), 7.53 (d, ^3J 7.5 Hz, 1H, Ar), 7.88 (s, 2H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 26.1 (NCH_3), 56.3 (2 × OCH_3), 60.9 (OCH_3), 107.8 (CH, Ar), 110.1 (2 × CH, Ar), 118.6 (CH, Ar), 121.8 (CH, Ar), 124.7 (C, Ar), 125.0 (C, Ar), 128.6 (CH, Ar), 129.4 (C, Ar), 137.3 (CH═), 140.7 (C, Ar), 142.0 (C, Ar), 152.7 (2 × C, Ar), 166.3 (C═O).

*1-Methyl-3-(thiophen-2-ylmethylene)indolin-2-one (**1h**).*[13c] 1-Methylindolin-2-one (1.186 g, 7.50 mmol) and thiophene-2-carbaldehyde (755 μL, 8.25 mmol) were stirred in ethanol (15 mL) and water (15 mL) in the presence of sodium hydroxide (600 mg, 15.00 mmol) for 3 h, yielding **1h** (1.340 g, 69%) as an orange oil. Two isomers **A**:**B** = 92:8. R_f = 0.34, 0.49 (ethyl acetate/petroleum ether; 1:3).

A: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 3.22 (s, 3H, NCH_3), 6.73 (d, ^3J 7.8 Hz, 1H, Ar), 6.99 (dd, ^3J 7.5, ^3J 7.6 Hz, 1H, Ar), 7.11 (dd, ^3J 3.7, ^3J 5.2 Hz, 1H, Ar), 7.21 (dd, ^3J 7.6, ^3J 7.7 Hz, 1H, Ar), 7.40 (d, ^3J 7.5 Hz, 1H, Ar), 7.58–7.61 (m, 2H, Ar, CH═), 7.74 (br. d, ^3J 3.7 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 25.8 (NCH_3), 107.9 (CH, Ar), 118.6 (CH, Ar), 121.3 (C, Ar), 121.6 (CH, Ar), 123.8 (C, Ar), 127.2 (CH, Ar), 127.9 (CH, Ar), 128.4 (CH, Ar), 133.5 (CH, Ar), 137.0 (CH═), 137.7 (C, Ar), 141.9 (C, Ar), 166.3 (C═O).

B: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 3.22 (s, 3H, NCH_3), 6.77 (d, ^3J 7.7 Hz, 1H, Ar), 6.97–7.03 (m, 1H, Ar), 7.14 (dd, ^3J 3.7, ^3J 5.0 Hz, 1H, Ar), 7.25 (dd, ^3J 7.7, ^3J 7.7 Hz, 1H, Ar), 7.53–7.56 (m, 2H, Ar), 7.90 (s, 1H, CH═), 8.17 (d, ^3J 7.7 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 26.2 (NCH_3), 108.1 (CH, Ar), 120.9 (C, Ar), 121.8 (CH, Ar), 122.6 (C, Ar), 123.4 (CH, Ar), 128.1 (CH, Ar), 128.3 (CH, Ar), 129.5 (CH, Ar), 130.5 (CH, Ar), 134.6 (CH═), 137.9 (C, Ar), 143.9 (C, Ar), 169.0 (C═O).

*1-Methyl-3-(pyridin-3-ylmethylene)indolin-2-one (**1i**).* 1-Methylindolin-2-one (1.186 g, 7.50 mmol) and nicotinaldehyde (775 μL, 8.25 mmol) were stirred in ethanol (15 mL) and water (15 mL) in the presence of sodium hydroxide (600 mg, 15.00 mmol) for 1 h, yielding **1i** (1.169 g, 61%) as an orange oil. Two isomers **A**:**B** = 58:42. R_f = 0.48, 0.56 (ethyl acetate/petroleum ether; 1:1).

A: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 3.22 (s, 3H, NCH_3), 6.79 (d, ^3J 7.7 Hz, 1H, Ar), 6.84 (dd, ^3J 7.7, ^3J 7.7 Hz, 1H, Ar), 7.25 (dd, ^3J 7.7, ^3J 7.7 Hz, 1H, Ar), 7.38 (dd, ^3J 4.9, ^3J 7.9 Hz, 1H, Ar), 7.45 (d, ^3J 7.7 Hz, 1H, Ar), 7.30 (s, 1H, CH═), 7.87–7.89 (m, 1H, Ar), 8.62 (dd, ^3J 4.9, ^4J 1.4 Hz, 1H, Ar), 8.85 (d, ^4J 1.4 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 26.2 (NCH_3), 108.4 (CH, Ar), 120.7 (C, Ar), 122.0 (CH, Ar), 122.6 (CH, Ar), 123.4 (CH, Ar), 129.3 (C, Ar), 130.5 (CH, Ar), 131.2 (C, Ar), 132.4 (CH, Ar), 136.4 (CH═), 144.6 (C, Ar), 149.9 (CH, Ar), 150.0 (CH, Ar), 167.8 (C═O).

B: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 3.20 (s, 3H, NCH_3), 6.76 (d, ^3J 7.8 Hz, 1H, Ar), 7.02 (dd, ^3J 7.5, ^3J 7.6 Hz, 1H, Ar), 7.27 (dd, ^3J 7.6, ^3J 7.8 Hz, 1H, Ar), 7.35 (dd, ^3J 4.8, ^3J 8.1 Hz, 1H, Ar), 7.39 (s, 1H, CH═), 7.49 (d, ^3J 7.5 Hz, 1H, Ar), 8.55 (dd, ^3J 4.8, ^4J 1.4 Hz, 1H, Ar), 8.93 (d, ^4J 1.4 Hz, 1H, Ar), 9.08–9.10 (m, 1H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 26.0 (NCH_3), 108.1 (CH, Ar), 119.4 (C, Ar), 122.1 (CH, Ar), 122.3 (CH, Ar), 123.2 (CH, Ar), 123.7 (CH, Ar), 129.7 (C, Ar), 130.0 (CH, Ar), 132.2 (C, Ar), 138.3 (CH═), 142.7 (C, Ar), 150.3 (CH, Ar), 152.5 (CH, Ar), 166.0 (C═O).

IR (film, cm^{-1}): 3430, 3120, 3070, 3055, 3025, 2930, 2885, 1920, 1905, 1705, 1680, 1605, 1560, 1490, 1470, 1415, 1375, 1340, 1310, 1260, 1185, 1150, 1125, 1090, 1050, 1035, 1025, 965, 935, 925, 915, 895, 880, 835, 810, 785, 775, 745, 700.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{13}N_2O$, 237.1022, found 237.1023.

General Procedure for the Synthesis of Cyclopropanes 2. A suspension of sodium hydride (2.2 equiv) and trimethylsulfoxonium iodide (2.0 equiv) in DMF was stirred at room temperature for 30 min, then solution of alkene **1** (1.0 equiv) in DMF was added dropwise. When addition was completed, the reaction mixture was stirred at room temperature for a specified time. Then, the reaction mixture was diluted with water and extracted with ethyl acetate. The organic layer was washed with water, dried with sodium sulfate, and concentrated under reduced pressure. The residue was washed with petroleum ether and dried.

*1′-Methyl-2-phenylspiro[cyclopropane-1,3′-indolin]-2′-one (**2a**).*[14a] A suspension of sodium hydride (468 mg, 11.70 mmol) and trimethylsulfoxonium iodide (2.340 g, 10.64 mmol) in DMF (6.0 mL) was stirred for 30 min; then solution of **1a** (1.250 g, 5.32 mmol) in DMF (30 mL) was added dropwise. The reaction mixture was stirred for additional 3 h, yielding **2a** (1.111 g, 84%) as yellow oil. Two diastereomers **A**:**B** = 74:26.

A: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.01 (dd, ^2J 4.5, ^3J 8.0 Hz, 1H, CH_2), 2.20 (dd, ^2J 4.5, ^3J 9.2 Hz, 1H, CH_2), 3.32–3.37 (m, 4H, CH, NCH_3), 5.97 (dd, ^3J 7.5, ^4J 0.5 Hz, 1H, Ar), 6.70 (ddd, ^3J 7.6, ^3J 7.6, ^4J 0.7 Hz, 1H, Ar), 6.86–6.91 (m, 1H, Ar), 7.16 (ddd, ^3J 7.7, ^3J 7.7, ^4J 1.1 Hz, 1H, Ar), 7.20 (d, ^3J 7.3 Hz, 2H, Ar), 7.23–7.35 (m, 3H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 22.4 (CH_2), 26.7 (NCH_3), 33.3 (C), 35.9 (CH), 107.8 (CH, Ar), 120.7 (CH, Ar), 121.5 (CH, Ar), 126.6 (CH, Ar), 127.4 (CH, Ar), 127.5 (C, Ar), 128.4 (2 × CH, Ar), 130.0 (2 × CH, Ar), 135.2 (C, Ar), 143.9 (C, Ar), 176.5 (C═O).

B: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.08 (dd, ^2J 4.9, ^3J 9.0 Hz, 1H, CH_2), 2.42 (dd, ^2J 4.9, ^3J 8.6 Hz, 1H, CH_2), 3.15–3.20 (m, 4H, CH, NCH_3), 6.86–6.91 (m, 1H, Ar), 6.99 (ddd, ^3J 7.4, ^4J 0.5, ^4J 0.5 Hz, 1H, Ar), 7.09 (ddd, ^3J 7.5, ^3J 7.5, ^4J 0.6 Hz, 1H, Ar), 7.23–7.35 (m, 6H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 22.5 (CH_2), 26.5 (NCH_3), 33.9 (C), 38.1 (CH), 107.8 (CH, Ar), 118.1 (CH, Ar), 121.9 (CH, Ar), 126.9 (CH, Ar), 127.2 (CH, Ar), 127.9 (2 × CH, Ar), 129.3 (2 × CH, Ar), 130.9 (C, Ar), 134.4 (C, Ar), 143.5 (C, Ar), 173.8 (C═O).

*2-(4-Bromophenyl)-1′-methylspiro[cyclopropane-1,3′-indolin]-2′-one (**2b**).*[14b] A suspension of sodium hydride (820 mg, 20.49 mmol) and trimethylsulfoxonium iodide (4.098 g, 18.63 mmol) in DMF (11 mL) was stirred for 30 min; then solution of **1b** (2.915 g, 9.31 mmol) in DMF (52 mL) was added dropwise. The reaction mixture was stirred for additional 3 h, yielding **2b** (2.982 g, 98%) as yellow oil. Two diastereomers **A**:**B** = 62:38.

A: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 1.93 (dd, ^2J 4.7, ^3J 7.9 Hz, 1H, CH_2), 2.19 (dd, ^2J 4.7, ^3J 9.2 Hz, 1H, CH_2), 3.25 (dd, ^3J 7.9, ^3J 9.2 Hz, 1H, CH), 3.33 (s, 3H, NCH_3), 5.99 (ddd, ^3J 7.5, ^4J 1.1, ^5J 0.5 Hz, 1H, Ar), 6.75 (ddd, ^3J 7.6, ^3J 7.6, ^4J 1.0 Hz, 1H, Ar), 6.87–6.91 (m, 1H, Ar), 7.05–7.10 (m, 2H, Ar), 7.16–7.22 (m, 1H, Ar), 7.40–7.44 (m, 2H, Ar);^{13}C NMR ($CDCl_3$, 150 MHz): δ = 22.3 (CH_2), 26.6 (NCH_3), 33.2 (C), 35.0 (CH), 107.88 (CH, Ar), 120.9 (CH, Ar), 121.4 (C, Ar), 121.6 (CH, Ar), 126.8 (CH, Ar), 127.1 (C, Ar), 131.5 (2 × CH, Ar), 131.6 (2 × CH, Ar), 134.3 (C, Ar), 143.9 (C, Ar), 176.1 (C═O).

B: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.08 (dd, ^2J 5.0, ^3J 9.1 Hz, 1H, CH_2), 2.35 (dd, ^2J 5.0, ^3J 8.6 Hz, 1H, CH_2), 3.08 (dd, ^3J 8.6, ^3J 9.1 Hz, 1H, CH), 3.19 (s, 3H, NCH_3), 6.87–6.91 (m, 1H, Ar), 6.97 (ddd, ^3J 7.4, ^4J 1.1, ^5J 0.4 Hz, 1H, Ar), 7.05–7.10 (m, 1H, Ar), 7.16–7.22 (m, 2H, Ar), 7.29 (ddd, ^3J 7.7, ^3J 7.7, ^4J 1.2 Hz, 1H, Ar), 7.40–7.44 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 22.4 (CH_2), 26.4 (NCH_3), 33.9 (C), 37.2 (CH), 107.91 (CH, Ar), 118.1 (CH, Ar), 121.2 (C, Ar), 122.0 (CH, Ar), 127.0 (CH, Ar), 130.5 (C, Ar), 130.9

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(2 × CH, Ar), 131.0 (2 × CH, Ar), 133.4 (C, Ar), 143.5 (C, Ar), 173.6 (C═O).

*1′-Methyl-2-(p-tolyl)spiro[cyclopropane-1,3′-indolin]-2′-one (**2c**).*[14a] A suspension of sodium hydride (631 mg, 15.79 mmol) and trimethylsulfoxonium iodide (3.158 g, 14.35 mmol) in DMF (8.0 mL) was stirred for 30 min; then solution of **1c** (1.787 g, 7.18 mmol) in DMF (40 mL) was added dropwise. The reaction mixture was stirred for additional 3 h, yielding **2c** (1.582 g, 84%) as yellow oil. Two diastereomers **A**:**B** = 71:29.

A: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 1.99 (dd, ^2J 4.5, ^3J 8.0 Hz, 1H, CH_2), 2.19 (dd, ^2J 4.5, ^3J 9.2 Hz, 1H, CH_2), 2.34 (s, 3H, CH_3), 3.32 (dd, ^3J 8.0, ^3J 9.2 Hz, 1H, CH), 3.34 (s, 3H, NCH_3), 6.03 (ddd, ^3J 7.5, ^4J 1.1, ^5J 0.5 Hz, 1H, Ar), 6.72 (ddd, ^3J 7.6, ^3J 7.6, ^4J 1.0 Hz, 1H, Ar), 6.86−6.90 (m, 1H, Ar), 7.07−7.14 (m, 4H, Ar), 7.16 (ddd, ^3J 7.7, ^3J 7.7, ^4J 1.2 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 21.1 (CH_3), 22.6 (CH_2), 26.6 (NCH_3), 33.3 (C), 35.6 (CH), 101.7 (CH, Ar), 120.8 (CH, Ar), 121.4 (CH, Ar), 126.5 (CH, Ar), 127.7 (C, Ar), 129.05 (2 × CH, Ar), 129.8 (2 × CH, Ar), 132.1 (C, Ar), 137.0 (C, Ar), 143.8 (C, Ar), 176.5 (C═O).

B: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.06 (dd, ^2J 4.9, ^3J 9.1 Hz, 1H, CH_2), 2.33 (s, 3H, CH_3), 2.40 (dd, ^2J 4.9, ^3J 8.6 Hz, 1H, CH_2), 3.14 (dd, ^3J 8.6, ^3J 9.1 Hz, 1H, CH), 3.19 (s, 3H, NCH_3), 6.86−6.90 (m, 1H, Ar), 6.98 (ddd, ^3J 7.4, ^4J 1.2, ^5J 0.5 Hz, 1H, Ar), 7.07−7.14 (m, 3H, Ar), 7.23 (d, ^3J 8.0 Hz, 2H, Ar), 7.29 (dd, ^3J 7.7, ^4J 1.2 Hz, 1H, CH_2); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 21.2 (CH_3), 22.6 (CH_2), 26.4 (NCH_3), 33.9 (C), 38.0 (CH), 107.7 (CH, Ar), 118.0 (CH, Ar), 121.8 (CH, Ar), 126.7 (CH, Ar), 128.7 (2 × CH, Ar), 129.09 (2 × CH, Ar), 131.0 (C, Ar), 131.3 (C, Ar), 136.7 (C, Ar), 143.5 (C, Ar), 173.9 (C═O).

*2-(4-Methoxyphenyl)-1′-methylspiro[cyclopropane-1,3′-indolin]-2′-one (**2d**).*[14a] A suspension of sodium hydride (2.139 g, 53.49 mmol) and trimethylsulfoxonium iodide (10.697 g, 48.63 mmol) in DMF (27 mL) was stirred for 30 min; then solution of **1d** (6.443 g, 24.31 mmol) in DMF (135 mL) was added dropwise. The reaction mixture was stirred for additional 3 h, yielding **2d** (6.053 g, 89%) as yellow oil. Two diastereomers **A**:**B** = 73:27.

A: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 1.96 (dd, ^2J 4.5, ^3J 8.0 Hz, 1H, CH_2), 2.18 (dd, ^2J 4.5, ^3J 9.2 Hz, 1H, CH_2), 3.28 (dd, ^3J 8.0, ^3J 9.2 Hz, 1H, CH), 3.33 (s, 3H, NCH_3), 3.80 (s, 3H, OCH_3), 5.98−6.02 (m, 1H, Ar), 6.72 (ddd, ^3J 7.6, ^3J 7.6, ^4J 1.0 Hz, 1H, Ar), 6.81−6.90 (m, 3H, Ar), 7.09−7.13 (m, 2H, Ar), 7.16 (ddd, ^3J 7.7, ^3J 7.7, ^4J 1.2 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 22.8 (CH_2), 26.6 (NCH_3), 33.4 (C), 35.3 (CH), 55.2 (OCH_3), 107.69 (CH, Ar), 113.8 (2 × CH, Ar), 120.8 (CH, Ar), 121.5 (CH, Ar), 126.5 (CH, Ar), 127.3 (C, Ar), 127.7 (C, Ar), 131.0 (2 × CH, Ar), 143.9 (C, Ar), 158.9 (C, Ar), 176.5 (C═O).

B: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.06 (dd, ^2J 4.9, ^3J 9.1 Hz, 1H, CH_2), 2.37 (dd, ^2J 4.9, ^3J 8.6 Hz, 1H, CH_2), 3.12 (dd, ^3J 8.6, ^3J 9.1 Hz, 1H, CH), 3.19 (s, 3H, NCH_3), 3.79 (s, 3H, OCH_3), 6.81−6.90 (m, 3H, Ar), 6.96−6.98 (m, 1H, Ar), 7.08 (ddd, ^3J 7.7, ^3J 7.7, ^4J 0.9 Hz, 1H, Ar), 7.25 (dd, ^3J 6.7, ^4J 1.7 Hz, 2H, Ar), 7.28 (ddd, ^3J 7.7, ^3J 7.7, ^4J 1.2 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 22.7 (CH_2), 26.4 (NCH_3), 33.9 (C), 37.8 (CH), 55.1 (OCH_3), 107.74 (CH, Ar), 113.4 (2 × CH, Ar), 118.0 (CH, Ar), 121.8 (CH, Ar), 126.3 (C, Ar), 126.7 (CH, Ar), 127.3 (C, Ar), 130.3 (2 × CH, Ar), 143.5 (C, Ar), 158.7 (C, Ar), 173.9 (C═O).

*2-(Benzo[d][1,3]dioxol-5-yl)-1′-methylspiro[cyclopropane-1,3′-indolin]-2′-one (**2e**).* A suspension of sodium hydride (473 mg, 11.83 mmol) and trimethylsulfoxonium iodide (2.366 g, 10.75 mmol) in DMF (6.0 mL) was stirred for 30 min; then solution of **1e** (1.500 g, 5.38 mmol) in DMF (30 mL) was added dropwise. The reaction mixture was stirred for additional 3 h, yielding **2e** (1.357 g, 86%) as yellow oil. Two diastereomers **A**:**B** = 74:26.

A: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 1.94 (dd, ^2J 4.6, ^3J 7.9 Hz, 1H, CH_2), 2.16 (dd, ^2J 4.6, ^3J 9.1 Hz, 1H, CH_2), 3.26 (dd, ^3J 7.9, ^3J 9.1 Hz, 1H, CH), 3.33 (s, 3H, NCH_3), 5.92 (s, 2H, OCH_2), 6.12 (d, ^3J 7.4 Hz, 1H, Ar), 6.64 (s, 1H, Ar), 6.70 (d, ^3J 7.9 Hz, 1H, Ar), 6.73−6.82 (m, 2H, Ar), 6.86−6.91 (m, 1H, Ar), 7.18 (dd, ^3J 7.7, ^3J 7.8 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 22.78 (CH_2), 26.6 (NCH_3), 33.4 (C), 35.7 (CH), 101.1 (OCH_2), 107.80 (CH, Ar), 108.1 (CH, Ar), 110.4 (CH, Ar), 120.7 (CH, Ar), 121.6 (CH, Ar), 123.0 (CH, Ar), 126.6 (CH, Ar), 127.5 (C, Ar), 129.0 (C, Ar), 143.8 (C, Ar), 146.8 (C, Ar), 147.6 (C, Ar), 176.4 (C═O).

B: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.04 (dd, ^2J 5.0, ^3J 9.0 Hz, 1H, CH_2), 2.33 (dd, ^2J 5.0, ^3J 8.5 Hz, 1H, CH_2), 3.10 (dd, ^3J 8.5, ^3J 9.0 Hz, 1H, CH), 3.21 (s, 3H, NCH_3), 5.93 (s, 2H, OCH_2), 6.73−6.82 (m, 3H, Ar), 6.86−6.91 (m, 1H, Ar), 6.95 (d, ^3J 7.3 Hz, 1H, Ar), 7.08 (dd, ^3J 7.5, ^3J 7.5 Hz, 1H, Ar), 7.29 (dd, ^3J 7.5, ^3J 7.8 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 22.75 (CH_2), 26.5 (NCH_3), 33.9 (C), 38.0 (CH), 101.0 (OCH_2), 107.80 (CH, Ar), 107.83 (CH, Ar), 109.7 (CH, Ar), 118.0 (CH, Ar), 121.9 (CH, Ar), 122.6 (CH, Ar), 126.8 (CH, Ar), 128.2 (C, Ar), 130.8 (C, Ar), 143.4 (C, Ar), 146.7 (C, Ar), 147.3 (C, Ar), 173.8 (C═O).

IR (film, cm^{-1}): 3055, 2930, 2885, 1700, 1690, 1615, 1505, 1495, 1475, 1455, 1420, 1380, 1355, 1345, 1295, 1255, 1240, 1195, 1130, 1105, 1090, 1075, 1065, 1040, 980, 940, 905, 890, 885, 855, 810, 755, 745, 730.

HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{18}H_{16}NO_3$, 294.1125, found 294.1121.

*2-(2,3-Dihydrobenzo[b][1,4]-dioxin-6-yl)-1′-methylspiro-[cyclopropane-1,3′-indolin]-2′-one (**2f**).* A suspension of sodium hydride (1.124 g, 28.12 mmol) and trimethylsulfoxonium iodide (5.624 g, 25.56 mmol) in DMF (14 mL) was stirred for 30 min; then solution of **1f** (3.745 g, 12.78 mmol) in DMF (70 mL) was added dropwise. The reaction mixture was stirred for additional 3 h, yielding **2f** (3.582 g, 91%) as yellow oil. Two diastereomers **A**:**B** = 74:26.

A: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 1.93 (dd, ^2J 4.5, ^3J 7.9 Hz, 1H, CH_2), 2.14 (dd, ^2J 4.5, ^3J 9.1 Hz, 1H, CH_2), 3.24 (dd, ^3J 7.9, ^3J 9.1 Hz, 1H, CH), 3.32 (s, 3H, NCH_3), 4.20−4.27 (m, 4H, OCH_2), 6.12 (ddd, ^3J 7.5, ^4J 1.2, ^5J 0.5 Hz, 1H, Ar), 6.65 (ddd, ^3J 8.3, ^4J 2.1, ^5J 0.8 Hz, 1H, Ar), 6.72 (dd, ^4J 2.1, ^5J 0.8 Hz, 1H, Ar), 6.73−6.80 (m, 2H, Ar), 6.86−6.89 (m, 1H, Ar), 7.17 (ddd, ^3J 7.7, ^3J 7.7, ^4J 1.2 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 22.6 (CH_2), 26.6 (NCH_3), 33.4 (C), 35.4 (CH), 64.29 (2 × OCH_2), 107.69 (CH, Ar), 117.0 (CH, Ar), 118.7 (CH, Ar), 120.8 (CH, Ar), 121.5 (CH, Ar), 122.8 (CH, Ar), 126.5 (CH, Ar), 127.6 (C, Ar), 128.4 (C, Ar), 142.83 (C, Ar), 143.3 (C, Ar), 143.8 (C, Ar), 176.41 (C═O).

B: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.02 (dd, ^2J 4.9, ^3J 9.1 Hz, 1H, CH_2), 2.32 (dd, ^2J 4.9, ^3J 8.6 Hz, 1H, CH_2), 3.06 (dd, ^3J 8.6, ^3J 9.1 Hz, 1H, CH), 3.20 (s, 3H, NCH_3), 4.20−4.27 (m, 4H, OCH_2), 6.73−6.80 (m, 2H, Ar), 6.83−6.84 (m, 1H, Ar), 6.86−6.89 (m, 1H, Ar), 6.94 (ddd, ^3J 7.4, ^4J 1.2, ^5J 0.5 Hz, 1H, Ar), 7.06 (ddd, ^3J 7.5, ^3J 7.5, ^4J 0.9 Hz, 1H, Ar), 7.27 (ddd, ^3J 7.7, ^3J 7.7, ^4J 1.2 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 22.7 (CH_2), 26.4 (NCH_3), 34.8 (C), 37.7 (CH), 64.33 (2 × OCH_2), 107.72 (CH, Ar), 116.7 (CH, Ar), 118.0 (CH, Ar), 118.2 (CH, Ar), 121.8 (CH, Ar), 122.2 (CH, Ar), 126.7 (CH, Ar), 127.6 (C, Ar), 130.9 (C, Ar), 142.75 (C, Ar), 143.0 (C, Ar), 143.5 (C, Ar), 173.8 (C═O).

IR (film, cm^{-1}): 3055, 2980, 2930, 2875, 1705, 1615, 1585, 1510, 1495, 1470, 1420, 1380, 1345, 1310, 1290, 1255, 1205, 1165, 1125, 1070, 1035, 930, 905, 885, 815, 750, 740, 700.

HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{19}H_{18}NO_3$, 308.1281, found 308.1275.

*1′-Methyl-2-(3,4,5-trimethoxyphenyl)spiro[cyclopropane-1,3′-indolin]-2′-one (**2g**).* A suspension of sodium hydride (626 mg, 15.65 mmol) and trimethylsulfoxonium iodide (3.130 g, 14.23 mmol) in DMF (8.0 mL) was stirred for 30 min; then solution of alkene **1g** (2.312 g, 7.11 mmol) in DMF (40 mL) was added dropwise. The reaction mixture was stirred for additional 3 h, yielding **2g** (2.190 g, 91%) as yellow oil. Two diastereomers **A**:**B** = 72:28.

A: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 1.94 (dd, ^2J 4.5, ^3J 7.9 Hz, 1H, CH_2), 2.16 (dd, ^2J 4.5, ^3J 9.2 Hz, 1H, CH_2), 3.28 (ddd, ^3J 7.9, ^3J 9.2, ^4J 0.7 Hz, 1H, CH), 3.33 (s, 3H, NCH_3), 3.75 (s, 6H, OCH_3), 3.83 (s, 3H, OCH_3), 6.11 (ddd, ^3J 7.5, ^4J 1.2, ^5J 0.5 Hz, 1H, Ar), 6.39 (d, ^4J 0.7 Hz, 2H, Ar), 6.74 (ddd, ^3J 7.6, ^3J 7.6, ^4J 1.0 Hz, 1H, Ar), 6.87 (d, ^3J 7.6 Hz, 1H, Ar), 7.17 (ddd, ^3J 7.7, ^3J 7.7, ^4J 1.2 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 22.9 (CH_2), 26.6 (NCH_3), 33.3 (C), 35.9 (CH), 56.2 (2 × OCH_3), 60.9 (OCH_3), 107.3 (2 × CH, Ar), 107.7 (CH, Ar), 120.9 (CH, Ar), 121.6 (CH, Ar), 126.6 (CH, Ar), 127.4 (C,

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Ar), 130.77 (C, Ar), 137.5 (C, Ar), 143.7 (C, Ar), 153.1 (2 × C, Ar), 176.4 (C═O).

B: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.06 (dd, ^2J 4.9, ^3J 9.1 Hz, 1H, CH_2), 2.35 (dd, ^2J 4.9, ^3J 8.7 Hz, 1H, CH_2), 3.08 (dd, ^3J 8.7, ^3J 9.1 Hz, 1H, CH), 3.21 (s, 3H, NCH_3), 3.83 (s, 3H, OCH_3), 3.84 (s, 6H, OCH_3), 6.57 (s, 2H, Ar), 6.90 (d, ^3J 7.8 Hz, 1H, Ar), 6.97 (ddd, ^3J 7.4, ^4J 1.1, ^5J 0.5 Hz, 1H, Ar), 7.08 (ddd, ^3J 7.6, ^3J 7.6, ^4J 1.0 Hz, 1H, Ar), 7.29 (ddd, ^3J 7.7, ^3J 7.7, ^4J 1.2 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 23.1 (CH_2), 26.5 (NCH_3), 34.2 (C), 38.6 (CH), 56.1 (2 × OCH_3), 60.8 (OCH_3), 106.5 (2 × CH, Ar), 107.8 (CH, Ar), 118.0 (CH, Ar), 121.9 (CH, Ar), 126.9 (CH, Ar), 130.0 (C, Ar), 130.82 (C, Ar), 137.5 (C, Ar), 143.5 (C, Ar), 152.7 (2 × C, Ar), 173.8 (C═O).

IR (film, cm^{-1}): 3055, 2995, 2935, 2835, 1705, 1615, 1590, 1510, 1495, 1465, 1415, 1385, 1355, 1325, 1290, 1240, 1185, 1160, 1130, 1075, 1055, 1040, 1005, 990, 980, 925, 905, 845, 825, 800, 775, 750, 700.

HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{20}H_{22}NO_4$, 340.1543, found 340.1541.

1′-Methyl-2-(thiophen-2-yl)spiro[cyclopropane-1,3′-indolin]-2′-one (**2h**).[14a] A suspension of sodium hydride (439 mg, 10.97 mmol) and trimethylsulfoxonium iodide (2.195 g, 9.98 mmol) in DMF (5.5 mL) was stirred for 30 min; then solution of **1h** (1.202 g, 4.99 mmol) in DMF (28 mL) was added dropwise. The reaction mixture was stirred for additional 4 h, yielding **2h** (1.105 g, 87%) as yellow oil. Two diastereomers **A**:**B** = 75:25.

A: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.05 (dd, ^2J 4.6, ^3J 7.6 Hz, 1H, CH_2), 2.28 (dd, ^2J 4.6, ^3J 9.2 Hz, 1H, CH_2), 3.30 (dd, ^3J 7.6, ^3J 9.2 Hz, 1H, CH), 3.34 (s, 3H, NCH_3), 6.26 (d, ^3J 7.6 Hz, 1H, Ar), 6.79 (ddd, ^3J 7.6, ^3J 7.6, ^4J 1.1 Hz, 1H, Ar), 6.88−6.94 (m, 2H, Ar), 6.97−7.00 (m, 1H, Ar), 7.18−7.24 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 23.7 (CH_2), 26.3 (NCH_3), 30.0 (CH), 34.1 (C), 107.9 (CH, Ar), 120.4 (CH, Ar), 121.7 (CH, Ar), 125.3 (CH, Ar), 126.8 (CH, Ar), 126.96 (CH, C, Ar), 127.5 (CH, Ar), 139.1 (C, Ar), 143.9 (C, Ar), 175.8 (C═O).

B: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.17 (dd, ^2J 5.0, ^3J 9.1 Hz, 1H, CH_2), 2.38 (dd, ^2J 5.0, ^3J 8.2 Hz, 1H, CH_2), 3.20−3.24 (m, 4H, CH, NCH_3), 6.88−6.94 (m, 1H, Ar), 6.95 (d, ^3J 7.4 Hz, 1H, Ar), 6.97−7.00 (m, 1H, Ar), 7.04−7.06 (m, 1H, Ar), 7.09 (ddd, ^3J 7.6, ^3J 7.6, ^4J 1.1 Hz, 1H, Ar), 7.18−7.24 (m, 1H, Ar), 7.31 (ddd, ^3J 7.6, ^3J 7.6, ^4J 1.1 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 24.0 (CH_2), 26.5 (NCH_3), 32.4 (CH), 34.3 (C), 107.9 (CH, Ar), 118.1 (CH, Ar), 121.8 (CH, Ar), 124.6 (CH, Ar), 126.7 (CH, Ar), 127.03 (CH, Ar), 127.1 (CH, Ar), 130.1 (C, Ar), 137.9 (C, Ar), 143.5 (C, Ar), 173.2 (C═O).

1′-Methyl-2-(pyridin-3-yl)spiro[cyclopropane-1,3′-indolin]-2′-one (**2i**). A suspension of sodium hydride (396 mg, 9.89 mmol) and trimethylsulfoxonium iodide (1.978 g, 8.99 mmol) in DMF (5.0 mL) was stirred for 30 min; then solution of alkene **1i** (1.061 g, 4.50 mmol) in DMF (25 mL) was added dropwise. The reaction mixture was stirred for additional 2 h, yielding **2i** (759 mg, 68%) as yellow oil. Two diastereomers **A**:**B** = 54:46.

A: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 1.98 (dd, ^2J 4.8, ^3J 7.9 Hz, 1H, CH_2), 2.23 (dd, ^2J 4.8, ^3J 9.1 Hz, 1H, CH_2), 3.24 (dd, ^3J 7.9, ^3J 9.1 Hz, 1H, CH), 3.32 (s, 3H, NCH_3), 6.71 (ddd, ^3J 7.6, ^3J 7.6, ^4J 0.9 Hz, 1H, Ar), 6.86−6.91 (m, 1H, Ar), 7.17 (ddd, ^3J 7.6, ^3J 7.7, ^4J 1.2 Hz, 1H, Ar), 7.21 (ddd, ^3J 4.8, ^3J 7.8, ^5J 0.5 Hz, 1H, Ar), 7.27−7.32 (m, 1H, Ar), 7.44−7.47 (m, 1H, Ar), 8.46 (d, ^4J 2.1 Hz, 1H, Ar), 8.49 (dd, ^3J 4.8, ^4J 1.2 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 21.5 (CH_2), 26.7 (NCH_3), 32.7 (CH), 32.9 (C), 108.1 (CH, Ar), 120.7 (CH, Ar), 121.7 (CH, Ar), 123.1 (CH, Ar), 126.6 (C, Ar), 127.0 (CH, Ar), 131.2 (C, Ar), 137.8 (CH, Ar), 144.0 (C, Ar), 148.6 (CH, Ar), 151.0 (CH, Ar), 175.9 (C═O).

B: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.13 (dd, ^2J 5.2, ^3J 9.1 Hz, 1H, CH_2), 2.37 (dd, ^2J 5.2, ^3J 8.5 Hz, 1H, CH_2), 3.09 (dd, ^3J 8.5, ^3J 9.1 Hz, 1H, CH), 3.17 (s, 3H, NCH_3), 5.93 (br. d, ^3J 7.5 Hz, 1H, Ar), 6.86−6.91 (m, 1H, Ar), 6.98 (br. d, ^3J 7.4 Hz, 1H, Ar), 7.09 (ddd, ^3J 7.5, ^3J 7.7, ^4J 1.0 Hz, 1H, Ar), 7.27−7.32 (m, 1H, Ar), 7.74−7.77 (m, 1H, Ar), 8.43 (dd, ^3J 4.8, ^4J 1.5 Hz, 1H, Ar), 8.51 (d, ^4J 2.1 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 21.8 (CH_2), 26.4 (NCH_3), 33.7 (C), 34.7 (CH), 108.1 (CH, Ar), 118.2 (CH, Ar), 122.1 (CH, Ar), 122.9 (CH, Ar), 127.3 (CH, Ar), 129.9 (C, Ar), 130.7 (C, Ar), 137.0 (CH, Ar), 143.6 (C, Ar), 147.4 (CH, Ar), 150.1 (CH, Ar), 173.3 (C═O).

IR (film, cm^{-1}): 3385, 3085, 3055, 3025, 3005, 2930, 2855, 2375, 2345, 1935, 1915, 1705, 1610, 1575, 1495, 1470, 1420, 1380, 1345, 1315, 1250, 1125, 1105, 1070, 1025, 1015, 970, 895, 840, 750, 715, 710, 695.

HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{16}H_{15}N_2O$, 251.1179, found 251.1177.

General Procedure for the Synthesis of Azides 3. A mixture of sodium azide (2.0 equiv), triethylamine hydrochloride (2.0 equiv), and cyclopropane **2** (1.0 equiv) in DMSO (0.5 M) were stirred at 100 °C (microwave reactor) for specified time. Then, the reaction mixture was diluted with water and extracted with ethyl acetate. The organic layer was washed with water, dried with sodium sulfate, and concentrated under reduced pressure. Azide **3** was purified by column chromatography on silica gel.

3-(2-Azido-2-phenylethyl)-1-methylindoline-2-one (**3a**). Cyclopropane **2a** (495 mg, 2.00 mmol), sodium azide (261 mg, 4.01 mmol), and triethylamine hydrochloride (551 mg, 4.01 mmol) in DMSO (4.0 mL) were stirred at 100 °C (microwave reactor) for 4 h, yielding **3a** (407 mg, 70%) as yellowish oil. Two diastereomers **A**:**B** = 53:47. R_f = 0.74 (ethyl acetate/petroleum ether; 1:1).

^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.16 (ddd, ^2J 14.3, ^3J 4.3, ^3J 8.6 Hz, 1H, CH_2, **A**), 2.24 (ddd, ^2J 14.0, ^3J 6.3, ^3J 8.4 Hz, 1H, CH_2, **B**), 2.41 (ddd, ^2J 14.3, ^3J 4.7, ^3J 10.6 Hz, 1H, CH_2, **A**), 2.46 (ddd, ^2J 14.0, ^3J 7.6, ^3J 7.6 Hz, 1H, CH_2, **B**), 3.08 (s, 3H, NCH_3, **B**), 3.23 (s, 3H, NCH_3, **A**), 3.41 (dd, ^3J 6.3, ^3J 7.6 Hz, 1H, C(3)H, **B**), 3.65 (dd, ^3J 4.7, ^3J 8.6 Hz, 1H, C(3)H, **A**), 4.95 (dd, ^3J 7.6, ^3J 8.4 Hz, 1H, CHN_3, **B**), 5.02 (dd, ^3J 4.3, ^3J 10.6 Hz, 1H, CHN_3, **A**), 6.79 (d, ^3J 7.8 Hz, 1H, Ar, **B**), 6.83 (d, ^3J 7.8 Hz, 1H, Ar, **A**), 7.04−7.09 (m, 2H, Ar), 7.24 (dd, ^3J 7.2, ^4J 0.5 Hz, 2H, Ar), 7.27−7.39 (m, 12H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 26.1 (NCH_3), 26.2 (NCH_3), 36.9 (CH_2), 37.6 (CH_2), 42.3 (CH), 42.5 (CH), 63.0 (2 × CHN_3), 108.2 (2 × CH, Ar), 122.41 (CH, Ar), 122.43 (CH, Ar), 123.7 (CH, Ar), 123.9 (CH, Ar), 126.9 (2 × CH, Ar), 127.5 (2 × CH, Ar), 128.1 (C, Ar), 128.19 (C, Ar), 128.20 (CH, Ar), 128.24 (CH, Ar), 128.5 (CH, Ar), 128.7 (CH, Ar), 128.8 (2 × CH, Ar), 128.9 (2 × CH, Ar), 138.3 (C, Ar), 139.3 (C, Ar), 144.2 (C, Ar), 144.3 (C, Ar), 176.9 (C═O), 177.4 (C═O).

IR (film, cm^{-1}): 2950, 2120, 1710, 1620, 1500, 1475, 1385, 1355, 1315, 1260, 1140, 1100, 1030, 985, 940, 765, 715.

HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{17}H_{17}N_4O$, 293.1397, found 293.1399.

3-(2-Azido-2-(4-bromophenyl)ethyl)-1-methylindoline-2-one (**3b**). Cyclopropane **2b** (948 mg, 2.90 mmol), sodium azide (377 mg, 5.80 mmol), and triethylamine hydrochloride (798 mg, 5.80 mmol) in DMSO (6.0 mL) were stirred at 100 °C (microwave reactor) for 4 h, yielding **3b** (459 mg, 43%) as yellowish oil. Two diastereomers **A**:**B** = 52:48. R_f = 0.67 (ethyl acetate/petroleum ether; 1:1).

A: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.10 (ddd, ^2J 14.3, ^3J 4.2, ^3J 8.7 Hz, 1H, CH_2), 2.35 (ddd, ^2J 14.3, ^3J 4.5, ^3J 10.7 Hz, 1H, CH_2), 3.21 (s, 3H, NCH_3), 3.62 (dd, ^3J 4.5, ^3J 8.7 Hz, 1H, C(3)H), 5.03 (dd, ^3J 4.2, ^3J 10.7 Hz, 1H, CHN_3), 6.82 (d, ^3J 7.8 Hz, 1H, Ar), 7.02−7.08 (m, 1H, Ar), 7.17−7.23 (m, 4H, Ar), 7.44−7.49 (m, 2H, Ar);^{13}C NMR ($CDCl_3$, 150 MHz): δ = 26.2 (NCH_3), 37.5 (CH_2), 42.3 (CH), 62.34 (CHN_3), 108.2 (CH, Ar), 122.4 (C, Ar), 122.5 (CH, Ar), 123.6 (CH, Ar), 128.0 (C, Ar), 128.3 (CH, Ar), 128.6 (2 × CH, Ar), 132.0 (2 × CH, Ar), 138.5 (C, Ar), 144.21 (C, Ar), 177.2 (C═O).

B: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.22 (ddd, ^2J 14.1, ^3J 6.0, ^3J 8.6 Hz, 1H, CH_2), 2.40 (ddd, ^2J 14.1, ^3J 7.3, ^3J 8.0 Hz, 1H, CH_2), 3.06 (s, 3H, NCH_3), 3.34 (dd, ^3J 6.0, ^3J 8.0 Hz, 1H, C(3)H), 4.91 (dd, ^3J 7.3, ^3J 8.6 Hz, 1H, CHN_3), 6.78 (d, ^3J 7.8 Hz, 1H, Ar), 7.02−7.08 (m, 1H, Ar), 7.17−7.23 (m, 2H, Ar), 7.25−7.30 (m, 2H, Ar), 7.44−7.49 (m, 2H, Ar);^{13}C NMR ($CDCl_3$, 150 MHz): δ = 26.1 (NCH_3), 36.6 (CH_2), 42.1 (CH), 62.27 (CHN_3), 108.2 (CH, Ar), 122.5 (CH, Ar), 122.6 (C, Ar), 123.8 (CH, Ar), 127.7 (C, Ar), 128.4 (CH, Ar), 129.2 (2 × CH, Ar), 131.9 (2 × CH, Ar), 137.3 (C, Ar), 144.16 (C, Ar), 176.7 (C═O).

IR (film, cm^{-1}): 3055, 2930, 2885, 2100, 1710, 1615, 1495, 1470, 1420, 1410, 1375, 1350, 1310, 1295, 1265, 1245, 1125, 1090, 1075, 1010, 965, 905, 825, 800, 750, 730.

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HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{16}BrN_4O$, 371.0502, found 371.0502.

*3-(2-Azido-2-(p-tolyl)ethyl)-1-methylindoline-2-one (**3c**).* Cyclopropane **2c** (501 mg, 1.90 mmol), sodium azide (247 mg, 3.80 mmol), and triethylamine hydrochloride (524 mg, 3.80 mmol) in DMSO (4.0 mL) were stirred at 100 °C (microwave reactor) for 3 h, yielding **3c** (297 mg, 51%) as yellowish oil. Two diastereomers **A**:**B** = 53:47. R_f = 0.72 (ethyl acetate/petroleum ether; 1:1).

^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.17 (ddd, ^2J 14.2, ^3J 4.5, ^3J 8.5 Hz, 1H, CH_2, **A**), 2.24 (ddd, ^2J 14.2, ^3J 6.4, ^3J 8.2 Hz, 1H, CH_2, **B**), 2.36 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 2.41 (ddd, ^2J 14.2, ^3J 4.9, ^3J 10.5 Hz, 1H, CH_2, **A**), 2.46 (ddd, ^2J 14.2, ^3J 7.6, ^3J 7.6 Hz, 1H, CH_2, **B**), 3.09 (s, 3H, NCH_3), 3.24 (s, 3H, NCH_3), 3.42 (dd, ^3J 6.4, ^3J 7.6 Hz, 1H, C(3)H, **B**), 3.63 (dd, ^3J 4.9, ^3J 8.5 Hz, 1H, C(3)H, (**A**), 4.94 (dd, ^3J 7.6, ^3J 8.2 Hz, 1H, CHN_3, **B**), 5.01 (dd, ^3J 4.5, ^3J 10.5 Hz, 1H, CHN_3, **A**), 6.80 (d, ^3J 7.7 Hz, 1H, Ar, **B**), 6.84 (d, ^3J 7.8 Hz, 1H, Ar, **A**), 7.05−7.11 (m, 2H, Ar), 7.17−7.22 (m, 4H, Ar), 7.23−7.28 (m, 6H, Ar), 7.29−7.33 (m, 2H, Ar);^{13}C NMR ($CDCl_3$, 150 MHz): δ = 21.11 (CH_3), 21.14 (CH_3), 26.0 (NCH_3), 26.2 (NCH_3), 36.9 (CH_2), 37.5 (CH_2), 42.4 (CH), 42.5 (CH), 62.9 (2 × CHN_3), 108.1 (2 × CH, Ar), 122.4 (2 × CH, Ar), 123.7 (CH, Ar), 123.9 (CH, Ar), 126.9 (2 × CH, Ar), 127.4 (2 × CH, Ar), 128.15 (CH, Ar), 128.20 (CH, C, Ar), 128.3 (C, Ar), 129.5 (2 × CH, Ar), 129.6 (2 × CH, Ar), 135.3 (C, Ar), 136.2 (C, Ar), 138.2 (C, Ar), 138.4 (C, Ar), 144.2 (C, Ar), 144.3 (C, Ar), 177.0 (C═O), 177.4 (C═O).

IR (film, cm^{-1}): 3055, 3025, 2925, 2885, 2100, 1710, 1615, 1515, 1495, 1470, 1420, 1375, 1350, 1310, 1245, 1205, 1185, 1125, 1090, 1020, 815, 750, 730, 700.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{19}N_4O$, 307.1553, found 307.1553.

*3-(2-Azido-2-(4-methoxyphenyl)ethyl)-1-methylindoline-2-one (**3d**).* Cyclopropane **2d** (1.767 g, 6.33 mmol), sodium azide (823 mg, 12.67 mmol), and triethylamine hydrochloride (1.742 g, 12.67 mmol) in DMSO (13 mL) were stirred at 100 °C (microwave reactor) for 3 h, yielding **3d** (1.157 g, 57%) as yellowish oil. Two diastereomers **A**:**B** = 52:48. R_f = 0.71 (ethyl acetate/petroleum ether; 1:1).

^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.15 (ddd, ^2J 14.3, ^3J 4.6, ^3J 8.4 Hz, 1H, CH_2, **A**), 2.22 (ddd, ^2J 13.9, ^3J 6.2, ^3J 8.5 Hz, 1H, CH_2, **B**), 2.40 (ddd, ^2J 14.3, ^3J 5.0, ^3J 10.5 Hz, 1H, CH_2, **A**), 2.44 (ddd, ^2J 13.9, ^3J 7.3, ^3J 7.6 Hz, 1H, CH_2, **B**), 3.07 (s, 3H, NCH_3), 3.23 (s, 3H, NCH_3), 3.41 (dd, ^3J 6.2, ^3J 7.3 Hz, 1H, C(3)H, **B**), 3.62 (dd, ^3J 5.0, ^3J 8.4 Hz, 1H, C(3)H, **A**), 3.80 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 4.88 (dd, ^3J 7.6, ^3J 8.5 Hz, 1H, CHN_3, **B**), 4.96 (dd, ^3J 4.6, ^3J 10.5 Hz, 1H, CHN_3, **A**), 6.79 (d, ^3J 7.8 Hz, 1H, Ar, **B**), 6.83 (d, ^3J 7.8 Hz, 1H, Ar, **A**), 6.87−6.92 (m, 4H, Ar), 7.05−7.10 (m, 2H, Ar), 7.22−7.32 (m, 8H, Ar);^{13}C NMR ($CDCl_3$, 150 MHz): δ = 26.0 (NCH_3), 26.2 (NCH_3), 36.7 (CH_2), 37.4 (CH_2), 42.3 (CH), 42.5 (CH), 55.3 (2 × OCH_3), 62.3 (2 × CHN_3), 108.1 (2 × CH, Ar), 114.1 (2 × CH, Ar), 114.2 (2 × CH, Ar), 122.4 (2 × CH, Ar), 123.9 (2 × CH, Ar), 128.1 (2 × CH, Ar), 128.2 (2 × CH, Ar), 128.8 (2 × CH, Ar), 130.1 (2 × C, Ar), 131.2 (2 × C, Ar), 144.2 (C, Ar), 144.3 (C, Ar), 159.7 (C, Ar), 159.8 (C, Ar), 177.0 (C═O), 177.4 (C═O).

IR (film, cm^{-1}): 2955, 2120, 1715, 1620, 1520, 1500, 1480, 1425, 1385, 1355, 1315, 1250, 1190, 1140, 1100, 1045, 980, 935, 905, 845, 765.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{18}H_{18}N_4O_2Na^+$, 345.1322, found 345.1331.

*3-(2-Azido-2-(benzo[d][1,3]dioxol-5-yl)ethyl)-1-methylindoline-2-one (**3e**).* Cyclopropane **2e** (745 mg, 2.54 mmol), sodium azide (331 mg, 5.09 mmol), and triethylamine hydrochloride (699 mg, 5.09 mmol) in DMSO (5.0 mL) were stirred at 100 °C (microwave reactor) for 4.5 h, yielding **3e** (389 mg, 46%) as yellowish oil. Two diastereomers **A**:**B** = 51:49. R_f = 0.67 (ethyl acetate/petroleum ether; 1:1).

^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.12 (ddd, ^2J 14.2, ^3J 4.7, ^3J 8.4 Hz, 1H, CH_2, **A**), 2.17 (ddd, ^2J 13.9, ^3J 6.2, ^3J 8.6 Hz, 1H, CH_2, **B**), 2.36 (ddd, ^2J 14.2, ^3J 4.8, ^3J 10.4 Hz, 1H, CH_2, **A**), 2.38 (ddd, ^2J 13.9, ^3J 7.2, ^3J 8.1 Hz, 1H, CH_2, **B**), 3.12 (s, 3H, NCH_3), 3.23 (s, 3H, NCH_3), 3.39 (dd, ^3J 6.2, ^3J 8.1 Hz, 1H, C(3)H, **B**), 3.61 (dd, ^3J 4.8, ^3J 8.4 Hz, 1H, C(3)H, **A**), 4.91 (dd, ^3J 7.2, ^3J 8.6 Hz, 1H, CHN_3, **B**), 4.94 (dd, ^3J 4.7, ^3J 10.4 Hz, 1H, CHN_3, **A**), 5.95−5.99 (m, 4H, OCH_2), 6.76−6.82 (m, 5H, Ar), 6.83 (d, ^3J 7.8 Hz, 1H, Ar), 6.86 (dd, ^3J 8.2, ^4J 1.6 Hz, 2H, Ar), 7.06 (ddd, ^3J 7.5, ^3J 7.5, ^4J 0.8 Hz, 1H, Ar), 7.08 (ddd, ^3J 7.5, ^3J 7.5, ^4J 0.8 Hz, 1H, Ar), 7.24 (d, ^3J 7.8, ^4J 0.5 Hz, 2H, Ar), 7.27−7.32 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 26.1 (NCH_3), 26.2 (NCH_3), 37.0 (CH_2), 37.5 (CH_2), 42.2 (CH), 42.5 (CH), 62.8 (CHN_3), 62.9 (CHN_3), 101.3 (2 × OCH_2), 107.1 (CH, Ar), 107.5 (CH, Ar), 108.15 (2 × CH, Ar), 108.23 (CH, Ar), 108.3 (CH, Ar), 120.7 (CH, Ar), 121.4 (CH, Ar), 122.4 (2 × CH, Ar), 123.7 (CH, Ar), 123.8 (CH, Ar), 128.1 (C, Ar), 128.16 (CH, C, Ar), 128.23 (CH, Ar), 132.1 (C, Ar), 133.0 (C, Ar), 144.16 (C, Ar), 144.23 (C, Ar), 147.7 (C, Ar), 147.8 (C, Ar), 148.1 (C, Ar), 148.2 (C, Ar), 177.0 (C═O), 177.4 (C═O).

IR (film, cm^{-1}): 2985, 2970, 2900, 2100, 1705, 1610, 1490, 1470, 1445, 1375, 1350, 1265, 1245, 1125, 1090, 1040, 935, 910, 865, 815, 735, 705.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{17}N_4O_3$, 337.1295, found 337.1299.

*3-(2-Azido-2-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)ethyl)-1-methylindoline-2-one (**3f**).* Cyclopropane **2f** (1.151 g, 3.75 mmol), sodium azide (487 mg, 7.50 mmol), and triethylamine hydrochloride (1.031 mg, 7.50 mmol) in DMSO (7.5 mL) were stirred at 100 °C (microwave reactor) for 4.5 h, yielding **3f** (646 mg, 49%) as yellowish oil. Two diastereomers **A**:**B** = 54:46. R_f = 0.64 (ethyl acetate/petroleum ether; 1:1).

^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.13 (ddd, ^2J 14.2, ^3J 4.7, ^3J 8.3 Hz, 1H, CH_2, **A**), 2.16 (ddd, ^2J 14.0, ^3J 6.4, ^3J 8.5 Hz, 1H, CH_2, **B**), 2.36 (ddd, ^2J 14.2, ^3J 5.0, ^3J 10.3 Hz, 1H, CH_2, **A**), 2.38 (ddd, ^2J 14.0, ^3J 7.3, ^3J 7.8 Hz, 1H, CH_2, **B**), 3.11 (s, 3H, NCH_3), 3.22 (s, 3H, NCH_3), 3.39 (dd, ^3J 6.4, ^3J 7.8 Hz, 1H, C(3)H, **B**), 3.60 (dd, ^3J 5.0, ^3J 8.3 Hz, 1H, C(3)H, **A**), 4.22−4.26 (m, 8H, OCH_2), 4.87 (dd, ^3J 7.3, ^3J 8.5 Hz, 1H, CHN_3, **B**), 4.89 (dd, ^3J 4.7, ^3J 10.3 Hz, 1H, CHN_3, **A**), 6.78−6.88 (m, 8H, Ar), 7.03−7.08 (m, 2H, Ar), 7.23 (dd, ^3J 7.4, ^4J 1.2 Hz, 2H, Ar), 7.26−7.31 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 26.1 (NCH_3), 26.2 (NCH_3), 36.9 (CH_2), 37.3 (CH_2), 42.3 (CH), 42.5 (CH), 62.5 (2 × CHN_3), 64.3 (4 × OCH_2), 108.1 (2 × CH, Ar), 115.9 (CH, Ar), 116.3 (CH, Ar), 117.5 (CH, Ar), 117.6 (CH, Ar), 120.0 (CH, Ar), 120.6 (CH, Ar), 122.4 (2 × CH, Ar), 123.7 (CH, Ar), 123.8 (CH, Ar), 128.1 (CH, Ar), 128.2 (CH, 2 × C, Ar), 131.5 (C, Ar), 132.3 (C, Ar), 143.66 (2 × C, Ar), 143.69 (C, Ar), 143.8 (C, Ar), 144.16 (C, Ar), 144.24 (C, Ar), 177.0 (C═O), 177.3 (C═O).

IR (film, cm^{-1}): 2930, 2100, 1700, 1610, 1590, 1510, 1495, 1470, 1435, 1420, 1375, 1350, 1290, 1265, 1205, 1155, 1125, 1090, 1070, 1050, 1020, 925, 890, 815, 730, 705.

HRMS (ESI-TOF) m/z: $[M - N_3]^+$ calcd for $C_{19}H_{18}NO_3$, 308.1279, found 308.1279.

*3-(2-Azido-2-(3,4,5-trimethoxyphenyl)ethyl)-1-methylindoline-2-one (**3g**).* Cyclopropane **2g** (1.180 g, 3.48 mmol), sodium azide (453 mg, 6.96 mmol), and triethylamine hydrochloride (957 mg, 6.96 mmol) in DMSO (7.0 mL) were stirred at 100 °C (microwave reactor) for 5 h, yielding **3g** (598 mg, 45%) as yellowish oil. Two diastereomers **A**:**B** = 56:44. R_f = 0.50 (ethyl acetate/petroleum ether; 1:1).

^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.09 (ddd, ^2J 14.3, ^3J 4.3, ^3J 8.6 Hz, 1H, CH_2, **A**), 2.21 (ddd, ^2J 14.0, ^3J 5.7, ^3J 8.9 Hz, 1H, CH_2, **B**), 2.36 (ddd, ^2J 14.3, ^3J 4.4, ^3J 10.6 Hz, 1H, CH_2, **A**), 2.41 (ddd, ^2J 14.0, ^3J 7.2, ^3J 7.9 Hz, 1H, CH_2, **B**), 2.97 (s, 3H, NCH_3), 3.15 (s, 3H, NCH_3), 3.34 (dd, ^3J 5.7, ^3J 7.9 Hz, 1H, C(3)H, **B**), 3.56 (dd, ^3J 4.4, ^3J 8.6 Hz, 1H, C(3)H, **A**), 3.76 (s, 3H, OCH_3), 3.77 (s, 9H, OCH_3), 3.79 (s, 6H, OCH_3), 4.74 (dd, ^3J 7.2, ^3J 8.9 Hz, 1H, CHN_3, **B**), 4.91 (dd, ^3J 4.3, ^3J 10.6 Hz, 1H, CHN_3, **A**), 6.42 (s, 2H, Ar), 6.50 (s, 2H, Ar), 6.69 (d, ^3J 7.8 Hz, 1H, Ar), 6.76 (d, ^3J 7.8 Hz, 1H, Ar), 6.96−7.02 (m, 2H, Ar), 7.16−7.23 (m, 4H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 25.9 (NCH_3), 26.1 (NCH_3), 36.2 (CH_2), 37.5 (CH_2), 42.2 (CH), 42.4 (CH), 56.05 (2 × OCH_3), 56.12 (2 × OCH_3), 60.65 (OCH_3), 60.68 (OCH_3), 63.2 (CHN_3), 63.3 (CHN_3), 103.8 (2 × CH, Ar), 104.5 (2 × CH, Ar), 108.0 (CH, Ar), 108.1 (CH, Ar), 122.3 (CH, Ar), 122.4 (CH, Ar), 123.6 (CH, Ar), 123.8 (CH, Ar), 127.8 (C, Ar), 128.0 (C, Ar), 128.2 (2 × CH, Ar), 133.4 (C, Ar), 135.0 (C, Ar), 137.9 (2 × C,

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Ar), 144.1 (C, Ar), 144.3 (C, Ar), 153.2 (2 × C, Ar), 153.5 (2 × C, Ar), 176.8 (C═O), 177.3 (C═O).

IR (film, cm^{-1}): 2920, 2095, 1700, 1615, 1510, 1495, 1460, 1420, 1375, 1345, 1325, 1265, 1235, 1185, 1150, 1125, 1090, 1005, 830, 755, 730, 700.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{23}N_4O_4$, 383.1714, found 383.1713.

*3-(2-Azido-2-(thiophen-2-yl)ethyl)-1-methylindoline-2-one (**3h**).* Cyclopropane **2h** (976 mg, 3.82 mmol), sodium azide (498 mg, 7.65 mmol), and triethylamine hydrochloride (1.053 g, 7.65 mmol) in DMSO (7.5 mL) were stirred at 100 °C (microwave reactor) for 4 h, yielding **3h** (616 mg, 55%) as yellowish oil. Two diastereomers **A**:**B** = 56:44. R_f = 0.51 (ethyl acetate/petroleum ether; 1:1).

^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.25−2.33 (m, 2H, CH_2), 2.45−2.53 (m, 2H, CH_2), 3.16 (s, 3H, NCH_3), 3.23 (s, 3H, NCH_3), 3.46 (dd, ^3J 7.2, ^3J 7.5 Hz, 1H, C(3)H), 3.68 (dd, ^3J 4.7, ^3J 8.6 Hz, 1H, C(3)H), 5.29−5.35 (m, 2H, CHN_3), 6.83 (d, ^3J 7.7 Hz, 1H, Ar), 6.86 (d, ^3J 7.7 Hz, 1H, Ar), 6.99−7.04 (m, 2H, Ar), 7.06−7.11 (m, 3H, Ar), 7.12−7.14 (m, 1H, Ar), 7.24−7.28 (m, 2H, Ar), 7.29−7.33 (m, 3H, Ar), 7.34 (d, ^3J 4.8 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 26.15 (NCH_3), 26.23 (NCH_3), 37.6 (CH_2), 37.7 (CH_2), 42.25 (CH), 42.32 (CH), 58.1 (CHN_3), 58.3 (CHN_3), 108.22 (CH, Ar), 108.23 (CH, Ar), 122.52 (CH, Ar), 122.53 (CH, Ar), 123.75 (CH, Ar), 123.83 (CH, Ar), 125.7 (CH, Ar), 125.8 (CH, Ar), 126.1 (CH, Ar), 126.88 (2 × CH, Ar), 126.89 (CH, Ar), 127.9 (C, Ar), 128.0 (C, Ar), 128.3 (2 × CH, Ar), 141.2 (C, Ar), 142.1 (C, Ar), 144.2 (C, Ar), 144.3 (C, Ar), 176.9 (C═O), 177.2 (C═O).

IR (film, cm^{-1}): 3055, 2925, 2855, 2095, 1700, 1610, 1495, 1470, 1435, 1420, 1375, 1345, 1310, 1265, 1240, 1215, 1155, 1125, 1090, 1040, 1020, 975, 945, 925, 895, 850, 830, 750, 730, 700.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{15}N_4OS$, 299.0961, found 299.0957.

*3-(2-Azido-2-(pyridine-3-yl)ethyl)-1-methylindoline-2-one (**3i**).* Cyclopropane **2i** (839 mg, 3.36 mmol), sodium azide (436 mg, 6.71 mmol), and triethylamine hydrochloride (923 mg, 6.71 mmol) in DMSO (7.0 mL) were stirred at 100 °C (microwave reactor) for 11 h, yielding **3i** (26 mg, 3%) as yellowish oil. Two diastereomers **A**:**B** = 52:48. R_f = 0.57 (ethyl acetate/petroleum ether; 1:1).

^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.10 (ddd, ^2J 14.2, ^3J 4.1, ^3J 9.1 Hz, 1H, CH_2, **A**), 2.31 (ddd, ^2J 14.2, ^3J 5.8, ^3J 8.7 Hz, 1H, CH_2, **B**), 2.43 (ddd, ^2J 14.2, ^3J 4.4, ^3J 10.8 Hz, 1H, CH_2, **A**), 2.49 (ddd, ^2J 14.2, ^3J 7.2, ^3J 7.8 Hz, 1H, CH_2, **B**), 3.04 (s, 3H, NCH_3), 3.23 (s, 3H, NCH_3), 3.39 (dd, ^3J 5.8, ^3J 7.8 Hz, 1H, C(3)H, **B**), 3.69 (dd, ^3J 4.4, ^3J 9.1 Hz, 1H, C(3)H, **A**), 4.92 (dd, ^3J 7.2, ^3J 8.7 Hz, 1H, CHN_3, **B**), 5.12 (dd, ^3J 4.1, ^3J 10.8 Hz, 1H, CHN_3, **A**), 6.81 (d, ^3J 7.8 Hz, 1H, Ar), 6.84 (d, ^3J 7.8 Hz, 1H, Ar), 7.06 (dd, ^3J 7.5, ^3J 7.5 Hz, 1H, Ar), 7.09 (dd, ^3J 7.6, ^3J 7.6 Hz, 1H, Ar), 7.21−7.36 (m, 6H, Ar), 7.70 (ddd, ^3J 7.9, ^4J 1.7, ^4J 1.7 Hz, 1H, Ar), 7.77 (ddd, ^3J 7.9, ^4J 1.8, ^4J 1.8 Hz, 1H, Ar), 8.40 (d, ^4J 1.6 Hz, 1H, Ar), 8.55−8.60 (m, 3H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 26.1 (NCH_3), 26.2 (NCH_3), 36.4 (CH_2), 37.5 (CH_2), 42.1 (CH), 42.2 (CH), 60.4 (CHN_3), 60.5 (CHN_3), 108.3 (CH, Ar), 108.4 (CH, Ar), 122.57 (CH, Ar), 122.61 (CH, Ar), 123.6 (CH, Ar), 123.8 (3 × CH, Ar), 127.4 (C, Ar), 127.7 (C, Ar), 128.4 (CH, Ar), 128.5 (CH, Ar), 134.2 (C, Ar), 134.5 (CH, Ar), 135.28 (CH, Ar), 135.33 (C, Ar), 144.1 (C, Ar), 144.2 (C, Ar), 148.3 (CH, Ar), 148.7 (CH, Ar), 149.7 (CH, Ar), 149.9 (CH, Ar), 176.5 (C═O), 177.1 (C═O).

IR (film, cm^{-1}): 3725, 3675, 3395, 3055, 2960, 2925, 2900, 2475, 2100, 1905, 1780, 1705, 1615, 1575, 1555, 1520, 1495, 1470, 1425, 1375, 1350, 1310, 1265, 1240, 1155, 1125, 1090, 1025, 980, 910, 810, 750, 735, 715.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{16}N_5O$, 294.1349, found 294.1348.

General Procedure for the Synthesis of Spiro[Pyrrolidine-3,3′-Oxindoles] 4. A mixture of azide **3** (1.0 equiv), aromatic aldehyde (1.5 equiv) and triphenylphosphane (1.05 equiv) in CH_2Cl_2 (1 m) was stirred under conditions specified. then the reaction mixture was concentrated under reduced pressure. product **4** was purified by column chromatography on silica gel.

*(2′Rs,3Sr,5′Rs)-1-Methyl-2′,5′-diphenylspiro[indoline-3,3′-pyrrolidin]-2-one (**4a**).* Azide **3a** (82 mg, 0.26 mmol), benzaldehyde (40 μL, 0.39 mmol), and triphenylphosphane (72 mg, 0.28 mmol) in CH_2Cl_2 (270 μL) were stirred at 39 °C (microwave reactor) for 12 h, yielding **4a** (63 mg, 68%) as yellow oil. Two diastereomers **A**:**B** = 90:10. R_f = 0.22 (ethyl acetate/petroleum ether; 1:4).

A: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.66 (dd, ^2J 13.7, ^3J 8.5 Hz, 1H, CH_2), 2.75 (dd, ^2J 13.7, ^3J 8.5 Hz, 1H, CH_2), 2.78 (s, 3H, NCH_3), 3.17 (br. s, 1H, NH), 4.58 (s, 1H, CH), 4.70 (dd, ^3J 8.5, ^3J 8.5 Hz, 1H, CH), 6.69 (d, ^3J 7.7 Hz, 1H, Ar), 6.90 (d, ^3J 7.4 Hz, 2H, Ar), 7.10−7.18 (m, 3H, Ar), 7.20 (dd, ^3J 7.5, ^3J 7.5 Hz, 1H, Ar), 7.31 (dd, ^3J 7.6, ^3J 7.6 Hz, 1H, Ar), 7.35 (t, ^3J 7.4 Hz, 1H, Ar), 7.45 (dd, ^3J 7.6, ^3J 7.6 Hz, 2H, Ar), 7.50 (d, ^3J 7.3 Hz, 1H, Ar), 7.79 (d, ^3J 7.4 Hz, 2H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 25.3 (NCH_3), 45.3 (CH_2), 60.3 (C), 65.3 (CH), 74.7 (CH), 107.9 (CH, Ar), 122.2 (CH, Ar), 122.7 (CH, Ar), 125.9 (2 × CH, Ar), 127.57 (CH, Ar), 127.64 (3 × CH, Ar), 127.7 (2 × CH, Ar), 128.1 (CH, Ar), 128.7 (2 × CH, Ar), 132.0 (C, Ar), 136.0 (C, Ar), 142.3 (C, Ar), 144.0 (C, Ar), 179.0 (C═O).

IR (film, cm^{-1}): 3060, 3030, 2960, 2935, 1705, 1615, 1495, 1470, 1455, 1420, 1375, 1350, 1305, 1265, 1130, 1090, 1025, 755, 700.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{24}H_{23}N_2O$, 355.1805, found 355.1803.

*(2′RS,3SR,5′RS)-5′-(4-Bromophenyl)-1-methyl-2′-phenylspiro-[indoline-3,3′-pyrrolidin]-2-one (**4b**).* Azide **3b** (102 mg, 0.28 mmol), benzaldehyde (40 μL, 0.41 mmol), and triphenylphosphane (76 mg, 0.29 mmol) in CH_2Cl_2 (280 μL) were stirred at 39 °C (microwave reactor) for 12 h, yielding **4b** (60 mg, 50%) as white solid, mp 124−125 °C. Two diastereomers **A**:**B** = 88:12. R_f = 0.26 (ethyl acetate/petroleum ether; 1:4).

A: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.56 (dd, ^2J 13.8, ^3J 8.3 Hz, 1H, CH_2), 2.73 (dd, ^2J 13.8, ^3J 8.6 Hz, 1H, CH_2), 2.76 (s, 3H, NCH_3), 3.15 (br. s, 1H, NH), 4.55 (s, 1H, CH), 4.65 (dd, ^3J 8.3, ^3J 8.6 Hz, 1H, CH), 6.68 (d, ^3J 7.8 Hz, 1H, Ar), 6.87 (d, ^3J 7.5 Hz, 2H, Ar), 7.09−7.13 (m, 2H, Ar), 7.15 (d, ^3J 7.1 Hz, 1H, Ar), 7.19 (ddd, ^3J 7.5, ^3J 7.5, ^4J 1.0 Hz, 1H, Ar), 7.31 (ddd, ^3J 7.7, ^3J 7.7, ^4J 0.6 Hz, 1H, Ar), 7.48 (d, ^3J 7.3 Hz, 1H, Ar), 7.53−7.57 (m, 2H, Ar), 7.66 (d, ^3J 8.4 Hz, 2H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 25.5 (NCH_3), 45.0 (CH_2), 60.1 (C), 62.6 (CH), 74.5 (CH), 107.9 (CH, Ar), 121.5 (C, Ar), 122.2 (CH, Ar), 122.8 (CH, Ar), 125.9 (2 × CH, Ar), 127.7 (3 × CH, Ar), 128.2 (CH, Ar), 129.5 (2 × CH, Ar), 131.6 (C, Ar), 131.8 (2 × CH, Ar), 135.7 (C, Ar), 141.4 (C, Ar), 143.9 (C, Ar), 178.8 (C═O).

IR (film, cm^{-1}): 3055, 2925, 2855, 1700, 1610, 1490, 1470, 1455, 1420, 1375, 1350, 1305, 1265, 1130, 1085, 1070, 1025, 1010, 820, 770, 750, 730, 695.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{24}H_{22}BrN_2O$, 433.0910, found 433.0918.

*(2′RS,3SR,5′RS)-1-Methyl-2′-phenyl-5′-(p-tolyl)spiro[indoline-3,3′-pyrrolidin]-2-one (**4c**).* Azide **3c** (130 mg, 0.42 mmol), benzaldehyde (65 μL, 0.64 mmol), and triphenylphosphane (117 mg, 0.45 mmol) in CH_2Cl_2 (430 μL) were stirred at 39 °C (microwave reactor) for 12 h, yielding **4c** (79 mg, 51%) as yellowish solid, mp 61−62 °C. Two diastereomers **A**:**B** = 92:8. R_f = 0.22 (ethyl acetate/petroleum ether; 1:4).

A: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.40 (s, 3H, CH_3), 2.66 (dd, ^2J 13.7, ^3J 8.5 Hz, 1H, CH_2), 2.74 (dd, ^2J 13.7, ^3J 8.5 Hz, 1H, CH_2), 2.78 (s, 3H, NCH_3), 3.31 (br. s, 1H, NH), 4.58 (s, 1H, CH), 4.70 (dd, ^3J 8.5, ^3J 8.5 Hz, 1H, CH), 6.70 (d, ^3J 7.6 Hz, 1H, Ar), 6.88 (d, ^3J 7.4 Hz, 2H, Ar), 7.10−7.14 (m, 2H, Ar), 7.14−7.17 (m, 1H, Ar), 7.20 (ddd, ^3J 7.5, ^3J 7.5, ^4J 1.0 Hz, 1H, Ar), 7.26 (d, ^3J 7.6 Hz, 2H, Ar), 7.31 (ddd, ^3J 7.7, ^3J 7.7, ^4J 1.2 Hz, 1H, Ar), 7.50 (ddd, ^3J 7.3, ^4J 0.6, ^4J 0.6 Hz, 1H, Ar), 7.68 (d, ^3J 8.0 Hz, 2H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 21.2 (CH_3), 25.5 (NCH_3), 45.2 (CH_2), 60.3 (C), 63.3 (CH), 74.6 (CH), 107.9 (CH, Ar), 122.3 (CH, Ar), 122.8 (CH, Ar), 125.9 (2 × CH, Ar), 127.57 (CH, Ar), 127.64 (2 × CH, Ar), 127.7 (2 × CH, Ar), 128.1 (CH, Ar), 129.4 (2 × CH, Ar), 131.9 (C, Ar), 135.8 (C, Ar), 137.3 (C, Ar), 139.0 (C, Ar), 143.9 (C, Ar), 179.0 (C═O).

IR (film, cm^{-1}): 3055, 3025, 2955, 2920, 2855, 1700, 1610, 1515, 1495, 1470, 1455, 1420, 1375, 1350, 1305, 1265, 1185, 1155, 1130, 1085, 1020, 960, 925, 900, 815, 780, 730, 695.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{25}H_{25}N_2O$, 369.1961, found 369.1975.

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*(2′RS,3SR,5′RS)-5′-(4-Methoxyphenyl)-1-methyl-2′-phenylspiro-[indoline-3,3′-pyrrolidin]-2-one (**4d**).* Azide **3d** (166 mg, 0.47 mmol), benzaldehyde (75 μL, 0.71 mmol), and triphenylphosphane (131 mg, 0.50 mmol) in CH_2Cl_2 (480 μL) were stirred at 39 °C (microwave reactor) for 12 h, yielding **4d** (101 mg, 55%) as yellowish solid, mp 97−98 °C. Two diastereomers **A**:**B** = 86:14. R_f = 0.14 (ethyl acetate/petroleum ether; 1:4).

A: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.63 (dd, ^2J 13.8, ^3J 8.4 Hz, 1H, CH_2), 2.73 (dd, ^2J 13.8, ^3J 8.5 Hz, 1H, CH_2), 2.78 (s, 3H, NCH_3), 3.17 (br. s, 1H, NH), 3.85 (s, 3H, OCH_3), 4.55 (s, 1H, CH), 4.66 (dd, ^3J 8.4, ^3J 8.5 Hz, 1H, CH), 6.70 (d, ^3J 7.7 Hz, 1H, Ar), 6.85 (d, ^3J 7.3 Hz, 2H, Ar), 6.96−7.00 (m, 2H, Ar), 7.08−7.13 (m, 2H, Ar), 7.13−7.17 (m, 1H, Ar), 7.18−7.21 (m, 1H, Ar), 7.31 (ddd, ^3J 7.7, ^3J 7.7, ^4J 1.1 Hz, 1H, Ar), 7.50 (d, ^3J 7.3 Hz, 1H, Ar), 7.69−7.72 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 28.4 (NCH_3), 48.3 (CH_2), 58.3 (OCH_3), 63.4 (C), 65.9 (CH), 77.5 (CH), 110.8 (CH, Ar), 117.0 (2 × CH, Ar), 125.1 (CH, Ar), 125.6 (CH, Ar), 128.7 (2 × CH, Ar), 130.4 (CH, Ar), 130.5 (2 × CH, Ar), 131.0 (CH, Ar), 131.8 (2 × CH, Ar), 134.9 (C, Ar), 137.2 (C, Ar), 138.8 (C, Ar), 146.8 (C, Ar), 162.0 (C, Ar), 182.0 (C═O).

IR (film, cm^{-1}): 3055, 3000, 2955, 2935, 2835, 1705, 1615, 1515, 1495, 1470, 1455, 1420, 1375, 1350, 1305, 1250, 1180, 1130, 1090, 1030, 835, 755, 735, 700.

HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{25}H_{25}N_2O_2$, 385.1911, found 385.1911.

*(2′RS,3SR,5′RS)-5′-(Benzo[d][1,4]dioxol-5-yl)-1-methyl-2′-phenylspiro[indoline-3,3′-pyrrolidin]-2-one (**4e**).* Azide **3e** (180 mg, 0.50 mmol), benzaldehyde (75 μL, 0.76 mmol), and triphenylphosphane (139 mg, 0.53 mmol) in CH_2Cl_2 (510 μL) were stirred at 39 °C (microwave reactor) for 18 h, yielding **4e** (118 mg, 59%) as white solid, mp 66−67 °C. Two diastereomers **A**:**B** = 79:21. R_f = 0.80 (ethyl acetate/petroleum ether; 1:1).

A: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.58 (dd, ^2J 13.7, ^3J 8.3 Hz, 1H, CH_2), 2.70 (dd, ^2J 13.7, ^3J 8.6 Hz, 1H, CH_2), 2.76 (s, 3H, NCH_3), 2.97 (br. s, 1H, NH), 4.53 (s, 1H, CH), 4.63 (dd, ^3J 8.3, ^3J 8.6 Hz, 1H, CH), 5.96 (d, ^2J 1.6 Hz, 1H, OCH_2), 5.97 (d, ^2J 1.6 Hz, 1H, OCH_2), 6.68 (d, ^3J 7.7 Hz, 1H, Ar), 6.84 (d, ^3J 7.9 Hz, 1H, Ar), 6.85−6.88 (m, 2H, Ar), 7.08−7.12 (m, 2H, Ar), 7.13−7.15 (m, 1H, Ar), 7.16−7.20 (m, 2H, Ar), 7.30 (ddd, ^3J 7.7, ^3J 7.7, ^4J 1.2 Hz, 1H, Ar), 7.38 (d, ^4J 1.7 Hz, 1H, Ar), 7.48 (dd, ^3J 7.3, ^4J 0.7 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 25.5 (NCH_3), 45.1 (CH_2), 60.2 (C), 63.2 (CH), 74.3 (CH), 101.0 (OCH_2), 107.9 (CH, Ar), 108.19 (CH, Ar), 108.23 (CH, Ar), 121.0 (CH, Ar), 122.4 (CH, Ar), 122.7 (CH, Ar), 125.9 (2 × CH, Ar), 127.60 (CH, Ar), 127.64 (2 × CH, Ar), 128.1 (CH, Ar), 131.8 (C, Ar), 135.7 (C, Ar), 136.1 (C, Ar), 143.9 (C, Ar), 147.1 (C, Ar), 148.0 (C, Ar), 178.9 (C═O).

IR (film, cm^{-1}): 3055, 2930, 2885, 1700, 1610, 1485, 1470, 1440, 1420, 1375, 1350, 1305, 1265, 1235, 1185, 1155, 1125, 1085, 1035, 985, 935, 870, 810, 790, 755, 730, 695.

HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{25}H_{23}N_2O_3$, 399.1703, found 399.1720.

*(2′RS,3SR,5′RS)-5′-(2,3-Dihydrobenzo[b][1,4]dioxin-6-yl)-1-methyl-2′-phenylspiro[indoline-3,3′-pyrrolidin]-2-one (**4f**).* Azide **3f** (154 mg, 0.41 mmol), benzaldehyde (65 μL, 0.62 mmol), and triphenylphosphane (114 mg, 0.44 mmol) in CH_2Cl_2 (420 μL) were stirred at 39 °C (microwave reactor) for 12 h, yielding **4f** (99 mg, 58%) as white solid, mp 66−67 °C. Two diastereomers **A**:**B** = 92:8. R_f = 0.55 (ethyl acetate/petroleum ether; 1:1).

A: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.61 (dd, ^2J 13.7, ^3J 8.4 Hz, 1H, CH_2), 2.71 (dd, ^2J 13.7, ^3J 8.5 Hz, 1H, CH_2), 2.78 (s, 3H, NCH_3), 3.14 (br. s, 1H, NH), 4.29 (s, 4H, OCH_2), 4.54 (s, 1H, CH), 4.61 (dd, ^3J 8.4, ^3J 8.5 Hz, 1H, CH), 6.69 (d, ^3J 7.6 Hz, 1H, Ar), 6.88 (d, ^3J 7.5 Hz, 2H, Ar), 6.94 (d, ^3J 8.3 Hz, 1H, Ar), 7.09−7.13 (m, 2H, Ar), 7.14−7.17 (m, 1H, Ar), 7.19 (ddd, ^3J 7.5, ^3J 7.5, ^4J 1.0 Hz, 1H, Ar), 7.27 (dd, ^3J 8.4, ^4J 1.9 Hz, 1H, Ar), 7.29−7.33 (m, 2H, Ar), 7.49 (ddd, ^3J 7.3, ^4J 0.6, ^4J 0.6 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 25.5 (NCH_3), 45.3 (CH_2), 60.3 (C), 63.0 (CH), 64.40 (OCH_2), 64.43 (OCH_2), 74.6 (CH), 107.9 (CH, Ar), 116.7 (CH, Ar), 117.4 (CH, Ar), 120.5 (CH, Ar), 122.2 (CH, Ar), 122.7 (CH, Ar), 125.9 (2 × CH, Ar), 127.5 (CH, Ar), 127.6 (2 × CH, Ar), 128.1 (CH, Ar), 132.0 (C, Ar), 135.6 (C, Ar), 135.9 (C, Ar), 143.0 (C, Ar), 143.6 (C, Ar), 144.0 (C, Ar), 178.9 (C═O).

IR (film, cm^{-1}): 3055, 2930, 2875, 1700, 1610, 1590, 1510, 1495, 1470, 1455, 1420, 1375, 1350, 1310, 1285, 1260, 1205, 1155, 1130, 1090, 1065, 1025, 925, 885, 815, 730, 695.

HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{26}H_{25}N_2O_3$, 413.1860, found 413.1871.

*(2′RS,3SR,5′RS)-1-Methyl-2′-phenyl-5′-(3,4,5-trimethoxyphenyl)-spiro[indoline-3,3′-pyrrolidin]-2-one (**4g**).* Azide **3g** (234 mg, 0.57 mmol), benzaldehyde (85 μL, 0.86 mmol), and triphenylphosphane (157 mg, 0.60 mmol) in CH_2Cl_2 (580 μL) were stirred at 39 °C (microwave reactor) for 12 h, yielding **4g** (142 mg, 56%) as yellowish solid, mp 71−72 °C. Two diastereomers **A**:**B** = 94:6. R_f = 0.45 (ethyl acetate/petroleum ether; 1:1).

A: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.64 (dd, ^2J 13.6, ^3J 8.1 Hz, 1H, CH_2), 2.73−2.80 (m, 4H, CH_2, NCH_3), 3.73 (br. s, 1H, NH), 3.87 (s, 3H, OCH_3), 3.94 (s, 6H, OCH_3), 4.59 (s, 1H, CH), 4.70 (dd, ^3J 8.1, ^3J 8.4 Hz, 1H, CH), 6.68 (d, ^3J 7.7 Hz, 1H, Ar), 6.85 (d, ^3J 7.6 Hz, 2H, Ar), 7.06 (s, 2H, Ar), 7.08−7.12 (m, 2H, Ar), 7.14 (t, ^3J 7.0 Hz, 1H, Ar), 7.18 (dd, ^3J 7.4, ^3J 7.4 Hz, 1H, Ar), 7.30 (dd, ^3J 7.7, ^3J 7.7 Hz, 1H, Ar), 7.49 (d, ^3J 7.1 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 26.5 (NCH_3), 44.5 (CH_2), 56.2 (2 × OCH_3), 60.0 (C), 60.8 (OCH_3), 63.4 (CH), 74.0 (CH), 104.7 (2 × CH, Ar), 108.0 (CH, Ar), 122.3 (CH, Ar), 122.9 (CH, Ar), 125.8 (2 × CH, Ar), 127.7 (3 × CH, Ar), 128.3 (CH, Ar), 131.3 (C, Ar), 135.1 (C, Ar), 137.4 (C, Ar), 137.5 (C, Ar), 143.9 (C, Ar), 153.5 (2 × C, Ar), 178.9 (C═O).

IR (film, cm^{-1}): 3055, 2930, 2840, 1700, 1610, 1590, 1510, 1495, 1465, 1420, 1375, 1350, 1325, 1265, 1250, 1230, 1185, 1155, 1125, 1090, 1025, 855, 830, 770, 730, 700.

HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{27}H_{29}N_2O_4$, 445.2122, found 445.2120.

*(2′RS,3SR,5′RS)-1-Methyl-2′-phenyl-5′-(thiophen-2-yl)spiro-[indoline-3,3′-pyrrolidin]-2-one (**4h**).* Azide **3h** (134 mg, 0.43 mmol), benzaldehyde (65 μL, 0.64 mmol), and triphenylphosphane (118 mg, 0.45 mmol) in CH_2Cl_2 (435 μL) were stirred at 39 °C (microwave reactor) for 12 h, yielding **4h** (72 mg, 47%) as yellowish oil. Two diastereomers **A**:**B** = 81:19. R_f = 0.36 (ethyl acetate/petroleum ether; 1:4).

A: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.72 (dd, ^2J 13.6, ^3J 8.4 Hz, 1H, CH_2), 2.77 (s, 3H, NCH_3), 2.80 (dd, ^2J 13.6, ^3J 8.4 Hz, 1H, CH_2), 3.18 (br. s, 1H, NH), 4.55 (s, 1H, CH), 4.98 (dd, ^3J 8.4, ^3J 8.4 Hz, 1H, CH), 6.69 (d, ^3J 7.7 Hz, 1H, Ar), 6.83−6.87 (m, 2H, Ar), 7.05 (dd, ^3J 3.5, ^3J 5.1 Hz, 1H, Ar), 7.09−7.13 (m, 2H, Ar), 7.13−7.16 (m, 1H, Ar), 7.18 (ddd, ^3J 7.6, ^3J 7.6, ^4J 1.0 Hz, 1H, Ar), 7.28 (ddd, ^3J 3.4, ^4J 1.0, ^4J 1.0 Hz, 1H, Ar), 7.29−7.32 (m, 2H, Ar), 7.47 (dd, ^3J 7.4, ^4J 1.2 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 25.6 (NCH_3), 45.4 (CH_2), 58.7 (CH), 60.2 (C), 74.4 (CH), 107.9 (CH, Ar), 122.2 (CH, Ar), 122.7 (CH, Ar), 124.7 (CH, Ar), 124.8 (CH, Ar), 125.9 (2 × CH, Ar), 126.9 (CH, Ar), 127.6 (CH, Ar), 127.7 (2 × CH, Ar), 128.2 (CH, Ar), 131.6 (C, Ar), 135.5 (C, Ar), 144.0 (C, Ar), 145.3 (C, Ar), 178.6 (C═O).

IR (film, cm^{-1}): 3055, 1700, 1610, 1495, 1470, 1380, 1350, 1265, 1190, 1125, 1090, 1025, 950, 900, 850, 735, 695.

HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{22}H_{21}N_2OS$, 361.1369, found 361.1372.

*(2′RS,3SR,5′RS)-2′-(4-Fluorophenyl)-1-methyl-5′-phenylspiro-[indoline-3,3′-pyrrolidin]-2-one (**4i**).* Azide **3a** (90 mg, 0.28 mmol), 4-fluorobenzaldehyde (45 μL, 0.42 mmol), and triphenylphosphane (77 mg, 0.29 mmol) in CH_2Cl_2 (285 μL) were stirred at 39 °C (microwave reactor) for 12 h, yielding **4i** (47 mg, 45%) as white solid, mp 131−132 °C. Two diastereomers **A**:**B** = 89:11. R_f = 0.28 (ethyl acetate/petroleum ether; 1:4).

A: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.66 (dd, ^2J 13.8, ^3J 8.4 Hz, 1H, CH_2), 2.78 (dd, ^2J 13.8, ^3J 8.8 Hz, 1H, CH_2), 2.83 (s, 3H, NCH_3), 3.81 (br. s, 1H, NH), 4.65 (s, 1H, CH), 4.79 (dd, ^3J 8.4, ^3J 8.8 Hz, 1H, CH), 6.71 (d, ^3J 7.7 Hz, 1H, Ar), 6.80 (dd, ^3J 8.8, ^3J 8.8 Hz, 2H, Ar), 6.88 (dd, $^3J_{HH}$ 8.6, $^4J_{HF}$ 5.5 Hz, 2H, Ar), 7.20 (ddd, ^3J 7.4, ^3J 7.4, ^4J 0.9 Hz, 1H, Ar), 7.32 (ddd, ^3J 7.7, ^3J 7.7, ^4J 1.2 Hz, 1H, Ar), 7.33−7.37 (m, 1H, Ar), 7.41−7.46 (m, 2H, Ar), 7.53 (d, ^3J 7.4 Hz, 1H, Ar), 7.73−7.79 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 25.7 (NCH_3),

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44.4 (CH_2), 59.7 (C), 63.1 (CH), 73.2 (CH), 108.1 (CH, Ar), 114.6 ($^2J_{CF}$ 21 Hz, 2 × CH, Ar), 122.5 (CH, Ar), 123.0 (CH, Ar), 127.7 ($^3J_{CF}$ 8 Hz, 2 × CH, Ar), 127.8 (2 × CH, Ar), 128.0 (CH, Ar), 128.4 (CH, Ar), 128.8 (2 × CH, Ar), 131.0 ($^4J_{CF}$ 2 Hz, C, Ar), 131.1 (C, Ar), 141.1 (C, Ar), 143.8 (C, Ar), 162.3 ($^1J_{CF}$ 247 Hz, C, Ar), 178.8 (C═O).

IR (film, cm^{-1}): 3055, 2925, 2855, 1700, 1610, 1510, 1495, 1470, 1455, 1420, 1375, 1350, 1305, 1265, 1225, 1155, 1130, 1090, 1025, 1015, 985, 960, 910, 865, 835, 795, 730, 700.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{24}H_{22}FN_2O$, 373.1711, found 373.1714.

*(2′RS,3SR,5′RS)-2′-(4-Bromophenyl)-1-methyl-5′-phenylspiro-[indoline-3,3′-pyrrolidin]-2-one (**4j**).* Azide **3a** (91 mg, 0.30 mmol), 4-bromobenzaldehyde (82 mg, 0.45 mmol), and triphenylphosphane (82 mg, 0.31 mmol) in CH_2Cl_2 (305 μL) were stirred at 39 °C (microwave reactor) for 12 h, yielding **4j** (52 mg, 40%) as white solid, mp 115−116 °C. Two diastereomers **A**:**B** = 94:6. R_f = 0.36 (ethyl acetate/petroleum ether; 1:4).

A: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.64 (dd, ^2J 13.8, ^3J 8.4 Hz, 1H, CH_2), 2.73 (dd, ^2J 13.8, ^3J 8.7 Hz, 1H, CH_2), 2.83 (s, 3H, NCH_3), 3.40 (br. s, 1H, NH), 4.54 (s, 1H, CH), 4.70 (dd, ^3J 8.4, ^3J 8.7 Hz, 1H, CH), 6.72 (d, ^3J 7.8 Hz, 1H, Ar), 6.78 (ddd, ^3J 8.6, ^4J 1.9, ^4J 1.9 Hz, 2H, Ar), 7.20 (ddd, ^3J 7.5, ^3J 7.5, ^4J 0.9 Hz, 1H, Ar), 7.24 (ddd, ^3J 8.6, ^4J 0.9, ^4J 0.9 Hz, 2H, Ar), 7.32 (ddd, ^3J 7.7, ^3J 7.7, ^4J 1.2 Hz, 1H, Ar), 7.34−7.36 (m, 1H, Ar), 7.42−7.45 (m, 2H, Ar), 7.49 (dd, ^3J 7.3, ^4J 0.6 Hz, 1H, Ar), 7.73−7.76 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 25.7 (NCH_3), 45.1 (CH_2), 59.9 (C), 63.3 (CH), 73.6 (CH), 108.1 (CH, Ar), 121.7 (C, Ar), 122.3 (CH, Ar), 122.9 (CH, Ar), 127.67 (2 × CH, Ar), 127.73 (2 × CH, Ar), 127.8 (CH, Ar), 128.4 (CH, Ar), 128.8 (2 × CH, Ar), 130.8 (2 × CH, Ar), 131.5 (C, Ar), 135.0 (C, Ar), 141.7 (C, Ar), 143.8 (C, Ar), 178.7 (C═O).

IR (film, cm^{-1}): 3030, 1700, 1615, 1520, 1495, 1470, 1460, 1420, 1375, 1350, 1305, 1265, 1130, 1090, 1025, 1010, 910, 820, 735, 700.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{24}H_{22}BrN_2O$, 433.0910, found 433.0912.

*(2′RS,3SR,5′RS)-1-Methyl-5′-phenyl-2′-(p-tolyl)spiro[indoline-3,3′-pyrrolidin]-2-one (**4k**).* Azide **3a** (122 mg, 0.42 mmol), 4-methylbenzaldehyde (75 μL, 0.63 mmol), and triphenylphosphane (115 mg, 0.44 mmol) in CH_2Cl_2 (425 μL) were stirred at 39 °C (microwave reactor) for 12 h, yielding **4k** (37 mg, 24%, 32% brsm) as yellowish oil. Two diastereomers **A**:**B** = 83:17. R_f = 0.24 (ethyl acetate/petroleum ether; 1:4).

A: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.23 (s, 3H, CH_3), 2.66 (dd, ^2J 13.8, ^3J 8.4 Hz, 1H, CH_2), 2.75 (dd, ^2J 13.8, ^3J 8.6 Hz, 1H, CH_2), 2.82 (s, 3H, NCH_3), 3.29 (br. s, 1H, NH), 4.59 (s, 1H, CH), 4.74 (dd, ^3J 8.4, ^3J 8.6 Hz, 1H, CH), 6.71 (d, ^3J 7.7 Hz, 1H, Ar), 6.76 (d, ^3J 8.1 Hz, 2H, Ar), 6.91 (d, ^3J 7.8 Hz, 2H, Ar), 7.19 (ddd, ^3J 7.5, ^3J 7.5, ^4J 1.0 Hz, 1H, Ar), 7.31 (ddd, ^3J 7.7, ^3J 7.7, ^4J 1.2 Hz, 1H, Ar), 7.34 (tt, ^3J 7.4, ^4J 1.3 Hz, 1H, Ar), 7.41−7.45 (m, 2H, Ar), 7.50 (ddd, ^3J 7.3, ^4J 0.5, ^4J 1.2 Hz, 1H, Ar), 7.74−7.80 (m, 2H, Ar);^{13}C NMR ($CDCl_3$, 150 MHz): δ = 21.1 (CH_3), 25.6 (NCH_3), 45.0 (CH_2), 60.1 (C), 63.3 (CH), 74.1 (CH), 107.9 (CH, Ar), 122.3 (CH, Ar), 122.8 (CH, Ar), 125.7 (2 × CH, Ar), 127.8 (3 × CH, Ar), 128.1 (CH, Ar), 128.4 (2 × CH, Ar), 128.8 (2 × CH, Ar), 131.8 (C, Ar), 132.4 (C, Ar), 137.2 (C, Ar), 141.7 (C, Ar), 143.9 (C, Ar), 179.1 (C═O).

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{25}H_{25}N_2O$, 369.1961, found 369.1967.

*(2′RS,3SR,5′RS)-1-Methyl-2′-(4-nitrophenyl)-5′-phenylspiro-[indoline-3,3′-pyrrolidin]-2-one (**4l**).* Azide **3a** (116 mg, 0.38 mmol), 4-nitrobenzaldehyde (86 mg, 0.57 mmol), and triphenylphosphane (105 mg, 0.40 mmol) in CH_2Cl_2 (385 μL) were stirred at room temperature for 4 h, yielding **4l** (38 mg, 25%) as yellow solid, mp 142−143 °C. R_f = 0.15 (ethyl acetate/petroleum ether; 1:4).

^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.65 (dd, ^2J 13.7, ^3J 8.7 Hz, 1H, CH_2), 2.73 (dd, ^2J 13.7, ^3J 8.4 Hz, 1H, CH_2), 2.81 (s, 3H, NCH_3), 2.93 (br. s, 1H, NH), 4.67 (s, 1H, CH), 4.72 (dd, ^3J 8.4, ^3J 8.7 Hz, 1H, CH), 6.74 (d, ^3J 7.7 Hz, 1H, Ar), 7.10 (d, ^3J 8.9 Hz, 2H, Ar), 7.23 (ddd, ^3J 7.5, ^3J 7.5, ^4J 0.9 Hz, 1H, Ar), 7.32−7.37 (m, 2H, Ar), 7.42−7.46 (m, 2H, Ar), 7.63 (dd, ^3J 7.4, ^4J 0.6 Hz, 1H, Ar), 7.72−7.76 (m, 2H, Ar), 7.99 (d, ^3J 8.9 Hz, 2H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 25.7 (NCH_3), 45.5 (CH_2), 59.8 (C), 63.5 (CH), 73.3 (CH), 108.2 (CH, Ar), 122.4 (CH, Ar), 122.9 (2 × CH, Ar), 123.1 (CH, Ar), 127.0 (2 × CH, Ar), 127.5 (2 × CH, Ar), 127.9 (CH, Ar), 128.7 (CH, Ar), 128.8 (2 × CH, Ar), 131.4 (C, Ar), 141.7 (C, Ar), 143.7 (C, Ar), 144.1 (C, Ar), 147.4 (C, Ar), 178.2 (C═O).

IR (film, cm^{-1}): 3030, 1705, 1610, 1520, 1495, 1470, 1450, 1420, 1375, 1345, 1265, 1130, 1090, 1025, 1015, 910, 850, 735, 700.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{24}H_{22}N_3O_3$, 400.1656, found 400.1661.

*(2′RS,3SR,5′RS)-2′-(3-Chlorophenyl)-1-methyl-5′-phenylspiro-[indoline-3,3′-pyrrolidin]-2-one (**4m**).* Azide **3a** (86 mg, 0.29 mmol), 3-chlorobenzaldehyde (50 μL, 0.44 mmol), and triphenylphosphane (81 mg, 0.31 mmol) in CH_2Cl_2 (300 μL) were stirred at 39 °C (microwave reactor) for 6 h, yielding **4m** (37 mg, 51%) as yellow oil. Two diastereomers **A**:**B** = 90:10. R_f = 0.34 (ethyl acetate/petroleum ether; 1:4).

A: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.64 (dd, ^2J 13.7, ^3J 8.5 Hz, 1H, CH_2), 2.73 (dd, ^2J 13.7, ^3J 8.5 Hz, 1H, CH_2), 2.83 (s, 3H, NCH_3), 3.08 (br. s, 1H, NH), 4.53 (s, 1H, CH), 4.67 (dd, ^3J 8.5, ^3J 8.5 Hz, 1H, CH), 6.74 (d, ^3J 7.8 Hz, 1H, Ar), 6.80 (dd, ^3J 7.8, ^4J 0.5 Hz, 1H, Ar), 6.85−6.87 (m, 1H, Ar), 7.06 (dd, ^3J 7.8, ^3J 7.9 Hz, 1H, Ar), 7.13−7.15 (m, 1H, Ar), 7.21 (ddd, ^3J 7.7, ^3J 7.7, ^4J 1.0 Hz, 1H, Ar), 7.32−7.37 (m, 2H, Ar), 7.44 (dd, ^3J 7.6, ^3J 7.8 Hz, 2H, Ar), 7.49 (ddd, ^3J 7.3, ^4J 0.5, ^4J 0.5 Hz, 1H, Ar), 7.73−7.77 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 25.6 (NCH_3), 45.4 (CH_2), 60.0 (C), 63.4 (CH), 73.8 (CH), 108.0 (CH, Ar), 122.2 (CH, Ar), 122.9 (CH, Ar), 124.1 (CH, Ar), 126.2 (CH, Ar), 127.6 (2 × CH, Ar), 127.67 (CH, Ar), 127.73 (CH, Ar), 128.4 (CH, Ar), 128.7 (2 × CH, Ar), 128.9 (CH, Ar), 131.7 (C, Ar), 133.6 (C, Ar), 138.5 (C, Ar), 142.0 (C, Ar), 143.9 (C, Ar), 178.6 (C═O).

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{24}H_{22}ClN_2O$, 389.1415, found 389.1420.

*(2′RS,3SR,5′RS)-2′-(2-Chlorophenyl)-1-methyl-5′-phenylspiro-[indoline-3,3′-pyrrolidin]-2-one (**4n**).* Azide **3a** (52 mg, 0.18 mmol), 2-chlorobenzaldehyde (30 μL, 0.27 mmol), and triphenylphosphane (49 mg, 0.19 mmol) in CH_2Cl_2 (180 μL) were stirred at 39 °C (microwave reactor) for 13 h, yielding **4n** (27 mg, 39%) as yellow oil. Two diastereomers **A**:**B** = 71:29. R_f = 0.26, 0.32 (ethyl acetate/petroleum ether; 1:4).

A: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.54 (dd, ^2J 13.0, ^3J 7.2 Hz, 1H, CH_2), 2.63 (dd, ^2J 13.0, ^3J 9.6 Hz, 1H, CH_2), 2.91 (s, 3H, NCH_3), 4.78 (dd, ^3J 7.2, ^3J 9.6 Hz, 1H, CH), 5.19 (s, 1H, CH), 6.71 (d, ^3J 7.9 Hz, 1H, Ar), 7.12−7.17 (m, 3H, Ar), 7.26−7.30 (m, 2H, Ar), 7.33 (ddd, ^3J 7.4, ^3J 7.4, ^4J 0.7 Hz, 1H, Ar), 7.43 (dd, ^3J 7.5, ^3J 7.5 Hz, 2H, Ar), 7.57 (d, ^3J 7.4 Hz, 1H, Ar), 7.74 (d, ^3J 7.6 Hz, 2H, Ar), 7.98 (d, ^3J 7.6 Hz, 1H, Ar). Signal of NH was not observed; ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 25.9 (NCH_3), 46.1 (CH_2), 59.1 (C), 62.8 (CH), 68.3 (CH), 107.7 (CH, Ar), 122.5 (CH, Ar), 123.3 (CH, Ar), 126.2 (CH, Ar), 127.4 (2 × CH, Ar), 127.6 (CH, Ar), 128.0 (CH, Ar), 128.5 (CH, Ar), 128.6 (2 × CH, Ar), 128.8 (CH, Ar), 129.9 (CH, Ar), 133.1 (C, Ar), 133.2 (C, Ar), 135.7 (C, Ar), 142.4 (C, Ar), 143.5 (C, Ar), 177.9 (C═O).

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{24}H_{22}ClN_2O$, 389.1415, found 389.1420.

*(2′RS,3SR,5′RS)-1-Methyl-5′-phenyl-2′-(thiophen-2-yl)spiro-[indoline-3,3′-pyrrolidin]-2-one (**4o**).* Azide **3a** (88 mg, 0.27 mmol), thiophene-2-carbaldehyde (40 μL, 0.41 mmol), and triphenylphosphane (75 mg, 0.29 mmol) in CH_2Cl_2 (275 μL) were stirred at 39 °C (microwave reactor) for 12 h, yielding **4o** (44 mg, 45%) as white solid, mp 108−109 °C. R_f = 0.25 (ethyl acetate/petroleum ether; 1:4).

^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.68 (dd, ^2J 13.8, ^3J 8.1 Hz, 1H, CH_2), 2.78 (dd, ^2J 13.8, ^3J 9.0 Hz, 1H, CH_2), 2.99 (s, 3H, NCH_3), 3.43 (br. s, 1H, NH), 4.75−4.81 (m, 1H, CH), 4.84 (s, 1H, CH), 6.65 (s, 1H, Ar), 6.79−6.84 (m, 2H, Ar), 7.05 (d, ^3J 5.0 Hz, 1H, Ar), 7.19 (t, ^3J 7.5 Hz, 1H, Ar), 7.32−7.37 (m, 2H, Ar), 7.43 (dd, ^3J 7.5, ^3J 7.5 Hz, 2H, Ar), 7.47 (d, ^3J 7.4 Hz, 1H, Ar), 7.75 (d, ^3J 7.6 Hz, 2H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 25.9 (NCH_3), 45.2 (CH_2), 59.6 (C), 63.4 (CH), 70.3 (CH), 108.2 (CH, Ar), 122.4 (CH, Ar), 123.0 (CH, Ar), 124.1 (CH, Ar), 124.2 (CH, Ar), 126.4 (CH, Ar), 127.8 (2 × CH,

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Ar), 127.9 (CH, Ar), 128.5 (CH, Ar), 128.8 (2 × CH, Ar), 130.7 (C, Ar), 138.1 (C, Ar), 141.1 (C, Ar), 144.3 (C, Ar), 179.0 (C═O).

IR (film, cm^{-1}): 2950, 2920, 2870, 2850, 1700, 1610, 1510, 1490, 1455, 1375, 1350, 1265, 1155, 1125, 1090, 1045, 1025, 1000, 975, 880, 855, 825, 790, 750, 700.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{22}H_{21}N_2OS$, 361.1369, found 361.1366.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b00529

Cell assay as well as copies of ^1H and ^{13}C NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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