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Article

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Stereocontrolled [3+2] Cycloaddition of Donor-Acceptor Cyclopropanes to Iminooxindoles: Access to Spiro[oxindole-3,2'-pyrrolidines]

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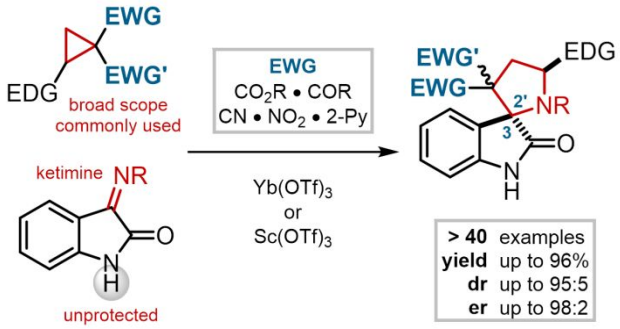


ABSTRACT: A novel stereocontrolled assembly of spiro[oxindole-3,2'-pyrrolidines] *via* [3+2]-cycloaddition of donor-acceptor cyclopropanes to electron poor ketimines, iminooxindoles, was developed. The method allows for efficient employment of common readily available donor-acceptor cyclopropanes, functionalized with ester, keto, nitro, cyano *etc*. groups, and *N*-unprotected iminooxindoles. The stereospecificity of the initial S_N2-like imine attack on a cyclopropane molecule together with high diastereoselectivity of further C–C bond formation facilitate a rapid access to spiro[oxindole-3,2'-pyrrolidines] in their optically active forms. Preliminary *in vitro* testing of the synthesized compounds against LNCaP (p53+) and PC-3 (p53-) cells revealed good antiproliferative activities and p53-selectivity indices for several compounds that are intriguing in terms of their further investigation as inhibitors of MDM2-p53 interaction.

INTRODUCTION

Over the past couple of decades, the design and development of synthetic strategies to access spirooxindole molecules have gained a lot of momentum.[1–3] Intense interest in these structures is determined by their various biological activities which provide ample opportunities for drug discovery.[4] Spiro[oxindolepyrrolidines] are of particular interest as potential anticancer agents. The most extensive investigations in this area are related to spiro[oxindole-3,3'-pyrrolidines], among which natural and artificial bioactive structures (*e.g.*, elacomine, horsfiline, spirotryprostatine A and B, MI-77301 and MI-888) are well-known[5] (Fig. 1, **A**). At the same time, the isomeric tricyclic spiro[oxindole-3,2'-pyrrolidine] systems, while also promising in the context of bioactivity, are rarely studied. Nevertheless, anticancer activity, particularly *via* inhibition of p53-MDM2 interaction, was revealed for the representatives of this subclass[6] (Fig. 1, **B**). Therefore, the development of efficient methods allowing for stereoselective synthesis of functionalized spiro[oxindole-3,2'-pyrrolidines] is highly desirable.

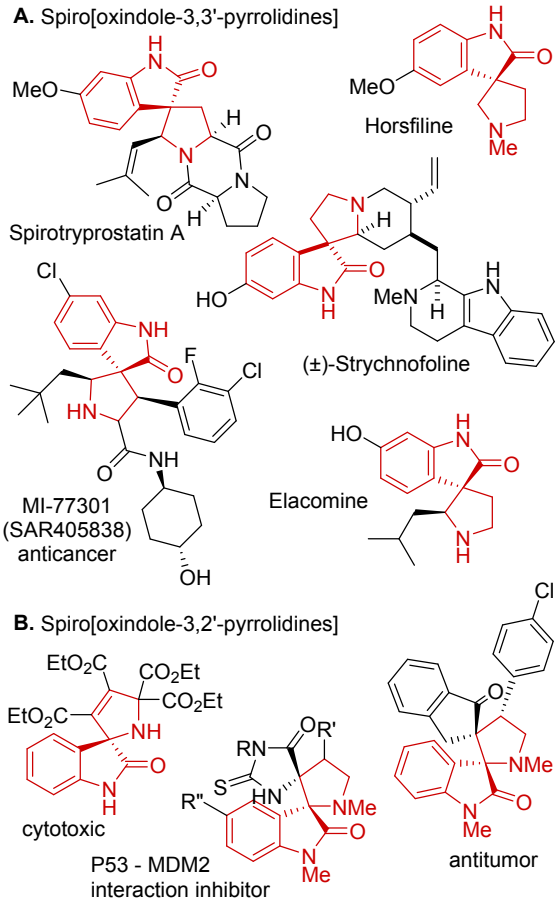


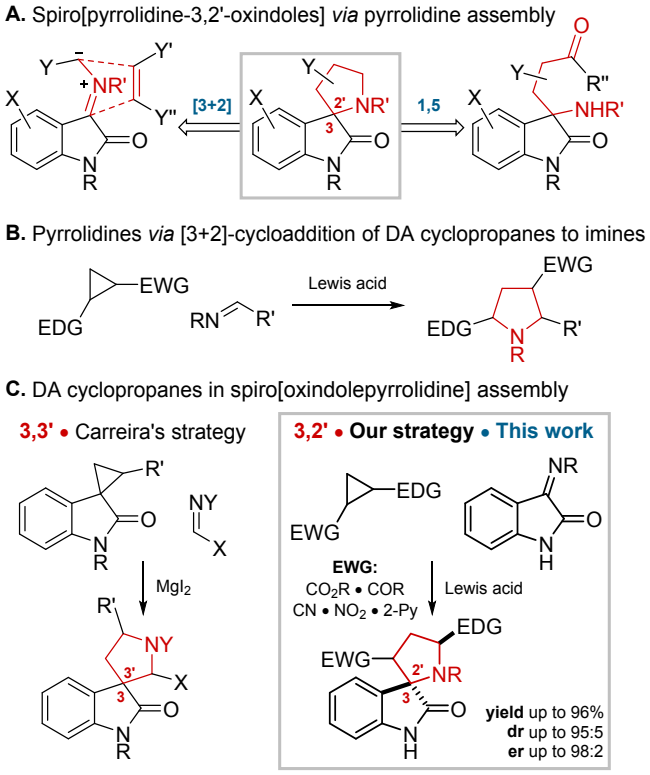
Figure 1. Examples of natural and synthetic bioactive spiro[oxindolepyrrolidines].

Among the typical synthetic approaches to these compounds, [3+2]-cycloaddition of isatin-derived azomethine ylides to dipolarophiles is the one reported most widely[7,8] (Scheme 1, **A**).

Some other approaches are based on the reactivity of iminooxindoles and involve 1,5-cyclization of oxindole-containing γ-aminocarbonyl compounds obtained *via* Mannich-*aza*-Michael reactions as well as *via* nucleophilic addition of organometallic compounds to iminooxindoles.[9–11] The possibility for assembling a pyrrolidine ring with a pre-existing oxindole bicycle is a common feature of the aforementioned methods.

In the recent years, Lewis acid (LA) catalyzed [3+2]-cycloaddition of donor-acceptor (DA) cyclopropanes[12] to imines emerged as a highly efficient alternative to the existing methods of pyrrolidine formation[13,14] (Scheme 1, **B**). Moreover, in their pioneering works, Carreira and co-workers successfully employed activated cyclopropanes in the synthesis of spiro[pyrrolidineoxindoles]. Their strategy relied upon MgI_2-catalyzed [3+2]-cycloaddition of spiro[oxindole-3,1'-cyclopropanes] to aldimines affording spiro[oxindole-3,3'-pyrrolidines] (Scheme 1, **C**), including (±) strychnofoline and (-)-spirotryprostatin B.[15]

Scheme 1. Overview and Strategy of This Work



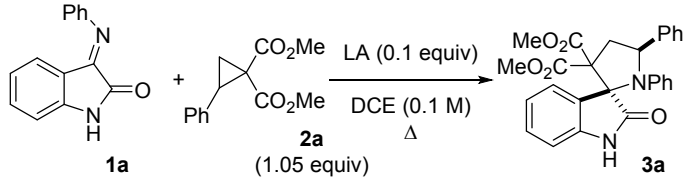
In this work, we report a new approach to isomeric spiro[oxindole-3,2'-pyrrolidines], applying [3+2]-cycloaddition of DA cyclopropanes to iminooxindoles for diastereo- and enantioselective assembly of the pyrrolidine unit. Recently, Pd-catalyzed [3+2]-cycloaddition of vinylcyclopropane-1,1-diesters to isatins was reported, leading to diastereo- and enantioselective construction of spiro[oxindole-3,2'-tetrahydrofurans].[16] Our technique provides possibilities for efficient employment of readily accessible DA cyclopropanes with ester groups as acceptors.

Moreover, cyclopropanes functionalized with COR, CN, NO_2, *etc*. groups were employed as well. This method allows for a direct synthesis of biologically relevant spiro[oxindole-3,2'-pyrrolidines] with an *N*-unprotected oxindole unit, thus avoiding redundant *N*-protection/deprotection steps. In this work, [3+2]-cycloaddition proceeds with high diastereo- and enantioselectivity. This mechanism facilitates the synthesis of optically active spiro[oxindole-3,2'-pyrrolidines] from enantiomerically enriched DA cyclopropanes.

RESULTS AND DISCUSSION

In order to optimize the reaction conditions, we carried out a short series of experiments using iminooxindole **1a** and cyclopropane-1,1-diester **2a** as model substrates (Table 1). Several LA, such as MgI_2, $Sc(OTf)_3$ and $Yb(OTf)_3$, typically used as catalysts in reactions with DA cyclopropanes, were examined. We found that, at ambient temperature, MgI_2 did not trigger the formation of spiro[oxindole-3,2'-pyrrolidine] **3a** at all, while the use of $Sc(OTf)_3$ resulted in trace amounts of **3a** under the same conditions (entries 1,2). An increase in temperature led to an increase in reaction efficiency. The heating of the reaction mixture in DCE under reflux for 2 h in the presence of $Sc(OTf)_3$ or $Yb(OTf)_3$ was found to be the most efficient, affording **3a** in 73% and 88% yields, respectively (entries 3,4). Further increase in the duration of the reaction (up to 8 h) led to a reduction in the yield of **3a** (entries 5,6). It is noteworthy that the use of MgI_2 under similar conditions induced an incomplete conversion of **2a** and gave the product **3a** in a moderate yield, whereas in the presence of $MgBr_2 \cdot OEt_2$ the reaction did not occur at all (entries 7,9). The increase in concentration and MgI_2 loading allowed for complete conversion of **2a** in 5 h and formation of **3a** in 76% yield (entry 8). All successful experiments displayed similar diastereoselectivity in regard to the formation of **3a**. Therefore, heating of the reaction mixture in DCE under reflux for 2 h in the presence of $Yb(OTf)_3$ (entry 4) was determined as optimal in terms of selecting conditions for further experiments.

Table 1. Optimization of [3+2]-Cycloaddition between **1a** and **2a**



Entry	LA	T (°C)	t (h)	Yield (%) [dr][a]
1	MgI_2	25	6	-[b]

2	$Sc(OTf)_3$	25	6	-[c]
3	$Sc(OTf)_3$	83	2	73 [92:8]
4	**$Yb(OTf)_3$**	**83**	**2**	**88 [93:7]**
5	$Sc(OTf)_3$	83	8	29 [95:5]
6	$Yb(OTf)_3$	83	8	69 [92:8]
7[d]	MgI_2	83	8	50 [94:6]
8	MgI_2[e]	83	5	76 [94:6]
9	$MgBr_2 \cdot OEt_2$	83	8	-[b]

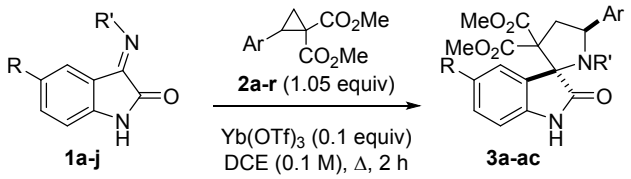
[a]Diastereomeric ratios [dr] were determined by NMR analysis of crude products. [b]No reaction. [c]Trace amounts of **3a** were formed. [d]77%-Conversion of **2a** was observed. [e]MgI_2 (0.2 equiv.), DCE (0.7 M).

Under the optimized conditions, a series of iminooxindoles **1a–j**, containing various substituents in their benzene unit as well as at the imine N center, and cyclopropane-1,1-diesters **2b–r** with a variety of aryl and hetaryl substituents at C2 were examined in the [3+2]-cycloaddition reaction (Table 2). In most cases, reactions proceeded with high efficiency, leading to desired products **3** in 47–96% yields. The introduction of halogens into the oxindole fragment of imines **1b–d** had no significant influence on the reaction outcome, affording **3b–h** in high yields. Similarly, **1e–j**, bearing both electron-donating and electron-withdrawing groups in the aromatic substituent at the imine N atom, efficiently reacted with **2a** and gave **3i–n** in high yields. Unfortunately, when using imines **1** with alkyl groups (*e.g.* Bu, **1k**) at the N atom, slow degradation of imines was observed with no formation of the desired [3+2]-cycloadduct **3**. The replacement of $Yb(OTf)_3$ with MgI_2 also did not facilitate a reaction with **1k**.

Varying substituents at the C2 atom of **2** allowed us to reveal a tendency to decelerate for the reaction involving **2i–k** which contain aryls with acceptor groups, such as NO_2, CO_2Me, CN. As a result, the reaction time was increased to 16–20 h, leading to noticeable tarring and a reasonable decrease in the yields of **3v–x** (as low as 51%). Moreover, the presence of an *ortho*-group (**2d**) also led to significant deceleration and decline in the yield of the corresponding spiro[oxindole-3,2'-pyrrolidine] **3q**. On the other hand, for electron-abundant aryls (**2e–h**), shorter time (1 h) was required to achieve a complete conversion of the reactants into the corresponding products **3**. 2-Thienyl derivative **2n** displayed good tolerance to the reaction

conditions, efficiently yielding **3aa** (92%). However, for the reactions of acidophobic indolyl-derivatives **2o**,**p**, the decrease in the yields of the corresponding products **3ab,ac** was observed, owing to significant tarring. Meanwhile, *N*-Me-pyrrolyl derivative **2q** and the even more tolerant *N*-Ts-pyrrolyl derivative **2r** underwent complete polymerization under the studied conditions.

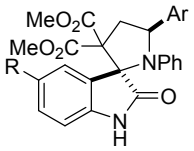
Table 2. [3+2]-Cycloaddition between Imines **1a–j** and 2-Arylcyclopropane-1,1-diesters **2a–r**[a]



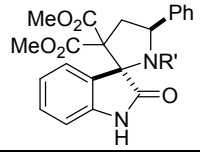
1a: R = H, R' = Ph
1b: R = F, R' = Ph
1c: R = Cl, R' = Ph
1d: R = Br, R' = Ph
1e: R = H, R' = 4-FC_6H_4
1f: R = H, R' = 4-ClC_6H_4
1g: R = H, R' = 2-ClC_6H_4
1h: R = H, R' = 4-BrC_6H_4
1i: R = H, R' = 4-MeC_6H_4
1j: R = H, R' = 4-$MeOC_6H_4$

2a: Ar = Ph
2b: Ar = 4-FC_6H_4
2c: Ar = 4-BrC_6H_4
2d: Ar = 2-BrC_6H_4
2e: Ar = 4-MeC_6H_4
2f: Ar = 4-$MeOC_6H_4$
2g: Ar = 3,4-$(MeO)_2C_6H_3$
2h: Ar = 3,4,5-$(MeO)_3C_6H_2$
2i: Ar = 4-$O_2NC_6H_4$
2j: Ar = 4-$MeO_2CC_6H_4$

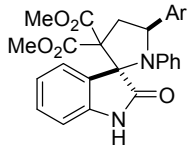
2k: Ar = 4-NCC_6H_4
2l: Ar = α-naphtyl
2m: Ar = β-naphtyl
2n: Ar = 2-thienyl
2o: Ar = 2-(*N*-Me)indolyl
2p: Ar = 4-(*N*-Me)indolyl
2q: Ar = 2-(*N*-Me)pyrrolyl
2r: Ar = 2-(*N*-Ts)pyrrolyl



3a: R = H, Ar = Ph, 88%, dr 93:7
3b: R = F, Ar = Ph, 90%, dr 94:6
3c:[b] R = F, Ar = 4-MeC_6H_4, 89%, dr 94:6
3d: R = Cl, Ar = Ph, 85%, dr 94:6
3e: R = Cl, Ar = 4-FC_6H_4, 95%, dr 93:7
3f: R = Br, Ar = Ph, 90%, dr 94:6
3g:[b] R = Br, Ar = 4-MeC_6H_4, 90%, dr 93:7
3h:[b] R = Br, Ar = 4-$MeOC_6H_4$, 95%, dr 95:5



3i: R' = 4-FC_6H_4, 92%, dr 94:6
3j: R' = 4-ClC_6H_4, 91%, dr 94:6
3k: R' = 2-ClC_6H_4, 83%, dr 95:5
3l: R' = 4-BrC_6H_4, 89%, dr 94:6
3m: R' = 4-MeC_6H_4, 89%, dr 93:7
3n: R' = 4-$MeOC_6H_4$, 93%, dr 92:8



3o: Ar = 4-FC_6H_4, 96%, dr 91:9
3p: Ar = 4-BrC_6H_4, 92%, dr 91:9
3q:[c] Ar = 2-BrC_6H_4, 49%, dr 91:9
3r:[b] Ar = 4-MeC_6H_4, 89%, dr 93:7
3s:[b] Ar = 4-$MeOC_6H_4$, 79%, dr 93:7
3t:[b] Ar = 3,4-$(MeO)_2C_6H_3$, 79%, dr 93:7
3u:[b] Ar = 3,4,5-$(MeO)_3C_6H_2$, 81%, dr 93:7
3v:[c] Ar = 4-$O_2NC_6H_4$, 51%, dr 91:9
3w:[d] Ar = 4-$MeO_2CC_6H_4$, 54%, dr 92:8
3x:[d] Ar = 4-NCC_6H_4, 60%, dr 91:9
3y: Ar = α-naphtyl, 91%, dr 93:7
3z: Ar = β-naphtyl, 71%, dr 93:7
3aa: Ar = 2-thienyl, 92%, dr 91:9
3ab: Ar = 2-(*N*-Me)indolyl, 58%, dr 93:7
3ac: Ar = 4-(*N*-Me)indolyl, 47%, dr 93:7
3ad: Ar = 2-(*N*-Me)pyrrolyl, 0%
3ae: Ar = 2-(*N*-Ts)pyrrolyl, 0%

[a]Diastereomeric ratios (dr) were determined by NMR analysis of crude products. [b]Reactions were carried out for 1 h. [c]Reactions were carried out for 20 h, extra portions of $Yb(OTf)_3$ (0.1 equiv) were added in 8 and 16 h; 86%-conversion of **2** was observed. [d]Reactions were carried out for 16 h, extra portion of $Yb(OTf)_3$ (0.1 equiv) was added in 8 h.

The studied reactions exhibited high diastereoselectivity, affording products **3**, predominantly as *trans*-isomers (dr 91:9 to 95:5). Relative configuration was initially assigned according to the results of a NOESY experiment for **3a**. The presence of the characteristic H^4-H^{ortho} cross-peak (Fig. 2) allowed us to assign the major isomer to *trans*-**3a**. Thereafter, this conclusion was supported by the results of single crystal X-ray analysis for the major isomers of **3f**,**g**,**r**.[17]

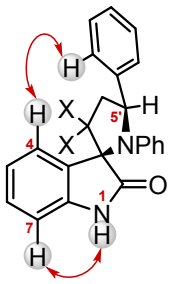
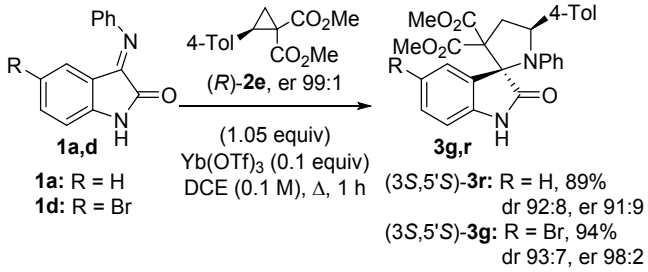


Figure 2. Representative NOE interactions for *trans*-**3a**.

We succeeded in the synthesis of optically active spiro[oxindole-3,2'-pyrrolidines] **3** *via* [3+2]-cycloaddition of the enantiomerically enriched cyclopropane (*R*)-**2e** (er 99:1) to imines **1a**,**d** (Scheme 2). The reaction of (*R*)-**2e** with imine **1a** yielded (3*S*,5'*S*)-**3r** with 91:9 er (with a slight loss in er *vs*. the initial cyclopropane **2e**). The use of Br-derivative **1d** afforded (3*S*,5'*S*)-**3g** with no notable decline in er. The recently reported [3+2]-cycloaddition between triphenyl-1,3,5-triazinane and (*S*)-2-phenylcyclopropane-1,1-diester exhibited a significant loss in stereochemical information.[13b] The absolute configuration of stereocenters in (3*S*,5'*S*)-**3g** was supported by single crystal X-ray analysis.[17] Without imines **1**, (*R*)-**2e** underwent complete racemization under similar conditions.

Scheme 2. Synthesis of Optically Active (3*S*,5'*S*)-**3g**,**r** from Enantiomerically Enriched Cyclopropane (*R*)-**2e**

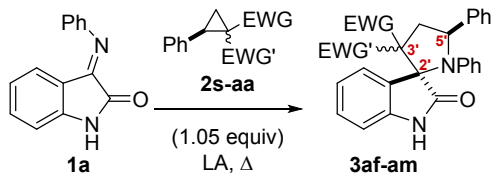


In order to determine the scope of EWG variation, we examined [3+2]-cycloaddition with D-A cyclopropanes **2s–aa** functionalized with keto, nitro, cyano, 2-pyridyl and sulfonyl groups (Table 3). Keto-derived cyclopropanes **2s–u** were able to undergo [3+2]-cycloaddition at lower temperatures (DCM under reflux instead of DCE), although the reaction time increased. The

replacement of the CO_2Me group (**2s**) by the bulkier CO_2Et (**2t**) led to deceleration; thus, an additional amount of the catalyst was required. For the nitro derivative **2v**, the complete conversion of the reactant was observed only under heating in DCE. The desired [3+2]-cycloadduct **3ai** was actually formed; however, only in a moderate yield (41%). Meanwhile, methyl 5-phenyl-4,5-dihydro-1,2-oxazole-3-carboxylate 2-oxide was formed as the major product (49%) *via* Cloke-like rearrangement of nitrocyclopropane **2v**. In reactions with cyano derivatives **2w**,**x**, $Yb(OTf)_3$ was found to be unsuitable as a catalyst. This is apparently related to the shift of complexation equilibrium toward a relatively strong complex between the CN group and $Yb(OTf)_3$, precluding further interactions. As a result, $Yb(OTf)_3$ loses its catalytic ability. Subsequently, the yield of [3+2]-cycloadduct **3** corresponds to the amount of $Yb(OTf)_3$ added to the reaction mixture. $Sc(OTf)_3$ was found to be more appropriate as a catalyst in this reaction; however, in the case of dinitrile **2x**, an equivalent of $Sc(OTf)_3$ was added in total. Moreover, the reactions could only be facilitated by replacing DCE by toluene which has a higher boiling point. A significant increase in reaction time and temperature led to **3ak** only forming in a 35% yield due to considerable tarring. The reactions between **1a** and 2-pyridyl-derived cyclopropane **2y** as well as cyclopropane **2z** (bearing a fragment of Meldrum's acid) exhibited similar efficiencies, affording the corresponding products **3al** and **3am** in 56% and 51% yields respectively. The sulfonyl derivative **2aa** was found to be inert under heating in DCE in the presence of both $Yb(OTf)_3$ and $Sc(OTf)_3$. Heating in toluene led to a slow decay of **2aa**.

The reactions with **2s–z** proceeded with very high diastereoselectivities in regard to the relative configurations of C2' and C5' stereocenters. Similarly to diesters **3a–ac**, the products **3af–am** were formed as *trans*-C2'-C5' isomers (dr > 95:5). However, for compounds **3af**,**ag**,**ai**,**aj**,**al** containing the third stereocenter at C3', the diastereomeric ratios of C3'-epimers were not very high and varied from 60:40 to 80:20 (Table 3). It is noteworthy that these ratios differ from those for the initial cyclopropanes **2s,t,v,w,y**.

Table 3. [3+2]-Cycloaddition with Variation of Electron-Withdrawing Groups in Cyclopropanes **2**



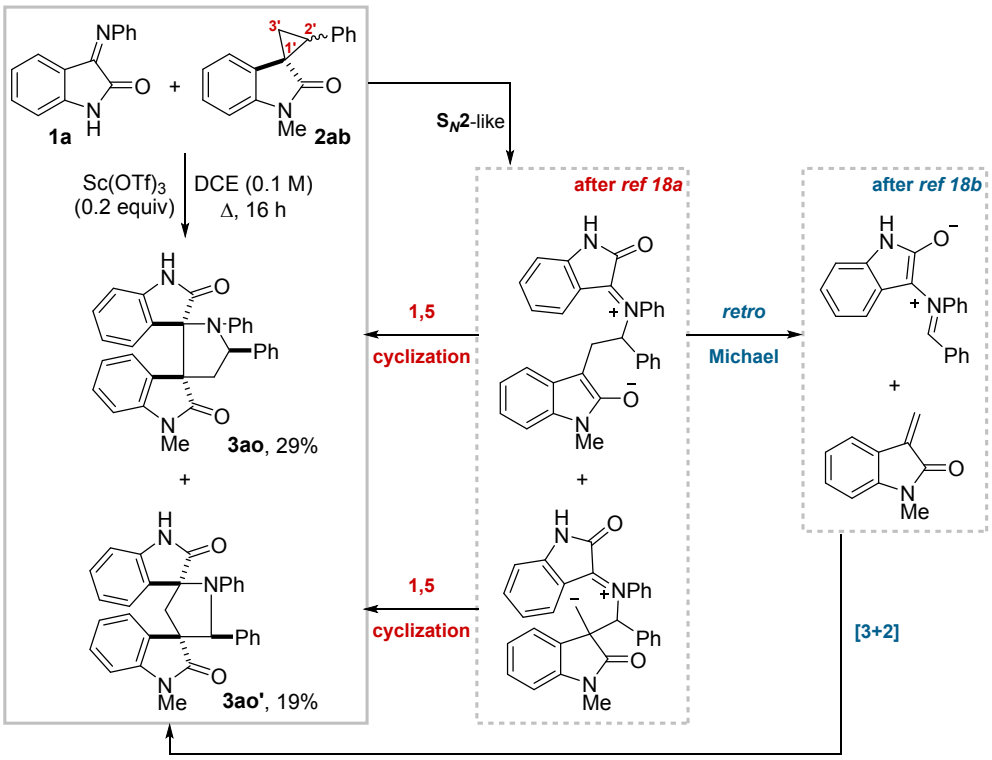
2	EWG	EWG'	LA (equiv)	t (h)	**3**	Yield (%) [dr][a]

s	CO_2Me	COMe	$Yb(OTf)_3$ (0.1)[b]	4	**af**	90 [60:40]
t	CO_2Et	COMe	$Yb(OTf)_3$ (0.1)[b,c]	12	**ag**	73 [63:37]
u	COMe	COMe	$Yb(OTf)_3$ (0.1)[b]	4	**ah**	89
v	CO_2Me	NO_2	$Yb(OTf)_3$ (0.1)[d]	2	**ai**[e]	41 [80:20]
w	CO_2Me	CN	$Sc(OTf)_3$ (0.2)[f]	8	**aj**[g]	73 [64:36]
x	CN	CN	$Sc(OTf)_3$ (0.5)[f, h]	16	**ak**[g]	35
y	CO_2Me	2-Py	$Yb(OTf)_3$ (0.1)[d]	8	**al**[g]	56 [71:29]
z	Meldrum's acid		$Yb(OTf)_3$ (0.1)[b]	2	**am**	51
aa	CO_2Me	SO_2Ph	$Sc(OTf)_3$ (0.2)[d]	12	**an**	-[i]

[a]Diastereomeric ratios (dr) for 3'-epimers were determined by NMR analysis of crude products; dr associated with C2'-C5' related configuration were > 95:5. [b]DCM was used as a solvent. [c]Extra portion of $Yb(OTf)_3$ (0.1 equiv) was added in 8 h. [d]DCE was used as a solvent. [e]Methyl 5-phenyl-4,5-dihydro-1,2-oxazole-3-carboxylate 2-oxide was obtained as the major product in a 49% yield. [f]Toluene was used as a solvent. [g]95% conversion of **1a** was observed. [h]Extra portion of $Sc(OTf)_3$ (0.5 equiv) was added in 8 h. [i]No reaction.

An unexpected result was obtained in the reaction of imine **1a** with the DA cyclopropane **2ab** containing the oxindole unit as an acceptor (Scheme 3). Besides the regular [3+2]-cycloadduct **3ao** forming *via* the insertion of **1a** into the C1'–C2' bond of **2ab**, regioisomer **3ao'** was also obtained. A similar reactivity of DA cyclopropanes was earlier observed in the reactions of 2-arylcyclopropane-1,1-diesters with diazenes and nitrosoarenes. It was associated with insertion into the C2'-C3' bond of cyclopropanes or fragmentation /recombination of reaction intermediates.[18] The structures of **3ao** and **3ao'** were unambiguously proved by single crystal X-ray analysis.[17]

Scheme 3. Reaction of Imine **1a** with Spiro[cyclopropane-3,1'-oxindole] **2ab**



We carried out preliminary *in vitro* tests for a series of synthesized spiro[oxindole-3,2'-pyrrolidines] **3** against human prostate cancer cell lines LNCaP (p53+) and PC-3 (p53-), noting the potential ability of spiro[oxindole-3,2'-pyrrolidines] to inhibit MDM2-p53 interaction that can result in regression of cancer cells. Nutlin-3a was used as a reference compound. The samples containing **3a,k,l,o–r,v,aa**, were found to have no significant antiproliferative effect against these cells (IC_{50} > 100 μM). Compounds **3i**,**y**,**z**,**ai** exhibited an antiproliferative effect towards LNCaP comparable to that of Nutlin-3a (Table 4). However, the selectivity that is associated with the difference between the effects against p53-containing LNCaP and 53-free PC-3 was not observed. Meanwhile, **3j**,**s**,**x** displayed high selectivity against LNCaP (p53+) in combination with an acceptable IC_{50} value. Within the examined series, compound **3j** was found to be the most promising for its further investigation as a selective inhibitor of MDM2-p53 interaction.

Table 4. Cell Assay

Compound	IC_{50} (μM)[a]	
	PC-3 (p53-)	LNCaP (p53+)
3i	8.2–9.3	6.2–8.3
3j	>100	6.3–7.4

3m,n,w	>50	>20
3s	>100	18–20
3t	18–20	18–20
3u	17–20	17–20
3x	>100	18–20
3y	13–16	6.7–8.2
3z	9.8–11.2	7.9–8.9
3af	>20	>20
3ai	6.8–8.5	6.2–7.9
Nutlin-3a	28.1–29.6	2.4–2.8

[a]MTS assay was used.

CONCLUSIONS

A new approach to spiro[oxindole-3,2'-pyrrolidines] was developed based on the [3+2]-cycloaddition of DA cyclopropanes to iminooxindoles. Commonly used 2-substituted cyclopropane-1,1-diesters were found to be highly appropriate substrates in their efficient transformations into the desired heterocycles under catalytic conditions with $Yb(OTf)_3$ or $Sc(OTf)_3$. The extension of this method to DA cyclopropanes of other types revealed that keto, cyano, nitro, 2-pyridyl-functionalized derivatives can undergo similar transformations quite efficiently.

The reactions exhibit high diastereoselectivity, producing spiro[oxindole-3,2'-pyrrolidine] with a strong predominance of *trans*-C3–C5' isomers. Moreover, the use of enantiomerically enriched DA cyclopropanes results in straightforward formation of optically active products with high er. The stereochemical results allow for a mechanistic explanation that relies upon stereospecific C–N bond formation *via* an initial S_N2-like attack of the imine on the DA cyclopropane-LA complex, followed by diastereoselective pyrrolidine ring closure. This mechanism is in agreement with the reported ones.

In vitro tests of a series of the synthesized compounds towards p53-containing and p53-free cell lines, LNCaP (p53+) and PC-3 (p53-), allow for selection of several structures that are promising in terms of their further investigation as p53-MDM inhibitors.

EXPERIMENTAL SECTION

General Information

NMR spectra were acquired either on Bruker Avance 600 MHz spectrometer at room temperature; the chemical shifts δ were measured in ppm with respect to solvent (^{1}H: $CDCl_3$, δ = 7.27 ppm; DMSO-d_6, δ = 2.50 ppm; $^{13}C\{^1H\}$: $CDCl_3$, δ = 77.0 ppm; DMSO-d_6, δ = 39.5 ppm). Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, double doublet. Coupling constants (*J*) are given in Hertz (Hz). The structures of compounds were elucidated with the aid of 1D NMR (^{1}H, $^{13}C\{^1H\}$) and 2D NMR (^{1}H-^{1}H COSY, ^{1}H-^{1}H NOESY, ^{1}H-^{13}C HSQC and HMBC) spectroscopy. High resolution and accurate mass measurements were carried out using a BrukermicroTOF-Q™ ESI-TOF (Electro Spray Ionization / Time of Flight) and Thermo Scientific™ LTQ Orbitrap mass spectrometers. IR spectra were recorded on Agilent FTIR Cary 630 spectrometers with ATR (Attenuated Total Reflectance) module. Melting points (mp) were determined using Electrothermal IA 9100 capillary melting point apparatus. Crystallographic data were collected using MoKα (λ = 0.71073 Å) using a w-scan mode. Absorption corrections based on measurements of equivalent reflections were applied. For **3f** and **3r**, the X-ray single crystal data have been collected on a Bruker D8Venture (Photon100 CMOS detector, IμS-microsource, focusing mirrors) diffractometer equipped with a Cryostream (Oxford Cryosystems) open-flow nitrogen cryostats at the temperature 120.0(2) K. For (3*RS*,5'*RS*)-**3g**, (3*S*,5'*S*)-**3g**, **3ao**, and **3ao'**, the X-ray single crystal data have been collected on a Bruker SMART(Photon II CMOS detector, fine-focus sealed X-ray tube) diffractometer equipped with a Cryostream (Oxford Cryosystems) open-flow nitrogen cryostats at the temperature 150.0(2) K. All structures were solved by direct method and refined by full-matrix least squares on F2 for all data using Olex21[19] and SHELXTL2[20] software. Analytical thin layer chromatography (TLC) was carried out with silica gel plates (silica gel 60, F_{254}, supported on aluminium) visualized with UV lamp (254 nm). Column chromatography was performed on silica gel 60 (230-400 mesh). Cyclopropanes **2** were synthesized according to procedures reported earlier: **2a-r**,**w**,**y-ab**,[21] **2s-u**,**x**,[22] **2v**,[23] (*R*)-**2e**.[24] The samples of cyclopropanes **2** used here were identical to those used in our previous works.[3h,25]

Synthesis of iminooxindoles 1 (General procedure).[26] The suspension of isatin (1.0 equiv) in ethanol was heated under reflux. After isatin dissolving, acetic acid (3 drops) and amine (1.0

equiv) were added to the reaction mixture. Then the reaction mixture was heated under reflux for the specified time and cooled down to room temperature. The precipitate was collected by filtration, washed with cold water and dried under reduced pressure.

3-(Phenylimino)-1,3-dihydro-2*H*-indol-2-one (1a).[27a] A mixture of indoline-2,3-dione (5.000 g, 34.01 mmol) and aniline (3.1 mL, 34.01 mmol) in ethanol (75 mL) in the presence of acetic acid was heated under reflux for 6 h yielding **1a** (6.508 g, 86%) as yellow solid, mp 220–221 °C. Two diastereomers *E*:*Z* = 85:15. (*E*)-**1a**: ^{1}H NMR (DMSO-d_6, 600 MHz): δ = 6.33 (d, ^3J 7.6 Hz, 1H, Ar), 6.70 (ddd, ^3J 7.6, ^3J 7.7, ^4J 0.7 Hz, 1H, Ar), 6.89 (d, ^3J 7.8 Hz, 1H, Ar), 6.96–7.00 (m, 2H, Ar), 7.25 (t, ^3J 7.4 Hz, 1H, Ar), 7.33 (ddd, ^3J 7.7, ^3J 7.8, ^4J 1.1 Hz, 1H, Ar), 7.46 (dd, ^3J 7.4, ^3J 8.4 Hz, 2H, Ar), 10.99 (br. s, 1H, NH); ^{13}C{^{1}H} NMR (DMSO-d_6, 150 MHz): δ = 111.5 (CH, Ar), 117.2 (2 × CH, Ar), 119.1 (C, Ar), 121.7 (CH, Ar), 124.9 (CH, Ar), 125.4 (CH, Ar), 129.6 (2 × CH, Ar), 134.4 (CH, Ar), 147.0 (C, Ar), 150.6 (C, Ar), 155.0 (C=N), 163.5 (C=O). (*Z*)-**1a**: ^{1}H NMR (DMSO-d_6, 600 MHz): δ = 6.86 (d, ^3J 7.8 Hz, 1H, Ar), 6.96–7.00 (m, 2H, Ar), 7.05 (ddd, ^3J 7.6, ^3J 7.8, ^4J 0.7 Hz, 1H, Ar), 7.10 (t, ^3J 7.4 Hz, 1H, Ar), 7.28–7.31 (m, 2H, Ar), 7.43–7.46 (m, 1H, Ar), 7.58 (d, ^3J 7.2 Hz, 1H, Ar), 10.87 (br. s, 1H, NH); ^{13}C{^{1}H} NMR (DMSO-d_6, 150 MHz): δ = 110.8 (CH, Ar), 115.7 (2 × CH, Ar), 121.4 (C, Ar), 122.3 (CH, Ar), 122.8 (CH, Ar), 124.4 (CH, Ar), 128.3 (2 × CH, Ar), 134.2 (CH, Ar), 145.7 (C, Ar), 149.0 (C, Ar), 152.8 (C=N), 158.4 (C=O).

5-Fluoro-3-(phenylimino)-1,3-dihydro-2*H*-indol-2-one (1b).[27b] A mixture of 5-fluoroindoline-2,3-dione (1.000 g, 6.06 mmol) and aniline (550 µL, 6.06 mmol) in ethanol (20 mL) in the presence of acetic acid was heated under reflux for 6 h yielding **1b** (1.253 g, 86%) as orange solid, mp 237–238 °C. Two diastereomers *E*:*Z* = 82:18. (*E*)-**1b**: ^{1}H NMR (DMSO-d_6, 600 MHz): δ = 5.95 (dd, $^3J_{HF}$ 8.5, ^4J 2.7 Hz, 1H, Ar), 6.89 (dd, ^3J 8.6, $^4J_{HF}$ 4.3 Hz, 1H, Ar), 6.97–7.00 (m, 2H, Ar), 7.19 (ddd, ^3J 8.6, $^3J_{HF}$ 9.2, ^4J 2.7 Hz, 1H, Ar), 7.25–7.29 (m, 1H, Ar), 7.48 (dd, ^3J 7.5, ^3J 8.4 Hz, 2H, Ar), 10.99 (br. s, 1H, NH); ^{13}C{^{1}H} NMR (DMSO-d_6, 150 MHz): δ = 111.87 ($^3J_{CF}$ 10 Hz, C, Ar), 111.92 ($^2J_{CF}$ 26 Hz, CH, Ar), 112.6 ($^3J_{CF}$ 8 Hz, CH, Ar), 117.2 (2 × CH, Ar), 120.8 ($^2J_{CF}$ 24 Hz, CH, Ar), 125.3 (CH, Ar), 129.7 (2 × CH, Ar), 143.3 (C, Ar), 150.1 (C, Ar), 154.6 ($^4J_{CF}$ 2 Hz, C=N, Ar), 156.7 ($^1J_{CF}$ 238 Hz, C, Ar), 163.5 (C=O). (*Z*)-**1b**: ^{1}H NMR (DMSO-d_6, 600 MHz): δ = 6.85 (dd, ^3J 8.6, $^4J_{HF}$ 4.1 Hz, 1H, Ar), 7.01–7.03 (m, 2H, Ar), 7.12 (t, ^3J 7.4 Hz, 1H, Ar), 7.25–7.29 (m, 1H, Ar), 7.31 (dd, ^3J 7.4, ^3J 8.3 Hz, 2H, Ar), 7.37 (dd, $^3J_{HF}$ 7.6, ^4J 2.6 Hz, 1H, Ar), 10.99 (br. s, 1H, NH); ^{13}C{^{1}H} NMR (DMSO-d_6, 150 MHz): δ = 109.7 ($^2J_{CF}$ 25 Hz, CH, Ar), 116.0 ($^3J_{CF}$ 8 Hz, CH, Ar), 119.2 (2 × CH, Ar), 120.4 ($^2J_{CF}$ 24 Hz, CH, Ar), 122.6 ($^3J_{CF}$ 8 Hz, C, Ar), 124.8 (CH, Ar), 128.3 (2 × CH, Ar), 141.9 (C, Ar), 148.6 (C, Ar), 152.5 ($^4J_{CF}$ 3 Hz, C=N, Ar), 158.2 ($^1J_{CF}$ 238 Hz, C, Ar), 158.5 (C=O).

5-Chloro-3-(phenylimino)-1,3-dihydro-2*H*-indol-2-one (1c).[27c] A mixture of 5-chloroindoline-2,3-dione (1.000 g, 5.51 mmol) and aniline (500 µL, 5.51 mmol) in ethanol (18 mL) in the presence of acetic acid was heated under reflux for 12 h yielding **1c** (1.113 g, 79%) as orange solid, mp 256–257 °C. Two diastereomers *E*:*Z* = 83:17. (*E*)-**1c**: ^{1}H NMR (DMSO-d_6, 600 MHz): δ = 6.20 (dd, ^{4}J 2.3, ^{5}J 0.5 Hz, 1H, Ar), 6.90 (dd, ^{3}J 8.4, ^{5}J 0.5 Hz, 1H, Ar), 6.98–7.01 (m, 2H, Ar), 7.29 (t, ^{3}J 7.5 Hz, 1H, Ar), 7.38 (dd, ^{3}J 8.4, ^{4}J 2.3 Hz, 1H, Ar), 7.49 (dd, ^{3}J 7.5, ^{3}J 8.4 Hz, 2H, Ar), 11.10 (br. s, 1H, NH); ^{13}C{^{1}H} NMR (DMSO-d_6, 150 MHz): δ = 113.1 (CH, Ar), 116.8 (C, Ar), 117.2 (2 × CH, Ar), 124.7 (CH, Ar), 125.26 (C, Ar), 125.29 (CH, Ar), 129.7 (2 × CH, Ar), 133.7 (CH, Ar), 145.7 (C, Ar), 150.2 (C, Ar), 154.2 (C=N), 163.2 (C=O). (*Z*)-**1c**: ^{1}H NMR (DMSO-d_6, 600 MHz): δ = 6.87 (dd, ^{3}J 8.4, ^{5}J 0.4 Hz, 1H, Ar), 7.02–7.04 (m, 2H, Ar), 7.13 (t, ^{3}J 7.5 Hz, 1H, Ar), 7.31 (dd, ^{3}J 7.5, ^{3}J 8.4 Hz, 2H, Ar), 7.47 (dd, ^{3}J 8.4, ^{4}J 2.2 Hz, 1H, Ar), 7.55 (dd, ^{4}J 2.2, ^{5}J 0.4 Hz, 1H, Ar), 11.10 (br. s, 1H, NH); ^{13}C{^{1}H} NMR (DMSO-d_6, 150 MHz): δ = 112.3 (CH, Ar), 119.3 (2 × CH, Ar), 122.3 (CH, Ar), 123.0 (C, Ar), 124.9 (CH, Ar), 126.4 (C, Ar), 128.3 (2 × CH, Ar), 133.4 (CH, Ar), 144.3 (C, Ar), 148.5 (C, Ar), 152.0 (C=N), 158.2 (C=O).

5-Bromo-3-(phenylimino)-1,3-dihydro-2*H*-indol-2-one (1d).[26d,27c] A mixture of 5-bromoindoline-2,3-dione (452 mg, 2.00 mmol) and aniline (180 µL, 2.00 mmol) in ethanol (6.7 mL) in the presence of acetic acid was heated under reflux for 6 h yielding **1d** (510 mg, 85%) as orange solid, mp 261–262 °C. Two diastereomers *E*:*Z* = 84:16. (*E*)-**1d**: ^{1}H NMR (DMSO-d_6, 600 MHz): δ = 6.34 (dd, ^{4}J 2.1, ^{5}J 0.3 Hz, 1H, Ar), 6.86 (dd, ^{3}J 8.4, ^{5}J 0.3 Hz, 1H, Ar), 6.98–7.00 (m, 2H, Ar), 7.29 (t, ^{3}J 7.5 Hz, 1H, Ar), 7.47–7.52 (m, 3H, Ar), 11.11 (br. s, 1H, NH); ^{13}C{^{1}H} NMR (DMSO-d_6, 150 MHz): δ = 112.9 (C, Ar), 113.5 (CH, Ar), 117.2 (2 × CH, Ar), 117.3 (C, Ar), 125.3 (CH, Ar), 127.6 (CH, Ar), 129.7 (2 × CH, Ar), 136.5 (CH, Ar), 146.0 (C, Ar), 150.2 (C, Ar), 154.1 (C=N), 163.0 (C=O). (*Z*)-**1d**: ^{1}H NMR (DMSO-d_6, 600 MHz): δ = 6.83 (dd, ^{3}J 8.3, ^{5}J 0.4 Hz, 1H, Ar), 7.02–7.04 (m, 2H, Ar), 7.13 (t, ^{3}J 7.4 Hz, 1H, Ar), 7.32 (dd, ^{3}J 7.4, ^{3}J 8.3 Hz, 2H, Ar), 7.60 (dd, ^{3}J 8.3, ^{4}J 2.1 Hz, 1H, Ar), 7.67 (dd, ^{4}J 2.1, ^{5}J 0.4 Hz, 1H, Ar), 11.11 (br. s, 1H, NH); ^{13}C{^{1}H} NMR (DMSO-d_6, 150 MHz): δ = 112.8 (CH, Ar), 113.9 (C, Ar), 119.3 (2 × CH, Ar), 123.4 (C, Ar), 124.9 (CH, Ar), 125.0 (CH, Ar), 128.3 (2 × CH, Ar), 136.2 (CH, Ar), 144.7 (C, Ar), 148.5 (C, Ar), 151.8 (C=N), 158.0 (C=O).

3-[(4-Fluorophenyl)imino]-1,3-dihydro-2*H*-indol-2-one (1e).[27a] A mixture of indoline-2,3-dione (1.000 g, 6.80 mmol) and 4-fluoroaniline (645 µL, 6.80 mmol) in ethanol (15 mL) in the presence of acetic acid was heated under reflux for 10 h yielding **1e** (1.318 g, 81%) as red solid, mp 221–222 °C. Two diastereomers *E*:*Z* = 81:19. (*E*)-**1e**: ^{1}H NMR (DMSO-d_6, 600 MHz): δ = 6.44 (d, ^{3}J 7.8 Hz, 1H, Ar), 6.75 (ddd, ^{3}J 7.7, ^{3}J 7.8, ^{4}J 1.0 Hz, 1H, Ar), 6.89 (d, ^{3}J 7.8 Hz, 1H,

Ar), 7.04 (dd, ^3J 8.9, $^4J_{HF}$ 5.0 Hz, 2H, Ar), 7.30 (dd, $^3J_{HF}$ 8.8, ^3J 8.9 Hz, 2H, Ar), 7.34 (ddd, ^3J 7.7, ^3J 7.8, ^4J 1.2 Hz, 1H, Ar), 10.98 (br. s, 1H, NH); $^{13}C\{^1H\}$ NMR (DMSO-d_6, 150 MHz): δ = 111.6 (CH, Ar), 115.6 (C, Ar), 116.4 ($^2J_{CF}$ 23 Hz, 2 × CH, Ar), 119.4 ($^3J_{CF}$ 8 Hz, 2 × CH, Ar), 121.8 (CH, Ar), 125.3 (CH, Ar), 134.5 (CH, Ar), 146.7 ($^4J_{CF}$ 2 Hz, C, Ar), 147.0 (C, Ar), 155.5 (C=N), 159.7 ($^1J_{CF}$ 242 Hz, C, Ar), 163.4 (C=O). (*Z*)-**1e**: ^{1}H NMR (DMSO-d_6, 600 MHz): δ = 6.86 (d, ^3J 7.8 Hz, 1H, Ar), 7.02–7.06 (m, 1H, Ar), 7.07–7.10 (m, 2H, Ar), 7.13 (dd, ^3J 8.9, $^3J_{HF}$ 8.9 Hz, 2H, Ar), 7.44 (ddd, ^3J 7.7, ^3J 7.8, ^4J 1.3 Hz, 1H, Ar), 7.57 (dd, ^3J 7.5, ^4J 0.6 Hz, 1H, Ar), 10.86 (br. s, 1H, NH); $^{13}C\{^1H\}$ NMR (DMSO-d_6, 150 MHz): δ = 110.7 (CH, Ar), 114.9 ($^2J_{CF}$ 23 Hz, 2 × CH, Ar), 121.4 ($^3J_{CF}$ 9 Hz, 2 × CH, Ar), 121.5 (C, Ar), 122.3 (CH, Ar), 122.7 (CH, Ar), 134.2 (CH, Ar), 145.1 ($^4J_{CF}$ 2 Hz, C, Ar), 145.6 (C, Ar), 153.4 (C=N), 158.5 (C=O), 159.7 ($^1J_{CF}$ 242 Hz, C, Ar).

3-[(4-Chlorophenyl)imino]-1,3-dihydro-2*H*-indol-2-one (1f).[27a] A mixture of indoline-2,3-dione (1.000 g, 6.80 mmol) and 4-chloroaniline (867 mg, 6.80 mmol) in ethanol (15 mL) in the presence of acetic acid was heated under reflux for 10 h yielding **1f** (1.537 g, 88%) as orange solid, mp 259–260 °C. Two diastereomers *E*:*Z* = 77:23. (*E*)-**1f**: ^{1}H NMR (DMSO-d_6, 600 MHz): δ = 6.43 (d, ^3J 7.7 Hz, 1H, Ar), 6.75 (dd, ^3J 7.6, ^3J 7.7 Hz, 1H, Ar), 6.90 (d, ^3J 7.8 Hz, 1H, Ar), 7.02 (d, ^3J 8.5 Hz, 2H, Ar), 7.31–7.37 (m, 1H, Ar), 7.50 (d, ^3J 8.5 Hz, 2H, Ar), 10.99 (br. s, 1H, NH); $^{13}C\{^1H\}$ NMR (DMSO-d_6, 150 MHz): δ = 111.9 (CH, Ar), 115.7 (C, Ar), 119.6 (2 × CH, Ar), 122.1 (CH, Ar), 125.6 (CH, Ar), 129.3 (C, Ar), 129.8 (2 × CH, Ar), 135.0 (CH, Ar), 147.2 (C, Ar), 149.3 (C, Ar), 155.6 (C=N), 163.6 (C=O). (*Z*)-**1f**: ^{1}H NMR (DMSO-d_6, 600 MHz): δ = 6.87 (d, ^3J 7.8 Hz, 1H, Ar), 7.00–7.03 (m, 2H, Ar), 7.06 (dd, ^3J 7.2, ^3J 7.7 Hz, 1H, Ar), 7.31–7.37 (m, 2H, Ar), 7.45 (ddd, ^3J 7.7, ^3J 7.8, ^4J 0.6 Hz, 1H, Ar), 7.57 (d, ^3J 7.2 Hz, 1H, Ar), 10.88 (br. s, 1H, NH); $^{13}C\{^1H\}$ NMR (DMSO-d_6, 150 MHz): δ = 111.1 (CH, Ar), 121.1 (2 × CH, Ar), 121.3 (C, Ar), 122.6 (CH, Ar), 123.2 (CH, Ar), 128.5 (2 × CH, Ar), 128.7 (C, Ar), 134.7 (CH, Ar), 146.0 (C, Ar), 148.1 (C, Ar), 153.8 (C=N), 158.7 (C=O).

3-[(2-Chlorophenyl)imino]-1,3-dihydro-2*H*-indol-2-one (1g).[27a] A mixture of indoline-2,3-dione (1.000 g, 6.80 mmol) and 2-chloroaniline (715 µL, 6.80 mmol) in ethanol (15 mL) in the presence of acetic acid was heated under reflux for 10 h yielding **1g** as a 35:65 mixture with the starting isatin. Yield **1g** (343 mg, 20%). Two diastereomers *E*:*Z* = 77:23. (*E*)-**1g**: ^{1}H NMR (DMSO-d_6, 600 MHz): δ = 6.25 (d, ^3J 7.6 Hz, 1H, Ar), 6.74 (dd, ^3J 7.6, ^3J 7.6 Hz, 1H, Ar), 6.88–6.93 (m, 1H, Ar), 7.07–7.11 (m, 1H, Ar), 7.24–7.28 (m, 1H, Ar), 7.36 (dd, ^3J 7.7, ^3J 7.7 Hz, 1H, Ar), 7.40–7.43 (m, 1H, Ar), 7.54–7.59 (m, 1H, Ar), 11.02 (br. s, 1H, NH); $^{13}C\{^1H\}$ NMR (DMSO-d_6, 150 MHz): δ = 112.0 (CH, Ar), 116.0 (C, Ar), 119.1 (CH, Ar), 121.3 (C, Ar), 122.4 (CH, Ar), 125.3 (CH, Ar), 126.5 (CH, Ar), 128.7 (CH, Ar), 130.3 (CH, Ar), 135.4 (CH, Ar),

147.2 (C, Ar), 147.4 (C, Ar), 156.8 (C=N), 163.4 (C=O). (*Z*)-**1g**: ^{1}H NMR (DMSO-d_6, 600 MHz): δ = 6.88–6.93 (m, 1H, Ar), 6.99–7.02 (m, 1H, Ar), 7.24–7.28 (m, 1H, Ar), 7.40 (dd, ^{3}J 7.5, ^{3}J 7.5 Hz, 1H, Ar), 7.45–7.48 (m, 2H, Ar), 7.54–7.59 (m, 1H, Ar), 7.64 (d, ^{3}J 7.4 Hz, 1H, Ar), 11.02 (br. s, 1H, NH); ^{13}C{^{1}H} NMR (DMSO-d_6, 150 MHz): δ = 111.3 (CH, Ar), 119.9 (CH, Ar), 120.7 (C, Ar), 121.9 (C, Ar), 122.8 (CH, Ar), 123.5 (CH, Ar), 125.4 (CH, Ar), 127.5 (CH, Ar), 129.3 (CH, Ar), 135.2 (CH, Ar), 146.4 (C, Ar), 147.0 (C, Ar), 155.1 (C=N), 158.5 (C=O).

3-[(4-Bromophenyl)imino]-1,3-dihydro-2*H*-indol-2-one (1h).[27a] A mixture of indoline-2,3-dione (1.000 g, 6.80 mmol) and 4-bromoaniline (1.163 g, 6.80 mmol) in ethanol (15 mL) in the presence of acetic acid was heated under reflux for 6 h yielding **1h** (1.825 g, 89%) as orange solid, mp 272–273 °C. Two diastereomers *E*:*Z* = 77:23. (*E*)-**1h**: ^{1}H NMR (DMSO-d_6, 600 MHz): δ = 6.44 (dd, ^{3}J 7.8, ^{4}J 0.9 Hz, 1H, Ar), 6.77 (ddd, ^{3}J 7.7, ^{3}J 7.8, ^{4}J 0.9 Hz, 1H, Ar), 6.90 (d, ^{3}J 7.8 Hz, 1H, Ar), 6.95–6.99 (m, 2H, Ar), 7.36 (ddd, ^{3}J 7.7, ^{3}J 7.8, ^{4}J 1.1 Hz, 1H, Ar), 7.64 (d, ^{3}J 8.7 Hz, 2H, Ar), 10.97 (br. s, 1H, NH); ^{13}C{^{1}H} NMR (DMSO-d_6, 150 MHz): δ = 111.6 (CH, Ar), 115.6 (C, Ar), 117.1 (C, Ar), 119.8 (2 × CH, Ar), 121.9 (CH, Ar), 125.4 (CH, Ar), 132.5 (2 × CH, Ar), 134.7 (CH, Ar), 147.1 (C, Ar), 149.6 (C, Ar), 155.3 (C=N), 163.3 (C=O). (*Z*)-**1h**: ^{1}H NMR (DMSO-d_6, 600 MHz): δ = 6.86 (d, ^{3}J 7.8 Hz, 1H, Ar), 6.95–6.99 (m, 2H, Ar), 7.06 (ddd, ^{3}J 7.5, ^{3}J 7.8, ^{4}J 0.8 Hz, 1H, Ar), 7.44–7.48 (m, 3H, Ar), 7.58 (d, ^{3}J 7.6, ^{4}J 0.8 Hz, 1H, Ar), 10.97 (br. s, 1H, NH); ^{13}C{^{1}H} NMR (DMSO-d_6, 150 MHz): δ = 110.8 (CH, Ar), 116.7 (C, Ar), 121.19 (C, Ar), 121.23 (2 × CH, Ar), 122.4 (CH, Ar), 123.0 (CH, Ar), 131.1 (2 × CH, Ar), 134.5 (CH, Ar), 145.9 (C, Ar), 148.4 (C, Ar), 153.5 (C=N), 158.5 (C=O).

3-[(4-Methylphenyl)imino]-1,3-dihydro-2*H*-indol-2-one (1i).[27a] A mixture of indoline-2,3-dione (1.349 g, 9.18 mmol) and *p*-toluidine (982 mg, 9.18 mmol) in ethanol (20 mL) in the presence of acetic acid was heated under reflux for 6 h yielding **1i** (1.887 g, 87%) as yellow solid, mp 225–226 °C. Two diastereomers *E*:*Z* = 86:14. (*E*)-**1i**: ^{1}H NMR (DMSO-d_6, 600 MHz): δ = 2.35 (s, 3H, CH_3), 6.48 (d, ^{3}J 7.4 Hz, 1H, Ar), 6.72 (ddd, ^{3}J 7.4, ^{3}J 7.6, ^{4}J 0.6 Hz, 1H, Ar), 6.87–6.90 (m, 3H, Ar), 7.26 (d, ^{3}J 8.1 Hz, 2H, Ar), 7.33 (ddd, ^{3}J 7.6, ^{3}J 7.7, ^{4}J 1.0 Hz, 1H, Ar), 10.96 (br. s, 1H, NH); ^{13}C{^{1}H} NMR (DMSO-d_6, 150 MHz): δ = 20.58 (CH_3), 111.5 (CH, Ar), 115.7 (C, Ar), 117.5 (2 × CH, Ar), 121.7 (CH, Ar), 125.2 (CH, Ar), 130.0 (2 × CH, Ar), 134.2 (C, Ar), 134.3 (CH, Ar), 146.9 (C, Ar), 147.8 (C, Ar), 154.8 (C=N), 163.6 (C=O). (*Z*)-**1i**: ^{1}H NMR (DMSO-d_6, 600 MHz): δ = 2.29 (s, 3H, CH_3), 6.85 (d, ^{3}J 7.8 Hz, 1H, Ar), 6.94 (d, ^{3}J 8.2 Hz, 2H, Ar), 7.04 (dd, ^{3}J 7.4, ^{3}J 7.6 Hz, 1H, Ar), 7.11 (d, ^{3}J 8.2 Hz, 2H, Ar), 7.43 (ddd, ^{3}J 7.6, ^{3}J 7.8, ^{4}J 1.1 Hz, 1H, Ar), 7.56 (d, ^{3}J 7.4 Hz, 1H, Ar), 10.96 (br. s, 1H, NH); ^{13}C{^{1}H} NMR (DMSO-d_6, 150 MHz): δ = 20.61 (CH_3), 110.7 (CH, Ar), 119.7 (2 × CH, Ar), 122.3 (CH, Ar),

122.6 (CH, Ar), 128.8 (2 × CH, Ar), 133.96 (CH, C, Ar), 133.99 (C, Ar), 145.4 (C, Ar), 146.2 (C, Ar), 152.5 (C=N), 158.5 (C=O).

3-[(4-Methoxyphenyl)imino]-1,3-dihydro-2*H*-indol-2-one (1j).[27a] A mixture of indoline-2,3-dione (1.294 g, 8.80 mmol) and 4-methoxyaniline (1.083 g, 8.80 mmol) in ethanol (20 mL) in the presence of acetic acid was heated under reflux for 6 h yielding **1j** (2.007 g, 90%) as orange solid, mp 234–235 °C. Two diastereomers *E*:*Z* = 83:17. (*E*)-**1j**: ^{1}H NMR (DMSO-d_6, 600 MHz): δ = 3.79 (s, 3H, OCH_3), 6.65 (d, ^3J 7.7 Hz, 1H, Ar), 6.73 (ddd, ^3J 7.6, ^3J 7.7, ^4J 0.8 Hz, 1H, Ar), 6.87–6.90 (m, 1H, Ar), 6.98 (d, ^3J 8.9 Hz, 2H, Ar), 7.02 (d, ^3J 8.9 Hz, 2H, Ar), 7.32 (ddd, ^3J 7.7, ^3J 7.8, ^4J 1.2 Hz, 1H, Ar), 10.92 (br. s, 1H, NH); ^{13}C{^{1}H} NMR (DMSO-d_6, 150 MHz): δ = 55.3 (OCH_3), 111.5 (CH, Ar), 114.7 (2 × CH, Ar), 115.8 (C, Ar), 119.5 (2 × CH, Ar), 121.7 (CH, Ar), 125.0 (CH, Ar), 134.2 (CH, Ar), 143.1 (C, Ar), 146.8 (C, Ar), 154.5 (C, Ar), 157.1 (C=N), 163.7 (C=O). (*Z*)-**1j**: ^{1}H NMR (DMSO-d_6, 600 MHz): δ = 3.76 (s, 3H, OCH_3), 6.84 (d, ^3J 7.8 Hz, 1H, Ar), 6.87–6.90 (m, 2H, Ar), 7.01–7.04 (m, 1H, Ar), 7.18 (d, ^3J 8.9 Hz, 2H, Ar), 7.40 (ddd, ^3J 7.7, ^3J 7.8, ^4J 1.2 Hz, 1H, Ar), 7.54 (d, ^3J 7.4 Hz, 1H, Ar), 10.92 (br. s, 1H, NH); ^{13}C{^{1}H} NMR (DMSO-d_6, 150 MHz): δ = 55.2 (OCH_3), 110.6 (CH, Ar), 113.4 (2 × CH, Ar), 115.8 (C, Ar), 122.2 (CH, Ar), 122.3 (CH, Ar), 122.8 (2 × CH, Ar), 133.5 (CH, Ar), 141.1 (C, Ar), 145.0 (C, Ar), 151.6 (C, Ar), 157.6 (C=N), 158.7 (C=O).

3-(Butylimino)-1,3-dihydro-2*H*-indol-2-one (1k).[27d] A mixture of indoline-2,3-dione (3.000 g, 20.41 mmol) and butylamine (2.0 mL, 20.41 mmol) in ethanol (30 mL) was stirred for 2 h yielding **1k** (3.760 g, 91%) as yellow solid, mp 102–103 °C. Two diastereomers *E*:*Z* = 75:25. (*E*)-**1k**: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 0.94–0.99 (m, 3H, CH_3), 1.43–1.55 (m, 2H, CH_2), 1.89–1.95 (m, 2H, CH_2), 4.02 (t, ^3J 7.1 Hz, 2H, NCH_2), 6.97 (d, ^3J 7.8 Hz, 1H, Ar), 6.99–7.05 (m, 1H, Ar), 7.34 (ddd, ^3J 7.6, ^3J 7.8, ^3J 0.8 Hz, 1H, Ar), 7.63 (d, ^3J 7.5 Hz, 1H, Ar), 10.31 (br. s, 1H, NH); ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ = 13.78 (CH_3), 20.8 (CH_2), 32.6 (CH_2), 54.1 (NCH_2), 111.9 (CH, Ar), 117.1 (C, Ar), 122.74 (CH, Ar), 126.8 (CH, Ar), 133.2 (CH, Ar), 145.1 (C, Ar), 154.7 (C=N), 165.9 (C=O). (*Z*)-**1k**: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 0.94–0.99 (m, 3H, CH_3), 1.43–1.55 (m, 2H, CH_2), 1.75–1.81 (m, 2H, CH_2), 4.38 (t, ^3J 7.2 Hz, 2H, NCH_2), 6.86 (d, ^3J 7.7 Hz, 1H, Ar), 6.99–7.05 (m, 1H, Ar), 7.29 (ddd, ^3J 7.7, ^3J 7.7, ^4J 1.0 Hz, 1H, Ar), 7.57 (d, ^3J 7.5 Hz, 1H, Ar), 9.57 (br. s, 1H, NH); ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ = 13.84 (CH_3), 20.6 (CH_2), 33.3 (CH_2), 52.0 (NCH_2), 110.6 (CH, Ar), 121.9 (CH, Ar), 122.1 (C, Ar), 122.74 (CH, Ar), 132.4 (CH, Ar), 143.2 (C, Ar), 153.1 (C=N), 160.6 (C=O).

Methyl 2-phenyl-1-(phenylsulfonyl)cyclopropanecarboxylate (2aa). A mixture of benzaldehyde (1.700 g, 16 mmol), methyl 2-(phenylsulfonyl)acetate (2.3 mL, 14 mmol), piperidine (135 μL) and acetic acid (160 μL) in benzene (7 mL) was heated at reflux temperature

with a Dean-Stark trap for 1 h. After cooling to ambient temperature, the reaction mixture was washed twice with brine, dried with Na_2SO_4, and concentrated under reduced pressure. The resulting alkene (3.729 g, 88%) was further used without purification. To a suspension of NaH (892 mg, 13.38 mmol, 60% suspension in mineral oil) in dry DMSO (10 mL) Me_3SOI (2.706 g, 12.26 mmol) was added in one portion under inert atmosphere. After stirring for 25 min at ambient temperature, solution of alkene (3.370 g, 11.15 mmol) in DMSO (20 mL) was added dropwise under vigorous stirring. The mixture was stirred for additional 3.5 h, quenched with ice water and extracted with EtOAc. Combined organic fractions were washed with water, dried with Na_2SO_4 and concentrated under reduced pressure yielding **2aa** (2.7 g, 77%) as yellowish oil, dr 93:7. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.41 (dd, ^2J 5.7, ^3J 8.5 Hz, 1H, CH_2), 2.46 (dd, ^2J 5.7, ^3J 10.0 Hz, 1H, CH_2), 3.25 (s, 3H, OCH_3), 3.47 (dd, ^3J 8.5, ^3J 10.0 Hz, 1H, CH), 7.04–7.07 (m, 2H, Ar), 7.20–7.24 (m, 3H, Ar), 7.58–7.62 (m, 2H, Ar), 7.67–7.71 (m, 1H, Ar), 8.05–8.08 (m, 2H, Ar); ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ = 17.6 (CH_2), 32.9 (CH), 52.16 (OCH_3), 52.22 (C), 127.7 (CH, Ar), 128.2 (2 × CH, Ar), 128.4 (2 × CH, Ar), 128.7 (2 × CH, Ar), 129.1 (2 × CH, Ar), 132.8 (C, Ar), 133.7 (CH, Ar), 139.5 (C, Ar), 164.2 (CO_2Me). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{17}H_{17}O_4S^+$, 317.0842, found 317.0837.

Synthesis of spiro[oxindole-3,2'-pyrrolidines] 3 (General procedure).

The solution of iminooxindole **1** (1.0 equiv), cyclopropane **2** (1.05 equiv) and Lewis acid in appropriate solvent (0.1 M) was heated under reflux for specified time. Then the reaction mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel.

Dimethyl (3*RS*,5'*RS*)-2-oxo-1',5'-diphenyl-1,2-dihydro-3'*H*-spiro[indole-3,2'-pyrrolidine]-3',3'-dicarboxylate (3a). A solution of imine **1a** (117 mg, 0.53 mmol), cyclopropane **2a** (130 mg, 0.56 mmol) and $Yb(OTf)_3$ (33 mg, 0.05 mmol) in DCE (5.3 mL) was heated under reflux for 2 h yielding **3a** (213 mg, 88%) as yellow foam. R_f = 0.50 (ethyl acetate/petroleum ether; 1:1), dr 93:7. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.79 (dd, ^2J 13.7, ^3J 7.8 Hz, 1H, CH_2), 3.37 (dd, ^2J 13.7, ^3J 8.5 Hz, 1H, CH_2), 3.56 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3), 5.77 (dd, ^3J 7.8, ^3J 8.5 Hz, 1H, CH), 6.66–6.69 (m, 2H, Ar), 6.72 (t, ^3J 7.3 Hz, 1H, Ar), 6.76 (ddd, ^3J 7.8, ^4J 0.9, ^5J 0.5 Hz, 1H, Ar), 6.90 (dd, ^3J 7.3, ^3J 8.6 Hz, 2H, Ar), 7.06 (ddd, ^3J 7.6, ^3J 7.6, ^4J 1.0 Hz, 1H, Ar), 7.17 (t, ^3J 7.4 Hz, 1H, Ar), 7.24–7.29 (m, 3H, Ar), 7.36–7.38 (m, 1H, Ar), 7.48–7.50 (m, 2H, Ar), 7.70 (br. s, 1H, NH); ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ = 40.5 (CH_2), 52.6 (OCH_3), 53.0 (OCH_3), 62.3 (CH), 66.4 (C), 76.3 (C), 110.1 (CH, Ar), 122.1 (2 × CH, Ar), 122.48 (CH, Ar), 122.50 (CH, Ar), 125.4 (CH, Ar), 127.0 (CH, Ar), 127.2 (2 × CH, Ar), 128.2 (C, Ar), 128.26 (2 × CH, Ar), 128.33 (2 × CH, Ar), 129.9 (CH, Ar), 141.3 (C, Ar), 142.3 (C, Ar), 143.5 (C, Ar), 169.4 (CO_2Me), 169.6

(CO_2Me), 176.5 (C=O). IR (film, cm^{-1}): 3305, 2950, 2915, 2850, 1730, 1615, 1595. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{27}H_{25}N_2O_5$, 457.1758, found 457.1758.

Dimethyl (3*RS*,5'*RS*)-5-fluoro-2-oxo-1',5'-diphenyl-1,2-dihydro-3'*H*-spiro[indole-3,2'-pyrrolidine]-3',3'-dicarboxylate (3b). A solution of imine **1b** (184 mg, 0.77 mmol), cyclopropane **2a** (188 mg, 0.80 mmol) and $Yb(OTf)_3$ (48 mg, 0.08 mmol) in DCE (7.7 mL) was heated under reflux for 2 h yielding **3b** (326 mg, 90%) as yellow foam. R_f = 0.36 (ethyl acetate/petroleum ether; 1:1), dr 94:6. ^1H NMR ($CDCl_3$, 600 MHz): δ = 2.77 (dd, ^2J 13.6, ^3J 7.6 Hz, 1H, CH_2), 3.42 (dd, ^2J 13.6, ^3J 8.5 Hz, 1H, CH_2), 3.60 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3), 5.79 (dd, ^3J 7.6, ^3J 8.5 Hz, 1H, CH), 6.65 (dd, ^3J 8.5, $^4J_{HF}$ 4.2 Hz, 1H, Ar), 6.68–6.71 (m, 2H, Ar), 6.73 (t, ^3J 7.4 Hz, 1H, Ar), 6.91 (dd, ^3J 7.4, ^3J 8.6 Hz, 2H, Ar), 6.95 (ddd, ^3J 8.5, $^3J_{HF}$ 8.8, ^4J 2.6 Hz, 1H, Ar), 7.16 (dd, ^3J 8.2, ^4J 2.6 Hz, 1H, Ar), 7.20 (t, ^3J 7.4 Hz, 1H, Ar), 7.29 (dd, ^3J 7.6, ^3J 7.9 Hz, 2H, Ar), 7.49–7.51 (m, 2H, Ar), 8.78 (br. s, 1H, NH); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ = 40.5 (CH_2), 52.7 (OCH_3), 53.0 (OCH_3), 62.5 (CH), 66.3 (C), 76.6 (C), 111.0 ($^3J_{CF}$ 8 Hz, CH, Ar), 113.1 ($^2J_{CF}$ 26 Hz, CH, Ar), 116.3 ($^2J_{CF}$ 23 Hz, CH, Ar), 121.9 (2 × CH, Ar), 122.6 (CH, Ar), 127.1 (3 × CH, Ar), 128.4 (4 × CH, Ar), 129.7 ($^3J_{CF}$ 7 Hz, C, Ar), 137.5 (C, Ar), 141.9 (C, Ar), 143.2 (C, Ar), 158.9 ($^1J_{CF}$ 241 Hz, C, Ar), 169.1 (CO_2Me), 169.3 (CO_2Me), 177.3 (C=O). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{27}H_{24}FN_2O_5$, 475.1664, found 475.1668.

Dimethyl (3*RS*,5'*RS*)-5-fluoro-5'-(4-methylphenyl)-2-oxo-1'-phenyl-1,2-dihydro-3'*H*-spiro[indole-3,2'-pyrrolidine]-3',3'-dicarboxylate (3c). A solution of imine **1b** (174 mg, 0.73 mmol), cyclopropane **2e** (189 mg, 0.76 mmol) and $Yb(OTf)_3$ (45 mg, 0.07 mmol) in DCE (7.3 mL) was heated under reflux for 1 h yielding **3c** (316 mg, 89%) as yellowish foam. R_f = 0.40 (ethyl acetate/petroleum ether; 1:1), dr 94:6. ^1H NMR ($CDCl_3$, 600 MHz): δ = 2.29 (s, 3H, CH_3), 2.74 (dd, ^2J 13.7, ^3J 7.6 Hz, 1H, CH_2), 3.39 (dd, ^2J 13.7, ^3J 8.5 Hz, 1H, CH_2), 3.60 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3), 5.75 (dd, ^3J 7.6, ^3J 8.5 Hz, 1H, CH), 6.65 (dd, ^3J 8.5, $^4J_{HF}$ 4.2 Hz, 1H, Ar), 6.67–6.70 (m, 2H, Ar), 6.73 (t, ^3J 7.3 Hz, 1H, Ar), 6.91 (dd, ^3J 7.4, ^3J 8.7 Hz, 2H, Ar), 6.95 (ddd, ^3J 8.5, $^3J_{HF}$ 8.8, ^4J 2.6 Hz, 1H, Ar), 7.09 (d, ^3J 7.7 Hz, 2H, Ar), 7.15 (dd, ^3J 8.2, ^4J 2.6 Hz, 1H, Ar), 7.37 (d, ^3J 8.1 Hz, 2H, Ar), 8.66 (br. s, 1H, NH); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ = 21.0 (CH_3), 40.6 (CH_2), 52.7 (OCH_3), 53.0 (OCH_3), 62.3 (CH), 66.3 (C), 76.5 (C), 111.0 ($^3J_{CF}$ 8 Hz, CH, Ar), 113.2 ($^2J_{CF}$ 26 Hz, CH, Ar), 116.3 ($^2J_{CF}$ 23 Hz, CH, Ar), 121.8 (2 × CH, Ar), 122.5 (CH, Ar), 127.0 (2 × CH, Ar), 128.3 (2 × CH, Ar), 129.1 (2 × CH, Ar), 129.9 ($^3J_{CF}$ 7 Hz, C, Ar), 136.6 (C, Ar), 137.5 (C, Ar), 138.9 (C, Ar), 143.3 (C, Ar), 158.9 ($^1J_{CF}$ 241 Hz, C, Ar), 169.1 (CO_2Me), 169.4 (CO_2Me), 177.3 (C=O). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{28}H_{26}FN_2O_5$, 489.1820, found 489.1833.

Dimethyl (3*RS*,5'*RS*)-5-chloro-2-oxo-1',5'-diphenyl-1,2-dihydro-3'*H*-spiro[indole-3,2'-pyrrolidine]-3',3'-dicarboxylate (3d). A solution of imine **1c** (161 mg, 0.63 mmol), cyclopropane **2a** (154 mg, 0.66 mmol) and $Yb(OTf)_3$ (39 mg, 0.06 mmol) in DCE (6.3 mL) was heated under reflux for 2 h yielding **3d** (262 mg, 85%) as yellowish oil. R_f = 0.52 (ethyl acetate/petroleum ether; 1:1), dr 94:6. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.78 (dd, ^2J 13.6, ^3J 7.3 Hz, 1H, CH_2), 3.41 (dd, ^2J 13.6, ^3J 8.8 Hz, 1H, CH_2), 3.64 (s, 3H, OCH_3), 3.69 (s, 3H, OCH_3), 5.76 (dd, ^3J 7.3, ^3J 8.8 Hz, 1H, CH), 6.63 (dd, ^3J 8.3, ^5J 0.3 Hz, 1H, Ar), 6.70–6.73 (m, 2H, Ar), 6.76 (t, ^3J 7.3 Hz, 1H, Ar), 6.92 (dd, ^3J 7.3, ^3J 8.6 Hz, 2H, Ar), 7.19 (t, ^3J 7.4 Hz, 1H, Ar), 7.21 (dd, ^3J 8.3, ^3J 2.1 Hz, 1H, Ar), 7.29 (dd, ^3J 7.4, ^3J 7.9 Hz, 2H, Ar), 7.37 (dd, ^4J 2.1, ^5J 0.3 Hz, 1H, Ar), 7.50–7.52 (m, 2H, Ar), 8.50 (br. s, 1H, NH); ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ = 40.3 (CH_2), 52.8 (OCH_3), 53.0 (OCH_3), 62.5 (CH), 66.3 (C), 76.5 (C), 111.3 (CH, Ar), 122.6 (2 × CH, Ar), 123.1 (CH, Ar), 125.7 (CH, Ar), 127.1 (CH, Ar), 127.2 (2 × CH, Ar), 127.8 (C, Ar), 128.3 (2 × CH, Ar), 128.4 (2 × CH, Ar), 129.6 (C, Ar), 129.8 (CH, Ar), 140.1 (C, Ar), 141.8 (C, Ar), 143.1 (C, Ar), 169.2 (CO_2Me), 169.4 (CO_2Me), 177.1 (C=O). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{27}H_{24}ClN_2O_5$, 491.1368, found 491.1357.

Dimethyl (3*RS*,5'*RS*)-5-chloro-5'-(4-fluorophenyl)-2-oxo-1'-phenyl-1,2-dihydro-3'*H*-spiro[indole-3,2'-pyrrolidine]-3',3'-dicarboxylate (3e). A solution of imine **1c** (171 mg, 0.67 mmol), cyclopropane **2b** (176 mg, 0.70 mmol) and $Yb(OTf)_3$ (41 mg, 0.07 mmol) in DCE (6.7 mL) was heated under reflux for 2 h yielding **3e** (321 mg, 95%) as yellowish foam. R_f = 0.46 (ethyl acetate/petroleum ether; 1:1), dr 93:7. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.76 (dd, ^2J 13.7, ^3J 6.9 Hz, 1H, CH_2), 3.41 (dd, ^2J 13.7, ^3J 9.0 Hz, 1H, CH_2), 3.66 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 5.71 (dd, ^3J 6.9, ^3J 9.0 Hz, 1H, CH), 6.59 (dd, ^3J 8.2, ^5J 0.3 Hz, 1H, Ar), 6.76–6.81 (m, 3H, Ar), 6.92 (dd, ^3J 7.4, ^3J 8.6 Hz, 2H, Ar), 6.95 (dd, ^3J 8.7, $^3J_{HF}$ 8.8 Hz, 2H, Ar), 7.19 (dd, ^3J 8.2, ^4J 2.1 Hz, 1H, Ar), 7.35 (dd, ^4J 2.1, ^5J 0.3 Hz, 1H, Ar), 7.52 (dd, ^3J 8.7, $^4J_{HF}$ 5.4 Hz, 2H, Ar), 8.55 (br. s, 1H, NH); ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ = 40.1 (CH_2), 52.8 (OCH_3), 52.9 (OCH_3), 61.7 (CH), 65.9 (C), 76.6 (C), 111.3 (CH, Ar), 115.1 ($^2J_{CF}$ 21 Hz, 2 × CH, Ar), 123.87 (2 × CH, Ar), 123.91 (CH, Ar), 125.8 (CH, Ar), 127.6 (C, Ar), 128.4 (2 × CH, Ar), 128.9 (C, Ar), 129.0 ($^3J_{CF}$ 8 Hz, 2 × CH, C, Ar), 129.9 (CH, Ar), 137.4 ($^4J_{CF}$ 2 Hz, C, Ar), 140.3 (C, Ar), 142.8 (C, Ar), 161.9 ($^1J_{CF}$ 244 Hz, C, Ar), 169.50 (CO_2Me), 169.54 (CO_2Me), 177.2 (C=O). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{27}H_{23}ClFN_2O_5$, 509.1274, found 509.1263.

Dimethyl (3*RS*,5'*RS*)-5-bromo-2-oxo-1',5'-diphenyl-1,2-dihydro-3'*H*-spiro[indole-3,2'-pyrrolidine]-3',3'-dicarboxylate (3f). A solution of imine **1d** (128 mg, 0.43 mmol), cyclopropane **2a** (105 mg, 0.45 mmol) and $Yb(OTf)_3$ (26 mg, 0.04 mmol) in DCE (4.3 mL) was heated under reflux for 2 h yielding **3f** (205 mg, 90%) as yellowish crystals, mp 203–204 °C. R_f

= 0.52 (ethyl acetate/petroleum ether; 1:1), dr 94:6. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.79 (dd, ^2J 13.6, ^3J 7.2 Hz, 1H, CH_2), 3.41 (dd, ^2J 13.6, ^3J 8.8 Hz, 1H, CH_2), 3.65 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 5.76 (dd, ^3J 7.2, ^3J 8.8 Hz, 1H, CH), 6.58 (d, ^3J 8.3 Hz, 1H, Ar), 6.71–6.74 (m, 2H, Ar), 6.76 (t, ^3J 7.4 Hz, 1H, Ar), 6.92 (dd, ^3J 7.4, ^3J 8.6 Hz, 2H, Ar), 7.19 (t, ^3J 7.4 Hz, 1H, Ar), 7.29 (dd, ^3J 7.4, ^3J 7.9 Hz, 2H, Ar), 7.35 (dd, ^3J 8.3, ^3J 2.0 Hz, 1H, Ar), 7.50–7.53 (m, 3H, Ar), 8.63 (br. s, 1H, NH); ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ = 40.2 (CH_2), 52.8 (OCH_3), 53.0 (OCH_3), 62.4 (CH), 66.3 (C), 76.5 (C), 111.9 (CH, Ar), 114.9 (C, Ar), 122.7 (2 × CH, Ar), 123.1 (CH, Ar), 127.1 (CH, Ar), 127.2 (2 × CH, Ar), 128.3 (2 × CH, Ar), 128.4 (2 × CH, Ar), 128.5 (CH, Ar), 129.8 (C, Ar), 132.7 (CH, Ar), 140.7 (C, Ar), 141.8 (C, Ar), 143.1 (C, Ar), 169.2 (CO_2Me), 169.4 (CO_2Me), 177.0 (C=O). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{27}H_{24}{}^{79}BrN_2O_5$, 535.0863, found 535.0849.

Dimethyl (3*RS*,5'*RS*)-5-bromo-5'-(4-methylphenyl)-2-oxo-1'-phenyl-1,2-dihydro-3'*H*-spiro[indole-3,2'-pyrrolidine]-3',3'-dicarboxylate (3g). A solution of imine **1d** (174 mg, 0.58 mmol), cyclopropane **2e** (151 mg, 0.61 mmol) and $Yb(OTf)_3$ (36 mg, 0.06 mmol) in DCE (5.8 mL) was heated under reflux for 1 h yielding **3g** (284 mg, 90%) as yellowish crystals, mp 231–232 °C. R_f = 0.54 (ethyl acetate/petroleum ether; 1:1), dr 93:7. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.30 (s, 3H, CH_3), 2.78 (dd, ^2J 13.6, ^3J 7.4 Hz, 1H, CH_2), 3.39 (dd, ^2J 13.6, ^3J 8.7 Hz, 1H, CH_2), 3.64 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 5.74 (dd, ^3J 7.4, ^3J 8.7 Hz, 1H, CH), 6.57 (d, ^3J 8.3 Hz, 1H, Ar), 6.71–6.73 (m, 2H, Ar), 6.75 (t, ^3J 7.3 Hz, 1H, Ar), 6.92 (dd, ^3J 7.3, ^3J 8.7 Hz, 2H, Ar), 7.10 (d, ^3J 8.2 Hz, 2H, Ar), 7.35 (dd, ^3J 8.3, ^4J 2.0 Hz, 1H, Ar), 7.40 (d, ^3J 8.2 Hz, 2H, Ar), 7.51 (d, ^4J 2.0 Hz, 1H, Ar), 8.73 (br. s, 1H, NH); ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ = 21.0 (CH_3), 40.3 (CH_2), 52.7 (OCH_3), 52.9 (OCH_3), 62.2 (CH), 66.3 (C), 76.4 (C), 111.9 (CH, Ar), 114.9 (C, Ar), 122.4 (2 × CH, Ar), 122.9 (CH, Ar), 127.1 (2 × CH, Ar), 128.3 (2 × CH, Ar), 128.4 (CH, Ar), 129.0 (2 × CH, Ar), 130.0 (C, Ar), 132.6 (CH, Ar), 136.6 (C, Ar), 138.8 (C, Ar), 140.6 (C, Ar), 143.2 (C, Ar), 169.1 (CO_2Me), 169.4 (CO_2Me), 177.0 (C=O). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{28}H_{26}{}^{79}BrN_2O_5$, 549.1020, found 549.1020.

Dimethyl (3*S*,5'*S*)-5-bromo-5'-(4-methylphenyl)-2-oxo-1'-phenyl-1,2-dihydro-3'*H*-spiro[indole-3,2'-pyrrolidine]-3',3'-dicarboxylate ((3*S*,5'*S*)-**3g)** was obtained by the same procedure from **1d** and (*R*)-**2e** (er 99:1); NMR spectra coincide with that of **3g**. Yellowish crystals, mp 211–212 °C. $[\alpha]_D^{25}$ = +172.0 (c 0.50, EtOH), er 98:2.

Dimethyl (3*RS*,5'*RS*)-5-bromo-5'-(4-methoxyphenyl)-2-oxo-1'-phenyl-1,2-dihydro-3'*H*-spiro[indole-3,2'-pyrrolidine]-3',3'-dicarboxylate (3h). A solution of imine **1d** (132 mg, 0.44 mmol), cyclopropane **2f** (122 mg, 0.46 mmol) and $Yb(OTf)_3$ (27 mg, 0.04 mmol) in DCE (4.4

mL) was heated under reflux for 1 h yielding **3h** (235 mg, 95%) as yellowish foam. R_f = 0.46 (ethyl acetate/petroleum ether; 1:1), dr 95:5. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.79 (dd, ^2J 13.7, ^3J 7.2 Hz, 1H, CH_2), 3.39 (dd, ^2J 13.7, ^3J 8.8 Hz, 1H, CH_2), 3.66 (s, 3H, OCH_3), 3.66 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 5.71 (dd, ^3J 7.2, ^3J 8.8 Hz, 1H, CH), 6.53 (d, ^3J 8.2 Hz, 1H, Ar), 6.74–6.77 (m, 3H, Ar), 6.82 (d, ^3J 8.9 Hz, 2H, Ar), 6.91 (dd, ^3J 7.3, ^3J 8.8 Hz, 2H, Ar), 7.33 (dd, ^3J 8.2, ^4J 2.0 Hz, 1H, Ar), 7.46 (d, ^3J 8.9 Hz, 2H, Ar), 7.51 (d, ^4J 2.0 Hz, 1H, Ar), 8.83 (br. s, 1H, NH); ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ = 40.2 (CH_2), 52.7 (OCH_3), 52.9 (OCH_3), 55.0 (OCH_3), 61.8 (CH), 66.0 (C), 76.4 (C), 111.8 (CH, Ar), 113.6 (2 × CH, Ar), 114.7 (C, Ar), 123.0 (2 × CH, Ar), 123.2 (CH, Ar), 128.2 (2 × CH, Ar), 128.4 (3 × CH, Ar), 129.7 (C, Ar), 132.5 (CH, Ar), 133.7 (C, Ar), 140.7 (C, Ar), 143.0 (C, Ar), 158.5 (C, Ar), 169.3 (CO_2Me), 169.4 (CO_2Me), 177.1 (C=O). HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd for $C_{28}H_{26}{}^{79}BrN_2O_6$, 565.0969, found 565.0947.

Dimethyl (3*RS*,5'*RS*)-1'-(4-fluorophenyl)-2-oxo-5'-phenyl-1,2-dihydro-3'*H*-spiro[indole-3,2'-pyrrolidine]-3',3'-dicarboxylate (3i). A solution of imine **1e** (150 mg, 0.63 mmol), cyclopropane **2a** (154 mg, 0.66 mmol) and Yb(OTf)$_3$ (39 mg, 0.06 mmol) in DCE (6.3 mL) was heated under reflux for 2 h yielding **3i** (272 mg, 92%) as yellow foam. R_f = 0.46 (ethyl acetate/petroleum ether; 1:1), dr 94:6. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.82 (dd, ^2J 13.7, ^3J 7.2 Hz, 1H, CH_2), 3.40 (dd, ^2J 13.7, ^3J 9.0 Hz, 1H, CH_2), 3.65 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 5.67 (dd, ^3J 7.2, ^3J 9.0 Hz, 1H, CH), 6.57 (dd, $^3J_{HF}$ 8.4, ^3J 9.2 Hz, 2H, Ar), 6.71 (ddd, ^3J 7.8, ^4J 0.9, ^5J 0.5 Hz, 1H, Ar), 6.77 (dd, ^3J 9.2, $^4J_{HF}$ 4.9 Hz, 2H, Ar), 7.06 (ddd, ^3J 7.6, ^3J 7.6, ^4J 0.9 Hz, 1H, Ar), 7.18 (t, ^3J 7.4 Hz, 1H, Ar), 7.23 (ddd, ^3J 7.6, ^3J 7.8, ^4J 1.1 Hz, 1H, Ar), 7.24–7.28 (m, 2H, Ar), 7.37 (ddd, ^3J 7.6, ^4J 1.1, ^5J 0.5 Hz, 1H, Ar), 7.53–7.55 (m, 2H, Ar), 8.22 (br. s, 1H, NH); ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ = 40.3 (CH_2), 52.7 (OCH_3), 52.9 (OCH_3), 62.5 (CH), 65.9 (C), 76.8 (C), 110.3 (CH, Ar), 114.9 ($^2J_{CF}$ 22 Hz, 2 × CH, Ar), 122.3 (CH, Ar), 125.5 (CH, Ar), 125.8 ($^3J_{CF}$ 8 Hz, 2 × CH, Ar), 127.1 (C, Ar), 127.2 (CH, Ar), 127.6 (2 × CH, Ar), 128.3 (2 × CH, Ar), 130.1 (CH, Ar), 139.1 ($^4J_{CF}$ 2 Hz, C, Ar), 141.7 (C, Ar), 141.8 (C, Ar), 159.1 ($^1J_{CF}$ 243 Hz, C, Ar), 169.8 (CO_2Me), 169.9 (CO_2Me), 177.4 (C=O). IR (film, cm^{-1}): 3290, 3065, 2955, 2880, 1735, 1720, 1700, 1620, 1600. HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd for $C_{27}H_{24}FN_2O_5$, 475.1664, found 475.1673.

Dimethyl (3*RS*,5'*RS*)-1'-(4-chlorophenyl)-2-oxo-5'-phenyl-1,2-dihydro-3'*H*-spiro[indole-3,2'-pyrrolidine]-3',3'-dicarboxylate (3j). A solution of imine **1f** (166 mg, 0.65 mmol), cyclopropane **2a** (159 mg, 0.68 mmol) and Yb(OTf)$_3$ (40 mg, 0.06 mmol) in DCE (6.5 mL) was heated under reflux for 2 h yielding **3j** (287 mg, 91%) as yellow foam. R_f = 0.46 (ethyl acetate/petroleum ether; 1:1), dr 94:6. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.80 (dd, ^2J 13.7, ^3J 7.8

Hz, 1H, CH_2), 3.35 (dd, ^2J 13.7, ^3J 8.5 Hz, 1H, CH_2), 3.54 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 5.73 (dd, ^3J 7.8, ^3J 8.5 Hz, 1H, CH), 6.58 (d, ^3J 9.0 Hz, 2H, Ar), 6.77 (d, ^3J 7.8 Hz, 1H, Ar), 6.85 (d, ^3J 9.0 Hz, 2H, Ar), 7.07 (ddd, ^3J 7.6, ^3J 7.6, ^4J 0.9 Hz, 1H, Ar), 7.20 (t, ^3J 7.3 Hz, 1H, Ar), 7.26–7.30 (m, 3H, Ar), 7.36 (d, ^3J 7.5 Hz, 1H, Ar), 7.45–7.48 (m, 2H, Ar), 8.37 (br. s, 1H, NH); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ = 40.6 (CH_2), 52.6 (OCH_3), 53.0 (OCH_3), 62.6 (CH), 66.4 (C), 76.3 (C), 110.5 (CH, Ar), 122.6 (CH, Ar), 122.9 (2 × CH, Ar), 125.1 (CH, Ar), 127.1 (2 × CH, Ar), 127.2 (CH, Ar), 127.4 (C, Ar), 127.9 (C, Ar), 128.4 (2 × CH, Ar), 128.5 (2 × CH, Ar), 130.2 (CH, Ar), 141.4 (C, Ar), 141.7 (C, Ar), 142.1 (C, Ar), 169.2 (CO_2Me), 169.4 (CO_2Me), 176.6 (C=O). IR (film, cm^{-1}): 3160, 3090, 2950, 2915, 2850, 1750, 1720, 1700, 1615, 1600. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{27}H_{23}ClN_2NaO_5$, 513.1188, found 513.1190.

Dimethyl (3*RS*,5'*RS*)-1'-(2-chlorophenyl)-2-oxo-5'-phenyl-1,2-dihydro-3'*H*-spiro[indole-3,2'-pyrrolidine]-3',3'-dicarboxylate (3k). A solution of imine **1g** (166 mg, 0.65 mmol), cyclopropane **2a** (159 mg, 0.68 mmol) and $Yb(OTf)_3$ (40 mg, 0.06 mmol) in DCE (6.5 mL) was heated under reflux for 2 h yielding **3k** (264 mg, 83%) as yellow foam. R_f = 0.42 (ethyl acetate/petroleum ether; 1:1), dr 95:5. ^1H NMR ($CDCl_3$, 600 MHz, 328 K): δ = 3.05 (dd, ^2J 13.8, ^3J 6.7 Hz, 1H, CH_2), 3.44 (dd, ^2J 13.8, ^3J 9.4 Hz, 1H, CH_2), 3.69 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 5.53 (br. s, 1H, CH), 6.58 (d, ^3J 7.7 Hz, 1H, Ar), 6.82 (ddd, ^3J 7.6, ^3J 7.6, ^4J 1.5 Hz, 1H, Ar), 6.90–6.94 (m, 2H, Ar), 7.00 (dd, ^3J 7.4, ^3J 7.4 Hz, 1H, Ar), 7.11 (ddd, ^3J 7.7, ^3J 7.7, ^4J 1.1 Hz, 1H, Ar), 7.15 (t, ^3J 7.3 Hz, 1H, Ar), 7.19–7.22 (m, 2H, Ar), 7.52 (d, ^3J 7.7 Hz, 1H, Ar), 7.68–7.73 (m, 4H, Ar, NH); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz, 328 K): δ = 40.1 (CH_2), 52.57 (OCH_3), 52.59 (OCH_3), 64.9 (CH), 65.6 (C), 77.8 (C), 109.3 (CH, Ar), 121.5 (CH, Ar), 124.5 (C, Ar), 126.8 (CH, Ar), 127.3 (CH, Ar), 127.5 (CH, Ar), 127.6 (CH, Ar), 127.8 (2 × CH, Ar), 128.5 (CH, Ar), 129.2 (2 × CH, Ar), 130.0 (CH, Ar), 130.1 (CH, Ar), 135.2 (C, Ar), 140.76 (C, Ar), 140.84 (C, Ar), 141.6 (C, Ar), 170.2 (CO_2Me), 170.5 (CO_2Me), 177.9 (C=O). IR (film, cm^{-1}): 3330, 3060, 3030, 2950, 1725, 1715, 1700, 1620, 1600. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{27}H_{23}ClN_2NaO_5^+$, 513.1188, found 513.1190.

Dimethyl (3*RS*,5'*RS*)-1'-(4-bromophenyl)-2-oxo-5'-phenyl-1,2-dihydro-3'*H*-spiro[indole-3,2'-pyrrolidine]-3',3'-dicarboxylate (3l). A solution of imine **1h** (177 mg, 0.59 mmol), cyclopropane **2a** (145 mg, 0.62 mmol) and $Yb(OTf)_3$ (37 mg, 0.06 mmol) in DCE (5.9 mL) was heated under reflux for 2 h yielding **3l** (280 mg, 89%) as yellow foam. R_f = 0.61 (ethyl acetate/petroleum ether; 1:1), dr 94:6. ^1H NMR ($CDCl_3$, 600 MHz): δ = 2.79 (dd, ^2J 13.7, ^3J 7.8 Hz, 1H, CH_2), 3.35 (dd, ^2J 13.7, ^3J 8.4 Hz, 1H, CH_2), 3.53 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3), 5.73 (dd, ^3J 7.8, ^3J 8.4 Hz, 1H, CH), 6.51 (d, ^3J 9.0 Hz, 2H, Ar), 6.77 (d, ^3J 7.8 Hz, 1H, Ar), 7.00 (d, ^3J 9.0 Hz, 2H, Ar), 7.07 (ddd, ^3J 7.6, ^3J 7.6, ^4J 0.9 Hz, 1H, Ar), 7.21 (t, ^3J 7.3 Hz, 1H, Ar),

7.27–7.30 (m, 3H, Ar), 7.36 (d, ^3J 7.4 Hz, 1H, Ar), 7.44–7.47 (m, 2H, Ar), 8.22 (br. s, 1H, NH); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ = 40.6 (CH_2), 52.6 (OCH_3), 53.0 (OCH_3), 62.5 (CH), 66.5 (C), 76.1 (C), 110.5 (CH, Ar), 115.0 (C, Ar), 122.7 (CH, Ar), 123.0 (2 × CH, Ar), 125.1 (CH, Ar), 127.1 (2 × CH, Ar), 127.2 (CH, Ar), 127.9 (C, Ar), 128.5 (2 × CH, Ar), 130.2 (CH, Ar), 131.3 (2 × CH, Ar), 141.3 (C, Ar), 141.7 (C, Ar), 142.7 (C, Ar), 169.1 (CO_2Me), 169.3 (CO_2Me), 176.3 (C=O). HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{27}H_{23}{}^{79}BrN_2NaO_5$, 557.0683, found 557.0669.

Dimethyl (3*RS*,5'*RS*)-1'-(4-methylphenyl)-2-oxo-5'-phenyl-1,2-dihydro-3'*H*-spiro[indole-3,2'-pyrrolidine]-3',3'-dicarboxylate (3m). A solution of imine **1i** (146 mg, 0.62 mmol), cyclopropane **2a** (152 mg, 0.65 mmol) and $Yb(OTf)_3$ (38 mg, 0.06 mmol) in DCE (6.2 mL) was heated under reflux for 2 h yielding **3m** (260 mg, 89%) as yellow foam. R_f = 0.52 (ethyl acetate/petroleum ether; 1:1), dr 93:7. ^1H NMR ($CDCl_3$, 600 MHz): δ = 2.02 (s, 3H, CH_3), 2.79 (dd, ^2J 13.6, ^3J 7.3 Hz, 1H, CH_2), 3.39 (dd, ^2J 13.6, ^3J 8.8 Hz, 1H, CH_2), 3.58 (s, 3H, OCH_3), 3.69 (s, 3H, OCH_3), 5.74 (dd, ^3J 7.3, ^3J 8.8 Hz, 1H, CH), 6.62 (d, ^3J 8.6 Hz, 2H, Ar), 6.67 (d, ^3J 8.6 Hz, 2H, Ar), 6.71 (d, ^3J 7.8 Hz, 1H, Ar), 7.05 (ddd, ^3J 7.6, ^3J 7.6, ^4J 0.9 Hz, 1H, Ar), 7.17 (t, ^3J 7.3 Hz, 1H, Ar), 7.23 (ddd, ^3J 7.6, ^3J 7.8, ^4J 1.2 Hz, 1H, Ar), 7.25–7.28 (m, 2H, Ar), 7.38 (d, ^3J 7.6 Hz, 1H, Ar), 7.51–7.54 (m, 2H, Ar), 8.32 (br. s, 1H, NH); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ = 20.5 (CH_3), 40.5 (CH_2), 52.6 (OCH_3), 52.9 (OCH_3), 62.3 (CH), 66.2 (C), 76.6 (C), 110.3 (CH, Ar), 122.3 (CH, Ar), 122.7 (2 × CH, Ar), 125.4 (CH, Ar), 126.9 (CH, Ar), 127.3 (2 × CH, Ar), 127.9 (C, Ar), 128.2 (2 × CH, Ar), 128.8 (2 × CH, Ar), 129.8 (CH, Ar), 132.2 (C, Ar), 140.8 (C, Ar), 141.6 (C, Ar), 142.4 (C, Ar), 169.65 (CO_2Me), 169.72 (CO_2Me), 177.4 (C=O). IR (film, cm^{-1}): 3125, 3070, 3020, 2950, 2890, 2835, 1730, 1700, 1685, 1620, 1600. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{28}H_{27}N_2O_5$, 471.1914, found 471.1908.

Dimethyl (3*RS*,5'*RS*)-1'-(4-methoxyphenyl)-2-oxo-5'-phenyl-1,2-dihydro-3'*H*-spiro[indole-3,2'-pyrrolidine]-3',3'-dicarboxylate (3n). A solution of imine **1j** (158 mg, 0.63 mmol), cyclopropane **2a** (154 mg, 0.66 mmol) and $Yb(OTf)_3$ (39 mg, 0.06 mmol) in DCE (6.3 mL) was heated under reflux for 2 h yielding **3n** (284 mg, 93%) as yellow foam. R_f = 0.33 (ethyl acetate/petroleum ether; 1:1), dr 92:8. ^1H NMR ($CDCl_3$, 600 MHz): δ = 2.81 (dd, ^2J 13.7, ^3J 6.8 Hz, 1H, CH_2), 3.43 (dd, ^2J 13.7, ^3J 9.3 Hz, 1H, CH_2), 3.49 (s, 3H, OCH_3), 3.66 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 5.66 (dd, ^3J 6.8, ^3J 9.3 Hz, 1H, CH), 6.39 (d, ^3J 9.1 Hz, 2H, Ar), 6.64 (d, ^3J 7.8 Hz, 1H, Ar), 6.81 (d, ^3J 9.1 Hz, 2H, Ar), 7.04 (ddd, ^3J 7.6, ^3J 7.6, ^4J 0.9 Hz, 1H, Ar), 7.15 (t, ^3J 7.3 Hz, 1H, Ar), 7.19 (ddd, ^3J 7.6, ^3J 7.8, ^4J 1.2 Hz, 1H, Ar), 7.25 (dd, ^3J 7.7, ^3J 7.7 Hz, 2H, Ar), 7.37 (d, ^3J 7.6 Hz, 1H, Ar), 7.57–7.59 (m, 2H, Ar), 8.29 (br. s, 1H, NH); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ = 40.2 (CH_2), 52.6 (OCH_3), 52.7 (OCH_3), 54.8 (OCH_3), 62.3 (CH), 65.6

(C), 77.0 (C), 110.2 (CH, Ar), 113.2 (2 × CH, Ar), 122.0 (CH, Ar), 125.5 (CH, Ar), 126.5 (2 × CH, Ar), 126.9 (CH, Ar), 127.0 (C, Ar), 127.8 (2 × CH, Ar), 128.1 (2 × CH, Ar), 129.8 (CH, Ar), 135.9 (C, Ar), 141.9 (C, Ar), 142.3 (C, Ar), 156.1 (C, Ar), 170.0 (CO_2Me), 170.2 (CO_2Me), 178.0 (C=O). IR (film, cm^{-1}): 3280, 3030, 2950, 2835, 1720, 1700, 1695, 1620, 1600. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{28}H_{26}N_2NaO_6^+$, 509.1683, found 509.1679.

Dimethyl (3*RS*,5'*RS*)-5'-(4-fluorophenyl)-2-oxo-1'-phenyl-1,2-dihydro-3'*H*-spiro[indole-3,2'-pyrrolidine]-3',3'-dicarboxylate (3o). A solution of imine **1a** (126 mg, 0.57 mmol), cyclopropane **2b** (150 mg, 0.60 mmol) and $Yb(OTf)_3$ (35 mg, 0.06 mmol) in DCE (5.7 mL) was heated under reflux for 2 h yielding **3o** (257 mg, 96%) as yellow foam. R_f = 0.46 (ethyl acetate/petroleum ether; 1:1), dr 91:9. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.75 (dd, ^2J 13.7, ^3J 7.2 Hz, 1H, CH_2), 3.38 (dd, ^2J 13.7, ^3J 8.9 Hz, 1H, CH_2), 3.60 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3), 5.73 (dd, ^3J 7.2, ^3J 8.9 Hz, 1H, CH), 6.69–6.72 (m, 3H, Ar), 6.73–6.77 (m, 1H, Ar), 6.90 (dd, ^3J 7.6, ^3J 8.3 Hz, 2H, Ar), 6.94 (dd, ^3J 8.7, $^3J_{HF}$ 8.7 Hz, 2H, Ar), 7.06 (ddd, ^3J 7.6, ^3J 7.7, ^4J 0.6 Hz, 1H, Ar), 7.23 (ddd, ^3J 7.7, ^3J 7.8, ^4J 1.0 Hz, 1H, Ar), 7.35 (d, ^3J 7.6 Hz, 1H, Ar), 7.49 (dd, ^3J 8.7, $^4J_{HF}$ 5.5 Hz, 2H, Ar), 8.03 (br. s, 1H, NH); ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ = 40.4 (CH_2), 52.6 (OCH_3), 52.9 (OCH_3), 61.6 (CH), 66.1 (C), 76.5 (C), 110.3 (CH, Ar), 115.1 ($^2J_{CF}$ 22 Hz, 2 × CH, Ar), 122.4 (CH, Ar), 123.0 (2 × CH, Ar), 123.1 (CH, Ar), 125.3 (CH, Ar), 127.6 (C, Ar), 128.3 (2 × CH, Ar), 128.9 ($^3J_{CF}$ 7 Hz, 2 × CH, Ar), 130.0 (CH, Ar), 137.9 ($^4J_{CF}$ 2 Hz, C, Ar), 141.6 (C, Ar), 143.1 (C, Ar), 161.8 ($^1J_{CF}$ 244 Hz, C, Ar), 169.6 (CO_2Me), 169.7 (CO_2Me), 176.9 (C=O). IR (film, cm^{-1}): 3300, 3060, 2990, 2955, 2915, 2850, 1730, 1700, 1620, 1595. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{27}H_{24}FN_2O_5$, 475.1664, found 475.1669.

Dimethyl (3*RS*,5'*RS*)-5'-(4-bromophenyl)-2-oxo-1'-phenyl-1,2-dihydro-3'*H*-spiro[indole-3,2'-pyrrolidine]-3',3'-dicarboxylate (3p). A solution of imine **1a** (112 mg, 0.51 mmol), cyclopropane **2c** (166 mg, 0.53 mmol) and $Yb(OTf)_3$ (31 mg, 0.05 mmol) in DCE (5.1 mL) was heated under reflux for 2 h yielding **3p** (250 mg, 92%) as yellow foam. R_f = 0.44 (ethyl acetate/petroleum ether; 1:1), dr 91:9. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.73 (dd, ^2J 13.6, ^3J 7.0 Hz, 1H, CH_2), 3.38 (dd, ^2J 13.6, ^3J 9.1 Hz, 1H, CH_2), 3.62 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 5.70 (dd, ^3J 7.0, ^3J 9.1 Hz, 1H, CH), 6.70–6.73 (m, 3H, Ar), 6.78 (t, ^3J 7.3 Hz, 1H, Ar), 6.91 (dd, ^3J 7.3, ^3J 8.6 Hz, 2H, Ar), 7.06 (ddd, ^3J 7.6, ^3J 7.6, ^4J 1.0 Hz, 1H, Ar), 7.24 (ddd, ^3J 7.7, ^3J 7.7, ^4J 1.2 Hz, 1H, Ar), 7.34 (ddd, ^3J 7.6, ^4J 0.6, ^5J 0.6 Hz, 1H, Ar), 7.38 (d, ^3J 8.6 Hz, 2H, Ar), 7.41 (d, ^3J 8.6 Hz, 2H, Ar), 7.58 (br. s, 1H, NH); ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ = 40.1 (CH_2), 52.7 (OCH_3), 53.0 (OCH_3), 61.6 (CH), 66.0 (C), 76.5 (C), 110.2 (CH, Ar), 120.8 (C, Ar), 122.4 (CH, Ar), 123.3 (2 × CH, Ar), 123.5 (CH, Ar), 125.4 (CH, Ar), 127.4 (C, Ar), 128.3 (2 × CH, Ar), 129.2 (2 × CH, Ar), 130.1 (CH, Ar), 131.4 (2 × CH, Ar), 141.4 (C, Ar), 141.5 (C, Ar), 143.0 (C,

Ar), 169.6 (CO_2Me), 169.7 (CO_2Me), 176.6 (C=O). IR (film, cm^{-1}): 3295, 2955, 2915, 2870, 2850, 1730, 1700, 1620, 1595. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{27}H_{24}{}^{79}BrN_2O_5$, 535.0863, found 535.0863.

Dimethyl (3*RS*,5'*RS*)-5'-(2-bromophenyl)-2-oxo-1'-phenyl-1,2-dihydro-3'*H*-spiro[indole-3,2'-pyrrolidine]-3',3'-dicarboxylate (3q). A solution of imine **1a** (106 mg, 0.48 mmol), cyclopropane **2d** (156 mg, 0.50 mmol) and $Yb(OTf)_3$ (30 mg, 0.05 mmol) in DCE (4.8 mL) was heated under reflux for 20 h yielding **3q** (125 mg, 49%, 58% brsm) as brown oil. Extra portions of $Yb(OTf)_3$ (30 mg, 0.05 mmol) were added twice in 8 and 16 h. R_f = 0.61 (ethyl acetate/petroleum ether; 1:1), dr 91:9. ^1H NMR ($CDCl_3$, 600 MHz): δ = 2.62 (dd, ^2J 13.7, ^3J 6.7 Hz, 1H, CH_2), 3.57 (s, 3H, OCH_3), 3.65 (dd, ^2J 13.7, ^3J 9.1 Hz, 1H, CH_2), 3.71 (s, 3H, OCH_3), 6.09 (dd, ^3J 6.7, ^3J 9.1 Hz, 1H, CH), 6.64–6.67 (m, 2H, Ar), 6.75 (t, ^3J 7.3 Hz, 1H, Ar), 6.76 (d, ^3J 7.5 Hz, 1H, Ar), 6.91 (dd, ^3J 7.4, ^3J 8.6 Hz, 2H, Ar), 7.05 (ddd, ^3J 7.5, ^3J 7.8, ^4J 1.7 Hz, 1H, Ar), 7.08 (ddd, ^3J 7.6, ^3J 7.6, ^4J 1.0 Hz, 1H, Ar), 7.20 (ddd, ^3J 7.6, ^3J 7.6, ^4J 0.9 Hz, 1H, Ar), 7.28 (ddd, ^3J 7.7, ^3J 7.7, ^4J 1.2 Hz, 1H, Ar), 7.36 (d, ^3J 7.5 Hz, 1H, Ar), 7.52 (dd, ^3J 7.9, ^4J 1.1 Hz, 1H, Ar), 7.69 (dd, ^3J 7.8, ^4J 1.7 Hz, 1H, Ar), 7.98 (br. s, 1H, NH); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ = 38.1 (CH_2), 52.6 (OCH_3), 53.0 (OCH_3), 61.4 (CH), 66.3 (C), 76.3 (C), 110.4 (CH, Ar), 121.8 (2 × CH, Ar), 122.4 (CH, Ar), 122.6 (CH, Ar), 123.2 (C, Ar), 125.3 (CH, Ar), 127.3 (CH, Ar), 127.9 (C, Ar), 128.37 (CH, Ar), 128.42 (2 × CH, Ar), 128.9 (CH, Ar), 130.1 (CH, Ar), 132.5 (CH, Ar), 141.1 (C, Ar), 141.6 (C, Ar), 143.4 (C, Ar), 169.37 (CO_2Me), 169.41 (CO_2Me), 176.5 (C=O). IR (film, cm^{-1}): 3295, 2950, 2920, 2850, 1735, 1720, 1700, 1620, 1595. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{27}H_{24}{}^{81}BrN_2O_5$, 537.0843, found 537.0842.

Dimethyl (3*RS*,5'*RS*)-5'-(4-methylphenyl)-2-oxo-1'-phenyl-1,2-dihydro-3'*H*-spiro[indole-3,2'-pyrrolidine]-3',3'-dicarboxylate (3r). A solution of imine **1a** (129 mg, 0.58 mmol), cyclopropane **2e** (151 mg, 0.61 mmol) and $Yb(OTf)_3$ (36 mg, 0.06 mmol) in DCE (5.8 mL) was heated under reflux for 1 h yielding **3r** (244 mg, 89%) as yellowish crystals, mp 189–190 °C. R_f = 0.45 (ethyl acetate/petroleum ether; 1:1), dr 93:7. ^1H NMR ($CDCl_3$, 600 MHz): δ = 2.29 (s, 3H, CH_3), 2.78 (dd, ^2J 13.6, ^3J 7.9 Hz, 1H, CH_2), 3.34 (dd, ^2J 13.6, ^3J 8.3 Hz, 1H, CH_2), 3.51 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 5.78 (dd, ^3J 7.9, ^3J 8.3 Hz, 1H, CH), 6.63 (d, ^3J 7.9 Hz, 2H, Ar), 6.69 (t, ^3J 7.3 Hz, 1H, Ar), 6.75 (d, ^3J 7.8 Hz, 1H, Ar), 6.89 (dd, ^3J 7.3, ^3J 8.5 Hz, 2H, Ar), 7.05 (ddd, ^3J 7.6, ^3J 7.6, ^4J 0.7 Hz, 1H, Ar), 7.09 (d, ^3J 7.9 Hz, 2H, Ar), 7.25 (ddd, ^3J 7.6, ^3J 7.8, ^4J 0.8 Hz, 1H, Ar), 7.35–7.39 (m, 3H, Ar), 8.50 (br. s, 1H, NH); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ = 21.0 (CH_3), 40.7 (CH_2), 52.5 (OCH_3), 53.0 (OCH_3), 62.1 (CH), 66.5 (C), 76.2 (C), 110.4 (CH, Ar), 121.1 (2 × CH, Ar), 121.8 (CH, Ar), 122.5 (CH, Ar), 125.1 (CH, Ar), 126.9 (2 × CH, Ar), 128.3 (2 × CH, Ar), 128.5 (C, Ar), 129.1 (2 × CH, Ar), 129.9 (CH, Ar), 136.5 (C, Ar), 139.2

(C, Ar), 141.3 (C, Ar), 143.5 (C, Ar), 169.2 (CO_2Me), 169.5 (CO_2Me), 176.9 (C=O). IR (film, cm^{-1}): 3340, 3000, 2950, 2915, 2850, 1730, 1710, 1595. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{28}H_{27}N_2O_5$, 471.1914, found 471.1918.

Dimethyl (3*S*,5'*S*)-5'-(4-methylphenyl)-2-oxo-1'-phenyl-1,2-dihydro-3'*H*-spiro[indole-3,2'-pyrrolidine]-3',3'-dicarboxylate ((3*S*,5'*S*)-**3r)** was obtained by the same procedure from **1a** and (*R*)-**2e** (er 99:1); NMR spectra coincide with that of **3r**. $[\alpha]_D^{25}$ = +137.9 (c 0.50, EtOH), er 91:9.

Dimethyl (3*RS*,5'*RS*)-5'-(4-methoxyphenyl)-2-oxo-1'-phenyl-1,2-dihydro-3'*H*-spiro[indole-3,2'-pyrrolidine]-3',3'-dicarboxylate (3s). A solution of imine **1a** (142 mg, 0.64 mmol), cyclopropane **2f** (177 mg, 0.67 mmol) and $Yb(OTf)_3$ (40 mg, 0.06 mmol) in DCE (6.4 mL) was heated under reflux for 1 h yielding **3s** (244 mg, 79%) as yellow foam. R_f = 0.51 (ethyl acetate/petroleum ether; 1:1), dr 93:7. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.77 (dd, ^2J 13.6, ^3J 7.6 Hz, 1H, CH_2), 3.34 (dd, ^2J 13.6, ^3J 8.5 Hz, 1H, CH_2), 3.56 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 5.73 (dd, ^3J 7.6, ^3J 8.5 Hz, 1H, CH), 6.66–6.69 (m, 2H, Ar), 6.70–6.74 (m, 2H, Ar), 6.81 (d, ^3J 8.8 Hz, 2H, Ar), 6.89 (dd, ^3J 7.4, ^3J 8.6 Hz, 2H, Ar), 7.05 (ddd, ^3J 7.5, ^3J 7.7, ^4J 0.9 Hz, 1H, Ar), 7.23 (ddd, ^3J 7.7, ^3J 7.7, ^4J 1.1 Hz, 1H, Ar), 7.37 (d, ^3J 7.5 Hz, 1H, Ar), 7.42 (d, ^3J 8.8 Hz, 2H, Ar), 8.10 (br. s, 1H, NH); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ = 40.6 (CH_2), 52.6 (OCH_3), 52.9 (OCH_3), 55.1 (OCH_3), 61.8 (CH), 66.3 (C), 76.3 (C), 110.2 (CH, Ar), 113.7 (2 × CH, Ar), 122.2 (2 × CH, Ar), 122.4 (CH, Ar), 122.5 (CH, Ar), 125.3 (CH, Ar), 128.1 (C, Ar), 128.2 (2 × CH, Ar), 128.3 (2 × CH, Ar), 129.9 (CH, Ar), 134.3 (C, Ar), 141.4 (C, Ar), 143.4 (C, Ar), 158.5 (C, Ar), 169.5 (CO_2Me), 169.6 (CO_2Me), 176.8 (C=O). IR (film, cm^{-1}): 3295, 2955, 2915, 2850, 1730, 1700, 1615, 1595. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{28}H_{27}N_2O_6$, 487.1864, found 487.1871.

Dimethyl (3*RS*,5'*RS*)-5'-(3,4-dimethoxyphenyl)-2-oxo-1'-phenyl-1,2-dihydro-3'*H*-spiro[indole-3,2'-pyrrolidine]-3',3'-dicarboxylate (3t). A solution of imine **1a** (208 mg, 0.94 mmol), cyclopropane **2g** (289 mg, 0.98 mmol) and $Yb(OTf)_3$ (58 mg, 0.09 mmol) in DCE (9.4 mL) was heated under reflux for 1 h yielding **3t** (383 mg, 79%) as white solid, mp 119–120 °C. R_f = 0.36 (ethyl acetate/petroleum ether; 1:1), dr 93:7. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.78 (dd, ^2J 13.6, ^3J 7.6 Hz, 1H, CH_2), 3.34 (dd, ^2J 13.6, ^3J 8.5 Hz, 1H, CH_2), 3.54 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 5.72 (dd, ^3J 7.6, ^3J 8.5 Hz, 1H, CH), 6.65–6.68 (m, 2H, Ar), 6.69–6.75 (m, 3H, Ar), 6.89 (dd, ^3J 7.4, ^3J 8.5 Hz, 2H, Ar), 6.95 (dd, ^3J 8.2, ^4J 2.0 Hz, 1H, Ar), 7.04 (ddd, ^3J 7.6, ^3J 7.6, ^4J 0.9 Hz, 1H, Ar), 7.18 (d, ^4J 2.0 Hz, 1H, Ar), 7.22 (ddd, ^3J 7.6, ^3J 7.8, ^4J 1.1 Hz, 1H, Ar), 7.36 (d, ^3J 7.6 Hz, 1H, Ar), 8.44 (br. s, 1H, NH); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ = 40.6 (CH_2), 52.5 (OCH_3), 52.9 (OCH_3), 55.7 (2 × OCH_3), 62.0 (CH), 66.2 (C), 76.2 (C), 110.4 (2 × CH, Ar), 110.8 (CH, Ar), 119.3 (CH, Ar), 122.0 (2 × CH,

Ar), 122.3 (CH, Ar), 122.4 (CH, Ar), 125.1 (CH, Ar), 128.1 (C, Ar), 128.2 (2 × CH, Ar), 129.9 (CH, Ar), 134.8 (C, Ar), 141.5 (C, Ar), 143.4 (C, Ar), 147.8 (C, Ar), 148.9 (C, Ar), 169.4 (CO_2Me), 169.6 (CO_2Me), 176.9 (C=O). IR (film, cm^{-1}): 3295, 2955, 2915, 2850, 1730, 1700, 1620, 1595. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{29}H_{29}N_2O_7$, 517.1969, found 517.1973.

Dimethyl (3*RS*,5'*RS*)-5'-(3,4,5-trimethoxyphenyl)-2-oxo-1'-phenyl-1,2-dihydro-3'*H*-spiro[indole-3,2'-pyrrolidine]-3',3'-dicarboxylate (3u). A solution of imine **1a** (193 mg, 0.87 mmol), cyclopropane **2h** (296 mg, 0.91 mmol) and $Yb(OTf)_3$ (54 mg, 0.09 mmol) in DCE (8.7 mL) was heated under reflux for 1 h yielding **3u** (385 mg, 81%) as white solid, mp 210–211 °C. R_f = 0.25 (ethyl acetate/petroleum ether; 1:1), dr 93:7. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.76 (dd, ^2J 13.7, ^3J 7.8 Hz, 1H, CH_2), 3.33 (dd, ^2J 13.7, ^3J 8.4 Hz, 1H, CH_2), 3.52 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 3.76 (s, 6H, OCH_3), 3.79 (s, 3H, OCH_3), 5.72 (dd, ^3J 7.8, ^3J 8.4 Hz, 1H, CH), 6.67 (d, ^3J 7.8 Hz, 2H, Ar), 6.71–6.75 (m, 4H, Ar), 6.91 (dd, ^3J 7.5, ^3J 8.3 Hz, 2H, Ar), 7.03 (dd, ^3J 7.5, ^3J 7.5 Hz, 1H, Ar), 7.23 (ddd, ^3J 7.5, ^3J 7.6, ^4J 0.8 Hz, 1H, Ar), 7.36 (d, ^3J 7.6 Hz, 1H, Ar), 8.41 (br. s, 1H, NH); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ = 40.6 (CH_2), 52.5 (OCH_3), 52.9 (OCH_3), 55.9 (2 × OCH_3), 60.7 (OCH_3), 62.4 (CH), 66.3 (C), 76.1 (C), 103.9 (2 × CH, Ar), 110.4 (CH, Ar), 121.7 (2 × CH, Ar), 122.2 (CH, Ar), 122.3 (CH, Ar), 125.1 (CH, Ar), 128.2 (C, Ar), 128.3 (2 × CH, Ar), 129.9 (CH, Ar), 136.5 (C, Ar), 138.0 (C, Ar), 141.5 (C, Ar), 143.4 (C, Ar), 153.0 (2 × C, Ar), 169.2 (CO_2Me), 169.5 (CO_2Me), 176.5 (C=O). IR (film, cm^{-1}): 3340, 2955, 2915, 2870, 2850, 1740, 1730, 1710, 1615, 1595. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{30}H_{31}N_2O_8$, 547.2075, found 547.2081.

Dimethyl (3*RS*,5'*RS*)-5'-(4-nitrophenyl)-2-oxo-1'-phenyl-1,2-dihydro-3'*H*-spiro[indole-3,2'-pyrrolidine]-3',3'-dicarboxylate (3v). A solution of imine **1a** (127 mg, 0.57 mmol), cyclopropane **2i** (168 mg, 0.60 mmol) and $Yb(OTf)_3$ (36 mg, 0.06 mmol) in DCE (5.7 mL) was heated under reflux for 20 h yielding **3v** (147 mg, 51%, 60% brsm) as brown oil. Extra portions of $Yb(OTf)_3$ (36 mg, 0.06 mmol) were added twice in 8 and 16 h. R_f = 0.54 (ethyl acetate/petroleum ether; 1:1), dr 91:9. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.74 (dd, ^2J 13.7, ^3J 6.7 Hz, 1H, CH_2), 3.49 (dd, ^2J 13.7, ^3J 9.4 Hz, 1H, CH_2), 3.64 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 5.85 (dd, ^3J 6.7, ^3J 9.4 Hz, 1H, CH), 6.70 (d, ^3J 7.8 Hz, 1H, Ar), 6.74–6.79 (m, 3H, Ar), 6.90 (dd, ^3J 7.3, ^3J 8.5 Hz, 2H, Ar), 7.07 (ddd, ^3J 7.6, ^3J 7.7, ^4J 1.0 Hz, 1H, Ar), 7.24 (ddd, ^3J 7.7, ^3J 7.8, ^4J 1.2 Hz, 1H, Ar), 7.34 (d, ^3J 7.6 Hz, 1H, Ar), 7.72 (d, ^3J 8.8 Hz, 2H, Ar), 8.12 (d, ^3J 8.8 Hz, 2H, Ar), 8.27 (br. s, 1H, NH); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ = 39.7 (CH_2), 52.8 (OCH_3), 52.9 (OCH_3), 61.6 (CH), 65.8 (C), 76.6 (C), 110.5 (CH, Ar), 122.4 (CH, Ar), 123.55 (2 × CH, Ar), 123.60 (2 × CH, Ar), 124.0 (CH, Ar), 125.3 (CH, Ar), 126.8 (C, Ar), 128.3 (2 × CH, Ar), 128.4 (2 × CH, Ar), 130.2 (CH, Ar), 141.8 (C, Ar), 142.7 (C, Ar), 147.0 (C, Ar), 150.1 (C, Ar), 169.3

(CO_2Me), 169.7 (CO_2Me), 177.0 (C=O). IR (film, cm^{-1}): 3305, 2950, 2915, 2850, 1730, 1700, 1620, 1595. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{27}H_{24}N_3O_7$, 502.1609, found 502.1617.

Dimethyl (3*RS*,5'*RS*)-5'-[4-(methoxycarbonyl)phenyl]-2-oxo-1'-phenyl-1,2-dihydro-3'*H*-spiro[indole-3,2'-pyrrolidine]-3',3'-dicarboxylate (3w). A solution of imine **1a** (109 mg, 0.49 mmol), cyclopropane **2j** (150 mg, 0.51 mmol) and $Yb(OTf)_3$ (30 mg, 0.05 mmol) in DCE (4.9 mL) was heated under reflux for 16 h yielding **3w** (135 mg, 54%) as yellow foam. An extra portion of $Yb(OTf)_3$ (30 mg, 0.05 mmol) was added in 8 h. R_f = 0.51 (ethyl acetate/petroleum ether; 1:1), dr 92:8. ^1H NMR ($CDCl_3$, 600 MHz): δ = 2.76 (dd, ^2J 13.6, ^3J 7.3 Hz, 1H, CH_2), 3.42 (dd, ^2J 13.6, ^3J 8.8 Hz, 1H, CH_2), 3.56 (s, 3H, OCH_3), 3.69 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 5.83 (dd, ^3J 7.3, ^3J 8.8 Hz, 1H, CH), 6.67–6.69 (m, 2H, Ar), 6.71–6.74 (m, 2H, Ar), 6.88 (dd, ^3J 7.4, ^3J 8.6 Hz, 2H, Ar), 7.06 (ddd, ^3J 7.6, ^3J 7.7, ^4J 0.9 Hz, 1H, Ar), 7.24 (ddd, ^3J 7.7, ^3J 7.8, ^4J 1.1 Hz, 1H, Ar), 7.35 (d, ^3J 7.6 Hz, 1H, Ar), 7.58 (d, ^3J 8.4 Hz, 2H, Ar), 7.95 (d, ^3J 8.4 Hz, 2H, Ar), 8.37 (br. s, 1H, NH); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ = 40.1 (CH_2), 51.9 (OCH_3), 52.6 (OCH_3), 52.9 (OCH_3), 62.1 (CH), 66.2 (C), 76.4 (C), 110.4 (CH, Ar), 122.2 (2 × CH, Ar), 122.4 (CH, Ar), 122.9 (CH, Ar), 125.2 (CH, Ar), 127.3 (2 × CH, Ar), 127.7 (C, Ar), 128.3 (2 × CH, Ar), 128.9 (C, Ar), 129.7 (2 × CH, Ar), 130.0 (CH, Ar), 141.6 (C, Ar), 143.1 (C, Ar), 147.8 (C, Ar), 167.0 (CO_2Me), 169.35 (CO_2Me), 169.38 (CO_2Me), 176.9 (C=O). IR (film, cm^{-1}): 3265, 2950, 2915, 2870, 2850, 1720, 1700, 1695, 1685, 1615, 1595. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{29}H_{27}N_2O_7$, 515.1813, found 515.1810.

Dimethyl (3*RS*,5'*RS*)-5'-(4-cyanophenyl)-2-oxo-1'-phenyl-1,2-dihydro-3'*H*-spiro[indole-3,2'-pyrrolidine]-3',3'-dicarboxylate (3x). A solution of imine **1a** (61 mg, 0.28 mmol), cyclopropane **2k** (75 mg, 0.29 mmol) and $Yb(OTf)_3$ (17 mg, 0.03 mmol) in DCE (2.8 mL) was heated under reflux for 16 h yielding **3x** (80 mg, 60%) as yellowish foam. An extra portion of $Yb(OTf)_3$ (17 mg, 0.03 mmol) was added in 8 h. R_f = 0.43 (ethyl acetate/petroleum ether; 1:1), dr 91:9. ^1H NMR ($CDCl_3$, 600 MHz): δ = 2.72 (dd, ^2J 13.6, ^3J 6.7 Hz, 1H, CH_2), 3.45 (dd, ^2J 13.6, ^3J 9.3 Hz, 1H, CH_2), 3.63 (s, 3H, OCH_3), 3.69 (s, 3H, OCH_3), 5.78 (dd, ^3J 6.7, ^3J 9.3 Hz, 1H, CH), 6.70 (d, ^3J 7.7 Hz, 1H, Ar), 6.74 (d, ^3J 8.3 Hz, 2H, Ar), 6.79 (t, ^3J 7.3 Hz, 1H, Ar), 6.91 (dd, ^3J 7.3, ^3J 8.3 Hz, 2H, Ar), 7.07 (dd, ^3J 7.6, ^3J 7.7 Hz, 1H, Ar), 7.24 (ddd, ^3J 7.7, ^3J 7.7, ^4J 0.8 Hz, 1H, Ar), 7.33 (d, ^3J 7.6 Hz, 1H, Ar), 7.55 (d, ^3J 8.2 Hz, 2H, Ar), 7.66 (d, ^3J 8.2 Hz, 2H, Ar), 7.95 (br. s, 1H, NH); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ = 39.8 (CH_2), 52.8 (OCH_3), 53.0 (OCH_3), 61.8 (CH), 65.8 (C), 76.6 (C), 110.4 (CH, Ar), 110.8 (CN), 118.9 (C, Ar), 122.4 (CH, Ar), 123.7 (2 × CH, Ar), 124.0 (CH, Ar), 125.4 (CH, Ar), 126.8 (C, Ar), 128.3 (2 × CH, Ar), 128.4 (2 × CH, Ar), 130.2 (CH, Ar), 132.2 (2 × CH, Ar), 141.7 (C, Ar), 142.7 (C, Ar), 148.0 (C, Ar), 169.4 (CO_2Me), 169.7 (CO_2Me), 176.8 (C=O). IR (film, cm^{-1}): 3305, 2955, 2915, 2870,

2850, 2340, 1730, 1720, 1700, 1620, 1595. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{28}H_{24}N_3O_5$, 482.1710, found 482.1715.

Dimethyl (3*RS*,5'*RS*)-5'-(naphtalen-1-yl)-2-oxo-1'-phenyl-1,2-dihydro-3'*H*-spiro[indole-3,2'-pyrrolidine]-3',3'-dicarboxylate (3y). A solution of imine **1a** (125 mg, 0.56 mmol), cyclopropane **2l** (168 mg, 0.59 mmol) and $Yb(OTf)_3$ (35 mg, 0.06 mmol) in DCE (5.6 mL) was heated under reflux for 2 h yielding **3y** (259 mg, 91%) as white solid, mp 262–263 °C. R_f = 0.43 (ethyl acetate/petroleum ether; 1:1), dr 93:7. ^{1}H NMR ($CDCl_3$, 600 MHz, 328 K): δ = 2.77 (dd, ^2J 13.5, ^3J 7.3 Hz, 1H, CH_2), 3.51 (s, 3H, OCH_3), 3.74 (dd, ^2J 13.5, ^3J 8.9 Hz, 1H, CH_2), 3.76 (s, 3H, OCH_3), 6.58 (dd, ^3J 7.3, ^3J 8.9 Hz, 1H, CH), 6.65–6.67 (m, 2H, Ar), 6.70 (t, ^3J 7.3 Hz, 1H, Ar), 6.80 (d, ^3J 7.7 Hz, 1H, Ar), 6.88 (dd, ^3J 7.3, ^3J 8.7 Hz, 2H, Ar), 7.10 (ddd, ^3J 7.6, ^3J 7.6, ^4J 0.9 Hz, 1H, Ar), 7.30 (ddd, ^3J 7.7, ^3J 7.7, ^4J 1.1 Hz, 1H, Ar), 7.37 (dd, ^3J 7.7, ^3J 7.7 Hz, 1H, Ar), 7.45 (d, ^3J 7.5 Hz, 1H, Ar), 7.52 (ddd, ^3J 6.9, ^3J 8.0, ^4J 0.9 Hz, 1H, Ar), 7.62 (ddd, ^3J 6.9, ^3J 8.4, ^4J 1.3 Hz, 1H, Ar), 7.71 (d, ^3J 8.1 Hz, 1H, Ar), 7.76 (d, ^3J 7.3 Hz, 1H, Ar), 7.89 (d, ^3J 8.1 Hz, 1H, Ar), 8.03 (br. s, 1H, NH), 8.34 (br. d, ^3J 8.0 Hz, 1H, Ar); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz, 328 K): δ = 39.6 (CH_2), 52.4 (OCH_3), 52.9 (OCH_3), 58.9 (CH), 66.9 (C), 76.4 (C), 110.3 (CH, Ar), 120.9 (2 × CH, Ar), 121.8 (CH, Ar), 122.6 (CH, Ar), 123.1 (CH, Ar), 124.1 (CH, Ar), 125.3 (CH, Ar), 125.6 (CH, Ar), 125.7 (CH, Ar), 126.1 (CH, Ar), 127.2 (CH, Ar), 128.4 (2 × CH, Ar), 128.9 (C, Ar), 129.0 (CH, Ar), 130.0 (CH, Ar), 131.4 (C, Ar), 134.1 (C, Ar), 137.5 (C, Ar), 141.7 (C, Ar), 144.2 (C, Ar), 169.0 (CO_2Me), 169.4 (CO_2Me), 176.6 (C=O). IR (film, cm^{-1}): 3295, 3050, 2955, 2915, 2850, 1725, 1700, 1620, 1600. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{31}H_{27}N_2O_5$, 507.1914, found 507.1913.

Dimethyl (3*RS*,5'*RS*)-5'-(naphtalen-2-yl)-2-oxo-1'-phenyl-1,2-dihydro-3'*H*-spiro[indole-3,2'-pyrrolidine]-3',3'-dicarboxylate (3z). A solution of imine **1a** (125 mg, 0.56 mmol), cyclopropane **2m** (168 mg, 0.59 mmol) and $Yb(OTf)_3$ (35 mg, 0.06 mmol) in DCE (5.6 mL) was heated under reflux for 2 h yielding **3z** (203 mg, 71%) as yellowish solid, mp 124–125 °C. R_f = 0.44 (ethyl acetate/petroleum ether; 1:1), dr 93:7. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.91 (dd, ^2J 13.7, ^3J 7.7 Hz, 1H, CH_2), 3.48 (dd, ^2J 13.7, ^3J 8.5 Hz, 1H, CH_2), 3.57 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 6.00 (dd, ^3J 7.7, ^3J 8.5 Hz, 1H, CH), 6.70 (t, ^3J 7.3 Hz, 1H, Ar), 6.75–6.78 (m, 3H, Ar), 6.89 (dd, ^3J 7.3, ^3J 8.7 Hz, 2H, Ar), 7.10 (ddd, ^3J 7.6, ^3J 7.6, ^4J 0.9 Hz, 1H, Ar), 7.27 (ddd, ^3J 7.7, ^3J 7.7, ^4J 1.2 Hz, 1H, Ar), 7.41–7.45 (m, 2H, Ar), 7.47 (d, ^3J 7.5 Hz, 1H, Ar), 7.78–7.82 (m, 4H, Ar), 7.88 (s, 1H, Ar), 8.60 (br. s, 1H, NH); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ = 40.5 (CH_2), 52.6 (OCH_3), 53.0 (OCH_3), 62.5 (CH), 66.4 (C), 76.5 (C), 110.5 (CH, Ar), 121.8 (2 × CH, Ar), 122.35 (CH, Ar), 122.42 (CH, Ar), 125.17 (CH, Ar), 125.21 (CH, Ar), 125.5 (CH, Ar), 125.8 (CH, Ar), 126.2 (CH, Ar), 127.6 (CH, Ar), 127.8 (CH, Ar), 128.16 (C, Ar), 128.23 (CH,

Ar), 128.3 (2 × CH, Ar), 129.9 (CH, Ar), 132.8 (C, Ar), 133.3 (C, Ar), 139.8 (C, Ar), 141.6 (C, Ar), 143.4 (C, Ar), 169.4 (CO_2Me), 169.6 (CO_2Me), 177.1 (C=O). IR (film, cm^{-1}): 3270, 3055, 2950, 2915, 2850, 1725, 1700, 1615, 1595. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{31}H_{27}N_2O_5$, 507.1914, found 507.1922.

Dimethyl (3*RS*,5'*RS*)-2-oxo-1'-phenyl-5'-(thien-2-yl)-1,2-dihydro-3'*H*-spiro[indole-3,2'-pyrrolidine]-3',3'-dicarboxylate (3aa). A solution of imine **1a** (122 mg, 0.55 mmol), cyclopropane **2n** (138 mg, 0.58 mmol) and $Yb(OTf)_3$ (34 mg, 0.05 mmol) in DCE (5.5 mL) was heated under reflux for 2 h yielding **3aa** (232 mg, 92%) as yellow foam. R_f = 0.44 (ethyl acetate/petroleum ether; 1:1), dr 91:9. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.94 (dd, ^2J 13.7, ^3J 7.1 Hz, 1H, CH_2), 3.40 (dd, ^2J 13.7, ^3J 8.7 Hz, 1H, CH_2), 3.62 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3), 6.06 (dd, ^3J 7.1, ^3J 8.7 Hz, 1H, CH), 6.70 (d, ^3J 7.7 Hz, 1H, Ar), 6.77–6.79 (m, 3H, Ar), 6.84 (dd, ^3J 3.5, ^3J 5.0 Hz, 1H, Ar), 6.93 (dd, ^3J 7.0, ^3J 8.8 Hz, 2H, Ar), 7.01 (dd, ^3J 3.5, ^4J 1.0 Hz, 1H, Ar), 7.05 (ddd, ^3J 7.6, ^3J 7.7, ^4J 1.0 Hz, 1H, Ar), 7.13 (dd, ^3J 5.0, ^4J 1.0 Hz, 1H, Ar), 7.22 (ddd, ^3J 7.7, ^3J 7.7, ^4J 1.2 Hz, 1H, Ar), 7.39 (d, ^3J 7.6 Hz, 1H, Ar), 8.22 (br. s, 1H, NH); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ = 40.7 (CH_2), 52.6 (OCH_3), 52.9 (OCH_3), 58.5 (CH), 66.0 (C), 76.3 (C), 110.2 (CH, Ar), 122.4 (CH, Ar), 123.2 (2 × CH, Ar), 123.4 (CH, Ar), 124.6 (CH, Ar), 125.2 (CH, Ar), 125.4 (CH, Ar), 126.1 (CH, Ar), 127.7 (C, Ar), 128.2 (2 × CH, Ar), 129.9 (CH, Ar), 141.4 (C, Ar), 143.1 (C, Ar), 146.9 (C, Ar), 169.3 (CO_2Me), 169.5 (CO_2Me), 176.9 (C=O). IR (film, cm^{-1}): 3300, 2955, 2915, 2850, 1730, 1700, 1620, 1595. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{25}H_{23}N_2O_5S$, 463.1322, found 463.1319.

Dimethyl (3*RS*,5'*RS*)-5'-(1-methyl-1*H*-indol-2-yl)-2-oxo-1'-phenyl-1,2-dihydro-3'*H*-spiro[indole-3,2'-pyrrolidine]-3',3'-dicarboxylate (3ab). A solution of imine **1a** (124 mg, 0.56 mmol), cyclopropane **2o** (169 mg, 0.59 mmol) and $Yb(OTf)_3$ (35 mg, 0.06 mmol) in DCE (5.6 mL) was heated under reflux for 2 h yielding **3ab** (165 mg, 58%) as yellow oil. R_f = 0.42 (ethyl acetate/petroleum ether; 1:1), dr 93:7. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.98 (dd, ^2J 13.4, ^3J 7.7 Hz, 1H, CH_2), 3.49 (dd, ^2J 13.4, ^3J 8.3 Hz, 1H, CH_2), 3.56 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 3.93 (s, 3H, NCH_3), 6.11 (dd, ^3J 7.7, ^3J 8.3 Hz, 1H, CH), 6.43 (s, 1H, Ar), 6.72–6.78 (m, 4H, Ar), 6.94 (dd, ^3J 7.4, ^3J 8.5 Hz, 2H, Ar), 7.06–7.12 (m, 2H, Ar), 7.18–7.21 (m, 1H, Ar), 7.28 (ddd, ^3J 7.7, ^3J 7.7, ^4J 1.1 Hz, 1H, Ar), 7.33 (d, ^3J 8.3 Hz, 1H, Ar), 7.46 (d, ^3J 7.2 Hz, 1H, Ar), 7.51 (d, ^3J 7.8 Hz, 1H, Ar), 8.67 (br. s, 1H, NH); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ = 30.1 (NCH_3), 38.5 (CH_2), 52.6 (OCH_3), 53.0 (OCH_3), 55.8 (CH), 66.3 (C), 75.8 (C), 100.7 (CH, Ar), 108.7 (CH, Ar), 110.4 (CH, Ar), 119.2 (CH, Ar), 120.4 (CH, Ar), 120.8 (CH, Ar), 121.2 (2 × CH, Ar), 122.3 (CH, Ar), 122.6 (CH, Ar), 125.4 (CH, Ar), 127.6 (C, Ar), 128.1 (C, Ar), 128.3 (2 × CH, Ar), 129.9 (CH, Ar), 137.6 (C, Ar), 140.5 (C, Ar), 141.4 (C, Ar), 143.4 (C, Ar), 168.8

(CO_2Me), 169.4 (CO_2Me), 176.8 (C=O). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{30}H_{28}N_3O_5$, 510.2023, found 510.2029.

Dimethyl (3*RS*,5'*RS*)-5'-(1-methyl-1*H*-indol-4-yl)-2-oxo-1'-phenyl-1,2-dihydro-3'*H*-spiro[indole-3,2'-pyrrolidine]-3',3'-dicarboxylate (3ac). A solution of imine **1a** (141 mg, 0.63 mmol), cyclopropane **2p** (191 mg, 0.67 mmol) and $Yb(OTf)_3$ (39 mg, 0.06 mmol) in DCE (6.3 mL) was heated under reflux for 2 h yielding **3ac** (153 mg, 47%) as yellow oil. R_f = 0.44 (ethyl acetate/petroleum ether; 1:1), dr 93:7. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.86 (dd, ^2J 13.6, ^3J 8.2 Hz, 1H, CH_2), 3.43 (s, 3H, OCH_3), 3.57 (dd, ^2J 13.6, ^3J 8.0 Hz, 1H, CH_2), 3.77 (s, 3H, OCH_3), 3.81 (s, 3H, NCH_3), 6.30 (dd, ^3J 8.0, ^3J 8.2 Hz, 1H, CH), 6.56–6.59 (m, 2H, Ar), 6.64 (t, ^3J 7.3 Hz, 1H, Ar), 6.82 (d, ^3J 7.8 Hz, 1H, Ar), 6.83 (d, ^3J 3.1 Hz, 1H, Ar), 6.88 (dd, ^3J 7.3, ^3J 8.5 Hz, 2H, Ar), 7.08 (ddd, ^3J 7.6, ^3J 7.6, ^4J 0.5 Hz, 1H, Ar), 7.12 (dd, ^3J 7.7, ^3J 7.7 Hz, 1H, Ar), 7.14 (d, ^3J 3.1 Hz, 1H, Ar), 7.17 (d, ^3J 7.1 Hz, 1H, Ar), 7.20 (d, ^3J 8.1 Hz, 1H, Ar), 7.28 (ddd, ^3J 7.6, ^3J 7.8, ^4J 0.8 Hz, 1H, Ar), 7.45 (d, ^3J 7.6 Hz, 1H, Ar), 8.76 (br. s, 1H, NH); ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ = 32.9 (NCH_3), 39.6 (CH_2), 52.4 (OCH_3), 53.0 (OCH_3), 60.3 (CH), 67.1 (C), 75.9 (C), 99.1 (CH, Ar), 107.8 (CH, Ar), 110.5 (CH, Ar), 116.4 (CH, Ar), 118.8 (2 × CH, Ar), 120.5 (CH, Ar), 121.7 (CH, Ar), 122.6 (CH, Ar), 125.2 (CH, Ar), 126.5 (C, Ar), 128.3 (2 × CH, Ar), 128.5 (CH, Ar), 129.3 (C, Ar), 129.8 (CH, Ar), 133.9 (C, Ar), 136.7 (C, Ar), 141.2 (C, Ar), 144.2 (C, Ar), 168.7 (CO_2Me), 169.4 (CO_2Me), 176.8 (C=O). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{30}H_{28}N_3O_5$, 510.2023, found 510.2029.

Methyl 3'-acetyl-2-oxo-1',5'-diphenyl-1,2-dihydrospiro[indole-3,2'-pyrrolidine]-3'-carboxylate (3af). A solution of imine **1a** (113 mg, 0.51 mmol), cyclopropane **2s** (116 mg, 0.53 mmol) and $Yb(OTf)_3$ (32 mg, 0.05 mmol) in DCM (5.1 mL) was heated under reflux for 4 h yielding **3af** (201 mg, 90%) as yellow oil. R_f = 0.56, 0.62 (ethyl acetate/petroleum ether; 1:1), mixture of C3'-epimers, dr 60:40. **A**: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.22 (s, 3H, CH_3), 2.81 (dd, ^2J 13.2, ^3J 7.0 Hz, 1H, CH_2), 3.32 (dd, ^2J 13.2, ^3J 8.9 Hz, 1H, CH_2), 3.57 (s, 3H, OCH_3), 5.77 (dd, ^3J 7.0, ^3J 8.9 Hz, 1H, CH), 6.66–6.73 (m, 4H, Ar), 6.86–6.90 (m, 2H, Ar), 7.05 (dd, ^3J 7.6, ^3J 7.7 Hz, 1H, Ar), 7.17–7.21 (m, 1H, Ar), 7.23 (dd, ^3J 7.7, ^3J 7.7 Hz, 1H, Ar), 7.27–7.30 (m, 2H, Ar), 7.33–7.36 (m, 1H, Ar), 7.53 (d, ^3J 7.3 Hz, 2H, Ar), 8.52 (br. s, 1H, NH); ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ = 28.5 (CH_3), 39.5 (CH_2), 52.4 (OCH_3), 62.1 (CH), 72.1 (C), 76.7 (C), 110.5 (CH, Ar), 122.2 (3 × CH, Ar), 122.6 (CH, Ar), 125.3 (CH, Ar), 127.0 (CH, Ar), 127.2 (2 × CH, Ar), 127.7 (C, Ar), 128.21 (2 × CH, Ar), 128.27 (2 × CH, Ar), 129.9 (CH, Ar), 141.5 (C, Ar), 142.25 (C, Ar), 143.3 (C, Ar), 170.1 (CO_2Me), 177.3 (C=O), 201.81 (C=O). **B**: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 1.94 (s, 3H, CH_3), 2.76 (dd, ^2J 13.6, ^3J 8.6 Hz, 1H, CH_2), 3.24 (dd, ^2J 13.6, ^3J 7.7 Hz, 1H, CH_2), 3.74 (s, 3H, OCH_3), 5.77 (dd, ^3J 7.7, ^3J 8.6 Hz, 1H, CH), 6.58–6.61

(m, 2H, Ar), 6.66–6.73 (m, 1H, Ar), 6.76 (d, ^3J 7.8 Hz, 1H, Ar), 6.86–6.90 (m, 2H, Ar), 7.08 (dd, ^3J 7.6, ^3J 7.7 Hz, 1H, Ar), 7.17–7.21 (m, 1H, Ar), 7.27–7.30 (m, 3H, Ar), 7.33–7.36 (m, 1H, Ar), 7.47 (d, ^3J 7.3 Hz, 2H, Ar), 8.81 (br. s, 1H, NH); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ = 28.9 (CH_3), 40.3 (CH_2), 52.9 (OCH_3), 62.4 (CH), 72.0 (C), 76.2 (C), 110.8 (CH, Ar), 120.7 (2 × CH, Ar), 121.7 (CH, Ar), 123.0 (CH, Ar), 125.9 (CH, Ar), 126.8 (2 × CH, Ar), 128.21 (C, Ar), 128.27 (3 × CH, Ar), 128.4 (2 × CH, Ar), 130.1 (CH, Ar), 141.2 (C, Ar), 142.25 (C, Ar), 143.7 (C, Ar), 170.5 (CO_2Me), 177.4 (C=O), 201.81 (C=O). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{27}H_{25}N_2O_4$, 441.1809, found 441.1811.

Ethyl 3'-acetyl-2-oxo-1',5'-diphenyl-1,2-dihydrospiro[indole-3,2'-pyrrolidine]-3'-carboxylate (3ag). A mixture of imine **1a** (78 mg, 0.35 mmol), cyclopropane **2t** (86 mg, 0.37 mmol) and $Yb(OTf)_3$ (22 mg, 0.04 mmol) in DCM (3.5 mL) was heated under reflux for 12 h yielding **3ag** (117 mg, 73%) as yellow oil. An extra portion of $Yb(OTf)_3$ (22 mg, 0.04 mmol) was added in 8 h. R_f = 0.66 (ethyl acetate/petroleum ether; 1:1), mixture of C3'-epimers, dr 63:37. **A**: ^1H NMR ($CDCl_3$, 600 MHz): δ = 1.07 (t, ^3J 7.1 Hz, 3H, CH_3), 2.22 (s, 3H, CH_3), 2.78 (dd, ^2J 13.2, ^3J 7.2 Hz, 1H, CH_2), 3.29 (dd, ^2J 13.2, ^3J 8.8 Hz, 1H, CH_2), 3.94 (dq, ^2J 10.8, ^3J 7.1 Hz, 1H, OCH_2), 4.16 (dq, ^2J 10.8, ^3J 7.1 Hz, 1H, OCH_2), 5.76 (dd, ^3J 7.2, ^3J 8.8 Hz, 1H, CH), 6.65–6.68 (m, 2H, Ar), 6.69–6.72 (m, 1H, Ar), 6.86–6.90 (m, 2H, Ar), 7.04 (ddd, ^3J 7.6, ^3J 7.7, ^4J 0.8 Hz, 1H, Ar), 7.16–7.20 (m, 1H, Ar), 7.24 (ddd, ^3J 7.6, ^3J 7.7, ^4J 1.2 Hz, 1H, Ar), 7.26–7.29 (m, 3H, Ar), 7.37 (ddd, ^3J 7.6, ^4J 0.8, ^5J 0.6 Hz, 1H, Ar), 7.50–7.52 (m, 2H, Ar), 8.21 (br. s, 1H, NH); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ = 13.6 (CH_3), 28.6 (CH_3), 39.6 (CH_2), 61.9 (OCH_2), 62.2 (CH), 72.1 (C), 76.6 (C), 110.4 (CH, Ar), 121.9 (2 × CH, Ar), 122.3 (CH, Ar), 122.4 (CH, Ar), 125.6 (CH, Ar), 126.98 (CH, Ar), 127.2 (2 × CH, Ar), 128.0 (C, Ar), 128.25 (2 × CH, Ar), 128.31 (2 × CH, Ar), 129.8 (CH, Ar), 141.4 (C, Ar), 142.4 (C, Ar), 143.5 (C, Ar), 169.6 (CO_2Et), 177.0 (C=O), 201.8 (C=O). **B**: ^1H NMR ($CDCl_3$, 600 MHz): δ = 1.25 (t, ^3J 7.1 Hz, 3H, CH_3), 1.95 (s, 3H, CH_3), 2.75 (dd, ^2J 13.6, ^3J 8.3 Hz, 1H, CH_2), 3.25 (dd, ^2J 13.6, ^3J 7.9 Hz, 1H, CH_2), 4.19–4.26 (m, 2H, OCH_2), 5.74 (dd, ^3J 7.9, ^3J 8.3 Hz, 1H, CH), 6.61–6.63 (m, 2H, Ar), 6.69–6.72 (m, 2H, Ar), 6.74 (ddd, ^3J 7.7, ^4J 1.0, ^5J 0.6 Hz, 1H, Ar), 6.86–6.90 (m, 2H, Ar), 7.07 (ddd, ^3J 7.6, ^3J 7.7, ^4J 0.8 Hz, 1H, Ar), 7.16–7.20 (m, 1H, Ar), 7.26–7.29 (m, 2H, Ar), 7.35 (ddd, ^3J 7.6, ^4J 0.8, ^5J 0.6 Hz, 1H, Ar), 7.46–7.48 (m, 2H, Ar), 8.37 (br. s, 1H, NH); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ = 13.7 (CH_3), 29.1 (CH_3), 40.1 (CH_2), 62.1 (OCH_2), 62.3 (CH), 71.9 (C), 76.3 (C), 110.6 (CH, Ar), 121.5 (2 × CH, Ar), 122.2 (CH, Ar), 122.9 (CH, Ar), 126.2 (CH, Ar), 126.98 (CH, Ar), 127.03 (2 × CH, Ar), 128.0 (C, Ar), 128.25 (2 × CH, Ar), 128.4 (2 × CH, Ar), 130.1 (CH, Ar), 141.2 (C, Ar), 142.3 (C, Ar), 143.7 (C, Ar), 170.2 (CO_2Et), 177.3 (C=O), 202.1 (C=O). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{28}H_{27}N_2O_4$, 455.1965, found 455.1975.

(3*RS*,5'*RS*)-3',3'-Diacetyl-1',5'-diphenylspiro[indole-3,2'-pyrrolidine]-2(1*H*)-one (3ah). A solution of imine **1a** (144 mg, 0.65 mmol), cyclopropane **2u** (138 mg, 0.68 mmol) and $Yb(OTf)_3$ (40 mg, 0.07 mmol) in DCM (6.5 mL) was heated under reflux for 4 h yielding **3ah** (247 mg, 89%) as yellow oil. R_f = 0.76 (ethyl acetate/petroleum ether; 1:1). ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.09 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 2.85 (dd, ^2J 13.2, ^3J 7.3 Hz, 1H, CH_2), 3.32 (dd, ^2J 13.2, ^3J 8.8 Hz, 1H, CH_2), 5.80 (dd, ^3J 7.3, ^3J 8.8 Hz, 1H, CH), 6.70–6.75 (m, 4H, Ar), 6.89 (dd, ^3J 7.4, ^3J 8.6 Hz, 2H, Ar), 7.04 (ddd, ^3J 7.6, ^3J 7.6, ^4J 1.0 Hz, 1H, Ar), 7.20 (t, ^3J 7.3 Hz, 1H, Ar), 7.23 (ddd, ^3J 7.7, ^3J 7.7, ^4J 1.2 Hz, 1H, Ar), 7.27–7.31 (m, 3H, Ar), 7.48–7.50 (m, 3H, Ar), 8.49 (br. s, 1H, NH); ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ = 29.3 (CH_3), 30.2 (CH_3), 38.8 (CH_2), 61.7 (CH), 78.2 (C), 110.7 (CH, Ar), 122.45 (CH, Ar), 122.53 (2 × CH, Ar), 122.9 (CH, Ar), 125.9 (CH, Ar), 127.0 (CH, Ar), 127.1 (2 × CH, Ar), 127.2 (C, Ar), 128.2 (2 × CH, Ar), 128.4 (2 × CH, Ar), 129.9 (CH, Ar), 141.5 (C, Ar), 142.0 (C, Ar), 143.2 (C, Ar), 177.5 (C=O), 204.0 (C=O), 205.7 (C=O). Signal of C was not observed. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{27}H_{25}N_2O_3$, 425.1860, found 425.1860.

Methyl 3'-nitro-2-oxo-1',5'-diphenyl-1,2-dihydrospiro[indole-3,2'-pyrrolidine]-3'-carboxylate (3ai). A solution of imine **1a** (198 mg, 0.89 mmol), cyclopropane **2v** (207 mg, 0.94 mmol) and $Yb(OTf)_3$ (55 mg, 0.09 mmol) in DCE (8.9 mL) was heated under reflux for 2 h yielding **3ai** (162 mg, 41%) as yellowish oil. R_f = 0.62 (ethyl acetate/petroleum ether; 1:1), mixture of C3'-epimers, dr 80:20. (5-Phenyl-4,5-dihydro-1,2-oxazole-3-carboxylate 2-oxide was also obtained under these conditions in 49% yield; the NMR data are coincident with that reported earlier).[28] **A**: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 3.07 (dd, ^2J 15.3, ^3J 6.2 Hz, 1H, CH_2), 3.64 (dd, ^2J 15.3, ^3J 9.6 Hz, 1H, CH_2), 3.79 (s, 3H, OCH_3), 5.79 (dd, ^3J 6.2, ^3J 9.6 Hz, 1H, CH), 6.68 (d, ^3J 7.8 Hz, 1H, Ar), 6.81–6.89 (m, 3H, Ar), 6.96 (d, ^3J 7.8 Hz, 1H, Ar), 7.09 (ddd, ^3J 7.6, ^3J 7.7, ^4J 0.9 Hz, 1H, Ar), 7.18–7.21 (m, 1H, Ar), 7.24–7.30 (m, 4H, Ar), 7.33 (d, ^3J 7.7 Hz, 1H, Ar), 7.51 (br. s, 1H, NH), 7.56–7.58 (m, 2H, Ar); ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ = 40.7 (CH_2), 53.8 (OCH_3), 61.3 (CH), 77.0 (C), 101.0 (C), 110.4 (CH, Ar), 123.1 (CH, Ar), 125.3 (CH, Ar), 125.5 (3 × CH, Ar), 127.5 (CH, Ar), 127.7 (2 × CH, Ar), 128.4 (2 × CH, Ar), 128.6 (2 × CH, Ar), 130.91 (CH, Ar), 138.6 (C, Ar), 140.7 (C, Ar), 141.4 (C, Ar), 142.3 (C, Ar), 164.7 (CO_2Me), 175.5 (C=O). **B**: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 3.25 (dd, ^2J 14.9, ^3J 6.9 Hz, 1H, CH_2), 3.29 (dd, ^2J 14.9, ^3J 9.2 Hz, 1H, CH_2), 3.76 (s, 3H, OCH_3), 5.99 (dd, ^3J 6.9, ^3J 9.2 Hz, 1H, CH), 6.43 (d, ^3J 7.8 Hz, 2H, Ar), 6.57 (t, ^3J 7.3 Hz, 1H, Ar), 6.66 (d, ^3J 7.8 Hz, 1H, Ar), 6.81–6.89 (m, 3H, Ar), 6.93 (dd, ^3J 7.1, ^3J 8.5 Hz, 2H, Ar), 7.18–7.21 (m, 1H, Ar), 7.24–7.30 (m, 2H, Ar), 7.60–7.62 (m, 2H, Ar), 8.13 (br. s, 1H, NH); ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ = 41.7 (CH_2), 53.7 (OCH_3), 63.8 (CH), 74.3 (C), 102.7 (C), 110.2 (CH, Ar), 118.5 (2 × CH, Ar), 120.0 (CH, Ar), 123.5 (CH, Ar), 125.1 (CH, Ar), 127.57 (CH, Ar), 127.61 (2 × CH, Ar), 128.1 (2 ×

CH, Ar), 128.3 (2 × CH, Ar), 130.91 (CH, Ar), 140.7 (C, Ar), 141.6 (C, Ar), 142.05 (C, Ar), 142.10 (C, Ar), 163.3 (CO_2Me), 177.5 (C=O). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{25}H_{22}N_3O_5$, 444.1554, found 444.1565.

Methyl 3'-cyano-2-oxo-1',5'-diphenyl-1,2-dihydrospiro[indole-3,2'-pyrrolidine]-3'-carboxylate (3aj). A solution of imine **1a** (118 mg, 0.53 mmol), cyclopropane **2w** (112 mg, 0.56 mmol) and $Sc(OTf)_3$ (52 mg, 0.10 mmol) in toluene (5.3 mL) was heated under reflux for 8 h yielding **2aj** (163 mg, 73%, 78% brsm) as yellowish foam. R_f = 0.50, 0.57 (ethyl acetate/petroleum ether; 1:1), mixture of C3'-epimers, dr 64:36. **A**: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.71 (dd, ^2J 13.2, ^3J 4.2 Hz, 1H, CH_2), 3.67 (s, 3H, OCH_3), 3.87 (dd, ^2J 13.2, ^3J 9.2 Hz, 1H, CH_2), 5.61 (dd, ^3J 4.2, ^3J 9.2 Hz, 1H, CH), 6.55 (d, ^3J 7.9 Hz, 2H, Ar), 6.75 (t, ^3J 7.3 Hz, 1H, Ar), 6.84 (d, ^3J 7.8 Hz, 1H, Ar), 6.95 (dd, ^3J 7.4, ^3J 8.7 Hz, 2H, Ar), 7.22 (ddd, ^3J 7.6, ^3J 7.6, ^4J 0.9 Hz, 1H, Ar), 7.28–7.32 (m, 1H, Ar), 7.34–7.41 (m, 3H, Ar), 7.56–7.59 (m, 2H, Ar), 7.94 (d, ^3J 7.6 Hz, 1H, Ar), 8.90 (br. s, 1H, NH); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ = 40.2 (CH_2), 54.0 (OCH_3), 55.2 (C), 63.7 (CH), 75.5 (C), 111.0 (CH, Ar), 116.9 (CN), 117.4 (CH, Ar), 119.2 (2 × CH, Ar), 121.6 (CH, Ar), 123.4 (CH, Ar), 126.0 (C, Ar), 126.6 (2 × CH, Ar), 128.6 (CH, Ar), 128.7 (4 × CH, Ar), 129.0 (CH, Ar), 140.5 (C, Ar), 141.3 (C, Ar), 143.7 (C, Ar), 164.9 (CO_2Me), 176.4 (C=O). **B**: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 3.09 (dd, ^2J 13.5, ^3J 6.2 Hz, 1H, CH_2), 3.13 (dd, ^2J 13.4, ^3J 10.3 Hz, 1H, CH_2), 3.32 (s, 3H, OCH_3), 5.62 (dd, ^3J 6.2, ^3J 10.3 Hz, 1H, CH), 6.39 (d, ^3J 8.0 Hz, 2H, Ar), 6.66 (t, ^3J 7.3 Hz, 1H, Ar), 6.88 (d, ^3J 7.8 Hz, 1H, Ar), 6.91 (dd, ^3J 7.4, ^3J 8.6 Hz, 2H, Ar), 7.14 (ddd, ^3J 7.6, ^3J 7.6, ^4J 0.8 Hz, 1H, Ar), 7.28–7.32 (m, 1H, Ar), 7.34–7.41 (m, 3H, Ar), 7.44–7.48 (m, 3H, Ar), 9.60 (br. s, 1H, NH); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ = 42.8 (CH_2), 53.5 (OCH_3), 55.9 (C), 62.6 (CH), 111.3 (CH, Ar), 116.3 (CN), 120.5 (CH, Ar), 123.1 (CH, Ar), 125.5 (CH, Ar), 126.08 (2 × CH, Ar), 126.13 (2 × CH, Ar), 127.3 (C, Ar), 127.6 (2 × CH, Ar), 127.8 (CH, Ar), 130.77 (2 × CH, Ar), 130.80 (CH, Ar), 140.0 (C, Ar), 140.1 (C, Ar), 143.4 (C, Ar), 164.0 (CO_2Me), 175.3 (C=O). Signal of C_{spiro} was not observed. IR (film, cm^{-1}): 3325, 3060, 3025, 2960, 1745, 1735, 1720, 1615, 1595. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{26}H_{22}N_3O_3$, 424.1656, found 424.1656.

(3*RS*,5'*RS*)-2-Oxo-1',5'-diphenyl-1,2-dihydro-3'*H*-spiro[indole-3,2'-pyrrolidine]-3',3'-dicarbonitrile (3ak). A solution of imine **1a** (162 mg, 0.73 mmol), cyclopropane **2x** (129 mg, 0.77 mmol) and $Sc(OTf)_3$ (180 mg, 0.37 mmol) in toluene (7.3 mL) was heated under reflux for 16 h yielding **3ak** (100 mg, 35%, 40% brsm) as white solid, mp 116–117 °C. An extra portion of $Sc(OTf)_3$ (180 mg, 0.37 mmol) was added in 8 h. R_f = 0.76 (ethyl acetate/petroleum ether; 1:1). ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.92 (dd, ^2J 13.1, ^3J 2.8 Hz, 1H, CH_2), 3.95 (dd, ^2J 13.1, ^3J 9.7 Hz, 1H, CH_2), 5.56 (dd, ^3J 2.8, ^3J 9.7 Hz, 1H, CH), 6.59–6.62 (m, 2H, Ar), 6.83 (t, ^3J 7.4 Hz, 1H,

Ar), 6.92 (ddd, ^3J 7.8, ^4J 0.9, ^5J 0.6 Hz, 1H, Ar), 7.00 (dd, ^3J 7.4, ^3J 8.9 Hz, 2H, Ar), 7.23 (ddd, ^3J 7.6, ^3J 7.7, ^4J 0.9 Hz, 1H, Ar), 7.33 (t, ^3J 7.4 Hz, 1H, Ar), 7.40–7.43 (m, 3H, Ar), 7.54–7.57 (m, 2H, Ar), 7.91 (ddd, ^3J 7.6, ^4J 0.9, ^5J 0.6 Hz, 1H, Ar), 8.52 (br. s, 1H, NH); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ = 41.1 (CH_2), 42.4 (C), 64.0 (CH), 76.2 (C), 111.5 (CH, Ar), 112.5 (CN), 113.4 (CN), 119.9 (2 × CH, Ar), 122.7 (C, Ar), 122.8 (CH, Ar), 123.9 (CH, Ar), 126.6 (CH, Ar), 126.7 (2 × CH, Ar), 128.2 (CH, Ar), 128.9 (2 × CH, Ar), 129.0 (2 × CH, Ar), 131.8 (CH, Ar), 140.2 (C, Ar), 140.3 (C, Ar), 143.1 (C, Ar), 175.1 (C=O). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{25}H_{19}N_4O$, 391.1553, found 391.1550.

Methyl 2-oxo-1',5'-diphenyl-3'-(pyridin-2-yl)-1,2-dihydrospiro[indole-3,2'-pyrrolidine]-3'-carboxylate (3al). A solution of imine **1a** (135 mg, 0.61 mmol), cyclopropane **2y** (161 mg, 0.64 mmol) and $Yb(OTf)_3$ (38 mg, 0.06 mmol) in DCE (6.1 mL) was heated under reflux for 8 h yielding **3al** (162 mg, 56%, 63% brsm) as yellowish foam. R_f = 0.44 (ethyl acetate/petroleum ether; 1:1), mixture of C3'-epimers, dr 71:29. **A**: ^1H NMR ($CDCl_3$, 600 MHz): δ = 3.06 (dd, ^2J 13.6, ^3J 7.9 Hz, 1H, CH_2), 3.72 (s, 3H, OCH_3), 3.77 (dd, ^2J 13.6, ^3J 8.6 Hz, 1H, CH_2), 6.09 (dd, ^3J 7.9, ^3J 8.6 Hz, 1H, CH), 6.19 (d, ^3J 7.6 Hz, 1H, Ar), 6.56 (d, ^3J 7.7 Hz, 1H, Ar), 6.65 (ddd, ^3J 7.6, ^3J 7.6, ^4J 0.9 Hz, 1H, Ar), 6.68–6.73 (m, 3H, Ar), 6.90 (dd, ^3J 7.4, ^3J 8.6 Hz, 2H, Ar), 7.03 (ddd, ^3J 7.7, ^3J 7.7, ^4J 1.1 Hz, 1H, Ar), 7.07–7.10 (m, 1H, Ar), 7.22 (t, ^3J 7.4 Hz, 1H, Ar), 7.31 (dd, ^3J 7.6, ^3J 7.9 Hz, 2H, Ar), 7.47–7.52 (m, 4H, Ar), 8.34 (ddd, ^3J 4.8, ^4J 1.6, ^5J 1.0 Hz, 1H, Ar), 8.84 (br. s, 1H, NH); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ = 42.5 (CH_2), 52.6 (OCH_3), 61.6 (CH), 66.6 (C), 78.7 (C), 110.17 (CH, Ar), 121.2 (2 × CH, Ar), 121.8 (CH, Ar), 121.9 (CH, Ar), 122.2 (CH, Ar), 124.2 (CH, Ar), 125.8 (CH, Ar), 126.6 (CH, Ar), 126.67 (2 × CH, C, Ar), 128.2 (2 × CH, Ar), 128.38 (2 × CH, Ar), 129.1 (CH, Ar), 135.50 (CH, Ar), 141.5 (C, Ar), 142.8 (C, Ar), 144.1 (C, Ar), 147.6 (CH, Ar), 158.9 (C, Ar), 172.7 (CO_2Me), 178.2 (C=O). **B**: ^1H NMR ($CDCl_3$, 600 MHz): δ = 3.12 (dd, ^2J 13.1, ^3J 6.5 Hz, 1H, CH_2), 3.21 (s, 3H, OCH_3), 3.78 (dd, ^2J 13.1, ^3J 7.9 Hz, 1H, CH_2), 5.66 (dd, ^3J 6.5, ^3J 7.9 Hz, 1H, CH), 6.43–6.46 (m, 2H, Ar), 6.63–6.66 (m, 1H, Ar), 6.68–6.73 (m, 1H, Ar), 7.07–7.12 (m, 2H, Ar), 7.16 (ddd, ^3J 4.8, ^3J 7.4, ^4J 0.9 Hz, 1H, Ar), 7.24 (t, ^3J 7.3 Hz, 1H, Ar), 7.28 (ddd, ^3J 7.7, ^3J 7.7, ^4J 1.2 Hz, 1H, Ar), 7.35 (dd, ^3J 7.5, ^3J 7.8 Hz, 2H, Ar), 7.39 (ddd, ^3J 8.0, ^4J 0.9, ^5J 0.9 Hz, 1H, Ar), 7.47–7.52 (m, 3H, Ar), 7.53–7.57 (m, 1H, Ar), 7.74 (d, ^3J 7.6 Hz, 1H, Ar), 8.51 (ddd, ^3J 4.9, ^4J 1.8, ^5J 0.9 Hz, 1H, Ar), 8.80 (br. s, 1H, NH); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ = 41.0 (CH_2), 51.8 (OCH_3), 63.0 (CH), 66.7 (C), 77.3 (C), 110.22 (CH, Ar), 117.6 (2 × CH, Ar), 119.6 (CH, Ar), 122.2 (CH, Ar), 122.5 (CH, Ar), 123.5 (CH, Ar), 126.74 (2 × CH, Ar), 127.0 (CH, Ar), 127.7 (C, Ar), 128.3 (2 × CH, Ar), 128.41 (2 × CH, Ar), 128.7 (CH, Ar), 129.5 (CH, Ar), 135.54 (CH, Ar), 141.1 (C, Ar), 142.5 (C, Ar), 144.6 (C, Ar), 148.4 (CH, Ar), 156.3 (C, Ar), 171.5 (CO_2Me), 177.2 (C=O). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{30}H_{26}N_3O_3$, 476.1969, found 476.1957.

(3*RS*,5'*RS*)-2'',2''-Dimethyl-1',5'-diphenyl-1,2-dihydrodispiro[indole-3,2'-pyrrolidine-3',5''-[1,3]dioxane]-2,4'',6''-trione (3am). A solution of imine **1a** (44 mg, 0.20 mmol), cyclopropane **2z** (58 mg, 0.21 mmol) and $Yb(OTf)_3$ (12 mg, 0.02 mmol) in DCM (2.0 mL) was heated under reflux for 2 h yielding **3am** (48 mg, 51%) as yellowish oil. R_f = 0.64 (ethyl acetate/petroleum ether; 1:1). ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 1.29 (s, 3H, CH_3), 1.56 (s, 3H, CH_3), 2.97 (dd, ^2J 13.2, ^3J 8.8 Hz, 1H, CH_2), 3.25 (dd, ^2J 13.2, ^3J 7.5 Hz, 1H, CH_2), 5.93 (dd, ^3J 7.5, ^3J 8.8 Hz, 1H, CH), 6.52–6.55 (m, 2H, Ar), 6.65 (t, ^3J 7.3 Hz, 1H, Ar), 6.78 (d, ^3J 7.8 Hz, 1H, Ar), 6.84 (dd, ^3J 7.3, ^3J 8.6 Hz, 2H, Ar), 7.17 (ddd, ^3J 7.6, ^3J 7.8, ^4J 0.9 Hz, 1H, Ar), 7.22 (t, ^3J 7.3 Hz, 1H, Ar), 7.29–7.35 (m, 3H, Ar), 7.49–7.52 (m, 2H, Ar), 7.61 (d, ^3J 7.5 Hz, 1H, Ar), 8.74 (br. s, 1H, NH); ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ = 26.8 (CH_3), 30.5 (CH_3), 39.8 (CH_2), 64.0 (C), 64.2 (CH), 79.0 (C), 106.2 (C), 111.1 (CH, Ar), 120.4 (2 × CH, Ar), 121.8 (CH, Ar), 123.4 (CH, Ar), 126.9 (2 × CH, C, Ar), 127.3 (CH, Ar), 127.5 (CH, Ar), 128.4 (2 × CH, Ar), 128.6 (2 × CH, Ar), 130.8 (CH, Ar), 140.1 (C, Ar), 141.5 (C, Ar), 143.6 (C, Ar), 165.1 (C=O), 165.5 (C=O), 176.1 (C=O). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{28}H_{25}N_2O_5$, 469.1758, found 469.1775.

Synthesis of dispiro-compounds 3ao and 3ao'. The solution of iminooxindole **1a** (100 mg, 0.45 mmol), cyclopropane **2ab** (118 mg, 0.47 mmol) and $Sc(OTf)_3$ (44 mg, 0.09 mmol) in DCE (4.5 mL) was heated under reflux for 16 h. Then the resulting mixture was concentrated under reduce pressure. The residue was purified by column chromatography on silica gel.

(3*RS*,3'*RS*,5'*RS*)-1''-Methyl-1',5'-diphenyl-1,1'',2,2''-tetrahydrodispiro[indole-3,2'-pyrrolidine-3',3''-indole]-2,2''-dione (3ao). Compound **3ao** was obtained in 29% yield (34% brsm, 64 mg) as white solid, mp 160–161 °C. R_f = 0.37 (ethyl acetate/petroleum ether; 1:1). ^{1}H NMR (DMSO-d_6, 600 MHz): δ = 2.59 (dd, ^2J 12.8, ^3J 9.2 Hz, 1H, CH_2), 2.91 (dd, ^2J 12.8, ^3J 7.0 Hz, 1H, CH_2), 3.00 (s, 3H, NCH_3), 6.18 (dd, ^3J 7.0, ^3J 9.2 Hz, 1H, CH), 6.18–6.21 (m, 2H, Ar), 6.30 (dd, ^3J 7.6, ^4J 0.7 Hz, 1H, Ar), 6.53–6.57 (m, 2H, Ar), 6.68 (d, ^3J 7.3 Hz, 1H, Ar), 6.84 (d, ^3J 7.8 Hz, 1H, Ar), 6.93 (dd, ^3J 7.3, ^3J 8.8 Hz, 2H, Ar), 7.05 (ddd, ^3J 7.5, ^3J 7.6, ^4J 1.0 Hz, 1H, Ar), 7.13 (ddd, ^3J 7.8, ^3J 7.8, ^4J 1.2 Hz, 1H, Ar), 7.23–7.28 (m, 2H, Ar), 7.33–7.39 (m, 4H, Ar), 7.47 (d, ^3J 7.2 Hz, 1H, Ar), 10.50 (br. s, 1H, NH); ^{13}C{^{1}H} NMR (DMSO-d_6, 150 MHz): δ = 25.9 (NCH_3), 41.4 (CH_2), 59.4 (C), 61.7 (CH), 76.2 (C), 107.7 (CH, Ar), 110.0 (CH, Ar), 115.6 (2 × CH, Ar), 117.7 (CH, Ar), 120.8 (CH, Ar), 121.6 (CH, Ar), 124.5 (CH, C, Ar), 125.6 (CH, Ar), 126.3 (2 × CH, Ar), 126.8 (CH, Ar), 128.3 (2 × CH, Ar), 128.6 (2 × CH, Ar), 128.8 (CH, Ar), 129.4 (C, Ar), 129.7 (CH, Ar), 140.7 (C, Ar), 142.2 (C, Ar), 144.2 (C, Ar), 144.3 (C, Ar), 173.5 (C=O), 174.5 (C=O). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{31}H_{26}N_3O_2$, 472.2020, found 472.2011.

(3*RS*,4'*R*S,5'*RS*)-1''-Methyl-1',5'-diphenyl-1,1'',2,2''-tetrahydrodispiro[indole-3,2'-pyrrolidine-4',3''-indole]-2,2''-dione (3ao'). Compound **3ao'** was obtained in 19% yield (21% brsm, 40 mg) as white solid, mp 330–331 °C (dec.). R_f = 0.45 (ethyl acetate/petroleum ether; 1:1). ^{1}H NMR (DMSO-d_6, 600 MHz): δ = 2.44 (d, ^2J 13.8 Hz, 1H, CH_2), 3.08 (s, 3H, NCH_3), 3.15 (d, ^2J 13.8 Hz, 1H, CH_2), 6.02 (s, 1H, CH), 6.61–6.63 (m, 2H, Ar), 6.72–6.74 (m, 2H, Ar), 6.81 (t, ^3J 7.3 Hz, 1H, Ar), 6.83–6.89 (m, 5H, Ar), 6.90–6.94 (m, 2H, Ar), 7.05–7.12 (m, 2H, Ar), 7.21 (ddd, ^3J 7.5, ^3J 7.5, ^4J 1.0 Hz, 1H, Ar), 7.29 (ddd, ^3J 7.7, ^3J 7.7, ^4J 1.2 Hz, 1H, Ar), 7.92 (d, ^3J 7.4 Hz, 1H, Ar), 8.05–8.07 (m, 1H, Ar), 10.14 (br. s, 1H, NH); ^{13}C{^{1}H} NMR (DMSO-d_6, 150 MHz): δ = 26.2 (NCH_3), 45.2 (CH_2), 56.8 (C), 71.2 (C), 71.3 (CH), 108.0 (CH, Ar), 110.0 (CH, Ar), 121.8 (CH, Ar), 122.5 (CH, Ar), 123.5 (CH, Ar), 123.8 (2 × CH, Ar), 125.0 (CH, Ar), 125.1 (CH, Ar), 126.7 (CH, Ar), 127.1 (2 × CH, Ar), 127.2 (2 × CH, Ar), 127.78 (CH, Ar), 127.83 (2 × CH, Ar), 129.6 (CH, Ar), 131.6 (C, Ar), 132.0 (C, Ar), 135.7 (C, Ar), 142.5 (C, Ar), 142.7 (C, Ar), 144.3 (C, Ar), 176.4 (C=O), 178.7 (C=O). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{31}H_{26}N_3O_2$, 472.2020, found 472.2019.

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ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

X-ray crystallography data, HPLC data, cell assay, copies of ^{1}H and ^{13}C{^{1}H} NMR spectra (PDF), CIF files

Accession Codes

CCDC 1879867, 1879868, 1879869, 1880076, 1879843, and 1879844 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif

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Notes

The authors declare no competing financial interest.

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