Copper(I)-Catalyzed Dearomative (3+2) Cycloaddition of 3-Nitroindoles with Propargylic nucleophiles: a Straightforward access to Cyclopenta[*b*]indolines

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*Cyclopenta[*b*]indolines, dearomatization, (3+2) cycloaddition, 3-nitroindoles, copper(I)-catalysis.*

ABSTRACT: The copper(I)-catalyzed dearomatization of 3-nitroindoles with propargylic nucleophiles is described. In mild reaction conditions, this original dearomative (3+2) cycloaddition process gives access to a wide variety of cyclopenta[*b*]indolines in good to excellent yields, with high functional group tolerance. Furthermore, an enantioselective version of this reaction is reachable by employing chiral phosphorous ligands. A mechanism proposal is given, based on kinetic studies.

Indolines constitute an important family of naturally occurring molecules,[1] within which several biologically active compounds, such as Vindolinine, Polyveoline, Spermacoceine and Kopsinitarine E, display a 2,3-fused cyclopentane ring (Figure 1).[2]

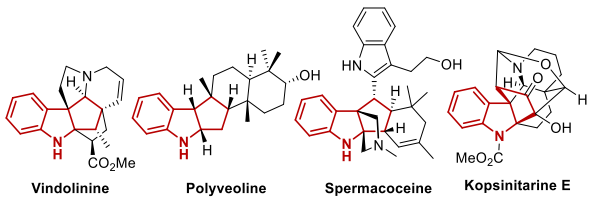
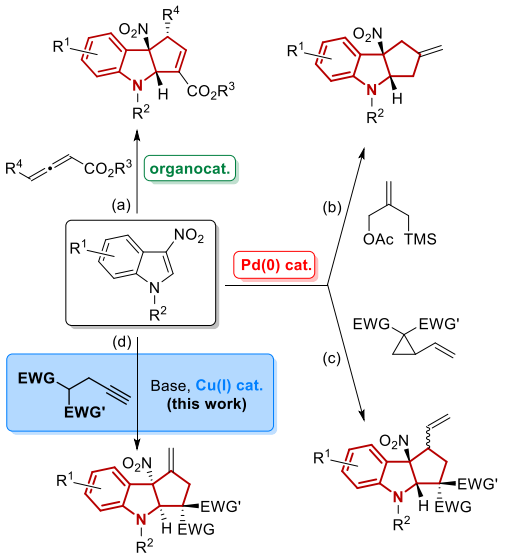


Figure 1. Relevant natural products containing a cyclopenta[*b*]indoline core.

For this reason, the cyclopenta[*b*]indoline core has attracted a lot of attention and many efforts have been dedicated to the preparation of this particular scaffold.[3] Among all possible methods, the direct introduction of the cyclopentane ring by means of a formal (3+2) cycloaddition process between an all-carbon 1,3-dipole and an indole partner remains undeniably the most straightforward.[3] Such a dearomative annulation strategy, which has long depended on the use of electron-rich indoles, based upon the seminal work of Kerr *et al.*,[4] has recently witnessed a change in paradigm, wherein electron-deficient indoles could be employed instead.[5-7]

More specifically, in direct connection with the seminal works from the groups of Chataigner and Gribble that showcased the unconventionally high reactivity of some nitroaromatics towards nitrogen-based 1,3-dipoles,[8] others and we demonstrated that cyclopenta[*b*]indolines could be straightforwardly obtained when 3-nitroindoles were engaged with all-carbon 1,3-dipoles.[5-7] In this field, in addition to recent achievements based on the use of allenoates (or surrogates) via nucleophilic organocatalysis (Scheme 1, (a)),[5] metal catalysis revealed itself a privileged approach.[6-7] In particular, Trost *et al.* reported the dearomative (3+2) cycloaddition reaction of 3-nitroindoles via transiently generated palladium trimethylenemethane complexes (Scheme 1, (b)),[6] a metal-catalyzed strategy which our group and that of Hyland later adopted by capitalizing on the palladium(0)-catalyzed ring opening of vinylcyclopropanes (Scheme 1, (c)).[7,9]



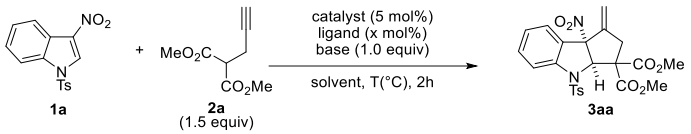
Scheme 1. Dearomative (3+2) cycloaddition reaction of 3-nitroindoles with *in situ* generated all-carbon 1,3-dipoles.

In continuation of our interest for such dearomative processes,[7a,10] we wish to report here that, by merging the use of a base with that of a catalytic copper(I) complex, cyclopenta[*b*]indolines can alternatively be obtained via the

formal (3+2) cycloaddition of 3-nitroindole with simple and easily accessible propargylic nucleophiles (Scheme 1, (d)).

At the onset of our study, inspired by the work of Dulcère *et al.* regarding the base-catalyzed annellation of nitrostyrene with propargylic nucleophiles,[11] we wondered if 3-nitroindoles could behave likewise and would afford cyclopenta[*b*]indolines. To this aim, we studied the formal (3+2) cycloaddition of *N*-tosyl-3-nitroindole **1a** with dimethyl propargylmalonate **2a** (1.5 equiv) (Table 1). However, in the reaction conditions previously reported by Dulcère *et al.*,[11] in the presence of Triton B (benzyltrimethylammonium hydroxide) at 50°C in dichloromethane, only traces of the desired cycloaddition product **3aa** could be observed (Table 1, Entry 1). For this reason, based on our previous interest for the metal-catalyzed carbocyclizations of formyl alkynes and other literature precedents, including Balme's and Dixon's seminal works,[12,13] we decided to evaluate if, using cesium carbonate as base (1 equiv), the use of a π-Lewis acid metal catalyst (5 mol%) could favour the desired dearomative process. Among the various metal sources which were tested, $Pd(OAc)_2$, PPh_3AuNTf_2 and $FeCl_3$ could not promote the expected reaction (Table 1, Entry 2-4). Nevertheless, we were pleased to witness that several silver salts, including silver nitrate or its bis(triflimide) analogue, permitted the desired dearomatization reaction to take place with good yields of 72% and 84%, respectively (Table 1, Entry 5-6). Encouraged by these results, we turned ourselves toward less expensive metal sources such as copper. In the presence of triphenylphosphine, copper(I) bromide, copper(I) iodide and copper(II) triflate, all allowed to obtained the cycloaddition product **3aa** in good yields, comparable to that obtained with $AgNO_3$ (Table 1, entries 7-9). Worthy of note, in absence of triphenylphosphine, copper(II) triflate showed poorly capable of activating **2a** ((Table 1, entry 10). In accord with previous observations,[13e,f] we concluded that $Cu(OTf)_2$ is actually a precatalyst and that, in such case, triphenylphosphine serves both as ligand and as reductant to promote the *in situ* generation of the more catalytically competent copper(I) trifluoromethanesulfonate complex.

Table 1. Optimization of the dearomative (3+2) cycloaddition of *N*-tosyl-3-nitroindole **1a** with dimethyl propargylmalonate **2a**.

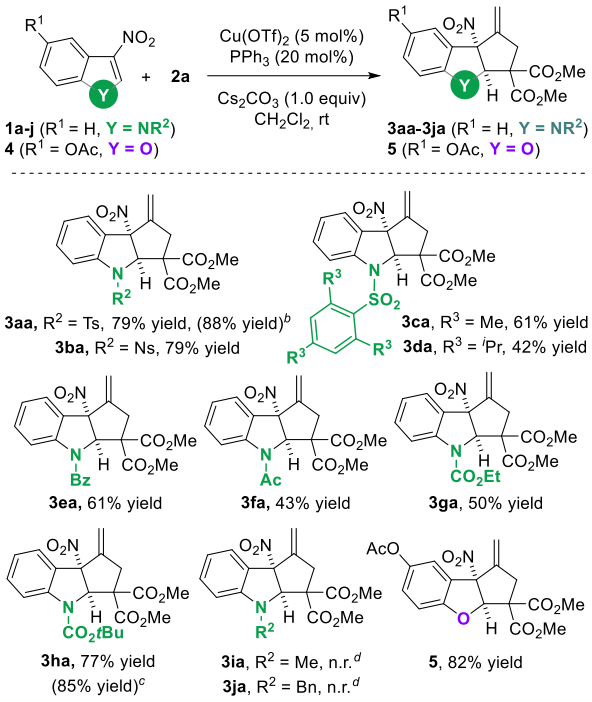


Entry	Catalyst	Ligand (x mol%)	Base	Solvent	Temperature (°C)	Yield (%)[b]
1	-	-	Triton B	CH_2Cl_2	50°C	1
2	$Pd(OAc)_2$	-	Cs_2CO_3	CH_2Cl_2	50°C	-[c]
3	PPh_3AuNTf_2	-	Cs_2CO_3	CH_2Cl_2	50°C	-[c]
4	$FeCl_3$	-	Cs_2CO_3	CH_2Cl_2	50°C	-[c]
5	$AgNO_3$	-	Cs_2CO_3	CH_2Cl_2	50°C	72
6	$AgNTf_2$	-	Cs_2CO_3	CH_2Cl_2	50°C	84
7	CuBr	PPh3 (20)	Cs_2CO_3	CH_2Cl_2	50°C	69
8	CuI	PPh3 (20)	Cs_2CO_3	CH_2Cl_2	50°C	66
9	$Cu(OTf)_2$	PPh3 (20)	Cs_2CO_3	CH_2Cl_2	50°C	72
10	$Cu(OTf)_2$	-	Cs_2CO_3	CH_2Cl_2	50°C	16
11[d]	$AgNTf_2$	-	Cs_2CO_3	CH_2Cl_2	rt	55
12[d]	$AgNO_3$	-	Cs_2CO_3	CH_2Cl_2	rt	63
13	$Cu(OTf)_2$	PPh3 (20)	Cs_2CO_3	CH_2Cl_2	rt	86
14	$Cu(OTf)_2$	PPh3 (20)	K_2CO3	CH_2Cl_2	rt	18
15	$Cu(OTf)_2$	PPh3 (20)	Li_2CO3	CH_2Cl_2	rt	-[c]
16	$Cu(OTf)_2$	PPh3 (20)	Cs_2CO_3	toluene	rt	81
17	$Cu(OTf)_2$	PPh3 (20)	Cs_2CO_3	MeOH	rt	30
18	$Cu(OTf)_2$	PPh3 (20)	Cs_2CO_3	1,2-DCE	rt	71
19	$Cu(OTf)_2$	PPh3 (20)	Cs_2CO_3	THF	rt	71
20	$Cu(OTf)_2$	PPh3 (20)	Cs_2CO_3	DMF	rt	64
21[f]	$Cu(OTf)_2$	PPh3 (20)	Cs_2CO_3	CH_2Cl_2	rt	91 (79)[e]

[a] Reaction conditions: **1a** (0.4 mmol), **2a** (0.6 mmol), catalyst (5 mol%), ligand (x mol%), base (0.4 mmol) in 2 mL of solvent (0.2M) for 2 hours. [b] ^1H NMR yields determined using propylene carbonate as internal standard. [c] No reaction occurred. [d] Reaction run overnight. [e] Isolated yield. [f] Reaction run with 1.1 equiv **2a.**

In order to reach milder reaction conditions, the cycloaddition reaction was then surveyed at room temperature. While, even after prolonged reaction times, silver salts exhibited a poorer reactivity in these new reaction conditions (Table 1, Entry 11-12), we were pleased to witness that the $Cu(OTf)_2/PPh_3$ system allowed to obtain **3aa** in 86% ^1H NMR yield after only two hours. The screening of a larger variety of bases and solvents led to no significant improvements (Table 1, Entries 14-20), but the desired dearomative cycloaddition worked as efficiently when only 1.1 equiv of propargylic derivative **1a** was used. In the later reaction conditions, which we used for the rest of our studies, the cyclopenta[*b*]indoline **3aa** was obtained in good 79% isolated yield (Table 1, entry 21).

With these optimized reaction conditions in hands, we then investigated the scope of this original dearomatization reaction, starting by evaluating the influence of the indole *N*-substitution pattern (Scheme 2).



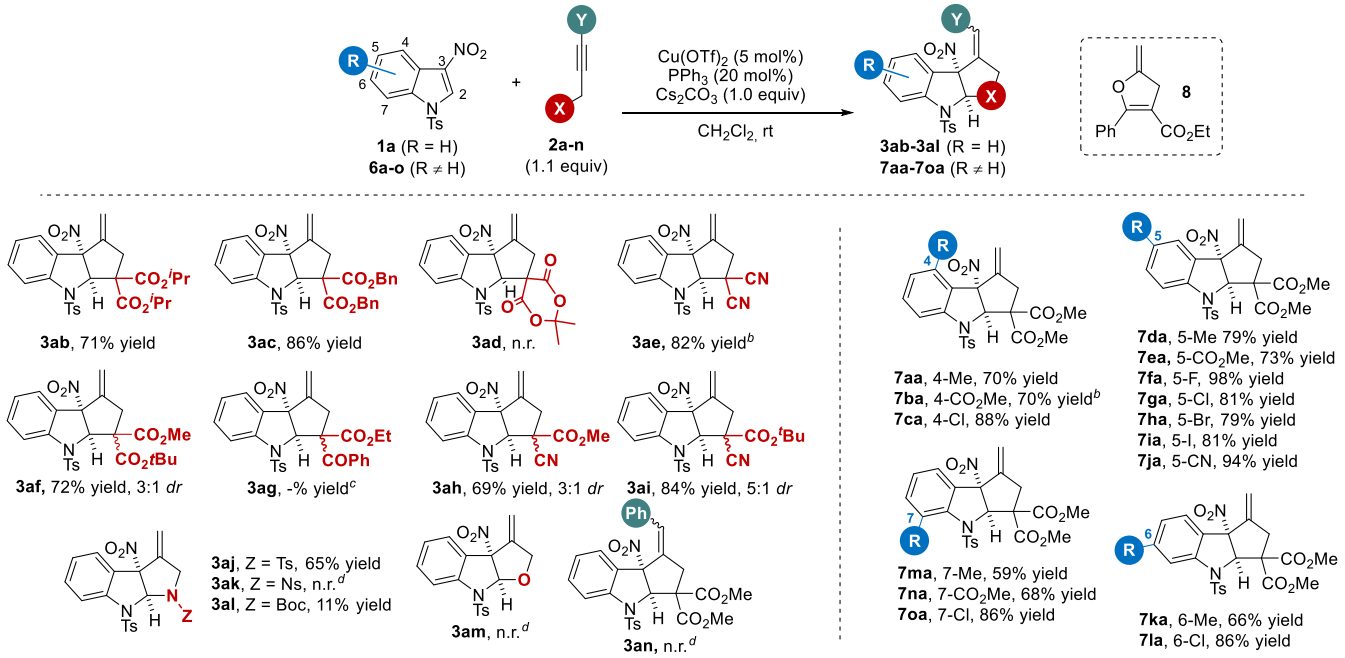
[a] Reaction conditions: **1a-j** or **4** (0.40 mmol), **2a** (0.44 mmol, 1.1 equiv), $Cu(OTf)_2$ (5 mol%), PPh_3 (20 mol%), Cs_2CO_3 (0.40 mmol) in 2 mL of CH_2Cl_2 (0.2M) at rt. [b] Starting from **1a** (2.50 mmol), 1.08 g of **3aa** was obtained. [c] With **1h** (2 equiv.). [d] No reaction occurred.

Scheme 2. Scope of the reaction – Influence of the nitrogen substitution pattern of the nitroindole partner – Extension to a 3-nitrobenzofuran.[a]

Whereas the model reaction of **1a** with **2a** could be scaled up to the gram scale preparation of **3aa** with good 88% yield, replacing the tosyl protecting group by a nosyl moiety had no detrimental effect (**3ba**, 79% yield). On the other hand, increasing the steric demand on the sulfonyl aromatic group tended to hamper the cyclization process. Indeed, the 3-nitroindole **1c** possessing a 2,4,6-trimethylbenzene sulfonyl moiety and its 2,4,6-tri*iso*propyl analogue **1d** led to the corresponding dearomatized products **3ca** and **3da** in lower 61% and 42% yields, respectively. The reaction proved also compatible with carbonyl-based protected indoles such as **1e** (benzoyl), **1f** (acetyl), **1g** (ethoxycarbonyl) and **1h** (*tert*-butoxycarbonyl), although competitive *N*-deprotection could also be observed, especially for **1e** and **1g**. In the case of the Boc-substituted substrate **1h**, the inherent steric hindrance of this protecting group limited this side process, which allowed to obtained the cyclopenta[*b*]indoline **3ha** in good 77% yield in the standard reaction conditions, and up to 85% yield when **1h** was used in excess. Reminiscent of previous studies,[7] the *N*-methyl and *N*-benzyl substrates **1i** an **1j**, in which a push-pull effect is supposed to happen, remained completely unreactive. Additionally, such a dearomatization strategy could be successfully applied to the efficient preparation of the cyclopenta[*b*]benzofuran **5** in 82% yield (starting from the 3-nitrobenzofuran **4**), suggesting that this dearomatization process is compatible with a wider range of nitroaromatics.

We next explored the scope of propargylic nucleophiles compatible with this annelative process. For this purpose, nitroindole **1a** was engaged with **2b-m** (Scheme 3, left). Employing other malonate derivatives, such as the di*iso*propyl propargylmalonate **2b** or its dibenzyl analogue **2c**, allowed to obtain the corresponding cyclopenta[*b*]indoles **3ab** and **3ac** in 71% and 86% yield, respectively. However, in the case of the Meldrum's acid propargyl derivative **2d**, no (3+2) cycloaddition product could be detected. We assume that in this case, the deprotonated form of **2d**, in line with the low p*K*a of such compounds (Meldrum's acid p*K*a ≈ 5), possesses a nucleophilicity so weak that the initial Michael addition step would become inoperative. Nevertheless, the less acidic propargyl malonitrile **2e** could be employed to generate **3ae** in satisfactory 82% yield. A slow cyclization rate was observed, which could be easily overcome by using 10 mol% of $Cu(OTf)_2$ and 40 mol% PPh_3. We next envisioned using unsymmetrical activated methylene derivatives (**2f-i**) to probe the diastereoselectivity of this cycloaddition reaction. Starting from the *tert*-butyl methyl propargyl malonate **2f**, the corresponding cycloadduct **3af** was isolated as a 3:1 mixture of diastereomers. On the other hand, the phenylketone derivative **2g** did not afford the expected product **3ag** and provided the intramolecular cyclization product **8** in 87% yield instead.[14] Better results were obtained with the propargylic cyanoacetates **2h** and **2i**, with which up to 5:1 *dr* and 84% yield were reached in the latter case, probably due to a better steric discrimination between the *tert*-butoxycarbonyl and the cyano groups. Heteroatom-based propargylic nucleophiles were tested next. While the *N*-Ts protected **2j** allowed to successfully obtain the corresponding desired pyrroloindoline **3aj** in 65% yield, the *N*-Ns equivalent **2k** remained completely unreactive and the *N*-Boc propargylamine **2l** only afforded a few of **3al** (11% yield). On the other hand, neither the propargyl alcohol **2m** nor the non-terminal phenyl-substituted propargylic malonate allowed the preparation of the corresponding cycloadducts **3am** and **3an**.

With regard to the influence of the indole aromatic substitution, we assessed it by engaging a variety of diversely substituted *N*-tosyl 3-nitroindoles **6a-o** with dimethyl propargyl malonate **1a** (Scheme 3, right).

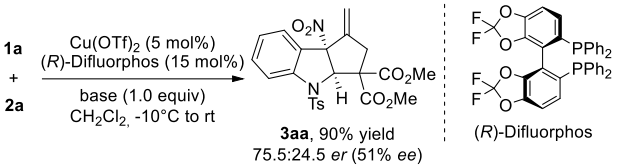


[a] Reaction conditions: **1a** or **6a-o** (0.40 mmol), **2a-l** (0.44 mmol, 1.1 equiv), $Cu(OTf)_2$ (5 mol%), PPh_3 (20 mol%), Cs_2CO_3 (0.40 mmol) in 2 mL of CH_2Cl_2 (0.2M) at rt. [b] 10 mol% $Cu(OTf)_2$, 40 mol% PPh_3 were used. [c] **8** was isolated in 87% yield. [d] No reaction occured.

Scheme 3. Scope of the reaction – Influence of both the propargylic nucleophile and the nitroindole aromatic substitution.[a]

In either position 4, 5, 6 or 7, we were pleased to observe little influence of the substitution pattern of the starting nitroarene onto the efficiency of this new dearomatization process. Indeed, in all the cases studied, the desired cyclopenta[*b*]indolines **7aa-7la** (15 examples) were obtained in good yields ranging from 66% to 98%. Various electron-donating (Me) as well as electron-withdrawing (halogens, CN, CO_2Me) groups were well tolerated.

In order to test the feasibility of developing an enantioselective version of this reaction, a screening of few chiral diphosphine ligands was performed. To our delight, after a quick optimization study,[15] we could demonstrate that the readily available atropoisomeric diphosphine (*R*)-Difluorphos[16] allowed to induce a significant level of enantioselectivity in the model reaction of nitroindole **1a** with dimethyl propargylmalonate **2a**. Indeed, when starting the reaction at -10°C and slowly warming up the reaction mixture to room temperature, the cyclopenta[*b*]indoline **3aa** was obtained in encouraging 51% enantiomeric excess (Scheme 4).

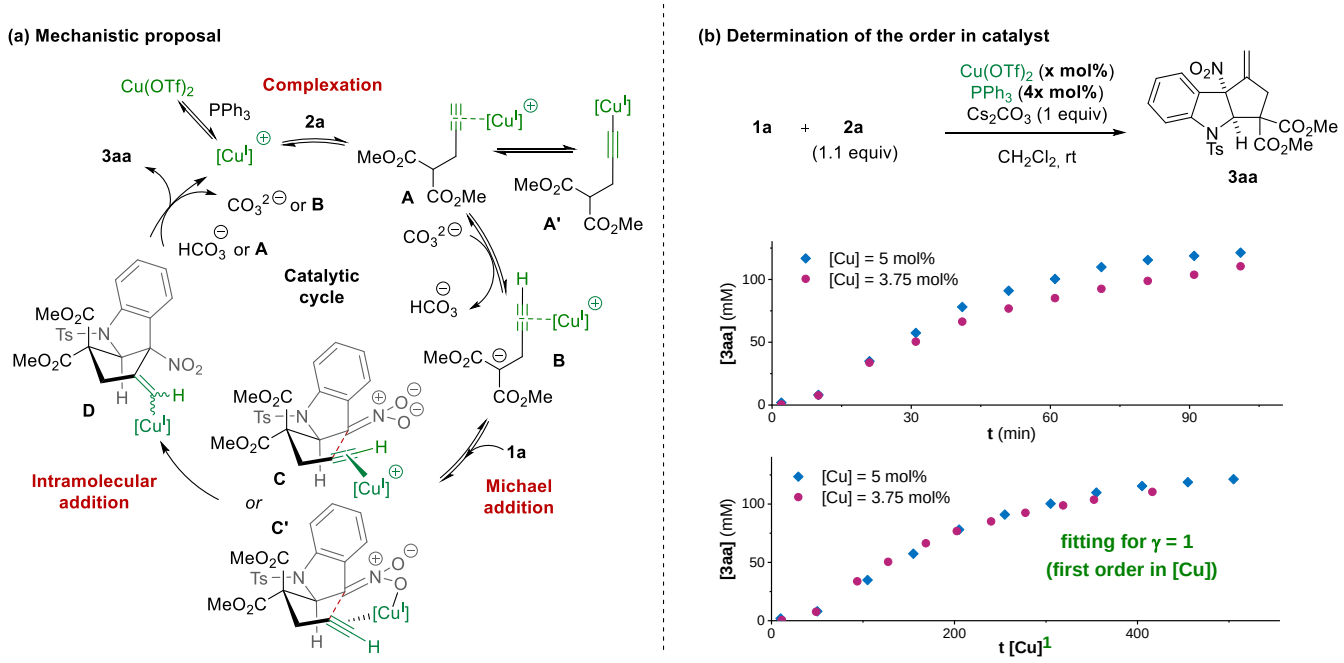


Scheme 4. Proof of concept for an enantioselective version of this dearomatization process.

This result represents the proof of concept that the development of an enantioselective version of this dearomative cycloaddition process is reachable, even if higher stereocontrol would require an in-depth chiral ligand screening.

From a mechanistic perspective (Scheme 5, (a)), in line with previous works,[12,13] we propose that the copper(I) complex resulting from the reduction of copper(II) triflate with triphenylphosphine may form the π-alkyne copper intermediate **A** in the presence of a propargylic nucleophile. While in basic reaction conditions **A** may likely exist in equilibrium with the corresponding alkynylcopper(I) derivative **A'**, the former would be prone to deprotonation in the presence of cesium carbonate and should generate the pseudo all carbon 1,3-dipole **B**, thereby. Upon Michael addition onto the 3-nitroindole, the resulting nitronate would then cyclize according to a chair like transition state through either an *anti*-carbocupration (**C**) or a *syn*-carbocupration (**C'**) pathway to afford the vinylcopper(I) intermediate **D**.[17] After protodecupration, either mediated by hydrogenocarbonate, **2a** or **A**, the dearomatization product would be released, together with the regeneration of the catalytically competent copper(I) complex.

To support this mechanistic picture further, we decided to perform some kinetic analyses. More specifically, we aimed to determine the order in catalyst so as to rule out a mechanistic scenario in which alkyne activation would entail the formation of a π-coordinated copper(I)acetylide copper(I) complex (second order in copper(I)). Indeed, the involvement of such binuclear copper intermediates, uncovered by Fokin in the context of the copper(I)-catalyzed alkyne/azide cycloaddition,[18] could have explained why the non-terminal propargylic derivative **2n** did not allow to obtain the corresponding dearomatization product **3an**.



Scheme 5. Mechanistic proposal and kinetic analyses

For this purpose, considering the dearomatization reaction of **1a** with **2a**, we applied the Variable Time Normalization Analysis (VTNA) method developed by Burés.[19] The concentration of cycloadduct **3aa** was monitored over time by ^{1}H NMR while employing two different initial catalyst loadings (Scheme 5, (b)).[19] By plotting product concentration against t[Cu]$^\gamma$ for several values of γ (0.5, 1, 2), the best overlay was obtained when γ=1,[15] which allowed to confirm a first order in catalyst, in line with our mechanistic proposal, and to infirm the occurrence of binuclear copper intermediates.

In conclusion, we have developed a straightforward access to cyclopenta[*b*]indolines. This new method, which is based on a copper(I)-catalyzed dearomative (3+2) cycloaddition reaction between 3-nitroindoles and propargylic nucleophiles, occurs with remarkably mild reaction conditions and is compatible with a large substrate scope. Chiral phosphorus ligands can be used and induce relevant levels of enantioselectivity, thereby. Finally, a plausible mechanistic proposal is given, supported by kinetic analyses.

EXPERIMENTAL SECTION

General Methods. All reactions were run under argon atmosphere unless specified. Reaction vessels were oven-dried, cooled under vacuum and flushed with argon before use. Cyclohexane and ethyl acetate were distilled under reduced pressure prior silica gel chromatography. 1,2-dichloroethan was distilled over calcium hydride. Methanol was distilled over sodium. THF, CH_2Cl_2, DMF and toluene were dried over alumina columns. Reagent grade di*iso*propyl ether and hexane were purchased and used without further purification. Every reagent was either purified following the methods described in the literature or used without further purification. Starting materials **1a-j**, **4**, **2a-n** and **6a-o** were prepared according to known protocols.[7,9,15]

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded at 400 MHz. Chemical shifts are reported in delta (*δ*) units part per million (ppm) relative to the residual protiated solvent. Coupling constants are reported in Hertz (Hz). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, sept = septuplet, m = multiplet, brs = broad singlet. Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded at 101 MHz. Chemical shifts are reported in delta (*δ*) units part per million (ppm) relative to the centre line of the triplet at 77.16 ppm for deuterochloroform. ^{13}C NMR experiments were routinely run with ^{1}H broadband decoupling. Fluorine-19 nuclear magnetic resonance (^{19}F NMR) spectra were recorded at 376 MHz.

HRMS analyses were performed at Sorbonne Université by ESI (electrospray ionization) using a HRMS/MS instrument. Melting point values were recorded on a Kofler bench. Enantiomeric excesses (*ees*) were determined by high-performance liquid chromatography using a chiral stationary phase (Chiralpak IA). Optical rotation value was measured with instruments operating at λ = 589 nm, corresponding to the sodium D line at the temperatures indicated.

5-iodo-3-nitro-1-tosyl-1H-indole (6i). Obtained according to the procedure described by Hyland *et al.*,[9] starting from 5-iodo-*N*-tosylindole (1.27 g, 3.2 mmol), as a pale yellow solid (461 mg, 35% yield) after trituration in methanol. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.60 (s, 1H), 8.50 (s, 1H), 7.90 – 7.80 (m, 2H), 7.75 (dd, *J* = 1.8, 1.2 Hz, 2H), 7.40 – 7.29 (m, 2H), 2.41 (s, 3H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) *δ* 147.0, 135.7, 133.7, 132.9, 132.1, 130.8 (2C), 130.2, 128.4, 127.6 (2C), 123.7, 115.4, 90.7, 21.9 ppm; IR (film): ν 3145, 2360, 2338,

1738, 1535, 1386, 1220 cm^{-1}; mp (°C) = 206-208; HRMS (ESI) [M+Na$^+$] calculated for $(C_{15}H_{11}IN_2O_4SNa)^+$: 509.0989, found 509.0987.

General protocol for the (3+2) cycloaddition reaction. In a screw-capped vial under argon atmosphere, cesium carbonate (130.4 mg, 0.40 mmol), nitroindole (0.40 mmol) and dichloromethane (800 µL) were successively added. To the resulting mixture was added the propargylated derivative (0.44 mmol) and the mixture was stirred at room temperature for 5 minutes. A solution of $Cu(OTf)_2$ (7.2 mg, 0.02 mmol) and PPh_3 (21.0 mg, 0.08 mmol) in dichloromethane (800 µL), previously stirred at room temperature for 30 minutes, was then transferred via cannula. The cannula was washed with additional dichloromethane (400 µL) (total volume of solvent = 2.0 mL) and the mixture was stirred at room temperature until TLC indicated full conversion of the starting nitroindole. The mixture was diluted with dichloromethane (10 mL), loaded onto a small silica plug, eluted with dichloromethane (40 mL) and evaporated under reduced pressure. The resulting crude mixture was purified by flash column chromatography or trituration to afford the desired cycloadduct.

Analytical data for the major isomer of compounds **3af**, **3ah** and **3ai** are described below. Selected ^{1}H NMR peaks for minor isomers of compounds **3af**, **3ah** and **3ai** are also reported.

(±)-Dimethyl 1-methylene-8b-nitro-4-tosyl-1,3a,4,8b-tetrahydrocyclopenta[*b*]indole-3,3(2H)-dicarboxylate (3aa). Obtained following the general procedure with dimethyl 2-(prop-2-yn-1-yl)malonate **2a** (75 mg, 0.44 mmol), starting from **1a** (127 mg, 0.40 mmol), as a white solid (158 mg, 81% yield) after flash column chromatography (petroleum ether/ methyl tert-butyl ether 9:1 to 8:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dt, J = 8.3, 0.8 Hz, 1H), 7.53 – 7.40 (m, 4H), 7.23 (td, J = 7.6, 1.0 Hz, 1H), 7.17 – 7.07 (m, 2H), 6.50 (s, 1H), 5.29 – 5.22 (m, 1H), 5.21 – 5.14 (m, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.07 (dt, J = 16.1, 2.5 Hz, 1H), 2.94 (dq, J = 16.1, 1.1 Hz, 1H), 2.33 (s, 3H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.6, 167.3, 145.2, 144.0, 143.2, 132.9, 132.3, 129.9 (2C), 127.7 (2C), 127.3, 127.2, 126.3, 118.3, 110.5, 100.1, 73.3, 63.9, 53.8, 53.5, 40.5, 21.7 ppm; IR (film): ν 2950, 2161, 2020, 1732, 1547, 1292, 1169 cm^{-1}; mp (°C) = 147-149; HRMS (ESI) [M+NH_4^+] calculated for $(C_{23}H_{22}N_2O_8SNH_4)^+$: 504.1435, found 504.1433.

(-)-Dimethyl 1-methylene-8b-nitro-4-tosyl-1,3a,4,8b-tetrahydrocyclopenta[*b*]indole-3,3(2H)-dicarboxylate ((-)-3aa). Obtained following the general procedure starting from **1a** (127 mg, 0.40 mmol), **2a** (75 mg, 0.44 mmol), $Cu(OTf)_2$ (8.6 mg, 0,024 mmol) and (*R*)-Difluorphos (41 mg, 0,06 mmol). The reaction was started at -10°C and slowly warmed up to room temperature. **3aa** was obtained as a white solid (175 mg, 90% yield). The enantiomeric excess (51%) was determined by HPLC (Daicel Chiralpak IA, T = 20 °C, 254 nm, 2-propanol:dichloromethane = 85:15, flow rate = 0.4 mL.min^{-1},): t_R (minor) = 16.69 min, t_R (major) = 19.95 min. $[\alpha]_D^{20}$ = -2.4 (*c* 0.01, dichloromethane).

(±)-Dimethyl 1-methylene-8b-nitro-4-((2-nitrophenyl)sulfonyl)-1,3a,4,8b-tetrahydrocyclopenta[*b*]indole-3,3(2H)-dicarboxylate (3ba). Obtained following the general procedure with dimethyl 2-(prop-2-yn-1-yl)malonate **2a** (75 mg, 0.44 mmol), starting from **1b** (139 mg, 0.40 mmol), as a pale yellow solid (164 mg, 79% yield) after trituration in di*iso*propyl ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, J = 8.0, 1.3 Hz, 1H), 7.70 (td, J = 7.8, 1.4 Hz, 1H), 7.67 – 7.60 (m, 1H), 7.62 – 7.51 (m, 3H), 7.55 – 7.46 (m, 1H), 7.30 (td, J = 7.6, 1.1 Hz, 1H), 6.62 (d, J = 0.6 Hz, 1H), 5.52 – 5.41 (m, 1H), 5.34 – 5.25 (m, 1H), 3.90 (s, 3H), 3.72 (s, 3H), 3.22 – 3.06 (m, 1H), 3.05 – 2.94 (m, 1H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.5, 167.3, 148.5, 143.0, 142.7, 135.1, 132.5, 131.7, 131.2, 129.8, 127.0, 126.8, 126.6, 124.5, 117.9, 111.9, 99.8, 72.9, 63.2, 53.9, 53.5, 40.9 ppm; IR (film): ν 3103, 2957, 2360, 2173, 1978, 1732, 1546 cm^{-1}; mp (°C) = 201-203; HRMS (ESI) [M+NH_4^+] calculated for $(C_{22}H_{19}N_3O_{10}SNH_4)^+$: 525.1129, found 525.1130.

(±)-Dimethyl 4-(mesitylsulfonyl)-1-methylene-8b-nitro-1,3a,4,8b-tetrahydrocyclopenta[*b*]indole-3,3(2H)-dicarboxylate (3ca). Obtained following the general procedure with dimethyl 2-(prop-2-yn-1-yl)malonate **2a** (75 mg, 0.44 mmol), starting from **1c** (138 mg, 0.40 mmol), as a brownish solid (126 mg, 61% yield) after trituration in di*iso*propyl ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.51 (m, 2H), 7.46 – 7.40 (m, 1H), 7.28 (dd, J = 7.6, 1.1 Hz, 1H), 6.98 – 6.85 (m, 2H), 6.22 (s, 1H), 5.32 – 5.23 (m, 1H), 5.23 – 5.14 (m, 1H), 3.78 (s, 3H), 3.69 (s, 3H), 3.09 – 2.86 (m, 2H), 2.45 (s, 6H), 2.29 (s, 3H) ppm;

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.6, 167.2, 144.4, 144.2, 144.0, 141.2, 132.6 (3C), 131.8, 131.1, 127.4 (2C), 126.3, 119.9, 110.4, 100.4, 72.5, 63.4, 53.7, 53.4, 40.8, 23.5 (2C), 21.2 ppm; IR (film): ν 2950, 2360, 2338, 1737, 1550, 1355, 1166 cm^{-1}; mp (°C) =158-160; HRMS (ESI) [M+NH_4^+] calculated for $(C_{25}H_{26}N_2O_8SNH_4)^+$: 532.1748, found 532.1748.

(±)-Dimethyl 1-methylene-8b-nitro-4-((2,4,6-tri*iso*-*propyl*phenyl)sulfonyl)-1,3a,4,8b-tetrahydrocyclopenta[*b*]indole-3,3(2H)-dicarboxylate (3da). Obtained following the general procedure with dimethyl 2-(prop-2-yn-1-yl)malonate **2a** (75 mg, 0.44 mmol), starting from **1d** (171 mg, 0.40 mmol), as a white solid (100 mg, 42% yield) after flash column chromatography (petroleum ether/ ethyl acetate 98:2 to 8:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.48 (m, 2H), 7.44 (td, J = 7.6, 1.4 Hz, 1H), 7.25 (td, J = 7.6, 1.1 Hz, 1H), 7.12 (s, 2H), 6.30 (s, 1H), 5.33 – 5.24 (m, 1H), 5.22 – 5.12 (m, 1H), 3.95 (hept, J = 6.7 Hz, 2H), 3.79 (s, 3H), 3.71 (s, 3H), 3.03 (dt, J = 16.0, 2.3 Hz, 1H), 2.98 – 2.79 (m, 2H), 1.25 (d, J = 5.4 Hz, 6H), 1.23 (d, J = 5.4 Hz, 6H), 0.89 (s, 6H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.5, 167.3, 154.2, 152.0 (2C), 144.2, 143.9, 131.7, 130.1, 127.9, 127.4, 126.4, 124.6 (2C), 120.0, 110.3, 99.8, 72.0, 63.4, 53.6, 53.3, 40.7, 34.3, 30.9 (2C), 24.9 (2C), 24.8 (2C), 23.61, 23.57 ppm; IR (film): ν 2955, 2359, 1735, 1600, 1551, 1172 cm^{-1}; mp (°C) = 197-199; HRMS (ESI) [M+H$^+$] calculated for $(C_{31}H_{38}N_2O_8SH)^+$: 599.2422, found 599.2423.

(±)-Dimethyl 4-benzoyl-1-methylene-8b-nitro-1,3a,4,8b-tetrahydrocyclopenta[*b*]indole-3,3(2H)-dicarboxylate (3ea). Obtained following the general procedure with dimethyl 2-(prop-2-yn-1-yl)malonate **2a** (150 mg, 0.88 mmol), starting from **1e** (213 mg, 0.80 mmol), as a

yellow oil (223 mg, 61% yield) after flash column chromatography (petroleum ether/ ethyl acetate 8:2 to 6:4). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dt, J = 7.7, 0.9 Hz, 1H), 7.57 (s, 1H), 7.55 (p, J = 2.0 Hz, 2H), 7.52 (t, J = 1.5 Hz, 1H), 7.48 (dd, J = 7.9, 6.6 Hz, 2H), 7.26 – 7.18 (m, 1H), 7.14 (t, J = 7.6 Hz, 1H), 6.78 (s, 1H), 5.77 (q, J = 1.8 Hz, 1H), 5.39 (q, J = 1.9 Hz, 1H), 3.65 (s, 3H), 3.48 (s, 3H), 3.27 (dt, J = 16.2, 2.0 Hz, 1H), 3.04 (d, J = 16.4 Hz, 1H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.3, 169.1, 167.4, 142.9, 142.7, 135.3, 131.6, 131.1, 128.7 (2C), 127.6 (2C), 126.5, 126.0, 124.7, 116.2, 112.7, 98.3, 73.3, 61.4, 53.5, 53.1, 41.4 ppm; IR (film): ν 3008, 2953, 2360, 1732, 1660, 1550, 1378 cm^{-1}; HRMS (ESI) [M+H$^+$] calculated for $(C_{23}H_{20}N_2O_7H$: 437.1343)$^+$, found 437.1344.

(±)-Dimethyl 4-acetyl-1-methylene-8b-nitro-1,3a,4,8b-tetrahydrocyclopenta[*b*]indole-3,3(2H)-dicarboxylate (3fa). Obtained following the general procedure with dimethyl 2-(prop-2-yn-1-yl)malonate **2a** (150 mg, 0.88 mmol), starting from **1f** (163 mg, 0.80 mmol), as a pale brown solid (128 mg, 43% yield) after flash column chromatography (petroleum ether/ ethyl acetate 9:1 to 8:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (brs, 1H), 7.60 (d, J = 7.7 Hz, 1H), 7.42 (td, J = 7.7, 1.4 Hz, 1H), 7.20 (td, J = 7.6, 1.0 Hz, 1H), 6.66 (s, 1H), 5.58 (dt, J = 2.5, 1.3 Hz, 1H), 5.33 (dt, J = 2.5, 1.3 Hz, 1H), 3.85 (s, 3H), 3.57 (s, 3H), 3.30 (d, J = 16.6 Hz, 1H), 3.02 (d, J = 16.6 Hz, 1H), 2.41 (s, 3H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.2, 169.5, 167.4, 143.3, 142.2, 132.2, 126.5, 125.5, 125.1, 118.1, 111.5, 99.9, 72.1, 62.7, 53.9, 53.4, 40.7, 23.9 ppm; IR (film): ν 3008, 2957, 2360, 1756, 1732, 1677, 1543 cm^{-1}; mp (°C) = 118-120; HRMS (ESI) [M+H$^+$] calculated for $(C_{18}H_{18}N_2O_7H)^+$: 375.1187, found 375.1186.

(±)-4-ethyl 3,3-dimethyl 1-methylene-8b-nitro-1,2,3a,8b-tetrahydrocyclopenta[*b*]indole-3,3,4-tricarboxylate (3ga). Obtained following the general procedure with dimethyl 2-(prop-2-yn-1-yl)malonate **2a** (75 mg, 0.44 mmol), starting from **1g** (94 mg, 0.40 mmol), as a yellow oil (81 mg, 50% yield) after flash column chromatography (petroleum ether/ ethyl acetate 9:1 to 8:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (brs, 1H), 7.65 (dd, J = 7.6, 1.3 Hz, 1H), 7.48 – 7.35 (m, 1H), 7.13 (td, J = 7.6, 1.1 Hz, 1H), 6.56 (s, 1H), 5.69 (dt, J = 3.3, 1.6 Hz, 1H), 5.36 (dt, J = 2.9, 1.5 Hz, 1H), 4.37 – 4.13 (m, 2H), 3.86 (s, 3H), 3.49 (s, 3H), 3.23 (dt, J = 15.9, 1.9 Hz, 1H), 3.10 (dt, J = 15.9, 2.2 Hz, 1H), 1.35 (t, J = 7.2 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.7, 167.8, 152.3, 144.0, 142.7, 132.1, 126.5, 124.7, 123.9, 115.6, 112.4, 99.3, 72.4, 62.6, 62.1, 53.5, 53.1, 41.9, 14.4 ppm; IR (film): ν 2955, 2359, 1731, 1551, 1273, 1067 cm^{-1}; HRMS (ESI) [M+H$^+$] calculated for $(C_{19}H_{20}N_2O_8H)^+$: 405.1292, found 405.1292.

(±)-4-(*tert*-butyl) 3,3-dimethyl 1-methylene-8b-nitro-1,2,3a,8b-tetrahydrocyclopenta[*b*]indole-3,3,4-tricarboxylate (3ha). Obtained following the general procedure with dimethyl 2-(prop-2-yn-1-yl)malonate **2a** (75 mg, 0.44 mmol), starting from **1h** (105 mg, 0.40 mmol), as a yellow solid (133 mg, 77% yield) after flash column chromatography (petroleum ether/ methyl tert-butyl ether 9:1 to 7:3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (brs, 1H), 7.62 (dd, J = 7.6, 1.1 Hz, 1H), 7.45 – 7.34 (m, 1H), 7.11 (td, J = 7.6, 1.1 Hz, 1H), 6.56 (s, 1H), 5.72 – 5.51 (m, 1H), 5.40 – 5.23 (m, 1H), 3.86 (s, 3H), 3.56 (s, 3H), 3.29 – 3.01 (m, 2H), 1.56 (s, 9H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.8, 168.0, 151.4, 144.3, 143.1, 132.1, 126.6, 124.8, 123.6, 115.8, 111.5, 99.4, 83.0, 72.3, 62.5, 53.6, 53.2, 41.8, 28.3 (3C) ppm; IR (film): ν 2996, 2968, 2360, 2342, 1734, 1716, 1548 cm^{-1}; mp (°C) = 123-125; HRMS (ESI) [M+Na$^+$] calculated for $(C_{21}H_{24}N_2O_8Na)^+$: 455.1425, found 455.1424.

(±)-Dimethyl 7-acetoxy-1-methylene-8b-nitro-1,2,3a,8b-tetrahydro-3H-cyclopenta[*b*]benzofuran-3,3-dicarboxylate (5). Obtained following the general procedure with dimethyl 2-(prop-2-yn-1-yl)malonate **2a** (75 mg, 0.44 mmol), starting from **4** (89 mg, 0.40 mmol), as a pale yellow solid (129 mg, 82% yield) after flash column chromatography (petroleum ether/ ethyl acetate 9:1 to 8:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 2.4 Hz, 1H), 7.06 (dd, J = 8.8, 2.4 Hz, 1H), 6.82 (d, J = 8.8 Hz, 1H), 6.57 (d, J = 1.2 Hz, 1H), 5.69 – 5.54 (m, 1H), 5.36 – 5.23 (m, 1H), 3.83 (s, 3H), 3.75 (s, 3H), 3.27 – 3.10 (m, 1H), 3.10 – 2.96 (m, 1H), 2.28 (s, 3H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.6, 168.9, 166.7, 157.3, 145.5, 143.8, 126.0, 123.3, 119.1, 111.9, 111.1, 101.1, 92.1, 63.3, 53.7, 53.3, 39.3, 21.1 ppm; IR (film): ν 3019, 2955, 2359, 1738, 1556, 1481, 1216 cm^{-1}; mp (°C) = 136-138; HRMS (ESI) [M+NH_4^+] calculated for $(C_{18}H_{17}NO_9NH_4)^+$: 409.1242, found 409.1242.

(±)-Dimethyl 8-methyl-1-methylene-8b-nitro-4-tosyl-1,3a,4,8b-tetrahydrocyclopenta[*b*]indole-3,3(2H)-dicarboxylate (7aa). Obtained following the general procedure with dimethyl 2-(prop-2-yn-1-yl)malonate **2a** (75 mg, 0.44 mmol), starting from **6a** (132 mg, 0.40 mmol), as a pale brown solid (140 mg, 70% yield) after flash column chromatography (petroleum ether/ methyl *tert*-butyl ether 9:1 to 7:3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 7.9 Hz, 1H), 7.48 – 7.40 (m, 2H), 7.36 (t, J = 7.9 Hz, 1H), 7.16 – 7.08 (m, 2H), 6.98 (d, J = 7.9 Hz, 1H), 6.38 (d, J = 1.0 Hz, 1H), 5.41 – 5.31 (m, 1H), 5.07 – 4.96 (m, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 3.06 (dt, J = 15.5, 2.6 Hz, 1H), 2.89 (dd, J = 15.5, 0.9 Hz, 1H), 2.35 (s, 3H), 2.24 (s, 3H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.6, 167.1, 145.2, 144.1, 141.8, 139.4, 133.1, 132.3, 129.9 (2C), 129.3, 127.7 (2C), 124.5, 116.4, 113.6, 101.6, 74.0, 63.5, 53.9, 53.6, 40.9, 21.7, 18.6 ppm; IR (film): ν 3004, 2955, 2360, 2342, 1732, 1552, 1171 cm^{-1}; mp (°C) = 176-178; HRMS (ESI) [M+NH_4^+] calculated for $(C_{24}H_{24}N_2O_8SNH_4)^+$: 518.1592, found 518.1590.

(±)-Trimethyl 1-methylene-8b-nitro-4-tosyl-1,3a,4,8b-tetrahydrocyclopenta[*b*]indole-3,3,8(2H)-tricarboxylate (7ba). Obtained following the general procedure with dimethyl 2-(prop-2-yn-1-yl)malonate **2a** (75 mg, 0.44 mmol), starting from **6b** (151 mg, 0.40 mmol), as a pale pink solid (153 mg, 70% yield) after trituration in di*iso*propyl ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, J = 8.3, 1.1 Hz, 1H), 7.75 (dd, J = 7.7, 1.1 Hz, 1H), 7.58 – 7.47 (m, 3H), 7.23 – 7.14 (m, 2H), 5.92 (s, 1H), 5.37 – 5.31 (m, 2H), 3.87 (s, 3H), 3.87 (s, 3H), 3.74 (s, 3H), 2.93 (d, J = 1.6 Hz, 2H), 2.35 (s, 3H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.4, 167.1, 165.0, 145.6, 145.6, 139.7, 132.9, 132.0, 130.1 (2C), 128.27, 128.25, 128.0, 127.9 (2C), 122.1, 117.4, 97.8, 76.6, 63.4, 53.8, 53.6, 52.4, 41.5, 21.8 ppm; IR (film): ν 3004, 2955, 2359, 2340, 1731, 1559, 1365 cm^{-1}; mp (°C) = 163-165; HRMS (ESI) [M+NH_4^+] calculated for $(C_{25}H_{24}N_2O_{10}SNH_4)^+$: 562.1490, found 562.1486.

(±)-Dimethyl 8-chloro-1-methylene-8b-nitro-4-tosyl-1,3a,4,8b-tetrahydrocyclopenta[*b*]indole-3,3(2H)-dicarboxylate (7ca). Obtained following the general procedure with dimethyl 2-(prop-2-yn-1-yl)malonate **2a** (75 mg, 0.44 mmol), starting from **6c** (140 mg, 0.40 mmol), as a white solid (182 mg, 88% yield) after flash column chromatography (petroleum ether/methyl *tert*-butyl ether 8:2 to 7:3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, J = 8.3, 0.9 Hz, 1H), 7.48 – 7.34 (m, 3H), 7.20 – 7.11 (m, 3H), 6.24 (d, J = 1.1 Hz, 1H), 5.45 (dt, J = 2.6, 1.0 Hz, 1H), 5.19 (dt, J = 2.7, 0.7 Hz, 1H), 3.88 (s, 3H), 3.88 (s, 3H), 3.07 (dt, J = 15.7, 2.6 Hz, 1H), 2.96 (dd, J = 15.7, 1.1 Hz, 1H), 2.36 (s, 3H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.4, 167.0, 145.7, 145.6, 139.6, 134.0, 133.2, 132.6, 130.1 (2C), 128.1, 127.5 (2C), 124.1, 117.0, 116.3, 100.4, 75.0, 63.5, 53.9, 53.6, 40.8, 21.7 ppm; IR (film): ν 3020, 2957, 2358, 2338, 1731, 1552, 1365 cm^{-1}; mp (°C) = 147-149; HRMS (ESI) [M+NH_4^+] calculated for $(C_{23}H_{21}ClN_2O_8SNH_4)^+$: 538.1045, found 538.1045.

(±)-Dimethyl 7-methyl-1-methylene-8b-nitro-4-tosyl-1,3a,4,8b-tetrahydrocyclopenta[*b*]indole-3,3(2H)-dicarboxylate (7da). Obtained following the general procedure with dimethyl 2-(prop-2-yn-1-yl)malonate **2a** (75 mg, 0.44 mmol), starting from **6d** (132 mg, 0.40 mmol), as a yellow solid (158 mg, 79% yield) after trituration in di*iso*-propyl ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.3 Hz, 1H), 7.48 – 7.40 (m, 2H), 7.28 – 7.21 (m, 1H), 7.21 – 7.15 (m, 1H), 7.10 (d, J = 8.1 Hz, 2H), 6.47 (d, J = 0.9 Hz, 1H), 5.24 – 5.18 (m, 1H), 5.18 – 5.05 (m, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 3.05 (dt, J = 16.1, 2.5 Hz, 1H), 2.91 (dq, J = 16.1, 1.1 Hz, 1H), 2.33 (s, 3H), 2.31 (s, 3H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.6, 167.2, 145.0, 144.0, 140.8, 136.3, 133.2, 132.8, 129.8 (2C), 127.7 (2C), 127.4, 127.1, 118.0, 110.3, 100.1, 73.4, 63.8, 53.7, 53.4, 40.3, 21.6, 21.2 ppm; IR (film): ν 3002, 2957, 2359, 1735, 1561, 1170 cm^{-1}; mp (°C) = 176-178; HRMS (ESI) [M+NH_4^+] calculated for $(C_{24}H_{24}N_2O_8SNH_4)^+$: 518.1592, found 518.1591.

(±)-Trimethyl 1-methylene-8b-nitro-4-tosyl-1,3a,4,8b-tetrahydrocyclopenta[*b*]indole-3,3,7(2H)-tricarboxylate (7ea). Obtained following the general procedure with dimethyl 2-(prop-2-yn-1-yl)malonate **2a** (75 mg, 0.44 mmol), starting from **6e** (151 mg, 0.40 mmol), as a pale brown solid (160 mg, 73% yield) after trituration in di*iso*-propyl ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 – 8.03 (m, 2H), 7.74 (dd, J = 8.6, 0.6 Hz, 1H), 7.56 – 7.39 (m, 2H), 7.21 – 7.02 (m, 2H), 6.54 (d, J = 1.0 Hz, 1H), 5.44 – 5.29 (m, 1H), 5.29 – 5.14 (m, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 3.82 (s, 3H), 3.08 (dt, J = 16.2, 2.4 Hz, 1H), 2.97 (dq, J = 16.2, 1.2 Hz, 1H), 2.31 (s, 3H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.4, 167.15, 165.7, 146.6, 145.6, 143.1, 133.9, 132.8, 130.0 (2C), 129.0, 128.2, 127.5 (2C), 127.3, 117.3, 111.5, 99.3, 73.8, 63.8, 53.8, 53.5, 52.4, 40.6, 21.7 ppm; IR (film): ν 3012, 2955, 2360, 2342, 1737, 1718, 1558 cm^{-1}; mp (°C) = 181-183; HRMS (ESI) [M+NH_4^+] calculated for $(C_{25}H_{24}N_2O_{10}SNH_4)^+$: 562.1490, found 562.1486.

(±)-Dimethyl 7-fluoro-1-methylene-8b-nitro-4-tosyl-1,3a,4,8b-tetrahydrocyclopenta[*b*]indole-3,3(2H)-dicarboxylate (7fa). Obtained following the general procedure with dimethyl 2-(prop-2-yn-1-yl)malonate **2a** (75 mg, 0.44 mmol), starting from **6f** (135 mg, 0.40 mmol), as a white solid (197 mg, 98% yield) after flash column chromatography (petroleum ether/methyl *tert*-butyl ether 8:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, J = 8.9, 4.4 Hz, 1H), 7.48 – 7.38 (m, 2H), 7.21 – 7.08 (m, 4H), 6.48 (d, J = 1.0 Hz, 1H), 5.20 (ddt, J = 7.9, 2.6, 1.3 Hz, 2H), 3.88 (s, 3H), 3.86 (s, 3H), 3.07 (dt, J = 16.2, 2.6 Hz, 1H), 2.95 (dq, J = 16.2, 1.2 Hz, 1H), 2.35 (s, 3H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.4, 167.1, 160.8 (d, $J_{C\text{-}F}$ = 246.6 Hz), 145.5, 143.8, 139.3, 132.4, 130.0 (2C), 129.0 (d, $J_{C\text{-}F}$ = 8.9 Hz), 127.7 (2C), 119.79 (d, $J_{C\text{-}F}$ = 8.5 Hz), 119.77 (d, $J_{C\text{-}F}$ = 23.8 Hz), 114.2 (d, $J_{C\text{-}F}$ = 25.0 Hz), 110.9, 99.6, 73.7, 63.9, 53.9, 53.6, 40.3, 21.7 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.77 (m) ppm; IR (film): ν 3008, 2955, 2360, 2338, 1732, 1547, 1483, 1167 cm^{-1}; mp (°C) = 150-152; HRMS (ESI) [M+NH_4^+] calculated for $C_{23}H_{21}FN_2O_8SNH_4$: 522.1341, found 522.13437.

(±)-Dimethyl 7-chloro-1-methylene-8b-nitro-4-tosyl-1,3a,4,8b-tetrahydrocyclopenta[*b*]indole-3,3(2H)-dicarboxylate (7ga). Obtained following the general procedure with dimethyl 2-(prop-2-yn-1-yl)malonate **2a** (75 mg, 0.44 mmol), starting from **6g** (140 mg, 0.40 mmol), as a white solid (168 mg, 81% yield) after flash column chromatography (petroleum ether/methyl *tert*-butyl ether 8:2 to 7:3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (dd, J = 8.6, 0.6 Hz, 1H), 7.50 – 7.42 (m, 2H), 7.46 – 7.36 (m, 2H), 7.21 – 7.11 (m, 2H), 6.48 (s, 1H), 5.24 (dt, J = 2.5, 1.2 Hz, 1H), 5.20 (dt, J = 2.6, 1.2 Hz, 1H), 3.88 (s, 3H), 3.85 (s, 3H), 3.08 (dt, J = 16.2, 2.6 Hz, 1H), 2.95 (dq, J = 16.2, 1.1 Hz, 1H), 2.35 (s, 3H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.4, 167.1, 145.5, 143.5, 141.8, 132.5, 132.5, 131.7, 130.0 (2C), 128.7, 127.6 (2C), 127.4, 119.3, 111.1, 99.5, 73.6, 63.8, 53.8, 53.5, 40.4, 21.7 ppm; IR (film): ν 3103, 2998, 2359, 1736, 1563, 1171 cm^{-1}; mp (°C) = 156-158; HRMS (ESI) [M+NH_4^+] calculated for $(C_{23}H_{21}ClN_2O_8SNH_4)^+$: 538.1045, found 538.1046.

(±)-Dimethyl 7-bromo-1-methylene-8b-nitro-4-tosyl-1,3a,4,8b-tetrahydrocyclopenta[*b*]indole-3,3(2H)-dicarboxylate (7ha). Obtained following the general procedure with dimethyl 2-(prop-2-yn-1-yl)malonate **2a** (75 mg, 0.44 mmol), starting from **6h** (159 mg, 0.40 mmol), as a yellow solid (165 mg, 79% yield) after trituration in di*iso*-propyl ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.53 (m, 3H), 7.49 – 7.44 (m, 2H), 7.19 – 7.14 (m, 2H), 6.48 (d, J = 0.9 Hz, 1H), 5.25 (dt, J = 2.6, 1.2 Hz, 1H), 5.21 (dt, J = 2.6, 1.3 Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.08 (dt, J = 16.2, 2.5 Hz, 1H), 2.96 (dq, J = 16.1, 1.1 Hz, 1H), 2.36 (s, 3H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.4, 167.2, 145.6, 143.5, 142.3, 135.4, 132.6, 130.4, 130.1 (C2), 129.0, 127.7 (2C), 119.7, 119.1, 111.2, 99.5, 73.5, 63.9, 53.9, 53.6, 40.5, 21.8 ppm; IR (film): ν 2998, 2955, 2360, 2342, 2024, 1736, 1171 cm^{-1}; mp (°C) = 164-166; HRMS (ESI) [M+NH_4^+] calculated for $(C_{23}H_{21}BrN_2O_8SNH_4)^+$: 582.0540, found 582.0543.

(±)-Dimethyl 7-iodo-1-methylene-8b-nitro-4-tosyl-1,3a,4,8b-tetrahydrocyclopenta[*b*]indole-3,3(2H)-dicarboxylate (7ia). Obtained following the general procedure with dimethyl 2-(prop-2-yn-1-yl)malonate **2a** (75 mg, 0.44 mmol), starting from **6i** (177 mg, 0.40 mmol), as a brown solid (199 mg, 81% yield) after trituration in di*iso*-propyl ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.66 (m, 2H), 7.53 – 7.43 (m, 3H), 7.21 – 7.10 (m, 2H), 6.46 (d, J = 0.9 Hz, 1H), 5.27 – 5.22 (m, 1H), 5.22 – 5.16 (m, 1H), 3.88 (s, 3H), 3.85 (s, 3H), 3.08 (dt, J = 16.2, 2.6 Hz, 1H), 2.95 (dq, J = 16.2,

1.1 Hz, 1H), 2.36 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 169.4, 167.1, 145.5, 143.4, 143.0, 141.2, 136.2, 132.6, 130.1 (2C), 129.2, 127.6 (2C), 119.9, 111.2, 99.4, 89.4, 73.3, 63.9, 53.9, 53.6, 40.5, 21.7 ppm; IR (film): ν 2953, 2360, 2342, 1736, 1562, 1173 cm^{-1}; mp (°C) = 173-175; HRMS (ESI) $[M+NH_4^+]$ calculated for$(C_{23}H_{21}IN_2O_8SNH_4)^+$: 630.0402, found 630.0403.

(±)-Dimethyl 7-cyano-1-methylene-8b-nitro-4-tosyl-1,3a,4,8b-tetrahydrocyclopenta[*b*]indole-3,3(2H)-dicarboxylate(7ja). Obtained following the general procedure with dimethyl 2-(prop-2-yn-1-yl)malonate 2a (75 mg, 0.44 mmol), starting from **6j** (137 mg, 0.40 mmol), as a white solid (192 mg, 94% yield) after flash column chromatography (petroleum ether/methyl *tert*-butyl ether 8:2 to 6:4). ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, J = 8.4, 0.7 Hz, 1H), 7.77 – 7.68 (m, 2H), 7.54 – 7.46 (m, 2H), 7.21 – 7.14 (m, 2H), 6.53 (d, J = 0.9 Hz, 1H), 5.33 (dt, J = 2.7, 1.5 Hz, 1H), 5.30 – 5.24 (m, 1H), 3.88 (s, 3H), 3.82 (s, 3H), 3.08 (dt, J = 16.4, 2.4 Hz, 1H), 3.01 (dq, J = 16.4, 1.3 Hz, 1H), 2.34 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 169.2, 167.1, 146.4, 146.0, 142.9, 136.1, 132.6, 131.7, 130.2 (2C), 127.9, 127.4 (2C), 118.2, 117.8, 111.9, 109.7, 99.0, 73.6, 63.7, 53.9, 53.6, 40.6, 21.7 ppm; IR (film): ν 3000, 2959, 2359, 2234, 1737, 1566, 1171 cm^{-1}; mp (°C) = 130-140; HRMS (ESI) $[M+NH_4^+]$ calculated for $(C_{24}H_{21}N_3O_8SNH_4)^+$: 529.1388, found 529.13874.

(±)-Dimethyl 6-methyl-1-methylene-8b-nitro-4-tosyl-1,3a,4,8b-tetrahydrocyclopenta[*b*]indole-3,3(2H)-dicarboxylate (7ka). Obtained following the general procedure with dimethyl 2-(prop-2-yn-1-yl)malonate **2a** (75 mg, 0.44 mmol), starting from **6k** (132 mg, 0.40 mmol), as a pale brown solid (132 mg, 66% yield) after trituration in di*iso*propyl ether. ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 1H), 7.51 – 7.43 (m, 2H), 7.29 (d, J = 8.0 Hz, 1H), 7.16 – 7.08 (m, 2H), 7.03 (dq, J = 8.0, 0.7 Hz, 2H), 6.47 (d, J = 0.9 Hz, 1H), 5.20 (dt, J = 2.4, 1.1 Hz, 1H), 5.14 (dt, J = 2.5, 1.2 Hz, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 3.07 (dt, J = 16.0, 2.6 Hz, 1H), 2.92 (dq, J = 16.0, 1.1 Hz, 1H), 2.42 (t, J = 0.7 Hz, 3H), 2.33 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 169.5, 167.2, 145.0, 144.0, 143.2, 143.1, 132.8, 129.8 (2C), 127.5 (2C), 127.3, 126.7, 124.3, 118.5, 110.0, 99.9, 73.4, 63.7, 53.7, 53.4, 40.3, 21.9, 21.6 ppm; IR (film): ν 2957, 2359, 2023, 1749, 1724, 1550, 1172 cm^{-1}; mp (°C) = 177-179; HRMS (ESI) $[M+NH_4^+]$ calculated for $(C_{24}H_{24}N_2O_8SNH_4)^+$: 518.1592, found 518.1583.

(±)-Dimethyl 6-chloro-1-methylene-8b-nitro-4-tosyl-1,3a,4,8b-tetrahydrocyclopenta[*b*]indole-3,3(2H)-dicarboxylate (7la). Obtained following the general procedure with dimethyl 2-(prop-2-yn-1-yl)malonate **2a** (75 mg, 0.44 mmol), starting from **6l** (140 mg, 0.40 mmol), as a white solid (178 mg, 86% yield) after flash column chromatography (petroleum ether/methyl *tert*-butyl ether 8:2 to 7:3). ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 1.8 Hz, 1H), 7.57 – 7.44 (m, 2H), 7.35 (d, J = 8.3 Hz, 1H), 7.22 – 7.13 (m, 3H), 6.49 (d, J = 0.9 Hz, 1H), 5.27 – 5.21 (m, 1H), 5.21 – 5.18 (m, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.09 (dt, J = 16.2, 2.5 Hz, 1H), 2.96 (dq, J = 16.2, 1.1 Hz, 1H), 2.35 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 169.4, 167.2, 145.6, 144.2, 143.6, 138.6, 132.7, 130.1 (2C), 128.2, 127.7 (2C), 126.7, 125.6, 118.3, 110.9, 99.5, 73.7, 63.8, 53.9, 53.6, 40.5, 21.7 ppm; IR (film): ν 3026, 2959, 2359, 2338, 1748, 1727, 1551 cm^{-1}; mp (°C) = 190-192; HRMS (ESI) $[M+NH_4^+]$ calculated for $(C_{23}H_{21}ClN_2O_8SNH_4)^+$: 538.1045, found 538.1046.

(±)-Dimethyl 5-methyl-1-methylene-8b-nitro-4-tosyl-1,3a,4,8b-tetrahydrocyclopenta[*b*]indole-3,3(2H)-dicarboxylate (7ma). Obtained following the general procedure with dimethyl 2-(prop-2-yn-1-yl)malonate **2a** (75 mg, 0.44 mmol), starting from **6m** (132 mg, 0.40 mmol), as a white solid (118 mg, 59% yield) after trituration in di*iso*propyl ether. ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 1H), 7.31 – 7.24 (m, 1H), 7.28 – 7.21 (m, 3H), 7.15 – 7.07 (m, 2H), 6.42 (s, 1H), 5.04 – 4.96 (m, 2H), 3.89 (s, 3H), 3.85 (s, 3H), 2.83 – 2.70 (m, 2H), 2.55 (s, 3H), 2.38 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 169.5, 167.2, 145.7, 145.5, 142.4, 134.6, 132.6, 131.9, 130.3, 129.9 (2C), 128.4 (2C), 127.8, 125.4, 109.2, 99.5, 73.4, 64.0, 53.8, 53.5, 39.6, 21.8, 20.2 ppm; IR (film): ν 3034, 2955, 2359, 2340, 1730, 1544, 1163 cm^{-1}; mp (°C) = 174-176; HRMS (ESI) $[M+NH_4^+]$ calculated for $(C_{24}H_{24}N_2O_8SNH_4)^+$: 518.1592, found 518.1584.

(±)-Trimethyl 1-methylene-8b-nitro-4-tosyl-1,3a,4,8b-tetrahydrocyclopenta[*b*]indole-3,3,5(2H)-tricarboxylate (7na). Obtained following the general procedure with dimethyl 2-(prop-2-yn-1-yl)malonate **2a** (75 mg, 0.44 mmol), starting from **6n** (151 mg, 0.40 mmol), as a yellow solid (148 mg, 68% yield) after flash column chromatography (petroleum ether/ methyl *tert*-butyl ether 8:2 to 6:4). ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, J = 7.7, 1.4 Hz, 1H), 7.59 (dd, J = 7.7, 1.4 Hz, 1H), 7.39 (t, J = 7.7 Hz, 1H), 7.26 (d, J = 8.1 Hz, 2H), 7.11 (d, J = 8.1 Hz, 2H), 6.35 (s, 1H), 5.13 – 5.06 (m, 2H), 3.94 (s, 3H), 3.92 (s, 3H), 3.85 (s, 3H), 2.99 (dt, J = 16.3, 2.6 Hz, 1H), 2.92 – 2.86 (m, 1H), 2.37 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 169.4, 167.1, 166.6, 145.8, 144.9, 141.4, 133.7, 131.8, 130.7, 130.0 (2C), 129.9, 128.2 (2C), 127.2, 125.8, 110.1, 99.6, 73.6, 63.9, 53.8, 53.5, 52.5, 39.8, 21.8 ppm; IR (film): ν 3094, 3026, 2955, 2357, 1734, 1555, 1433 cm^{-1}; mp (°C) = 164-166; HRMS (ESI) $[M+NH_4^+]$ calculated for $(C_{25}H_{24}N_2O_{10}SNH_4)^+$: 562.1490, found 562.14825.

(±)-Dimethyl 5-chloro-1-methylene-8b-nitro-4-tosyl-1,3a,4,8b-tetrahydrocyclopenta[*b*]indole-3,3(2H)-dicarboxylate (70a). Obtained following the general procedure with dimethyl 2-(prop-2-yn-1-yl)malonate **2a** (75 mg, 0.44 mmol), starting from **6o** (140 mg, 0.40 mmol), as a white solid (179 mg, 86% yield) after flash column chromatography (petroleum ether/ ethyl acetate 8:2 to 6:4). ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.54 (m, 2H), 7.49 (dd, J = 7.8, 1.2 Hz, 1H), 7.39 (dd, J = 7.8, 1.2 Hz, 1H), 7.27 (t, J = 7.8 Hz, 1H), 7.23 – 7.17 (m, 2H), 6.59 (s, 1H), 5.14 (ddt, J = 7.2, 2.9, 1.5 Hz, 2H), 3.81 (s, 3H), 3.67 (s, 3H), 2.95 – 2.82 (m, 2H), 2.40 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 169.4, 167.0, 145.5, 144.8, 141.0, 133.6, 133.2, 132.3, 129.8 (2C), 128.7, 128.5 (2C), 127.1, 126.3, 110.6, 99.8, 74.4, 63.4, 53.8, 53.5, 39.6, 21.8 ppm; IR (film): ν 3020, 2953, 2360, 2342, 1729, 1546, 1432 cm^{-1}; mp (°C) = 163-165; HRMS (ESI) $[M+NH_4^+]$ calculated for $(C_{23}H_{21}ClN_2O_8SNH_4)^+$: 538.1045, found 538.1044.

(±)-Di*isopropyl* 1-methylene-8b-nitro-4-tosyl-1,3a,4,8b-tetrahydrocyclopenta[*b*]indole-3,3(2H)-dicarboxylate (3ab). Obtained following the general procedure with **2b** (100 mg, 0.44 mmol), starting from **1a** (127 mg,

0.40 mmol), as a white solid (155 mg, 71% yield) after flash column chromatography (petroleum ether/ methyl *tert*-butyl ether 9:1 to 8:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, J = 8.2, 0.8 Hz, 1H), 7.51 – 7.39 (m, 4H), 7.23 (td, J = 7.6, 1.0 Hz, 1H), 7.09 (dd, J = 8.0, 0.7 Hz, 2H), 6.49 (s, 1H), 5.28 – 5.14 (m, 2H), 5.18 – 5.11 (m, 1H), 5.07 (hept, J = 6.3 Hz, 1H), 3.16 – 2.99 (m, 1H), 2.99 – 2.76 (m, 1H), 2.32 (s, 3H), 1.42 (d, J = 6.3 Hz, 3H), 1.34 (d, J = 6.3 Hz, 3H), 1.30 (d, J = 6.3 Hz, 3H), 1.29 (d, J = 6.3 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.6, 166.5, 145.1, 144.6, 143.4, 133.0, 132.2, 129.8, 127.7, 127.5, 127.4, 126.3, 118.6, 110.1, 100.4, 73.2, 71.1, 70.4, 63.8, 40.9, 21.8, 21.7 (3C), 21.6 ppm; IR (film): ν 3447, 2981, 2933, 2360, 2025, 1724, 1551, 1167 cm^{-1}; mp (°C) = 132-134; HRMS (ESI) [M+NH_4^+] calculated for $(C_{27}H_{30}N_2O_8SNH_4)^+$: 560.2061, found 560.2061.

(±)-Dibenzyl 1-methylene-8b-nitro-4-tosyl-1,3a,4,8b-tetrahydrocyclopenta[*b*]indole-3,3(2H)-dicarboxylate (3ac). Obtained following the general procedure with **2c** (142 mg, 0.44 mmol), starting from **1a** (127 mg, 0.40 mmol), as a white solid (219 mg, 86% yield) after flash column chromatography (petroleum ether/ methyl *tert*-butyl ether 85:15 to 8:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, J = 8.6, 1.0 Hz, 1H), 7.47 – 7.36 (m, 4H), 7.30 (m, 8H), 7.26 – 7.15 (m, 3H), 7.10 – 7.01 (m, 2H), 6.51 (s, 1H), 5.34 (d, J = 12.2 Hz, 1H), 5.24 – 5.18 (m, 1H), 5.18 (d, J = 5.6 Hz, 2H), 5.13 (d, J = 12.2 Hz, 1H), 5.12 – 5.05 (m, 1H), 3.04 (dt, J = 16.0, 2.5 Hz, 1H), 2.93 (dq, J = 16.0, 1.2 Hz, 1H), 2.29 (s, 3H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.8, 166.6, 145.2, 144.0, 143.2, 135.2, 134.9, 132.8, 132.3, 129.9 (2C), 128.7 (2C), 128.63 (2C), 128.62, 128.57 (2C), 128.55 (2C), 128.4, 127.7 (2C), 127.2, 127.1, 126.2, 118.3, 110.6, 100.1, 73.3, 68.6, 68.5, 64.1, 40.6, 21.7 ppm; IR (film): ν 3018, 2360, 1722, 1595, 1552, 1162 cm^{-1}; mp (°C) = 135-137; HRMS (ESI) [M+NH_4^+] calculated for $(C_{35}H_{30}N_2O_8SNH_4)^+$: 656.2061, found 656.2063.

(±)-1-methylene-8b-nitro-4-tosyl-1,3a,4,8b-tetrahydrocyclopenta[*b*]indole-3,3(2H)-dicarbonitrile (3ae). Obtained following the general procedure with **2e** (46 mg, 0.44 mmol), starting from **1a** (127 mg, 0.40 mmol), as a brown solid (138 mg, 82% yield) after trituration in a mixture di*iso*propyl ether /hexane (1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dt, J = 8.3, 0.8 Hz, 1H), 7.69 – 7.62 (m, 1H), 7.60 – 7.53 (m, 3H), 7.30 (td, J = 7.7, 1.0 Hz, 1H), 7.19 (dd, J = 8.0, 0.6 Hz, 2H), 5.91 (dq, J = 2.4, 1.3 Hz, 1H), 5.85 (s, 1H), 5.67 – 5.62 (m, 1H), 3.39 (dt, J = 15.6, 2.4 Hz, 1H), 3.22 (dt, J = 15.6, 1.4 Hz, 1H), 2.36 (s, 3H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 146.1, 142.2, 139.5, 133.3, 132.5, 130.3 (2C), 127.6 (2C), 126.7, 126.6, 125.2, 118.9, 117.6, 113.1, 111.4, 97.4, 75.8, 43.6, 41.1, 21.8 ppm; IR (film): ν 3008, 2360, 2338, 2022, 1743, 1557, 1370 cm^{-1}; mp (°C) = 178-180; HRMS (ESI) [M+NH_4^+] calculated for $(C_{21}H_{16}N_4O_4SNH_4)^+$: 438.1231, found 438.1230.

(±)-3-(*tert*-butyl) 3-methyl 1-methylene-8b-nitro-4-tosyl-1,3a,4,8b-tetrahydrocyclopenta[*b*]indole-3,3(2H)-dicarboxylate (3af). Obtained following the general procedure with **2f** (93 mg, 0.44 mmol), starting from **1a** (127 mg, 0.40 mmol), as an orange oil (159 mg, 72% yield, *dr* 3:1) after flash column chromatography (petroleum ether/ methyl *tert*-butyl ether 85:15 to 8:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ **maj** : 7.76 – 7.69 (m, 1H), 7.50 – 7.42 (m, 2H), 7.46 – 7.38 (m, 2H), 7.27 – 7.18 (m, 1H), 7.12 – 7.04 (m, 2H), 6.47 (s, 1H), 5.20 – 5.16 (m, 1H), 5.16 – 5.12 (m, 1H), 3.86 (s, 3H), 3.03 (dt, J = 16.3, 2.5 Hz, 1H), 2.90 – 2.80 (m, 1H), 2.31 (s, 3H), 1.51 (s, 9H) ppm; **min** (selected signals) : 6.43 (s, 1H), 5.21 (dt, J = 2.2, 1.0 Hz, 1H), 3.81 (s, 3H), 3.00 – 2.90 (m, 2H), 1.51 (s, 9H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ **maj** : 170.1, 165.4, 145.1, 144.5, 143.4, 132.9, 132.2, 129.8 (2C), 127.6 (2C), 127.5, 127.4, 126.3, 118.6, 110.3, 100.4, 83.8, 73.2, 64.2, 53.4, 40.5, 27.7, 21.6 ppm; **min** : 170.1, 167.6, 145.1, 144.4, 143.1, 132.8, 132.2, 129.8(2C), 127.6 (2C), 127.4, 127.2, 126.2, 118.3, 109.7, 100.0, 83.5, 73.0, 64.5, 53.2, 40.5, 27.7, 21.6 ppm; IR (film): ν 2978, 2359, 1729, 1551, 1367, 1170 cm^{-1}.; HRMS (ESI) [M+NH_4^+] calculated for $(C_{26}H_{28}N_2O_8SNH_4)^+$: 545.1905, found 546.1904.

(±)-Methyl-3-cyano-1-methylene-8b-nitro-4-tosyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole-3-carboxylate (3ah). Obtained following the general procedure with **2h** (60 mg, 0.44 mmol), starting from **1a** (127 mg, 0.40 mmol), as a yellow oil (125 mg, 69% yield, *dr* 3:1) after flash column chromatography (petroleum ether/ methyl *tert*-butyl ether 8:2 to 7:3). ^{1}H NMR (400 MHz, $CDCl_3$) δ **maj** : 7.86 (dt, J = 8.3, 0.8 Hz, 1H), 7.69 (ddd, J = 7.9, 1.3, 0.6 Hz, 1H), 7.59 – 7.52 (m, 2H), 7.56 – 7.48 (m, 1H), 7.30 – 7.22 (m, 1H), 7.22 – 7.15 (m, 2H), 5.91 (ddd, J = 2.9, 1.6, 1.0 Hz, 1H), 5.88 (s, 1H), 5.60 – 5.54 (m, 1H), 4.03 (s, 3H), 3.36 (dt, J = 15.6, 2.8 Hz, 1H), 3.06 (dd, J = 15.6, 0.8 Hz, 1H), 2.35 (s, 3H) ppm; **min** (selected signals) : 7.49 – 7.46 (m, 1H), 7.17 – 7.13 (m, 2H), 5.94 (s, 1H), 5.61 (m, 1H), 5.41 (m, 1H), 3.85 (s, 3H), 3.13 – 3.09 (m, 2H), 2.33 (s, 3H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ **maj** : 167.1, 145.6, 142.3, 141.6, 132.8, 132.5, 130.1 (2C), 127.3 (2C), 126.9, 126.3, 125.8, 118.1, 117.1, 116.8, 98.0, 75.9, 54.8, 54.5, 43.1, 21.7 ppm; **min** : 164.7, 145.1, 142.6, 142.4, 133.0, 132.4, 130.1 (2C), 127.5 (2C), 127.3, 126.4, 126.3, 117.6, 115.0, 113.6, 99.1, 76.017, 54.3, 52.1, 41.7, 21.7 ppm; IR (film): ν 3022, 2055, 2360, 2340, 1748, 1555, 1170 cm^{-1}; HRMS (ESI) [M+NH_4^+] calculated for $(C_{22}H_{19}N_3O_6SNH_4)^+$: 471.1333, found 471.1332.

(±)-*Tert*-butyl-3-cyano-1-methylene-8b-nitro-4-tosyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole-3-carboxylate (3ai). Obtained following the general procedure with **2i** (79 mg, 0.44 mmol), starting from **1a** (127 mg, 0.40 mmol), as a brown oil (167 mg, 84% yield, *dr* 5:1) after flash column chromatography (petroleum ether/ methyl *tert*-butyl ether 9:1 to 7:3). ^{1}H NMR (400 MHz, $CDCl_3$) δ **maj** : 7.84 (dd, J = 8.4, 1.3 Hz, 1H), 7.66 (dd, J = 7.9, 1.3 Hz, 1H), 7.55 – 7.52 (m, 2H), 7.52 – 7.47 (m, 1H), 7.23 (m, 1.1 Hz, 1H), 7.16 (m, 2H), 5.92 (s, 1H), 5.86 – 5.79 (m, 1H), 5.54 – 5.48 (m, 1H), 3.26 (dt, J = 15.5, 2.8 Hz, 1H), 3.08 – 2.99 (m, 1H), 2.32 (d, J = 2.0 Hz, 3H), 1.64 (s, 9H) ppm; **min** (selected signals) : 7.74 – 7.69 (m, 1H), 7.63 – 7.59 (m, 1H), 7.13 (d, J = 8.2 Hz, 2H), 5.90 (s, 1H), 5.62 (q, J = 1.9 Hz, 1H), 5.39 (q, J = 1.9 Hz, 1H), 3.21 – 3.10 (m, 2H), 2.31 (s, 3H), 1.42 (s, 9H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ **maj** : 165.0, 145.4, 142.4, 141.9, 132.9, 132.6, 130.0 (2C), 127.3 (2C), 126.3, 125.9, 125.7, 117.4, 117.0, 115.3, 98.3, 86.1, 75.3, 55.2, 43.5, 27.8, 21.6 ppm; **min** : 163.1, 145.6, 143.2, 142.8, 132.4, 132.2, 130.0 (2C), 127.4 (2C), 126.7, 126.7, 126.1, 118.1, 117.0, 113.7, 99.4, 85.9, 76.3, 52.7, 42.1, 27.5, 21.6 ppm; IR (film): ν 2979, 2931, 1737, 1555, 1369, 1171, 1151 cm^{-1}; HRMS (ESI) [M+NH_4^+] calculated for $(C_{25}H_{25}N_3O_6SNH_4)^+$: 513.1802, found 513.1802.

(±)-3-methylene-3a-nitro-1,8-ditosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-*b*]indole (3aj). Obtained following the general procedure with **2j** (184 mg, 0.88 mmol), starting from **1a** (253 mg, 0.80 mmol), as an orange oil (275 mg, 65% yield) after flash column chromatography (petroleum ether/ ethyl acetate 8:2 to 6:4). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.91 (m, 2H), 7.62 – 7.52 (m, 3H), 7.48 – 7.38 (m, 2H), 7.38 – 7.30 (m, 2H), 7.19 (td, J = 7.6, 1.1 Hz, 1H), 7.17 – 7.11 (m, 2H), 6.94 (s, 1H), 5.41 (q, J = 1.7 Hz, 1H), 5.18 (q, J = 1.8 Hz, 1H), 4.38 (dt, J = 14.6, 1.5 Hz, 1H), 3.74 (dt, J = 14.7, 2.3 Hz, 1H), 2.43 (s, 3H), 2.33 (s, 3H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 145.1, 144.3, 141.8, 141.1, 135.5, 133.4, 132.3, 129.8 (2C), 129.7 (2C), 128.0 (2C), 127.5 (2C), 126.8, 126.1, 125.2, 117.8, 110.1, 99.0, 84.2, 52.5, 21.5, 21.5 ppm; IR (film): ν 2917, 2359, 2340, 1748, 1597, 1553, 1160 cm^{-1}; HRMS (ESI) [M+NH_4^+] calculated for $(C_{25}H_{23}N_3O_6S_2NH_4)^+$: 543.1367, found 543.1364.

(±)-*tert*-butyl-3-methylene-3a-nitro-8-tosyl-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indole-1(2H)-carboxylate 3al). Obtained following the general procedure with **2l** (137 mg, 0.88 mmol), starting from **1a** (253 mg, 0.80 mmol), as a yellow oil (42 mg, 11% yield) after flash column chromatography (petroleum ether/ methyl *tert*-butyl ether 9:1 to 8:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.2 Hz, 1H), 7.63 (s, 1H), 7.53 (dd, J = 7.7, 1.3 Hz, 1H), 7.48 – 7.39 (m, 1H), 7.36 – 7.27 (m, 1H), 7.22 – 7.09 (m, 3H), 5.42 (dd, J = 2.7, 1.5 Hz, 1H), 5.25 (q, J = 1.8 Hz, 1H), 4.52 (dt, J = 15.2, 1.6 Hz, 1H), 3.76 (d, J = 15.3 Hz, 1H), 2.34 (s, 3H), 1.58 (s, 9H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 153.2, 144.9, 143.0, 142.0, 133.9, 132.1, 129.9 (2C), 128.6, 127.7 (2C), 126.6, 125.6, 117.5, 110.3, 98.7, 83.4, 82.5, 51.0, 28.5, 21.7 ppm; IR (film): ν 2974, 2927, 2871, 2359, 2340, 1704, 1553 cm^{-1}; HRMS (ESI) [M+Na^+] calculated for $(C_{23}H_{25}N_3O_6SNa)^+$: 494.1356, found 494.1354.

Ethyl 5-methylene-2-phenyltetrahydrofuran-3-carboxylate (8). Obtained following the general procedure starting from **2g** (101 mg, 0.44 mmol), as a colourless oil (88 mg, 87% yield) after flash column chromatography (pure petroleum ether to petroleum ether/ methyl *tert*-butyl ether 95:5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.80 (m, 2H), 7.50 – 7.34 (m, 3H), 4.72 (q, J = 2.9 Hz, 1H), 4.33 (q, J = 2.9 Hz, 1H), 4.16 (q, J = 7.1 Hz, 2H), 3.82 (t, J = 2.9 Hz, 2H), 1.23 (t, J = 7.1 Hz, 3H) ppm. Spectral data of the product were in accordance with those reported in the literature.[14]

ASSOCIATED CONTENT

Supporting Information. Copies of ^{1}H and ^{13}C NMR Spectra for all new compounds and more details concerning the screening of chiral ligands for the enantioselective version and the kinetic studies.

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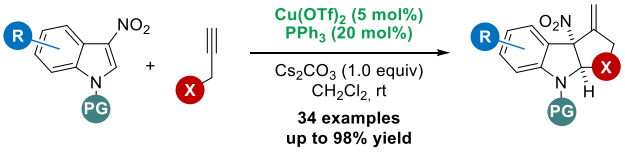
R
NO2
N
PG
+
X
Cu(OTf)2 (5 mol%)
PPh3 (20 mol%)
Cs2CO3 (1.0 equiv)
CH2Cl2, rt
34 examples
up to 98% yield
R
O2N
X
N
H
PG