JOC The Journal of Organic Chemistry

Article

Pd-catalyzed Dearomative [3 + 2] Cycloaddition of 3-Nitroindoles with 2-Vinylcyclopropane-1,1-dicarboxylates

Yi Sing Gee, Daniel J Rivinoja, Steven Mark Wales, Michael G. Gardiner, John H. Ryan, and Christopher J. T. Hyland

J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.7b02624 • Publication Date (Web): 12 Nov 2017

Just Accepted

ACS Publications

The Journal of Organic Chemistry is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Pd-catalyzed Dearomative [3 + 2] Cycloaddition of 3-Nitroindoles with 2-Vinylcyclopropane-1,1-dicarboxylates

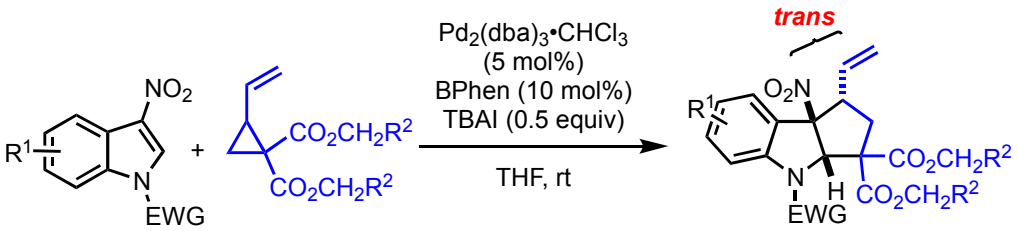
Yi Sing Gee,† Daniel J. Rivinoja,† Steven M. Wales,† Michael G. Gardiner,# John H. Ryan,§ and Christopher J. T. Hyland*†

†School of Chemistry, University of Wollongong, Wollongong, New South Wales 2522, Australia

#School of Physical Sciences - Chemistry, University of Tasmania, Hobart, Tasmania 7001, Australia

§CSIRO Manufacturing Flagship, Ian Wark Laboratory, Bayview Avenue, Clayton, Victoria 3168, Australia

Table of Contents Graphic

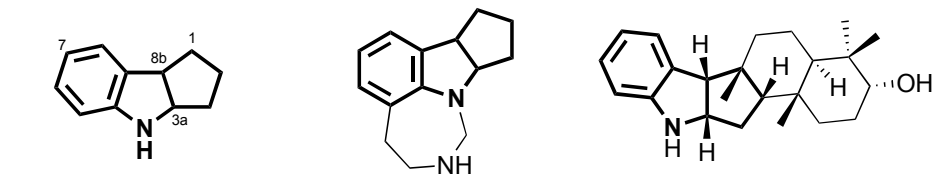


Abstract

A *trans*-diastereoselective Pd-catalyzed dearomative [3 + 2] cycloaddition between vinylcyclopropane dicarboxylates and 3-nitroindoles has been developed. The reaction provides densely functionalised cyclopenta[*b*]indolines with versatile vinyl and nitro-groups. The addition of a halide additive was found to be critical for the diastereoselectivity of the reaction, which is proposed to be a result of a rapid π-σ-π interconversion between the intermediates allowing for Curtin–Hammett control. A switch in diastereoselectivity to afford products with the vinyl and nitro groups *cis* to each other is observed with a 4-substituted 3-nitroindole.

Introduction

Indoline-derived heterocycles are prevalent in a host of important biologically active molecules, therefore new methods for their preparation is a major area of investigation for synthetic chemists. An important class of indolines containing the cyclopenta[*b*]indoline core are found in bioactive molecules such as diazepinoindoline (treatment and prevention of central nervous system disorders) and polyveoline (antitrypanosomal alkaloid) (Figure 1).[1] Traditionally, cyclopenta[*b*]indolines are prepared in several steps by photochemical cyclization or heterocyclization of alkenylarylamines.[2] Recently, Gilbertson et al. prepared cyclopenta[*b*]indoline in a step-efficient manner via a Pd-N-heterocyclic carbene-catalyzed cyclopentannulation of diazabicyclic olefins with *ortho*-functionalised aryl halides.[3] Although this method proceeded with high diastereoselectivity, it could not provide access to cyclopenta[*b*]indoline derivatives with electron-withdrawing groups or a halogen at C7, nor a substituent at C8b. The [3 + 2] dearomative cycloaddition of 1,3-dipoles to the indole skeleton is perhaps the most atom-efficient method to prepare cyclopenta[*b*]indolines.[4] Alkynyl Fischer carbene complexes have been used by Barluenga for the asymmetric [3 + 2] cyclopentannulation of indoles.[5] Lian and Davies reported a Rh-catalyzed version of this reaction with vinyldiazoacetates, while Doyle and co-workers developed an asymmetric Rh-catalyzed variant with enoldiazoacetamides.[6]

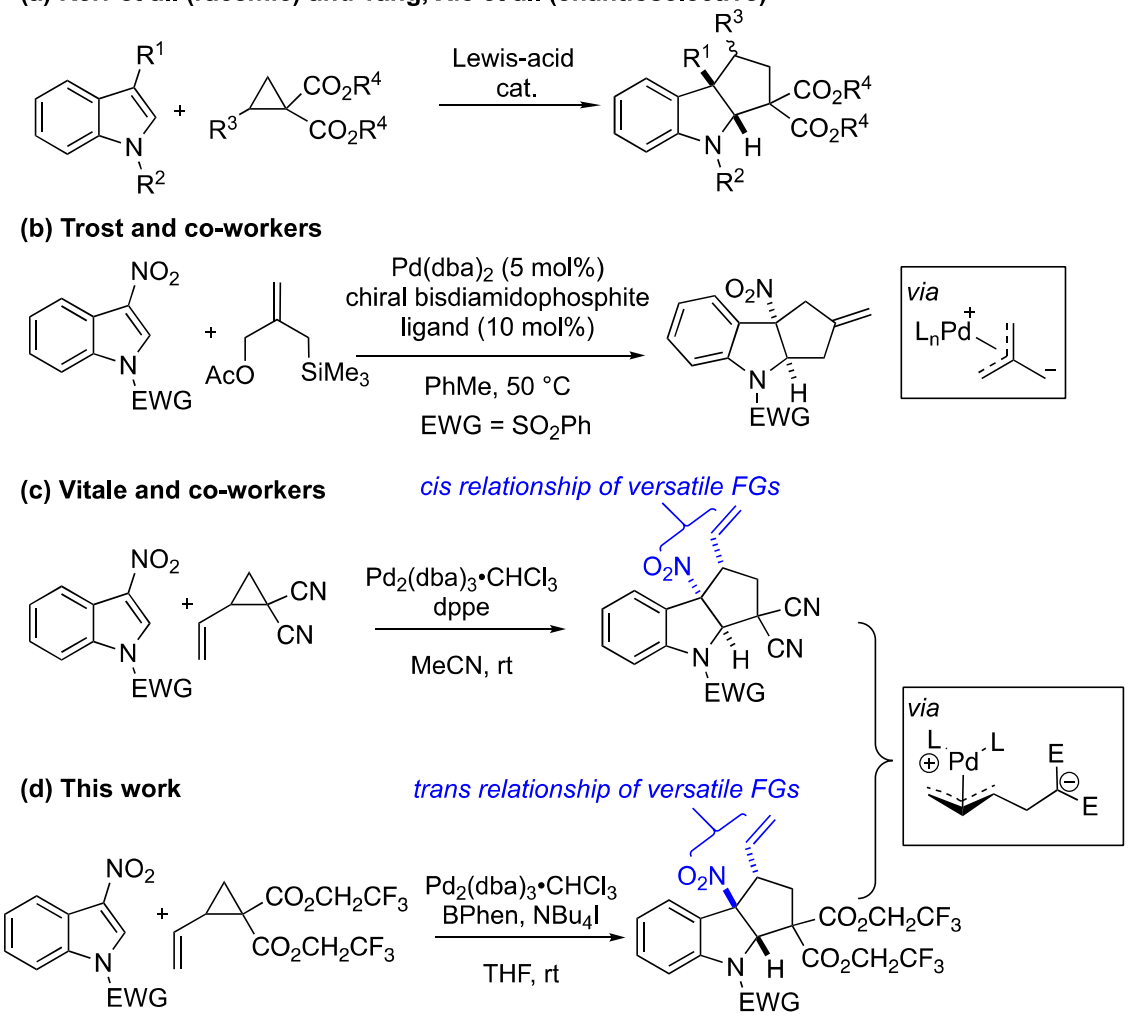


Cyclopenta[*b*]indoline core **Diazepinoindoline** **Polyveoline**

Figure 1. *Cyclopenta[b]indoline core and bioactive molecules that feature this core.*

Perhaps the most atom efficient [3 + 2] dearomative indole cycloaddition is when cyclopropane dicarboxylates are used as the formal 1,3-dipole. In seminal work in this area, Kerr et al. reported the $Yb(OTf)_3$-catalyzed formal [3 + 2] annulation of 3-alkylindoles with 1,1-cyclopropanediesters as formal 1,3-dipoles to provide cyclopenta[*b*]indolines in high yield and diastereoselectivity (Scheme 1a).[7] More recently, an enantioselective cyclopentannulation of electron-rich indoles with 1,1-

cyclopropanediesters using a BOX/Cu(II)-catalyst has been reported (Scheme 1a).[8] While these are highly efficient methods for the preparation of cyclopenta[*b*]indoline core, they afford derivatives with an aryl group at C1, which limits opportunities for subsequent functionalization. These approaches are also distinguished by their use of electron-rich indoles, whereas a reversal of polarity using electron-poor indoles as the cycloaddition partners is relatively unexploited to date. Trost made an important seminal contribution in this area with the [3 + 2] cycloaddition reactions of Pd-trimethylenemethane (TMM) to electron-deficient aromatics, including 3-nitro-1-phenylsulfonyl indoles to give cyclopenta[*b*]indolines (Scheme 1b).[9] This is an efficient and innovative route to these compounds, however this method cannot easily place functionality at the C1 position of the cyclopentane ring. We recently reported the Pd(0)-catalyzed diastereoselective dearomative [3 + 2] cycloaddition of *N*-Ts vinylaziridines to electron-deficient 3-nitroindoles to afford pyrroloindolines.[10,11] We therefore considered whether vinylcyclopropane-1,1-dicarboxylates (VCPs) could undergo a similar cycloaddition with 3-nitroindoles via a Pd-stabilized all-carbon zwitterionic dipole[12] to give cyclopenta[*b*]indolines bearing a manipulable vinyl group and nitro groups (Scheme 1d).[13] Such products would have increased utility beyond the cyclopenta[*b*]indolines substituted with alkyl and aryl groups, derived from electron-rich indoles and cyclopropane-1,1-dicarboxylates with vicinal donor aryl groups (Scheme 1a).



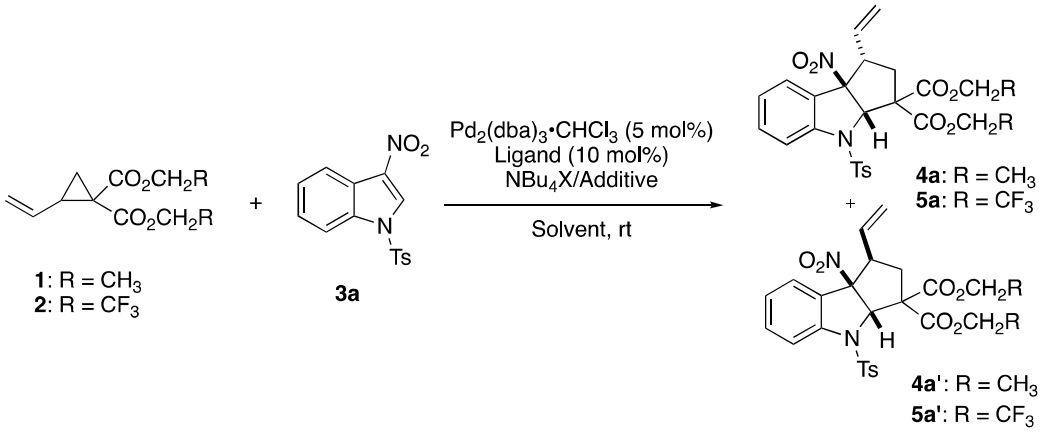
Scheme 1. *Representative previous and current studies on Pd-catalyzed dearomative [3 + 2] cycloaddition reactions to give cyclopenta[b]indolines.*

Herein, we report the Pd-catalyzed diastereoselective synthesis of functionalised cyclopenta[*b*]indolines under mild conditions using the economical and air-stable BPhen ligand. Concurrently, as this study was compiled for publication, Vitale et al. reported the Pd(0)/dppe-catalyzed [3 + 2] cycloaddition of 3-nitroindoles with 2-vinylcyclopropane-1,1-dicarbonitrile with reverse *dr* to that reported here (Scheme 1c), rendering the current report complementary.[14]

Results and Discussion

We began our study with 3-nitro-1-tosylindole **3a** and diethyl 2-vinylcyclopropane-1,1,-dicarboxylate **1** as reaction partners to investigate the proposed dearomative cycloaddition. At the outset of the investigation, we identified the combination of BPhen and $Pd_2(dba)_3 \cdot CHCl_3$ as a suitable catalyst system for the transformation, based on efficacy in our previously reported cycloaddition between vinylaziridines and electron-deficient indoles.[10] Gratifyingly, the reaction proceeded in good yield, providing the desired cyclopenta[*b*]indoline **4a/4a'**, but as a mixture of *cis* (favoured) and *trans* diastereoisomers in low *dr* (Table 1, entry 1). It was postulated that the reversible addition of the VCP-derived zwitterionic dipole to the 3-nitroindole could play a role in determining the ultimate diastereoselectivity of the reaction. As such the di(trifluoroethyl) ester analogue **2** was investigated as this would afford a more stable dipole and potentially facilitate this reversible addition. Interestingly, **2** reversed the sense of selectivity, favouring *trans* cyclopenta[*b*]indoline **5a** in MeCN, while switching the solvent to THF increased the *dr* moderately (entries 2 and 3). It was postulated that π-σ-π interconversion between the two diastereomeric zwitterionic π-allylpalladium complexes derived from the vinylcyclopropane adding to the 3-nitroindole could be an important control factor in determining the *dr* of the reaction.[15] Given that halide additives are known to increase the rate of π-σ-π interconversion these were then investigated in the reaction. In line with this, it was found that the use of halide additives had a positive effect on the *dr* of the reaction (entries 4-9), with 0.5 equiv of nBu$_4$NI proving optimal (entry 8). The introduction of a perchlorate additive only resulted in a slight increase in *dr* (entry 10). Lowering of the temperature (entry 11) had no effect on the *dr,* but resulted in a slight decrease in yield. A screen of other solvents (entries 12-15) resulted in lower yields and diastereoselectivity, indicating that THF was optimal. Using THF as the solvent a selection of other ligands were trialled in the reaction (entries 16-21), including dppe and other diamine ligands, but while some resulted in an increased yield the *dr* was lower than BPhen for all cases. As such, the reaction scope was investigated with the optimum conditions in entry 8. The catalyst/ligand loading can be lowered to 2.5 mol%/5 mol% respectively, however a noticeable drop in *dr* was observed (Entry 22).

Table 1. *Optimization of dearomative cycloaddition between vinylcyclopropane-1,1-dicarboxylates and 3-nitro-1-tosylindole.*[a]



Entry	R	NBu_4X (Equiv)	Solvent	Ligand	dr (*trans:cis*)[b]	Yield[c]
1	CH_3		MeCN	BPhen	1:1.3	62
2	CF_3		MeCN	BPhen	1.3:1	95
3	CF_3		THF	BPhen	1.7:1	95
4[d]	CF_3	I (0.3)	THF	BPhen	3.1:1	95
5[d]	CF_3	Br (0.3)	THF	BPhen	2.8:1	97
6[d]	CF_3	Cl (0.3)	THF	BPhen	2.6:1	92
7	CF_3	I (1.0)	THF	BPhen	3.7:1	74
8[d]	CF_3	I (0.5)	THF	BPhen	4.3:1	(80)
9[d]	CF_3	LiI (0.5)	THF	BPhen	N/A	Trace
10	CF_3	ClO_4 (0.5)	THF	BPhen	2.0:1	75

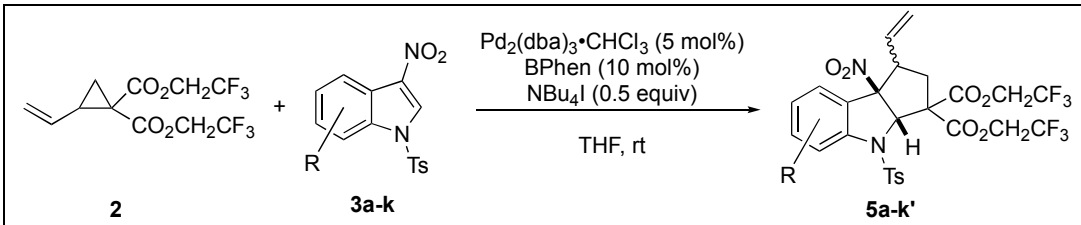
11[e]	CF_3	I (0.5)	THF	BPhen	4.2:1	77
12	CF_3	I (0.5)	DCM	BPhen	1.7:1	74
13	CF_3	I (0.5)	Dioxane	BPhen	2.4:1	74
14	CF_3	I (0.5)	MeCN	BPhen	1.8:1	75
15	CF_3	I (0.5)	PhMe	BPhen	4.0:1	64
16[d]	CF_3	I (0.5)	THF	dppe	2.2:1	76
17[d]	CF_3	I (0.5)	THF	Bipy	1.9:1	92
18[d]	CF_3	I (0.5)	THF	Phen	2.7:1	97
19[d]	CF_3	I (0.5)	THF	Neocuproine	2.0:1	84
20[d]	CF_3	I (0.5)	THF	Phen-Dione	1.9:1	25
21[d]	CF_3	I (0.5)	THF	Hydroxy Phen	1.8:1	96
22[d]	CF_3	I (0.5)	THF	BPhen[f]	3.1:1	82

[a] Reactions carried out at 0.1 M, rt with 5 mol% $Pd_2(dba)_3 \cdot CHCl_3$ and 10 mol% ligand with 1.0 eq. of VCP **1/2** and 1.3 eq. of indole **3a**. **4a/5a** refers to the *trans* diastereoisomer and **4a'/5a'** to the *cis* diastereoisomer. [b] Determined from the ^{1}H NMR of the crude reaction mixture.[c] Yield was calculated from ^{1}H NMR of the reaction mixture using mesitylene as an internal standard, with isolated yield in brackets where applicable. [d] 1:1 molar ratio of indole:VCP utilised. [e] 0 °C. [f] Pd-catalyst = 2.5 mol% instead of 5 mol%; i.e. Pd (2.5 mol%), BPhen (5 mol%) (Halving catalyst & ligand loadings).

Using the optimized experimental conditions, various substituted *N*-tosyl-3-nitroindoles **3** were subjected to the dearomatization reaction with VCP **2** (Table 2). In most cases, the reaction proceeded

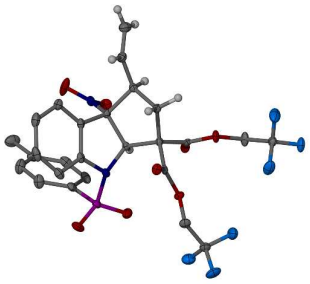
in high yield (73 – 88%) and good diastereoselectivity (3:1 to 4.3:1). Halogen substituents were tolerated by the Pd(0)-catalyst, providing products **5b**, **5c, 5i** and **5j**, which would be amenable to further coupling reactions. Strongly electron-withdrawing groups (products **5d, 5e** and **5f**) and an inductively donating methyl group (**5g**) also afforded the desired products. However, a 5-methoxy substituted 3-nitro-indole proved unreactive – presumably due to mesomeric donation rendering the indole insufficiently electron-poor to undergo dearomatization. Curiously, when methyl ester substituent was present at the 4-position of the starting indole an inseparable mixture of products resulting from multiple VCP additions to the indole was obtained using the standard optimized conditions. However, when the nBu$_4$NI additive was removed the reaction proceeded smoothly to provide the *trans* diastereoisomer **5k'** with almost complete selectivity. The relative stereochemistry of product **5k'** was determined by X-ray crystallographic analysis of its ester hydrolysis product (Scheme 4c). A similar reversal in diastereoselectivity was observed with the analogous vinylaziridine substrate in our previous work and is discussion below.[10]

Table 2. *Substrate scope with various functionalised 3-nitroindoles.*[a]



2 **3a-k** **5a-k'**

X-ray structure:



5a 80% yield
4.3:1 *dr*

5b 88% yield
3:1 *dr*

5c 87% yield
3.4:1 *dr*

5d 84% yield
3.2:1 *dr*

5e 82% yield
3:1 *dr*

5f 73% yield
3.1:1 *dr*

5g 78% yield
3.1:1 *dr*

5h no reaction

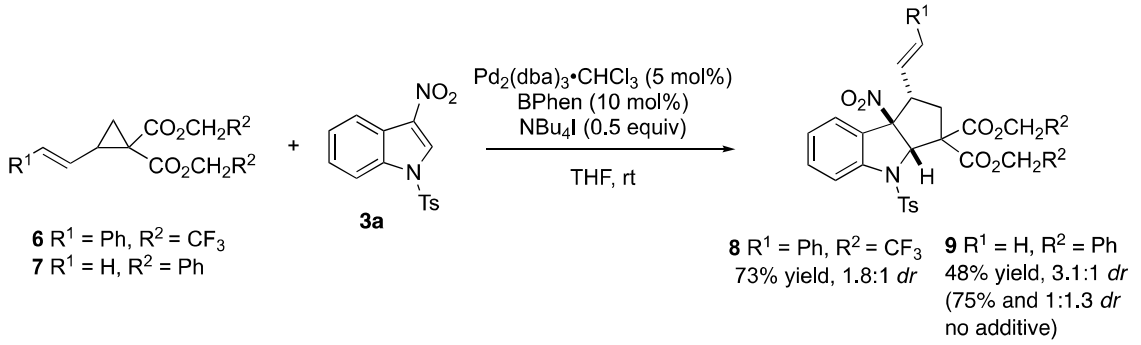
5i 88% yield
3.6:1 *dr*

5j 88% yield
3.2:1 *dr*

5k' 88% yield
<1:49 *dr*
(without additive)

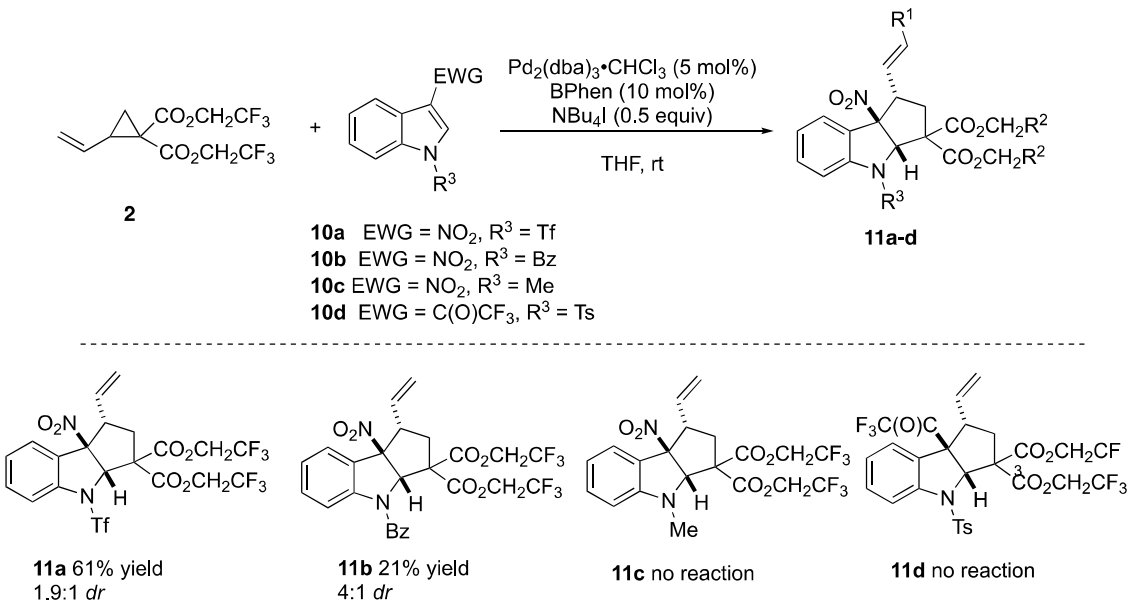
[a] Diastereoselectivity (*trans:cis*) was determined from the ^{1}H NMR of the crude reaction mixture. All yields are for isolated products after chromatographic purification.

Variation of the VCP was next investigated and interestingly, when a styryl-cyclopropane **6** was used, product **8** was obtained but a significant decrease in diastereoselectivity was observed (Scheme 2). Use of dibenzyl 2-vinylcyclopropane-1,1-dicarboxylate **7** gave the product **9** with slightly lowered *dr* and as expected, when the NBu_4I additive was absent, the *dr* dropped to 1:1.3 where the *cis* isomer is the major diastereomer. These two experiments provide additional evidence for our theory of reversible Michael attack and a π-σ-π interconversion being important for the selectivity.



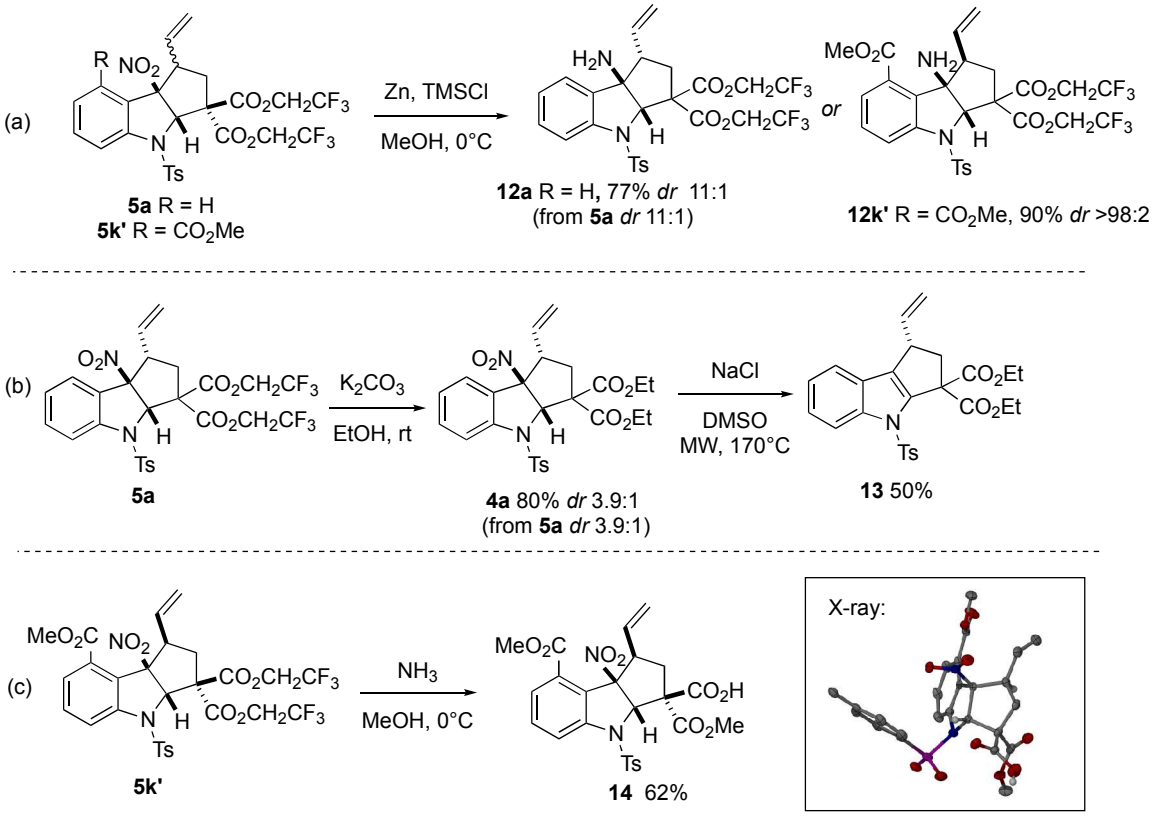
Scheme 2. *Variation of the vinycyclopropane.*

The focus was then switched to the electron-withdrawing groups on the indole substrate, as they are likely crucial to the reactivity of the indole starting material to the dearomatization process (Scheme 3). The diastereoselectivity decreases when the indole nitrogen is protected with trifluoromethanesulfonate group (product **11a**, Scheme 3). Having an *N*-benzoyl-protected indole nitrogen gives similar diastereoselectivity to that of the tosyl counterpart but with a poor yield (product **11b**, Scheme 3). Furthermore, in the case of the *N*-Bz cycloadduct, the conditions reported here provide an improved diastereoselectivity compared to the reported diastereoselectivity of 1:1 where dppe ligand and acetonitrile were used in the absence of tetrabutylammonium halide.[8] As a control experiment, no reaction occurred when the indole bears an *N*-methyl group, which is as anticipated for a less electrophilic, electron-rich dipolarophile (product **11c**, Scheme 3). Lastly, an *N*-tosyl indole bearing a trifluoroketone at C3 instead of nitro group was subjected to the reaction conditions, but no conversion was observed, suggesting the presence of a nitro group at C3 is vital for reactivity (product **11d**, Scheme 3).



Scheme 3. *Variation of the N-protecting group on the 3-nitro-indole.*

To demonstrate the synthetic utility of the densely functionalised cyclopenta[*b*]indoline products, the nitro group of **5a** and **5k'** was reduced with zinc powder under acidic conditions to provide the corresponding amines **12a** and **12k'** in high yield and with the same *dr* as the starting cyclopent[*b*]indoline (Scheme 4a). Further, a transesterification in ethanol converted **5a** to diethyl ester **4a**, which when subjected to Krapcho decarboxylation conditions underwent a denitration reaction to give the cyclopent[*b*]indole **13** (Scheme 4b). This cyclopent[*b*]indole features as the core unit of many alkaloids that display broad spectrum of pharmacological properties, such as paspaline (Maxi-K channel antagonist, potential treatment for Alzheimer's disease) and yuehchukene (antifertility agent).[16]



Scheme 4. *Chemical transformation of densely functionalised cyclopenta[b]indolines.*

Importantly, treatment of **5k'** with ammonia in methanol allowed for differentiation of the geminal ester groups by providing carboxylic acid **14** in 62% yield (Scheme 4c). Interestingly, the ester on the concave face underwent transesterification to the methyl ester, while that on the convex was ultimately hydrolyzed to the carboxylic acid by adventitious water. The origin of this chemoselectivity is potentially due to the dimethylester initially being formed and then a subsequent selective hydrolysis at the less hindered convex face to provide **14**. This reaction highlights the utility of the di-ester group and allows selective facial differentiation of the ester groups. The resulting acid was also highly crystalline, which enabled determination of the *cis*-relationship between the nitro and vinyl groups in **14** by X-ray crystallographic analysis, thereby confirming the switch in diastereoselectivity for substrate **3k**.

The reaction mechanism likely proceeds via initial oxidative addition of the Pd(0)-catalyst to the VCP (**2**) to form Pd-stabilized zwitterionic 1,3-dipole **A**, which undergoes a *reversible* Michael addition to the electron-deficient indole **3** and subsequently an *irreversible* ring-closure via transitions states **TS1** or **TS2** to form cyclopenta[*b*]indoline products **5/5'** (Figure 2). Through control experiments we demonstrated that the ring-closure step is irreversible (Scheme 5). Subjecting a mixture of **5a**/**5a'** with low diastereo-enrichment to the reaction conditions resulted in recovery of the starting materials with an identical *dr*. Further, a cross-over experiment where **9** (originating cycloaddition of VCP **7** to 3-nitroindole) was subjected to the reaction conditions in the presence of VCP **2** resulted in recovery of the original cycloadduct without any incorporation of VCP **2**.

The stereochemical outcome of the reaction is intriguing, especially as a reversal of the sense of diastereoselectivity is observed in the present system when compared to the recent report from Vitale and co-workers.[14] It is important to note that during the Michael addition, the racemic 1,3-dipole **A** – which has planar chirality – can either attack the *re* or the *si* face of indole **3**. As such, the Michael addition of **A** (in the depicted configuration) will provide one of two diastereomeric transition states **TS1** or **TS2**, which lead to products **5** and **5'**, respectively. Alternatively, π-σ-π isomerisation of the Pd-π-allyl moiety could occur before ring closure for each Michael intermediate, leading to products epimeric at the vinyl-bearing stereocentre. Although the current process is racemic, it is important to consider both enantiomers of the dipole (**A** and ***enant.* A)** and their resultant Michael adducts to illustrate the stereochemical consequences of the π-σ-π epimerisation process, which enables products of the same absolute configuration to arise from opposite enantiomers of the dipole **A**. These factors have important implications in the future development of dynamic enantioselective variants. An equilibrium between **A** and *enant.* **A** is also likely to exist (not shown) by a π-σ-π-racemisation process. Irreversible ring-closure of **TS1** and ***enant.*-TS1** lead to the formation of the *trans* diastereomer **5** and is the favoured pathway for most substrates – this is tentatively attributed to stabilization of **TS1** by a cation-π interaction between the indole skeleton and the cationic π–allyl Pd complex.[17] It appears from the experimental results that this selectivity relies upon the reversibility of the initial Michael attack *and* facile π-σ-π interconversion between **TS1** and **TS2** and their

enantiomers. For example, the reaction for the formation of **9** (Scheme 2) favours the *trans* diastereomer in the presence of the halide additive, but reverts back to a poorly diastereoselective reaction in its absence. This suggests, as postulated by Trost,[15] that Curtin–Hammett conditions are operating in the presence of the halide additive, as this enables rapid interconversion of the intermediate Pd-allyl complexes, thereby allowing the reaction to proceed selectively via **TS1**, which is presumably lower in energy than **TS2**.

Comparing the reaction of diethyl 2-vinylcyclopropane-1,1-dicarboxylate **1** and the trifluoroethyl-analogue **2** in the absence of additives (entries 1 and 2, Table 1) a switch in diastereoselectivity is observed. This suggests that greater stability of the malonyl-anion **A**, derived from **2** allows for some interconversion of **TS1** and **TS2** outside of the π-σ-π pathway. For indole substrate **3k**, which has a C-4 ester substituent the diastereoselectivity of the reaction completely favors the *cis* cyclopenta[*b*]indoline product – this complete selectivity is possibly due to a deleterious steric interaction between the C-4 ester and the Pd-allyl unit in **TS1** over-riding the π-stacking interaction.

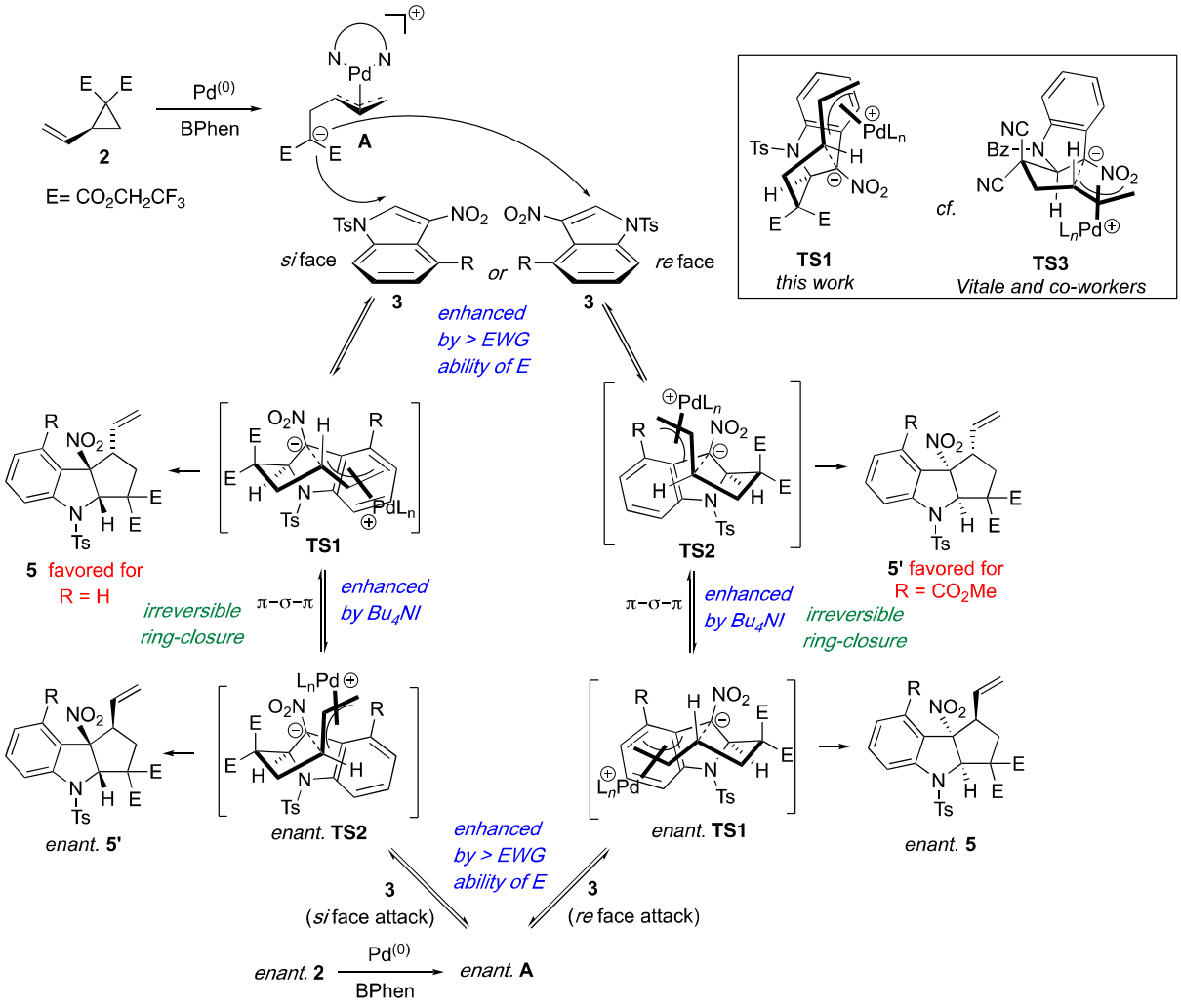
Vitale and co-workers invoked **TS3** (Figure 2, box) in the cycloaddition of dicyano vinylcyclopropanes to 3-nitroindoles as this places the Pd-allyl moiety in a pseudo-equatorial position to minimise diaxial interactions, however such a transition state is likely disfavored in the current reaction for steric reasons. Primarily, in **TS3** one of the cyano-groups occupies a pseudo-axial position adjacent to the indole skeleton – an arrangement that is likely to be sterically unfavourable for the larger ester groups of the 1,1-diester-derived vinylcyclopropanes.

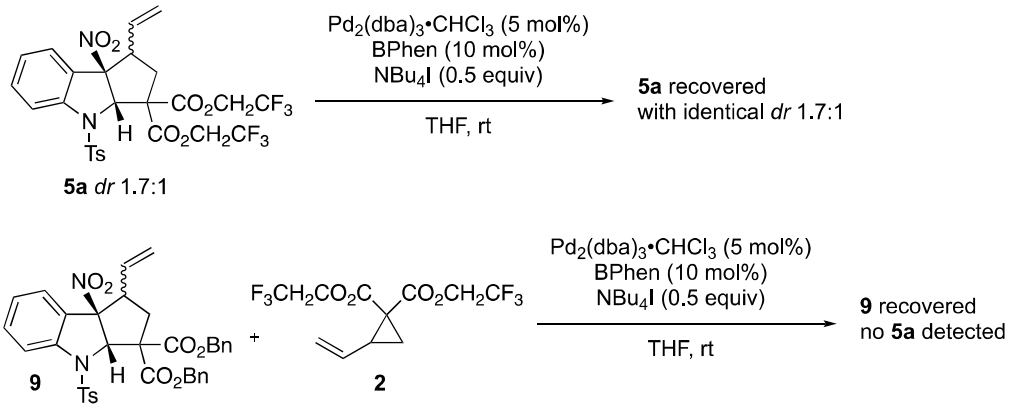
Conclusion

In summary, the Pd-catalyzed dearomative [3 + 2] cycloaddition of 3-nitroindoles with 2-vinylcyclopropane-1,1-dicarboxylates was achieved in high yields and moderate-good diastereoselectivity. Critically, this diastereoselectivity was complementary to the only existing report on vinylcyclopropane addition to electron-deficient indoles, which is proposed to be due to the presence of a halide additive allowing for Curtin–Hammett control of the reaction. Furthermore, the

densely functionalised cyclopenta[*b*]indoline products demonstrate potential to undergo further chemical transformation and provide access to other core structures. Of particular note is the facial differentiation of the geminal diester group, highlighting the versatility of 1,1-diester-derived vinylcyclopropanes, which can also be prepared in a single step from commercial materials and are easily handled and stored. We are currently conducting computational studies in order to gain further insight into the reaction diastereoselectivity and developing enantioselective variants – these results will be reported in due course.

Figure 2. *Proposed mechanism.*





Scheme 5. *Control experiments demonstrating irreversibility of the final ring-closure step.*

Experimental

General experimental details. Unless stated specifically, all chemicals were purchased from commercial suppliers and used without purification. All reactions were conducted in oven-dried glassware under nitrogen atmosphere. Reaction solvents were dried by passing through a column of activated alumina and then stored over 4Å molecular sieves. Progress of reactions was tracked by TLC and was performed on aluminium backed silica gel sheets (Grace Davison, UV254). TLC plates were visualised under UV lamp at 254 nm and/or by treatment with one of the following TLC stains: Phosphomolybdic acid (PMA) stain: PMA (10 g), absolute EtOH (100 mL); Potassium permanganate stain: $KMnO_4$ (1.5 g), 10% NaOH (1.25 mL), water (200 mL); Vanillin stain: Vanillin (15 g), concentrated H_2SO_4 (2.5 mL), EtOH (250 mL). For NMR spectroscopy analytes were dissolved in deuterated chloroform or stated otherwise. NMR spectra for each compound were collected from one of the following instrument: Mercury 2000 spectrometer operates at 500 and 125 MHz for ^{1}H and ^{13}C NMR respectively; Bruker spectrometer operates at 400, 100 and 470 MHz for ^{1}H, ^{13}C and ^{19}F NMR respectively. NMR data are expressed in parts per million (ppm) and referenced to the solvent (7.26 ppm for ^{1}H NMR and 77.16 ppm for ^{13}C NMR). The following abbreviations are used to assign the multiplicity of the ^{1}H NMR signal: s = singlet; bs = broad singlet; d = doublet; t = triplet; q = quartet; quin = quintet; dd = doublet of doublets; m = multiplet. NMR assignments were made on the basis of

HMBC, HSQC, COSY and DEPT experiments. For mass spectrometry analytes were dissolved in HPLC grade methanol or dichloromethane. High-resolution mass spectra were collected from a Waters Xevo G1 QTOF mass spectrophotometer. Infrared spectra were obtained from a Shimadzu IRAffinity-1 Fourier transform infrared spectrophotometer with ATR attachment. Melting point measurements were taken on a Buchi M-560.

Preparation of 2-vinylcyclopropane-1,1-dicarboxylates. 2-vinylcyclopropane-1,1-dicarboxylates **1** and **2** were prepared based on previously reported methods.[18]

*Bis(2,2,2-trifluoroethyl) (E)-2-styrylcyclopropane-1,1-dicarboxylate (**6**).* A solution of **2** (158.4 mg, 0.495 mmol, 1 equiv), Grubbs Catalyst 2nd Generation (10.2 mg, 12.0 μmol, 2.4 mol%) and styrene (1.1 mL, 996.6 mg, 9.57 mmol, 19.3 equiv) in dichloromethane (4 mL) was heated at 40°C for 1 h then concentrated under reduced pressure. After column chromatography (5 – 20% ethyl acetate in hexane), the title compound was obtained as a colourless oil (155.4 mg) in 79% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.30 (d, *J* = 4.5 Hz, 4H, CH_{Ar}) , 7.26 – 7.23 (m, 1H, CH_{Ar}), 6.69 (d, *J* = 15.5 Hz, 1H, Ph-C*H*=CH), 5.83 (dd, *J* = 16.0, 8.5 Hz, 1H, Ph-CH=C*H*), 4.63 – 4.44 (m, 4H, OCH_2), 2.91 (q, *J* = 8.5 Hz, 1H, Ph-CH=CH-C*H*), 2.05 – 2.02 (m, 1H, C*H*$_2$-C$(CO_2CH_2CF_3)_2$), 1.85 (dd, *J* = 9.0, 5.0 Hz, 1H, C*H*$_2$-C$(CO_2CH_2CF_3)_2$) ppm. **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ 167.4 (C=O), 165.4 (C=O), 136.1 (C_{Ar}), 135.4 (Ph-*C*H=CH), 128.6 (CH_{Ar}), 128.0 (CH_{Ar}), 126.2 (CH_{Ar}), 122.4 (Ph-CH=*C*H), 61.3 (q, *J* = 37.5 Hz, OCH_2), 61.2 (q, *J* = 36.3 Hz, OCH_2), 35.3 (*C*$(CO_2CH_2CF_3)_2$), 33.4 (Ph-CH=CH-*C*H), 22.3 (*C*H$_2$-C$(CO_2CH_2CF_3)_2$) ppm. **IR** (Neat): 3033, 1743, 1412, 1273, 1159, 1113 cm^{-1}. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{14}F_6O_4Na$ 419.0694; Found 419.0686.

*Dibenzyl 2-vinylcyclopropane-1,1-dicarboxylate (**7**).* A suspension of dibenzyl malonate (0.44 mL, 500.3 mg, 1.76 mmol, 1 equiv), *trans*-1,4-dibromo-2-butene (372.8 mg, 1.74 mmol, 1 equiv) and caesium carbonate (1.4393 g, 4.42 mmol, 2.5 equiv) in THF (35 mL) was heated at 60°C for 24 h. The suspension was cooled to room temperature and filtered. The filtrate was diluted with diethyl ether (70 mL) and washed with saturated sodium bicarbonate solution (50 mL), water (50 mL) then brine (50 mL). After the solution was dried over sodium sulfate and concentrated under reduced

pressure, column chromatography (50% dichloromethane in hexane) was performed to yield the title compound as a colourless oil (494.6 mg, 1.47 mmol) in 84% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.32 – 7.26 (m, 10H, CH_{Ar}), 5.44 – 5.37 (m, 1H, C*H*=CH_2), 5.28 (d, *J* = 17.0 Hz, 1H, CH=C*H*$_2$), 5.08-5.20 (m, 5H, CH=C*H*$_2$ and 2 × OCH_2), 2.63 (q, *J* = 8.5 Hz, 1H, C*H*-CH=CH2), 1.76 (dd, *J* = 7.5, 5.0 Hz, 1H, C*H*$_2$-C(CO_2Bn)$_2$), 1.60 (dd, *J* = 9.0, 4.5 Hz, 1H, C*H*$_2$-C(CO_2Bn)$_2$) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 169.4 (C=O), 167.2 (C=O), 135.5 (C_{Ar}), 135.4 (C_{Ar}), 132.8 (*C*H=CH_2), 128.5 (CH_{Ar}), 128.4 (CH_{Ar}), 128.3 (CH_{Ar}), 128.23 (CH_{Ar}), 128.21 (CH_{Ar}), 128.0 (CH_{Ar}), 118.8 (CH=*C*H_2), 67.4 (OCH_2), 67.3 (OCH_2), 35.9 (*C*-(CO_2Bn)$_2$), 31.7 (*C*H-CH=CH_2), 20.8 (*C*H_2-C-(CO_2Bn)$_2$) ppm. **IR** (Neat): 3034, 1722, 1498, 1455, 1379, 1317, 1266, 1189, 1123 cm^{-1}. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{20}O_4Na$ 359.1259; Found 359.1273.

Preparation of 3-nitroindoles. Indole derivatives **3a-k** and **10c** were prepared based on reported method.[10]

*3-Nitro-1-((trifluoromethyl)sulfonyl)-1H-indole (**10a**)*. A solution of 3-nitro-1*H*-indole[19,20] (100.9 mg, 0.622 mmol, 1 equiv), DMAP (81.9 mg, 0.670 mmol, 1.1 equiv) and triethylamine (0.35 mL, 253.8 mg, 2.51 mmol, 4 equiv) in dichloromethane (6 mL) was cooled to 0°C prior to the addition of trifluoromethanesulfonic anhydride (0.35 mL, 587.0 mg, 2.08 mmol, 3.3 equiv). After the addition, the solution was allowed to warm to room temperature and stirred overnight. Reaction was quenched with ice-cold water (5 mL). Organic layer was isolated and the aqueous layer was extracted with ethyl acetate (3 × 20 mL). After the combined organic extracts were dried over sodium sulfate and concentrated under reduced pressure, column chromatography (20 – 40% ethyl acetate in hexane) was performed to yield the title compound as a yellow solid (118.1 mg, 0.401 mmol) in 65% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.37 – 8.34 (m, 2H, CH_{Ar} and *H*C=C-NO_2), 7.96 (d, *J* = 6.8 Hz, 1H, CH_{Ar}), 7.62 – 7.58 (m, 2H, CH_{Ar}) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 135.8 (C_{Ar}), 134.7 (C_{Ar}), 128.2 (CH_{Ar}), 127.7 (H*C*=C-NO_2), 127.3 (CH_{Ar}), 121.81 (C_{Ar}), 121.77 (CH_{Ar}), 119.3 (q, *J* = 320 Hz, CF_3), 113.9 (CH_{Ar}) ppm. **^{19}F NMR** (470 Hz, $CDCl_3$): δ −74.64 (s, CF_3) ppm. **IR** (Neat): 3170, 1591, 1560, 1513, 1478, 1443, 1416, 1355, 1316, 1267, 1215, 1142, 1124, 1101, 1067 cm^{-1}. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_9H_5F_3N_2O_4SNa$ 316.9820; Found 316.9815. **Melting point**: 89.1 – 92.9 °C

*(3-Nitro-1H-indol-1-yl)(phenyl)methanone (**10b**).* The title compound was prepared from (3-nitro-1*H*-indol-1-yl)(phenyl)methanone[10,21] based on a reported method.[10] Recrystallization from hot methanol gave the title compound as a white solid (132.1 mg, 11% yield). **IR** (Neat): 3141, 1708, 1545, 1479, 1450, 1387, 1370, 1317, 1299, 1213, 1145, 1120 cm^{-1}. NMR data consistent with the literature.[14]

*2,2,2-Trifluoro-1-(1-tosyl-1H-indol-3-yl)ethan-1-one (**10d**).* Ground sodium hydroxide pearls (206.1 mg, 5.15 mmol, 5.5 equiv) was added to a solution of 2,2,2-trifluoro-1-(1*H*-indol-3-yl)ethan-1-one[22] (199.4 mg, 0.935 mmol, 1 equiv) and tetrabutylammonium bisulfate (32.8 mg, 0.0966 mmol, 0.1 equiv) in dichloromethane (10 mL). The solution was stirred for 10 mins before the addition of tosyl chloride (270.4 mg, 1.42 mmol, 1.5 equiv). The reaction was left stirring overnight at room temperature. Tetrabutylammonium bisulfate (33.2 mg, 0.0978 mmol) and ground sodium hydroxide pearls (179.8 mg, 4.50 mmol, 4.8 equiv) were added to the suspension. The reaction was left stirring overnight at 55°C before the addition of saturated ammonium chloride solution (20 mL). The solution was stirred for 2 h then the organic fraction was isolated and the aqueous fraction was extracted with dichloromethane (2 × 10 mL). The combined organic extracts were dried over magnesium sulfate and concentrated under reduced pressure. After column chromatography (20% ethyl acetate in hexane), the title compound was collected as an oily white solid (22.6 mg, 0.062 mmol) in 7% yield. NMR data consistent with literature.[22]

Typical procedure for Pd-catalyzed dearomative [3 + 2] cycloaddition of 3-nitroindole with 2-vinylcyclopropane-1,1-dicarboxylates. An oven-dried 3 mL reaction vial equipped with a magnetic stir bar was charged with the 2-vinylcyclopropane-1,1-dicarboxylate derivative (0.05 mmol, 1.0 equiv), the indole derivative (0.05 mmol, 1 equiv), $Pd_2(dba)_3 \cdot CHCl_3$ (2.6 mg, 0.0025 mmol, 5 mol %), BPhen (1.7 mg, 0.0050 mmol, 10 mol %) and NBu_4I (10.1 mg, 0.02 mmol, 0.5 equiv). The vial was fitted with a septum cap and purged with N_2. Anhydrous THF (0.82 mL) was added and the reaction

was stirred till the consumption of both substrates as indicated from TLC. The solvent was removed under reduced pressure and the crude residue was purified by column chromatography.

*Diethyl (1S,3aS,8bR)-8b-nitro-4-tosyl-1-vinyl-1,3a,4,8b-tetrahydrocyclopenta[b]indole-3,3(2H)-dicarboxylate (**4a/4a'**).* Based on the typical procedure, the title compound was obtained as a pale yellow oil (53.7 mg, 101.6 mmol) in 99% yield after column chromatography (20 % ethyl acetate in hexane). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.73 (t, *J* = 8.5 Hz, 2H, CH_{Ar}), 7.52 - 7.51 (m, 3H, CH_{Ar}), 7.47 - 7.43 (m, 2H, CH_{Ar}), 7.41 (d, *J* = 8.5 Hz, 2H, CH_{Ar}), 7.37 (d, *J* = 8.0 Hz, 1H, CH_{Ar}), 7.22 (t, *J* = 7.5 Hz, 1H, CH_{Ar}), 7.15 (t, *J* = 7.5 Hz, 1H, CH_{Ar}), 7.10 (dd, *J* = 13.5, 8.0 Hz, 3H, CH_{Ar}), 6.36 (s, 1H, Ts-N-C*H* major), 6.31 (s, 1H, Ts-N-C*H* minor), 5.78 (ddd, *J* = 17.4, 10.0, 7.5 Hz, 1H, C*H*=CH_2 major), 5.53 (dt, *J* = 17.0, 9.5 Hz, 1H, C*H*=CH_2 minor), 5.28 - 5.11 (m, 4H, CH=CH_2), 4.48 - 4.16 (m, 8H, OC$H_2$$CH_3$), 3.41 (app q, *J* = 7.0 Hz, 1H, C*H*-CH=CH_2 major), 3.30 (dt, *J* = 14.0, 6.5 Hz, 1H, C*H*-CH=CH_2 minor), 2.59 (dd, *J* = 13.5, 6.5 Hz, 1H, CHCH_2 major), 2.40 (dd, *J* = 13.5, 56.5 Hz, 1H, CHCH_2 minor), 2.31 - 2.28 (m, 7H, CH_3 and CHCH_2), 2.21 (app t, *J* = 14.0 Hz, 1H, CHCH_2 major), 1.40-1.31 (m, 12H, OCH_2CH_3) ppm. **^{13}C{^{1}H}** NMR (125 MHz, $CDCl_3$): δ 169.8 (2 × overlapping C=O), 167.9 (C=O), 166.7 (C=O), 145.1 (C_{Ar}), 145.0 (C_{Ar}), 144.5 (C_{Ar}), 142.6 (C_{Ar}), 133.0 (C_{Ar}), 132.8 (*C*H=CH_2), 132.4 (*C*H=CH_2), 132.1 (CH_{Ar}), 132.0 (CH_{Ar}), 129.80 ($CH_{Ar\ Tosyl}$), 129.79 ($CH_{Ar\ Tosyl}$), 128.9 (CH_{Ar}), 128.6 (C_{Ar}), 127.8 ($CH_{Ar\ Tosyl}$), 127.7 ($CH_{Ar\ Tosyl}$), 126.5 (CH_{Ar}), 126.0 (CH_{Ar}), 125.3 (CH_{Ar}), 124.7 (C_{Ar}), 121.1 (CH=*C*H_2), 120.7 (CH=*C*H_2), 118.3 (CH_{Ar}), 117.8 (CH_{Ar}), 102.7 (C-NO_2), 101.3 (C-NO_2), 73.7 (Ts-N-*C*H), 73.3 (Ts-N-*C*H), 64.9 (*C*-(CO_2Et)$_2$), 64.1 (*C*-(CO_2Et)$_2$), 62.85 (O*C*$H_2$$CH_3$), 62.80 (O*C*$H_2$$CH_3$), 62.65 (O*C*$H_2$$CH_3$), 62.61 (O*C*$H_2$$CH_3$), 53.8 (*C*H-CH=$CH_2$), 50.5 (*C*H-CH=$CH_2$), 39.6 (CH*C*$H_2$), 37.5 (CH*C*$H_2$), 21.71 ($CH_3$), 21.70 ($CH_3$), 14.18 ($CO_2CH_2$*C*$H_3$), 14.14 ($CO_2CH_2$*C*$H_3$), 14.10 ($CO_2CH_2$*C*$H_3$), 14.08 ($CO_2CH_2$*C*$H_3$) ppm. **IR** (Neat): 2987, 1730, 1551, 1368, 1265, 1172, 1091, 734, 664 cm^{-1}. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{28}N_2O_8SNa$ 551.1464; Found 551.1445.

*Bis(2,2,2-trifluoroethyl) (3aS,8bR)-8b-nitro-4-tosyl-1-vinyl-1,3a,4,8b-tetrahydrocyclopenta[b]indole-3,3(2H)-dicarboxylate (**5a**).* Based on the typical procedure, the title compound was obtained as a white solid (28.3 mg, 0.04 mmol) in 80% yield after column chromatography (25 – 50% diethyl ether in hexane). The major isomer was isolated by recrystallization in methanol and dichloromethane. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.5 Hz, 1H, CH_{Ar}), 7.49 (t, *J* = 8.0 Hz, 1H, CH_{Ar}), 7.43 (d, *J* = 8.5 Hz, 2H, $CH_{Ar\ Tosyl}$), 7.38 (d, *J* = 7.5 Hz, 1H, CH_{Ar}), 7.18 (t, *J* = 7.5 Hz, 1H, CH_{Ar}), 7.13 (d, *J* = 8.0 Hz, 2H, $CH_{Ar\ Tosyl}$), 6.24 (s, 1H, C*H*-NTs), 5.75 (ddd, *J* = 17.4, 10.5, 7.5 Hz, 1H, C*H*=CH_2), 5.31 (d, *J* = 10.5 Hz, 1H, CH=CH_2), 5.17 (d, *J* = 17.0 Hz, 1H, CH=CH_2), 5.02 – 4.95 (m, 1H, OCH_2CF_3), 4.84 – 4.77 (m, 1H, OCH_2CF_3), 4.57 – 4.50 (m, 1H, OCH_2CF_3), 4.47 – 4.40 (m, 1H, OCH_2CF_3), 3.30 (dt, *J* = 14.0, 6.5 Hz, 1H, C*H*-CH=CH_2), 2.47 (dd, *J* = 13.5, 5.5 Hz, 1H, CH_2-CH-CH=CH_2), 2.34 (s, 3H, CH_3), 2.28 (app t, *J* = 14.0 Hz, 1H, CH_2-CH-CH=CH_2) ppm. **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ 167.7 (C=O), 164.5 (C=O), 145.5 (C_{Ar}), 144.0 (C_{Ar}), 132.3 (CH_{Ar}), 132.1 (C_{Ar}), 131.6 (*C*H=CH_2), 129.8 ($CH_{Ar\ Tosyl}$), 128.6 (CH_{Ar}). 127.7 ($CH_{Ar\ Tosyl}$), 125.3 (CH_{Ar}), 123.9 (C_{Ar}), 122.5 (q, *J* = 275 Hz, *C*F_3), 122.4 (q, *J* = 270 Hz, *C*F_3), 121.2 (CH=*C*H_2), 117.9 (CH_{Ar}), 100.8 (C-NO_2), 73.6 (*C*H-NTs), 63.7 (*C*($CO_2CH_2CF_3$)$_2$), 62.1 (q, *J* = 37.5 Hz, O*C*H_2CF_3), 61.9 (q, *J* = 37.5 Hz, O*C*H_2CF_3), 50.2 (*C*H-CH=CH_2), 37.4 (*C*H_2-CH-CH=CH_2), 21.6 (CH_3) ppm. **^{19}F NMR** (470 Hz, $CDCl_3$): δ −73.61 (t, *J* = 8.0 Hz, CF_3), −73.75 (t, *J* = 8.9 Hz, CF_3) ppm. **IR** (Neat): 1751, 1551, 1461, 1420, 1370, 1285, 1241, 1157, 1072 cm^{-1}. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{22}F_6N_2O_8SNa$ 659.0899; Found 659.0928. **Melting point**: 185.2 – 187.2 °C

*Bis(2,2,2-trifluoroethyl)(3aS,8bR)-7-chloro-8b-nitro-4-tosyl-1-vinyl-1,3a,4,8b tetrahydrocyclopenta[b]indole-3,3(2H)-dicarboxylate (**5b/5b'**).* Based on the typical procedure, the title compound was obtained as a colourless film (31.1 mg, 0.046 mmol) in 88% yield after column chromatography (10 – 20% ethyl acetate in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.69 – 7.65 (m, 2H, $CH_{Ar\ Major}$ and $CH_{Ar\ Minor}$), 7.52 – 7.41 (m, 7H, 3 × $CH_{Ar\ Major}$ and 4 × $CH_{Ar\ Minor}$), 7.34 (d, *J* = 2.0 Hz, 1H, $CH_{Ar\ Major}$), 7.18 – 7.16 (m, 4H, 2 × $CH_{Ar\ Major}$ and 2 × $CH_{Ar\ Minor}$), 6.28 (s, 1H, Ts-N-C*H* $_{Minor}$), 6.24 (d, *J* = 0.8 Hz, 1H, Ts-N-C*H* $_{Major}$), 5.74 (ddd, *J* = 17.3, 10.2, 7.6 Hz, 1H, C*H*=$CH_{2\ Major}$), 5.51 –

5.44 (m, 1H, C*H*=$CH_{2\ Minor}$), 5.38 (d, *J* = 10.4 Hz, 1H, CH=C$H_{2\ Major}$), 5.31 – 5.25 (m, 2H, CH=C$H_{2\ Minor}$), 5.19 (d, *J* = 17.2 Hz, 1H, CH=C$H_{2\ Major}$), 5.01 – 4.92 (m, 1H, OC$H_2CF_{3\ Major}$), 4.88 – 4.70 (m, 1H of OC$H_2CF_{3\ Major}$ and 2H of OC$H_2CF_{3\ Minor}$), 4.59 – 4.50 (m, 2H, OC$H_2CF_{3\ Major}$ and OC$H_2CF_{3\ Minor}$), 4.47 – 4.37 (m, 2H, OC$H_2CF_{3\ Major}$ and OC$H_2CF_{3\ Minor}$), 3.42 (app q, *J* = 6.8 Hz, 1H, C*H*-CH=$CH_{2\ Minor}$), 3.29 (dt, *J* = 14.4, 6.4 Hz, 1H, C*H*-CH=$CH_{2\ Major}$), 2.66 (dd, *J* = 14.0, 6.4 Hz, 1H, CH-C$H_{2\ Minor}$), 2.50 (dd, *J* = 14.0, 4.4 Hz, 1H, CH-C$H_{2\ Major}$), 2.40 (dd, *J* = 12.6, 5.6 Hz, 1H, CH-C$H_{2\ Minor}$), 2.36 (s, 3H, $CH_{3\ Tosyl\ Major}$), 2.35 (s, 3H, $CH_{3\ Tosyl\ Minor}$), 2.28 (app t, *J* = 14.4 Hz, 1H, CH-C$H_{2\ Major}$) ppm. **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$): δ 167.6 (C=$O_{\ Major}$), 167.4 (C=$O_{\ Minor}$), 165.9 (C=$O_{\ Minor}$), 164.4 (C=$O_{\ Major}$), 145.8 ($C_{Ar\ Major}$), 145.7 ($C_{Ar\ Minor}$), 142.7 ($C_{Ar\ Major}$), 140.9 ($C_{Ar\ Minor}$), 132.6 ($CH_{Ar\ Major}$), 132.4 ($CH_{Ar\ Minor}$), 132.0 ($C_{Ar\ Minor}$), 131.9 ($C_{Ar\ Major}$), 131.6 ($C_{Ar\ Minor}$), 131.3 (*C*H=$CH_{2\ Minor}$), 130.94 (*C*H=$CH_{2\ Major}$), 130.87 ($C_{Ar\ Major}$), 130.1 ($CH_{Ar\ Tosyl\ Major}$), 130.0 ($CH_{Ar\ Tosyl\ Minor}$), 129.3 ($C_{Ar\ Minor}$), 129.0 ($CH_{Ar\ Minor}$), 128.6 ($CH_{Ar\ Major}$), 127.64 ($CH_{Ar\ Tosyl\ Major}$), 127.58 ($CH_{Ar\ Tosyl\ Minor}$), 125.5 ($C_{Ar\ Major}$), 122.5 (q, *J* = 275 Hz, $CF_{3\ Major}$ and $CF_{3\ Minor}$), 122.4 (q, *J* = 276 Hz, $CF_{3\ Major}$ and $CF_{3\ Minor}$), 122.2 (CH=*C*$H_{2\ Minor}$), 121.9 (CH=*C*$H_{2\ Major}$), 118.8 ($CH_{Ar\ Major}$), 118.7 ($CH_{Ar\ Minor}$), 101.7 (C-$NO_{2\ Minor}$), 100.4 (C-$NO_{2\ Major}$), 73.9 (Ts-N-*C*H $_{Major}$ and Ts-N-*C*H $_{Minor}$), 64.6 (*C*-$(CO_2CH_2CF_3)_{2\ Minor}$), 63.8 (*C*-$(CO_2CH_2CF_3)_{2\ Major}$), 62.7 – 61.4 (m, *C*$H_2CF_{3\ Major}$ and *C*$H_2CF_{3\ Minor}$), 53.8 (*C*H-CH=$CH_{2\ Minor}$), 50.2 (*C*H-CH=$CH_{2\ Major}$), 39.6 (CH-*C*$H_{2\ Minor}$), 37.4 (CH-*C*$H_{2\ Major}$), 21.6 ($CH_{3\ Major}$ and $CH_{3\ Minor}$) ppm. **^{19}F NMR** (470 Hz, $CDCl_3$): δ −73.51 (t, *J* = 8.0 Hz, $CF_{3\ Minor}$), −73.61 (t, *J* = 7.5 Hz, $CF_{3\ Major}$), −73.70 (t, *J* = 8.5 Hz, $CF_{3\ Minor}$), −73.75 (t, *J* = 8.5 Hz, $CF_{3\ Major}$) ppm. **IR** (Neat): 1751, 1553, 1472, 1419, 1373, 1285, 1241, 1158, 1105, 1091, 1068 cm^{-1}. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{21}ClF_6N_2O_8SNa$ 693.0509; Found 693.0511.

*Bis(2,2,2-trifluoroethyl)(3aS,8bR)-7-bromo-8b-nitro-4-tosyl-1-vinyl-1,3a,4,8b-tetrahydrocyclopenta[b]indole-3,3(2H)-dicarboxylate (**5c/5c'**).* Based on the typical procedure, the title compound was obtained as an off-white solid (34.6 mg, 0.048 mmol) in 87% yield after column chromatography (15 – 40% ethyl acetate in hexane). **^1H NMR** (500 MHz, $CDCl_3$): δ 7.63 – 7.59 (m, 5H, 2 × $CH_{Ar\ Major}$ and 3 × $CH_{Ar\ Minor}$), 7.52 (d, *J* = 8.0 Hz, 2H, $CH_{Ar\ Minor}$), 7.48 (d, *J* = 1.5 Hz, 1H,

$CH_{Ar\ Major}$), 7.44 (d, J = 8.0 Hz, 2H, $CH_{Ar\ Major}$), 7.17 (d, J = 7.5 Hz, 4H, 2 × $CH_{Ar\ Major}$ and 2 × $CH_{Ar\ Minor}$), 6.27 (s, 1H, Ts-N-C*H* $_{Minor}$), 6.23 (s, 1H, Ts-N-C*H* $_{Major}$), 5.74 (ddd, J = 17.3, 10.3, 7.5 Hz, 1H, C*H*=$CH_{2\ Major}$), 5.50 – 5.43 (m, 1H, C*H*=$CH_{2\ Minor}$), 5.38 (d, J = 10.5 Hz, 1H, CH=C$H_{2\ Major}$), 5.31 – 5.25 (m, 2H, CH=C$H_{2\ Minor}$), 5.19 (d, J = 17.0 Hz, 1H, CH=C$H_{2\ Major}$), 5.00 – 4.93 (m, 1H, OC$H_2CF_{3\ Major}$), 4.87 – 4.71 (m, 1H of OC$H_2CF_{3\ Major}$ and 2H of OC$H_2CF_{3\ Minor}$), 4.58 – 4.50 (m, 2H, OC$H_2CF_{3\ Major}$ and OC$H_2CF_{3\ Minor}$), 4.46 – 4.38 (m, 2H, OC$H_2CF_{3\ Major}$ and OC$H_2CF_{3\ Minor}$), 3.42 (app q, J = 8.5 Hz, 1H, C*H*-CH=$CH_{2\ Minor}$), 3.28 (dt, J = 14.0, 6.5 Hz, 1H, C*H*-CH=$CH_{2\ Major}$), 2.66 (dd, J = 14.0, 6.5 Hz, 1H, CH-C$H_{2\ Minor}$), 2.49 (dd, J = 14.0, 4.5 Hz, 1H, CH-C$H_{2\ Major}$), 2.42 – 2.39 (m, 1H, CH-C$H_{2\ Minor}$), 2.37 (s, 3H, $CH_{3\ Tosyl\ Major}$), 2.36 (s, 3H, $CH_{3\ Tosyl\ Minor}$), 2.28 (app t, J = 14.0 Hz, 1H, CHC$H_{2\ Major}$) ppm. **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ 167.5 (C=O $_{Major}$), 165.8 (C=O $_{Minor}$), 164.4 (C=O $_{Major}$), 145.8 ($C_{Ar\ Major}$), 145.7 ($C_{Ar\ Minor}$), 143.2 ($C_{Ar\ Major}$), 141.4 ($C_{Ar\ Minor}$), 135.4 ($CH_{Ar\ Major}$), 135.3 ($CH_{Ar\ Minor}$), 132.0 ($C_{Ar\ Minor}$), 131.9 ($C_{Ar\ Major}$), 131.5 ($CH_{Ar\ Major}$), 131.2 (*C*H=$CH_{2\ Minor}$), 130.9 (*C*H=$CH_{2\ Major}$), 130.1 ($CH_{Ar\ Tosyl\ Major}$), 130.0 ($CH_{Ar\ Tosyl\ Minor}$), 129.6 ($C_{Ar\ Minor}$), 129.4 ($CH_{Ar\ Minor}$), 127.63 ($CH_{Ar\ Tosyl\ Major}$), 127.57 ($CH_{Ar\ Tosyl\ Minor}$), 125.7 ($C_{Ar\ Major}$), 122.5 (q, J = 276 Hz, $CF_{3\ Major}$ and $CF_{3\ Minor}$), 122.4 (q, J = 276 Hz, $CF_{3\ Major}$ and $CF_{3\ Minor}$), 122.2 (CH=*C*$H_{2\ Minor}$), 121.9 (CH=*C*$H_{2\ Major}$), 119.2 ($CH_{Ar\ Major}$), 119.0 ($CH_{Ar\ Minor}$), 118.9 ($C_{Ar\ Minor}$), 118.2 ($C_{Ar\ Major}$), 101.7 (C-$NO_{2\ Minor}$), 100.3 (C-$NO_{2\ Major}$), 73.8 (Ts-N-*C*H $_{Major}$ and Ts-N-*C*H $_{Minor}$), 64.6 (*C*-$(CO_2CH_2CF_3)_{2\ Minor}$), 63.7 (*C*-$(CO_2CH_2CF_3)_{2\ Major}$), 62.6 – 61.5 (m, *C*$H_2CF_{3\ Major}$ and *C*$H_2CF_{3\ Minor}$), 53.8 (*C*H-CH=$CH_{2\ Minor}$), 50.2 (*C*H-CH=$CH_{2\ Major}$), 39.6 (CH-*C*$H_{2\ Minor}$), 37.4 (CH-*C*$H_{2\ Major}$), 21.7 ($CH_{3\ Major}$ and $CH_{3\ Minor}$) ppm. **^{19}F NMR** (470 Hz, $CDCl_3$): δ −73.51 (t, J = 8.0 Hz, $CF_{3\ Minor}$), −73.61 (t, J = 8.0 Hz, $CF_{3\ Major}$), −73.69 (t, J = 8.5 Hz, $CF_{3\ Minor}$), −73.74 (t, J = 8.5 Hz, $CF_{3\ Major}$) ppm. **IR** (Neat): 1751, 1559, 1555, 1472, 1419, 1370, 1283, 1250, 1161, 1103, 1068 cm^{-1}. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{21}BrF_6N_2O_8SNa$ 737.0004; Found 737.0034.

*7-Methyl 3,3-bis(2,2,2-trifluoroethyl) (3aS,8bR)-8b-nitro-4-tosyl-1-vinyl-1,3a,4,8b-tetrahydrocyclopenta[b]indole-3,3,7(2H)-tricarboxylate (**5d/5d'**).* Based on the typical procedure, the title compound was obtained as a colourless film (30.5 mg, 0.044 mmol) in 84% yield after column

chromatography (20 – 30% ethyl acetate in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.21 – 8.15 (m, 3H, $CH_{Ar\ Major}$ and 2 × $CH_{Ar\ Minor}$), 8.02 (d, *J* = 1.2 Hz, 1H, $CH_{Ar\ Major}$), 7.79 (d, *J* = 8.8 Hz, 1H, $CH_{Ar\ Major}$), 7.75 (d, *J* = 8.8 Hz, 1H, $CH_{Ar\ Minor}$), 7.56 (d, *J* = 8.0 Hz, 2H, $CH_{Ar\ Tosyl\ Minor}$), 7.48 (d, *J* = 8.4 Hz, 2H, $CH_{Ar\ Tosyl\ Major}$), 7.18 – 7.15 (m, 4H, 2 × $CH_{Ar\ Tosyl\ Major}$ and 2 × $CH_{Ar\ Tosyl\ Minor}$), 6.39 (s, 1H, Ts-N-C*H* $_{Minor}$), 6.29 (d, *J* = 0.8 Hz, 1H, Ts-N-C*H* $_{Major}$), 5.80 (ddd, *J* = 17.3, 10.2, 7.2 Hz, 1H, C*H*=$CH_{2\ Major}$), 5.57 – 5.49 (m, 1H, C*H*=$CH_{2\ Minor}$), 5.39 (d, *J* = 10.4 Hz, 1H, CH=C*H*$_{2\ Major}$), 5.31 (d, *J* = 16.8 Hz, 1H, CH=C*H*$_{2\ Minor}$), 5.27 (d, *J* = 10.0 Hz, 1H, CH=C*H*$_{2\ Minor}$), 5.20 (d, *J* = 17.2 Hz, 1H, CH=C*H*$_{2\ Major}$), 5.01 – 4.91 (m, 1H, OC*H*$_2CF_{3\ Major}$), 4.87 – 4.73 (m, 1H of OC*H*$_2CF_{3\ Major}$ and 2H of OC*H*$_2CF_{3\ Minor}$), 4.60 – 4.50 (m, 2H, OC*H*$_2CF_{3\ Major}$ and OC*H*$_2CF_{3\ Minor}$), 4.48 – 4.39 (m, 2H, OC*H*$_2CF_{3\ Major}$ and OC*H*$_2CF_{3\ Minor}$), 3.92 (s, 3H, $OCH_{3\ Minor}$), 3.91 (s, 3H, $OCH_{3\ Major}$), 3.49 (app q, *J* = 7.2 Hz, 1H, C*H*-CH=$CH_{2\ Minor}$), 3.35 (dt, *J* = 14.4, 6.4 Hz, 1H, C*H*-CH=$CH_{2\ Major}$), 2.71 – 2.64 (m, 1H, CH-C*H*$_{2\ Minor}$), 2.52 (ddd, *J* = 13.8, 5.4, 0.8 Hz, 1H, CH-C*H*$_{2\ Major}$), 2.45 (dd, *J* = 14.0, 7.6 Hz, 1H, CH-C*H*$_{2\ Minor}$), 2.34 (s, 3H, $CH_{3\ Tosyl\ Major}$), 2.33 (s, 3H, $CH_{3\ Tosyl\ Minor}$), 2.28 – 2.25 (m, 1H, CH-C*H*$_{2\ Major}$) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 167.6 (C=O $_{Major}$), 167.5 (C=O $_{Minor}$), 165.8 (C=O $_{Minor}$), 165.6 (C=O $_{Major}$), 164.4 (C=O $_{Major}$), 147.7 ($C_{Ar\ Major}$), 145.9 ($C_{Ar\ Major}$), 145.81 ($C_{Ar\ Minor}$), 145.77 ($C_{Ar\ Minor}$), 134.0 ($CH_{Ar\ Major}$), 133.9 ($CH_{Ar\ Minor}$), 132.4 ($C_{Ar\ Minor}$), 132.1 ($C_{Ar\ Major}$), 131.4 (*C*H=$CH_{2\ Minor}$), 131.1 (*C*H=$CH_{2\ Major}$), 130.2 ($CH_{Ar\ Major}$), 130.1 ($CH_{Ar\ Tosyl\ Major}$ and $CH_{Ar\ Tosyl\ Minor}$), 128.2 ($CH_{Ar\ Minor}$), 128.1 ($C_{Ar\ Minor}$), 127.8 ($C_{Ar\ Minor}$), 127.6 ($CH_{Ar\ Tosyl\ Major}$), 127.5 ($CH_{Ar\ Tosyl\ Minor}$), 127.4 ($C_{Ar\ Major}$), 124.2 ($C_{Ar\ Major}$), 122.5 (q, *J* = 280 Hz, $CF_{3\ Major}$ and $CF_{3\ Minor}$), 122.4 (q, *J* = 280 Hz, $CF_{3\ Major}$ and $CF_{3\ Minor}$), 122.1 (CH=*C*H$_{2\ Minor}$), 121.7 (CH=*C*H$_{2\ Major}$), 117.0 ($CH_{Ar\ Major}$), 116.7 ($CH_{Ar\ Minor}$), 101.8 (C-$NO_{2\ Minor}$), 100.2 (C-$NO_{2\ Major}$), 74.2 (Ts-N-*C*H $_{Major}$), 73.9 (Ts-N-*C*H $_{Minor}$), 64.6 (*C*-$(CO_2CH_2CF_3)_{2\ Minor}$), 63.7 (*C*-$(CO_2CH_2CF_3)_{2\ Major}$), 62.6 – 61.5 (m, *C*$H_2CF_{3\ Major}$ and *C*$H_2CF_{3\ Minor}$), 53.4 (*C*H-CH=$CH_{2\ Minor}$), 52.5 ($OCH_{3\ Major}$ and $OCH_{3\ Minor}$), 49.9 (*C*H-CH=$CH_{2\ Major}$), 39.7 (CH-*C*H$_{2\ Minor}$), 37.5 (CH-*C*H$_{2\ Major}$), 21.64 ($CH_{3\ Major}$), 21.61 ($CH_{3\ Minor}$) ppm. **^{19}F NMR** (470 Hz, $CDCl_3$): δ −73.54 (t, *J* = 8.5 Hz, $CF_{3\ Minor}$), −73.62 (t, *J* = 8.0 Hz, $CF_{3\ Major}$), −73.68 (t, *J* = 8.0 Hz, $CF_{3\ Minor}$), −73.74 (t, *J* = 8.0 Hz, $CF_{3\ Major}$) ppm. **IR** (Neat): 1754, 1722, 1555, 1374, 1287, 1243, 1165, 1111, 1088 cm^{-1}. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{24}F_6N_2O_{10}SNa$ 717.0954; Found 717.0928.

*Bis(2,2,2-trifluoroethyl) (3aS,8bR)-7-cyano-8b-nitro-4-tosyl-1-vinyl-1,3a,4,8b-tetrahydrocyclopenta[b]indole-3,3(2H)-dicarboxylate (**5e/5e'**)*. Based on the typical procedure, the title compound was obtained as a colourless film (31.0 mg, 0.047 mmol) in 82% yield after column chromatography (20 – 30% ethyl acetate in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.85 – 7.82 (m, 3H, $CH_{Ar\ Major}$ and 2 × $CH_{Ar\ Minor}$), 7.77 – 7.74 (m, 2H, $CH_{Ar\ Major}$ and $CH_{Ar\ Minor}$), 7.68 (d, J = 4.0 Hz, 1H, $CH_{Ar\ Major}$), 7.55 (d, J = 8.0 Hz, 2H, $CH_{Ar\ Minor}$), 7.47 (d, J = 8.0 Hz, 2H, $CH_{Ar\ Major}$), 7.22 – 7.19 (m, 4H, 2 × $CH_{Ar\ Major}$ and 2 × $CH_{Ar\ Minor}$), 6.30 (d, J = 1.6 Hz, 2H, Ts-N-C*H* $_{Major}$ and Ts-N-C*H* $_{Minor}$), 5.74 (ddd, J = 17.3, 10.4, 7.2 Hz, 1H, C*H*=$CH_{2\ Major}$), 5.51 – 5.42 (m, 1H, C*H*=$CH_{2\ Minor}$), 5.43 (d, J = 10.4 Hz, 1H, CH=C$H_{2\ Major}$) 5.35 – 5.30 (m, 2H, CH=C$H_{2\ Minor}$), 5.23 (d, J = 17.2 Hz, 1H, CH=C$H_{2\ Major}$), 4.99 – 4.89 (m, 1H, OC$H_2CF_{3\ Major}$), 4.87 – 4.76 (m, 2H, OC$H_2CF_{3\ Major}$ and OC$H_2CF_{3\ Minor}$), 4.74 – 4.67 (m, 1H, OC$H_2CF_{3\ Minor}$), 4.61 – 4.52 (m, 2H, OC$H_2CF_{3\ Major}$ and OC$H_2CF_{3\ Minor}$), 4.49 – 4.38 (m, 2H, OC$H_2CF_{3\ Major}$ and OC$H_2CF_{3\ Minor}$), 3.43 (app q, J = 8.0 Hz, 1H, C*H*-CH=$CH_{2\ Minor}$), 3.33 (dt, J = 16.0, 8.0 Hz, 1H, C*H*-CH=$CH_{2\ Major}$), 2.68 (dd, J = 16.0, 8.0 Hz, 1H, CH-C$H_{2\ Minor}$), 2.57 (ddd, J = 14.0, 5.6, 1.2 Hz, 1H, CH-C$H_{2\ Major}$), 2.44 (dd, J = 13.8, 9.6 Hz, 1H, CH-C$H_{2\ Minor}$), 2.37 (s, 3H, $CH_{3\ Tosyl\ Major}$), 2.36 (s, 3H, $CH_{3\ Tosyl\ Minor}$), 2.26 (app t, J = 14.8 Hz, 1H, CH-C$H_{2\ Major}$) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 167.3 (C=O_{Major}), 167.2 (C=O_{Minor}), 165.9 (C=O_{Minor}), 164.3 (C=O_{Major}), 147.5 ($C_{Ar\ Major}$), 146.3 ($C_{Ar\ Major}$), 146.2 ($C_{Ar\ Minor}$), 145.6 ($C_{Ar\ Minor}$), 136.2 ($CH_{Ar\ Major}$), 136.0 ($CH_{Ar\ Minor}$), 132.8 ($CH_{Ar\ Major}$), 132.0 ($C_{Ar\ Minor}$), 131.9 ($C_{Ar\ Major}$), 130.85 (*C*H=$CH_{2\ Minor}$), 130.80 ($CH_{Ar\ Minor}$), 130.6 (*C*H=$CH_{2\ Major}$), 130.2 ($CH_{Ar\ Tosyl\ Major}$ and $CH_{Ar\ Tosyl\ Minor}$), 128.5 ($C_{Ar\ Minor}$), 127.5 ($CH_{Ar\ Tosyl\ Major}$), 127.4 ($CH_{Ar\ Tosyl\ Minor}$), 124.8 ($C_{Ar\ Major}$), 122.8 (CH=*C*$H_{2\ Minor}$), 122.48 (CH=*C*$H_{2\ Major}$), 122.45 (q, J = 275 Hz, $CF_{3\ Major}$ and $CF_{3\ Minor}$), 122.39 (q, J = 276 Hz, $CF_{3\ Major}$ and $CF_{3\ Minor}$), 118.0 ($CH_{Ar\ Major}$), 117.72 ($C_{Ar\ Major}$), 117.69 ($CH_{Ar\ Minor}$), 109.6 (C≡N_{Minor}), 109.0 (C≡N_{Major}), 101.3 (C-$NO_{2\ Minor}$), 99.9 (C-$NO_{2\ Major}$), 74.1 (Ts-N-*C*H $_{Minor}$), 74.0 (Ts-N-*C*H $_{Major}$), 64.5 (*C*-$(CO_2CH_2CF_3)_{2\ Minor}$), 63.7 (*C*-$(CO_2CH_2CF_3)_{2\ Major}$), 62.8 – 61.6 (m, *C*$H_2CF_{3\ Major}$ and *C*$H_2CF_{3\ Minor}$), 54.0 (*C*H-CH=$CH_{2\ Minor}$), 50.0 (*C*H-CH=$CH_{2\ Major}$), 40.0 (CH-*C*$H_{2\ Minor}$), 37.5 (CH-*C*$H_{2\ Major}$), 21.7 ($CH_{3\ Major}$ and $CH_{3\ Minor}$) ppm. **^{19}F NMR** (470 Hz, $CDCl_3$): δ −73.50 (t, J = 8.5 Hz, $CF_{3\ Minor}$), −73.60 (t, J = 8.0 Hz, $CF_{3\ Major}$), −73.69 (t, J = 8.0 Hz, CF_3

$_{Minor}$), −73.72 (t, J = 7.5 Hz, $CF_{3\ Major}$) ppm. **IR** (Neat): 2232, 1754, 1555, 1373, 1287, 1241, 1169, 1089, 1066 cm^{-1}. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{21}F_6N_3O_8SNa$ 684.0851; Found 684.0836.

*Bis(2,2,2-trifluoroethyl)(3aS,8bR)-7,8b-dinitro-4-tosyl-1-vinyl-1,3a,4,8b-tetrahydrocyclopenta[b]indole-3,3(2H)-dicarboxylate (**5f/5f'**).* Based on the typical procedure, the title compound was obtained as a colourless oil film (29.6 mg, 0.043 mmol) in 73% yield after column chromatography (20% ethyl acetate in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.38 (dd, J = 9.0, 2.0 Hz, 3H, 1 × $CH_{Ar\ Major}$ and 2 × $CH_{Ar\ Minor}$), 8.24 (d, J = 2.0 Hz, 1H, $CH_{Ar\ Major}$), 7.88 – 7.84 (m, 2H, $CH_{Ar\ Major}$ and $CH_{Ar\ Minor}$), 7.58 (d, J = 4.2 Hz, 2H, $CH_{Ar\ Minor}$), 7.51 (d, J = 8.4 Hz, 2H, $CH_{Ar\ Major}$), 7.21 (d, J = 8.0 Hz, 4H, 2 × $CH_{Ar\ Major}$ and 2 × $CH_{Ar\ Minor}$), 6.37 (s, 1H, Ts-N-C$H_{\ Minor}$), 6.35 (s, 1H, Ts-N-C$H_{\ Major}$), 5.81 (ddd, J = 17.3, 10.2, 7.2 Hz, 1H, CH=$CH_{2\ Major}$), 5.55 – 5.45 (m, 2H, CH=$CH_{2\ Minor}$ and CH=C$H_{2\ Major}$), 5.38 – 5.33 (m, 2H, CH=C$H_{2\ Minor}$), 5.24 (d, J = 17.2 Hz, 1H, CH=C$H_{2\ Major}$), 4.99 – 4.90 (m, 1H, OC$H_2CF_{3\ Major}$), 4.88 – 4.68 (m, 1H of OC$H_2CF_{3\ Major}$ and 2H of OC$H_2CF_{3\ Minor}$), 4.62 – 4.51 (m, 2H, OC$H_2CF_{3\ Major}$ and OC$H_2CF_{3\ Minor}$), 4.49 – 4.39 (m, 2H, OC$H_2CF_{3\ Major}$ and OC$H_2CF_{3\ Minor}$), 3.49 (app q, J = 6.8 Hz, 1H, CH-CH=$CH_{2\ Minor}$), 3.37 (dt, J = 14.4, 6.4 Hz, 1H, CH-CH=$CH_{2\ Major}$), 2.71 (dd, J = 14.0, 6.4 Hz, 1H, CH-C$H_{2\ Minor}$), 2.59 (dd, J = 18.0, 4.8 Hz, 1H, CH-C$H_{2\ Major}$), 2.48 (dd, J = 14.0, 8.8 Hz, 1H, CH-C$H_{2\ Minor}$), 2.37 (s, 6H, $CH_{3\ Tosyl\ Major}$ and $CH_{3\ Tosyl\ Minor}$), 2.29 (app t, J = 14.0 Hz, 1H, CH-C$H_{2\ Major}$) ppm. **^{13}C{^{1}H} NMR** (100MHz, $CDCl_3$): δ 167.3 (C=O $_{Major}$), 167.2 (C=O $_{Minor}$), 165.8 (C=O $_{Minor}$), 164.3 (C=O $_{Major}$), 149.0 ($C_{Ar\ Major}$), 147.1 ($C_{Ar\ Minor}$), 146.4 ($C_{Ar\ Major}$), 146.3 ($C_{Ar\ Minor}$), 144.8 ($C_{Ar\ Major}$), 132.0 ($C_{Ar\ Minor}$), 131.9 ($C_{Ar\ Major}$), 130.7 (CH=$CH_{2\ Minor}$), 130.4 (CH=$CH_{2\ Major}$), 130.3 ($CH_{Ar\ Tosyl\ Major}$ and $CH_{Ar\ Tosyl\ Minor}$), 128.4 ($C_{Ar\ Minor}$), 128.2 ($CH_{Ar\ Major}$), 128.0 ($CH_{Ar\ Minor}$), 127.5 ($CH_{Ar\ Tosyl\ Major}$), 127.4 ($CH_{Ar\ Tosyl\ Minor}$), 124.8 ($C_{Ar\ Major}$), 124.7 ($CH_{Ar\ Major}$), 122.9 (CH=CH$_{2\ Minor}$), 122.8 ($CH_{Ar\ Minor}$), 122.6 (CH=CH$_{2\ Major}$), 122.44 (q, J = 275 Hz, $CF_{3\ Major}$ and $CF_{3\ Minor}$), 122.37 (q, J = 276 Hz, $CF_{3\ Major}$ and $CF_{3\ Minor}$), 117.1 ($CH_{Ar\ Major}$), 116.9 ($CH_{Ar\ Minor}$), 101.1 (C-$NO_{2\ Minor}$), 99.6 (C-$NO_{2\ Major}$), 74.6 (Ts-N-CH $_{Major}$ and Ts-N-CH $_{Minor}$), 64.5 (C-$(CO_2CH_2CF_3)_{2\ Minor}$), 63.7 ($C$-$(CO_2CH_2CF_3)_{2\ Major}$), 62.8 – 61.6 (m, CH$_2CF_{3\ Major}$ and CH$_2CF_{3\ Minor}$), 53.7 (CH-CH=CH_2

$_{Minor}$), 49.8 (*C*H-CH=$CH_{2\ Major}$), 39.9 (CH-*C*$H_{2\ Minor}$), 37.5 (CH-*C*$H_{2\ Major}$), 21.7 ($CH_{3\ Major}$ and $CH_{3\ Minor}$) ppm. **^{19}F NMR** (470 Hz, $CDCl_3$): δ −73.50 (t, *J* = 8.5 Hz, $CF_{3\ Minor}$), −73.59 (t, *J* = 8.0 Hz, $CF_{3\ Major}$), −73.67 (t, *J* = 8.5 Hz, $CF_{3\ Minor}$), −73.71 (t, *J* = 8.9 Hz, $CF_{3\ Major}$) ppm. **IR** (Neat): 1753, 1558, 1529, 1375, 1344, 1287, 1248, 1165, 1085 cm^{-1}. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{21}F_6N_3O_{10}SNa$ 704.0750; Found 704.0750.

*Bis(2,2,2-trifluoroethyl)(3aS,8bR)-7-methyl-8b-nitro-4-tosyl-1-vinyl-1,3a,4,8b-tetrahydrocyclopenta[b]indole-3,3(2H)-dicarboxylate (**5g**).* Based on the typical procedure, the title compound was obtained as an off-white solid (30.3 mg, 0.047 mmol) in 78% yield after column chromatography (20 – 30% ethyl acetate in hexane). The major isomer was isolated by recrystallization in methanol. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.0 Hz, 1H, CH_{Ar}), 7.43 (d, *J* = 8.0 Hz, 2H, CH_{Ar}), 7.30 – 7.27 (m, 1H, CH_{Ar}), 7.13 (d, *J* = 8.0 Hz, 3H, CH_{Ar}), 6.21 (d, *J* = 1.2 Hz, 1H, Ts-N-C*H*), 5.76 (ddd, *J* = 17.4, 10.2, 7.6 Hz, 1H, C*H*=CH_2), 5.31 (d, *J* = 10.4 Hz, 1H, CH=CH_2), 5.17 (d, *J* = 17.2 Hz, 1H, CH=CH_2), 5.02 – 4.93 (m, 1H, OCH_2CF_3), 4.85 – 4.76 (m, 1H, OCH_2CF_3), 4.57 – 4.48 (m, 1H, OCH_2CF_3), 4.47 – 4.38 (m, 1H, OCH_2CF_3), 3.28 (dt, *J* = 16.0, 5.6 Hz, 1H, C*H*-CH=CH_2), 2.45 (ddd, *J* = 13.6, 5.6, 1.2 Hz, 1H, CH-CH_2), 2.34 (s, 6H, CH_3), 2.28 (app t, *J* = 14.0 Hz, 1H, CH-CH_2) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 167.8 (C=O), 164.5 (C=O), 145.3 (C_{Ar}), 141.8 (C_{Ar}), 135.4 (C_{Ar}), 133.2 (CH_{Ar}), 132.2 (C_{Ar}), 131.7 (*C*H=CH_2), 129.8 ($CH_{Ar\ Tosyl}$), 128.7 (CH_{Ar}), 127.7 ($CH_{Ar\ Tosyl}$), 124.0 (C_{Ar}), 121.1 (CH=*C*H_2), 117.6 (CH_{Ar}), 100.9 (C-NO_2), 73.7 (Ts-N-*C*H), 63.7 (*C*-($CO_2CH_2CF_3$)$_2$), 62.1 (q, *J* = 38.0 Hz, *C*H_2CF_3), 61.9 (q, *J* = 37.0 Hz, *C*H_2CF_3), 50.3 (*C*H-CH=CH_2), 37.4 (CH-*C*H_2), 21.6 (CH_3), 21.2 (CH_3) ppm. **^{19}F NMR** (470 Hz, $CDCl_3$): δ −73.62 (t, *J* = 8.0 Hz, CF_3), −73.75 (t, *J* = 8.5 Hz, CF_3) ppm. **IR** (Neat): 1751, 1550, 1486, 1419, 1370, 1285, 1244, 1158, 1092, 1071 cm^{-1}. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{24}F_6N_2O_8SNa$ 673.1055; Found 673.1056. **Melting point**: 199.5 – 202.6 °C

*Bis(2,2,2-trifluoroethyl) (3aS,8bR)-6-chloro-8b-nitro-4-tosyl-1-vinyl-1,3a,4,8b-tetrahydrocyclopenta[b]indole-3,3(2H)-dicarboxylate (**5i/5i'**).* Based on the typical procedure, the title compound was obtained as a colourless oil (34.1 mg, 0.051 mmol) in 88% yield after column chromatography (30% diethyl ether in hexane). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.76 (d, *J* = 1.5 Hz, 1H, $CH_{Ar\ Major}$), 7.73 (s, 1H, $CH_{Ar\ Minor}$), 7.55 (d, *J* = 8.0 Hz, 2H, $CH_{Ar\ Minor}$), 7.47 (d, *J* = 8.0 Hz, 2H, $CH_{Ar\ Major}$), 7.30 (d, *J* = 8.0 Hz, 2H, $CH_{Ar\ Major}$ and $CH_{Ar\ Minor}$), 7.19 – 7.14 (m, 6H, 3 × $CH_{Ar\ Major}$ and 3 × $CH_{Ar\ Minor}$), 6.29 (s, 1H, Ts-N-C*H* $_{Minor}$), 6.24 (s, 1H, Ts-N-C*H* $_{Major}$), 5.73 (ddd, *J* = 17.3, 10.3, 7.5 Hz, 1H, C*H*=$CH_{2\ Major}$), 5.50 – 5.43 (m, 1H, C*H*=$CH_{2\ Minor}$), 5.33 (d, *J* = 10.5 Hz, 1H, CH=C$H_{2\ Major}$), 5.29 – 5.24 (m, 2H, CH=C$H_{2\ Minor}$), 5.18 (d, *J* = 17.0 Hz, 1H, CH=C$H_{2\ Major}$), 5.01 – 4.94 (m, 1H, OC$H_2CF_{3\ Major}$), 4.88 – 4.74 (m, 1H of OC$H_2CF_{3\ Major}$ and 2H of OC$H_2CF_{3\ Minor}$), 4.58 – 4.50 (m, 2H, OC$H_2CF_{3\ Major}$ and OC$H_2CF_{3\ Minor}$), 4.46 – 4.39 (m, 2H, OC$H_2CF_{3\ Major}$ and OC$H_2CF_{3\ Minor}$), 3.42 (app q, *J* = 7.0 Hz, 1H, C*H*-CH=$CH_{2\ Minor}$), 3.29 (dt, *J* = 14.0, 6.5 Hz, 1H, C*H*-CH=$CH_{2\ Major}$), 2.67 (dd, *J* = 13.5, 6.5 Hz, 1H, CH-C$H_{2\ Minor}$), 2.50 (dd, *J* = 13.8, 5.0 Hz, 1H, CH-C$H_{2\ Major}$), 2.43 – 2.40 (m, 1H, CH-C$H_{2\ Minor}$), 2.36 (s, 6H, $CH_{3\ Tosyl\ Major}$ and $CH_{3\ Tosyl\ Minor}$), 2.29 (app t, *J* = 14.0 Hz, 1H, CH-C$H_{2\ Major}$) ppm. **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ 167.6 (C=O), 164.4 (C=O), 145.8 (C_{Ar}), 145.2 (C_{Ar}), 138.7 (C_{Ar}), 131.9 (C_{Ar}), 131.2 (*C*H=CH_2), 130.1 ($CH_{Ar\ Tosyl}$), 129.3 (CH_{Ar}), 127.7 ($CH_{Ar\ Tosyl}$), 125.7 (CH_{Ar}), 122.5 (q, *J* = 276.3 Hz, CF_3), 122.4 (q, *J* = 276.3 Hz, CF_3), 122.3 (C_{Ar}), 121.6 (CH=*C*H_2), 118.0 (CH_{Ar}), 100.3 (C-NO_2), 74.0 (Ts-N-*C*H), 63.7 (*C*-($CO_2CH_2CF_3$)$_2$), 62.1 (q, *J* = 36.3 Hz, *C*H_2CF_3), 62.0(q, *J* = 36.3 Hz, *C*H_2CF_3), 50.1 (*C*H-CH=CH_2), 37.4 (CH-*C*H_2), 21.7 (CH_3) ppm. **^{19}F NMR** (470 Hz, $CDCl_3$): δ −73.54 (t, *J* = 8.5 Hz, $CF_{3\ Minor}$), −73.62 (t, *J* = 8.9 Hz, $CF_{3\ Major}$), −73.69 (t, *J* = 8.5 Hz, $CF_{3\ Minor}$), −73.74 (t, *J* = 7.5 Hz, $CF_{3\ Major}$) ppm. **IR** (Neat): 1757, 1751, 1551, 1417, 1373, 1288, 1238, 1173, 1153 cm^{-1}. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{21}ClF_6N_2O_8SNa$ 693.0509; Found 693.0501.

*Bis(2,2,2-trifluoroethyl) (3aS,8bR)-5-chloro-8b-nitro-4-tosyl-1-vinyl-1,3a,4,8b-tetrahydrocyclopenta[b]indole-3,3(2H)-dicarboxylate (**5j/5j'**).* Based on the typical procedure, the title compound was obtained as beige solid (32.7 mg, 0.048 mmol) in 88% yield after column

chromatography (20 – 40% ethyl acetate in hexane). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.56 – 7.17 (m, 14H, $CH_{Ar\ Major}$ and $CH_{Ar\ Minor}$), 6.40 (s, 1H, Ts-N-C*H* $_{Minor}$), 6.38 (s, 1H, Ts-N-C*H* $_{Major}$), 5.62 (ddd, *J* = 17.4, 10.3, 7.5 Hz, 1H, C*H*=$CH_{2\ Major}$), 5.50 – 5.42 (m, 1H, C*H*=$CH_{2\ Minor}$), 5.30 (d, *J* = 10.0 Hz, 1H, CH=C*H*$_{2\ Major}$), 5.24 – 5.21 (m, 2H, CH=C*H*$_{2\ Minor}$), 5.10 (d, *J* = 15.0 Hz, 1H, CH=C*H*$_{2\ Major}$), 5.01 – 4.94 (m, 1H, OC*H*$_2CF_{3\ Major}$), 4.84 – 4.73 (m, 3H, OC*H*$_2CF_{3\ Major}$ and OC*H*$_2CF_{3\ Minor}$), 4.57 – 4.42 (m, 2H, OC*H*$_2CF_{3\ Major}$ and OC*H*$_2CF_{3\ Minor}$), 4.25 – 4.11 (m, 2H, OC*H*$_2CF_{3\ Major}$ and OC*H*$_2CF_{3\ Minor}$), 3.36 – 3.24 (m, 2H, C*H*-CH=$CH_{2\ Major}$ and C*H*-CH=$CH_{2\ Minor}$), 2.49 (dd, *J* = 13.8, 7.0 Hz, 1H, CH-C*H*$_{2\ Minor}$), 2.40 (s, 6H, $CH_{3\ Tosyl\ Major}$ and $CH_{3\ Tosyl\ Minor}$), 2.34 (dd, *J* = 14.0, 5.5 Hz, 1H, CH-C*H*$_{2\ Major}$), 2.26 (dd, *J* = 14.0, 8.5 Hz, 1H, CH-C*H*$_{2\ Minor}$), 2.06 (app t, *J* = 14.0 Hz, 1H, CH-C*H*$_{2\ Major}$) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 167.6 (C=O $_{Major}$), 167.4 (C=O $_{Minor}$), 165.7 (C=O $_{Minor}$), 164.3 (C=O $_{Major}$), 146.0 ($C_{Ar\ Major}$), 145.7 ($C_{Ar\ Minor}$), 141.6 ($C_{Ar\ Major}$), 139.8 ($C_{Ar\ Minor}$), 134.1 ($C_{Ar\ Minor}$), 133.9 ($CH_{Ar\ Major}$), 133.5 ($CH_{Ar\ Minor}$), 132.3 ($C_{Ar\ Minor}$), 132.1 ($C_{Ar\ Major}$), 131.5 (*C*H=$CH_{2\ Minor}$), 130.9 (*C*H=$CH_{2\ Major}$), 130.0 ($CH_{Ar\ Tosyl\ Major}$), 129.8 ($CH_{Ar\ Tosyl\ Minor}$), 128.9 ($CH_{Ar\ Minor}$), 128.6 ($C_{Ar\ Major}$), 128.5 ($CH_{Ar\ Tosyl\ Minor}$), 128.4 ($CH_{Ar\ Tosyl\ Major}$), 127.64 ($CH_{Ar\ Major}$), 127.61 ($CH_{Ar\ Major}$), 127.1 ($C_{Ar\ Major}$), 126.9 ($C_{Ar\ Minor}$), 125.0 ($CH_{Ar\ Minor}$), 122.4 (q, *J* = 276 Hz, $CF_{3\ Major}$ and $CF_{3\ Minor}$), 122.3 (q, *J* = 276 Hz, $CF_{3\ Major}$ and $CF_{3\ Minor}$), 122.0 (CH=*C*$H_{2\ Minor}$), 121.7 (CH=*C*$H_{2\ Major}$), 101.2 (C-$NO_{2\ Minor}$), 100.7 (C-$NO_{2\ Major}$), 74.4 (Ts-N-*C*H $_{Minor}$), 74.0 (Ts-N-*C*H $_{Major}$), 64.3 (*C*-$(CO_2CH_2CF_3)_{2\ Minor}$), 63.7 (*C*-$(CO_2CH_2CF_3)_{2\ Major}$), 62.7 – 61.5 (m, *C*$H_2CF_{3\ Major}$ and *C*$H_2CF_{3\ Minor}$), 54.7 (*C*H-CH=$CH_{2\ Minor}$), 51.7 (*C*H-CH=$CH_{2\ Major}$), 38.4 (CH-*C*$H_{2\ Minor}$), 36.8 (CH-*C*$H_{2\ Major}$), 21.7 ($CH_{3\ Major}$ and $CH_{3\ Minor}$) ppm. **^{19}F NMR** (470 Hz, $CDCl_3$): δ −73.63 - −73.78 (m, $CF_{3\ Major}$ and $CF_{3\ Minor}$) ppm. **IR** (Neat): 1757, 1559, 1465, 1457, 1378, 1288, 1241, 1172 cm^{-1}. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{21}ClF_6N_2O_8SNa$ 693.0509; Found 693.0504.

*8-Methyl 3,3-bis(2,2,2-trifluoroethyl) (1S,3aS,8bR)-8b-nitro-4-tosyl-1-vinyl-1,3a,4,8b-tetrahydrocyclopenta[b]indole-3,3,8(2H)-tricarboxylate (**5k'**).* Based on the typical procedure with the exclusion of tetrabutylammonium iodide, the title compound was obtained as a colourless oil (34.0 mg, 0.048 mmol) in 88% yield after column chromatography (20 – 30% ethyl acetate in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.96 (dd, *J* = 8.4, 0.8 Hz, 1H, CH_{Ar}), 7.73 (dd, *J* = 7.6, 0.8 Hz, 1H, CH_{Ar}),

7.55 (t, J = 8.0 Hz, 1H, CH_{Ar}), 7.49 (d, J = 8.4 Hz, 2H, $CH_{Ar\ Tosyl}$), 7.17 (d, J = 8.0 Hz, 2H, $CH_{Ar\ Tosyl}$), 6.03 (s, 1H, Ts-N-C*H*), 6.00 – 5.91 (m, 1H, C*H*=CH_2), 5.09 (d, J = 10.4 Hz, 1H, CH=CH_2), 5.08 (d, J = 16.8 Hz, 1H, CH=CH_2), 4.87 – 4.74 (m, 2H, OC$H_2$$CF_3$), 4.57 – 4.47 (m, 1H, OC$H_2$$CF_3$), 4.46 – 4.37 (m, 1H, OC$H_2$$CF_3$), 3.81 (app q, J = 7.2 Hz, 1H, C*H*-CH=CH_2), 3.75 (s, 3H, OCH_3), 2.65 (dd, J = 14.0, 8.0 Hz, 1H, CH-CH_2), 2.54 (dd, J = 16.0, 8.0 Hz, 1H, CH-CH_2), 2.35 (s, 3H, $CH_{3\ Tosyl}$) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 167.7 (C=O), 165.9 (C=O), 165.7 (C=O), 145.7 (C_{Ar}), 143.9 (C_{Ar}), 133.9 (*C*H=CH_2), 132.1 (C_{Ar}), 132.0 (CH_{Ar}), 130.0 ($CH_{Ar\ Tosyl}$), 129.4 (C_{Ar}), 128.2 (CH_{Ar}), 127.71 ($CH_{Ar\ Tosyl}$), 127.66 (C_{Ar}), 122.5 (q, J = 280 Hz, CF_3), 122.4 (q, J = 280 Hz, CF_3), 121.4 (CH_{Ar}), 119.0 (CH=*C*H_2), 102.2 (C-NO_2), 76.7 (Ts-N-*C*H), 64.1 (*C*-($CO_2CH_2CF_3$)$_2$), 62.6 – 61.1 (m, *C*H_2CF_3), 53.3 (*C*H-CH=CH_2), 52.5 (OCH_3), 40.7 (CH-*C*H_2), 21.6 ($CH_{3\ Tosyl}$) ppm. **^{19}F NMR** (470 Hz, $CDCl_3$): δ −73.79 - −73.84 (m, CF_3) ppm. **IR** (Neat): 1753, 1733, 1731, 1557, 1371, 1286, 1242, 1169, 1089 cm^{-1}. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{24}F_6N_2O_{10}SNa$ 717.0954; Found 717.0950.

*Bis(2,2,2-trifluoroethyl)(3aS,8bR)-8b-nitro-1-styryl-4-tosyl-1,3a,4,8b-tetrahydrocyclopenta[b]indole-3,3(2H)-dicarboxylate (**8/8′**)*. Based on the typical procedure, the title compound was obtained as a colourless film (29.2 mg, 0.041 mmol) in 73% yield after column chromatography (20% ethyl acetate in hexane). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.78 – 7.12 (m, 26H, $CH_{Ar\ Major}$ and $CH_{Ar\ Minor}$), 6.57 (d, J = 15.0 Hz, 1H, CH=C*H*-Ph $_{Minor}$), 6.46 (d, J = 15.0 Hz, 1H, CH=C*H*-Ph $_{Major}$), 6.35 (s, 1H, Ts-N-*C*H $_{Minor}$), 6.27 (s, 1H, Ts-N-*C*H $_{Major}$), 6.01 (dd, J = 15.0, 10.0 Hz, 1H, C*H*=CH-Ph $_{Major}$), 5.78 (dd, J = 15.0, 10.0 Hz, 1H, C*H*=CH-Ph $_{Minor}$), 5.03 – 4.96 (m, 1H, OC$H_2$$CF_{3\ Major}$), 4.86 – 4.73 (m, 1H of OC$H_2$$CF_{3\ Major}$ and 2H of OC$H_2$$CF_{3\ Minor}$), 4.60 – 4.52 (m, 2H, OC$H_2$$CF_{3\ Major}$ and OC$H_2$$CF_{3\ Minor}$), 4.50 – 4.42 (m, 2H, OC$H_2$$CF_{3\ Major}$ and OC$H_2$$CF_{3\ Minor}$), 3.62 (app q, J = 10.0 Hz, 1H, C*H*-CH=$CH_{2\ Minor}$), 3.48 (dt, J = 15.0, 10.0 Hz, 1H, C*H*-CH=$CH_{2\ Major}$), 2.73 (dd, J = 12.5, 5.0 Hz, 1H, CH-C$H_{2\ Minor}$), 2.56 (dd, J = 15.0, 5.0 Hz, 1H, CH-C$H_{2\ Major}$), 2.48 (dd, J = 12.5, 5.0 Hz, 1H, CH-C$H_{2\ Minor}$), 2.38 (app t, J = 15.0 Hz, 1H, CH-C$H_{2\ Major}$), 2.33 (s, 3H, $CH_{3\ Major}$), 2.32 (s, 3H, $CH_{3\ Minor}$) ppm. **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ 167.74 (C=O $_{Major}$), 167.66 (C=O $_{Minor}$), 166.0 (C=O $_{Minor}$), 164.5 (C=O $_{Major}$), 145.5

($C_{Ar\ Major}$), 145.4 ($C_{Ar\ Minor}$), 144.2 ($C_{Ar\ Major}$), 142.2 ($C_{Ar\ Minor}$), 136.6 (CH=*C*H-Ph $_{Minor}$), 135.8 ($C_{Ar\ Major}$), 135.6 ($C_{Ar\ Minor}$), 135.5 (CH=*C*H-Ph $_{Major}$), 132.3 ($CH_{Ar\ Major}$), 132.1 ($C_{Ar\ Major}$ and $CH_{Ar\ Minor}$), 129.9 ($CH_{Ar\ Tosyl\ Major}$ and $CH_{Ar\ Tosyl\ Minor}$), 128.8 ($CH_{Ar\ Major}$), 128.7 ($CH_{Ar\ Minor}$), 128.6 ($CH_{Ar\ Minor}$), 128.5 (2 × $CH_{Ar\ Major}$), 128.0 ($C_{Ar\ Minor}$), 127.7 ($CH_{Ar\ Tosyl\ Major}$), 127.6 ($CH_{Ar\ Tosyl\ Minor}$), 126.7 ($CH_{Ar\ Minor}$), 126.5 ($CH_{Ar\ Major}$), 126.4 ($CH_{Ar\ Minor}$), 126.2 ($CH_{Ar\ Minor}$), 125.4 ($CH_{Ar\ Major}$), 124.1 ($C_{Ar\ Major}$), 122.6 (q, *J* = 275 Hz, $CF_{3\ Major}$ and $CF_{3\ Minor}$), 122.5 (q, *J* = 275 Hz, $CF_{3\ Major}$ and $CF_{3\ Minor}$), 122.5 (*C*H=CH-Ph $_{Major}$), 122.3 (*C*H=CH-Ph $_{Minor}$), 118.0 ($CH_{Ar\ Major}$), 117.6 ($CH_{Ar\ Minor}$), 102.3 (C-$NO_{2\ Minor}$), 101.3 (C-$NO_{2\ Major}$), 73.6 (Ts-N-*C*H $_{Major}$ and Ts-N-*C*H $_{Minor}$), 64.8 (*C*-$(CO_2CH_2CF_3)_{2\ Minor}$), 63.9 (*C*-$(CO_2CH_2CF_3)_{2\ Major}$), 62.6 – 61.5 (m, *C*$H_2CF_{3\ Major}$ and *C*$H_2CF_{3\ Minor}$), 53.6 (*C*H-CH=Ph $_{Minor}$), 49.9 (*C*H-CH=Ph $_{Major}$), 40.3 (CH-*C*$H_{2\ Minor}$), 38.0 (CH-*C*$H_{2\ Major}$), 21.6 ($CH_{3\ Major}$ and $CH_{3\ Minor}$) ppm. **^{19}F NMR** (470 Hz, $CDCl_3$): δ −73.48 (t, *J* = 8.0 Hz, $CF_{3\ Minor}$), −73.59 (t, *J* = 8.0 Hz, $CF_{3\ Major}$), −73.67 - −73.73 (m, $CF_{3\ Major}$ and $CF_{3\ Minor}$) ppm. **IR** (Neat): 1752, 1549, 1464, 1417, 1370, 1286, 1246, 1170, 1089, 1071 cm^{-1}. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{26}F_6N_2O_8SNa$ 735.1212; Found 735.1186.

*Dibenzyl (3aS,8bR)-8b-nitro-4-tosyl-1-vinyl-1,3a,4,8b-tetrahydrocyclopenta[b]indole-3,3(2H)-dicarboxylate (**9/9'**).* Based on the typical procedure, the title compound was obtained as a colourless film (18.0 mg, 0.028 mmol) in 48% yield after column chromatography (20 – 50% ethyl acetate in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.4 Hz, 1H, $CH_{Ar\ Major}$), 7.64 (d, *J* = 8.0 Hz, 1H, $CH_{Ar\ Minor}$), 7.51 – 7.06 (m, 34H, $CH_{Ar\ Major}$ and $CH_{Ar\ Minor}$), 6.40 (s, 1H, Ts-N-C*H* $_{Minor}$), 6.33 (s, 1H, Ts-N-C*H* $_{Major}$), 5.74 (ddd, *J* = 17.4, 10.2, 7.6 Hz, 1H, C*H*=$CH_{2\ Major}$), 5.48 – 5.39 (m, 1H of CH=C$H_{2\ Major}$ and 1H of C*H*=$CH_{2\ Minor}$), 5.30 – 5.06 (m, 11H, 1 × CH=C$H_{2\ Major}$, 2 × OC$H_{2\ Major}$, 1 × CH=C$H_{2\ Minor}$ and 2 × OC$H_{2\ Minor}$), 3.40 (app q, *J* = 8.0 Hz, 1H, C*H*-CH=$CH_{2\ Minor}$), 3.24 (dt, *J* = 14.4, 6.4 Hz, 1H, C*H*-CH=$CH_{2\ Major}$), 2.59 (dd, *J* = 13.6, 6.8 Hz, 1H, CH-C$H_{2\ Minor}$), 2.43 (dd, *J* = 13.6, 5.2 Hz, 1H, CH-C$H_{2\ Major}$), 2.37 – 2.29 (m, 7H, $CH_{3\ Major}$, $CH_{3\ Minor}$ and CH-C$H_{2\ Minor}$), 2.22 (app t, *J* = 14.0 Hz, 1H, CH-C$H_{2\ Major}$) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 169.40 (C=O $_{Major}$), 169.37 (C=O $_{Minor}$), 167.5 (C=O $_{Minor}$), 166.3 (C=O $_{Major}$), 145.0 ($C_{Ar\ Major}$), 144.9 ($C_{Ar\ Minor}$), 144.4 ($C_{Ar\ Major}$), 142.5 (C_{Ar}

$_{Minor}$), 135.2 ($C_{Ar\ Major}$), 135.0 ($C_{Ar\ Minor}$), 134.9 ($C_{Ar\ Minor}$), 134.7 ($C_{Ar\ Major}$), 132.8 ($C_{Ar\ Minor}$), 132.6 ($C_{Ar\ Major}$), 132.5 (*C*H=$CH_{2\ Minor}$), 132.2 (*C*H=$CH_{2\ Major}$), 132.0 ($CH_{Ar\ Major}$), 131.9 ($CH_{Ar\ Minor}$), 129.7 ($CH_{Ar\ Major}$ and $CH_{Ar\ Minor}$), 128.58 ($CH_{Ar\ Major}$), 128.56 ($CH_{Ar\ Major}$), 128.55 ($CH_{Ar\ Major}$), 128.50 ($CH_{Ar\ Minor}$), 128.48 ($CH_{Ar\ Minor}$), 128.4 ($CH_{Ar\ Major}$), 128.3 ($C_{Ar\ Minor}$), 128.2 ($CH_{Ar\ Minor}$), 127.7 ($CH_{Ar\ Major}$), 127.6 ($CH_{Ar\ Minor}$), 126.3 ($CH_{Ar\ Minor}$), 125.9 ($CH_{Ar\ Minor}$), 125.1 ($CH_{Ar\ Major}$), 124.4 ($C_{Ar\ Major}$), 121.0 (CH=*C*$H_{2\ Minor}$), 120.6 (CH=*C*$H_{2\ Major}$), 118.1 ($CH_{Ar\ Major}$), 117.7 ($CH_{Ar\ Minor}$), 102.6 (C-$NO_{2\ Minor}$), 101.1 (C-$NO_{2\ Major}$), 73.7 (Ts-N-*C*H $_{Major}$), 73.3 (Ts-N-*C*H $_{Minor}$), 68.6 ($OCH_{2\ Major}$), 68.4 ($OCH_{2\ Major}$), 68.3 ($OCH_{2\ Minor}$), 68.2 ($OCH_{2\ Minor}$), 65.0 (*C*-$(CO_2Bn)_{2\ Minor}$), 64.2 (*C*-$(CO_2Bn)_{2\ Major}$), 53.6 (*C*H-CH=$CH_{2\ Minor}$), 50.4 (*C*H-CH=$CH_{2\ Major}$), 39.6 (CH-*C*$H_{2\ Minor}$), 37.6 (CH-*C*$H_{2\ Major}$), 21.6 ($CH_{3\ Major}$ and $CH_{3\ Minor}$) ppm. **IR** (Neat): 1730, 1550, 1456, 1368, 1269, 1241, 1170, 1089, 1068 cm^{-1}. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{36}H_{32}N_2O_8SNa$ 675.1777; Found 675.1780.

*Bis(2,2,2-trifluoroethyl) (3aS,8bR)-8b-nitro-4-((trifluoromethyl)sulfonyl)-1-vinyl-1,3a,4,8b-tetrahydrocyclopenta[b]indole-3,3(2H)-dicarboxylate (**11a/11a'**).* Based on the typical procedure, the title compound was obtained as a white solid (18.3 mg, 0.030 mmol) in 61% yield after column chromatography (20% ethyl acetate in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.0 Hz, 1H, CH_{Ar}), 7.64 (d, *J* = 8.0 Hz, 1H, CH_{Ar}), 7.58 – 7.49 (m, 4H, CH_{Ar}), 7.40 – 7.31 (m, 2H, CH_{Ar}), 6.56 (s, 1H, Tf-N-C*H*), 6.49 (s, 1H, Tf-N-C*H*), 5.90 (ddd, *J* = 17.3, 10.2, 7.2 Hz, 1H, C*H*=CH_2), 5.64 (ddd, *J* = 17.6, 9.2, 8.4 Hz, 1H, C*H*=CH_2), 5.43 – 5.36 (m, 3H, CH=CH_2), 5.30 (d, *J* = 20.0 Hz, 1H, CH=CH_2), 4.89 – 4.49 (m, 6H, OCH_2CF_3), 4.40 – 4.28 (m, 2H, OCH_2CF_3), 3.54 – 3.44 (m, 2H, C*H*-CH=CH_2), 2.75 (dd, *J* = 13.6, 6.4 Hz, 1H, CH-CH_2), 2.59 (ddd, *J* = 14.0, 5.6, 1.2 Hz, 1H, CH-CH_2), 2.53 (dd, *J* = 13.6, 9.2 Hz, 1H, CH-CH_2), 2.33 (app t, *J* = 14.0 Hz, 1H, CH-CH_2) ppm. **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ 167.0 (C=O), 166.8 (C=O), 165.3(C=O), 164.5 (C=O), 141.4 (C_{Ar}), 139.6 (C_{Ar}), 133.0 (CH_{Ar}), 132.7 (CH_{Ar}), 131.3 (*C*H=CH_2), 131.0 (*C*H=CH_2), 129.1 (CH_{Ar}), 127.2 (CH_{Ar}), 127.1 (CH_{Ar}), 127.0 (C_{Ar}), 126.5 (CH_{Ar}), 123.1 (C_{Ar}), 122.5 (CH=*C*H_2), 122.33 (q, *J* = 275 Hz, CF_3), 122.31 (q, *J* = 275 Hz, CF_3), 122.2 (q, *J* = 275 Hz, CF_3), 122.1 (q, *J* = 275 Hz, CF_3), 121.9 (CH=*C*H_2), 115.9 (CH_{Ar}), 115.5 (CH_{Ar}), 101.6 (C-NO_2), 100.5 (C-NO_2), 74.7 (Tf-N-*C*H), 74.3 (Tf-N-*C*H), 64.0 (*C*-

$(CO_2CH_2CF_3)_2$), 63.5 (*C*-$(CO_2CH_2CF_3)_2$), 62.7 – 61.3 (m, *C*H_2CF_3), 53.4 (*C*H-CH=CH_2), 50.0 (*C*H-CH=CH_2), 40.0 (CH-*C*H_2), 37.9 (CH-*C*H_2) ppm. **^{19}F NMR** (470 Hz, $CDCl_3$): δ −71.39 (s, N-SO_2-CF_3 $_{Major}$), −72.11 (s, N-SO_2-CF_3 $_{Minor}$), −73.52 (t, *J* = 8.0 Hz, CH_2CF_3 $_{Minor}$), −73.61 (t, *J* = 8.5 Hz, CH_2CF_3 $_{Major}$), −73.74 - −73.80 (m, CH_2CF_3 $_{Major}$ and CH_2CF_3 $_{Minor}$) ppm. **IR** (Neat): 1756, 1559, 1465, 1412, 1350, 1286, 1222, 1168, 1142, 1073 cm^{-1}. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{15}F_9N_2O_8SNa$ 637.0303; Found 637.0276.

*Bis(2,2,2-trifluoroethyl)(3aS,8bR)-4-benzoyl-8b-nitro-1-vinyl-1,3a,4,8b tetrahydrocyclopenta[b]indole-3,3(2H)-dicarboxylate (**11b/11b'**).* Based on the typical procedure, the title compound was obtained as a colourless oil (7.0 mg, 0.011 mmol) in 21% yield. NMR data consistent with literature.[8] **IR** (Neat): 1751, 1749, 1658, 1550, 1480, 1379, 1349, 1281, 1158 cm^{-1} (IR provided as not previously reported in the literature).

Chemical transformation of cyclopenta[*b*]indoline derivatives.

*Bis(2,2,2-trifluoroethyl)(3aS,8bR)-8b-amino-4-tosyl-1-vinyl-1,3a,4,8b-tetrahydrocyclopenta[b]indole-3,3(2H)-dicarboxylate (**12a**).* A solution of **5a** (30.1 mg, 47.3 μmol, 1 equiv) and trimethylsilyl chloride (0.15 mL, 128.4 mg, 1.18 mmol, 25 equiv) in methanol was cooled to 0°C prior to the slow addition of zinc powder (62.4 mg, 0.954 mmol, 20 equiv). After the reaction was stirred at 0°C for 2 h 20 mins, another portion of trimethylsilyl chloride (0.05 mL, 42.8 mg, 0.394 mmol, 8 equiv) was added and the reaction was stirred at room temperature for 2 h then 70°C for 30 mins. The reaction was cooled to room temperature and filtered. The insoluble solid was washed with methanol (1 mL) and dichloromethane (3 × 1 mL). The filtrate and the combined washings were treated with saturated sodium bicarbonate solution (10 mL) and diluted with dichloromethane (10 mL). The organic fraction was isolated and the aqueous fraction was extracted with dichloromethane (2 × 10 mL). The combined organic fractions were dried over sodium sulfate then concentrated under reduced pressure. ^{1}H NMR analysis of the crude residue revealed that approximately 66% conversion was completed. In order to maximise the conversion, a solution of the crude residue and trimethylsilyl

chloride (0.1 mL, 85.6 mg, 0.788 mmol, 17 equiv) in methanol (1 mL) was cooled to 0 °C prior to the slow addition of zinc powder (33.5 mg, 0.512 mmol, 11 equiv). The reaction was stirred for 35 mins at 0°C then filtered. Washing and extraction were carried out as previous. After column chromatography (40% ethyl acetate in hexane), the title compound was obtained as a colourless oil film (22.0 mg, 36.3 μmol) in 77% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.0 Hz, 1H, CH_{Ar}), 7.55 (d, *J* = 8.0 Hz, 2H, CH_{Ar}), 7.38 – 7.34 (m, 1H, CH_{Ar}), 7.16 (d, *J* = 8.0 Hz, 2H, CH_{Ar}), 7.09 – 7.03 (m, 2H, CH_{Ar}), 5.72 (ddd, *J* = 17.4, 10.0, 7.2 Hz, 1H, C*H*=CH_2), 5.61 (s, 1H, Ts-N-C*H*), 5.19 (d, *J* = 8.0 Hz, 1H, CH=C*H*$_2$), 5.08 (d, *J* = 16.0 Hz, 1H, CH=C*H*$_2$), 5.01 – 4.91 (m, 1H, OC*H*$_2$$CF_3$), 4.81 – 4.72 (m, 1H, OC*H*$_2$$CF_3$), 4.53 – 4.37 (m, 2H, OC*H*$_2$$CF_3$), 4.08 (bs, 2H, NH_2), 2.85 (dt, *J* = 16.0, 4.0 Hz, 1H, C*H*-CH=CH_2), 2.35 – 2.30 (m, 4H, CH_3 and CH-C*H*$_2$), 2.19 (app t, *J* = 16.0 Hz, 1H, CH-C*H*$_2$) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 168.6 (C=O), 165.6 (C=O), 144.7 (C_{Ar}), 143.7 (C_{Ar}), 134.7 (*C*H=CH_2), 133.3 (C_{Ar}), 130.6 (CH_{Ar}), 129.5 ($CH_{Ar\ Tosyl}$), 128.7 (C_{Ar}), 127.7 ($CH_{Ar\ Tosyl}$), 126.7 (CH_{Ar}), 124.8 (CH_{Ar}), 122.7 (q, *J* = 280 Hz, CF_3), 122.6 (q, *J* = 280 Hz, CF_3), 118.5 (CH=*C*H_2), 117.6 (CH_{Ar}), 79.7 (C-NH_2), 70.5 (Ts-N-*C*H), 63.4 (*C*-($CO_2CH_2CF_3$)$_2$), 61.7 (q, *J* = 40.0 Hz, *C*H_2CF_3), 61.6 (q, *J* = 40.0 Hz, *C*H_2CF_3), 45.1 (*C*H-CH=CH_2), 36.3 (CH-*C*H_2), 21.5 (CH_3) ppm. **^{19}F NMR** (470 Hz, $CDCl_3$): δ −73.62 (t, *J* = 8.0 Hz, CF_3), −73.71 (t, *J* = 8.5 Hz, CF_3) ppm. **IR** (Neat): 3510, 3263, 1751, 1598, 1459, 1412, 1363, 1286, 1164, 1092, 1065 cm^{-1}. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{24}F_6N_2O_6SNa$ 629.1157; Found 629.1144.

*8-Methyl 3,3-bis(2,2,2-trifluoroethyl) (1S,3aS,8bR)-8b-amino-4-tosyl-1-vinyl-1,3a,4,8b-tetrahydrocyclopenta[b]indole-3,3,8(2H)-tricarboxylate (**12k'**).* Zinc powder (76.7 mg, 1.17 mmol, 23 equiv) was slowly added to a solution of **5k'** (36.0 mg, 51.8 μmol, 1 equiv), trimethylsilyl chloride (0.14 mL, 119.8 mg, 1.10 mmol, 21 equiv) in methanol (0.6 mL) at 0°C. After stirring the reaction suspension at 0°C for 30 mins, the suspension was filtered and the solids were washed with dichloromethane (3 × 1 mL). The filtrate was diluted with dichloromethane (10 mL) and treated with saturated sodium bicarbonate solution (5 mL). Organic fraction was isolated and aqueous fraction was extracted with dichloromethane (2 × 10 mL). The combined organic fractions were dried over

magnesium sulfate and concentrated under reduced pressure. After column chromatography (40% ethyl acetate in hexane), the title compound was collected as a colourless oil (31.1 mg, 46.8 μmol) in 90% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.98 (dd, *J* = 8.2, 0.8 Hz, 1H, CH_{Ar}), 7.70 – 7.66 (m, 3H, CH_{Ar}), 7.40 (t, *J* = 8.0 Hz, 1H, CH_{Ar}), 7.19 (d, *J* = 8.0 Hz, CH_{Ar}), 5.76 – 5.66 (m, 1H, C*H*=CH_2), 5.56 (s, 1H, Ts-N-C*H*), 5.09 – 5.05 (m, 2H, CH=CH_2), 4.92 – 4.75 (m, 2H, OCH_2CF_3), 4.49 – 4.34 (m, 2H, OCH_2CF_3), 3.83 (s, 3H, OCH_3), 3.20 – 3.14 (m, 1H, C*H*-CH=CH_2), 2.52 (dd, *J* = 13.6, 7.2 Hz, 1H, CH-CH_2), 2.36 – 2.32 (m, 4H, CH-CH_2 and $CH_{3\ Tosyl}$) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 168.9 (C=O), 167.3 (C=O), 166.5 (C=O), 144.7 (C_{Ar}), 144.1 (C_{Ar}), 134.4 (*C*H=CH_2), 133.9 (C_{Ar}), 133.8 (C_{Ar}), 129.9 (CH_{Ar}), 129.6 ($CH_{Ar\ Tosyl}$), 128.1 ($CH_{Ar\ Tosyl}$), 127.62 (C_{Ar}), 127.59 (CH_{Ar}), 122.7 (q, *J* = 275.0 Hz, CF_3), 120.6 (CH_{Ar}), 118.1 (CH=*C*H_2), 80.2 (C-NH_2), 74.6 (Ts-N-*C*H), 64.8 (*C*-($CO_2CH_2CF_3$)$_2$), 61.7 (q, *J* = 40.0 Hz, O*C*H_2CF_3), 61.5 (q, *J* = 40.0 Hz, O*C*H_2CF_3), 52.9 (*C*H-CH=CH_2), 52.6 (OCH_3), 40.8 (CH-*C*H_2), 21.6 ($CH_{3\ Tosyl}$) ppm. **^{19}F NMR** (470 Hz, $CDCl_3$): δ −73.57 (t, *J* = 7.0 Hz, CF_3), −73.58 (t, *J* = 7.5 Hz, CF_3) ppm. **IR** (Neat): 1751, 1715, 1445, 1363, 1279, 1162, 1090 cm^{-1}. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{27}F_6N_2O_8S$ 665.1392; Found 665.1415.

*Diethyl (3aS,8bR)-8b-nitro-4-tosyl-1-vinyl-1,3a,4,8b-tetrahydrocyclopenta[b]indole-3,3(2H)-dicarboxylate (**4a/4a'**)*. A suspension of **5a/5a'** (mixture of diastereomers, 28.3 mg, 44.5 μmol, 1 equiv) and potassium carbonate (14.1 mg, 102 μmol, 2.3 equiv) in ethanol (3 mL) was stirred overnight at room temperature. The reaction was diluted with water (5 mL). Organic fraction was isolated and aqueous fraction was extracted with diethyl ether (3 × 10 mL). Combined organic fractions were washed with brine (5 mL) and dried over sodium sulfate. After column chromatography (20% ethyl acetate in hexane), the title compound was collected as a white oil film (18.8 mg, 35.6 μmol) in 80% yield. The data collected for this compound matches that obtained for the direct cycloaddition.

*Diethyl 4-tosyl-1-vinyl-1,4-dihydrocyclopenta[b]indole-3,3(2H)-dicarboxylate (**13**).* A suspension of **4a** (19.8 mg, 37.5 µmol, 1 equiv), sodium chloride (4.8 mg, 82 µmol, 2.2 equiv) and water (1 drop) in DMSO (0.5 mL) was heated in a microwave reactor at 170 °C for 5 mins. The reaction was diluted with water (4 mL) then extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were dried over sodium sulfate and concentrated under reduced pressure. After column chromatography (20% ethyl acetate in hexane), the title compound was obtained as an off-white oil film (9.0 mg, 18.7 µmol) in 50% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.4 Hz, 2H, CH_{Ar}), 7.60 (dd, *J* = 7.0, 1.6 Hz, 1H, CH_{Ar}), 7.43 – 7.40 (m, 1H, CH_{Ar}), 7.23 (d, *J* = 8.0 Hz, 2H, CH_{Ar}), 7.20 – 7.13 (m, 2H, CH_{Ar}), 5.91 (ddd, *J* = 17.3, 9.4, 8.0 Hz, 1H, C*H*=CH_2), 5.22 (d, *J* = 17.2 Hz, 1H, CH=C*H*$_2$), 5.11 (d, *J* = 10.0 Hz, 1H, CH=C*H*$_2$), 4.31 – 4.17 (m, 4H, OC*H*$_2$$CH_3$), 3.88 (app q, *J* = 6.0 Hz, 1H, C*H*-$CH=CH_2$), 3.46 (dd, *J* = 13.2, 7.6 Hz, 1H, CH-C*H*$_2$), 2.93 (dd, *J* = 12.8, 5.6 Hz, 1H, CH-C*H*$_2$), 2.34 (s, 3H, $CH_{3\ Tosyl}$), 1.29 (t, *J* = 7.2 Hz, 6H, OCH_2CH_3) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 170.2 (C=O), 169.5 (C=O), 144.6 (C_{Ar}), 140.0 (C_{Ar}), 139.1 (C_{Ar}), 138.8 (*C*H=CH_2), 136.1 (C_{Ar}), 130.8 (C_{Ar}), 129.6 ($CH_{Ar\ Tosyl}$), 127.7 ($CH_{Ar\ Tosyl}$), 125.4 (C_{Ar}), 124.5 (CH_{Ar}), 123.0 (CH_{Ar}), 119.8 (CH_{Ar}), 116.0 (CH=*C*H_2), 114.3 (CH_{Ar}), 62.5 (*C*-$(CO_2Et)_2$), 62.1 (OCH_2CH_3), 48.3 (CH-*C*H_2), 40.9 (*C*H-CH=CH_2), 21.6 ($CH_{3\ Tosyl}$), 14.0 (OCH_2CH_3) ppm. **IR** (Neat): 1727, 1446, 1366, 1252, 1173 cm^{-1}. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{27}NO_6SNa$ 504.1457; Found 504.1475.

*(1R,3S,3aS,8bR)-3,8-Bis(methoxycarbonyl)-8b-nitro-4-tosyl-1-vinyl-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indole-3-carboxylic acid (**14**).* Ammonia solution (7 N in methanol, 2 mL) was added to **5k'** (33.5 mg, 48.2 mmol) at 5 °C. The reaction solution was stirred at 5 °C for 1 h then concentrated under reduced pressure. After column chromatography (5% methanol in dichloromethane), the title compound was obtained as a white solid (16.3 mg, 29.9 mmol) in 62% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.98 (d, *J* = 5.0 Hz, 1H, CH_{Ar}), 7.72 (d, *J* = 10.0 Hz, 1H, CH_{Ar}), 7.54 (t, *J* = 10.0 Hz, 1H, CH_{Ar}), 7.47 (d, *J* = 10.0 Hz, 2H, $CH_{Ar\ Tosyl}$), 7.17 (d, *J* = 5.0 Hz, 2H, $CH_{Ar\ Tosyl}$), 6.05 (ddd, *J* = 17.3, 9.8, 8.0 Hz, 1H, C*H*=CH_2), 5.90 (s, 1H, Ts-N-C*H*), 5.80 (bs, 1H, CO_2H), 5.08 (t, *J* = 15.0 Hz, 2H, CH=C*H*$_2$), 3.83 – 3.78 (m, 1H, C*H*-CH=CH_2), 3.74 (s, 3H, OCH_3), 3.57 (s,

3H, OCH_3), 2.78 (dd, *J* = 15.0, 10.0 Hz, 1H, CH-C*H*$_2$), 2.49 (dd, *J* = 15.0, 10.0 Hz, 1H, CH-C*H*$_2$), 2.35 (s, 3H, $CH_{3\ Tosyl}$) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 171.4 (C=O), 170.2 (C=O), 165.8 (C=O), 145.7 (C_{Ar}), 143.9 (C_{Ar}), 135.2 (*C*H=CH_2), 132.3 (C_{Ar}), 131.6 (CH_{Ar}), 130.0 (CH_{Ar}), 129.7 (C_{Ar}), 128.7 (C_{Ar}), 128.0 (CH_{Ar}), 127.5 (CH_{Ar}), 120.7 (CH_{Ar}), 118.1 (CH=*C*H_2), 103.0 (C-NO_2), 78.2 (Ts-N-*C*H), 64.0 (*C*-CO_2H), 52.82 (*C*H-CH=CH_2 or OCH_3), 52.77 (*C*H-CH=CH_2 or OCH_3), 52.6 (OCH_3), 41.2 (CH-*C*H_2), 21.7 ($CH_{3\ Tosyl}$) ppm. **IR** (Neat): 3438, 3196, 2954, 1730, 1688, 1685, 1553, 1436, 1374, 1294, 1238, 1173 cm^{-1}. **LRMS** (ESI) = 567, $(M+Na)^+$. **Melting point**: 194.3 – 196.4 °C

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

NMR (^{1}H, ^{13}C and ^{19}F) spectra for all new compounds and X-ray Crystallographic Information for **5a** and **14** (PDF)

Crystallographic data for **5a** and **14** (CIF)

References

[1] a) Welmaker, G. S.; Sabalski, J. E.; Smith, M. D. US20020058689A1, 2002. (b) Ngantchou, I.; Nyasse, B.; Denier, C.; Blonski, C.; Hannaert, V.; Schneider, B., *Bioorg. Med. Chem. Lett*. **2010**, *20*, 3495.

[2] (a) Welmaker, G. S.; Sabalski, J. E., *Tetrahedron Lett*. **2004**, *45*, 4851. (b) Murphy, J. A.; Scott, K. A.; Sinclair, R. S.; Lewis, N., *Tetrahedron Lett*. **1997**, *38,* 7295. (c) Gataullin, R. R.; Ishberdina, R. R.; Shitikova, O. V.; Minnigulov, F. F.; Spirikhin, L. V.; Abdrakhmanov, I. B., *Chemistry of Heterocyclic Compounds* **2006**, *42*, 1025. (d) Chapman, O. L.; Eian, G. L., *J. Am. Chem. Soc.* **1968**, *90*, 5329.

[3] Prasad, B. A. B.; Buechele, A. E.; Gilbertson, S. R. *Org. Lett.* **2010**, *12*, 5422.

[4] Roche, S. P.; J-J. Y. Tendoung; Treguier, B. *Tetrahedron,* **2015**, *71*, 3549.

[5] Barluenga, J.; Tudela, E.; Ballesteros, A.; Tomás, M. *J. Am. Chem. Soc.* **2009**, *131*, 2096.

[6] a) Lian, Y.; Davies, H. M. L. *J. Am. Chem. Soc.* **2010**, *132*, 440. b) Jing, C.; Cheng, Q-Q.; Deng, Y.; Arman, H.; Doyle, M. P. *Org. Lett.* **2016** *18*, 4550.

[7] a) Kerr, M. A.; Keddy, R. G. *Tetrahedron Lett*. **1999**, *40*, 5671. b) England, D. B.; Kuss, T. D. O.; Keddy, R. G.; Kerr, M. A. *J. Org. Chem.* **2001**, *66* , 4704.

[8] Xiong, H.; Xu, H.; Liao, S.; Xie, Z.; Tang, Y. *J. Am. Chem. Soc.* **2013**, *135*, 7851.

[9] Trost, B. M.; Ehmke, V.; O'Keefe, B. M.; Bringley, D. A. *J. Am. Chem. Soc.* **2014**, *136*, 8213.

[10] Rivinoja, D. J.; Gee, Y. S.; Gardiner, M. G.; Ryan, J. H.; Hyland, C. J. T. *ACS Catal.* **2017**, *7*, 1053.

[11] For a review on approaches to pyrroloindoline syntheses, see: Repka, L. M.; Reisman, S. E. *J. Org. Chem.* **2013**, *78*, 12314. For selected recent examples of pyrroloindoline syntheses, see: (a) Li, Q.; Xia, T.; Yao, L.; Deng, H.; Liao, X. *Chem. Sci.* **2015**, *6*, 3599−3605. (b) Acharya, A.; Anumandla, D.; Jeffrey, C. S. *J. Am. Chem. Soc.* **2015**, *137*, 14858– 14860. (c) DiPoto, M. C.; Hughes, R. P.; Wu, J. *J. Am. Chem. Soc.* **2015**, *137*, 14861– 14864. (d) Chai, Z.; Zhu, Y. M.; Yang, P. J.; Wang, S.; Wang, S.; Liu, Z.; Yang, G. *J. Am. Chem. Soc.* **2015**, *137*, 10088– 10091. (e) Liu, C.; Yi, J. C.; Zheng, Z. B.; Tang, Y.; Dai, L. X.; You, S. L. *Angew. Chem., Int. Ed.* **2016**, *55*, 751– 754.

[12] For an example of the reaction of oxindoles with Pd-stabilized all-carbon zwitterionic dipoles derived from vinylcyclopropanes, see: Cao, R.; Zhang, J.; Zhou, H.; Yang, H.; Jiang, G. *Org. Biomol. Chem.* **2016**, *14*, 2191.

[13] For examples of Pd-catalyzed vinylcyclopropane [3 + 2] cycloaddition to nitroalkenes, see: Wei, F.; Ren, C.-L.; Wang, D.; Liu, L., *Chem. Eur. J.* **2015**, *21*, 2335-2338.

[14] Laugeois, M.; Ling, J.; Férard, C.; Michelet, V.; Ratovelomanana-Vidal, V.; Vitale, M. R. *Org. Lett.* **2017**, *19*, 2266.

[15] Trost, B. M.; Toste, F. D *J. Am. Chem. Soc*. **1999**, *121*, 4545.

[16] (a) Sharpe, R. J.; Johnson, J. S. *J. Org. Chem.* **2015**, *80*, 9740-9766; (b) Bergman, J.; Venemalm, L.,*Tetrahedron* **1992**, *48*, 759-768.

[17] For evidence for the interaction of an indole ring with a quaternary trimethylammonium group via a cation-π interaction, see: Aoki, K.; Murayama, K.; Nishiyama, H. *Chem. Commun.* **1995**, 2221–2222.

[18] a) Mei, L.-y.; Wei, Y.; Xu, Q.; Shi, M. *Organometallics* **2013**, *32*, 3544. b) Sherry, B. D.; Furstner, A. *Chem. Commun.* **2009**, 7116. c) Trost, B. M.; Morris, P. J.; Sprague, S. J. *J. Am. Chem. Soc.* **2012**, *134*, 17823.

[19] Nowrouzi, N.; Mehranpour, A. M.; Bashiri, E.; Shayan, Z. *Tetrahedron Lett.* **2012**, *53*, 4841.

[20] Stokes, B. J.; Liu, S.; Driver, T. G. *J. Am. Chem. Soc.* **2011**, *133*, 4702.

[21] Ren, W.; Yamane, M. *J. Org. Chem.* **2010**, *75*, 8410.

[22] Raimer, B.; Wartmann, T.; Jones, P. G.; Lindel, T. *Eur. J. Org. Chem.* **2014**, *2014*, 5509.