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ARTICLE TYPE

# Maleimide as efficient nucleophilic partner in *aza*-Morita-Baylis-Hillman reaction: Synthesis of chiral 3-substituted-3-aminooxindoles

**Akshay Kumar, Vivek Sharma, Jasneet Kaur, Naveen Kumar and Swapandeep Singh Chimni***

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A highly enantioselective Morita-Baylis-Hillman reaction of maleimides with isatin derived ketimines has been developed to obtain enantiomerically enriched 3-substituted-3-aminooxindoles using *β*-isocupreidine as an organocatalyst. Maleimide acting as a nucleophile provide products with up to 99% ee.

## Introduction

Morita-Baylis-Hillman reaction is the important atom economical Carbon-Carbon bond forming reaction in organic synthesis, which is used for the synthesis of densely functionalized *β*-hydroxy carbonyl or *β*-amino carbonyl functionalities involving the addition of *α*,*β*-unsaturated carbonyl compounds to aldehydes or aldimines[1] respectively. Since its discovery in 1968 by Morita[2] and later in 1972 by A.B. Baylis and M.E.D. Hillman,[3] it went through a dormant period. It was rarely explored for nearly three decades but in last few years, it has witnessed a great deal of interest for the synthesis of multifunctional molecules and its green chemistry relevance. The reasons for its fast growth can be attributed to several advantages like atom economic nature, catalysis by nucleophilic organocatalyts and mild reaction conditions. In place of aldehydes, activated imines also serve as suitable substrates for this reaction, leading to *α*-methylene-*β*-amino carbonyl compounds, which are commonly referred to as the *aza*-Morita–Baylis–Hillman adducts.[4] While the use of aldimine electrophiles[4a-h] has shown to be quite successful but the addition of nucleophiles to cyclic ketimines still remains a challenging task because of their lower reactivity. Due to this, there are only few reports on the enantioselective organocatalytic MBH reactions in which ketimines have been used as electrophiles.[4i-k] Two independent reports on the enantioselective MBH reaction of isatin derived ketimines with methyl vinyl ketone and acrylates were published by the research groups of Shi and Feng.[5] Besides these reports, no other donor has been used till date with isatin ketimine in the Morita-Baylis-Hillman reaction.We thought of using maleimide as a MBH donor which is more challenging task because maleimides are traditionally Michael acceptors used for the synthesis of chiral succinimide derivatives.[6] They can also be used in asymmetric cascade reactions providing chiral disubstituted succinimides. However, the use of maleimides as a nucleophilic partners in catalytic asymmetric transformation is very rare.[7]

In continuation of our ongoing programme of developing enantioselective carbon–carbon bond-forming reactions by the application of *Cinchona* alkaloid derivatives,[8] herein, we report an organocatalytic *aza*-MBH reaction of maleimides with isatin derived ketimines to obtain chiral 3-substituted-3-amino-2-oxindole derivatives.[9]

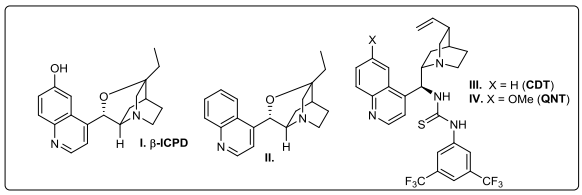



**Figure 1**. *Cinchona*-derived organocatalysts for the MBH reaction

## Result and Discussion

Initially, we investigated the model reaction of isatin imine (**2a**) with *N*-phenyl maleimide (**1a**) using *β*-isocupreidine-a quinidine derived oxaza-twistanes (**Figure 1**).This catalyst has proven to be an excellent catalyst for various reactions including MBH reaction,[10] since it possesses special characteristics as compared to other modified *Cinchona* alkaloids due to extra constrained ring between C9 and C3. Moreover, *β*-isocupreidine has less conformations due to extra ring. In addition to this its quinuclidine *N*-atom is more basic and has more nucleophilic character due to extra cycle (**Figure 2**).

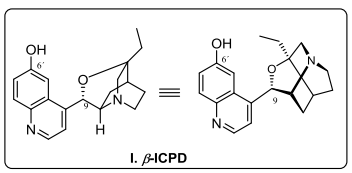
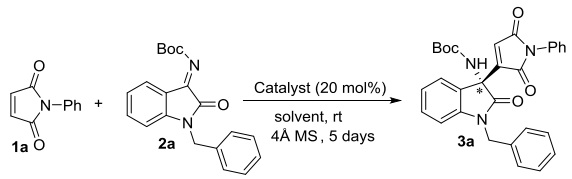



**Figure 2**: *β*-isocupreidine: Quinidine derived oxaza-twistanes

*β*-Isocupreidine catalyzed reaction of **2a** with **1a** yielded the desired adduct with good enantioselectivity of 89% but poor yield of 38%. The addition of freshly dried 4Å molecular sieves was found to increase the yield upto 53% without affecting the enantioselectivity. Since, the catalyst *β*-

isocupreidine **I** provided the best results in terms of product yield and enantioselectivity, the catalytic potential of the analogous catalyst **II** was also evaluated for the model reaction. This reaction provided **3a** in 70% ee and 36% yield. The other natural *Cinchona* alkaloids and their thiourea derivatives were also investigated but without any success. Since *β*-isocupreidine **I** was found to be a superior catalyst for this reaction so all further optimization was performed with it.

**Table 1. Screening of catalysts and solvents**[a]



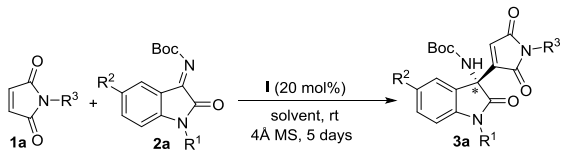

| Entry | Catalyst | Solvent | Yield[%][b] | ee [%][c] |
|---|---|---|---|---|
| 1 | I | THF | 53 | 89 |
| 2 | II | THF | 36 | 70 |
| 3 | III | THF | - | n.d. |
| 4 | IV | THF | - | n.d. |
| 5 | I | DCM | 51 | 88 |
| 6 | I | $CHCl_3$ | 55 | 95 |
| 7 | I | Toluene | 51 | 95 |
| 8 | I | Xylene | 45 | 92 |
| 9 | I | MTBE | 50 | 90 |
| 10 | I | 1,4-Dioxane | 79 | 86 |
| 11 | I | Ethyl acetate | 67 | 81 |

[a]Reaction conditions: 0.1mmol *N*-benzylisatin imine **2a**, 0.3mmol of *N*-phenylmaleimide **1a**, 4Å molecular sieves (50 mg) and catalyst (20 mol%) in dry solvent (0.5 ml). [b]Yield refers to isolated yield after column chromatography. [c]Enantiomeric excess (ee) determined by chiral HPLC.

A screening of different organic solvents using catalyst **I** for the model reaction was carried out. On using chloroform as the solvent, **3a** was isolated in 55% yield and 95% enantioselectivity (**Table 1**, **entry 6**). Other solvents such as toluene, xylene, MTBE, 1,4-dioxane provided better enantioselectivity but lower yields as compared to reaction in chloroform (**Table 1**, **entry 7-11**). Solvent screening revealed that the reaction proceeded better in chloroform than ethereal solvents. Based on the above screenings, the substrate scope was investigated using chloroform as a solvent at room temperature, using 20 mol% of catalyst **I**.

This protocol was successful in the reaction of variety of different substituted isatin imines and maleimide derivatives. The reaction of *N*-phenylmaleimide with *N*-benzylisatin imines provided adducts (**3a-3e**) in modest yield (55-76%) and excellent enantioselectivity (95-99%) (**Table 2, entry 1-5**). 5-Methoxy-*N*-benzylisatin imine (**2f**) gave product (**3f**) in 47% yield with 96% ee (**Table 2, entry 6**). The *N*-allylisatin imine (**2g)** also reacts smoothly with *N*-phenylmaleimide (**1a)** to provide the corresponding adduct **3g** in 58% yield and 95% enantioselectivity (**Table 2, entry 7**). The 5-fluoro, 5-chloro, 5-bromo and 5-iodo-*N*-allylisatin imine (**2h-2k**) also reacted efficiently with *N*-phenylmaleimide (**1a**) to provide the products (**3h-3k**) in 46-66% yield and with > 95% ee (**Table 2**, **entry 8-11**). The *N*-allylisatin imine (**2l**) substituted with electron donating group in the aromatic ring gave adduct (**3l**) in 35% yield and 95% enantioselectivity (**Table 2, entry 12**). The addition of *N*-phenylmaleimide to 5-chloro-*N*-substituted isatin imines **2m** and **2n** yielded adducts **3m** and **3n** in 55-77% yield and excellent enantioselectivity (96-98%) (**Table 2, entry 13-14**). The *N*-phenylisatin imine (**2o**) also reacted with *N*-phenylmaleimide (**1a)** resulting in the desired product **3o** in moderate yield but with good enantioselectivity of 92% (**Table 2, entry 15**). Further exploration of the substrate scope was concentrated on varying the substituents of maleimides.

**Table 2. Reaction of maleimides (1a-1e) with *N*-substituted isatin imines (2a-2o)**[a]




| Entry | 1($R^3$) | 2 ($R^1$, $R^2$) | 3 | Yield[b] (%) | ee[c] (%) |
|---|---|---|---|---|---|
| 1 | **1a** (Ph) | **2a** ($R_1$=$CH_2C_6H_5$, $R_2$=H) | **3a** | 55 | 95 |
| 2 | **1a** (Ph) | **2b** ($R_1$=$CH_2C_6H_5$, $R_2$=F) | **3b** | 66 | 96 |
| 3 | **1a** (Ph) | **2c** ($R_1$=$CH_2C_6H_5$, $R_2$=Cl) | **3c** | 75 | 96 |
| 4 | **1a** (Ph) | **2d** ($R_1$=$CH_2C_6H_5$,$R_2$=Br) | **3d** | 57 | 96 |
| 5 | **1a** (Ph) | **2e** ($R_1$= $CH_2C_6H_5$, $R_2$=I) | **3e** | 76 | 99 |
| 6 | **1a** (Ph) | **2f**($R_1$=$CH_2C_6H_5$, $R_2$=OMe) | **3f** | 47 | 96 |
| 7 | **1a** (Ph) | **2g** ($R_1$=$CH_2CHCH_2$, $R_2$=H) | **3g** | 58 | 95 |
| 8 | **1a** (Ph) | **2h** ($R_1$=$CH_2CHCH_2$, $R_2$=F) | **3h** | 62 | 96 |
| 9 | **1a** (Ph) | **2i** ($R_1$=$CH_2CHCH_2$, $R_2$=Cl) | **3i** | 66 | 95 |
| 10 | **1a** (Ph) | **2j** ($R_1$=$CH_2CHCH_2$, $R_2$=Br) | **3j** | 46 | 95 |
| 11 | **1a** (Ph) | **2k** ($R_1$= $CH_2CHCH_2$, $R_2$=I) | **3k** | 63 | 90 |
| 12 | **1a** (Ph) | **2l** ($R_1$= $CH_2CHCH_2$, $R_2$=OMe) | **3l** | 35 | 95 |
| 13 | **1a** (Ph) | **2m** ($R_1$=$CH_2C(CH_3)CH_2$, $R_2$=Cl) | **3m** | 77 | 98 |
| 14 | **1a** (Ph) | **2n** ($R_1$= $CH_2CHCHCH_3$, $R_2$=Cl) | **3n** | 55 | 96 |
| 15 | **1a** (Ph) | **2o** ($R_1$=Ph, $R_2$=H) | **3o** | 75 | 92 |
| 16 | **1b**(-$CH_2$Ph) | **2g** ($R_1$=$CH_2CHCH_2$, $R_2$=H) | **3p** | 64 | 76 |
| 17 | **1c** (- Me) | **2g** ($R_1$=$CH_2CHCH_2$, $R_2$=H) | **3q** | 30 | 71 |
| 18 | **1d**(-$CH_2$ $CH_2$Ph) | **2g** ($R_1$=$CH_2CHCH_2$, $R_2$=H) | **3r** | 76 | 70 |
| 19 |  **1e** | **2g** ($R_1$=$CH_2CHCH_2$, $R_2$=H) | **3s** | 79 | 75 |

[a] Reaction conditions: 0.1 mmol of isatin imines **2**, 0.3 mmol maleimide derivatives **1a**, 4Å molecular sieves (50 mg) and catalysts **I** (20 mol%) in chloroform. [b]Yield refers to isolated yield after column chromatography. [c]Enantiomeric excess (ee) determined by chiral HPLC

The reactions of *N*-allylisatin imine (**2g**) with *N*-benzylmaleimide (**1b)** and *N*-methylmaleimide (**1c)** were

carried out. The reaction of *N*-allylisatin imine (**2g**) with *N*-benzylmaleimide (**1b**) gave the adduct **3p** in 64% yield and 76% enantioselectivity (**Table 2, entry 16**). The reaction with *N*-methylmaleimide (**1c**) gave the adduct in 30% yield and 71% enantioselectivity (**Table 2, entry 17**). The reaction of **2g** with 2-phenylethylmaleimide (**1d**) provided the adduct **3r** in 76% yield and 70% enantioselectivity (**Table 2, entry 18**). Furthermore, the reaction of **2a** with maleimide was unsuccessful even after five days.

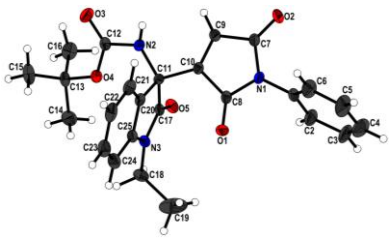


**Figure 3.** ORTEP diagram of the molecule (**3g**) at 20% probability.

The (*R*) absolute configuration of adducts was assigned on the basis of single-crystal X-ray diffraction analysis of compound **3g** (**Figure 3**)[11].

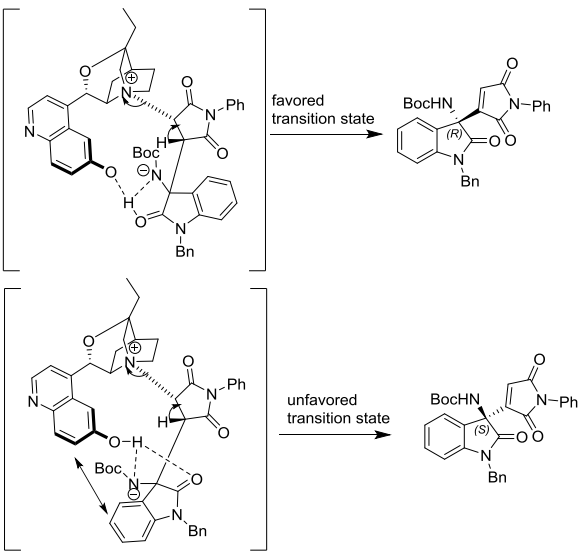



**Figure 4: Proposed Transition State**.

In the proposed transition state (**Figure 4**), the tertiary amine of the catalyst adds on to maleimide resulting in the formation of enolate, which simultaneously attacks on the isatin imine to form the favourable *R* enantiomer. On the other hand, in the unfavourable transition state leading to *S* enantiomer of the product, the steric crowding resulting from the close proximity of the aromatic ring of substrate and aryl group of the catalyst.

## Conclusions

We have developed an organocatalytic enantioselective *aza*-MBH reaction of maleimide derivatives with various *N*-substituted isatin imine derivatives by employing chiral *β*-ICPD **I** as a catalyst. Through this methodology, a wide variety of 3-substituted 3-aminoindolin-2-ones were synthesized in good yields (up to 77%) and good enantioselectivities (up to 99% ee).

## Experimental section

### General information

All reactions were performed in oven-dried glassware. All solvents and commercially available chemical were used without further purification. The molecular sieves were activated at 200 ˚C for 2 hours in an oven. The column chromatography was carried out on a column packed with silica gel 60-120 using mixtures of hexane and ethyl acetate as an eluents. $^1$H NMR spectra were recorded in $CDCl_3$ on a BRUKER AVANCE III (500 MHz), BRUKER AVANCE II (400 MHz) and JEOL (300 MHz) spectrometer. $^{13}$C NMR spectra were recorded in $CDCl_3$ on BRUKER AVANCE III (125 MHz), BRUKER AVANCE II (100 MHz) and JEOL (75 MHz). Chemical shifts ($\delta$) are expressed in ppm downfield from internal TMS. MS were recorded on micrOTOF-Q II 10356 Mass Spectrometer. Optical rotation was determined with AUTOPOL IV polarimeter at 25˚C using sodium D light. Enantiomeric excess was determined by using Shimadzu LC-20AD using Daicel Chiralpak IA, IB and IC column.

### General Procedure for the *aza*-Morita–Baylis–Hillman reaction

To the solution of ketimines derived from isatins **2a** (0.1 mmol), maleimides **1a** (0.30 mmol), 4Å MS (50 mg) in 0.3 mL of chloroform, the catalyst *β*-ICPD (**I**, 20 mol%) was added at 25 °C. The reaction mixture was stirred for 5 days and the progress of the reaction was monitored at regular intervals by thin layer chromatography (tlc). After the completion of reaction, the crude reaction mixture was purified by column chromatography on silica gel (mesh 60–120) using hexane–ethyl acetate (1:1) as eluent. The enantiomeric excess of the purified **3** were determined using Diacel Chiralpak columns. The racemic standards were prepared using DABCO (20 mol%) as a catalyst.

**(*R*)-*tert*-Butyl-1-benzyl-3-(2,5-dioxo-1-phenyl-2,5-dihydro-1H-pyrrol-3-yl)-2-oxoindolin-3-ylcarbamate (3a):** White solid; m.p. 110-112℃; yield 55%; $[\alpha]_{20}^{D}$= -176 (*c* 0.50, $CHCl_3$); 95% ee; HPLC[Chiralpak IA, hexane/*i*-PrOH, 80:20, 1 mL/min, 254 nm, $t_R$ = 16.4 min (minor) and $t_R$ = 22.8 min (major)]; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.29-7.63 (m, 15H), 7.10 (t, *J*= 15.0 Hz, 1H), 6.81 (d, *J*= 10.0 Hz, 1H), 6.41 (s, 1H), 6.19 (s, 1H), 5.05 (dd, *J*= 75.0 Hz, *J*= 15.0 Hz, 2H), 1.39 (s, 9H); $^{13}$C (125 MHz, $CDCl_3$) $\delta$ 28.15, 44.67, 61.48, 81.26, 109.9, 123.6, 125.3, 126.0, 127.3, 127.8, 128.2, 128.5, 128.9, 129.1, 130.1, 135.1, 142.7, 143.7, 153.9, 167.6, 167.9, 172.8; HRMS calcd. for $C_{30}H_{27}N_3O_5$ $[M + Na]^+$ 532.1848; found 532.1835.

**(*R*)-*tert*-Butyl-1-benzyl-3-(2,5-dioxo-1-phenyl-2,5-dihydro-1H-pyrrol-3-yl)-5-fluoro-2-oxoindolin-3-ylcarbamate (3b):** White semisolid; yield 66%; $[\alpha]_{20}^{D}$= -56.9 (*c* 0.5, $CHCl_3$); 96% ee; HPLC[Chiralpak IA, hexane/*i*-PrOH, 80:20, 1 mL/min, 254 nm, $t_R$ = 15.2 min (major) and $t_R$ = 24.1 min (minor)]; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.26-

7.46 (m, 11H), 6.95 (s, 1H), 6.71 (d, *J*= 3.6 Hz, 1H), 6.51 (s, 1H), 6.16 (s, 1H), 5.02 (dd, *J*= 37.8 Hz, *J*= 14.7 Hz, 2H), 1.39 (s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 28.16, 44.84, 61.55, 81.55, 110.5, 110.7, 113.5, 113.7, 116.4, 116.5, 126.0, 127.2, 127.9, 128.3, 129.0, 129.1, 129.2, 130.7, 134.8, 138.7, 138.8, 143.2, 153.9, 158.5, 160.5, 167.4, 167.7, 172.7; HRMS calcd. for $C_{30}H_{26}FN_3O_5$ $[M+H]^+$ 528.1935; found 528.2216.

**(*R*)-*tert*-Butyl-1-benzyl-5-chloro-3-(2,5-dioxo-1-phenyl-2,5-dihydro-1H-pyrrol-3-yl)-2-oxoindolin-3-ylcarbamate (3c):** White semisolid; yield 75%; $[\alpha]_{20}^{D}$= -65.9 (c 0.15, $CHCl_3$); 96% ee; HPLC[Chiralpak IA, hexane/*i*-PrOH, 80:20, 1 mL/min, 254 nm, $t_R$ = 14.1 min (major) and $t_R$ = 29.4 min (minor)]; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.26-7.71 (m, 11H), 6.87 (d, *J*= 3.0 Hz, 1H), 6.64 (d, *J*= 6.0 Hz, 1H), 6.50 (s, 1H), 6.21 (s, 1H), 5.01 (dd, *J*= 27.9 Hz, *J*= 16.2 Hz, 2H), 1.39 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 29.71, 44.50, 61.39, 81.61, 110.9, 125.6, 126.0, 126.1, 127.3, 127.9, 128.0, 128.2, 129.0, 129.1, 129.2, 129.3, 130.1, 130.7, 131.2, 134.2, 134.7, 141.3, 143.2, 153.8, 167.4, 167.8, 169.5, 172.5; HRMS calcd. for $C_{30}H_{26}ClN_3O_5$ $[M+H]^+$ 544.1639; found 544.1586.

**(*R*)-*tert*-Butyl-1-benzyl-5-bromo-3-(2,5-dioxo-1-phenyl-2,5-dihydro-1H-pyrrol-3-yl)-2-oxoindolin-3-ylcarbamate (3d):** Brown semisolid; yield 57%; $[\alpha]_{20}^{D}$ = - 42.7 (*c* 0.50, $CHCl_3$); 96% ee; HPLC[Chiralpak IB, hexane/*i*-PrOH, 80:20, 1 mL/min, 254 nm, $t_R$ = 6.44 min (major) and $t_R$ = 12.0 min (minor)]; $^1$H NMR (300 MHz,$CDCl_3$) $\delta$ 7.29-7.88 (m, 13H), 6.52-6.59 (m, 2H), 6.22 (s, 1H), 5.09 (dd, *J*= 27.0 Hz, *J*= 15.0 Hz, 2H), 1.43 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 29.70, 44.79, 61.31, 81.63, 111.5, 116.2, 126.0, 126.1, 127.3, 127.9, 128.0, 128.3, 128.9, 129.0, 129.1, 129.2, 129.5, 130.7, 132.9, 134.2, 134.7, 141.0, 143.1, 153.8, 167.3, 167.7, 169.5, 172.5; HRMS calcd. for $C_{30}H_{26}BrN_3O_5$ $[M + Na]^+$ 610.0948; found 610.0889.

**(*R*)-*tert*-Butyl-1-benzyl-3-(2,5-dioxo-1-phenyl-2,5-dihydro-1H-pyrrol-3-yl)-5-iodo-2-oxoindolin-3-ylcarbamate (3e):** White semisolid; yield 76%; $[\alpha]_{20}^{D}$= -43.6 (*c* 0.50, $CHCl_3$); 99% ee; HPLC[Chiralpak IA, hexane/*i*-PrOH, 80:20, 1 mL/min, 254 nm, $t_R$ = 16.8 min (major) and $t_R$ = 40.8 min (minor)]; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.85 (s, 1H), 7.29-7.47 (m, 10H), 6.87 (s, 1H), 6.53 (t, *J*= 10.5 Hz, 2H), 6.19 (s, 1H), 5.00 (dd, *J*= 27.0 Hz, J= 15.0 Hz, 2H), 1.39 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 28.17, 44.74, 61.16, 81.62, 86.08, 112.0, 126.0, 126.1, 127.3, 127.9, 128.0, 128.3, 128.4, 129.0, 129.1, 129.8, 130.7, 133.7, 134.2, 134.7, 138.9, 142.6, 143.1, 153.8, 167.3, 167.7, 169.5, 172.3; HRMS calcd. for $C_{30}H_{26}IN_3O_5$ $[M + Na]^+$ 658.0814; found 658.0876.

**(*R*)-*tert*-Butyl-1-benzyl-3-(2,5-dioxo-1-phenyl-2,5-dihydro-1H-pyrrol-3-yl)-5-methoxy-2-oxoindolin-3-ylcarbamate (3f):** White semisolid; yield 47%; $[\alpha]_{20}^{D}$= - 52.3 (*c* 0.50, $CHCl_3$); 96% ee; HPLC[Chiralpak AD-H, hexane/*i*-PrOH, 80:20, 1 mL/min, 254 nm, $t_R$ = 17.8 min (minor) and $t_R$ = 36.9 min (major)]; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.31-7.46 (m, 11H), 6.78 (t, *J*= 7.5 Hz, 1H), 6.71 (d, *J*= 5.0 Hz, 1H), 6.48 (s, 1H), 6.21 (s, 1H), 5.01 (dd, J= 70.0 Hz, *J*= 15.0 Hz, 2H), 3.77 (s, 3H), 1.41 (s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 28.17, 44.74, 55.82, 61.83, 81.28, 110.4, 112.4, 114.6, 126.0, 127.3, 127.9, 128.1, 128.8, 128.9, 129.1, 135.2, 143.7, 156.5, 167.5, 167.8, 172.6; HRMS calcd. for $C_{31}H_{29}N_3O_6$ $[M + H]^+$ 540.2129; found 540.2139.

**(*R*)-*tert*-Butyl-1-allyl-3-(2,5-dioxo-1-phenyl-2,5-dihydro-1H-pyrrol-3-yl)-2-oxoindolin-3-ylcarbamate (3g):** White solid; m.pt. 125-126℃; yield 58%; $[\alpha]_{20}^{D}$= - 161 (*c* 0.50, $CHCl_3$); 95% ee; HPLC[Chiralpak IA, hexane/*i*-PrOH, 80:20, 1 mL/min, 254 nm, $t_R$ = 8.91 min (minor) and $t_R$ = 19.7 min (major)]; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.27-7.72 (m, 8H), 6.82 (t, *J*= 15.0 Hz, 1H), 6.54 (s, 1H), 6.12 (s, 1H), 5.83-5.89 (m, 1H), 5.27-5.32 (m, 2H), 4.44 (dd, *J*= 59.4 Hz, *J*= 16.5 Hz, 2H), 1.37 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 28.10, 43.01, 61.41, 81.14, 109.7, 118.1, 123.5, 125.1, 127.8, 127.9, 128.3, 128.4, 128.8, 129.9, 130.8, 134.2, 135.7, 142.6, 143.7, 153.9, 165.4, 165.7, 172.5; HRMS calcd. for $C_{26}H_{25}N_3O_5$ $[M + Na]^+$ 482.1691; found 482.1678.

**(*R*)-*tert*-Butyl-1-allyl-3-(2,5-dioxo-1-phenyl-2,5-dihydro-1H-pyrrol-3-yl)-5-fluoro-2-oxoindolin-3-ylcarbamate (3h):** White semisolid; yield 62%; $[\alpha]_{20}^{D}$= - 151 (*c* 0.50, $CHCl_3$); 96% ee; HPLC[Chiralpak IA, hexane/*i*-PrOH, 80:20, 1 mL/min, 254 nm, $t_R$ = 6.97 min (minor) and $t_R$ = 13.2 min (major)]; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.05-7.45 (m, 7H), 6.83-6.87 (m, 2H), 6.54 (s, 1H), 6.08 (s, 1H), 5.77-5.89 (m, 1H), 5.27-5.38 (m, 2H), 4.36-4.54 (m, 2H), 1.37 (s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 28.14, 43.25, 61.46, 81.49, 110.4, 110.5, 113.6, 113.7, 116.4, 116.6, 118.3, 126.0, 128.2, 129.1, 129.2, 130.6, 134.2, 138.8, 138.9, 1143.3, 153.8, 158.5, 160.4, 167.4, 167.7, 172.2; HRMS calcd. for $C_{17}H_{20}ClN_3O_5$ $[M + Na]^+$ 404.0984; found 404.0996.

**(*R*)-*tert*-Butyl-1-allyl-5-chloro-3-(2,5-dioxo-1-phenyl-2,5-dihydro-1H-pyrrol-3-yl)-2-oxoindolin-3-ylcarbamate (3i):** White semisolid; yield 66%; $[\alpha]_{20}^{D}$= - 9.03 (*c* 0.50, $CHCl_3$); 95% ee; HPLC[Chiralpak IA, hexane/*i*-PrOH, 80:20, 1 mL/min, 254 nm, $t_R$ = 6.72 min (minor) and $t_R$ = 12.0 min (major)]; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.31-7.61 (m, 7H), 6.86 (t, *J*= 10.0 Hz, 1H), 6.58 (s, 1H), 6.22 (s, 1H), 5.87-5.90 (m, 1H), 5.29-5.39 (m, 2H), 4.33-4.57 (m, 2H), 1.39 (s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 28.15, 43.23, 61.30, 81.57, 110.8, 118.4, 126.0, 128.2, 128.9, 129.1, 130.1, 130.5, 141.4, 143.2, 153.9, 167.4, 167.7, 172.2; HRMS calcd. for $C_{17}H_{20}ClN_3O_5$ $[M+Na]^+$ 404.0984; found 404.0996.

**(*R*)-*tert*-Butyl-1-allyl-5-bromo-3-(2,5-dioxo-1-phenyl-2,5-dihydro-1H-pyrrol-3-yl)-2-oxoindolin-3-ylcarbamate (3j):** Brownish semisolid; yield 46%; $[\alpha]_{20}^{D}$= - 88.5 (*c* 0.50, $CHCl_3$); 95% ee; HPLC[Chiralpak

IB, hexane/*i*-PrOH, 80:20, 1 mL/min, 254 nm, $t_R$ = 5.77 min (major) and $t_R$ = 8.46 min (minor)]; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.26-7.71 (m, 8H), 6.81 (t, *J*= 15.0 Hz, 1H), 6.13 (s, 1H), 5.90 (s, 1H), 5.86-5.88 (m, 1H), 5.30-5.84 (m, 2H), 4.36-4.51 (m, 2H), 1.38 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 28.16, 43.20, 61.24, 81.59, 111.3, 116.1, 118.4, 126.0, 126.1, 127.9, 128.1, 128.3, 128.9, 129.2, 129.5, 130.4, 130.7, 132.9, 134.2, 141.9, 143.2, 153.6, 167.4,167.6, 169.5, 172.1; HRMS calcd. for $C_{26}H_{24}BrN_3O_5$ $[M + Na]^+$ 560.0797; found 560.0763.

**(*R*)-*tert*-Butyl-1-allyl-3-(2,5-dioxo-1-phenyl-2,5-dihydro-1H-pyrrol-3-yl)-5-iodo-2-oxoindolin-3-ylcarbamate (3k):** White semisolid; yield 63%; $[\alpha]_{20}^{D}$= - 111 (*c* 0.50, $CHCl_3$); 90% ee; HPLC[Chiralpak IA, hexane/*i*-PrOH, 80:20, 1 mL/min, 254 nm, $t_R$ = 7.23 min (minor) and $t_R$ =13.9 min (major)]; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.26-7.71 (m, 7H), 6.80-6.86 (m, 2H), 6.77 (s, 1H), 5.83-6.54 (m, 1H), 5.27-5.81 (m, 2H), 4.44 (dd, *J*= 60.0 Hz, *J*= 15.0 Hz, 2H), 1.38 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 28.14, 43.14, 61.05, 81.58, 85.90, 111.8, 118.4, 126.0, 126.1, 128.2, 128.8, 129.1, 129.8, 130.5, 130.7, 133.7, 134.2, 134.9, 142.6, 143.2, 153.8, 167.4, 167.6, 171.9; HRMS calcd. for $C_{26}H_{24}IN_3O_5$ $[M+Na]^+$ 608.0658; found 608.0690.

**(*R*)-*tert*-Butyl-1-allyl-3-(2,5-dioxo-1-phenyl-2,5-dihydro-1H-pyrrol-3-yl)-5-methoxy-2-oxoindolin-3-ylcarbamate (3l):** White semisolid; yield 35%; $[\alpha]_{20}^{D}$= - 59.7 (*c* 0.50, $CHCl_3$); 95% ee; HPLC[Chiralpak AD-H, hexane/*i*-PrOH, 80:20, 1 mL/min, 254 nm, $t_R$ = 10.2 min (minor) and $t_R$ =30.1 min (major)]; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 6.82-7.46 (m, 8H), 6.49 (s, 1H), 6.13 (s, 1H), 5.84-5.93 (m, 1H), 5.25-5.37 (m, 2H), 4.42 (dd, *J*= 69.3 Hz, *J*= 16.2 Hz, 2H), 3.77 (s, 3H), 1.36 (s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 28.15, 43.17, 55.86, 61.75, 81.23, 110.3, 112.3, 114.6, 118.1, 126.0, 128.1, 128.7, 129.1, 130.9, 136.0, 143.8, 153.9, 156.5, 167.6, 167.7, 172.1; HRMS calcd. for $C_{27}H_{27}N_3O_6$ $[M+Na]^+$ 512.1797; found 512.1792.

**(*R*)-*tert*-Butyl-5-chloro-3-(2,5-dioxo-1-phenyl-2,5-dihydro-1H-pyrrol-3-yl)-1-(2-methylallyl)-2-oxoindolin-3-ylcarbamate (3m):** Brown semisolid; yield 77%; $[\alpha]_{20}^{D}$= -83.1 (*c* 0.50, $CHCl_3$); 98% ee; HPLC[Chiralpak IA, hexane/*i*-PrOH, 80:20, 1 mL/min, 218 nm, $t_R$ = 5.90 min (minor) and $t_R$ = 9.34 min (major)]; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.29-7.62 (m, 8H), 6.85 (d, *J*= 9.0 Hz, 1H), 6.54 (s, 1H), 6.13 (s, 1H), 4.99 (s, 2H), 4.36 (dd, *J*= 60.0 Hz, *J*= 15.0 Hz, 2H), 1.82 (s, 3H), 1.39 (s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 20.06, 28.15, 46.85, 61.28, 81.53, 110.9, 113.2, 125.6, 126.0, 126.1, 128.2, 128.9, 129.1, 129.2, 130.1, 134.2, 138.3, 141.6, 153.8, 167.4, 167.7, 172.3; HRMS calcd. for $C_{27}H_{26}ClN_3O_5$ $[M+Na]^+$ 530.1453; found 530.1435.

**(*R*)-(*E*)-*tert*-Butyl 1-(but-2-enyl)-5-chloro-3-(2,5-dioxo-1-phenyl-2,5-dihydro-1H-pyrrol-3-yl)-2-oxoindolin-3-ylcarbamate (3n):** Yellowish semisolid; yield 55%; $[\alpha]_{20}^{D}$= -84.1 (*c* 0.50, $CHCl_3$); 96% ee; HPLC[Chiralpak IA, hexane/*i*-PrOH, 90:10, 1 mL/min, 254 nm, $t_R$ = 11.5 min (minor) and $t_R$ = 24.1 min (major)]; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.30-7.61 (m, 7H), 6.85 (t, *J*= 6.0 Hz, 1H), 6.53 (s, 1H), 6.13 (s, 1H), 4.99 (s, 2H), 4.35 (dd, *J*= 60.0 Hz, *J*= 15.9 Hz, 2H), 1.38 (s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 17.73, 28.15, 42.73, 61.29, 81.53, 110.8, 123.4, 125.7, 126.0, 126.1, 128.2, 128.9, 129.1, 130.0, 130.2, 141.5, 143.2, 153.9, 167.4, 167.7, 172.0; HRMS calcd. for $C_{27}H_{26}ClN_3O_5$ $[M+Na]^+$ 530.1453; found 530.1449.

**(*R*)-*tert*-Butyl-3-(2,5-dioxo-1-phenyl-2,5-dihydro-1H-pyrrol-3-yl)-2-oxo-1-phenylindolin-3-ylcarbamate (3o):** Brown semisolid; yield 75%; $[\alpha]_{20}^{D}$= -96.8 (*c* 0.50, $CHCl_3$); 92% ee; HPLC[Chiralpak IA, hexane/*i*-PrOH, 80:20, 1 mL/min, 254 nm, $t_R$ = 9.05 min (minor) and $t_R$ = 13.5 min (major)]; $^1$H NMR (500 MHz,$CDCl_3$) $\delta$ 6.87-7.66 (m, 14H), 6.68 (s, 1H), 6.25 (s, 1H), 1.40 (s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 28.19, 61.62, 81.36, 110.2, 123.8, 125.4, 126.1, 126.7, 128.2, 128.6, 128.7, 129.1, 129.8, 130.1, 134.2, 143.9, 154.1, 167.7, 169.5, 172.4; HRMS calcd. for $C_{31}H_{29}N_3O_5$ $[M+Na]^+$ 546.2005; found 546.2416.

**(*R*)-*tert*-Butyl-1-allyl-3-(1-benzyl-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)-2-oxoindolin-3-ylcarbamate (3p):** Light Brown semisolid; yield 64%; $[\alpha]_{20}^{D}$= -67.8 (*c* 0.50, $CHCl_3$); 76% ee; HPLC[Chiralpak IB, hexane/*i*-PrOH, 90:10, 1 mL/min, 254 nm, $t_R$ = 8.39 min (major) and $t_R$ = 11.7 min (minor)]; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.05-7.54 (m, 8H), 6.87 (d, *J*= 6.0 Hz, 1H), 6.29 (s, 1H), 6.14 (s, 1H), 5.83-5.92 (m, 1H), 5.24-5.35 (m, 2H), 4.26-4.67 (m, 4H), 1.31 (s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 28.10, 41.77, 43.00, 61.40, 81.13, 109.7, 118.1, 123.5, 125.1, 127.9, 128.3, 128.4, 128.7, 129.9, 130.8, 142.5, 143.8, 153.9, 168.5, 168.7, 172.5; HRMS calcd. for $C_{27}H_{27}N_3O_5$ $[M+H]^+$ 474.2023; found 474.2037.

**(*R*)-*tert*-Butyl-1-allyl-3-(1-methyl-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)-2-oxoindolin-3-ylcarbamate (3q):** Brown semisolid; yield 30%; $[\alpha]_{20}^{D}$= -79.8 (*c* 0.50, $CHCl_3$); 71% ee; HPLC[Chiralpak IA, hexane/*i*-PrOH, 80:20, 1 mL/min, 254 nm, $t_R$ = 10.8 min (minor) and $t_R$ = 15.5 min (major)]; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.06-7.54 (m, 3H), 6.89 (d, *J*= 9.0 Hz, 1H), 6.34 (s, 1H), 6.11 (s, 1H), 5.86-5.88 (m, 1H), 5.25-5.37 (m, 2H), 4.31-4.58 (m, 2H), 2.97 (s, 3H), 1.33 (s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 28.11, 33.92, 43.03, 61.37, 81.13, 109.7, 118.1, 123.4, 125.1, 127.8, 128.4, 129.9, 130.8, 142.7, 144.0, 153.8, 168.8, 168.9, 172.5; HRMS calcd. for $C_{21}H_{23}N_3O_5$ $[M+Na]^+$ 420.1530; found 420.1530.

**(*R*)-*tert*-Butyl-1-allyl-3-(2,5-dioxo-1-phenethyl-2,5-dihydro-1H-pyrrol-3-yl)-2-oxoindolin-3-ylcarbamate (3r):**

White semisolid; yield 76%; $[\alpha]_{20}^{D}$= -59.3 (*c* 0.50, $CHCl_3$); 70% ee; HPLC[Chiralpak IB, hexane/*i*-PrOH,

90:10, 1 mL/min, 254 nm, $t_R$ = 7.80 min (major) and $t_R$ = 13.2 min (minor)]; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.22-7.48 (m, 8H), 6.87 (s, *J*= 6.0 Hz, 1H), 6.28 (s, 1H), 6.07 (s, 1H), 5.82-5.91 (m, 1H), 5.25-5.39 (m, 2H), 4.42 (dd, *J*= 78.0 Hz, *J*= 18.0 Hz, 2H), 3.66-3.78 (m, 4H), 1.33 (s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 20.53, 28.12, 40.19, 43.01, 67.36, 81.08, 109.6, 123.4, 126.7, 126.8, 128.1, 128.6, 128.7, 128.8, 129.9, 137.4, 137.6, 142.6, 153.8, 169.6, 169.8, 172.9; HRMS calcd. for $C_{28}H_{29}N_3O_5$ [M + Na]+ 510.1999; found 510.1970.

**(*R*)-*tert*-Butyl 1-allyl-3-(1-(naphthalen-1-ylmethyl)-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)-2-oxoindolin-3-ylcarbamate (3s):** White semisolid; yield 79%; $[\alpha]_{20}^{D}$= -67.9 (*c* 0.50, $CHCl_3$); 75% ee; HPLC [Chiralpak IA, hexane/*i*-PrOH, 90:10, 1 mL/min, 254 nm, $t_R$ = 37.1 min (minor) and $t_R$ = 40.1 min (major)]; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.17 (d, *J*= 9.0 Hz, 1H), 6.88-7.83 (m, 10H), 6.30 (s, 1H), 6.11 (s, 1H), 5.82-5.85 (m, 1H), 5.09-5.35 (m, 1H), 4.41 (dd, *J*= 76.8 Hz, *J*= 15.6 Hz, 2H), 1.30 (s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 28.10, 39.63, 43.00, 61.41, 81.13, 109.7, 123.1, 123.5, 125.2, 125.8, 126.6, 128.7, 129.9, 130.8, 142.6, 143.8, 153.9, 168.6, 168.9, 172.5; HRMS calcd. for $C_{31}H_{29}N_3O_5$ [M + Na]$^+$ 546.2005; found 546.2417.

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## Notes and references

*Department of Chemistry, U.G.C. Centre of Advance Studies in Chemistry, Guru Nanak Dev University, Amritsar, India.*
*Fax: (+)91-183-2258820*
*E-mail: sschimni@yahoo.com, sschimni.chem@gndu.ac.in*

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11 CCDC 1037308 (**3g**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.a- c.uk/data_request/cif.