

PALLADIUM CATALYZED CARBONYLATIVE CROSS-COUPLING REACTION OF INDOLYLBORATES WITH PROP-2-YNYL CARBONATES

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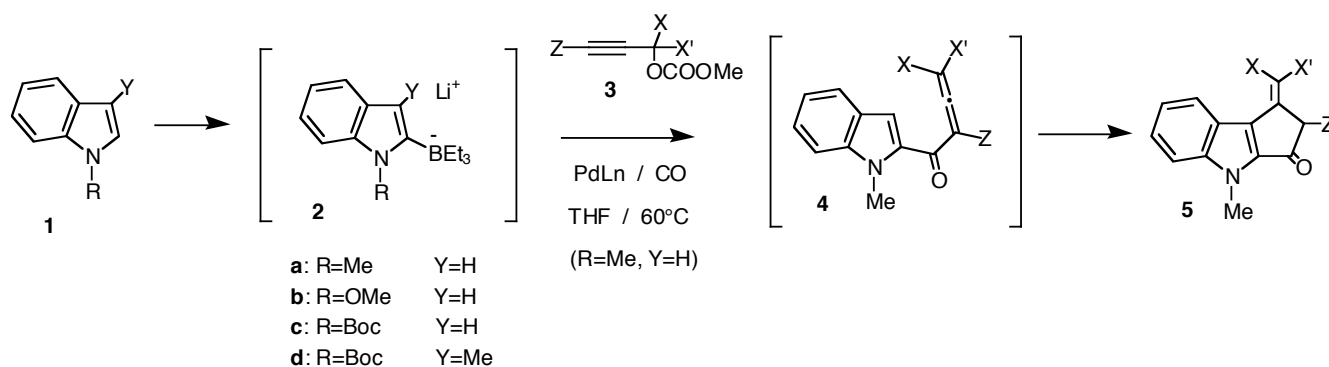
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Abstract – Palladium catalyzed carbonylative cross-coupling reaction of 1-methylindolylborate (**2a**) with prop-2-ynyl carbonates (**3**) produced cyclopenta-[*b*]indole derivatives in a one-pot manner. Hence, the use of indolylborates (**2c, d**) for the reaction with **3** allowed the isolation of indol-2-yl allenyl ketones (**4**).

Transition metals catalyzed cross-coupling reactions have been of current and continuing importance in organic synthetic transformations. In particular, increased attention has been devoted to the application of organoboron compounds to this reaction.¹

In our previous reports, we have presented both the widespread applicability of indolylborates (**2**), derived from indoles (**1**) *in situ*,^{2b} to cross-coupling reactions² and palladium catalyzed carbonylative cross-coupling reaction.³ In this context, we were curious as to whether the carbonylative cross-coupling reaction of indolylborate (**2**) with prop-2-ynyl carbonate (**3**) might offer a versatile approach to functionalized allenyl indol-2-yl ketones, as well. This paper presents the results of our investigation, a part of which has been reported previously.⁴

Initially, indolylborate (**2a**) was treated with **3** in the presence of a catalytic amount of PdCl₂(PPh₃)₂ in THF under a carbon monoxide atmosphere (10 atm) at 60°C for 20 h (Scheme 1).

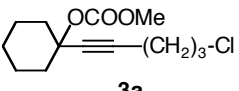
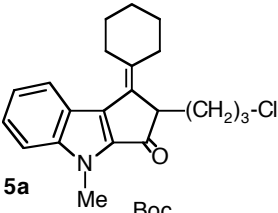
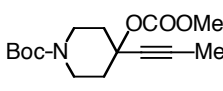
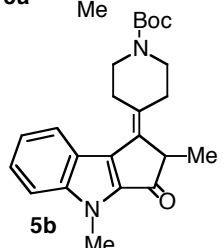
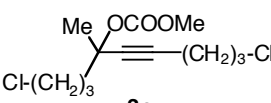
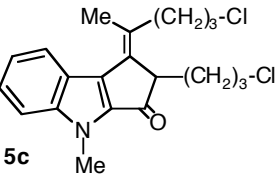
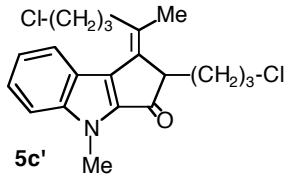
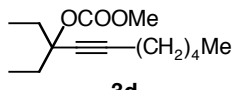
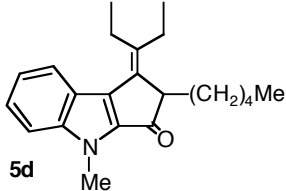


Scheme 1

This reaction proceeded smoothly, and cyclopenta[*b*]indoles (**5**) were obtained in good yields (Table 1). Herein, the intermediary formation of allenyl indolyl ketone (**4**), followed by the 1,4-addition of C-3 carbon in the indole ring to the internal allenic carbon would have to be postulated to accommodate the formation of **5**.

Notably, the employment of **3c** in the reaction with **2c** produced a 1:1 mixture of geometrical isomers (**5c** and **5c'**), which are ascribable to the intermediary generation of allenyl ketone (**4**).⁴

Table 1 Formation of cyclopenta[*b*]indoles (**5**)

3	5	Yield (%) ^a
 <p>3a</p>	 <p>5a</p>	60
 <p>3b</p>	 <p>5b</p>	—
 <p>3c</p>	 <p>5c</p>  <p>5c'</p>	64 ^b
 <p>3d</p>	 <p>5d</p>	68

^a Isolated yields (%) based on **1**.

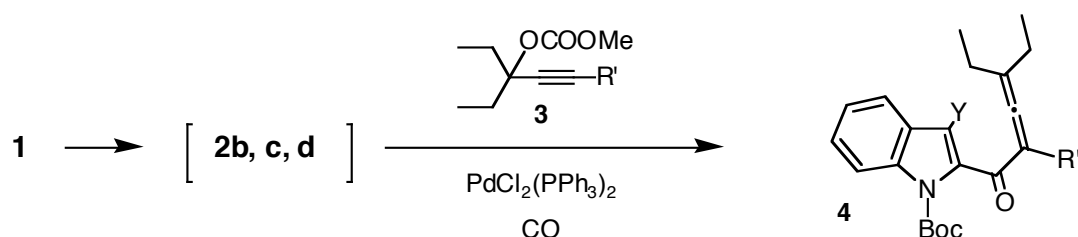
^b a 1:1 mixture

The formation of **5** from **1** in a “one-pot” manner was encouraging, since the expected carbonylative cross-coupling reaction of **2a** with **3e** did not occur. Furthermore, we have sought to develop an adequate set of conditions for the isolation of allenyl indolyl ketone (**4a**). Thereupon, it was anticipated that the presence of an electron-withdrawing group at the nitrogen might lead to the suppression of nucleophilicity of the C-3 carbon in indole ring of **4**, so that allenyl indolyl ketone (**4**) would not react further. Thus, we investigated the reaction using **2b** and **2c**.

Unfortunately, the carbonylation reaction of **2b** with **3d** in the presence of a catalytic amount of

$\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ resulted in the formation of complex mixtures, from which a trace amount of **5e** was isolated. Fortunately, the carbonylation reaction of **2c** with **3d** in the presence of a catalytic amount of $\text{PdCl}_2(\text{PPh}_3)_2$ at 60°C for 20 h under pressurized carbon monoxide (10 atm) afforded the desired allenyl ketone (**4a**) in 26 % yield, and the yield of **4a** increased to 38 % with increased reaction time (40 h). Similar treatment of **2c** with **3e** and **3f** provided **4b** and **4c**, respectively (Table 2). Otherwise, when **2c** was subjected to the reaction with **3d** at a higher temperature (100°C) using toluene as a solvent for 60 h, **5e** was the only isolable product in a 33 % yield.

Table 2 Formation of indol-2-yl allenyl ketones (**4**)



2	3	conditions	4	Yield (%) ^a
2b	3d	THF / 60°C / 40 h	_____ ^b	
2c	3d	THF / 60°C / 40 h	a: $\text{R}' = -(\text{CH}_2)_4\text{-Me}$ $\text{Y} = \text{H}$	38
2c	3d	toluene / 100°C / 60 h	_____ ^c	
2c	3e ($\text{R}' = -(\text{CH}_2)_3\text{-Cl}$)	THF / 60°C / 40 h	b: $\text{R}' = -(\text{CH}_2)_3\text{-Cl}$ $\text{Y} = \text{H}$	38
2c	3f ($\text{R}' = -(\text{CH}_2)_2\text{-OTHP}$)	THF / 60°C / 40 h	c: $\text{R}' = -(\text{CH}_2)_2\text{-OTHP}$ $\text{Y} = \text{H}$	35
2d	3d	THF / 60°C / 40 h	d: $\text{R}' = -(\text{CH}_2)_4\text{-Me}$ $\text{Y} = \text{Me}$	27

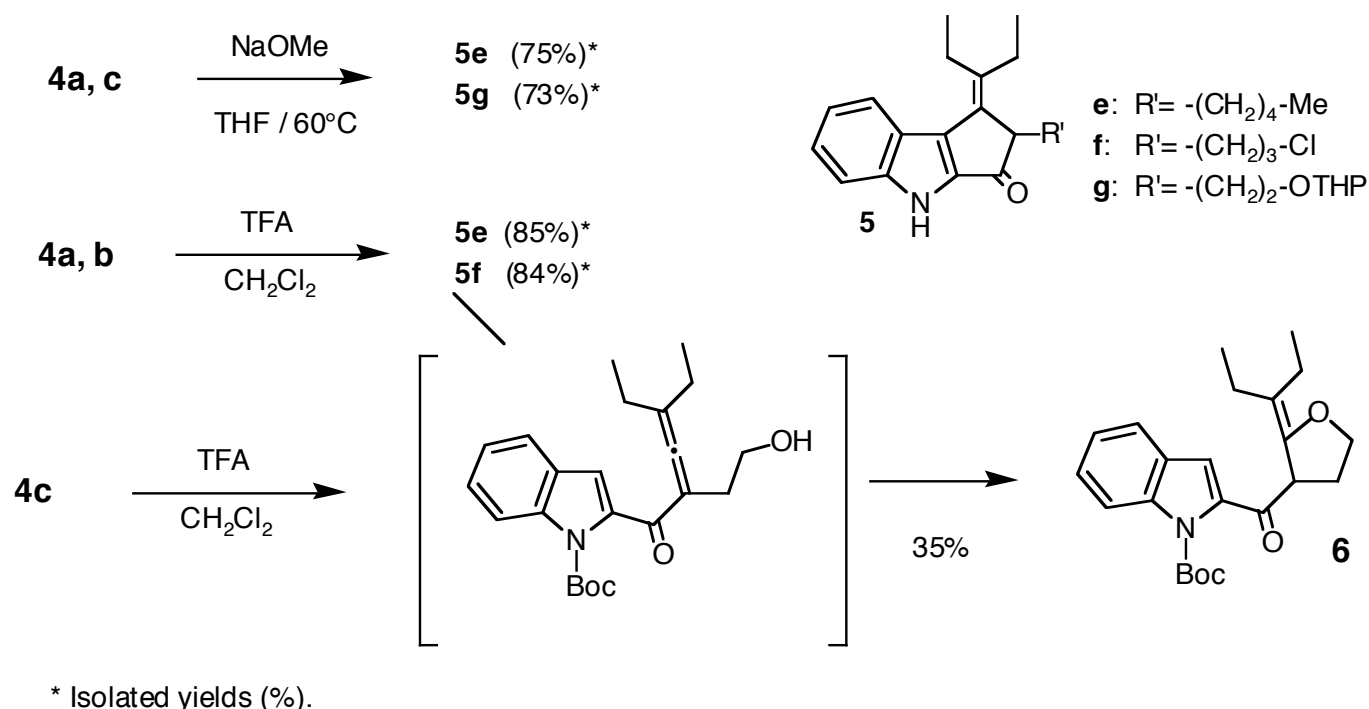
^a Isolated yields (%) based on **1**.
isolated in a 33% yield.

^b **5e** was isolated in a 7 % yield.

^c **5e** was

Next, cyclization of **4a** was attempted under thermal conditions (100°C in toluene for 20 h), resulting in the recovery of unchanged **4a**. Hence, on heating **4a** and **4c** in the presence of NaOMe in THF at 60°C , the cyclization could be promoted to give **5e** and **5g**, respectively (Scheme 2).

Because of the known Lewis acid-promoted ring closure of allenyl phenyl ketones,⁵ **4a** and **4b** were subjected to acidic treatment with TFA in CH_2Cl_2 at room temperature, cleanly producing **5e** and **5f**, respectively. Otherwise, on a similar acidic treatment of **4c**, the deprotection of the THP group in **4c** predominated, followed by the 1,4-addition of OH group to provide **6**.



Scheme 2

We have developed a simple protocol for the formation of allenyl indol-2-yl ketone (**4**) based on the palladium catalyzed carbonylative cross-coupling reaction of indolylborate (**2c**) with prop-2-ynyl esters (**3**).

ACKNOWLEDGEMENTS

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EXPERIMENTAL

Melting points were recorded on a Yamato MP21 and are uncorrected. MS and high-resolution MS were recorded on a Micromass AutoSpec 3100 mass spectrometer. IR spectra were measured on a Hitachi Model 270-30 spectrophotometer. The NMR experiments were performed with a JEOL JNM-LA300 or JNM-EX400 spectrometer, and chemical shifts are expressed in ppm (δ) with TMS as an internal reference. Medium pressure liquid column chromatography (MPLC) and flash column chromatography were performed on silica gel (Silica gel 60N, Kanto Chemical Co., Inc.). HPLC was performed on Mightysil RP-18 GP250-10 (5 μm) (Kanto Chemical Co. Inc.). Dehydrated THF was purchased from Kanto Chemical Co. Inc.

General procedure for the palladium catalyzed carbonylative cross-coupling reaction of **2 with **3**:**

Indolylborates (**2**) were generated from the corresponding indoles (**1**) (2 mmol) in THF (10 mL) under argon atmosphere *in situ*,^{2b} and then, the reaction apparatus was filled with carbon monoxide. Prop-2-ynyl carbonates (**3**) and PdCl₂(PPh₃)₂ (0.05 mmol) were added at once, and carbon monoxide was introduced up to 10 atm. Then, the mixture was heated at 60°C for 20 h. After cooling, the mixture was treated with 10% NaOH (5 mL) and 30% H₂O₂ (1 mL) under ice-cooling. The mixture was diluted with AcOEt (100 mL), and the organic layer was washed with brine and dried over anhydrous MgSO₄. The solvent was removed, and the residue was separated by MPLC with AcOEt-hexane as an eluent to give **4** and **5**. Geometrical isomers (**5c** and **5c'**) were separated by HPLC with MeOH:H₂O=10:1 as an eluent.

tert-Butyl 2-(4-Ethyl-2-pentylhexa-2,3-dienoyl)indole-1-carboxylate (**4a**).

mp 85-86°C (from AcOEt-hexane). IR (CHCl₃): 1736, 1648 cm⁻¹. ¹H-NMR (CDCl₃) δ: 0.90 (t, 3H, *J*=7.5 Hz), 0.92 (t, 6H, *J*=7.5 Hz), 1.30-1.55 (m, 6H), 1.57 (s, 3H), 1.90-2.10 (m, 4H), 2.37 (t, 2H, *J*=7.5 Hz), 6.67 (s, 1H), 7.23 (dt, 1H, *J*=1.0, 7.8 Hz), 7.35 (ddd, 1H, *J*=1.0, 7.8, 8.3 Hz), 7.54 (d, 1H, *J*=7.8 Hz), 8.12 (d, 1H, *J*=8.3 Hz). ¹³C-NMR (CDCl₃) δ: 12.1, 14.0, 22.5, 25.3, 27.2, 27.7, 27.8, 31.6, 84.3, 111.3, 111.9, 112.5, 115.0, 121.6, 123.0, 125.7, 128.0, 136.8, 138.3, 149.3, 188.9, 210.8. MS *m/z*: 409 (M⁺). *Anal.* Calcd for C₂₆H₃₅NO₃: C, 76.24; H, 8.61; N, 3.42. Found: C, 76.20; H, 8.73; N, 3.33.

tert-Butyl 2-[2-(3-Chloropropyl)-4-ethylhexa-2,3-dienoyl]indole-1-carboxylate (**4b**).

mp 54-56°C (from AcOEt-hexane). IR (CHCl₃): 1942, 1730, 1646 cm⁻¹. ¹H-NMR (CDCl₃) δ: 0.92 (t, 6H, *J*=7.3 Hz), 1.59 (s, 9H), 1.90-2.05 (m, 6H), 2.54 (t, 2H, *J*=7.8 Hz), 3.63 (t, 2H, *J*=6.8 Hz), 6.69 (s, 1H), 7.25 (t, 1H, *J*=6.8 Hz), 7.54 (d, 1H, *J*=7.3 Hz), 8.10 (d, 1H, *J*=8.3 Hz). ¹³C-NMR (CDCl₃) δ: 12.2, 25.0, 25.3, 27.9, 31.1, 44.5, 84.5, 110.4, 111.4, 113.3, 115.1, 121.3, 123.1, 125.9, 128.0, 136.7, 138.0, 149.3, 188.6, 210.3. MS *m/z*: 415 (M⁺). *Anal.* Calcd for C₂₄H₃₀NO₃Cl: C, 68.62; H, 7.32; N, 3.34. Found: C, 68.63; H, 7.39; N, 3.20.

tert-Butyl 2-[2-(2-(2*H*-3,4,5,6-Tetrahydropyran-2-yloxy)ethyl-4-ethylhexa-2,3-dienoyl)indole-1-carboxylate (**4c**).

mp 68-69°C (from pet. ether). IR (CHCl₃): 1944, 1744, 1660 cm⁻¹. ¹H-NMR (CDCl₃) δ: 0.93 (t, 3H, *J*=7.3 Hz), 0.93 (t, 3H, *J*=7.3 Hz), 1.45-1.60 (m, 7H), 1.58 (s, 9H), 1.90-2.01 (m, 3H), 2.71 (t, 3H, *J*=7.3 Hz), 3.50-3.60 (m, 2H), 3.85-3.90 (m, 2H), 4.60-4.65 (m, 1H), 6.70 (s, 1H), 7.25 (t, 1H, *J*=7.3 Hz), 7.35 (dt, 1H, *J*=1.0, 7.3 Hz), 7.54 (d, 1H, *J*=7.8 Hz), 8.13 (d, 1H, *J*=9.3 Hz). ¹³C-NMR (CDCl₃) δ: 12.0, 12.1, 19.6, 25.3, 25.5, 26.8, 27.8, 28.0, 30.7, 62.2, 65.7, 84.4, 98.3, 108.5, 111.5, 112.8, 115.1, 121.7, 123.1, 125.8, 128.0, 136.9, 138.1, 149.3, 188.5, 210.9. MS *m/z*: 467 (M⁺). *Anal.* Calcd for C₂₈H₃₇NO₅: C, 71.91; H, 7.98; N, 3.00. Found: C, 72.10; H, 8.40; N, 3.06.

tert-Butyl 2-(4-Ethyl-2-pentylhexa-2,3-dienoyl)-3-methylindole-1-carboxylate (**4d**).

symp. IR (neat): 1940, 1724, 1652 cm⁻¹. ¹H-NMR (CDCl₃) δ: 0.78 (t, 6H, *J*=7.8 Hz), 0.91 (t, 3H, *J*=7.3 Hz), 1.30-1.45 (m, 4H), 1.45-1.55 (m, 2H), 1.59 (s, 9H), 1.70-1.90 (m, 4H), 2.19 (s, 3H), 2.40 (t, 2H, *J*=7.8 Hz), 7.24 (t, 1H, *J*=7.3 Hz), 7.22 (dt, 1H, *J*=1.0, 7.3 Hz), 7.47 (d, 1H, *J*=7.8 Hz), 8.07 (d, 1H, *J*=8.3 Hz).

$J=8.3$ Hz). $^{13}\text{C-NMR}$ (CDCl_3) δ : 8.6, 12.1, 14.0, 22.5, 24.8, 26.8, 27.6, 28.0, 31.6, 84.1, 112.9, 115.3, 117.3, 119.3, 122.7, 125.3, 130.0, 134.2, 135.2, 149.3, 191.3, 209.6. HR-MS m/z : Calcd for $\text{C}_{27}\text{H}_{37}\text{NO}_3$: 423.2773. Found: 423.2769.

2-(3-Chloropropyl)-1-cyclohexylidene-4-methyl-3-oxo-2,3-dihydrocyclopenta[2,1-*b*]indole (**5a**).

mp 83-85°C (from AcOEt-hexane). IR (CHCl_3): 1678 cm^{-1} . $^1\text{H-NMR}$ (CDCl_3) δ : 1.50-2.00 (m, 9H), 2.10-2.23 (m, 1H), 2.30-2.40 (m, 2H), 2.80-2.95 (m, 2H), 3.40-3.60 (m, 3H), 3.95 (s, 3H), 7.21 (t, 1H, $J=7.8$ Hz), 7.37 (d, 1H, $J=7.8$ Hz), 7.44 (t, 1H, $J=8.3$ Hz), 7.99 (d, 1H, $J=8.3$ Hz). $^{13}\text{C-NMR}$ (CDCl_3) δ : 26.4, 28.0, 28.1, 28.2, 29.7, 30.1, 32.3, 33.6, 45.2, 55.1, 111.0, 120.6, 124.4, 124.7, 126.8, 134.0, 139.4, 140.5, 145.3, 194.8. MS m/z : 341 (M^+). Anal. Calcd for $\text{C}_{21}\text{H}_{24}\text{NOCl}$: C, 73.78; H, 7.08; N, 4.10. Found: C, 73.82; H, 7.20; N, 4.28.

tert-Butyl 4-(2,4-Dimethyl-2,3-dihydrocyclopenta[1,2-*b*]indolylidene)piperidine-1-carboxylate (**5b**).

symp. IR (neat): 1676 cm^{-1} . $^1\text{H-NMR}$ (CDCl_3) δ : 1.39 (d, 1H, $J=7.3$ Hz), 1.50 (s, 9H), 2.47 (t, 2H, $J=5.8$ Hz), 2.83-2.95 (m, 1H), 3.00-3.10 (m, 1H), 3.25-3.38 (m, 2H), 3.45 (q, 1H, $J=7.3$ Hz), 3.70-3.90 (m, 2H), 3.96 (s, 3H), 7.23 (t, 1H, $J=7.8$ Hz), 7.39 (d, 1H, $J=8.3$ Hz), 7.45 (t, 1H, $J=7.8$ Hz), 7.96 (d, 1H, $J=8.3$ Hz). $^{13}\text{C-NMR}$ (CDCl_3) δ : 18.1, 28.5, 30.1, 30.8, 32.5, 44.5, 51.3, 79.6, 111.2, 120.8, 121.0, 124.4, 126.8, 127.3, 129.1, 138.6, 138.8, 145.4, 154.8, 195.1. HR-MS m/z : Calcd for $\text{C}_{23}\text{H}_{28}\text{N}_2\text{O}_3$: 380.2098. Found: 380.2117.

(*E*)-1-(5-Chloro-1-methylpentylidene)-2-(3-chloropropyl)-4-methyl-3-oxo-2,3-dihydrocyclopenta[2,1-*b*]indole (**5c**).

mp 83-84°C (from AcOEt-hexane). IR (CHCl_3): 1678 cm^{-1} . $^1\text{H-NMR}$ (CDCl_3) δ : 1.68-1.90 (m, 2H), 1.90-2.15 (m, 3H), 2.15-2.25 (m, 1H), 2.34 (s, 3H), 2.43 (t, 2H, $J=7.0$ Hz), 3.50-3.59 (m, 3H), 3.60-3.70 (m, 2H), 3.95 (s, 3H), 7.21 (t, 1H, $J=7.8$ Hz), 7.38 (d, 1H, $J=8.3$ Hz), 7.44 (t, 1H, $J=8.3$ Hz), 8.12 (d, 1H, $J=8.3$ Hz). $^{13}\text{C-NMR}$ (CDCl_3) δ : 21.3, 27.9, 29.6, 30.2, 31.0, 33.3, 44.8, 45.1, 54.9, 111.0, 120.7, 121.1, 124.8, 126.9, 127.0, 129.1, 139.0, 140.4, 145.3, 194.4. MS m/z : 363 (M^+). Anal. Calcd for $\text{C}_{20}\text{H}_{23}\text{NOCl}_2$: C, 65.93; H, 6.36; N, 3.84. Found: C, 65.78; H, 6.45; N, 3.86.

(*Z*)-1-(5-Chloro-1-methylpentylidene)-2-(3-chloropropyl)-4-methyl-3-oxo-2,3-dihydrocyclopenta[2,1-*b*]indole (**5c'**).

symp. IR (neat): 1690 cm^{-1} . $^1\text{H-NMR}$ (CDCl_3) δ : 1.65-1.90 (m, 2H), 1.90-2.20 (m, 4H), 1.98 (s, 3H), 2.75-2.83 (m, 1H), 2.90-3.00 (m, 1H), 3.49-3.55 (m, 3H), 3.67 (t, 2H, $J=7.0$ Hz), 3.95 (s, 3H), 7.21 (t, 1H, $J=7.8$ Hz), 7.38 (d, 1H, $J=8.3$ Hz), 7.45 (t, 1H, $J=7.8$ Hz), 8.02 (d, 1H, $J=8.3$ Hz). $^{13}\text{C-NMR}$ (CDCl_3) δ : 20.3, 27.9, 28.7, 30.1, 31.6, 34.4, 44.8, 45.1, 55.3, 111.2, 120.7, 121.0, 124.3, 126.9, 127.6, 128.8, 139.2, 139.5, 145.3, 194.6. HR-MS m/z : Calcd for $\text{C}_{20}\text{H}_{23}\text{NOCl}_2$: 363.1155. Found: 363.1143.

1-Ethylpropylidene-4-methyl-2-pentyl-3-oxo-2,3-dihydrocyclopenta[2,1-*b*]indole (**5d**).

symp. IR (neat): 1690 cm^{-1} . $^1\text{H-NMR}$ (CDCl_3) δ : 0.81 (t, 3H, $J=5.0$ Hz), 1.12 (t, 3H, $J=7.8$ Hz), 1.25 (t, 3H, $J=7.8$ Hz), 1.10-1.25 (m, 6H), 1.75-1.85 (m, 1H), 1.95-2.05 (m, 1H), 2.20 (t, 2H, $J=7.8$ Hz), 2.55

2.67 (m, 1H), 2.75-2.85 (m, 1H), 3.44 (dd, 1H, $J=3.4, 7.3$ Hz), 3.96 (s, 3H), 7.22 (t, 1H, $J=7.8$ Hz), 7.37 (d, 1H, $J=8.3$ Hz), 7.43 (t, 1H, $J=7.8$ Hz), 8.00 (d, 1H, $J=8.3$ Hz). ^{13}C -NMR (CDCl_3) δ : 13.1, 14.1, 14.5, 22.4, 24.4, 26.1, 26.3, 30.0, 32.2, 32.5, 55.8, 110.9, 120.7, 121.0, 124.4, 126.6, 127.6, 136.4, 139.4, 140.0, 145.2, 195.5. HR-MS m/z : Calcd for $\text{C}_{22}\text{H}_{29}\text{NO}$: 323.2249. Found: 323.2237.

Treatment of **4a**, **b**, **c** with TFA: General procedure

A mixture of **4a**, **4b**, **4c** (100 mg) and TFA (0.5 mL) in CH_2Cl_2 (20 mL) was stirred at rt for 2 h, and 10% NaOH (10 mL) was poured into the mixture. The mixture was extracted with AcOEt (100 mL), and the extract was washed with water and dried over anhydrous MgSO_4 . The solvent was removed and the residue was separated by MPLC with AcOEt-hexane as an eluent to give **5e**, **5f**, **6**, respectively.

Treatment of **4a**, **c** with NaOMe: General procedure

A mixture of **4a**, **c** (100 mg) and NaOMe (50 mg) in THF (20 mL) was heated at 60°C for 4 h, and the mixture was extracted with AcOEt (100 mL). The extract was washed with water and dried over anhydrous MgSO_4 . The solvent was removed and the residue was separated by MPLC with AcOEt-hexane as an eluent to give **5e**, **g**, respectively.

1-Ethylpropylidene-2-pentyl-3-oxo-2,3-dihydrocyclopenta[2,1-*b*]indole (**5e**).

mp $159\text{--}161^\circ\text{C}$ (from pet. ether). IR (CHCl_3): $3192, 1662\text{ cm}^{-1}$. ^1H -NMR (CDCl_3) δ : 0.79 (t, 3H, $J=6.8$ Hz), 1.15 (t, 3H, $J=7.8$ Hz), 1.27 (t, 3H, $J=7.8$ Hz), 1.10-1.40 (m, 5H), 2.00-2.15 (m, 1H), 2.29-2.40 (m, 2H), 2.33 (q, 2H, $J=7.8$ Hz), 2.60-2.70 (m, 1H), 2.78-2.88 (m, 1H), 3.49-3.54 (m, 1H), 7.21 (t, 1H, $J=7.8$ Hz), 7.41 (t, 1H, $J=7.3$ Hz), 7.57 (d, 1H, $J=8.3$ Hz), 8.00 (d, 1H, $J=8.3$ Hz), 10.3 (br s, 1H). ^{13}C -NMR (CDCl_3) δ : 13.1, 14.0, 14.5, 22.4, 24.3, 26.1, 26.3, 32.2, 32.5, 55.3, 114.0, 121.0, 121.2, 124.3, 127.1, 128.0, 137.7, 139.5, 142.4, 144.7, 195.9. MS m/z : 309 (M^+). Anal. Calcd for $\text{C}_{21}\text{H}_{27}\text{NO}$: C, 81.50; H, 8.80; N, 4.53. Found: C, 81.60; H, 8.93; N, 4.49.

2-(3-Chloropropyl)-1-ethylpropylidene-3-oxo-2,3-dihydrocyclopenta[2,1-*b*]indole (**5f**).

mp $188\text{--}189^\circ\text{C}$ (from MeOH). IR (CHCl_3): $3632, 1660\text{ cm}^{-1}$. ^1H -NMR (CDCl_3) δ : 1.17 (t, 3H, $J=7.8$ Hz), 1.28 (t, 3H, $J=7.8$ Hz), 1.64-1.76 (m, 1H), 1.78-1.90 (m, 1H), 1.90-2.60 (m, 1H), 2.23-2.40 (m, 1H), 2.35 (q, 2H, $J=7.3$ Hz), 2.60-2.70 (m, 1H), 2.78-2.90 (m, 1H), 3.50 (t, 2H, $J=6.8$ Hz), 3.54-3.61 (m, 1H), 7.22 (t, 1H, $J=7.3$ Hz), 7.43 (t, 1H, $J=7.3$ Hz), 7.60 (d, 1H, $J=8.3$ Hz), 8.00 (d, 1H, $J=8.3$ Hz), 10.5 (br s, 1H). ^{13}C -NMR (CDCl_3) δ : 13.1, 14.5, 26.2, 26.3, 27.8, 29.6, 45.2, 54.3, 114.1, 121.2, 124.3, 127.2, 127.4, 138.5, 139.1, 142.6, 144.9, 195.2. MS m/z : 315 (M^+). Anal. Calcd for $\text{C}_{19}\text{H}_{22}\text{NOCl}$: C, 72.35; H, 7.04; N, 4.44. Found: C, 72.09; H, 7.09; N, 4.43.

2-[3-(2*H*-3,4,5,6-Tetrahydropyran-2-yl)propyl]-1-ethylpropylidene-3-oxo-2,3-dihydrocyclopenta[2,1-*b*]indole (**5g**).

mp $138\text{--}139^\circ\text{C}$ (from AcOEt-hexane). IR (CHCl_3): $3640, 1663\text{ cm}^{-1}$. ^1H -NMR (CDCl_3) δ : 1.15 (t, 3H, $J=7.3$ Hz), 1.25-1.60 (m, 4H), 1.27 (t, 3H, $J=7.3$ Hz), 1.60-1.75 (m, 1H), 2.00-2.15 (m, 1H), 2.30-2.50 (m, 2H), 2.56-2.70 (m, 1H), 2.80-2.90 (m, 1H), 2.95-3.20 (m, 1H), 3.22-3.55 (m, 2H), 3.60-3.65 (m, 1H), 7.22 (t, 1H, $J=7.3$ Hz), 7.43 (t, 1H, $J=7.3$ Hz), 7.60 (d, 1H, $J=8.3$ Hz), 8.00 (d, 1H, $J=8.3$ Hz), 10.5 (br s, 1H).

3.65-3.75 (m, 1H), 3.75-3.90 (m, 2H), 4.29 (s, 1H), 4.48 (s, 1H), 7.21 (dt, 1H, $J=1.0, 7.3$ Hz), 7.40 (t, 1H, $J=7.3$ Hz), 7.56 (d, 1H, $J=8.3$ Hz), 7.98 (1H, $J=8.3$ Hz). ^{13}C -NMR (CDCl_3) δ : 13.0, 14.5, 18.8, 19.2, 25.3, 25.4, 25.9, 26.0, 26.3, 30.3, 30.4, 32.4, 32.6, 98.1, 99.0, 114.1, 120.9, 121.2, 121.3, 124.1, 127.1, 127.4, 137.8, 139.1, 139.2, 141.9, 142.0, 144.9, 145.0, 195.5. MS m/z : 367 (M^+). Anal. Calcd for $\text{C}_{23}\text{H}_{29}\text{NO}_3$: C, 75.17; H, 7.95; N, 3.81. Found: C, 75.10; H, 7.99; N, 3.79.

tert-Butyl 2-[(2-Ethylpropylidene-2,3,4,5-tetrahydrofuran-3-yl)carbonyl]indole-1-carboxylate (**6**).

symp. IR (neat): 1732, 1620 cm^{-1} . ^1H -NMR (CDCl_3) δ : 0.67 (t, 6H, $J=7.3$ Hz), 1.20-1.32 (m, 2H), 1.50-1.60 (m, 2H), 1.63 (s, 9H), 2.48-2.51 (m, 1H), 3.14 (t, 2H, $J=9.8$ Hz), 4.58 (t, 2H, $J=9.8$ Hz), 6.80 (s, 1H), 7.28 (t, 1H, $J=6.8$ Hz), 7.40 (t, 1H, $J=7.3$ Hz), 7.59 (d, 1H, $J=7.8$ Hz), 8.21 (d, 1H, $J=8.3$ Hz). ^{13}C -NMR (CDCl_3) δ : 12.0, 24.9, 28.1, 30.9, 50.3, 70.6, 84.4, 113.9, 115.7, 118.4, 121.3, 123.5, 125.8, 127.8, 128.3, 136.8, 149.1, 158.3, 201.1. HR-MS m/z : Calcd for $\text{C}_{23}\text{H}_{29}\text{NO}_4$: 383.2096. Found: 383.2098.

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