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A Concise Access to 2-Allenylindole Derivatives Based on the Palladium Catalyzed Cross-Coupling Reaction of Indolylborates

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Abstract: The palladium catalyzed cross-coupling reaction of trialkyl(indol-2-yl)borates with prop-2-ynyl carbonates was developed for the preparation of 2-allenylindole derivatives. When the reaction of indolylborates with *tert*-prop-2-ynyl carbonates was carried out, 2-allenylindoles were obtained solely. Otherwise, indolylborates reacted with *sec*-prop-2-ynyl carbonates, giving rise to 2-allenylindoles and/or 3-(prop-2-ynyl)-indoles depending on the catalyst used. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords : indolylborate; allenylindole; cross-coupling reaction; prop-2-ynylindole

Interest in natural and synthetic indole derivatives has been focused on their biological and pharmacological activities and has prompted extensive development of synthetic methodology for indole derivatives.[1] Allenic compounds have been characterized as a distinctive class of compounds and various recent reports demonstrate their synthetic versatility.[2] In considering newer synthetic approaches to indole derivatives, the rich chemistry of allenic compounds would have wide-spread utility in the design of processes for the construction of indole derivatives in a convergent manner.[3] Among literature pertaining to the preparation of allenic compounds,[4] the usefulness of prop-2-ynyl halides and esters is well documented by Tsuji et al.[5] Within this context and in connection with our ongoing studies of the use of indolylborate as a potential synthetic intermediate,[6] the cross-coupling methodology with indolylborates and prop-2-ynyl carbonates is of special interest, with the aim of developing a procedure to introduce an allenyl group to the indole ring. We describe herein the palladium catalyzed cross-coupling reaction of indolylborates with prop-2-ynyl carbonates leading to 2-allenylindole derivatives, which has been partly reported in our previous communication.[7]

Indolylborates (**2**), [generated *in situ* from indoles (**1**) and *n*- or *tert*-butyllithium (BuLi), followed by treatment with triethylborane (Et_3B)], were first subjected to the reaction with *tert*-prop-2-ynyl carbonates (**3**, **4**) in the presence of a catalytic amount of a palladium complex (5 mol%) in tetrahydrofuran (THF), leading to the sole formation of 2-allenylindoles (**5**, **6**) (Scheme 1).

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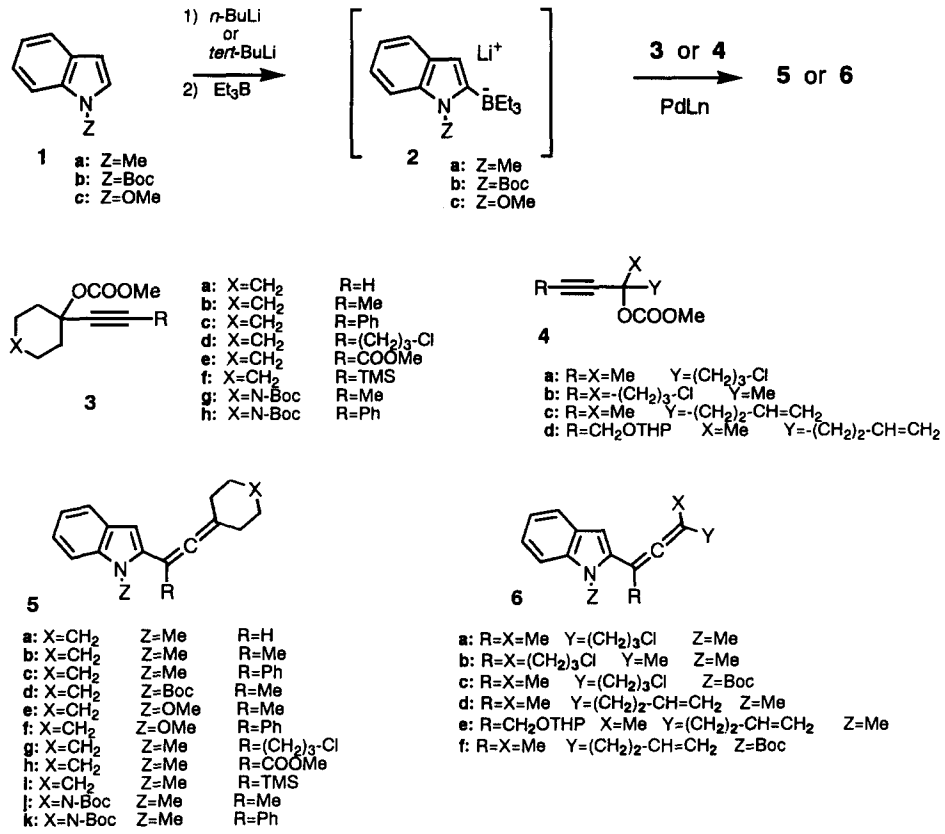


Scheme 1

As can be seen in Table 1, the reaction performed with **2a** appeared to be successful, and carbonates (**3**, **4**) possessing various functional groups were tolerable under the present reaction conditions. A number of Pd(0) and Pd(II) salts could be used as a catalyst, and entered the catalytic cycles, forming **5** and **6** (Table 1).

Treatment of indolylborate (**2b**) with carbonate (**3b**) in the presence of $Pd_2(dba)_3CHCl_3$ produced allenylindole (**5d**) in 50% yield. However, the reaction was markedly suppressed on the subjection of **2b** to **3b** in the presence of $Pd_2(dba)_3CHCl_3$ with 8PPh_3, and **3c** in the presence of either $Pd_2(dba)_3CHCl_3$ or $Pd_2(dba)_3CHCl_3$ with 8PPh_3, which result can be ascribed to the fact that the bulky *tert*-butoxycarbonyl (Boc) group at the 1-position of **2b** sterically interferes with the reaction compared with the cases of **2a**. Indolylborate (**2c**) was also subjected to the reaction with **3b** and **3c**, which provided **5e** and **5f** in moderate yields.

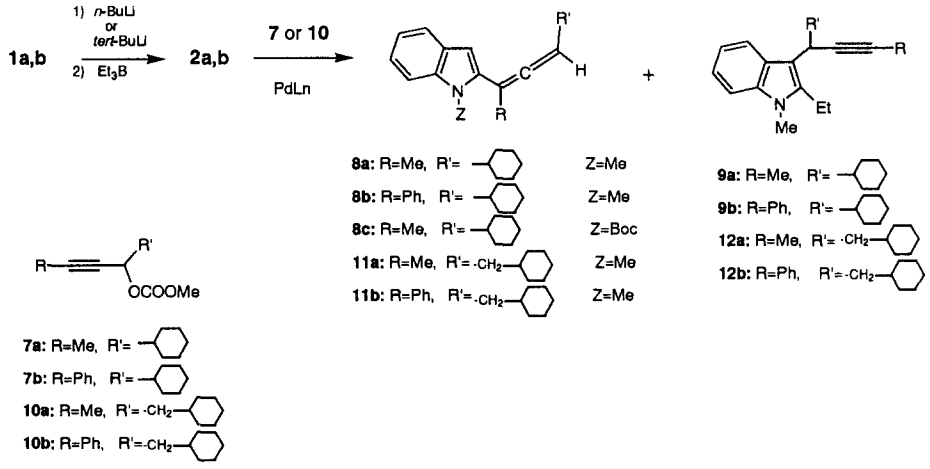
We next examined the reaction of **2a** and **2b** with *sec*-prop-2-ynyl carbonates (**7**, **10**) under similar conditions as above, and the results are summarized in Table 2. As can be seen, the present reaction resulted in the isolation of 2-allenylindoles (**8**, **11**) and/or 3-(prop-2-ynyl)indoles (**9**, **12**), whose ratio was found to depend on the catalyst used. The proportion of **8** or **11** declined in the presence of a palladium complex coordinated by triphenylphosphine, while increased propensity for the formation of **9** or **12** resulted to a greater extent. In

Table 1. Reaction of Indolylborates (**2**) with *tert*-Prop-2-ynyl Carbonates (**3**, **4**)

2	Carbonate	PdLn[a]	Product Compd	Yield(%)[b]	2	Carbonate	PdLn[a]	Product Compd	Yield(%)[b]
2a	**3a**	A	**5a**	57	**2b**	**3b**	D	**5d**	50
2a	**3a**	B	**5a**	29	**2b**	**3c**	C	—	—
2a	**3a**	C	**5a**	60	**2b**	**3c**	D	—	—
2a	**3a**	D	**5a**	42	**2c**	**3b**	C	**5e**	16
2a	**3a**	E	**5a**	28	**2c**	**3b**	D	**5e**	46
2a	**3a**	F	**5a**	34	**2c**	**3c**	C	**5f**	20
2a	**3b**	A	**5b**	44	**2c**	**3c**	D	**5f**	45
2a	**3b**	B	**5b**	45	**2a**	**3d**	B	**5g**	65
2a	**3b**	C	**5b**	49	**2a**	**3e**	B	**5h**	54
2a	**3b**	D	**5b**	51	**2a**	**3f**	B	**5i**	40
2a	**3b**	E	**5b**	28	**2a**	**3g**	B	**5j**	55
2a	**3b**	F	**5b**	44	**2a**	**3h**	B	**5k**	53
2a	**3c**	A	**5c**	64	**2a**	**4a**	D	**6a**	74
2a	**3c**	B	**5c**	63	**2a**	**4b**	D	**6b**	64
2a	**3c**	C	**5c**	63	**2b**	**4a**	D	**6c**	60
2a	**3c**	D	**5c**	65	**2a**	**4c**	B	**6d**	34
2a	**3c**	E	**5c**	51	**2a**	**4d**	B	**6e**	64
2a	**3c**	F	**5c**	60	**2a**	**4e**	B	**6f**	45
2b	**3b**	C	**5d**	10	**2b**	**4c**	D	**6g**	60

[a] A; $Pd(PPh_3)_4$ B; $PdCl_2(PPh_3)_2$ C; $Pd_2(dba)_3CHCl_3$+ $8PPh_3$ D; $Pd_2(dba)_3CHCl_3$
E; $Pd(OAc)_2$ F; $PdCl_2(CH_3CN)_2$ [b] Yields(%) based on indole (**1**)

contrast, treatment of **2b** with carbonate (**7a**) in the presence of $Pd_2(dba)_3CHCl_3$ furnished the sole formation of allenylindole (**8c**) in 51% yield. Further exposure of **2b** to **7a** in the presence of $Pd_2(dba)_3CHCl_3$ with $8PPh_3$ or to **7b** in the presence of $Pd_2(dba)_3CHCl_3$ and $Pd_2(dba)_3CHCl_3$ with $8PPh_3$ did not give either 2-allenylindole or 3-(prop-2-yny)lindole, resulting in the recovery of indole (**1b**).



Scheme 2

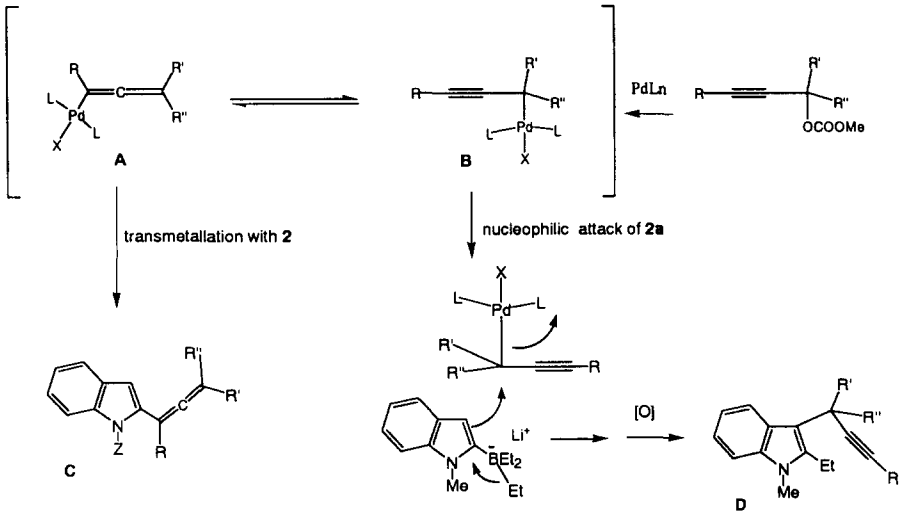
Table 2. Reaction of Indolylborates (**2**) with *sec*-Prop-2-ynyl Carbonates (**7**, **10**)

2	Carbonate	PdLn[a]	Product Compd	Product Compd	2	Carbonate	PdLn[a]	Product Compd	Product Compd
2a	**7a**	A	—	**9a** (30)[b]	**2b**	**7a**	C	—	—
2a	**7a**	B	**8a** (23)[b]	**9a** (39)[b]	**2b**	**7a**	D	**8c** (51)[b]	—
2a	**7a**	C	—	**9a** (30)[b]	**2b**	**7b**	C	—	—
2a	**7a**	D	**8a** (54)[b]	—	**2b**	**7b**	D	—	—
2a	**7a**	E	**8a** (45)[b]	—	**2a**	**10a**	A	—	**12a** (60)[b]
2a	**7a**	F	**8a** (40)[b]	—	**2a**	**10a**	B	**11a** (20)[b]	**12a** (38)[b]
2a	**7b**	A	—	**9b** (30)[b]	**2a**	**10a**	C	—	**12a** (61)[b]
2a	**7b**	B	**8b** (41)[b]	**9b** (5)[b]	**2a**	**10a**	D	**11a** (68)[b]	—
2a	**7b**	C	—	**9b** (27)[b]	**2a**	**10b**	A	—	**12b** (60)[b]
2a	**7b**	D	**8b** (60)[b]	—	**2a**	**10b**	B	**11b** (16)[b]	**12b** (31)[b]
2a	**7b**	E	**8b** (24)[b]	—	**2a**	**10b**	C	—	**12b** (60)[b]
2a	**7b**	F	**8b** (44)[b]	—	**2a**	**10b**	D	**11b** (47)[b]	–

[a] A; $Pd(PPh_3)_4$ B; $PdCl_2(PPh_3)_2$ C; $Pd_2(dba)_3CHCl_3$+ $8PPh_3$ D; $Pd_2(dba)_3CHCl_3$ E; $Pd(OAc)_2$ F; $PdCl_2(CH_3CN)_2$ [b] Yields(%) based on indole (**1**)

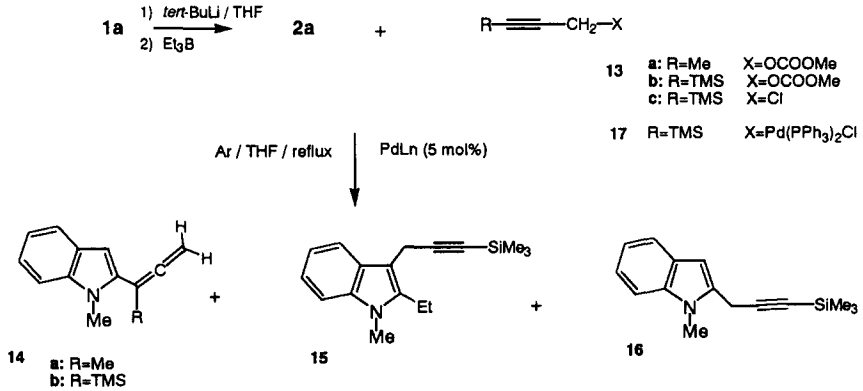
Prop-2-ynyl chloride is known to add oxidatively to $Pd(PPh_3)_4$ to form a σ-allenyl-palladium complex and σ-prop-2-ynylpalladium complex.[8] Most of the known reactions with prop-2-ynyl halides and esters are based on the σ-allenylpalladium complex, leading to the formation of allenic compounds.[5,9] There are, however, only a few reports that are ascribable to the reaction *via* the σ-prop-2-ynylpalladium complex.[10] Hence, the present results can be also rationalized by the reaction course in Scheme 3. The palladium complex undergoes the known oxidative addition to prop-2-ynyl carbonate in a S_N2' manner, coming to equilibrium between allenylpalladium complex (**A**) and prop-2-ynylpalladium complex (**B**), where the spatial size of the substituents of complexes (**A**, **B**) affects the equilibrium.[9] Therefore, the formation of 2-allenylindole (**C**) can be explained by the transmetallation between complex (**A**) and indolylborates (**2**).

On the other hand, the nucleophilic attack of **2** to complex (**B**) accompanied with an intramolecular alkyl migration and an oxidation process leads to 3-(prop-2-ynyl)indole (**D**), which is a rare example of the reaction *via* a σ-prop-2-ynylpalladium complex. In the cases of sterically encumbered *tert*-prop-2-ynyl carbonates (**3**, **4**), quite sluggish as the nucleophilic attack of **2** to complex (**B**) is, the transmetallation process becomes more operative, leading to the exclusive formation of 2-allenylindoles (**5**, **6**). The reaction *via* the equilibrium between complex (**A**) and complex (**B**) arising from *sec*-prop-2-ynyl carbonates (**7**, **10**) is more complicated. The formation of 3-(prop-2-ynyl)indoles (**9**, **12**) preponderates over allenylindoles (**8a**, **8b**, **11**) on reaction of **2a** with **7** and **10** in the presence of a palladium catalyst coordinated by triphenylphosphine. This leads to one to presume that the coordination of triphenylphosphine to palladium tends to form complex (**B**) preferably as the steric repulsion between substituent (R) and PdL_2X, L being PPh_3, in complex (**A**) increases, where complex (**B**) takes part in the nucleophilic attack by **2a** more likely. The participation of palladium in this nucleophilic process was evidenced by the reaction of **2a** with **7a** without a palladium complex, where the formation of 3-(prop-2-ynyl)indole could not be seen, and only the recovery of substantial amounts of 2-ethyl-1-methylindole resulted. The reduced nucleophilicity by the electron-withdrawing effect of a 1-Boc group in **2b** retards the formation of 3-(prop-2-ynyl)indole on reaction with **7**.



Scheme 3

We also tried the reaction of **2a** with *prim*-prop-2-ynyl carbonates (**13**), providing more variable results (Scheme 4). The reaction of **2a** with **13a** gave only allenylindole (**14a**), whereas exposure of **13b** to the reaction with **2a** allowed the isolation of allenylindole (**14b**), 3-(prop-2-ynyl)indole (**15**), and 2-(prop-2-ynyl)indole (**16**). We believe that complex (**B**) arising from **13a** participates in the destructive side process on the nucleophilic reaction with **2a** due to its higher lability compared to complex (**B**) arising from **13b** in which a trimethylsilyl group exerts some influence on the stabilization of the complex (**B**), allowing the interaction between the complex (**B**) and **2a** to form **15** and **16**. The formation of **16** would be understood by the transmetallation between complex (**B**) and **2a**. The results are summarized in Table 3, where chloride (**13c**) reacted as well. Moreover, an equimolar amount of prop-2-ynylpalladium complex (**17**)[9] was simply treated with **2a** in THF at 60°C, giving **14b**, **15**, and **16** in 30%, 13%, and 14% yields, respectively. The observed generation of **14b** demonstrates the propensity of **17** to come to equilibrium between complex (**A**) and complex (**B**) in the reaction medium.



Scheme 4

Table 3. Reaction of Indolylborate (**2a**) with *prim*-Prop-2-ynyl Carbonates (**13a, b**) and Chloride (**13c**)

Carbonate (**13**)	PdLn	Yield (%) **14**	**15**	**16**
13a	$PdCl_2(PPh_3)_2$	38 (**14a**)	----	----
13b	$PdCl_2(PPh_3)_2$	5 (**14b**)	----	30
13b	$Pd_2(dba)_3CHCl_3$	21 (**14b**)	----	13
13b	$Pd_2(dba)_3CHCl_3$+8PPh_3	----	12	----
13c	$PdCl_2(PPh_3)_2$	9 (**14b**)	----	30
13c	$Pd_2(dba)_3CHCl_3$	14 (**14b**)	----	10
13c	$Pd_2(dba)_3CHCl_3$+8PPh_3	----	10	----

In conclusion, the palladium catalyzed cross-coupling of indolylborate (**2**) with prop-2-ynyl carbonates having various functional groups has been demonstrated as an effective procedure for the preparation of 2-allenylindole derivatives which show potential for further transformation leading to various indole derivatives. Work along this line is in progress.

Experimental Section

Melting points were recorded on Yamato MP 21. All melting points and boiling points are uncorrected. MS and high resolution MS (HR-MS) were recorded on Shimadzu GCMS 9100-MK or JEOL JMS DX-303 mass spectrometers. IR spectra were measured on a Hitachi Model 270-30 spectrometer. The NMR experiments were performed with a JEOL JNM-LA300 or JNM-EX400 spectrometer in $CDCl_3$, and chemical shifts are expressed in ppm (δ) with tetramethylsilane (TMS) as an internal reference. The following abbreviations are used: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, br=broad. Medium pressure liquid chromatography (MPLC) was performed on silica gel (Silica gel 60N, Kanto Chemical Co., Inc.). Dehydrated tetrahydrofuran (THF) and diethyl ether were purchased from Kanto Chemical Co., Inc.

Representative Procedure for the Preparation of Prop-2-ynyl Carbonates. Preparation of 1-Methyl-1-prop-1-ynylpent-4-enylmethoxyformate (4c)

n-BuLi (1.6M solution in hexane, 40 ml, 64 mmol) was added to a THF (10 ml) solution of 1-bromo-1-propene (5.4g, 45 mmol) at -78°C under an argon atmosphere, and the mixture was stirred for 2 h.[10] To this solution, was added 5-hexen-2-one (2.9g, 30 mmol), and the mixture was stirred for another 1 h. Then, methyl chloroformate (3.4g, 36 mmol) was added dropwise, and the whole was gradually raised to room temperature over 1 h. The mixture was diluted with EtOAc (50 ml), washed with brine, and dried over $MgSO_4$. The solvent was removed, and the residue was distilled under the reduced pressure to give 5.4g (70%) of **4c**.

Other carbonates (**3, 4, 7, 10**) were prepared from the reaction of lithium acetylides, [generated from 1-bromo-1-propene,[11] phenylacetylene,[4b] 5-chloro-1-pentyne,[4b] tetrahydro-2-(2-propynyloxy)-2H-pyran,[4b] tetrahydro-2-(5-hexynyloxy)-2H-pyran,[4b] and trimethylsilylacetylene[4b] in THF or diethyl ether, respectively], with the corresponding aldehydes or ketones, followed by the treatment with methyl chloroformate. Physicochemical data for these carbonates are summarized in Tables 4 and 5.

Preparation of Methyl 3-(Acetyloxycyclohexyl)prop-2-ynoate (3e)

n-BuLi (1.6M solution in hexane, 56.3 ml, 88mmol) was added to a THF solution of 1-ethynyl-1-cyclohexanol (5g, 40 mmol) at -78°C under an argon atmosphere. After stirring for 30 min, methyl chloroformate (8.4g, 88mmol) was added, and the whole was gradually raised to room temperature over 1 h. The mixture was diluted with EtOAc (50 ml), washed with brine, and dried over $MgSO_4$. The solvent was removed, and the residue was distilled under reduced pressure to give 5.5g (76%) of **3e**. Physicochemical data for **3e** are summarized in Table 4 and 5.

Table 4. Physicochemical Data for Prop-2-ynyl Carbonates (**3**, **4**, **7**, **10**)

Compd	Formula	bp (°C / mmHg)	Analysis (%) or HR-MS m/z (Calcd)
3a	$C_{10}H_{14}O_3$	110 / 15	C: 66.15; H: 7.87 (C: 65.91; H: 7.74)
3b	$C_{11}H_{16}O_3$	130 / 15	196.10870 (196.10988)
3c	$C_{16}H_{18}O_3$	140 / 1	258.12191 (258.12552)
3d	$C_{13}H_{19}ClO_3$	125 / 1	C: 60.55; H: 7.48 (C: 60.35; H: 7.40)
3e	$C_{12}H_{16}O_5$	130 / 1	C: 59.98; H: 6.78 (C: 59.99; H: 6.71)
3f	$C_{13}H_{22}O_3Si$	135 / 15	254.13211 (254.13373)
3g	$C_{15}H_{23}NO_5$	------	281.16170 (281.16261)
3h	$C_{20}H_{25}NO_5$	------	359.17682 (359.17317)
4a	$C_{10}H_{15}ClO_3$	100 / 1	C: 55.18; H: 6.98 (C: 54.92; H: 6.91)
4b	$C_{12}H_{18}Cl_2O_3$	145 / 0.5	C: 51.40; H: 6.46 (C: 51.25; H: 6.45)
4c	$C_{11}H_{16}O_3$	75 / 1	C: 67.20; H: 8.13 (C: 67.32; H: 8.22)
4d	$C_{16}H_{24}O_5$	150 / 0.5	C: 65.14; H: 8.17 (C: 64.84; H: 8.16)
7a	$C_{12}H_{18}O_3$	107 / 1	C: 68.41; H: 9.06 (C: 68.21; H: 9.06)
7b	$C_{17}H_{22}O_3$	160 / 1	272.14427 (272.14116)
10a	$C_{13}H_{20}O_3$	110 / 0.5	C: 69.49; H: 8.94 (C: 69.61; H: 8.98)
10b	$C_{18}H_{22}O_3$	170 / 0.5	C: 75.56; H: 7.88 (C: 75.49; H: 7.74)

Generation of Indolylborates (2) from Indoles (1)

Triethyl(1-methylindol-2-yl)borate (2a): *tert*-BuLi (1.6 M solution in pentane, 1.5 ml, 2.4 mmol) was added to a THF (10 ml) solution of 1-methylindole (**1a**) under an argon atmosphere at 0°C, and the mixture was stirred for 1 h at room temperature. Triethylborane (Et_3B) (1 M solution in hexane, 2.4 ml, 2.4 mmol) was added, and the whole was stirred for another 1 h at room temperature, and the resulting solution was used for the further reaction.

Triethyl(1-tert-butoxycarbonylindol-2-yl)borate (2b): *tert*-BuLi (1.6 M solution in pentane, 1.5 ml, 2.4 mmol) was added to a THF (10 ml) solution of 1-*tert*-butoxy-carbonylindole (**1b**) under an argon atmosphere at -78°C.[12] After stirring for 2 h, Et_3B (1 M solution in hexane, 2.4 ml, 2.4 mmol) was added, and the whole was gradually raised to room temperature over 1 h, and stirred for another 1 h at room temperature, and the resulting solution was used for the further reaction.

Triethyl(1-methoxyindol-2-yl)borate (2c): *n*-BuLi (1.6 M solution in hexane, 1.5 ml, 2.4 mmol) was added to a THF (10 ml) solution of 1-methoxyindole (**1c**)[13] under an argon atmosphere at -30°C. After stirring for 20 min, Et_3B (1 M solution in hexane, 2.4 ml, 2.4 mmol) was added. Then the whole was gradually raised to room temperature over 1 h, and stirred for another 1 h at room temperature, and the resulting solution was subjected to the further reaction.

Table 5. Physicochemical Data for Prop-2-ynyl Carbonates (**3**, **4**, **7**, **10**)

Compd	IR(neat) cm^{-1}	^{1}H-NMR ($CDCl_3$) δ:	^{13}C-NMR ($CDCl_3$) δ:
3a	1754	1.27-1.44 (1H, m), 1.52-1.73 (5H, m), 1.84-1.92 (2H, m), 2.16-2.20 (2H, m), 2.65 (1H, s), 3.78 (3H, s)	22.5, 25.0, 36.8, 54.2, 74.9, 77.2, 83.0, 153.4
3b	1752	1.27-1.36 (1H, m), 1.52-1.67 (6H, m), 1.84 -1.92 (1H, m), 1.89 (3H, s), 2.07-2.15 (2H, m), 3.67 (3H, s)	3.7, 22.7, 25.3, 37.2, 54.1, 78.2, 78.6, 82.7, 153.4
3c	1754	1.25-1.43 (1H, m), 1.54-1.77 (5H, m), 1.89-2.04 (2H, m), 2.24-2.42 (2H, m), 3.78 (3H, s), 7.26-7.34 (3H, m), 7.42-7.49 (2H, m)	22.8, 25.1, 37.1, 54.2, 78.2, 86.7, 88.4, 122.6, 128.2, 128.4, 131.9, 153.3
3d	1752	1.23-1.38 (1H, m), 1.48-1.72 (5H, m), 1.79-1.88 (2H, m), 1.93-2.01 (2H, m), 2.09-2.16 (2H, m), 2.45 (2H, t, J=7Hz), 3.70 (2H, t, J=7Hz), 3.76 (3H, s)	16.2, 22.8, 25.1, 31.3, 37.2, 43.5, 54.1, 78.0, 80.7, 85.2, 153.3
3e	1758 1720	1.31-1.42 (1H, m), 1.53-1.71 (5H, m), 1.88-1.96 (2H, m), 2.17-2.21 (2H, m), 3.78 (3H, s), 3.79 (3H, s)	22.3, 24.8, 36.2, 52.7, 54.6, 76.4, 76.8, 86.2, 153.2, 153.6
3f	1754	0.00(9H, s), 1.06-1.19 (2H, m), 1.32-1.53 (4H, m), 1.61-1.70 (2H, m), 1.94-1.99 (2H, m), 3.58 (3H, s)	0.0, 22.8, 25.2, 37.0, 54.2, 78.1, 91.6, 104.6, 153.2
3g	1754 1692	1.45 (9H, s), 1.89 (3H, s), 1.90-2.00 (2H, m), 2.10-2.20 (2H, m), 3.20-3.35 (2H, m), 3.70-3.80 (2H, m), 3.77 (3H, s)	3.4, 28.1, 36.4, 40.2, 54.1, 75.8, 77.3, 79.5, 83.8, 153.1, 154.3
3h	1752	1.46 (9H, s), 2.00-2.10 (2H, m), 2.25-2.30 (2H, m), 3.30-3.45 (2H, m), 3.79 (3H, s), 3.80-3.90 (2H, m), 7.28-7.35 (3H, m), 7.42-7.50 (2H, m)	28.4, 36.5, 40.4, 54.5, 76.1, 79.8, 86.5, 87.7, 121.9, 128.2, 128.8, 131.9, 153.2, 154.5
4a	1756	1.68 (3H, s), 1.86 (3H, s), 1.89-2.06 (4H, m), 2.22-2.29 (2H, m), 3.75 (3H, s)	3.6, 26.7, 27.7, 39.5, 44.8, 54.2, 77.2, 78.3, 82.3, 153.4
4b	1754	1.70 (3H, s), 1.89-2.09 (6H, m), 2.42 (2H, t, J=7Hz), 3.52-3.68(4H, m), 3.75 (3H, s)	15.9, 26.5, 27.5, 31.0, 39.0, 43.3, 44.5, 54.1, 76.8, 80.2, 84.6, 153.2
4c	1754	1.69 (3H, s), 1.83-1.91 (1H, m), 1.87 (s, 3H), 1.99-2.07 (1H, m), 2.22-2.29 (2H, m), 3.75 (3H, s), 4.98 (1H, qd, J=1.5, 10Hz), 5.05 (1H, qd, J=1.5, 17Hz), 5.80-5.87 (1H, m)	3.6, 26.6, 28.6, 40.9, 54.2, 77.6, 78.6, 82.1, 114.8, 137.7, 153.5
4d	1754	1.52-1.65 (4H, m), 1.71 (3H, s), 1.73-1.94 (3H, m), 2.01-2.09 (1H, m), 2.19-2.34 (2H, m), 3.50-3.56 (1H, m), 3.75 (3H, s), 3.77 (1H, t, J=1.5Hz), 4.31 (2H, s), 4.84 (1H, s), 4.97 (1H, d, J=10Hz), 5.06 (1H, d, J=17Hz), 5.77-5.87 (1H, m)	19.1, 25.4, 26.3, 28.5, 30.3, 40.6, 54.1, 54.3, 62.0, 77.4, 82.1, 85.1, 96.5, 115.0, 137.5, 153.4
7a	1756	1.02-1.32 (5H, m), 1.63-1.90 (6H, m), 1.86 (3H, d, J=2Hz), 3.79 (3H, s), 4.99-5.03 (1H, m)	3.6, 25.7, 25.8, 26.2, 28.1, 28.4, 42.2, 54.8, 73.1, 75.1, 83.2, 155.3
7b	1746	1.12-1.31 (5H, m), 1.59-1.95 (6H, m), 3.82 (3H, s), 5.29 (1H, d, J=6Hz), 7.28-7.34 (3H, m), 7.43-7.47 (2H, m)	25.7, 25.8, 26.1, 28.1, 42.1, 54.9, 73.0, 84.9, 86.8, 122.3,128.2, 128.3, 128.6, 131.9, 155.2
10a	1750	0.87-0.99 (2H, m), 1.08-1.30 (3H, m), 1.41-1.77 (8H, m), 1.84 (3H, t, J=3Hz), 3.79 (3H, s), 5.20-5.30 (1H, m)	3.4, 25.9, 26.3, 32.8, 32.9, 33.7, 42.4, 54.6, 66.9, 76.4, 82.3, 155.0
10b	1750	0.95-1.04 (2H, m), 1.14-1.32 (3H, m), 1.51-1.91 (8H, m), 3.81 (3H, s), 5.53 (1H, t, J=7Hz), 7.25-7.34 (3H, m), 7.40-7.45 (2H, m)	26.0, 26.1, 26.3, 33.0, 33.1, 34.0, 42.3, 54.8, 67.0, 86.0, 86.2, 122.2, 128.2, 128.6, 131.8, 155.1

General Procedure for the Palladium Catalyzed Cross-Coupling Reaction of Indolylborates (2) with Prop-2-ynyl Carbonates

To a THF solution of indolylborates (**2**), generated *in situ* under an argon atmosphere as above, was added prop-2-ynyl carbonates (1.5 equiv) and palladium salt (0.1 equiv), and the mixture was heated at 60°C for 30 min. The reaction mixture was treated with 10% NaOH (10 ml) and 30% H_2O_2 (2 ml) under ice-cooling for 10 min. The mixture was diluted with EtOAc (50 ml), washed with brine, and dried over $MgSO_4$. The solvent was removed, and the residue was separated by MPLC with hexane-EtOAc (200:1) as an eluent to give **5**, **6**, **8**, **9**, **11**, **12**, **14**, **15**, and **16**.

2-(2-Cyclohexylidenevinyl)-1-methylindole (5a): mp 81-82°C. ^{1}H-NMR ($CDCl_3$) δ: 1.50-1.80 (6H, m), 2.20-2.30 (4H, m), 3.77 (3H, s), 6.20-6.25 (1H, s), 6.41 (1H, s), 7.05 (1H, dt, J=1, 6.8 Hz), 7.15 (1H, dt, J=1, 6.8 Hz), 7.25 (1H, d, J=7.8 Hz), 7.51 (1H, d, J=8.3 Hz). ^{13}C-NMR ($CDCl_3$) δ: 25.9, 26.9, 30.2, 31.3, 83.6, 100.7, 105.0, 108.7, 119.4, 119.8, 121.0, 127.9, 134.5, 138.4, 200.5. *Anal.* Calcd for $C_{17}H_{19}N$: C, 86.03; H, 8.07; N, 5.90. Found: C, 85.93; H, 8.30; N, 5.89.

2-(2-Cyclohexylidene-1-methylvinyl)-1-methylindole (5b): mp 90-91°C. ^{1}H-NMR ($CDCl_3$) δ: 1.60-1.75 (6H, m), 2.13 (3H, s), 2.15-2.30 (4H, m), 3.75 (3H, s), 6.42 (1H, s), 7.05 (1H, ddd, J=1, 6.8, 7.8 Hz), 7.16 (1H, ddd, J=1, 6.8, 7.8 Hz), 7.25 (1H, d, J=8.3 Hz), 7.52 (1H, d, J=7.8 Hz). ^{13}C-NMR ($CDCl_3$) δ: 20.2, 25.9, 26.8, 31.2, 31.7, 91.1, 100.0, 103.0, 108.8, 119.9, 121.2, 127.6, 137.8, 138.4, 199.0. *Anal.* Calcd for $C_{18}H_{21}N$: C, 86.00; H, 8.42; N, 5.57. Found: C, 85.94; H, 8.51; N, 5.38.

2-(2-Cyclohexylidene-1-phenylvinyl)-1-methylindole (5c): mp 108-109°C. ^{1}H-NMR ($CDCl_3$) δ: 1.50-1.80 (6H, m), 2.20-2.45 (4H, m), 3.62 (3H, s), 6.43 (1H, s), 7.10 (1H, t, J=6.8 Hz), 7.20-7.35 (7H, m), 7.58 (1H, d, J=7.8 Hz). ^{13}C-NMR ($CDCl_3$) δ: 25.9, 27.3, 30.6, 31.2, 98.7, 102.4, 105.5, 109.2, 119.4, 120.3, 121.2, 126.7, 127.1, 127.9, 128.3, 136.5, 137.7, 137.8, 200.7. *Anal.* Calcd for $C_{23}H_{23}N$: C, 88.13; H, 7.40; N, 4.47. Found: C, 88.37; H, 7.39; N, 4.36.

***tert*-Butyl 2-(2-Cyclohexylidene-1-methylvinyl)indole-1-carboxylate (5d)**: mp 95-96°C. IR ($CHCl_3$) : 1730 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.50-1.70 (6H, m), 1.64 (9H, s), 2.02 (3H, s), 2.08-2.30 (4H, m), 6.38 (1H, s), 7.10-7.35 (2H, m), 7.43 (1H, d, J=7.8 Hz), 8.07 (1H, d, J=8.3 Hz). ^{13}C-NMR ($CDCl_3$) δ: 20.8, 26.1, 27.4, 28.0, 31.4, 83.5, 92.9, 102.3, 108.3, 115.2, 120.1, 122.6, 123.6, 129.4, 139.8, 198.2. *Anal.* Calcd for $C_{22}H_{27}NO_2$: C, 78.30; H, 8.07; N, 4.15. Found: C, 78.20; H, 8.17; N, 4.22.

2-(2-Cyclohexylidene-1-methylvinyl)-1-methoxyindole (5e): ^{1}H-NMR ($CDCl_3$) δ: 1.50-1.80 (6H, m), 2.11 (3H, s), 2.20-2.38 (4H, m), 3.89 (3H, s), 6.22 (1H, s), 7.05 (1H, t, J=6.8 Hz), 7.17 (1H, t, J=7.8 Hz), 7.35 (1H, d, J=7.8 Hz), 7.49 (1H, dd, J=1, 8.3 Hz). ^{13}C-NMR ($CDCl_3$) δ: 14.1, 19.3, 22.6, 26.1, 27.1, 31.6, 64.1, 88.8, 96.9, 102.8, 107.9, 120.0, 120.2, 122.0, 123.8, 134.5, 137.7, 199.7 High-resolution MS m/z: Calcd for $C_{18}H_{21}NO$: 267.1622. Found: 267.1657.

2-(2-Cyclohexylidene-1-phenylvinyl)-1-methoxyindole (5f): ^{1}H-NMR ($CDCl_3$) δ: 1.40-1.80 (6H, m), 2.20-2.40 (4H, m), 3.88 (3H, s), 6.24 (1H, s), 7.07 (1H, dt J=1, 6.8 Hz), 7.16-7.26 (2H, m), 7.28-7.35 (2H, m), 7.38-7.48 (3H, m), 7.50 (1H, d, J=8.3 Hz). ^{13}C-NMR ($CDCl_3$) δ: 26.0, 27.2, 31.2, 64.6, 97.3, 99.4, 105.5, 108.2, 120.1, 120.5, 122.1, 123.9, 126.9, 127.7, 128.2, 132.9, 133.9, 137.6, 201.3. High-resolution MS m/z: Calcd for $C_{23}H_{23}NO$: 329.1778. Found: 329.1745.

2-[1-(3-Chloropropyl)-2-cyclohexylidenevinyl]-1-methylindole (5g): ^{1}H-NMR ($CDCl_3$) δ: 1.50-1.70 (6H, m), 2.00-2.10 (2H, m), 2.15-2.30 (4H, m), 2.59 (2H, t, J=7 Hz), 3.60(2H, t, J=7 Hz), 3.72 (3H, s), 6.44 (1H, s), 7.05 (1H, dt, J=1, 6.8 Hz), 7.16 (1H, dt, J=1, 6.8 Hz), 7.25 (1H, d, J=7.8 Hz), 7.54 (1H, d, J=7.8 Hz). ^{13}C-NMR ($CDCl_3$) δ: 25.9, 26.9, 29.8, 30.9, 31.1, 31.6, 44.4, 94.6, 99.9, 105.3, 108.9, 119.4, 120.0, 121.4, 127.6, 136.9, 138.3, 198.4. High-resolution MS m/z : Calcd for $C_{20}H_{24}ClN$: 313.1596. Found: 313.1588.

Methyl 3-Cyclohexylidene-2-(1-methylindol-2-yl)prop-2-enoate (5h): IR (neat) : 1720 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.50-1.80 (6H, m), 2.20-2.40 (4H, m), 3.66 (3H, s), 3.79 (3H, s), 6.57 (1H, s), 7.08 (1H, dt, J=1, 6.8 Hz), 7.19 (1H, dt, J=1, 6.8 Hz), 7.29 (1H, d, J=7.8 Hz), 7.58 (1H, d, J=7.8 Hz). ^{13}C-

NMR ($CDCl_3$) δ: 25.6, 26.6, 30.3, 30.6, 103.0, 106.5, 109.2, 119.5, 120.5, 121.6, 127.6, 132.7, 137.7, 166.7, 207.4. High-resolution MS m/z : Calcd for $C_{19}H_{21}NO_2$: 295.1571. Found: 295.1543

4-Cyclohexylidene-2,2-dimethyl-3-(1-methylindol-2-yl)-2-silabut-3-ene (5i): mp 92-93°C. IR ($CHCl_3$) : 1932 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.23 (9H, s), 1.50-1.80 (6H, m), 2.10-2.30 (4H, m), 3.71 (3H, s), 6.31 (1H, s), 7.05 (1H, dt, J=1, 6.8 Hz), 7.13 (1H, dt, J=1, 6.8 Hz), 7.25 (1H, d, J=8.3 Hz), 7.52 (1H, J=7.8 Hz). ^{13}C-NMR ($CDCl_3$) δ: 0.1, 26.4, 27.3, 31.0, 31.1, 90.5, 97.5, 101.0, 109.3, 119.6, 120.1, 121.3, 128.4, 136.6, 138.1, 204.8. *Anal.* Calcd for $C_{20}H_{27}NSi$: C, 77.61; H, 8.79; N, 4.52. Found: C, 77.70; H, 8.92; N, 4.59.

***tert*-Butyl 4-[2-(1-Methylindol-2-yl)prop-1-enylidene]piperidine-1-carboxylate (5j)**: mp 109-110°C. IR ($CHCl_3$) : 1682 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.48 (9H, s), 2.16 (3H, s), 2.20-2.40 (4H, m), 3.40-3.60(4H, m), 3.74 (3H, s), 6.46 (1H, s), 7.06 (1H, t, J=6.8 Hz), 7.18 (1H, t, J=6.8 Hz), 7.26 (1H, d, J=8.3 Hz), 7.55 (1H, d, J=7.8 Hz). ^{13}C-NMR ($CDCl_3$) δ: 20.3, 28.4, 30.9, 31.3, 44.4, 79.7, 92.6, 99.4, 100.7, 108.9, 119.5, 120.1, 121.6, 127.5, 137.1, 138.5, 154.7, 199.6. *Anal.* Calcd for $C_{22}H_{28}N_2O_2$: C, 74.96; H, 8.01; N, 7.95. Found: C, 74.80; H, 7.98; N, 7.75.

***tert*-Butyl 4-[2-(1-Methylindol-2-yl)-2-phenylvinylidene]piperidine-1-carboxylate (5k)**: IR (neat) : 1688 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.48 (9H, s), 2.40-2.50 (4H, m), 3.45-3.58 (2H, m), 3.60-3.70 (2H, m), 3.60 (3H, s), 6.45 (1H, s), 7.11 (1H, t, J=6.8 Hz), 7.20-7.28 (2H, m), 7.28-7.36 (5H, m), 7.59 (1H, d, J=7.8 Hz). ^{13}C-NMR ($CDCl_3$) δ: 28.4, 30.4, 30.7, 44.8, 79.7, 100.2, 101.7, 102.8, 109.3, 119.6, 120.4, 121.5, 127.1, 127.2, 127.7, 128.4, 135.7, 137.0, 137.8, 154.5, 201.0. High-resolution MS m/z : Calcd for $C_{27}H_{30}N_2O_2$: 414.2305. Found: 414.2336.

2-(6-Chloro-1,3-dimethylhexa-1,2-dienyl)-1-methylindole (6a): ^{1}H-NMR ($CDCl_3$) δ: 1.83 (3H, s), 1.88-1.97 (2H, m), 2.14 (3H, s), 2.15-2.30 (2H, m), 3.54 (2H, t, J=6.5 Hz), 3.72 (3H, s), 6.44 (1H, s), 7.06 (1H, t, J=6.8 Hz), 7.18 (1H, t, J=6.8 Hz), 7.26 (1H, d, J=8.3 Hz), 7.55 (1H, d, J=7.8 Hz). ^{13}C-NMR ($CDCl_3$) δ: 19.5, 19.9, 30.4, 31.1, 31.5, 44.5, 93.6, 99.6, 100.5, 108.9, 119.4, 120.0, 121.5, 127.5, 137.2, 138.5, 201.7. High-resolution MS m/z : Calcd for $C_{17}H_{20}ClN$: 273.1283. Found: 273.1292.

2-[6-Chloro-1-(3-chloropropyl)-3-methylhexa-1,2-dienyl]-1-methylindole (6b): ^{1}H-NMR ($CDCl_3$) δ: 1.81 (3H, s), 1.80-2.05 (4H, m), 2.10-2.20 (2H, m), 2.58 (2H, t, J=7.5 Hz), 3.47 (2H, t, J=6.4 Hz), 3.56 (2H, t, J=7.5 Hz, 3.66 (3H, s), 6.44 (1H, s), 7.05 (1H, t, J=6.8 Hz), 7.16 (1H, dt, J=1, 6.8 Hz), 7.23 (1H, d, J=7.8 Hz), 7.53 (1H, d, J=7.8 Hz). ^{13}C-NMR ($CDCl_3$) δ: 19.2, 30.1, 30.3, 30.9, 31.0, 31.4, 44.3, 44.4, 97.0, 100.3, 101.5, 108.9, 119.4, 120.0, 121.5, 127.5, 136.1, 138.3, 201.3. High-resolution MS m/z : Calcd for $C_{19}H_{23}Cl_2N$: 335.1206. Found: 335.1205.

***tert*-Butyl 2-(6-Chloro-1,3-dimethylhexa-1,2-dienyl)indole-1-carboxylate (6c)**: IR (neat) : 1732 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.67 (9H, s), 1.75 (3H, s), 1.90-2.03 (2H, m), 2.10-2.20 (2H, m), 3.55 (2H, t, J=6 Hz), 6.41 (1H, s), 7.10-7.30 (2H, m), 7.46 (1H, dt, J=1, 7.8 Hz), 8.05 (1H, dd, J=1, 8.3 Hz). ^{13}C-NMR ($CDCl_3$) δ: 19.0, 20.4, 28.1, 30.5, 31.2, 44.6, 83.7, 95.5, 98.2, 108.3, 115.2, 120.2, 122.6, 123.7, 129.3, 137.0, 139.1, 149.9, 201.0. High-resolution MS m/z : Calcd for $C_{21}H_{26}ClNO_2$: 302.0947. Found: 302.0957.

2-(1,3-Dimethylhepta-1,2,6-trienyl)-1-methylindole (6d): ^{1}H-NMR ($CDCl_3$) δ: 1.80 (3H, s), 2.12 (3H, s), 2.10-2.30 (4H, m), 3.69 (3H, s), 4.94 (1H, d, J=10 Hz), 4.97 (1H, d, J=17 Hz), 5.70-5.90 (1H, m), 6.42 (1H, s), 7.05 (1H, dt, J=1, 6.8 Hz), 7.13 (1H, dt, J=1, 6.8 Hz), 7.23 (1H, d, J=8.3 Hz), 7.54 (1H, d, J=7.8 Hz). ^{13}C-NMR ($CDCl_3$) δ: 19.4, 20.0, 31.7, 33.9, 93.2, 100.3, 100.4, 108.8, 114.9, 119.3, 120.0,

121.4, 127.7, 137.6, 138.1, 138.6, 202.1. High-resolution MS m/z : Calcd for $C_{18}H_{21}N$: 251.1672. Found: 251.1674.

2-[4-Methyl-2-(1-methylindol-2-yl)octa-2,3,7-trienyloxy]perhydro-2H-pyran (6e): ^{1}H-NMR ($CDCl_3$) δ: 1.40-1.90 (6H, m), 1.84 (3H, s), 2.10-2.30 (4H, m), 3.43-3.60 (4H, m), 3.73 (3H, s), 3.85-4.00 (1H, m), 4.41 (1H, t, J=12 Hz), 4.56 (1H, t, J=12 Hz), 4.75-4.83 (1H, m), 4.93 (1H, d, J=10 Hz), 5.01 (1H, d, J=16 Hz), 5.70-5.90 (1H, m), 6.65 (1H, s), 7.06 (1H, dt, J=1, 6.8 Hz), 7.18 (1H, dt, J=1, 6.8 Hz), 7.27 (1H, d, J=8.3 Hz), 7.55 (1H, d, J=7.8 Hz). ^{13}C-NMR ($CDCl_3$) δ: 19.1, 19.2, 19.4, 19.5, 25.5, 30.7, 31.1, 31.7, 33.7, 33.8, 62.1, 62.2, 68.5, 68.6, 95.6, 95.7, 97.2, 97.6, 100.8, 100.9, 101.9, 102.1, 109.0, 115.0, 119.4, 120.3, 121.5, 127.8, 135.1, 137.9, 138.0, 138.4, 202.7, 202.9. High-resolution MS m/z : Calcd for $C_{23}H_{29}NO_2$: 351.2196. Found: 351.2209.

***tert*-Butyl 2-(1,3-Dimethylhepta-1,2,6-trienyl)indole-1-carboxylate (6f)**: IR (neat): 1732 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.67 (9H, s), 1.75 (3H, s), 2.01 (3H, s), 2.00-2.20 (2H, m), 2.20-2.30 (2H, m), 4.95 (1H, d, J=10 Hz), 5.03 (1H, dd, J=1.5, 17 Hz), 5.80-5.95 (1H, m), 6.41 (1H, s), 7.15-7.30 (2H, m), 7.46 (1H, d, J=7.8 Hz), 8.06 (1H, d, J=8.3 Hz). ^{13}C-NMR ($CDCl_3$) δ: 18.9, 20.5, 28.1, 31.9, 33.7, 83.6, 94.9, 99.1, 108.2, 114.5, 115.2, 120.1, 122.6, 123.6, 125.0, 129.3, 137.1, 138.4, 139.5, 201.3. High-resolution MS m/z : Calcd for $C_{21}H_{25}NO_2$: 282.1493. Found: 282.1504.

2-(3-Cyclohexyl-1-methylpropa-1,2-dienyl)-1-methylindole (8a): ^{1}H-NMR ($CDCl_3$) δ: 1.10-1.23 (3H, m), 1.23-1.35 (2H, m), 1.60-1.67 (1H, m), 1.68-1.76 (2H, m), 1.76-1.85 (2H, m), 2.05-2.20 (1H, m), 2.16 (3H, d, J=3 Hz), 3.78 (3H, s), 5.40-5.45 (1H, m), 6.44 (1H, s), 7.06 (1H, t, J=6.8 Hz), 7.17 (1H, ddd, J=1, 6.8, 7.8 Hz), 7.26 (1H, d, J=8.3 Hz), 7.55 (1H, d, J=7.8 Hz). ^{13}C-NMR ($CDCl_3$) δ: 20.3, 25.9, 26.1, 31.5, 32.8, 32.9, 38.1, 94.4, 98.8, 100.4, 108.9, 119.3, 120.0, 121.5, 127.5, 136.9, 138.6, 203.5. High-resolution MS m/z : Calcd for $C_{19}H_{23}N$: 265.1829. Found: 265.1826.

2-(3-Cyclohexyl-1-phenylpropa-1,2-dienyl)-1-methylindole (8b): ^{1}H-NMR ($CDCl_3$) δ: 1.10-1.38 (5H, m), 1.60-1.70 (1H, m), 1.70-1.80 (2H, m), 1.83-1.95 (2H, m), 2.15-2.28 (1H, m), 357 (3H, s), 5.69 (1H, d, J=6 Hz), 6.49 (1H, s), 7.11 (1H, t, J=6.8 Hz), 7.13-7.25 (2H, m), 7.25-7.40 (5H, m), 7.60 (1H, d, J=7.8 Hz). ^{13}C-NMR ($CDCl_3$) δ: 25.9, 30.6, 32.9, 33.0, 37.8, 100.1, 101.8, 102.5, 109.2, 119.5, 120.4, 121.3, 126.6, 126.9, 127.9, 128.4, 135.7, 136.7, 137.8, 204.7. High-resolution MS m/z : Calcd for $C_{24}H_{25}N$: 327.1985. Found: 327.1983.

***tert*-Butyl 2-(3-Cyclohexyl-1-methylpropa-1,2-dienyl)indole-1-carboxylate (8c)**: ^{1}H-NMR ($CDCl_3$) δ: 1.00-1.50 (6H, m), 1.41 (9H, s), 1.50-1.90 (4H, m), 2.06 (3H, s), 5.20-5.30 (1H, m), 6.53 (1H, s), 7.10-7.30 (2H, m), 7.45 (1H, d, J=7.8 Hz), 8.08 (1H, d, J=8.3 Hz). ^{13}C-NMR ($CDCl_3$) δ: 20.4, 26.0, 28.1, 33.1, 37.5, 83.5, 96.2, 97.1, 108.3, 115.1, 120.1, 122.6, 123.1, 129.3, 137.1, 138.8, 149.9, 202.8. High-resolution MS m/z : Calcd for $C_{23}H_{29}NO_2$: 351.2197. Found: 351.2201.

3-(3-Cyclohexyl-1-methylprop-2-ynyl)-2-ethyl-1-methylindole (9a): mp 99-100°C. ^{1}H-NMR ($CDCl_3$) δ: 0.80-0.98 (1H, m), 1.00-1.30 (4H, m), 1.21 (3H, t, J=7.3 Hz), 1.40-1.65 (3H, m), 1.70-1.83 (2H, m), 1.80 (3H, d, J=2.5 Hz), 2.20-2.30 (1H, m), 2.82 (2H, q, J=7.3 Hz), 3.40-3.55 (1H, m), 3.65 (3H, s), 7.05 (1H, ddd, J=1, 6.8, 7.8 Hz), 7.14 (1H, ddd, J=1, 6.8, 7.8 Hz), 7.23 (1H, d, J=8.3 Hz), 7.73 (1H, d, J=7.8 Hz). ^{13}C-NMR ($CDCl_3$) δ: 3.6, 14.3, 17.9, 26.4, 29.4, 31.5, 35.3, 43.4, 76.9, 80.7, 108.5, 109.9, 118.5, 119.6, 120.4, 126.8, 136.7, 138.4. *Anal.* Calcd for $C_{21}H_{27}N$: C, 85.95; H, 9.27; N, 4.77. Found: C, 85.94; H, 9.32; N, 4.68.

3-(3-Cyclohexyl-1-phenylprop-2-ynyl)-2-ethyl-1-methylindole (9b): ^{1}H-NMR ($CDCl_3$) δ: 0.95-1.30 (5H, m), 1.24 (3H, t, J=7 Hz), 1.55-1.70 (3H, m), 1.85-1.95 (2H, m), 2.25-2.35 (1H, m), 2.80-3.00 (2H, m), 3.67 (3H, s), 3.82 (1H, d, J=8.3 Hz), 7.07 (1H, dt, J=1, 6.8 Hz), 7.16 (1H, dt, J=1, 6.8 Hz), 7.20-7.30 (4H, m), 7.35-7.40 (2H, m), 7.80 (1H, d, J=8.3 Hz). ^{13}C-NMR ($CDCl_3$) δ: 14.4, 18.0, 26.3, 26.4, 29.4, 31.6, 35.9, 43.8, 82.1, 91.9, 108.6, 109.1, 118.7, 119.5, 120.5, 124.3, 126.9, 127.3, 128.0, 131.5, 136.7, 138.6. High-resolution MS m/z : Calcd for $C_{26}H_{29}N$: 355.2298. Found: 355.2265.

2-(4-Cyclohexyl-1-methylbuta-1,2-dienyl)-1-methylindole (11a): mp 61-62°C. ^{1}H-NMR ($CDCl_3$) δ: 0.80-1.90 (11H, m), 2.00-2.10 (2H, m), 2.02 (3H, s), 3.76 (3H, s), 5.30-5.45 (1H, m), 6.28 (1H, s), 7.06 (1H, dt, J=1, 6.8 Hz), 7.18 (1H, t, J=6.8 Hz), 7.27 (1H, d, J=8.3 Hz), 7.55 (1H, d, J=7.8 Hz). ^{13}C-NMR ($CDCl_3$) δ: 20.2, 26.2, 26.5, 31.3, 33.0, 37.3, 38.0, 91.3, 92.8, 100.3, 108.9, 119.3, 120.0, 121.4, 127.6, 137.0, 138.5, 204.9. *Anal.* Calcd for $C_{20}H_{25}N$: C, 85.97; H, 9.02; N, 5.01. Found: C, 86.08; H, 9.05; N, 4.78.

2-(4-Cyclohexyl-1-phenylbuta-1,2-dienyl)-1-methylindole (11b): ^{1}H-NMR ($CDCl_3$) δ: 0.85-1.00 (2H, m), 1.10-1.30 (3H, m), 1.40-1.50 (1H, m), 1.60-1.90 (4H, m), 2.12 (1H, dt, J=2, 7.5 Hz), 3.57 (3H, s), 6.49 (1H, s), 7.11 (1H, dt, J=1, 6.8 Hz), 7.15-7.40 (7H, m), 7.60 (1H, d, J=8.3 Hz). ^{13}C-NMR ($CDCl_3$) δ: 26.2, 26.4, 30.7, 33.0, 33.1, 36.7, 38.0, 92.8, 100.4, 102.6, 109.2, 119.5, 120.4, 121.3, 126.9, 127.0, 127.9, 128.4, 135.7, 136.8, 137.8, 206.1. High-resolution MS m/z : Calcd for $C_{25}H_{27}N$: 341.2142. Found: 341.2121.

3-(4-Cyclohexyl-1-methylbut-2-ynyl)-2-ethyl-1-methylindole (12a): mp 90-92°C. ^{1}H-NMR ($CDCl_3$) δ: 0.80-1.00 (2H, m), 1.00-1.30 (4H, m), 1.18 (3H, t, J=7.3 Hz), 1.40-2.00 (8H, m), 1.78 (3H, d, J=2.5 Hz), 2.70-2.85 (2H, m), 3.56 (3H, s), 3.87-4.00 (1H, m), 7.05 (1H, t, J=6.8 Hz), 7.12 (1H, t, J=6.8 Hz), 7.19 (1H, d, J=7.8 Hz), 7.75 (1H, d, J=7.8 Hz). ^{13}C-NMR ($CDCl_3$) δ: 14.5, 17.8, 26.1, 26.2, 26.6, 29.2, 32.7, 33.7, 35.4, 45.1, 81.1, 92.8, 108.7, 110.7, 118.7, 119.1, 120.6, 124.2, 126.3, 127.3, 128.1, 131.5, 136.7, 137.8. *Anal.* Calcd for $C_{22}H_{29}N$: C, 85.94: H, 9.51; N, 4.56. Found: C, 85.79; H, 9.67; N, 4.58.

3-(4-Cyclohexyl-1-phenylbut-2-ynyl)-2-ethyl-1-methylindole (12b): ^{1}H-NMR ($CDCl_3$) δ: 0.90-1.10 (2H, m), 1.10-1.40 (3H, m), 1.23 (3H, t, J=7 Hz), 1.55-1.80 (5H, m), 1.80-1.95 (2H, m), 2.00-2.15 (1H, m), 2.80-3.00 (2H, m), 3.64 (3H, s), 4.19 (1H, dd, J=6, 9 Hz), 7.08 (1H, dt, J=1, 6.8 Hz), 7.16 (1H, dt, J=1, 6.8 Hz), 7.20-7.30 (4H, m), 7.35-7.40 (2H, m), 7.82 (1H, d, J=7.8 Hz). ^{13}C-NMR ($CDCl_3$) δ: 3.6, 14.1, 14.6, 17.8, 22.6, 27.7, 28.5, 29.3, 31.6, 37.5, 76.0, 81.8, 108.6, 111.1, 118.6, 119.3, 120.6, 126.3, 136.8, 137.9. High-resolution MS m/z : Calcd for $C_{27}H_{31}N$: 369.2454. Found: 369.2463.

1-Methyl-2-(1-methylpropa-1,2-dienyl)indole (14a): IR (neat) : 1936 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.16 (3H, t, J=3 Hz), 3.79 (3H, s), 5.06 (2H, q, J=3 Hz), 6.45 (1H, s), 7.06 (1H, dt, J=1, 6.8 Hz), 7.18 (1H, dt, J=1, 6.8 Hz), 7.26 (1H, d, J=8.3 Hz), 7.55 (1H, d, J=7.8 Hz). ^{13}C-NMR ($CDCl_3$) δ: 19.6, 31.4, 77.2, 93.2, 100.6, 109.0, 119.4, 120.1, 121.6, 127.5, 135.9, 138.5, 209.0. High-resolution MS m/z : Calcd for $C_{13}H_{13}N$: 183.1047. Found: 183.1057.

2,2-Dimethyl-3-(1-methylindol-2-yl)-2-silapenta-3,4-diene (14b): IR (neat) : 1918 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.25 (9H, s), 3.73 (3H, s), 4.68 (2H, s), 6.32 (1H, s), 6.81 (1H, t, J=7.8 Hz), 6.90 (1H, t, J=6.8 Hz), 7.01 (1H, d, J=6.8 Hz), 7.52 (1H, d, J=8.3 Hz). ^{13}C-NMR ($CDCl_3$) δ: 0.9, 31.6, 71.2, 91.5,

101.6, 109.9, 120.2, 120.8, 122.0, 128.9, 135.3, 138.6, 211.8. High-resolution MS m/z : Calcd for $C_{15}H_{19}NSi$: 241.1285. Found: 241.1312.

5-(2-Ethyl-1-methylindol-3-yl)-2,2-dimethyl-2-silapent-3-yne (15): ^{1}H-NMR ($CDCl_3$) δ: 1.08 (3H, t, J=8.5 Hz), 2.67 (2H, q, J=6 Hz), 3.47 (3H, s), 3.54 (2H, s), 6.96 (1H, t, J=6.8 Hz), 7.02 (1H, t, J=6.8 Hz), 7.08 (1H, d, J=8.3 Hz), 7.50 (1H, d, J=7.8 Hz). ^{13}C-NMR ($CDCl_3$) δ: 0.0, 14.1, 15.3, 17.7, 29.2, 83.7, 104.7, 105.6, 108.6, 118.2, 118.8, 120.7, 127.0, 136.3, 138.8. High-resolution MS m/z : Calcd for $C_{17}H_{23}NSi$: 269.1598. Found: 269.1598.

2,2-Dimethyl-5-(1-methylindol-2-yl)-2-silapent-3-yne (16): mp 90-91°C. ^{1}H-NMR ($CDCl_3$) δ: 0.00 (9H, s), 3.54 (3H, s), 3.55 (2H, s), 6.22 (1H, s), 6.91 (1H, t, J=6.8 Hz), 7.02 (1H, t, J=6.8 Hz), 7.10 (1H, d, J=8.3 Hz), 7.39 (1H, d, J=7.8 Hz). ^{13}C-NMR ($CDCl_3$) δ: 0.0, 19.0, 29.7, 86.8, 100.3, 101.7, 108.9, 119.5, 120.2, 121.2, 127.6, 134.8, 137.7. *Anal.* Calcd for $C_{15}H_{19}NSi$: C, 74.63; H, 7.93; N, 5.80. Found: C, 74.49; H, 7.91; N, 5.74.

Reaction of Equimolar Amounts of 2a and Complex (17)

A mixture of complex (**17**) (1.6 g, 2 mmol), prepared according to the literature,[9] and **2a**, generated in THF from 1-methylindole (262 mg, 2 mmol) as above, was heated at 60°C for 30 min under an argon atmosphere. The reaction mixture was treated with 10% NaOH (10 ml) and 30% H_2O_2 (2 ml) under ice-cooling for 10 min. The mixture was diluted with EtOAc (50 ml), washed with brine, and dried over $MgSO_4$. The solvent was removed, and the residue was separated by MPLC with hexane-EtOAc (200:1) as an eluent to afford 144 mg of **14b** (30 %), 69 mg of **15** (13 %), and 72 mg of **16** (15%).

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