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ALLYLIC ALKYLATION OF INDOLES WITH BUTADIENE PROMOTED BY PALLADIUM CATALYST AND TRIETHYLBORANE

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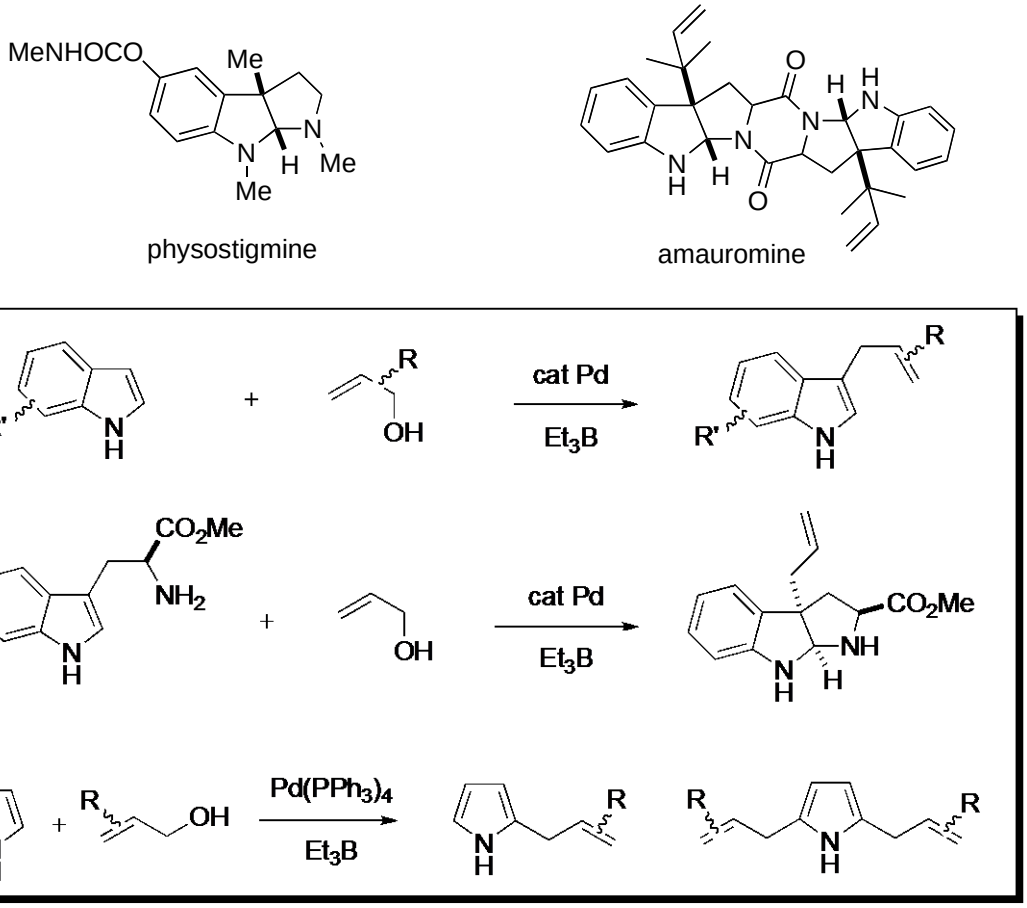
Abstract – Triethylborane promotes the Pd-catalyzed allylic alkylation of a wide variety of indoles with 1,3-butadiene to provide C3-octadienylindoles and C3-bis(octadienyl)indolenines in good to excellent yields under mild conditions.

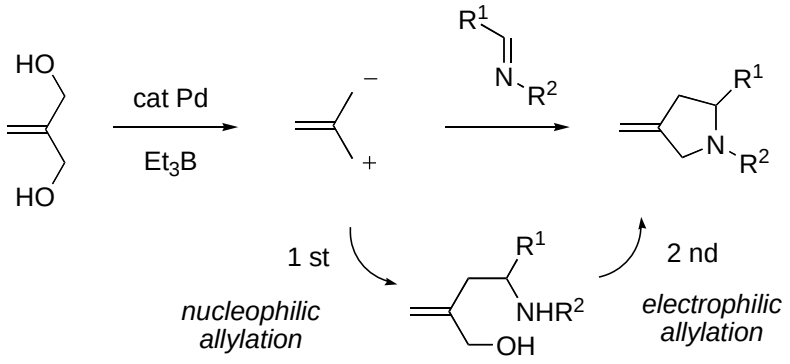
Pd-catalyzed allylic alkylation is one of the most attractive strategies for constructing important fundamental constituents of complicated molecules and fine chemicals.[1] Allylation of indoles is a particularly efficient and successful method for the construction of vital elements found in a diverse range of biologically and physiologically active molecules.[2]

Recently, we have demonstrated that a Pd(0) species in the presence of Et_3B catalytically activates allylic alcohols to undergo electrophilic *C*-allylation of active methylene compounds[3] and *N*-allylation of primary and secondary aromatic and aliphatic amines.[4] Furthermore, the Pd/Et_3B catalytic system worked effectively for the C3 selective allylation of indoles by direct use of allylic alcohols and provided 3-allylindoles in excellent yields (Scheme 1).[5] The same procedure was applied to the diastereofacial selective alkylative cyclic amination on the C2-C3 double bond of tryptophan methyl ester and furnished hexahydropyrrolo[2,3-*b*]indole skeletons, found widely in many alkaloids such as physostigmine and amauromine. We have also found that the combination of Et_3B and Pd catalyst effectively activates a wide variety of allylic alcohols to undergo either selective monoallylic alkylation of pyrroles at the C2 position with disubstituted allylic alcohols or diallylic alkylation at the C2 and C5 positions with monosubstituted allylic alcohols.[6] It is possible to shift the selectivity in favor of monoallylation under conditions employing an excess amount of pyrrole and triethylamine as promoters. Moreover, we have also reported the Pd/Et_3B system promoted the amphiphilic allylation of aldimines, which are prepared from a wide variety of amines and aldehydes with 2-methylenepropane-1,3-diol to construct nitrogen

heterocyclic compounds such as pyrrolidines (Scheme 2).[7] Thus, the combination of Pd(0) catalyst and Et_3B works for the generation of both allyl cationic and anionic species directly from allylic alcohols to achieve amphiphilic allylation.



Scheme 1. Pd/Et_3B Promoted Allylation of Indole and Pyrrole with Allylic Alcohols



Scheme 2. Amphiphilic Allylation of Aldimine

Since the development of η^3-bis-π-allylpalladium species from Pd catalysts and conjugated dienes,[8] the transition-metal catalyzed telomerization of conjugated dienes with nucleophiles has become an efficient method of C-C bond and C-hetero atom bond formation.[9] Conjugated dienes are important building

blocks for cosmetic chemicals and industrial polymers as well as physiologically active molecules such as terpenoids.[10]

Herein we report that the combination of Et_3B and Pd catalyst promoted the dimerization of butadiene followed by electrophilic allylation at the C3 position of indole to provide 3-(2,7-octadienyl)indole **1**, and the further allylated product, 3,3-bis(2,7-octadienyl)indolenine **2**, in good to excellent yields (eq 1).

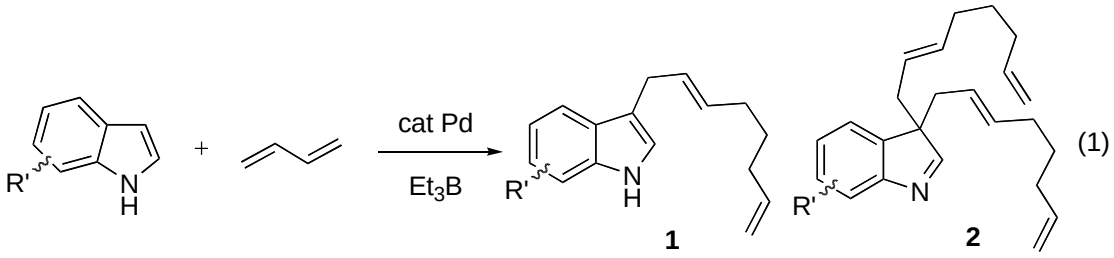


Table 1. Pd-Et_3B Catalyzed Allylation of Indole with Butadiene[a]

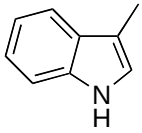
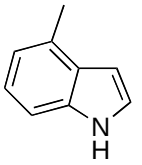
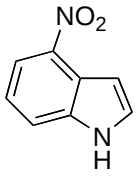
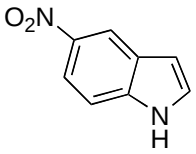
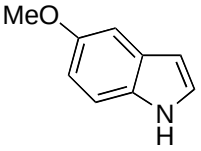
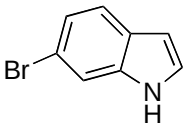
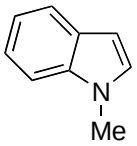
run	butadiene (mmol)	Et_3B (mmol)	time (hour)	% isolated yield [ratio]	
				1a	**2a**
1	4	0	48	0	0
2	4	0.3	24	21	trace
3	4	1.2	24	49	12
4	4	2.4	46	65	32
5	6	2.4	24	0	95

[a] Reaction conditions: indole (1 mmol), $Pd(PPh_3)_4$ (5 mol %), butadiene and Et_3B in THF (5 mL) under N_2.

The reaction was performed simply by combining a homogeneous mixture of indole, $Pd(PPh_3)_4$ catalyst, 1,3-butadiene, and Et_3B (30–240 mol %) in dry THF at room temperature under nitrogen atmosphere.[11] Both $Pd(PPh_3)_4$ and Et_3B are indispensable for the reaction; in the absence of either, no reaction takes place. The reactions of indole with 4 equivalents of 1,3-butadiene with various amounts of Et_3B are summarized in Table 1. A catalytic amount of Et_3B accelerated the dimerization of butadiene and the subsequent electrophilic allylation of indole gave rise to 3-(2,7-octadienyl)indole **1a** in moderate yield (run 2, Table 1). Increasing the amount of Et_3B generated a higher yield of the further octadienylated product, bis(2,7-octadienyl)indolenine **2a** (runs 2-4, Table 1).

In the presence of excess butadiene (6 equivalents) and Et_3B (2.4 equivalents), indolenine **2a** was obtained as the sole product (run 5, Table 1). Next, we examined a wide variety of substituted indoles under similar catalytic systems. These results are summarized in Table 2. 3-Methylindole (skatole) was found to be an efficient substrate for the allylic alkylation (run 1, Table 2).

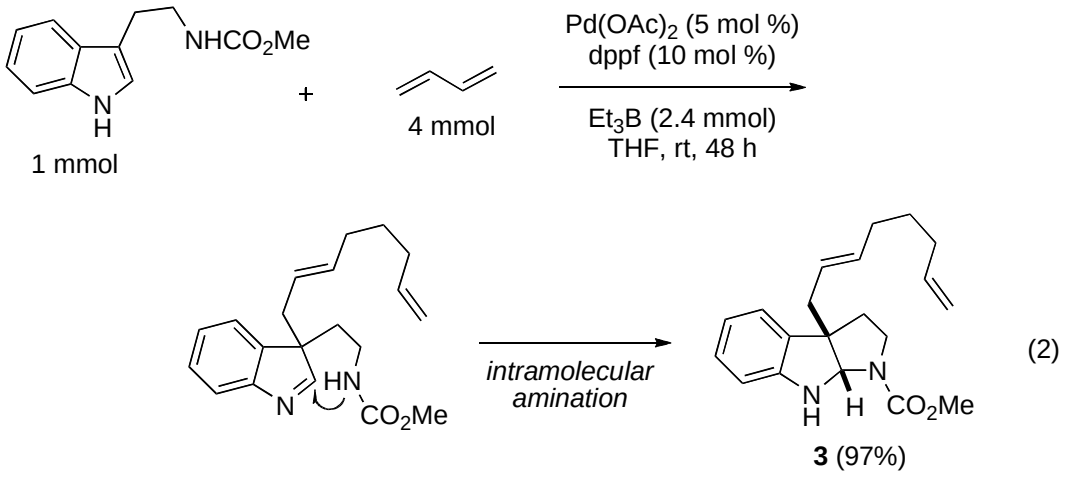
Table 2. Pd-Et_3B Promoted Octadienylation of Various Indoles with Butadiene[a]

run	indole	time (hour)	% isolated yield	
			1	**2**
1		2	**1b**: 83	-
2		5	**1c**: 87	**2c**: 10
3		5	**1d**: 77	**2d**: 23
4		14	**1e**: 74	**2e**: trace
5[b]		48	**1f**: 80	**2f**: 13
6[b]		48	**1g**: 74	**2g**: 17
7		24	no reaction	

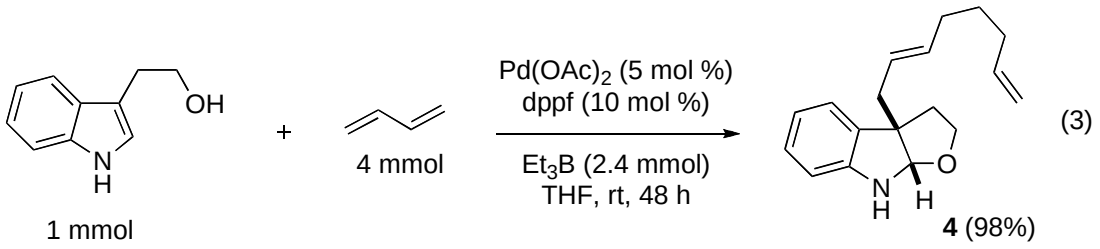
[a] Reaction conditions: indole (1 mmol), $Pd(PPh_3)_4$ (5 mol %), butadiene (4 mmol), and Et_3B (2.4 mmol) in THF (5 mL) at room temperature under N_2. [b] Reaction conditions: indole (1 mmol), $Pd(OAc)_2$ (5 mol %), dppf (10 mol %), butadiene (4 mmol), and Et_3B (2.4 mmol) in THF (5 mL) at room temperature under N_2.

Treatment of skatole with 2.0 equivalents of 1,3-butadiene provided 3-methyl-3-(2,7-octadienyl)indolenine **1b** in reasonable yield within 2 hours. Thus, the electrophilic alkylation reaction occurs smoothly with 3-alkyl substituted indoles with their enhanced nucleophilicity on the C3 carbon.[5] 4-Methylindole underwent a similar reaction to give octadienylindole **1c** as a major product along with a trace amount of bis(octadienyl)indolenine **2c** (run 2, Table 2). Nitro, methoxy, and bromo substituted indoles also participated in the reaction and the desired products were obtained in good to reasonable yields irrespective of the steric and electronic nature of the substituents (runs 3-6, Table 2).

The indole NH group is required for the reaction to proceed; *N*-methyl substituted indole did not undergo the reaction at all under this catalytic system and was recovered quantitatively (run 7, Table 2). These results imply that Et_3B coordinates to the nitrogen atom of indole, increasing its acidity, and thus activating the C3 enamine carbon atom towards electrophilic alkylation.

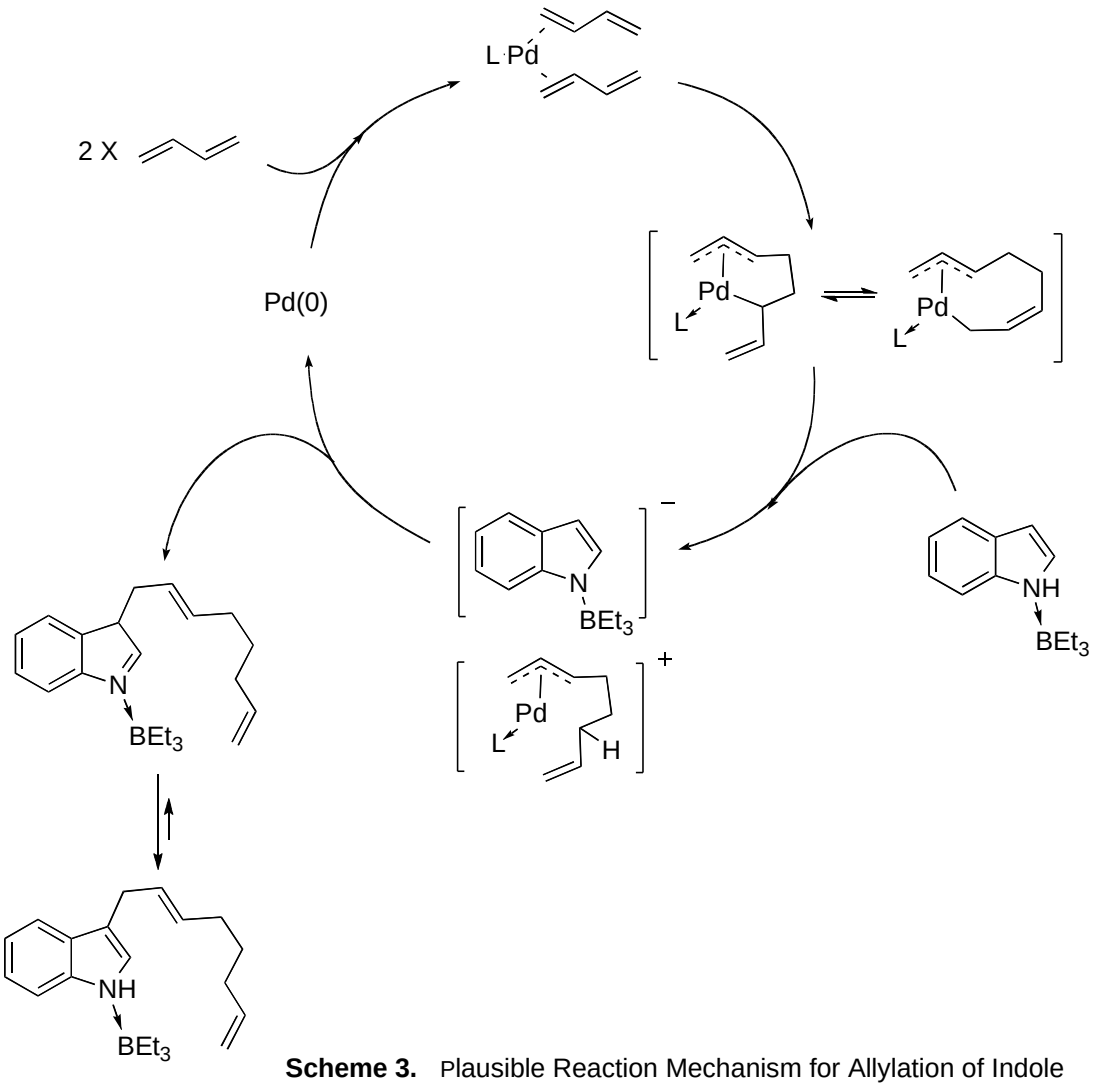


The present reaction was applied to the diastereoselective alkylation of tryptamine derivatives to afford pyrroloindoles. Under this catalytic system, 1,3-butadiene underwent the dimerization with concomitant electrophilic allylation at the C3 carbon atom of tryptamine and the subsequent intramolecular amination toward the electrophilic imine carbon atom furnished the pyrroloindole skeleton (eq 2). Tryptophol also underwent the consecutive allylic alkylation and amination processes involving dimerization of butadiene to give 2*H*-furo[2,3-*b*]indole in excellent yield (eq 3). This transformation has the potential for the efficient construction of vital indole alkaloid frameworks.



On the basis of these results, a plausible reaction mechanism via dimerization of butadiene promoted by Pd catalyst and Et_3B is illustrated in Scheme 3. The Pd(0)-catalyzed dimerization of butadiene affords an η^1,η^3-octadienylpalladium species, which subsequently undergoes protonation at the C6 position to give the η^3-allylpalladium indolyltriethylborate intermediate. Since indole is a heterocyclic compound containing a weakly Lewis basic nitrogen, Et_3B is capable of serving as a Lewis acid to enhance the nucleophilicity of the C3 position by abstraction of a hydrogen atom from the NH bond. The activated indole readily undergoes Friedel-Crafts alkylation with the η^3-octadienylpalladium species to provide

3-(2,7-octadienyl)indole, along with regeneration of the Pd(0) active species.



Scheme 3. Plausible Reaction Mechanism for Allylation of Indole

In summary, we have shown that a combination of Pd(0) catalyst and Et_3B effectively activates butadiene to undergo the *C*-allylation of indole via oligomerization of the diene. The C3 carbon atom of the parent indole moiety serves as a good nucleophile to undergo exhaustive allylations to furnish the C3 bis(octadienyl)indolenine in high yield. Tryptamine and tryptophol also underwent similar allylic alkylations followed by intramolecular cyclization to afford pyrrolo[2,3-*b*]indole and 2*H*-furo[2,3-*b*]indole frameworks, respectively.

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work was partially supported by the Asahi Glass Foundation.

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11. Typical reaction procedure (run 4, Table 1): Into a N_2 purged flask containing indole (117 mg, 1 mmol), $Pd(PPh_3)_4$ (55.6 mg, 0.05 mmol) purged with nitrogen were successively added THF (5 mL), 1,3-butadiene (400 μL, 4 mmol; liquefied by cooling at -78 ˚C prior to use under argon atmosphere) and triethylborane (2.4 mL, 1 M hexane; Aldrich) were introduced successively *via* a syringe. The reaction mixture was stirred at room temperature for 24 h, during which the reaction was monitored by means of TLC. After dilution with ethyl acetate (30 mL), the mixture was washed with sat. NaCl (30 mL). The organic layer was dried ($MgSO_4$) and the solvent was removed in vacuo. The residue was subjected to the column chromatography over silica gel (Fujisirisia NH; eluent: hexane/EtOAc = 32:1) and 3-[(*E*)-octa-2,7-dienyl]-1*H*-indole (**1a**): and 3,3-bis[(*E*)-octa-2,7-dienyl]-3*H*-indole (**2a**) were obtained in 65% and 32% yields, respectively. **3-[(*E*)-Octa-2,7-dienyl]-1*H*-indole** (**1a**): IR (neat) 3418 (s), 2926 (s), 1639 (s), 968 (s), 741 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.48 (quint, J = 7.0 Hz, 2 H), 1.98 – 2.07 (m, 4 H), 3.48 (d, J = 7.0 Hz, 2 H), 4.93 (dd, J = 3.4, 10.1 Hz, 1 H), 4.99 (dd, J = 3.4, 17.1 Hz, 1 H), 5.57 (dt, J = 14.2, 7.0 Hz, 1 H), 5.67 (dt, J = 14.2, 7.0 Hz, 1 H), 5.80 (ddt, J = 10.1, 17.1, 7.0 Hz, 1 H), 6.96 (br s, 1 H), 7.09 (t, J

= 7.4 Hz, 1 H), 7.20 (t, *J* = 7.4 Hz, 1 H), 7.34 (d, *J* = 7.4 Hz, 1 H), 7.59 (d, *J* = 7.4 Hz, 1 H), 7.90 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 28.6, 28.8, 31.2, 110.9, 114.2, 115.5, 119.0, 121.2, 121.8, 127.4, 128.8, 130.8, 136.3, 138.7, 141.9. High-resolution MS, calcd for $C_{16}H_{19}N$: 225.3288, Found *m/z* (relative intensity): 225.1490 (M^+, 100), 225 (10), 182 (20).

3,3-Di[(*E*)-octa-2,7-dienyl]-3*H*-indole (2a): IR (neat) 2926 (s), 1639 (s), 970 (s), 910 (s), 742 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.30 (quint, *J* = 7.0 Hz, 4 H), 1.82 – 1.98 (m, 8 H), 2.39 – 2.54 (m, 4 H), 4.91 (dd, *J* = 3.4, 10.1 Hz, 2 H), 4.93 (dd, *J* = 3.4, 17.5 Hz, 2 H), 5.09 (dt, *J* = 13.9, 7.0 Hz, 2 H), 5.34 (dt, *J* = 13.9, 7.0 Hz, 2 H), 5.72 (ddt, *J* = 10.1, 17.5, 7.0 Hz, 2 H), 7.19 – 7.33 (m, 3 H), 7.59 (d, *J* = 7.8 Hz, 1 H), 8.00 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 28.4, 31.7, 32.9, 37.4, 61.5, 114.3, 121.2, 122.1, 123.9, 125.6, 127.5, 134.3, 138.5, 141.7, 155.5, 177.9. High-resolution MS, calcd for $C_{24}H_{31}N$: 333.5096, Found *m/z* (relative intensity): 333.2451 (M^+, 100), 265 (15).

Other new compound's data are as follows.

3-Methyl-3-[(*E*)-octa-2,7-dienyl]-3*H*-indole (1b): IR (neat) 2925 (s), 1639 (s), 1603 (s), 972 (s), 910 (s), 743 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.22 – 1.42 (m, 2 H), 1.34 (s, 3 H), 1.80 – 1.98 (m, 4 H), 2.39 (dd, *J* = 7.4, 13.7 Hz, 1 H), 2.44 (dd, *J* = 7.4, 13.7 Hz, 1 H), 4.92 (br d, *J* = 10.0 Hz, 1 H), 4.60 (br d, *J* = 17.6 Hz, 1 H), 5.15 (dt, *J* = 15.1, 7.4 Hz, 1 H), 5.40 (dt, *J* = 15.1, 7.4 Hz, 1 H), 5.75 (ddt, *J* = 10.0, 17.6, 7.4 Hz, 1 H), 7.22 – 7.38 (m, 3 H), 7.62 (d, *J* = 7.8 Hz, 1 H), 8.03 (s, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.0, 29.0, 32.2, 33.4, 39.6, 57.9, 114.8, 121.5, 122.0, 124.7, 126.3, 128.0, 134.9, 139.0, 143.8, 155.2, 179.4. High-resolution MS, calcd for $C_{17}H_{21}N$: 239.1674, Found *m/z* (relative intensity): 239.1666 (M^+, 94), 224 (7), 170 (100).

4-Methyl-3-[(*E*)-octa-2,7-dienyl-1*H*-indole (**1c**): IR (neat) 3411 (s), 3321 (s), 2925 (m), 2856 (s), 1963 (m), 1618 (m), 1504 (s), 1436 (m), 1342 (m), 1155 (m), 970 (m), 910 (m), 746 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.46 (quint, *J* = 7.4, 2 H), 2.04 (dtd, *J* = 7.4, 6.8, 1.2 Hz, 4 H), 2.68 (s, 3 H), 3.62 (dd, *J* = 6.1, 1.2 Hz, 2 H), 4.93 (dd, *J* = 10.2, 2.2 Hz, 1 H), 4.98 (dd, *J* = 17.1, 2.2 Hz, 1 H), 5.46 (dtt, *J* = 17.1, 6.7, 1.2 Hz, 1 H), 5.73 (dtt, *J* = 17.1, 6.1, 1.2 Hz, 1 H), 5.80 (ddt, *J* = 17.1, 10.2, 6.8 Hz, 1 H), 6. 81 (d, *J* = 7.2 Hz, 1 H), 6.91 (s, 1 H), 7.03 (dd, *J* = 7.9, 7.4 Hz, 1 H), 7.17 (d, *J* = 7.9, 1 H), 7.89 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.1, 28.8, 30.4, 31.9, 33.3, 108.8, 114.3, 116.3, 120.7, 121.7, 121.9 125.9, 123.0, 130.8, 136.8, 130.9, 136.8, 138.7. High-resolution MS, calcd for $C_{17}H_{21}N$: 239.1674, Found *m/z* (relative intensity): 239.1680 (M^+, 100).

4-Methyl-3,3-di[(*E*)-octa-2,7-dienyl]-3*H*-indole (**2c**): IR (neat) 3076 (w), 2926 (m), 2854 (w), 1639 (w), 1529 (s), 1441 (w), 1354 (s), 1331 (w), 968 (m), 912 (m), 741 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.22 (quint, *J* = 7.3 Hz, 4 H), 1.80 (dt, *J* = 13.7, 7.3 Hz, 8 H), 2.41 (s, 3 H), 2.60 (dd, *J* = 13.7, 7.1 Hz, 2 H), 2.72 (dd, *J* = 13.7, 7.1 Hz, 2 H), 4.84 - 4.91 (m, 6 H), 5.33 (dt, *J* = 15.1, 7.1 Hz, 2 H), 5.68 (ddt, *J* = 17.8, 9.5, 6.6 Hz, 2 H), 6.96 (d, *J* = 7.6 Hz, 1 H), 7.19 (t, *J* = 7.6 Hz, 1 H), 7.38 (d,

J = 7.6 Hz, 1 H), 7.91 (s, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.4, 28.3, 31.5, 32.7, 36.0, 62.9, 114.2, 118.6, 124.0, 127.7, 127.8, 132.8, 133.4, 138.4, 138.6, 156.1, 177.8. HRMS calcd for $C_{25}H_{33}N$: 347.2613. Found *m*/*z* (relative intensity): 347.2608 (M^+, 100).

4-Nitro-3-[(*E*)-octa-2,7-dienyl]-1*H*-indole (**1d**): IR (neat) 3385 (m), 2926 (m), 2853 (w), 1514 (s), 1443 (m), 1325 (s), 1290 (m), 1250 (m), 1111 (m), 972 (m), 912 (m), 787 (m), 732 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.42 (quint, *J* = 7.6 Hz, 2 H), 2.00 (dt, *J* = 7.6, 6.6 Hz, 4 H), 3.55 (d, *J* = 6.3 Hz, 2 H), 4.92 (ddt, *J* = 10.3, 2.2, 1.2 Hz, 1 H), 4.97 (ddt, *J* = 17.1, 2.2, 1.7 Hz, 1 H), 5.39 (dtt, *J* = 15.1, 6.6, 1.3 Hz, 1 H), 5.56 (dtt, *J* = 15.1, 6.3, 1.3 Hz, 1 H), 5.78 (ddt, *J* = 17.1, 10.3, 6.6 Hz, 1 H), 7.20 (s, 1 H), 7.60 (dd, *J* = 8.0, 0.9 Hz, 1 H), 7.76 (dd, *J* = 8.0, 0.9 Hz, 1 H), 8.30 - 8.46 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.7, 30.3, 31.9, 33.2, 114.2, 115.5, 116.5, 117.1, 119.0, 120.6, 126.3, 127.9, 128.9, 131.2, 138.7, 138.9. HRMS calcd for $C_{16}H_{18}N_2O_2$: 270.1368. Found *m*/*z* (relative intensity): 270.1369 (M^+, 100).

4-Nitro-3,3-di[(*E*)-octa-2,7-dienyl]-3*H*-indole (**2d**): IR (neat) 3074 (m), 2926 (s), 2853 (s), 1639 (s), 1593 (w), 1562 (m), 1440 (s), 1416 (m), 964 (s), 910 (s), 789 (s), 748 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.13 (quint, *J* = 6.8 Hz, 4 H), 1.71 (dt, *J* = 7.3, 6.8 Hz, 8 H), 2.77 (dd, *J* = 13.9, 6.8 Hz, 2 H), 2.98 (dd, *J* = 13.9, 6.8 Hz, 2 H), 4.77 (dt, *J* = 14.3, 6.8 Hz, 2 H), 4.89 (dd, *J* = 16.3, 2.2 Hz, 2 H), 4.86 (dd, *J* = 10.7, 2.2 Hz, 2 H), 5.30 (dt, *J* = 14.3, 7.3 Hz, 2 H), 5.63 (ddt, *J* = 16.3, 10.7, 6.8 Hz, 2 H), 7.48 (dd, *J* = 8.3, 7.6 Hz, 1 H), 7.86 (d, *J* = 7.6 Hz, 1 H), 8.00 (d, *J* = 8.3 Hz, 1 H), 8.08 (s, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.2, 31.4, 32.6, 35.1, 66.4, 114.3, 121.5, 123.2, 126.7, 128.9, 134.4, 135.6, 138.4, 146.1, 159.2, 180.6. HRMS calcd for $C_{24}H_{30}N_2O_2$: 378.2307. Found *m*/*z* (relative intensity): 378.2297 (M^+, 100).

5-Nitro-3-[(*E*)-octa-2,7-dienyl]-1*H*-indole (**1e**): IR (neat) 3375 (s), 2926 (m), 2839 (w), 1624 (w), 1510 (m), 1470 (m), 1319 (s), 1221 (m), 1101 (m), 968 (w), 912 (w), 738 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.49 (quint, *J* = 7.4 Hz, 2 H), 2.03 - 2.09 (m, 4 H), 3.49 (dd, *J* = 5.1, 0.7 Hz, 2 H), 4.93 (ddt, *J* = 10.3, 2.2, 1.2 Hz, 1 H), 4.99 (d, *J* = 17.1, 2.2, 1.7 Hz, 1 H), 5.56 - 5.69 (m, 2 H), 5.80 (ddt, *J* = 17.1, 10.3, 6.8 Hz, 1 H), 7.11 (s, 1 H), 7.36 (d, *J* = 9.0 Hz, 1 H), 8.10 (dd, *J* = 9.0, 2.2 Hz, 1 H), 8.27 - 8.38 (br s, 1 H), 8.57 (d, *J* = 2.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.3, 28.7, 28.3, 31.8, 33.2, 110.8, 114.4, 116.5, 117.6, *117.7*, 118.2, 126.8, 127.7, 131.8, 138.6, 139.3, 141.4. HRMS calcd for $C_{16}H_{18}N_2O_2$: 270.1368. Found *m*/*z* (relative intensity): 270.1369 (M^+, 100), 269 (7).

5-Methoxy-3-[(*E*)-octa-2,7-dienyl]-1*H*-indole (**1f**): IR (neat) 3417 (s), 2927 (s), 2831(m), 1624(s), 1585(m), 1485 (m), 1454 (s), 1215 (m), 1172 (m), 968 (m), 914 (m), 831 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.49 (quint, *J* = 7.3, 2 H), 2.05 (dt, *J* = 6.6, 7.3 Hz, 4 H), 3.41 (d, *J* = 6.1 Hz, 2 H), 3.84 (s, 3 H), 4.92 (dd, *J* = 10.2, 2.0 Hz, 1 H), 4.98 (dd, *J* = 17.1, 2.0 Hz, 1 H), 5.58 (dd, *J* = 15.2, 6.6 Hz, 1 H), 5.66 (dd, *J* = 15.3, 6.1 Hz, 1 H), 5.79 (ddt, *J* = 17.1, 10.2, 6.6 Hz, 1 H), 6.83 (dd, *J* = 8.8, 2.4

Hz, 1 H), 6.93 (s, 3 H), 7.03 (d, *J* = 2.4 Hz, 1 H), 7.22 (d, *J* = 8.8 Hz, 1 H), 7.88 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 28.7, 28.8, 31.9, 33.2, 55.9, 111.6, 112.0, 114.3, 115.1, 122.1, 127.8, 128.7, 130.8 131.5, 138.7, 153.7. High-resolution MS, calcd for $C_{17}H_{21}NO$: 255.1623, Found *m/z* (relative intensity): 255.1620 (M^+, 100).

5-Methoxy-3-bis[(*E*)-octa-2,7-dienyl]-3*H*-indole (**2f**): IR (neat) 3074 (s), 2925 (s), 2837(m), 1963(s), 1591(m), 1554 (m), 1469 (s), 1336 (m), 1228 (m), 1176 (m), 966 (m), 910 (m), 810 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.31 (quint, *J* = 7.3 Hz, 4 H), 1.89 - 1.93 (m, 8 H), 2.39 (dd, *J* = 13.4, 6.8 Hz, 2 H), 2.46 (dd, *J* = 13.3, 7.4 Hz, 2 H), 3.82 (s, 3 H), 4.90 (dd, *J* = 10.2, 3.2 Hz, 1 H), 4.91 (dd, *J* = 10.2, 3.2 Hz, 1 H), 4.92 (dd, *J* = 17.1, 3.2 Hz, 1 H), 4.93 (dd, *J* = 17.1, 3.2 Hz, 1 H), 5.10 (dd, *J* = 15.1, 6.8 Hz, 2 H), 5.37 (dt, *J* = 15.1, 7.4 Hz, 2 H), 5.72 (ddt, *J* = 17.1, 10.2, 6.6 Hz, 2 H), 6. 80 - 6.84 (m, 2 H), 7.74 - 7.50 (m, 1 H), 7.88 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 28.5, 31.7, 32.9, 37.5, 55.7, 62.6, 109.0, 112.1, 114.3, 121.1, 124.0, 134.3, 138.5 143.5, 149.3, 158.2, 175.9. High-resolution MS, calcd for $C_{25}H_{33}NO$: 363.2562, Found *m/z* (relative intensity): 363.2568 (M^+, 66), 309 (100).

6-Bromo-3-[(*E*)-octa-2,7-dienyl]-1*H*-indole (**1g**): IR (neat): 3425 (s), 2925 (s), 2854 (m), 1640 (m), 1614 (m), 1454 (m), 1332 (m), 1089 (m), 968 (m), 802 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.46 (quint, *J* = 7.4 Hz, 2 H), 2.04 (dt, *J* = 7.4, 6.3 Hz, 1 H), 2.04 (dt, *J* = 7.4, 6.7, 1.8 Hz, 1 H), 3.42 (dd, *J* = 6.1, 1.1Hz, 1 H), 4.93 (dd, *J* = 10.1, 1.8 Hz, 1 H), 4.98 (dq, *J* = 17.1, 1.8 Hz, 1 H), 5.59 (dt, *J* = 16.3, 6.3 Hz, 1 H), 5.63 (dt, *J* = 16.3, 6.1 Hz, 1 H), 5.79 (ddt, *J* = 17.1, 10.1, 6.7 Hz, 1 H), 6.93 (t, *J* = 1.1 Hz, 1 H), 7.18 (dd, *J* = 8.4, 1.7 Hz, 1 H), 7.44 (d, *J* = 8.4 Hz, 1 H), 7.49 (d, *J* = 1.7 Hz, 1 H), 7.90 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.5, 28.7, 31.8, 33.2, 113.8, 114.3, 115.4, 115.7, 120.3, 121.9, 122.4, 126.3, 128.4, 131.1, 138.6. High-resolution MS, calcd for $C_{16}H_{18}BrN$: 303.0623, Found *m/z* (relative intensity): 303.0629 (M^+, 49), 249 (100).

6-Bromo-3,3-bis[(*E*)-octa-2,7-dienyl]-3*H*-indole (**2g**): IR (neat) 3074 (m), 2925 (s), 2825 (m), 1639 (s), 1593 (s), 1471 (s), 970 (s), 910 (s), 802 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.31 (quint, *J* = 7.5 Hz, 4 H), 1.82 - 1.95 (m, 8 H), 2.41 (dd, *J* = 13.9, 7.8 Hz, 2 H), 2.47 (dd, *J* = 13.9, 7.8 Hz, 2 H), 4.92 (dd, *J* = 10.4, 1.6 Hz, 2 H), 4.94 (dq, *J* = 17.0, 1.6 Hz, 2 H), 5.03 (dt, *J* = 14.9, 7.8 Hz, 2 H), 5.36 (dt, *J* = 14.9, 6.9 Hz, 2 H), 5.73 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 2 H), 7.12 (dd, *J* = 8.0 Hz, 1 H), 7.36 (dd, *J* = 8.0, 1.8 Hz, 1 H), 7.73 (d, *J* = 1.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.4 (2C), 32.9 (4C), 37.2 (2C), 61.7, 114.4 (2C), 120.9, 123.3, 123.5 (4C), 124.4, 128.5, 134.7 138.4 (2C), 140.6, 157.0. High-resolution MS, calcd for $C_{24}H_{30}BrN$: 411.1562, Found *m/z* (relative intensity): 411.1556 (M^+, 100).

1,2,3,3a,8,8a-Hexahydro-1-methoxycarbonyl-3a-(2,7-octadienyl)-pyrrolo[2,3-*b*]indole (**3**): IR (neat) 2925 (s), 2856 (s), 1705 (s), 1639 (s), 1606 (s), 1490 (s), 1448 (s), 1386 (s), 1211 (s), 968 (s),

740 (s); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.43 (quint, J = 7.4 Hz, 2 H), 2.01 - 2.14 (m, 4 H), 2.37 (d, J = 6.3 Hz, 2 H), 3.03 (d, J = 3.2 Hz, 1 H), 3.57 (dt, J = 2.7, 7.3 Hz, 1 H), 3.58 (dd, J = 2.7, 10.0 Hz, 1 H), 3.64 (s, 3 H), 4.97 (dd, J = 2.0, 17.1 Hz, 1 H), 4.93 (dd, J = 1.9, 10.2 Hz, 1 H), 5.12 (s, 1 H), 5.44 (dt, J = 6.3, 14.9 Hz, 2 H), 5.77 (ddt, J = 6.7, 10.2, 17.1 Hz, 1 H), 6.53 - 6.58 (m, 2 H), 6.75 - 6.70 (m, 2 H), 7.00 - 7.05 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.6, 31.9, 33.1, 34.9, 41.0, 45.8, 52.4, 57.3, 80.1, 109.1, 114.3, 118.5, 123.0, 125.0, 128.1, 131.8, 134.1, 138.5, 155.4. Anal. Calcd for $C_{20}H_{26}N_2O_2$: C, 73.59; H, 8.03; N, 8.58; O, 9.80. Found: C, 73.42; H, 8.40; N, 8.38.

3,3a,8,8a-Tetrahydro-3a-(2,7-octadienyl)-2*H*-furo[2,3-*b*]indole (**4**): IR (neat) 3352 (s), 2858 (s), 1639 (s), 1611 (s), 910 (s), 742 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.40 (quint, J = 7.4 Hz, 2 H), 1.90 – 2.02 (m, 6 H), 2.41 (dd, J = 7.8, 14.1 Hz, 1 H), 2.51 (dd, J = 6.3, 14.1 Hz, 1 H), 3.54 (m, 1 H), 3.94 (m, 1 H), 4.54 (br s, 1 H), 4.93 (br d, J = 10.3 Hz, 1 H), 4.96 (br d, J = 14.3 Hz, 1 H), 5.33 (m, 1 H), 5.35 (br s, 1 H), 5.46 (m, 1 H), 5.76 (dddd, J = 6.3, 7.8, 10.3, 14.3 Hz, 1 H), 6.57 (d, J = 7.6 Hz, 1 H), 6.74 (t, J = 7.6 Hz, 1 H), 7.03 – 7.07 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.6, 31.9, 33.0, 39.5, 41.2, 57.9, 67.1, 97.4, 108.1, 114.3, 118.6, 123.5, 125.6, 127.9, 132.4, 133.8, 138.6, 149.4. High-resolution MS, calcd for $C_{18}H_{23}NO$: 269.1780, Found *m/z* (relative intensity): 269.1780 (M^+, 100), 215 (11).