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Synthesis of Tetrasubstituted Cyclopentadienes via Palladium-Catalyzed Reaction of (*Z*)-2-En-4-yn Acetates and *N*-Methyl Indoles

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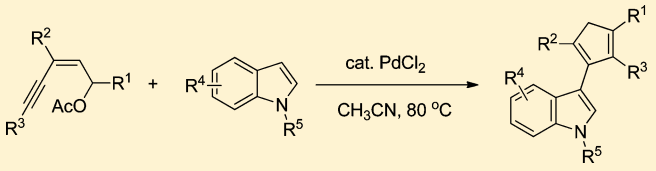
Supporting Information

ABSTRACT: An efficient approach for the synthesis of tetrasubstituted cyclopentadienes through Pd-catalyzed reactions of (*Z*)-2-en-4-yn acetates with substituted indoles was developed. This methodology has the advantages of broad scope, simple conditions and easily accessible starting materials.



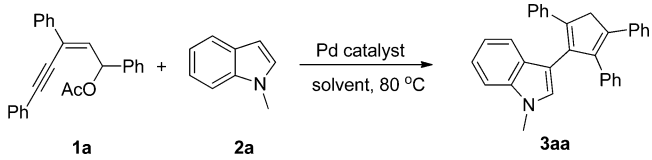
(*Z*)-2-En-4-yn-1-ols and their derivatives are important key building blocks for diversity-oriented organic synthesis. Many heterocycles such as dihydrofurans, furans,[1−6] butenolides,[7] phthalans,[8,10,11] dihydroisoquinolines,[9] isochromenes[9−12] and 2-(1-alkenyl) furans[13] have been synthesized by the intramolecular cyclization of this category of substrates. On the other hand, the intermolecular cyclization of (*Z*)-enynols with nucleophiles such as amines, furans and indoles catalyzed by transition metals (Au, Ag, Cu and Bi) has been proved as an effective method for the construction of heterocycles[14−18] and carbocycles.[19−24] However, (*Z*)-enynol derivatives have never been used for the construction of cyclopentadienes, which lend themselves to the synthesis of fulvenes.[25]

Cyclopentadienes are useful not only as a reactive diene component in the Diels−Alder reaction[26−29] but also as a precursor for the preparation of transition-metal complexes with Cp-type ligands.[30−33] The traditional method for the synthesis of substituted cyclopentadiene is the reduction of tetracyclone.[34,35] Nevertheless, the development of synthetic routes of tetrasubstituted cyclopentadienes under mild, simple and neutral conditions remains an important synthetic goal.

Recently, Iwasawa et al. have reported a novel method for the preparation of highly substituted cyclopentadiene derivatives based on the Pt(II)-catalyzed cyclization of 1,2,4-trienes.[24] This work prompted us to examine possible synthesis of multisubstituted cyclopentadienes by cyclization of (*Z*)-enynols, which can be precursors of 1,2,4-trienes. Herein, we wish to report an approach for the synthesis of tetrasubstituted cyclopentadienes through Pd-catalyzed reactions of (*Z*)-2-en-4-ynyl acetates with substituted indoles.

We commenced our studies by probing a variety of Pd catalysts and solvents for the reaction between (*Z*)-1,3,5-triphenylpent-2-en-4-ynyl acetate **1a** and *N*-methyl indole **2a** (Scheme 1). To our delight, treatment of **1a** and **2a** (1.1 equiv) in the presence of 10 mol % of $PdCl_2$ in CH_3CN at 80 °C for 0.5 h gave the desired product 1-methyl-3-(2,4,5-triphenylcyclopenta-1,4-dienyl)-1*H*-indole **3aa** in 86% yield (see Supporting Information). Other Lewis acids did not promote the transformation. Thus, the condition was selected as the general conditions.

Scheme 1. Model Reaction for the Formation of Tetrasubstituted Cyclopentadiene



We used a range of (*Z*)-2-en-4-yn acetates **1** and *N*-methyl indoles **2** to investigate the scopes and limits of this reaction. The electronic effect of R^1, R^2, and R^3 were examined by employing a series of enynol acetates bearing electron-withdrawing and electron-donating substituents to this reaction. The results are summarized in Table 1. An electron-donating substituent (Me) on the aryl group of R^1 afforded the corresponding product **3ba** in 76% yield (entry 2), but electron-withdrawing substituents (Cl, Br) on R^1 lead to lower yields (entries 3−4). Either an electron-withdrawing or electron-donating substituent on aryl group of R^2 resulted in a moderate yield (51−64%, entries 5−7). However, a strong electron-withdrawing substituent on R^2 such as cyano group had a negative effect on this reaction, which afforded a yield of only 25% (entry 8). The electronic effect on R^3 is similar to R^1. The reaction could proceed well when aryl group was substituted by electron-donating substituents (Me, OMe) (entries 9−10). The structure of **3ea** and **3ia** was unambiguously confirmed by X-ray crystallographic analysis (see Supporting Information). Moreover, when the substrate

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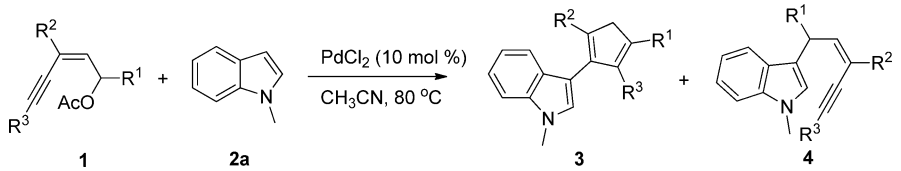
Table 1. $PdCl_2$-Catalyzed Reactions of (*Z*)-2-En-4-yn acetates with *N*-Methyl Indole[a]



1 2a 3 4

entry	enynol acetate	R^1	R^2	R^3	product	yield [%][b]
1	**1a**	Ph	Ph	Ph	**3aa**	86
2	**1b**	*p*-MeC_6H_4	Ph	Ph	**3ba**	76
3	**1c**	*p*-ClC_6H_4	Ph	Ph	**3ca**	51
4	**1d**	*p*-BrC_6H_4	Ph	Ph	**3da**	62
5	**1e**	Ph	*p*-MeC_6H_4	Ph	**3ea**	60
6	**1f**	Ph	*p*-BrC_6H_4	Ph	**3fa**	64
7	**1g**	Ph	*p*-ClC_6H_4	Ph	**3ga**	51
8	**1h**	Ph	*p*-CNC_6H_4	Ph	**3ha**	25
9	**1i**	Ph	Ph	*p*-MeC_6H_4	**3ia**	76
10	**1j**	Ph	Ph	*p*-$OMeC_6H_4$	**3ja**	71
11	**1k**	Ph	Ph	*p*-ClC_6H_4	**3ka**	64
12	**1l**	Ph	Ph	*n*-C_3H_7	**3la**	57
13	**1m**	Ph	Ph	*o*-MeC_6H_4	**3ma**	45
14	**1n**	Ph	Ph	*m*-MeC_6H_4	**3na**	62
15	**1o**	*n*-C_3H_7	Ph	Ph	**4oa**	40
16	**1p**	2,4-dichloro-C_6H_4	*p*-ClC_6H_4	Ph	**4pa**	50
17	**1q**	Ph	Ph	TMS	**4qa**	84

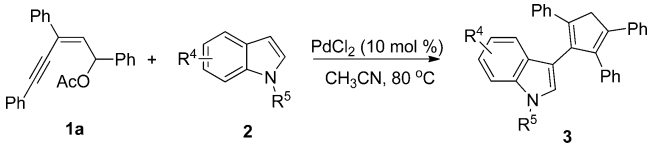
[a]All of the reactions were carried out using 10 mol % of $PdCl_2$ and 1.1 equiv of *N*-methyl indole at 80 °C in CH_3CN, 0.1 mmol scale. [b]Isolated yields.

with C-5 alkyl substituent instead of aryl group was examined, we obtained the expected product **3la** in a moderate yield of 57% (entry 12). However, when substrates **1o**, **1p** and **1q** were used, only Fridel–Crafts arylation products were observed (entries 15–17).

The present method could also be applied successfully to various indoles. As shown in Table 2, electron-donating group (Me, OMe) on C-5 position of *N*-methyl indole led to moderate yields (60 and 50%, entries 1–2), but an electron-withdrawing group such as Br could promote the reaction to 80% yield (entry 3). Even a cyano group could afford a yield of 71% (entry 4). C-7 substituted *N*-methyl indole was also effective for the conversion (entry 5). Interestingly, when unprotected indole **2g** was used, the preconceived product **3ag** was also obtained in 68% yield (entry 6). Other substituted indoles could also proceed the reaction, although the yields were lower (enties 7–10).

We next applied this cyclization reaction to other nucleophiles. When (*Z*)-1,3,5-triphenylpent-2-en-4-ynyl acetate **1a** was treated with 1.2 equiv of CuX_2, 10 mol % of $Pd(acac)_2$ and 20 mol % of $(C_6F_5)_3P$ in 1,4-dioxane, the reaction proceed smoothly to give the halogen-substituted cyclopentadienes **5a** and **6a**, despite the yield being low (46 and 10%, Scheme 2).

Table 2. Reaction of (*Z*)-1,3,5-Triphenylpent-2-en-4-ynyl Acetate 1a with Substituted Indoles[a]

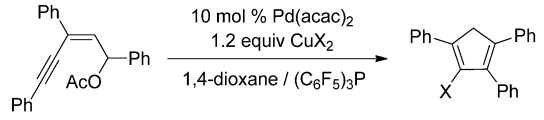


1a 2 3

entry	R^4	R^5	indole	product	yield [%][b]
1	5-CH_3	CH_3	**2b**	**3ab**	60
2	5-OCH_3	CH_3	**2c**	**3ac**	50
3	5-Br	CH_3	**2d**	**3ad**	80
4	5-CN	CH_3	**2e**	**3ae**	73
5	7-CH_3	CH_3	**2f**	**3af**	71
6	H	H	**2g**	**3ag**	68[c]
7	5-CH_3	H	**2h**	**3ah**	41[c]
8	5-OCH_3	H	**2i**	**3ai**	38[c]
9	5-Br	H	**2j**	**3aj**	50[c]
10	7-CH_3	H	**2k**	**3ak**	36[c]

[a]Unless noted, all of the reactions were carried out using 10 mol % of $PdCl_2$ and 1.1 equiv of substituted indole at 80 °C in CH_3CN, 0.1 mmol scale. [b]Isolated yields. [c]The solvent is CH_3NO_2.

Scheme 2. Palladium-Catalyzed Reaction of (*Z*)-1,3,5-Triphenylpent-2-en-4-ynyl Acetate 1a to Give Halogen Substituted Cyclopentadienes 5a and 6a



1a

5a: X = Cl, t = 100 °C, 46%
6a: X = Br, t = 85 °C, 10%

To understand the reaction mechanism, the arylate product **4aa** has been isolated by heating **1a** and **2a** in CH_3CN at 80 °C (Scheme 3). The structure of **4aa** can be confirmed by previous work.[17] The intramolecular cyclization of **4aa** catalyzed by $PdCl_2$ proceeded smoothly to provide the same product of **3aa** as observed in the model reaction. The results indicate that **3** was formed through intermediate **4**, and the formation of **4** was not a Pd-catalyzed process. The structure of **3ea** unambiguously indicated that the reaction involves an indole-migration process.

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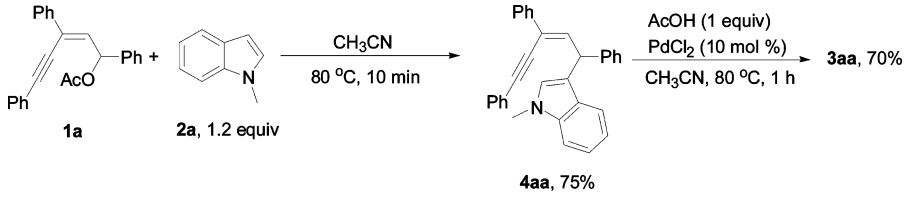
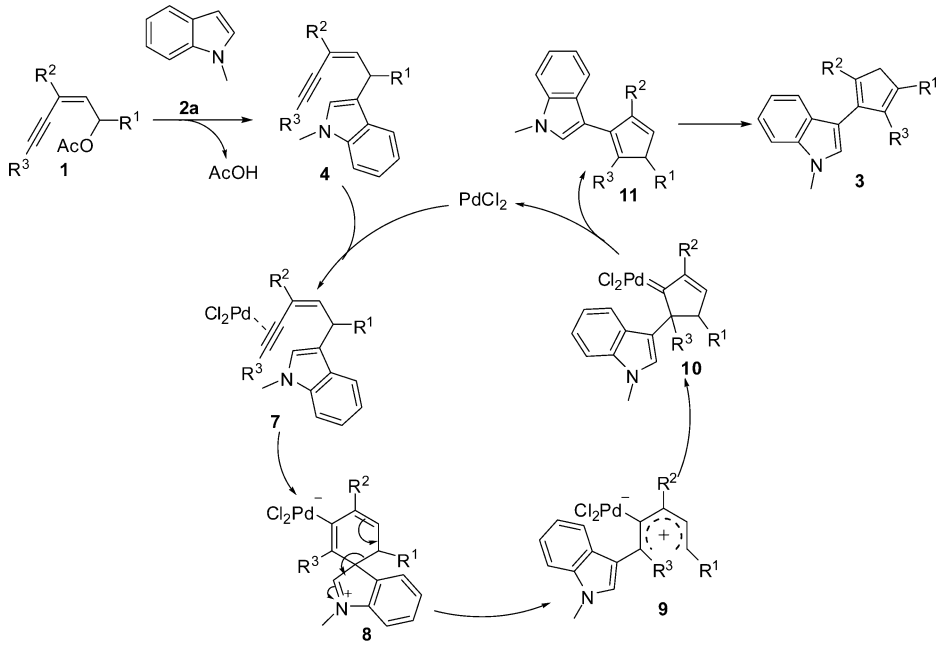
Scheme 3. Investigation of Possible Reaction Intermediates



Scheme 4. Reaction Mechanism of $PdCl_2$-Catalyzed Tandem Reaction of (*Z*)-2-En-4-yn Acetates with *N*-Methyl Indole



On the basis of the results above together with some literature reports, the mechanism was envisioned (Scheme 4). The reaction starts with the direct attack of indole **2a** to substrate **1**. The C−C triple bond of the resulting Fridel-Crafts arylation product **4** was activated by $PdCl_2$ to form Pd(II)-complex **7**. A *6-endo-dig* addition of the indole C-3 position onto **7** results in the formation of a spirocyclic intermediate **8**. Then the C−C double bond migration leads to the C−C fragmention of **8**, which results in the formation of an achiral pentadienyl cation intermediate **9**.[36] **9** undergoes Nazarov-type 4π electrocyclization to afford palladium-carbene intermediate **10**,[24,37−40] which then undergoes a 1,2-indole migration to give **11** with regeneration of the palladium catalyst.[41−49] The structure of **3ea** indicates that the migration group is indole. Isomerization of **11** give the final product **3**.

In summary, we have developed a $PdCl_2$-catalyzed reaction of (*Z*)-2-en-4-yn acetates with substituted indoles for the synthesis of tetrasubstituted cyclopentadienes. The cyclopentadiene formation proceeds through a Fridel−Crafts arylation/1,5-indole migaration/Nazarov electrocyclization/1,2-indole migration sequence. The method is mild, simple and has wide applicability. Furthermore, we have succeed in applying this cyclization reaction to other nucleophiles to give the halogen substituted cyclopentadienes.

EXPERIMENTAL SECTION

General Remarks. Column chromatography was carried out on silica gel using EtOAc and petroleum ether as solvents. ^{1}H NMR spectra were recorded on 400 MHz in $CDCl_3$, and ^{13}C NMR spectra were recorded on 100 MHz in $CDCl_3$ using TMS as internal standard. IR spectra were recorded on a FT-IR spectrometer, and only major peaks are reported in cm. All new compounds were further characterized by high-resolution mass spectrometry. HRMS was obtained using a Q-TOF instrument equipped with APCI. Copies of their ^{1}H NMR and ^{13}C NMR spectra are provided. Commercially available reagents and solvents were used without further purification.

Starting Materials. (*Z*)-2-En-4-yn acetates were prepared according to the literature.[14] *N*-Methyl indoles were prepared according to the literature.[50]

Typical Procedure for the Preparation of Tetrasubstituted Cyclopentadienes. A mixture of (*Z*)-1,3,5-triphenylpent-2-en-4-ynyl acetate **1a** (0.1 mmol), *N*-methyl indole **2a** (0.11 mmol), and $PdCl_2$ (17.7 mg, 10 mol %) in CH_3CN was stirred at 80 °C for 0.5 h. When the reaction was considered complete as determined by TLC analysis, the reaction was allowed to cool to room temperature and quenched by water, and the mixture was extracted with EtOAc. The combined organic layer was washed with saturated NH_4Cl (aq), water and brine, dried over Na_2SO_4 and filtered. The solvent was removed in vacuo, and the crude product was purified by column chromatography to afford 1-Methyl-3-(2,4,5-triphenyl-cyclopenta-1,4-dienyl)-1*H*-indole **3aa**.

Characterization Data of Compounds. *1-Methyl-3-(2,4,5-triphenyl-cyclopenta-1,4-dienyl)-1H-indole (**3aa**).* Yellow oil, 36 mg, 86% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.250−7.233 (t, 2H), 7.146−7.126 (d, J = 8 Hz, 3H), 7.102−7.097 (d, J = 2 Hz, 1H), 7.085−7.081 (d, J = 1.6 Hz, 1H), 7.065 (s, 1H), 7.055−7.026 (m, 5H), 7.014 (s, 1H), 6.995−6.978 (m, 2H), 6.967−6.965 (d, J = 0.8 Hz, 1H), 6.945−6.928 (m, 1H), 6.919−6.913 (d, J = 2.4 Hz, 1H), 6.777−6.738 (m, 1H), 6.272 (s, 1H), 4.019 (s, 2H), 3.507 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 139.6, 139.3, 137.3, 137.2, 137.0, 136.7, 129.9, 128.6, 128.1, 128.0, 127.8, 127.3, 126.8, 126.6, 126.2, 126.0, 121.2, 121.1, 118.9, 110.3, 108.7, 45.7, 32.6; IR (neat, cm^{-1}) 3433, 3052,

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2924, 1599, 1484, 1378, 1330, 1239, 1070, 1021, 742, 696, 408; HRMS (APCI) Calcd for $C_{32}H_{26}N$ M + H = 424.2060, found 424.2061.

*3-(2,5-Diphenyl-4-p-tolyl-cyclopenta-1,4-dienyl)-1-methyl-1H-indole (**3ba**).* Brown oil, 33 mg, 76% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.388−7.370 (d, J = 7.2 Hz, 2H), 7.284−7.263 (m, 1H), 7.195−7.185 (m, 4H), 7.166 (s, 2H), 7.149 (s, 1H), 7.132 (s, 1H), 7.115 (s, 1H), 7.097−7.032 (m, 5H), 6.917−6.880 (t, J = 7.2 Hz, 1H), 6.411 (s, 1H), 4.140 (s, 2H), 3.642 (s, 3H), 2.337 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 139.3, 139.2, 137.4, 137.3, 137.0, 136.7, 135.9, 133.8, 129.9, 128.8, 128.6, 128.0, 127.8, 127.7, 127.2, 126.8, 126.5, 125.9, 121.2, 121.1, 118.9, 110.4, 108.7, 45.7, 32.6, 21.1; IR (neat, cm^{-1}) 3827, 3433, 2923, 1621, 1461, 1380, 1260, 1096, 1029, 805, 740, 698, 407; HRMS (APCI) Calcd for $C_{33}H_{28}N$ M + H = 438.2216, found 438.2223.

*3-[4-(4-Chloro-phenyl)-2,5-diphenyl-cyclopenta-1,4-dienyl]-1-methyl-1H-indole (**3ca**).* Yellow oil, 23 mg, 51% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.317−7.300 (d, J = 6.8 Hz, 2H), 7.227−7.205 (d, J = 8.8 Hz, 1H), 7.158−7.025 (m, 12H), 6.988−6.969 (m, 2H), 6.851−6.814 (t, J = 7.2 Hz, 1H), 6.339 (s, 1H), 4.053 (s, 2H), 3.587 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2, 139.8, 137.9, 137.0, 137.0, 136.9, 136.7, 135.1, 131.8, 129.7, 129.0, 128.6, 128.2, 128.0, 127.2, 126.8, 126.7, 126.2, 121.2, 121.1, 118.9, 110.1, 108.8, 45.5, 32.7; IR (neat, cm^{-1}) 3827, 3441, 3053, 2941, 2327, 1485, 1383, 1091, 1013, 821, 741, 697, 470; HRMS (APCI) Calcd for $C_{32}H_{25}ClN$ M + H = 458.1670, found 458.1674.

*3-[4-(4-Bromo-phenyl)-2,5-diphenyl-cyclopenta-1,4-dienyl]-1-methyl-1H-indole (**3da**).* Deep yellow oil, 31 mg, 62% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.316−7.298 (d, J = 7.2 Hz, 2H), 7.216−7.199 (d, J = 6.8 Hz, 1H), 7.154−7.112 (m, 8H), 7.088−7.026 (m, 4H), 6.990−6.969 (dd, J_1 = 6.8 Hz, J_2 = 1.6 Hz, 2H), 6.850−6.812 (t, J = 7.6 Hz, 1H), 6.337 (s, 1H), 4.048 (s, 2H), 3.576 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2, 139.8, 137.9, 137.0, 137.0, 136.9, 136.7, 135.1, 131.8, 129.7, 129.0, 128.6, 128.2, 128.0, 127.2, 126.8, 126.7, 126.2, 121.2, 121.1, 118.9, 110.1, 108.8, 45.5, 32.6; IR (neat, cm^{-1}) 3827, 3435, 3053, 2928, 2318, 1600, 1566, 1486, 1379, 1335, 1264, 1207, 1093, 1018, 821, 140, 698, 407; HRMS (APCI) Calcd for $C_{32}H_{25}BrN$ M + H = 502.1165, found 502.1167.

*3-(4,5-Diphenyl-2-p-tolyl-cyclopenta-1,4-dienyl)-1-methyl-1H-indole (**3ea**).* Yellow oil, 26 mg, 60% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.226−7.197 (m, 5H), 7.173−7.155 (d, J = 7.2 Hz, 2H), 7.134−7.078 (m, 7H), 7.003−6.981 (dd, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 2H), 6.910−6.890 (d, J = 8 Hz, 2H), 6.872−6.835 (t, J = 7.2 Hz, 1H), 6.358 (s, 1H), 4.073 (s, 2H), 3.586 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 139.8, 138.8, 137.3, 136.7, 136.7, 136.3, 135.7, 134.3, 129.9, 128.7, 128.5, 128.1, 127.8, 127.8, 127.1, 127.0, 126.6, 126.1, 121.2, 121.1, 118.9, 110.5, 108.7, 45.7, 32.6, 21.1; IR (neat, cm^{-1}) 3439, 3053, 2922, 2322, 1621, 1496, 1475, 1379, 1332, 1264, 1072, 1022, 812, 738, 699, 407; HRMS (APCI) Calcd for $C_{33}H_{28}N$ M + H = 438.2216, found 438.2225.

*3-[2-(4-Bromo-phenyl)-4,5-diphenyl-cyclopenta-1,4-dienyl]-1-methyl-1H-indole (**3fa**).* Deep yellow oil, 32 mg, 64% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.233−7.175 (m, 7H), 7.157−7.090 (m, 7H), 7.056−7.036 (d, J = 8 Hz, 1H), 6.989−6.966 (dd, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 2H), 6.892−6.854 (t, J = 7.6 Hz, 1H), 6.331 (s, 1H), 4.042 (s, 2H), 3.581 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 139.6, 138.0, 137.8, 137.0, 136.7, 136.5, 136.1, 131.1, 129.8, 128.7, 128.6, 128.1, 127.9, 127.8, 126.7, 126.5, 126.4, 121.3, 121.0, 119.7, 119.1, 109.9, 108.9, 45.5, 32.7; IR (neat, cm^{-1}) 3828, 3743, 3436, 3053, 2921, 2358, 1482, 1383, 1336, 1204, 1072, 1016, 816, 741, 696, 407; HRMS (APCI) Calcd for $C_{32}H_{25}BrN$ M + H = 502.1165, found 502.1166.

*3-[2-(4-Chloro-phenyl)-4,5-diphenyl-cyclopenta-1,4-dienyl]-1-methyl-1H-indole (**3ga**).* Yellow oil, 23 mg, 51% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.390−7.326 (q, J = 8.4 Hz, 4H), 7.246−7.227 (m, 2H), 7.207−7.202 (d, J = 2 Hz, 2H), 7.182−7.126 (m, 6H), 6.989−6.969 (d, J = 8 Hz, 3H), 6.896−6.859 (t, J = 7.6 Hz, 1H), 6.332 (s, 1H), 4.101 (s, 2H), 3.618 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 141.6 141.3, 140.7, 136.8, 136.7, 136.1, 131.8, 129.9, 128.8, 128.2, 128.0, 127.9, 127.3, 126.9, 126.8, 126.1, 121.6, 120.8, 119.4, 109.6, 109.1, 108.6, 45.3, 32.7; IR (neat, cm^{-1}) 3828, 3742, 3443, 2359, 1646, 1483, 1384, 1090, 1017, 822, 742, 696, 408; HRMS (APCI) Calcd for $C_{32}H_{25}ClN$ M + H = 458.1670, found 458.1674.

*4-[2-(1-Methyl-1H-indol-3-yl)-3,4-diphenyl-cyclopenta-1,3-dienyl]-benzonitrile (**3ha**).* Yellow oil, 11 mg, 25% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.378−7.356 (d, J = 8.8 Hz, 2H), 7.328−7.307 (d, J = 8.4 Hz, 2H), 7.254−7.114 (m, 10 H), 6.987−6.969 (m, 3H), 6.887−6.850 (t, J = 7.2 Hz, 1H), 6.328 (s 1H), 4.083 (s, 2H), 3.595 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 141.6, 141.2, 140.6, 136.7, 136.7, 136.1, 131.8, 129.8, 128.7, 128.2, 128.0, 127.8, 127.3, 126.9, 126.7, 126.1, 121.6, 120.8, 119.38, 119.35, 109.5, 109.1, 108.6; IR (neat, cm^{-1}) 3828, 3742, 3442, 2359, 2222, 1646, 1511, 1463, 1384, 1097, 1021, 834, 743, 693, 407; HRMS (APCI) Calcd for $C_{33}H_{25}N_2$ M + H =449.2012, found 449.2022.

*3-(2,4-Diphenyl-5-p-tolyl-cyclopenta-1,4-dienyl)-1-methyl-1H-indole (**3ia**).* Yellow oil, 33 mg, 76% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.305−7.287 (d, J = 7.2 Hz, 2H), 7.222−7.107 (m, 5H), 7.090−6.992 (m, 6H), 6.920−6.865 (q, J = 8 Hz, 4H), 6.848−6.811 (t, J = 7.6 Hz, 1H), 6.359 (s, 1H), 4.068 (s, 2H), 3,549 (s, 3H), 2.243 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 139.6, 139.1, 137.3, 137.1, 136.8, 136.7, 136.1, 134.1, 129.7, 128.58, 128.55, 128.0, 127.9, 127.8, 127.2, 126.9, 126.1, 126.0, 121.1, 118.9, 110.4, 108.7, 45.7, 32.6, 21.2. IR (neat, cm^{-1}) 3829, 3743, 3437, 3053, 2920, 2360, 1684, 1611, 1518, 1463, 1375, 1333, 1074, 823, 743, 695, 407; HRMS (APCI) Calcd for $C_{33}H_{28}N$ M + H = 438.2216, found 438.2223.

*3-[5-(4-Methoxy-phenyl)-2,4-diphenyl-cyclopenta-1,4-dienyl]-1-methyl-1H-indole (**3ja**).* Yellow oil, 32 mg, 71% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.315−7.294 (m, 2H), 7.238−7.213 (m, 3H), 7.186−7.149 (m, 2H), 7.126−7.027 (m, 6H), 6.922−6.894 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 2H), 6.861−6.822 (t, J = 8 Hz, 1H), 6.672−6.650 (d, J = 8.8 Hz, 2H), 6.382 (s, 1H), 4.068 (s, 2H), 3.719 (s, 3H), 3.605 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 145.1, 139.6, 139.0, 137.3, 137.1, 136.9, 136.7, 131.0, 129.5, 128.6, 128.1, 128.0, 127.8, 127.2, 126.9, 126.1, 126.0, 121.2, 121.1, 118.9, 113.3, 110.4, 108.8, 55.0, 45.6, 32.7; IR (neat, cm^{-1}) 3845, 3742, 3436, 2360, 1691, 1646, 1611, 1512, 1463, 1383, 1244, 1098, 1032, 835, 744, 693, 407; HRMS (APCI) Calcd for $C_{33}H_{28}NO$ M + H = 454.2165, found 454.2180.

*3-[5-(4-Chloro-phenyl)-2,4-diphenyl-cyclopenta-1,4-dienyl]-1-methyl-1H-indole (**3ka**).* Brown amorphous solid, 29 mg, 64% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.230−7.209 (m, 2H), 7.173−7.145 (m, 1H), 7.117−7.107 (d, J = 4 Hz, 4H), 7.086−6.966 (m, 8H), 6.854−6.833 (d, J = 7.6 Hz, 2H), 6.799−6.762 (t, J = 7.2 Hz, 1H), 6.320 (s, 1H), 4.002 (s, 2H), 3.556 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 140.2, 140.0, 137.0, 136.8, 136.5, 136.4, 135.6, 132.5, 131.3, 128.3, 128.2, 128.1, 128.0, 127.9, 127.2, 126.8, 126.5, 126.2, 121.4, 120.9, 119.1, 110.2, 108.9, 45.9, 32.7; IR (neat, cm^{-1}) 3440, 2928, 1627, 1485, 1381, 1089, 911, 833, 740, 696; HRMS (APCI) Calcd for $C_{32}H_{25}ClN$ M + H = 458.1670, found 458.1673.

*3-(2,4-Diphenyl-5-propyl-cyclopenta-1,4-dienyl)-1-methyl-1H-indole (**3la**).* Deep yellow oil, 22 mg, 57% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.491−7.470 (m, 2H), 7.410−7.330 (m, 6H), 7.260−7.207 (m, 6H), 6.079−6.990 (m, 4H), 6.951 (s, 1H), 3.917 (s, 2H), 3.834 (s, 3H), 2.428−2.388 (t, J = 8 Hz, 2H), 1.287−1.192 (m, 2H), 0.663−0.627 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 141.2, 138.2, 138.0, 137.6, 137.0, 128.4, 128.0, 127.8, 127.6, 127.0, 126.9, 126.0, 125.8, 121.5, 120.6, 119.2, 111.2, 109.0, 45.6, 32.9, 29.1, 22.7, 14.2; IR (neat, cm^{-1}) 3435, 1635, 1374, 1101, 687; HRMS (APCI) Calcd for $C_{29}H_{28}N$ M + H = 390.2216, found 390.2222.

*3-(2,4-Diphenyl-5-o-tolylcyclopenta-1,4-dienyl)-1-methyl-1H-indole (**3ma**).* Yellow oil, 20 mg, 45% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.327−7.308 (d, J = 8.4 Hz, 2H), 7.236−7.111 (m, 6H), 7.094−7.051 (m, 6H), 7.026−6.987 (t, J = 7.6 Hz, 1H), 6.952−6.933 (d, J = 7.6 Hz, 1H), 6.850−6.786 (dd, J_1 = 18 Hz, J_2 = 7.6 Hz, 3H), 6.348 (s, 1H), 4.080 (s, 2H), 3.564 (s, 3H), 2.119 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8, 139.4, 139.0, 137.3, 137.2, 137.2, 137.1, 136.7, 136.7, 130.4, 128.6, 128.0, 128.0, 128.0, 127.3, 127.2, 127.0, 126.9, 126.1, 126.0, 121.2, 121.1, 118.8, 110.4, 108.7, 45.6, 32.6, 32.6, 21.3, 21.3; IR (neat, cm^{-1}) 3436, 3052, 3013, 2925, 1597, 1487, 1379, 1335, 1214, 1070, 1032, 797, 751, 695, 524; HRMS (APCI) Calcd for $C_{33}H_{28}N$ M + H = 438.2216, found 438.2221.

*3-(2,4-Diphenyl-5-m-tolylcyclopenta-1,4-dienyl)-1-methyl-1H-indole (**3na**).* Yellow oil, 27 mg, 62% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.323−7.304 (d, J = 7.9 Hz, 2H), 7.231−7.124 (m, 5H), 7.085−6.981 (m, 7H), 6.945−6.927 (d, J = 7.2 Hz, 1H), 6.830−6.786 (m, 3H), 6.343 (s, 1H), 4.072 (s, 2H), 3.541 (s, 3H), 2.111 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8, 139.4, 139.0, 137.3, 137.2, 137.2, 137.1, 136.7, 136.7, 130.4, 128.6, 128.0, 128.0, 127.7, 127.7, 127.3, 127.2, 127.0, 126.9, 126.1, 126.0, 121.2, 121.1, 118.8, 110.4, 108.7, 45.6, 32.6, 32.5, 21.3, 21.2; IR (neat, cm^{-1}) 3436, 3052, 3019, 2923, 1596, 1487, 1379, 1333, 1214, 1070, 1032, 797, 751, 694, 523; HRMS (APCI) Calcd for $C_{33}H_{28}N$ M + H = 438.2216, found 438.2218.

*(Z)-1-Methyl-3-(1,3,5-triphenylpent-2-en-4-ynyl)-1H-indole (**4aa**).* Yellow oil, 31 mg, 75% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.709−7.687 (m, 2H), 7.537−7.496 (m, 3H), 7.437−7.419 (d, J = 7.2 Hz, 2H), 7.344−7.307 (m, 6H), 7.287−7.234 (m, 3H), 7.219−7.171 (m, 2H), 7.035−6.996 (m, 1H), 6.916−6.891 (d, J = 10 Hz, 1H), 6.788 (s, 1H), 5.846−5.821 (d, J = 10 Hz, 1H), 3.691 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 139.8, 138.1, 137.5, 131.7, 128.6, 128.5, 128.3, 127.8, 127.4, 127.0, 127.0, 126.5, 126.4, 123.5, 123.0, 121.8, 120.1, 119.1, 116.8, 109.3, 95.9, 86.9, 44.7, 44.7, 32.8, 32.7; IR (neat, cm^{-1}) 3457, 3055, 2925, 1596, 1487, 1380, 1339, 1239, 1211, 1147, 1124, 1084, 1062, 1022, 885, 798, 750, 694, 571; HRMS (APCI) Calcd for $C_{32}H_{26}N$ M + H = 424.2060, found 424.2061.

*3-(3,5-Diphenyl-1-propyl-pent-2-en-4-ynyl)-1-methyl-1H-indole (**4oa**).* Yellow oil, 16 mg, 40% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.846−7.826 (d, J = 8.0 Hz, 1H), 7.657−7.638 (d, J = 7.6 Hz, 2H), 7.586−7.563 (dd, J_1 = 8 Hz, J_2 = 1.6 Hz, 2H), 7.374−7.175 (m, 9H), 7.087−7.049 (t, J = 7.6 Hz, 1H), 6.911 (s, 1H), 6.506−6.481 (d, J = 10 Hz, 1H), 4.552−4.490 (td, J_1= 7.4 Hz, J_2 = 6 Hz, 1H), 3.722 (s, 3H), 2.067−1.867 (m, 2H), 1.576−1.459 (m, 2H), 1.022−0.985 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 138.2, 137.2, 131.6, 128.5, 128.3, 128.3, 127.6, 127.5, 126.2, 125.2, 123.7, 122.3, 121.6, 119.9, 118.9, 117.6, 109.2, 95.3, 87.4, 38.6, 37.4, 32.7, 20.9, 14.3; IR (neat, cm^{-1}) 3435, 3037, 2957, 2143, 1635, 1253, 1374, 1101, 908, 871, 844, 735, 699, 687; HRMS (APCI) Calcd for $C_{29}H_{28}N$ M + H = 390.2216, found 390.2213.

*(Z)-3-(3-(4-Chlorophenyl)-1-(2,4-dichlorophenyl)-5-phenylpent-2-en-4-yn-1-yl)-1-methyl-1H-indole (**4pa**).* Yellow oil, 26 mg, 50% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.625−7.604 (d, J = 8.4 Hz, 2H), 7.503−7.471 (m, 3H), 7.435−7.430 (d, J = 2 Hz, 1H), 7.311−7.277 (m, 6H), 7.221−7.159 (m, 3H), 7.059−7.022 (d, J = 7.2 Hz, 1H), 6.766−6.742 (d, J = 9.6 Hz, 1H), 6.657 (s, 1H), 6.202−6.178 (d, J = 9.6 Hz, 1H), 3.685 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 138.1, 137.4, 136.2, 134.7, 133.8, 132.7, 131.6, 130.4, 129.6, 128.6, 128.5, 128.4, 127.6, 127.3, 126.9, 126.8, 123.6, 122.9, 121.9, 119.6, 119.2, 115.7, 109.3, 97.1, 85.8, 41.0, 32.7, 32.7; IR (neat, cm^{-1}) 3458, 3052, 2923, 1596, 1487, 1458, 1380, 1337, 1239, 1214, 1149, 1124, 1084, 1062, 1022, 885, 798, 750, 694, 571; HRMS (APCI) Calcd for $C_{32}H_{23}Cl_3N$ M + H = 526.0891, found 526.0888.

*(Z)-3-(1,3-Diphenyl-5-(trimethylsilyl)pent-2-en-4-ynyl)-1-methyl-1H-indole (**4qa**).* Yellow oil, 35 mg, 84% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.752−7.734 (d, J = 7.2 Hz, 2H), 6.656−6.636 (d, J = 8 Hz, 1H), 7.531−7.512 (d, J = 7.6 Hz, 2H), 7.445−7.270 (m, 8H), 7.169−7.132 (t, J = 7.6 Hz, 1H), 7.018−6.992 (d, J = 10.4 Hz, 1H), 6.867 (s, 1H), 5.909−5.884 (d, J = 10 Hz, 1H), 3.800 (s, 3H), 0.406 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 140.6, 137.6, 137.4, 128.5, 128.3, 128.2, 127.7, 127.3, 126.8, 126.4, 126.2, 122.9, 121.7, 120.1, 118.9, 116.8, 109.2, 102.3, 101.3, 44.4, 32.6, 0.1; IR (neat, cm^{-1}) 3058, 3027, 2958, 2926, 2854, 2248, 2145, 1062, 1545, 1473, 1373, 1331, 1251, 1012, 987, 908, 871, 843, 735, 699, 646; HRMS (APCI) Calcd for $C_{29}H_{30}NSi$ M + H = 420.2142, found 420.2143.

*1,5-Dimethyl-3-(2,4,5-triphenyl-cyclopenta-1,4-dienyl)-1H-indole (**3ab**).* Brown oil, 26 mg, 60% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.147−7.129 (m, 2H), 7.101−7.084 (d, J = 6.8 Hz, 2H), 7.064−7.044 (m, 2H), 7.030−6.969 (m, 8H), 6.943−6.920 (dd, J_1 = 7.2 Hz, J_2 = 2 Hz, 2H), 6.851−6.830 (d, J = 8.4 Hz, 1H), 6.229 (s, 1H), 4.012 (s, 2H), 3.470 (s, 3H), 2.103 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 139.4, 139.2, 137.3, 137.3, 137.2, 136.7, 135.1, 129.9, 128.6, 128.1, 127.9, 127.8, 127.3, 127.1, 126.6, 126.2, 125.9, 122.7, 120.9, 109.7, 108.3, 45.7, 32.6, 21.2; IR (neat, cm^{-1}) 3439, 1633, 1495, 1440, 1379, 1254, 1063, 699; HRMS (APCI) Calcd for $C_{33}H_{28}N$ M + H = 438.2216, found 438.2224.

*5-Methoxy-1-methyl-3-(2,4,5-triphenyl-cyclopenta-1,4-dienyl)-1H-indole (**3ac**).* Deep yellow oil, 22 mg, 50% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.332−7.313 (d, J = 7.6 Hz, 2H), 7.233−7.226 (d, J = 2.8 Hz, 1H), 7.207 (s, 1H), 7.185−7.125 (m, 5H), 7.118−7.090 (m, 4H), 7.068−7.031 (m, 3H), 6.748−6.720 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 6.387−6.382 (d, J = 2 Hz, 1H), 6.265 (s, 1H), 4.098 (s, 2H), 3.549 (s, 3H), 3.410 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 145.3, 139.6, 138.9, 137.6, 137.3, 137.0, 136.7, 131.9, 130.0, 129.3, 128.1, 128.0, 127.9, 127.8, 127.4, 126.8, 126.7, 126.2, 126.0, 111.9, 109.6, 109.5, 102.5, 55.3, 45.9, 32.8; IR (neat, cm^{-1}) 3434, 2912, 2360, 1629, 1489, 1437, 1381, 1216, 1146, 1098, 1029, 741, 695, 613; HRMS (APCI) Calcd for $C_{33}H_{28}NO$ M + H = 454.2165, found 454.2181.

*5-Bromo-1-methyl-3-(2,4,5-triphenyl-cyclopenta-1,4-dienyl)-1H-indole (**3ad**).* Yellow oil, 40 mg, 80% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.283−7.266 (d, J = 6.8 Hz, 2H), 7.209−7.190 (d, J = 7.6 Hz, 2H), 7.159−7.057 (m, 11H), 7.004−6.985 (d, J = 7.6 Hz, 3H), 6.361 (s, 1H), 4.062 (s, 2H), 3.495 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 140.3, 139.4, 137.1, 136.9, 136.5, 136.3, 135.3, 129.7, 129.5, 128.5, 128.1, 127.9, 127.8, 127.3, 126.7, 126.3, 124.0, 123.5, 112.4, 110.3, 110.1, 45.7, 32.8; IR (neat, cm^{-1}) 3440, 2921, 2360, 1622, 1478, 1382, 1145, 1053, 908, 788, 751, 696, 598; HRMS (APCI) Calcd for $C_{32}H_{25}BrN$ M + H = 502.1165, found 502.1166.

*1-Methyl-3-(2,4,5-triphenyl-cyclopenta-1,4-dienyl)-1H-indole-5-carbonitrile (**3ae**).* Brown oil, 32 mg, 73% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.227−7.202 (dd, J_1 = 8.8 Hz, J_2 = 1.6 Hz, 1H), 7.179−7.108 (m, 6H), 7.091−7.010 (m, 9H), 6.920−6.897 (m, 2H), 6.428 (s, 1H), 4.021 (s, 2H), 3.546 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 141.0, 139.8, 138.0, 136.9, 136.7, 136.3, 135.4, 130.5, 129.7, 128.2, 128.1, 128.1, 127.7, 127.3, 126.9, 126.6, 126.5, 126.4, 124.3, 120.6, 111.6, 109.8, 102.0, 45.8, 32.9; IR (neat, cm^{-1}) 3434, 2360, 2220, 1629, 1490, 1448, 1382, 1145, 1098, 800, 737, 696, 660, 605; HRMS (APCI) Calcd for $C_{33}H_{25}N_2$ M + H = 449.2012, found 449.2021.

*1,7-Dimethyl-3-(2,4,5-triphenyl-cyclopenta-1,4-dienyl)-1H-indole (**3af**).* Brown oil, 31 mg, 71% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.247−7.227 (d, J = 8 Hz, 2H), 7.138−7.119 (d, J = 7.6 Hz, 3H), 7.097−6.998 (m, 8H), 6.975−6.958 (d, J = 6.8 Hz, 1H), 6.928−6.907 (m, 2H), 6.851−6.832 (d, J = 7.6 Hz, 1H), 6.713−6.695 (d, J = 7.2 Hz, 1H), 6.631−6.593 (t, J = 7.6 Hz, 1H), 6.157 (s, 1H), 4.007 (s, 2H), 3.747 (s, 3H), 2.623 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 139.6, 139.2, 137.3, 137.2, 137.0, 136.7, 135.4, 130.1, 129.9, 128.1, 128.0, 127.9, 127.8, 127.8, 127.2, 126.6, 126.2, 126.0, 124.0, 120.6, 119.3, 110.1, 45.6, 36.6, 36.57, 19.7; IR (neat, cm^{-1}) 3434, 3053, 2922, 2360, 1600, 1488, 1450, 1373, 1263, 1204, 1073, 1032, 854, 745, 696; HRMS (APCI) Calcd for $C_{33}H_{28}N$ M + H = 438.2216, found 438.2223.

*3-(2,4,5-Triphenyl-cyclopenta-1,4-dienyl)-1H-indole (**3ag**).* Brown oil, 28 mg, 68% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.865 (s, 1H), 7.322−7.301 (m, 2H), 7.268−7.247 (d, J = 8.4 Hz, 3H), 7.231−7.205 (m, 2H), 7.186−7.047 (m, 9H), 7.014−6.990 (m, 2H), 6.874−6.837 (t, J = 7.2 Hz, 1H), 6.519−6.513 (d, J = 2.4 Hz, 1H), 4.110 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 140.1, 139.4, 137.2, 137.0, 136.9, 136.6, 135.7, 129.8, 128.1, 128.0, 127.9, 127.8, 127.2, 126.6, 126.3, 126.3, 126.1, 123.8, 121.7, 120.9, 119.4, 112.0, 110.7, 45.7; IR (neat, cm^{-1}) 3434, 3052, 2924, 2322, 1685, 1616, 1456, 1382, 1258, 1199, 1093, 800, 747, 697, 605; HRMS (APCI) Calcd for $C_{31}H_{24}N$ M + H = 410.1903, found 410.1905.

*5-Methyl-3-(2,4,5-triphenyl-cyclopenta-1,4-dienyl)-1H-indole (**3ah**).* Yellow oil, 17 mg, 41% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.783 (s, 1H), 7.327−7.309 (d, J = 7.2 Hz, 2H), 7.231−7.050 (m, 12H), 7.016−7.003 (d, J = 5.2 Hz, 2H), 6.905−6.885 (d, J = 8 Hz, 1H), 6.843 (s, 1H), 6.489 (s, 1H), 4.104 (s, 2H), 2.188 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 140.0, 139.3, 137.3, 137.2, 136.7, 134.1, 129.8, 128.5, 128.1, 128.0, 127.9, 127.8, 127.3, 126.7, 126.6, 126.2, 126.1, 123.9, 123.3, 120.7, 111.5, 110.2, 45.7, 21.3; IR (neat, cm^{-1}) 3435, 3052, 2924, 2323, 1633, 1496, 1443, 1379, 1254, 1063,

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800, 745, 699; HRMS (APCI) Calcd for $C_{32}H_{26}N$ M + H = 424.2060, found 424.2065.

*Methoxy-3-(2,4,5-triphenyl-cyclopenta-1,4-dienyl)-1H-indole (**3ai**).* Yellow oil, 17 mg, 38% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.798 (s, 1H), 7.318−7.300 (d, J = 7.2 Hz, 2H), 7.229−7.026 (m, 14 H), 6.721−6.694 (dd, J_1 = 8.8 Hz, J_2 = 2 Hz, 1H), 6.452−6.418 (dd, J_1 = 11.2 Hz, J_2 = 2.4 Hz, 2H), 4.105 (s, 2H), 3.428 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7, 145.2, 139.6, 137.5, 137.3, 136.9, 130.7, 129.9, 128.09, 128.06, 128.0, 127.8, 127.4, 126.7, 126.5, 126.3, 126.1, 124.7, 112.5, 111.6, 111.3, 102.2, 55.3, 45.8; IR (neat, cm^{-1}) 3434, 2911, 2357, 1631, 1491, 1442, 1383, 1216, 1147, 1098, 1029, 741, 699, 608; HRMS (APCI) Calcd for $C_{32}H_{26}NO$ M + H = 440.2009, found 440.2019.

*5-Bromo-3-(2,4,5-triphenyl-cyclopenta-1,4-dienyl)-1H-indole (**3aj**).* Yellow oil, 24 mg, 50% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.877 (s, 1H), 7.289−7.266 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 2H), 7.223−7.073 (m, 14H), 7.008−6.985 (m, 2H), 6.540−6.534 (d, J = 2.4 Hz, 1H), 4.090 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 140.8, 139.5, 137.1, 136.8, 136.5, 136.2, 134.3, 129.7, 128.2, 128.1, 128.0, 127.8, 127.3, 126.7, 126.4, 126.3, 124.9, 124.6, 123.4, 112.8, 112.2, 111.8, 45.7; IR (neat, cm^{-1}) 3443, 2922, 2355, 1622, 1478, 1387, 1144, 1057, 908, 788, 751, 696, 601; HRMS (APCI) Calcd for $C_{31}H_{23}BrN$ M + H = 488.1008, found 488.1010.

*7-Methyl-3-(2,4,5-triphenyl-cyclopenta-1,4-dienyl)-1H-indole (**3ak**).* Yellow oil, 15 mg, 36% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.819 (s, 1H), 7.316−7.298 (d, J = 7.2 Hz, 2H), 7.239−7.043 (m, 11H), 7.019−6.996 (dd, J_1 = 7.6 Hz, J_2 = 2 Hz, 2H), 6.949−6.929 (d, J = 8 Hz, 1H), 6.895−6.878 (d, J = 6.8 Hz, 1H), 6.793−6.755 (t, J = 7.6 Hz, 1H), 6.514−6.508 (d, J = 2.4 Hz, 1H), 4.107 (s, 2H), 2.421 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 140.0, 139.4, 137.3, 137.1, 137.1, 136.7, 135.4, 129.9, 128.1, 128.0, 127.9, 127.8, 127.2, 126.6, 126.2, 126.1, 125.9, 123.6, 122.3, 119.7, 119.5, 118.8, 112.4, 45.7, 16.6; IR (neat, cm^{-1}) 3434, 3053, 2922, 2358, 1611, 1489, 1450, 1380, 1265, 1204, 1073, 1040, 847, 748, 696; HRMS (APCI) Calcd for $C_{32}H_{26}N$ M + H = 424.2060, found 424.2066.

*(3-Chlorocyclopenta-1,3-diene-1,2,4-triyl)tribenzene (**5a**).* Yellow oil, 29 mg, 46% yield (0.2 mmol scale): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.830−7.811 (d, J = 7.6 Hz, 2H), 7.428−7.284 (m, 8H), 7.230−7.125 (m, 5H), 3.939 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 139.5, 136.2, 135.5, 134.8, 134.6, 130.2, 130.0, 128.5, 128.3, 127.8, 127.5, 127.3, 127.1, 127.0, 43.9; IR (neat, cm^{-1}) 3437, 3070, 3024, 2854, 2360, 1766, 1682, 1587, 1489, 1451, 1374, 1317, 1259, 1211, 1174, 1104, 1045, 941, 910, 874, 792, 757, 695; HRMS (APCI) Calcd for $C_{23}H_{18}Cl$ M + H = 329.1092, found 329.1094.

*(3-Bromocyclopenta-1,3-diene-1,2,4-triyl)tribenzene (**6a**).* Yellow oil, 8 mg, 10% yield (0.2 mmol scale): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.823−7.804 (d, J = 7.6 Hz, 2H), 7.433−7.371 (m, 5H), 7.327−7.294 (m, 3H), 7.167−7.123 (m, 5H), 3.935 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 140.1, 139.7, 135.7, 135.4, 135.3, 130.0, 128.4, 128.4, 128.3, 127.8, 127.5, 127.4, 127.0, 120.6, 45.5; IR (neat, cm^{-1}) 3437, 3070, 3024, 2854, 2360, 1766, 1682, 1587, 1489, 1451, 1374, 1317, 1259, 1211, 1174, 1104, 1045, 941, 910, 874, 792, 757, 695; HRMS (APCI) Calcd for $C_{23}H_{18}Br$ M + H = 373.0586, found 373.0584.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of the ^{1}H NMR and ^{13}C NMR spectra for all new products and crystal data (CIF) for **3ea** and **3ia**. This material is available free of charge via the Internet at http://pubs.acs.org

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Notes

The authors declare no competing financial interest.

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