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Platinum-Catalyzed Multistep Reactions of Indoles with Alkynyl Alcohols

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Abstract: $PtCl_2$ effectively catalyzes the multistep reaction of *N*-methyl indole (**1a**) with pent-3-yn-1-ol (**2a**) in THF at room temperature for 2 h to give indole derivative **3a**, which contains a five-membered cyclic ether group at C3 in 93 % yield. Under similar reaction conditions, various substituted *N*-methyl indoles **1b**–**h** and indole (**1i**) reacted efficiently with **2a** to afford the corresponding indole derivatives **3b**–**h** and **3i** in 48–91 and 72 % yields. The results showed that *N*-methyl indoles with electron-donating substituents were more reactive affording higher product yields than those with electron-withdrawing groups. Likewise, various substituted but-3-yn-1-ols **2b**–**e** and other longer chain alkynyl alcohols **2f**–**i** also underwent a cyclization–addition reaction with *N*-methyl indole (**1a**) to provide the corresponding cyclization–addition products **3j**–**m** and **3a**, **3j**, and **3n**–**o** in good to excellent yields. The present platinum-catalyzed cyclization–addition reaction can be further extended into *N*-methyl pyrrole. Mechanistically, the catalytic reaction proceeds by an intramolecular hydroalkoxylation of alkynyl alcohol to afford cyclic enol ether followed by the addition of the C–H bond of indole to the unsaturated moiety of cyclic enol ether providing the final product. Experimental evidence to support this proposed mechanism is provided.

Keywords: catalysis · electrophilic metallation · gold · Lewis acids · platinum

Introduction

The transition-metal-catalyzed intramolecular nucleophilic addition of an O–H bond to a carbon–carbon multiple bond (hydroalkoxylation reaction) is a practical method to construct complex cyclic ethers under mild reaction conditions.[1] Many polycyclic ether-based biologically active compounds and natural products[2] as well as antiviral nucleosides[3] and oligosaccharides[4] were synthesized by using this methodology. The development of mild and convenient methods for the functionalization of arenes and heteroarenes is fundamentally important in organic synthesis. The transition-metal-catalyzed direct addition of the C–H bond of arenes or heteroarenes to carbon–carbon multiple bonds through electrophilic metallation is one of the convenient methods for functionalizing arenes or heteroarenes.[5,6,9] These types of reactions are highly atom-economical and environmentally friendly as no prefunctionalization, such as halogenation is required. Indeed, if the above two highly efficient transition-metal-catalyzed transformations occur in one pot without isolating the intermediate and changing the reaction conditions, it would be very useful in organic synthesis for maximized molecular complexity with minimized organic wastes.[7]

With the assistance of metal complexes such as palladium, platinum, and gold, alkynyl alcohols are capable of undergoing intramolecular hydroalkoxylation reactions to give cyclic enol ether derivatives.[8] In addition, these metal complexes also readily activate the unreactive C–H bond of arenes or heteroarenes which further endures addition reactions with carbon–carbon multiple bonds to give the corresponding hydroarylation product.[5–7,9] Although a number of reports describe the addition reaction of the C–H bond of arenes, heteroarenes, or active methylenes to carbon–carbon multiple bonds (alkynes and alkenes),[5–7,9] the addition reaction with cyclic enol ether is still rare. Recently, Li et al. reported a gold-catalyzed addition reaction of the C–H bond of active methylenes with cyclic enol ethers.[10]

Our continuous interest in metal-catalyzed multistep reactions prompted us to investigate the possibility of carrying out the above two transformations in one pot.[11–12] In this article, we wish to report a platinum-catalyzed domino reaction of indole with alkynyl alcohol to give an indole derivative with a cyclic ether group at the 3-position through two

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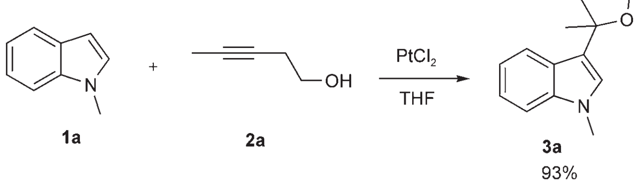
consecutive O–H and C–H bond additions. Nitrogen or oxygen-containing heterocycles are important building blocks in natural products and various pharmaceutical agents. The present reaction provides an efficient method for the functionalization of indoles and pyrrole.

Results and Discussion

In the presence of platinum dichloride (5 mol %), *N*-methyl indole (**1a**) reacted with pent-3-yn-1-ol (**2a**) in THF at room temperature for 2 h to give indole derivative **3a** containing a five-membered ether ring group attached at C3 in 93 % isolated yield (Scheme 1). This product, thoroughly characterized by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry, appears to result from an intramolecular O–H bond addition and an intermolecular C–H bond addition of indole (**1a**) to the unsaturated moiety of the alkynyl alcohol. The reaction is completely atom economic with no loss of any atom in the product compared with the two reactants. In this reaction, the cyclization step is likely to occur by means of the attack of the hydroxy group at C4 of the alkynyl alcohol **2a** (a 5-*endo-dig* pathway) to give a five-membered ether ring group.[13]



Scheme 1. Platinum-catalyzed cyclization–addition reaction of *N*-methyl indole (**1a**) with pent-3-yn-1-ol (**2a**).

In view of the fact that some gold complexes show similar Lewis acid catalytic activity to that of $PtCl_2$, we also examined the catalytic activities of $AuCl_3$, $AuCl(PPh_3)$, and $NaAuCl_4{\cdot}2H_2O$ for the reaction of **1a** with **2a** (Table 1).

Table 1. Effect of catalyst and solvent on the cyclization–addition reaction of *N*-methyl indole (**1a**) with pent-3-yn-1-ol (**2a**).[a]

Entry	Catalyst	Solvent	Yield [%][b]
1	$AuCl_3$	THF	70
2	$AuCl(PPh_3)$	THF	0
3	$NaAuCl_4{\cdot}2H_2O$	THF	75
4	$AuCl(PPh_3)/AgSbF_6$	THF	45[c]
5	$PtCl_2$	THF	97
6	$PtCl_2$	CH_3CN	85
7	$PtCl_2$	DCE	60
8	$PtCl_2$	toluene	55
9	$PtCl_2$	MeOH	35

[a] All reactions were carried out by using *N*-methyl indole (**1a**) (1.00 mmol), pent-3-yn-1-ol (**2a**) (1.20 mmol), catalyst (0.005 mmol, 5 mol %) and THF (3.0 mL) at room temperature for 10 h. [b] Yields were measured from crude products by the ^{1}H NMR spectroscopic integration method by using mesitylene as an internal standard. [c] Additive $AgSbF_6$ (0.020 mmol, 20 mol %) was added in the reaction mixture.

Under similar reaction conditions, [$AuCl_3$] and $NaAuCl_4{\cdot}2H_2O$ exhibited substantial catalytic activity giving **3a** in 70 and 75 % yields, but $AuCl(PPh_3)$ was totally inactive (entries 1–3). However, if the chloride in $AuCl(PPh_3)$ (5 mol %) was removed by $AgSbF_6$ (20 mol %), the gold complex became active for the reaction giving **3a** in 45 % yield (entry 4). Thus, $PtCl_2$ appears to show the highest catalytic activity among these platinum and gold complexes (entry 5). Several solvents were tested for the [$PtCl_2$]-catalyzed reaction of **1a** with **2a** at room temperature. The results revealed that THF was the solvent of choice giving **3a** in 97 % yield (entry 5). CH_3CN was also effective affording **3a** in 85 % yield (entry 6). Other solvents, DCE (1,2-dichloroethane), toluene, and MeOH provided **3a** in 60, 55, and 35 % yields, respectively (entries 7–9).

This platinum-catalyzed addition reaction was successfully extended to different substituted indoles **1b–i** and substituted alkynyl alcohols **2b–e**. The results of these studies are listed in Table 2. Treatment of 5-methoxy-substituted indole **1b** with **2a** provided the expected product **3b** in 91 % yield (entry 1). Similarly, 6-methoxy (**1c**), 7-methoxy (**1d**), 5-bromo (**1e**), 5-iodo (**1f**), and 5-nitro- (**1g**) substituted indoles reacted with **2a** affording products **3c–g** in 58–90 % yields, respectively (entries 2–6). The reaction of **1h** possessing a methyl group at the C2-position with **2a** also proceeded smoothly to give the addition product **3h** albeit in lower yield (entry 7). The nature of the substituents on the N-moiety of indole greatly influences the yield of the product. While N-methyl indole (**1a**) gave **3a** in the highest, 93 %, yield (Scheme 1), indole (**1i**) was comparatively less effective affording **3i** in 72 % yield (entry 8). *N*-acetyl indole and *N*-sulphonyl indole were totally ineffective. These results indicate that an electron-donating substituent at the benzo-ring or at the nitrogen atom of the indole moiety favors product formation, while an electron-withdrawing group greatly hinders the reaction (entries 1–8).

Under the optimized reaction conditions, other but-3-yn-1-ol derivatives that have substituents, such as Et (**2b**), Ph (**2c**), and 2-thienyl (**2d**) at one of the alkyne carbons also reacted efficiently with *N*-methyl indole (**1a**), providing **3j–l** in 73–89 % yields (entries 9–11). The substituent at one of the alkyne carbons of **2** shows a substantial steric effect on the yield of product **3**. Thus, Et-substituted alkynyl alcohol **2b** affords **3j** in 89 % yield, but the bulkier Ph or 2-thienyl-substituted alkynyl alcohol **2c** and **2d** provide **3k** and **3l** in 75 and 73 % yields, respectively. In addition to **3k**, a non-cyclized addition product **3k′** containing an *E* and *Z* mixture

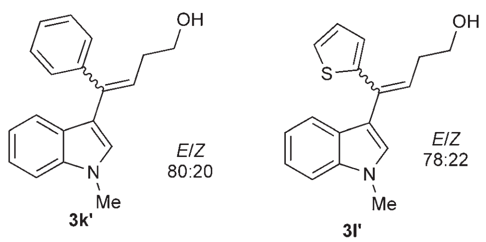
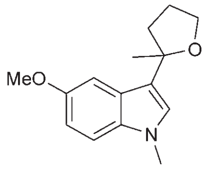
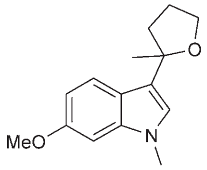
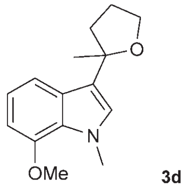
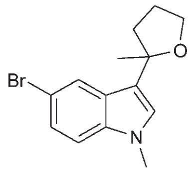
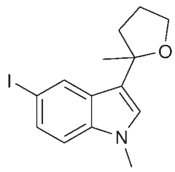
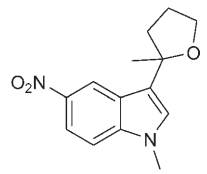
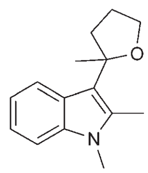
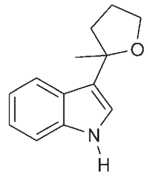
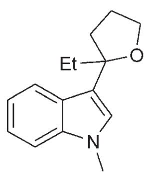


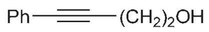
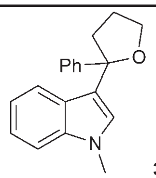
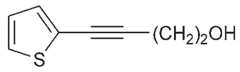
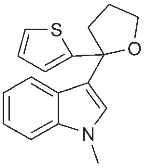
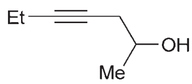
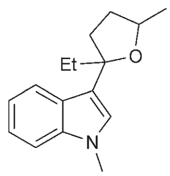
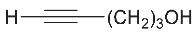
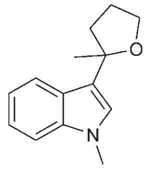
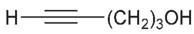
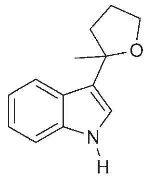
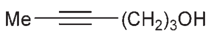
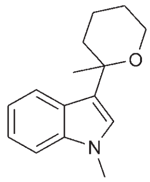
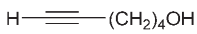
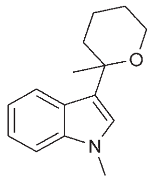
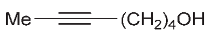
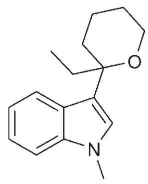
Table 2. Results of the platinum-catalyzed cyclization–addition reaction of substituted indoles **1b**–**i** with alkynyl alcohols **2a**–**i**.[a]

Entry	1	2	Product 3	Yield [%][b]
1	**1b**	Me—≡—$(CH_2)_2OH$ **2a**	 **3b**	91
2	**1c**	Me—≡—$(CH_2)_2OH$ **2a**	 **3c**	85
3	**1d**	Me—≡—$(CH_2)_2OH$ **2a**	 **3d**	90
4	**1e**	Me—≡—$(CH_2)_2OH$ **2a**	 **3e**	89
5	**1f**	Me—≡—$(CH_2)_2OH$ **2a**	 **3f**	90
6	**1g**	Me—≡—$(CH_2)_2OH$ **2a**	 **3g**	58
7	**1h**	Me—≡—$(CH_2)_2OH$ **2a**	 **3h**	48
8	**1i**	Me—≡—$(CH_2)_2OH$ **2a**	 **3i**	72
9	**1a**	Et—≡—$(CH_2)_2OH$ **2b**	 **3j**	89

in a 80:20 ratio in 15% combined yield was also observed from the reaction of **2c** with **1a**. Similarly, addition product **3l′** with an *E*/*Z* ratio of 78:22 in 17% combined yield was also observed for the reaction of **2d** with **1a**. For but-3-yn-1-ol derivative **2e**, which contains an ethyl group at one of the alkyne carbons and a methyl group at the α-position to the alcohol group affords the corresponding cyclization–addition product **3m** in 85% yield. The product consists of a 1:1 ratio of diastereomers (entry 12). All of these reactions are highly regioselective, giving only five-membered cyclization products (entries 1–12). While various internal alkynyl alcohols **2a**–**e** react smoothly with **1** to give cyclization–addition product **3**, terminal alkynyl alcohol but-3-yn-1-ol showed no activity with indoles **1a** and **1i** under the optimized reaction conditions.

Surprisingly, for the terminal alkyne,[7d] pent-4-yn-1-ol (**2f**), which is one carbon longer than but-3-yn-1-ol, the cyclization–addition reaction with **1a** proceeded successfully to give product **3a** in 85% yield (Table 2, entry 13). The product is exactly the same as that from **1a** and pent-3-yn-1-ol (**2a**) (Scheme 1). Similarly, indole **1i** reacts with **2f** to afford **3i** in 79% yield (entry 14).[5f,g] The product is also exactly the same as that from **1i** and pent-3-yn-1-ol (**2a**) (entry 8). Internal alkynyl alcohol **2g** also undergoes a cyclization–addition reaction smoothly, but to give two products, **3j** and **3n** (Scheme 2). The former is the major product in 67% yield and shows a structure the same as that from **1a** and **2b** (entry 9), while the latter is minor and is a six-membered cyclic ether ring (entry 15). It is noteworthy that the reaction of **1a** or **1i** with substituted pent-4-yn-1-ol **2f** af-

Table 2. (Continued)

Entry	1	2	Product 3	Yield [%][b]
10	**1a**	 **2c**	 **3k**	75[c]
11	**1a**	 **2d**	 **3l**	73[c]
12	**1a**	 **2e**	 **3m**	85[d]
13	**1a**	 **2f**	 **3a**	85
14	**1i**	 **2f**	 **3i**	79
15	**1a**	 **2g**	**3j + 3n**  **3n**	67+20
16	**1a**	 **2h**	 **3n**	87[e]
17	**1a**	 **2i**	 **3o**	85[e]

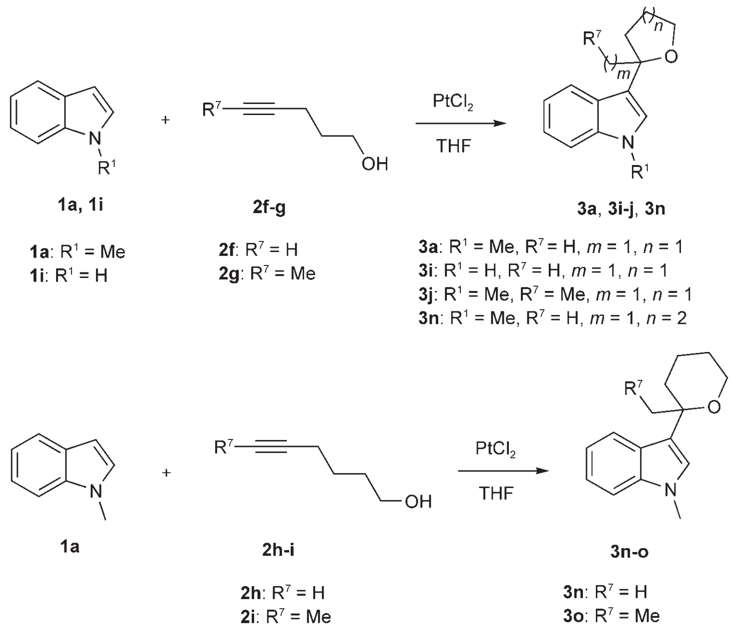
[a] All reactions were carried out by using indoles **1** (1.00 mmol), alkynyl alcohol **2** (1.20 mmol), $PtCl_2$ (0.005 mmol, 5 mol%) and THF (3.0 mL) at room temperature for 2 h. [b] Isolated yields. [c] Reaction was carried out at room temperature for 8 h. [d] Diasteroisomeric ratio 1:1. [e] Reaction was carried out at 60°C for 8 h.

fords only five-membered cyclic ether ring products (entries 13–14), whereas the reaction of **1a** with **2g** gives five-membered as well as six-membered ring products **3j** and **3n**, respectively (entry 15, Table 2 and Scheme 2).

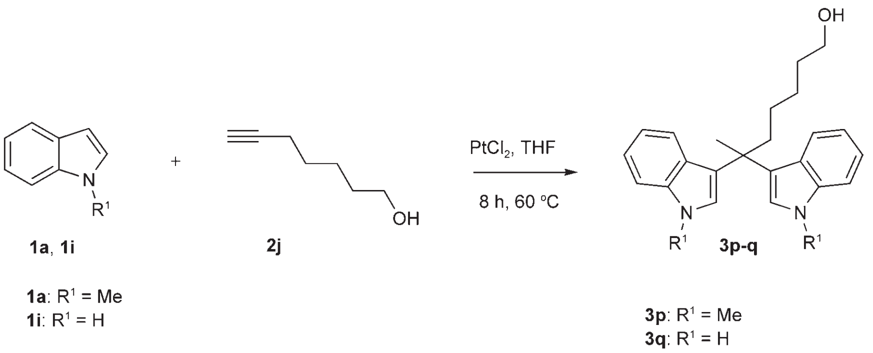
The present catalytic reaction was further tested with longer chain alkynyl alcohols by using hex-5-yn-1-ol (**2h**) and hept-5-yn-1-ol (**2i**, see Scheme 2). In both cases, the catalytic reaction proceeded smoothly and is highly regioselective. For example, the reaction of **2h** with **1a** afforded six-membered ether ring **3n** exclusively in 87% yield (entry 16). In a similar manner, **2i** reacted with **1a** providing product **3o**, which contains a six-membered ether ring in 85% yield (entry 17). It is important to say that in the reaction of **2i** with **1a**, only a six-membered ether ring product is observed and no seven-membered-ring product formed.

Unlike **2h** and **2i**, the reaction of **2j** with indoles **1a** and **1i** did not give the expected seven-membered cyclic ether derivatives. Instead, the reaction products are bis(3-indolyl) species **3p** and **3q** in 85 and 79% yields, respectively (Scheme 3).

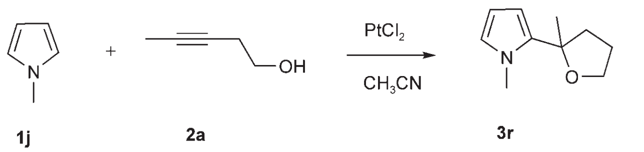
The scope of the present platinum-catalyzed cyclization–addition reaction can be further extended to *N*-methyl pyrrole. Treatment of *N*-methyl pyrrole (**1j**) (4.0 mmol) with pent-3-yn-1-ol (**2a**) (1.0 mmol) in the presence of $PtCl_2$ in CH_3CN at room temperature for 30 min afforded 2-substituted pyrrole derivative **3r** in 75% yield (Scheme 4). When the reaction was carried out in nearly an equal ratio of **1j** (1.0 mmol) to **2a** (1.2 mmol), multicyclic ether substituted pyrrole products were observed. These products cannot be separated by column chromatography.



Scheme 2. Platinum-catalyzed cyclization–addition reaction of substituted indoles **1a** and **1i** with substituted pent-4-yn-1-ols **2f–g** and hex-5-yn-1-ols **2h–i**.



Scheme 3. Platinum-catalyzed addition reaction of substituted indoles **1a** and **1i** with hept-6-yn-1-ol **2j**.



Scheme 4. Platinum-catalyzed cyclization–addition reaction of *N*-methyl pyrrole (**1j**) with pent-3-yn-1-ol (**2a**).

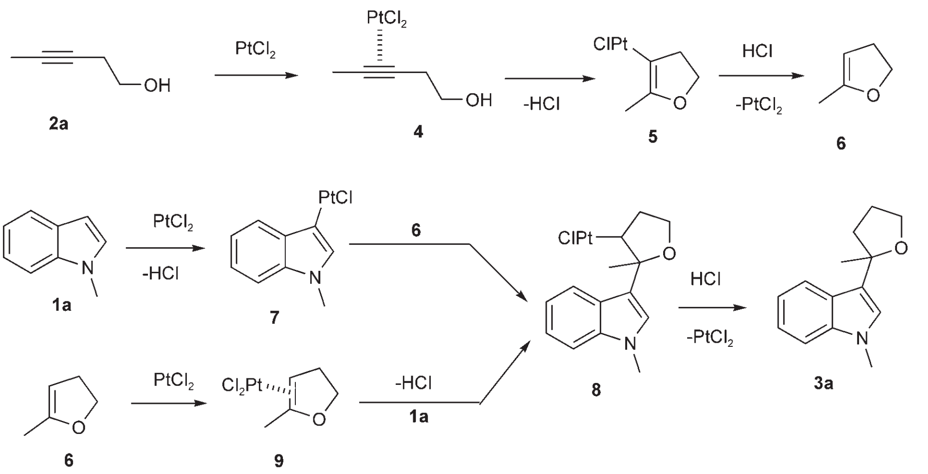
Based on the known chemistry of the metal-catalyzed intramolecular hydroalkoxylation of alkynyl alcohols[1,8] and the metal-catalyzed C–H bond addition of arenes to carbon-carbon multiple bonds,[5–7,9] a possible mechanism for the present platinum-catalyzed reaction of alkynyl alcohol **2a** with indole **1a** is proposed in Scheme 5. First, a $PtCl_2$-catalyzed intramolecular hydroalkoxylation of alkynyl alcohol likely occurs to give 2,3-dihydro-5-methylfuran (**6**). Then, a C–H bond addition of indole to intermediate **6** catalyzed by $PtCl_2$ again leads to the final product **3a**.

For the intimate mechanism of the intramolecular hydroalkoxylation of alkynyl alcohol, $PtCl_2$ likely acts as a Lewis acid to which the carbon–carbon triple bond of alkynyl alcohol **2a** is coordinated to give intermediate **4**. Intramolecular nucleophilic addition of the OH bond to alkyne in intermediate **4** by an 5-*endo-dig* cyclization affords intermediate **5**. Protonation of the resulting organoplatinum complex **5** affords cyclic enol ether **6** and regenerates $PtCl_2$.

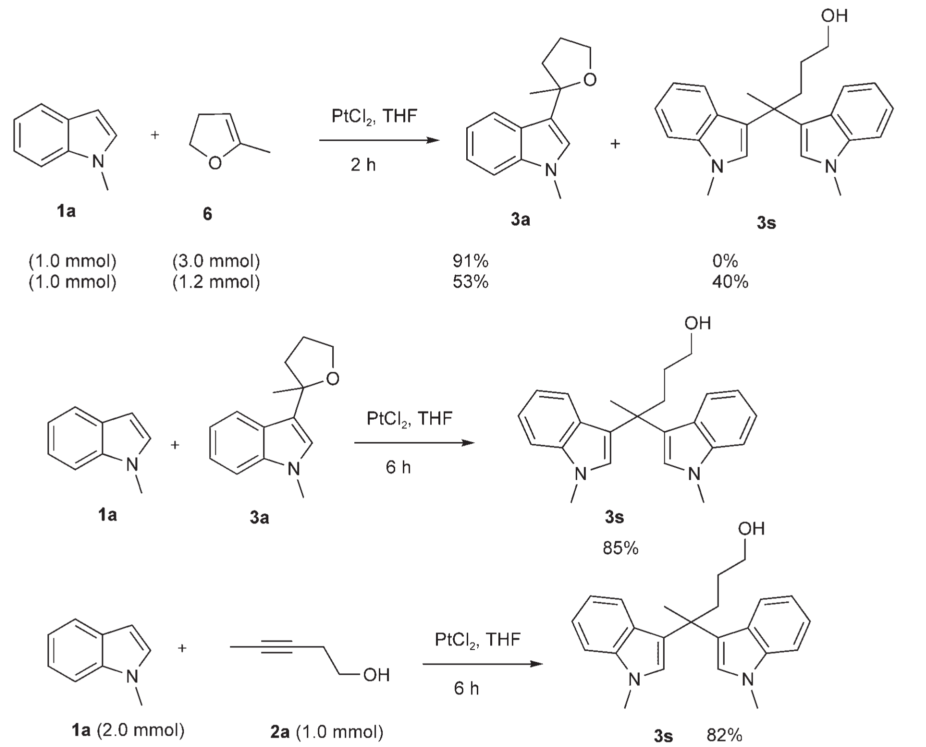
For the mechanism of the addition of indole **1a** to the cyclic enol ether **6**, there are two possible routes (Scheme 5). One involves an electrophilic metallation reaction of indole **1a** with $PtCl_2$ to form complex **7**,[6] followed by insertion of the carbon–carbon double bond of cyclic enol ether **6** to give complex **8**. Subsequent protonation of complex **8** affords product **3a** and regenerates $PtCl_2$. The other possible pathway is the coordination of the carbon–carbon double bond of cyclic enol ether **6** to $PtCl_2$ to afford intermediate **9**. C–H addition of indole **1a** at the coordinated double bond in **9** provides intermediate **8**. Protonation of complex **8** gives product **3** with regeneration of the catalyst.

The proposed key intermediate **6** is strongly supported by the results of the following reactions. Treatment of indole **1a** (1.0 mmol) with 2,3-dihydro-5-methylfuran (**6**) available commercially (3 mmol) in the presence of $PtCl_2$ at room temperature gave product **3a** in 91% yield (Scheme 6). Interestingly, as the relative amount of **1a** to **6** increases, another product **3s**, a product from double addition of indole **1a** to **6**, starts to appear. To explain the formation of **3s**, product **3a** was further treated with indole **1a** in the presence of $PtCl_2$ further transforming **3a** to the double-addition product **3s** in 85% yield (Scheme 6). In agreement with the results of the reaction of excess **1a** with **6**, the reaction of indole **1a** (2.00 mmol) with alkynyl alcohol **2** (1.00 mmol) (Scheme 1) also gave only the double-addition product **3s** in 82% yield (Scheme 6). The formation of **3s** can be explained by the coordination of the oxygen of **3a** to $PtCl_2$ followed by C–H addition of indole to the highly substituted carbon of the cyclic ether of **3a** to give double-addition product **3s** with regeneration of the catalyst. The selective ring-opening of cyclic ether has been a subject of intense interest in organic synthesis for the past few decades.[14] In the present reaction, we have reported for the first time that the catalytic amount of $PtCl_2$ selectively cleaves the C–O quaternary carbon of cyclic ether under mild reaction conditions.

The addition reaction of indole **1a** with cyclic enol ether **6** is a crucial step for the present reaction (Scheme 6). It is



Scheme 5. Proposed mechanism for the cyclization–addition reaction of indole **1** with alkynyl alcohol **2**.

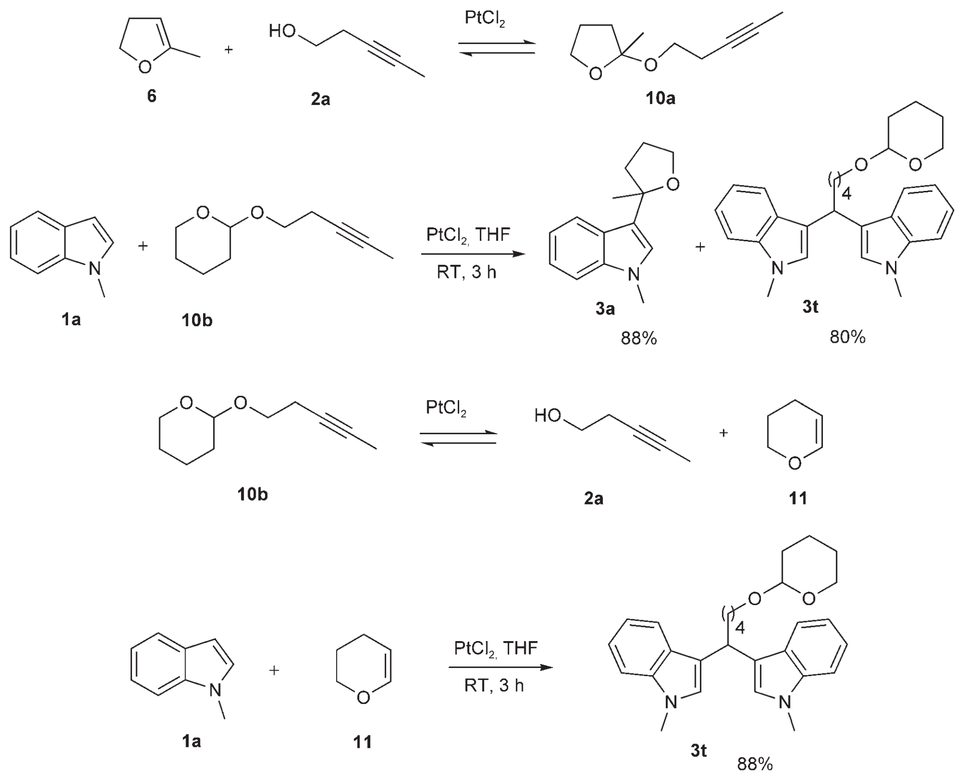


Scheme 6. Result of the platinum-catalyzed addition reaction of *N*-methylindole (**1a**) with 2,3-dihydro-5-methylfuran (**6**).

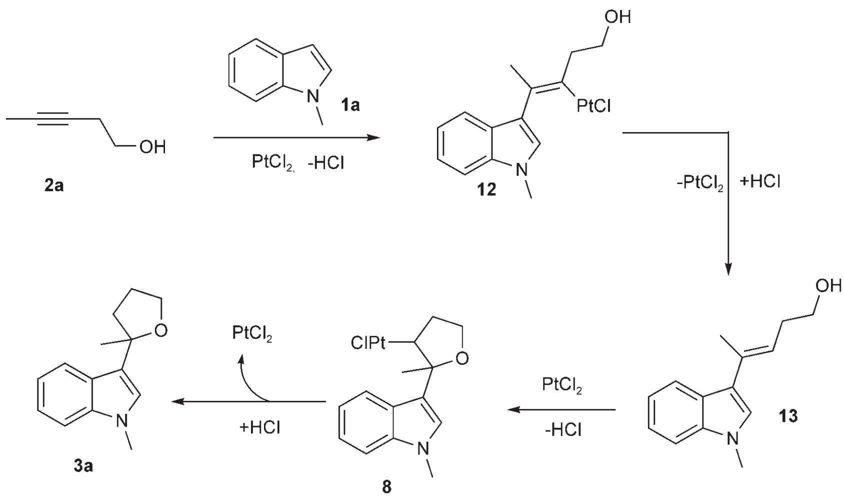
well known that cyclic enol ether is an excellent protecting reagent for alcohols.[15] With the assistance of $PtCl_2$, alkynyl alcohol **2a** underwent an intramolecular hydroalkoxylation reaction to give cyclic enol ether **6** (Scheme 5). Once, cyclic enol ether **6** is formed in the reaction mixture, there is a competition from the nucleophilic addition of the OH bond of alkynyl alcohol **2a**.[8a–b] It is likely that in the presence of $PtCl_2$, the nucleophilic addition of an OH bond of alkynyl alcohol **2a** to cyclic enol ether **6** to give **10a** is faster than the indole C–H bond addition (Scheme 7), but the reaction is reversible. On the other hand, the addition of *N*-methyl indole to **6** is an irreversible process leading to **3a** instead of **10a** as the final product. This is strongly supported by the following experiment in which the reaction of **1a** with tetrahydro-2-(pent-3-ynyloxy)-2*H*-pyran (**10b**) in the presence of $PtCl_2$ in THF at room temperature for 3 h gave products **3a** and **3t** in 88 and 80 % yields, respectively (Scheme 7). The above reaction clearly revealed that in the presence of $PtCl_2$, **10b** is cleaved into two moieties, alkynyl alcohol **2a** and cyclic enol ether **11**. Alkynyl alcohol **2a** then reacted with **1a** in the presence of $PtCl_2$ to give **3a** by the pathway shown in Scheme 5. In meantime, **11** reacted with two molecules of indole **1a** to afford a double-addition product which further reacted with another molecule of **11** to give product **3t** by the pathway shown in Scheme 6. It is noteworthy that the same product **3t** in 88 % yield was also observed from the reaction of **1a** (1.0 mmol) with **11** (1.2 mmol) in the presence of $PtCl_2$ (Scheme 7).

An alternative mechanism can also be proposed for the present addition–cyclization reaction of indole **1** with alkynyl alcohol **2** (Scheme 8). The carbon–carbon triple bond of alkynyl alcohol **2a** reacts first with indole **1a** catalyzed by $PtCl_2$ to give intermediate **12**. Protonolysis of **12** affords **13** and regenerates $PtCl_2$. Subsequently, the carbon–carbon double bond of alkene in **13** is activated by $PtCl_2$ and is followed by intramolecular nucleophilic addition of an OH bond to alkene by a 5-*endo-trig* pathway[13] to yield intermediate **8**. This intermediate further undergoes protonolysis to give the final product **3a** and regenerates $PtCl_2$. This mechanism can not be totally ruled out, but is highly unlikely on the basis of following studies.

In the reaction of *N*-methyl indole (**1a**) with 4-phenylbut-3-yn-1-ol (**2c**), in addition to the expected cyclic ether derivative **3k**, alkenyl alcohol **3k′** (*E* and *Z* mixture) was obtained in 15 % combined yield. The corresponding addition products were further treated with $PtCl_2$ in THF at room



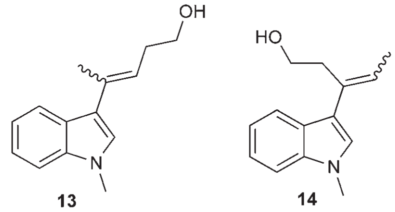
Scheme 7. Results of the addition reaction of *N*-methyl indole (**1a**) with 3-tetrahydro-2-(pent-3-ynyloxy)-2*H*-pyran (**10b**).



Scheme 8. Alternative mechanism for the addition and cyclization reaction of indole **1** with alkynyl alcohol **2**.

temperature for 12 h, but no **3k** was observed. This observation clearly indicates that the formation of **3k** did not go through **3k′** as the intermediate. Thus, the mechanism proposed in Scheme 8 is highly unlikely.

The regiochemistry and the ring size of the cyclic ether group in products **3** (see Table 2) also favors the proposed mechanism shown in Scheme 5. The main difference between the two proposed mechanisms (Schemes 5 and 8) for the $PtCl_2$-catalyzed cyclization and addition is the reaction sequence of the substrates. The mechanism in Scheme 5, in which the intramolecular cyclization of alkynyl alcohol **2** to give the corresponding cyclic enol ether occurs before the C–H addition of indole, explains very well the regiochemistry and the ring size of the substituted cyclic ether groups in the products based on the known Baldwin's rule.[13] On the other hand, the mechanism in Scheme 8, in which the C–H addition to the alkyne moiety of **2** occurs first, cannot distinguish the two alkynyl carbons and would lead to two different products (**13** and **14**). This is in contrast to the results shown in Table 2 in which the reactions show very high regioselectivity for the formation of a cyclic ether group.



13 **14**

Conclusion

We have developed a highly regioselective platinum-catalyzed multistep reaction of indoles with alkynyl alcohols. The methodology offers a simple and mild method for the preparation of 3-substituted five-membered tetrahydrofuran and six-membered tetrahydro-2*H*-pyran indole derivatives. Ring closure of these alkynyl alcohols is highly regioselective. Based on these observations, a mechanism involving successive $PtCl_2$-catalyzed cyclization of alkynyl alcohol to give the corresponding cyclic enol ether and addition of indole derivative to the cyclic enol ether is proposed to account for the present platinum-catalyzed reaction of indole with alkynyl alcohols. The proposed mechanism is strongly supported by the following reactions: 1) addition reaction of *N*-methyl indole with 2,3-dihydro-5-methylfuran and 2) *E* and *Z* mixture of 4-(1-methyl-1*H*-indol-3-yl)-4-phenylbut-3-en-1-ol derived from the reaction of *N*-methyl indole with 4-phenylbut-3-yn-1-ol do not give the corresponding cyclization product. Further extension of this work to the addition reaction of arenes or heteroarenes to propargyl alcohols and alkynyl amines, and the detailed study of the mechanism are in progress.

Experimental Section

General: All reactions were conducted under a nitrogen atmosphere on a dual-manifold Schlenk line unless otherwise mentioned by using oven-dried glass ware. Reagents and chemicals were used as purchased without further purification. Substituted indoles **1b–h**,[16a] alkynyl alcohols **2g**,[15] **2i**[15] and **2j**,[16b] and tetrahydro-2-(pent-3-ynyloxy)-2*H*-pyran (**10b**)[15] were synthesized according to the reported procedures.

General procedure for the cyclization–addition reaction of indole 1 with alkynyl alcohol 2: A 25 mL round-bottomed flask containing $PtCl_2$ (0.050 mmol, 5.0 mol%) was evacuated and purged with nitrogen gas three times. Freshly distilled THF (3.0 mL), indole (1.00 mmol) and alkynyl alcohol (1.20 mmol) were sequentially added to the system and the reaction mixture was stirred at room temperature for 2 h. The mixture was filtered through a short Celite and silica-gel pad and washed with dichloromethane several times. The filtrate was concentrated and the residue was purified on a silica gel column by using hexanes/ethyl acetate as an eluent to afford the cyclization product **3**. Products **3a–k** were synthesized according to this procedure, but for products **3l–m** the reactions proceeded for 8 h at room temperature, for products **3n–o** for 8 h at 60 °C, and for products **3p–q**, *N*-methyl indole (2.00 mmol) was used for 8 h at 60 °C. Product **3r** was synthesized according to a similar procedure by using pyrrole **1j** (4.0 mmol) instead of indole.

Spectral data of compounds **3a–c**, **3i–j**, **3n–p**, and **3r** are listed bellow. Experimental procedure for the preparation of compounds **3s** and **3t**, spectral data of remaining compounds, and copies of ^{1}H and ^{13}C NMR spectra of all compounds are given in the Supporting Information.

3-(Tetrahydro-2-methylfuran-2-yl)-1-methyl-1*H*-indole (3a): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 8.5 Hz, 1H; HC=), 7.26 (d, *J* = 8.0 Hz, 1H; HC=), 7.19 (t, *J* = 7.0 Hz, 1H; HC=), 7.08 (t, *J* = 8.0 Hz, 1H; HC=), 6.94 (s, 1H; HC=), 4.00–3.92 (m, 2H; O−CH_2), 3.73 (s, 3H; N−CH_3), 2.39–2.36 (m, 1H; CH_2), 2.05–1.89 (m, 3H; CH_2), 1.66 ppm (s, 3H; CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.38 (C), 125.41 (C), 125.20 (CH), 121.58 (C), 121.30 (CH), 120.37 (CH), 118.73 (CH), 109.27 (CH), 81.77 (C), 67.22 (CH_2), 38.48 (CH_2), 32.61 (N−CH_3), 28.70 (CH_3), 26.08 ppm (CH_2); HRMS: *m*/*z*: calcd for $C_{14}H_{17}ON$: 215.1310; found: 215.1305.

3-(Tetrahydro-2-methylfuran-2-yl)-5-methoxy-1-methyl-1*H*-indole (3b): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.16 (s, 1H; HC=), 7.15 (d, *J* = 8.0 Hz, 1H; HC=), 6.90 (s, 1H; HC=), 6.85 (d, *J* = 8.0 Hz, 1H; HC=), 4.03–3.90 (m, 2H; O−CH_2), 3.86 (s, 3H; O−CH_3), 3.69 (s, 3H; N−CH_3), 2.38–2.35 (m, 1H; CH_2), 2.03–1.87 (m, 3H; CH_2), 1.65 ppm (s, 3H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.46 (C), 133.17 (C), 125.83 (CH), 125.70 (C), 120.85 (C), 111.26 (CH), 109.92 (CH), 102.82 (CH), 81.71 (C), 67.18 (CH_2), 50.08 (O-CH_3), 38.29 (CH_2), 32.77 (N-CH_3), 28.48 (CH_3), 26.06 ppm (CH_2); HRMS: *m*/*z*: calcd for $C_{15}H_{19}O_2N$: 245.1416; found: 245.1417.

3-(Tetrahydro-2-methylfuran-2-yl)-6-methoxy-1-methyl-1*H*-indole (3c): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.55 (d, *J* = 9.0 Hz, 1H; HC=), 6.82 (s, 1H; HC=), 6.75 (d, *J* = 8.5 Hz, 1H; HC=), 6.71 (d, *J* = 2.5 Hz, 1H; HC=), 3.99–3.92 (m, 2H; O−CH_2), 3.86 (s, 3H; O−CH_3), 3.66 (s, 3H; N−CH_3), 2.35–2.32 (m, 1H; CH_2), 2.03–1.92 (m, 3H; CH_2), 1.64 ppm (s, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.08 (C), 138.36 (C), 124.05 (CH), 121.55 (C), 121.03 (CH), 119.85 (C), 108.64 (CH), 92.84 (CH), 81.71 (C), 67.20 (CH_2), 55.71 (O-CH_3), 38.47 (CH_2), 32.62 (N-CH_3), 28.70 (CH_3), 26.04 ppm (CH_2); HRMS: *m*/*z*: calcd for $C_{15}H_{19}O_2N$: 245.1416; found: 245.1425.

3-(Tetrahydro-2-methylfuran-2-yl)-1-methyl-1*H*-indole (3i): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.19 (s, 1H; N−H), 7.74 (d, *J* = 7.6 Hz, 1H; HC=), 7.32 (d, *J* = 8.0 Hz, 1H; HC=), 7.20 (t, *J* = 7.2 Hz, 1H; HC=), 7.14 (t, *J* = 7.2 Hz, 1H; HC=), 7.06 (d, *J* = 2.4 Hz, 1H; HC=), 4.04–3.99 (m, 2H; O−CH_2), 2.40–2.38 (m, 1H; CH_2), 2.07–1.97 ppm (m, 3H; CH_2), 1.68 ppm (s, 3H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.00 (C), 124.95 (C), 122.81 (CH), 121.65 (CH), 120.43 (CH), 120.20 (CH), 119.23 (CH), 111.23 (CH), 81.81 (C), 67.21 (CH_2), 38.30 (CH_2), 28.40 (CH_3), 26.02 ppm (CH_2); HRMS: *m*/*z*: calcd for $C_{13}H_{15}ON$: 201.1154; found: 201.1152.

3-(2-Ethyl-tetrahydrofuran-2-yl)-1-methyl-1*H*-indole (3j): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 8.0 Hz, 1H; HC=), 7.30 (d, *J* = 8.4 Hz, 1H; HC=), 7.22 (t, *J* = 8.0 Hz, 1H; HC=), 7.10 (t, *J* = 8.4 Hz, 1H; HC=), 6.96 (s, 1H; HC=), 3.98–3.93 (m, 2H; O−CH_2), 3.76 (s, 3H; N−CH_3), 2.35–2.32 (m, 1H; CH_2), 2.08–1.90 (m, 5H; CH_2), 0.82 ppm (t, *J* = 7.2 Hz, 3H; CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.67 (C), 126.22 (CH), 125.63 (C), 121.17 (CH), 120.46 (CH), 119.74 (C), 118.59 (CH), 109.18 (CH), 85.14 (C), 67.14 (CH_2), 36.79 (CH_2), 33.79 (CH_2), 32.63 (N−CH_3), 25.86 (CH_2), 9.21 ppm (CH_3); HRMS: *m*/*z*: calcd for $C_{15}H_{19}ON$: 229.1467; found: 229.1471.

3-(Tetrahydro-2-methyl-2*H*-pyran-2-yl)-1-methyl-1*H*-indole (3n): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 8.0 Hz, 1H; HC=), 7.31 (d, *J* = 8.0 Hz, 1H; HC=), 7.26 (t, *J* = 8.0 Hz, 1H; HC=), 7.14 (t, *J* = 8.0 Hz, 1H; HC=), 6.88 (s, 1H; HC=), 3.75 (s, 3H; N−CH_3), 3.74–3.73 (m, 1H; O−CH_2), 3.54–3.48 (m, 1H; O−CH_2), 2.24–2.20 (m, 1H; CH_2), 1.83–1.63 (m, 4H; CH_2), 1.59 (s, 3H; CH_3), 1.46–1.44 ppm (m, 1H; CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.39 (C), 126.35 (CH), 126.27 (C), 121.57 (CH), 121.42 (CH), 118.87 (CH), 118.29 (C), 118.31 (C), 109.03 (CH), 74.15 (C), 62.69 (CH_2), 35.49 (CH_2), 32.68 (N−CH_3), 31.46 (CH_3), 25.70 (CH_2), 20.20 ppm (CH_2); HRMS: *m*/*z*: calcd for $C_{15}H_{19}ON$: 229.1467; found: 229.1473.

3-(2-Ethyl-tetrahydro-2*H*-pyran-2-yl)-1-methyl-1*H*-indole (3o): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 8.0 Hz, 1H; HC=), 7.32 (d, *J* = 8.4 Hz, 1H; HC=), 7.25 (t, *J* = 8.0 Hz, 1H; HC=), 7.12 (t, *J* = 8.0 Hz, 1H; HC=), 6.85 (s, 1H; HC=), 3.74 (s, 3H; N−CH_3), 3.73–3.72 (m, 1H; O−CH_2), 3.57–3.51 (m, 1H; O−CH_2), 2.23–2.20 (m, 1H; CH_2), 2.05–2.01 (m, 1H; CH_2), 1.81–1.63 (m, 5H; CH_2), 1.44–1.41 (m, 1H; CH_2), 0.73 ppm (t, *J* = 7.6 Hz, 3H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.46 (C), 127.54 (CH), 126.68 (C), 121.81 (CH), 121.30 (CH), 118.79 (CH), 116.05 (C), 109.67 (CH), 77.66 (C), 62.59 (CH_2), 36.23 (CH_2), 33.09 (N-CH_3), 32.67 (CH_3), 22.95 (CH_2), 20.03 (CH_2), 8.43 ppm (CH_3); HRMS: *m*/*z*: calcd for $C_{16}H_{21}ON$: 243.1623; found: 243.1627.

6,6-Bis(1-methyl-1*H*-indol-3-yl)heptan-1-ol (3p): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 8.0 Hz, 2H; HC=), 7.25 (d, *J* = 8.0 Hz, 2H; HC=), 7.10 (t, *J* = 7.2 Hz, 2H; HC=), 6.88 (m, 4H; HC=), 3.75 (s, 6H; N−CH_3), 3.50 (t, *J* = 7.2 Hz, 2H; OCH_2), 2.36 (t, *J* = 8.0 Hz, 2H; CH_2), 1.83 (s, 3H; CH_3), 1.49–1.16 ppm (m, 6H; CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.61 (C), 126.74 (C), 126.07 (CH), 122.84 (C), 121.38 (CH), 120.76 (CH), 117.92 (CH), 108.94 (CH), 62.96 (CH_2), 40.59 (CH_2), 38.37 (C), 32.65 (CH_2), 32.57 (N−CH_3), 27.25 (CH_3), 26.23 (CH_2), 24.28 ppm (CH_2); IR: $\tilde{\nu}$ = 3471.24 cm^{-1} (OH); HRMS: *m*/*z*: calcd for $C_{25}H_{30}ON_2$: 374.2358; found: 374.2363.

2-(Tetrahydro-2-methylfuran-2-yl)-1-methyl-1*H*-pyrrole (3r): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.53 (t, *J* = 2.0 Hz, 1H; HC=), 5.98 (m, 2H; HC=), 3.96–3.92 (m, 1H; O−CH_2), 3.75–3.71 (m, 4H; N−CH_3, O−CH_2), 2.43–2.38 (m, 1H; CH_2), 2.01–1.94 (m, 2H; CH_2), 1.88–1.86 (m, 1H; CH_2), 1.51 ppm (s, 3H; CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 135.94 (C), 123.92 (CH), 105.96 (CH), 105.77 (CH), 80.88 (C), 67.15 (CH_2), 38.03 (CH_2), 35.75 (N−CH_3), 27.58 (CH_3), 25.54 ppm (CH_2); HRMS: *m*/*z*: calcd for $C_{10}H_{15}ON$: 165.1154; found: 165.1155.

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