JOC The Journal of Organic Chemistry

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Friedel–Crafts-Type Allylation of Nitrogen-Containing Aromatic Compounds with Allylic Alcohols Catalyzed by a [$Mo_3S_4Pd(\eta^3$-allyl)] Cluster

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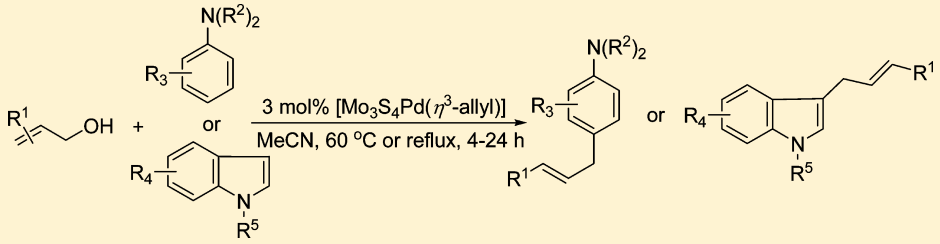
Supporting Information



ABSTRACT: With the direct use of allylic alcohols as allylating agents, the Friedel–Crafts-type allylic alkylation of nitrogen-containing aromatic compounds catalyzed by a [$Mo_3S_4Pd(\eta^3$-allyl)] cluster is achieved. With a 3 mol % catalyst loading in acetonitrile at reflux or 60 °C, a variety of *N*,*N*-dialkylanilines and indoles reacted smoothly with allylic alcohols to afford the Friedel–Crafts-type allylation products in good to excellent yields with high levels of regioselectivity.

Green chemistry has been attracting increasing interest from both academic and industrial communities owing to its great potential on lowering the environmental pressure brought about by pollutive chemical processes.[1] Among the various criteria used to define a green process, one significant facet is to minimize or, ideally, to completely avoid the formation of waste byproducts. To this end, replacing the reactants that produce undesired byproducts by less or nonwaste-producing ones provides an excellent solution. Consequently, a number of environmentally benign chemical processes have been developed on the basis of this strategy. The Friedel–Crafts-type allylic alkylation of aromatic and heteroaromatic compounds represents a typical member among the category of allylatively alkylating transformations and constitutes one of the most important tools for the construction of the carbon–carbon bond.[2] Most frequently, allylic compounds such as allyl acetate, carbonate, and halide are employed as allylic substrates in the allylic alkylation reactions. However, the use of these substrates would inevitably produce waste byproducts in stoichiometric amount. Alternatively, from a viewpoint of economy and environment, the ideal substrate for allylic alkylation should be allylic alcohols since water is the only byproduct in such case.

Although the studies with the direct use of allylic alcohols as allylating agents are limited because of the poor leaving-group character of the hydroxyl function, reports toward this project are increasing.[3] In the specific case of Friedel–Crafts-type allylic alkylation of aromatic and heteroaromatic compounds with allylic alcohols as substrate, two kinds of activator have been reported, stoichiometric or catalytic Brønsted/Lewis acid and transition-metal complex in catalytic amounts, respectively.[4] In contrast, the latter one is more favorable in terms of the efficiency of the promoter. In the context of transition-metal catalysis for Friedel–Crafts-allylating with allylic alcohols, ruthenium and palladium complexes are most studied, as exemplified by the elegant research work from the groups of Hidai,[5] Pregosin,[6] Tamaru,[7] Trost,[8] and Breit.[9] Given the salient advantages associated with the direct use of allylic alcohols as allylating agent, the development of more efficient and practical catalyst system for this process is still in high demand.

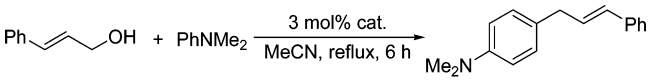
As a part of our ongoing project aimed at developing environmentally benign chemical transformations, we have recently shown that the novel cubane-type sulfido cluster incorporating Mo and Pd, $[(Cp^*Mo)_3(\mu_3\text{-}S)_4Pd(\eta^3\text{-allyl})][PF_6]_2$, ($Cp^* = \eta^5\text{-}C_5Me_5$) (**1**) could efficiently catalyze the allylation of amines and active methylene compounds in excellent regioselectivity with the direct use of allylic alcohols as allylating agent.[10] Note that Hidai and coworkers have first demonstrated the unique catalytic activities of cubane-type Mo_3MS_4 (M = Pd, Ni) clusters for organic synthesis.[11] As a logical extension of our previous work, we further find that the Friedel–Crafts-type allylation of *N*,*N*-dialkylaniline and indole could occur smoothly under the catalysis of the Mo, Pd-based cubane-type sulfido cluster. We wish to present herein the experimental results.

The first experiments were focused on the identification of the optimal reaction conditions. Thus, the Friedel–Crafts reaction of *N*,*N*-dimethylaniline (**3a**) with cinnamyl alcohol (**2a**) was chosen as the model reaction. Subjection of the two reactants to the

Received: December 2, 2011
Published: February 16, 2012

catalysis of 3 mol % of various promoters in acetonitrile at reflux was evaluated so as to identify the best catalyst, and the results are compiled in Table 1.

Table 1. Evaluation of Reaction Conditions[a]



2a **3a** **4aa**

entry	cat.	yield[b] (%)
1	*p*-TsOH·H_2O	nr
2	HPF_6 (60%)	nr
3	$AuCl_3$	nr
4	$FeCl_3$	nr
5	$ZnCl_2$	nr
6	$PdCl_2$	nr
7	$[(\eta^3\text{-allyl})PdCl]_2$	nr
8	$Pd(PPh_3)_4$	nr
9	$[(Cp^*Mo)_3(\mu_3\text{-}S)_4Pd(dba)][PF_6]$	38
10	$[(Cp^*Mo)_3(\mu_3\text{-}S)_4Pd(\eta^3\text{-allyl})][PF_6]_2$ (**1**)	87
11	$[\{(Cp^*Mo)_3(\mu_3\text{-}S)_4Ni\}_2(cod)][PF_6]_2$	nr
12	$[(Cp^*Mo)_3(\mu_3\text{-}S)_4RuH_2(PPh_3)][PF_6]$	nr

[a]Reaction conditions: *N*,*N*-dimethylaniline (0.4 mmol), cinnamyl alcohol (0.4 mmol), cat. (0.012 mmol), MeCN (1 mL), reflux, 6 h. [b]Isolated yield.

The Brønsted acids, *p*-TsOH·H_2O and HPF_6, failed to catalyze this reaction probably due to the scavenging of the proton by the basic *N*,*N*-dimethylaniline (entries 1−2). Notably, no allylation was observed when $AuCl_3$[12] or $FeCl_3$[13] was used as catalyst (entries 3 and 4), which in contrast showed high efficiency on the allylic alkylation of phenols and benzylation of aromatic compounds, respectively. $ZnCl_2$, a typical Lewis acid, did not work for this process either (entry 5). Despite the sporadic reports wherein palladium complexes exhibited excellent performance in the allylation of aromatic and heteroaromatic compounds with allylic alcohols, simple palladium catalysts, such as $PdCl_2$, $[(\eta^3\text{-allyl})PdCl]_2$, and $Pd(PPh_3)_4$, could not promote the model reaction (entries 6−8). When a cubane-type sulfido cluster involving Pd in combination with dba as a ligand[14] was examined, however, a 38% product yield was obtained (entry 9). Gratifyingly, further investigation showed that the cubane-type sulfido cluster $[(Cp^*Mo)_3(\mu_3\text{-}S)_4Pd(\eta^3\text{-allyl})][PF_6]_2$, ($Cp^* = \eta^5\text{-}C_5Me_5$) (**1**) could catalyze the allylation reaction smoothly in 87% product yield (entry 10). Other cubane-type sulfido clusters involving Ru[14] or Ni[15] showed no catalytic activity toward this transformation (entries 11 and 12).

With the optimal reaction conditions in hand, we next investigated the substrate scope of the Friedel−Crafts-type allylation with allylic alcohols. Compared to alkylbenzenes, phenols, and anisoles, *N*,*N*-dialkylanilines are rarely employed as substrate in the transition metal or Lewis acid catalyzed Friedel−Crafts-type allylation with allylic alcohols as the allylating agent. It is worthy of note that our catalyst system is especially effective for allylating *N*,*N*-dialkylaniline compounds. From Table 2, we can see that various *N*,*N*-dialkylanilines could be allylated smoothly under the standard reaction conditions (entries 1−4, 6, and 7). Notably, the substitution manner of methyl group on the benzene ring exhibited marked influence on the reactivity of the aniline substrate, as can be seen in the cases of **3e**, **3f**, and **3g**. The *m*-methyl-substituted *N*,*N*-dimethylaniline (**3g**) is most reactive, affording the product in 84% yield. While the *p*-methyl-substituted *N*,*N*-dimethylaniline (**3e**) gave a low product yield of 35%, the *o*-methyl-substituted one (**3f**) is completely unreactive. This fact may be due to a combination of the steric and electronic effects. Interestingly, *m*-bromo-*N*,*N*-dimethylaniline (**3h**) underwent the reaction smoothly, affording the product in 91% yield, which can be further manipulated by coupling reactions. The substrate scope in terms of allylic alcohol was also examined, with **2b**, **2c**, and **2d** reacting smoothly with **3a** to furnish the corresponding product in high yield, respectively. The fact that allylic alcohols **2a** and **2b** gave the same allylated product indicates that a common π-allylpalladium intermediate exists in this process. A final remark concerns the allylation of secondary amine *N*-methyaniline (**3i**), and it was found both nitrogen and *p*-carbon were allylated in such cases.

The indole moiety is a significant motif in a vast number of bioactive natural alkaloids and synthetic drugs. As such, the synthesis and functionalization of indole has been drawn much attention from synthetic and pharmaceutical chemists.[16] After the allylation of *N*,*N*-dialkylaniline was successfully investigated, we focused our attention on the allylic alkylation of indoles. Very recently, Breit and co-workers documented the first palladium catalyst system with self-assembling ligands based on complementary hydrogen-bonding, which allowed the allylation of indoles with the direct use of allylic alcohols as allylating agents.[9] Comparably, when indole (**5a**) was treated with cinnamyl alcohol (**2a**) over our cubane-type palladium catalyst, to our delight, the desired allylation product was obtained in 83% yield (Table 3, entry 1). Some other representative substituted indoles, such as 5-methoxyindole (**5b**), 5-bromoindole (**5c**), and 2-methylindole (**5d**), could serve as reactive substrates as well (entries 2−4). In addition, *N*-methyl- and *N*-phenylindole (**5e**, **5f**) were also allylated smoothly by cinnamyl alcohol (**2a**) (entries 5 and 6). The allylic alcohols **2b** and **2a** afforded the same product when treated with indole (entry 7), again indicating a common π-allylpalladium intermediate involved in this process.

Although no experimental details were provided to probe the insights into the reaction mechanism, we surmise that the pathway of the current transformation resembles that of the allylation of active methylene compounds just reported by our group.[10b]

In summary, we have discovered that the novel cubane-type sulfido cluster $[(Cp^*Mo)_3(\mu_3\text{-}S)_4Pd(\eta^3\text{-allyl})][PF_6]_2$ is a valuable catalyst with unique catalytic activities, which allows the highly efficient Friedel−Crafts-type allylation of nitrogen-containing aromatic compounds including *N*,*N*-dialkylaniline and indole with the direct use of allylic alcohols as allylating agents. We anticipate that this process would find use in the synthesis of natural alkaloids.

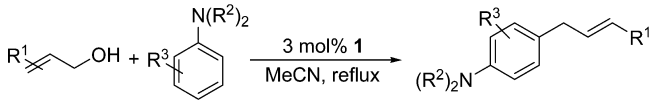
EXPERIMENTAL SECTION

All manipulations were carried out under an argon atmosphere using conventional Schlenk techniques. All commercially available reagents were used as received unless otherwise noted. All solvents were dried and distilled by standard methods before use. The cubane-type catalysts, $[(Cp^*Mo)_3(\mu_3\text{-}S)_4Pd(dba)][PF_6]$,[14] $[(Cp^*Mo)_3(\mu_3\text{-}S)_4RuH_2(PPh_3)][PF_6]$,[14] $[\{(Cp^*Mo)_3(\mu_3\text{-}S)_4Ni\}_2(cod)][PF_6]_2$,[15] and $[(Cp^*Mo)_3(\mu_3\text{-}S)_4Pd(\eta^3\text{-allyl})][PF_6]_2$ (**1**),[10b] were synthesized according to literature procedures. NMR spectra were recorded on a 400 MHz spectrometer. Chemical shifts were reported in ppm relative to TMS.

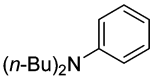
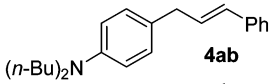
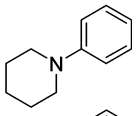
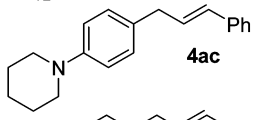
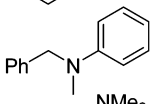
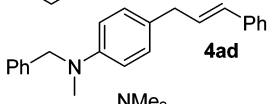
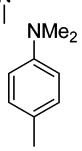
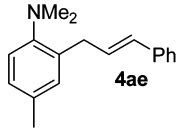
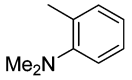
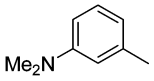
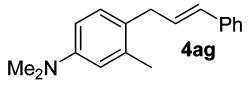
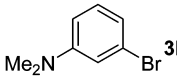
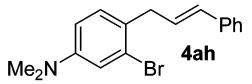
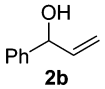
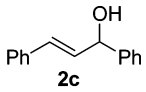
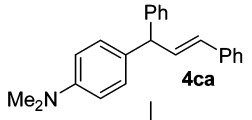
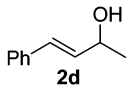
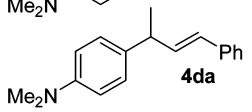
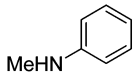
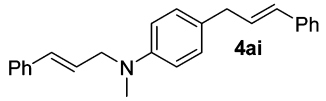
General Reaction Procedure for the Friedel−Crafts-type Allylation of *N*,*N*-Dialkylated Anilines and Indoles. $[(Cp^*Mo)_3(\mu_3\text{-}S_4)Pd(\eta^3\text{-allyl})][PF_6]_2$ (**1**) (0.012 mmol) was added to a 25 mL Schlenk tube under argon, and then MeCN (1 mL), aniline or indole compounds (0.4 mmol), and allylic alcohol (0.4 mmol) were added

dx.doi.org/10.1021/jo2024812 | J. Org. Chem. 2012, 77, 2942−2946

Table 2. Friedel–Crafts-Type Reaction of Anilines with Allylic Alcohols Catalyzed by 1[a]



2 3 4

entry	allylic alcohol	aniline		time (h)	product	yield (%)[b]
1	**2a**		**3b**	8	 **4ab**	80
2	**2a**		**3c**	8	 **4ac**	82
3	**2a**		**3d**	6	 **4ad**	90
4	**2a**		**3e**	12	 **4ae**	35
5	**2a**		**3f**	12	nr	
6	**2a**		**3g**	6	 **4ag**	84
7	**2a**		**3h**	6	 **4ah**	91
8	 **2b**		**3a**	6	**4aa**	84
9	 **2c**		**3a**	6	 **4ca**	85
10	 **2d**		**3a**	6	 **4da**	81
11	**2a**		**3i**	24	 **4ai**	55[c]

[a]Reaction conditions: **1** (0.012 mmol), **2** (0.4 mmol), **3** (0.4 mmol), MeCN (1 mL), reflux. [b]Isolated yield. [c]**1** (0.02 mmol), **2a** (0.8 mmol), **3i** (0.4 mmol).

stepwise. The tube was sealed and heated to the appointed temperature. The reaction was monitored by TLC. The products were obtained by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 20/1).

***N,N*-Dimethyl-4-cinnamylaniline, 4aa.** Following the general procedure, **4aa** was obtained as a light yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.91(s, 6 H), 3.45(d, J = 6.4 Hz, 2 H,), 6.34 (dt, J = 15.9, 6.4 Hz, 1 H), 6.43 (d, J = 15.9 Hz, 1 H), 6.71(d, J = 8.6 Hz, 2 H), 7.11(d, J = 8.6 Hz, 2 H), 7.18 (m, 1 H), 7.27 (m, 2 H), 7.34 (d, J = 7.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.4, 40.9, 113.1, 126.1, 126.9, 128.3, 128.5, 129.3, 130.2, 130.4, 137.8, 149.3.

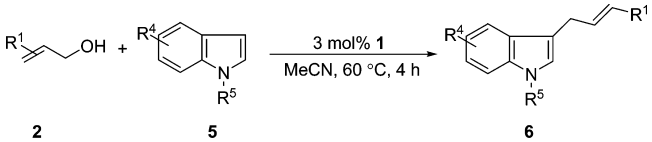
***N,N*-Dibutyl-4-cinnamylaniline, 4ab.** Following the general procedure, **4ab** was obtained as a light yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (t, J = 7.2 Hz, 6 H), 1.29–1.36 (m, 4 H), 1.51–1.58 (m, 4 H), 3.23 (t, J = 7.6 Hz, 4 H), 3.43 (d, J = 6.5 Hz, 2 H), 6.34 (dt, J = 15.9, 6.5 Hz, 1 H), 6.43 (d, J = 15.9 Hz, 1 H), 6.60 (d, J = 8.6 Hz, 2 H), 7.07 (d, J = 8.6 Hz, 2 H), 7.27 (m, 2 H), 7.17 (m, 1 H), 7.35 (d, J = 7.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 20.5, 29.5, 38.5, 51.0, 112.1, 126.18, 126.53, 126.95, 128.5, 129.5, 130.29, 130.5, 137.9, 146.8; HRMS (APCI, positive) calcd for $C_{23}H_{32}N$ ($[M + H]^+$) 322.2535, found 322.2525.

***(E)*-1-(4-Cinnamylphenyl)piperidine, 4ac.** Following the general procedure, **4ac** was obtained as a light yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.69 (m, 4 H), 1.54 (m, 2 H), 3.10 (t, J = 5.4 Hz, 4 H), 3.45 (d, J = 6.4 Hz, 2 H), 6.33 (dt, J = 15.8, 6.4 Hz, 1 H), 6.42 (d, J = 15.8 Hz, 1 H), 6.89 (d, J = 8.5 Hz, 2 H), 7.11 (d, J = 8.5 Hz, 2 H), 7.17 (m, 1 H), 7.27 (m, 2 H), 7.34 (d, J = 7.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.4, 26.0, 38.5, 51.1, 116.9, 126.2, 127.0, 128.5, 129.3, 129.97, 130.6, 130.85, 137.7, 150.9; HRMS (APCI, positive) calcd for $C_{20}H_{24}N$ ($[M + H]^+$) 278.1909, found 278.1917.

***N*-Benzyl-4-cinnamyl-*N*-methylaniline, 4ad.** Following the general procedure, **4ad** was obtained as a light yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.99 (s, 3 H), 3.45 (d, J = 4.0 Hz, 2 H), 4.50 (s, 2 H), 6.30–6.44 (m, 2 H), 6.69–7.36 (m, 14 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.41, 38.65, 56.9, 112.7, 126.1, 126.84, 126.87, 126.93, 128.0, 128.48, 128.57, 129.4, 130.23, 130.37, 137.8, 139.2,

dx.doi.org/10.1021/jo2024812 | J. Org. Chem. 2012, 77, 2942–2946

Table 3. Friedel–Crafts-type Reaction of Indoles with Allylic Alcohols Catalyzed by 1[a]



2 5 6

entry	allylic alcohol	indole	product	yield (%)[b]
1	2a	5a	6aa	83
2	2a	5b	6ab	86
3	2a	5c	6ac	78
4	2a	5d	6ad	67
5	2a	5e	6ae	93
6	2a	5f	6af	71
7	2b	5a	6aa	82

[a]Reaction conditions: **1** (0.012 mmol), **2** (0.4 mmol), **5** (0.4 mmol), MeCN (1 mL), 60 °C. [b]Isolated yield.

148.4; HRMS (APCI, positive) calcd for $C_{23}H_{24}N$ ([M + H]$^+$) 314.1909, found 314.1904.

2-Cinnamyl-4-methyl-*N*,*N*-dimethylaniline, 4ae. Following the general procedure, **4ae** was obtained as a light yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.27 (s, 3 H), 2.68 (s, 6 H), 3.63 (d, J = 6.4 Hz, 2 H), 6.37 (dt, J = 15.8, 6.4 Hz, 1 H), 6.48 (d, J = 15.8 Hz, 1 H), 7.02–7.05 (m, 3 H), 7.20 (m, 1 H), 7.29 (m, 2 H), 7.37 (d, J = 7.3 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 34.0, 45.3, 119.3, 126.1, 126.9, 127.5, 128.5, 130.0, 130.85, 130.90, 132.7, 134.6, 137.8, 150.2; HRMS (APCI, positive) calcd for $C_{18}H_{22}N$ ([M + H]$^+$) 252.1752, found 252.1754.

3-Methyl-4-cinnamyl-*N*,*N*-dimethylaniline, 4ag. Following the general procedure, **4ag** was obtained as a light yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3 H), 2.91 (s, 6 H), 3.45(d, J = 4.7 Hz, 2 H,), 6.33 (m, 2 H), 6.58 (m, 2 H), 7.06(d, J = 8.0 Hz, 1 H), 7.17 (m, 1 H), 7.26 (m, 2 H), 7.33 (d, J = 7.3 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.2, 36.2, 41.1, 110.9, 115.1, 126.2, 126.7, 127.0, 128.6, 129.77, 130.14, 130.36, 137.2, 137.9, 149.7; HRMS (APCI, positive) calcd for $C_{18}H_{22}N$ ([M + H]$^+$) 252.1752, found 252.1747.

3-Bromo-4-cinnamyl-*N*,*N*-dimethylaniline, 4ah. Following the general procedure, **4ah** was obtained as a light yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.91 (s, 6 H), 3.56 (d, J = 6.2 Hz, 2 H), 6.32 (dt, J = 15.9, 6.2 Hz, 1 H), 6.41 (d, J = 15.9 Hz, 1 H), 6.63 (dd, J = 8.5, 2.4 Hz, 1 H), 6.91 (d, J = 2.4 Hz, 1 H), 7.10 (d, J = 8.5 Hz, 1 H), 7.18 (m, 1 H), 7.27 (m, 2 H), 7.35 (d, J = 7.5 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 137.8, 131.1, 130.8, 128.74, 128.63, 127.2, 127.0, 126.3, 125.5, 116.5, 112.2, 40.7, 38.5; HRMS (APCI, positive) calcd for $C_{17}H_{19}BrN$ ([M + H]$^+$) 316.0701, found 316.0704.

(*E*)-4-(1,3-Diphenylallyl)-*N*,*N*-dimethylaniline, 4ca. Following the general procedure, **4ca** was obtained as a white solid: mp 79.5–82.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.91 (s, 6 H), 4.81 (d, J = 7.5 Hz, 1 H), 6.33 (d, J = 15.9 Hz, 1H), 6.65 (dd, J = 15.9, 7.5 Hz, 1 H), 6.70 (d, J = 8.6 Hz, 2 H), 7.10 (d, J = 8.6 Hz, 2 H), 7.17–7.32 (m, 8 H), 7.36 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.8, 53.4, 112.8, 126.3, 126.4, 127.2, 128.47, 128.56, 128.72, 129.4, 130.9, 131.6, 133.4, 137.6, 144.3, 149.3; HRMS (APCI, positive) calcd for $C_{23}H_{24}N$ ([M + H]$^+$) 314.1909, found 314.1905.

(*E*)-*N*,*N*-Dimethyl-4-(4-phenylbut-3-en-2-yl)aniline, 4da. Following the general procedure, **4da** was obtained as a light yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.43 (d, J = 7.0 Hz, 3 H), 2.91 (s, 6 H), 3.56 (m, 1 H), 6.33 (m, 2 H), 6.72 (d, J = 8.7 Hz, 2 H), 7.14–7.20 (m, 3 H), 7.27 (m, 2 H), 7.35 (d, J = 7.3 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 41.0, 41.6, 113.1, 126.2, 126.9, 127.94, 127.95, 128.5, 133.8, 136.1, 137.9, 149.3; HRMS (APCI, positive) calcd for $C_{18}H_{22}N$ ([M + H]$^+$) 252.1752, found 252.1759.

***N*,4-Dicinnamyl-*N*-methylaniline, 4ai.** Following the general procedure, **4ai** was obtained as a light yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.95 (s, 3 H), 3.46 (d, J = 8 Hz, 2 H), 4.06 (d, J = 8 Hz, 2 H), 6.21–6.54 (m, 4 H), 6.75 (d, J = 8 Hz, 2 H), 7.11 (d, J = 8 Hz, 2 H), 7.17–7.27 (m, 10 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.4, 38.6, 55.4, 113.2, 126.0, 126.3, 126.5, 127.1, 127.6, 128.3, 128.63, 128.70, 129.6, 130.37, 130.53, 131.5, 137.1, 137.9, 148.3; HRMS (APCI, positive) calcd for $C_{25}H_{26}N$ ([M + H]$^+$) 340.2065, found 340.2068.

3-Cinnamylindole, 6aa. Following the general procedure, **6aa** was obtained as a white solid: mp 89–91 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.69 (d, J = 8.0 Hz, 2 H), 6.43–6.52 (m, 2 H), 7.04–7.65 (m, 10 H), 7.98 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.0, 111.2, 114.6, 119.2, 119.4, 121.9, 122.1, 126.2, 127.0, 127.5, 128.6, 129.4, 130.5, 136.5, 137.8.

3-Cinnamyl-5-methoxyindole, 6ab. Following the general procedure, **6ab** was obtained as a light yellow solid: mp 80.5–82.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.64 (d, J = 8 Hz, 2 H), 3.83 (s, 3 H), 6.42–6.55 (m, 2 H), 6.84–7.36 (m, 9 H), 7.90 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.0, 55.9, 101.0, 111.9, 112.2, 114.2, 122.7, 126.1, 127.0, 127.9, 128.5, 129.2, 130.5, 131.6, 137.7, 153.9.

3-Cinnamyl-5-bromoindole, 6ac. Following the general procedure, **6ac** was obtained as a light yellow solid: mp 99–103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.61 (d, J = 8 Hz, 2 H), 6.37–6.52 (m, 2 H), 7.0–7.74 (m, 9 H), 7.96 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.7, 112.59, 112.67, 114.4, 121.7, 123.1, 124.9, 126.2, 127.1, 128.55, 128.72, 129.3, 130.8, 135.0, 137.6.

2-Methyl-3-cinnamylindole, 6ad. Following the general procedure, **6ad** was obtained as a light yellow solid: mp 69–71 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3 H), 3.61 (d, J = 4 Hz, 2 H), 6.33–6.45 (m, 2 H), 7.04–7.54 (m, 9 H), 7.75 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.7, 27.8, 109.4, 110.2, 118.3, 119.2, 121.0, 126.1, 126.8, 128.4, 128.8, 129.60,129.79, 131.4, 135.3, 137.8.

3-Cinnamyl-*N*-methylindole, 6ae. Following the general procedure, **6ae** was obtained as a light yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.64 (d, J = 8 Hz, 2 H), 3.67 (s, 3 H), 6.39–6.53 (m, 2 H), 6.83–7.32 (m, 10 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.0, 32.7, 109.3, 113.1, 118.9, 119.3, 121.7, 126.2, 126.8, 127.1, 128.0, 128.6, 129.6, 130.4, 137.3, 137.9.

3-Cinnamyl-*N*-phenylindole, 6af. Following the general procedure, **6af** was obtained as a light yellow solid: mp 57.5–59.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.74 (d, J = 4 Hz, 2 H), 6.46–6.61 (m, 2 H), 7.08–7.50 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.9, 110.6, 115.7, 119.5, 120.0, 122.5, 124.1, 125.7, 126.14, 126.16, 127.1, 128.5, 128.90, 128.93, 129.6, 130.8, 136.2, 137.7, 139.9; HRMS (APCI, positive) calcd for $C_{23}H_{20}N$ ([M + H]$^+$) 310.1596, found 310.1618.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of NMR spectra of the products. 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.

dx.doi.org/10.1021/jo2024812 | J. Org. Chem. 2012, 77, 2942–2946

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Nos. 20806012 and 20972022) and the "111" project of Ministry of Education of China.

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