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Friedel–Crafts-Type Alkylation of Indoles in Water Using Amphiphilic Resin-Supported 1,10-Phenanthroline–Palladium Complex under Aerobic Conditions

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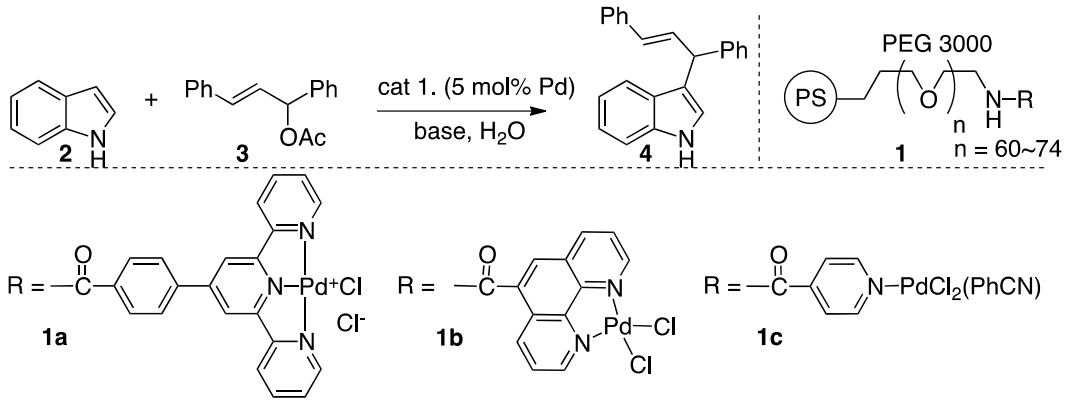
Abstract: The palladium-catalyzed Friedel-Crafts-type alkylation of indoles in water has been achieved using amphiphilic polystyrene-poly(ethylene glycol) (PS-PEG) resin-supported phenanthroline-palladium complexes in water under aerobic conditions, affording the corresponding products with good-to-high yield. The polymeric catalyst was also found to promote the C3-alkylation reaction to give a thermodynamic alkylation product with high selectivity. The polymeric catalyst was recovered and reused several times without any loss of catalytic activity.

Keywords: aqueous media; polymer-support; Friedel-Crafts reaction

1. Introduction

The Friedel-Crafts reaction is one of the considerably important carbon–carbon bond forming reactions to employ Lewis acids as promoters since the pioneering study by Friedel and Crafts [1,2]. Recently, the original procedure (for which stoichiometric amounts of a Lewis acid were required) has been replaced by catalytic Friedel-Crafts-type reactions for the alkylation and acylation of aromatic and heteroarene compounds [3,4]. While widespread research has been devoted to the catalytic Friedel-Crafts reactions of allyl compounds with electron-rich aromatics, research on the catalytic Friedel-Crafts reactions has took place in organic solvent [5–15] or in water solvent [16,17] under homogeneous conditions. If the Friedel-Crafts reactions were performed in water with recyclable palladium catalysts, where neither aqueous-organic solvent wastes nor metal-contaminated wastes were yielded, this would go a long way to meeting green chemical requirements.

Nowadays, we have developed amphiphilic polystyrene-poly(ethylene glycol) (PS-PEG) resin-supported terpyridine-palladium complexes that promote varied catalytic transformations [18–28] smoothly in water [29–32] under heterogeneous conditions [33–36]. Herein, we aimed for the Friedel-Crafts reaction of π-allylic palladium intermediates with indoles in water under aerobic conditions in the presence of amphiphilic PS-PEG resin-bound pyridine skeleton ligand-palladium complexes **1a–c** (Scheme 1).



Scheme 1. Friedel-Crafts-type alkylation of indole in water using polymeric catalysts **1.**

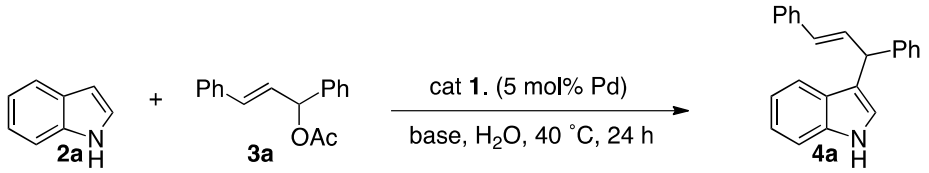
2. Results

Alkylation Reaction

First, the polymeric catalyst **1b** was prepared from phenanthroline carboxylic acid, PS-PEG resin, and palladium in accordance with previously reported procedures [26], and we then examined different bases and catalysts in the alkylation reaction in water to distinguish which bases and catalysts were most suitable for use in the reaction (Table 1). Thus, the alkylation reaction of indole (**2a**) and 1,3-diphenyl-2-propenyl acetate (**3a**) was carried out in water with Et_3N (3.0 equivalent) in the presence of the polymeric catalyst **1b** (5 mol.% to Pd) at 40 °C for 24 h. After completion of the reaction, the reaction mixture was filtered, and the recovered resin beads were rinsed with a small portion of water and extracted with EtOAc to give an 88% yield of 3-(1,3-diphenyl-2-propenyl)-1*H*-indole (**4a**) (entry 2, Table 1). The scope of suitable bases for the C3-alkylation of indole in water using catalyst **1b** was examined. lithium carbonate, sodium carbonate, potassium carbonate, cesium carbonate, sodium hydrogen carbonate, and DBU gave 27%, 12%, 13%, 16%, 28%, and 30% yields, respectively (entries 4–9, Table 1). Next, we tested several catalysts using Et_3N as a base for the C3-alkylation reaction, which produced **4a** with 43%–88% yields (entries 1–3, Table 1). The most effective catalyst proved to be polymer-supported 1,10-phenanthroline-palladium complex **1b**, which gave **4a** in an impressive 88% yield (entry 2, Table 1). In addition, these reaction conditions were applicable to scale up the reaction (entry 10, Table 1). Thus, the reaction was performed using 20 times the amount of indole of entry 2 to give the corresponding product in 94% yield.

With the optimal conditions in hand, we examined the polymer-supported 1,10-phenanthroline-palladium catalyzed alkylation of several indoles, and the results are summarized in Table 2. The 2-methylindole gave a 78% yield of 3-allyl-2-methyl-1*H*-indole **4b** (entry 2, Table 2). Due to the low dissolubility of 2-phenylindole (**2c**), the reaction of the **2c** with **3a** afforded the 3-allyl-2-phenyl-1*H*-indole **4c** in only a 27% yield (entry 3, Table 2). The 5-methylindole (**2d**) and 7-methylindole (**2e**) also underwent the alkylation to give **4d** and **4e** in 91% and 77% yields, respectively (entries 4 and 5, Table 2). The alkylation of indoles **2f** and **2g** having an electron withdrawing group at the 5-position afforded the 3-allyl-5-bromo-1*H*-indole **4f** and 3-allyl-2-chloro-1*H*-indole **4g** in 74% and 64% yields, respectively (entries 6 and 7, Table 2). The 5-substituted indoles **2h** and **2i** having an electron donating group (OCH_3 or OBn) furnished the 3-allyl-5-methoxy-1*H*-indole **4h** and 3-allyl-2-benzyloxy-1*H*-indole **4i** in 52% and 33% yields, respectively (entries 8 and 9, Table 2). The cyclic substrate was also examined, but the alkylation reaction did not proceed at all (entry 10).

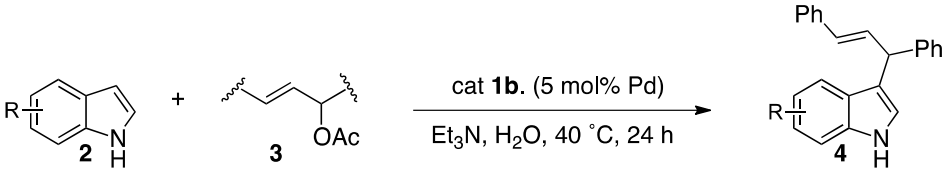
Table 1. Friedel–Crafts-type alkylation of indole in water using catalysts **1** and several bases [a].



Entry	Catalyst	Bases (3 equiv.)	Yield of 4a (%)
1	**1a**	Et_3N	43
2	**1b**	Et_3N	88
3	**1c**	Et_3N	53
4	**1b**	Li_2CO_3	27
5	**1b**	Na_2CO_3	12
6	**1b**	K_2CO_3	13
7	**1b**	Cs_2CO_3	16
8	**1b**	$NaHCO_3$	28
9	**1b**	DBU	30
10 [b]	**1b**	Et_3N	94 [c]

[a]: All reactions were performed in water at 40 °C for 24 h. The ratio of **3** (mol)/indoles (mol)/base (mol)/Pd (mol)/H_2O (mL) = 1.5/1/3/0.05/1.5. Yields were determined by gas chromatography (GC) based on *n*-dodecane as an internal standard. [b]: This reaction was performed under scaled-up conditions (**3** (3 mmol)/indoles (2 mmol)/base (6 mmol)/Pd (0.1 mmol)/H_2O (15 mL). [c]: One day later, the yield of **4a** in extract was the same. It means that the reaction did not proceed without the polymeric catalyst.

Table 2. Friedel–Crafts-type alkylation of indoles **2** with allyl esters **3** in H_2O.



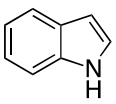
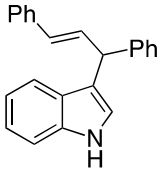
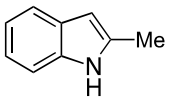
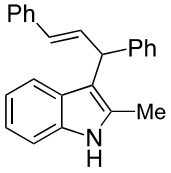
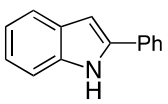
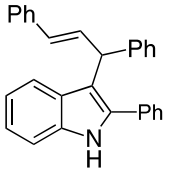
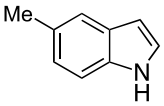
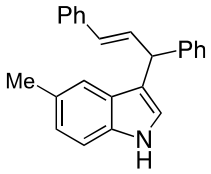
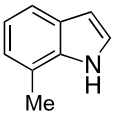
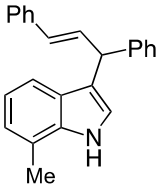
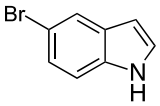
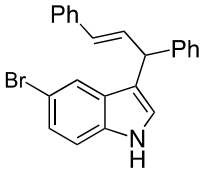
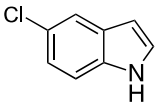
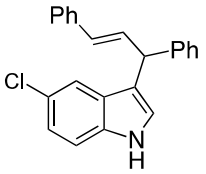
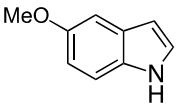
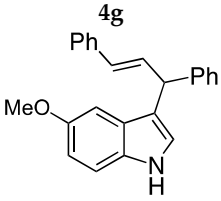
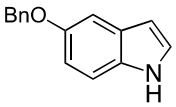
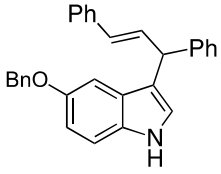
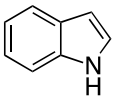
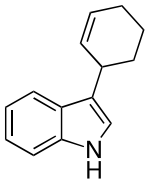
Entry	2	4	Yield (%) [a]
1	 **2a**	 **4a**	**88**
2	 **2b**	 **4b**	**78**
3	 **2c**	 **4c**	**27**

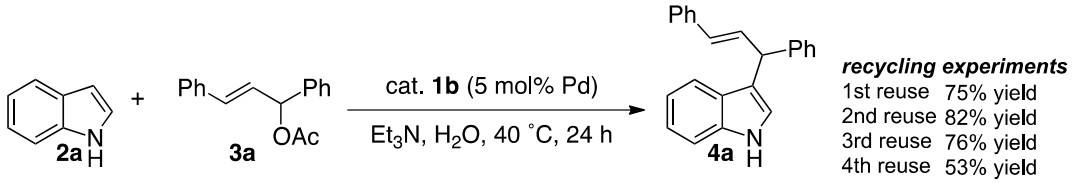
Table 2. *Cont.*

Entry	2	4	Yield (%) [a]
4	 **2d**	 **4d**	**91**
5	 **2e**	 **4e**	**77**
6	 **2f**	 **4f**	**74**
7	 **2g**	 **4g**	**64**
8	 **2h**	 **4h**	**52**
9	 **2i**	 **4i**	**33**
10	 **2j**	 **4j**	**0**

[a]: All reactions were performed in water at 40 °C for 24 h. The ratio of **3** (mol)/indoles (mol)/triethylamine (mol)/Pd (mol)/H_2O (mL) = 1.5/1/3/0.05/1.5.

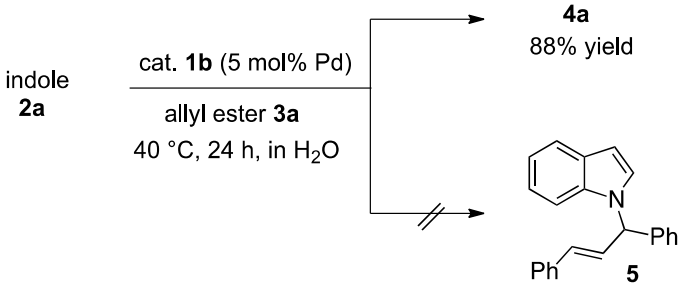
Recycling experiments were tested for alkylation of indole (**2a**) with the allyl ester **3a**. After the first use of the polymeric palladium catalyst **1b** (Table 1, entry 1) to give an 88% yield of the C3-allylindole **4a**, the recovered catalyst beads were taken on for a 3rd reuse and exhibited stable

catalytic activity (Scheme 2). After the recycling experiments, inductively coupled plasma-atomic emission spectrometry (ICP-AES) analysis showed that the concentration of Pd leached into the aqueous solution was <0.3 ppm.



Scheme 2. Recycling experiments.

Bandini and co-workers reported that while low coordinating solvents would favor the generation of C3-alkylation product **4a**, the use of highly coordinating solvents would drive the regiochemistry toward the formation of *N*-alkylation product **5** (Scheme 3) [9]. It is noteworthy that the C3-allylindole **4a** was obtained as a sole product using polymeric catalyst **1b** with triethylamine in water. These results suggested that the Friedel–Crafts-type reaction of indole in water with polymeric catalyst **1b** proceeded in the polystyrene moiety of the polystyrene-poly(ethylene glycol) matrix to give thermodynamic alkylation product **4a** in 88% yield.



Scheme 3. Regioselective alkylation of indole.

3. Materials and Methods

3.1. General Methods

All manipulations were conducted under aerobic conditions. Water was deionized with a Millipore Milli-Q Gradient A10 system. NMR spectra were recorded on a Bruker AVANCE spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C); ^{1}H and ^{13}C spectra were recorded in $CDCl_3$, CD_3OD, and DMSO-d_6 at 25 °C. Chemical shifts of ^{13}C are given relative to $CDCl_3$, CD_3OD, and DMSO-d_6 as internal standards (δ77.0, δ49.0, δ39.7 ppm). Mass spectra were measured on a JEOL JMS-T100GCv MS detector (gas chromatography (GC)-MS) and a JEOL JMS-T100LP MS detector (LC-MS); the base peak is denoted as "bp." GC and IR analyses were performed on a Shimadzu GC-2014 instrument and a Jasco FTIR-410 detector, respectively. ICP-AES spectra were measured on a Shimadzu ICPE-9000 instrument.

3.2. Materials

The PS-PEG-supported phenanthroline-palladium complex (PS-PEG-phenanthroline-Pd; **1b**) was prepared from a PS-PEG amino-resin (TentaGel S NH_2, average diameter 90 μm, 1% divinylbenzene cross-linked, loading value of amino residue 0.29 mmol/g; purchased from Rapp Polymer), a polymeric phenanthroline ligand, and $(C_6H_5CN)_2PdCl_2$ in accordance with previously reported procedures [26]. The loading level of Pd in polymeric catalyst **1b** was 0.26 mmol/g.

3.3. Synthesis of Polymer-Supported Ligand

First, 5-methyl-1,10-phenanthroline (99 mg, 0.51 mmol) and SeO_2 (115 mg, 1.0 mmol) were suspended in ortho-dichlorobenzene (20 mL) and the mixture was heated at reflux for 6 h, and then cooled to room temperature. Filtration was followed by the addition of 5M aqueous citric acid (10 mL) to the filtrate. The aqueous phase was collected and washed with dichloromethane and then neutralized by the addition of 10M NaOHaq (15 mL). Dichloromethane was added, and extraction was repeated 5 times with dichloromethane. The corrected organic layers were washed with saturated NaCl and dried over $MgSO_4$. The solvent was removed by an evaporator and dried in vacuum to give a 76% yield of 1,10-phenanthroline-5-carbaldehyde. ^{1}H NMR ($CDCl_3$): δ10.42 (s, 1H), 9.81 (dd, *J* = 8.1, 1.3 Hz, 1H), 9.38 (dd, *J* = 3.9, 1.3 Hz, 1H), 9.33 (d, *J* = 2.7 Hz, 1H), 8.47 (dd, *J* = 8.0, 1.4 Hz, 1H), 8.41 (s, 1H), 7.83–7.79 (m, 2 H); ^{13}C NMR ($CDCl_3$): δ192.6, 153.4, 151.1, 148.0, 146.0, 139.7, 137.5, 134.2, 130.4, 126.8, 125.5, 124.4, 123.9; IR (ATR) (cm^{-1}): *v* 2970, 1681, 1506; HR-EI-MS: Calculated for $C_{13}H_9N_2O$ (M+) 208.0636, found 208.0637.

To a solution of the crude 1,10-phenanthroline-5-carbaldehyde (81 mg, 0.39 mmol) in THF (9.0 mL) and *t*-BuOH (9.0 mL), 2-methyl-2-butene (318 mg, 4.5 mmol) was added. The solution of $NaClO_2$ (105 mg, 1.2 mmol) and $NaH_2PO_4{\cdot}2H_2O$ (182 mg, 1.2 mmol) in 3.0 mL water was added to the reaction mixture and the mixture was stirred vigorously at 25 °C for 24 h, after which a white suspension was obtained. To a reaction mixture, 43 mL of 0.70 M NaOH was added, and the combined reaction mixture was washed with CH_2Cl_2 to remove residual starting materials. The water layers were neutralized with 10 mL of 0.5 M critic acid to generate a white precipitate via crystallization at 0 °C. The precipitate was filtered and washed with water. The precipitate was further purified by heating under reflux for 1 h in MeOH. The 5-carboxy-1,10-phenanthroline (13.7 mg, 16% yield) was collected by filtration. ^{1}H-NMR (CD_3OD): δ9.52 (dd, *J* = 8.5, 1.6 Hz, 1H), 9.17 (dd, *J* = 4.4, 1.6 Hz, 1 H), 9.11 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.72–8.69 (m, 1H), 8.59 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.85–7.82 (m, 2H); ^{13}C-NMR (DMSO-d_6): δ.168.0, 152.5, 150.4, 147.2, 146.0, 138.1, 134.8, 132.1, 127.1, 126.8, 126.6, 124.3, 124.0; IR (ATR) (cm^{-1}): *v* 3669 (br), 2997, 1683, 1508; HR-ESI-MS: Calculated for $C_{13}H_9N_2O_2$ (M + H) 225.0664, found 225.0665.

3.4. Preparation of PS–PEG Resin-Supported Phenanthroline–Palladium Complex **1b**

A Merrifield vessel was charged with PS-PEG-NH_2 (348 mg, 0.10 mmol), phenanthroline-COOH ligand (35.0 mg, 0.16 mmol), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (39.4 mg, 0.21 mmol), 1-hydroxybenzotriazole (27.4 mg, 0.2 mmol), and DMSO (6 mL). The reaction mixture was shaken at 25 °C for 17 h. The consumption of the primary amino residue of the resin was monitored by the Kaiser negative test. The reaction mixture was filtered, and the resin was washed with DMSO and CH_2Cl_2. The resin was dried under reduced pressure to provide the polymer-supported phenanthroline.

Another Merrifield vessel was charged with the obtained resin-supported phenanthroline ligand (0.10 mmol) and toluene (6 mL). To a suspension, $(C_6H_5CN)_2PdCl_2$ (45.9 mg, 0.12 mmol) was added, and the mixture was shaken (CM-1000) at 25 °C for 2 h. The mixture was filtered, and the resin was washed with toluene and CH_2Cl_2. The resulting resin was dried under reduced pressure to provide the polymer-supported palladium complex **1b** (loading value of Pd: 0.26 mmol/g). IR (ATR) (cm^{-1}); **1**; v 2868, 1683, 1102, 700.

3.5. Palladium-Catalyzed Friedel-Crafts-Type Alkylation of Indoles with Allyl Esters

The reaction conditions and results are shown in Table 1. A typical procedure is given for the reaction with indole **2a** and 1,3-diphenyl-2-propenyl acetate **3a** in water in entry 1. To a solution of catalyst **1** (38.0 mg, 0.01 mmol), 1,3-diphenyl-2-propenyl acetate (75 mg, 0.30 mmol), and indole **2a** (23.4 mg, 0.2 mmol) in H_2O (1.5 mL), triethylamine (60.7 mg, 0.60 mmol) was added, and the mixture was stirred at 40 °C for 24 h. The reaction mixture was filtered and the recovered resin beads were rinsed three times with AcOEt. The combined filtrate was extracted with AcOEt. The combined extracts were washed with aqueous sodium chloride and dried over anhydrous magnesium sulfate.

The solvent was evaporated and the residue was chromatographed on silica gel (hexane/ethyl acetate = 95/5) to give a mixture of the corresponding substituted products and indole. The indole was removed from a mixture of products and indole by distillation to give 3-(1,3-diphenyl-2-propenyl)-1*H*-indole in 88% yield (54.5 mg, 0.18 mmol). (To remove the other indoles **2b**–**h**, the mixture of products and indoles was separated by recycle HPLC (JAI LC-9201)).

The compounds and CAS registry numbers are as follows: 3-(1,3-diphenyl-2-propenyl)-1*H*-indole (**4a**), 3-(1,3-diphenyl-2-propenyl)-2-methyl-1*H*-indole (**4b**), 3-(1,3-diphenyl-2-propenyl)-2-phenyl-1*H*-indole (**4c**), 3-(1,3-diphenyl-2-propenyl)-5-methyl-1*H*-indole (**4d**), 3-(1,3-diphenyl-2-propenyl)-7-methyl-1*H*-indole (**4e**), 3-(1,3-diphenyl-2-propenyl)-5-bromo-1*H*-indole (**4f**), 3-(1,3-diphenyl-2-propenyl)-5- chloro-1*H*-indole (**4g**), 3-(1,3-diphenyl-2-propenyl)-5-methoxy-1*H*-indole (**4h**), 3-(1,3-diphenyl-2-propenyl)-5-benzyloxy-1*H*-indol (**4i**); and 1265313-04-9, 956480-06-6, 769929-40-0, 1264750-28-8, 1264750-28-8, 769929-44-4, 1264750-26-6, 957777-42-3, 769929-42-2, respectively.

Spectral and analytical data for the **4** are shown below:

(*R*)-3-(1,3-diphenyl-2-propenyl)-1*H*-indole (**4a**): ^{1}H NMR ($CDCl_3$): δ8.01 (br, 1 H), 7.27–7.44 (m, 14 H), 7.16–7.24 (m, 1 H), 6.73 (dd, *J* = 7.4, 15.8 Hz, 1 H), 6.45 (d, *J* = 15.1 Hz, 1 H), 5.13 (d, *J* = 7.3 Hz, 1 H). ^{13}C NMR ($CDCl_3$): δ143.3, 137.5, 136.6, 132.5, 130.5, 128.5 (2C), 128.4 (2C), 127.1 (2C), 126.7 (2C), 126.4 (2C), 126.3, 122.6, 122.1, 119.9, 119.4, 118.7, 111.1, 46.2. MS (EI): *m/z* (rel%) 309 (bp, M^+), 232 (36), 130 (30), 130 (29), 77 (16). IR (ATR): (cm^{-1}) *v* 3419 (br), 3056, 3024. EI-HRMS: Calcd for $C_{23}H_{19}N$ 309.1517, found 309.1516.

3-(1,3-diphenyl-2-propenyl)-2-methyl-1*H*-indole (**4b**): ^{1}H NMR ($CDCl_3$): δ7.62 (br, 1 H), 7.36–7.31 (m, 5 H), 7.26–7.20 (m, 4 H), 7.18–7.14 (m, 3 H), 7.05 (td, *J* = 7.1, 1.1 Hz, 1 H), 6.95 (td, *J* = 7.1, 1.1 Hz, 1 H), 6.81 (dd *J* = 15.8, 7.2 Hz, 1 H), 6.39 (d, *J* = 15.8 Hz, 1 H), 5.11 (d, *J* = 7.2 Hz, 1 H), 2.27 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ143.4, 137.4, 135.2, 132.1, 131.5, 130.5, 128.4 (2C), 128.2 (2C), 127.8 (2C), 127.0 (2C), 126.2 (2C), 126.0, 120.8, 119.3, 119.1, 112.7, 110.2, 45.0, 12.2. MS (EI): *m/z* (rel%) 323 (bp, M^+), 308 (67), 246 (38), 218 (36), 144 (42), 77 (14). IR (ATR): (cm^{-1}) *v* 3379 (br), 2982. EI-HRMS: Calcd for $C_{24}H_{21}N$ 323.1674, found 323.1682.

3-(1,3-diphenyl-2-propenyl)-2-phenyl-1*H*-indole (**4c**): ^{1}H NMR ($CDCl_3$): δ8.05 (br, 1 H), 7.53–7.51 (m, 2 H), 7.45–7.41 (m, 3 H), 7.38–7.31 (m, 6 H), 7.27–7.23 (m, 4 H), 7.20–7.14 (m, 3 H), 6.99 (td, *J* = 8.0, 1.0 Hz, 1 H), 6.88 (dd, *J* = 15.8, 7.2 Hz, 1 H), 6.39 (dd, *J* = 15.8, 1.0 Hz, 1 H), 5.27 (d, *J* = 7.2 Hz, 1 H). ^{13}C NMR ($CDCl_3$): δ143.4, 137.4, 136.2, 135.5, 132.9, 132.2, 131.0, 128.7 (2C), 128.5 (2C), 128.4 (2C), 128.2 (2C), 128.2, 128.0, 127.9, 127.0, 126.2 (2C), 126.0, 122.0, 121.2, 119.6, 113.8, 110.9, 45.1. MS (EI): *m/z* (rel%) 385 (bp, M^+), 294 (89), 206 (41), 91 (13). IR (ATR): (cm^{-1}) *v* 3408 (br), 3056, 3023. EI-HRMS: Calcd for $C_{29}H_{23}N$ 385.1830, found 385.1835.

3-(1,3-diphenyl-2-propenyl)-5-methyl-1*H*-indole (**4d**): ^{1}H NMR ($CDCl_3$): δ7.74 (br, 1 H), 7.35–7.16 (m, 12 H), 6.97 (dd, *J* = 8.2, 1.4 Hz, 1 H), 6.77 (dd, *J* = 2.3, 0.6 Hz, 1 H), 6.69 (dd, *J* = 15.8, 7.2 Hz, 1 H), 6.39 (dd, *J* = 16.4 Hz, 1 H), 5.07 (d, *J* = 7.2 Hz, 1 H), 2.35 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ143.4, 137.5, 134.9, 132.6, 130.4, 128.5 (2C), 128.4 (2C), 128.4, 128.3 (2C), 127.0, 127.0, 126.2, 126.2 (2C), 123.7, 122.7, 119.3, 118.0, 110.7, 46.0, 21.5. MS (EI): *m/z* (rel%) 323 (bp, M^+), 246 (42), 220 (28), 191 (20), 144 (14), 91 (8). IR (ATR): (cm^{-1}) *v* 3404 (br), 2982. EI-HRMS: Calcd for $C_{24}H_{21}N$ 323.1674, found 323.1679.

3-(1,3-diphenyl-2-propenyl)-7-methyl-1*H*-indole (**4e**): ^{1}H NMR ($CDCl_3$): δ7.69 (br, 1 H), 7.33–7.10 (m, 11 H), 6.95–6.91 (m, 2 H), 6.76 (dd, *J* = 2.4, 0.8 Hz, 1 H), 6.69 (dd, *J* = 15.8, 7.3 Hz, 1 H), 6.40 (dd, *J* = 15.8, 0.5 Hz, 1 H), 5.07 (d, *J* = 7.3 Hz, 1 H), 2.37 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ143.4, 137.4, 136.1, 132.5, 130.4, 128.4 (2C), 128.4 (2C), 128.3 (2C), 127.0, 126.3, 126.3, 126.2 (2C), 122.5, 122.2, 120.1, 119.6, 119.0, 117.5, 46.2, 16.4. MS (EI): *m/z* (rel%) 323 (bp, M^+), 246 (38), 220 (28), 191 (20), 144 (22), 91 (7). IR (ATR): (cm^{-1}) *v* 3429 (br), 3024. EI-HRMS: Calcd for $C_{24}H_{21}N$ 323.1674, found 323.1670.

3-(1,3-diphenyl-2-propenyl)-5-bromo-1*H*-indole (**4f**): ^{1}H NMR ($CDCl_3$): δ7.84 (br, 1 H), 7.52 (d, *J* = 1.8 Hz, 1 H), 7.33–7.16 (m, 11 H), 7.10 (d, *J* = 8.8 Hz, 1 H), 6.79 (d, *J* = 2.4 Hz, 1 H), 6.64 (dd, *J* = 15.8, 7.3 Hz, 1 H), 6.37 (d, *J* = 15.8 Hz, 1 H), 5.00 (d, *J* = 7.2 Hz, 1 H). ^{13}C NMR ($CDCl_3$): δ142.8, 137.2, 135.1,

132.0, 130.0, 128.4 (2C), 128.4, 128.4 (2C), 128.3 (2C), 127.2, 126.5, 126.2 (2C), 124.9, 123.7, 122.1, 118.2, 112.6, 112.5, 45.8. MS (EI): *m/z* (rel%) 389 (42), 387 (M^+, 47), 231 (25), 233 (25), 130 (45), 68 (bp). IR (ATR): (cm^{-1}) *v* 3364 (br), 2982. EI-HRMS: Calcd for $C_{23}H_{18}{}^{79}BrN$ 387.0622, found 387.0638.

3-(1,3-diphenyl-2-propenyl)-5-chloro-1*H*-indole (**4g**): ^1H NMR ($CDCl_3$): δ7.84 (br, 1 H), 7.37–7.14 (m, 12 H), 7.07 (dd, *J* = 8.6, 1.9 Hz, 1 H), 6.81 (dd, *J* = 2.2, 0.5 Hz, 1 H), 6.64 (dd, *J* = 15.8, 7.3 Hz, 1 H), 6.38 (d, *J* = 15.8 Hz, 1 H), 5.01 (d, *J* = 7.3 Hz, 1 H). ^{13}C NMR ($CDCl_3$): δ142.8, 137.2, 134.9, 132.0, 130.7, 128.4 (2C), 128.4 (2C), 128.3 (2C), 127.8, 127.2, 126.5, 126.2 (2C), 125.0, 123.9, 122.3, 119.1, 118.3, 112.1, 45.8. MS (EI): *m/z* (rel%) 343 (bp, M^+), 266 (35), 240 (29), 191 (27), 115 (26). IR (ATR): (cm^{-1}) *v* 3853 (br), 3025. EI-HRMS: Calcd for $C_{23}H_{18}{}^{35}ClN$ 343.1127, found 343.1131.

3-(1,3-diphenyl-2-propenyl)-5-methoxy-1*H*-indole (**4h**): ^1H NMR ($CDCl_3$): δ7.75 (br, 1 H), 7.34–7.11 (m, 12 H), 6.84–6.65 (m, 4 H), 6.41 (d, *J* = 15.8, 1 H), 5.03 (d, *J* = 7.2 Hz, 1 H), 3.67 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ153.7, 143.2, 137.4, 132.4, 131.7, 130.4, 128.4 (2C), 128.3 (3C), 127.1 (2C), 126.3 (2C), 126.2 (2C), 123.4, 118.1, 112.0, 111.7, 101.8, 55.7, 46.1. MS (EI): *m/z* (rel%) 339 (bp, M^+), 262 (38), 236 (25), 115 (12). IR (ATR): (cm^{-1}) *v* 3420 (br), 3024. EI-HRMS: Calcd for $C_{24}H_{21}NO$ 339.1623, found 339.1624.

3-(1,3-diphenyl-2-propenyl)-5-benzyloxy-1*H*-indole (**4i**): ^1H NMR ($CDCl_3$): δ7.66 (br, 1 H), 7.34–7.13 (m, 15 H), 7.06 (d, *J* = 8.8 Hz, 1 H), 6.92 (d, *J* = 2.3 Hz, 1 H), 6.85 (dd, *J* = 8.7, 2.4 Hz, 1 H), 6.99 (d, *J* = 2.0 Hz, 1 H), 6.64 (dd, *J* = 15.8, 7.3 Hz, 1 H), 6.38 (d, *J* = 15.8 Hz, 1 H), 4.99 (d, *J* = 7.3 Hz, 1 H), 4.90 (s, 2 H). ^{13}C NMR ($CDCl_3$): δ152.8, 143.2, 137.5, 137.4, 132.4, 131.8, 130.4, 128.4 (2C), 128.3 (2C), 128.3, 127.6 (2C), 127.5 (2C), 127.0 (2C), 127.0 (2C), 126.3, 126.2 (2C), 123.4, 118.0, 112.8, 111.7, 103.3, 70.8, 46.1. MS (ESI): *m/z* (rel%) 438 (bp, M+Na). IR (ATR): (cm^{-1}) *v* 3426 (br), 3025. ESI-HRMS: Calcd for $C_{30}H_{25}NONa$ 438.1833, found 438.1836.

4. Conclusions

In summary, we have developed a practical protocol for the Friedel-Crafts-type alkylation of indoles with allylic ester using the PS-PEG resin-supported phenanthroline-palladium complex to give the 3-allyl-1*H*-indoles with up to 91% yield. This polymeric catalyst was also found to promote the C3-alkylation reaction to give a thermodynamic alkylation product with high selectivity. This catalyst was recovered and reused several times without any loss of activity.

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