Tetrahedron xxx (2013) 1–7

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

MCM-41-immobilized bidentate nitrogen copper(I) complex: a highly efficient and recyclable catalyst for Buchwald N-arylation of indoles

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ARTICLE INFO

Article history:
Received 4 February 2013
Received in revised form 14 April 2013
Accepted 23 April 2013
Available online xxx

Keywords:
Immobilized catalyst
Bidentate nitrogen copper(I) complex
N-Arylation
Indole
Heterogeneous catalysis

ABSTRACT

The heterogeneous N-arylation reaction of indoles with aryl halides was achieved in toluene at 110 °C by using 4 mol % MCM-41-immobilized bidentate nitrogen copper(I) complex [MCM-41–2N-CuI] as catalyst and K_3PO_4 as base, yielding a variety of *N*-arylindoles in good to excellent yields. The heterogeneous copper catalyst exhibited as high activity as homogeneous CuI/diamine catalytic system and can be easily prepared by a simple two-step procedure from commercially available and cheap reagents and recovered by a simple filtration of the reaction solution and reused for 10 cycles with almost consistent activity.

1. Introduction

The *N*-aryl nitrogen heterocycle motif is present in numerous natural products and biologically active pharmaceutical products.[1] Various strategies have been developed for the N-arylation of heterocycles. The Ullmann-type coupling of aryl halides with nitrogen heterocycles represents a straightforward, inexpensive approach to *N*-aryl nitrogen heterocycles.[2] These copper-catalyzed reactions usually suffer from several limitations such as high reaction temperatures, generally 140 °C or more, use of stoichiometric amounts of copper reagents, long reaction times, and low yields. The palladium-catalyzed N-arylation of heterocycles is an alternative method under mild reaction conditions.[3] However, use of expensive palladium limits the attractiveness of this method for industrial applications. The efficiency of copper-catalyzed Ullmann reactions has been improved by the correct choice of copper sources, bases, ligands, and other additives in the past few years, several mild and efficient methods have been reported for the N-arylation of indoles.[4] Ligands based on diamines,[5] oxime–phosphine oxide,[6] amino-acids,[7] phosphoramidite,[8] proline,[9] and diimines[10] have been used to promote copper-catalyzed N-arylation of indoles and other heterocycles.

Although these copper-catalyzed N-arylations of indoles or other heterocycles are highly efficient, the problem with homogeneous catalysis is the difficulty to separate the catalyst from the reaction mixture and the impossibility to reuse it in consecutive reactions. In addition, homogeneous catalysis might result in unacceptable copper contamination of the desired isolated product, which is a particularly significant drawback for its application in the pharmaceutical industry. To overcome these problems, the development of highly efficient and recyclable heterogeneous catalysts, such as immobilization of catalytically active species, i.e., organometallic complexes, onto a solid support to produce a molecular heterogeneous catalyst is essential.[11] Heterogeneous catalysis also helps to minimize wastes derived from reaction workup, contributing to the development of green chemical processes.[12] In spite of tremendous effort dedicated to the immobilization of homogeneous palladium complexes over the last two decades,[13] very few examples of carbon–carbon or carbon–heteroatom bond formation reactions catalyzed by heterogeneous copper catalysts have appeared.[14] Therefore, the development of a stable heterogeneous copper catalyst that allows for highly efficient N-arylation of a wide range of substrates (indoles and aryl halides) is worthwhile.

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0040-4020/$ – see front matter © 2013 Published by Elsevier Ltd.
http://dx.doi.org/10.1016/j.tet.2013.04.106

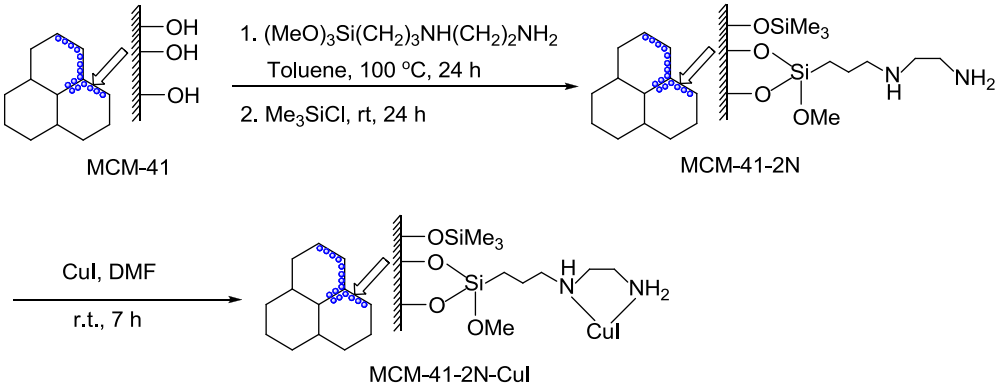
Developments on the mesoporous material MCM-41 provided a new possible candidate for a solid support for immobilization of homogeneous catalysts.[15] MCM-41 has a regular pore diameter of ca.5 nm and a specific surface area >700 $m^2 g^{-1}$.[16] Its large pore size allows passage of large molecules such as organic reactants and metal complexes through the pores to reach to the surface of the channel.[17] To date, some palladium and rhodium complexes on functionalized MCM-41 support have been prepared and successfully used in organic reactions.[11b,18] Very recently, we reported the synthesis of the first MCM-41-immobilized bidentate nitrogen copper(I) complex and found that it is a highly efficient and recyclable heterogeneous catalyst for the homo- and heterocoupling of terminal alkynes.[14d] However, to the best of our knowledge, no N-arylation of indoles catalyzed by immobilization of copper in MCM-41 has been described in the open literature. In continuing our efforts to develop greener synthetic pathways for organic transformations, herein we wish to report a highly efficient, heterogeneous N-arylation of indoles with aryl halides catalyzed by an MCM-41-immobilized bidentate nitrogen copper(I) complex under mild reaction conditions.

2. Results and discussion

The MCM-41-immobilized bidentate nitrogen copper(I) complex (MCM-41–2N-CuI) was conveniently prepared starting from commercially available and inexpensive 3-(2-aminoethylamino) propyltrimethoxysilane and CuI according to our previous procedure[14d] (Scheme 1). Firstly, the mesoporous material MCM-41 reacted with 3-(2-aminoethylamino)propyltrimethoxysilane in toluene at 100 °C for 24 h, followed by the silylation with Me_3SiCl in toluene at room temperature for 24 h to generate 3-(2-aminoethylamino)propyl-functionalized MCM-41 (MCM-41–2N). The latter was subsequently treated with CuI in DMF at room temperature for 7 h to generate the MCM-41-immobilized bidentate nitrogen copper(I) complex (MCM-41–2N-CuI) as a pale blue powder, the copper content of the complex was found to be 0.45 mmol g^{-1} according to the ICP-AES measurements.

be the most effective (Table 1, entry 7), DMF and NMP also afforded good yields (Table 1, entries 12 and 14). While other solvents such as xylene, DCE, and benzene were substantially less effective (Table 1, entries 13, 15, and 16). The effect of reaction temperature and time on the reaction was also investigated. It was found that the reaction was accomplished when it was carried out in toluene at 110 °C for 24 h. Reducing the reaction temperature resulted in a decrease in yield (Table 1, entries 17 and 18). Finally, the amount of supported copper catalyst was also screened, and 4.0 mol % loading of copper was found to be optimal, a lower yield was observed when the amount of the catalyst was decreased (Table 1, entry 19). Increasing the amount of copper catalyst could shorten the reaction time, but did not increase the yield of *N*-phenylindole (Table 1, entry 20). The N-arylation reaction did not take place in the absence of the catalyst (Table 1, entry 21). Thus, the optimized reaction conditions for this N-arylation reaction of indole are the MCM-41–2N-CuI (4.0 mol %) in toluene using K_3PO_4 as base at 110 °C under Ar for 24 h (Table 1, entry 7).

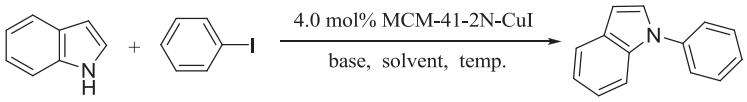
With this promising result in hand, we started to investigate the scope of this reaction under the optimized conditions. The scope of both indoles and aryl halides was explored, and the results are summarized in Table 2. As shown in Table 2, the N-arylation reaction of indole with a variety of aryl iodides proceeded smoothly under mild conditions affording the corresponding *N*-arylindoles **3a**–**o** in good to excellent yields (entries 1–15). Various electron-donating and electron-withdrawing substituents such as $-CH_3$, $-OCH_3$, $-NH_2$, $-Cl$, $-F$, $-CF_3$, $-CN$, $-CO_2CH_3$, $-COCH_3$, and $-NO_2$ on aryl iodides were well tolerated. The reactivity of aryl iodides having electron-withdrawing groups was higher than that of aryl iodides having electron-donating groups. The reactions of sterically hindered aryl iodides such as 2-iodotoluene and 2-iodoanisole with indole also provided good yields of the desired *N*-arylindoles **3b** and **3e** under the optimized reaction conditions, respectively (entries 2 and 5). The N-arylation of heteroaryl iodides such as 2-iodothiophene and 3-iodopyridine with indole gave the corresponding *N*-heteroarylindoles **3p** and **3q** in 90 and 94% yields, respectively (entries 16 and 17). The bulky 1-iodonaphthalene also



Scheme 1.

In our initial screening experiments, the N-arylation reaction of indole with iodobenzene was investigated to optimize the reaction conditions, and the results are summarized in Table 1. At first, the base effect was examined, and a significant base effect was observed. It is evident that good to high yields were obtained when Bu_3N, Na_2CO_3, Cs_2CO_3, K_2CO_3, K_3PO_4, and Et_3N were used as the base (Table 1, entries 1–3, 6–8), whereas DBU, *t*-BuOK, and CsF afforded low to moderate yields (Table 1, entries 5, 9, 10) and KF was ineffective (Table 1, entry 4), so K_3PO_4 was finally selected as the base for the reaction. The N-arylation reaction did not occur without base (Table 1, entry 11). Our next studies focused on the effect of solvent on the model reaction. Among the solvents examined, toluene was found to reacted effectively with indole to afford the desired *N*-(1-naphthyl) indole (**3r**) in good yield (entry 18). This heterogeneous copper catalyst exhibited as high activity as homogeneous CuI/diamine catalytic system. For example, the N-arylation reaction of 4-iodonitrobenzene (1.2 equiv) with indole in the presence of 4 mol % of MCM-41–2N-CuI in toluene using K_3PO_4 (2.0 equiv) as base at 110 °C for 24 h gave a 98% yield of the *N*-arylated product **3m** (entry 13), the same reaction of indole (1.2 equiv) with 4-iodonitrobenzene in the presence of 1 mol % of CuI and 10 mol % of racemic *trans*-1,2-cyclohexanediamine in dioxane using K_3PO_4 (2.1 equiv) as base at 110 °C for 24 h gave **3m** in 99% yield.[5a] Comparison with homogeneous analogous catalysts such as CuI/

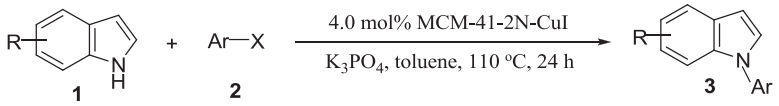
Table 1
Reaction condition screening for the N-arylation of indole with iodobenzene[a]



Entry	Base	Solvent	Temp (°C)	Time (h)	Yield[b] (%)
1	Bu_3N	Toluene	110	24	81
2	Na_2CO_3	Toluene	110	24	79
3	Cs_2CO_3	Toluene	110	24	70
4	KF	Toluene	110	24	Trace
5	*t*-BuOK	Toluene	110	24	37
6	K_2CO_3	Toluene	110	24	75
7	K_3PO_4	Toluene	110	24	92
8	Et_3N	Toluene	110	24	77
9	DBU	Toluene	110	24	57
10	CsF	Toluene	110	24	30
11	None	Toluene	110	48	0
12	K_3PO_4	DMF	140	24	81
13	K_3PO_4	Xylene	130	24	52
14	K_3PO_4	NMP	110	24	82
15	K_3PO_4	DCE	80	36	67
16	K_3PO_4	Benzene	80	36	72
17	K_3PO_4	Toluene	100	30	85
18	K_3PO_4	Toluene	80	48	76
19[c]	K_3PO_4	Toluene	110	48	81
20[d]	K_3PO_4	Toluene	110	15	91
21[e]	K_3PO_4	Toluene	110	48	0

[a] Reaction conditions: indole (1.0 mmol), iodobenzene (1.2 mmol), copper catalyst (4.0 mol %), base (2.0 mmol), solvent (2.0 mL).
[b] Isolated yield.
[c] Copper catalyst (2.0 mol %) was used.
[d] Copper catalyst (8.0 mol %) was used.
[e] No copper catalyst.

Table 2
Heterogeneous copper-catalyzed N-arylation of indoles with aryl halides[a]



Entry	R	Ar/X	Product	Yield[b] (%)
1	H	Ph/I	**3a**	92
2	H	2-$CH_3C_6H_4$/I	**3b**	83
3	H	3-$CH_3C_6H_4$/I	**3c**	92
4	H	4-$CH_3C_6H_4$/I	**3d**	91
5	H	2-$CH_3OC_6H_4$/I	**3e**	79
6	H	4-$CH_3OC_6H_4$/I	**3f**	90
7	H	3-$CF_3C_6H_4$/I	**3g**	93
8	H	4-$NH_2C_6H_4$/I	**3h**	89
9	H	4-$CH_3OCOC_6H_4$/I	**3i**	96
10	H	4-ClC_6H_4/I	**3j**	94
11	H	4-FC_6H_4/I	**3k**	91
12	H	3-$O_2NC_6H_4$/I	**3l**	95
13	H	4-$O_2NC_6H_4$/I	**3m**	98
14	H	4-$CH_3COC_6H_4$/I	**3n**	96
15	H	4-NCC_6H_4/I	**3o**	95
16	H	2-Thienyl/I	**3p**	90
17	H	3-Pyridinyl/I	**3q**	94
18	H	1-Naphthyl/I	**3r**	79
19	2-CH_3	4-ClC_6H_4/I	**3s**	87
20	2-CH_3	3-Pyridinyl/I	**3t**	90
21	5-CH_3	4-ClC_6H_4/I	**3u**	92
22	5-CH_3	3-Pyridinyl/I	**3v**	94
23	5-CHO	4-ClC_6H_4/I	**3w**	89
24	5-CHO	3-Pyridinyl/I	**3x**	91
25[c]	H	4-PhenylC_6H_4/Br	**3y**	78
26[c]	H	4-$CH_3COC_6H_4$/Br	**3n**	83
27[c]	H	4-$O_2NC_6H_4$/Br	**3m**	88
28[c]	H	4-$NH_2C_6H_4$/Br	**3h**	59
29[c]	H	4-$O_2NC_6H_4$/Cl	**3m**	57
30[c]	H	4-$NH_2C_6H_4$/Cl	**3h**	0

[a] Reaction conditions: indole (1.0 mmol), aryl halide (1.2 mmol), MCM-41−2N-CuI (4.0 mol %), K_3PO_4 (2.0 mmol), toluene (2.0 mL) at 110 °C for 24 h.
[b] Isolated yield.
[c] For 48 h.

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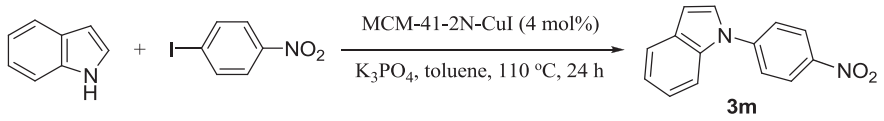
$H_2N(CH_2)_2NH_2$ was also made in order to assess the immobilization effect on activity. When 4 mol % of CuI and 10 mol % of $H_2N(CH_2)_2NH_2$ were used as the catalytic system, the N-arylation reaction of 4-iodonitrobenzene (1.2 equiv) with indole in toluene using K_3PO_4 (2.0 equiv) as base at 110 °C for 24 h afforded **3m** in 85% yield.

The optimized reaction conditions were also applied to the N-arylation reactions of a variety of substituted indoles such as 2-methylindole, 5-methylindole, and indole-5-carboxaldehyde with various aryl iodides, the results are also summarized in Table 2. As shown in Table 2, the reactions of a variety of substituted indoles having either electron-donating or electron-withdrawing groups with aryl iodides also proceeded smoothly to give the corresponding *N*-arylated indoles **3s**–**x** in high yields (entries 19–24). The reactivity of 2-methylindole was slightly lower than that of 5-methyl-indole due to the steric effect. The method provides a quite general route for the synthesis of *N*-arylindoles having various functionalities. The results above prompted us to investigate the reaction of indole with aryl bromides or chlorides. The reactions of indole with various aryl bromides could proceed efficiently under the optimized reaction conditions to afford the desired *N*-arylated indoles in moderate to good yields on longer reaction times (entries 25–28). The reactivity of aryl chlorides was obviously lower than that of aryl bromides, the reaction of only 4-nitrochlorobenzene with indole could give a moderate yield of desired product **3m** after 48 h (entry 29).

In order to determine whether the catalysis was due to the MCM-41–2N-CuI complex or to a homogeneous copper complex that comes off the support during the reaction and then returns to the support at the end, we performed the hot filtration test.[19] We focused on the N-arylation reaction of indole with iodobenzene. We filtered off the MCM-41–2N-CuI complex after 5 h of reaction time and the filtered solution was concentrated under reduced pressure. To the residue were added 10 mol % of racemic *trans*-1,2-cyclohexanediamine in dioxane (2 mL) and K_3PO_4 (2.0 mmol) and the mixture was stirred at 110 °C under Ar for 24 h to give **3a** in 41% yield. The catalyst filtration was performed at the reaction temperature (110 °C) in order to avoid possible recoordination or precipitation of soluble copper upon cooling. The reaction of indole with iodobenzene at 110 °C for 5 h before the hot filtration could afford **3a** in 42% yield. We found that, after this hot filtration, no further reaction was observed. This result suggests that the copper catalyst remains on the MCM-41 support at elevated temperatures during the reaction and points to a process of heterogeneous nature.

For a heterogeneous transition-metal catalyst, it is important to examine its ease of separation, recoverability, and reusability. We also investigated the recyclability of the MCM-41–2N-CuI by using the N-arylation reaction of indole with 4-nitroiodobenzene. After carrying out the reaction, the catalyst was separated by simple filtration and washed with distilled water, ethanol, and diethyl ether. After being air-dried, it can be reused directly without further purification. The recovered copper catalyst was used in the next run, and almost consistent activity was observed for 10 consecutive cycles (Table 3, entries 1–10). In addition, copper leaching in the immobilized catalyst was also determined. The copper content of the catalyst was found by ICP analysis to be 0.43 mmol g^{-1} after 10 consecutive runs, only 4.4% of copper had been lost from the MCM-41 support. The high stability and excellent reusability of the catalyst should result from the chelating action of bidentate 2-aminoethylamino ligand on copper and the mesoporous structure of the MCM-41 support. The result is important from a practical point of view. The high catalytic activity, excellent reusability, and the easy accessibility of the MCM-41–2N-CuI make it a highly attractive heterogeneous copper catalyst for the parallel solution phase synthesis of diverse libraries of compounds.

Table 3
N-Arylation reaction of indole with 4-nitroiodobenzene catalyzed by the recycled catalyst[a]



Cycle	Yield[b] (%)	Cycle	Yield[b] (%)
1	98	2	97
3	98	4	97
5	97	6	96
7	95	8	96
9	95	10	95

[a] Reaction was carried out with indole (1 mmol), 4-nitroiodobenzene (1.2 mmol), MCM-41–2N-CuI (4.0 mol %), K_3PO_4 (2.0 mmol), toluene (2.0 mL) at 110 °C for 24 h.
[b] Isolated yield.

3. Conclusions

In summary, we have developed a novel, practical, and environmentally friendly method for the synthesis of *N*-arylindoles through the reaction of indoles with aryl halides by using an MCM-41-immobilized bidentate nitrogen copper complex as catalyst under mild reaction conditions. The reactions generated the corresponding *N*-arylindoles in good to excellent yields and were applicable to various indoles and a variety of aryl iodides or bromides. This heterogeneous copper catalyst can be very conveniently prepared by a simple two-step procedure from commercially available and cheap reagents. In addition, this methodology offers the competitiveness of recyclability of the catalyst without significant loss of catalytic activity, and the catalyst could be easily recovered and reused for at least 10 cycles, thus making this procedure environmentally more acceptable.

4. Experimental

4.1. Physical measurements and materials

All chemicals were reagent grade and used as purchased. All solvents were dried and distilled before use. The products were purified by flash chromatography on silica gel and a mixture of EtOAc and petroleum ether was generally used as eluent. IR spectra were determined on a Perkin–Elmer 683 instrument. ^1H NMR spectra (400 MHz) were recorded on a Bruker Avance 400 MHz spectrometer with TMS as an internal standard in $CDCl_3$ as solvent. ^{13}C NMR spectra (100 MHz) were recorded on a Bruker Avance 400 MHz spectrometer in $CDCl_3$ as solvent. Microanalyses were measured by using a Yanaco MT-3 CHN microelemental analyzer. The MCM-41–2N-CuI complex was prepared according to our previous procedure, the copper content was 0.45 mmol g^{-1}.[14d]

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4.2. Typical experimental procedure for the synthesis of *N*-arylindoles

To a resealable Schlenk tube were added indole (1.0 mmol), K_3PO_4 (0.424 g, 2.0 mmol), and MCM-41–2N-CuI (88 mg, 0.04 mmol), and the reaction vessel was fitted with a rubber septum. The vessel was evacuated and back-filled with argon and this evacuation/back-fill procedure was repeated one additional time. The aryl halide (1.2 mmol) and toluene (2 mL) were then added under a stream of argon. The reaction tube was quickly sealed and the contents were stirred while heating in an oil bath at 110 °C for 24–48 h. After completion of the reaction, the reaction mixture was cooled to room temperature, diluted with ethyl acetate (5 mL), and filtered. The MCM-41–2N-CuI complex was washed with distilled water (2×5 mL), ethanol (2×5 mL), and Et_2O (2×5 mL) and reused in the next run. The filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (petroleum/ethyl acetate=50:1 to 4:1) to provide the desired product.

*4.2.1. N-Phenylindole (**3a**).* Colorless oil.[20] ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.68 (d, *J*=8.0 Hz, 1H), 7.55 (d, *J*=8.0 Hz, 1H), 7.50–7.47 (m, 4H), 7.35–7.31 (m, 2H), 7.21 (t, *J*=7.2 Hz, 1H), 7.16 (t, *J*=7.2 Hz, 1H), 6.67 (d, *J*==2.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=139.8, 135.8, 129.6, 129.3, 127.9, 126.4, 124.3, 122.3, 121.1, 120.3, 110.5, 103.5. IR (film, cm^{-1}): 2924, 1596, 1502, 1138, 745, 688.

*4.2.2. N-(2-Methylphenyl)indole (**3b**).* Colorless oil.[21] ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.71–7.69 (m, 1H), 7.37–7.31 (m, 4H), 7.18–7.13 (m, 3H), 7.06–7.03 (m, 1H), 6.67 (d, *J*=3.2 Hz, 1H), 2.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=138.3, 137.0, 135.9, 131.2, 128.7, 128.3, 128.2, 128.1, 126.8, 122.0, 120.9, 119.9, 110.6, 102.5, 17.7. IR (film, cm^{-1}): 2924, 1583, 1512, 1496, 1462, 1331, 1235, 742.

*4.2.3. N-(3-Methylphenyl)indole (**3c**).* Colorless oil.[20] ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.67 (d, *J*=7.6 Hz, 1H), 7.55 (d, *J*=8.0 Hz, 1H), 7.34 (t, *J*=7.6 Hz, 1H), 7.29–7.26 (m, 3H), 7.22–7.11 (m, 3H), 6.64 (d, *J*=2.8 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=139.8, 139.7, 135.9, 129.5, 129.4, 128.1, 127.3, 125.1, 122.4, 121.5, 121.2, 120.4, 110.7, 103.5, 21.6. IR (film, cm^{-1}): 2920, 1608, 1590, 1515, 1494, 1459, 1335, 1215, 741, 698.

*4.2.4. N-(4-Methylphenyl)indole (**3d**).* Colorless oil.[5d] ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.67 (d, *J*=7.6 Hz, 1H), 7.51 (d, *J*=8.0 Hz, 1H), 7.35 (d, *J*=8.4 Hz, 2H), 7.28–7.26 (m, 3H), 7.21–7.12 (m, 2H), 6.64 (d, *J*=3.2 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=137.4, 136.4, 136.1, 130.3, 129.3, 128.2, 124.4, 122.3, 121.2, 120.3, 110.6, 103.3, 21.2. IR (film, cm^{-1}): 2921, 1608, 1519, 1457, 1333, 1213, 821, 740.

*4.2.5. N-(2-Methoxyphenyl)indole (**3e**).* Colorless oil.[5d] ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.66 (d, *J*=8.0 Hz, 1H), 7.38–7.32 (m, 2H), 7.27–7.02 (m, 6H), 6.64 (d, *J*=3.2 Hz, 1H), 3.71 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=154.6, 136.9, 129.5, 128.7, 128.6, 128.3, 128.2, 122.6, 122.0, 120.9, 120.0, 112.6, 110.9, 102.6, 55.8. IR (film, cm^{-1}): 2926, 1578, 1249, 1112, 1013, 822, 789.

*4.2.6. N-(4-Methoxyphenyl)indole (**3f**).* Colorless oil.[5d] ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.68 (d, *J*=7.6 Hz, 1H), 7.45 (d, *J*=8.4 Hz, 1H), 7.40 (d, *J*=8.8 Hz, 2H), 7.27 (d, *J*=3.2 Hz, 1H), 7.20 (t, *J*=7.6 Hz, 1H), 7.15 (t, *J*=7.6 Hz, 1H), 7.03 (d, *J*=8.8 Hz, 2H), 6.65 (d, *J*=3.2 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=158.2, 136.3, 132.8, 129.0, 128.3, 126.0, 122.2, 121.0, 120.1, 114.7, 110.4, 102.9, 55.6. IR (film, cm^{-1}): 2925, 1641, 1565, 1519, 1458, 1249, 1163, 1075, 836, 747.

*4.2.7. N-(3-Trifluoromethylphenyl)indole (**3g**).* Colorless oil.[22] ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.76 (s, 1H), 7.69–7.65 (m, 2H), 7.62–7.58 (m, 2H), 7.53 (d, *J*=8.0 Hz, 1H), 7.30 (d, *J*=3.2 Hz, 1H), 7.24 (t, *J*=7.6 Hz, 1H), 7.19 (t, *J*=7.6 Hz, 1H), 6.70 (d, *J*=3.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=140.3, 135.6, 132.2 (q, $^2J_{CF}$=33.0 Hz), 130.3, 129.5, 127.5, 127.3, 123.7 (q, $^1J_{CF}$=271.0 Hz), 122.9 (q, $^3J_{CF}$=4.0 Hz), 121.4, 120.9 (q, $^3J_{CF}$=4.0 Hz), 110.1, 104.7. IR (film, cm^{-1}): 1596, 1520, 1496, 1463, 1321, 1130, 1068, 742.

*4.2.8. N-(4-Aminophenyl)indole (**3h**).* Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.67 (d, *J*=7.2 Hz, 1H), 7.43 (d, *J*=7.6 Hz, 1H), 7.24–7.11 (m, 5H), 6.72 (d, *J*=8.4 Hz, 2H), 6.62 (d, *J*=3.2 Hz, 1H), 3.71 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=145.3, 136.5, 130.9, 128.9, 128.5, 126.1, 122.0, 121.0, 119.9, 115.7, 110.5, 102.5. IR (film, cm^{-1}): 3455, 3371, 1622, 1520, 1458, 1282, 1135, 832, 743. Anal. Calcd for $C_{14}H_{12}N_2$: C, 80.75; H, 5.81; N, 13.45. Found: C, 80.52; H, 5.54; N, 13.53.

*4.2.9. N-(4-Methoxycarbonylphenyl)indole (**3i**).* White solid.[5d] ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.17 (d, *J*=8.4 Hz, 2H), 7.68 (d, *J*=7.6 Hz, 1H), 7.62 (d, *J*=8.0 Hz, 1H), 7.56 (d, *J*=8.4 Hz, 2H), 7.35 (d, *J*=3.2 Hz, 1H), 7.27–7.18 (m, 2H), 6.71 (d, *J*=3.2 Hz, 1H), 3.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=166.5, 143.8, 135.4, 131.3, 129.8, 127.6, 127.5, 123.3, 122.9, 121.5, 121.0, 110.6, 105.0, 52.3. IR (KBr, cm^{-1}): 1710, 1639, 1617, 1457, 1285, 1135, 1069, 953, 861.

*4.2.10. N-(4-Chlorophenyl)indole (**3j**).* Colorless oil.[21] ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.68 (d, *J*=8.0 Hz, 1H), 7.51–7.41 (m, 5H), 7.27 (d, *J*=3.2 Hz, 1H), 7.25–7.17 (m, 2H), 6.68 (d, *J*=3.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=138.2, 135.6, 131.8, 129.7, 129.3, 127.6, 125.4, 122.6, 121.2, 120.6, 110.2, 104.0. IR (film, cm^{-1}): 1641, 1567, 1517, 1495, 1455, 1333, 1134, 1089, 954, 831, 739.

*4.2.11. N-(4-Fluorophenyl)indole (**3k**).* Colorless oil.[22] ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.65 (d, *J*=8.0 Hz, 1H), 7.41 (d, *J*=8.0 Hz, 1H), 7.34–7.30 (m, 2H), 7.19–7.06 (m, 4H), 6.62 (d, *J*=3.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=161.2 (d, $^1J_{CF}$=245.0 Hz) 136.3, 136.0 (d, $^4J_{CF}$=3.0 Hz), 129.4, 128.2, 126.3 (d, $^3J_{CF}$=8.0 Hz), 122.7, 121.4, 120.7, 116.6 (d, $^2J_{CF}$=23.0 Hz), 110.4, 103.8. IR (film, cm^{-1}): 1515, 1458, 1334, 1213, 1135, 838, 742.

*4.2.12. N-(3-Nitrophenyl)indole (**3l**).* Pale yellow solid.[5c] ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.39 (t, *J*=4.0 Hz, 1H), 8.19 (d, *J*=8.0 Hz, 1H), 7.87 (d, *J*=8.0 Hz, 1H), 7.71 (t, *J*=8.0 Hz, 2H), 7.59 (d, *J*=8.0 Hz, 1H), 7.37 (d, *J*=3.2 Hz, 1H), 7.29 (t, *J*=7.4 Hz, 1H), 7.23 (t, *J*=7.6 Hz, 1H), 6.76 (d, *J*=3.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=149.1, 140.9, 135.4, 130.6, 129.7, 129.6, 127.3, 123.3, 121.6, 121.3, 120.8, 118.7, 110.1, 105.4. IR (KBr, cm^{-1}): 1638, 1618, 1537, 1348, 1068, 984, 864, 728.

*4.2.13. N-(4-Nitrophenyl)indole (**3m**).* Pale yellow solid.[5d] ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.40 (d, *J*=8.8 Hz, 2H), 7.72–7.64 (m, 4H), 7.38 (d, *J*=2.8 Hz, 1H), 7.32–7.24 (m, 2H), 6.78 (d, *J*=2.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=145.3, 145.1, 135.3, 130.1, 127.1, 125.6, 123.4, 123.3, 121.7, 121.6, 110.5, 106.2. IR (KBr, cm^{-1}): 1641, 1594, 1566, 1505, 1456, 1326, 1137, 1069, 953, 854.

*4.2.14. N-(4-Acetylphenyl)indole (**3n**).* White solid.[5d] ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.09 (d, *J*=8.4 Hz, 2H), 7.69 (d, *J*=7.6 Hz, 1H), 7.64 (d, *J*=8.0 Hz, 1H), 7.58 (d, *J*=8.4 Hz, 2H), 7.36 (d, *J*=1.6 Hz, 1H), 7.26 (t, *J*=7.2 Hz, 1H), 7.20 (t, *J*=7.2 Hz, 1H), 6.72 (s, 1H), 2.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=197.0, 143.8, 135.4, 134.5, 130.1, 129.9, 127.4, 123.3, 123.0, 121.5, 121.1, 110.6, 105.1, 26.7. IR (KBr, cm^{-1}): 1673, 1600, 1516, 1458, 1357, 1163, 1075, 952, 860, 732.

*4.2.15. N-(4-Cyanophenyl)indole (**3o**).* White solid.[23] ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.73 (d, *J*=8.4 Hz, 2H), 7.67 (d, *J*=7.6 Hz, 1H), 7.58–7.54 (m, 3H), 7.29 (d, *J*=3.6 Hz, 1H), 7.25 (t, *J*=7.6 Hz, 1H), 7.20 (d, *J*=7.2 Hz, 1H), 6.72 (d, *J*=3.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=143.6, 135.3, 133.8, 130.0, 127.1, 123.9, 123.3, 121.7, 121.4, 118.5,

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110.4, 109.4, 105.8. IR (KBr, cm^{-1}): 2221, 1604, 1512, 1456, 1134, 1068, 953, 839, 732.

*4.2.16. N-(2-Thienyl)indole (**3p**).* Colorless oil.[22] ^1H NMR (400 MHz, $CDCl_3$): δ=7.64 (d, J=8.0 Hz, 1H), 7.57 (d, J=8.4 Hz, 1H), 7.26–7.10 (m, 4H), 7.04–6.98 (m, 2H), 6.63 (d, J=2.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=141.6, 137.0, 129.2, 128.9, 126.0, 122.8, 121.5, 121.0, 120.8, 120.3, 110.6, 104.1. IR (film, cm^{-1}): 1611, 1551, 1460, 1312, 1227, 1202, 841, 742.

*4.2.17. N-(3-Pyridinyl)indole (**3q**).* Colorless oil.[5d] ^1H NMR (400 MHz, $CDCl_3$): δ=8.80 (s, 1H), 8.56 (d, J=4.0 Hz, 1H), 7.76 (d, J=7.2 Hz, 1H), 7.68 (d, J=7.2 Hz, 1H), 7.49 (d, J=8.0 Hz, 1H), 7.40–7.37 (m, 1H), 7.27 (d, J=3.2 Hz, 1H), 7.25–7.16 (m, 2H), 6.70 (d, J=2.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=147.4, 145.5, 136.3, 135.6, 131.2, 129.4, 127.3, 124.0, 122.8, 121.3, 120.8, 109.9, 104.7. IR (film, cm^{-1}): 1722, 1584, 1518, 1487, 1456, 1334, 1214, 809, 742.

*4.2.18. N-(1-Naphthyl)indole (**3r**).* White solid.[24] ^1H NMR (400 MHz, $CDCl_3$): δ=7.93 (d, J=7.6 Hz, 2H), 7.74 (d, J=7.6 Hz, 1H), 7.56–7.43 (m, 3H), 7.37 (d, J=8.0 Hz, 1H), 7.34–7.32 (m, 2H), 7.18–7.09 (m, 2H), 7.02 (d, J=8.0 Hz, 1H), 6.75 (d, J=2.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=137.9, 136.0, 134.4, 130.5, 129.7, 128.4, 128.2, 126.9, 126.6, 125.4, 125.1, 123.3, 122.1, 120.9, 120.1, 110.8, 102.9. IR (KBr, cm^{-1}): 1640, 1594, 1567, 1454, 1404, 1141, 1071, 954, 778.

*4.2.19. N-(4-Chlorophenyl)-2-methylindole (**3s**).* White solid. ^1H NMR (400 MHz, $CDCl_3$): δ=7.58 (d, J=8.4 Hz, 1H), 7.49 (d, J=8.8 Hz, 2H), 7.27 (d, J=8.8 Hz, 2H), 7.14–7.06 (m, 3H), 6.41 (s, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=138.1, 136.8, 136.6, 133.5, 129.8, 129.3, 128.3, 121.4, 120.4, 119.8, 109.9, 101.8, 13.4. IR (KBr, cm^{-1}): 2919, 1593, 1557, 1493, 1458, 1322, 1088, 1013, 823, 738. Anal. Calcd for $C_{15}H_{12}NCl$: C, 74.52; H, 5.00; N, 5.79. Found: C, 74.31; H, 5.11; N, 5.58.

*4.2.20. 2-Methyl-N-(3-pyridinyl)indole (**3t**).* White solid. ^1H NMR (400 MHz, $CDCl_3$): δ=8.67–8.65 (m, 2H), 7.67–7.64 (m, 1H), 7.56 (d, J=8.4 Hz, 1H), 7.46–7.42 (m, 1H), 7.13–7.05 (m, 3H), 6.43 (s, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=149.1, 148.7, 138.1, 136.6, 135.2, 134.6, 128.4, 124.0, 121.6, 120.6, 119.8, 109.5, 102.4, 13.3. IR (KBr, cm^{-1}): 2920, 1610, 1585, 1557, 1483, 1458, 1425, 1318, 781, 747. Anal. Calcd for $C_{14}H_{11}N_2$: C, 80.75; H, 5.81; N, 13.45. Found: C, 80.81; H, 5.64; N, 13.32.

*4.2.21. N-(4-Chlorophenyl)-5-methylindole (**3u**).* White solid. ^1H NMR (400 MHz, $CDCl_3$): δ=7.45–7.36 (m, 6H), 7.21 (d, J=3.2 Hz, 1H), 7.04 (d, J=8.4 Hz, 1H), 6.58 (d, J=3.2 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=138.6, 134.1, 131.7, 130.0, 129.8, 129.7, 127.7, 125.3, 124.3, 121.0, 110.0, 103.7, 21.4. IR (KBr, cm^{-1}): IR (film, cm^{-1}): 2919, 1596, 1497, 1333, 1221, 1091, 834, 794, 717. Anal. Calcd for $C_{15}H_{12}NCl$: C, 74.52; H, 5.00; N, 5.79. Found: C, 74.28; H, 4.77; N, 5.54.

*4.2.22. 5-Methyl-N-(3-pyridinyl)indole (**3v**).* White solid. ^1H NMR (400 MHz, $CDCl_3$): δ=8.80 (s, 1H), 8.56 (d, J=4.0 Hz, 1H), 7.77 (d, J=8.0 Hz, 1H), 7.46 (s, 1H), 7.41–7.38 (m, 2H), 7.25 (d, J=2.8 Hz, 1H), 7.06 (d, J=8.4 Hz, 1H), 6.63 (d, J=2.8 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=147.3, 145.4, 136.6, 134.1, 131.1, 130.3, 129.9, 127.4, 124.5, 124.1, 121.1, 109.8, 104.5, 21.4. IR (KBr, cm^{-1}): 2919, 1585, 1490, 1429, 1222, 1159, 909, 794, 711. Anal. Calcd for $C_{14}H_{12}N_2$: C, 80.75; H, 5.81; N, 13.45. Found: C, 80.49; H, 5.59; N, 13.21.

*4.2.23. N-(4-Chlorophenyl)indole-5-carboxaldehyde (**3w**).* White solid. ^1H NMR (400 MHz, $CDCl_3$): δ=10.1 (s, 1H), 8.22 (d, J=0.8 Hz, 1H), 7.82–7.79 (m, 1H), 7.57–7.53 (m, 3H), 7.45 (d, J=8.8 Hz, 2H), 7.39 (d, J=3.6 Hz, 1H), 6.85 (d, J=2.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=192.2, 139.1, 137.5, 133.1, 130.3, 130.1, 129.8, 129.1, 126.4, 125.9, 122.9, 110.9, 105.6. IR (KBr, cm^{-1}): 1683, 1640, 1607, 1564, 1492, 1137, 1069, 954, 864. Anal. Calcd for $C_{15}H_{10}NOCl$: C, 70.45; H, 3.94; N, 5.47. Found: C, 70.21; H, 4.07; N, 5.22.

*4.2.24. N-(3-Pyridinyl)indole-5-carboxaldehyde (**3x**).* White solid. ^1H NMR (400 MHz, $CDCl_3$): δ=10.1 (s, 1H), 8.85 (s, 1H), 8.70 (d, J=4.0 Hz, 1H), 8.24 (s, 1H), 7.88–7.81 (m, 2H), 7.58–7.52 (m, 2H), 7.43 (d, J=3.6 Hz, 1H), 6.90 (d, J=3.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=192.1, 148.5, 146.0, 139.1, 135.7, 131.9, 130.5, 129.5, 129.3, 126.4, 124.3, 123.3, 110.6, 106.3. IR (KBr, cm^{-1}): 1681, 1640, 1564, 1417, 1259, 1122, 1069, 954, 864. Anal. Calcd for $C_{14}H_{10}N_2O$: C, 75.67; H, 4.54; N, 12.60. Found: C, 75.39; H, 4.61, N, 12.42.

*4.2.25. N-(4-Biphenyl)indole (**3y**).* White solid.[22] ^1H NMR (400 MHz, $CDCl_3$): δ=7.74–7.69 (m, 3H), 7.65–7.56 (m, 5H), 7.48 (t, J=7.6 Hz, 2H), 7.41–7.37 (m, 2H), 7.25–7.18 (m, 2H), 6.70 (d, J=3.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=139.8, 138.9, 138.5, 135.4, 128.9, 128.5, 127.8, 127.4, 127.1, 126.6, 124.1, 122.0, 120.7, 120.0, 110.1, 103.3. IR (KBr, cm^{-1}): 1642, 1567, 1486, 1458, 1135, 1070, 954, 862, 753.

Acknowledgements

We thank the National Natural Science Foundation of China (no. 21272044) and Key Laboratory of Functional Small Organic Molecule, Ministry of Education (no. KLFS-KF-201213) for financial support.

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Please cite this article in press as: Xiao, R.; et al., Tetrahedron (2013), http://dx.doi.org/10.1016/j.tet.2013.04.106