Heterogeneous gold(III)-catalysed double hydroamination of 2-alkynylanilines with terminal alkynes leading to *N*-vinylindoles

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Heterogeneous double hydroamination of 2-alkynylanilines with terminal alkynes was achieved by using a magnetic nanoparticles-supported gold(III)-2,2′-bipyridine complex and silver trifluoromethanesulfonate as catalysts to afford the corresponding *N*-vinylindoles in moderate to good yields under mild and solvent-free conditions. The heterogeneous gold catalyst can easily be separated from the reaction mixture by simply applying an external magnet and can be recycled up to seven times without significant loss of activity.

Keywords: hydroamination, *N*-vinylindole, magnetic nanoparticles, gold(III)-2,2′-bipyridine complex, heterogeneous catalysis

Indoles play an important role in organic synthesis and exhibit a wide range of biological and pharmacological activities.[1–5] Among the various indole derivatives, *N*-vinylindoles are important chemicals because they represent key structural motifs in numerous natural products and biologically active compounds.[6–8] In addition, *N*-vinylindole compounds are of increasing importance in materials science as monomers for preparation of poly(*N*-vinylindoles), which can be used as semiconductors and photosensitive materials.[9–12] Of the various synthetic routes to *N*-vinylindoles, the transition metal-catalysed cross-coupling reaction of indoles with prefunctionalised alkenes, such as vinyl halides[13–15] and vinyl trifluoromethanesulfonates,[16] is one of the most efficient approaches. Palladium-catalysed oxidative cross-coupling of *N*-tosylhydrazones with indoles has proven to be an alternative method for the synthesis of *N*-vinylindoles.[17] Recently, the Verma[18–20] and Wacharasindhu[21] groups have reported base-mediated or copper-catalysed intermolecular hydroaminations of alkynes with indoles leading to *N*-vinylindoles. Also, acid-promoted condensation of alkyl or aryl α-branched aldehydes with indole derivatives can produce *N*-vinylindoles.[22] Despite significant progress made in the preparation of *N*-vinylindoles, the narrow scope of substrates, high cost and harsh reaction conditions make these protocols of limited synthetic utility. Considering the importance of *N*-vinylindoles and the drawbacks of the existing methods, the development of a more efficient and practical approach to construct *N*-vinylindoles is highly desirable.

Homogeneous catalysis of organic reactions by gold complexes has become a highly efficient and powerful tool for the synthesis of valuable building blocks.[23–27] Recently, gold-catalysed construction of *N*-heterocyclic compounds such as pyrroles,[28–30] indoles[31–33] and oxazoles[34–36] has attracted great interest due to their high efficiency and mild reaction conditions, which greatly enriched the synthetic methods for *N*-heterocycles. However, applications of these homogeneous gold complexes in large-scale synthesis or multistep syntheses remain a challenge because they are expensive, not recyclable and difficult to separate from the product mixture. Recycling of homogeneous precious metal catalysts is a task of great economic and environmental importance in the chemical and pharmaceutical industries. The heterogenisation of the existing homogeneous catalysts appears to be a logical solution to this problem.[37] Moreover, heterogeneous catalysis can reduce waste derived from reaction workup, contributing to the development of green and sustainable chemical processes.[38] However, to the best of our knowledge, no examples of heterogeneous gold complex-catalysed construction of indoles have been described until now, despite the practical benefits of heterogeneous catalysis.

To solve the problems of catalyst recovery and recycling, magnetic nanoparticles-supported catalysts are a good choice because their magnetic separation is an alternative to filtration or centrifugation and it prevents loss of catalyst and improves the reusability.[39–41] Recently, we reported the synthesis of a magnetic nanoparticles-supported gold(III)-bipy (bipy = 2,2′-bipyridine) complex (Fe_3O_4@SiO_2-bipy-$AuCl_3$) and its successful application to the oxidative α-cyanation of tertiary amines.[42] To expand applications of this heterogeneous gold(III) catalyst, we report here a double hydroamination reaction of *o*-alkynylanilines with terminal alkynes catalysed by Fe_3O_4@SiO_2-bipy-$AuCl_3$ leading to *N*-vinylindoles in moderate to good yields. The heterogeneous gold(III) catalyst can be easily separated from the reaction mixture by simply applying an external magnet and its catalytic efficiency remains unaltered even after recycling seven times.

Results and discussion

The magnetic nanoparticles-supported gold(III)-bipy complex (Fe_3O_4@SiO_2-bipy-$AuCl_3$) was prepared by a simple two-step procedure as shown in Scheme 1.[42] Firstly, the silica-coated Fe_3O_4 (Fe_3O_4@SiO_2)[43] was reacted with 4,4′-bis[3-(triethoxysilyl)-propylaminomethyl]-2,2′-bipyridine (BTESBPY)[44] in toluene under reflux for 24 h to generate the bipyridine-functionalised magnetic nanoparticles (Fe_3O_4@SiO_2-bipy). The latter were treated with $AuCl_3$ in methanol at 65 ºC for 24 h to give the magnetic nanoparticles-supported gold(III)-bipy complex (Fe_3O_4@SiO_2-bipy-$AuCl_3$) as brown nanoparticles. The gold content was determined to be 0.62 mmol g^{-1} by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

The magnetic nanoparticles-supported gold(III)-bipy complex (Fe_3O_4@SiO_2-bipy-$AuCl_3$) was then used as the catalyst for the double hydroamination reaction of *o*-alkynylanilines with terminal alkynes. In our initial screening, the double hydroamination of 2-(phenylethynyl)aniline (**1a**) with phenylacetylene (**2a**) under neat conditions was selected as the model reaction to optimise the reaction conditions and the results are summarised in Table 1. When $AuCl_3$ was used as the catalyst, the reaction at 60 ºC gave the desired product **3a** in 69% yield (Table 1, entry 1). Various silver salts such as AgOTf (silver trifluoromethanesulfonate), $AgSbF_6$ and $AgBF_4$ could also catalyse this transformation, but the yield of **3a** was moderate (Table 1, entries 2–4). However, a combination of $AuCl_3$ (5 mol%) and AgOTf (15 mol%) proved to be more efficient and afforded an 83% yield at room temperature (Table 1, entry 5). We next examined the catalytic efficiency

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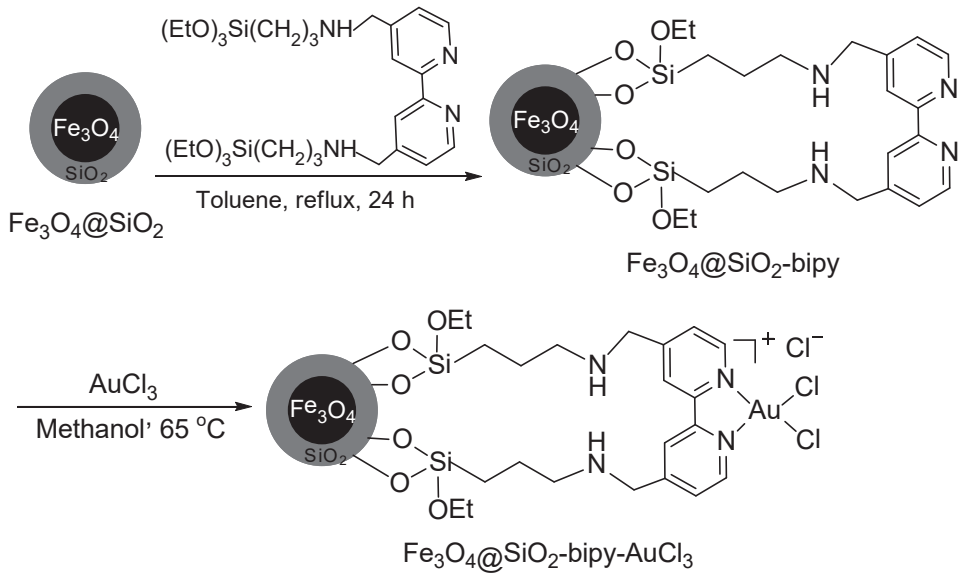
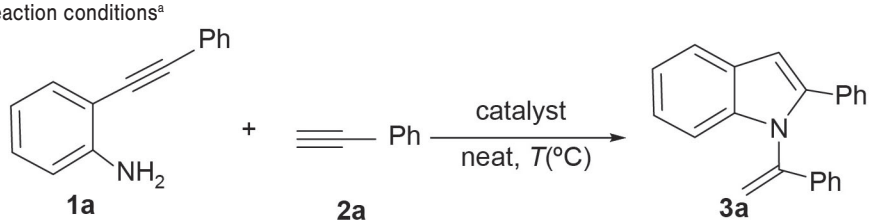


Scheme 1

Table 1 Optimisation of reaction conditions[a]



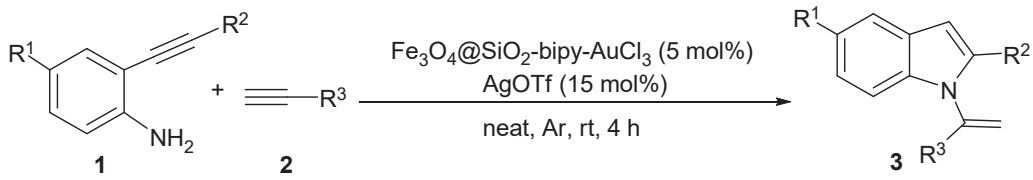
Entry	Catalyst (%)	T (°C)	Time (h)	Yield (%)[b]
1	$AuCl_3$ (5)	60	2	69
2	AgOTf (5)	60	2	58
3	$AgSbF_6$ (5)	60	2	51
4	$AgBF_4$ (5)	60	2	55
5	$AuCl_3$ (5)/AgOTf (15)	r.t.	2	83
6	Fe_3O_4@SiO_2-bipy-$AuCl_3$ (5)	60	2	65
7	Fe_3O_4@SiO_2-bipy-$AuCl_3$ (5)/AgOTf (15)	r.t.	4	81
8	Fe_3O_4@SiO_2-bipy-$AuCl_3$ (5)/$AgSbF_6$ (15)	r.t.	4	71
9	Fe_3O_4@SiO_2-bipy-$AuCl_3$ (5)/$AgBF_4$ (15)	r.t.	4	75
10	Fe_3O_4@SiO_2-bipy-$AuCl_3$ (5)/AgOTf (15)	60	2	78
11	Fe_3O_4@SiO_2-bipy-$AuCl_3$ (2.5)/AgOTf (7.5)	r.t.	10	76

[a]All reactions were performed using **1a** (0.2 mmol), **2a** (0.4 mmol) under Ar.
[b]Isolated yield.

of Fe_3O_4@SiO_2-bipy-$AuCl_3$ in this reaction. The use of Fe_3O_4@SiO_2-bipy-$AuCl_3$ alone at 60 ºC gave the desired **3a** in only 65% yield (Table 1, entry 6). To our delight, use of various silver salts as co-catalysts allowed the reaction to proceed smoothly at room temperature to give **3a** in 71–81% yields (Table 1, entries 7–9). AgOTf was found to be most efficient. When Fe_3O_4@SiO_2-bipy-$AuCl_3$ (5 mol%) and AgOTf (15 mol%) were used as catalysts, the reaction at 60 ºC afforded a slightly lower yield (Table 1, entry 10). Reducing the amount of the catalysts resulted in a lower yield and a longer reaction time was required (Table 1, entry 11). Therefore, the optimised reaction conditions for this transformation are Fe_3O_4@SiO_2-bipy-$AuCl_3$ (5 mol%) and AgOTf (15 mol%) at room temperature under Ar for 4 h (Table 1, entry 7).

Subsequently, we investigated the scope of this heterogeneous gold(III)-catalysed double hydroamination reaction by using various 2-alkynylanilines and a range of terminal alkynes as the substrates and the results are summarised in Table 2. The double hydroamination reactions of both electron-rich and electron-deficient arylacetylenes **2b–f** with 2-(phenylethynyl) aniline (**1a**) proceeded smoothly under the optimised conditions to afford the corresponding *N*-vinylindoles **3b–f** in good yields (Table 2, entries 2–6). Aliphatic alkynes appeared less reactive. For instance, the reaction of cyclopropylacetylene (**2g**) with **1a** gave the desired product **3g** in only 43% yield (Table 2, entry 7). On the other hand, the reactivity of alkyl-substituted acetylenic anilines was lower than that of phenyl-substituted acetylenic anilines. Reactions of alkyl-substituted acetylenic anilines **1b–d** with arylacetylenes provided the desired *N*-vinylindoles **3h–k** in moderate yields (Table 2, entries 8–11). 2-(4-Chlorophenylethynyl)aniline (**1e**) was also a suitable substrate and the reactions with arylacetylenes produced the expected products **3l** and **3m** in good yields (Table 2, entries 12 and 13). In addition, halo-substituted 2-(phenylethynyl) anilines **1f–h** also proved to be good substrates and showed a similar reactivity to 2-(phenylethynyl)aniline (**1a**). For

Table 2 Heterogeneous Au(III)-catalysed double hydroamination of 2-alkynylanilines with terminal alkynes[a]



Entry	R^1	R^2	R^3	Product	Yield (%)[b]
1	H	Ph	Ph	**3a**	81
2	H	Ph	4-MeC_6H_4	**3b**	78
3	H	Ph	4-$MeOC_6H_4$	**3c**	70
4	H	Ph	4-ClC_6H_4	**3d**	75
5	H	Ph	4-FC_6H_4	**3e**	69
6	H	Ph	2-ClC_6H_4	**3f**	66
7	H	Ph	Cyclopropyl	**3g**	43
8	H	*n*-Bu	Ph	**3h**	51
9	H	Cyclohexyl	Ph	**3i**	42
10	H	Cyclopropyl	Ph	**3j**	44
11	H	Cyclopropyl	4-ClC_6H_4	**3k**	41
12	H	4-ClC_6H_4	Ph	**3l**	68
13	H	4-ClC_6H_4	4-ClC_6H_4	**3m**	66
14	Cl	Ph	Ph	**3n**	75
15	Cl	Ph	4-MeC_6H_4	**3o**	74
16	Cl	Ph	4-$MeOC_6H_4$	**3p**	71
17	Br	Ph	Ph	**3q**	73
18	Br	Ph	4-ClC_6H_4	**3r**	70
19	Br	Ph	4-MeC_6H_4	**3s**	72
20	Br	Ph	1-Naphthyl	**3t**	65
21	F	Ph	Ph	**3u**	67
22	Me	4-ClC_6H_4	Ph	**3v**	65
23	Me	4-ClC_6H_4	4-MeC_6H_4	**3w**	63

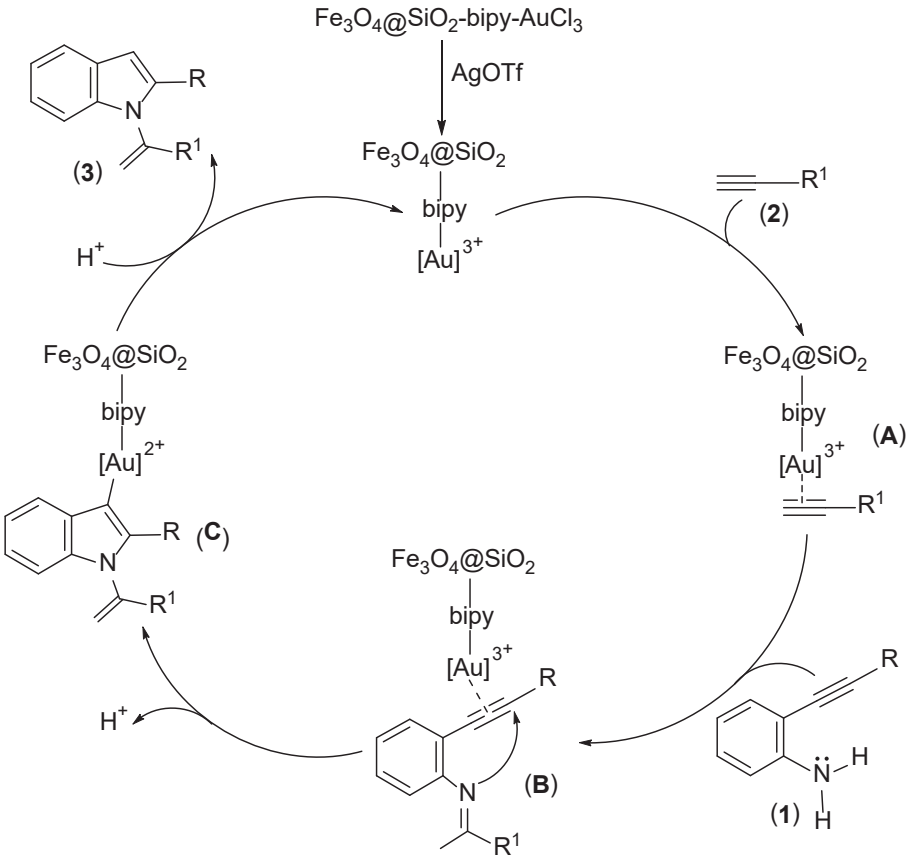
[a]Reaction conditions: **1** (0.2 mmol), **2** (0.4 mmol), Fe_3O_4@SiO_2-bipy-$AuCl_3$ (5 mol%), AgOTf (15 mol%), room temperature under Ar for 4 h.
[b]Isolated yield.

example, 4-chloro-2-(phenylethynyl)aniline (**1f**), 4-bromo-2-(phenylethynyl)aniline (**1g**) and 4-fluoro-2-(phenylethynyl) aniline (**1h**) could undergo the double hydroamination with various arylacetylenes effectively to furnish the corresponding 5-halo-substituted *N*-vinylindoles **3n–s** and **3u** in 67–75% yields (Table 2, entries 14–19 and 21). Interestingly, the reaction of 4-bromo-2-(phenylethynyl)aniline (**1g**) with bulky 1-ethynylnaphthalene (**2h**) also gave the desired product **3t** in 65% yield (Table 2, entry 20). It is noteworthy that 4-methyl-2-(4-chlorophenylethynyl)aniline (**1i**) was also a suitable substrate and afforded the expected products **3v** and **3w** in good yields (Table 2, entries 22 and 23).

A possible mechanism for this heterogeneous gold(III)-catalysed double hydroamination reaction of 2-alkynylanilines **1** with terminal alkynes **2** is outlined in Scheme 2.[31] Firstly, coordination of the Fe_3O_4@SiO_2-bipy-Au$(OTf)_3$ complex generated *in situ* from Fe_3O_4@SiO_2-bipy-$AuCl_3$ and AgOTf to the carbon–carbon triple bond in terminal alkyne **2** affords a magnetic nanoparticles-bound bipy-Au(III) alkyne complex **A**. Intermediate **A** further reacts with 2-alkynylaniline **1** to give the first hydroamination product, which is followed by coordination of Fe_3O_4@SiO_2-bipy-Au$(OTf)_3$ to the alkyne moiety in the product again to generate intermediate **B**. Intermediate **B** undergoes an intramolecular nucleophilic addition of the imine nitrogen to the carbon–carbon triple bond to form intermediate **C**. Finally, the C-3 position of indole in intermediate **C** is protonated to afford the desired product **3** and regenerate the Fe_3O_4@SiO_2-bipy-Au$(OTf)_3$ complex.

For the practical application of a heterogeneous precious metal catalyst, its stability and reusability are important factors. We next investigated the recycling of the Fe_3O_4@SiO_2-bipy-$AuCl_3$ complex by using the double hydroamination of 2-(phenylethynyl)aniline (**1a**) with phenylacetylene (**2a**) as a model reaction. After the reaction was completed, the reaction mixture was diluted with EtOAc and more than 99% of the gold catalyst could be recovered by simply fixing a magnet near to the reaction vessel. The recovered catalyst was washed with MeOH, air-dried and used directly in the next run without further purification. The recovered gold catalyst was used for seven further consecutive cycles using fresh substrates under identical conditions and the results are presented in Fig. 1. As shown in Fig. 1, the yield of the desired product **3a** in all cases was found to be closely similar, which confirmed that the developed heterogeneous gold(III) catalyst can be recycled efficiently for at least seven times without significant loss of activity. It is noteworthy that the reaction catalysed by the recovered catalyst did not need the addition of AgOTf because Fe_3O_4@SiO_2-bipy-$AuCl_3$ had been changed to Fe_3O_4@SiO_2-bipy-Au$(OTf)_3$ after the first cycle. The excellent reusability of the catalyst may result from the chelating action of the bidentate bipyridine ligand on gold and the magnetic separation. The result is important from industrial and environmental points of view.

In conclusion, we have developed a novel, efficient and practical method for the synthesis of *N*-vinylindoles through



Scheme 2

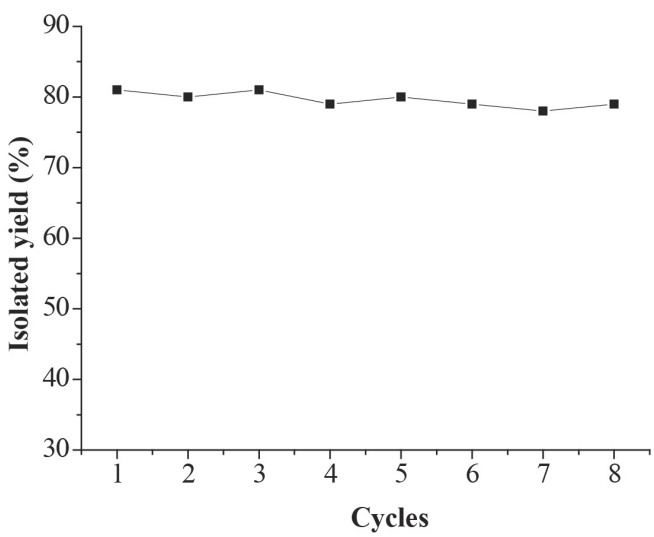


Fig. 1 Recycling of the Fe_3O_4@SiO_2-bipy-$AuCl_3$ catalyst.

the double hydroamination reaction of 2-alkynylanilines with terminal alkynes by using a magnetic nanoparticles-supported gold(III)-bipy complex (Fe_3O_4@SiO_2-bipy-$AuCl_3$) and AgOTf as catalysts. The reactions generated a variety of *N*-vinylindole derivatives in moderate to good yields under mild and solvent-free conditions. Importantly, this heterogeneous gold catalyst can be recovered by simply applying an external magnet and recycled up to seven times without significant loss of activity. The Fe_3O_4@SiO_2-bipy-$AuCl_3$ catalyst not only solves the basic problems of catalyst separation and recovery but also avoids the use of AgOTf in the recycling process. This makes our protocol facile, economical and environmentally benign.

Experimental

All reagents were used as received without further purification. 2-Alkynylanilines **1a–i** were prepared by palladium/copper-catalysed Sonogashira coupling reactions of 2-iodoanilines with terminal alkynes according to a literature method.[31] The Fe_3O_4@SiO_2-bipy-$AuCl_3$ complex was prepared according to our previous procedure.[42] The gold content was determined to be 0.62 mmol g^{-1}. All reactions were carried out under Ar in oven-dried glassware with magnetic stirring. ^{1}H NMR spectra were recorded on a Bruker Avance 400 (at 400 MHz) spectrometer with TMS as an internal standard using $CDCl_3$ as the solvent. ^{13}C NMR spectra were recorded on a Bruker Avance 400 (at 100 MHz) spectrometer using $CDCl_3$ as the solvent. HRMS spectra were recorded on a quadrupole-time of flight Bruker MicroTOF-Q II mass spectrometer equipped with an ESI and APCI source. Gold content was determined using ICP-AES on an Atomscan16 instrument (TJA Corporation).

*Synthesis of 2-phenyl-1-(1-phenylvinyl)-1*H*-indole (**3a**); general procedure*

Fe_3O_4@SiO_2-bipy-$AuCl_3$ (16 mg, 0.01 mmol) and AgOTf (8 mg, 0.03 mmol) were added to a mixture of 2-(phenylethynyl)aniline (0.2 mmol) and phenylacetylene (0.4 mmol) under Ar at room temperature. The reaction mixture was stirred at room temperature. During this procedure the reaction mixture became a deep black liquid very quickly. After 4 h the resulting mixture was diluted with ethyl acetate and the supported catalyst was magnetically separated. The reaction solution was evaporated and the residue was purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 25:1) to give the desired product **3a**. The recovered catalyst was washed with MeOH (2 × 2 mL) and air-dried. When appropriate it could be used directly for the next run.

*2-Phenyl-1-(1-phenylvinyl)-1*H*-indole* (**3a**):[31] Oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 7.2 Hz, 2H), 7.28–7.20 (m, 6H), 7.19–7.11 (m, 5H), 6.77 (s, 1H), 5.89 (s, 1H), 5.25 (s,

1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.6, 141.3, 139.1, 137.3, 132.8, 128.8, 128.6, 128.4, 128.3, 128.1, 127.5, 125.9, 122.3, 120.7, 120.5, 113.8, 111.5, 103.7.

*2-Phenyl-1-(1-*p*-tolylvinyl)-1*H*-indole* (**3b**):[31] Oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68–7.62 (m, 1H), 7.51–7.46 (m, 2H), 7.28–7.18 (m, 3H), 7.18–7.06 (m, 5H), 7.04 (d, *J* = 8.2 Hz, 2H), 6.77 (s, 1H), 5.84 (s, 1H), 5.16 (s, 1H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5, 141.3, 139.1, 138.8, 134.4, 132.8, 129.3, 128.9, 128.4, 128.1, 127.4, 125.8, 122.2, 120.5, 120.4, 113.0, 111.6, 103.6, 21.2.

*1-[1-(4-Methoxyphenyl)vinyl]-2-phenyl-1*H*-indole* (**3c**):[31] Oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 7.0 Hz, 1H), 7.51–7.46 (m, 2H), 7.28–7.21 (m, 3H), 7.16–7.10 (m, 5H), 6.76 (d, *J* = 8.4 Hz, 2H), 6.74 (s, 1H), 5.78 (s, 1H), 5.13 (s, 1H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 143.1, 141.3, 139.1, 132.8, 130.9, 128.9, 128.3, 128.1, 127.4, 127.3, 122.2, 120.5, 120.4, 114.0, 111.9, 111.5, 103.5, 55.2.

*1-[1-(4-Chlorophenyl)vinyl]-2-phenyl-1*H*-indole* (**3d**): Oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 6.8 Hz, 1H), 7.45 (d, *J* = 6.8 Hz, 2H), 7.27–7.23 (m, 3H), 7.19–7.12 (m, 5H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.77 (s, 1H), 5.89 (s, 1H), 5.31 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.7, 141.2, 139.0, 135.8, 134.7, 132.6, 128.8, 128.4, 128.3, 128.2, 127.6, 127.2, 122.4, 120.8, 120.6, 114.2, 111.3, 103.9; HRMS calcd for $C_{22}H_{16}{}^{35}ClN^+$: [M$^+$]: 329.0971; found: 329.0980.

*1-[1-(4-Fluorophenyl)vinyl]-2-phenyl-1*H*-indole* (**3e**):[31] Oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 7.4 Hz, 1H), 7.46 (d, *J* = 7.8 Hz, 2H), 7.28–7.24 (m, 3H), 7.19–7.15 (m, 3H), 7.12–7.06 (m, 2H), 6.88 (t, *J* = 8.0 Hz, 2H), 6.76 (s, 1H), 5.84 (s, 1H), 5.29 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.0 (d, $^1J_{C–F}$ = 247.4 Hz), 142.8, 141.2, 139.0, 133.5 (d, $^4J_{C–F}$ = 2.9 Hz), 132.7, 130.9, 128.3, 128.1, 127.7 (d, $^3J_{C–F}$ = 8.3 Hz), 127.5, 122.3, 120.8, 120.6, 115.5 (d, $^2J_{C–F}$ = 21.7 Hz), 113.4, 111.3, 103.8.

*1-[1-(2-Chlorophenyl)vinyl]-2-phenyl-1*H*-indole* (**3f**): Oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66–7.64 (m, 1H), 7.44–7.40 (m, 3H), 7.25–7.17 (m, 6H), 7.05–7.00 (m, 1H), 6.96–6.92 (m, 1H), 6.75–6.72 (m, 1H), 6.67 (s, 1H), 5.91 (s, 1H), 5.74 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.7, 140.4, 139.0, 136.1, 133.0, 132.2, 130.3, 129.2, 128.6, 128.5, 128.0, 127.4, 126.5, 122.4, 120.8, 120.6, 117.1, 111.2, 104.2; HRMS calcd for $C_{22}H_{16}{}^{35}ClN^+$: [M$^+$]: 329.0971; found: 329.0965.

*1-(1-Cyclopropylvinyl)-2-phenyl-1*H*-indole* (**3g**): Oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 7.8 Hz, 2H), 7.61 (d, *J* = 7.4 Hz, 1H), 7.43–7.38 (m, 3H), 7.34 (d, *J* = 7.2 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.13 (t, *J* = 7.4 Hz, 1H), 6.69 (s, 1H), 5.33 (s, 1H), 5.24 (s, 1H), 1.34–1.28 (m, 1H), 0.54–0.52 (m, 2H), 0.41–0.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.0, 140.1, 138.8, 133.5, 132.2, 128.5, 128.3, 128.2, 127.6, 122.1, 120.3, 111.0, 110.9, 103.1, 16.4, 7.8; HRMS calcd for $C_{19}H_{17}N^+$: [M$^+$]: 259.1361; found: 259.1357.

*2-Butyl-1-(1-phenylvinyl)-1*H*-indole* (**3h**):[31] Oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 7.6 Hz, 1H), 7.31–7.27 (m, 3H), 7.16–7.10 (m, 3H), 7.07 (t, *J* = 7.4 Hz, 2H), 6.39 (s, 1H), 6.06 (s, 1H), 5.42 (s, 1H), 2.51 (t, *J* = 7.4 Hz, 2H), 1.63–1.58 (m, 2H), 1.34–1.28 (m, 2H), 0.84 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.0, 141.9, 138.0, 137.1, 128.9, 128.7, 128.2, 125.7, 121.0, 119.9, 119.6, 113.7, 110.5, 100.4, 30.71, 26.7, 22.3, 13.8.

*2-Cyclohexyl-1-(1-phenylvinyl)-1*H*-indole* (**3i**): Oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.4 Hz, 1H), 7.34 (d, *J* = 7.4 Hz, 1H), 7.29–7.23 (m, 3H), 7.12 (d, *J* = 6.8 Hz, 2H), 7.06 (t, *J* = 7.4 Hz, 2H), 6.42 (s, 1H), 6.09 (s, 1H), 5.45 (s, 1H), 2.97–2.77 (m, 1H), 1.98–1.41 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.6, 143.2, 138.0, 137.1, 128.9, 128.7, 128.5, 125.6, 121.1, 119.9, 119.7, 114.1, 110.4, 98.1, 37.5, 33.6, 29.7, 25.3; HRMS calcd for $C_{22}H_{23}N^+$: [M$^+$]: 301.1830; found: 301.1819.

*2-Cyclopropyl-1-(1-phenylvinyl)-1*H*-indole* (**3j**):[45] Oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54–7.52 (m, 1H), 7.31–7.27 (m, 3H), 7.19–7.16 (m, 2H), 7.15–7.12 (m, 1H), 7.09–7.03 (m, 2H), 6.19 (s, 1H), 6.05 (s, 1H), 5.49 (s, 1H), 1.67–1.60 (m, 1H), 0.79–0.71 (m, 2H), 0.70–0.63 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.0, 143.2, 138.1, 137.4, 128.8, 128.6, 128.0, 125.9, 121.1, 120.0, 119.7, 113.6, 110.4, 97.7, 8.2, 7.8.

*1-[1-(4-Chlorophenyl)vinyl]-2-cyclopropyl-1*H*-indole* (**3k**): Oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54–7.52 (m, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.12–7.09 (m, 2H), 7.08–7.05 (m, 3H), 6.19 (s, 1H), 6.04 (s, 1H), 5.50 (s, 1H), 1.64–1.60 (m, 1H), 0.79–0.74 (m, 2H), 0.70–0.62 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.8, 142.2, 138.0, 135.9, 134.8, 128.8, 128.1, 127.2, 121.3, 120.1, 119.8, 114.1, 110.3, 98.1, 8.2, 7.8; HRMS calcd for $C_{19}H_{16}{}^{35}ClN^+$: [M$^+$]: 293.0971; found: 293.0976.

*2-(4-Chlorophenyl)-1-(1-phenylvinyl)-1*H*-indole* (**3l**): Green solid; m.p. 77–79 °C (lit.[45] 123–124 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 7.6 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.24–7.20 (m, 4H), 7.19–7.09 (m, 6H), 6.76 (s, 1H), 5.92 (s, 1H), 5.28 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5, 139.9, 139.2, 137.1, 133.4, 131.3, 129.5, 129.0, 128.6, 128.4, 128.2, 125.8, 122.6, 120.8, 120.6, 113.9, 111.5, 104.0.

*2-(4-Chlorophenyl)-1-[1-(4-chlorophenyl)vinyl]-1*H*-indole* (**3m**): Oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70–7.64 (m, 1H), 7.41–7.36 (m, 2H), 7.25–7.22 (m, 2H), 7.21–7.19 (m, 1H), 7.18–7.15 (m, 4H), 7.06–7.02 (m, 2H), 6.76 (s, 1H), 5.92 (s, 1H), 5.33 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.5, 139.8, 139.0, 135.5, 134.9, 133.6, 131.1, 129.4, 128.9, 128.5, 128.2, 127.1, 122.7, 121.0, 120.7, 114.4, 111.3, 104.2; HRMS calcd for $C_{22}H_{15}{}^{35}Cl_2NNa^+$: [M + Na]$^+$: 386.0479; found: 386.0468.

*5-Chloro-2-phenyl-1-(1-phenylvinyl)-1*H*-indole* (**3n**): Oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (s, 1H), 7.47–7.44 (m, 2H), 7.28–7.19 (m, 6H), 7.13–7.11 (m, 2H), 7.07–7.03 (m, 2H), 6.69 (s, 1H), 5.90 (s, 1H), 5.25 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.4, 142.6, 137.4, 136.9, 132.3, 129.3, 129.0, 128.7, 128.4, 128.2, 127.8, 126.3, 125.8, 122.5, 119.8, 114.1, 112.5, 103.1.; HRMS calcd for $C_{22}H_{16}{}^{35}ClN^+$: [M$^+$]: 329.0971; found: 329.0962.

*5-Chloro-2-phenyl-1-(1-*p*-tolylvinyl)-1*H*-indole* (**3o**): Oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (s, 1H), 7.47 (d, *J* = 6.4 Hz, 2H), 7.28–7.21 (m, 3H), 7.04–7.02 (m, 6H), 6.69 (s, 1H), 5.84 (s, 1H), 5.15 (s, 1H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.2, 142.6, 139.1, 137.4, 134.0, 132.3, 129.4, 129.3, 128.4, 128.2, 127.8, 126.2, 125.7, 122.4, 119.8, 113.3, 112.6, 103.0, 21.2; HRMS calcd for $C_{23}H_{18}{}^{35}ClN^+$: [M$^+$]: 343.1128; found: 343.1140.

*5-Chloro-1-[1-(4-methoxyphenyl)vinyl]-2-phenyl-1*H*-indole* (**3p**): Oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (s, 1H), 7.47 (d, *J* = 6.6 Hz, 2H), 7.29–7.22 (m, 3H), 7.11–7.00 (m, 4H), 6.75 (d, *J* = 8.8 Hz, 2H), 6.69 (s, 1H), 5.78 (s, 1H), 5.12 (s, 1H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 143.0, 142.6, 137.5, 132.4, 129.5, 129.3, 128.4, 128.1, 127.7, 127.2, 126.2, 122.4, 119.8, 114.1, 112.5, 112.1, 102.9, 55.2; HRMS calcd for $C_{23}H_{18}{}^{35}ClNNaO^+$: [M + Na]$^+$: 382.0975; found: 382.0973.

*5-Bromo-2-phenyl-1-(1-phenylvinyl)-1*H*-indole* (**3q**): Oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (s, 1H), 7.47–7.43 (m, 2H), 7.29–7.17 (m, 6H), 7.14–6.97 (m, 4H), 6.69 (s, 1H), 5.89 (s, 1H), 5.25 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.3, 142.4, 137.7, 136.8, 132.2, 130.0, 129.0, 128.7, 128.5, 128.2, 127.8, 125.8, 125.1, 122.9, 114.1, 113.8, 112.9, 103.0; HRMS calcd for $C_{22}H_{16}{}^{79}BrNNa^+$: [M + Na]$^+$: 396.0364; found: 396.0371.

*5-Bromo-1-[1-(4-chlorophenyl)vinyl]-2-phenyl-1*H*-indole* (**3r**): Oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (s, 1H), 7.43–7.41 (m, 2H), 7.28–7.16 (m, 6H), 7.03–7.00 (m, 3H), 6.69 (s, 1H), 5.89 (s, 1H), 5.31 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.3, 141.2, 136.5, 134.3, 133.8, 131.0, 128.9, 127.8, 127.3, 127.2, 126.9, 126.0, 124.1, 122.0, 113.5, 112.9, 111.6, 102.1; HRMS calcd for $C_{22}H_{15}{}^{79}Br^{35}ClNNa^+$: [M + Na]$^+$: 429.9974; found: 429.9971.

*5-Bromo-2-phenyl-1-(1-*p*-tolylvinyl)-1*H*-indole* (**3s**): Oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (s, 1H), 7.48–7.46 (m, 2H), 7.27–7.24 (m, 3H), 7.18–7.14 (m, 1H), 7.08–7.02 (m, 4H), 6.97 (d, *J* = 8.6 Hz, 1H), 6.70 (s, 1H), 5.85 (s, 1H), 5.16 (s, 1H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.2, 142.4, 139.1, 137.7, 134.0, 132.2, 129.9, 129.4, 128.4, 128.2, 127.8, 125.7, 125.0, 122.9, 113.8, 113.3, 113.0, 102.8, 21.2; HRMS calcd for $C_{23}H_{18}{}^{79}BrNNa^+$: [M + Na]$^+$: 410.0520; found: 410.0515.

*5-Bromo-1-[1-(naphthalen-1-yl)vinyl]-2-phenyl-1*H*-indole* (**3t**): Beige solid; m.p. 159–161 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.6 Hz, 1H), 7.77 (d, *J* = 1.6 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.40–7.37 (m, 1H), 7.35–7.30 (m, 1H), 7.29–7.24 (m, 3H), 7.24–7.20 (m, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.12–7.04 (m, 3H), 7.02–6.97 (m, 1H), 6.57 (s, 1H), 5.78 (s, 1H), 5.68 (s, 1H); ^{13}C NMR

(100 MHz, $CDCl_3$): δ 142.4, 141.7, 137.4, 135.1, 133.8, 132.5, 130.7, 130.3, 129.3, 128.6, 128.5, 127.9, 127.7, 126.8, 126.6, 125.7, 125.3, 124.9, 124.5, 123.1, 116.4, 114.0, 112.9, 103.8; HRMS calcd for $C_{26}H_{18}{}^{79}BrNNa^+$: $[M + Na]^+$: 446.0520; found: 446.0527.

*5-Fluoro-2-phenyl-1-(1-phenylvinyl)-1*H-*indole* (**3u**): Brown solid; m.p. 82–84 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, J = 6.6 Hz, 2H), 7.29–7.27 (m, 1H), 7.26–7.22 (m, 6H), 7.16–7.13 (m, 2H), 7.06–7.01 (m, 1H), 6.87–6.82 (m, 1H), 6.72 (s, 1H), 5.89 (s, 1H), 5.25 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.4 (d, $^1J_{C–F}$ = 233.9 Hz), 143.5, 142.9, 137.0, 135.6, 132.5, 128.9, 128.7, 128.6 (d, $^3J_{C–F}$ = 9.4 Hz), 128.4, 128.2, 127.7, 125.9, 114.0, 112.2 (d, $^3J_{C–F}$ = 9.5 Hz), 110.5 (d, $^2J_{C–F}$ = 25.9 Hz), 105.2 (d, $^2J_{C–F}$ = 23.4 Hz), 103.5 (d, $^4J_{C–F}$ = 4.3 Hz); HRMS calcd for $C_{22}H_{16}FN^+$: $[M^+]$: 313.1267; found 313.1276.

*2-(4-Chlorophenyl)-5-methyl-1-(1-phenylvinyl)-1*H-*indole* (**3v**): Brown solid; m.p. 136–138 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (s, 1H), 7.39 (d, J = 8.4 Hz, 2H), 7.25–7.18 (m, 5H), 7.15–7.11 (m, 2H), 7.04 (d, J = 8.4 Hz, 1H), 6.95 (d, J = 8.2 Hz, 1H), 6.68 (s, 1H), 5.89 (s, 1H), 5.24 (s, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.7, 140.0, 137.7, 137.2, 133.3, 132.5, 131.5, 130.1, 129.5, 128.9, 128.6, 128.3, 125.9, 124.1, 120.2, 113.6, 111.1, 103.6, 21.3; HRMS calcd for $C_{23}H_{18}{}^{35}ClN^+$: $[M^+]$: 343.1128; found 343.1133.

*2-(4-Chlorophenyl)-5-methyl-1-(1-*p*-tolylvinyl)-1*H-*indole* (**3w**): Beige solid; m.p. 145–147 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (s, 1H), 7.43–7.38 (m, 2H), 7.23–7.19 (m, 2H), 7.08–7.00 (m, 5H), 6.96–6.93 (m, 1H), 6.68 (s, 1H), 5.84 (s, 1H), 5.15 (s, 1H), 2.44 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.4, 140.0, 139.0, 137.7, 134.2, 133.2, 131.4, 130.1, 129.4, 128.5, 128.4, 125.8, 124.1, 120.2, 112.9, 111.3, 103.5, 21.5, 21.3; HRMS calcd for $C_{24}H_{20}{}^{35}ClNNa^+$: $[M + Na]^+$: 380.1182; found: 380.1173.

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