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PAPER

Domino cyclization–alkylation protocol for the synthesis of 2,3-functionalized indoles from *o*-alkynylanilines and allylic alcohols†

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A practical and efficient protocol for the one-pot synthesis of 2,3-substituted indoles was developed *via* a palladacycle catalyzed domino cyclization–alkylation reaction involving 2-alkynylanilines and allylic alcohols under mild conditions without any additives.

Introduction

The development of facile, economical and environmentally friendly synthetic methods targeting the generation of the indole nucleus, a common structural motif in many bioactive natural products and pharmaceuticals, has attracted continued research interest.[1] Numerous methods have also been developed for the alkylation of 2-substituted indoles to yield 2,3-disubstituted indoles – a key synthetic task in the preparation of relevant molecules incorporating the indole nuclei.[2] Recent literature reports show efforts being directed at developing methods that allow the one-pot/sequential/domino formation of 2,3-disubstituted indoles. Notable amongst these include the $PdCl_2$ catalyzed domino-cyclization-Heck of 2-ethynylphenylcarbamates in the presence of reoxidant and excess Bu_4NF,[3] a one-pot three component Sonogashira–Cacchi domino sequence involving 2-iodo-*N*-triflouroacetylanilides, alkynes and arylbromides using Pd $(OAc)_2$ and PPh_3,[4] the $PdBr_2$(BINAP)-complex catalyzed reaction of arylamines with α-diketones under reductive conditions[5] and the *N*-arylation and Fischer cyclization of *N*-tosylhydrazones with benzyne.[6]

Our aim was to develop a protocol that involves a domino catalytic sequence consisting of cyclization of unprotected *o*-alkynylanilines (readily available *via* Sonogashira-type reactions) to yield C-2 substituted indoles and their subsequent regioselective alkylation at C-3 using allylic alcohols. The development of such a one-pot reaction which allows low catalyst loading, avoids use of protecting agents (at the risk of *N*-alkylated products) and tolerates the use of benign alcohols (as opposed to conventional Lewis acids) as alkylating agents (in spite of their acidic nature and poor leaving group behavior) is highly challenging, yet desirable.

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We have recently reported the use of palladacycles **I** and **IV** (Fig. 1) as efficient promoters for P–H additions[7] and for the one-pot synthesis of 2-allylanilines from allylic alcohols respectively.[8] We herein report the results of our studies on the use of palladacycle **I** to achieve the aforementioned domino sequence towards 2,3-substituted indoles under mild conditions in one-pot without the need for any additive or protecting agent.

Results and discussion

Transition metal catalyzed cyclization of 2-alkynylaniline derivatives to 2-substituted indoles is an efficient approach for the synthesis of indoles.[9] Unfortunately, only a few such methods can deal with unprotected primary 2-alkynylaniline.[10] With the palladacycle **I** in hand, we attempted the cyclization of unprotected 2-(phenylethynyl)aniline (**1a**) as our first step. Excellent yields (up to 99%) of free NH 2-substituted indoles (**2a**) were obtained (Table 1).

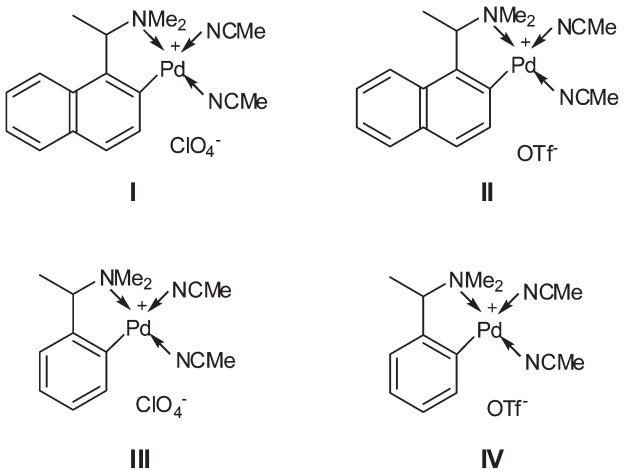
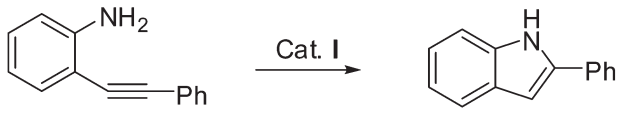


Fig. 1 Palladacycle catalysts.

Subsequently the allylic alkylation of **2a** with 1,3-diphenyl-2-propenol (**3a**) was also attempted (Table 2). Such alkylations with allylic alcohols to give C3- or N-substituted indoles, have hitherto been achieved using Lewis acids, Brønsted acids, and iodine as catalysts *via* the Friedel–Crafts pathway[11] and transition metal catalyzed alkylations.[12] Recently, Hirashita *et al.* reported that allylic alcohols reacted with indoles in the absence of catalyst in ion-exchanged water at 220 °C.[13] We were gratified to find that the alkylation in low-coordinating solvents (toluene, dichloroethane) gave clean conversion to **4a** at only 70 °C. No trace of *N*-allylic substituted indole was observed.

Table 1 Optimization of reaction conditions for the formation of **2a**[a]



1a **2a**

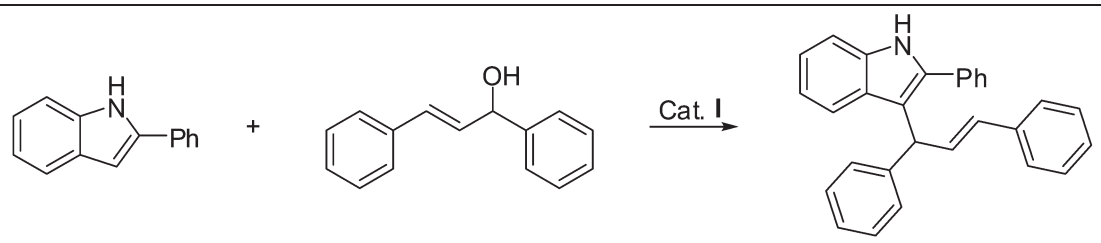
Entry	Catalyst (mol%)	Temperature/°C	Time/h	Solvent	Yield[b] (%)
1	10	110	24	Tol	91
2	20	110	24	Tol	78
3	5	110	24	Tol	93
4	10	110	9	Tol	91
5	10	90	24	ACN	97
6	10	80	24	DCE	91
7	10	80	9	DCE	99
8	10	70	9	DCE	98
9	10	60	9	DCE	90

[a] The reaction was carried out with 2-alkynlaniline (0.1 mmol, 1 equiv.), catalyst **I** (10 mol%) in 2 mL of specified solvent. [b] Yields were determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

In order to test whether the two steps can be integrated into one single operative procedure, we treated **1a**, **3a** and 10% catalyst **I** in dichloroethane at 70 °C for 9 h, **4a** was formed with a yield of up to 98% (Table 3, entry 1). We further investigated the other three palladacycles (Fig. 1) under the same conditions and the summarized results are shown in Table 3. The results show that catalyst **I** and **II** were much more effective than their benzyl amine analogues **III** and **IV**, which is possibly indicative of the difference in electronic influence of the C_{naphyl}–Pd bond and C_{benzyl}–Pd bonds on the Pd center. From the results, **I** and **II** are comparable, indicating that the anion effect does not play an important role. We therefore chose the well characterized **I** as our catalyst.

To further probe the general feasibility of this protocol, various 2-alkynylanilines bearing different functional groups on the aromatic ring were reacted with 1,3-diphenyl-2-propenol and substituted 1,3-diphenyl-2-propenol (Table 4). The results show that these 2-alkynylanilines can react with 1,3-diphenyl-2-propenol very efficiently to afford the desired 2,3-substituted indoles with excellent yields and regio-selectivities (Table 4, entries 1–5). We further reacted the 2-alkynylanilines with the unsymmetrical allylic alcohol **3b**. The results show that the reaction can also afford the 2,3-substituted indole exclusively in excellent yields but the product was a mixture of the isomers **4** and **4′**. The regioselectivity ratio however could not be determined accurately due to the extensive overlap of the ^{1}H NMR signals. However the lack of regioselectivity is in line with the literature[14] and indicated that the alkylation step maybe proceeding *via* the Tsuji–Trost pathway rather than the Friedel–Crafts pathway. It should be mentioned that the formation of trace amounts of black solid (no NMR signals in ^{1}H NMR spectrum) on the sides of the reaction flask was observed upon completion of the reaction, which is also consistent with the Tsuji–Trost mechanism. However in order to confirm that the formation of the black solid is not indicative of a palladium nanoparticle

Table 2 Optimization of reaction conditions for the formation of **4a**[a]

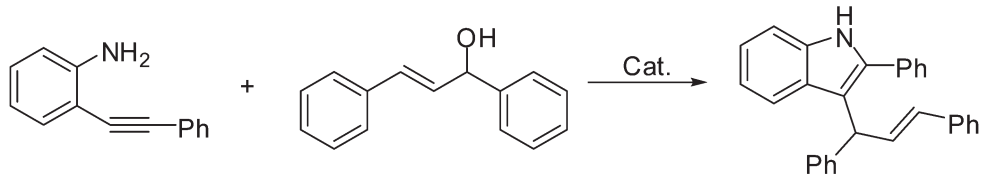


2a **3a** **4a**

Entry	Catalyst (mol%)	Temperature/°C	Time/h	Solvent	Yield[b] (%)
1	20	110	24	Tol	71
2	10	110	24	Tol	97
3	10	90	24	ACN	NR
4	10	80	24	THF	80
5	10	80	24	DCE	84
6	10	70	9	Tol	91
7	10	70	9	DCE	91
8	10	60	9	DCE	NR

[a] The reaction was carried out with 2-alkynlaniline (0.1 mmol, 1 equiv.), catalyst **I** (10 mol%) in 2 mL of specified solvent. [b] Yields were determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

Table 3 Optimization of reaction conditions for the formation of **4a**[a]



1a **3a** **4a**

Entry	Catalyst (mol%)	Temperature/°C	Time/h	Yield[b] (%)
1	**I** (10)	70	9	98
2	**II** (10)	70	9	98
3	**III** (10)	70	9	NR[c]
4	**IV** (10)	70	9	18
5	**I** (10)	60	9	NR[c]
6	**I** (10)	70	3	75
7	**I** (10)	70	6	91
8	**I** (5)	70	9	64

[a] The reaction was carried out with 2-alkynlaniline (0.1 mmol, 1 equiv.), 1,3-diphenyl-2-propenol (0.1 mmol, 1 equiv.), catalyst, 2 mL of dichloroethane. [b] Yields were determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. [c] Almost quantitative amount of **2a** was obtained together with un-reacted allylic alcohol.

catalyzed mechanism, we isolated the black solid and conducted a fresh reaction. The solid however did catalyze neither the cyclization nor the alkylation step. A blank experiment was also conducted in the absence of the catalyst and it did not yield any products. Palladium acetate as the catalyst under the reaction conditions could catalyze the cyclization step but it could not yield the alkylation product. We also attempted the reaction of 2-alkynylanilines with 4-phenyl-3-buten-2-ol and cinnamyl alcohol. Unfortunately, only cyclized products were obtained.

Although a detailed mechanism deserves further investigations, based on the previously reported mechanistic studies a reaction mechanism as described in Scheme 1 is proposed to rationalize the formation of 2,3-substituted indoles.[9a,15] Firstly, intramolecular nucleophilic attack by the amino group towards the Pd-activated C–C triple bond occurs (**5**), leading to the formation of a palladium intermediate (**6**). This palladium intermediate undergoes a rapid proton–palladium exchange and regenerates the catalyst with the formation of indole. Subsequently, the indole as a nucleophile attacks the π-allylpalladium intermediate (**7**),[15c] yielding the 2,3-substituted indole, which undergoes protonation to form the final product.

Conclusion

In conclusion, we have developed a very simple, clean and atom-efficient protocol for the synthesis of 2,3-substituted indoles from 2-alkynylanilines and allylic alcohols. The one-pot domino cyclization–alkylation reaction proceeds under mild conditions with no additives and provides an alternative method to access 2,3-substituted indoles. The method more importantly allows the incorporation of hithero unavailable substituents at the C-3 position of C-2 substituted indoles which have potential for further functionalization *via* the C=C bond. Further investigations on the detailed reaction mechanism, extension to other hereo cycle systems as well as work on an asymmetric protocol are currently underway in our laboratory.

Experimental

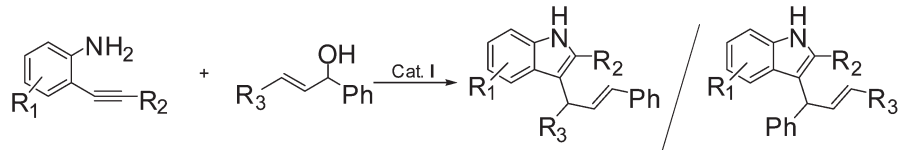
All reactions and manipulations were carried out under dry, oxygen-free nitrogen using the standard Schlenk technique. NMR spectra were recorded on a Bruker AV 300 spectrometer (^{1}H at 300 MHz, ^{13}C at 75 MHz) or a Bruker AV 400 (^{1}H at 400 MHz, ^{13}C at 100 MHz). Chemical shifts are given in ppm and are referenced to the residual solvent peak in the respective deutero-solvents. HR-MS spectra were obtained in the ESI mode on a Waters Q-Tof Premier MS system. Solvents were degassed prior to use when necessary. DCE, toluene, THF, acetone and acetonitrile were purchased from TEDIA COMPANY (AR) and used as supplied. Column chromatography was conducted on Silica gel 60 (Merck).

The four palladacycles catalysts **I–IV** were prepared by treating the corresponding chloro-bridged dimeric palladium compounds[16] with silver perchlorate–triflate in acetonitrile *via* a procedure reported previously.[17] *o*-Alkynylanilines were prepared according to the published procedure.[18] All the other reactants and reagents were used as supplied.

Typical procedure for the palladacycle catalyzed cyclization of 1a

Compound **1a** (19.3 mg, 0.1 mmol), catalyst **I** (4.9 mg, 10 mol %), and 2 mL of varying solvents were placed in a 25 mL argon-filled sealed Schlenk tube and stirred at the given temperature for the stipulated reaction time. Upon completion of the reaction, internal standard, 1,3,5-trimethoxybenzene, was added into the mixture. The reaction mixture was then filtered through celite. The filtrate was evacuated to dryness and the resulting residue was dissolved in deuterated solvent and analyzed by ^{1}H NMR

Table 4 Palladacycle catalyzed domino cyclization–alkylation with *o*-alkynylanilines and allylic alcohols[a]



1 **3** **4** **4'**

3a: R3 = Ph
3b: R3 = 4-MePh

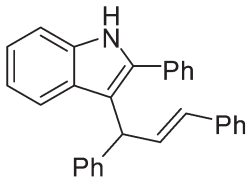
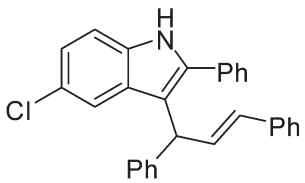
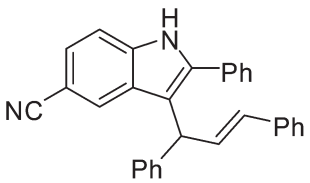
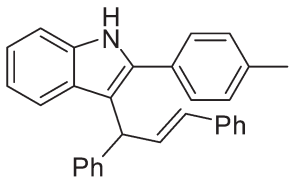
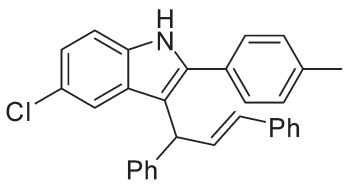
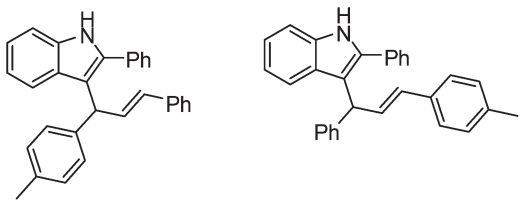
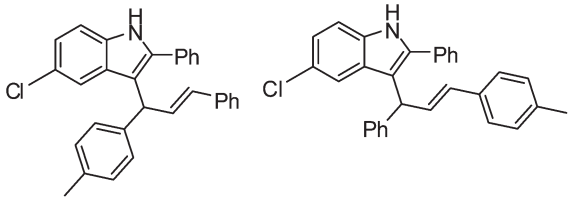
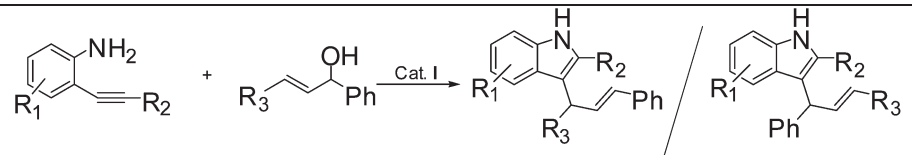
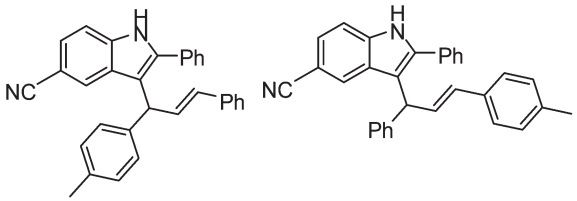
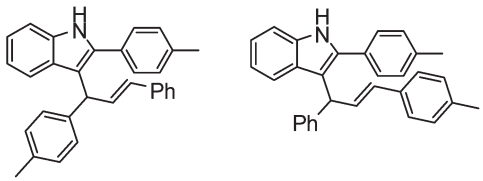
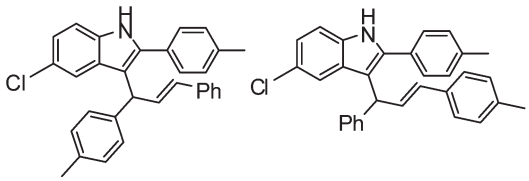
Entry	R_1	R_2	Allylic alcohol	Product	Overall yield[b] (%)
1	H	Ph	**3a**		98
2	Cl	Ph	**3a**		95
3	CN	Ph	**3a**		90
4	H	4-MePh	**3a**		94
5	Cl	4-MePh	**3a**		90
6	H	Ph	**3b**		91
7	Cl	Ph	**3b**		98

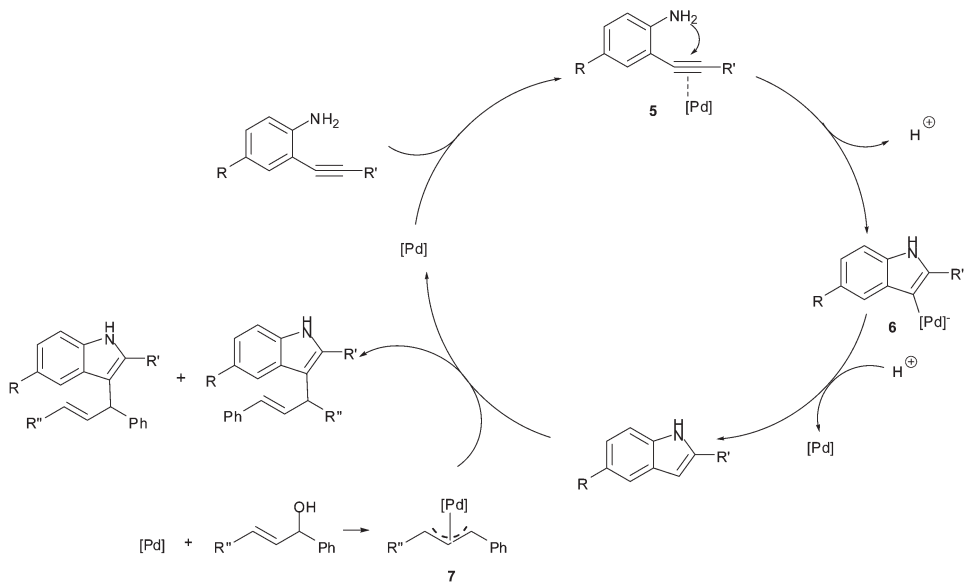
Table 4 *(Contd.)*



3a: R3 = Ph
3b: R3 = 4-MePh

Entry	R_1	R_2	Allylic alcohol	Product	Overall yield[b] (%)
8	CN	Ph	**3b**		96
9	H	4-MePh	**3b**		94
10	Cl	4-MePh	**3b**		98

[a] The reaction was carried out with 2-alkynlaniline (0.1 mmol, 1 equiv.), allylic alcohol (0.1 mmol, 1 equiv.), catalyst **I** (10 mol%) in 2 mL of dichloroethane at 70 °C for 9 h. [b] Overall yields (combined yields of two isomers for entries 6–10) were determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.



Scheme 1 Proposed mechanism.

spectroscopy with 1,3,5-trimethoxybenzene as an internal standard. The signals due to product **2a** were confirmed by comparisons with values obtained from the literature.[19]

Typical procedure for the palladacycle catalyzed allylic alkylation of 2a with 3a

Compound **2a** (19.3 mg, 0.1 mmol), **3a** (21.0 mg, 0.1 mmol), catalyst **I** (4.9 mg, 10 mol%), and 2 mL of varying solvents were placed in a 25 mL argon-filled sealed Schlenk tube and stirred at the given temperature for the stipulated reaction time. Upon completion of the reaction time, internal standard, 1,3,5-trimethoxybenzene, was added and dissolved in the mixture. The reaction mixture was then filtered through celite. The filtrate was evacuated to dryness and the resulting residue was dissolved in deuterated solvent and analyzed by ^{1}H NMR spectroscopy with 1,3,5-trimethoxybenzene as an internal standard. The signals due to product **4a** were confirmed by comparisons with values obtained from the literature.[20]

Typical procedure for the palladacycle catalyzed domino cyclization–alkylation of 1a with 3a

1a (19.3 mg, 0.1 mmol), **3a** (21.0 mg, 0.1 mmol), an appropriate amount of varying catalyst as shown in Table 3, as well as 2 mL of dichloroethane were placed in a 25 mL argon-filled sealed Schlenk tube and stirred at the given temperature for the stipulated reaction time. Upon completion of the reaction, internal standard, 1,3,5-trimethoxybenzene, was added and dissolved into the mixture. The reaction mixture was then filtered through celite. The filtrate was evacuated to dryness and the resulting residue was dissolved in deuterated solvent and analyzed by ^{1}H NMR spectroscopy with 1,3,5-trimethoxybenzene as an internal standard. The signals due to the product **4a** were confirmed by comparisons with values obtained from the literature.[20]

Typical procedure for the palladacycle catalyzed domino cyclization–alkylation of *o*-alkynlanilines with allylic alcohols

o-Alkynylaniline (0.1 mmol, 1 equiv.), allylic alcohol (0.1 mmol, 1 equiv.), catalyst **I** (10 mol%), and 2 mL of dichloroethane were placed in a 25 mL argon-filled sealed Schlenk tube and stirred at 70 °C for 9 h. Upon completion of the reaction time, internal standard, 1,3,5-trimethoxybenzene, was added and dissolved into the mixture. The reaction mixture was then filtered through celite. The filtrate was evacuated to dryness and the resulting residue was dissolved in deuterated solvent and analyzed by ^{1}H NMR spectroscopy with 1,3,5-trimethoxybenzene as an internal standard. The analytically pure products were obtained by flash chromatography using hexane–DCM.

4b: pale yellow paste (25.9 mg, 62%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.14 (s, 1H, N*H*), 7.53–7.11 (m, 18H, Ar), 6.83 (dd, 1H, J = 15.9, 7.5 Hz, C*H*═CHPh), 6.41 (d, 1H, J = 15.8 Hz, CH═C*H*Ph), 5.25 (d, 1H, J = 7.2 Hz, C*H*CH═CH); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 143.0, 137.3, 137.0, 134.6, 132.5, 131.6, 131.5, 128.9, 128.6, 128.5, 128.4, 128.2, 127.3, 126.4, 125.3, 122.5, 120.4, 113.7, 111.9, 44.9. HRMS (ESI): calcd for $C_{29}H_{23}NCl$ $[M + H]^+$: 420.1519; found: 420.1527.

4c: yellow paste (21.7 mg, 53%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.45 (s, 1H, N*H*), 7.72–7.26 (m, 18H, Ar), 6.82 (dd, 1H, J = 15.9, 7.2 Hz, C*H*═CHPh), 6.40 (d, 1H, J = 15.9 Hz, CH═C*H*Ph), 5.29 (d, 1H, J = 7.2 Hz, C*H*CH═CH); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 142.7, 137.9, 137.8, 137.0, 131.8, 131.8, 131.1, 129.1, 128.9, 128.6, 128.6, 128.5, 128.0, 127.6, 127.5, 126.6, 126.5, 126.4, 125.2, 120.8, 114.8, 111.8, 102.9, 44.7. HRMS (ESI): calcd for $C_{30}H_{23}N_2$ $[M + H]^+$: 411.1861; found: 411.1859.

4d: pale yellow paste (22.7 mg, 57%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.04 (s, 1H, N*H*), 7.43–6.96 (m, 18H, Ar), 6.88 (dd, 1H, J = 15.9, 7.2 Hz, C*H*═CHPh), 6.40 (d, 1H, J = 15.9 Hz, CH═C*H*Ph), 5.27 (d, 1H, J = 7.2 Hz, C*H*CH═CH), 2.40 (s, 3H, Me); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 143.6, 138.0, 137.6, 136.2, 135.7, 132.4, 131.0, 130.1, 129.6, 128.5, 128.5, 128.3, 128.3, 127.1, 126.3, 126.1, 122.0, 121.2, 119.7, 113.6, 110.9, 45.2, 21.3. HRMS (ESI): calcd for $C_{30}H_{26}N$ $[M + H]^+$: 400.2065; found: 400.2067.

4e: pale yellow paste (23.4 mg, 54%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.09 (s, 1H, N*H*), 7.42–7.09 (m, 18H, Ar), 6.82 (dd, 1H, J = 15.6, 7.2 Hz, C*H*═CHPh), 6.39 (d, 1H, J = 15.6 Hz, CH═C*H*Ph), 5.23 (d, 1H, J = 7.2 Hz, C*H*CH═CH), 2.41 (s, 3H, Me); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.1, 138.4, 137.4, 137.2, 134.5, 131.7, 131.4, 129.6, 129.6, 129.0, 128.5, 128.5, 128.4, 128.2, 127.2, 126.4, 126.3, 125.2, 122.3, 120.3, 113.4, 111.9, 45.0, 21.3. HRMS (ESI): calcd for $C_{30}H_{25}NCl$ $[M + H]^+$: 434.1676; found: 434.1679.

4f/f′: pale yellow paste (20.0 mg, 50%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.10 (s, 1H, N*H*), 7.55–6.92 (m, 18H, Ar), 6.89–6.79 (m, 1H, C*H*═CHPh), 6.42–6.35 (m, 1H, CH═C*H*Ph), 5.28–5.23 (m, 1H, C*H*CH═CH), 2.30 (s, 3H, Me); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 143.6, 140.4, 137.6, 136.9, 136.3, 135.6, 134.7, 133.0, 132.5, 131.3, 131.0, 130.9, 129.1, 129.0, 128.8, 128.6, 128.4, 128.3, 128.2, 128.2, 128.0, 128.0, 127.1, 126.3, 126.2, 126.1, 122.1, 121.3, 121.3, 120.0, 114.1, 110.9, 45.1, 44.8, 21.1, 21.0. HRMS (ESI): calcd for $C_{30}H_{26}N$ $[M + H]^+$: 400.2065; found: 400.2073.

4g/g′: pale yellow paste (20.8 mg, 48%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.13 (s, 1H, N*H*), 7.54–7.08 (m, 18H, Ar), 6.84–6.74 (m, 1H, C*H*═CHPh), 6.41–6.35 (m, 1H, CH═C*H*Ph), 5.24–5.20 (m, 1H, C*H*CH═CH), 2.32–2.32 (m, 3H, Me); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.2, 139.9, 137.4, 137.1, 137.0, 137.0, 135.8, 134.6, 134.6, 132.5, 131.9, 127.2, 126.4, 126.3, 125.2, 122.5, 120.5, 120.4, 113.9, 111.9, 44.9, 44.6, 21.2, 21.0. HRMS (ESI): calcd for $C_{30}H_{25}NCl$ $[M + H]^+$: 434.1676; found: 434.1688.

4h/h′: yellow paste (17.8 mg, 42%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.43 (s, 1H, N*H*), 7.73–7.09 (m, 18H, Ar), 6.83–6.73 (m, 1H, C*H*═CHPh), 6.41–6.35 (m, 1H, CH═C*H*Ph), 5.28–5.23 (m, 1H, C*H*CH═CH), 2.33–2.32 (m, 3H, Me); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.8, 139.5, 137.9, 137.7, 137.7, 137.3, 137.1, 136.1, 134.3, 131.8, 131.7, 131.6, 131.4, 130.1, 129.3, 129.3, 129.1, 128.8, 128.6, 128.6, 128.5, 128.3, 128.1, 127.9, 127.7, 127.4, 126.6, 126.6, 126.4, 126.3, 126.0, 125.1, 120.8, 120.8, 115.0, 111.8, 102.8, 102.8, 44.7, 44.4, 21.2, 21.0. HRMS (ESI): calcd for $C_{31}H_{25}N_2$ $[M + H]^+$: 425.2018; found: 425.2030.

4i/i′: pale yellow paste (21.5 mg, 52%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.11 (s, 1H, N*H*), 7.49–7.02 (m, 18H, Ar),

6.90–6.84 (m, 1H, C*H*═CHPh), 6.43–6.39 (m, 1H, CH═C*H*Ph), 5.30–5.26 (m, 1H, C*H*CH═CH), 2.45 (s, 3H, Me), 2.35 (s, 3H, Me); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 143.7, 140.5, 138.0, 137.7, 136.8, 136.2, 135.7, 135.6, 135.5, 134.8, 132.6, 131.4, 130.9, 130.8, 130.1, 129.5, 129.1, 129.0, 128.5, 128.4, 128.3, 128.2, 128.2, 128.0, 127.0, 126.3, 126.2, 126.0, 121.9, 121.2, 121.2, 119.6, 113.7, 110.8, 45.2, 44.9, 21.3, 21.2, 21.0. HRMS (ESI): calcd for $C_{31}H_{28}N$ $[M + H]^+$: 414.2222; found: 414.2222.

4j/j′: pale yellow paste (22.4 mg, 50%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.09 (s, 1H, N*H*), 7.41–7.10 (m, 18H, Ar), 6.80–6.73 (m, 1H, C*H*═CHPh), 6.41–6.34 (m, 1H, CH═C*H*Ph), 5.23–5.18 (m, 1H, C*H*CH═CH), 2.41 (s, 3H, Me), 2.32 (s, 3H, Me); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 143.2, 140.0, 138.3, 137.1, 137.1, 137.0, 135.7, 134.6, 134.5, 132.0, 131.3, 131.2, 130.7, 129.6, 129.2, 129.1, 129.0, 128.5, 128.3, 128.2, 128.0, 127.2, 126.3, 126.2, 125.1, 122.3, 120.3, 113.5, 111.8, 44.9, 44.6, 21.3, 21.2, 21.0. HRMS (ESI): calcd for $C_{31}H_{27}NCl$ $[M + H]^+$: 448.1832; found: 448.1835.

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