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A facile route to 5-methyl-5*H*-indeno[1,2-*c*]quinolones via palladium-catalyzed cyclization of 2-alkynylbromobenzenes with *N*, *N*-dimethyl-2-alkynylanilines

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A tandem reaction catalyzed by palladium is developed to provide a facile and simple route for the synthesis of 5-methyl-5*H*-indeno[1,2-*c*]quinolones, which can introduce diversity and complexity into the products from readily available starting materials. This transformation proceeds well with good functional group tolerance.

1. Introduction

Cyclic compounds especially heterocycles have made profound impact on organic chemistry due to their special properties and potential biological activity.[1] As a result, a series of strategies for access to heterocyclic skeletons such as indoles, isoquinolines and benzofurans have been developed,[2] among which, the domino reaction has been utilized widely because of its high efficiency and convenience.[3] Recently, our group focused intense attention on constructing fused polycycles via palladium-catalyzed domino reactions involving double insertion of triple bonds as the key step.[4] In these protocols, 2-alkynylhalobenzenes as powerful electrophiles undergo cyclization with different alkynes as nucleophiles by a sequence of carbopalladation and reductive elimination to generate functionalized polycyclic compounds.

In our attempt to synthesize *N*-substituted 5*H*-indeno[1,2-c] quinolones with our previous reported method,[4a] we found that the substrates *N*-mono-alkylated-2-alkynylaniline were very difficult to synthesize. The direct Buchwald cross coupling of aryl bromide and amine usually suffers from low yields.[5] The alkylation of the 2-alkynylaniline would generate a large amount of undesired *N*, *N* -disubstituted product. So a long synthetic route including protection-alkylation-deprotection is typically needed.[5] However, the recent reported the chemistry of *N*, *N*-dimethyl 2-alkynylaniline give us a new insight of this synthetic route. We hypothesize that our desired product can also be synthesized by utilizing this easy-synthesizing substrate with a C-N bond cleavage.

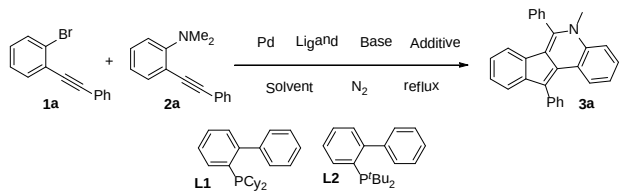
As part of our ongoing research, we wish to report herein the cyclizative reaction of *N*, *N*-dimethyl-2-alkynylaniline with 2-alkynylbromobenzene takes place efficiently to afford the multi-substituted 5*H*-indeno[1,2-*c*]quinoline **3** (Scheme 1). This approach not only introduces more diversity and complexity into the products, but also avoids the unexpected oxidative compounds 11*H*-indeno[1,2-*c*]quinolin-11-ol comparing to the previous works.[4a-b] The construction of versatile substituted 5*H*-indeno[1,2-*c*]quinolines will potentially help find molecules with anticancer activity.[6]

2. Results and discussion

We investigated the model reaction of 1-bromo-2-(phenylethynyl)benzene **1a** and *N*, *N*-dimethyl-2-(phenylethynyl)aniline **2a** in the presence of 5 mol% palladium catalyst at 102 °C under various reaction conditions (Table 1). Our initial attempt focused on screening ligands. The transformation did not occur in the use of PCy_3 (entry 1), and a trace amount of desired product **3a** was detected under the condition of $P(^tBu)_3{\cdot}HBF_4$ (entry 2). Several other ligands, such as DPPF (1,1'-bis(diphenylphosphino)ferrocene), DPPM (bis(diphenylphosphino)methane), DPE Phos (bis[2-(diphenylphosphino)phenyl] ether) and L1, utilized as the replacement of the above ligands could improve the final outcome to moderate yields (entries 3-6). Interestingly, the reaction gave rise to **3a** in 53% yield without the addition of ligand (entry 7). L2 was proved to be the most effective ligand improving the yield to 67% and PPh_3 afforded the desired product in similar yield of 62% (entries 8-9). Subsequently, the examination of bases showed that *t*-BuONa was the best choice and the others could not increase yields (entries 10-13). Further screening of solvents showed the reaction proceeded the most efficiently in 1,4-dioxane (entries 14-17). Various palladium sources were explored only to find Pd_2dba_3 could give a similar yield while other palladium catalysts lowered the yield of 3a (entries 18-20). Further exploration proved that additive was necessary and TBAI (n-Bu_4NI) was the best choice. No other additives could enhance the isolated yield (entries 21-25). Subsequently, the reaction did not proceed well when the temperature was lowered, while higher temperature could not promote the conversion obviously (entries 26-29).

Having established the optimal reaction conditions (5 mol % of $Pd(OAc)_2$, 10 mol % of L2, 2.0 equiv of *t*-BuONa, 1.2 equiv of TBAI, 1,4-dioxane, under reflux), we then focused on the scope of this palladium-catalyzed tandem reaction of 2-alkynylbromobenzenes **1** with *N*, *N*-dimethyl-2-

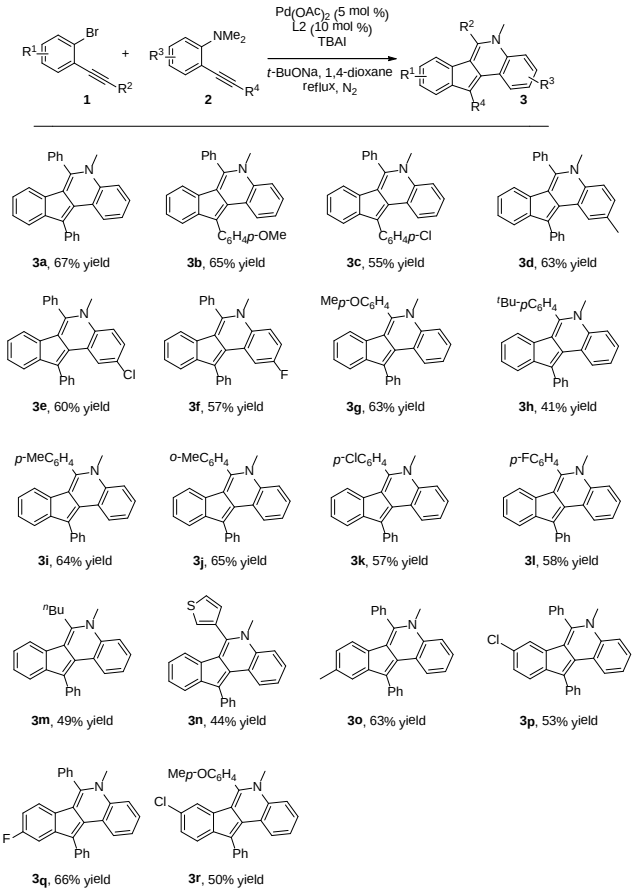
Table 1 Palladium-catalyzed domino reaction of 2-alkynylbromobenzene **1a**, *N*, *N*-dimethyl-2-(phenylethynyl)aniline **2a**.[a]



Entry	Ligand	Pd	Base	Solvent	Additive	Yield (%)
1	PCy_3	$Pd(OAc)_2$	*t*-BuONa	1,4-dioxane	TBAI	n.r
2	$P(t\text{-}Bu)_3 HBF_4$	$Pd(OAc)_2$	*t*-BuONa	1,4-dioxane	TBAI	trace
3	DPPF	$Pd(OAc)_2$	*t*-BuONa	1,4-dioxane	TBAI	47
4	DPPM	$Pd(OAc)_2$	*t*-BuONa	1,4-dioxane	TBAI	40
5	DPEPhos	$Pd(OAc)_2$	*t*-BuONa	1,4-dioxane	TBAI	45
6	L1	$Pd(OAc)_2$	*t*-BuONa	1,4-dioxane	TBAI	43
7	-	$Pd(OAc)_2$	*t*-BuONa	1,4-dioxane	TBAI	53
8	PPh_3	$Pd(OAc)_2$	*t*-BuONa	1,4-dioxane	TBAI	62
9	L2	$Pd(OAc)_2$	*t*-BuONa	1,4-dioxane	TBAI	67
10	L2	$Pd(OAc)_2$	*t*-BuOK	1,4-dioxane	TBAI	n.r.
11	L2	$Pd(OAc)_2$	Cs_2CO_3	1,4-dioxane	TBAI	40
12	L2	$Pd(OAc)_2$	K_3PO_4	1,4-dioxane	TBAI	60
13	L2	$Pd(OAc)_2$	KOH	1,4-dioxane	TBAI	56
14	L2	$Pd(OAc)_2$	*t*-BuONa	DMSO	TBAI	n.r.
15	L2	$Pd(OAc)_2$	*t*-BuONa	DMF	TBAI	trace
16	L2	$Pd(OAc)_2$	*t*-BuONa	Toluene	TBAI	21
17	L2	$Pd(OAc)_2$	*t*-BuONa	Diglyme	TBAI	45
18	L2	$PdCl_2(PhCN)_2$	*t*-BuONa	1,4-dioxane	TBAI	trace
19	L2	Pd_2dba_3	*t*-BuONa	1,4-dioxane	TBAI	61
20	L2	$PdCl_2(PPh_3)_2$	*t*-BuONa	1,4-dioxane	TBAI	44
21	L2	$Pd(OAc)_2$	*t*-BuONa	1,4-dioxane	-	n.r.
22	L2	$Pd(OAc)_2$	*t*-BuONa	1,4-dioxane	TBAB	n.r.
23	L2	$Pd(OAc)_2$	*t*-BuONa	1,4-dioxane	KI	n.r.
24	L2	$Pd(OAc)_2$	*t*-BuONa	1,4-dioxane	TBAC	38
25	L2	$Pd(OAc)_2$	*t*-BuONa	1,4-dioxane	nBu_4OAc	43
26	L2[b]	$Pd(OAc)_2$	*t*-BuONa	1,4-dioxane	TBAI	50
27	L2[c]	$Pd(OAc)_2$	*t*-BuONa	1,4-dioxane	TBAI	63
28	L2[d]	$Pd(OAc)_2$	*t*-BuONa	1,4-dioxane	TBAI	68
29	L2[e]	$Pd(OAc)_2$	*t*-BuONa	1,4-dioxane	TBAI	64

[a] Isolated yield based on 2-alkynylaniline **2**. [b,c,d,e] The reaction was performed at 90 °C, 100 °C, 105 °C, 110 °C.

alkynylanilines **2**. The results are summarized in Scheme 1. With respect to the scope of 2-alkynylbromobenzenes **1,** various electron-donating or electron-withdrawing substituents attached on the aromatic ring (R^1 group) or the triple bond (R^2 group) were well tolerated. It is notable that 1-bromo-2-(phenylethynyl)benzene derivatives with heterocyclic (**1n**), alkyl (**1m**), bulky groups (**1j**) serve as viable substrates for synthesizing indeno[1,2-*c*]quinolones. The reaction was also smoothly performed with moderate yields for *N*, *N*-dimethyl-2-alkynylanilines **2** bearing either electron-rich or electron-poor groups in the R^3 or R^4 position.



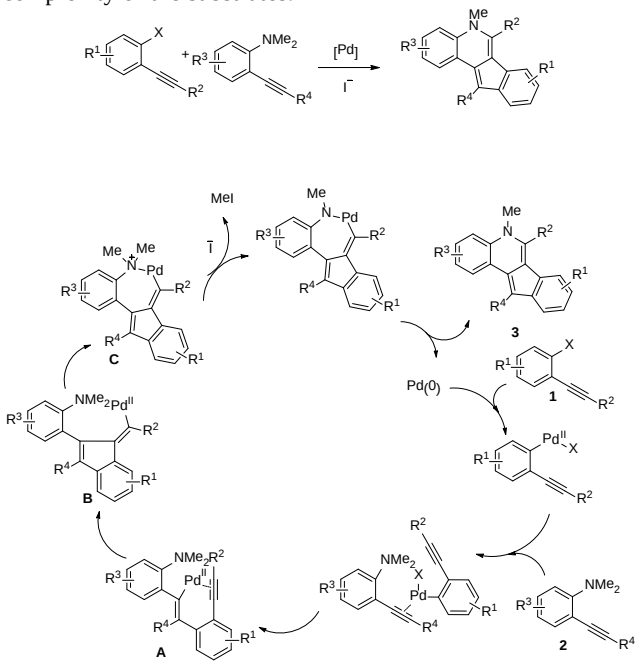
Scheme 1 Palladium-catalyzed tandem reaction of 2-alkynylbromobenzene **1** with *N*, *N*-dimethyl-2-alkynylaniline **2**

[a] Isolated yield based on *N*, *N*-dimethyl-2-alkynylaniline **2**

A plausible reaction pathway is depicted in Scheme 2. The active intermediate ($R\text{-}Pd^{II}X$), generated from the oxidative addition of 2-alkynylbromobenzene **1** to Pd^0, reacted with *N*, *N*-dimethyl-2-alkynylaniline **2** via intermolecular insertion of the triple bond to provide **A**. The subsequent intramolecular insertion of the triple bond occurred to give rise to **B**, which went through intramolecular C-N bond formation to afford the quaternary ammonium intermediate **C**. In the presence of TBAI, *N*-demethylation by S_N2 attack of I^- to **C** proceeded,[7] followed by reductive elimination to furnish the desired product **3** and Pd^0.

In conclusion, we have disclosed a simple and convenient access to 5-methyl-5*H*-indeno[1,2-*c*]quinolones via a palladium-catalyzed tandem reaction of 2-

alkynylbromobenzenes with *N*, *N*-dimethyl-2-alkynylanilines. The conversion tolerate different functional groups, and more diverse substituents can be easily introduced from readily available starting materials to promote the diversity and complexity of the substrates.



Scheme 2 Plausible Reaction Pathway

Experimental Section

General experimental procedure for palladium-catalyzed reaction of 2-alkynylbromobenzene **1**, *N*, *N*-dimethyl-2-alkynylaniline **2**: *N*, *N*-dimethyl-2-alkynylaniline (0.20 mmol) was added to a mixture of $Pd(OAc)_2$ (5 mol %), L2 (10 mol %), *t*-BuONa (0.4 mmol), TBAI (0.24 mmol) in a test tube. This test tube was applied with vaccum and filled with N_2. Then a solution of 2-alkynylbromobenzene (0.24 mmol) in 1, 4-dioxane (2.0 mL) was added to the system. The mixture was heated under reflux. After *N*, *N*-dimethyl-2-alkynylaniline was consumed completely as indicated by TLC, the reaction was cooled and the solvent was diluted by EtOAc (10 mL), washed with saturated brine (2 × 10 mL), and dried by anhydrous Na_2SO_4. Evaporation of the solvent followed by purification on silica gel provides the products **3a-3r**.

5-Methyl-6,11-diphenyl-5*H*-indeno[1,2-*c*]quinoline (**3a**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 7.9 Hz, 1H), 7.59-7.50 (m, 7H), 7.46-7.31 (m, 6H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.88 (t, *J* = 7.3 Hz, 1H), 6.31 (d, *J* = 7.8 Hz, 1H), 3.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.1, 142.5, 138.7, 136.1, 135.5, 130.6, 129.5, 129.0, 128.8, 126.6, 125.6, 125.4, 124.3, 123.0, 120.6, 120.4, 120.0, 118.3, 116.2, 115.5, 36.2. HRMS (ESI) calcd for $C_{29}H_{22}N^+$: 384.1747 (M + H^+), found: 384.1753.

11-(4-Methoxyphenyl)-5-methyl-6-phenyl-5*H*-indeno[1,2-*c*]quinoline (**3b**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 8.1 Hz, 1H), 7.64-7.36 (m, 10H), 7.25-7.20 (m, 1H), 7.14-7.08 (m, 3H), 6.90-6.86 (m, 1H), 6.32 (d, *J* = 7.9 Hz, 1H), 3.91 (s, 3H), 3.56 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.4, 143.9, 142.7, 136.2, 135.6, 132.7, 131.6, 130.8, 129.5, 129.1, 126.5, 125.6, 125.4, 124.3, 123.2, 123.0, 120.6, 120.3, 119.8, 118.3, 116.2, 115.4, 114.3, 113.9, 55.3, 36.3. HRMS (ESI) calcd for $C_{30}H_{24}NO^+$: 414.1852 (M + H^+), found: 414.1870.

11-(4-Chlorophenyl)-5-methyl-6-phenyl-5*H*-indeno[1,2-*c*]quinoline (**3c**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06-8.03 (m, 1H), 7.67-7.66 (m, 3H), 7.56-7.50 (m, 7H), 7.46-7.40 (m, 2H), 7.26-7.22 (m, 1H), 7.19-7.15 (m, 1H), 6.90 (d, *J* = 7.1 Hz, 1H), 6.32 (d, *J* = 8.0 Hz, 1H), 3.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.3, 142.2, 137.3, 136.1, 135.5, 132.3, 132.1, 130.6, 129.7, 129.6, 129.1, 126.8, 125.8, 125.6, 124.5, 123.2, 122.9, 120.7, 120.5, 118.5, 118.0, 116.3, 115.7, 36.4. HRMS (ESI) calcd for $C_{29}H_{21}ClN^+$: 418.1357 (M + H^+), found: 418.1361.

2,5-Dimethyl-6,11-diphenyl-5*H*-indeno[1,2-*c*]quinoline (**3d**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (s, 1H), 7.63-7.38 (m, 12H), 7.24-7.19 (m, 2H), 6.87 (t, *J* = 7.6 Hz, 1H), 6.32 (d, *J* = 8.0 Hz, 1H), 3.54 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.9, 142.3, 138.8, 135.6, 134.1, 132.5, 130.6, 129.5, 129.1, 128.6, 127.7, 126.5, 125.8, 125.5, 124.2, 123.0, 120.6, 120.2, 119.7, 118.3, 116.0, 115.4, 36.3, 21.0. HRMS (ESI) calcd for $C_{30}H_{24}N^+$: 398.1903 (M + H^+), found: 398.1904.

2-Chloro-5-methyl-6,11-diphenyl-5*H*-indeno[1,2-*c*]quinoline (**3e**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99-7.98 (m, 1H), 7.65-7.53 (m, 7H), 7.47-7.45 (m, 4H), 7.38-7.36 (m, 1H), 7.30-7.21 (m, 2H), 6.91 (t, *J* = 7.6 Hz, 1H), 6.32 (d, *J* = 8.0 Hz, 1H), 3.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.9, 142.3, 137.8, 135.2, 134.7, 131.5, 130.3, 129.7, 129.6, 129.0, 128.9, 128.5, 127.0, 126.4, 124.8, 124.6, 124.3, 124.2, 121.3, 120.9, 120.7, 118.6, 116.8, 116.4, 36.4. HRMS (ESI) calcd for $C_{29}H_{21}ClN^+$: 418.1357 (M + H^+), found: 418.1351.

2-Fluoro-5-methyl-6,11-diphenyl-5*H*-indeno[1,2-*c*]quinoline (**3f**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71-7.64 (m, 4H), 7.59-7.44 (m, 9H), 7.26-7.22 (m, 1H), 7.12-7.07 (m, 1H), 6.93-6.89 (m, 1H), 6.33 (d, *J* = 8.0 Hz, 1H), 3.91 (s, 3H), 3.56 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.4 (d, J_{CF} = 241.1 Hz), 144.0, 142.2, 137.9, 135.3, 132.7, 130.5, 129.7, 129.6, 129.1, 128.9, 127.0, 124.6, 124.5, 121.0, 120.7 (d, $^3J_{CF}$ = 6.5 Hz), 118.6, 117.1 (d, $^3J_{CF}$ = 8.7 Hz), 115.5, 114.0 (d, $^2J_{CF}$ = 24.0 Hz), 110.8 (d, $^2J_{CF}$ = 23.6 Hz), 36.6. HRMS (ESI) calcd for $C_{29}H_{21}FN^+$: 402.1653 (M + H^+), found: 402.1656.

6-(4-Methoxyphenyl)-5-methyl-11-phenyl-5*H*-indeno[1,2-*c*]quinoline (**3g**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.0 Hz, 1H), 7.61-7.59 (m, 2H), 7.55-7.51 (m, 2H), 7.48-7.35 (m, 6H), 7.26-7.22 (m, 1H), 7.12-7.08 (m, 3H), 6.93 (t, *J* = 7.8 Hz, 1H), 6.47 (d, *J* = 7.4 Hz, 1H), 3.93 (s, 3H), 3.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.4, 144.1, 142.4, 138.8, 136.2, 130.6, 130.4, 129.2, 128.8, 127.6, 126.5, 125.6, 125.4, 124.3, 123.0, 122.9, 120.7, 120.4, 119.9, 118.3, 116.6, 115.6, 114.9, 55.4, 36.2. HRMS (ESI) calcd for $C_{30}H_{24}NO^+$: 414.1852 (M + H^+), found: 414.1850.

6-(4-(*tert*-Butyl)phenyl)-5-methyl-11-phenyl-5*H*-indeno[1,2-*c*]quinoline (**3h**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.1 Hz, 1H), 7.62 (d, *J* = 8.2 Hz, 4H), 7.55-7.49 (m, 3H), 7.45-7.39 (m, 5H), 7.25-7.21 (m, 1H), 7.11 (t, *J* = 7.8 Hz, 1H), 6.88 (t, *J* = 7.8 Hz, 1H), 6.33 (t, *J* = 7.9 Hz, 1H), 3.58 (s, 3H), 1.47 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ

152.8, 144.4, 142.4, 138.8, 136.2, 132.5, 130.7, 129.2, 128.7, 128.7, 126.5,126.4, 125.7, 125.4, 124.2, 123.1, 123.0, 120.7, 120.3, 119.9, 118.2, 116.4, 115.5, 36.4, 35.0, 31.4. HRMS (ESI) calcd for $C_{33}H_{30}N^+$: 440.2373 (M + H^+), found: 440.2370.

5-Methyl-11-phenyl-6-(*p*-tolyl)-5*H*-indeno[1,2-*c*]quinoline (**3i**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07-8.05 (m, 1H), 7.62-7.36 (m, 12H), 7.26-7.19 (m, 1H), 7.12-7.09 (m, 1H), 6.93-6.89 (m, 1H), 6.42 (d, *J* = 7.9 Hz, 1H), 3.56 (s, 3H), 2.55 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.4, 142.4, 139.5, 138.8, 136.2, 132.6, 130.7, 130.2, 129.2, 128.9, 128.8, 126.5, 125.7, 125.5, 124.3, 123.1, 123.0, 120.7, 120.3, 119.9, 118.3, 116.3, 115.5, 36.3, 21.6. HRMS (ESI) calcd for $C_{30}H_{24}N^+$: 398.1903 (M + H^+), found: 398.1884.

5-Methyl-11-phenyl-6-(*o*-tolyl)-5*H*-indeno[1,2-*c*]quinoline (**3j**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 8.1 Hz, 1H), 7.63-7.36 (m, 12H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.27 (d, *J* = 7.9 Hz, 1H), 3.58 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5, 142.5, 138.7, 136.8, 136.1, 135.0, 130.9, 130.7, 129.9, 129.2, 129.0, 128.8, 127.1, 126.5, 125.8, 125.3, 124.3, 123.2, 123.0, 120.5, 120.2, 120.1, 118.3, 115.9, 115.5, 35.4, 19.3. HRMS (ESI) calcd for $C_{30}H_{24}N^+$: 398.1903 (M + H^+), found: 398.1904.

6-(4-Chlorophenyl)-5-methyl-11-phenyl-5*H*-indeno[1,2-*c*]quinoline (**3k**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 8.1 Hz, 1H), 7.65-7.39 (m, 12H), 7.28-7.23 (m, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.95 (t, *J* = 7.6 Hz, 1H), 6.42 (d, *J* = 7.8 Hz, 1H), 3.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.7, 142.6, 138.5, 136.1, 135.8, 134.0, 130.7, 130.6, 130.0, 128.8, 126.7, 125.8, 125.4, 124.6, 123.2, 123.0, 120.6, 120.5, 118.5, 116.5, 115.5, 36.4. HRMS (ESI) calcd for $C_{29}H_{21}ClN^+$: 418.1357 (M + H^+), found: 418.1345.

6-(4-Fluorophenyl)-5-methyl-11-phenyl-5*H*-indeno[1,2-*c*]quinoline (**3l**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.1 Hz, 1H), 7.60-7.20 (m, 13H), 7.11 (t, *J* = 7.4 Hz, 1H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.35 (d, *J* = 7.9 Hz, 1H), 3.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.3 (d, J_{CF} = 248.8 Hz), 142.9, 142.6, 138.5, 136.1, 131.5, 131.2, 131.1, 130.6, 129.0, 128.8, 126.7, 125.7, 125.4, 124.5, 123.1, 123.0, 120.5 (d, $^3J_{CF}$ = 7.7 Hz), 120.4, 118.5, 116.8 (d, $^2J_{CF}$ = 21.6 Hz), 116.7, 115.5, 36.2. HRMS (ESI) calcd for $C_{29}H_{21}FN^+$: 402.1653 (M + H^+), found: 402.1648.

6-Butyl-5-methyl-11-phenyl-5*H*-indeno[1,2-*c*]quinoline (**3m**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03-8.95 (m, 2H), 7.59-7.51 (m, 5H), 7.44-7.28 (m, 5H), 7.04 (t, *J* = 7.2 Hz, 1H), 3.78 (s, 3H), 3.38 (m, 2H), 1.92-1.84 (m, 2H), 1.72-1.63 (m, 2H), 1.07 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.5, 142.4, 138.9, 136.3, 130.8, 128.8, 128.3, 126.5, 126.4, 125.7, 125.4, 123.9, 122.9, 122.7, 120.9, 120.7, 119.1, 118.8, 115.3, 115.0, 34.4, 30.5, 30.2, 23.1, 13.9. HRMS (ESI) calcd for $C_{27}H_{26}N^+$: 364.2060 (M + H^+), found: 364.2038.

5-Methyl-11-phenyl-6-(thiophen-3-yl)-5*H*-indeno[1,2-*c*]quinoline (**3n**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 8.1 Hz, 1H), 7.68-7.66 (m, 1H), 7.61-7.59 (m, 2H), 7.55-7.37 (m, 7H), 7.28-7.24 (m, 1H), 7.21-7.20 (m, 1H), 7.11 (t, *J* = 7.7 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.49 (d, *J* = 7.9 Hz, 1H), 3.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.5, 139.2, 138.6, 136.2, 135.3, 130.6, 129.0, 128.8, 128.0, 127.8, 126.6, 126.0, 125.7, 125.2, 124.5, 123.1, 123.0, 120.6, 120.4, 120.3, 118.4, 117.2, 115.5, 36.2. HRMS (ESI) calcd for $C_{27}H_{20}NS^+$: 390.1311 (M + H^+), found: 390.1335.

5,9-Dimethyl-6,11-diphenyl-5*H*-indeno[1,2-*c*]quinoline (**3o**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.1 Hz, 1H), 7.63-7.35 (m, 12H), 7.23 (s, 1H), 7.09 (t, *J* = 7.9 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 6.21 (d, *J* = 8.0 Hz, 1H), 3.56 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.3, 142.9, 138.9, 136.1, 135.7, 134.2, 130.7, 129.5, 129.2, 128.8, 126.8, 126.5, 126.4, 125.7, 123.0, 122.9, 121.9, 120.4, 119.9, 118.4, 116.3, 115.4, 36.3, 21.8. HRMS (ESI) calcd for $C_{30}H_{24}N^+$: 398.1903 (M + H^+), found: 398.1884.

8-Chloro-5-methyl-6,11-diphenyl-5*H*-indeno[1,2-*c*]quinoline (**3p**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.1 Hz, 1H), 7.65-7.49 (m, 8H), 7.44-7.39 (m, 5H), 7.13 (t, *J* = 7.7 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 6.18 (d, *J* = 8.5 Hz, 1H), 3.57 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.6, 143.5, 138.0, 136.0, 135.1, 130.6, 130.3, 129.8, 129.6, 128.9, 127.2, 126.9, 126.8, 126.7, 125.8, 123.4, 122.9, 121.5, 120.3, 119.1, 117.8, 115.7, 115.6, 36.4. HRMS (ESI) calcd for $C_{29}H_{21}ClN^+$: 418.1357 (M + H^+), found: 418.1331.

9-Fluoro-5-methyl-6,11-diphenyl-5*H*-indeno[1,2-*c*]quinoline (**3q**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.0 Hz, 1H), 7.66-7.39 (m, 12H), 7.15-7.06 (m, 2H), 6.62-6.57 (m, 1H), 6.23-6.19 (m, 1H), 3.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.4 (d, J_{CF} = 239.5 Hz), 143.9, 143.8, 138.5, 136.0, 135.3, 130.5, 129.7, 129.6, 129.0, 128.9, 127.1, 126.9, 126.8, 125.8, 125.2, 123.2, 122.6, 121.6 (d, $^3J_{CF}$ = 9.4 Hz), 119.5, 115.7, 115.6, 108.1 (d, $^2J_{CF}$ = 24.0 Hz), 103.7 (d, $^2J_{CF}$ = 22.7 Hz), 36.4. HRMS (ESI) calcd for $C_{29}H_{21}FN^+$: 402.1653 (M + H^+), found: 402.1663.

8-Chloro-6-(4-methoxyphenyl)-5-methyl-11-phenyl-5*H*-indeno[1,2-*c*]quinoline (**3r**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.0 Hz, 1H), 7.58-7.51 (m, 5H), 7.45-7.33 (m, 6H), 7.19-7.10 (m, 4H), 6.38 (s, 1H), 3.97 (s, 3H), 3.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.7, 145.1, 140.5, 138.3, 136.2, 130.6, 130.3, 130.2, 128.8, 127.1, 126.8, 126.7, 125.9, 125.6, 124.3, 123.4, 123.1, 120.5, 119.3, 119.1, 115.8, 115.1, 55.6, 36.4. HRMS (ESI) calcd for $C_{30}H_{23}ClNO^+$: 448.1463 (M + H^+), found: 448.1461.

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Notes and references

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