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Note

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Synthesis of Quinolines and Pyrido[3,2-*g* or 2,3-*g*]quinolines Catalyzed by Heterogeneous Propylphosphonium Tetrachloroindate Ionic Liquid

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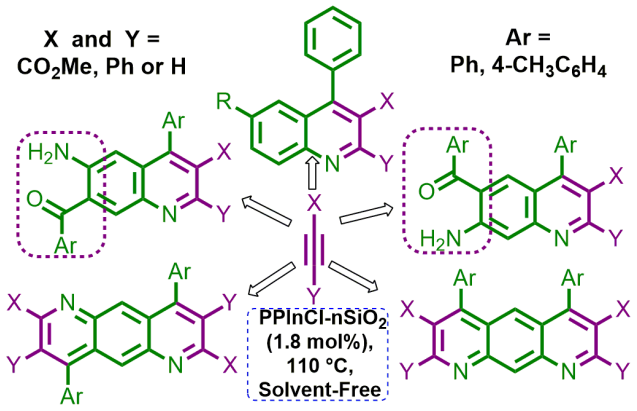
ABSTRACT



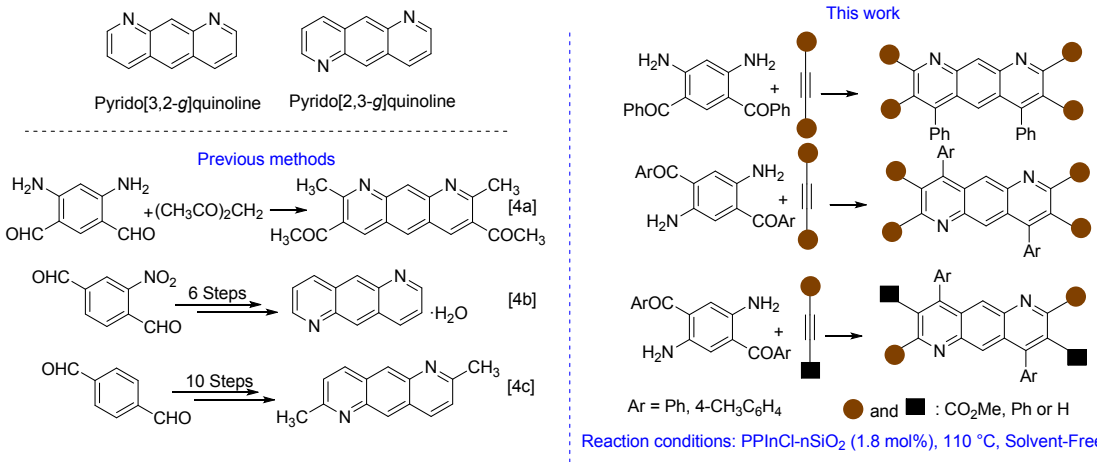
This report explains an efficient method for synthesis of an array of quinolines, via the reaction of 2-aminoaryl ketones with terminal and internal alkynes in the presence of propylphosphonium tetrachloroindate ionic liquid supported on nano-silica (PPInCl-nSiO_2) as a heterogeneous and reusable catalyst under solvent-free conditions. Inspired by this catalytic system, the first easy one-step synthesis of symmetric and unsymmetric pyrido[3,2-*g* or 2,3-*g*]quinolines was investigated through the reaction of diaroylphenylenediamines with one alkyne or two different alkynes.

Quinolines are an important class of nitrogen containing heterocycles, which has been investigated extensively in terms of biological activities, medicinal applications, electric and photonic usages.[1] Due to their importance, several methods such as Skraup, Combes, Friedlander and Doebner–Von have been reported for the synthesis of quinolines.[2] Recently, the condensation of 2-aminoaryl ketones and alkynes in the presence of various catalysts and reagents under different reaction conditions have also been used fot the synthesis of these compounds.[3] However, some of the reported methods suffer from one or more of the disadvantages such as the use of toxic reagents and solvents, costly catalysts, unsatisfactory reaction times and yields, large amounts of catalysts, tedious workup and lack of recovery and reuse of the catalyst from homogenous reaction mixture. More importantly, the simple quinoline derivatives are mostly synthesized by these procedures. In addition, during the past years, little attention has been paid to the synthesis of pyrido[3,2-*g*]quinolines and pyrido[2,3-*g*]quinolines, and only a few reports

involving harsh conditions and multi-steps reactions are available for the prepartation of some derivatives of thes heterocycles[4] (Scheme 1).

In continuation of our interest on the constraction of quinoline deriveitives using heterogeneous catalysts,[5] herein, we describe a straightforward method for the synthesis of various substituted quinolines, novel quinolines containing one 2-aminoaryl ketone unit in the backbone, novel symmetric and unsymmetric pyrido[3,2-*g* or 2,3-*g*]quinolines using propylphosphonium tetrachloroindate ionic liquid supported on nano-silica (PPInCl-nSiO_2) as an efficient heterogeneous catalyst under solvent-free conditions (Scheme 1).

Scheme 1. Some examples and the proposed strategy for synthesis of pyrido[3,2-*g*]quinolines and pyrido[2,3-*g*]quinolines



Recently, we reported propylphosphonium hydrogen carbonate ionic liquid supported on nano-silica (PPHC-nSiO_2) for the synthesis of various fully substituted pyridines.[6] In the present study, after some preliminary experiments upon the effect of catalyst on the yield of quinolines, the propylphosphonium tetrachloroindate ionic liquid supported on nano-silica (PPInCl-nSiO_2, Figure 1) was prepared and selected as catalyst for quinoline synthesis (for more details, see the Experimental section and Supporting information). The indium content of PPInCl-nSiO_2 is 0.725 mmol per gram of the catalyst as determined by ICP analysis.

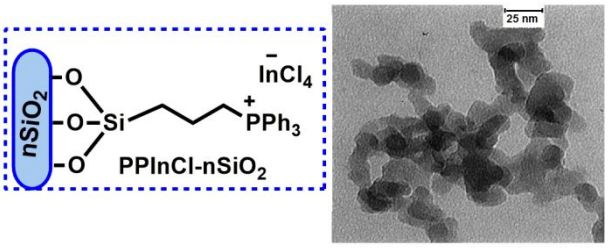


Figure 1. The schematic structure of PPInCl-nSiO_2 along with its TEM image

The reaction conditions of 2-amino-5-chlorobenzophenone **1b** and dimethyl acetylenedicarboxylate (DMAD, **2a**) was investigated in point of molar ratios of substrates, the amount of catalyst and temperature. The optimized conditions to give the highest yield of the desired quinoline was found to be; 1:1.3 molar ratio of **1b**:**2a**, 1.8 mol% PPInCl-nSiO_2 (25 mg of catalyst) at 110 °C under solvent-free conditions (Table 1, entry 7).

Table 1: Optimization of reaction conditions

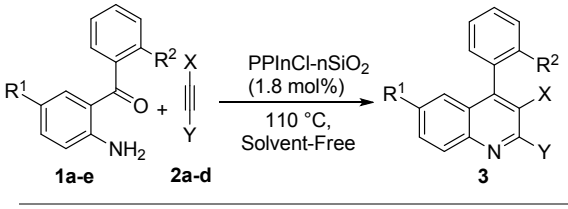
Entry	Catalyst (mol%)[a]	1b:2a (eq:eq)[b]	T (°C)	Time (h)	Yield (%)[c]
1	3.6	1:1.5	110	0.5	99
2	1.8	1:1.5	110	0.5	99
3	1.0	1:1.5	110	2	76
4	3.6	1:1	110	2	70
5	1.8	1:1	110	2	67
6	1.8	1:1.2	110	2	86
7	1.8	1:1.3	110	0.5	99
8	1.8	1:1.3	80	2	64
9	1.8	1:1.3	100	2	81
10	1.8	1:1.3	120	0.5	98

[a] Reaction of 2-amino-5-chlorobenzophenone **1b** and DMAD **2a** in the presence of PPInCl-nSiO_2, according to ICP analysis : 50 mg (3.6 mol% In), 25 mg (1.8 mol% In) and 15 mg (1.0 mol% In). [b] 2-Amino-5-chlorobenzophenone **1b** : DMAD **2a**. [c] Isolated yield.

The substrates scope of this protocol was then investigated using the optimized conditions. As shown in Scheme 2, different 2-aminoaryl ketones were reacted with internal alkynes such as DMAD **2a** or diphenylacetylene **2b** in the presence of PPInCl-nSiO_2, to afford the desired 2,3,4-trisubstituted quinolines (**3aa**-**3ea** and **3bb**-**3eb**) in good to excellent yields (65-99%). Furthermore, the reaction of 2-aminoaryl ketones with terminal alkynes including methyl propiolate **2c** and phenylacetylene **2d** was performed under the same conditions in orther to find out the selectivity of this catalyst. When methyl propiolate **2c** were treated with 2-amino-5-chlorobenzophenone **1b** and/or 2-amino-5-chloro-2´-

fluorobenzophenone **1d**, good yields of the corresponding 3,4-disubstituted quinolines (**3bc** and **3dc**) were selectively obtained. On the contrary, the reaction of phenylacetylene **2d** with 2-aminoaryl ketones selectively gave the corresponding 2,4-disubstituted quinolines (**3bd-3ed**) in 50-95% yields. The structures of **3dc** and **3cd** as representative compounds were confirmed by X-ray crystallographic analysis (Figure 2, CCDC of **3dc**: 1857298 and CCDC of **3cd**: 1857297).

Scheme 2. Reaction of 2-aminoaryl ketones and alkynes catalyzed by PPInCl-nSiO_2



2a: X = Y = CO_2Me

3aa, R^1 = H, R^2 = H, 98% (20 min)
3ba, R^1 = Cl, R^2 = H, 99% (30 min)
3ca, R^1 = Cl, R^2 = Cl, 88% (20 min)
3da, R^1 = Cl, R^2 = F, 98% (20 min)
3ea, R^1 = NO_2, R^2 = H, 75% (25 min)

2b: X = Y = Ph

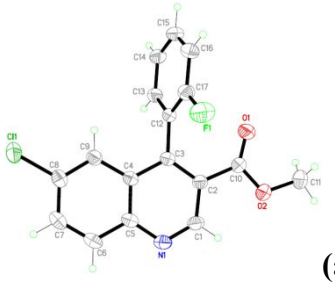
3bb, R^1 = Cl, R^2 = H, 67% (1 h)
3cb, R^1 = Cl, R^2 = Cl, 72% (1 h)
3eb, R^1 = NO_2, R^2 = H, 65% (1 h)

2c: X = CO_2Me, Y = H

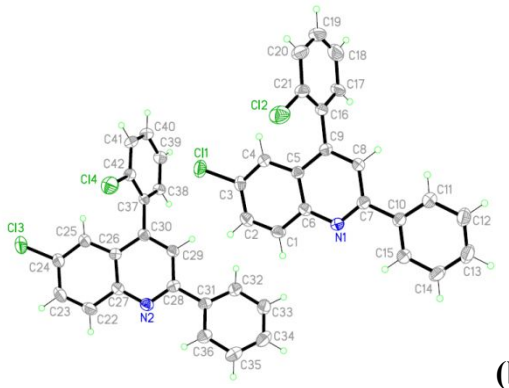
3bc, R^1 = Cl, R^2 = H, 79% (1 h)
3dc, R^1 = Cl, R^2 = F, 66% (1 h)

2d: X = H, Y = Ph

3bd, R^1 = Cl, R^2 = H, 87% (45 min)
3cd, R^1 = Cl, R^2 = Cl, 98% (35 min)
3dd, R^1 = Cl, R^2 = F, 95% (35 min)
3ed, R^1 = NO_2, R^2 = H, 50% (1 h)



(a)



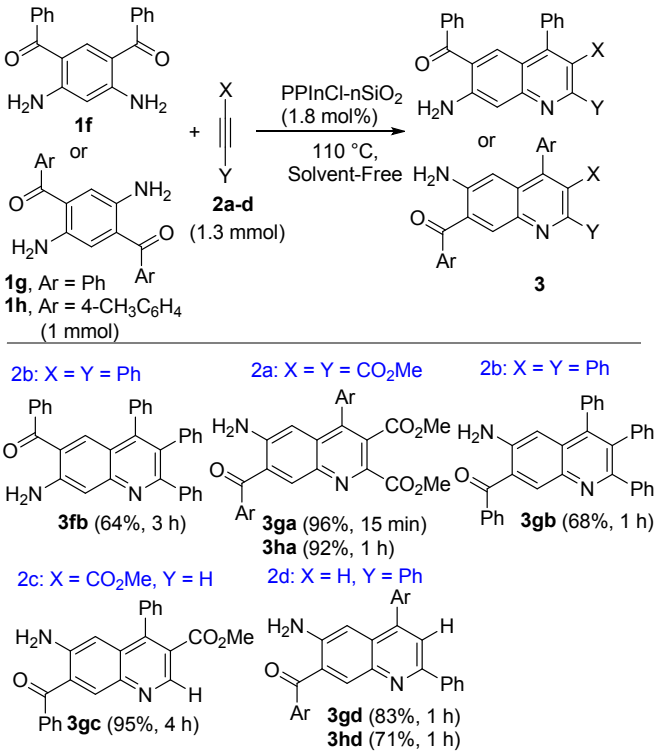
(b)

Figure 2. Molecular structures of **3dc** (a) and **3cd** (b), showing 40% probability displacement ellipsoids and the atomic numbering

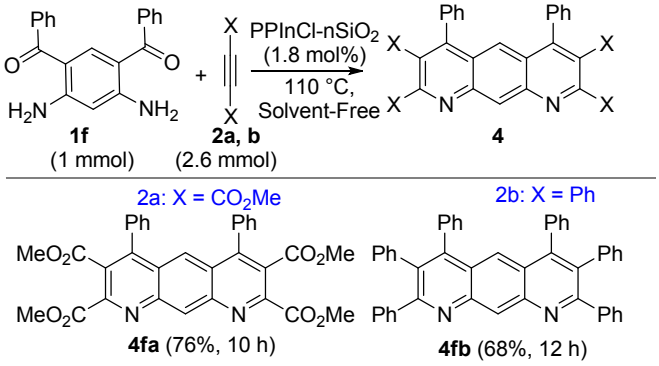
The synthesis of quinolines was also examined with substrates containing two 2-aminoaryl ketone units such as 4,6-dibenzoyl-1,3-phenylenediamine **1f**, 2,5-dibenzoyl-1,4-phenylenediamine **1g** and 2,5-ditolyl-1,4-phenylendiamine **1h**. As shown in Scheme 3, when compounds **1f-h** were reacted with alkynes **2a-d** in 1:1.3 molar ratios, only one of the 2-aminoaryl ketone groups took part selectively to afford the respected quinolines in high yields. Importantly, the remaining 2-aminoaryl ketone group on the quinoline backbone can be transformed to some other useful functional groups.

Another exceptional aspect of this catalytic system lies in the preparation of various pyrido[3,2-*g*]quinolines and pyrido[2,3-*g*]quinolines. As evident from Scheme 4, treatment of 4,6-dibenzoyl-1,3-phenylenediamine **1f** (1 mmol) and alkynes **2a**, **2b** (2.6 mmol) in the presence of PPInCl-nSiO_2 at 110 °C provided the related pyrido[3,2-*g*]quinolines in high yields within 10-12 h.

Scheme 3. Selective synthesis of quinolines containing 2-aminoaryl ketone group

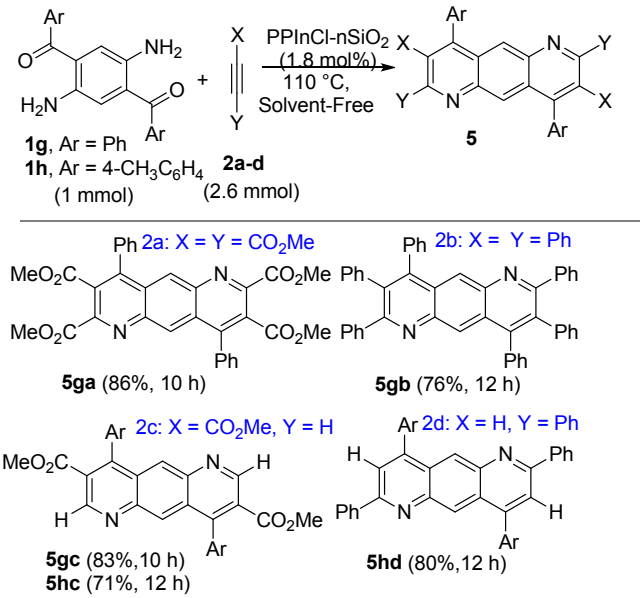


Scheme 4. Preparation of pyrido[3,2-*g*] quinolines



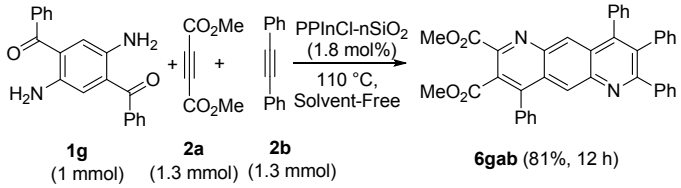
Similarly, the reaction of 2,5-diaroyl-1,4-phenylenediamines (**1g** and **1h**, 1 mmol) with alkynes **2a-d** (2.6 mmol) under the optimized conditions led to a variety of symmetric pyrido[2,3-*g*]quinolines in high yields (Scheme 5).

Scheme 5. Synthesis of symmetric pyrido[2,3-*g*]quinolines



Encouraged by the above mentioned promising results, we turned our attention to the one-pot, three-component reaction of 2,5-dibenzoyl-1,4-phenylenediamine **1g** (1 mmol) with two different alkynes, DMAD **2a** (1.3 mmol) and diphenylacetylene **2b** (1.3 mmol). Interestingly, the corresponding unsymmetric pyrido[2,3-*g*]quinoline **6gab** was obtained in 81% yield (Scheme 6). It is worth mentioning that the synthesis of quinolines and pyrido[3,2-*g* or 2,3-*g*]quinolines (Schemes 3-6) from diaroylphenylenediamines **1f-h** is reported for the first time which clearly indicates the novelty and applicability of this catalytic method and makes this protocol very useful and effective for the preparation of these vital heterocyclic compounds. Another outstanding feature of this method is that such complex molecules are prepared via a single step.

Scheme 6. Synthesis of unsymmetric pyrido[2,3-*g*]quinoline



As reported in the literature, tetrachloroindate(III) ionic liquid has been used as a Lewis acidic catalyst. [7] Accordingly, a plausible mechanism for the selective synthesis of 3,4- and 2,4-disubstituted quinolines in the presence of PPInCl-nSiO_2 is proposed in Scheme S1. First, the amino group of 2-aminoaryl ketone **1** attacks the terminal carbon of methyl propiolate **2c** in the presence of the catalyst to give

intermediate **A**, in which the negative charge is stabilized by the carbonyl group of the ester. Then, **A** is converted to β-enamino ester **B** by a prototropic shift from nitrogen to carbon. Finally, intramolecular nucleophilic addition of carbon of β-enamino ester to the activated carbonyl group affords intermediate **C**, which upon dehydration in the presence of the catalyst results in the desired 3,4-disubstituted quinoline selectively. For selective formation of 2,4-disubstituted quinoline, on the basis of observed regiochemistry confirmed by X-ray analysis of **3cd**, it is reasonable to assume that nucleophilic addition of phenylacetylene to the activated carbonyl group of 2-aminoaryl ketone **1** gives intermediate **D**, in which prototropic shift from carbon to oxygen affords propargylic alcohol **E**. Next, the alcohol is transformed to the corresponding enone **G** by Meyer-Schuster rearrangement (via the intermediate allenol **F**),[8] which upon cyclization and subsequent dehydration in the presence of the catalyst gives the related 2,4-disubstituted quinoline selectively.

The reusability of PPInCl-nSiO_2 which is very important from environmental and economical points of view, was examined in the synthesis of **3ba**. Upon reaction completion, the mixture was diluted with EtOAc and the catalyst was separated, dried and then reused for subsequent reactions. The catalyst could be reused at least 5 times without a significant loss of its activity (Table 2).

Table 2: Reusability of PPInCl-nSiO_2 in the synthesis of 3ba

Entry [a]	1	2	3	4	5	6
Yield (%)[b]	99	99	98	97	97	95

[a] Reaction conditions: 2-amino-5-chlorobenzophenone (**1b,** 1 mmol), DMAD (**2a,** 1.3 mmol) and PPInCl-nSiO_2 catalyst (1.8 mol%), 110 °C. [b] Isolated yield.

To sum up, we presented a new catalytic strategy for the efficient synthesis of quinolines via the reaction of various 2-aminoaryl ketones with terminal and internal alkynes in the presence of

heterogeneous propylphosphonium tetrachloroindate ionic liquid supported on nano-silica catalyst (PPInCl-nSiO_2) under solvent-free conditions. Selective synthesis of novel quinolines containing one 2-amino arylketone group was also carried out using this catalytic system. Also, for the first time, a variety of symmetric and unsymmetric pyrido[3,2-*g*]quinolines and pyrido[2,3-*g*]quinolines were prepared by the reaction of diaroylphenylenediamines with one alkyne or two different alkynes. Notably, the PPInCl-nSiO_2 catalyst could be recovered and reused several times by preserving its activity.

EXPERIMENTAL SECTION

General information

The chemicals used in this work were purchased from Fluka and Merck chemical companies. The substrates containing two 2-aminoaryl ketone units **1f-h** were prepared according to reported method.[9] Melting points were determined with a Stuart Scientific SMP2 apparatus. FT-IR spectra were recorded on a Nicolet-Impact 400D spectrophotometer. ^{1}H and ^{13}C NMR (400 and 100 MHz) spectra were recorded on a Bruker Avance 400 MHz spectrometer using $CDCl_3$ solvent. The UV–vis diffuse reflectance spectra of the samples were recorded on a JASCO V-670 spectrophotometer. Elemental analysis was performed on a LECO, CHNS-932 analyzer. Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer STA 6000 instrument under argon flow at a uniform heating rate of 20 °C min^{-1} in the range 30-600 °C. The scanning electron microscope (SEM) measurement was carried out on a Hitachi S-4700 field emission-scanning electron microscope. The transmission electron microscopy (TEM) was carried out on a Philips CM10 instrument operating at 100 kV. The indium content of the catalyst was determined by a Jarrell-Ash 1100 ICP analyzer.

Preparation and characterization of propylphosphonium tetrachloroindate ionic liquid supported on nano-silica (PPInCl-nSiO_2)

First, a mixture of 3 mL 3-chloropropyltrimethoxysilane (CPTMS) and nano-SiO_2 (2 g) in 25 mL anhydrous toluene was refluxed for 24 h. The reaction mixture was cooled to room temperature and

filtered. The solid material was washed with toluene (40 mL) and a mixture of water-ethanol (40 mL, 1:1) to give chloropropylated nano-silica (CP-nSiO_2). Then, a mixture of CP-nSiO_2 (2 g) and triphenylphosphine (8 g) in anhydrous toluene (25 mL) was refluxed under N_2 atmosphere for 24 h. After cooling to room temperature, the mixture was filtered and the solid material was washed with toluene (40 mL) and ethanol (20 mL) to afford propylphosphonium chloride supported on nano-silica (PPCl-nSiO_2). Finally, a mixture of PPCl-nSiO_2 (0.5 g) and indium chloride (0.442 g, 2 mmol) in toluene (10 mL) was stirred vigorously at 50 °C under N_2 atmosphere for 12 h. The mixture was filtrated and the solid material was washed with toluene (20 mL) and then dried under vacuum at 70 °C to afford propylphosphonium tetrachloroindate ionic liquid supported on nano-silica (PPInCl-nSiO_2, Supporting information, Figure S1). The prepared nanocatalyst was characterized by FT-IR, diffuse reflectance UV–vis spectroscopy, TGA/DTG, SEM, TEM, and ICP. FT-IR spectra of nano-silica (nSiO_2) and propylphosphonium tetrachloroindate ionic liquid supported on nano-silica (PPInCl-nSiO_2) are presented in Figure S2. The characteristic bands at 3060 (sp^2 C–H), 2931 and 1438 (C–H stretching of the alkyl chain), 1101, 807 and 468 (Si–O), 1620 (C=C), 1482 and 789 cm^{-1} (P–C) were detected which indicate the desired catalyst (PPInCl-nSiO_2) has been prepared. The diffuse reflectance UV–vis spectra of nSiO_2, PPCl–nSiO_2 and PPInCl-nSiO_2 are shown in Figure S3. No absorption peak was observed for nano-silica in the UV–vis spectrum. But PPCl-nSiO_2 showed two significant absorption peaks at 228 nm corresponds to $\pi \rightarrow \pi^*$ transition of C=C phenyl groups and at 271 nm related to $n \rightarrow \pi^*$ lone electron pair in P-Ph.[10] The same absorption peaks at 230 and 271 nm were detected for PPInCl-nSiO_2 catalyst. Also, a new absorption peak was observed at 196 nm which is related to a d-d transition of indium.[11] The TGA/DTG curves for PPInCl-nSiO_2 catalyst was shown in Figure S4. The observed total weight loss is 44.35%. The first step loss relates to removal of the physically adsorbed water (100-130 °C, 3.03 %), whereas, the main weight loss corresponds to removal of the organic moieties from the surface (350-600 °C, 41.32%). As indicated, the decomposition occurred in the range of 350-600 °C. This high thermal stability provides good activity of the catalyst without any considerable leaching of the active species at high temperature reaction. The morphology of the nano-SiO_2 and PPInCl-nSiO_2 catalysts was investigated by scanning electron microscopy (Figure S5). The morphology of the catalyst

is different from that of nano-SiO_2, indicating IL has been immobilized on the nanoparticles. The energy dispersive X-ray (EDX) results, obtained from SEM analysis of PPInCl-nSiO_2, is shown in Figure S6. The presence of all the expected elements C, O, Si, Cl, P and In, indicates that the catalyst (PPInCl-nSiO_2) has been prepared. The size and morphology of the PPInCl-nSiO_2 catalyst was also investigated by transmission electron microscopy (TEM, Figure S7). The dark colored regions or black spots in the photograph correspond to the indium species, while the colorless parts are related to nano-silica particles.[12] The histogram of size distribution showed that the particles diameter are in the range of 18-26 nm (Figure S8).

Investigation of the effect of catalyst for the synthesis of quinoline: In order to demonstrate the usefulness of the catalyst, the reaction of 2-amino-5-chlorobenzophenone **1b** and dimethylacetylenedicarboxylate (DMAD, **2a**) was performed in the absence of the catalyst at 110 °C; no desired product was obtained under this conditions even after 10 h (Table S1). Then, the reaction was performed in the presence of different catalysts such as $H_3PW_{12}O_{40}$, *p*-TSA, $BiCl_3$, $FeCl_3$, $ZnCl_2$, $AlCl_3$, nano-silica, propylphosphonium hydrogen carbonate ionic liquid supported on nano-silica (PPHC-nSiO_2),[6] propylphosphonium tetrachloroindate ionic liquid supported on nano-silica (PPInCl-nSiO_2). The results listed in Table S1, clearly indicate that PPInCl-nSiO_2 is the best catalyst for this transformation. In order to show the advantages of supporting of IL on nanoparticles and also to examine the effect of particle size on the activity of the catalyst, the model reaction was also performed in the presence of $InCl_3$ and homogenous butylphosphonium tetrachloroindate ([BuP]$InCl_4$). Under these conditions the desired product was obtained in 60% and 71% for $InCl_3$ and [BuP]$InCl_4$, respectively, which are considerably lower than the yield obtained with PPInCl-nSiO_2. These results clearly showed that the supporting of IL on nano-silica leads to isolation of the active sites and therefore, the activity of the catalyst is improved compared to the bulk $InCl_3$ and butylphosphonium tetrachloroindate.

Synthesis of quinoline derivatives catalyzed by PPInCl-nSiO_2 (Scheme 2): A mixture of 2-aminoaryl ketone (1 mmol), alkyne (1.3 mmol), and PPInCl-nSiO_2 catalyst (25 mg, containing 0.018 mmol In, 1.8 mol%) was stirred at 110 °C under solvent-free conditions. The progress of the reaction

was monitored by TLC. After completion of the reaction, the mixture was cooled to room temperature and then EtOAc (10 mL) was added. The catalyst was separated by filtration and washed with EtOAc (10 mL). The filtrate was evaporated and the crude product was purified by recrystallization from EtOH or silica gel column chromatography to afford the pure product.

*Dimethyl4-phenylquinoline-2,3-dicarboxylate (**3aa**):* Purified by recrystallization from EtOH. Yield: 98% (314.60 mg). M.p = 124-126 °C (124-125 °C)[13]. FT-IR (KBr): ν_{max} = 3446, 3064, 2993, 2951, 2924, 2853, 1739, 1616, 1561, 1484, 1447, 1370, 1305, 1244, 1204, 1100, 1049, 975, 849, 757 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.67 (s, 3H), 4.10 (s, 3H), 7.38-7.40 (m, 2H), 7.52-7.54 (m, 3H), 7.62-7.68 (m, 2H), 7.83-7.88 (m, 1H), 8.35 (d, *J* = 8.8 Hz, 1H).

*Dimethyl 6-chloro-4-phenylquinoline-2,3-dicarboxylate (**3ba**):* Purified by recrystallization from EtOH. Yield: 99% (349.71 mg). M.p = 160-162 °C (164-165 °C)[13]. FT-IR (KBr): ν_{max} = 3426, 3049, 2952, 2923, 1907, 1742, 1722, 1604, 1558, 1480, 1446, 1395, 1366, 1294, 1240 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.66 (s, 3H), 4.09 (s, 3H), 7.36-7.38 (m, 2H), 7.55-7.56 (m, 3H), 7.62 (d, *J* = 2.0 Hz, 1H), 7.77 (dd, ^1J = 6.8 Hz, ^2J = 2.4 Hz, 1H), 8.28 (d, *J* = 9.2 Hz, 1H).

*Dimethyl 6-chloro-4-(2-chlorophenyl)quinoline-2,3-dicarboxylate (**3ca**):* Purified by silica gel column chromatography (eluent: petroleum ether/EtOAc, 2:1). Yield: 88% (342.12 mg). M.p = 188-190 °C (190-192 °C)[14]. FT-IR (KBr): ν_{max} = 3431, 3065, 2923, 2962, 2662, 1787, 1729, 1557, 1470, 1439, 1396, 1365, 1318, 1300, 1242, 1222, 1129, 1062 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.66 (s, 3H), 4.07 (s, 3H), 7.26 (s, 1H), 7.28-7.32 (m, 2H), 7.49 (t, *J* = 2.0 Hz, 1H), 7.53-7.57 (m, 1H), 7.77 (dd, ^1J = 6.8 Hz, ^2J = 2.4 Hz, 1H), 8.27 (d, *J* = 9.2 Hz, 1H).

*Dimethyl 6-chloro-4-(2-fluorophenyl)quinoline-2,3-dicarboxylate (**3da**):* Purified by recrystallization from EtOH. Yield: 98% (365.07 mg). M.p = 199-201 °C. FT-IR (KBr): ν_{max} = 3427, 3077, 2954, 2850, 1728, 1665, 1612, 1559, 1480, 1442, 1399, 1303, 1247, 1224, 1146, 1104, 1053, 957, 835 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.66 (s, 3H), 4.09 (s, 3H), 7.28 (dd, ^1J = 6.0 Hz, ^2J = 1.6 Hz, 1H), 7.39 (d, *J* = 2.0 Hz, 1H), 7.43 (td, ^1J = 6.4 Hz, ^2J = 1.2 Hz, 1H), 7.49 (td, ^1J = 6.4 Hz, ^2J = 1.6 Hz, 1H), 7.59 (dd, ^1J = 6.8 Hz, ^2J = 1.2 Hz, 1H), 7.78 (dd, ^1J = 6.8 Hz, ^2J = 2 Hz, 1H), 8.30 (d, *J* =9.2 Hz, 1H). ^{13}C NMR

(100 MHz, $CDCl_3$): δ = 166.3, 164.7, 160.2 (d, $^1J_{CF}$ = 240 Hz), 145.1, 144.8, 141.3, 135.5, 131.9, 131.8, 131.2, 131.1, 130.7, 130.6, 127.9, 127.7, 124.5, 123.9, 123.8, 121.1, 120.9, 115.6 (d, $^2J_{CF}$ = 20 Hz), 53.1, 52.2. Anal. Calcd for $C_{19}H_{13}ClFNO_4$: C, 61.06; H, 3.51; N, 3.75. Found: C, 61.19; H, 3.55; N, 3.68.

*Dimethyl 6-nitro-4-phenylquinoline-2,3-dicarboxylate (**3ea**):* Purified by silica gel column chromatography (eluent: petroleum ether/EtOAc, 2:1). Yield: 75% (273.24 mg). M.p = 190-192 °C. FT-IR (KBr): ν_{max} = 3440, 3097, 2955, 2924, 2853, 1917, 1746, 1728, 1620, 1575, 1535, 1482, 1438, 1370, 1347, 1218, 1151, 1088, 1051 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.69 (s, 3H), 4.12 (s, 3H), 7.39-7.41 (m, 2H), 7.59-7.61 (m, 3H), 8.49-8.51 (m, 1H), 8.59-8.61 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.2, 164.4, 149.9, 148.4, 147.7, 146.8, 132.5, 132.0, 129.3, 128.7, 128.3, 128.1, 126.5, 123.9, 122.9, 53.3, 52.3. Anal. Calcd for $C_{19}H_{14}N_2O_6$: C, 62.30; H, 3.85; N, 7.65. Found: C, 62.40; H, 3.80; N, 7.58.

*6-Chloro-2,3,4-triphenylquinoline (**3bb**):* Purified by silica gel column chromatography (eluent: petroleum ether/EtOAc, 4:1). Yield: 67% (260.34 mg). M.p = 191-193 °C (193-194 °C)[3a]. FT-IR (KBr): ν_{max} = 3426, 3059, 3021, 2959, 2923, 1802, 1730, 1603, 1543, 1468, 1443, 1367, 1344, 1287, 1122, 1075, 1024, 699 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.86-6.89 (m, 2H), 7.00-7.02 (m, 2H), 7.11-7.13 (m, 2H), 7.21-7.22 (m, 2H), 7.25-7.26 (m, 1H), 7.28-7.30 (m, 3H), 7.35-7.37 (m, 2H), 7.54-7.55 (m, 1H), 7.65-7.74 (m, 2H), 8.17-8.20 (m, 1H).

*6-Chloro-4-(2-chlorophenyl)-2,3-diphenylquinoline (**3cb**):* Purified by silica gel column chromatography (eluent: petroleum ether/EtOAc, 2:1). Yield: 72% (304.50 mg). M.p = 184-186 °C. FT-IR (KBr): ν_{max} = 3423, 3058, 2921, 2654, 1725, 1607, 1588, 1468, 1440, 1343, 1263, 1223, 1153, 1111, 1078, 1030, 929, 756, 700 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.86-6.87 (m, 1H), 7.03-7.04 (m, 4H), 7.16-7.20 (m, 1H), 7.21-7.24 (m, 4H), 7.31 (d, J = 2.2 Hz, 1H), 7.38-7.41 (m, 4H), 7.66 (dd, ^1J = 6.7 Hz, ^2J = 2.3 Hz, 1H), 8.19 (d, J = 8.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.4, 145.6, 144.4, 140.5, 137.7, 135.6, 134.2, 133.7, 132.8, 131.7, 131.5, 130.7, 130.5, 129.9, 129.5, 129.4, 127.9, 127.8, 127.3, 126.9, 126.8, 126.6, 124.8. Anal. Calcd for $C_{27}H_{17}Cl_2N$: C, 76.06; H, 4.02; N, 3.29. Found: C, 76.19; H, 3.98; N, 3.21.

*6-Nitro-2,3,4-triphenylquinoline (**3eb**):* Purified by silica gel column chromatography (eluent: petroleum ether/EtOAc, 2:1). Yield: 65% (259.98 mg). M.p = 179-181 °C. FT-IR (KBr): ν_{max} = 3430, 3056, 3028, 2966, 2952, 2922, 1808, 1728, 1616, 1597, 1576, 1549, 1521, 1464, 1339, 1282, 1123, 1074, 1027, 700 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.88 (dd, ^1J = 5.8 Hz, ^2J = 1.5 Hz, 2H), 7.04-7.05 (m, 3H), 7.12-7.14 (m, 2H), 7.33-7.35 (m, 3H), 7.38 (dd,^1J = 6.2 Hz, ^2J = 1.4 Hz, 3H), 7.52-7.55 (m, 1H), 7.74 (d, J = 7.2 Hz, 1H), 8.35 (d, J = 9.2 Hz, 1H), 8.48 (dd, ^1J = 6.7 Hz, ^2J = 2.5 Hz, 1H), 8.55 (d, J = 2.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.5, 149.7, 149.4, 145.6, 140.3, 137.3, 135.4, 134.8, 131.5, 131.1, 130.1, 129.9, 128.4, 128.3, 128.2, 127.9, 127.7, 126.9, 125.9, 123.8, 122.9. Anal. Calcd for $C_{27}H_{18}N_2O_2$: C, 85.58; H, 4.51; N, 6.96. Found: C, 85.73; H, 4.54; N, 7.03.

*Methyl 6-chloro-4-phenylquinoline-3-carboxylate (**3bc**):* Purified by silica gel column chromatography (eluent: petroleum ether/EtOAc, 2:1). Yield: 79% (230.87 mg). yellow gummy mass[13]. FT-IR (KBr): ν_{max} = 3436, 3060, 2951, 2850, 1727, 1577, 1483, 1439, 1353, 1300, 1260, 1216, 1126, 1077, 840, 758 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.71 (s, 3H), 7.29-7.32 (m, 2H), 7.55-7.57 (m, 3H), 7.59 (d, J = 2.0 Hz, 1H), 7.75 (dd, ^1J = 6.8 Hz, ^2J = 2.0 Hz, 1H), 8.18 (d, J = 9.2 Hz, 1H), 9.35 (s, 1H).

*Methyl 6-chloro-4-(2-fluorophenyl)quinoline-3-carboxylate (**3dc**):* Purified by silica gel column chromatography (eluent: petroleum ether/EtOAc, 2:1). Yield: 66% (205.68 mg). M.p = 164-166 °C. FT-IR (KBr): ν_{max} = 3432, 3028, 2959, 2924, 2853, 1726, 1616, 1575, 1483, 1443, 1355, 1286, 1214, 1125, 1102, 1074, 600 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.79 (s, 3H), 7.24-7.28 (m, 1H), 7.31-7.37 (m, 2H), 7.53-7.56 (m, 2H), 7.76 (dd, ^1J = 6.6 Hz, ^2J = 2.3 Hz, 1H), 8.16 (d, J = 9.0 Hz, 1H), 9.45 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.1, 158.3, 149.9, 142.1 (d, $^1J_{CF}$ = 160 Hz), 131.8, 130.9, 130.4, 130.3, 130.1, 130.0, 128.5, 127.7, 125.2, 123.7, 123.6, 115.3 (d, $^2J_{CF}$ = 22 Hz), 52.0. Anal. Calcd for $C_{17}H_{11}ClFNO_2$: C, 64.67; H, 3.51; N, 4.44. Found: C, 64.89; H, 3.48; N, 4.37.

*6-Chloro-2,4-diphenylquinoline (**3bd**):* Purified by silica gel column chromatography (eluent: petroleum ether/EtOAc, 2:1). Yield: 87% (273.15 mg). M = 98-99 °C (98-99 °C)[5a]. FT-IR (KBr): ν_{max} = 3431, 3056, 3028, 2927, 1896, 1588, 1538, 1480, 1443, 1355, 1240, 1146, 1074, 886, 823, 788, 700

Cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.49-7.60 (m, 8H), 7.69 (dd, ^1J = 6.6 Hz, ^2J = 2.3 Hz, 1H), 7.87 (s, 1H), 7.89 (d, J = 2.3 Hz, 1H), 8.19-8.22 (m, 3H).

*6-Chloro-4-(2-chlorophenyl)-2-phenylquinoline (**3cd**):* Purified by recrystallization from EtOH. Yield: 98% (341.62 mg). M.p = 110-112 °C (112-114 °C)[5a]. FT-IR (KBr): ν_{max} = 3429, 3344, 3214, 3056, 3025, 2920, 2660, 1598, 1585, 1542, 1470, 1435, 1353, 1227, 1156, 1128, 1053, 1029, 885, 829 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.40 (dd, ^1J = 5.4 Hz, ^2J = 1.8 Hz, 1H), 7.46-7.58 (m, 6H), 7.62 (dd, ^1J = 6.3 Hz, ^2J = 1.6 Hz, 1H), 7.69 (dd, ^1J = 6.7 Hz, ^2J = 2.3 Hz, 1H), 7.85 (s, 1H), 8.20 (s, 2H), 8.21-8.23 (m, 1H).

*6-Chloro-4-(2-fluorophenyl)-2-phenylquinoline (**3dd**):* Purified by recrystallization from EtOH. Yield: 95% (314.74 mg). M.p = 125-127 °C (124-126 °C)[5a]. FT-IR (KBr): ν_{max} = 3426, 3059, 3032, 1615, 1588, 1542, 1479, 1447, 1360, 1352, 1256, 1232, 1207, 1073, 1025, 884, 753 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ =7.40-7.49 (m, 2H), 7.54-7.67 (m, 5H), 7.76-7.80 (m, 2H), 7.98 (s, 1H), 8.29-8.31 (m, 3H).

*6-Nitro-2,4-diphenylquinoline (**3ed**):* Purified by silica gel column chromatography (eluent: petroleum ether/EtOAc, 2:1). Yield: 50% (161.7 mg). M.p: 265-266 °C (265-266 °C)[5a]. FT-IR (KBr): ν_{max} = 3414, 3067, 2958, 2924, 2855, 1729, 1647, 1462, 1381, 1339, 1282, 1122, 1078, 1041, 743, 700 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ =7.52-7.65 (m, 8H), 7.99 (s, 1H), 8.24 (dd, ^1J = 6.4 Hz, ^2J = 1.7 Hz, 2H), 8.33 (d, J = 9.2 Hz, 1H), 8.49 (dd, ^1J = 6.7 Hz, ^2J = 2.5 Hz, 1H), 8.86 (d, J = 2.4 Hz, 1H).

Synthesis of quinolines contains 2-aminoaryl ketone group catalyzed by PPInCl-nSiO_2 (Scheme 3): The substrates containing two parts of 2-aminoaryl ketones [**1f**, **1g** and **1h (**1 mmol)],[9] alkyne (1.3 mmol) and PPInCl-nSiO_2 catalyst (25 mg, containing 0.018 mmol In, 1.8 mol%) was stirred at 110 °C under solvent-free conditions. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was cooled to room temperature and then EtOAc (10 mL) was added. The catalyst was separated by filtration and washed with EtOAc (10 mL). The filtrate was evaporated and the crude product was purified by silica gel column chromatography to afford the pure desired quinolines.

*(7-Amino-2,3,4-triphenylquinoline-6-yl)(phenyl)methanone (**3fb**):* Purified by silica gel column chromatography (eluent: petroleum ether/EtOAc, 1.5:1). Yield: 64% (301.30 mg). M.p = 99-100 °C. FT-IR (KBr): ν_{max} = 3429, 3067, 2957, 2926, 2857, 1730, 1642, 1458, 1879, 1282, 1123, 1072, 744, 700, 465 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.80 (s, 2H), 6.76-6.78 (m, 2H), 6.90-6.92 (m, 3H), 6.93-6.96 (m, 2H), 7.02-7.04 (m, 3H), 7.13-7.15 (m, 3H), 7.28-7.31 (m, 5H), 7.36 (s, 1H), 7.54 (m, 2H), 7.69 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.5, 149.3, 141.0, 138.8, 138.2, 136.4, 135.9, 131.9, 131.5, 129.9, 129.8, 129.7, 129.6, 129.2, 128.2, 128.1, 127.9, 127.8, 127.7, 127.6, 127.4, 127.3, 126.2, 122.2, 118.7, 111.2. Anal. Calcd for $C_{34}H_{24}N_2O$: C, 85.69; H, 5.08; N, 5.88. Found: C, 85.82; H, 5.11; N, 5.78.

Anal. Calcd for $C_{34}H_{24}N_2O$: C, 85.69; H, 5.08; N, 5.88. Found: C, 85.82; H, 5.11; N, 5.78.

*Dimethyl 6-amino-7-benzoyl-4-phenylquinoline-2,3-dicarboxylate (**3ga**):* Purified by recrystallization from EtOH. Yield: 96% (418.15 mg). M.p = 183-185 °C. FT-IR (KBr): ν_{max} = 3474, 3370, 3056, 2948, 2924, 2857, 1722, 1644, 1619, 1591, 1484, 1429, 1388, 1283, 1250, 1221, 1176 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.65 (s, 3H), 4.03 (s, 3H), 5.82 (s, 2H), 6.69 (s, 1H), 7.37-7.39 (m, 2H), 7.53-7.55 (m, 5H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.77 (d, *J* = 7.2 Hz, 2H), 8.47 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ =195.5, 171.1, 166.6, 142.5, 138.1, 136.8, 132.6, 129.8, 129.7, 129.4, 129.3, 129.2, 128.9, 128.6, 128.5, 127.3, 108.1, 53.4, 52.5. Anal. Calcd for $C_{26}H_{20}N_2O_5$: C, 70.90; H, 4.58; N, 6.36. Found: C, 71.04; H, 4.54; N, 6.28.

*Dimethyl 6-amino-7-(4-methylbenzoyl)-4-(p-tolyl)quinoline-2,3-dicarboxylate (**3ha**):* Purified by recrystallization from EtOH. Yield: 92% (428.32 mg). M.p = 258-260 °C. FT-IR (KBr): ν_{max} = 3453, 3355, 3056, 2922, 2854, 1744, 1714, 1617, 1486, 1439, 1391, 1299, 1247, 1214, 1183, 1053, 879 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.48 (s, 6H), 3.68 (s, 3H), 4.03 (s, 3H), 5.72 (s, 2H), 6.72 (s, 1H), 7.26-7.29 (m, 1H), 7.31 (t, *J* = 7.4 Hz, 5H), 7.70 (d, *J* = 8.1 Hz, 2H), 8.44 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.5, 165.6, 152.0, 148.5, 143.5, 139.9, 138.7, 137.6, 135.9, 133.6, 132.1, 131.4, 130.1, 129.3, 129.2, 127.7, 126.3, 108.1, 53.4, 52.5, 21.7, 21.4. Anal. Calcd for $C_{28}H_{24}N_2O_5$: C, 71.78; H, 5.16; N, 5.98. Found: C, 71.91; H, 5.19; N, 5.89.

*(6-Amino-2,3,4-triphenylquinoline-7-yl)(phenyl) methanone (**3gb**):* Purified by silica gel column chromatography (eluent: petroleum ether/EtOAc, 2:1). Yield: 68% (320.78 mg). M.p = 268-270 °C. FT-IR (KBr): ν_{max} = 3470, 3350, 3057, 3026, 2954, 1721, 1637, 1609, 1581, 1525, 1478, 1448, 1411, 1317, 1246, 1202, 1177, 1068, 954, 750, 695 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.83 (s, 2H), 6.32 (s, 1H), 7.28 (s, 1H), 7.33-7.43 (m, 7H), 7.51-7.60 (m, 6H), 7.73-7.75 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.5, 169.4, 146.9, 140.2, 139.5, 137.5, 134.2, 131.5, 131.2, 129.3, 129.1, 128.8, 128.4, 128.3, 127.7, 126.3, 119.4, 115.5. Anal. Calcd for $C_{34}H_{24}N_2O$: C, 85.69; H, 5.08; N, 5.88. Found: C, 85.57; H, 5.05; N, 5.97.

*Methyl 6-amino-7-benzoyl-4-phenylquinoline-2-carboxylate (**3gc**):* Purified by recrystallization from EtOH. Yield: 95% (359.14 mg). M.p = 190-193 °C. FT-IR (KBr): ν_{max} = 3474, 3370, 3056, 2948, 2924, 2857, 1722, 1644, 1619, 1591, 1484, 1429, 1388, 1283, 1250, 1221, 1176 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ =3.69 (s, 3H), 5.58 (s, 2H), 6.71 (s, 1H), 7.30 (dd, ^1J = 5.6 Hz, ^2J = 1.6 Hz, 1H), 7.50-7.56 (m, 5H), 7.61-7.65 (m, 1H), 7.72-7.74 (m, 1H), 7.80 (d, J = 7.1 Hz, 2H), 8.31 (s, 1H), 9.04 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.7, 166.9, 146.9, 146.88, 146.85, 136.4, 132.5, 131.2, 131.1, 130.9, 129.9, 129.3, 129.1, 128.8, 128.7, 128.5, 128.3, 128.2, 109.6, 52.3. Anal. Calcd for $C_{24}H_{18}N_2O_3$: C, 75.38; H, 4.74; N, 7.33. Found: C, 75.51; H, 4.70; N, 7.26.

*(6-Amino-2,4-diphenylquinoline-7-yl)(phenyl) methanone (**3gd**):* Purified by silica gel column chromatography (eluent: petroleum ether/EtOAc, 2:1). Yield: 83% (330.25 mg). M.p = 261-263 °C. FT-IR (KBr): ν_{max} = 3467, 3344, 3313, 3197, 3057, 3028, 2921, 2851, 2250, 1722, 1609, 1577, 1526, 1445, 1412, 1318, 1244, 1205, 1177, 1069, 954, 883, 696 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.83 (s, 2H), 6.32 (s, 1H), 7.23 (s, 1H), 7.35 (t, J = 7.2 Hz, 3H), 7.40-7.43 (m, 2H), 7.50-7.54 (m, 4H), 7.57-7.60 (m, 2H), 7.73-7.75 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.5, 169.5, 147.0, 140.2, 139.5, 137.5, 134.2, 134.1, 133.6, 131.5, 131.2, 130.6, 130.3, 129.6, 129.3, 129.2, 129.1, 128.9, 128.3, 126.3, 119.4, 115.5. Anal. Calcd for $C_{28}H_{20}N_2O$: C, 83.98; H, 5.03; N, 7.00. Found: C, 83.85; H, 4.99; N, 7.08.

*(6-Amino-2-phenyl-4-(p-tolyl)quinoline-7-yl)(p-tolyl)methanone (**3hd**):* Purified by silica gel column chromatography (eluent: petroleum ether/EtOAc, 2:1). Yield: 71% (300.70 mg). M.p = 101-103 °C. FT-IR (KBr): ν_{max} = 3466, 3365, 3028, 2951, 2921, 2734, 2587, 1911, 1724, 1644, 1619, 1598, 1528, 1491,

1451, 1356, 1289, 1213, 1179, 1072, 895, 769 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.40 (s, 3H), 2.42 (s, 3H), 5.42 (s, 2H), 7.01 (s, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 6.8 Hz, 2H), 7.36-7.43 (m, 5H), 7.65 (s, 1H), 7.68 (d, *J* = 8.1 Hz, 2H), 7.99-8.01 (m, 2H), 8.27 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.2, 157.2, 151.6, 149.6, 144.7, 143.1, 140.6, 134.8, 132.9, 130.2, 130.0, 129.4, 129.3, 129.1, 128.8, 127.1, 124.3, 121.4, 119.8, 108.1, 21.3. Anal. Calcd for $C_{30}H_{24}N_2O$: C, 84.08; H, 5.65; N, 6.54. Found: C, 84.20; H, 5.61; N, 6.45.

Synthesis of pyrido[3,2-*g*]quinolines catalyzed by PPInCl-nSiO_2 (Scheme 4): A mixture of 4,6-dibenzoyl-1,3-phenylenediamine (**1f**, 1 mmol), alkyne (2.6 mmol) and PPInCl-nSiO_2 catalyst (50 mg, containing 0.036 mmol In, 1.8 mol%) was stirred at 110 °C under solvent-free conditions. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was cooled to room temperature and then EtOAc (10 mL) was added. The catalyst was separated by filtration and washed with EtOAc (10 mL). The filtrate was evaporated and the crude product was purified by silica gel column chromatography to afford the pure desired pyrido[3,2-*g*]quinolines.

*Tetramethyl 4,6-diphenylpyrido[3,2-g]quinoline-2,3,7,8-tetracarboxylate (**4fa**):* Purified by silica gel column chromatography (eluent: petroleum ether/EtOAc, 1.5:1). Yield: 76% (421.56 mg). M.p = 124-126 °C. FT-IR (KBr): ν_{max} = 3442, 3330, 2959, 2925, 2856, 2741, 1729, 1602, 1440, 1377, 1262, 1123, 1070, 997, 744 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ =3.91 (s, 6H), 3.97 (s, 6H), 7.55-7.72 (m, 6H), 7.73-7.79(m, 5H), 8.70 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.3, 164.4, 139.2, 134.3, 132.6, 130.9, 130.0, 129.5, 129.3, 128.8, 128.7, 128.2, 53.3, 53.2. Anal. Calcd for $C_{32}H_{24}N_2O_8$: C, 68.08; H, 4.29; N, 4.96. Found: C, 68.21; H, 4.33; N, 4.88.

*2,3,4,6,7,8-Hexaphenylpyrido[3,2-g]quinoline (**4fb**):* Purified by silica gel column chromatography (eluent: petroleum ether/EtOAc, 2:1). Yield: 68% (429.38 mg). M.p = 143-145 °C. FT-IR (KBr): ν_{max} = 3467, 3306, 3055, 3028, 2959, 2923, 2853, 1952, 1725, 1688, 1593, 1553, 1445, 1490, 1377, 1282, 1119, 1072, 1025, 761, 698 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.84-6.86 (m, 2H), 6.90-6.95 (m, 7H), 7.03-7.05 (m, 3H), 7.07-7.09 (m, 1H), 7.12-7.16 (m, 2H), 7.17-7.19 (m, 3H), 7.23-7.29 (m, 4H), 7.30-7.34 (m, 2H), 7.38-7.40 (m, 3H), 7.42-7.48 (m, 3H), 7.69-7.75 (m, 2H). ^{13}C NMR (100 MHz,

$CDCl_3$): δ = 161.1, 131.4, 130.8, 130.1, 130.0, 129.9, 129.4, 128.5. 128.3, 127.9, 127.7, 127.6, 127.4, 127.1. Anal. Calcd for $C_{48}H_{32}N_2$: C, 90.54; H, 5.07; N, 4.40. Found: C, 90.40; H, 5.04; N, 4.47

Synthesis of symmetric pyrido[2,3-*g*]quinolines catalyzed by PPInCl-nSiO_2 (Scheme 5): A mixture of 2,5-dibenzoyl-1,4-phenylenediamine **1g** / or 2,5-ditolyl-1,4-phenylendiamine **1h** (1 mmol), alkyne (2.6 mmol) and PPInCl-nSiO_2 catalyst (50 mg, containing 0.036 mmol In, 1.8 mol%) was stirred at 110 ^oC under solvent-free condition. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was cooled to room temperature and then EtOAc (10 mL) was added. The catalyst was separated by filtration and washed with EtOAc (10 mL). The filtrate was evaporated and the crude product was purified by silica gel column chromatography to afford the pure desired symmetric pyrido[2,3-*g*]quinolines.

*Tetramethyl 4,9-diphenylpyrido[2,3-g]quinoline-2,3,7,8-tetracarboxylate (**5ga**):* Purified by silica gel column chromatography (eluent: petroleum ether/EtOAc, 1.5:1). Yield: 86% (482.45 mg). M.p >300 °C. FT-IR (KBr): ν_{max} = 3431, 3060, 2951, 2924, 2854, 1734, 1654, 1570, 1525, 1442, 1353, 1259, 1216, 1146, 1111, 974, 700, 469 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ =3.58 (s, 6H), 3.99 (s, 6H), 7.35-7.37 (m, 5H), 7.47-7.50 (m, 5H), 8.72 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.3, 164.2, 157.0, 150.9, 144.3, 133.8, 130.3, 129.9, 129.4, 129.3, 128.8, 128.7, 53.8, 52.7. Anal. Calcd for $C_{32}H_{24}N_2O_8$: C, 68.08; H, 4.29; N, 4.96. Found: C, 67.92; H, 4.25; N, 5.04.

*2,3,4,7,8,9-Hexaphenylpyrido[2,3-g]quinoline (**5gb**):* Purified by silica gel column chromatography (eluent: petroleum ether/EtOAc, 2:1). Yield: 76% (480.12 mg). M.p= 288-290 °C. FT-IR (KBr): ν_{max} = 3427, 3056, 3026, 2922, 2850, 1952, 1725, 1619, 1574, 1464, 1441, 1315, 1260, 1150, 1075, 1025, 764 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.72-6.80 (m, 3H), 6.91-6.97 (m, 5H), 7.08-7.11 (m, 6H), 7.17 (s, 2H), 7.21-7.28 (m, 9H), 7.31-7.42 (m, 3H), 7.73-7.75 (m, 2H), 7.81 (s, 1H), 7.83-7.85 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.8, 147.1, 138.1, 137.5, 136.5, 131.5, 131.2, 130.3, 130.2, 129.8, 129.5, 128.9, 128.3, 128.1, 127.9, 127.7, 127.4, 126.4, 116.4. Anal. Calcd for $C_{48}H_{32}N_2$: C, 90.54; H, 5.07; N, 4.40. Found: C, 90.51; H, 5.11; N, 4.30.

*Dimethyl 4,9-diphenylpyrido[2,3-g]quinoline-2,7-dicarboxylate (**5gc**):* Purified by silica gel column chromatography (eluent: petroleum ether/EtOAc, 2:1). Yield: 83% (368.54 mg). M.p = 157-160 °C. FT-

IR (KBr): ν_{max} = 3445, 3049, 2955, 2926, 2856, 1731, 1595, 1538, 1491, 1438, 1348, 1282, 1212, 1121, 1072, 1034, 769, 700 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.74 (s, 6H), 7.39-7.41 (m, 4H), 7.55-7.60 (m, 8H), 8.61 (s, 1H), 9.40 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.2, 168.8, 162.4, 151.6, 130.9, 129.5, 128.8, 128.77, 128.73, 128.5, 116.4 52.5. Anal. Calcd for $C_{28}H_{20}N_2O_4$: C, 74.99; H, 4.50; N, 6.25. Found: C, 75.15; H, 4.53; N, 6.17.

*Dimethyl 4,9-di-p-tolylpyrido[2,3-g]quinoline-3,8-dicarboxylate (**5hc**):* Purified by silica gel column chromatography (eluent: petroleum ether/EtOAc, 2:1). Yield: 71% (332.90 mg). M.p = 235-237 °C. FT-IR (KBr): ν_{max} = 3466, 3365, 3028, 2951, 2921, 2734, 2587, 1911, 1724, 1644, 1619, 1598, 1528, 1491, 1451, 1356, 1289, 1213, 1072, 895, 769 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.43 (s, 6H), 3.62 (s, 3H), 3.99 (s, 3H), 7.23-7.31 (m, 8H), 7.45-7.48 (m, 2H), 7.63-7.65 (m, 1H), 8.72 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.4, 149.5, 144.3, 139.4, 130.9, 130.8, 130.3, 129.4, 129.2, 129.1, 128.8, 128.6, 53.8, 52.7, 23.7, 23.0. Anal. Calcd for $C_{30}H_{24}N_2O_4$: C, 75.62; H, 5.08; N, 5.88. Found: C, 75.48; H, 5.12; N, 5.95.

*3,8-Diphenyl-4,9-di-p-tolylpyrido[2,3-g]quinoline (**5hd**):* Purified by silica gel column chromatography (eluent: petroleum ether/EtOAc, 2:1).Yield: 80% (408.65 mg). M.p >300 °C. FT-IR (KBr): ν_{max} = 3427, 2948, 2924, 2867, 2734, 1737, 1609, 1500, 1445, 1360, 1252, 1219, 1114, 1048, 788 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.46 (s, 6H), 7.35 (d, *J* = 7.8 Hz, 4H), 7.41-7.48 (m, 7H), 7.53 (d, *J* = 7.9 Hz, 4H), 7.79 (s, 2H), 8.14 (d, *J* = 7.1 Hz, 3H), 8.81 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.5, 130.0, 129.7, 129.6, 129.5, 129.4, 129.0, 128.9, 128.8, 127.7, 127.6, 127.2, 126.9, 119.6, 21.4. Anal. Calcd for $C_{38}H_{28}N_2$: C, 89.03; H, 5.51; N, 5.46. Found: C, 89.17; H, 5.49; N, 5.27.

Synthesis of unsymmetric pyrido[2,3-*g*]quinolines catalyzed by PPInCl-nSiO_2 (Scheme 6): A three-component reaction of 2,5-dibenzoyl-1,4-phenylenediamine **1g** (1 mmol) with DMAD **2a** (1.3 mmol) and diphenyl acetylene **2b** (1.3 mmol) in the presence of PPInCl-nSiO_2 catalyst (50 mg, containing 0.036 mmol In, 1.8 mol%) was stirred at 110 °C under solvent-free conditions. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was cooled to room temperature and then EtOAc (10 mL) was added. The catalyst was separated by filtration and

washed with EtOAc (10 mL). The filtrate was evaporated and the crude product was purified by silica gel column chromatography to afford the pure desired unsymmetric pyrido[2,3-*g*]quinolines.

*Dimethyl 4,7,8,9-tetraphenylpyrido[2,3-g]quinoline-2,3-dicarboxylate (**6gab**):* Purified by silica gel column chromatography (eluent: petroleum ether/EtOAc, 2:1). Yield: 81% (484.35 mg). M.p>310 °C. FT-IR (KBr): ν_{max} = 3439, 3060, 2955, 2924, 2730, 1969, 1732, 1579, 1526, 1446, 1358, 1259, 1218, 1111, 1051, 977, 756, 702 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.69 (s, 3H), 4.09 (s, 3H), 7.51-7.56 (m, 10H), 7.60-7.65 (m, 6H), 7.72-7.74 (m, 1H), 7.94 (s, 1H), 8.20 (dd, ^1J = 6.4 Hz, ^2J = 1.4 Hz, 2H), 8.64 (s, 1H), 9.01 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.5, 173.6, 150.7, 149.4, 131.4, 131.0, 130.3 129.6, 129.4, 129.0, 128.9, 128.8, 128.6, 128.3, 128.1, 127.8, 120.5, 118.3, 105.6, 53.7, 52.6. Anal. Calcd for $C_{40}H_{28}N_2O_4$: C, 79.98; H, 4.70; N, 4.66. Found: C, 80.11; H, 4.66; N, 4.57.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications websiteat.

Detailed preparation and characterization of PPInCl-nSiO_2 catalyst, proposed mechanism, copies of ^1H and ^{13}C NMR spectra of the products and X-ray crystallographic data (PDF).

X-ray crystallographic data for compound 3cd (CIF)

X-ray crystallographic data for compound 3dc (CIF)

Accession Codes

CCDC 1857297 and 1857298 contain the supplementary crystallographic data for this paper.

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Notes

The authors declare no competing financial interest.

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