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Synthesis of Sterically Congested Polycyclic Aromatic Hydrocarbons: Rhodium(III)-Catalyzed Cascade Oxidative Annulation of Aryl Ketoximes with Diphenylacetylene by Sequential Cleavage of Multiple C–H Bonds

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Abstract: The rhodium(III)-catalyzed oxidative annulations of aryl ketoximes with diphenylacetylene by the cleavage of three C–H bonds, one C–O bond and the formation of four C–C bonds, one C–N bonds simultaneously have been developed. This protocol is scalable and compatible with various functional groups, providing an expeditious access to highly congested polycyclic aromatic/heteroaromatic hydrocarbons.

Keywords: alkynes; C–H activation; oxidative annulation; polycyclic aromatic hydrocarbons (PAHs); rhodium

Introduction

Polycyclic aromatic and heteroaromatic hydrocarbons are an important class of compounds because of their wide applications in materials science, as nanotubes, light emitters, semiconductors, light-absorption dyes, and in liquid crystals.[1] Numerous synthetic methodologies for the construction of these polycyclic aromatic systems have been developed in the past decades,[2] among which, transition metal-catalyzed cross-coupling reactions of organometallic reagents with organic halides are popular methods for the formation of functionalized polycyclic aromatic and heteroaromatic hydrocarbons.[3] However, these methods are typically limited by the availability of the starting materials and multistep procedures. Moreover, the construction of more densely arylated arenes still poses a significant challenge, since the cross-coupling reactions are usually sensitive to steric hindrance.

Transition metal-catalyzed direct C–H bond functionalization has unimpeachably emerged as a powerful tool for the step- and atom-economical construction of complex organic molecules in modern organic chemistry.[4] Recently, the Rh(III)-catalyzed oxidative annulations of various aromatic substrates with alkynes have been extensively investigated.[5–7] This kind of reaction typically uses heteroatoms to direct cyclometalation at the *ortho* C–H bond, followed by oxidative annulation with alkynes (Figure 1). Miura,[5a] Fagnou[5b] and several groups have achieved tremendous successes for the synthesis of heterocycles *via* heterocyclization with 1 equivalent of alkynes in the presence of $[Cp^*RhCl_2]_2/AgSbF_6/Cu(OAc)_2$ catalyst system (Figure 1, a).[5] The construction of polycyclic aromatic hydrocarbons *via* oxidative annulations with 2 equivalents of alkynes has also been well investigated (Figure 1, b).[6] In these reports, however, the oxidative annulation reactions are mainly restricted to the coupling of various aromatic substrates with one or two equivalents alkynes *via* the cleavage of one or two C–H bonds.[5,6] Our continued interest in metal-catalyzed C–H activation[9] and the reactions through the cleavage of more than one C–H bonds promoted us to explore the synthesis of highly congested isoquinolines through C–H activation.[6d,e] Herein we describe a new process in which aryl ketoximes undergo an efficient oxidative annulation with three equivalents of diphenylacetylene, by the cleavage of three C–H bonds, one C–O bond with formation of four C–C bonds and one C–N bond simultaneously. This protocol provides an expeditious access to the highly

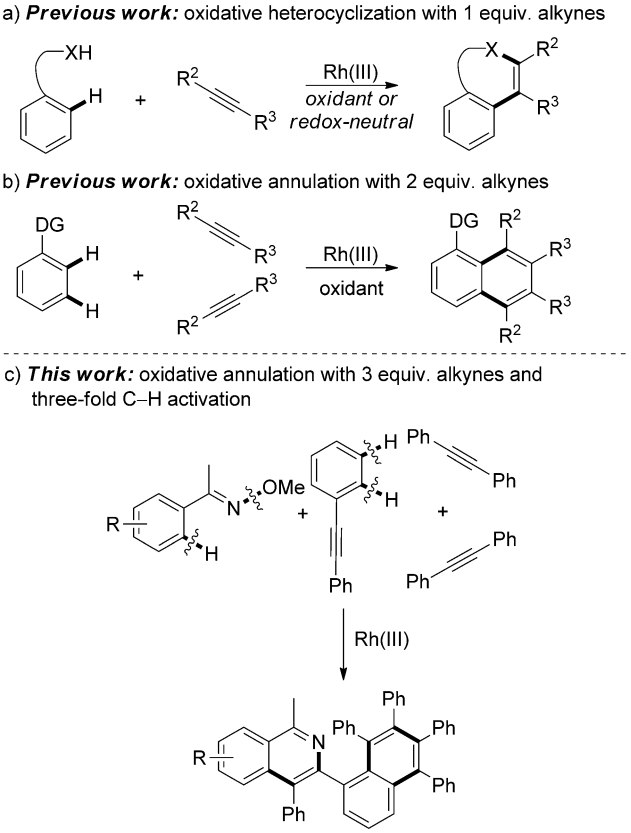


Figure 1. Rh(III)-catalyzed oxidative annulation with alkynes *via* C–H activation.

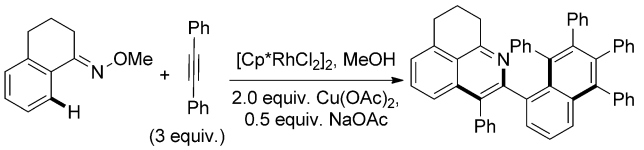
congested 1-methyl-4-phenyl-3-(5,6,7,8-tetraphenylnaphthalen-1-yl)isoquinolines.

Results and Discussion

We commenced our study by investigating the coupling of 3,4-dihydronaphthalen-1(2*H*)-one *O*-methyl oxime **1a** and 3 equivalents of diphenylacetylene **2a** with $[Cp^*RhCl_2]_2$ (5.0 mol%) as catalyst in the presence of $Cu(OAc)_2$ under N_2 in MeOH at 110 °C. The reaction proceeded smoothly to afford the product in 70% yield (Table 1, entry 1). The yield was reduced when the reaction was carried out at 100 °C or in the absence of NaOAc (entries 2 and 3). We were delighted to find that the yield was improved to 83% when the reaction was run for only 2 h even with the reduced loading of catalyst (entry 6, 2.5 mol% $[Cp^*RhCl_2]_2$). The yield dropped dramatically when the reaction was conducted under an air atmosphere (entry 6).

With the optimized conditions in hand, the substrate scope of this annulation process was explored extensively (Table 2). Substrates bearing both electron-withdrawing groups and electron-donating

Table 1. Optimization of reaction conditions.[a]



1a 2a 3a

Entry	Oxidant	*T* [°C]	$[Cp^*RhCl_2]_2$ [mol%]	Time [h]	Yield [%]
1	$Cu(OAc)_2$	110	5	24	70
2	$Cu(OAc)_2$	100	5	24	67
3[b]	$Cu(OAc)_2$	110	5	24	43
4	$Cu(OAc)_2$	110	5	3	83
5	$Cu(OAc)_2$	110	2.5	3	83
6	$Cu(OAc)_2$	110	2.5	2	83
7[c]	$Cu(OAc)_2$	110	2.5	2	38

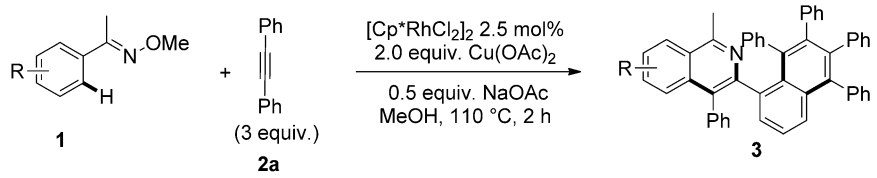
[a] *Reaction conditions:* **1a** (0.4 mmol), $[Cp^*RhCl_2]_2$, **2a** (1.2 mmol), $Cu(OAc)_2$ (0.8 mmol), NaOAc (0.2 mmol), in 2 mL MeOH. Yields are given for isolated products after chromatography.
[b] NaOAc was not added.
[c] Under air.

groups were compatible with the optimized conditions and reacted efficiently with diphenylacetylene to give the corresponding highly congested annulation products (up to 96% yield). Aryl ketoxime **1c** bearing an *ortho*-methyl group gave a reduced yield (entry 2, 23%), likely due to the steric hindrance. When *meta*-substituted aryl ketoximes were applied, good regioselectivity favoring activation of the less hindered C–H bonds was achieved (entries 3, 5 and 9). The unprotected phenol group is also compatible with the present reaction protocol; affording **3h** in 81% yield (entry 7). Various ketoximes bearing other valuable functional groups, such as acetylamino, chloro, fluoro and trifluoromethyl, could react smoothly with alkyne **2a** to afford the annulated products in good yields (entries 7–12).

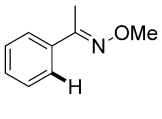
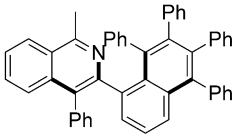
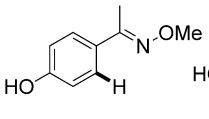
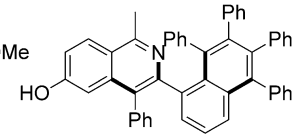
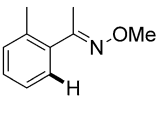
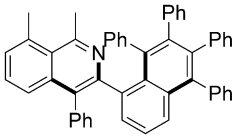
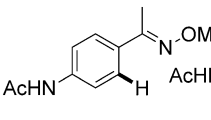
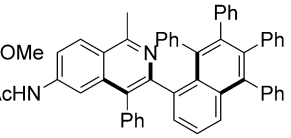
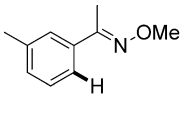
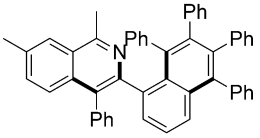
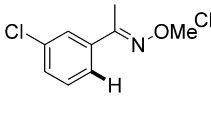
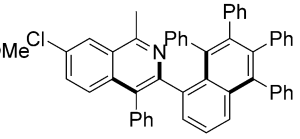
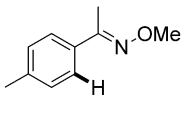
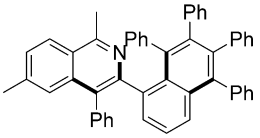
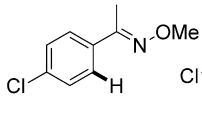
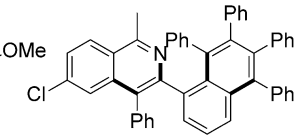
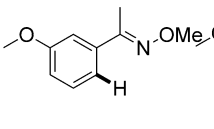
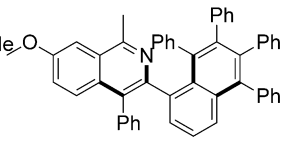
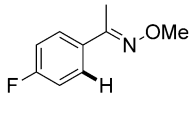
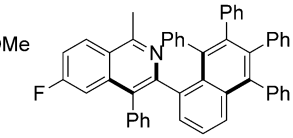
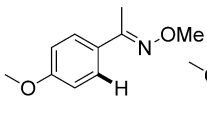
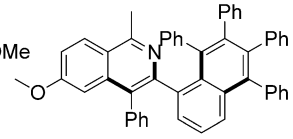
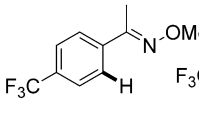
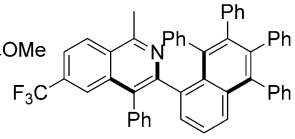
We were delighted to find that the Rh(III)-catalyzed annulation reaction was also compatible with heteroaromatic ketoximes (Table 3). Heteroarenes, such as pyrrole, thiophene and indole, all reacted with alkyne **2a** in good to excellent yields (entries 1–4). When 3-substituted thiophene was applied, activation of the C-4 position was achieved regioselectively under standard reaction conditions (entry 3). Moreover, the congested polycyclic structure was confirmed by an X-ray analysis of compound **3q** (Table 3).[10] However, complicated mixtures were obtained when other substituted diphenylacetylenes were employed to this reaction protocol.

To compare the activity difference of aryl ketoximes, we performed a set of intermolecular competition experiments between ketoximes **1g** and **1k** with alkyne **2a** under the standard reaction conditions. The result indicated that electron-rich ketoxime **1g** was

Table 2. Substrate scope of aryl ketoximes.[a]



1 2a 3

Entry	Substrate	Product	Yield	Entry	Substrate	Product	Yield
1	 1b	 3b	73%	7	 1h	 3h	81%
2	 1c	 3c	23%	8	 1i	 3i	71%
3	 1d	 3d	69%	9	 1j	 3j	71%
4	 1e	 3e	79%	10	 1k	 3k	80%
5	 1f	 3f	70%	11	 1l	 3l	76%
6	 1g	 3g	96%	12	 1m	 3m	76%

[a] Yields are given for isolated products after chromatography.

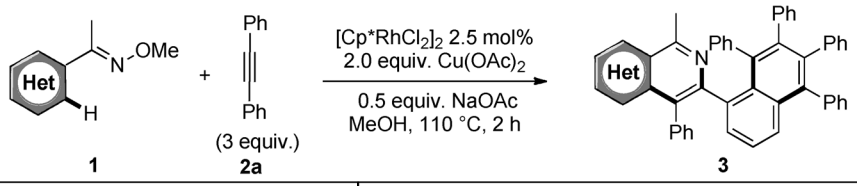
transformed preferentially (Scheme 1), hence rendering an electrophilic C–H bond activation.

To further evaluate the efficiency and practicality of this reaction, a 4-mmol scale reaction was conducted using **1b** as substrate and the reaction proceeded smoothly to furnish the product **3b** in good yield (Scheme 2, 76% yield, 1.95 g of **3b**).

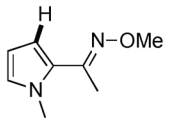
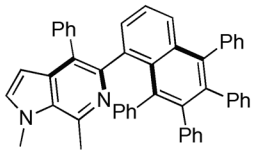
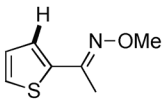
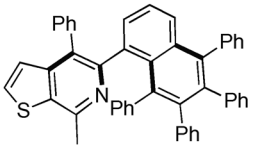
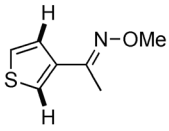
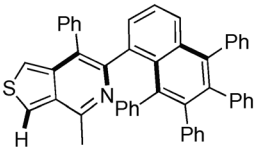
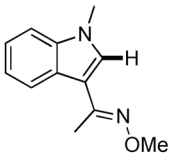
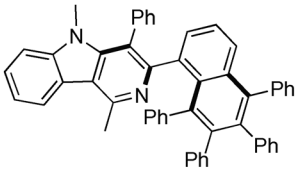
To gain further insight into the mechanism of this cascade reaction, we carried out a deuterium competition experiment between substrate **1b** and **1b**-d_5 under the standard reaction conditions and the reaction was stopped after 10 min. A primary KIE value ($k_H/k_D = 3$) was obtained, indicating that the cleavage of the C–H bond in the phenyl ring of ketoxime is most likely involved in the rate-determining step (Scheme 3).[11]

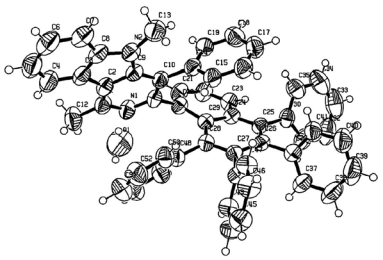
On the basis of these preliminary results and literature precedents,[5,6] a plausible mechanism for the present catalytic process is proposed (Figure 2). The $[Cp^*RhCl_2]_2$ presumably dissociates into the coordinatively unsaturated monomer, which can exchange with acetate ligand to form $Cp^*Rh(OAc)_2$. The first

Table 3. Synthesis of sterically congested polycyclic heteroaromatic hydrocarbons.



1 2a 3

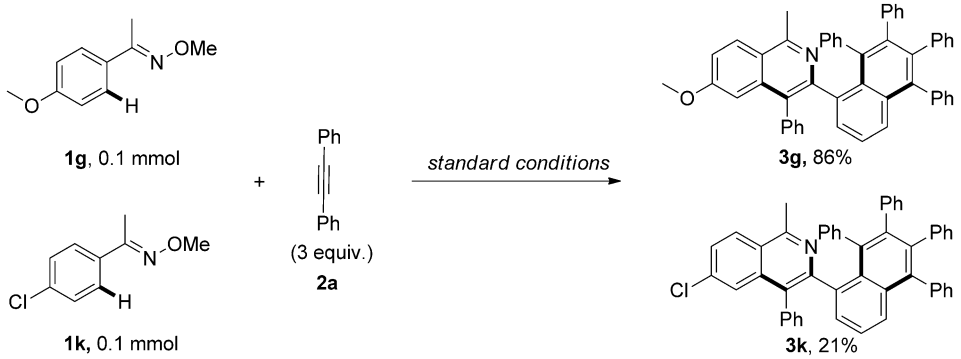
Entry	Substrate	Product	Yield
1			87%
	1n	3n	
2			83%
	1o	3o	
3			80%
	1p	3p	
4			96%
	1q	3q	



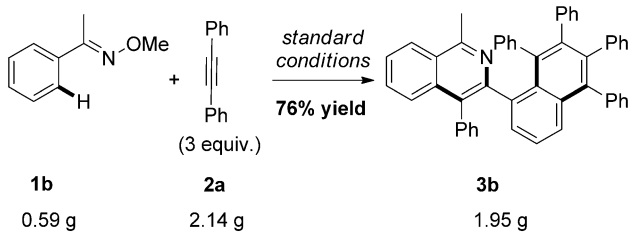
step is likely to be a rate-determining *ortho*-C–H bond activation of aryl ketoxime **1** with the assistance of the oxime nitrogen to give arylrhodium intermediate **A**. Alkyne may then coordinate with **A**, followed by regioselective insertion into the Rh–C bond of **A** to afford the seven-membered intermediate **B**. Finally, subsequent C–N bond formation and N–O bond cleavage of intermediate **B** *via* a concerted redox process in a redox neutral manner in the presence of NaOAc affords the first-step product **C** and regenerates the active Rh(III) species[5f] for the next catalytic cycle and the second-step annulation. The mechanism of the second-step annulation of functionalized 1-methyl-3,4-diphenylisoquinoline **C** with alkyne is consistent with that reported by Li[6c] and Miura.[6a,d]

Conclusions

In conclusion, we have demonstrated a rhodium(III)-catalyzed cascade oxidative annulation reaction of aryl/heteroaryl ketoximes with diphenylacetylene



Scheme 1. Intermolecular competition experiments between ketoximes **1g** and **1h**.



Scheme 2. Gram-scale synthesis of **3b**.

using $Cu(OAc)_2$ as an oxidant, generating highly congested 1-methyl-4-phenyl-3-(5,6,7,8-tetraphenylnaphthalen-1-yl)isoquinolines in good yields. This reaction protocol features a short reaction time, high compatibility with various functional groups and high yields.

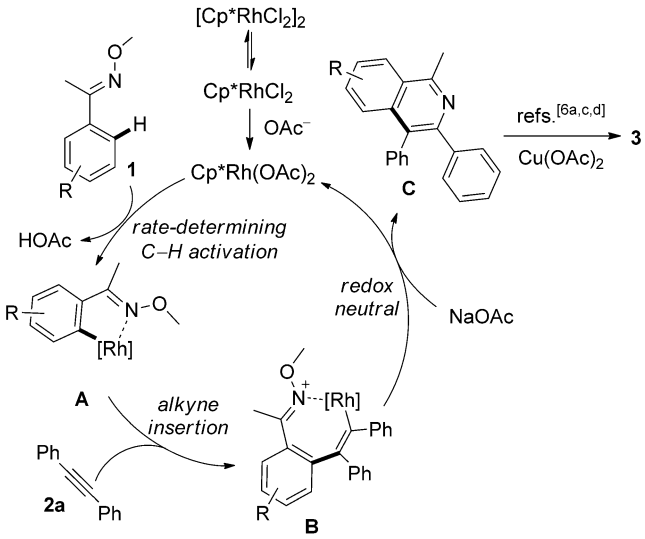


Figure 2. Proposed mechanism.

Experimental Section

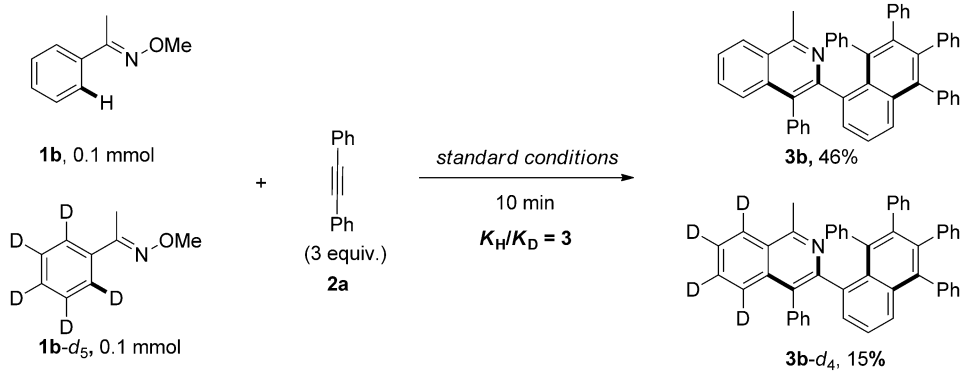
General Methods

Commercial grade solvents were dried by known procedures. The other materials and solvents were purchased from commercial suppliers and used without additional purification. Aryl ketoximes **1a**–**1p** were prepared according to the literature.[12] NMR spectra were recorded for ^1H at 400 MHz, and ^{13}C at 100 MHz using TMS as internal standard. Chemical shifts are given relative to $CDCl_3$ (7.26 ppm for ^1H NMR, 77.16 ppm for ^{13}C NMR). Data are presented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz). Mass spectroscopy data of the products were collected on an HR-MS-TOF instrument or a low-resolution MS instrument using EI ionization.

General Procedure for the Annulation of Aryl Ketoximes with Internal Alkynes

A mixture of aryl ketoxime **1** (0.4 mmol), $[Cp^*RhCl_2]_2$ (0.01 mmol, 0.025 equiv.), diphenylacetylene **2a** (1.2 mmol, 3.0 equiv.), $Cu(OAc)_2$ (0.8 mmol, 2.0 equiv.), NaOAc (0.2 mmol, 0.5 equiv.) and 2 mL MeOH in a 50-mL Schlenck tube (purged with N_2) was heated at 110 °C for 2 h. Then the reaction mixture was cooled to room temperature and a saturated solution of Na_2S (2 mL) was added and the whole stirred for 5 min. The resulting mixture was extracted with dichloromethane. The organic layer was dried over Na_2SO_4, concentrated under reduced pressure and separated on a silica gel column with petroleum ether/ethyl acetate as the eluent to give the desired product **3**.

3-Phenyl-2-(5,6,7,8-tetraphenylnaphthalen-1-yl)-8,9-dihydro-7*H*-benzo[*de*]quinoline (3a): obtained as a yellow solid according to the general procedure; yield: 224 mg (83%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.43$–7.38 (m, 3H), 7.34–7.31 (m, 1H), 7.27- 7.08 (m, 10H), 7.03–6.99 (m, 2H), 6.96 (m, $J = 7.2$ Hz, 1 H), 6.87–6.81 (m, 1H), 6.78–6.66 (m, 9H), 6.56–6.50 (m, 3H), 6.16 (t, $J = 7.2$ Hz, 1H), 3.13–2.98 (m, 4H), 2.15- 2.08 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 157.5, 151.7, 141.0, 140.9, 140.8, 140.1, 140.0, 139.3, 138.3, 138.1, 137.7, 135.5, 133.4, 133.3, 132.1, 131.5, 131.3, 131.0, 130.5, 130.2, 129.3, 129.0, 127.6, 127.3, 127.1, 127.0, 126.4,



Scheme 3. Kinetic isotope effect.

126.3, 125.9, 125.3, 125.2, 125.0, 124.7, 124.4, 124.1, 123.5, 123.2, 34.2, 30.8, 23.3; HR-MS (EI-TOF): m/z = 675.2932, calcd. for $C_{52}H_{37}N$ (M^+): 675.2926.

1-Methyl-4-phenyl-3-(5,6,7,8-tetraphenylnaphthalen-1-yl)-isoquinoline (3b): obtained as a white solid according to the general procedure; yield: 190 mg (73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85–7.82 (m, 1H), 7.39–7.29 (m, 6H), 7.28–7.19 (m, 5H), 7.17–7.11 (m, 4H), 7.03 (d, J = 7.6 Hz, 1H), 6.98 (d, J = 7.6 Hz, 1H), 6.89–6.83 (m, 2H), 6.80–6.65 (m, 9H), 6.55–6.54 (m, 2H), 6.46 (t, J = 7.4 Hz, 1H), 6.13 (t, J = 7.4 Hz, 1H), 2.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.2, 151.1, 140.9, 140.8, 140.2, 139.1, 138.2, 137.8, 137.5, 135.2, 133.5, 133.4, 132.1, 131.6, 131.4, 131.3, 131.2, 131.0, 130.5, 130.3, 129.4, 129.2, 127.6, 127.4, 127.2, 127.1, 126.6, 126.5, 126.4, 126.3, 126.1, 125.9, 125.8, 125.3, 125.2, 125.1, 125.0, 124.7, 124.5, 22.3; HR-MS (EI-TOF): m/z = 649.2770, calcd. for $C_{50}H_{35}N$ (M^+): 649.2770.

***d*$_4$-1-Methyl-4-phenyl-3-(5,6,7,8-tetraphenylnaphthalen-1-yl)isoquinoline (3b-*d*$_4$):** obtained as a white solid according to the general procedure; yield: 10 mg (15%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.37 (m, 3H), 7.28–7.20 (m, 4H), 7.18–7.11 (m, 4H), 7.03 (d, J = 7.2 Hz, 1H), 6.98 (d, J = 7.6 Hz, 1H), 6.89–6.82 (m, 2H), 6.79–6.65 (m, 9 H), 6.5–6.53 (m, 2H), 6.46 (t, J = 7.4 Hz, 1H), 6.12 (t, J = 7.4 Hz, 1H), 2,74 (s, 3H).

1,8-Dimethyl-4-phenyl-3-(5,6,7,8-tetraphenylnaphthalen-1-yl)isoquinoline (3c): obtained as a white solid according to the general procedure; yield: 60 mg (23%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.39 (m, 2H), 7.35–7.32 (m, 1H), 7.27–7.18 (m, 7H), 7.17–7.10 (m, 4H), 7.02–6.92 (m, 2H), 6.91 (t, J = 7.4 Hz, 1H), 6.85–6.83 (m, 1H), 6.77–6.65 (m, 9H), 6.54–6.49 (m, 3H), 6.13 (t, J = 7.4H, 1H), 2.89 (s, 3H), 2. 83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.9, 151.0, 141.0, 140.9, 140.8, 140.2, 140.1, 138.9, 138.3, 138.2, 138.1, 137.7, 137.2, 135.4, 133.4, 133.3, 132.0, 131.4, 131.3, 131.2, 131.0, 129.5, 129.4, 128.5, 127.6, 127.4, 127.1, 126.8, 126.6, 126.4, 126.3, 125.8, 125.2, 125.0, 124.6, 124.5, 29.3, 25.9; HR-MS (EI-TOF): m/z = 663.2930, calcd. for $C_{51}H_{37}N$ (M^+): 663.2926.

1,7-Dimethyl-4-phenyl-3-(5,6,7,8-tetraphenylnaphthalen-1-yl)isoquinoline (3d): obtained as a white solid according to the general procedure; yield: 184 mg (69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 (s, 1H), 7.42–7.32 (m, 4H), 7.28–7.17 (m, 5H), 7.15–7.10 (m, 4H), 7.03 (d, J = 7.6 Hz, 1H), 6.98 (d, J = 7.6 Hz, 1H), 6.89–6.82 (m, 2H), 6.79–6.69 (m, 8H), 6.66 (d, J = 7.6 Hz, 1H), 6.54 (d, J = 6.4 Hz, 1 H), 6.48 (d, J = 7.4 Hz, 1H), 6.15 (t, J = 7.6 Hz, 1H), 2.71 (s, 3H), 2,50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.4, 150.9, 140.9, 140.2, 140.1, 139.2, 139.3, 138.3, 138.2, 137.8, 137.7, 135.8, 133.4, 132.1, 131.4, 131.3, 131.2, 131.1, 130.4, 130.3, 129.1, 127.6, 127.4, 127.0, 126.6, 126.4, 126.2, 125.8, 125.3, 125.2, 125.0, 124.7, 124.5, 124.1, 22.3, 22.0; HR-MS (EI-TOF): m/z = 663.2933, calcd. for $C_{51}H_{37}N$ (M^+): 663.2926.

1,6-Dimethyl-4-phenyl-3-(5,6,7,8-tetraphenylnaphthalen-1-yl)isoquinoline (3e): obtained as a white solid according to the general procedure; yield: 211 mg (79%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, J = 8.4 Hz, 1H), 7.41–7.37 (m, 3H), 7.28–7.19 (m, 6H), 7.16–7.10 (m, 4H), 7.04–6.98, (m, 2H), 6.91 (t, J = 7.4 Hz, 1H), 6.87–6.82 (m, 1H), 6.79–6.62 (m, 9H), 6.54–6.48 (m, 3H), 6.13 (t, J = 7.4H, 1H), 2.70 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.8, 151.8, 140.9, 140.8, 140.0, 139.3, 138.3, 138.1, 137.8, 137.6, 135.4, 133.4, 133.3, 132.2, 131.5, 131.4, 131.2, 131.0, 130.4, 130.3, 128.9, 128.2, 127.8, 127.3, 127.1, 127.0, 126.6, 126.5, 126.4, 126.2, 125.9, 125.4, 125.2, 125.0, 124.8, 124.7, 124.4, 124.2, 22.2, 22.1; HR-MS (EI-TOF): m/z = 663.2934, calcd. for $C_{51}H_{37}N$ (M^+): 663.2926.

7-Methoxy-1-methyl-4-phenyl-3-(5,6,7,8-tetraphenylnaphthalen-1-yl)isoquinoline (3f): obtained as a white solid according to the general procedure; yield: 190 mg (70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (s, 1H), 7.45–7.35 (m, 5H), 7.29–7.21 (m, 4H), 7.19–7.13 (m, 4H), 7.03 (d, J = 7.2 Hz, 1H), 6.98 (d, J = 7.6 Hz, 1H), 6.92–6.83 (m, 2H), 6.80–6.70 (m, 8H), 6.66 (d, J = 6.8 Hz, 1H), 6.57–6.50 (m, 3H), 6.19 (t, J = 7.4 Hz, 1H), 2.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.6, 155.5, 152.9, 141.4, 141.0, 140.8, 140.2, 139.8, 139.2, 138.2, 138.0, 137.9, 133.4, 133.0, 132.5, 131.4, 131.3, 130.9, 130.4, 129.9, 129.2, 127.7, 127.6, 127.3, 126.5, 126.4, 126.2, 125.8, 125.5, 125.4, 125.2, 125.0, 124.8, 124.6, 124.3, 117.8, 109.8, 55.6, 22.9; HR-MS (EI-TOF): m/z = 679.2870, calcd. for $C_{51}H_{37}NO$ (M^+): 679.2875.

6-Methoxy-1-methyl-4-phenyl-3-(5,6,7,8-tetraphenylnaphthalen-1-yl)isoquinoline (3g): obtained as a white solid according to the general procedure; yield: 260 mg (96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, J = 9.2 Hz, 1H), 7.42–7.38 (m, 3H), 7.24–7.19 (m, 3H), 7.18–7.11 (m, 4H), 7.09–7.06 (m, 1H), 7.04–6.99 (m, 3H), 6.91 (t, J = 7.4 Hz, 1H), 6.87–6.82 (m, 1H), 6.80–6.78 (m,3H), 6.75–6.67 (m, 7H), 6.57–6.50 (m, 3H), 6,19 (t, J = 7.2 Hz, 1H), 3.68 (s, 3H), 2.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.1, 155.5, 152.4, 140.9, 140.8, 140.2, 140.1, 140.0, 139.3, 138.3, 138.1, 137.8, 137.7, 137.2, 133.5, 133.4, 133.3, 132.1, 131.5, 131.2, 131.0, 130.4, 130.1, 128.7, 127.6, 127.5, 127.4, 127.2, 127.1, 127.0, 126.6, 126.5, 126.4, 126.3, 125.8, 125.3, 125.2, 125.0, 124.7, 124.4, 121.5, 118.7, 55.2, 22.2; HR-MS (EI-TOF): m/z = 679.2883, calcd. for $C_{51}H_{37}NO$ (M^+): 679.2875.

1-Methyl-4-phenyl-3-(5,6,7,8-tetraphenylnaphthalen-1-yl)-isoquinolin-6-ol (3h): obtained as a white solid according to the general procedure; yield: 216 mg (81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72–7.69 (m, 1H), 7.35–7.31 (m, 2H), 7.22–7.18 (m, 1H), 7.14–7.11 (m, 3H), 7.06–6.91 (m, 8H), 6.85–6.81 (m, 1H), 6.78–6.74 (m, 2H), 6.73–6.64 (m, 6H), 6.59 (s, 1H), 6.53–6.47 (m, 3H), 6.13 (t, J = 7.4 Hz, 1H), 2,58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.3, 140.8, 140.7, 140.1, 138.4, 138.1, 137.6, 133.4, 133.2, 132.2, 131.4, 131.3, 131.2, 131.1, 131.0, 130.9, 130.5, 129.9, 127.6, 127.5, 127.3, 127.0, 126.6, 126.5, 126.4, 126.3, 126.0, 125.4, 125.3, 125.1, 124.8, 124.3, 107.9, 21.2; HR-MS (EI-TOF): m/z = 665.2720, calcd. for $C_{50}H_{35}NO$ (M^+): 665.2719.

***N*-(1-Methyl-4-phenyl-3-(5,6,7,8-tetraphenylnaphthalen-1-yl)isoquinolin-6-yl)acetamide (3i):** obtained as a yellow solid according to the general procedure; yield: 200 mg (71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (s, 2H), 7.42–7.36 (m, 4H), 7,29 (s, 1H), 7.24–7.20 (m, 4H), 7.16–7.13 (m, 4H), 7.02 (d, J = 7.2 Hz, 1H), 6.98 (d, J = Hz, 1H), 6.90–6.82 (m, 2H), 6.79–6.76 (m, 2H), 6.75–6.65 (m, 7H), 6.57–6.37 (m, 4H), 6.16 (t, J = 7.4 Hz, 1H), 2.70 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.5, 155.8, 140.9, 140.8, 140.1, 139.0, 138.2, 137.7, 137.4, 136.0, 133.5, 133.2, 132.0, 131.5, 131.4, 131.3, 131.1, 131.0, 130.5, 130.1, 128.7, 127.6, 127.5, 127.4, 127.3, 127.1, 126.6, 126.5, 126.4, 126.3, 125.8, 125.4, 125.3, 125.0, 124.8, 124.4, 123.0, 119.7, 113.5, 24.8,

22.1; HR-MS (EI-TOF): m/z = 706.2976, calcd. for $C_{52}H_{38}N_2O$ (M^+): 706.2984.

7-Chloro-1-methyl-4-phenyl-3-(5,6,7,8-tetraphenylnaphthalen-1-yl)isoquinoline (3j): obtained as a yellow solid according to the general procedure; yield: 193 mg (71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (s, 1H), 7.45–7.35 (m, 5H), 7.29–7.21 (m, 4H), 7.19–7.13 (m, 4H), 7.03 (d, J = 7.2 Hz, 1H), 6.98 (d, J = 7.6 Hz, 1H), 6.92–6.83 (m, 2H), 6.80–6.70 (m, 8H), 6.66 (d, J = 6.8 Hz, 1H), 6.57–6.50 (m, 3H), 6.19 (t, J = 7.4 Hz, 1H), 2.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.3, 152.2, 140.9, 140.8, 140.7, 140.3, 140.1, 138.7, 138.5, 138.3, 137.6, 136.9, 133.6, 133.5, 133.4, 131.9, 131.8, 131.4, 131.3, 131.1, 131.0, 126.3, 125.9, 125.4, 125.3, 125.1, 124.9, 124.4, 124.1, 22.2; HR-MS (EI-TOF): m/z = 683.2385, calcd. for $C_{50}H_{34}ClN$ (M^+): 683.2380.

6-Chloro-1-methyl-4-phenyl-3-(5,6,7,8-tetraphenylnaphthalen-1-yl)isoquinoline (3k): obtained as a yellow solid according to the general procedure; yield: 220 mg (80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, J = 8.8 Hz, 1H), 7.44–7.36 (m, 5H), 7.28–7.21 (m, 4H), 7.18–7.12 (m, 4H), 7.03 (d, J = 7.6 Hz, 1H), 6.98 (d, J = 8.0 Hz, 1H), 6.92–6.82 (m, 2H), 6.80–6.75 (m, 3H), 6.73–6.66 (m, 6H), 6.57–6.49 (m, 3H), 6.18 (t, J = 7.2 Hz, 1H), 2.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.2, 153.1, 140.9, 140.8, 140.7, 140.3, 140.0, 138.7, 138.5, 138.3, 137.6, 136.7, 136.3, 135.8, 133.5, 133.3, 131.9, 131.4, 131.3, 131.2, 131.1, 131.0, 130.5, 130.1, 128.5, 127.6, 127.4, 127.3, 127.0, 126.9, 126.8, 126.4, 126.3, 125.9, 125.5, 125.3, 125.1, 124.8, 124.4, 124.0, 22.3; HR-MS (EI-TOF): m/z = 683.2379, calcd. for $C_{50}H_{34}ClN$ (M^+): 683.2380.

6-Fluoro-1-methyl-4-phenyl-3-(5,6,7,8-tetraphenylnaphthalen-1-yl)isoquinoline (3l): obtained as a white solid according to the general procedure; yield: 203 mg (76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (dd, J_1 = 4.2 Hz, J_2 = 8.8 Hz, 1H), 7.44–7.36 (m, 3H), 7.29–7.22(m, 5H), 7.18–7.11 (m, 4H), 7.06–6.92 (m, 3H), 6.89–6.82 (m, 2H), 6.79–6.65 (m, 9H), 6.59–6.54 (m, 2H), 6.48 (t, J = 7.4 Hz, 1H), 6.18 (t, J = 7.4 Hz, 1H), 2,73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.0 (d $J_{C.F}$ = 233.8 Hz), 156.0, 152.8, 140.9, 140.8, 140.7, 140.3, 140.1, 138.8, 138.5, 138.3, 137.6, 137.0, 131.9, 131.4, 131.3, 131.1, 131.0, 130.6, 130.0, 128.1 (d, $J_{C.F}$ = 9.5 Hz), 127.6, 127.4, 127.3, 126.8, 126.6 (d, $J_{C.F}$ = 3.4 Hz), 126.4, 126.3, 125.8, 125.4, 125.3, 125.1, 124.8, 124.4, 123.0, 116.0(d, $J_{C.F}$=25.3 Hz), 109.5 (d, $J_{C.F}$ = 21.9 Hz), 22.4; HR-MS (EI-TOF): m/z = 667.2668, calcd. for $C_{50}H_{34}FN$ (M^+): 667.2675.

1-Methyl-4-phenyl-3-(5,6,7,8-tetraphenylnaphthalen-1-yl)-6-(trifluoromethyl)isoquinoline (3m): obtained as a white solid according to the general procedure; yield: 219 mg (76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, J = 8.4 Hz, 1H), 7.76 (s,1H), 7.62 (dd, J_1 = 1.2 Hz, J_2 = 8.0 Hz, 1H). 7.45 (d, J = 8.4 Hz, 1H), 7.31–7.23 (m, 4H), 7.17–7.11 (m, 4H), 7.03 (d, J = 7.2 Hz, 1H), 6.98 (d, J = 7.6 Hz, 1H), 6.92–6.83 (m, 2H), 6.79–6.70 (m, 9H), 6.54–6.46 (m, 3H), 6.12 (t, J = 7.6 Hz, 1H), 2,78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.3, 153.4, 140.9, 140.8, 140.6, 140.3, 140.0, 138.6, 138.5, 138.3, 137.5, 136.3, 134.5, 133.5, 133.4, 131.9, 131.4, 131.3, 130.9, 130.5, 130.2, 129.8, 127.7, 127.6, 127.5, 127.4, 126.6, 126.5 (d, $J_{C.F}$ = 3.8 Hz), 126.4, 126.0, 125.3, 125.1, 124.8, 124.5, 123.6 (d, $J_{C.F}$ = 3.6 Hz), 122.7, 121.8, 22.4; HR-MS (EI-TOF): m/z = 717.2638, calcd. for $C_{51}H_{34}F_3N$ (M^+): 717.2643.

1,7-Dimethyl-4-phenyl-5-(5,6,7,8-tetraphenylnaphthalen-1-yl)-1*H*-pyrrolo[2,3-*c*]pyridine (3n): obtained as a yellow solid according to the general procedure; yield: 227 mg (87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (dd, J_1 = 1.2 Hz, J_2 = 4.4 Hz, 1H), 7.37 (dd, J_1 = 1.2 Hz, J_2 = 6.8 Hz, 1H), 6.94–6.93 (m, 2H), 6.85–6.75(m, 4H), 6.74–6.65 (m, 7H), 6.59–6.53 (m, 2H), 6.49–6.44(m, 1H), 6,28 (t, J = 8.0 Hz, 1H), 3,96 (s, 3H), 2.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.0, 141.1, 140.4, 140.2, 139.6, 138.3, 137.7, 134.2, 133.7, 133.3, 133.0, 132.0, 131.7, 131.4, 131.2, 130.8, 130.3, 129.9, 129.4, 127.7, 127.5, 127.4, 127.3, 127.0, 126.5, 126.4, 126.3, 126.2, 126.1, 125.8, 125.2, 125.1, 124.8, 124.7, 124.6, 124.1, 36.9, 22.6; HR-MS (EI-TOF): m/z = 652.2877, calcd. for $C_{49}H_{36}N_2$ (M^+): 652.2878.

7-Methyl-4-phenyl-5-(5,6,7,8-tetraphenylnaphthalen-1-yl)thieno[2,3-*c*]pyridine (3o): obtained as a yellow solid according to the general procedure; yield: 218 mg (83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (d, J = 8.4 Hz, 1H), 7.45 (d, J = 5.2 Hz, 1H), 7.28–7.24 (m, 2H), 7.22–7.13 (m, 7H), 7.08–7.04 (m, 3H), 6.93 (d, J = 7.6 Hz, 1H), 6.86–6.80 (m 2H), 6.78–6.76 (m, 2H), 6.75–6.62 (m, 5H), 6.63–6.60 (m, 2H), 6.55–6.49 (m, 2H), 6.25 (t, J = 7.4 Hz, 1H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.8, 150.0, 144.5, 140.9, 140.8, 140.4, 140.2, 138.6, 138.5, 138.3, 138.0, 137.6, 133.8, 133.6, 131.9, 131.5, 131.3, 131.2, 131.1,130.3, 130.1, 128.2, 127.6, 127.5, 127.4, 126.6, 126.5, 126.4, 126.2, 125.5, 125.1, 125.0, 124.5, 124.1, 23.3; HR-MS (EI-TOF): m/z = 655.2331, calcd. for $C_{48}H_{33}NS$ (M^+): 655.2334.

4-Methyl-7-phenyl-6-(5,6,7,8-tetraphenylnaphthalen-1-yl)thieno[3,4-*c*]pyridine(3p): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (m,1H), 7.42 (m, 1H), 7.33–7.28 (m, 2H), 7.26–7.24 (m, 2H), 7.23–7.19 (m, 6H), 7.17–7.13 (m, 3H), 7.08 (d, J = 7.2 Hz, 1H), 6.96 (d, J = 7.6 Hz, 1H), 6.85–6.81 (m, 2H), 6.80–6.66 (m,8H), 6.60 (d, J = 6.8 Hz, 1H), 6.54–6.48 (m, 2H), 6.32 (t, J = 7.6 Hz, 1H), 2.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.7, 151.3, 148.3, 140.9, 140.8, 140.4, 140.1, 138.6, 138.3, 138.2, 137.5, 133.6, 133.4, 131.8, 131.6, 131.4, 131.2, 131.0, 130.3, 129.4, 127.8, 127.6, 127.4, 127.2, 126.7, 126.5, 126.4, 126.3, 125.7, 125.3, 125.1, 125.0, 124.6, 124.5, 122.3, 22.4; HR-MS (ESI): m/z = 655.2336, calcd, for $C_{48}H_{33}NS$ (M^+): 655.2334.

1,5-Dimethyl-4-phenyl-3-(5,6,7,8-tetraphenylnaphthalen-1-yl)-5*H*-pyrido[4,3-*b*]indole (3q): obtained as a yellow solid according to the general procedure; yield: 270 mg (96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, J = 8.0 Hz, 1H), 7.49–7.39 (m, 3H), 7.33–7.28 (m, 3H), 7.24–7.11 (m, 9H), 7.06 (d, J = 7.6 Hz, 1H), 7.01 (d, J = 7.6 Hz, 1H), 6.87–6.77 (m, 6H), 6.74–6.61 (m, 5H), 6,63–6,57 (m, 2H), 6.44 (t, J = 7.6 Hz, 1H), 6.21 (t, J = 7.2 Hz, 1H), 3,12 (s, 1H), 2. 85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.8, 150.5, 143.1, 142.2, 140.9, 140.8, 140.7, 140.2, 140.1, 138.6, 138.4, 138.2, 138.0, 136.7, 133.7, 133.2, 132.3, 131.9, 131.4, 131.2, 131.1, 130.9, 130.4, 127.6, 127.3, 127.0, 126.6, 126.4, 126.2, 125.9, 125.7, 125.2, 125.0, 124.5, 124.3, 122.3, 122.0, 120.5, 117.5, 116.7, 32.3, 23.3; HR-MS (EI-TOF): m/z = 702.3028, calcd. for $C_{53}H_{38}N_2$ (M^+): 702.3035.

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