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Rhodium-Catalyzed One-Pot Access to N-Polycyclic Aromatic Hydrocarbons from Aryl Ketones through Triple C−H Bond Activations

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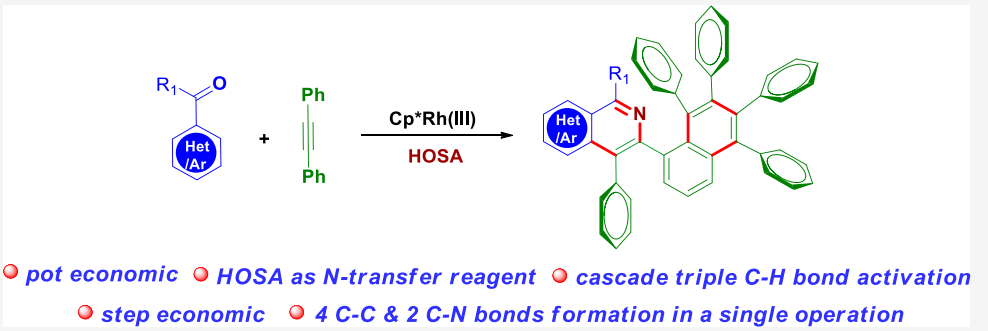

ABSTRACT: A Rh-catalyzed pot and step economic synthesis of aza-polycyclic aromatic hydrocarbons (N-PAHs) from readily available aryl ketones and alkynes has been disclosed. Additionally, a novel synthetic application of the well-known aminating reagent hydroxylamine-*O*-sulfonic acid (HOSA) has been explored as an in situ redox-neutral directing group for the formation of N-PAHs via isoquinoline. Multiple bond formation in a single operation through a cascade of triple C−H bond activations is the beauty of this protocol. The challenging annulations of two different alkynes in a regioselective fashion have been demonstrated effectively. Mechanistic studies reveal that 3,4-diphenyl-1-methylisoquinoline is an active intermediate for this one-pot transformation.

INTRODUCTION

Over the past few decades, synthesis of polycyclic aromatic hydrocarbons (PAHs) has gained significant attention among synthetic and material chemists. These compounds have been extensively employed in optoelectronics and advanced organic materials, which can be attributed to their structural features.[1] It has been observed that incorporation of heteroatoms such as boron (B), nitrogen (N), and sulfur (S) into the aromatic frameworks of PAHs could modulate its electronic properties.[2] Particularly, nitrogen-containing PAHs (N-PAHs) have a key significance in organic electronics because of nitrogen's influence on electronic modulation and the role in stabilizing the PAHs.[3] Moreover, nitrogen-atom-containing π-extended organic compounds are of prominent interest in organic light-emitting diodes (OLEDs) and organic field-effect transistors (OFETs).[4] Because of the unique electronics of the nitrogen atom, N-containing compounds are being used as model synthetic equivalents for nitrogen-doped graphene in current studies.[4d,e] Hence, the presence of heterocyclic rings in PAHs has a dramatic impact on organic solar cells, sensors, field-effect transistors, and the photophysical properties. Despite much exploration and advancement in this field, the common issues involved in this field are complicated and involves multistep syntheses of N-PAHs. Consequently, developing a straightforward methodology for the construction of highly conjugated PAHs is highly desirable.

During the past few decades, transition metal-catalyzed directed C−H bond functionalization has greatly improved the arsenal of synthetic chemistry by creating an attractive transformative platform for the construction of complex organic scaffolds.[5] Miura et al. have reported the Rh-catalyzed synthesis of polyarylated naphthyl- and anthrylazoles en route to the cleavage of multiple C−H bonds by taking *N*-phenylazoles and diarylalkynes as reacting partners.[6a] Likewise, Jioa and co-workers have disclosed the synthesis of polyarylated naphthylamides and isoquinolinone derivatives from benzamides and alkynes.[6b] Very recently, Dong et al. have addressed the synthesis of azahelicenes from *N*-phenyl-7-azaindole, which has significant applications in photophysics.[6c] Moreover, the

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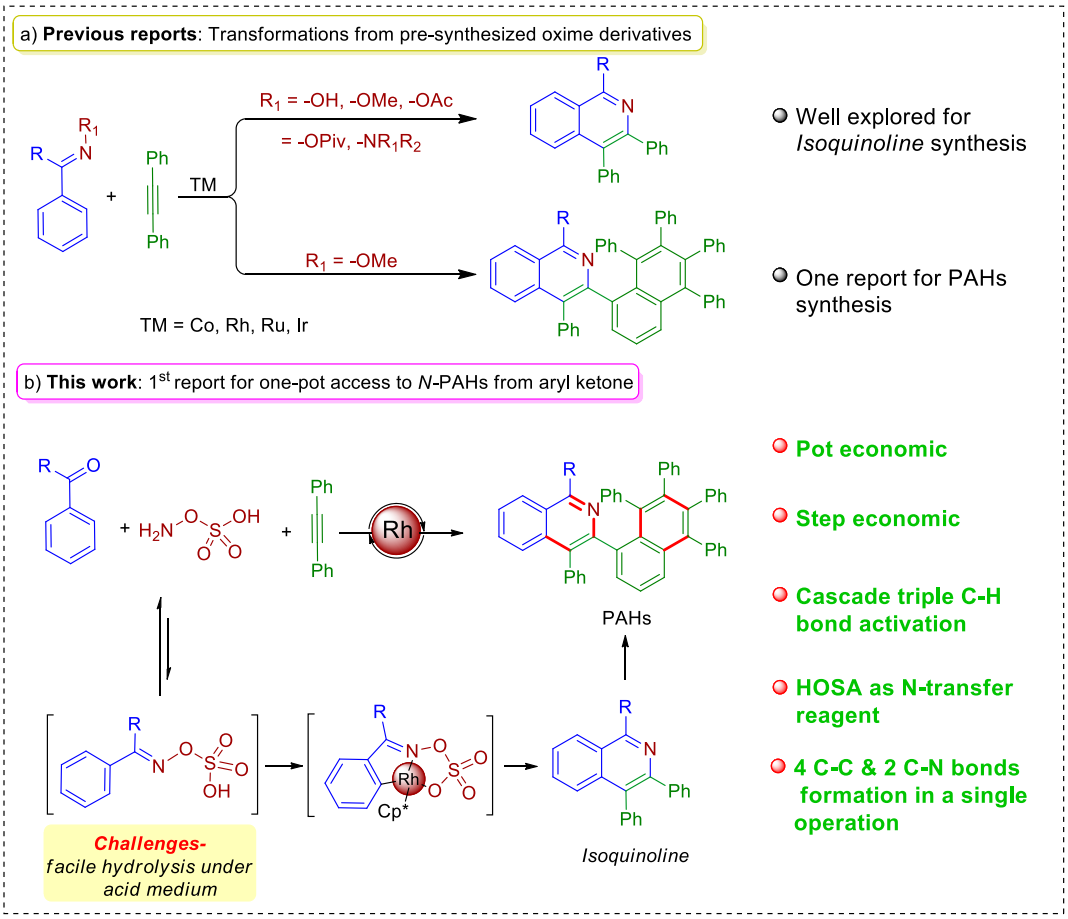

Figure 1. Transition metal-catalyzed oxidative annulation reactions with alkyne.

Ackerman group has developed a rhoda-electrocatalyzed synthesis of N-PAHs enabled by cascade of C−H activations.[6d] In addition, the use of redox-neutral directing groups is of current interest in the synthetic community. Such methodologies contribute greatly toward green synthesis, as it obviates the use of extra metal oxidants.[7]

In transition metal-catalyzed C−H bond activation, various types of redox-neutral directing groups have been well documented for different transformations.[8] In this context, isoquinoline synthesis has been depicted by taking different preinstalled redox-neutral directing groups with Rh, Co, Ru, and Ir (Figure 1a).[9] Although there are several reports on the synthesis of isoquinolines employing redox-neutral strategy with preformed imines, the synthesis of N-PAHs is limited to only one report (Figure 1a).[10] Thus, development of a simpler protocol to achieve complex value-added scaffolds is highly desirable in synthetic organic chemistry.

In this context, a pot economy protocol is being considered as an efficient approach in synthetic organic chemistry. One-pot synthesis is a promising green approach to contemporary synthesis because it minimizes the steps, pursues multiple new bond formations in a single operation, addresses the waste of chemicals, and more importantly minimizes wasteful efforts.[11] In our previous work, we documented the synthetic application of the well-known aminating reagent hydroxylamine-*O*-sulfonic acid (HOSA) as a new redox-neutral directing group for the one-pot synthesis of isoquinolines from readily available aryl ketones.[8f] In our continuous pursuit to expand our stockpile of new synthetic applications of HOSA, we envisaged the possibility of using acetophenone and alkyne for the synthesis of polyarylated aromatic hydrocarbons in a one-pot strategy through a cascade of triple C−H bond activations (Figure 1b). Salient features of this methodology includes (i) pot as well as step economic synthesis, (ii) a novel application of obscure redox-neutral directing group HOSA, (iii) cascade of triple C−H bond functionalization, and (iv) four C−C and two C−N bond formations in single reactor.

RESULTS AND DISCUSSION

We commenced our investigation by taking acetophenone (**1a**), diphenylacetylene (**2a**) as model substrate, and HOSA as N-transfer reagent (Table 1). To our delight, a preliminary attempt with 5 mol % of (1,2,3,4,5-pentamethylcyclopentadienyl rhodium(III) chloride dimer {[Cp*RhCl$_2$]$_2$}, 50 mol % of AgOAc as additive, and 2 equiv of Cu(OAc)$_2$ as oxidant in 1 mL of MeOH at 70 °C afforded 30% isolated yield of the desired product **3aa** along with 12% of **4aa** (Table 1, entry 1). Addition of 1 equiv of AgOAc lowered the overall yields. As addition of extra additive gave lower yield of **3aa** (entry 2), we presumed that lowering the additive loading for the first annulation step could improve the yields. To our delight, when the oxidant Cu(OAc)$_2$ was added after the complete conversion of acetophenone (5 h) to isoquinoline (**4aa**), we obtained 21% of **3aa** along with improved yield of isoquinoline **4aa** to 57%, which is the active starting material for the second and third C−H bond activations (Table 1, entry 3). Next, we moved to screen the reaction at different temperatures (Table 1, entries 4−6). From these screenings, 110 °C was found to be the optimal

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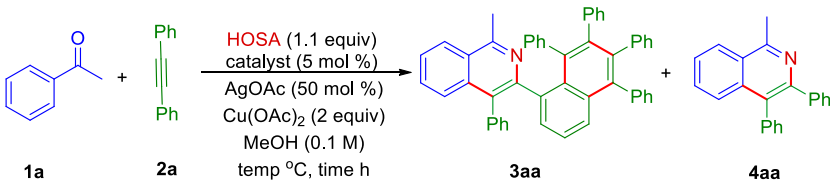
Table 1. Optimization of Reaction Conditions[a,b]



entry	catalyst	additive	oxidant	temp and time	(3aa/4aa)[b]
1	$[Cp^*Rh(Cl)_2]_2$	AgOAc	$Cu(OAc)_2$	70 °C, 12 h	30/12
2	$[Cp^*Rh(Cl)_2]_2$	AgOAc (100 mol %)	$Cu(OAc)_2$	70 °C, 12 h	25/14
3[c]	$[Cp^*Rh(Cl)_2]_2$	AgOAc	$Cu(OAc)_2$	70 °C, 12 h	21/57
4[c]	$[Cp^*Rh(Cl)_2]_2$	AgOAc	$Cu(OAc)_2$	100 °C, 12 h	27/22
5[c]	$[Cp^*Rh(Cl)_2]_2$	AgOAc	$Cu(OAc)_2$	110 °C, 12 h	61/11
6[c]	$[Cp^*Rh(Cl)_2]_2$	AgOAc	$Cu(OAc)_2$	120 °C, 12 h	34/18
7[c]	$[Cp^*Rh(Cl)_2]_2$	AgOAc	$Cu(OAc)_2$ (1)	110 °C, 12 h	23/60
8[c]	$[Cp^*Rh(Cl)_2]_2$	AgOAc	$Cu(OAc)_2$ (1.5)	110 °C, 12 h	46/37
9[c]	$[Cp^*Rh(Cl)_2]_2$	AgOAc	$Cu(OAc)_2$ (2.5)	110 °C, 12 h	55/trace
10[c,d]	$[Cp^*Rh(Cl)_2]2$	AgOAc	$Cu(OAc)_2$	110 °C, 18 h	71/trace
11[c,e]	$[Cp^*Rh(Cl)_2]_2$	AgOAc	$Cu(OAc)_2$	110 °C, 18 h	21/nd
12[c,f]	$[Cp^*Rh(Cl)_2]_2$	AgOAc	$Cu(OAc)_2$	110 °C, 18 h	nd/50
13[c,g]	$[Cp^*Rh(Cl)_2]_2$	AgOAc	$Cu(OAc)_2$	110 °C, 18 h	nd/nd
14[c]	$[Cp^*Rh(CH_3CN)_3][SbF_6]_2$	–	$Cu(OAc)_2$	110 °C, 18 h	11/67
15[c]	$[Cp^*Co(CO)I_2]$	AgOAc	$Cu(OAc)_2$	110 °C, 18 h	nd/nd
16[c]	$[RuCl_2(p\text{-cymene})]_2$	AgOAc	$Cu(OAc)_2$	110 °C, 18 h	nd/nd
17[c]	$[Cp^*Rh(Cl)_2]_2$	–	$Cu(OAc)_2$	110 °C, 18 h	nd/nd
18[c]	$[Cp^*Rh(Cl)_2]_2$	AgOAc	–	110 °C, 18 h	trace/85
19[c]	–	AgOAc	$Cu(OAc)_2$	110 °C, 18 h	nd/nd

[a]Reaction conditions: **1a** (0.10 mmol), **2a** (0.45 mmol), HOSA (0.11 mmol), catalyst (5 mol %), AgOAc (50 mol %), solvent (0.1 M), temp (°C), 12 h. [b]NMR yields by using 1,3,5-trimethoxybenzene as internal standard. [c]Reactions were heated at 70 °C for 5 h without $Cu(OAc)_2$, and then $Cu(OAc)_2$ was added followed by stirring. [d]Isolated yield. [e]DCE as the solvent. [f]CH_3CN as the solvent. [g]TFE as the solvent. nd = not detected.

temperature (Table 1, entry 5). A few conditions were screened to know the influence of oxidant equivalents (Table 1, entries 7−9). It was observed that increasing or lowering the equivalents of oxidant did not improve the yield of **3aa**.

A better yield of **3aa** was observed on increasing the reaction time to 18 h with almost total consumption of the starting material (entry 10). The reaction failed to produce better results when we attempted to replace MeOH by DCE, CH_3CN, and TFE (Table 1, entries 11−13). The replacement of catalytic system $[Cp^*RhCl_2]_2$ and AgOAc with cationic rhodium catalyst $[Cp^*Rh(CH_3CN)_3][SbF_6]_2$ had a deleterious impact on the reaction, resulting in only 11% of **3aa** (Table 1, entry 14). Similarly, attempts to replace the catalyst $[Cp^*RhCl_2]_2$ by $[Cp^*Co(CO)I_2]$ and $[RuCl_2(p\text{-cymene})]_2$ resulted in complete loss of reactivity (Table 1, entries 15 and 16). Next, to check the influence of $[Cp^*RhCl_2]_2$, AgOAc and $Cu(OAc)_2$ on the reaction, three control experiments were carried out (Table 1, entries 17−19). The reaction did not furnish isoquinoline **4aa** in the absence of silver additive (Table 1, entry 17). This indicates that AgOAc is playing a major role to make the active catalyst $Cp^*Rh(OAc)_2$. Moreover, the presence of $Cu(OAc)_2$ is also essential as oxidant to regenerate the catalyst (Table 1, entry 18). Similarly, we did not observe the formation of **3aa** in the absence of $[Cp^*RhCl_2]_2$ (Table 1, entry 19).

With the acquired optimized reaction conditions, we started examining various substituted acetophenones. We were pleased to see that this protocol is quite general with many structurally and electronically diverse compounds. Acetophenone bearing electron-donating groups such as *p*-Me, *p*-OMe, *m*-Me, and *o*-OMe afforded good to excellent yields of the respective annulated product (Scheme 1, **3ba**, **3ca**, **3ia**, **3ka**). The protocol also worked smoothly with thiomethyl and trifluoromethyl groups, delivering 57% yields of **3da** and **3ea**, respectively. Delightfully, substrates with easily transformable halo groups, F, Br, and I, also behaved smoothly under the reaction conditions, giving moderate to good yields of **3fa**, **3ga**, **3ha**, and **3ja**. This protocol was found compatible with a free hydroxy substituent, affording 78% of **3la**. To make more conjugated molecules, we examined this protocol with 4-phenylacetophenone and 1-acetylnaphthalene, which delivered their respective products **3ma** and **3na** in good yields.

Acetophenone having a dioxolane ring reacted in a completely regioselective fashion, yielding **3oa** in 31% yield. It is noteworthy that heteroaromatic aryl ketones such as furan, thiophene, and indole delivered their respective products **3pa**, **3qa**, and **3ra** in moderate to very good yields. It is worth mentioning that the unsymmetrical ketones **1i**, **1j**, **1l**, and **1o** underwent annulation in a regioselective manner, delivering their respective products **3ia**, **3ja**, **3la**, and **3oa**. Pleasingly, when 1-tetralone was subjected to the standard reaction condition, 55% of the corresponding N-PAH (**3sa**) was isolated. A variety of carbonyl compounds obtained by the replacement of the methyl group of acetophenone (**1t**, **1u**, **1v**, **1w**, and **1x**) were also investigated for the formation of N-PAHs under the standard reaction conditions. Of these carbonyl compounds, propiophenone (**1u**) was only successful in providing the desired N-PAHs (**3ua**). To extend the generality of this protocol, various disubstituted alkynes were investigated. Diaryl alkynes such as 4,4′-dichlorodiphenylacetylene (**2b**) afforded the corresponding annulated product **3cb** in moderate yield. In contrast, the alkynes having electron-donating groups such as Me and OMe are very less reactive and produced **3ac** and **3ad**, respectively, in

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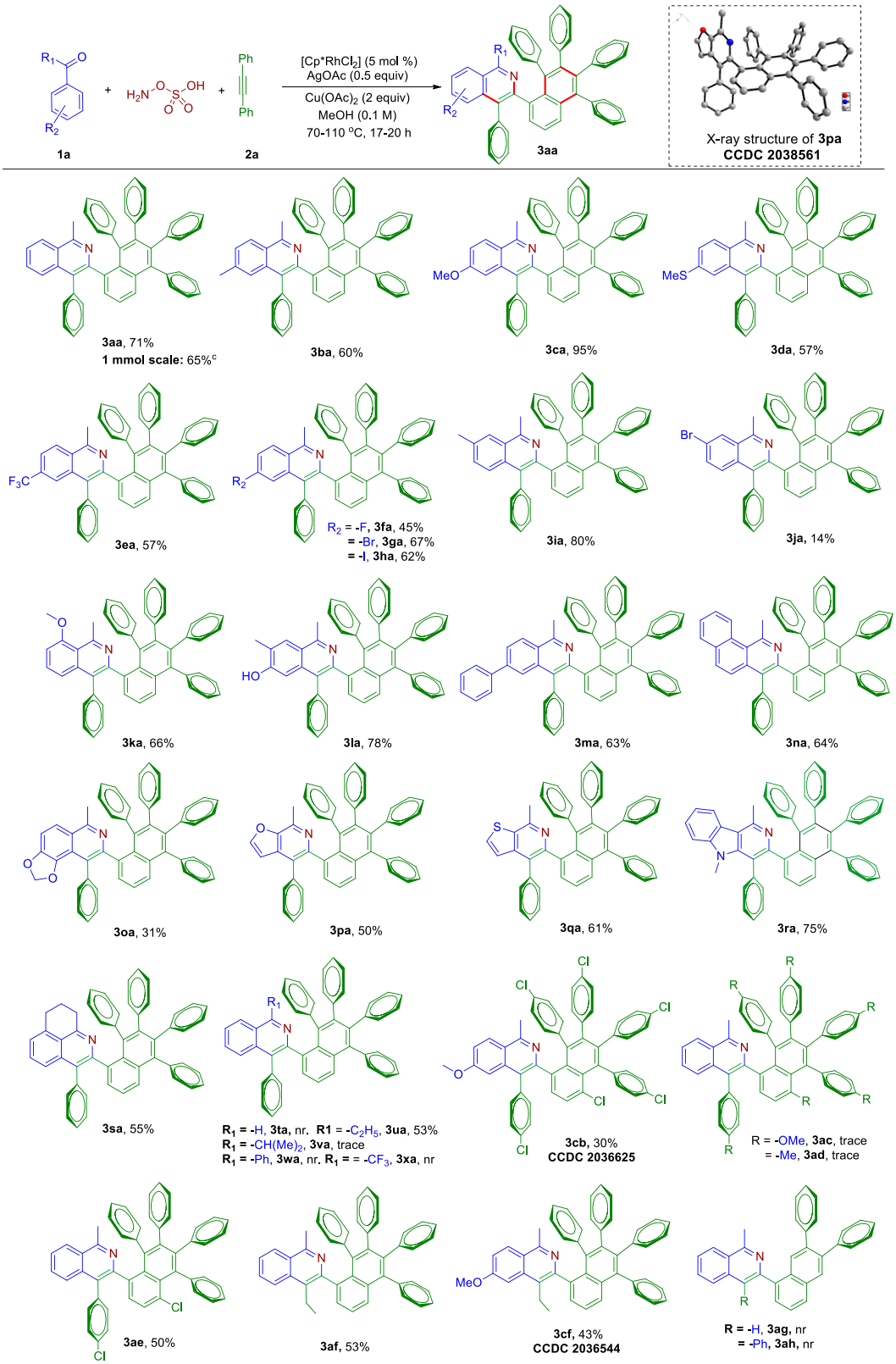
Scheme 1. Evaluation of Aryl Ketones for One-Pot Synthesis of N-Polycyclic Aromatic Hydrocarbons[a,b]



[a]Reaction conditions: **1a** (0.10 mmol), **2a** (0.45 mmol), HOSA (0.11 mmol), $[Cp^*RhCl_2]_2$ (5 mol %), AgOAc (50 mol %), MeOH (0.1 M), 70–110 °C, 12–18 h. [b]Isolated yields. [c]Isolated yield of 1 mmol scale reaction.

trace amounts. Taking advantage of the sequential addition of different alkynes, we hypothesized to construct unsymmetrical annulated products by using two different types of alkynes (alk-1 and alk-2). Gratifyingly, when **1a** was reacted with **2b** and **2a**, it delivered 50% of **3ae**. In a similar vein, we were able to construct **3af** and **3cf** in 53% and 43% yields, respectively. Unfortunately,

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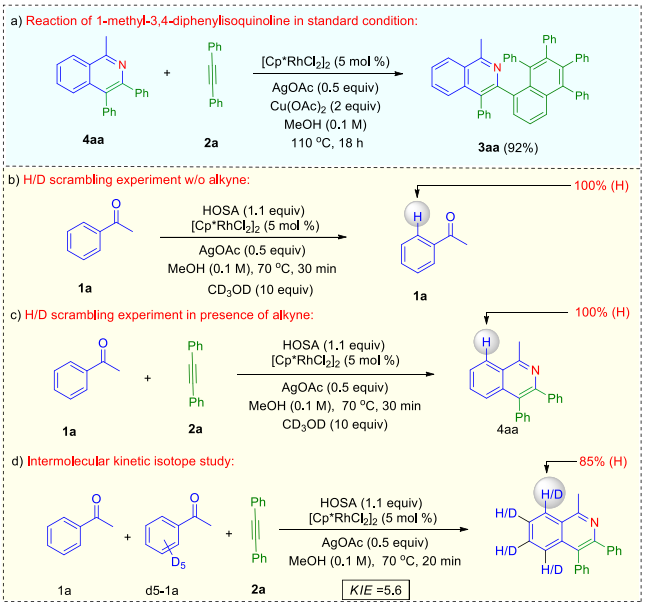
terminal alkynes failed to produce **3ag** and **3ah** under the standard reaction conditions. Further, to show the synthetic utility of this protocol, a 1 mmol scale reaction was performed, which gave 65% of **3aa** (Scheme 1).

To gain mechanistic insight, we have performed few control experiments. When 1-methyl-3,4-diphenylisoquinoline (**4aa**) was subjected to the standard reaction conditions, it afforded 92% of **3aa** (Scheme 2a). This indicates that formation of **3aa** is

Scheme 2. Mechanistic and Kinetic Experiments



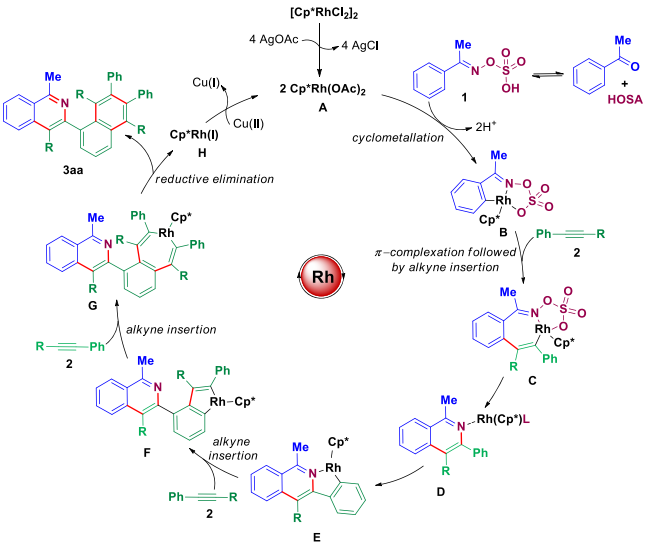
going through intermediate **4aa**. To understand the catalytic activity, a few kinetic experiments were conducted (Scheme 2b–d). No H/D scrambling could be confirmed at the ortho-position of acetophenone **1a** when the standard reaction was carried out with CD_3OD in the absence or presence of a coupling partner (Scheme 2b,c). Moreover, a kinetic isotope effect (KIE) for the intermolecular kinetic experiment was found to be 5.6 (Scheme 2d). All these experiments indicate that the Rh-catalyzed C–H activation step might be involved in the rate-limiting step.[12]

A plausible mechanism has been proposed for the formation of **3aa** based on the performed mechanistic experiments and previous literature reports (Scheme 3).[8f,10] At first, active rhodium catalyst **A** is generated from $[Cp^*RhCl_2]_2$ and AgOAc, which then undergoes cyclometalation irreversibly with in situ-generated arylmethyl imine **1**, giving cyclometalated species **B**. The coordination and insertion of alkyne into the C–Rh bond of **B** gave **C**, followed by cyclization in a redox-neutral manner to give the annulated product **D**. The catalyst activates the second C–H bond directed by the coordinating N atom from isoquinoline. Subsequent insertion of 2 equiv of alkyne led to intermediates **F** and **G**. Intermediate **G** undergoes reductive elimination, affording **3aa** and Cp*Rh(I) catalyst, which is again reoxidized by Cu(II) salt, to participate in the next catalytic cycle.

CONCLUSION

In summary, highly arylated N-PAHs have been synthesized in a one-pot strategy from readily available aryl ketones and alkynes through a cascade of three C–H bond activations. The well-

Scheme 3. Proposed Catalytic Cycle



known amination reagent HOSA has been used here as N-transfer reagent, thus exploring the synthetic applications of this aminating reagent. Control experiments and mechanistic studies clarify the role of each reagent and details of the mechanism. This methodology tolerates a wide range of functional groups including a free hydroxy (OH) group, showing the importance of this protocol. Moreover, the easily synthesizable, highly arylated N-PAH products could be applicable in optoelectronics. We expect that this synthetic protocol could gain the attention of synthetic and material chemists significantly.

EXPERIMENTAL SECTION

General Information.[8f] Acetophenone derivatives were bought from Sigma-Aldrich, Alfa-Aesar, Avra, TCI, and Spectrochem and used without any further purification. For column chromatography, silica gel (230–400 mesh) from Acme Co. was used. A gradient elution using distilled hexane and ethyl acetate was performed, based on Merck aluminum TLC sheets. All isolated compounds were characterized by ^1H NMR and ^{13}C NMR spectroscopy (Bruker-400 MHz) and HRMS. Copies of the ^1H NMR, ^{13}C NMR, and ^{19}F NMR can be found in Supporting Information. Nuclear magnetic resonance spectra were recorded on a Bruker 400 MHz instrument. HRMS signal analysis was performed using micro a TOF Q-II mass spectrometer. X-ray analysis was conducted using a Rigaku Smartlab X-ray diffractometer in our institute. All ^1H NMR experiments were reported in parts per million (ppm) and were measured relative to the signals for residual chloroform (7.26 ppm) in the deuterated solvent. All ^{13}C NMR spectra were reported in ppm relative to $CDCl_3$ (77.36 ppm). Chemical shift multiplicities are represented as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, dt = doublet of triplet, td = tripet of doublet. The starting materials **2b**,[13] **2c**,[13] **2d**,[13] acetophenone-d_5,[14] and **4aa**[8f] were prepared by following the reported procedure.

General Procedure for Rhodium-Catalyzed Annulation Reaction (A). To an oven-dried 25 mL Schlenk tube, charged with a magnetic stirring bar, were added dry MeOH (0.1 M, 1 mL), aryl ketone (0.1 mmol, 1 equiv), and HOSA (0.11 mmol, 1.1 equiv) sequentially under nitrogen atmosphere. To this solution were added alkyne (0.45 mmol, 4.5 equiv), $[Cp^*RhCl_2]_2$(0.005 mmol, 0.05 equiv), and AgOAc (0.05 mmol, 0.5 equiv). Then the reaction mixture was stirred (500 rpm) at 70 °C in a preheated aluminum block for 5–7 h. The reaction was monitored by TLC. After complete conversion of aryl ketone to corresponding isoquinoline, the reaction mixture was allowed to attain ambient temperature. To the above reaction mixture was added $Cu(OAc)_2$ (0.2 mmol, 2 equiv) under nitrogen atmosphere and

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again heated at 110 °C in a preheated aluminum block for 12−20 h. The reaction was monitored by TLC. After complete conversion, the reaction mixture was transferred in to a 50 mL round-bottom flask. The reaction vial was washed two to three times with ethyl acetate (10−15 mL). The solvent was removed under reduced pressure to obtain a crude mixture which was extracted with ethyl acetate (3 × 10 mL) and saturated sodium bicarbonate (10 mL). The organic layer was dried over anhydrous Na_2SO_4 and then purified through column chromatography by using 230−400 mesh silica, giving 46 mg (71%) of **3aa**.

General Procedure for Rhodium-Catalyzed Annulation Reaction (B). To an oven-dried 25 mL Schlenk tube, charged with a magnetic stirring bar, were added dry MeOH (0.1 M, 1 mL), aryl ketone (0.11 mmol, 1.1 equiv), and HOSA (0.12 mmol, 1.2 equiv) sequentially under nitrogen atmosphere. To this solution were added alkyne-1 (0.1 mmol, 1 equiv), $[Cp^*RhCl_2]_2$(0.005 mmol, 0.05 equiv), and AgOAc (0.05 mmol, 0.5 equiv). Then the reaction mixture was stirred (500 rpm) at 70 °C in a preheated aluminum block for 5−7 h. The reaction was monitored by TLC. After complete conversion of aryl ketone to the corresponding isoquinoline, the reaction mixture was allowed to attain ambient temperature. To the above reaction mixture was added alkyne-2 (0.35 mmol, 3.5 equiv) and $Cu(OAc)_2$ (0.2 mmol, 2 equiv) under nitrogen atmosphere and again heated at 110 °C in a preheated aluminum block for 12−20 h. The reaction was monitored by TLC. After complete conversion, the reaction mixture was transferred in to a 50 mL round-bottom flask. The reaction vial was washed two to three times with ethyl acetate (10−15 mL). The solvent was removed under reduced pressure to obtain a crude mixture which was extracted with ethyl acetate (3 × 10 mL) and saturated sodium bicarbonate (10 mL). The organic layer was dried over anhydrous Na_2SO_4 and then purified by column chromatography using 230−400 mesh silica, giving the corresponding N-PAHs.

General Procedure for a 1 mmol Scale Reaction To Synthesize 3aa. To an oven-dried 25 mL Schlenk tube, charged with a magnetic stirring bar, were added dry MeOH (0.1 M, 10 mL), aryl ketone (1 mmol, 1 equiv), and hydroxylamine-*O*-sulfonic acid (1.1 mmol, 1.1 equiv) sequentially under nitrogen atmosphere. To this solution were added alkyne (4.5 mmol, 4.5 equiv), $[Cp^*RhCl_2]_2$ (0.05 mmol, 0.05 equiv), and AgOAc (0.5 mmol, 0.5 equiv). Then the reaction mixture was stirred (500 rpm) at 70 °C in a preheated aluminum block for 5 h. The reaction was monitored by TLC. After complete conversion of aryl ketone to the corresponding isoquinoline, the reaction mixture was allowed to attain ambient temperature. To the above reaction mixture was added $Cu(OAc)_2$ (2 mmol, 2 equiv) under nitrogen atmosphere and again heated at 110 °C in a preheated aluminum block for 18 h. The reaction was monitored by TLC. After complete conversion, the reaction mixture was transferred to a 50 mL round-bottom flask. The reaction vial was washed two to three times with ethyl acetate (20−30 mL). The solvent was removed under reduced pressure to afford a crude mixture which was extracted with ethyl acetate (3 × 10 mL) and saturated sodium bicarbonate (10 mL). The organic layer was dried over anhydrous Na_2SO_4 and then purified by column chromatography using 230−400 mesh silica, giving 422 mg (65%) of **3aa**.

*1-Methyl-4-phenyl-3-(5,6,7,8-tetraphenylnaphthalen-1-yl)-isoquinoline (**3aa**).*[10] Prepared according to general procedure A. The crude reaction mixture was purified by column chromatography, giving a pale brown solid (45 mg) in 71% yield; mp 143−145 °C; R_f = 0.2 (10% EtOAc/hexane); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.92−7.90 (m, 1H), 7.45−7.38 (m, 6H), 7.26−7.20 (m, 4H), 7.17−7.11 (m, 4H), 7.02 (t, J = 8.0 Hz, 2H), 6.91−6.88 (m, 1H), 6.85−6.82 (m, 1H), 6.79−6.66 (m, 9H), 6.54 (d, J = 4.0 Hz, 2H), 6.47 (t, J = 8.0 Hz, 1H), 6.12 (t, J = 8.0 Hz, 1H), 2.76 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 156.3, 141.1, 141.0, 140.9, 140.3 (2C), 138.5, 138.4, 137.9, 135.4, 133.6, 133.5, 132.2, 131.7, 131.6 (2C), 131.5, 131.4 (2C), 131.3, 131.2, 130.6, 130.4, 127.7, 127.6, 127.5, 127.4, 126.7 (2C), 126.6, 126.4, 126.3, 126.1, 126.0, 125.9, 125.5, 125.4, 125.3, 125.2, 124.8, 124.6, 22.3; IR (KBr, cm^{-1}): 3056, 2870, 1602, 1441; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{50}H_{36}N$ 650.2842; found 650.2878.

*1,6-Dimethyl-4-phenyl-3-(5,6,7,8-tetraphenylnaphthalen-1-yl)-isoquinoline (**3ba**).*[10] Prepared according to general procedure A. The crude reaction mixture was purified by column chromatography, giving a brown solid (40 mg) in 60% yield; mp 173−175 °C; R_f = 0.3 (10% EtOAc/hexane); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80 (d, J = 8.0 Hz, 1H), 7.41−7.38 (m, 3H), 7.27 (d, J = 8.0 Hz, 2H), 7.23−7.19 (m, 4H), 7.16−7.10 (m, 4H), 7.02 (t, J = 8.0 Hz, 2H), 6.92 (t, J = 8.0 Hz, 1H), 6.85−6.83 (m, 1H), 6.79−6.77 (m, 3H), 6.74−6.67 (m, 6H), 6.53−6.48 (m, 3H), 6.13 (t, J = 8.0 Hz, 1H), 2.72 (s, 3H), 2.36 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 156.0, 141.1 (2C), 141.0, 140.3, 140.2, 138.5, 138.3, 137.9, 135.6, 133.6, 133.4, 132.3, 131.7, 131.6 (2C), 131.5, 131.4, 131.3, 131.2, 130.6, 130.4, 128.5, 127.8, 127.5, 127.3, 127.2, 126.7 (2C), 126.6, 126.5, 126.4, 126.1, 125.5, 125.4, 125.2 (2C), 124.9, 124.8, 124.6, 124.3, 22.3, 22.1; IR (KBr, cm^{-1}): 3054, 2868, 1600, 1440.

*6-Methoxy-1-methyl-4-phenyl-3-(5,6,7,8-tetraphenylnaphthalen-1-yl)isoquinoline (**3ca**).*[10] Prepared according to general procedure A. The crude reaction mixture was purified by column chromatography, giving a pale yellow solid (65 mg) in 95% yield; mp 144−146 °C; R_f = 0.2 (20% EtOAc/hexane); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.77 (d, J = 8.0 Hz, 1H), 7.39−7.34 (m, 3H), 7.21−7.16 (m, 4H), 7.10 (q, J = 8.0 Hz, 4H), 7.03−6.99 (m, 3H), 6.91−6.87 (m, 1H), 6.83−6.79 (m, 1H), 6.75−6.73 (m, 3H), 6.70−6.62 (m, 7H), 6.53−6.48 (m, 3H), 6.16 (t, J = 8.0 Hz, 1H), 3.64 (s, 3H), 2.67 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 160.4, 155.6, 141.0 (2C), 140.9, 140.3, 140.2, 138.5, 138.2, 137.9, 137.8, 137.3, 133.6, 133.4, 132.2, 131.6, 131.4 (2C), 131.3 (2C), 131.1, 130.6, 130.2, 127.7, 127.6, 127.5, 127.4, 127.2, 126.7, 126.6 (2C), 126.4, 126.0, 125.4 (2C), 125.1, 124.9, 124.6, 121.6, 118.3, 104.4, 55.4, 22.2; IR (KBr, cm^{-1}): 3055, 2868, 1618, 1441, 1028.

*1-Methyl-6-(methylthio)-4-phenyl-3-(5,6,7,8-tetraphenylnaphthalen-1-yl)isoquinoline (**3da**).* Prepared according to general procedure A. The crude reaction mixture was purified by column giving a pale yellow solid (40 mg) in 57% yield; mp 145−147 °C; R_f = 0.2 (10% EtOAc/hexane); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.78 (d, J = 8.0 Hz, 1H), 7.43−7.38 (m, 3H), 7.29 (dd, J = 8.0 Hz, 4 Hz, 1H), 7.25−7.21 (m, 4H), 7.17−7.10 (m, 5H), 7.03−6.98 (m, 2H), 6.91 (t, J = 8.0 Hz, 1H), 6.87−6.83 (m, 1H), 6.79−6.67 (m, 9H), 6.56−6.50 (m, 3H), 6.18 (t, J = 8.0 Hz, 1H), 2,69 (s, 3H), 2.32 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 156.0, 152.7, 141.1, 141.0, 140.9, 140.2 (2C), 139.2, 138.5, 138.3, 137.8, 137.4, 135.7, 133.6, 133.4, 132.2, 131.6, 131.5, 131.4 (2C), 131.3 (2C), 131.1, 130.6, 130.3, 128.4, 127.7, 127.6, 127.5, 127.3, 127.2, 126.7 (2C), 126.5, 126.4, 126.0, 125.6, 125.5, 125.4, 125.2, 125.0, 124.9, 124.6, 123.5, 120.3, 22.2, 15.1; IR (KBr, cm^{-1}): 3055, 2837, 1601, 1440; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{51}H_{38}NS$ 696.2719; found 696.2690.

*1-Methyl-4-phenyl-3-(5,6,7,8-tetraphenylnaphthalen-1-yl)-6-(trifluoromethyl)isoquinoline (**3ea**).*[10] Prepared according to general procedure A. The crude reaction mixture was purified by column chromatography, giving a pale yellow solid (25 mg) in 57% yield; mp 119−121 °C; R_f = 0.3 (10% EtOAc/hexane); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.02 (d, J = 8.8 Hz, 1H), 7.76 (s, 1H), 7.62 (dd, J = 8.4 Hz, 1.2 Hz, 1H), 7.45 (dd, J = 8.4 Hz, 1.2 Hz, 1H),7.40−7.36 (m, 2H), 7.30−7.11 (m, 9H), 7.04 (d, J = 7.2 Hz, 1H), 6.99 (d, J = 7.6 Hz, 1H), 6.89 (t, J = 7.6 Hz, 1H), 6.85−6.82 (m, 1H), 6.78−6.76 (m, 2H), 6.74−6.66 (m, 6H), 6.56−6.52 (m, 2H), 6.47 (t, J = 7.6 Hz, 1H), 6.13 (t, J = 7.6 Hz, 1H), 2.78 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 156.5, 153.6, 141.1, 141.0, 140.8, 140.6, 140.2, 138.8, 138.7, 138.6, 137.7, 136.5, 134.7, 133.8, 133.6, 132.1, 131.6 (2C), 131.5, 131.4, 131.3, 131.1, 131.0, 130.7, 130.3, 130.0, 127.9, 127.8, 127.7, 127.6 (2C), 127.2, 126.9 (q, J_{C-F} = 270.8 Hz), 126.8, 126.6 (2C), 126.5, 126.1, 125.6, 125.5, 125.3, 125.0, 124.6, 123.8 (q, J_{C-F} = 4.0 Hz), 121.9 (q, J_{C-F} = 2.9 Hz), 22.5; ^{19}F NMR ($CDCl_3$, 376 MHz): δ −62.7; IR (KBr, cm^{-1}): 3057, 2852, 1601, 1441, 1311.

*6-Fluoro-1-methyl-4-phenyl-3-(5,6,7,8-tetraphenylnaphthalen-1-yl)isoquinoline (**3fa**).*[10] Prepared according to general procedure A. The crude reaction mixture was purified by column chromatography, giving a brown solid (30 mg) in 45% yield; mp 135−137 °C; R_f = 0.3 (10% EtOAc/hexane); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.94−7.90 (m, 1H), 7.44−7.36 (m, 3H), 7.28 (d, J = 8.0 Hz, 1H), 7.23−7.19 (m, 3H),

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7.17−7.12 (m, 5H), 7.06−6.97 (m, 3H), 6.89−6.82 (m, 2H), 6.79−6.70 (m, 8H), 6.66 (d, J = 8.0 Hz, 1H), 6.59−6.54 (m, 2H), 6.48 (t, J = 8.0 Hz, 1H), 6.19−6.16 (m, 1H), 2.73 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 163.1 (d, J_{C-F} = 248.0 Hz), 156.2, 153.0, 141.1, 141.0, 140.9, 140.4, 140.2, 139.9, 138.6, 138.4, 137.8, 137.3 (d, J_{C-F} = 10.0 Hz), 137.2, 133.7, 133.5, 132.0, 131.6 (2C), 131.5, 131.4 (d, J_{C-F} = 3 Hz), 131.3, 131.2, 130.7, 130.2, 128.3 (2C), 127.8, 127.6 (d, J_{C-F} = 3.0 Hz), 127.5, 126.9, 126.7 (d, J_{C-F} = 3.0 Hz), 126.6 (2C), 126.5, 126.0, 125.5, 125.4, 125.2, 124.9, 124.6, 123.2, 116.3 (d, J_{C-F} = 25 Hz), 109.7 (d, J_{C-F} = 22 Hz), 22.5; ^{19}F NMR ($CDCl_3$, 376 MHz): δ −108.6; IR (KBr, cm^{-1}): 3055, 2852, 1601, 1400, 1188.

*6-Bromo-1-methyl-4-phenyl-3-(5,6,7,8-tetraphenylnaphthalen-1-yl)isoquinoline (**3ga**).* Prepared according to general procedure A. The crude reaction mixture was purified by column chromatography, giving a pale yellow solid (49 mg) in 67% yield; mp 113−115 °C; R_f = 0.3 (10% EtOAc/hexane); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.74 (d, J = 8.0 Hz, 1H), 7.55 (d, J = 4.0 Hz, 1H), 7.49 (dd, J = 8.8 Hz, 0.8 Hz, 1H), 7.41−7.36 (m, 2H), 7.35 (dd, J = 6.8 Hz, 0.8 Hz, 1H), 7.28 (d, J = 8 Hz, 1H), 7.20 (dt, J = 7.2 Hz, 2.4 Hz, 3H), 7.13−7.12 (m, 3H), 7.09−7.07 (m, 1H), 7.01−6.96 (m, 2H), 6.89 (t, J = 8.0 Hz, 1H), 6.84−6.80 (m, 1H), 6.76−6.71 (m, 3H), 6.69−6.65 (m, 5H), 6.61 (d, J = 4.0 Hz, 1H), 6.54−6.47 (m, 3H), 6.16 (t, J = 8.0 Hz, 1H), 2.70 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 156.4, 153.2, 141.1, 141.0, 140.8, 140.4, 140.2, 138.8, 138.6, 138.4, 137.7, 136.8, 136.7, 133.7, 133.5, 132.1, 131.6, 131.5, 131.4 (2C), 131.3 (2C), 131.1, 130.6, 130.3, 129.7, 128.2, 127.8, 127.6 (2C), 127.5, 127.1, 127.0, 126.7 (2C), 126.6 (2C), 126.5, 126.1, 125.7, 125.5, 125.2, 125.0, 124.6, 124.3, 22.4; IR (KBr, cm^{-1}): 3056, 2852, 1599, 1441, 652; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{50}H_{35}BrN$ 728.1947; found 728.1949.

*6-Iodo-1-methyl-4-phenyl-3-(5,6,7,8-tetraphenylnaphthalen-1-yl)isoquinoline (**3ha**).* Prepared according to general procedure A. The crude reaction mixture was purified by column chromatography, giving a pale yellow solid (48 mg) in 62% yield; mp 117−119 °C; R_f = 0.3 (10% EtOAc/hexane); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.82 (d, J = 1.6 Hz, 1H), 7.72 (dd, J = 8.8 Hz, 1.6 Hz, 1H), 7.61 (d, J = 8.8 Hz, 1H), 7.42 (dd, J = 8.4 Hz, 1.2 Hz, 1H), 7.36 (dd, J = 6.8 Hz, 1.6 Hz, 1H), 7.30−7.28 (m, 1H), 7.23−7.22 (m, 1H), 7.21−7.20 (m, 1H), 7.17−7.14 (m, 2H), 7.13−7.10 (m, 2H), 7.02 (d, J = 7.6 Hz, 1H), 6.98 (td, J = 7.6 Hz, 1.2 Hz, 1H), 6.92−6.88 (m, 1H), 6.86−6.83 (m, 1H), 6.79−6.75 (m, 4H), 6.73−6.66 (m, 7H), 6.54−6.49 (m, 3H), 6.18−6.14 (m, 1H), 2.70 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 156.5, 141.1, 141.0, 140.8, 140.4, 140.2, 138.6, 138.4, 137.7, 136.8 (2C), 135.1, 134.8, 133.6, 133.4, 132.1, 131.6 (2C), 131.5 (2C), 131.4, 131.3 (2C), 131.1, 130.6, 130.3, 127.8, 127.7, 127.6, 127.4, 126.9, 126.8, 126.7(2C), 126.6, 126.5, 126.1, 125.7, 125.4, 125.2, 125.0, 124.6, 97.2, 22.2; IR (KBr, cm^{-1}): 3056, 2856, 1592, 1440, 583; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{50}H_{35}IN$ 776.1809; found 776.1793.

*1,7-Dimethyl-4-phenyl-3-(5,6,7,8-tetraphenylnaphthalen-1-yl)-isoquinoline (**3ia**).*[10] Prepared according to general procedure A. The crude reaction mixture was purified by column chromatography, giving a pale brown solid (53 mg) in 80% yield; mp 152−154 °C; R_f = 0.2 (10% EtOAc/hexane); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.66 (s, 1H), 7.42−7.32 (m, 4H), 7.28−7.25 (m, 2H), 7.22−7.18 (m, 3H), 7.15−7.10 (m, 4H), 7.01 (dd, J = 16.0 Hz, 8.0 Hz, 2H), 6.88 (t, J = 8.0 Hz, 1H), 6.84−6.82 (m, 1H), 6.79−6.70 (m, 8H), 6.66 (d, J = 4.0 Hz, 1H), 6.55 (d, J = 8.0 Hz, 2H), 6.48 (t, J = 8.0 Hz, 1H), 6.16−6.13 (m, 1H), 2.71 (s, 3H), 2.49 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 155.6, 151.1, 141.1, 141.0, 140.3, 140.2, 139.4, 138.5, 138.3, 137.9, 137.8, 135.9, 133.6, 133.5, 132.3, 131.7 (2C), 131.6 (2C), 131.5 (2C), 131.4, 131.3, 131.2, 130.6, 130.4, 129.2, 127.7, 127.5, 127.3, 127.2, 126.7 (2C), 126.5, 126.4, 126.1, 125.9, 125.5, 125.4, 125.1, 124.8, 124.6, 124.2, 22.4, 22.1; IR (KBr, cm^{-1}): 3055, 2917, 1601, 1410.

*7-Bromo-1-methyl-4-phenyl-3-(5,6,7,8-tetraphenylnaphthalen-1-yl)isoquinoline (**3ja**).* Prepared according to general procedure A. The crude reaction mixture was purified by column chromatography, giving a brown solid (10 mg) in 14% yield; mp 140−142 °C; R_f = 0.2 (10% EtOAc/hexane); ^1H NMR ($CDCl_3$, 400 MHz): δ 8.05 (s, 1H), 7.50 (d, J = 8.8 Hz, 1H), 7.43 (d, J = 8.4 Hz, 1H), 7.39−7.31 (m, 4H), 7.23−7.21 (m, 3H), 7.18−7.12 (m, 5H), 7.03 (d, J = 7.6 Hz, 1H), 6.98 (d, J = 7.6 Hz, 1H), 6.90 (t, J = 7.6 Hz, 1H), 6.84−6.82 (m, 1H), 6.80−6.79 (m, 2H), 6.74−6.69 (m, 5H), 6.65 (d, J = 7.2 Hz, 1H), 6.56−6.50 (m, 3H), 6.20−6.18 (m, 1H), 2.70 (s, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 155.4, 152.5, 141.1, 141.0, 140.9, 140.4, 140.2, 138.8, 138.7, 138.4, 137.0, 134.0, 133.7, 133.5, 132.9, 132.0, 131.6 (2C), 131.4, 131.3, 131.2, 130.6, 130.3, 128.1, 127.8, 127.7, 127.6, 127.5 (2C), 127.0, 126.9, 126.8, 126.7, 126.6, 126.5, 126.1, 125.6, 125.5, 125.2, 125.1, 124.6, 120.2, 22.4; IR (KBr, cm^{-1}): 3055, 2852, 1601, 1408, 651; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{50}H_{35}BrN$ 728.1947; found 728.1987.

*8-Methoxy-1-methyl-4-phenyl-3-(5,6,7,8-tetraphenylnaphthalen-1-yl)isoquinoline (**3ka**).* Prepared according to general procedure A. The crude reaction mixture was purified by column chromatography, giving a pale yellow solid (45 mg) in 66% yield; mp 273−275 °C; R_f = 0.2 (10% EtOAc/hexane); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.41−7.34 (m, 3H), 7.28 (t, J = 8.0 Hz, 1H), 7.22−7.09 (m, 8H), 7.01 (dd, J = 16.0 Hz, 8.0 Hz, 2H), 6.91 (dd, J = 16.0 Hz, 8.0 Hz, 2H), 6.85−6.81 (m, 1H), 6.78−6.66 (m, 10H), 6.58−6.55 (m, 2H), 6.51 (t, J = 8.0 Hz, 1H), 6.22−6.19 (m, 1H), 3.92 (s, 3H), 2.89 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 158.1, 156.1, 152.0, 141.1, 141.0, 140.9, 140.3, 140.2, 139.3, 138.5, 138.3, 138.2, 138.0, 133.6, 133.4, 132.1, 131.7, 131.6 (2C), 131.5, 131.4 (2C), 131.3, 131.2, 130.6, 130.3, 129.5, 128.5, 127.7, 127.5, 127.3, 127.2, 126.7, 126.6, 126.5 (2C), 126.4, 126.0, 125.4 (2C), 125.1, 124.9, 124.6, 118.9, 118.3, 105.8, 55.8, 28.9; IR (KBr, cm^{-1}): 3055, 2877, 2837, 1611, 1440, 1027; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{51}H_{38}NO$ 680.2948; found 680.2932.

*1,7-Dimethyl-4-phenyl-3-(5,6,7,8-tetraphenylnaphthalen-1-yl)-isoquinolin-6-ol (**3la**).* Prepared according to general procedure A. The crude reaction mixture was purified by column chromatography, giving a pale brown solid (53 mg) in 78% yield; mp 242−244 °C; R_f = 0.2 (30% EtOAc/hexane); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.55 (s, 1H), 7.27 (d, J = 8.4 Hz, 1H), 7.17−7.09 (m, 4H), 7.05 (d, J = 6.8 Hz, 1H), 7.02−7.00 (m, 1H), 6.98−6.91 (m, 3H), 6.89−6.85 (m, 1H), 6.81−6.75 (m, 6H), 6.71−6.65 (m, 5H), 6.63−6.60 (m, 1H), 6.59 (s, 1H), 6.54−6.49 (m, 3H), 6.45 (d, J = 7.6 Hz, 1H), 6.16−6.13 (m, 1H), 2.50 (s, 3H), 2.31 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 154.4, 141.0 (2C), 140.9, 140.2, 140.1, 138.3, 138.1, 137.9, 137.8, 136.4, 133.6, 133.2, 132.5, 131.6, 131.4 (2C), 131.3, 131.2, 130.5, 129.8, 128.5, 127.7, 127.5 (2C), 127.2, 127.0, 126.9, 126.7 (2C), 126.6, 126.5, 126.4, 126.1 (2C), 125.5, 125.4, 125.2, 124.9, 124.2, 121.3, 107.3, 21.0, 17.2; IR (KBr, cm^{-1}): 3443, 3056, 2868, 1440; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{51}H_{38}NO$ 680.2948; found 680.2906.

*1-Methyl-4,6-diphenyl-3-(5,6,7,8-tetraphenylnaphthalen-1-yl)-isoquinoline (**3ma**).* Prepared according to general procedure A. The crude reaction mixture was purified by column chromatography, giving a pale yellow solid (45 mg) in 63% yield; mp 155−157 °C; R_f = 0.2 (10% EtOAc/hexane); ^1H NMR ($CDCl_3$, 400 MHz): δ 8.03 (d, J = 8.0 Hz, 1H), 7.76 (s, 1H), 7.62 (dd, J = 12.0 Hz, 4.0 Hz, 1H), 7.45 (dd, J = 12.0 Hz, 4.0 Hz, 1H),7.40−7.36 (m, 2H), 7.29−7.13 (m, 11H), 7.04 (d, J = 8.0 Hz, 1H), 6.99 (d, J = 8.0 Hz, 1H), 6.90 (t, J = 8.0 Hz, 1H), 6.86−6.83 (m, 1H), 6.80−6.66 (m, 11H), 6.55−6.52 (m, 2H), 6.48 (t, J = 8.0 Hz, 1H), 6.13 (t, J = 8.0 Hz, 1H), 2.78 (s, 3H);$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 156.2, 153.2, 140.8, 140.6, 140.5, 140.2, 139.8, 138.4, 138.3, 138.2, 137.3, 136.1, 134.3, 133.4, 133.2, 131.7, 131.3, 131.2, 131.1 (2C), 131.0, 130.8, 130.3, 130.0, 129.6, 127.5 (2C), 127.4, 127.3 (2C), 126.9, 126.4 (2C), 126.3 (2C), 126.2, 125.8, 125.3, 125.2, 125.0, 124.7, 124.3, 123.4 (2C), 121.6 (2C), 22.2; IR (KBr, cm^{-1}): 3056, 2857, 1600, 1441; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{56}H_{40}N$ 726.3155; found 726.3129.

*1-Methyl-4-phenyl-3-(5,6,7,8-tetraphenylnaphthalen-1-yl)-benzo[h]isoquinoline (**3na**).* Prepared according to general procedure A. The crude reaction mixture was purified by column chromatography, giving a brown solid (45 mg) in 64% yield; mp 258−259 °C; R_f = 0.2 (10% EtOAc/hexane); ^1H NMR ($CDCl_3$, 400 MHz): δ 8.62 (d, J = 12.0 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.69 (t, J = 8.0 Hz, 1H), 7.65−7.58 (m, 2H), 7.53 (d, J = 8.0 Hz, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.35 (d, J = 8.0 Hz, 1H), 7.33−7.25 (m, 3H), 7.24−7.20 (m, 2H), 7.16−7.09 (m, 4H), 7.03 (d, J = 8.0 Hz, 1H), 7.00−6.95 (m, 2H), 6.87−6.83 (m, 1H), 6.78−6.65 (m, 9H), 6.56−6.44 (m, 2H), 6.39 (d, J = 8.0 Hz, 1H), 5.95 (t, J = 8.0 Hz, 1H), 3.08 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 154.1, 153.5, 141.0 (2C), 140.8, 140.2, 138.5, 138.3, 137.8

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(2C), 136.1, 133.4 (2C), 133.0, 132.3, 131.6 (2C), 131.5 (2C), 131.4, 131.3 (2C), 131.0, 130.9, 130.7, 130.5, 130.4, 129.9, 128.8, 127.8, 127.6, 127.5, 127.4, 127.3, 126.7 (3C), 126.6 (3C), 126.5, 126.4, 126.2, 125.8, 125.4, 125.2, 124.6 (2C), 124.3, 123.8, 29.9; IR (KBr, cm^{-1}): 3054, 2856, 1601, 1440; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{54}H_{38}N$ 700.2999; found 700.2983.

*6-Methyl-9-phenyl-8-(5,6,7,8-tetraphenylnaphthalen-1-yl)-[1,3]-dioxolo[4,5-f]isoquinoline (**3oa**).* Prepared according to general procedure A. The crude reaction mixture was purified by column chromatography, giving a gray solid (21 mg) in 31% yield; mp 155−137 °C; R_f = 0.5 (30% EtOAc/hexane); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.54 (d, J = 8.0 Hz, 1H), 7.39 (dd, J = 8.0 Hz, 4.0 Hz, 1H), 7.36−7.33 (m, 1H), 7.31 (dd, J = 7.2 Hz, 1.2 Hz, 1H), 7.23−7.19 (m, 2H), 7.17−7.10 (m, 6H), 7.05−7.00 (m, 2H), 6.98 (d, J = 8.0 Hz, 1H), 6.91 (t, J = 8.0 Hz, 1H), 6.87−6.83 (m, 1H), 6.79−6.68 (m, 9H), 6.64 (d, J = 8.0 Hz, 1H), 6.55−6.51 (m, 2H), 6.22 (t, J = 8.0 Hz, 1H), 5.83 (d, J = 1.2 Hz, 1H), 5.73 (d, J = 1.2 Hz, 1H), 2.67 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 156.4, 152.6, 147.4, 141.1, 141.0 (2C), 140.3, 140.2, 138.5, 138.4, 138.3, 137.9, 133.7, 133.4, 132.3, 131.6 (2C), 131.5, 131.4, 131.3 (2C), 131.1 (2C), 130.7, 130.3, 127.7, 127.5, 127.2, 126.7 (2C), 126.6, 126.5, 126.4, 126.3, 126.2, 126.0, 125.6, 125.4, 125.2, 124.9, 124.5, 123.2, 121.9, 120.7, 110.5, 101.5, 23.1; IR (KBr, cm^{-1}): 3054, 2873, 1600, 1441, 1278; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{51}H_{36}NO_2$ 694.2741; found 694.2727.

*7-Methyl-4-phenyl-5-(5,6,7,8-tetraphenylnaphthalen-1-yl)furo-[2,3-c]pyridine (**3pa**).* Prepared according to general procedure A. The crude reaction mixture was purified by column chromatography, giving a pale yellow solid (32 mg) in 50% yield; mp 239−241 °C; R_f = 0.3 (10% EtOAc/hexane); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.58 (d, J = 2.0 Hz, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.29 (t, J = 8.0 Hz, 1H), 7.23−7.11 (m, 8H), 7.07−7.04 (m, 2H), 6.92 (d, J = 4.0 Hz, 1H), 6.83 (d, J = 8.0 Hz, 2H), 6.78−6.63 (m, 8H), 6.57−6.50 (m, 4H), 6.34 (t, J = 8.0 Hz, 1H), 2.56 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 151.4, 149.4, 147.2, 141.0 (2C), 140.9, 140.6, 140.3, 140.1, 139.0, 138.7, 138.5, 137.6, 137.5, 133.8, 133.5, 133.0, 131.9, 131.7, 131.6 (2C), 131.5, 131.4, 131.2 (2C), 130.4, 130.1, 127.8 (2C), 127.6 (2C), 126.9, 126.8, 126.7, 126.6 (2C), 126.5, 126.3, 125.7, 125.4, 125.2, 125.1, 124.8 (2C), 106.6, 18.5; IR (KBr, cm^{-1}): 3056, 2853, 1601, 1441; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{48}H_{34}NO$ 640.2635; found 640.2646.

*7-Methyl-4-phenyl-5-(5,6,7,8-tetraphenylnaphthalen-1-yl)-thieno[2,3-c]pyridine (**3qa**).*[10] Prepared according to general procedure A. The crude reaction mixture was purified by column chromatography, giving a brown solid (43 mg) in 61% yield; mp 110−112 °C; R_f = 0.3 (10% EtOAc/hexane); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.49 (d, J = 8.0 Hz, 1H), 7.45 (d, J = 5.2 Hz, 1H), 7.37 (d, J = 6.0 Hz, 1H), 7.28−7.13 (m, 10H), 7.09−7.04 (m, 2H), 6.93 (d, J = 4.0 Hz, 1H), 6.86−6.80 (m, 2H), 6.78−6.67 (m, 7H), 6.62−6.61 (m, 2H), 6.55−6.50 (m, 2H), 6.25 (t, J = 8.0 Hz, 1H), 2.59 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 152.9, 150.1, 144.6, 141.0 (3C), 140.5, 140.3, 138.8, 138.7, 138.5, 138.1, 137.7, 133.9, 133.7, 133.5, 132.1, 131.6 (2C), 131.5, 131.4, 131.3, 131.2, 130.5, 130.2, 128.3, 127.8, 127.7, 127.6, 126.8, 126.7, 126.6 (2C), 126.5, 126.4, 125.7, 125.4, 125.2 (2C), 124.7, 124.6, 124.3, 23.4; IR (KBr, cm^{-1}): 3054, 2855, 1600, 1440.

*1,5-Dimethyl-4-phenyl-3-(5,6,7,8-tetraphenylnaphthalen-1-yl)-5H-pyrido[4,3-b]indole (**3ra**).*[10] Prepared according to general procedure A. The crude reaction mixture was purified by column chromatography, giving a brown solid (53 mg) in 75% yield; mp 124−126 °C; R_f = 0.5 (50% EtOAc/hexane); ^1H NMR ($CDCl_3$, 400 MHz): δ 8.08 (d, J = 8.0 Hz, 1H), 7.47 (t, J = 8.0 Hz, 1H), 7.43−7.40 (m, 2H), 7.34−7.28 (m, 3H), 7.23−7.20 (m, 4H), 7.17−7.12 (m, 4H), 7.06 (d, J = 8.0 Hz, 1H), 7.01 (d, J = 8.0 Hz, 1H), 6.85−6.77 (m, 5H), 6.74−6.68 (m, 5H), 6.63 (d, J = 8.0 Hz, 1H), 6.59−6.57 (m, 1H), 6.44 (t, J = 8.0 Hz, 1H), 6.22 (t, J = 8.0 Hz, 1H), 3.12 (s, 3H), 2.86 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 154.9, 150.6, 143.3, 142.3, 141.1, 141.0, 140.9, 140.4, 140.3, 138.5, 138.4, 138.1, 133.8, 133.4, 132.4, 132.0, 131.6 (2C), 131.5, 131.4, 131.3, 131.2, 131.1, 130.6, 130.5, 127.8, 127.5 (2C), 127.2, 126.9, 126.8, 126.6 (2C), 126.5, 126.4, 126.0, 125.9, 125.4, 125.2, 124.7, 124.5, 122.4, 122.1, 120.6, 117.7, 116.8, 109.1, 32.4, 23.5; IR (KBr, cm^{-1}): 3055, 2852, 1601, 1441.

*3-Phenyl-2-(5,6,7,8-tetraphenylnaphthalen-1-yl)-8,9-dihydro-7H-benzo[de]quinoline (**3sa**).*[10] Prepared according to general procedure A. The crude reaction mixture was purified by column chromatography, giving a pale brown solid (37 mg) in 55% yield; mp 125−127 °C; R_f = 0.3 (20% EtOAc/hexane); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.43−7.39 (m, 3H), 7.36−7.32 (m, 1H), 7.28−7.24 (m, 4H), 7.22−7.19 (m, 2H), 7.17−7.14 (m, 2H), 7.12−7.09 (m, 2H), 7.04−6.99 (m, 2H), 6.92 (t, J = 7.6 Hz, 1H), 6.88−6.83 (m, 1H), 6.79−6.75 (m, 3H), 6.71−6.67 (m, 6H), 6.57−6.51 (m, 3H), 6.17 (t, J = 7.6 Hz, 1H), 3.09−3.00 (m, 4H), 2.14−2.10 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 157.6, 141.2, 141.0, 140.9, 140.3, 140.2, 138.5, 138.3, 138.2, 137.8, 135.6, 133.5, 133.4, 132.3, 131.6, 131.5(2C), 131.4(2C), 131.3, 131.1, 130.7, 130.4, 127.7, 127.5, 127.3, 127.2, 126.7(2C), 126.5(2C), 126.4, 126.1, 125.5, 125.4, 125.2, 124.8, 124.6, 124.3, 123.6, 123.3, 34.3, 30.9, 23.5; IR (KBr, cm^{-1}): 3056, 2867, 1601, 1441.

*1-Ethyl-4-phenyl-3-(5,6,7,8-tetraphenylnaphthalen-1-yl)-isoquinoline (**3ua**).* Prepared according to general procedure A. The crude reaction mixture was purified by column chromatography, giving a pale yellow solid (35 mg) in 53% yield; mp 106−108 °C; R_f = 0.2 (5% EtOAc/hexane); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.98−7.95 (m, 1H), 7.48−7.40 (m, 6H), 7.28−7.25 (m, 2H), 7.23−7.20 (m, 2H), 7.16−7.14 (m, 2H), 7.12−7.09 (m, 2H), 7.05 (t, J = 7.6 Hz, 1H), 6.98 (d, J = 7.6 Hz, 1H), 6.90−7.83 (m, 2H), 6.78−6.75 (m, 3H), 6.72−6.64 (m, 6H), 6.50−6.45 (m, 3H), 6.11 (t, J = 7.6 Hz, 1H), 3.29−3.20 (m, 1H), 3.03−2.94 (m, 1H), 1.38 (t, J = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 161.0, 152.1, 141.1(2C), 141.0, 140.3, 140.1, 139.6, 138.4, 138.2, 137.8, 137.6, 135.6, 133.4, 132.3, 131.6, 131.5(2C), 131.4(2C), 131.3, 131.1, 130.6, 130.5, 129.3, 127.8, 127.5(2C), 127.2, 127.1, 126.7(2C), 126.6, 126.5(2C), 126.4(2C), 126.2, 126.1, 125.5, 125.4, 125.2, 125.1, 125.0, 124.6, 29.2, 14.3; IR (KBr, cm^{-1}): 3055, 2930, 1601, 1441; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{51}H_{38}N$ 664.2999; found 664.3055.

*3-(4-Chloro-5,6,7,8-tetrakis(4-chlorophenyl)naphthalen-1-yl)-4-(4-chlorophenyl)-6-methoxy-1-methylisoquinoline (**3cb**).* Prepared according to general procedure A. The crude reaction mixture was purified by column chromatography, giving a pale yellow solid (26 mg) in 30% yield; mp 128−130 °C; R_f = 0.3 (20% EtOAc/hexane); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.94 (d, J = 9.2 Hz, 1H), 7.51−7.47 (m, 2H), 7.24 (d, J = 2.4 Hz, 1H), 7.19 (s, 2H), 7.15 (dd, J = 8.8 Hz, 2.4 Hz, 2H), 7.08 (d, J = 8.4 Hz, 1H), 6.99−6.94 (m, 2H), 6.86−6.79 (m, 4H), 6.77−6.73 (m, 2H), 6.67 (d, J = 2.4 Hz, 1H), 6.51−6.45 (m, 3H), 6.39 (d, J = 8.4 Hz, 1H), 6.25 (dd, J = 8.0 Hz, 2 Hz, 1H), 6.04−5.98 (m, 2H), 3.70 (s, 3H), 2.75 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 161.0, 157.3, 139.2, 138.6, 138.2, 138.1, 137.7, 137.3, 136.4, 136.0, 135.6 (2C), 134.6, 132.9 (2C), 132.7, 132.5, 132.4, 132.3, 132.2, 132.1, 132.0, 131.9, 131.6, 131.4, 130.9, 130.4, 130.1, 129.1, 128.3, 128.1, 127.8 (2C), 127.7 (3C), 127.5 (2C), 127.2, 126.8, 121.5, 119.1, 103.6, 55.5, 22.1; IR (KBr, cm^{-1}): 2855, 1412, 1027, 771; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{51}H_{32}C_{l6}NO$ 884.0610; found 884.0593.

*3-(4-Chloro-5,6,7,8-tetraphenylnaphthalen-1-yl)-4-(4-chlorophenyl)-1-methylisoquinoline (**3ae**).* Prepared according to general procedure B. The crude reaction mixture was purified by column chromatography, giving a pale yellow solid (36 mg) in 50% yield; mp 274−276 °C; R_f = 0.3 (20% EtOAc/hexane); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.96−7.92 (m, 1H), 7.49−7.42 (m, 5H), 7.32−7.23 (m, 3H), 7.16−7.07 (m, 3H), 6.96−6.91 (m, 3H), 6.89−6.83 (m, 2H), 6.78−6.73 (m, 4H), 6.72−6.66 (m, 2H), 6.63−6.56 (m, 3H), 6.42 (dd, J = 8.0 Hz, 4 Hz, 1H), 6.33 (d, J = 8.0 Hz, 1H), 6.07 (d, J = 8.0 Hz, 1H), 5.94 (t, J = 8.0 Hz, 1H), 2.69 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 157.2, 151.3, 141.3, 140.8, 140.6, 140.3, 140.0, 139.8, 138.9, 138.0, 136.3, 135.8, 135.7, 134.6, 133.4, 133.0, 132.2, 132.0, 131.8, 131.6 (2C), 131.4, 131.0, 130.5, 130.2, 130.0 (2C), 129.8, 128.9, 128.5, 128.1, 127.3, 127.2, 127.0, 126.9, 126.8, 126.7, 126.6, 126.3, 126.0, 125.8, 125.6, 125.5, 125.4, 125.2, 22.2; IR (KBr, cm^{-1}): 3066, 2852, 1441, 696; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{50}H_{34}Cl_2N$ 718.2063; found 718.2028.

*4-Ethyl-1-methyl-3-(5,6,7,8-tetraphenylnaphthalen-1-yl)-isoquinoline (**3af**).* Prepared according to general procedure B. The

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crude reaction mixture was purified by column chromatography, giving a pale yellow solid (32 mg) in 53% yield; mp 240−242 °C; R_f = 0.2 (10% EtOAc/hexane); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.91 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.55−7.52 (m, 1H), 7.46−7.39 (m, 3H), 7.28−7.24 (m, 4H), 7.20−7.16 (m, 1H), 6.81−6.74 (m, 6H), 6.68−6.57 (m, 6H), 6.35−6.32 (m, 1H), 6.20 (t, J = 8.0 Hz, 1H), 5.95 (t, J = 8.0 Hz, 1H), 2.79 (s, 3H), 2.72 (q, J = 8.0 Hz, 1H), 2.62 (q, J = 8.0 Hz, 1H), 1.17 (t, J = 8.0 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 154.9, 152.4, 141.3, 141.0 (2C), 140.6, 140.5, 140.1, 139.1, 138.6, 134.8, 133.9, 131.9, 131.8, 131.5 (2C), 131.4, 131.3 (2C), 130.5, 130.2 (2C), 129.4, 128.9, 128.2, 127.8, 127.7, 126.7, 126.6, 126.3, 126.2, 125.9, 125.8, 125.4, 125.1 (2C), 125.0, 124.6, 124.5, 123.8, 23.8, 22.4, 15.2; IR (KBr, cm^{-1}): 3056, 2873, 1601, 1441; HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{46}H_{36}N$ 602.2842; found 602.2804.

*4-Ethyl-6-methoxy-1-methyl-3-(5,6,7,8-tetraphenylnaphthalen-1-yl)isoquinoline (**3cf**).* Prepared according to general procedure B. The crude reaction mixture was purified by column chromatography, giving a brown solid (27 mg) in 43% yield; mp 147−149 °C; R_f = 0.3 (20% EtOAc/hexane); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.82 (d, J = 8.0 Hz, 1H), 7.43 (dd, J = 8.4 Hz, 1.2 Hz, 1H), 7.45−7.41 (m, 1H), 7.38 (dd, J = 6.8 Hz, 1.2 Hz, 1H), 7.29−7.22 (m, 4H), 7.20−7.16 (m, 1H), 7.09 (dd, J = 9.2 Hz, 2.4 Hz, 1H), 6.92 (d, J = 2.4 Hz, 1H), 6.83−6.74 (m, 6H), 6.70−6.63 (m, 5H), 6.60−6.58 (m, 1H), 6.39−6.36 (m, 1H), 6.23 (t, J = 8.0 Hz, 1H), 6.01 (t, J = 7.6 Hz, 1H), 3.91 (s, 3H), 2.74 (s, 3H), 2.61 (q, J = 8.0 Hz, 2H), 1.17 (t, J = 8.0 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 160.3, 154.2, 141.3, 141.1, 141.0, 140.5, 139.1 (2C), 138.6, 136.7, 133.9, 131.9, 131.8, 131.6, 131.5, 131.4, 131.3, 131.2, 130.5, 130.2, 130.1, 128.2, 128.1, 127.9, 127.8, 127.7, 126.7, 126.6, 126.3, 126.2, 125.4, 125.1, 125.0, 124.8, 124.6 (2C), 122.4, 117.7, 102.4, 55.6, 23.9, 22.2, 14.6; IR (KBr, cm^{-1}): 3055, 2871, 1440, 1027; HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{47}H_{38}NO$ 632.2948; found 632.2921.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02582.

Mechanistic studies and control experiments, NMR spectra (^{1}H, ^{13}C, and ^{19}F) of **3aa−3ua**, **3cb**, **3cf**, **3ae**, and **3af**, and X-ray crystallography data (PDF)

FAIR data, including the primary NMR FID files, for compounds **3aa−3ua**, **3cb**, **3cf**, **3ae**, and **3af** (ZIP)

Accession Codes

CCDC 2036544, 2036625, and 2038561 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Rieger, R.; Müllen, K. Forever Young: Polycyclic Aromatic Hydrocarbons as Model Cases for Structural and Optical Studies. *J. Phys. Org. Chem.* **2010**, *23*, 315−325. (b) Narita, A.; Wang, X.-Y.; Feng, X.; Müllen, K. New Advances in Nanographene Chemistry. *Chem. Soc. Rev.* **2015**, *44*, 6616−6643. (c) Brasholz, M. Super-Reducing" Photocatalysis: Consecutive Energy and Electron Transfers with Polycyclic Aromatic Hydrocarbons. *Angew. Chem., Int. Ed.* **2017**, *56*, 10280.

(2) (a) Yang, L.; Jiang, S.; Zhao, Y.; Zhu, L.; Chen, S.; Wang, X.; Wu, Q.; Ma, J.; Ma, Y.; Hu, Z. Boron-Doped Carbon Nanotubes as Metal Free Electrocatalysts for the Oxygen Reduction Reaction. *Angew. Chem., Int. Ed.* **2011**, *50*, 7132−7135. (b) Matsuo, K.; Saito, S.; Yamaguchi, S. Photo dissociation of B-N Lewis Adducts: A Partially Fused Trinaphthyl borane with Dual Fluorescence. *J. Am. Chem. Soc.* **2014**, *136*, 12580−12583. (c) Kahan, R. J.; Hirunpinyopas, W.; Cid, J.; Ingleson, M. J.; Dryfe, R. A. W. Well-Defined Boron/Nitrogen-Doped Polycyclic Aromatic Hydrocarbons Are Active Electrocatalysts for the Oxygen Reduction Reaction. *Chem. Mater.* **2019**, *31* (6), 1891−1898. (d) Tang, R.; Wang, X. Y.; Zhang, W. Z.; Zhuang, X. D.; Bi, S.; Zhang, W. B.; Zhang, F. Aromatic Azaheterocycle-Cored Luminogens with Tunable Physical Properties via Nitrogen Atoms for Sensing Strong Acids. *J. Mater. Chem. C* **2016**, *4*, 7640−7648. (e) Li, M.; Yuan, Y.; Chen, Y. Acid-induced multicolor fluorescence of pyridazine derivative. *ACS Appl. Mater. Interfaces* **2018**, *10*, 1237−1243. (f) Jiang, W.; Zhou, Y.; Geng, H.; Jiang, S.; Yan, S.; Hu, W.; Wang, Z.; Shuai, Z.; Pei, J. Solution-Processed, High-Performance Nanoribbon Transistors Based on Dithioperylene. *J. Am. Chem. Soc.* **2011**, *133*, 1−3.

(3) (a) Miao, Q. Ten Years of N-Heteropentacenes as Semiconductors for Organic Thin-Film Transistors. *Adv. Mater.* **2014**, *26*, 5541. (b) MateoAlonso, A. Pyrene-fused pyrazaacenes: from small molecules to nanoribbons. *Chem. Soc. Rev.* **2014**, *43*, 6311. (c) Bunz, U. H. F. The Larger Linear N-Heteroacenes. *Acc. Chem. Res.* **2015**, *48*, 1676. (d) Li, J.; Zhang, Q. Linearly Fused Azaacenes: Novel Approaches and New Applications Beyond Field-Effect Transistors (FETs). *ACS Appl. Mater. Interfaces* **2015**, *7*, 28049.

(4) (a) Kulkarni, A. P.; Tonzola, C. J.; Babel, A.; Jenekhe, S. A. Electron Transport Materials for Organic Light-Emitting Diodes. *Chem. Mater.* **2004**, *16*, 4556−4573. (b) Li, Y. N.; Sonar, P.; Murphy, L.; Hong, W. High mobility diketopyrrolopyrrole (DPP)-based organic semiconductor materials for organic thin film transistors and photo-

https://dx.doi.org/10.1021/acs.joc.0c02582
J. Org. Chem. XXXX, XXX, XXX−XXX

voltaics. *Energy Environ. Sci.* **2013**, *6*, 1684−1710. (c) Gsanger, M.; Bialas, D.; Huang, L. Z.; Stolte, M.; Wurthner, F. Organic Semiconductors based on Dyes and Color Pigments. *Adv. Mater.* **2016**, *28*, 3615−3645. (d) Wang, H.; Maiyalagan, T.; Wang, X. Review on Recent Progress in Nitrogen-Doped Graphene: Synthesis, Characterization, and Its Potential Applications. *ACS Catal.* **2012**, *2*, 781. (e) Kong, X.-K.; Chen, C.-L.; Chen, Q.-W. Doped graphene for metal-free catalysis. *Chem. Soc. Rev.* **2014**, *43*, 2841.

(5) (a) Godula, K.; Sames, D. C-H Bond Functionalization in Complex Organic Synthesis. *Science* **2006**, *312*, 67−72. (b) Yamaguchi, J.; Yamaguchi, A. D.; Itami, K. C-H Bond Functionalization: Emerging Synthetic Tools for Natural Products and Pharmaceuticals. *Angew. Chem., Int. Ed.* **2012**, *51*, 8960−9009. (c) McMurray, L.; O'Hara, F.; Gaunt, M. J. Recent Developments in Natural Product Synthesis Using Metal-Catalysed C-H Bond Functionalisation. *Chem. Soc. Rev.* **2011**, *40*, 1885. (d) He, R.; Huang, Z.-T.; Zheng, Q.-Y.; Wang, C. Isoquinoline Skeleton Synthesis via Chelation-Assisted C-H Activation. *Tetrahedron Lett.* **2014**, *55*, 5705−5713.

(6) (a) Umeda, N.; Tsurugi, H.; Satoh, T.; Miura, M. Fluorescent Naphthyl- and Anthrylazoles from the Catalytic Coupling of Phenylazoles with Internal Alkynes through the Cleavage of Multiple C-H Bonds. *Angew. Chem., Int. Ed.* **2008**, *47*, 4019. (b) Shi, Z.; Tang, C.; Jiao, N. Chemoselective Synthesis of Naphthylamides and Isoquinolinones via Rhodium-Catalyzed Oxidative Dehydrogenative Annulation of Benzamides with Alkynes. *Adv. Synth. Catal.* **2012**, *354*, 2695. (c) Li, S. S.; Liu, C. F.; Zhang, G. T.; Xia, Y. Q.; Li, W. H.; Dong, L. A Convenient One-Pot Route to Screw-Shaped [5]Azahelicenes via Rhodium(III)-Catalyzed Multiple C-H Bond Activation. *Chem. - Asian J.* **2017**, *12*, 415. (d) Kong, W.-J.; Shen, Z.; Finger, L. H.; Ackermann, L. Electrochemical Access to Aza-Polycyclic Aromatic Hydrocarbons: Rhoda-Electrocatalyzed Domino Alkyne Annulations. *Angew. Chem., Int. Ed.* **2020**, *59*, 5551−5556.

(7) (a) Mo, J.; Wang, L.; Liu, Y.; Cui, X. Transition-Metal-Catalyzed Direct C-H Functionalization under External-Oxidant-Free Conditions. *Synthesis* **2015**, *47*, 439−459. (b) Huang, H.; Ji, X.; Wu, W.; Jiang, H. Transition Metal-Catalyzed C-H Functionalization of N-Oxyenamine Internal Oxidants. *Chem. Soc. Rev.* **2015**, *44*, 1155−1171.

(8) (a) Guimond, N.; Gouliaras, C.; Fagnou, K. Rhodium(III)-Catalyzed Isoquinolone Synthesis: The N-O Bond as a Handle for C-N Bond Formation and Catalyst Turnover. *J. Am. Chem. Soc.* **2010**, *132*, 6908−6909. (b) Guimond, N.; Gorelsky, S. I.; Fagnou, K. Rhodium(III)-Catalyzed Heterocycle Synthesis Using an Internal Oxidant: Improved Reactivity and Mechanistic Studies. *J. Am. Chem. Soc.* **2011**, *133*, 6449−6457. (c) Wang, H.; Grohmann, C.; Nimphius, C.; Glorius, F. Mild Rh(III)-Catalyzed C-H Activation and Annulation with Alkyne MIDA Boronates: Short, Efficient Synthesis of Heterocyclic Boronic Acid Derivatives. *J. Am. Chem. Soc.* **2012**, *134*, 19592−19595. (d) Zhao, D.; Lied, F.; Glorius, F. Rh(III)-Catalyzed C-H Functionalization/Aromatization Cascade with 1,3-Dienes: A Redox-Neutral and Regioselective Access to Isoquinolines. *Chem. Sci.* **2014**, *5*, 2869. (e) Shi, Z.; Boultadakis-Arapinis, M.; Koester, D. C.; Glorius, F. Rh(III)-Catalyzed Intramolecular Redox-Neutral Cyclization of Alkenes via C-H Activation. *Chem. Commun.* **2014**, *50*, 2650. (f) Biswal, P.; Pati, B. V.; Chebolu, R.; Ghosh, A.; Ravikumar, P. C. Hydroxylamine-*O* -Sulfonic Acid (HOSA) as a Redox-Neutral Directing Group: Rhodium Catalyzed, Additive Free, One-Pot Synthesis of Isoquinolines from Arylketones. *Eur. J. Org. Chem.* **2020**, *2020*, 1006−1014.

(9) (a) Guimond, N.; Fagnou, K. Isoquinoline Synthesis via Rhodium-Catalyzed Oxidative Cross-Coupling/Cyclization of Aryl Aldimines and Alkynes. *J. Am. Chem. Soc.* **2009**, *131*, 12050−12051. (b) Sen, M.; Kalsi, D.; Sundararaju, B. Cobalt(III)-Catalyzed Dehydrative [4 + 2] Annulation of Oxime with Alkyne by C-H and N-OH Activation. *Chem. - Eur. J.* **2015**, *21*, 15529−15533. (c) Pawar, A. B.; Agarwal, D.; Lade, D. M. Cp*Co(III)-Catalyzed C-H/N-N Functionalization of Arylhydrazones for the Synthesis of Isoquinolines. *J. Org. Chem.* **2016**, *81*, 11409−11415. (d) Li, X.-C.; Du, C.; Zhang, H.; Niu, J.-L.; Song, M.-P. Cp*-Free Cobalt-Catalyzed C-H Activation/Annulations by Traceless N,O-Bidentate Directing Group: Access to Isoquinolines. *Org. Lett.* **2019**, *21*, 2863−2866. (e) Dey, A.; Volla, C. M. R. Traceless Bidentate Directing Group Assisted Cobalt-Catalyzed sp^2-C-H Activation and [4 + 2]-Annulation Reaction with 1,3-Diynes. *Org. Lett.* **2020**, *22* (19), 7480−7485 and references have cited therein.

(10) Liu, B.; Hu, F.; Shi, B.-F. 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. *Adv. Synth. Catal.* **2014**, *356*, 2688.

(11) Hayashi, Y. Pot Economy and One-Pot Synthesis. *Chem. Sci.* **2016**, *7*, 866−880.

(12) Simmons, E. M.; Hartwig, J. F. On the Interpretation of Deuterium Kinetic Isotope Effects in C-H Bond Functionalizations by Transition-Metal Complexes. *Angew. Chem., Int. Ed.* **2012**, *51*, 3066−3072.

(13) Mio, M. J.; Kopel, L. C.; Braun, J. B.; Gadzikwa, T. L.; Hull, K. L.; Brisbois, R. G.; Markworth, C. J.; Grieco, P. A. *Org. Lett.* **2002**, *4*, 3199−3202.

(14) Wang, H.; Koeller, J.; Liu, W.; Ackermann, L. *Chem. - Eur. J.* **2015**, *21*, 15525−15528.

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