JOC The Journal of Organic Chemistry

Article

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Palladium-Catalyzed Intramolecular C(sp^2)-H Imidoylation for the Synthesis of Six-Membered N-Heterocycles

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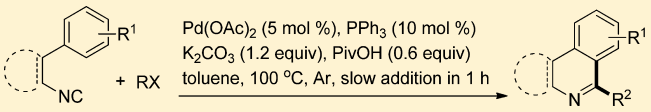
Supporting Information

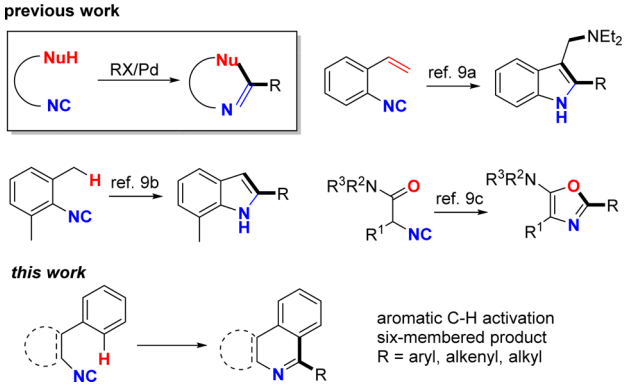
ABSTRACT: A new strategy for the construction of phenanthridine and isoquinoline scaffolds, starting from arenes containing a pending isocyanide moiety under palladium catalysis, has been developed. This process involves sequential intermolecular isocyanide insertion to an aryl palladium(II) intermediate and intramolecular aromatic C−H activation as key steps. Alkyl palladium(II) intermediate lacking β-hydrogen is also applicable to this reaction, generating unique bisheterocyclic scaffolds with three C−C bonds being formed consecutively.



INTRODUCTION

The versatility of isocyanide in generating molecular complexity has been adequately demonstrated in Ugi and related multicomponent reactions (MCRs) since the 1960s.[1] In the past decade, another important and unique reactivity of isocyanide has been increasingly recognized, that is, the palladium-catalyzed imidoylation process.[2] Similar to carbon monoxide (CO) as its isoelectronic equivalent, isocyanide can undergo migratory insertion to a Pd(II) intermediate, followed by substitution with various nucleophiles and reductive elimination to generate amidines,[3a] amides,[3b,4] ketimines,[5] imidates, or thiomidates[6] accordingly. This palladium-catalyzed imidoylation reaction is particularly powerful in the construction of heterocyclic skeletons through nonfunctionalized or functionalized isocyanide strategies. In the nonfunctionalized isocyanide approach, only the terminal carbon of isocyanide is present in the constructed heterocyclic ring by reacting isocyanide with molecules either bearing two nucleophiles[7] or containing a nucleophile and a precursor of the Pd(II) intermediate ready for isocyanide insertion.[8] In the functionalized isocyanide strategy, however, the isocyanide substrate not only participates in migratory insertion but also provides inbuilt functional groups which can further react with the imidoyl palladium intermediate (Scheme 1).[9] As a result, the isocyanide nitrogen is included in the cyclized product as a ring member. Therefore, this strategy for heterocycle synthesis takes full advantage of RNC in having a diversifiable R group over CO. For instance, in 2002, Takahashi reported a three-component coupling reaction of aryl iodides, *o*-alkenylphenyl isocyanides, and secondary amines (Scheme 1).[9a] In this reaction, the imidoyl palladium intermediate was trapped by the *ortho*-styrenic moiety followed by nucleophilic substitution and reductive elimination to build the indole scaffold. Ten years later, Takemoto reported a Pd-catalyzed cascade process consisting of isocyanide insertion and benzylic C(sp^3)-H activation, leading to indole derivatives as well (Scheme 1).[9b] Very recently, we used α-isocyanoacetamides as a novel class of functionalized isocyanide for the synthesis of C2 diversified

Scheme 1. Functionalized Isocyanide in Palladium-Catalyzed Imidoylative Cyclization



oxazoles[9c] as well as 2,2′-bisoxazoles.[9d] Herein, we would like to report a sequential process using arene-containing isocyanides as substrates to construct six-membered N-heterocycles including phenanthridines[10] and isoquinolines via intramolecular aromatic C−H activation as a key step (Scheme 1).

2-Isocyano-1,1′-biphenyls were originally selected as idea substrates in testing the hypothesis. In recent years, reactions using 2-isocyano-1,1′-biphenyls as radical acceptors to form multisubstituted phenanthridines have been frequently reported. Some carbon-centered radicals including aryl,[11] CF_3,[12] alkyl,[13] acyl,[14] and alkoxycarbonyl[15] radicals as well as heteroatom-centered ones[16] were applied to react with 2-isocyano-1,1′-biphenyls, forming various imidoyl radical intermediates for the following the intramolecular homolytic aromatic substitution (HAS) process.[17] In these radical based reactions, however, no examples of corresponding alkenylation or alkynylation were realized. Given the fruitfulness of Pd chemistry, we anticipated that an alternative palladium-catalyzed imidoylation process would provide a new approach

Received: December 3, 2014
Published: January 22, 2015

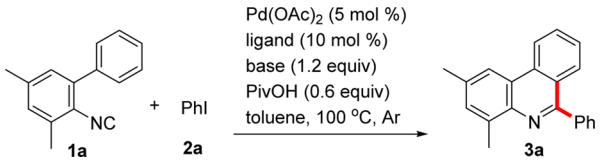
DOI: 10.1021/jo502731n
J. Org. Chem. 2015, 80, 2223−2230

to multisubstituted six-membered N-heterocycles by using arene-containing isocyanides as a new class of functionalized isocyanides.

RESULTS AND DISCUSSION

Our initial effort was focused on using 2-isocyano-5-methyl-1,1′-biphenyl as a model substrate in a reaction with iodobenzene under palladium catalysis. Unfortunately, unstable products derived from consecutive isocyanide insertion were obtained. This unwanted side reaction was probably due to the unfavorable reaction distance between the phenyl ring and the Pd catalyst after isocyanide insertion. To circumvent multi-isocyanide insertion, an additional substituent at the C3 position of the 2-isocyano-1,1′-biphenyl substrate was introduced to force the Pd center in a position closer to the pending phenyl ring. Indeed, when 2-isocyano-3,5-dimethyl-1,1′-biphenyl **1a** (0.2 mmol scale) was chosen in a reaction with iodobenzene **2a** in the presence of $Pd(OAc)_2$ (5 mol %), Ad_2PnBu (10 mol %), and 1.2 equiv of Cs_2CO_3 in toluene at 100 °C, 2,4-dimethyl-6-phenylphenanthridine **3a** was formed in 20% yield (entry 1, Table 1). When Cs_2CO_3 was replaced by

Table 1. Optimization of the Reaction Conditions[a]



1a 2a 3a

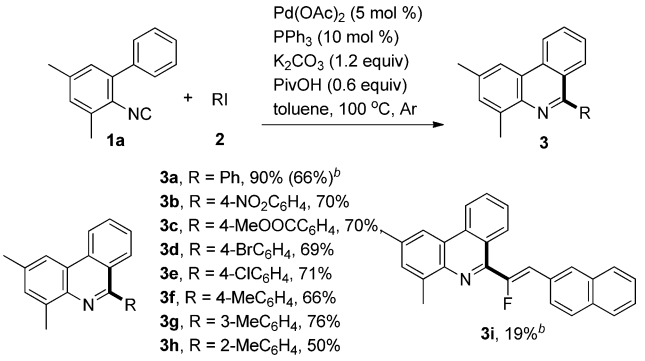
entry	base	ligand	additive	yield[b]
1	Cs_2CO_3	Ad_2PnBu		20%
2	CsOPiv	Ad_2PnBu		78%
3	CsOPiv	Cy_3P		78%
4	CsOPiv	dppe		76%
5	CsOPiv	PPh_3		77%
6	CsOPiv	BINAP		78%
7	Cs_2CO_3	PPh_3	PivOH	84%
8	CsF	PPh_3	PivOH	80%
9	K_2CO_3	PPh_3	PivOH	88%
10	Na_2CO_3	PPh_3	PivOH	trace
11[c]	K_2CO_3	PPh_3	PivOH	90%

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv, in 1 mL of toluene), **2a** (0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (5 mol %), ligand (10 mol %), base (1.2 equiv), additive (0.6 equiv), toluene (0.5 mL), 100 °C, Ar, syringe pump addition within 1 h. [b]Isolated yield of **3a**. [c]**1a** (0.5 mmol), in the same amount of solvent (0.5 + 1 mL).

CsOPiv, the reaction was improved significantly to give **3a** in 78% yield (entry 2). It was found that the influence of phosphine ligand on the reaction efficiency was minimal (entries 3−6). Since CsOPiv was highly hygroscopic, in situ formation of CsOPiv by mixing Cs_2CO_3 and PivOH was preferred, which indeed gave a slightly improved result (entry 7).[18] K_2CO_3 was proved the base of choice among the bases screened (entries 8−10). The reaction proceeded equally well in 0.5 mmol scale in the same amount of solvent (1.5 mL), and the product **3a** was isolated in 90% yield (entry 11). It is notable that in all of these cases, slow addition of a solution of **1a** in toluene via a syringe pump to a prestirred reaction mixture is applied to achieve maximum and reproducible results (see Experimental Section for details).

With the optimal conditions in hand, we first investigated the scope of halides in this Pd-catalyzed imidoylative cyclization reaction with **1a** (Scheme 2). Aryl iodides bearing a variety of

Scheme 2. Scope of Halides[a]



[a]Reaction conditions: **1a** (0.5 mmol, 1.0 equiv, in 1 mL of toluene), **2** (0.75 mmol, 1.5 equiv), $Pd(OAc)_2$ (5 mol %), PPh_3 (10 mol %), PivOH (0.6 equiv), K_2CO_3 (1.2 equiv), toluene (0.5 mL), 100 °C, Ar, syringe pump addition within 1 h. Isolated yields of **3** were reported. [b]Corresponding bromide was used.

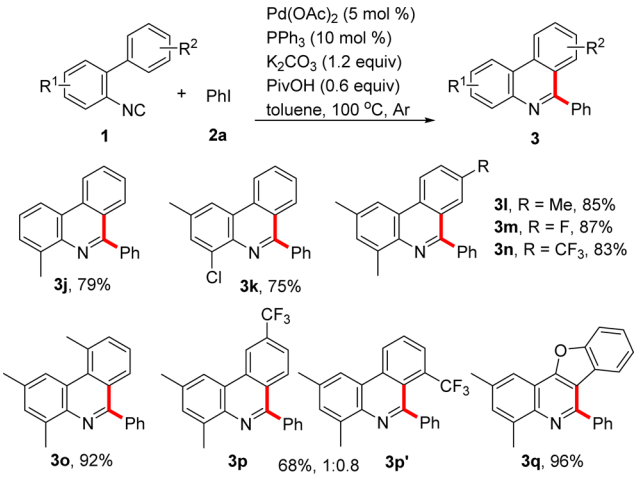
functional groups including electron-withdrawing NO_2, methoxycarbonyl, Br, and Cl as well as electron-donating methyl at the para position gave the corresponding products **3b**−**3f** in yields ranging from 66 to 71%. 3-Methylphenyl iodide reacted smoothly with **1a** to give **3g** in 76% yield, while a methyl group located at the ortho position of phenyl iodide affected the product formation significantly (**3h**, 50%). Phenyl bromide could also be used in this reaction, furnishing the same product **3a** in 66% yield. Besides, alkenylated phenanthridine derivative **3i** was also accessible by employing the corresponding vinyl bromide[19] as a substrate, albeit in only 19% yield. Unfortunately, a reaction between **1a** and bromoethynylbenzene under otherwise identical conditions could not yield the desired product.

Then the reaction was investigated using various substituted 2-isocyano biphenyls (Scheme 3). Changing the substituent on the 2-position from methyl to chloride also gave the desired product **3k** in 75% yield. The reaction was not sensitive to the electronic nature of substituents on the nonisocyano bearing aromatic ring, delivering F-, CF_3-, and Me-substituted 6-phenyl phenanthridines **3l**−**3m** in good yields. 2-Isocyano-3,5,2′-trimethyl-1,1′-biphenyl furnished **3o** in a surprisingly high yield (92%). Unfortunately, poor regio-selectivity was obtained for *meta*-CF_3 substituted 2-isocyano biphenyl (**3p** and **3p′**). The C−H bond in a heteroaromatic ring could also be activated by the imidoyl palladium(II) intermediate, giving benzofuro-[3,2-*c*]quinolone derivative **3q** in an excellent 96% yield.

It was anticipated that alkyl Pd(II)-intermediate lacking *β*-hydrogen was also applicable to this reaction to generate alkyl substituted phenanthridine derivatives. Therefore, a cascade process involving oxidative addition of Pd(0) to aryl iodides **4** linking a 2-propene moiety and alkene insertion, followed by imidoylative cyclization, was investigated (Scheme 4). Indeed, a range of unique bisheterocyclic scaffolds with a methylene tether were obtained in moderate to good yields (**5a**−**5d**). When 2-iodophenyl methacrylate was used, the desired intramolecular alkene insertion to aryl Pd(II) intermediate did not take place, furnishing aryl-substituted phenanthridine **3r** in 51% yield. Satisfyingly, when the terminal alkene was one

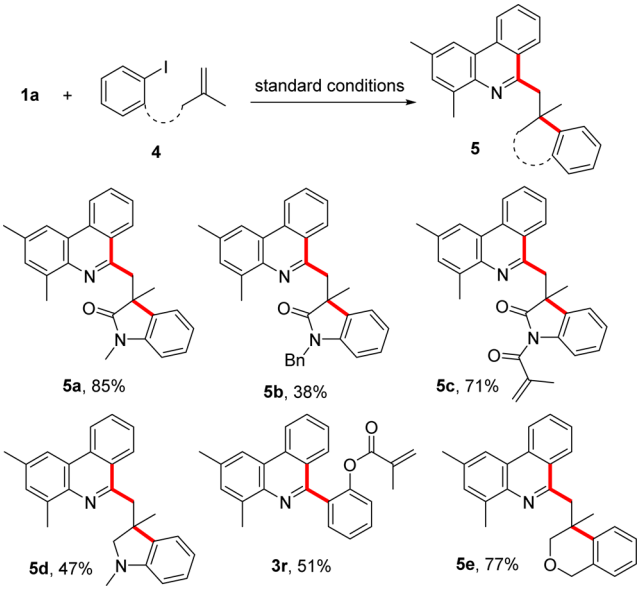
DOI: 10.1021/jo502731n
J. Org. Chem. 2015, 80, 2223−2230

Scheme 3. Scope of 2-Isocyano Biphenyls[a]



[a]Reaction conditions: **1** (0.5 mmol, 1.0 equiv, in 1 mL of toluene), **2a** (0.75 mmol, 1.5 equiv), $Pd(OAc)_2$ (5 mol %), PPh_3 (10 mol %), PivOH (0.6 equiv), K_2CO_3 (1.2 equiv), toluene (0.5 mL), 100 °C, Ar, syringe pump addition within 1 h. Isolated yields of **3** were reported

Scheme 4. Cascade Imidoylative Cyclization[a]



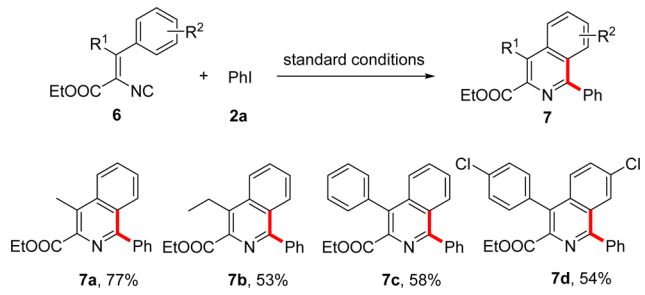
[a]Standard conditions, isolated yields of **5** and **3r**.

more carbon away from the aryl ring in a benzyl ether substrate, the cascade reaction occurred again (**5e**, 77%). It was notable that three C−C bonds were formed consecutively in this one-pot reaction, enabling the installation of indolinone, indoline, or isochromane to phenanthridine with high step and bond-forming efficiency.

To extend this Pd-catalyzed functionalized isocyanide strategy to other six-membered heterocycle synthesis, vinyl isocyanides **6** were used as substrates under the same reaction conditions (Scheme 5).[20] Ethyl 4-methyl(ethyl)-1-phenyl-isoquinoline-3-carboxylates **7a−b** were prepared smoothly starting from the corresponding vinyl isocyanides. 1,4-Diaryl isoquinolines **7c−d** were also accessible by employing this method in acceptable yields.

To gain insight into the reaction mechanism, the intramolecular kinetic isotope effect was investigated using 2,6-

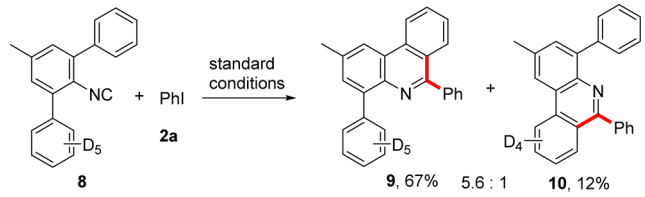
Scheme 5. Synthesis of Isoquinolines[a]



[a]Standard conditions, isolated yields of **7**.

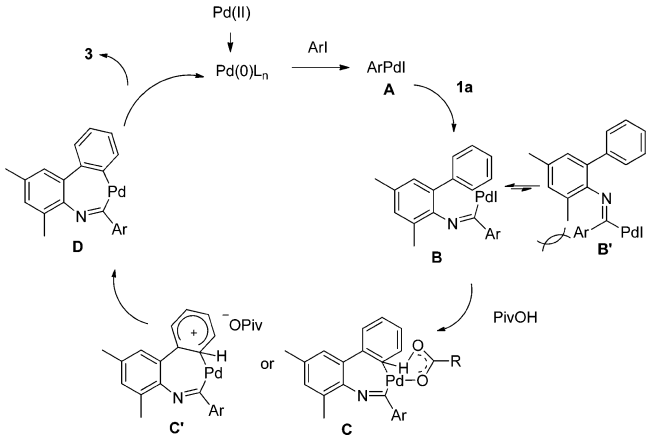
diphenyl aryl isocyanide **8** with one of the phenyl rings fully deuterium labeled. The ratio of **9** to **10**, determined by ^1H NMR, was about 5.6:1, which indicated that C−H cleavage might be a rate-limiting step (Scheme 6).

Scheme 6. Mechanistic Study



A plausible mechanism of this imidoylative cyclization process is depicted in Scheme 7.[5] Initial oxidative addition of

Scheme 7. Possible mechanism



aryl halide to Pd(0) affords aryl Pd(II) intermediate **A**. Then, coordination and migratory insertion of the isocyano moiety to intermediate **A** generates imidoyl palladium species **B** and **B′**. The steric hindrance of the *ortho*-methyl group helps the presence of conformer **B** in equilibrium. Next, activation of the $C(sp^2)$-H bond aided by the coordinated pivalate through a concerted metalation deprotonation (CMD) intermediate **C** gives palladacycle **D**.[21] Finally, reductive elimination delivers the cyclized phenanthridine product **3** and regenerates Pd(0) for the next catalytic cycle. However, an electrophilic aromatic substitution process involving intermediate **C′** cannot be excluded.

DOI: 10.1021/jo502731n
J. Org. Chem. 2015, 80, 2223−2230

CONCLUSIONS

In summary, we have demonstrated the feasibility of the functionalized isocyanide strategy in palladium-catalyzed imidoylation in heterocycle synthesis. In this imidoylative cyclization process, 2-isocyano-1,1′-biphenyls as well as *Z*-2-isocyanostyrenes react smoothly with arylhalides to generate aryl-substituted six-membered phenanthridines and isoquinolines, respectively. Aryl iodides bearing *ortho*-alkenes by a variety of N or O linkages are also applied in this reaction. Therefore, a process including alkene insertion, migratory insertion of isocyanide, and intramolecular C(sp^2)-H activation takes place sequentially, allowing the installation of other heterocycles to phenanthridine by a methylene tether. Three C−C bonds are formed consecutively, representing high bond-forming efficiency of the reaction. The mechanistic study suggests that C(sp^2)-H activation is likely a rate-determining step.

EXPERIMENTAL SECTION

General Information. Reactions were monitored using thin-layer chromatography (TLC) on commercial silica gel plates (GF254). Solvents for flash column chromatography (FC), crystallization, and extractions have been distilled once. Visualization of the developed plates was performed under UV light (254 nm). Flash column chromatography was performed on silica gel (200−300 mesh). ^{1}H and ^{13}C NMR spectra were recorded on a 400 or 500 MHz spectrometer. Chemical shifts (δ) were reported in ppm referenced to an internal tetramethylsilane standard for ^{1}H NMR. Chemical shifts of ^{13}C NMR are reported relative to $CDCl_3$ (δ 77.0). Coupling constants, *J*, were reported in hertz (Hz). High resolution mass spectra (HRMS) were obtained on an ESI-LC-MS/MS spectrometer.

General Procedure A. An oven-dried 25 mL Schlenk tube was charged with $Pd(OAc)_2$ (0.025 mmol, 5.6 mg), PPh_3 (0.05 mmol, 13.1 mg), K_2CO_3 (0.6 mmol, 84 mg), and PivOH (0.3 mmol, 31 mg), and the tube was refilled with Ar 3 times. Then a solution of aryl(vinyl) halide **2** (0.75 mmol) in 0.5 mL of toluene was added. After the mixture was stirred at 100 °C for 0.5 h, 2-isocyano-1,1′-biphenyl **1** (0.5 mmol) was dissolved in 1.0 mL of toluene, and the solution was added via a syringe pump within 1 h. The crude reaction mixture was extracted with ethyl acetate (20 mL × 3) and washed with brine (20 mL). The organic phase was concentrated in vacuum, and product **3** was purified by flash chromatography using ethyl acetate and petroleum ether (1:100) as an eluent.

General Procedure B. An oven-dried 25 mL Schlenk tube was charged with $Pd(OAc)_2$ (0.025 mmol, 5.6 mg), PPh_3 (0.05 mmol, 13.1 mg), K_2CO_3 (0.6 mmol, 84 mg), and PivOH (0.3 mmol, 31 mg), and the tube was refilled with Ar 3 times. Then, 0.5 mL of toluene was added, and the mixture was stirred at 100 °C for 0.5 h. To this mixture, a solution of aryl iodide **4** containing an ortho pending alkene moiety (0.75 mmol) in 0.5 mL of toluene was added. Besides, a solution of 2-isocyano-3,5-dimethyl-1,1′-biphenyl (**1a**, 0.5 mmol, 103.6 mg) in 0.5 mL of toluene was introduced via a syringe pump within 1 h. The crude reaction mixture was extracted with ethyl acetate (20 mL × 3) and washed with brine (20 mL). The organic phase was concentrated in vacuum, and product **5** was purified by flash chromatography using ethyl acetate and petroleum ether (1:50) as an eluent.

General Procedure C. An oven-dried 25 mL Schlenk tube was charged with $Pd(OAc)_2$ (0.01 mmol, 2.3 mg), PPh_3 (0.02 mmol, 5.3 mg), K_2CO_3 (0.24 mmol, 33 mg), and PivOH (0.12 mmol, 12 mg), and the tube was refilled with Ar 3 times. Then, a solution of PhI (**2a**, 0.3 mmol, 61.8 mg) in 0.5 mL of toluene was added. The mixture was stirred at 100 °C for 0.5 h, followed by the addition of a solution of vinyl isocyanide **6** (0.2 mmol) in 1.0 mL of toluene via a syringe pump within 1 h. The reaction mixture was extracted with ethyl acetate (20 mL × 3) and washed with brine (20 mL). The organic phase was concentrated in vacuum, and product **7** was purified by flash chromatography using ethyl acetate and petroleum ether (1:100) as an eluent.

2,4-Dimethyl-6-phenylphenanthridine (3a).[22] The title compound was prepared from 2-isocyano-3,5-dimethyl-1,1′-biphenyl (104 mg, 0.5 mmol, 1.0 equiv) and iodobenzene (153 mg, 0.75 mmol, 1.5 equiv) according to general procedure A. It was isolated as a white solid (128 mg, 0.45 mmol); yield 90%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (d, *J* = 8.4 Hz, 1H), 8.25 (s, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 7.82−7.78 (m, 3H), 7.60−7.49 (m, 4H), 7.45 (s, 1H), 2.85 (s, 3H), 2.60 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.3, 140.9, 137.8, 136.1, 133.6, 131.2, 130.2, 129.8, 128.5, 128.4, 128.1, 126.6, 124.8, 123.3, 122.4, 119.3, 21.9, 18.2. FTIR: ν_{max}/cm^{-1} 3047, 2910, 1566, 1517, 1442, 1360, 1319, 955, 850, 778, 761, 700, 672, 582. HRMS (ESI-TOF): calcd for $C_{21}H_{17}N$ (M + H$^+$) 284.1434; found, 284.1436; mp 123−125 °C.

2,4-Dimethyl-6-(4-nitrophenyl)phenanthridine (3b). The title compound was prepared from 2-isocyano-3,5-dimethyl-1,1′-biphenyl (104 mg, 0.5 mmol, 1.0 equiv) and 1-iodo-4-nitrobenzene (187 mg, 0.75 mmol, 1.5 equiv) according to general procedure A. It was isolated as a pale yellow solid (111 mg, 0.35 mmol); yield 70%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (d, *J* = 8.4 Hz, 1H), 8.42 (d, *J* = 8.4 Hz, 2H), 8.27 (s, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 8.8 Hz, 2H), 7.85 (t, *J* = 7.6 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.49 (s, 1H), 2.83 (s, 3H), 2.62 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.7, 147.9, 146.7, 140.8, 138.1, 137.1, 133.6, 131.6, 131.1, 130.3, 127.5, 127.1, 124.2, 123.5, 123.5, 122.8, 119.4, 22.0, 18.1. FTIR: ν_{max}/cm^{-1} 3069, 2919, 1597, 1517, 1348, 1319, 852, 773, 694, 584. HRMS (ESI-TOF): calcd for $C_{21}H_{16}N_2O_2$ (M + H$^+$) 329.1285; found, 329.1285; mp 213-215 °C.

Methyl 4-(2,4-dimethylphenanthridin-6-yl)benzoate (3c). The title compound was prepared from 2-isocyano-3,5-dimethyl-1,1′-biphenyl (104 mg, 0.5 mmol, 1.0 equiv) and methyl 4-iodobenzoate (196 mg, 0.75 mmol, 1.5 equiv) according to general procedure A. It was isolated as a white solid (120 mg, 0.35 mmol); yield 70%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (d, *J* = 8.0 Hz, 1H), 8.24 (s, 1H), 8.22 (d, *J* = 8.4 Hz, 2H), 8.08 (d, *J* = 8.4 Hz, 1H), 8.88 (d, *J* = 8.0 Hz, 2H), 7.81 (t, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.46 (s, 1H), 3.98 (s, 3H), 2.83 (s, 3H), 2.60 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.0, 157.1, 144.8, 140.9, 138.0, 136.6, 133.6, 131.4, 130.3, 130.1, 130.0, 129.5, 128.0, 126.8, 124.5, 123.4, 122.6, 119.3, 52.2, 22.0, 18.2. FTIR: ν_{max}/cm^{-1} 3070, 2919, 1724, 1609, 1434, 1321, 1288, 1103, 777, 704. HRMS (ESI-TOF): calcd for $C_{23}H_{19}NO_2$ (M + H$^+$) 342.1489; found, 342.1489; mp 191−193 °C.

6-(4-Bromophenyl)-2,4-dimethylphenanthridine (3d). The title compound was prepared from 2-isocyano-3,5-dimethyl-1,1′-biphenyl (104 mg, 0.5 mmol, 1.0 equiv) and 1-bromo-4-iodobenzene (212 mg, 0.75 mmol, 1.5 equiv) according to general procedure A. It was isolated as a white solid (126 mg, 0.35 mmol); yield 69%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (d, *J* = 8.0 Hz, 1H), 8.25 (s, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.84−7.80 (m, 1H), 7.69 (m, 4H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.46 (s, 1H), 2.83 (s, 3H), 2.60 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.0, 140.9, 139.3, 137.8, 136.4, 133.6, 131.8, 131.4, 130.0, 128.1, 126.8, 124.5, 123.3, 122.9, 122.6, 119.3, 22.0, 18.2. FTIR: ν_{max}/cm^{-1} 3070, 2920, 1485, 1370, 1361, 1317, 1912, 841, 831, 794, 767, 583. HRMS (ESI-TOF): calcd for $C_{21}H_{16}BrN$ (M + H$^+$) 362.0539; found, 362.0539; mp 176−178 °C.

6-(4-Chlorophenyl)-2,4-dimethylphenanthridine (3e). The title compound was prepared from 2-isocyano-3,5-dimethyl-1,1′-biphenyl (104 mg, 0.5 mmol, 1.0 equiv) and 1-chloro-4-iodobenzene (178 mg, 0.75 mmol, 1.5 equiv) according to general procedure A. It was isolated as a white solid (120 mg, 0.36 mmol); yield 71%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67 (d, *J* = 8.4 Hz, 1H), 8.24 (s, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.80 (t, *J* = 7.6 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.45 (s, 1H), 2.83 (s, 3H), 2.59 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.0, 140.8, 138.8, 137.8, 136.4, 134.6, 133.6, 131.5, 131.3, 130.0, 128.4, 128.1, 126.8, 124.6, 123.3, 122.6, 119.3, 22.0, 18.2. FTIR: ν_{max}/cm^{-1} 3072, 2919, 1488, 1362, 1318, 1090, 834, 795, 763. HRMS (ESI-TOF): calcd for $C_{21}H_{16}ClN$ (M + H$^+$) 318.1044; found, 318.1046; mp 187−189 °C.

DOI: 10.1021/jo502731n
J. Org. Chem. 2015, 80, 2223−2230

2,4-Dimethyl-6-(*p*-tolyl)phenanthridine (3f). The title compound was prepared from 2-isocyano-3,5-dimethyl-1,1′-biphenyl (104 mg, 0.5 mmol, 1.0 equiv) and 1-iodo-4-methylbenzene (164 mg, 0.75 mmol, 1.5 equiv) according to general procedure A. It was isolated as a white solid (99 mg, 0.33 mmol); yield 66%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (d, J = 8.4 Hz, 1H), 8.23 (s, 1H), 8.18 (d, J = 8.4 Hz, 1H), 7.78 (t, J = 6.8 Hz, 1H), 7.71 (d, J = 8.0 Hz, 2H), 7.56 (t, J = 7.6 Hz, 1H), 7.43 (s, 1H), 7.35 (d, J = 8.0 Hz, 2H), 2.84 (s, 3H), 2.59 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.3, 141.0, 138.3, 137.8, 137.6, 136.0, 133.6, 131.2, 130.2, 130.1, 129.9, 129.8, 128.9, 128.6, 128.2, 126.5, 124.9, 123.2, 122.4, 119.3, 22.0, 21.4, 18.3. FTIR: ν_{max}/cm^{-1} 3069, 2914, 1449, 1361, 1318, 1181, 845, 797, 769, 582. HRMS (ESI-TOF): calcd for $C_{22}H_{19}N$ (M + H$^+$) 298.1590; found, 298.1593; mp 139−141 °C.

2,4-Dimethyl-6-(*m*-tolyl)phenanthridine (3g). The title compound was prepared from 2-isocyano-3,5-dimethyl-1,1′-biphenyl (104 mg, 0.5 mmol, 1.0 equiv) and 1-iodo-3-methylbenzene (163 mg, 0.75 mmol, 1.5 equiv) according to general procedure A. It was isolated as a pale yellow solid (113 mg, 0.38 mmol); yield 76%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (d, J = 8.4 Hz, 1H), 8.24 (s, 1H), 8.14 (d, J = 8.0 Hz, 1H), 7.79 (t, J = 7.6 Hz, 1H), 7.60−7.53 (m, 3H), 7.45−7.41 (m, 2H), 7.32 (d, J = 7.6 Hz, 1H), 2.84 (s, 3H), 2.59 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.5, 141.0, 140.4, 137.8, 137.7, 136.0, 133.5, 131.2, 130.8, 130.2, 129.8, 129.2, 128.6, 128.5, 128.4, 128.2, 128.0, 127.3, 126.6, 126.5, 124.9, 123.3, 122.4, 122.3, 119.3, 22.0, 21.6, 18.3. FTIR: ν_{max}/cm^{-1} 3075, 2911, 1570, 1357, 1318, 849, 792, 779, 766, 706. HRMS (ESI-TOF): calcd for $C_{22}H_{19}N$ (M + H$^+$) 298.1590; found, 298.1591; mp 133−135 °C.

2,4-Dimethyl-6-(*o*-tolyl)phenanthridine (3h). The title compound was prepared from 2-isocyano-3,5-dimethyl-1,1′-biphenyl (104 mg, 0.5 mmol, 1.0 equiv) and 1-iodo-2-methylbenzene (163 mg, 0.75 mmol, 1.5 equiv) according to general procedure A. It was isolated as a pale yellow solid (75 mg, 0.25 mmol); yield 50%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67 (d, J = 8.0 Hz, 1H), 8.27 (s, 1H), 7.80−7.76 (m, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.53−7.49 (m, 1H), 7.45 (s, 1H), 7.42−7.32 (m, 4H), 2.81 (s, 3H), 2.60 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.0, 140.9, 139.8, 137.9, 136.8, 136.1, 133.1, 131.1, 130.4, 130.0, 129.9, 129.8, 128.4, 128.2, 126.7, 125.6, 125.5, 123.4, 122.3, 119.3, 21.9, 20.0, 18.4. FTIR: ν_{max}/cm^{-1} 3049, 2915, 1573, 1452, 1361, 1317, 854, 778, 760, 737, 726. HRMS (ESI-TOF): calcd for $C_{22}H_{19}N$ (M + H$^+$) 298.1590; found, 298.1592; mp 145−147 °C.

(*Z*)-6-(1-Fluoro-2-(naphthalen-2-yl)vinyl)-2,4-dimethylphenanthridine (3i). The title compound was prepared from 2-isocyano-3,5-dimethyl-1,1′-biphenyl (104 mg, 0.5 mmol, 1.0 equiv) and (*E*)-2-(2-bromo-2-fluorovinyl)naphthalene (188 mg, 0.75 mmol, 1.5 equiv) according to general procedure A. It was isolated as an orange solid (35 mg, 0.10 mmol); yield 19%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (d, J = 8.4 Hz, 1H), 8.60 (d, J = 9.2 Hz, 1H), 8.23 (d, J = 10.0 Hz, 1H), 7.98−7.95 (m, 1H), 7.91−7.83 (m, 4H), 7.73−7.69 (m, 1H), 7.53−7.48 (m, 3H), 7.01 (d, J = 38.4 Hz, 1H), 2.91 (s, 3H), 2.62 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.8 (d, J = 265.0 Hz, 1C), 149.3 (d, J = 30.6 Hz, 1C), 140.5, 138.0, 137.3, 133.6, 133.5, 132.8 (d, J = 1.6 Hz, 1C), 131.4, 131.1 (d, J = 3.6 Hz, 1C), 130.2, 129.0, 128.9, 128.3, 128.1, 127.6, 127.4, 127.2, 127.14, 127.07, 126.3, 126.2, 124.1, 123.9 (d, J = 3.6 Hz, 1C), 122.5, 119.4, 112.61, 112.56, 22.1, 18.2. FTIR: ν_{max}/cm^{-1} 3052, 2917, 1367,1313, 1165, 905, 817, 766, 748, 482. HRMS (ESI-TOF): calcd for $C_{27}H_{20}FN$ (M + H$^+$) 378.1653; found, 378.1654; mp 195−197 °C.

4-Methyl-6-phenylphenanthridine (3j).[23] The title compound was prepared from 2-isocyano-3-methyl-1,1′-biphenyl (97 mg, 0.5 mmol, 1.0 equiv) and iodobenzene (153 mg, 0.75 mmol, 1.5 equiv) according to general procedure A. It was isolated as a white solid (106 mg, 0.40 mmol); yield 79%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (d, J = 8.4 Hz, 1H), 8.45 (d, J = 8.0 Hz, 1H), 8.17 (d, J = 8.4 Hz, 1H),7.82−7.79 (m, 3H), 7.61−7.49 (m, 6H), 2.89 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.2, 142.6, 140.3, 138.2, 133.9, 130.2, 130.1, 129.4, 128.6, 128.5, 128.4, 128.2, 126.8, 126.4, 124.7, 123.4, 122.5, 119.7, 18.4. FTIR: ν_{max}/cm^{-1} 3059, 2957, 1567, 1467, 1361, 750, 689, 668. HRMS (ESI-TOF): calcd for $C_{20}H_{15}N$ (M + H$^+$) 270.1277; found, 270.1278; mp 137−139 °C.

4-Chloro-2-methyl-6-phenylphenanthridine (3k). The title compound was prepared from 3-chloro-2-isocyano-5-methyl-1,1′-biphenyl (114 mg, 0.5 mmol, 1.0 equiv) and iodobenzene (153 mg, 0.75 mmol, 1.5 equiv) according to general procedure A. It was isolated as a white solid (113 mg, 0.38 mmol); yield 75%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.65 (d, J = 8.0 Hz, 1H), 8.30 (s, 1H), 8.18 (d, J = 8.0 Hz, 1H), 7.86−7.81 (m, 3H), 7.70 (s, 1H), 7.63 (t, J = 8.0 Hz, 1H), 7.58−7.50 (m, 3H), 2.61 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.5, 139.6, 138.4, 136.8, 134.2, 133.1, 130.7, 130.5, 130.3, 128.9, 128.8, 128.3, 127.5, 125.2, 125.1, 122.4, 120.5, 21.7. FTIR: ν_{max}/cm^{-1} 3048, 2914, 1360, 1317, 855, 829, 779, 762, 702,673. HRMS (ESI-TOF): calcd for $C_{20}H_{14}ClN$ (M + H$^+$) 304.0888; found, 304.0886; mp 189−191 °C.

2,4,8-Trimethyl-6-phenylphenanthridine (3l). The title compound was prepared from 2-isocyano-3,4′,5-trimethyl-1,1′-biphenyl (111 mg, 0.5 mmol, 1.0 equiv) and iodobenzene (153 mg, 0.75 mmol, 1.5 equiv) according to general procedure A. It was isolated as a white solid (126 mg, 0.43 mmol); yield 85%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (d, J = 8.0 Hz, 1H), 8.19 (s, 1H), 7.91 (s, 1H), 7.81−7.78 (m, 1H), 7.62−7.48 (m, 4H), 7.40 (s, 1H), 2.83 (s, 3H), 2.57 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.0, 140.7, 140.6, 137.8, 136.5, 136.0, 131.6, 131.5, 130.8, 130.2, 128.3, 128.2, 127.8, 125.0, 123.4, 122.4, 119.1, 22.0, 21.7, 18.3. FTIR: ν_{max}/cm^{-1} 3050, 2919, 2850, 1565, 1524, 1441, 1365, 1315, 818, 766, 700, 581. HRMS (ESI-TOF): calcd for $C_{22}H_{19}N$ (M + H$^+$) 298.1590; found, 298.1592; mp 147−149 °C.

8-Fluoro-2,4-dimethyl-6-phenylphenanthridine (3m). The title compound was prepared from 4′-fluoro-2-isocyano-3,5-dimethyl-1,1′-biphenyl (113 mg, 0.5 mmol, 1.0 equiv) and iodobenzene (153 mg, 0.75 mmol, 1.5 equiv) according to general procedure A. It was isolated as a white solid (131 mg, 0.44 mmol); yield 87%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67−8.66 (m, 1H), 8.17 (s, 1H), 7.80−7.77 (m, 3H), 7.58−7.50 (m, 4H), 7.44 (s, 1H), 2.83 (s, 3H), 2.59 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.0 (d, J = 246.9 Hz, 1C), 157.4 (d, J = 4.1 Hz, 1C), 140.7, 139.9, 138.0, 136.6, 131.1, 130.2 (d, J = 1.8 Hz, 1C), 130.0, 128.6, 128.3, 126.0 (d, J = 7.9 Hz, 1C), 125.0 (d, J = 8.4 Hz, 1C), 122.9, 119.2, 119.03, 118.99, 112.8, 112.6, 22.0, 18.2. FTIR: ν_{max}/cm^{-1} 3057, 2917, 1524, 1372, 1315, 1196, 875, 824, 765, 693, 580. HRMS (ESI-TOF): calcd for $C_{21}H_{16}FN$ (M + H$^+$) 302.1340; found, 302.1343; mp 147−149 °C.

2,4-Dimethyl-6-phenyl-8(trifluoromethyl)phenanthridine (3n). The title compound was prepared from 2-isocyano-3,5-dimethyl-4′-(trifluoromethyl)-1,1′-biphenyl (138 mg, 0.5 mmol, 1.0 equiv) and iodobenzene (153 mg, 0.75 mmol, 1.5 equiv) according to general procedure A. It was isolated as a white solid (145 mg, 0.42 mmol); yield 83%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (d, J = 8.0 Hz, 1H), 8.45 (s, 1H), 8.20 (s, 1H), 7.97−7.94 (m, 1H), 7.80−7.78 (m, 2H), 7.60−7.52 (m, 3H), 7.49 (s, 1H), 2.83 (s, 3H), 2.58 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.0, 141.6, 139.5, 138.2, 136.9, 132.4, 130.2, 128.9, 128.5, 128.4 (q, J = 32.9 Hz, 1C), 125.9 (q, J = 4.1 Hz, 1C), 125.6 (q, J = 3.2 Hz, 1C), 124.1 (q, J = 273.5 Hz, 1C), 124.0, 123.5, 122.4, 119.5, 21.9, 18.2. FTIR: ν_{max}/cm^{-1} 3056, 2920, 1372, 1330, 1303, 1225, 1162, 1119, 828, 769. HRMS (ESI-TOF): calcd for $C_{22}H_{16}F_3N$ (M + H$^+$) 352.1308; found, 352.1309; mp 142−144 °C.

2,4,10-Trimethyl-6-phenylphenanthridine (3o). The title compound was prepared from 2-isocyano-2′,3,5-trimethyl-1,1′-biphenyl (111 mg, 0.5 mmol, 1.0 equiv) and iodobenzene (153 mg, 0.75 mmol, 1.5 equiv) according to general procedure A. It was isolated as a white solid (137 mg, 0.46 mmol); yield 92%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (s, 1H), 8.03 (d, J = 8.0 Hz, 1H), 7.76−7.74 (m, 2H), 7.63 (d, J = 4.0 Hz, 1H), 7.55−7.53 (m, 3H), 7.51−7.43 (m, 2H), 3.15 (s, 3H), 2.86 (s, 3H), 2.59 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.0, 141.9, 141.1, 137.7, 135.2, 134.8, 134.1, 133.2, 130.5, 130.2, 128.2, 128.1, 127.3, 126.5, 126.0, 124.7, 124.2, 27.1, 22.3, 18.9. FTIR: ν_{max}/cm^{-1} 3051, 2915, 1442, 1379, 1362, 1322, 845, 779, 766, 700. HRMS (ESI-TOF): calcd for $C_{22}H_{19}N$ (M + H$^+$) 298.1590; found, 298.1591; mp 161−163 °C.

2,4-Dimethyl-6-phenyl-9(trifluoromethyl)phenanthridine (3p). The title compound was prepared from 2-isocyano-3,5-dimethyl-3′-(trifluoromethyl)-1,1′-biphenyl (138 mg, 0.5 mmol, 1.0 equiv) and

DOI: 10.1021/jo502731n
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iodobenzene (153 mg, 0.75 mmol, 1.5 equiv) according to general procedure A. It was isolated as a white solid (67 mg, 0.19 mmol); yield 38%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.94 (s, 1H), 8.29 (d, J = 8.0 Hz, 1H), 8.25 (s, 1H), 7.80−7.76 (m, 3H), 7.59−7.54 (m, 3H), 7.51 (s, 1H), 2.85 (s, 3H), 2.63 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.6, 141.3, 139.8, 138.2, 137.1, 133.3, 132.1, 131.3 (q, J = 32.7 Hz, 1C), 130.1, 129.5, 128.8, 128.3, 126.1, 124.1 (q, J = 272.7 Hz, 1C), 122.8, 122.5 (q, J = 3.2 Hz, 1C), 120.0 (q, J = 4.0 Hz, 1C), 119.2, 21.9, 18.1. FTIR: ν_{max}/cm^{-1} 3063, 2920, 1349, 1316, 1161, 1152, 1119, 1072, 771, 703. HRMS (ESI-TOF): calcd for $C_{22}H_{16}F_3N$ (M + H$^+$) 352.1308; found, 352.1309; mp 187−189 °C.

2,4-Dimethyl-6-phenyl-7(trifluoromethyl)phenanthridine (3p′). Another isomer **3p′** was isolated as a white solid (57 mg, 0.15 mmol); yield 30%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.86 (d, J = 8.0 Hz, 1H), 8.17 (s, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.86 (t, J = 8.0 Hz, 1H), 7.62 (d, J = 4.0 Hz, 2H), 7.46−7.42 (m, 4H), 2.81 (s, 3H), 2.59 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.9, 143.6 (q, J = 1.8 Hz, 1C), 140.0, 137.5, 136.6, 135.5, 131.9, 129.3, 128.5, 128.4 (q, J = 31.5 Hz, 1C), 128.3, 127.6 (q, J = 6.2 Hz, 1C), 127.5, 126.2, 123.8 (q, J = 274.4 Hz, 1C), 121.7, 120.5, 119.0, 22.0, 17.7. FTIR: ν_{max}/cm^{-1} 3058, 2919, 1298, 1185, 1128, 1112, 1092, 822, 776, 700. HRMS (ESI-TOF): calcd for $C_{22}H_{16}F_3N$ (M + H$^+$) 352.1308; found, 352.1306; mp 199−201 °C.

2,4-Dimethyl-6-phenyl-9*H*-cyclopenta[4,5]furo[3,2-*c*]-quinolone (3q). The title compound was prepared from 2-(2-isocyano-3,5-dimethylphenyl)benzofuran (120 mg, 0.5 mmol, 1.0 equiv) and iodobenzene (153 mg, 0.75 mmol, 1.5 equiv) according to general procedure A. It was isolated as a white solid (151 mg, 0.48 mmol); yield 96%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04−8.01 (m, 3H), 7.80 (d, J = 8.0 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.62−7.54 (m, 3H), 7.46 (t, J = 8.0 Hz, 2H), 7.28−7.24 (m, 1H), 2.87 (s, 3H), 2.58 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.4, 156.0, 153.1, 144.7, 140.4, 137.6, 136.2, 132.1, 129.3, 129.1, 128.5, 126.7, 123.3, 123.2, 122.3, 117.4, 115.9, 114.1, 111.8, 21.8, 18.4. FTIR: ν_{max}/cm^{-1} 3050, 2916, 1589, 1489, 1446, 1355, 1319, 1185, 1120, 851, 775, 745, 694. HRMS (ESI-TOF): calcd for $C_{23}H_{17}NO$ (M + H$^+$) 324.1383; found, 324.1383; mp 185−187 °C.

3-((2,4-Dimethylphenanthridin-6-yl)methyl)-1,3-dimethylindolin-2-one (5a). The title compound was prepared from 2-isocyano-3,5-dimethyl-1,1′-biphenyl (104 mg, 0.5 mmol, 1.0 equiv) and *N*-(2-iodophenyl)-*N*-methylmethacrylamide (227 mg, 0.75 mmol, 1.5 equiv) according to general procedure B. It was isolated as a yellow solid (162 mg, 0.43 mmol); yield 85%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (d, J = 8.0 Hz, 1H), 8.27 (d, J = 8.0 Hz, 1H), 8.06 (s, 1H), 7.75−7.71 (m, 1H), 7.64−7.60 (m, 1H), 7.22 (s, 1H), 7.16−7.12 (m, 1H), 7.04−7.02 (m, 1H), 6.84−6.80 (m, 2H), 4.11 (d, J = 16.8 Hz, 1H), 4.04 (d, J = 16.8 Hz, 1H), 3.30 (s, 3H), 2.47 (s, 3H), 2.34 (s, 3H), 1.58 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 181.1, 154.0, 143.5, 140.3, 137.0, 135.4, 134.8, 132.5, 130.6, 129.7, 126.9, 126.7, 125.5, 125.2, 123.1, 122.5, 121.9, 121.8, 119.1, 107.9, 47.1, 40.8, 27.3, 26.4, 21.7, 18.2. FTIR: ν_{max}/cm^{-1} 3046, 2962, 1704, 1612, 1491, 1467, 1450, 1376, 1313, 791, 752. HRMS (ESI-TOF): calcd for $C_{26}H_{24}N_2O$ (M + H$^+$) 381.1961; found, 381.1963; mp 174−176 °C.

1-Benzyl-3-((2,4-dimethylphenanthridin-6-yl)methyl)-3-methylindolin-2-one (5b). The title compound was prepared from 2-isocyano-3,5-dimethyl-1,1′-biphenyl (104 mg, 0.5 mmol, 1.0 equiv) and *N*-benzyl-*N*-(2-iodophenyl)methacrylamide (283 mg, 0.75 mmol, 1.5 equiv) according to general procedure B. It was isolated as a yellow solid (87 mg, 0.19 mmol); yield 38%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (d, J = 8.0 Hz, 1H), 8.32 (d, J = 8.0 Hz, 1H), 8.09 (s, 1H), 7.73 (t, J = 7.6 Hz, 1H), 7.63 (t, J = 8.0 Hz, 1H), 7.23(s, 1H), 7.17−7.15 (m, 3H), 7.12−7.11 (m, 3H), 7.02 (t, J = 7.6 Hz, 1H), 6.83 (t, J = 7.6 Hz, 1H), 6.67 (d, J = 7.6 Hz, 1H), 5.32 (d, J = 15.6 Hz, 1H), 4.66 (d, J = 15.6 Hz, 1H), 4.17 (d, J = 16.4 Hz, 1H), 4.02 (d, J = 16.4 Hz, 1H), 2.49 (s, 3H), 2.34 (s, 3H), 1.66 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 180.9, 154.1, 142.4, 140.3, 137.1, 136.4, 135.5, 134.7, 132.7, 130.7, 129.7, 128.6, 127.3, 127.1, 126.9, 126.8, 125.8, 125.3, 123.2, 122.4, 122.3, 121.9, 119.1, 108.9, 47.6, 43.6, 40.8, 27.2, 21.2, 18.2. FTIR: ν_{max}/cm^{-1} 3060, 2914, 1718, 1613, 1489, 1464, 1340, 1305, 1168, 790, 746. HRMS (ESI-TOF): calcd for $C_{32}H_{28}N_2O$ (M + H$^+$) 457.2274; found, 457.2278; mp 174−176 °C.

3-((2,4-Dimethylphenanthridin-6-yl)methyl)-1-methacryloyl-3-methylindolin-2-one (5c). The title compound was prepared from 2-isocyano-3,5-dimethyl-1,1′-biphenyl (104 mg, 0.5 mmol, 1.0 equiv) and *N*-(2-iodophenyl)-*N*-methacryloylmethacrylamide (266 mg, 0.75 mmol, 1.5 equiv) according to general procedure B. It was isolated as a white solid (154 mg, 0.36 mmol); yield 71%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (d, J = 8.4 Hz, 1H), 8.27 (d, J = 8.0 Hz, 1H), 8.12 (d, J = 8.0 Hz, 1H), 8.06 (s, 1H), 7.78−7.74 (m, 1H), 7.68−7.64 (m, 1H), 7.25−7.21 (m, 1H), 7.10−7.08 (m, 1H), 7.03−6.99 (m, 1H), 5.40 (s, 1H), 5.37 (s, 1H), 4.21 (d, J = 16.0 Hz, 1H), 4.13 (d, J = 16.0 Hz, 1H), 2.47 (s, 3H), 2.28 (s, 3H), 2.05 (s, 3H), 1.67 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 180.3, 171.2, 153.0, 141.7, 140.2, 139.7, 137.2, 135.7, 134.6, 132.6, 131.0, 129.9, 127.3, 126.9, 125.1, 125.0, 124.7, 123.2, 122.6, 121.1, 119.8, 119.1, 115.7, 47.0, 41.2, 28.3, 21.7, 18.9, 18.4. FTIR: ν_{max}/cm^{-1} 3075, 2965, 1766, 1681, 1480, 1451, 1352, 1311, 1259, 1150, 790, 751. HRMS (ESI-TOF): calcd for $C_{29}H_{26}N_2O_2$ (M + H$^+$) 435.2067; found, 435.2065; mp 227−229 °C.

6-((1,3-Dimethylindolin-3-yl)methyl)-2,4-dimethylphenanthridine (5d). The title compound was prepared from 2-isocyano-3,5-dimethyl-1,1′-biphenyl (104 mg, 0.5 mmol, 1.0 equiv) and 2-iodo-*N*-methyl-*N*-(2-methylallyl)aniline (215 mg, 0.75 mmol, 1.5 equiv) according to general procedure B. It was isolated as a pale yellow oil (86 mg, 0.24 mmol); yield 47%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (d, J = 8.4 Hz, 1H), 8.17 (s, 1H), 8.10 (d, J = 8.4 Hz, 1H), 7.70 (t, J = 8.0 Hz, 1H), 7.51 (t, J = 8.0 Hz, 1H), 7.41 (s, 1H), 7.10 (t, J = 8.0 Hz, 1H), 6.97 (d, J = 8.0 Hz, 1H), 6.63 (t, J = 8.0 Hz, 1H), 6.51 (d, J = 8.0 Hz, 1H), 3.78−3.74 (m, 2H), 3.54 (d, J = 14.8 Hz, 1H), 4.22 (d, J = 8.8 Hz, 1H), 2.84 (s, 3H), 2.76 (s, 3H), 2.56 (s, 3H), 1.56 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.5, 152.2, 140.5, 138.9, 137.2, 135.5, 132.6, 130.9, 129.5, 127.7, 126.6, 126.3, 126.2, 123.1, 122.4, 122.3, 119.3, 117.6, 107.3, 68.2, 44.4, 43.2, 35.8, 24.6, 21.9, 18.6. FTIR: ν_{max}/cm^{-1} 3020, 2952, 2803, 1605, 1489, 1460, 1450, 1372, 1361, 1300, 849, 795, 777. HRMS (ESI-TOF): calcd for $C_{26}H_{26}N_2$ (M + H$^+$) 367.2169; found, 367.2169.

2-(2,4-Dimethylphenanthridin-6-yl)phenyl Methacrylate (3r). The title compound was prepared from 2-isocyano-3,5-dimethyl-1,1′-biphenyl (104 mg, 0.5 mmol, 1.0 equiv) and 2-iodophenyl methacrylate (216 mg, 0.75 mmol, 1.5 equiv) according to general procedure A. It was isolated as a pale yellow oil (93 mg, 0.26 mmol); yield 51%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.65 (d, J = 8.4 Hz, 1H), 8.25 (s, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.80−7.76 (m, 1H), 7.67−7.65 (m, 1H), 7.60−7.53 (m, 2H), 7.45−7.40 (m, 3H), 5.65 (s, 1H), 5.25 (s, 1H), 2.78 (s, 3H), 2.60 (s, 3H), 1.56 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.3, 155.1, 149.0, 140.9, 138.0, 136.4, 135.4, 133.0, 132.8, 131.7, 131.2, 130.0, 129.4, 128.3, 126.7, 126.6, 125.6, 125.3, 123.4, 123.1, 122.2, 119.3, 22.0, 18.2, 17.9. FTIR: ν_{max}/cm^{-1} 3068, 2923, 1737, 1447, 1363, 1319, 1294, 1196, 1130, 773, 758. HRMS (ESI-TOF): calcd for $C_{25}H_{21}NO_2$ (M + H$^+$) 368.1645; found, 368.1647.

2,4-Dimethyl-6-((4-methylisochroman-4-yl)mthyl)-phenanthridine (5e). The title compound was prepared from 2-isocyano-3,5-dimethyl-1,1′-biphenyl (104 mg, 0.5 mmol, 1.0 equiv) and 1-iodo-2-(((2-methylallyl)oxy)methyl)benzene (216 mg, 0.75 mmol, 1.5 equiv) according to general procedure B. It was isolated as a pale yellow oil (141 mg, 0.39 mmol); yield 77%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (d, J = 8.4 Hz, 1H), 8.22 (s, 1H), 8.18 (d, J = 8.0 Hz, 1H), 7.73 (t, J = 8.0 Hz, 1H), 5.02 (t, J = 14.8 Hz, 1H), 4.92 (d, J = 14.8 Hz, 1H), 4.29 (d, J = 11.6 Hz, 1H), 3.84 (d, J = 14.0 Hz, 1H), 3.76 (d, J = 13.6 Hz, 1H), 3.64 (d, J = 11.2 Hz, 1H), 2.86 (s, 3H), 2.60 (s, 3H), 1.47 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.6, 142.2, 140.5, 137.3, 135.6, 133.7, 132.7, 130.9, 129.4, 126.5, 126.5, 126.5, 125.8, 124.0, 123.1, 122.3, 119.3, 74.3, 69.1, 44.0, 38.0, 23.5, 21.9, 18.4. FTIR: ν_{max}/cm^{-1} 3071, 2921, 1578, 1490, 1453, 1363, 1097, 773, 795, 745. HRMS (ESI-TOF): calcd for $C_{26}H_{25}NO$ (M + H$^+$) 368.2009; found, 368.2009.

Ethyl 4-Methyl-1-phenylisoquinoline-3-carboxylate (7a).[24] The title compound was prepared from ethyl (*Z*)-2-isocyano-3-phenylbut-2-enoate (43 mg, 0.2 mmol, 1.0 equiv) and iodobenzene

DOI: 10.1021/jo502731n
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(61 mg, 0.3 mmol, 1.5 equiv) according to general procedure C. It was isolated as a pale yellow solid (45 mg, 0.16 mmol); yield 77%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, J = 8.4 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H), 7.80−7.76 (m, 1H), 7.71−7.68 (m, 2H), 7.61−7.57 (m, 1H), 7.54−7.46 (m, 3H), 4.50 (q, J = 8.0 Hz, 2H), 1.45 (t, J = 8.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.0, 158.7, 142.1, 139.1, 136.6, 130.3, 130.2, 128.6, 128.3, 128.2, 127.9, 126.9, 124.3, 61.6, 14.32, 14.27. FTIR: ν_{max}/cm^{-1} 3039, 2921, 1713, 1374, 1331, 1309, 1238, 1214, 1057, 772, 762, 704. HRMS (ESI-TOF): calcd for $C_{19}H_{17}NO_2$ (M + H$^+$) 292.1332; found, 292.1334; mp 92−94 °C.

Ethyl 4-Ethyl-1-phenylisoquinoline-3-carboxylate (7b). The title compound was prepared from ((*Z*)-1,1-diisocyanobut-1-en-2-yl)benzene (46 mg, 0.2 mmol, 1.0 equiv) and iodobenzene (61 mg, 0.3 mmol, 1.5 equiv) according to general procedure C. It was isolated as a pale yellow solid (33 mg, 0.11 mmol); yield 53%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, J = 8.8 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H), 7.79−7.75 (m, 1H), 7.70−7.68 (m, 2H), 7.57 (t, J = 8.0 Hz, 1H), 7.53−7.45 (m, 3H), 4.49 (q, J = 8.0 Hz, 2H), 3.27 (q, J = 8.0 Hz, 2H), 1.46−1.42(m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.9, 158.8, 141.9, 139.1, 135.7, 132.5, 130.3, 130.2, 128.6, 128.4, 128.3, 127.7, 127.3, 124.1, 61.6, 21.6, 15.4, 14.3. FTIR: ν_{max}/cm^{-1} 2966, 1716, 1445, 1372, 1309, 1286, 1256, 1208, 1160, 1071, 1052, 774, 705. HRMS (ESI-TOF): calcd for $C_{20}H_{19}NO_2$ (M + H$^+$) 306.1489; found, 306.1486; mp 91−93 °C.

Ethyl 1,4-Diphenylisoquinoline-3-carboxylate (7c).[25] The title compound was prepared from (*Z*)-ethyl 2-isocyano-3,3-diphenyl acrylate (55 mg, 0.2 mmol, 1.0 equiv) and iodobenzene (61 mg, 0.3 mmol, 1.5 equiv) according to general procedure C. It was isolated as a pale yellow solid (41 mg, 0.12 mmol); yield 58%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, J = 8.0 Hz, 1H), 7.78−7.41 (m, 13H), 4.12 (q, J = 8.0 Hz, 2H), 0.98 (t, J = 8.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.5, 160.3, 142.3, 138.9, 136.4, 136.1, 131.9, 130.5, 130.2, 130.0, 128.8, 128.5, 128.3, 128.2, 128.1, 128.0, 127.7, 127.0, 126.5, 61.2, 13.7. FTIR: ν_{max}/cm^{-1} 3061, 2977, 1732, 1723, 1401, 1384, 1227, 1185, 1113, 782, 758, 700, 672. HRMS (ESI-TOF): calcd for $C_{24}H_{19}NO_2$ (M + H$^+$) 354.1489; found, 354.1487; mp 108−110 °C.

Ethyl 7-Chloro-4-(4-chlorophenyl)-1-phenylisoquinoline-3-carboxylate (7d). The title compound was prepared from (*Z*)-4,4′-(2,2-diisocyanoethene-1,1-diyl)bis(chlorobenzene) (70 mg, 0.2 mmol, 1.0 equiv) and iodobenzene (61 mg, 0.3 mmol, 1.5 equiv) according to general procedure C. It was isolated as a pale yellow oil (46 mg, 0.11 mmol); yield 54%. ^{1}H NMR (400 MHz, CDCl3): δ 8.15 (s, 1H), 7.75−7.73 (m, 2H), 7.63−7.49 (m, 7H), 7.36−7.32 (m, 2H), 4.16 (q, J = 8.0 Hz, 2H), 1.07 (t, J = 8.0 Hz, 3H). ^{13}C NMR (125 MHz, CDCl3): δ 166.9, 159.7, 142.4, 138.2, 134.7, 134.53, 134.46, 134.1, 131.6, 131.3, 130.6, 130.1, 129.2, 128.7, 128.6, 128.1, 127.7, 126.6, 61.5, 13.8. FTIR: ν_{max}/cm^{-1} 3060, 2980, 1721, 1495, 1300, 1222, 1173, 1087, 841, 701, 533, 521; HRMS (ESI-TOF): calcd for $C_{24}H_{17}Cl_2NO_2$ (M + H$^+$) 422.0709; found, 422.0708.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Proton and carbon NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful to the National Science Foundation of China (21402203, 21472190) for the financial support of this work.

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DOI: 10.1021/jo502731n
J. Org. Chem. 2015, 80, 2223−2230