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Divergent Reaction Pathways of Homologous and Isosteric Propargyl Amides in Sequential Ru/Pd-Catalyzed Annulations for the Synthesis of Heterocycles

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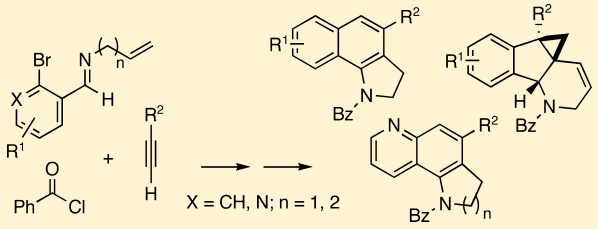
Supporting Information

ABSTRACT: Cu-catalyzed three-component coupling of imines with benzoyl chloride and terminal arylalkynes followed by enyne ring-closing metathesis (RCM) and Heck cyclization afforded medicinally relevant benzoindolines, cyclopropane-fused indenopyridines, pyrroloquinolines, or 1,7-tetrahydrophenanthrolines via divergent cyclization pathways. Unexpectedly, the Pd-catalyzed cyclization of heterocyclic dienes proceeded via regiodivergent 5-exo or 6-endo pathways depending on the ring size (n = 1, 2) or the presence of isosteric groups (CH vs N). A one-pot protocol for the enyne−RCM/Heck annulation featuring a sequential addition of the Ru and Pd catalysts was developed maximizing the synthetic efficiency.



INTRODUCTION

An important goal of the current synthetic organic chemistry is to maximize the efficiency of methodologies for the preparation of complex structures.[1] In the search for the "ideal synthesis", much effort has been directed toward improving the "step economy"[2] by the application of multicomponent reactions[3] and by performing sequences of reactions as one-pot operations.[4] This task has proven to be particularly difficult when transition-metal-catalyzed reactions were involved due to the likelihood of catalyst poisoning in complex reaction mixtures.[5] The recent advances in diversity-oriented synthesis underscore the value of divergent synthetic pathways that can be used to construct libraries of compounds with multiple distinct core structures.[6] Herein, we describe a divergent methodology that delivers structurally distinct N-heterocycles by applying multicomponent reactions[3] and one-pot sequential transition-metal-catalyzed transformations to homologous and isosteric[7] substrates (Figure 1).

Cu(I)-catalyzed coupling of imines, acyl chlorides, and alkynes[8] afforded enynes **I** that were subjected to Ru(II)-catalyzed ring-closing metathesis (RCM) and Pd(0)-catalyzed Heck annulation, unexpectedly yielding either benzoindolines **III** or cyclopropane-fused tetrahydroindenopyridines **IV** via divergent 6-endo and 5-exo Heck cyclization pathways, respectively, depending on the ring size (Figure 1). The course of the Heck cyclization was altered by the presence of the additional N-heteroatom in enynes **I** (X = N) delivering pyrroloquinolines **V** and 1,7-tetrahydrophenanthrolines **VI** via 6-endo Heck cyclization (Figure 1).

In previously reported studies, selectivity for possible divergent 5-exo vs 6-endo pathways of various Heck cyclizations has been controlled by steric effects of substituents on the vinyl component[9] or distinct conformational preferences of the substrates.[10] Alternatively, the regiocontrol was achieved by the choice of the catalyst composition[11] or by trapping of the product of 5-exo cyclization under reductive Heck conditions.[12] In our system, the structural features of the homologous and isosteric substrates determine whether the 5-exo or the 6-endo carbopalladation step leads to a synthetically productive pathway. The efficiency of the synthetic protocol described herein was maximized by uncovering reaction conditions that allowed for the Ru-catalyzed enyne RCM and the Pd(0)-catalyzed Heck reaction to be performed for the first time as a one-pot operation via a sequential addition of the transition metal catalysts. Sequences of Ru-catalyzed metatheses and Pd-catalyzed C−C bond-forming reactions, including Tsuji−Trost reaction, cross-coupling, and the Heck reaction, have been utilized in synthesis in the past.[13] However, only Trost and Grigg investigated the possibility of combining the two catalytic reactions into one-step processes. Trost described a one-pot enyne cross-metathesis (CM) followed by an enantioselective Tsuji−Trost allylation involving a sequential addition of the Ru and Pd catalysts for the preparation of N- and O-heterocycles.[13f] Grigg identified the difficulties arising from interactions of the components of the catalytic systems when diene RCM and the Heck annulations were performed in one pot with both sequential and concomitant additions of the two catalysts.[14] Notably, when challenging RCM reactions were involved, low yields of the heterocycles resulted both from the

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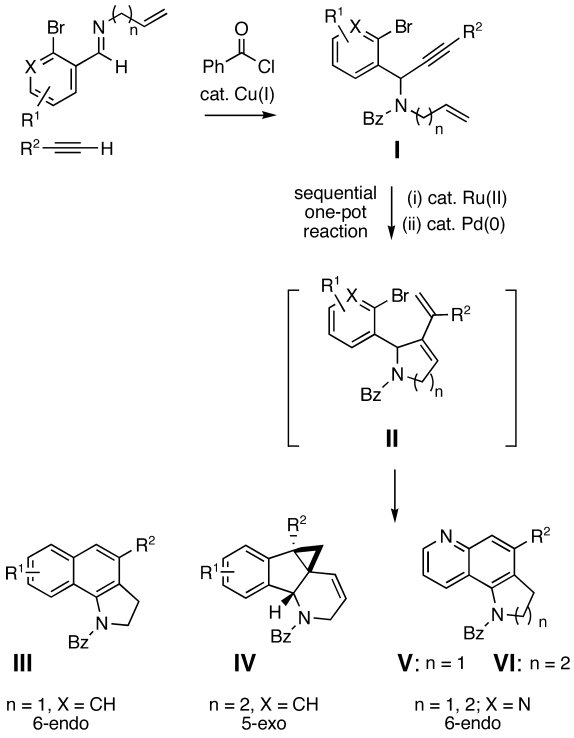


Figure 1. Synthetic methodology.

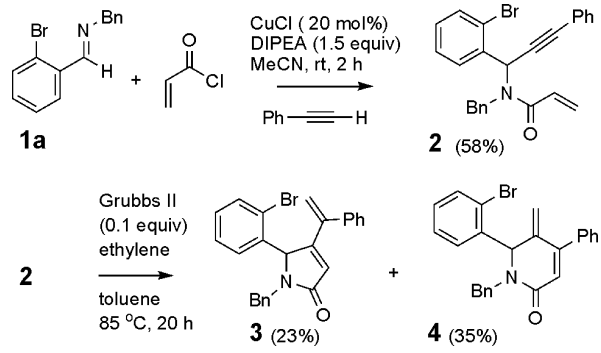
sequential and concomitant catalyst additions. This problem could only be addressed by a physical separation of the catalysts using solid-supported or fluorous phase-localized Pd catalysts for the Heck reactions.[14]

The one-pot sequential Ru/Pd-catalyzed protocol for the annulation of enyne amides **I** described herein provides an attractive and modular alternative to the synthetic methods currently available for the preparation of benzoindolines **III**, indenopyridines **IV**, pyrroloquinoline **V**, and 1,7-phenanthrolines **VI** and related heterocycles.[15] The most relevant known methods include Au-catalyzed annulation of diynes[15a] for benzolindolines, sequential hetero-Diels–Alder/Friedel–Crafts reaction[15c] yielding structures related to indenopyridines, and a classical stepwise annulation of the pyrrolidine ring[15f] for the synthesis of oxidized analogues of pyrroloquinolines. Heterocycles **III**–**VI** represent druglike scaffolds[16] potentially endowed with valuable medicinal properties.[17]

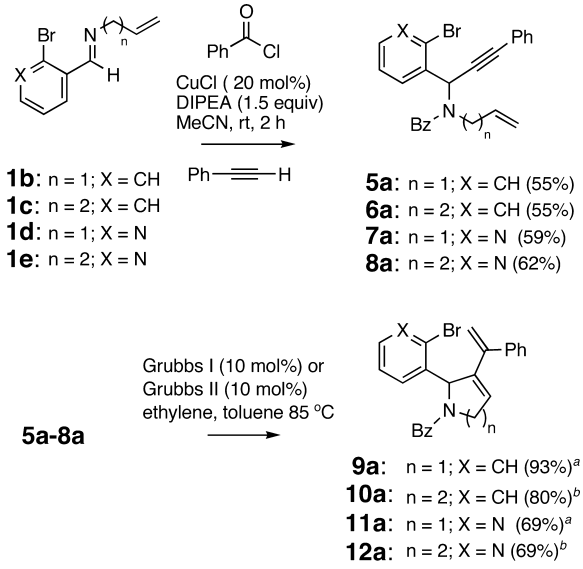
RESULTS AND DISCUSSION

Method Development. We envisioned that properly functionalized enynes incorporating the propargylic amide functional group would provide useful substrates for diverse sequences of transition-metal-catalyzed annulation reactions. Seeking the ideal arrangement of the functional groups, the Cu(I)-catalyzed coupling of *N*-benzylimine **1a**, acroyl chloride with phenylacetylene[8] was used to prepare *N*-benzyl enyne **2** (58%) (Scheme 1). However, enyne **2** proved to be a challenging substrate for the RCM reaction,[18] providing low yields of pyrrolidone **3** (23%) and cyclohexenenone **4** (35%) (Scheme 1). Alternatively, *N*-allyl- and *N*-homoallylimines **1b**–**e** derived from 2-bromobenzaldehyde and 2-bromopyridine-3-carbaldehyde afforded enyne amides **5a**–**8a** (55–62%) via the Cu-catalyzed coupling with benzoyl chloride and phenylacetylene (Scheme 2). The moderate yields of enynes **5a**–**8a** were caused by the formation of amide byproducts PhC(=O)NH$(CH_2)_n$CH=CH_2 (n = 1, 2) arising from a premature hydrolysis of the *N*-acyliminium salts. In contrast to enyne **2**, the RCM reaction with amides **5a**–**8a** under ethylene atmosphere proceeded efficiently to afford dienes **9a**–**12a** in good yields (69–93%).[18] The *N*-homoallylic analogs **6a** and **8a** (n = 2) performed better in reactions catalyzed by the more active Grubbs II catalyst (Scheme 1).[19] The pyrrolidine derivatives **9a** and **11a** (n = 1) proved to be somewhat unstable and had to be used within 24 h, whereas the piperidine analogues **10a** and **12a** (n = 2) were stable compounds.

Scheme 1. Cu(I)-Catalyzed Three-Component Coupling and RCM with Acroyl Chloride



Scheme 2. Cu(I)-Catalyzed Three-Component Coupling and RCM with Benzoyl Chloride



[a]Grubbs I catalyst was used [b]Grubbs II catalyst was used.

Next, we explored pathways available for Pd-catalyzed annulations of dienes **9a**–**12a** (Scheme 3). The Heck cyclization of dienes **9a**–**12a** may proceed via the kinetically favored 5-exo pathway[20] or the 6-endo route[20] generating an allylpalladium intermediate.[21] Initially, we anticipated that the 5-exo cyclization would be favored. To the contrary, catalysis of the cyclization of diene **9a**[22] either with the ligandless catalyst [conditions A: $Pd(OAc)_2$, NaOAc][8a] or with an added phosphine [conditions B: $Pd(OAc)_2/PPh_3/Cs_2CO_3$][22] both in DMF, afforded benzoindoline **13a** in 71% and 73% yields, respectively, pointing to the preference for 6-endo cyclization (Scheme 3). The homologous diene **10a** yielded cyclopropane-fused indenopyridine **14a** (55%) when treated under

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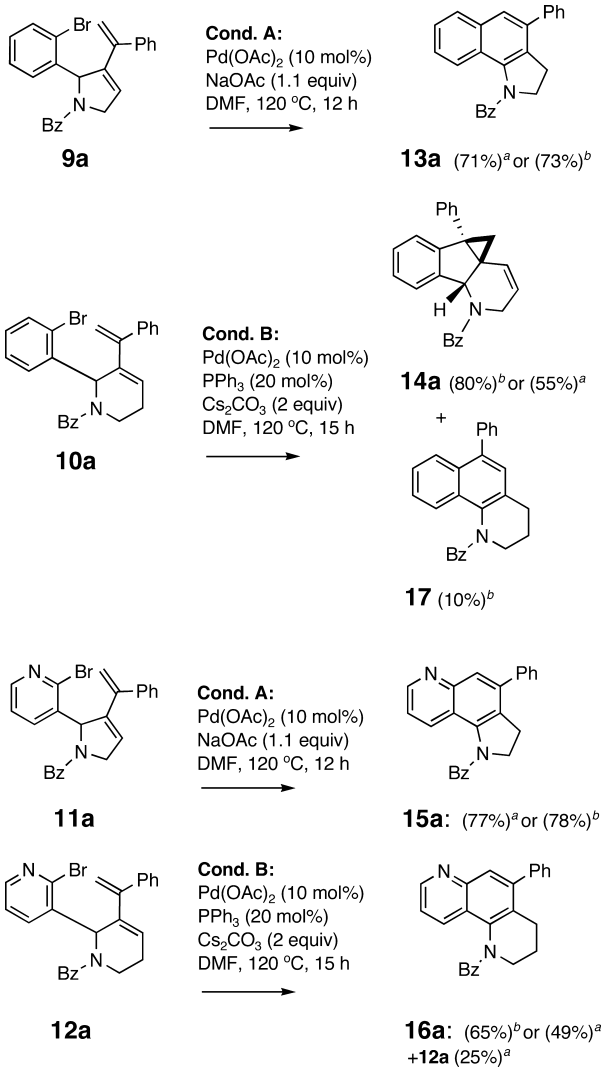
Scheme 3. Exploration of the Divergent Pathways in the Heck Cyclizations



[a]Conditions A were used. [b]Conditions B were used.

conditions A [$Pd(OAc)_2$, NaOAc] and the indenopyridine **14a** (80%) accompanied by a separable benzoquinoline **17** (10%) when treated under conditions B [$Pd(OAc)_2/PPh_3/Cs_2CO_3$] (Scheme 3). The results indicate the operation of the 5-exo pathway. The position of the phenyl substituent in benzoindolines **13a** and **17** and the relative stereochemistry in indenopyridine **14a** (vide infra) were established by X-ray crystallography, utilizing an indenopyridine analogue **14b** prepared as shown in Table 1 (vide infra).[23] The protocol was successfully extended to the synthesis of pyridine-fused N-heterocyclic cores (Scheme 3). Diene **11a** (X = N, n = 1) delivered the expected pyrroloquinoline **15a** upon the treatment under conditions A [$Pd(OAc)_2$/NaOAc] or conditions B [$Pd(OAc)_2/PPh_3/Cs_2CO_3$] in 77% and 78% yields, respectively. Unexpectedly, diene **12a** (X = N, n = 2) afforded tetrahydro-1,7-phenanthroline **16a** (65%) via the 6-endo cyclization when treated under conditions B [$Pd(OAc)_2/PPh_3/Cs_2CO_3$]. The application of conditions A [$Pd(OAc)_2$, NaOAc] for the reaction of diene **12a** afforded the same product **16a** (49%), but the conversion of substrate **12a** was not complete (Scheme 3). Apparently, the 5-exo cyclization pathway was disfavored by the N-heteroatom. The structures of heterocycles **15a** and **16a** were assigned by NMR analyses and X-ray crystallography on **16a**.[23]

The observed reactivity of dienes **9a**−**12a** suggests that the divergent reaction pathways are not controlled by the choice of the catalyst composition (conditions A vs B) but rather by the structural features of the substrates. We propose that intermediates **A** and **D** formed by oxidative addition of the Pd(0) catalysts initially undergo kinetically favored 5-exo cyclization[20] (Figure 2).

The intermediate **E** (n = 2), which is less conformationally restricted than the intermediate **B** (n = 1), rapidly undergoes 3-exo cyclization giving rise to the cyclopropane ring[24] in

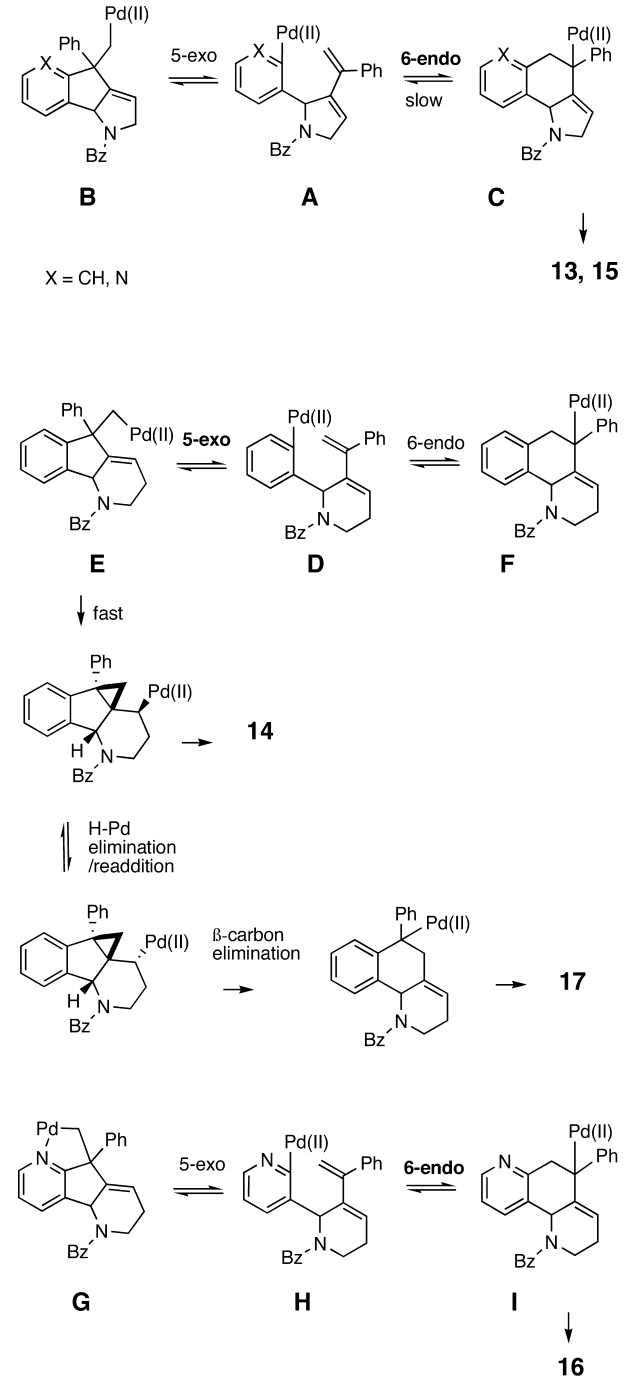


Figure 2. Proposed mechanistic rationale.

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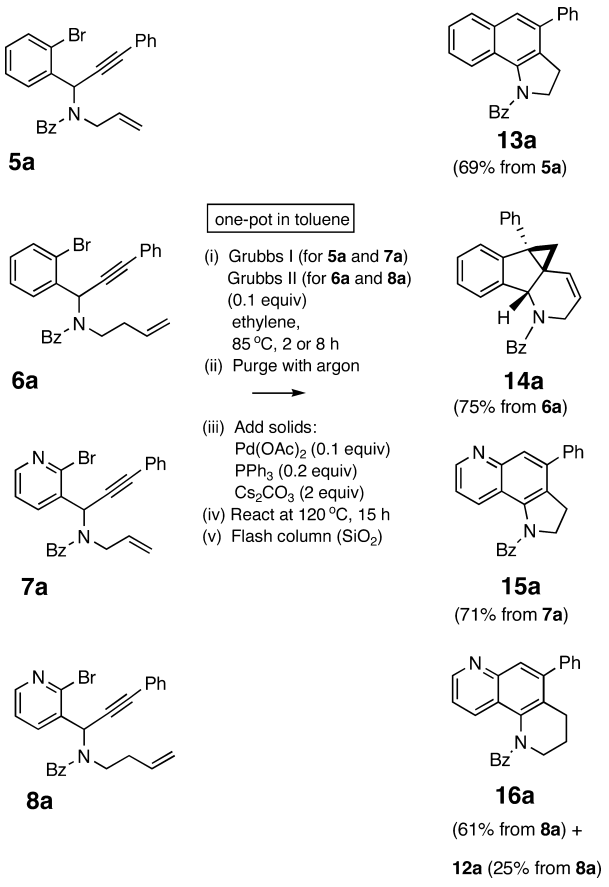
indenopyridines **14**. Reversible ß-hydride elimination, H–Pd(II) readdition, and β-carbon elimination[25] from the diastereomeric Pd-intermediate delivers the minor product **17**. In contrast, the conformationally restricted pyrrolidine-derived intermediate **B** (n = 1) engages in reversible carbopalladation, ultimately affording intermediate **C** and benzoindolines **13** or pyrroloquinolines **15** via 6-endo cyclization. The diene intermediate **H** (n = 2) carrying the additional N-heteroatom (X = N) also undergoes a fast 5-exo cyclization. However, the chelation of the N-heteroatom to the Pd(II) center in the intermediate **G** slows the 3-*exo-trig* cyclization, directing the reversible carbopalladation toward the 6-endo cyclization yielding the intermediate **I** and ultimately 1,7-tetrahydrophenanthrolines **16**.

Development of the One-Pot Protocol. To improve the synthetic efficiency of the method, we sought to perform the Ru- and Pd-catalyzed reactions as a one-pot operation. A catalytic system that could realize both the RCM and the Heck cyclizations in toluene was needed. Experimentation with different bases and additives for the Heck reaction revealed that achieving a good stability of the Pd catalyst by the addition of a phosphine ligand and identifying a base with a sufficient solubility in toluene were the critical factors. The solution to this problem was found when we employed the original conditions B [$Pd(OAc)_2/PPh_3/Cs_2CO_3$] (Scheme 4) for the Pd-catalyzed annulation in toluene instead of DMF as the solvent. The sequence of enyne–RCM/Heck reactions could then be performed successfully in one-pot with a sequential addition of the Ru and Pd catalysts via the series of operations

Scheme 4. Development of the One-Pot Protocol for Sequential Ru/Pd-Catalyzed Annulations



including (i) treatment of toluene solutions of the dienes **5a–8a** under an atmosphere of ethylene with the Grubbs I catalyst for 2 h for the *N*-allylic substrates or with the Grubbs II catalyst for 8 h for the *N*-homoallylic substrates; (ii) purging the reaction mixtures with argon; (iii) addition of the solid components of the Heck catalyst mixture [$Pd(OAc)_2$, PPh_3, Cs_2CO_3]; (iv) heating the reactions mixtures at 120 °C for 15 h; (v) and finally purification of the crude products by flash chromatography (Scheme 4). Using this one-pot protocol, heterocycles **13a**, **14a**, and **15a** were obtained in 69%, 75%, and 71% yields calculated per the enynes **5a**, **6a**, and **7a**, respectively (Scheme 4). The tetrahydrophenanthroline **16a** was accompanied by residual diene **12a** formed by the RCM reaction (Schemes 3 and 4). The crude mixture of **16a** and **12a** was easily separated by flash chromatography over silica, delivering pure tetrahydrophenanthroline **16a** in 61% yield calculated per the enyne **8a** (Scheme 4). The one-pot protocol provides for more economical syntheses by avoiding the expense of time, silica, and solvents involved in chromatographic purification of the RCM products **9a**, **10a**, **11a**, and **12a**. The most significant improvements in the yields of the target heterocycles were observed for the pyridine-derived pyrroloquinoline **15a** (71% from **7a**) and tetrahydrophenanthroline **16a** (61% from **8a**) when compared to the yields of **15a** (53% from **7a**, difference of 18%) and **16a** (44% from **8a**, difference of 17%) calculated from the yields of the two sequential reactions reported in Schemes 2 and 3. Elimination of the material loss during the chromatographic purification of dienes **11a** (69% yield via RCM) and **12a** (69% yield via RCM) appears to be largely responsible for the success of the one-pot protocol for the preparation of heterocycles **15a** and **16a**. The improvement in the yield of tetrahydrophenanthroline **16a** in the one-pot process despite the presence of unreacted diene **12a** is notable. The proposed involvement of the N–Pd chelation interactions en route to **16a** (Figure 2), as well as interferences of the RCM catalytic system with the Pd-catalyst provide for a challenging Heck cyclization process, and additional optimization may be needed to finetune this protocol specifically for the preparation of 1,7-phenanthrolines.

Scope of the Synthetic Methodology. To assess whether electronic effects may influence the regioselectivity of the Pd-catalyzed annulations, as well as to evaluate the scope and merits of the one-pot protocol, a series of substituted arylimines **1** (R^1 = 4,5-OMe, 5-F) and terminal arylalkynes (R^2 = 4-F, 4-OMe) were employed in the described method using both the two-step reaction sequence and the one-pot protocols (Table 1). The moderate yields of enynes **5–8** (45–58%) were caused by the formation simple amides [$PhC(=O)NH(CH_2)_nCH=CH_2$)] arising via a premature hydrolysis of the *N*-benzoyliminium ions. The enyne RCM reaction afforded dienes **9a–e** (63–93%) and **10a–e** (80–92%) in good yields. Lower yields of the RCM reaction providing the pyridine-derived (X = N) dienes **11a,b** (60–69%) and **12a–c** (58–69%) were caused by a strong retention of the products on the silica column during the purification steps, emphasizing need for the one-pot protocol. Enynes bearing the electron-rich *p*-methoxyphenyl substituent afforded the lowest yields in the RCM reactions. In fact, the diene bearing substituents X = N, n = 1, R^1 = H, R^2 = OMe could not be efficiently prepared via RCM in appreciable quantities. However, the subsequent Heck reaction on such diene (X = N, n = 1, R^1 = H, R^2 = OMe) was found to be facile. In all the cases, the regioselectivity of the Heck annulation uncovered in the original studies (Scheme 3)

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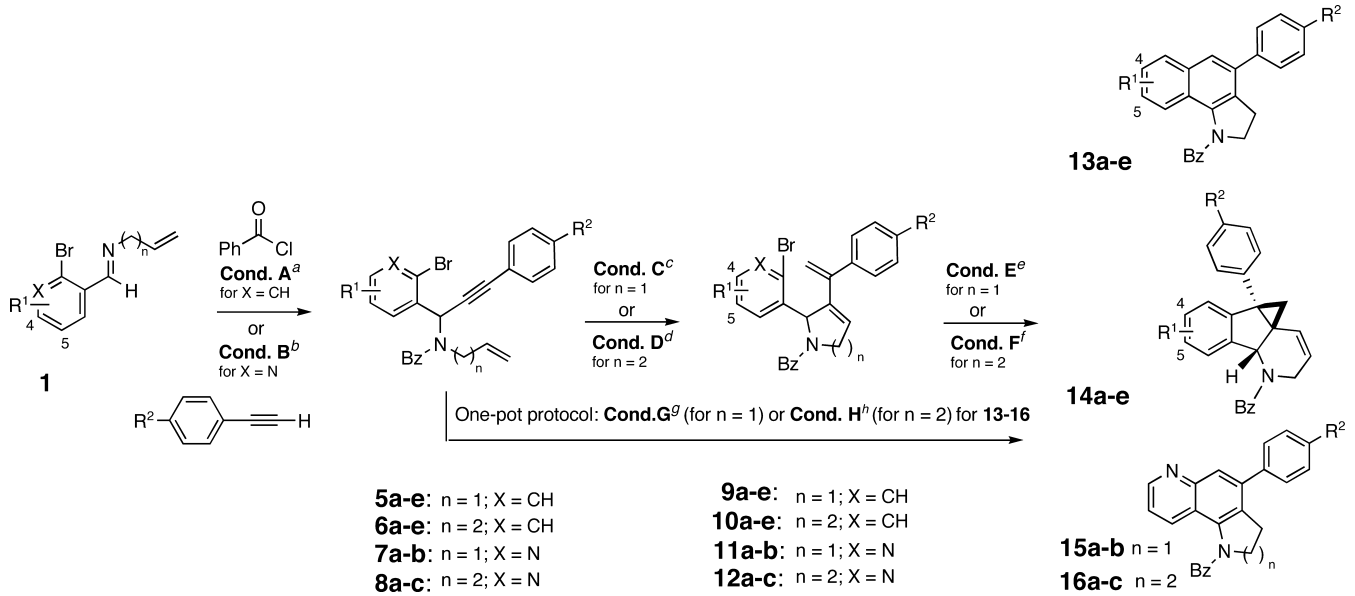
Table 1. Scope of the Two-Step and One-Pot Ru/Pd-Catalyzed Protocol



entry	1	*n*	X	R^1	R^2	5 – 8[i] (%)	9 – 12[i] (%)	13–16[i] (%) from 9–12	13–16[i] (%) from 5–8	yield increase in one pot[j] (%)
1	**1b**	1	CH	H	H	**5a** (55)	**9a** (93)	**13a** (71)	**13a** (69)	+3
2	**1f**	1	CH	4,5-$(OMe)_2$	H	**5b** (49)	**9b** (81)	**13b** (68)		
3	**1g**	1	CH	5-F	H	**5c** (52)	**9c** (72)	**13c** (65)	**13c** (61)	+14
4	**1b**	1	CH	H	F	**5d** (53)	**9d** (87)	**13d** (78)		
5	**1b**	1	CH	H	OMe	**5e** (61)	**9e** (63)	**13e** (66)	**13e** (64)	+22
6	**1c**	2	CH	H	H	**6a** (55)	**10a** (92)	**14a** (80)	**14a** (75)	+2
7	**1h**	2	CH	4,5-$(OMe)_2$	H	**6b** (45)	**10b** (87)	**14b** (78)		
8	**1i**	2	CH	5-F	H	**6c** (52)	**10c** (88)	**14c** (71)	**14c** (69)	+7
9	**1c**	2	CH	H	F	**6d** (58)	**10d** (85)	**14d** (81)		
10	**1c**	2	CH	H	OMe	**6e** (53)	**10e** (80)	**14e** (80)	**14e** (70)	+6
11	**1d**	1	N	H	H	**7a** (59)	**11a** (69)	**15a** (77)	**15a** (71)	+18
12	**1d**	1	N	H	F	**7b** (60)	**11b** (60)	**15b** (65)[k]		
13	**1e**	2	N	H	H	**8a** (62)	**12a** (69)	**16a** (65)	**16a** (61) +**12a** (25%)	+17
14	**1e**	2	N	H	F	**8b** (61)	**12b** (62)	**16b** (61)	**16b** (56) +**12b** (29%)	+18
15	**1e**	2	N	H	OMe	**8c** (63)	**12c** (58)	**16c** (59)		

[a]Conditions A: CuCl (20 mol %), DIPEA (1.5 equiv), MeCN, rt, 1 h. [b]Conditions B: Same as conditions A except for a reversed order of addition and DIPEA (1.2 equiv). [c]Conditions C: Grubbs **I** (Ru) (10 mol %), ethylene, toluene, 85 °C, 2 h. [d]Conditions D: Same as conditions C except for Grubbs **II** (Ru) (10 mol %) and 8 h. [e]Conditions E: $Pd(OAc)_2$ (10 mol %), NaOAc (1.1 equiv), DMF, 120 °C, 12 h. [f]Conditions F: $Pd(OAc)_2$ (10 mol %), Cs_2CO_3 (2.0 equiv), PPh_3 (20 mol %), DMF, 120 °C, 15 h. [g]Conditions G: One-pot protocol described in Scheme 4, using Grubbs I catalyst. [h]Conditions H: One-pot protocol described in Scheme 4 using Grubbs II catalyst. [i]Isolated yield. [j]Calcutated as the % yield (column 10) − [% yield (column 9) × % yield (column 8)/100]. [k]Obtained in a mixture with aromatized oxidation product (8.5% by GC–MS).

was followed, delivering the series of heterocycles **13a–e** (66–71%), **14a–e** (78–81%), **15a,b** (65–77%), and **16a–c** (59–65%) (Table 1). Thus, no electronic effects of the substituents on the course of the Pd-catalyzed annulations were detected. The ^1H NMR analyses of crude reaction mixtures from the reactions providing indenopyridines **14b–e** indicated the presence (less than 10%) of benzoquinoline byproducts analogous to heterocycle **17** (Scheme 3), which were easily separated by column chromatography and except for heterocycle **17** were not isolated and characterized. The electron-deficient pyrroloquinoline **15b** was isolated along with an impurity (8.5% by GC–MS) with the mass corresponding to the fully aromatized product of air oxidation, the content of which only increased upon further purification.

The yields of the products from both the two-step sequence and the one-pot protocol are provided in Table 1. The yields of heterocycles **13**, **14**, **15**, and **16** obtained via the one-pot protocol (56–75% calculated per the enynes **5**, **6**, **7**, and **8**) represent 2–22% improvement in comparison to the yields of heterocycles **13**, **14**, and **15** achieved via the two-step process from enynes **5**, **6**, **7**, and **8** (calculated from the data in Table 1) involving the isolation of the dienes resulting from the enyne–RCM. In agreement with prior results of the one-pot preparation of **16a**, phenanthroline **16b** was accompanied by unreacted RCM product **12b** in the crude reaction mixture. The mixture was easily separated by flash chromatography, affording the phenanthroline **16b** in 56% yield, that was 18% higher when compared to the calculated yield of **16b** from **8b** (38%) achieved via the two-step process.

■ CONCLUSIONS

In conclusion, a novel methodology for the construction of complex N-heterocycles via sequential transition-metal catalysis was described. Regiodivergent Heck annulation afforded

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distinct heterocyclic cores from homologous or isosteric (X = CH or N) substrates. A protocol for one-pot enyne−RCM/Heck annulation was developed, underscoring the practicality of the new methodology.

EXPERIMENTAL SECTION

General Methods. Unless otherwise indicated, all NMR data were collected at room temperature in $CDCl_3$ with internal $CHCl_3$ as the reference (δ 7.26 ppm for ^1H and 77.00 ppm for ^{13}C). IR spectra were measured as thin films on salt (NaCl) plates. Melting points are uncorrected and were taken in open capillary tubes. MS were measured under electrospray ionization (ES+) conditions. Analytical thin-layer chromatography (TLC) was carried out on commercial Merck silica gel 60 plates, 250 mm thickness, with fluorescent indicator (F-254) or stained with aqueous $KMnO_4$ solution. Column chromatography was performed with 32−63 mm silica gel (Sorbent) or with 150 mesh 58 Å pore size basic alumina. Where appropriate, neat liquid reagents were added via microliter syringes. Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone. Methylene chloride and toluene were distilled over CaH_2 and sodium metal, respectively. DMF and ACN were kept over 3 Å (8−12 mesh) molecular sieves under an atmosphere of dry argon; other solvents were used as received. Unless otherwise specified, all reactions were carried out under an atmosphere of dry argon in oven-dried (at least 6h at 140 °C) glassware. All imines were prepared[26] by condensation of a 1:1 mixture of aldehyde and amine in methylene chloride in the presence of activated 3 Å (8−12 mesh) molecular sieves for 24 h at rt followed by filtration through Celite and removal of solvent under vacuum to afford pure imines that were used immediately. Grubbs I catalyst, benzylidenebis(tricyclohexylphosphine)dichlororuthenium, and Grubbs II catalyst, (1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(phenylmethylene)(tricyclohexylphosphine)ruthenium, were purchased from a commercial supplier and used as such. Other materials were used as received from commercial suppliers.

General Procedure for the Synthesis of Enynes 2 and 5a−e and 6a−e (Conditions A, Table 1). Imines (1.0 equiv, 0.67−1.58 mmol), benzoyl chloride (1.5 equiv, 1.01−2.37 mmol), and alkynes (1.5 equiv, 1.01−2.37 mmol) were mixed in acetonitrile (5−10 mL) and stirred for 5 min at rt under argon. The resulting yellow solution and neat EtN-*i*-Pr_2 (1.5 equiv, 1.01−2.37 mmol) were added dropwise simultaneously to a solution of CuCl (0.2 equiv, 0.135−0.32 mmol) in acetonitrile (2 mL). The reaction mixture was stirred at rt under argon for 2 h. Solvents were removed under reduced pressure to afford crude products that were separated by flash chromatography over basic alumina eluting with EtOAc/hexanes mixtures to yield pure enynes **2**, **5a−e**, and **6a−e**.

*N-Benzyl-N-(1-(2-bromophenyl)-3-phenylprop-2-yn-1-yl)-acrylamide (**2**).* The treatment of imine **1a** (0.43 g, 1.58 mmol, 1.0 equiv), acryloyl chloride (195 μL, 2.37 mmol, 1.5 equiv), and phenylacetylene (225 μL, 2.37 mmol, 1.5 equiv) with EtN-*i*-Pr_2 (410 μL, 2.37 mmol, 1.5 equiv) and CuCl (0.031 g, 0.32 mmol, 0.2 equiv) according to the general procedure described above followed by flash chromatography over basic alumina eluting with EtOAc/hexane (1:4) afforded enyne **2** (0.393 g, 58%) as a colorless oil: R_f = 0.6 (EtOAc/hexane 3:7); ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (br s, 0.8H), 7.63 (br s, 0.2H), 7.51 (br s, 1H), 7.43−6.88 (m, 12H), 6.50−6.32 (m, 2H), 5.72 (br s, 1H), 4.75−4.44 (m, 2H). In the ^1H NMR, the signal for the methine proton was not detected due extensive broadening (see the temperature-dependent ^1H NMR spectra for **5a**): ^{13}C NMR (125 MHz, $CDCl_3$) δ (48.0), 48.1, (49.9), 50.9, (85.4), 85.6, 86.4, (86.9), (122.3), 124.5, 126.1 (2C), 127.0, 127.3, 127.8, 128.1, 128.2 (2C), (128.40), 128.46, (128.5), 128.6, (129.6), (129.8), 130.0, 131.0, 131.5, 131.7 (2C), 133.3 (2C), (135.8), 137.5, (137.6), 138.0, 166.6, (166.8). Signals for the minor rotamer are given in parentheses. Significant broadening of some signals in ^1H and ^{13}C NMR arises due to hindered rotation about the amide bond. Temperature-dependent ^1H NMR spectra were recorded (vide infra); IR (cm^{-1}) 1654, 1490, 1425; HRMS (ES^+) calcd for $C_{25}H_{21}BrNO$ $(M + H)^+$ 430.0807, found 430.0812.

*N-Allyl-N-(1-(2-bromophenyl)-3-phenylprop-2-yn-1-yl)-benzamide (**5a**).* The treatment of imine **1b** (0.33 g, 1.48 mmol, 1.0 equiv), benzoyl chloride (260 μL, 2.22 mmol, 1.5 equiv), and phenylacetylene (210 μL, 2.22 mmol, 1.5 equiv) with EtN-*i*-Pr_2 (385 μL, 2.22 mmol, 1.5 equiv) and CuCl (0.055 g, 0.55 mmol, 0.2 equiv) according to the general procedure described above followed by flash chromatography over basic alumina eluting with EtOAc/hexane (1:4) afforded enyne **5a** (0.349 g, 55%) as a light yellow solid: mp 98−101 °C; R_f = 0.55 (EtOAc/hexane 3:7); ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.6 Hz, 1H), 7.79 (br s, 1H), 7.67−7.57 (m, 4H), 7.49−7.33 (m, 7H), 7.25 (t, J = 6.8 Hz, 1H), 7.09 (br s, 0.5H), 6.08 (br s, 0.5H), 5.62 (br s, 1H), 4.86 (d, J = 10 Hz, 1.5H), 4.77 (br s, 0.5H), 4.01 (br s, 1.5H), 3.66 (br s, 0.5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 49.5, 50.8, 86.0, 116.5, 122.3, 124.6, 127.3 (2C), 127.5, 128.2 (2C), 128.4, 128.7, 129.8, 130.2, 131.70, 131.76 (2C), 133.4 (2C), 134.1, 135.4, 136.1, 170.7. Significant broadening of some signals in ^1H and ^{13}C NMR arises due to hindered rotation about the amide bond. Temperature-dependent ^1H NMR spectra were recorded (vide infra). In the ^{13}C NMR spectra only one signal for the two sp carbons was observed. IR (cm^{-1}) 2223, 1643, 1394; HRMS (ES^+) calcd for $C_{25}H_{21}BrNO$ $(M + H)^+$ 430.0807, found 430.0808.

*N-Allyl-N-(1-(2-bromo-4,5-dimethoxyphenyl)-3-phenylprop-2-yn-1-yl)benzamide (**5b**).* The treatment of imine **1f** (0.275 g, 0.97 mmol, 1.0 equiv), benzoyl chloride (170 μL, 1.46 mmol, 1.5 equiv), and phenylacetylene (139 μL, 1.46 mmol, 1.5 equiv) with EtN-*i*-Pr_2 (255 μL, 1.46 mmol, 1.5 equiv) and CuCl (0.029 g, 0.28 mmol, 0.2 equiv) according to the general procedure described above followed by flash chromatography over basic alumina eluting with EtOAc/hexane (1:3) afforded enyne **5b** (0.232 g, 49%) as a light yellow oil: R_f = 0.46 (EtOAc/hexane 3:7); ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (br s, 1.75H), 7.55 (t, J = 4.0 Hz, 3.25H), 7.49−7.34 (m, 6H), 7.06 (br s, 1H), 6.01 (br s, 1H), 5.69 (br s, 1H), 4.91 (d, J = 8.4 Hz, 1.25H), 4.83 (br s, 0.75H), 4.05 (br s, 1H), 3.93 (s, 3H), 3.92 (s, 3H), 3.70 (br s, 1H); In the ^1H NMR, the signal for the methine proton appeared to integrate for only 0.4H due to extensive broadening (see the temperature-dependent ^1H NMR spectra for **5a**). However, the signal was recorded as 1H (6.01 ppm). ^{13}C NMR (125 MHz, $CDCl_3$) δ 42.4, (45.9), 49.3, (50.3), (56.0), 56.1, (56.2), 56.3, 86.4, 114.4, 114.8, 115.8, 116.3, 122.4, 127.2, 128.2 (2C), 128.5 (2C), 128.6, 128.8, 129.8, 131.6 (2C), 134.4, 136.2 (2C), 148.0, 149.7, 171.5. Signals for the minor rotamer are given in parentheses. In the ^{13}C NMR spectra only one signal for the two sp carbons was observed. IR (cm^{-1}) 1643, 1477, 1236, 1035; HRMS (ES^+) calcd for $C_{27}H_{25}BrNO_3$ $(M + H)^+$ 490.1018, found 490.1018.

*N-Allyl-N-(1-(2-bromo-5-fluorophenyl)-3-phenylprop-2-yn-1-yl)-benzamide (**5c**).* The treatment of imine **1g** (0.276 g, 1.14 mmol, 1.0 equiv), benzoyl chloride (200 μL, 1.71 mmol, 1.5 equiv), and phenylacetylene (165 μL, 1.71 mmol, 1.5 equiv) with EtN-*i*-Pr_2 (295 μL, 1.71 mmol, 1.5 equiv) and CuCl (0.022 g, 0.22 mmol, 0.2 equiv) according to the general procedure described above followed by flash chromatography over basic alumina eluting with EtOAc/hexane (1:9) afforded enyne **5c** (0.264 g, 52%) as a colorless heavy oil: R_f = 0.65 (EtOAc/hexane 3:7); ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, J = 9.6 Hz, J = 3.2 Hz 1H), 7.60−7.53 (m, 4H), 7.49−7.36 (m, 7H), 6.99 (dt, J = 8.4 Hz, J = 2.8 Hz 1H), 5.63 (br s, 1H), 4.88 (dd, J = 10.0 Hz, J = 0.8 Hz 1H), 4.81 (br s, 1H), 4.06−3.97 (m, 1H), 3.79 (br s, 1H). In the ^1H NMR the signal for methine proton could not be detected likely due to extensive broadening (see the temperature-dependent ^1H NMR spectra for **5a**). ^{13}C NMR (125 MHz, $CDCl_3$) δ (46.2), 49.4, 50.5, (55.9), 85.2, 116.8, 117.2 (d, J = 22.3 Hz), 118.5 (d, J = 3.2 Hz), 119.0 (d, J = 24.5 Hz), (122.0), 125.5, 126.8, (127.3), 128.2 (2C), (128.44), 128.49 (2C), 128.7 (d, J = 26.1 Hz), 128.9, 129.9, 130.0, (130.4), 131.8 (2C), (133.8), 134.5 (d, J = 7.7 Hz), 135.9 (2C), (137.9), 161.8 (d, J = 246.2 Hz), 171.7. Signals for the minor rotamer are given in parentheses. In the ^{13}C NMR spectra only one signal for the two sp carbons was observed. IR (cm^{-1}) 1647, 1467; HRMS (ES^+) calcd for $C_{25}H_{20}BrFNO$ $(M + H)^+$ 448.0712 found, 448.0707.

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*N-Allyl-N-(1-(2-bromophenyl)-3-(4-fluorophenyl)prop-2-yn-1-yl)-benzamide (**5d**).* The treatment of imine **1b** (0.212 g, 0.95 mmol, 1.0 equiv), benzoyl chloride (165 μL, 1.42 mmol, 1.5 equiv), and *p*-fluorophenylacetylene (0.171 g, 1.42 mmol, 1.5 equiv) with EtN-*i*-Pr_2 (210 μL, 1.42 mmol, 1.5 equiv) and CuCl (0.019 g, 0.19 mmol, 0.2 equiv) according to the general procedure described above followed by flash chromatography over basic alumina eluting with EtOAc/hexane (1:9) afforded enyne **5d** (0.225 g, 53%) as a light white solid: mp 89−93 °C; R_f = 0.72 (EtOAc/hexane 3:7); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.6 Hz, 1H), 7.61 (br s, 2H), 7.58−7.50 (m, 3H), 7.49−7.36 (m, 4H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 8.0 Hz, 2H), 6.09 (br s, 1H), 5.62 (br s, 1H), 4.86 (dd, *J* = 10.0 Hz, *J* = 1.2 Hz 1H), 4.77 (br s, 1H), 4.01 (d, *J* = 14.0 Hz, 1H), 3.70 (br s, 1H). In the ^{1}H NMR, the signal for methine proton appeared to integrate for only 0.1H due to extensive broadening (see the temperature-dependent ^{1}H NMR spectra for **5a**). However, the signal was recorded as 1H (6.09 ppm). ^{13}C NMR (125 MHz, $CDCl_3$) δ 46.3, (49.0), 50.4, (56.1), 85.7, 115.7 (d, *J* = 21.8 Hz, 2C), 116.5, 118.4, 124.6, 127.2, 127.3 (2C), 128.2 (2C), 129.8, 130.2 (d, *J* = 43.8 Hz), 131.6, 133.4, 133.7 (d, *J* = 8.3 Hz, 2C), 133.9, 135.3, 136.1, 162.7 (d, *J* = 248.6 Hz), 171.7. Signals for the minor rotamer are given in parentheses. In the ^{13}C NMR spectra only one signal for the two sp carbons was observed. IR (cm^{-1}) 2227, 1643, 1506; HRMS (ES^+) calcd for $C_{25}H_{20}BrFNO$ $(M + H)^+$ 448.0712 found, 448.0707.

*N-Allyl-N-(1-(2-bromophenyl)-3-(4-methoxyphenyl)prop-2-yn-1-yl)benzamide (**5e**).* The treatment of imine **1b** (0.15 g, 0.673 mmol, 1.0 equiv), benzoyl chloride (120 μL, 1.01 mmol, 1.5 equiv), and *p*-methoxyphenylacetylene (122 μL, 1.01 mmol, 1.5 equiv) with EtN-*i*-Pr_2 (0.13 g, 174 μL, 1.01 mmol, 1.5 equiv) and CuCl (0.013 g, 0.135 mmol, 0.2 equiv) according to the general procedure described above followed by flash chromatography over basic alumina eluting with EtOAc/hexane (1:4) afforded enyne **5e** (0.19 g, 61%) as a colorless heavy oil: R_f = 0.55 (EtOAc/hexane 3:7); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.2 Hz, 1H), 7.82 (br s, 1H), 7.59 (br s, 2H), 7.50 (d, *J* = 8.8 Hz, 2H), 7.47−7.35 (m, 4H), 7.24 (t, *J* = 6.8 Hz, 1H), 7.08 (br s, 0.5H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.05 (br s, 0.5H), 5.61 (br s, 1H), 4.84 (d, *J* = 10.4 Hz, 1H), 4.7 (br s, 1H), 3.98 (br s, 1.5H), 3.86 (s, 3H), 3.68 (br s, 0.5H). In the ^{1}H NMR, the signal for the methine proton appeared as two broad singlets (7.08 and 6.05 ppm) that integrate for only 0.5H when combined due to extensive broadening (see the temperature-dependent ^{1}H NMR spectra for **5a**). However, the signals are presented herein as 0.5H (7.08 ppm) and 0.5H (6.05 ppm). ^{13}C NMR (125 MHz, $CDCl_3$) δ 44.0, (47.2), 48.6, 53.4, (54.4), 82.6, 112.1, 114.5, 122.6, 125.3 (2C), 125.5, 126.2 (2C), 126.4, 127.9, 128.2, 129.8 (2C), 131.2 (2C), 131.4, 132.1, 133.7, 134.3, 158.0, 169.7. Significant broadening of some signals in the ^{1}H and ^{13}C NMR arises due to hindered rotation about the amide bond (see the temperature-dependent ^{1}H NMR spectra for **5a**). In the ^{13}C NMR spectra only one signal for the two sp carbons was observed. IR (cm^{-1}) 2210, 1643, 1396, 1027; HRMS (ES^+) calcd for $C_{26}H_{23}BrNO_2$ $(M + H)^+$ 460.0912, found 460.0911.

*N-(1-(2-Bromophenyl)-3-phenylprop-2-yn-1-yl)-N-(but-3-en-1-yl)benzamide (**6a**).* The treatment of imine **1c** (0.325 g, 1.36 mmol, 1.0 equiv), benzoyl chloride (235 μL, 2.04 mmol, 1.5 equiv), and phenylacetylene (195 μL, 2.04 mmol, 1.5 equiv) with EtN-*i*-Pr_2 (350 μL, 2.04 mmol, 1.5 equiv) and CuCl (0.027 g, 0.27 mmol, 0.2 equiv) according to the general procedure described above followed by flash chromatography over basic alumina eluting with EtOAc/hexane (1:4) afforded enyne **6a** (0.332 g, 55%) as a white solid: mp 75−80 °C; R_f = 0.6 (EtOAc/hexane 3:7); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (br s, 1H), 7.79 (br s, 1H), 7.69−7.53 (m, 4H), 7.50−7.36 (m, 7H), 7.31−7.23 (m, 1H), 7.06 (br s, 0.5H), 6.05 (br s, 0.5H), 5.80−5.36 (m, 1H), 4.89 (br s, 2H), 3.58−2.86 (m, 2H), 2.46 (br s, 1H), 1.81 (br s, 1H). In the ^{1}H NMR the signal for the methine proton appeared as two broad singlets (7.06 and 6.05 ppm) that integrate for only 0.5H when combined, due to extensive broadening (see the temperature-dependent ^{1}H NMR spectra for **6a**). However, the signals are presented herein as 0.5H (7.06 ppm) and 0.5H (6.05 ppm). ^{13}C NMR (125 MHz, $CDCl_3$) δ 32.5, (33.9), 43.3, (46.0), (50.4), 56.2, 86.2, 116.3, (116.7), 122.2, 124.4, 127.1, 127.5 (2C), 127.6, 128.2, 128.41, 128.49, 128.7, (128.8), 129.8, 130.3, 131.3 (2C), 131.7 (2C), 133.5 (2C), (135.5), 136.4, 171.6. Signals for the minor rotamer are given in parentheses. In the ^{13}C NMR spectra only one signal for the two sp carbons was observed. IR (cm^{-1}) 2223, 1641, 1402; HRMS (ES^+) calcd for $C_{26}H_{22}BrNONa$ $(M + Na)^+$, 466.0782, found 466.0778.

*N-(1-(2-Bromo-4,5-dimethoxyphenyl)-3-phenylprop-2-yn-1-yl)-N-(but-3-en-1-yl)benzamide (**6b**).* The treatment of imine **1h** (0.329 g, 1.11 mmol, 1.0 equiv), benzoyl chloride (190 μL, 1.66 mmol, 1.5 equiv), and phenylacetylene (160 μL, 1.66 mmol, 1.5 equiv) with EtN-*i*-Pr_2 (285 μL, 1.66 mmol, 1.5 equiv) and CuCl (0.022 g, 0.22 mmol, 0.2 equiv) according to the general procedure described above followed by flash chromatography over basic alumina eluting with EtOAc/hexane (1:4) afforded enyne **6b** (0.248 g, 45%) as a colorless oil: R_f = 0.45 (EtOAc/hexane 3:7); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89−7.71 (m, 1H), 7.68−7.50 (m, 4H), 7.49−7.33 (m, 6H), 7.08 (br s, 1H), 7.05 (br s, 0.5H) 6.35−5.91 (m, 0.5H), 5.87−5.35 (m, 1H), 5.21−5.10 (m, 0.2H), 4.92 (br s, 1.8H), 3.95 (s, 3H), 3.92 (s, 3H), 3.60−2.86 (m, 2H), 2.67−2.25 (m, 1H), 1.88 (br s, 1H). In the ^{1}H NMR the signal for the methine proton appeared as a broad singlet and a multiplet (7.05 and 6.35−5.91 ppm) that integrate for only 0.5H when combined, due to extensive broadening (see the temperature-dependent ^{1}H NMR spectra for **6a**). However, the signals are presented herein as 0.5H (7.05 ppm) and 0.5H (6.35−5.91 ppm). ^{13}C NMR (125 MHz, $CDCl_3$) δ 32.6, (33.9), 43.1, (46.0), (50.1), 55.9, 56.21, 56.29, 86.6, 114.0, 114.6, (115.2), 115.9, (116.3), 117.4, (122.1), 126.8, (127.5), 128.2 (2C), 128.54 (2C), 128.58, (128.9), 129.8, 131.3, 131.6 (2C), 131.7, (134.7), 135.3, (135.6), 136.4 (2C), 148.1, 149.7, (167.4), 171.5. Signals for the minor rotamer are given in parentheses. In the ^{13}C NMR spectra only one signal for the two sp carbons was observed. IR (cm^{-1}) 2225, 1487, 1280, 1031; HRMS (ES^+) calcd for $C_{28}H_{26}BrNO_3Na$ $(M + Na)^+$, 526.0994, found 526.0985.

*N-(1-(2-Bromo-5-fluorophenyl)-3-phenylprop-2-yn-1-yl)-N-(but-3-en-1-yl)benzamide (**6c**).* The treatment of imine **1i** (0.32 g, 1.25 mmol, 1.0 equiv), benzoyl chloride (215 μL, 1.87 mmol, 1.5 equiv), and phenylacetylene (180 μL, 1.87 mmol, 1.5 equiv) with EtN-*i*-Pr_2 (240 μL, 1.87 mmol, 1.5 equiv) and CuCl (0.025 g, 0.25 mmol, 0.2 equiv) according to the general procedure described above, followed by flash chromatography over basic alumina eluting with EtOAc/hexane (1:9), afforded enyne **6c** (0.299 g, 52%) as a colorless oil: R_f = 0.6 (EtOAc/hexane 3:7); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 7.2 Hz, *J* = 1.2 Hz, 0.25H), 7.77 (d, *J* = 7.6 Hz, 1.25H), 7.71 (t, *J* = 7.2 Hz, 0.5H), 7.64−7.52 (m, 4H), 7.50−7.34 (m, 7H), 7.01 (td, *J* = 8.0 Hz, *J* = 2.8 Hz, 1H), 6.20−5.35 (m, 1H), 5.25−4.72 (m, 2H), 3.75−2.90 (m, 2H), 2.49 (br s, 1H), 2.16−2.05 (m, 0.15H), 1.92 (br s, 0.85H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (32.6), 33.8, 43.2, (46.3), (50.3), 56.0, 85.4, [115.4, (d, *J* = 24.7 Hz)], [116.5, (d, *J* = 3.2 Hz)], 117.3, (117.4), 118.3 (d, *J* = 3.3 Hz), 118.6 (d, *J* = 24.3 Hz), 126.8, (127.4), 128.3 (2C), 128.4 (d, *J* = 9.6 Hz), 128.5 (d, *J* = 8.0 Hz), 128.8, (129.0), 129.87 (2C), (129.89), (129.9), 130.3, 131.4, 131.8 (2C), 133.9, 134.8 (d, *J* = 7.7 Hz), [135.0, (d, *J* = 7.8 Hz)], (135.5), 136.2 (2C), (138.0), (164.1), 161.8 (d, *J* = 246.6 Hz), [161.9, (d, *J* = 246.8 Hz)], 171.7, (172.8). Signals for the minor rotamer are given in parentheses. In the ^{13}C NMR spectra only one signal for the two sp carbons was observed. Significant broadening of some signals in ^{1}H and ^{13}C NMR arises due to hindered rotation about the amide bond (see the temperature-dependent ^{1}H NMR spectra for **6a**). IR (cm^{-1}) 1643, 1467; HRMS (ES^+) calcd for $C_{26}H_{22}BrFNO$ $(M + H)^+$ 462.0869, found 462.0877.

*N-(1-(2-Bromophenyl)-3-(4-fluorophenyl)prop-2-yn-1-yl)-N-(but-3-en-1-yl)benzamide (**6d**).* The treatment of imine **1c** (0.193 g, 0.811 mmol, 1.0 equiv), benzoyl chloride (140 μL, 1.21 mmol, 1.5 equiv), and *p*-fluorophenylacetylene (0.145 g, 1.21 mmol, 1.5 equiv) with EtN-*i*-Pr_2 (210 μL, 1.21 mmol, 1.5 equiv) and CuCl (0.016 g, 0.16 mmol, 0.2 equiv) according to the general procedure described above followed by flash chromatography over basic alumina eluting with EtOAc/hexane (1:9) afforded enyne **6d** (0.22 g, 58%) as a colorless oil: R_f = 0.6 (EtOAc/hexane 3:7); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.6 Hz, 1H), 7.86−7.59 (m, 2H), 7.54 (dd, *J* = 5.2 Hz, *J* = 3.2 Hz, 2H), 7.49−7.39 (m, 4H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 8.0

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Hz, 2H), 7.03 (br s, 0.5H), 6.03 (br s, 0.5H), 5.83−5.27 (m, 1H), 4.89 (br s, 2H), 3.94−2.86 (m, 2H), 2.40 (br s, 1H), 1.81 (br s, 1H). In the ^{1}H NMR the signal for the methine proton appeared as two broad singlets (7.03 and 6.03 ppm) that integrate for only 0.5H when combined, due to extensive broadening (see the temperature-dependent ^{1}H NMR spectra for **6a**). However the signals are presented herein as 0.5H (7.03 ppm) and 0.5H (6.03 ppm). ^{13}C NMR (125 MHz, $CDCl_3$) δ 32.5, (33.8), 43.3, (46.0), 50.1, (56.1), 85.9, 115.8 (d, J = 21.6 Hz, 2C), 116.6, (118.3), 124.4, 125.5, (127.2), 127.5, 128.2, 128.4, 128.6, [128.7 (d, J = 5.2 Hz)], 129.8 (d, J = 5.2 Hz), 130.5, 131.2 (2C), 133.6 (2C), 133.7 (d, J = 8.3 Hz, 2C), (135.4), 136.3, 138.9, 162.8 (d, J = 248.6 Hz), (171.0), 172.6. Signals for the minor rotamer are given in parentheses. In the ^{13}C NMR spectra only one signal for the two sp carbons was observed. IR (cm^{-1}) 2225, 1643, 1400; HRMS (ES$^+$) calcd for $C_{26}H_{21}BrFNONa$ (M + Na)$^+$, 484.0688, found 484.0685.

*N-(1-(2-Bromophenyl)-3-(4-methoxyphenyl)prop-2-yn-1-yl)-N-(but-3-en-1-yl)benzamide (**6e**).* The treatment of imine **1c** (0.19 g, 0.798 mmol, 1.0 equiv), benzoyl chloride (140 μL, 1.19 mmol, 1.5 equiv), and *p*-methoxyphenylacetylene (155 μL, 1.19 mmol, 1.5 equiv) with EtN-*i*-Pr_2 (205 μL, 1.19 mmol, 1.5 equiv) and CuCl (0.016 g, 0.16 mmol, 0.2 equiv) according to the general procedure described above followed by flash chromatography over basic alumina eluting with EtOAc/hexane (1:4) afforded enyne **6e** (0.2 g, 53%) as a colorless oil: R_f = 0.6 (EtOAc/hexane 3:7); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (br s, 1H), 7.80 (br s, 1H), 7.60 (br s, 2H), 7.50 (d, J = 10.4 Hz, 2H), 7.47−7.38 (m, 4H), 7.30−7.22 (m, 1H), 7.04 (br s, 0.5H), 6.92 (d, J = 7.2 Hz, 2H), 6.03 (br s, 0.5H), 5.80−5.13 (m, 1H), 4.90 (br s, 2H), 3.86 (s, 3H), 3.56−2.82 (m, 2H), 2.47 (br s, 1H), 1.79 (br s, 1H). In the ^{1}H NMR the signal for the methine proton appeared as two broad singlets (7.04 and 6.03 ppm) that integrate for only 0.5H when combined, due to extensive broadening (see the temperature-dependent ^{1}H NMR spectra for **6a**). However the signals are presented herein as 0.5H (7.04 ppm) and 0.5H (6.03 ppm). ^{13}C NMR (125 MHz, $CDCl_3$) δ 32.4, (33.9), 43.3, (46.0), (50.4), 55.3, 56.3, 84.7, 114.3, 116.2, (116.8), 124.4, 126.9, 127.5 (2C), 128.2, 128.6, 129.8, 130.2, 131.4 (2C), 133.2 (2C), 133.4, 133.5 (2C), 135.6, 136.5, 160.0, 171.6. Signals for the minor rotamer are given in parentheses. In the ^{13}C NMR spectra only one signal for the two sp carbons was observed. IR (cm^{-1}) 2221, 1643, 1510, 1027; HRMS (ES$^+$) calcd for $C_{27}H_{25}BrNO_2$ (M + H)$^+$ 474.1069, found 474.1072.

General Procedure for the Preparation of Enynes 7a,b and 8a−c (Conditions B, Table 1). Imine (1.0 equiv, 0.5−0.694 mmol), benzoyl chloride (1.2 equiv, 0.6−0.832 mmol), and alkyne (1.2 equiv, 0.6−0.832 mmol) were mixed in acetonitrile (5 mL) and stirred at rt under argon for 5 min to afford a yellow solution. To this solution were added neat EtN-*i*-Pr_2 (1.2 equiv, 0.6−0.832 mmol) and the solution of CuCl (0.2 equiv, 0.1−0.14 mmol) in acetonitrile (1 mL) simultaneously dropwise. The reaction mixture was stirred at rt under argon for 1 h. Solvents were removed under reduced pressure, and the resulting crude product was separated by flash chromatography over silica eluting with EtOAc/hexanes mixtures to yield pure enynes **7a−b** and **8a−c**.

*N-Allyl-N-(1-(2-bromopyridin-3-yl)-3-phenylprop-2-yn-1-yl)-benzamide (**7a**).* The treatment of imine **1d** (0.12 g, 0.53 mmol, 1.0 equiv), benzoyl chloride (0.091 g, 75 μL, 0.64 mmol, 1.2 equiv), and phenylacetylene (0.065 g, 61 μL, 0.64 mmol, 1.2 equiv) with EtN-*i*-Pr_2 (0.082 g, 110 μL, 0.64 mmol, 1.2 equiv) and CuCl (0.011 g, 0.11 mmol, 0.2 equiv) according to the general procedure described above followed by flash chromatography over silica eluting with EtOAc/hexane (1:3) afforded enyne **7a** (0.135 g, 59%) as a colorless oil: R_f = 0.4 (EtOAc/hexane 3:7); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (dd, J = 4.6 Hz, J = 1.6 Hz, 1H), 8.30 (d, J = 7.6 Hz, 1H), 7.65 (br s, 1.5H), 7.56 (dd, J = 7.6 Hz, J = 2.4 Hz, 2.5H), 7.50−7.39 (m, 5.75H), 7.37 (dd, J = 7.6 Hz, J = 4.4 Hz, 1.25H), 5.69 (br s, 1H), 4.87 (d, J = 10.4 Hz, 1H), 4.76 (dd, J = 17.2 Hz, J = 1.2 Hz, 1H), 4.29−3.56 (m, 2H). In the ^{1}H NMR the signal for the methine proton was not detected due extensive broadening (see the temperature-dependent ^{1}H NMR spectra for **5a**); ^{13}C NMR (125 MHz, $CDCl_3$) δ 50.1, 55.8, 84.7, 99.9, 116.8, 121.9, 122.5 (2C), 127.3, 128.3 (2C), 128.5 (2C), 129.0, 130.1, 131.8(2C), 133.4, 133.9, 135.7, 139.9, 144.0, 149.8, 171.8. Signals for the minor rotamer are given in parentheses; IR (cm^{-1}) 2223, 1643, 1400; HRMS (ES$^+$)calcd for $C_{24}H_{19}BrN_2ONa$ (M + Na)$^+$, 453.0578, found 453.0571.

*N-Allyl-N-(1-(2-bromopyridin-3-yl)-3-(4-fluorophenyl)prop-2-yn-1-yl)benzamide (**7b**).* The treatment of imine **1d** (0.12 g, 0.53 mmol, 1.0 equiv), benzoyl chloride (0.091 g, 75 μL, 0.64 mmol, 1.2 equiv) and *p*-fluorophenylacetylene (0.076 g, 73 μL, 0.64 mmol, 1.2 equiv) with EtN-*i*-Pr_2 (0.082 g, 110 μL, 0.64 mmol, 1.2 equiv) and CuCl (0.011 g, 0.11 mmol, 0.2 equiv) according to the general procedure described above followed by flash chromatography over silica eluting with EtOAc/hexane (1:3) afforded enyne **7b** (0.142 g, 60%) as a colorless oil: R_f = 0.4 (EtOAc/hexane 3:7); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (br s, 1H), 8.27 (d, J = 6.0 Hz, 1H), 7.83 (br s, 0.75H), 7.77−7.31 (m, 7.25H), 7.09 (t, J = 7.6 Hz, 2H), 6.91 (br s, 0.5H), 6.40 (br s, 0.5H), 5.98 (br, 0.30H), 5.68 (br s, 0.70H), 5.25 (dd, J = 34.8 Hz, J = 16.8 Hz, 0.5H), 4.82 (dd, J = 42.8 Hz, J = 9.6 Hz, 1.5H), 4.72−4.42 (m, 2H). In the ^{1}H NMR the signal for the methine proton appeared as two broad singlets (6.91 and 6.40 ppm) that integrate for only 0.5H when combined, due to extensive broadening (see the temperature-dependent ^{1}H NMR spectra for **5a**). However, the signals are presented herein as 0.5H (6.91 ppm) and 0.5H (6.40 ppm). ^{13}C NMR (125 MHz, $CDCl_3$) δ 33.1, 84.4, 99.9, 115.8 (d, J = 22.0 Hz), 116.7, (116.9), (118.0), 122.6 (2C), (123.4), 126.9 (2C), 127.3, 128.5 (d, J = 27.3 Hz, 2C), 130.2, 131.5, (133.3), 133.8 (d, J = 9.3 Hz, 2C), 133.9, (134.2), 135.6, (138.0), 139.8, 144.0, 149.8, (154.5), 162.9 (d, J = 249.4 Hz), 171.9. Signals for the minor rotamer are given in parentheses. IR (cm^{-1}) 2223, 1643, 1400; HRMS (ES$^+$) calcd for $C_{24}H_{18}BrFN_2ONa$ (M + Na)$^+$, 471.0484, found 471.0487.

*N-(1-(2-Bromopyridin-3-yl)-3-phenylprop-2-yn-1-yl)-N-(but-3-en-1-yl)benzamide (**8a**).* The treatment of imine **1e** (0.12 g, 0.5 mmol, 1.0 equiv), benzoyl chloride (0.084 g, 70 μL, 0.6 mmol, 1.2 equiv), and phenylacetylene (0.061 g, 57 μL, 0.6 mmol, 1.2 equiv) with EtN-*i*-Pr_2 (0.078 g, 104 μL, 0.6 mmol, 1.2 equiv) and CuCl (0.010 g, 0.1 mmol, 0.2 equiv) according to the general procedure described above followed by flash chromatography over silica eluting with EtOAc/hexane (1:3) afforded enyne **8a** (0.137 g, 62%) as a colorless oil: R_f = 0.4 (EtOAc/hexane 3:7); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (dd, J = 4.4 Hz, J = 1.2 Hz, 1H), 8.32 (d, J = 5.4 Hz, 1H), 7.67 (br s, 2H), 7.56 (dd, J = 7.6 Hz, J = 2.4 Hz, 2H), 7.52−7.36 (m, 7H), 6.83 (br s, 0.5H), 6.05 (br s, 0.5H), 5.60 (br s, 1H), 4.97−4.81 (m, 2H), 3.55−3.43 (m, 1H), 3.25 (br s, 1H), 2.47 (br s, 1H), 1.95 (br s, 1H). In the ^{1}H NMR the signal for the methine proton appeared as two broad singlets (6.83 and 6.05 ppm) that integrate for only 0.5H when combined, due to extensive broadening (see the temperature-dependent ^{1}H NMR spectra for **6a**). However the signals are presented herein as 0.5H (6.83 ppm) and 0.5H (6.05 ppm). ^{13}C NMR (125 MHz, $CDCl_3$) δ 33.0, (33.6), 43.5, (47.0), 50.0, (55.4), 84.8, 117.0, 121.8, 122.7 (2C), 127.2, 128.3 (2C), 128.5 (2C), 128.8, 129.1, 129.8, 130.0, 131.7 (2C), 136.0, 139.5, 143.8, 149.8, 171.8. Signals for the minor rotamer are given in parentheses. In the ^{13}C NMR spectra only one signal for the two sp carbons was observed. IR (cm^{-1}) 1637, 1490, 1446; HRMS (ES$^+$) calcd for $C_{25}H_{21}BrN_2ONa$ (M + Na)$^+$, 467.0735, found 467.0741.

*N-(1-(2-Bromopyridin-3-yl)-3-(4-fluorophenyl)prop-2-yn-1-yl)-N-(but-3-en-1-yl)benzamide (**8b**).* The treatment of imine **1e** (0.15 g, 0.627 mmol, 1.0 equiv), benzoyl chloride (0.128 g, 106 μL, 0.752 mmol, 1.2 equiv), and *p*-fluorophenylacetylene (0.092 g, 87 μL, 0.752 mmol, 1.2 equiv) with EtN-*i*-Pr_2 (0.072 g, 97 μL, 0.752 mmol, 1.2 equiv) and CuCl (0.013 g, 0.13 mmol, 0.2 equiv) according to the general procedure described above followed by flash chromatography over silica eluting with EtOAc/hexane (1:3) afforded enyne **8b** (0.175 g, 61%) as a colorless oil: R_f = 0.4 (EtOAc/hexane 3:7); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (dd, J = 4.8 Hz, J = 2.0 Hz, 1H), 8.30 (br s, 1H), 7.78−7.58 (m, 2H), 7.57−7.51 (m, 2H), 7.49−7.37 (m, 4H), 7.10 (t, J = 8.4 Hz, 2H), 5.95−5.38 (m, 1H), 4.90 (dd, J = 22.8 Hz, J = 10.4 Hz, 2H), 3.60−3.40 (m, 1.25H), 3.23 (br s, 0.75H), 2.55−2.34 (m, 1H), 1.95 (br s, 1H). In the ^{1}H NMR the signal for the methine proton was not observed, due to extensive broadening (see the temperature-dependent ^{1}H NMR spectra for **6a**). ^{13}C NMR (125

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MHz, $CDCl_3$) δ 84.6, 115.9 (d, J = 22 Hz, 2C), (117.0), 117.5, (122.6), 122.7 (2C), 126.7, 127.2, 128.4 (2C), 128.5, 130.0, 131.4, 133.7 (d, J = 8.5 Hz, 2C), (135.3), 135.9, 139.4, 143.8, 149.9, 163.0 (d, J = 249 Hz), 171.8. In the ^{13}C NMR spectra only one signal for the two methylene carbons and only one signal for the two sp carbons was observed. No signal was observed for methine due to significant broadening. Signals for the minor rotamer are given in parentheses. IR (cm^{-1}) 2230, 1643, 1506, 1400; HRMS (ES^+) calcd for $C_{25}H_{20}BrFN_2ONa$ $(M + Na)^+$, 485.0641, found 485.0640.

*N-(1-(2-Bromopyridin-3-yl)-3-(4-methoxyphenyl)prop-2-yn-1-yl)-N-(but-3-en-1-yl)benzamide (**8c**).* The treatment of imine **1e** (0.166 g, 0.694 mmol, 1.0 equiv), benzoyl chloride (0.115 g, 95 μL, 0.832 mmol, 1.2 equiv), and *p*-methoxyphenylacetylene (0.110 g, 108 μL, 0.832 mmol, 1.2 equiv) with EtN-*i*-Pr_2 (0.107 g, 144 μL, 0.832 mmol, 1.2 equiv) and CuCl (0.014 g, 0.14 mmol, 0.2 equiv) according to the general procedure described above followed by flash chromatography over silica eluting with EtOAc/hexane (1:3) afforded enyne **8c** (0.207 g, 63%) as a colorless oil: R_f = 0.3 (EtOAc/hexane 3:7); ^1H NMR (400 MHz, $CDCl_3$) δ 8.41 (dd, J = 4.4 Hz, J = 1.2 Hz, 1H), 8.36−8.26 (m, 1.4H), 7.67 (br s, 1.6H), 7.53−7.36 (m, 6H), 6.92 (d, J = 8.4 Hz, 1H), 6.91 (br s, 0.5H), 6.80 (d, J = 9.2 Hz, 1H), 6.01 (br s, 0.5H), 5.76−5.44 (m, 1H), 5.04−4.76 (m, 2H), 3.86 (s, 2H), 3.82 (s, 1H), 3.57−2.87 (m, 2H), 2.45 (br s, 0.75H), 2.17−1.82 (m, 1.25H). In the ^1H NMR the signal for the methine proton appeared as two broad singlets (6.91 and 6.01 ppm) that integrate for only 0.7H when combined, due to extensive broadening (see the temperature-dependent ^1H NMR spectra for **6a**). However the signals are presented herein as 0.5H (6.91 ppm) and 0.5H (6.01 ppm). ^{13}C NMR (125 MHz, $CDCl_3$) δ 33.4, 49.1, 55.33, (55.39), 56.5, (83.4), 83.8, 88.7, 113.8, (113.9), 114.1, (114.6), 115.7, 122.6, 122.7 (2C), (127.3), 128.3 (2C), (130.0), (133.1), 133.2 (2C), 135.9, 136.0, 136.3, 139.6 (2C), (140.6), 143.8, 144.2, 149.1, (149.8), 159.7, 171.8; IR (cm^{-1}) 2221, 1641, 1510, 1029; HRMS (ES^+) calcd for $C_{26}H_{24}BrN_2O_2$ $(M + H)^+$ 475.1021, found 475.1017.

*1-Benzyl-5-(2-bromophenyl)-4-(1-phenylvinyl)-1,5-dihydro-2H-pyrrol-2-one (**3**) and 1-Benzyl-6-(2-bromophenyl)-5-methylene-4-phenyl-5,6-dihydropyridin-2(1H)-one (**4**).* The solution of enyne **2** (0.13 g, 0.30 mmol, 1.0 equiv) in toluene (20 mL) was degassed with ethylene for 5 min, Grubb's II catalyst (0.025 g, 0.03 mmol, 0.1 equiv) was added, and the reaction mixture was stirred at 85 °C under ethylene atmosphere for 20 h. The mixture was cooled to rt, directly loaded on a silica column, and purified by flash chromatography, eluting with EtOAc/hexane (1:9) to afford pure diene **4** (0.045 g, 35%) as a colorless heavy oil, and continuous elution with EtOAc/hexane (1:4) afforded pure diene **3** (0.03 g, 23%) as a colorless heavy oil.

*Analytical data for **3**:* R_f = 0.45 (EtOAc/hexane 3:7); ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.0 Hz, 1H), 7.37−7.31 (m, 5H), 7.25−7.16 (m, 7H), 7.07 (dd, J = 7.6 Hz, J = 1.6 Hz, 1H), 6.13 (s, 1H), 5.90 (s, 1H), 5.38 (s, 1H), 5.26 (s, 1H), 5.01 (d, J = 15.2 Hz, 1H), 3.71 (d, J = 15.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 44.0, 64.2, 120.1, 125.1, 127.3, 127.5, 128.00, 128.03 (2C), 128.2, 128.3 (2C), 128.4 (2C), 128.5 (2C), 130.2, 130.4, 133.2, 135.2, 137.2, 139.4, 141.6, 158.9, 170.8; IR (cm^{-1}) 1650, 1494, 1261; HRMS (ES^+) calcd for $C_{25}H_{21}BrNO$ $(M + H)^+$ 430.0807, found 430.0803.

*Analytical data for **4**:* R_f = 0.52 (EtOAc/hexane 3:7); ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.0 Hz, 1H), 7.53 (d, J = 7.6 Hz, 1H), 7.38−7.31 (m, 8H), 7.25−7.17 (m, 4H), 6.21 (s, 1H), 5.83 (s, 1H), 5.75 (s, 1H), 5.45 (d, J = 14.8 Hz, 1H), 5.16 (s, 1H), 3.57 (d, J = 14.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 46.1, 61.0, 119.1, 119.6, 121.3, 126.1, 126.2, 126.9, 127.15 (2C), 127.16 (2C), 127.18 (2C), 127.2 (2C), 127.8, 128.3, 132.2, 135.3, 135.5, 137.5, 138.9, 147.0, 162.8; IR (cm^{-1}) 1689, 1494, 1265; HRMS (ES^+) calcd for $C_{25}H_{21}BrNO$ $(M + H)^+$ 430.0807, found 430.0808.

General Procedure for the Preparation of Dihydropyrroles 9a−e and 11a,b (Conditions C, Table 1). The solution of 1,6-enynes **5a−e** or **7a,b** (1.0 equiv, 0.147−0.21 mmol) in toluene (5−15 mL) was degassed with ethylene for 5 min, Grubb's I catalyst (0.1 equiv, 0.015−0.02 mmol) was added, and the reaction mixture was stirred at 85 °C under ethylene atmosphere for 2 h. The mixture was cooled to rt, directly loaded on a silica column, and purified by flash chromatography eluting with EtOAc/hexane mixtures to afford pure dihydropyrroles **9a−e** and **11a,b**.

*N-Benzoyl-2-(2-bromophenyl)-3-(1-phenylvinyl)-2,5-dihydro-1H-pyrrole (**9a**).* The treatment of enyne **5a** (0.07 g, 0.16 mmol, 1.0 equiv) with Grubb's I catalyst (0.013 g, 0.016 mmol, 0.1 equiv) according to the general procedure described above followed by flash chromatography over silica eluting with EtOAc/hexane (1:4) afforded dihydropyrrole **9a** (0.065 g, 93%) as a colorless oil: R_f = 0.6 (EtOAc/hexane 3:7); ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.0 Hz, 1H), 7.54 (d, J = 6.4 Hz, 1H), 7.41 (t, J = 7.2 Hz, 3H), 7.35−7.31 (m, 4.3H), 7.24−7.19 (m, 2.7H), 7.14 (t, J = 7.6 Hz, 1H), 7.04−6.96 (m, 1H), 6.64 (s, 0.7H), 6.11 (s, 0.3H), 5.92 (s, 0.3H), 5.75 (s, 0.7H), 5.38 (s, 0.7H), 5.28 (s, 0.3H), 5.16 (s, 0.7H), 5.09 (s, 0.3H), 4.84−4.66 (m, 1.3H), 4.27 (d, J = 16.0 Hz, 0.7H). The signals that integrate for less than 1H arise due to hindered rotation as confirmed by the temperature-dependent ^1H NMR spectra recorded for the diene **9a**. ^{13}C NMR (125 MHz, $CDCl_3$) δ (54.3), 56.9, (60.4), 67.6, (116.9), 117.6, 125.0, 125.9, 127.2 (2C), 127.6, 127.7, 128.0, 128.1 (2C), 128.25 (2C), 128.28 (2C), 128.5, 129.1, (129.2), 130.1, 133.5, 136.1, (136.8), 139.5, (140.5), 140.7, 142.1, (142.2), 169.5, (171.1). Signals for the minor rotamer are given in parentheses. IR (cm^{-1}) 1643, 1492, 1469; HRMS (ES^+) calcd for $C_{25}H_{21}BrNO$ $(M + H)^+$ 430.0807, found 430.0801.

*N-Benzoyl-2-(2-bromo-4,5-dimethoxyphenyl)-3-(1-phenylvinyl)-2,5-dihydro-1H-pyrrole (**9b**).* The treatment of enyne **5b** (0.072 g, 0.15 mmol, 1.0 equiv) with Grubb's I catalyst (0.012 g, 0.015 mmol, 0.1 equiv) according to the general procedure described above followed by flash chromatography over silica eluting with EtOAc/hexane (1:3) afforded dihydropyrrole **9b** (0.058 g, 81%) as a yellow oil: R_f = 0.33 (EtOAc/hexane 3:7); ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.2 Hz, 1H), 7.46−7.38 (m, 3H), 7.36−7.26 (m, 4H), 7.22 (t, J = 6.8 Hz, 2H), 7.04 (d, J = 7.6 Hz, 2H), 6.82 (s, 0.5H), 6.48 (s, 0.5H), 5.93 (s, 0.4H), 5.76 (s, 0.6H), 5.36 (s, 0.7H), 5.25 (s, 0.3H), 5.17 (s, 0.7H), 5.10 (s, 0.3H), 4.83- 4.65 (m, 1.5H), 4.28 (d, J = 24.4 Hz, 0.5H), 3.87 (s, 2H), 3.86 (s, 2H), 3.82 (s, 2H). The signals that integrate for less than 1H arise due to hindered rotation as confirmed by the temperature-dependent ^1H NMR spectra recorded for the diene **9a**. ^{13}C NMR (125 MHz, $CDCl_3$) δ (54.2), (55.9), 56.0, 56.1, 56.9, 67.9, 116.0, (116.9), 117.6, 124.7, 125.9, 127.2 (2C), 127.71 (2C), 127.76, 128.0, 128.2 (2C), 128.3 (2C), 128.4, 129.2, 130.2, (130.9), 136.2, 140.7, 142.2, 148.6, 149.0, 169.7. Signals for the minor rotamer are given in parentheses. IR (cm^{-1}) 1643, 1444, 1159, 1026; HRMS (ES^+) calcd for $C_{27}H_{25}BrNO_3$ $(M + H)^+$ 490.1018, found 490.1024.

*N-Benzoyl-2-(2-bromo-5-fluorophenyl)-3-(1-phenylvinyl)-2,5-dihydro-1H-pyrrole (**9c**).* The treatment of enyne **5c** (0.094 g, 0.21 mmol, 1.0 equiv) with Grubb's I catalyst (0.018 g, 0.02 mmol, 0.1 equiv) according to the general procedure described above followed by flash chromatography over silica eluting with EtOAc/hexane (1:9) afforded dihydropyrrole **9c** (0.068 g, 72%) as a colorless oil: R_f = 0.75 (EtOAc/hexane 3:7); ^1H NMR (400 MHz, $CDCl_3$) δ 7.58−7.47 (m, 2H), 7.46−7.35 (m, 3H), 7.31 (t, J = 6.8 Hz, 3H), 7.24−7.14 (m, 2H), 7.09 (dd, J = 9.2 Hz, J = 2.8 Hz, 1H), 7.02 (d, J = 7.6 Hz, 0.75H), 6.87 (td, J = 8.4 Hz, J = 2.8 Hz, 1H), 6.74 (br s, 0.25H), 6.57 (s, 0.75H), 6.03 (s, 0.25H), 5.94 (s, 0.25H), 5.76 (s, 0.75H), 5.34 (s, 0.75H), 5.23 (s, 0.25H), 5.16 (s, 0.75H), 5.09 (s, 0.25H), 4.81- 4.63 (m, 1.25H), 4.26 (d, J = 16.0 Hz, 0.75H). The signals that integrate for less than 1H arise due to hindered rotation as confirmed by the temperature-dependent ^1H NMR spectra recorded for the diene **9a**. ^{13}C NMR (125 MHz, $CDCl_3$) δ (54.3), 56.7, 67.4, 116.5 (d, J = 22.3 Hz, 2C), 117.7, 125.3, (125.5), 125.9, (126.5), 127.2 (2C), 127.83, 127.89, 127.9, 128.25 (2C), 128.27 (d, J = 19.1 Hz, 2C), 128.6, (129.0), 129.4, 130.3, 134.6 (d, J = 7.6 Hz), 135.8, (136.6), (140.2), 140.5, (141.8), 142.0, 161.3 (d, J = 245.2 Hz), 169.6. Signals for the minor rotamer are given in parentheses. IR (cm^{-1}) 1641, 1465, 1400; HRMS (ES^+) calcd for $C_{25}H_{20}BrFNO$ $(M + H)^+$ 448.0712, found 448.0720.

*N-Benzoyl-2-(2-bromophenyl)-3-(1-(4-fluorophenyl)vinyl)-2,5-dihydro-1H-pyrrole (**9d**).* The treatment of enyne **5d** (0.079 g, 0.17 mmol, 1.0 equiv) with Grubb's I catalyst (0.015 g, 0.017 mmol, 0.1

equiv) according to the general procedure described above followed by flash chromatography over silica eluting with EtOAc/hexane (1:5) afforded dihydropyrrole **9d** (0.069 g, 87%) as a colorless heavy oil: R_f = 0.47 (EtOAc/hexane 3:7); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62−7.49 (m, 2H), 7.47−7.36 (m, 2H), 7.33 (t, J = 7.6 Hz, 1H), 7.68−7.10 (m, 5H), 7.02 (q, J = 8.8 Hz, 3H), 6.62 (s, 0.7H), 6.09 (s, 0.3H), 5.91 (s, 0.3H), 5.72 (s, 0.7H), 5.37 (s, 0.7H), 5.27 (s, 0.3H), 5.13 (s, 0.7H), 5.06 (s, 0.3H), 4.84−4.66 (m, 1.5H), 4.28 (d, J = 16.4 Hz, 0.5H). The signals that integrate for less than 1H arise due to hindered rotation as confirmed by the temperature-dependent ^{1}H NMR spectra recorded for the diene **9a**. ^{13}C NMR (125 MHz, $CDCl_3$) δ (54.3), 56.9, 67.6, 115.1 (d, J = 21.3 Hz, 2C), (117.0), 117.7, (124.0), 125.1, 125.9, 127.2 (2C), 127.7, 128.2 (2C), 128.5, 129.1, 129.2, [129.5, (d, J = 7.8 Hz,)], 129.5 (d, J = 8.0 Hz, 2C), 130.2, (132.6), 133.6, 136.1, (136.4), 136.7 (d, J = 3.1 Hz), (136.8), 139.4, 141.1, (141.2), (142.6), [162.4, (d, J = 245.5 Hz,)], 162.3 (d, J = 245.0 Hz), 169.6, (171.1). Signals for the minor rotamer are given in parentheses. IR (cm^{-1}) 1643, 1508, 1448; HRMS (ES$^+$) calcd for $C_{25}H_{19}BrFNONa$ (M + Na)$^+$ 470.0532, found 470.0537.

*N-Benzoyl-2-(2-bromophenyl)-3-(1-(4-fluorophenyl)vinyl)-2,5-dihydro-1H-pyrrole (**9e**).* The treatment of enyne **5e** (0.09 g, 0.2 mmol, 1.0 equiv) with Grubb's I catalyst (0.016 g, 0.02 mmol, 0.1 equiv) according to the general procedure described above, followed by flash chromatography over silica eluting with EtOAc/hexane (3:7) afforded dihydropyrrole **9e** (0.057 g, 63%) as a colorless oil: R_f = 0.45 (EtOAc/hexane 3:7); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60−7.52 (m, 2H), 7.46−7.36 (m, 3H), 7.32 (t, J = 7.6 Hz, 1H), 7.22 (d, J = 8.4 Hz, 2.5H), 7.18−7.09 (m, 1.5H), 7.00 (t, J = 7.2 Hz, 1H), 6.85 (t, J = 9.2 Hz, 2H), 6.62 (br s, 0.7H), 6.09 (br s, 0.3H), 5.93 (s, 0.4H), 5.76 (s, 0.6H), 5.32 (s, 0.6H), 5.20 (br s, 0.4H), 5.12 (s, 0.6H), 5.05 (s, 0.4H), 4.82−4.68 (m, 1.4H), 4.28 (d, J = 16.0 Hz, 0.6H), 3.82 (s, 3H). The signals that integrate for less than 1H arise due to hindered rotation as confirmed by the temperature-dependent ^{1}H NMR spectra recorded for the diene **9a**. ^{13}C NMR (125 MHz, $CDCl_3$) δ (54.3), 55.2, 56.9, 67.6, 115.9, 116.7, (124.0), 124.8, 125.9, 127.2 (2C), 127.6, (127.8), (128.1), 128.2 (2C), 128.4, 129.0 (2C), 129.2, 129.3 (2C), (129.7), 130.1, (132.6), 132.9, 133.2, 133.5, 136.2, (136.8), (139.5), 141.60, (141.65), (142.9), 159.1, (159.2), 169.5, (171.2). Signals for the minor rotamer are given in parentheses. IR (cm^{-1}) 1643, 1398, 1027; HRMS (ES$^+$) calcd for $C_{26}H_{23}BrNO_2$ (M + H)$^+$ 460.0912, found 460.0904.

*N-Benzoyl-2-(2-bromopyridin-3-yl)-3-(1-phenylvinyl)-2,5-dihydro-1H-pyrrole (**11a**).* The treatment of enyne **7a** (0.072 g, 0.17 mmol, 1.0 equiv) with Grubb's I catalyst (0.014 g, 0.017 mmol, 0.1 equiv) according to the general procedure described above followed by flash chromatography over silica eluting with EtOAc/hexane (1:3) afforded dihydropyrrole **11a** (0.05 g, 69%) as a colorless oil: R_f = 0.55 (EtOAc/hexane 7:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (ddd, J = 10.0 Hz, J = 6.0 Hz, J = 1.6 Hz, 0.7H), 8.19 (br s, 0.3H), 7.78 (dd, J = 7.6 Hz, J = 1.6 Hz, 0.5H), 7.71 (dd, J = 8.0 Hz, J = 1.6 Hz, 0.5H), 7.56 (d, J = 7.2 Hz, 2H), 7.42 (q, J = 7.2 Hz, 3H), 7.38−7.30 (m, 4H), 7.23−7.29 (m, 1H), 7.20 (br s, 1H), 7.03 (br s, 0.5H), 6.49 (s, 0.5H), 6.15−5.90 (m, 0.3H), 5.83 (s, 0.7H), 5.34 (s, 0.5H), 5.28 (s, 0.5H), 5.19 (d, J = 4.0 Hz, 0.7H), 5.11 (d, J = 11.2 Hz, 0.3H), 4.82−4.67 (m, 1.3H), 4.31 (d, J = 16.4 Hz, 0.7H). The signals that integrate for less than 1H arise due to hindered rotation as confirmed by the temperature-dependent ^{1}H NMR spectra recorded for the diene **9a**. ^{13}C NMR (125 MHz, $CDCl_3$) δ (54.3), 57.1, (66.4), 67.8, 117.4, (117.7), (122.6), 122.9, (125.7), 125.81, (125.89), 127.2 (2C), 127.91, 127.96, 128.1 (2C), 128.2 (2C), 128.4 (2C), 128.7, 128.8, (129.7), 130.4, (134.2), 135.7, (136.5), (140.0), 140.2, 142.0, (142.1), 148.7, (148.8), 149.1, (150.2), 169.9. Signals for the minor rotamer are given in parentheses. IR (cm^{-1}) 1643, 1497, 1400; HRMS (ES$^+$) calcd for $C_{24}H_{20}BrN_2O$ (M + H)$^+$ 431.0759, found 431.0769.

*N-benzoyl-2-(2-bromopyridin-3-yl)-3-(1-(4-fluorophenyl)vinyl)-2,5-dihydro-1H-pyrrole (**11b**).* The treatment of enyne **7b** (0.066 g, 0.147 mmol, 1.0 equiv) with Grubbs I catalyst (0.012 g, 0.015 mmol, 0.1 equiv) according to the general procedure described above followed by flash chromatography over silica eluting with EtOAc/hexane (1:3) afforded dihydropyrrole **11b** (0.039 g, 60%) as a colorless oil: R_f = 0.5 (EtOAc/hexane 7:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (br s, 0.8H), 8.1 (br s, 0.2H), 7.72 (d, J = 7.2 Hz, 1H), 7.56 (d, J = 6.4 Hz, 2H), 7.49−7.38 (m, 4H), 7.25−7.14 (m, 1H), 7.08−6.97 (m, 3.5H), 6.47 (s, 0.5H), 6.10−5.90 (m, 0.3H), 5.8 (s, 0.7H), 5.31 (s, 1H), 5.16 (s, 1H), 4.85−4.65 (m, 1.3H), 4.25 (d, J = 16.8 Hz, 0.7H). The signals that integrate for less than 1H arise due to hindered rotation as confirmed by the temperature-dependent ^{1}H NMR spectra recorded for the diene **9a**. ^{13}C NMR (125 MHz, $CDCl_3$) δ 57.9, 67.8, 115.2 (d, J = 21.3 Hz, 2C), 117.8, 122.9, (125.2), 125.7, 126.0, 127.2 (2C), 128.2 (d, J = 6.3 Hz), 128.42 (2C), 128.48, (128.8), (129.5), 129.8 (d, J = 7.7 Hz, 2C), 130.1, 130.5, (133.5), 135.7, 136.2, 141.1, 149.2, 162.3 (d, J = 245.2 Hz), 170.0. Signals for the minor rotamer are given in parentheses. IR (cm^{-1}) 1643, 1465, 1409; HRMS (ES$^+$) calcd for $C_{24}H_{18}BrFN_2ONa$ (M + Na)$^+$, 471.0484 found 471.0481.

General Procedure for the Synthesis of Dihydropyridines 10a−e and 12a−c (Conditions D, Table 1). The solution of 1,7-enynes **6a−e** or **8a−c** (1.0 equiv, 0.11−0.27 mmol) in toluene (5−10 mL) was degassed with ethylene for 5 min, Grubb's II catalyst (0.1 equiv, 0.011−0.027 mmol) was added, and the mixture was stirred at 85 °C under ethylene atmosphere for 8 h. The mixture was cooled to rt, directly loaded on a silica column, and purified by flash chromatography eluting with EtOAc/hexanes mixtures to afford dihydropyridines **10a−e** and **12a−c**.

*N-Benzoyl-2-(2-bromophenyl)-3-(1-phenylvinyl)-1,2,5,6-tetrahydropyridine (**10a**).* The treatment of enyne **6a** (0.12 g, 0.27 mmol, 1.0 equiv) with Grubb's II catalyst (0.023 g, 0.027 mmol, 0.1 equiv) according to the general procedure described above followed by flash chromatography over silica eluting with EtOAc/hexane (1:8) afforded dihydropyridine **10a** (0.108 g, 92%) as a colorless oil: R_f = 0.6 (EtOAc/hexane 3:7); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (br s, 1H), 7.51 (d, J = 7.6 Hz, 3H), 7.45−7.40 (m, 3H), 7.37−7.31 (m, 6H), 7.22 (t, J = 7.2 Hz, 1H), 6.97 (br s, 1H), 5.98 (br s, 1H), 5.15 (br s, 1H), 5.04 (br s, 1H), 3.57 (br s, 1H), 3.16 (br s, 1H), 2.26 (br s, 1H), 2.11 (br s, 1H). The broadening of some signals arise due to hindered rotation as suggested by the temperature-dependent ^{1}H NMR spectra recorded for the diene **9a**. ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.7, 40.1, 52.9, 115.1, 125.1, 126.8, 127.3, 127.5, 127.7, 128.0 (2C), 128.4, 128.9 (2C), 129.3, 129.9 (2C), 131.0, 133.8 (2C), 135.8, 137.1, 138.6, 141.1, 147.0, 171.3; IR (cm^{-1}) 1645, 1465, 1409; HRMS (ES$^+$) calcd for $C_{26}H_{23}BrNO$ (M + H)$^+$ 444.0963, found 444.0964.

*N-Benzoyl-2-(2-bromo-4,5-dimethoxyphenyl)-3-(1-phenylvinyl)-1,2,5,6-tetrahydropyridine (**10b**).* The treatment of enyne **6b** (0.055 g, 0.11 mmol, 1.0 equiv) with Grubb's II catalyst (0.0093 g, 0.011 mmol, 0.1 equiv) according to the general procedure described above followed by flash chromatography over silica eluting with EtOAc/hexane (1:4) afforded dihydropyridine **10b** (0.048 g, 87%) as a colorless heavy oil: R_f = 0.4 (EtOAc/hexane 3:7); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68−7.49 (m, 3H), 7.48−7.28 (m, 7H), 7.16 (br s, 1H), 7.02 (s, 1H), 6.88 (br s, 1H), 6.00 (br s, 1H), 5.20 (br s, 1H), 5.06 (br s, 1H), 3.91 (s, 3H), 3.88 (s, 3H), 3.61 (br s, 1H), 3.21 (br s, 1H), 2.28 (br s, 1H), 2.11 (br s, 1H). The broadening of some signals arise due to hindered rotation as suggested by the temperature-dependent ^{1}H NMR spectra recorded for the diene **9a**. ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.8, 40.2, 52.8, 56.18, 56.19, 114.1, 115.3, 116.4, 127.4, 127.5, 127.9, 128.1 (2C), 128.3, 128.6, 128.8 (2C), 129.9 (2C), 130.6, 135.9, 137.5, 141.0, 146.9, 147.6 (2C), 149.0, 171.1; IR (cm^{-1}) 1643, 1440, 1205, 1026; HRMS (ES$^+$) calcd for $C_{28}H_{26}BrNO_3Na$ (M + Na)$^+$, 526.0994, found 526.0994.

*N-Benzoyl-2-(2-bromo-5-fluorophenyl)-3-(1-phenylvinyl)-1,2,5,6-tetrahydropyridine (**10c**).* The treatment of enyne **6c** (0.09 g, 0.19 mmol, 1.0 equiv) with Grubb's II catalyst (0.016 g, 0.019 mmol, 0.1 equiv) according to the general procedure described above followed by flash chromatography over silica eluting with EtOAc/hexane (1:9) afforded dihydropyridine **10c** (0.079 g, 88%) as a yellow heavy oil: R_f = 0.55 (EtOAc/hexane 3:7); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (br s, 1H), 7.52−7.48 (m, 2H), 7.45−7.35 (m, 6H), 7.34−7.30 (m, 2H), 7.24 (dd, J = 9.6 Hz, J = 2.8 Hz, 1H), 7.10−6.75 (m, 2H), 6.01 (br s, 1H), 5.13 (br s, 1H), 5.06 (br s, 1H), 3.60 (br s, 1H), 3.14 (br s, 1H), 2.25 (br s, 1H), 2.11 (br s, 1H). The broadening of some signals arise due to hindered rotation as suggested by the temperature-dependent

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^{1}H NMR spectra recorded for the diene **9a**. ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.6, 40.2, 52.7, 115.2, 116.8, [117.7, (d, J = 22.1 Hz)], 118.2 (d, J = 24.0 Hz), (119.1), 126.8, 127.4 (d, J = 12.0 Hz, 2C), 128.1 (2C), 128.4, 128.81, 128.88 (2C), (129.3), 129.9, 130.1, 130.4, 133.8, 134.9 (d, J = 7.6 Hz, 2C), (135.6), 136.7, 140.8, 146.9, 161.6 (d, J = 245.1 Hz), [161.9, (d, J = 246.7 Hz)], (171.4), 172.6. Signals for the minor rotamer are given in parentheses. IR (cm^{-1}) 1649, 1465, 1445; HRMS (ES$^+$) calcd for $C_{26}H_{22}BrFNO$ (M + H)$^+$ 462.0869, found 462.0862.

*N-Benzoyl-2-(2-bromophenyl)-3-(1-(4-fluorophenyl)vinyl)-1,2,5,6-tetrahydropyridine (**10d**).* The treatment of enyne **6d** (0.08 g, 0.17 mmol, 1.0 equiv) with Grubb's II catalyst (0.015 g, 0.017 mmol, 0.1 equiv) according to the general procedure described above followed by flash chromatography over silica eluting with EtOAc/hexane (1:9) afforded dihydropyridine **10d** (0.068 g, 85%) as a colorless oil: R_f = 0.6 (EtOAc/hexane 3:7); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (br s, 1H), 7.62−7.47 (m, 4H), 7.44−7.38 (m, 3H), 7.36−7.30 (m, 2H), 7.24−7.30 (m, 1H), 7.05 (t, J = 8.4 Hz, 2H), 6.93 (br s, 1H), 5.98 (br s, 1H), 5.15 (br s, 1H), 5.02 (br s, 1H), 3.60 (br s, 1H), 3.17 (br s, 1H), 2.28 (br s, 1H), 2.12 (br s, 1H). The broadening of some signals arise due to hindered rotation as suggested by the temperature-dependent ^{1}H NMR spectra recorded for the diene **9a**. ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.7, 40.1, 53.0, 114.9 (d, J = 21.2 Hz, 2C), 115.4, 125.1, 126.8, 127.5, 128.4, 128.9, 129.4, 130.0 (2C), 130.4 (d, J = 7.8 Hz, 2C), 130.9, 133.9 (2C), 135.8, 136.9 (d, J = 3.3 Hz), 137.3, 138.5, 146.1, 160.2 (d, J = 244.5 Hz), 171.3; IR (cm^{-1}) 1643, 1440, 1402; HRMS (ES$^+$) calcd for $C_{26}H_{21}BrFNONa$ (M + Na)$^+$ 484.0688, found 484.0688.

*N-Benzoyl-2-(2-bromophenyl)-3-(1-(4-methoxyphenyl)vinyl)-1,2,5,6-tetrahydropyridine (**10e**).* The treatment of enyne **6e** (0.079 g, 0.17 mmol, 1.0 equiv) with Grubb's II catalyst (0.014 g, 0.017 mmol, 0.1 equiv) according to the general procedure described above followed by flash chromatography over silica eluting with EtOAc/hexane (1:8) afforded dihydropyridine **10e** (0.063 g, 80%) as a colorless oil: R_f = 0.45 (EtOAc/hexane 3:7); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (br s, 1H), 7.50 (d, J = 6.4 Hz, 3H), 7.46−7.37 (m, 3H), 7.34 (t, J = 7.6 Hz, 1H), 7.30−7.17 (m, 3H), 6.94 (br s, 1H), 6.91 (d, J = 8.8 Hz, 2H), 6.03 (br s, 1H), 5.11 (br s, 1H), 5.02 (br s, 1H), 3.84 (s, 3H), 3.56 (br s, 1H), 3.16 (br s, 1H), 2.27 (br s, 1H), 2.11 (br s, 1H). The broadening of some signals arise due to hindered rotation as suggested by the temperature-dependent ^{1}H NMR spectra recorded for the diene **9a**. ^{13}C NMR (125 MHz, $CDCl_3$) δ 25.3, 39.1, 52.0, 54.3, 112.3 (2C), 113.3, 124.3, 125.7, 126.5, 127.3, 127.6, 128.2, 128.90 (2C), 128.93 (2C), 130.0, 132.3, 132.8 (2C), 134.8, 136.4, 137.6, 145.6, 157.8, 170.3; IR (cm^{-1}) 1639, 1485, 1446; HRMS (ES$^+$) calcd for $C_{27}H_{25}BrNO_2$ (M + H)$^+$ 474.1069, found 474.1069.

*N-Benzoyl-2′-bromo-3-(1-phenylvinyl)-1,2,5,6-tetrahydro-2,3′-bipyridine (**12a**).* The treatment of enyne **8a** (0.065 g, 0.15 mmol, 1.0 equiv) with Grubb's II catalyst (0.012 g, 0.015 mmol, 0.1 equiv) according to the general procedure described above followed by flash chromatography over silica eluting with EtOAc/hexane (2:3) afforded dihydropyridine **12a** (0.045 g, 69%) as a colorless heavy oil: R_f = 0.3 (EtOAc/hexane 3:7); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.78 (d, J = 7.6 Hz, 1H), 7.53 (d, J = 7.2 Hz, 2H), 7.47−7.30 (m, 9H), 6.92 (s, 1H), 6.05 (s, 1H), 5.14 (s, 1H), 5.07 (s, 1H), 3.63 (br s, 1H), 3.05 (br s, 1H), 2.27 (br s, 1H), 2.11 (br s, 1H). The broadening of some signals arise due to hindered rotation as suggested by the temperature-dependent ^{1}H NMR spectra recorded for the diene **9a**. ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.5, 40.2, 52.3, 115.4, 122.2, 127.5 (2C), 127.7, 128.1 (2C), 128.4, 128.7 (2C), 129.5, 130.2 (2C), 135.5, 136.0, 136.2, 139.1, 140.6, 144.8, 146.8, 149.1, 171.7; IR (cm^{-1}) 1643, 1446, 1402; HRMS (ES$^+$) calcd for $C_{25}H_{21}BrN_2ONa$ (M + Na)$^+$ 467.0735, found 467.0742.

*N-Benzoyl-2′-bromo-3-(1-(4-fluorophenyl)vinyl)-1,2,5,6-tetrahydro-2,3′-bipyridine (**12b**).* The treatment of enyne **8b** (0.1 g, 0.22 mmol, 1.0 equiv) with Grubb's II catalyst (0.019 g, 0.022 mmol, 0.1 equiv) according to the general procedure described above followed by flash chromatography over silica eluting with EtOAc/hexane (2:3) afforded dihydropyridine **12b** (0.062 g, 62%) as a colorless oil: R_f = 0.35 (EtOAc/hexane 3:7); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.74 (dd, J = 7.2 Hz, J = 1.6 Hz, 1H), 7.52 (dd, J = 7.6 Hz, J = 1.2 Hz, 2H), 7.47−7.39 (m, 3H), 7.32 (dd, J = 4.8 Hz, J = 2.8 Hz, 1H), 7.30−7.22 (m, 2H), 7.06 (t, J = 8.6 Hz, 2H), 6.86 (br s, 1H), 6.08 (s, 1H), 5.13 (br s, 1H), 5.05 (s, 1H), 3.64 (br s, 1H), 3.05 (br s, 1H), 2.31 (br s, 1H), 2.14 (br s, 1H).The broadening of some signals arise due to hindered rotation as suggested by the temperature-dependent ^{1}H NMR spectra recorded for the diene **9a**. ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.5, 40.2, 52.4, 115.1 (d, J = 21.2 Hz, 2C), 115.66, 115.68, 122.1, 127.5 (2C), 128.5, 129.5, 130.2 (2C), 130.3 (d, J = 8.0 Hz, 2C), 135.4, 135.8, 136.4 (d, J = 3.2 Hz), 139.0, 144.8, 146.0, 149.2, 162.3 (d, J = 245 Hz), 171.7; IR (cm^{-1}) 1645, 1508, 1402; HRMS (ES$^+$) calcd for $C_{25}H_{20}BrFN_2ONa$ (M + Na)$^+$ 485.0641, found 485.0634.

*N-Benzoyl-2′-bromo-3-(1-(4-methoxyphenyl)vinyl)-1,2,5,6-tetrahydro-2,3′-bipyridine (**12c**).* The treatment of enyne **8c** (0.1 g, 0.21 mmol, 1.0 equiv) with Grubb's II catalyst (0.018 g, 0.021 mmol, 0.1 equiv) according to the general procedure described above followed by flash chromatography over silica eluting with EtOAc/hexane (2:3) afforded dihydropyridine **12c** (0.058 g, 58%) as a colorless oil: R_f = 0.3 (EtOAc/hexane 3:7); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 3.6 Hz, 1H), 7.75 (dd, J = 7.6 Hz, J = 1.6 Hz, 1H), 7.53 (dd, J = 7.6 Hz, J = 1.6 Hz, 2H), 7.48−7.39 (m, 3H), 7.30 (dd, J = 4.8 Hz, J = 2.8 Hz, 1H), 7.23 (d, J = 8.8 Hz, 2H), 6.94−6.88 (m, 2H), 6.87 (br s, 1H), 6.10 (s, 1H), 5.09 (br s, 1H), 5.04 (s, 1H), 3.85 (s, 3H), 3.64 (br s, 1H), 3.04 (br s, 1H), 2.31 (br s, 1H), 2.10 (br s, 1H). The broadening of some signals arise due to hindered rotation as suggested by the temperature-dependent ^{1}H NMR spectra recorded for the diene **9a**. ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.5, 40.3, 52.5, 55.1, 113.5 (2C), 114.8, 122.1, 127.5, 128.4 (2C), 129.1, 129.8 (2C), 130.1 (2C), 132.8, 135.5, 136.0, 136.6, 139.1, 144.8, 146.5, 149.1, 159.1, 171.7; IR (cm^{-1}) 1647, 1458, 1400; HRMS (ES$^+$) calcd for $C_{26}H_{24}BrN_2O_2$ (M + H)$^+$ 475.1021, found 475.1018.

General Procedure for the Synthesis of Benzoindolines 13a−e and Pyrroloquinolines 15a,b (Conditions E, Table 1). A solution of the dienes **9a−e** and **11a−b** (1 equiv, 0.065−0.12 mmol) in DMF (2 mL) was added to a mixture of solid $Pd(OAc)_2$ (0.1 equiv, 0.006−0.012 mmol) and NaOAc (1.1 equiv, 0.07−0.13 mmol) in a sealed tube. The tube was flushed with argon and capped, and the reaction mixture was stirred at 120 °C for 12 h. The mixture was cooled to rt, cold water (2 mL) was added, and the mixture was extracted with EtOAc (3 × 20 mL). Combined organic layers were washed with brine, dried (anhydrous $MgSO_4$), and solvents were removed under reduced pressure to afford the crude products that were purified by flash chromatography over silica eluting with EtOAc/hexane mixture to afford benzoindolines **13a−e** and pyrroloquinolines **15a−b**.

*N-Benzoyl-4-phenyl-2,3-dihydro-1H-benzo[g]indole (**13a**).* The treatment of diene **9a** (0.048 g, 0.11 mmol, 1.0 equiv) with $Pd(OAc)_2$ (0.0026 g, 0.01 mmol, 0.1 equiv) and NaOAc (0.01 g, 0.12 mmol, 1.1 equiv) according to the general procedure described above followed by flash chromatography over silica eluting with EtOAc/hexane (1:9) afforded benzoindoline **13a** (0.028 g, 71%) as a white solid: mp 178−180 °C; R_f = 0.6 (EtOAc/hexane 3:7); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91−7.82 (m, 3H), 7.81−7.76 (m, 1H), 7.74 (s, 1H), 7.58−7.35 (m, 9H), 7.43−7.38 (m, 1H), 4.29 (t, J = 7.6 Hz, 2H), 3.22 (t, J = 7.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.9, 55.1, 123.8, 125.2, 125.5, 125.7 126.4, 127.4, 128.3, 128.52 (2C), 128.54 (2C), 128.56 (2C), 128.9 (2C), 130.3, 131.5, 133.9, 135.9, 136.5, 139.5, 140.2, 170.8; IR (cm^{-1}) 1650, 1494, 1386; HRMS (ES$^+$) calcd for $C_{25}H_{19}NONa$ (M + Na)$^+$ 372.1364, found 372.1375.

*N-Benzoyl-7,8-dimethoxy-4-phenyl-2,3-dihydro-1H-benzo[g]-indole (**13b**).* The treatment of diene **9b** (0.035 g, 0.07 mmol, 1.0 equiv) with $Pd(OAc)_2$ (0.0016 g, 0.007 mmol, 0.1 equiv) and NaOAc (0.0063 g, 0.077 mmol, 1.1 equiv) according to the general procedure described above, followed by flash chromatography over silica eluting with EtOAc/hexane (1:3) afforded benzoindoline **13b** (0.02 g, 68%) as a yellow oil: R_f = 0.23 (EtOAc/hexane 3:7); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 6.8 Hz, 2H), 7.60 (s, 1H), 7.57−7.45 (m, 7H), 7.39 (t, J = 6.8 Hz, 1H), 7.18 (s, 1H), 7.02 (s, 1H), 4.28 (t, J = 7.2 Hz, 2H), 4.03 (s, 3H), 3.91 (s, 3H), 3.21 (t, J = 7.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.6, 55.2, 55.8, 55.9, 104.3 106.6, 119.6, 124.8,

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127.1, 128.4 (2C), 128.5 (2C), 128.6, 128.7 (2C), 130.0, 131.31, 131.35 (2C), 134.7, 136.3, 138.3, 140.4, 149.0, 149.9, 170.2; IR (cm^{-1}) 1649, 1498, 1161, 1012; HRMS (ES^+) calcd for $C_{27}H_{24}O_3N$ $(M + H)^+$ 410.1756, found 410.1756.

*N-Benzoyl-8-fluoro-4-phenyl-2,3-dihydro-1H-benzo[g]indole (**13c**).* The treatment of diene **9c** (0.029 g, 0.065 mmol, 1.0 equiv) with $Pd(OAc)_2$ (0.0015 g, 0.006 mmol, 0.1 equiv) and NaOAc (0.006 g, 0.07 mmol, 1.1 equiv) according to the general procedure described above followed by flash chromatography over silica eluting with EtOAc/hexane (1:9) afforded benzoindoline **13c** (0.016 g, 65%) as a heavy oil: R_f = 0.72 (EtOAc/hexane 3:7); ^1H NMR (400 MHz, $CDCl_3$) δ 7.95−7.82 (m, 3H), 7.75 (s, 1H), 7.64−7.38 (m, 8H), 7.28 (d, J = 1.2 Hz, 2H), 4.30 (t, J = 6.4 Hz, 2H), 3.23 (t, J = 6.8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.9, 55.0, 109.2 (d, J = 23.0 Hz), 116.3 (d, J = 25.2 Hz), 124.8 (d, J = 9.9 Hz), 126.3, 127.5 (2C), 128.5 (2C), 128.6 (2C), 128.8 (2C), 130.7, 130.8, 131.0, 131.5, 131.6, 135.7, 135.8 (d, J = 2.7 Hz), 139.3 (d, J = 5.4 Hz), 139.9, 160.1 (d, J = 245.1 Hz), 170.7; IR (cm^{-1}) 1650, 1496, 1357; HRMS (ES^+) calcd for $C_{25}H_{19}FNO$ $(M + H)^+$ 368.1451, found 368.1446.

*N-Benzoyl-4-(4-fluorophenyl)-2,3-dihydro-1H-benzo[g]indole (**13d**).* The treatment of diene **9d** (0.038 g, 0.085 mmol, 1.0 equiv) with $Pd(OAc)_2$ (0.002 g, 0.008 mmol, 0.1 equiv) and NaOAc (0.0078 g, 0.094 mmol, 1.1 equiv) according to the general procedure described above followed by flash chromatography over silica eluting with EtOAc/hexane (1:9) afforded benzoindoline **13d** (0.024 g, 78%) as a heavy oil: R_f = 0.75 (EtOAc/hexane 3:7); ^1H NMR (400 MHz, $CDCl_3$) δ 7.92−7.87 (m, 3H), 7.81 (t, J = 3.2 Hz, 1H), 7.72 (s, 1H), 7.61−7.58 (m, 1H), 7.53 (d, J = 7.6 Hz, 2H), 7.50−7.45 (m, 4H), 7.18 (t, J = 8.8 Hz, 2H), 4.31 (t, J = 7.6 Hz, 2H), 3.20 (t, J = 7.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.9, 55.1, 115.4 (d, J = 21.2 Hz, 2C), 123.9, 125.2, 125.6, 125.8, 126.3, 128.3, 128.5 (2C), 128.8 (2C), 130.15, 130.18 (d, J = 25.2 Hz, 2C), 131.6, 133.9, 135.5, 135.9, 136.2 (d, J = 10.4 Hz), 139.6, 162.1 (d, J = 245.0 Hz), 170.8; IR (cm^{-1}) 1650, 1504, 1446; HRMS (ES^+) calcd for $C_{25}H_{18}FNONa$ $(M + Na)^+$ 390.1270, found 390.1270.

*N-Benzoyl-4-(4-methoxyphenyl)-2,3-dihydro-1H-benzo[g]indole (**13e**).* The treatment of diene **9e** (0.055 g, 0.12 mmol, 1.0 equiv) with $Pd(OAc)_2$ (0.0027 g, 0.012 mmol, 0.1 equiv) and NaOAc (0.011 g, 0.13 mmol, 1.1 equiv) according to the general procedure described above followed by flash chromatography over silica eluting with EtOAc/hexane (1:4) afforded benzoindoline **13e** (0.03 g, 66%) as colorless oil: R_f = 0.45 (EtOAc/hexane 3:7); ^1H NMR (400 MHz, $CDCl_3$) δ 7.93−7.84 (m, 3H), 7.80 (d, J = 5.6 Hz, 1H), 7.73 (s, 1H), 7.61−7.50 (m, 3H), 7.49−7.43 (m, 4H), 7.02 (d, J = 8.8 Hz, 2H), 4.30 (t, J = 7.2 Hz, 2H), 3.89 (s, 3H), 3.23 (t, J = 7.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.0, 55.1, 55.3, 113.9 (2C), 123.6, 125.2, 125.3, 125.6, 126.1, 128.2, 128.5 (2C), 128.8 (2C), 129.6 (2C), 130.4, 131.5, 132.6, 134.0, 136.0, 136.1, 139.4, 159.0, 170.7; IR (cm^{-1}) 1650, 1446, 1074; HRMS (ES^+) calcd for $C_{26}H_{21}NO_2Na$ $(M + Na)^+$ 402.1470, found 402.1466.

*N-Benzoyl-4-phenyl-2,3-dihydro-1H-pyrrolo[2,3-f]quinoline (**15a**).* The treatment of diene **11a** (0.032 g, 0.07 mmol, 1.0 equiv) with $Pd(OAc)_2$ (0.0016 g, 0.007 mmol, 0.1 equiv) and NaOAc (0.0063 g, 0.077 mmol, 1.1 equiv) according to the general procedure described above followed by flash chromatography over silica eluting with EtOAc/hexane (2:3) afforded pyrroloquinoline **15a** (0.02 g, 77%) as a colorless oil: R_f = 0.2 (EtOAc/hexane 3:7); ^1H NMR (400 MHz, $CDCl_3$) δ 8.92 (d, J = 2.4 Hz, 1H), 8.23 (d, J = 8.4 Hz, 1H), 8.06 (s, 1H), 7.86 (d, J = 8.0 Hz, 2H), 7.62−7.47 (m, 7H), 7.43 (t, J = 7.2 Hz, 1H), 7.38 (dd, J = 8.4 Hz, J = 4.0 Hz, 1H), 4.33 (t, J = 7.6 Hz, 2H), 3.27 (t, J = 7.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.7, 55.2, 119.5, 120.0, 127.1, 127.9, 128.2, 128.5 (2C), 128.6 (2C), 128.70 (2C), 128.77 (2C), 130.9, 131.8, 134.4, 135.5, 139.3, 139.4, 140.1, 149.8, 170.9; IR (cm^{-1}) 1649, 1556, 1490; HRMS (ES^+) calcd for $C_{24}H_{19}N_2O$ $(M + H)^+$ 351.1497, found 351.1490.

*N-Benzoyl-4,4-fluorophenyl)-2,3-dihydro-1H-pyrrolo[2,3-f]-quinoline (**15b**).* The treatment of diene **9b** (0.03 g, 0.067 mmol, 1.0 equiv) with $Pd(OAc)_2$ (0.0015 g, 0.0067 mmol, 0.1 equiv) and NaOAc (0.006 g, 0.07 mmol, 1.1 equiv) according to the general procedure described above followed by flash chromatography over silica eluting with EtOAc/hexane (2:3) afforded pyrroloquinoline **15b** (0.016 g, 65%) as a yellow oil in a mixture with aromatized oxidation product (8.5% by GC−MS, M^+ 366.2; see the Supporting Information): R_f = 0.3 (EtOAc/hexane 3:7); ^1H NMR (400 MHz, $CDCl_3$) δ 8.92 (dd, J = 4.4 Hz, J = 1.6 Hz, 1H), 8.23 (d, J = 8.4 Hz, 1H), 8.01 (s, 1H), 7.85 (d, J = 7.2 Hz, 2H), 7.59 (d, J = 7.2 Hz, 1H), 7.55−7.51 (m, 4H), 7.38 (dd, J = 8.4 Hz, J = 4.0 Hz, 1H), 7.19 (t, J = 8.8 Hz, 2H), 4.34 (t, J = 7.6 Hz, 2H), 3.24 (t, J = 7.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.6, 55.1, 115.7 (d, J = 21.3 Hz, 2C), 119.4, 120.2, 127.3, 128.6 (2C), 128.7 (2C), 130.1 (d, J = 8.1 Hz, 2C), 130.6, 131.8, 134.0, 135.4, 130.5 (d, J = 3.2 Hz), 138.8, 139.4, 148.1, 150.3, 162.5 (d, J = 246 Hz), 171.0; IR (cm^{-1}) 1637, 1440, 1400; HRMS (ES^+) calcd for $C_{24}H_{17}FN_2ONa$ $(M + Na)^+$ 391.1223, found 391.1231.

General Procedure for the Preparation of Indenopyridines 14a−e and Tetrahydrophenanthrolines 16a−c (Conditions F, Table 1). To a mixture of solid $Pd(OAc)_2$ (0.1 equiv, 0.008−0.023 mmol), PPh_3 (0.2 equiv, 0.016−0.045 mmol), and Cs_2CO_3 (2.0 equiv, 0.16−0.45 mmol) in a sealed tube under argon was added a solution of dienes **10a−e** and **12a−c** (1.0 equiv, 0.08−0.23 mmol) in DMF (2.0 mL). The tube was flushed with argon and capped, and the reaction mixture was stirred at 120 °C for 15 h. The mixture was cooled to rt, water (2 mL) was added, and the mixture was extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine and dried (anhydrous $MgSO_4$), and solvents were removed under reduced pressure to afford crude products that were separated by flash chromatography over silica to afford indenopyridines **14a−e** and tetrahydrophenanthroline **16a−c**.

(4aR,5aR*,9bS*)-N-Benzoyl-5a-phenyl-2,5,5a,9b-tetrahydro-1H-cyclopropa[2,3]indeno[1,2-b]pyridine (**14a**) and N-Benzoyl-6-phenyl-1,2,3,4-tetrahydrobenzo[h]quinoline (**17**).* The treatment of diene **10a** (0.1 g, 0.23 mmol, 1.0 equiv) with $Pd(OAc)_2$ (0.005 g, 0.023 mmol, 0.1 equiv), Cs_2CO_3 (0.147 g, 0.45 mmol, 2.0 equiv), and PPh_3 (0.012 g, 0.045 mmol, 0.2 equiv) according to the general procedure described above followed by flash chromatography over silica eluting with EtOAc/hexane (1:8) afforded indenopyridine **14a** (0.066 g, 80%) as a fluffy white solid, and continuous elution with EtOAc/hexane (1:8) afforded benzoquinoline **17** (0.008 g, 10%) as a white solid.

*Analytical data for **14a**:* mp 73−78 °C; R_f = 0.45 (EtOAc/hexane 3:7); ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 7.2 Hz, 1H), 7.52−7.42 (m, 5H), 7.35 (t, J = 7.6 Hz, 2H), 7.30−7.22 (m, 4H), 7.20 (t, J = 6.8 Hz, 1H), 6.98 (d, J = 7.2 Hz, 1H), 6.09−6.01 (m, 2H), 5.47 (dd, J = 9.2 Hz, J = 2.8 Hz, 1H), 4.16−3.95 (m, 1H), 3.59 (d, J = 15.6 Hz, 1H), 2.31 (d, J = 5.6 Hz, 1H), 1.46 (d, J = 5.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.0, 40.1, 43.1, 46.5, 59.6, 123.6, 126.8 (2C), 126.9, 127.0, 127.1, 127.9, 128.4 (2C), 128.5 (2C), 129.2, 129.6, 129.7 (2C), 131.2, 136.5, 138.5, 142.8, 149.0, 170.5; IR (cm^{-1}) 1627, 1600, 1444; HRMS (ES^+) calcd for $C_{26}H_{21}NONa$ $(M + Na)^+$ 386.1521, found 386.1519.

*Analytical data for **17**:* mp 169−171 °C; R_f = 0.5 (EtOAc/hexane 3:7); ^1H NMR (400 MHz, $CDCl_3$) δ 7.89−7.80 (br m, 1.7H), 7.69−7.62 (m, 2.3H), 7.56−7.41 (m, 7H), 7.24−7.19 (m, 2H), 7.06 (t, J = 6.8 Hz, 0.7H), 6.98 (t, J = 7.2 Hz, 1.3H), 5.06−4.82 (m, 0.5H), 4.36−4.12 (m, 0.5H), 3.62−3.51 (m, 0.4H), 3.43−3.33 (m, 0.6H), 3.16−3.01 (m, 1H), 2.86−2.68 (m, 1H), 2.53−2.41 (m, 0.5H), 2.15−1.98 (m, 0.5H), 1.87−1.69 (m, 1H). The signals that integrate for less than 1H arise due to hindered rotation. ^{13}C NMR (125 MHz, $CDCl_3$) δ (24.8), 24.9, (25.3), 25.9, 43.1, (47.8), 122.6, (123.1), (125.5), (125.6), 125.7, 126.2, 126.8, (127.1), 127.30, (127.35), 127.4 (2C), (127.5), 127.6, (127.8), 128.02 (2C), (128.07), (128.2), (128.3), 128.3 (2C), 128.6, (129.4), 129.6 (2C), (129.9), 130.0, (130.1), 130.8, (130.9), (132.0), 132.2, 132.3, (136.0), 136.5, (136.7), 138.9, (139.6), 140.3, (140.9), 170.3, (172.6). Signals for the minor rotamer are given in the parentheses; IR (cm^{-1}) 1641, 1490, 1467; HRMS (ES^+) calcd for $C_{26}H_{22}NO$ $(M + H)^+$ 364.1701, found 364.1696.

(4aR,5aR*,9bS*)-N-Benzoyl-7,8-dimethoxy-5a-phenyl-2,5,5a,9b-tetrahydro-1H-cyclopropa[2,3]indeno[1,2-b]pyridine (**14b**).* The treatment of diene **10b** (0.04 g, 0.08 mmol, 1.0 equiv) with $Pd(OAc)_2$ (0.0018 g, 0.008 mmol, 0.1 equiv), Cs_2CO_3 (0.058 g, 0.16 mmol, 2.0 equiv), and PPh_3 (0.0042 g, 0.016 mmol, 0.2 equiv)

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according to the general procedure described above followed by flash chromatography over silica eluting with EtOAc/hexane (1:4) afforded indenopyridine **14b** (0.026 g, 78%) as a light yellow solid: mp 220−222 °C; R_f = 0.35 (EtOAc/hexane 3:7); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51−7.43 (m, 5H), 7.39−7.32 (m, 2H), 7.31−7.23 (m, 4H), 6.48 (s, 1H), 6.03−5.96 (m, 2H), 5.44 (dd, J = 9.2 Hz, J = 2.8 Hz, 1H), 4.08−3.98 (m, 1H), 3.80 (s, 3H), 3.75 (s, 3H), 3.61 (d, J = 15.6 Hz, 1H), 2.29 (d, J = 5.6 Hz, 1H), 1.40 (d, J = 5.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.0, 40.0, 43.1, 46.3, 56.0, 56.1, 59.7, 106.3, 109.4, 126.80, 126.84 (2C), 128.4 (2C), 128.5 (2C), 129.1, 129.4 (2C), 129.6, 131.3, 134.1, 136.5, 138.6, 140.9, 148.7, 149.2, 170.4; IR (cm^{-1}) 1625, 1423, 1130, 1116; HRMS (ES^+) calcd for $C_{28}H_{26}NO_3$ $(M + H)^+$ 424.1913, found 424.1913.

(4aR,5aR*,9bS*)-N-Benzoyl-8-fluoro-5a-phenyl-2,5,5a,9b-tetrahydro-1H-cyclopropa[2,3]indeno[1,2-b]pyridine (**14c**).* The treatment of diene **10c** (0.06 g, 0.13 mmol, 1.0 equiv) with $Pd(OAc)_2$ (0.003 g, 0.013 mmol, 0.1 equiv), Cs_2CO_3 (0.085 g, 0.26 mmol, 2.0 equiv), and PPh_3 (0.0068 g, 0.026 mmol, 0.2 equiv) according to the general procedure described above, followed by flash chromatography over silica eluting with EtOAc/hexane (1:4) afforded indenopyridine **14c** (0.034 g, 71%) as a colorless heavy oil: R_f = 0.5 (EtOAc/hexane 1:9); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52−7.40 (m, 6H), 7.32−7.28 (m, 2H), 7.30−7.21 (m, 3H), 6.90 (d, J = 6.4 Hz, 2H), 6.09−5.97 (m, 2H), 5.45 (dd, J = 9.2 Hz, J = 2.8 Hz, 1H), 4.13−4.01 (m, 1H), 3.60 (d, J = 16.0 Hz, 1H), 2.29 (d, J = 5.6 Hz, 1H), 1.44 (d, J = 5.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.9, 40.3, 43.2, 45.7, 59.3, 113.5 (d, J = 22.5 Hz), 115.1 (d, J = 23.0 Hz), 124.5 (d, J = 9.0 Hz), 126.8 (2C), 127.0, 128.4 (2C), 128.5 (2C), 129.1, 129.6 (2C), 129.7, 131.0, 136.2, 138.3, 144.5 (d, J = 2.7 Hz), 144.9 (d, J = 8.1 Hz), 162.1 (d, J = 242.8.1 Hz), 170.5; IR (cm^{-1}) 1625, 1600, 1483; HRMS (ES^+) calcd for $C_{26}H_{21}NFO$ $(M + H)^+$ 382.1607, found 382.1599.

(4aR,5aR*,9bS*)-N-Benzoyl-5a-(4-fluorophenyl)-2,5,5a,9b-tetrahydro-1H-cyclopropa[2,3]indeno[1,2-b]pyridine (**14d**).* The treatment of diene **10d** (0.06 g, 0.13 mmol, 1.0 equiv) with $Pd(OAc)_2$ (0.003 g, 0.013 mmol, 0.1 equiv), Cs_2CO_3 (0.084 g, 0.26 mmol, 2.0 equiv), and PPh_3 (0.007 g, 0.026 mmol, 0.2 equiv) according to the general procedure described above, followed by flash chromatography over silica eluting with EtOAc/hexane (1:9) afforded indenopyridine **14d** (0.04 g, 81%) as a colorless oil: R_f = 0.55 (EtOAc/hexane 3:7); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 7.2 Hz, 1H), 7.54−7.41 (m, 5H), 7.26−7.18 (m, 4H), 7.03 (t, J = 8.8 Hz, 2H), 6.94 (d, J = 7.6 Hz, 1H), 6.10−5.99 (m, 2H), 5.45 (dd, J = 9.2 Hz, J = 2.4 Hz, 1H), 4.13−4.01 (m, 1H), 3.56 (d, J = 15.6 Hz, 1H), 2.25 (d, J = 5.6 Hz, 1H), 1.46 (d, J = 5.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.2, 40.0, 43.0, 45.7, 59.5, 115.3 (d, J = 21.2 Hz, 2C), 123.4, 126.8 (2C), 127.1, 127.2, 128.0, 128.5 (2C), 129.3, 129.6, 131.1, 131.2 (d, J = 8.1 Hz, 2C), 134.3 (d, J = 3.1 Hz), 136.4, 142.7, 148.8, 161.4 (d, J = 244.1 Hz), 170.5; IR (cm^{-1}) 1625, 1598, 1427; HRMS (ES^+) calcd for $C_{26}H_{20}FNONa$ $(M + Na)^+$ 404.1427, found 404.1419.

(4aR,5aR*,9bS*)-N-Benzoyl-5a-(4-methoxyphenyl)-2,5,5a,9b-tetrahydro-1Hcyclopropa[2,3]indeno[1,2-b]pyridine (**14e**).* The treatment of diene **10e** (0.038 g, 0.08 mmol, 1.0 equiv) with $Pd(OAc)_2$ (0.002 g, 0.008 mmol, 0.1 equiv), Cs_2CO_3 (0.052 g, 0.16 mmol, 2.0 equiv), and PPh_3 (0.0042 g, 0.016 mmol, 0.2 equiv) according to the general procedure described above followed by flash chromatography over silica eluting with EtOAc/hexane (1:8) afforded indenopyridine **14e** (0.025 g, 80%) as a colorless oil: R_f = 0.4 (EtOAc/hexane 3:7); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 6.8 Hz, 1H), 7.52−7.42 (m, 5H), 7.26−7.15 (m, 4H), 6.95 (d, J = 7.2 Hz, 1H), 6.88 (d, J = 8.8 Hz, 2H), 6.09−5.99 (m, 2H), 5.48 (dd, J = 9.2 Hz, J = 2.8 Hz, 1H), 4.12−4.00 (m, 1H), 3.82 (s, 3H), 3.58 (d, J = 15.2 Hz, 1H), 2.24 (d, J = 5.6 Hz, 1H), 1.40 (d, J = 5.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.3, 39.9, 43.0, 45.9, 55.2, 59.5, 113.8 (2C), 123.5, 126.9 (2C), 127.0, 127.1, 127.9, 128.5 (2C), 129.0, 129.5, 130.6, 130.8 (2C), 131.5, 136.6, 142.6, 149.3, 158.5, 170.5; IR (cm^{-1}) 1625, 1598, 1245; HRMS (ES^+) calcd for $C_{27}H_{23}NO_2Na$ $(M + Na)^+$ 416.1626, found 416.1626.

*N-Benzoyl-5-phenyl-1,2,3,4-tetrahydro-1,7-phenanthroline (**16a**).* The treatment of diene **12a** (0.04 g, 0.09 mmol, 1.0 equiv) with $Pd(OAc)_2$ (0.002 g, 0.01 mmol, 0.1 equiv), Cs_2CO_3 (0.059 g, 0.18 mmol, 2.0 equiv), and PPh_3 (0.0065 g, 0.02 mmol, 0.2 equiv) according to the general procedure described above followed by flash chromatography over silica eluting with EtOAc/hexane (2:3) afforded phenanthroline **16a** (0.022 g, 65%) as a light yellow powder: mp 190−193 °C; R_f = 0.3 (EtOAc/hexane 3:7); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (br s, 0.2H), 8.68 (br s, 0.3H), 8.15 (d, J = 6.4 Hz, 0.3H), 8.05−7.90 (m, 1.5H), 7.82 (d, J = 5.2 Hz, 0.7H), 7.65−7.38 (m, 7H), 7.32−7.24 (m, 1H), 7.22 (d, J = 7.2 Hz, 1H), 7.09 (t, J = 7.2 Hz, 1H), 7.00 (t, J = 6.8 Hz, 1H), 4.86 (q, J = 8.4 Hz, 0.5H), 4.25 (br s, 0.5H), 3.57 (br s, 0.5H), 3.42 (br s, 0.5H), 3.14 (d, J = 15.2 Hz, 0.5H), 2.93−2.70 (m, 1.5H), 2.47 (br s, 0.5H), 2.06 (br s, 0.5H), 1.81 (br s, 1H). The signals that integrate for less than 1H arise due to hindered rotation as confirmed by the temperature-dependent ^{1}H NMR spectra recorded for the phenanthroline **16a**. ^{13}C NMR (125 MHz, $CDCl_3$) δ (24.9), 25.0, (25.8), 43.5, (47.9), 53.4, 120.3, (120.8), 122.8, (122.9), (127.5), 127.7 (2C), (127.8), 127.9, 128.1 (2C), (128.2), (128.3), 128.4 (2C), 128.8, (129.2), 129.5 (2C), 130.3, 131.0, (131.1), (132.1), 132.5, (135.1), (135.5), 136.0, 136.4, 139.6, (140.1), 142.6, (143.5), 146.7, 150.0, (170.2), 172.9. Signals for minor rotamer are given in the parentheses. IR (cm^{-1}) 1643, 1444, 1394; HRMS (ES^+) calcd for $C_{25}H_{20}N_2ONa$ $(M + Na)^+$ 387.1473, found 387.1475.

*N-Benzoyl-5-(4-fluorophenyl)-1,2,3,4-tetrahydro-1,7-phenanthroline (**16b**).* The treatment of diene **12d** (0.055 g, 0.12 mmol, 1.0 equiv) with $Pd(OAc)_2$ (0.0027 g, 0.012 mmol, 0.1 equiv), Cs_2CO_3 (0.078 g, 0.24 mmol, 2.0 equiv), and PPh_3 (0.0063 g, 0.024 mmol, 0.2 equiv) according to the general procedure described above followed by flash chromatography over silica eluting with EtOAc/hexane (2:3) afforded phenanthroline **16b** (0.03 g, 61%) as a colorless oil: R_f = 0.3 (EtOAc/hexane 3:7); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (br s, 0.25H), 8.67 (br s, 0.25H), 8.15 (d, J = 6.8 Hz, 0.25H), 7.91 (d, J = 8.8 Hz, 1.5H), 7.82 (d, J = 6.0 Hz, 0.75H), 7.62−7.52 (m, 1.25H), 7.51−7.35 (m, 2.75H), 7.25−7.15 (m, 4H), 7.09 (t, J = 7.6 Hz, 1H), 7.00 (t, J = 7.6 Hz, 1H), 4.94−4.80 (m, 0.5H), 4.30−3.05 (m, 0.5H), 3.72−3.72 (m, 0.5H), 3.42 (br s, 0.5H), 3.09 (d, J = 14.0 Hz, 0.5H), 2.85−2.70 (m, 1.5H), 2.48 (br s, 0.5H), 2.12−2.00 (m, 0.5H), 1.92−1.73 (m, 1H). The signals that integrate for less than 1H arise due to hindered rotation as confirmed by the temperature-dependent ^{1}H NMR spectra recorded for the phenanthroline **16a**. ^{13}C NMR (125 MHz, $CDCl_3$) δ (24.9), 25.0, (25.8), 43.4, 47.9, (53.4), 115.2, 115.5 (d, J = 21.3 Hz, 2C), [115.5 (d, J = 21.3 Hz,)], 120.4, (121.0), (122.9), 126.8, 127.7 (2C), (128.0), 128.1 (2C), 128.2, (128.5), (128.6), 128.8, (129.3), (129.9), (130.2), 130.3 (d, J = 5.0 Hz), [130.8 (d, J = 7.6 Hz,)], 130.9, 131.1 (d, J = 7.5 Hz, 2C), [131.4 (d, J = 8.2 Hz,)], 131.9, (132.3), (135.4), (135.6), 135.9, (136.6), 141.4, (142.3), 146.7, (149.5), 150.2, 162.5 (d, J = 247 Hz), 170.2, (172.9). Signals for the minor rotamer are given in parentheses. IR (cm^{-1}) 1643, 1467, 1402; HRMS (ES^+) calcd for $C_{25}H_{20}FN_2O$ $(M + H)^+$ 383.1560, found 383.1547.

*N-Benzoyl-5-(4-methoxyphenyl)-1,2,3,4-tetrahydro-1,7-phenanthroline (**16c**).* The treatment of diene **12c** (0.08 g, 0.169 mmol, 1.0 equiv) with $Pd(OAc)_2$ (0.0038 g, 0.017 mmol, 0.1 equiv), Cs_2CO_3 (0.11 g, 0.338 mmol, 2.0 equiv), and PPh_3 (0.009 g, 0.038 mmol, 0.2 equiv) according to the general procedure described above followed by flash chromatography over silica eluting with EtOAc/hexane (2:3) afforded phenanthroline **16c** (0.04 g, 59%) as a colorless oil: R_f = 0.25 (EtOAc/hexane 3:7); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (br s, 0.25H), 8.66 (br s, 0.5H), 8.11 (d, J = 6.1 Hz, 0.25H), 7.93 (d, J = 8.4 Hz, 1.5H), 7.82 (d, J = 5.2 Hz, 0.5H), 7.57 (s, 1.25H), 7.49−7.33 (m, 3H), 7.21 (d, J = 7.2 Hz, 1.25H), 7.13−6.96 (m, 4.5H), 4.91−4.78 (m, 0.5H), 4.27−3.99 (m, 0.5H), 3.92 (s, 2H), 3.90 (s, 1H), 3.70−3.52 (m, 0.5H), 3.41 (br s, 0.5H), 3.17 (d, J = 15.6 Hz, 0.5H), 2.93−2.70 (m, 1.5H), 2.47 (br s, 0.5H), 2.06 (br s, 0.5H), 1.92−1.75 (m, 1H). The signals that integrate for less than 1H arise due to hindered rotation as confirmed by the temperature-dependent ^{1}H NMR spectra recorded for the phenanthroline **16a**. ^{13}C NMR (125 MHz, $CDCl_3$) δ (25.0), 25.1, (25.8), 43.5, 47.9, (53.4), (55.3), 55.4, (113.7), 113.9 (2C), 120.2, (120.7), 122.7, (122.8), (126.8), 127.73 (2C), (127.76), 128.1 (2C), (128.2), (128.3), 128.6, 128.8, (130.3), 130.4, 130.7 (2C), 130.9, (131.1), 131.9, (132.5), 132.7, (135.0), (135.5), 136.0, 136.4, 142.2, (143.1), (146.8), 149.9, (159.0), 159.3, 170.2, (172.9). Signals

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for the minor rotamer is given in the parentheses. IR (cm^{-1}) 1637, 1402, 1027; HRMS (ES^+) calcd for $C_{26}H_{23}N_2O_2$ $(M + H)^+$ 395.1760, found 395.1763.

One-Pot Protocol for the Synthesis of Benzoindolines 13a, 13c, and 13e and Pyrroloquinoline 15a (Conditions G, Table 1). Ethylene was bubbled for 5 min through the solutions of enynes **5a**, **5c**, **5e**, and **7a** (1.0 equiv, 0.08−0.18 mmol) in toluene (3−4 mL) in a 25 mL two-neck round-bottom flask fitted with a reflux condenser. Grubbs I catalyst (0.1 equiv, 0.008−0.018 mmol) was added as a solid, and the reaction mixtures were stirred at 85 °C under ethylene atmosphere for 2 h, cooled to rt, and purged with argon for 10 min. $Pd(OAc)_2$ (0.1 equiv, 0.008−0.018 mmol), PPh_3 (0.2 equiv, 0.017−0.037 mmol), and Cs_2CO_3 (2.0 equiv, 0.17−0.37 mmol) were added as solids. The reaction mixtures were stirred at 120 °C for 15 h and cooled to rt. Upon evaporation of toluene the crude mixtures were loaded on silica columns and were purified by flash chromatography over silica eluting with EtOAc/hexane mixtures to afford pure benzoindolines **13a**, **13c**, **13e**, and pyrroloquinoline **15a**.

*N-Benzoyl-4-phenyl-2,3-dihydro-1H-benzo[g]indole (**13a**).* Treatment of enyne **5a** (0.08 g, 0.18 mmol) in toluene (4 mL) with Grubbs I catalyst (0.015 g, 0.018 mmol), $Pd(OAc)_2$ (0.004 g, 0.018 mmol), PPh_3 (0.012 g, 0.03 mmol), and Cs_2CO_3 (0.097 g, 0.37 mmol) according to the general procedure described above followed by flash chromatography over silica eluting with EtOAc/hexane (1:9) afforded pure benzoindoline **13a** (0.045 g, 69% yield) as a white solid.

*N-Benzoyl-8-fluoro-4-phenyl-2,3-dihydro-1H-benzo[g]indole (**13c**).* Treatment of enyne **5c** (0.037 g, 0.08 mmol) in toluene (4 mL) with Grubbs I catalyst (0.007 g, 0.008 mmol), $Pd(OAc)_2$ (0.002 g, 0.008 mmol), PPh_3 (0.005 g, 0.017 mmol), and Cs_2CO_3 (0.055 g, 0.17 mmol) according to the general procedure described above followed by flash chromatography over silica eluting with EtOAc/hexane (1:9) afforded pure benzoindoline **13c** (0.019 g, 61% yield) as a heavy oil.

*N-Benzoyl-4-(4-methoxyphenyl)-2,3-dihydro-1H-benzo[g]indole (**13e**).* Treatment of enyne **5e** (0.04 g, 0.087 mmol) in toluene (4 mL) with Grubbs I catalyst (0.008 g, 0.009 mmol) $Pd(OAc)_2$ (0.002 g, 0.009 mmol), PPh_3 (0.005 g, 0.017 mmol) and Cs_2CO_3 (0.055 g, 0.17 mmol) according to the general procedure described above, followed by flash chromatography over silica eluting with EtOAc/hexane (1:4) afforded pure benzoindoline **13e** (0.021 g, 64% yield) as a colorless oil.

*N-Benzoyl-4-phenyl-2,3-dihydro-1H-pyrrolo[2,3-f]quinoline (**15a**).* Treatment of enyne **7a** (0.051 g, 0.12 mmol) in toluene (4 mL) with Grubbs I catalyst (0.01 g, 0.012 mmol), $Pd(OAc)_2$ (0.003 g, 0.012 mmol), PPh_3 (0.009 g, 0.024 mmol), and Cs_2CO_3 (0.078 g, 0.24 mmol) according to the general procedure described above followed by flash chromatography over silica eluting with EtOAc/hexane (2:3) afforded pure benzoindoline **15a** (0.03 g, 71% yield) as a colorless oil.

One-Pot Protocol for the Synthesis of Indenopyridines 14a, 14c, and 14e and Phenanthrolines 16a and 16b (Conditions H, Table 1). Ethylene was bubbled for 5 min through the solutions of enynes **6a**, **6c**, **6e**, **8a**, and **8b** (1 equiv, 0.07−0.20 mmol) in toluene (3−10 mL) in a 25 mL two-neck round-bottom flask fitted with a reflux condenser. Grubbs II catalyst (0.1 equiv, 0.007−0.02 mmol) was added as a solid, and the reaction mixtures were stirred at 85 °C under ethylene atmosphere for 8 h, cooled to rt, and purged with argon for 10 min. $Pd(OAc)_2$ (0.1 equiv, 0.007−0.02 mmol), PPh_3 (0.2 equiv, 0.014−0.04 mmol), and Cs_2CO_3 (2.0 equiv, 0.14−0.46 mmol) were added as solids. The reaction mixtures were stirred at 120 °C for 15 h and cooled to rt. Upon evaporation of toluene, the crude mixtures were purified by flash chromatography eluting with EtOAc/hexane mixtures to afford indenopyridines **14a**, **14c**, and **14e** and phenanthrolines **16a** and **16b**.

(4aR,5aR*,9bS*)-N-Benzoyl-5a-phenyl-2,5,5a,9b-tetrahydro-1H-cyclopropa[2,3]indeno[1,2-b]pyridine (**14a**).* Treatment of enyne **6a** (0.103 g, 0.20 mmol) in toluene (10 mL) with Grubbs II catalyst (0.02 g, 0.02 mmol), $Pd(OAc)_2$ (0.0052 g, 0.02 mmol), PPh_3 (0.015 g, 0.04 mmol), and Cs_2CO_3 (0.122 g, 0.46 mmol) according to the general procedure described above followed by flash chromatography over silica eluting with EtOAc/hexane (1:8) afforded indenopyridine **14a** (0.063 g, 75%) as a white fluffy solid and benzoquinoline **17** (0.001 g, 12%) as a white solid.

(4aR,5aR*,9bS*)-N-Benzoyl-8-fluoro-5a-phenyl-2,5,5a,9b-tetrahydro-1H-cyclopropa[2,3]indeno[1,2-b]pyridine (**14c**).* Treatment of enyne **6c** (0.041 g, 0.09 mmol) in toluene (4 mL) with Grubbs II catalyst (0.008 g, 0.009 mmol) $Pd(OAc)_2$ (0.002 g, 0.009 mmol), PPh_3 (0.007 g, 0.018 mmol), and Cs_2CO_3 (0.059 g, 0.18 mmol) according to the general procedure described above, followed by flash chromatography over silica eluting with EtOAc/hexane (1:4) afforded indenopyridine **14c** (0.023 g, 69%) as a colorless heavy oil.

(4aR,5aR*,9bS*)-N-Benzoyl-5a-(4-methoxyphenyl)-2,5,5a,9b-tetrahydro-1H-cyclopropa[2,3]indeno[1,2-b]pyridine (**14e**).* Treatment of enyne **6e** (0.032 g, 0.07 mmol) in toluene (3 mL) with Grubbs II catalyst (0.006 g, 0.007 mmol), $Pd(OAc)_2$ (0.002 g, 0.007 mmol), PPh_3 (0.005 g, 0.014 mmol), and Cs_2CO_3 (0.046 g, 0.14 mmol) according to the general procedure described above followed by flash chromatography over silica eluting with EtOAc/hexane (1:8) afforded indenopyridine **14e** (0.019 g, 70%) as a colorless oil.

*N-Benzoyl-5-phenyl-1,2,3,4-tetrahydro-1,7-phenanthroline (**16a**).* Treatment of enyne **8a** (0.043 g, 0.1 mmol) in toluene (3 mL) with Grubbs II catalyst (0.008 g, 0.01 mmol), $Pd(OAc)_2$ (0.002 g, 0.01 mmol), PPh_3 (0.007 g, 0.02 mmol), and Cs_2CO_3 (0.065 g, 0.2 mmol) according to the general procedure described above followed by flash chromatography over silica eluting with EtOAc/hexane (2:3) afforded phenanthroline **16a** (0.022 g, 61%) as a light yellow powder along with diene **12a** (0.011 g, 25%).

*N-Benzoyl-5-(4-fluorophenyl)-1,2,3,4-tetrahydro-1,7-phenanthroline (**16b**).* Treatment of enyne **8b** (0.034 g, 0.07 mmol) in toluene (3 mL) with Grubbs II catalyst (0.006 g, 0.007 mmol), $Pd(OAc)_2$ (0.002 g, 0.007 mmol), PPh_3 (0.005 g, 0.014 mmol), and Cs_2CO_3 (0.046 g, 0.14 mmol) according to the general procedure described above followed by flash chromatography over silica eluting with EtOAc/Hexane (2:3) afforded phenanthroline **16b** (0.015 g, 56%) as a colorless oil along with diene **12b** (0.01g, 29%).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^1H and ^{13}C NMR spectra for all new compounds prepared in this study, 2D NMR data for compounds **3** and **4**, the variable-temperature ^1H NMR spectra for compounds **5a**, **6a**, **9a**, and **16a**, quantitative GC−MS chromatograms with MS spectra for compounds **15a**,**b**, **16a**−**c**, and thermal ellipsoid diagrams for compounds **13a**, **14b**, **16a**, and **17**. This material is available free of charge via Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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