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Redox-Neutral Cobalt(III)-Catalyzed C−H Activation/Annulation of α,β-Unsaturated Oxime Ether with Alkyne: One-Step Access to Multisubstituted Pyridine

Smruti Ranjan Mohanty, Bedadyuti Vedvyas Pati, Shyam Kumar Banjare, Gopal Krushna Das Adhikari, and Ponneri Chandrababu Ravikumar*

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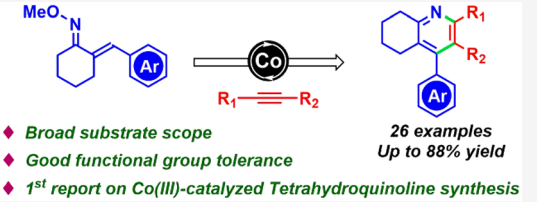
ABSTRACT: A redox neutral Co(III)-catalyzed annulation of α,β-unsaturated oxime ether with alkyne has been reported. Multisubstituted pyridines were synthesized in good yields without the use of any heavy metal oxidants. The developed methodology tolerates a variety of functional groups. Notably, this transformation has been applied to the late-stage modification of the bioactive molecule dehydropregnenolone.



INTRODUCTION

The transition-metal-catalyzed functionalization of C−H bonds is considered an atom economic process in organic synthesis.[1] Among all of the heterocycles, nitrogen-containing heterocycles hold significance in organic synthesis because of their presence in a wide range of natural products, pharmaceuticals, and agrochemicals.[2] Hence, the development of efficient synthetic methodology to obtain those molecules has received extensive importance over the years.

Multisubstituted pyridine (tetrahydroquinoline) is an important structural skeleton among all of the nitrogen-containing heterocycles and biologically active natural products, such as haplophyllidine[3] and megistosarcimine.[4] Moreover, molecules that contain the tetrahydroquinoline moiety have been found to show biological activities such as anti-HIV,[5] anticancer,[6] and antifungal[7] properties (Figure 1). Therefore, significant efforts have been dedicated to the development of methodologies for the synthesis of tetrahydroquinoline using mainly second and third row transition metal catalysts (Rh, Ir, and Pd).[8,9] However, these catalytic systems are associated with several undesirable factors: (i) the use of an expensive metal catalyst, (ii) harsh reaction conditions, and (iii) low functional group tolerance. Hence, in order to tackle the above-mentioned challenges, efficient and benign reaction conditions are of paramount importance.

So far, there is no report for the synthesis of tetrahydroquinoline by using a cobalt catalyst. Previously, Matsunaga,[10] Ackermann,[11] Sundararaju,[12] and Cheng[13] have reported the synthesis of isoquinoline from oxime and alkyne by using the Cp*Co(III) catalyst (Scheme 1a). However, all of the reports are based on arene C−H bond activation. The activation of nonaromatic vinylic C−H bonds is challenging, and it is less explored.[14] Yoshikai and Petit groups have accomplished vinylic C−H activation of α,β-unsaturated

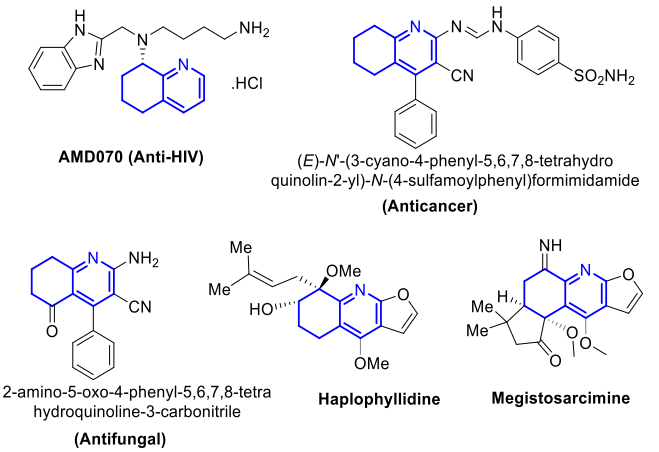


Figure 1. Representative examples of natural products and a bioactive molecule-containing tetrahydroquinoline moiety.

imines using a low valent cobalt catalyst and subsequent annulation with alkynes for the synthesis of dihydropyridines (Scheme 1b,c).[15,16] However, these method suffers from some drawbacks: (a) the metal complex that is highly sensitive to air, (b) the requirement of high temperatures in one case, which goes against the introduction of sensitive groups, and (c) the necessity of an extra step to access aromatic pyridine derivatives.[17] Therefore, direct synthesis of multisubstituted

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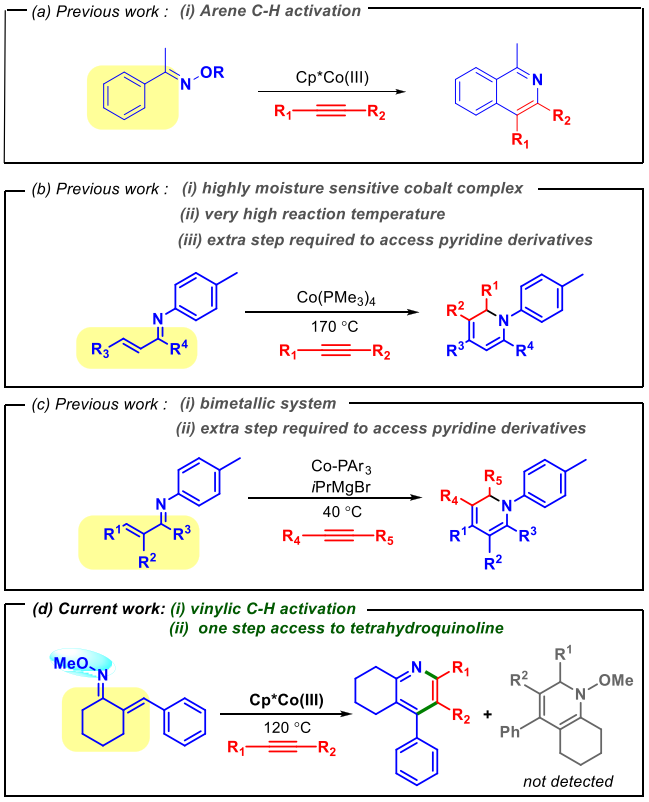
Scheme 1. Comparison with Previous Work



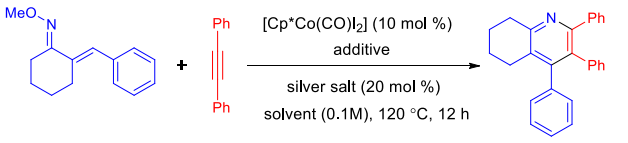
pyridine via olefinic C−H activation followed by annulations is still an unresolved problem.

Although there are a handful of reports on Co(III)-catalyzed olefinic C−H activation,[15,16,18−22,25] to the best of our knowledge, there is no report of Co(III)-catalyzed annulations of α,β-unsaturated oxime ether with alkyne to synthesize multisubstituted pyridine under redox neutral conditions (Scheme 1d). Hence, it is highly desirable to develop an efficient methodology for annulations of α,β-unsaturated oxime ether with alkyne using a cobalt catalyst.

RESULTS AND DISCUSSION

To achieve this goal, we initiated our optimization by taking (1*E*,2*E*)-2-benzylidenecyclohexanone *o*-methyl oxime ether **1a** as a model substrate and diphenylacetylene **2a** as a coupling partner, [CoCp*(CO)I_2] (10 mol %) as a catalyst, and $AgSbF_6$ (20 mol %) as an activator along with 1-adamantanecarboxylic acid (20 mol %) as an additive in tetrahydrofuran (THF). Unfortunately, we did not get any product (Table 1, entry 1). Keeping all other reaction conditions constant, we varied the solvent to dioxane and ethanol (Table 1, entries 2 and 3); unfortunately, we were again met with failure. Gratifyingly, when we performed the reaction with HFIP as a solvent, we obtained the desired product **3aa** in 9% yield (Table 1, entry 4). In order to improve the yield further, we decided to change the additive to trifluoroacetic acid (TFA), but we obtained only 7% yield of **3aa** (entry 5). Since acetates are known to promote the C−H activation reaction, we decided to explore various acetate-assisted bases such as NaOAc, LiOAc, AgOAc, CsOAc, and KOAc (Table 1, entries 6−10). Among the examined additives, KOAc was found to be the most effective in producing the desired annulated product **3aa** in 61% (Table 1, entry 10). For further improvement of the product yield, we

Table 1. Optimization of Reaction Conditions[a]



entry	silver salt (20 mol %)	additive (20 mol %)	solvent (0.1 M)	yield (%)[b]
1	$AgSbF_6$	1-AdCOOH	THF	nd
2	$AgSbF_6$	1-AdCOOH	1,4-dioxane	nd
3	$AgSbF_6$	1-AdCOOH	EtOH	nd
4	$AgSbF_6$	1-AdCOOH	HFIP	9
5	$AgSbF_6$	TFA	HFIP	7
6	$AgSbF_6$	NaOAc	HFIP	31
7	$AgSbF_6$	LiOAc	HFIP	34
8	$AgSbF_6$	AgOAc	HFIP	35
9	$AgSbF_6$	CsOAc	HFIP	37
10	$AgSbF_6$	KOAc	HFIP	61
11	$AgBF_4$	KOAc	HFIP	47
12	AgOTf	KOAc	HFIP	58
13	$AgNTf_2$	KOAc	HFIP	75
14	$AgNTf_2$	KOAc	HFIP	88[c]
15	$AgNTf_2$	KOAc	HFIP	53[d]
16	$AgNTf_2$	KOAc	HFIP	69[e]
17	$AgNTf_2$	KOAc	HFIP	nd[f]
18	$AgNTf_2$		HFIP	trace[g]
19		KOAc	HFIP	79[h]

[a]Reaction conditions: **1a** (0.112 mmol), **2a** (0.056 mmol), [Cp*Co(CO)I_2] (10 mol %), silver salt (20 mol %), additive (100 mol %), solvent (0.1 M), 120 °C for 12 h. [b]Isolated yield. [c]1 equiv of additive. [d]Reaction at 60 °C. [e]5 mol % of [Cp*Co(CO)I_2]. [f]Absence of cobalt catalyst. [g]Absence of additive. [h]Absence of $AgNTf_2$; nd = not detected.

screened different silver additives such as $AgBF_4$, AgOTf, and $AgNTf_2$ (Table 1, entries 11−13). Delightfully, $AgNTf_2$ produced the best yield of **3aa**, 75% (Table 1, entry 13). Further,when we increased the base (KOAc) equivalence from 20 mol % to 1 equiv, we obtained 88% of the desired product **3aa** (Table 1, entry 14). It was found that lower temperature and reduced catalyst loading were found to be ineffective to afford the annulation product in better yields (entries 15 and 16).

We performed a few control experiments to understand the influence of catalyst, silver additive, and base. In the absence of catalyst, no reaction could occur (Table 1, entry 17); in the absence of additive only, a trace amount of product was formed (Table 1, entry 18). Whereas without a silver additive, a 79% yield of **3aa** was obtained (Table 1, entry 19).

With the optimized reaction conditions in hand, the generality of the reaction was examined (Scheme 2). As seen before, unsubstituted oxime ether gave the desired product in excellent yield (88%). The structure of **3aa** was confirmed by single-crystal X-ray analysis. *para*-Halogen-substituted α,β-unsaturated oxime ethers (−F, −Br, −I) were found to be compatible and produced the desired product in good to excellent yields (Scheme 2, **3ba**, **3ca**, **3da**). The oxime ether with the electron-donating group at the *para*-position (−Me) furnished a good yield of the corresponding product (Scheme 2, **3ea**), whereas the electron-withdrawing group ($-NO_2$) at the *para*-position gave only 23% yield of the products (Scheme 2, **3fa**). Heterocycle-substituted oxime ether underwent

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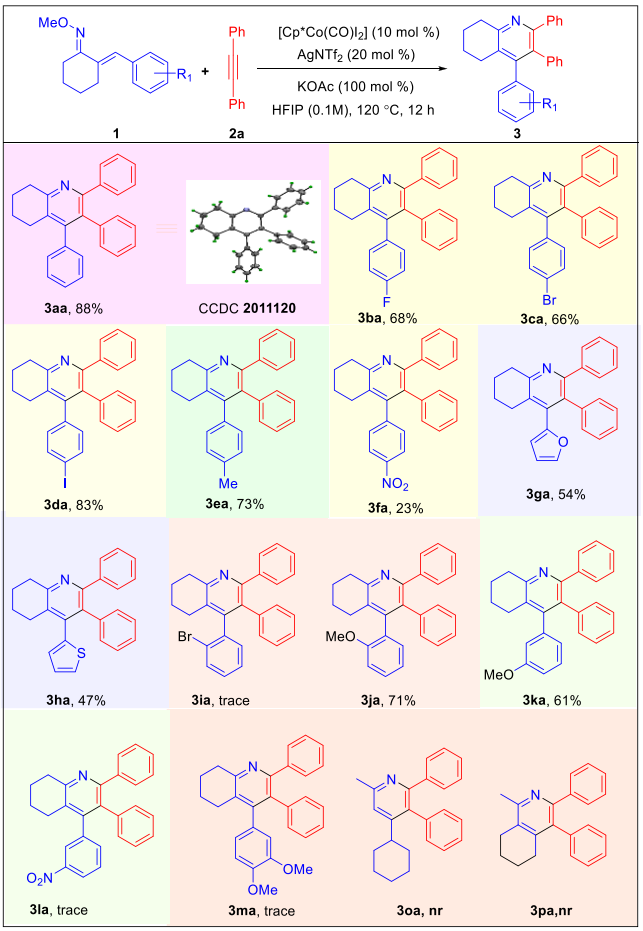
Scheme 2. Scope of α,β-Unsaturated Oxime Ethers

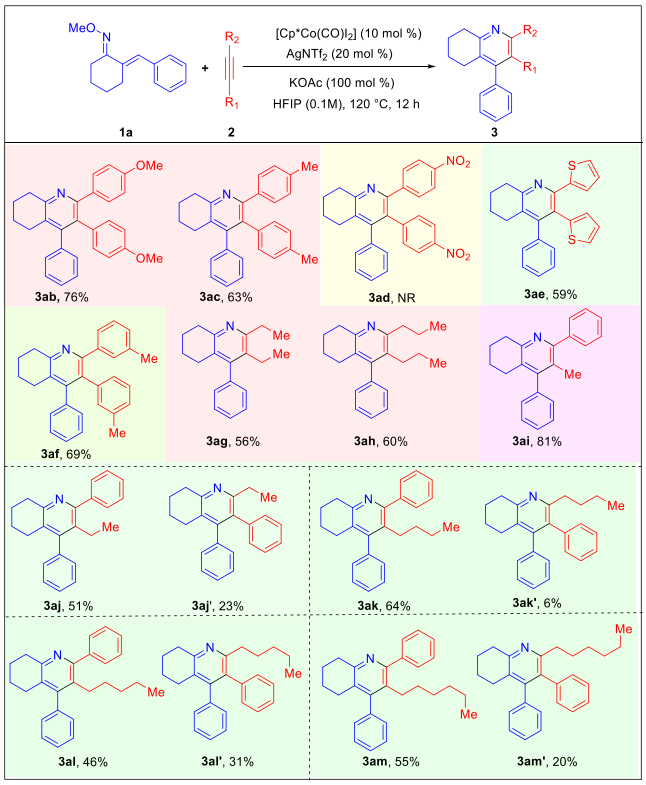


[a]Reaction conditions: **1a** (0.112 mmol), **2a** (0.056 mmol), [Cp*Co(CO)I_2] (10 mol %), $AgNTf_2$ (20 mol %), KOAc (100 mol %), HFIP (0.1 M), 120 °C for 12 h.

cyclization, producing a moderate yield of the products (Scheme 2, **3ga**, **3ha**). A trace amount of product was observed with *ortho*-Br-substituted oxime ether; it might be due to steric hindrance of the bulky −Br group near the reaction site (Scheme 2, **3ia**). Notably, the −OMe group substituted at the *ortho*-position gave the desired product (Scheme 2, **3ja**) in 71% yield. With *meta*-substituted oxime ether (*meta*-OMe), the desired product was obtained in 61% yield (Scheme 2, **3ka**), whereas, with *meta*-NO_2-substituted oxime ether, only a trace amount of product was formed (Scheme 2, **3la**). Dimethoxy-substituted oxime ether also gave a trace amount of the product (Scheme 2, **3ma**). Whereas acyclic unsaturated oxime ether failed to give the desired product, it might be due to the flexibility of the C−C bond in acyclic unsaturated imine, which might be restricting the formation of the five-membered planar cobaltacycle in the C−H activation step (Scheme 2, **3oa**, **3pa**).

Next, to extend the generality of this methodology, we examined the reaction using different alkynes (Scheme 3). The alkynes with electron-donating groups such as −OMe and −Me at the para position furnished the corresponding annulations product in good yields (Scheme 3, **3ab**, **3ac**). Surprisingly diphenylacetylene with an electron-withdrawing group (*p*-NO_2) failed to produce the annulation product **3ad**. Notably, heteroaryl alkyne such as di(2-thiophenyl)ethyne

Scheme 3. Scope of Alkynes

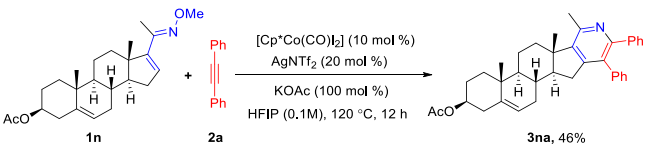


[a]Reaction conditions: **1a** (0.112 mmol), **2a** (0.056 mmol), [Cp*Co(CO)I_2] (10 mol %), $AgNTf_2$ (20 mol %), KOAc (100 mol %), HFIP (0.1 M), 120 °C for 12 h.

underwent cyclization in a good yield (Scheme 3, **3ae**). The *meta*-methyl substituted alkyne also gave an expected product in a good yield (Scheme 3, **3af**). Dialkyl-substituted alkynes such as 3-hexyne and 4-octyne gave the products in good yields (Scheme 3, **3ag**, **3ah**). Then, we turned our attention toward unsymmetrical aryl-alkyl alkynes. In the case of 1-phenel-1-propyne, we obtained a single isomer, where the aryl ring is oriented toward the nitrogen atom of tetrahydroquinoline (Scheme 3, **3ai**).[8,23] Other unsymmetrical alkynes such as 1-phenyl-1-butyne, 1-phenyl-1-hexyne, 1-phenyl-1-heptyne, and 1-phenyl-1-octyne smoothly gave the annulated product with good regioselectivity and good yields (Scheme 3, **3aj**−**3am**), wherein the aryl ring orienting toward the nitrogen atom of tetrahydroquinoline is the major product.[23] Formation of the major regio-isomeric product can be rationalized with the stabilization of intermediate **III** (Scheme 6) by the phenyl ring through π-interaction with the metal orbitals.

The scope of the developed annulation method has been extended to complex bioactive molecule dehydropregnenolone. To our delight, the desired annulated adduct was obtained in a moderate yield (Scheme 4, **3na**). These results

Scheme 4. Late-Stage Functionalization of Dehydropregnenolone



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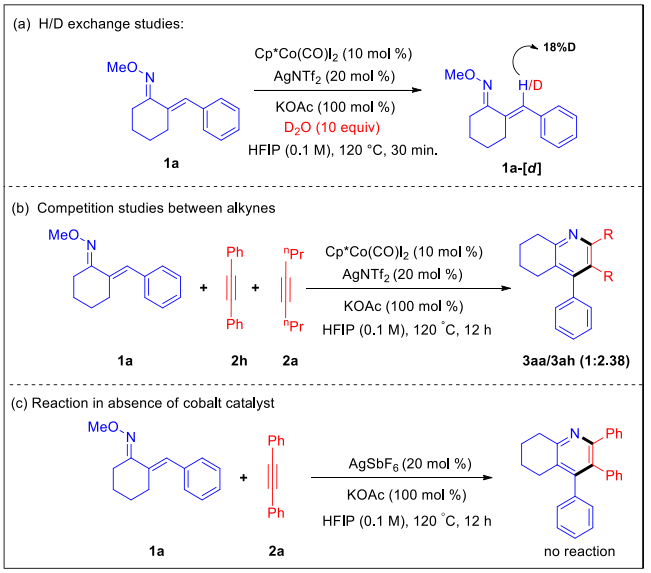
indicated that the annulations protocol developed may be useful for rapid generation of the derivatives of bioactive compounds. The synthetic applicability of this reaction in a larger scale was confirmed from a 1 mmol scale reaction, which gave **3aa** in a 66% yield.

In order to have better insight of the reaction mechanism, a few mechanistic experiments were performed. The deuterium labeling experiment of oxime ether **1a** with D_2O under the standard reaction condition showed 18% deuterium incorporation of the vinylic C-H of oxime ether **1a**, which indicates an acetate-assisted reversible cyclometalation pathway of the Co(III) catalyst (Scheme 5a).

Scheme 5. Competitive and Mechanistic Studies



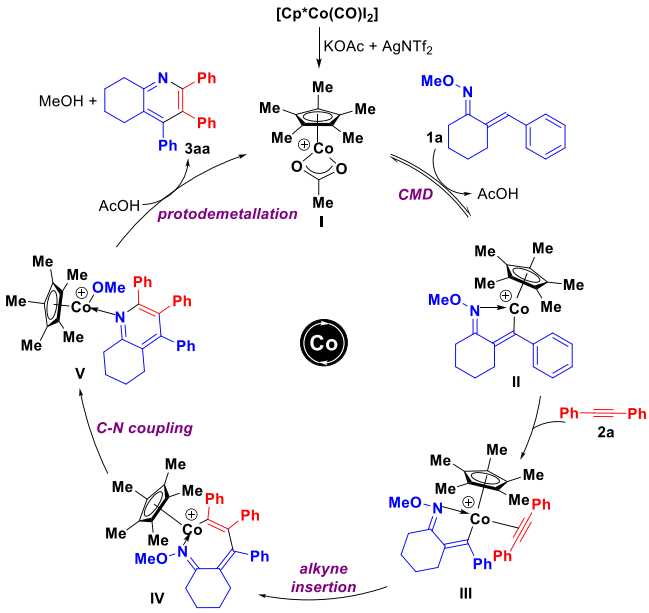
Further, an intermolecular competitive reaction between two different internal alkynes **2a** and **2h** with oxime ether **1a** resulted in **3aa**/**3ah** in a 1:2.38 ratio. The results of the above experiment indicate that the developed annulation protocol is favorable for the electron-rich alkyne (Scheme 5b). A control experiment was performed without a cobalt catalyst, but no product was observed, which confirms the vital role of the cobalt catalyst (Scheme 5c).

On the basis of the above mechanistic studies and previous literature reports,[24,25,12] we propose a plausible reaction mechanism (Scheme 6). Initially $[CoCp^*(CO)I_2]$ undergoes decarbonylation in the presence of $AgNTf_2$ and KOAc to give the cationic complex **I**. Co-ordination of olefinic oxime ether **1a** followed by reversible concerted cyclometalation deprotonation leads to cobaltacycle **II**. Coordination of alkyne **2a** to cobaltacycle **II** gives intermediate **III**; then, subsequent insertion of the alkyne into the Co−C bond of intermediate **III** affords a seven-membered cobaltacycle **IV**. The intermediate **IV** undergoes reductive elimination (C−N Coupling) followed by oxidative insertion of cobalt on to the weak N−O bond to give $[Cp^*Co(Pyridine)(OMe)]^+$. Finally, intermediate **V** undergoes protodemetalation to give the desired product **3aa** and the catalytically active species **I** and byproduct MeOH.

CONCLUSIONS

In conclusion, we have successfully developed an efficient strategy to access multisubstituted pyridines by Co(III)-

Scheme 6. Plausible Mechanism



catalyzed annulations of α,β-unsaturated oxime ether with alkyne. The importance of this reaction is the exclusive formation of multisubstituted pyridine. This methodology is applicable to a wide range of substrates and as well as compatible with a variety of functional group. This transformation has been applied to the late-stage functionalization of the bioactive molecule dehydropregnenolone.

EXPERIMENTAL SECTION

General Information.[26] Reactions were performed using a borosil-sealed tube vial under a N_2 atmosphere. Column chromatography was done by using 230−400 mesh silica gel of Acme synthetic chemicals company. A gradient elution was performed by using distilled petroleum ether and ethyl acetate. TLC plates were detected under UV light at 254 nm and vanillin. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker AV 400 MHz and Jeol ECZ-400 R spectrometers using $CDCl_3$ as the deuterated solvent.[27] Multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sept = septet, m = multiplet, dd = double of doublet, br = broad signal), integration, and coupling constants (J) in hertz (Hz). HRMS signal analysis was performed using a micro TOF Q-II mass spectrometer. Reagents and starting materials were purchased from Sigma-Aldrich, TCI, Avra, Spectrochem, and other commercially available sources, used without further purification unless otherwise noted. All aldol condensation derivatives,[28] imine derivative,[29] and alkyne derivatives[30] were prepared according to the reported literature procedure.

General Procedure A: The Synthesis of the Condensation Product.[28] The condensation reactions were performed according to a literature procedure.[28] Cycloalkanone (326 mmol, 2.91 equiv) was added to a solution of NaOH (6.52 g, 163 mmol, 1.45 equiv) in water (750 mL, 0.149 M) and stirred under ice bath for 5 min, followed by the addition of benzaldehyde (11.88 g, 112 mmol, 1.0 equiv). After 3 days of stirring, the reaction mixture was neutralized with glacial acetic acid. The product was extracted with toluene (3 × 200 mL) and purified by vacuum distillation, affording both the ketones as bright yellow solids. The analytical data of these synthesized compounds were well matched with known literature data.

General Procedure B: The Synthesis of (1E,2E)-2-Benzylidenecyclohexanone o-Methyl Oxime Ether.[29] (1E,2E)-2-Benzylidenecyclohexanone *o*-methyl oxime ether was prepared according to a previously reported procedure. α,β-Unsaturated ketone or aldehyde derivatives (5 mmol, 1.0 equiv) were taken in a 50 mL round-bottom

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flask. Then a mixture of water (10 mL, 0.5 M) and ethanol (5 mL, 1 M) was added to it. Further, alkoxylamine hydrochloride (15 mmol, 3.0 equiv) and sodium acetate (25 mmol, 5.0 equiv) were added to the suspension, respectively. The resulting suspension was refluxed at 80 °C for 1−4 h. The progress of the reaction was regularly checked by TLC. After complete consumption of the starting materials, additional water was added to the reaction mixture and extracted with ethyl acetate. The organic phase was dried over anhydrous sodium sulfate and concentrated under reduced pressure. Oxime ether **1a** was purified using silica gel flash column chromatography in 60−95% yield [eluent: hexane−ethyl acetate mixture (98:2 to 95:5)].

General Procedure C: The Synthesis of 2,3,4-Triphenyl-5,6,7,8-tetrahydroquinoline. An oven-dried Schlenk tube was equipped with a magnetic stir bar was charged with [Cp*Co(CO)I_2] (0.02 mmol, 0.1 equiv) and potassium acetate (0.2 mmol, 100 mol %). Subsequently, *o*-methyl oxime ether **1a** (0.4 mmol, 2.0 equiv), alkyne **2** (0.2 mmol, 1.0 equiv), and $AgNTf_2$ (0.04 mmol, 0.2 equiv) followed by HFIP (2 mL, 0.1 M) were added under a N_2 atmosphere. The reaction mixture was vigorously stirred (750 rpm) in a preheated aluminum block at 120 °C for 12 h. After 12 h (completion of the reaction as monitored by TLC analysis), the reaction mixture was cooled to room temperature and diluted with dichloromethane and passed through a short pad of Celite; the solvent was evaporated under reduced pressure, and the residue was purified by column chromatography using a 1:9 mixture of EtOAc/hexane on silica gel to give pure product **3**.

General Procedure D: Cobalt-Catalyzed Annulation Reaction between Olefinic Imine with Alkyne in a 1 mmol Scale. An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with [Cp*Co(CO)I_2] (0.02 mmol, 0.1 equiv) and potassium acetate (1.0 mmol, 100 mol %). Subsequently, *o*-methyl oxime ether **1a** (2.0 mmol, 2.0 equiv), alkyne **2a** (1.0 mmol, 1.0 equiv), and $AgNTf_2$ (0.2 mmol, 0.2 equiv) followed by HFIP (10 mL, 0.1 M) were added under a N_2 atmosphere. The reaction mixture was vigorously stirred (750 rpm) in a preheated aluminum block at 120 °C for 12 h. After 12 h (completion of reaction as monitored by TLC analysis), the reaction mixture was cooled to room temperature and diluted with dichloromethane and passed through a short pad of Celite; the solvent was evaporated under reduced pressure, and the residue was purified by column chromatography using a 1:9 mixture of EtOAc/hexane on silica gel to give pure product **3aa** (238 mg) with 66% yield.

General Procedure E: Deuterium Labeling Experiments. An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with [Cp*Co(CO)I_2] (0.02 mmol, 0.1 equiv) and potassium acetate (0.2 mmol, 100 mol %). Subsequently, *o*-methyl oxime ether **1a** (0.4 mmol, 2.0 equiv) and D_2O (2 mmol, 10.0 equiv), and $AgNTf_2$ (0.04 mmol, 0.2 equiv) followed by HFIP (2 mL, 0.1 M) were added under a N_2 atmosphere. The reaction mixture was vigorously stirred (750 rpm) in a preheated aluminum block at 120 °C for 30 min. After 30 min, the reaction mixture was cooled to room temperature, diluted with dichloromethane, and passed through a short pad of Celite; the solvent was evaporated under reduced pressure. The 18% H/D exchange was calculated by ^{1}H NMR analysis of the crude mixture.

General Procedure F: Competitive Experiment with Alkynes. An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with [Cp*Co(CO)I_2] (0.02 mmol, 0.1 equiv) and potassium acetate (0.2 mmol, 100 mol %). Subsequently, *o*-methyl oxime ether **1a** (0.4 mmol, 2.0 equiv), diphenylacetylene **2a** (0.2 mmol, 1.0 equiv) and 4-octyne **2h** (0.2 mmol, 1.0 equiv), and $AgNTf_2$ (0.04 mmol, 0.2 equiv) followed by HFIP (2 mL, 0.1 M) were added under a N_2 atmosphere. The reaction mixture was vigorously stirred (750 rpm) in a preheated aluminum block at 120 °C for 12 h. After 12 h (completion of reaction as monitored by TLC analysis), the reaction mixture was cooled to room temperature, diluted with dichloromethane, and passed through a short pad of Celite; the solvent was evaporated under reduced pressure, and the residue purified by column chromatography using a 1:9 mixture of EtOAc/hexane on silica gel afforded tetrahydroquinoline **3aa** and tetrahydroquinoline **3ah** with a combined yield of 75%. The ratio of **3aa**/**3ah** (1:2.38) was calculated using NMR.

Experimental Characterization Data for Olefinic Imines. *(1E,2E)-2-Benzylidenecyclohexanone o-Methyl Oxime (**1a**).* The compound was prepared according to general procedure B. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh) giving **1a** (93 mg) in 80% yield. Physical state: yellow liquid. R_f: 0.55 (5% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26−7.21 (m, 4H), 7.16−7.12 (m, 1H), 6.85 (s, 1H), 3.86 (s, 3H), 2.58 (t, J = 6.0 Hz, 2H), 2.51 (t, J = 6.4 Hz, 2H), 1.64−1.50 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.1, 137.3, 135.2, 130.1, 128.4, 127.8, 127.3, 62.0, 29.3, 26.0, 25.3, 23.7. IR (KBr, cm^{-1}): 2933, 1457, 1337, 1048. HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{14}H_{18}NO$, 216.1383; found, 216.1363.

*(1E,2E)-2-(4-Fluorobenzylidene)cyclohexanone o-Methyl Oxime (**1b**).* The compound was prepared according to general procedure B. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh) giving **1b** (78 mg) in 68% yield. Physical state: yellow liquid. R_f: 0.5 (5% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29−7.25 (m, 2H), 7.03−6.99 (m, 2H), 6.88 (s, 1H), 3.94 (s, 3H), 2.64−2.57 (m, 4H), 1.73−1.59 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.0 (d, J_{C-F}= 245 Hz), 159.9, 135.0 (d, J_{C-F} = 2 Hz), 133.3 (d, J_{C-F} = 4 Hz), 131.6 (d, J_{C-F}= 9 Hz), 126.6, 115.3 (d, J_{C-F} = 22 Hz), 62.0, 29.2, 25.9, 25.2, 23.7. IR (KBr, cm^{-1}): 2935, 1600, 1505, 1223, 1156, 1048. HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{14}H_{17}FNO$, 234.1289; found, 234.1301.

*(1E,2E)-2-(4-Bromobenzylidene)cyclohexanone o-Methyl Oxime (**1c**).* The compound was prepared according to general procedure B. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh) giving **1c** (92 mg) in 83% yield. Physical state: white solid. Mp: 61−63 °C. R_f: 0.5 (5% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 6.85 (s, 1H), 3.94 (s, 3H), 2.63−2.57 (m, 4H), 1.72−1.59 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.8, 136.2, 135.9, 131.6, 131.5, 126.5, 121.3, 62.0, 29.3, 25.9, 25.2, 23.7. IR (KBr, cm^{-1}): 2933, 1485, 1048, 870. HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{14}H_{17}BrNO$, 294.0488; found, 294.0507.

*(1E,2E)-2-(4-Iodobenzylidene)cyclohexanone o-Methyl Oxime (**1d**).* The compound was prepared according to general procedure B. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh) giving **1d** (80 mg) in 74% yield. Physical state: colorless oil. R_f: 0.8 (5% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66−7.63 (m, 2H), 7.03 (d, J = 7.6 Hz, 2H), 6.83 (s, 1H), 3.94 (s, 3H), 2.63−2.56 (m, 4H), 1.68−1.56 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.7, 137.5, 136.7, 136.0, 131.8, 126.6, 93.0, 62.1, 29.4, 26.0, 25.2, 23.7. IR (KBr, cm^{-1}): 2932, 1482, 1048, 508. HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{14}H_{17}INO$, 342.0349; found, 342.0334.

*(1E,2E)-2-(4-Methylbenzylidene)cyclohexanone o-Methyl Oxime (**1e**).* The compound was prepared according to general procedure B. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh) giving **1e** (88 mg) in 77% yield. Physical state: white solid. Mp: 58−60 °C. R_f: 0.55 (5% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 6.90 (s, 1H), 3.94 (s, 3H), 2.66 (td, J = 6.8, 1.6 Hz, 2H), 2.58 (t, J = 6.4 Hz, 2H), 2.34 (s, 3H), 1.72−1.58 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.2, 137.2, 134.4, 134.4, 130.0, 129.1, 127.8, 62.0, 29.4, 26.0, 25.2, 23.7, 21.6. IR (KBr, cm^{-1}): 2934, 1510, 1449, 1049. HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{15}H_{20}NO$, 230.1539; found, 230.1561.

*(1E,2E)-2-(4-Nitrobenzylidene)cyclohexanone o-Methyl Oxime (**1f**).* The compound was prepared according to general procedure B. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh) giving **1f** (69 mg) in 61% yield. Physical state: yellow solid. Mp: 92−94 °C. R_f: 0.25 (5% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21−8.17 (m, 2H), 7.47−7.43 (m, 2H), 6.96 (s, 1H), 3.96 (s, 3H), 2.66 (td, J = 6.4, 2.0 Hz, 2H), 2.61 (t, J = 6.8 Hz, 2H), 1.74−1.63 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.2, 146.7, 144.0, 139.0, 130.6, 125.4, 123.8, 62.2, 29.6, 25.9, 25.1, 23.5. IR (KBr, cm^{-1}): 2936, 1594, 1515, 1343,

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1047. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{17}N_2O_3$, 261.1234; found, 261.1241.

*(1E,2E)-2-(Furan-2-yl-methylene)cyclohexanone o-Methyl Oxime (**1g**).* The compound was prepared according to general procedure B. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh) giving **1g** (94 mg) in 81% yield. Physical state: yellow liquid. R_f: 0.5 (5% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, J = 1.6 Hz, 1H), 6.84 (t, J = 2.0 Hz, 1H), 6.42−6.41 (m, 1H), 6.37 (d, J = 3.2 Hz, 1H), 3.93 (s, 3H), 2.78−2.74 (m, 2H), 2.58−2.54 (m, 2H), 1.68−1.65 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 158.9, 153.5, 142.5, 132.2, 115.5, 111.8, 111.7, 62.1, 29.3, 25.9, 24.1, 23.0. IR (KBr, cm^{-1}): 2935, 1463, 1435,1049. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{12}H_{16}NO_2$, 206.1176; found, 206.1190.

*(1E,2E)-2-(Thiophen-2-yl-methylene)cyclohexanone o-Methyl Oxime (**1h**).* The compound was prepared according to general procedure B. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh) giving **1h** (86 mg) in 75% yield. Physical state: yellow liquid. R_f: 0.5 (5% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, J = 5.2 Hz, 1H), 7.21 (t, J = 2.0 Hz, 1H), 7.12 (d, J = 3.6 Hz, 1H), 7.04 (dd, J = 5.2, 3.6 Hz, 1H), 3.94 (s, 3H), 2.72 (m, 2H), 2.57 (t, J = 6.0 Hz, 2H), 1.70−1.66 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 159.2, 140.8, 131.9, 129.5, 127.3, 126.6, 120.7, 62.1, 29.4, 25.9, 24.0, 22.8. IR (KBr, cm^{-1}): 2933, 1615, 1461, 1421, 1048. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{12}H_{16}NOS$, 222.0947; found, 222.0964.

*(1E,2E)-2-(2-Bromobenzylidene)cyclohexanone o-Methyl Oxime (**1i**).* The compound was prepared according to general procedure B. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh) giving **1i** (80 mg) in 72% yield. Physical state: white solid. Mp: 53−55 °C. R_f: 0.45 (5% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59−7.57 (m, 1H), 7.26−7.25 (m, 2H), 7.13−7.08 (m, 1H), 6.87 (s, 1H), 3.96 (s, 3H), 2.62 (t, J = 6.8 Hz, 2H), 2.49 (td, J = 6.8, 1.6 Hz, 2H), 1.74−1.68 (m, 2H), 1.64−1.58 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 159.5, 137.3, 136.5, 132.9, 131.5, 128.9, 127.0, 126.9, 125.3, 62.0, 29.5, 26.0, 25.5, 24.0. IR (KBr, cm^{-1}): 2933, 1463, 1048, 1024, 746. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{17}BrNO$, 294.0488; found, 294.0496.

*(1E,2E)-2-(2-Methoxybenzylidene)cyclohexanone o-Methyl Oxime (**1j**).* The compound was prepared according to general procedure B. The crude reaction mixture was purified by column chromatography using silica gel (230- 400 mesh) giving **1j** (76 mg) in 66% yield. Physical state: yellow liquid. R_f: 0.3 (5% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28−7.24 (m, 2H), 6.88−6.85 (m, 3H), 3.94 (s, 3H), 3.81 (s, 3H), 2.66 (td, J = 6.4, 1.6 Hz, 2H), 2.58 (t, J = 6.8 Hz, 2H), 1.70−1.60 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.3, 158.9, 133.4, 131.5, 130.0, 128.7, 127.5, 113.8, 113.8, 61.9, 55.5, 29.3, 26.0, 25.2, 23.7. IR (KBr, cm^{-1}): 2934, 1604, 1463, 1177, 1048. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{20}NO_2$, 246.1489; found, 246.1501.

*(1E,2E)-2-(3-Methoxybenzylidene)cyclohexanone o-Methyl Oxime (**1k**).* The compound was prepared according to general procedure B. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh) giving **1k** (58 mg) in 51% yield. Physical state: colorless oil. R_f: 0.4 (5% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (t, J = 7.6 Hz, 1H), 6.83 (d, J = 5.6 Hz, 2H), 6.77 (s, 1H), 6.71 (dd, J = 8.0, 2.4 Hz, 1H), 3.86 (s, 3H), 3.71 (s, 3H), 2.60−2.57 (m, 2H), 2.51 (t, J = 6.4 Hz, 2H), 1.64−1.51 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 159.9, 159.6, 138.6, 135.4, 129.3, 127.6, 122.6, 115.5, 112.9, 61.9, 55.5, 29.4, 25.9, 25.2, 23.7. IR (KBr, cm^{-1}): 2934, 1596, 1487, 1157, 1048. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{20}NO_2$, 246.1489; found, 246.1508.

*(1E,2E)-2-(3-Nitrobenzylidene)cyclohexanone o-Methyl Oxime (**1l**).* The compound was prepared according to general procedure B. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh) giving **1l** (71 mg) in 63% yield. Physical state: yellow liquid. R_f: 0.25 (5% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.99 (d, J = 8.4 Hz, 1H), 7.53 (d, J = 7.6 Hz, 1H), 7.41 (t, J = 8 Hz, 1H), 6.86 (s, 1H), 3.86 (s, 3H), 2.57 (t, J = 5.6 Hz, 2H), 2.52 (t, J = 6.4 Hz, 2H), 1.66−1.53 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 159.0, 148.3, 138.8, 137.9, 135.8, 129.2, 124.9, 124.4, 121.9, 62.0, 29.2, 25.8, 25.0,, 23.4. IR (KBr, cm^{-1}): 2935, 1528, 1348, 1047. HRMS (ESI) m/z: $[M + H]^+$ calcd for, $C_{14}H_{17}N_2O_3$; 261.1234; found, 261.1238.

*(1E,2E)-2-(3,4-Dimethoxybenzylidene)cyclohexanone o-Methyl Oxime (**1m**).* The compound was prepared according to general procedure B. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh) giving **1m** (74 mg) in 66% yield. Physical state: yellow viscous liquid. R_f: 0.15 (5% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.92−6.82 (m, 4H), 3.94 (s, 3H), 3.88 (s, 3H), 3.86 (s, 3H), 2.68 (t, J = 5.6 Hz, 2H), 2.58 (t, J = 6.4 Hz, 2H), 1.72−1.60 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.2, 148.7, 148.5, 133.7, 130.3, 127.7, 122.9, 113.4, 111.1, 62.0, 56.2, 56.2, 29.4, 26.0, 25.2, 23.7. IR (KBr, cm^{-1}): 2934, 1513, 1463, 1255, 1140, 1048. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{22}NO_3$, 276.1594; found, 276.1595.

*(2Z,3E)-4-Cyclohexylbut-3-en-2-One o-Methyl Oxime (**1o**).* The compound was prepared according to general procedure B. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh) giving **1o** (77 mg) in 60% yield. Physical state: colorless liquid. R_f:0.6 (5% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.09−5.95 (m, 2H), 3.88 (s, 3H), 2.11−2.04 (m, 1H), 1.93 (s, 3H), 1.76−1.65 (m, 5H), 1.31−1.11 (m, 5H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 156.2, 142.0, 125.3, 61.9, 41.2, 32.9, 26.4, 26.3, 10.4. IR (KBr, cm^{-1}): 1062, 1257, 1452, 2900. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{11}H_{20}NO$, 182.1539; found, 182.1552.

*(E)-1-(Cyclohex-1-en-1-yl)ethan-1-One o-Methyl Oxime (**1p**).* The compound was prepared according to general procedure B. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh) giving **1p** (63 mg) in 51% yield. Physical state: colorless liquid. R_f:0.8 (5% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.13−6.10 (m, 1H), 3.88 (s, 3H), 2.30−2.27 (m, 2H), 2.18−2.15 (m, 2H), 1.93 (s, 3H), 1.66−1.59 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 156.4, 135.2, 129.3, 61.8, 26.3, 24.8, 22.8, 22.5, 10.6. IR (KBr, cm^{-1}): 1052, 1264, 1299, 1442, 2930. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_9H_{16}NO$, 154.1226; found, 154.1231.

Experimental Characterization Data for Annulated Products. *2,3,4-Triphenyl-5,6,7,8-tetrahydroquinoline (**3aa**).*[8] The compound was prepared according to general procedure C. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh) giving **3aa** (18 mg) in 88% yield. Physical state: white solid. Mp: 163−165 °C. R_f: 0.5 (10% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27−7.25 (m, 2H), 7.20−7.12 (m, 6H), 6.97−6.91 (m, 5H), 6.82−6.79 (m, 2H), 3.11 (t, J = 6.8 Hz, 2H), 2.46 (t, J = 6.4 Hz, 2H), 1.95−1.89 (m, 2H), 1.77−1.74 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 156.5, 155.2, 150.1, 141.4, 138.8, 138.6, 132.9, 131.5, 130.2, 129.5, 129.2, 128.1, 127.9, 127.5, 127.3, 127.0, 126.3, 33.6, 28.2, 23.4, 23.3. IR (KBr, cm^{-1}): 3056, 2934, 1634, 1443. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{27}H_{24}N$, 362.1903; found, 362.1921. The spectral data were in accordance with those reported in the literature.[8]

*4-(4-Fluorophenyl)-2,3-diphenyl-5,6,7,8-tetrahydroquinoline (**3ba**).* The compound was prepared according to general procedure C. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh) giving **3ba** (14 mg) in 68% yield. Physical state: white solid. Mp: 181−182 °C. R_f: 0.4 (10% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26−7.24 (m, 2H), 7.15−7.13 (m, 3H), 6.97−6.86 (m, 7H), 6.79−6.77 (m, 2H), 3.11 (t, J = 6.4 Hz, 2H), 2.45 (t, J = 6.4 Hz, 2H), 1.96−1.90 (m, 2H), 1.81−1.75 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.9 (d, J_{C-F} = 244 Hz), 156.7, 155.3, 149.2, 141.3, 138.7, 134.5 (d, J_{C-F} = 3 Hz), 133.1, 131.5, 131.2 (d, J_{C-F} = 8 Hz), 130.1, 129.4, 127.9, 127.7, 127.4, 126.4, 115.2 (d, J_{C-F} = 22 Hz), 33.6, 28.3, 23.4, 23.3. IR (KBr, cm^{-1}): 3056, 2936, 1603, 1510, 1221. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{27}H_{23}FN$, 380.1809; found, 380.1822.

*4-(4-Bromophenyl)-2,3-diphenyl-5,6,7,8tetrahydroquinoline (**3ca**).* The compound was prepared according to general procedure

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C. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh) giving **3ca** (16 mg) in 66% yield. Physical state: white solid. Mp: 161−163 °C. R_f: 0.45 (10% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 4.0 Hz, 2H), 7.14 (d, J = 3.6 Hz, 3H), 6.98 (d, J = 4.8 Hz, 3H), 6.84 (d, J = 8.0 Hz, 2H), 6.79 (d, J = 5.2 Hz, 2H), 3.11 (t, J = 6.4 Hz, 2H), 2.44 (t, J = 6.4 Hz, 2H), 1.96−1.91 (m, 2H), 1.80−1.74 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.8, 155.4, 148.9, 141.2, 138.5, 137.6, 132.8, 131.5, 131.4, 131.2, 130.1, 129.1, 127.9, 127.8, 127.4, 126.5, 121.3, 33.6, 28.3, 23.3, 23.2. IR (KBr, cm^{-1}): 3056, 2934, 1548, 1488, 1012. HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{27}H_{23}BrN$, 440.1008; found, 440.1026.

*4-(4-Iodophenyl)-2,3-diphenyl-5,6,7,8-tetrahydroquinoline (**3da**).* The compound was prepared according to general procedure C. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh) giving **3da** (23 mg) in 83% yield. Physical state: light yellow solid. Mp: 174−176 °C. R_f: 0.42 (10% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, J = 8.0 Hz, 2H), 7.26−7.23 (m, 2H), 7.14−7.13 (m, 3H), 6.98−6.95 (m, 3H), 6.79−6.77 (m, 2H), 6.71 (d, J = 8.4 Hz, 2H), 3.10 (t, J = 6.4 Hz, 2H), 2.43 (t, J = 6.4 Hz, 2H), 1.96−1.89 (m, 2H), 1.80−1.75 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.8, 155.4, 148.9, 141.3, 138.5, 138.3, 137.3, 132.7, 131.5, 131.5, 130.2, 129.0, 127.9, 127.8, 127.4, 126.6, 92.8, 33.6, 28.3, 23.4, 23.3. IR (KBr, cm^{-1}): 3060, 2933, 1545, 1484, 699. HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{27}H_{23}IN$, 488.0870; found, 488.0838.

2,3-Diphenyl-4-(p-tolyl)-5,6,7,8-tetrahydroquinoline (3ea). The compound was prepared according to general procedure C. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh) giving **3ea** (15 mg) in 73% yield. Physical state: white solid. Mp: 125−127 °C. R_f: 0.45 (10% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26−7.23 (m, 2H), 7.15−7.12 (m, 3H), 6.99 (d, J = 8.0 Hz, 2H), 6.96−6.93 (m, 3H), 6.84−6.79 (m, 4H), 3.11 (t, J = 6.8 Hz, 2H), 2.46 (t, J = 6.4 Hz, 2H), 2.26 (s, 3H), 1.95−1.89 (m, 2H), 1.79−1.73 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.4, 155.2, 150.3, 141.4, 138.9, 136.6, 135.5, 133.1, 131.6, 130.2, 129.5, 129.4, 128.8, 127.9, 127.5, 127.3, 126.2, 33.6, 28.3, 23.4, 23.3, 21.5. IR (KBr, cm^{-1}): 3055, 2931, 1546, 1444. HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{28}H_{26}N$, 376.2060; found, 376.2072.

*4-(4-Nitrophenyl)-2,3-diphenyl-5,6,7,8-tetrahydroquinoline (**3fa**).* The compound was prepared according to general procedure C. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh) giving **3fa** (5 mg) in 23% yield. Physical state: yellow solid. Mp: 218−220 °C. R_f: 0.3 (10% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, J = 8.0 Hz, 2H), 7.26 (br, 4H), 7.16 (d, J = 6.4 Hz, 4H), 6.97 (d, J = 4.8 Hz, 2H), 6.79 (d, J = 6.4 Hz, 2H), 3.13 (t, J = 6.0 Hz, 2H), 2.41 (t, J = 6.0 Hz, 2H), 1.98−1.92 (m, 2H), 1.82−1.76 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.1, 155.5, 147.9, 147.0, 146.0, 140.8, 138.0, 132.4, 131.3, 130.6, 130.1, 128.4, 128.0, 128.0, 127.7, 126.9, 123.5, 33.6, 28.2, 23.2, 23.1. IR (KBr, cm^{-1}): 3059, 2925, 1547, 1518, 1346. HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{27}H_{23}N_2O_2$, 407.1754; found, 407.1752.

*4-(Furan-2-yl)-2,3-diphenyl-5,6,7,8-tetrahydroquinoline (**3ga**).* The compound was prepared according to general procedure C. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh) giving **3ga** (11 mg) in 54% yield. Physical state: brown solid. Mp: 134−136 °C. R_f: 0.5 (10% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (s, 1H), 7.23 (d, J = 3.6 Hz, 2H), 7.15 (d, J = 2.8 Hz, 3H), 7.07 (d, J = 4.8 Hz, 3H), 6.89 (d, J = 4.4 Hz, 2H), 6.23 (d, J = 1.2 Hz, 1H), 5.83 (d, J = 2.8 Hz, 1H), 3.10 (t, J = 6.4 Hz, 2H), 2.69 (t, J = 6.4 Hz, 2H), 1.98−1.92 (m, 2H), 1.84−1.80 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.0, 155.5, 150.0, 142.2, 141.2, 139.5, 139.0, 133.9, 131.0, 130.8, 130.1, 127.9, 127.8, 127.4, 126.7, 111.3, 110.9, 33.5, 27.6, 23.2. IR (KBr, cm^{-1}): 3056, 2935, 1545, 1397, 1076. HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{25}H_{22}NO$, 352.1696; found, 352.1693.

*2,3-Diphenyl-4-(thiophen-2-yl)-5,6,7,8-tetrahydroquinoline (**3ha**).* The compound was prepared according to general procedure C. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh) giving **3ha** (10 mg) in 47% yield. Physical state: yellow solid. Mp: 135−137 °C. R_f: 0.5 (10% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26−7.24 (m, 2H), 7.20 (d, J = 4.8 Hz, 1H), 7.14 (d, J = 3.6 Hz, 3H), 7.02−7.01 (m, 3H), 6.90−6.86 (m, 3H), 6.68 (d, J = 3.2 Hz, 1H), 3.11 (t, J = 6.4 Hz, 2H), 2.64 (t, J = 6.4 Hz, 2H), 1.97−1.91 (m, 2H), 1.83−1.77 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.8, 155.3, 143.2, 141.3, 138.8, 138.6, 134.4, 131.2, 130.9, 130.1, 128.2, 127.9, 127.6, 127.4, 126.8, 126.6, 126.4, 33.6, 28.2, 23.3, 23.2. IR (KBr, cm^{-1}): 3060, 2924, 1744, 1398, 1086. HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{25}H_{22}NS$, 368.1467; found, 368.1458.

*4-(2-Bromophenyl)-2,3-diphenyl-5,6,7,8-tetrahydroquinoline (**3ia**).* The compound was prepared according to general procedure C. The crude reaction mixture was submitted for HRMS giving **3ia** in a trace amount. HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{27}H_{23}BrN$, 440.1008; found, 440.1011.

*4-(2-Methoxyphenyl)-2,3-diphenyl-5,6,7,8-tetrahydroquinoline (**3ja**).* The compound was prepared according to general procedure C. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh) giving **3ja** (16 mg) in 71% yield. Physical state: yellow solid. Mp: 152−154 °C. R_f: 0.4 (10% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26−7.23 (m, 2H), 7.13 (dd, J = 4.8, 1.6 Hz, 3H), 6.96−6.94 (m, 3H), 6.87 (d, J = 8.8 Hz, 2H), 6.81−6.78 (m, 2H), 6.73 (d, J = 8.8 Hz, 2H), 3.74 (s, 3H), 3.11 (t, J = 6.4 Hz, 2H), 2.48 (t, J = 6.4 Hz, 2H), 1.96−1.90 (m, 2H), 1.79−1.75 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.5, 156.5, 155.2, 149.9, 141.5, 139.0, 133.3, 132.6, 131.9, 131.6, 130.8, 130.6, 130.2, 129.7, 127.9, 127.6, 127.3, 126.2, 113.6, 55.4, 33.6, 28.3, 23.4, 23.3. IR (KBr, cm^{-1}): 3059, 2931, 1609, 1513, 1245. HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{28}H_{26}NO$, 392.2009; found, 392.2021.

*4-(3-Methoxyphenyl)-2,3-diphenyl-5,6,7,8 tetrahydroquinoline (**3ka**).* The compound was prepared according to general procedure C. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh) giving **3ka** (13 mg) in 61% yield. Physical state: yellow solid. Mp: 65−67 °C. R_f: 0.4 (10% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27−7.26 (m, 2H), 7.15−7.09 (m, 4H), 6.96−6.95 (m, 3H), 6.82 (d, J = 2.4 Hz, 2H), 6.69 (dd, J = 7.6, 1.8 Hz, 1H), 6.58 (d, J = 7.6 Hz, 1H), 6.48 (s, 1H), 3.64 (s, 3H), 3.11 (t, J = 6.4 Hz, 2H), 2.50 (t, J = 6.0 Hz, 2H), 1.96−1.90 (m, 2H), 1.80−1.73 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.4, 156.6, 155.2, 149.9, 141.4, 139.9, 138.8, 132.8, 131.5, 130.2, 129.2, 129.2, 127.9, 127.6, 127.3, 126.3, 122.1, 115.2, 112.8, 55.5, 33.6, 28.1, 23.4, 23.3. IR (KBr, cm^{-1}): 3056, 2934, 1600, 1491, 1229. HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{28}H_{26}NO$, 392.2009; found, 392.2020.

*4-(3-Nitrophenyl)-2,3-diphenyl-5,6,7,8-tetrahydroquinoline (**3la**).* The compound was prepared according to general procedure C. The crude reaction mixture was submitted for HRMS giving **3la** in a trace amount. HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{27}H_{23}N_2O_2$, 407.1754; found, 407.1771.

*4-(3,4-Dimethoxyphenyl)-2,3-diphenyl-5,6,7,8-tetrahydroquinoline (**3ma**).* The compound was prepared according to general procedure C. The crude reaction mixture was submitted for HRMS giving **3ma** in a trace amount. HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{29}H_{28}NO_2$, 422.2115; found, 422.2112.

*2,3-Bis(4-methoxyphenyl)-4-phenyl-5,6,7,8-tetrahydroquinoline (**3ab**).* The compound was prepared according to general procedure C. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh) giving **3ab** (18 mg) in 76% yield. Physical state: yellow solid. Mp: 171−173 °C. R_f: 0.2 (10% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22−7.14 (m, 5H), 6.95−6.93 (m, 2H), 6.71−6.68 (m, 4H), 6.52−6.49 (m, 2H), 3.74 (s, 3H), 3.65 (s, 3H), 3.09 (t, J = 6.4 Hz, 2H), 2.43 (t, J = 6.4 Hz, 2H), 1.93−1.88 (m, 2H), 1.76−1.73 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.9, 157.9, 156.2, 155.0, 150.4, 138.9, 134.2, 132.6, 132.3, 131.4, 131.3, 129.5, 128.9, 128.1, 126.9, 113.4, 113.1, 55.5, 55.3, 33.6, 28.2, 23.4, 23.3. IR (KBr, cm^{-1}): 3000, 2931, 1608, 1513,

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1288, 1245. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{29}H_{28}NO_2$, 422.2115; found, 422.2108.

*4-Phenyl-2,3-di-p-tolyl-5,6,7,8-tetrahydroquinoline (**3ac**).* The compound was prepared according to general procedure C. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh) giving **3ac** (14 mg) in 63% yield. Physical state: yellow solid. Mp: 168−170 °C. R_f: 0.35 (10% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24−7.17 (m, 3H), 7.08−6.96 (m, 10H), 3.07 (t, J = 6.4 Hz, 2H), 2.44 (t, J = 6.0 Hz, 2H), 2.29 (s, 3H), 2.27 (s, 3H), 1.93−1.87 (m, 2H), 1.76−1.71 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.0, 149.3, 140.1, 138.9, 138.0, 137.4, 136.5, 135.0, 132.0, 130.9, 130.4, 129.4, 129.2, 128.2, 127.3, 120.1, 92.0, 33.5, 28.4, 23.2, 23.1, 21.8, 21.5. IR (KBr, cm^{-1}): 3055, 2936, 1521, 1394. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{29}H_{28}N$, 390.2216; found, 390.2215.

*4-Phenyl-2,3-di(thiophen-2-yl)-5,6,7,8-tetrahydroquinoline (**3ae**).* The compound was prepared according to general procedure C. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh) giving **3ae** (12 mg) in 59% yield. Physical state: yellow solid. Mp: 182−184 °C. R_f: 0.75 (10% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26−7.17 (m, 5H), 7.02−7.00 (m, 2H), 6.82 (dd, J = 4.8, 4.0 Hz, 2H), 6.66 (dd, J = 3.2, 1.8 Hz, 1H), 6.56 (dd, J = 3.6, 1.8 Hz, 1H), 3.06 (t, J = 6.4 Hz, 2H), 2.37 (t, J = 6.4 Hz, 2H), 1.93−1.87 (m, 2H), 1.76−1.70 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.6, 152.2, 149.3, 139.4, 138.2, 130.0, 129.3, 129.1, 129.0, 128.1, 127.7, 127.5, 127.5, 127.3, 127.1, 126.9, 123.9, 33.5, 28.1, 23.3, 23.1. IR (KBr, cm^{-1}): 3100, 2934, 1491, 1436, 1389. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{20}NS_2$, 374.1032; found, 374.1048.

*4-Phenyl-2,3-di-m-tolyl-5,6,7,8-tetrahydroquinoline (**3af**).* The compound was prepared according to general procedure C. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh) giving **3af** (15 mg) in 69% yield. Physical state: yellow solid. Mp: 115−117 °C. R_f: 0.5 (10% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20−7.12 (m, 4H), 7.00−6.93 (m, 5H), 6.82 (t, J = 7.6 Hz, 1H), 6.74 (d, J = 7.6 Hz, 1H), 6.61−6.57 (m, 2H), 3.11 (t, J = 6.8 Hz, 2H), 2.45 (d, J = 5.6 Hz, 2H), 2.23 (s, 3H), 2.03 (s, 3H), 1.94−1.90 (m, 2H), 1.79−1.73 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.3, 155.3, 150.1, 141.3, 138.8, 138.6, 137.3, 136.8, 133.1, 132.4, 130.9, 129.5, 129.1, 128.7, 128.6, 128.0, 127.5, 127.3, 127.3, 127.0, 126.9, 33.6, 28.2, 23.4, 23.3, 21.7, 21.5. IR (KBr, cm^{-1}): 3059, 2933, 1545, 1394. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{29}H_{28}N$, 390.2216; found, 390.2243.

*2,3-Diethyl-4-phenyl-5,6,7,8-tetrahydroquinoline (**3ag**).*[8] The compound was prepared according to general procedure C. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh) giving **3ag** (8 mg) in 56% yield. Physical state: yellow solid. Mp: 61−63 °C. R_f: 0.4 (10% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (t, J = 7.2 Hz, 2H), 7.36 (t, J = 7.2 Hz, 1H), 7.09 (d, J = 8.0 Hz, 2H), 2.93 (t, J = 6.4 Hz, 2H), 2.83 (q, J = 7.6 Hz, 2H), 2.35 (q, J = 7.6 Hz, 2H), 2.21 (t, J = 6.4 Hz, 2H), 1.85−1.79 (m, 2H), 1.68−1.62 (m, 2H), 1.32 (t, J = 7.6 Hz, 3H), 0.93 (t, J = 7.6 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.7, 154.1, 150.1, 139.4, 132.0, 128.7, 128.6, 128.0, 127.4, 33.2, 28.6, 27.9, 23.4, 23.3, 22.6, 15.7, 15.1. IR (KBr, cm^{-1}): 3055, 2931, 1565, 1406. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{24}N$, 266.1903; found, 266.1894. The spectral data were in accordance with those reported in the literature.[8]

*4-Phenyl-2,3-dipropyl-5,6,7,8-tetrahydroquinoline (**3ah**).* The compound was prepared according to general procedure C. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh) giving **3ah** (10 mg) in 60% yield. Physical state: white solid. Mp: 68−70 °C. R_f: 0.5 (10% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44−7.33 (m, 3H), 7.08 (d, J = 8.0 Hz, 2H), 2.92 (t, J = 6.4 Hz, 2H), 2.76−2.72 (m, 2H), 2.28−2.19 (m, 4H), 1.83−1.63 (m, 6H), 1.35−1.29 (m, 2H), 1.04 (t, J = 7.2 Hz, 3H), 0.73 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.7, 154.0, 150.2, 139.4, 130.9, 128.7, 127.9, 127.4, 37.8, 33.2, 31.9, 28.0, 24.7, 24.3, 23.4, 23.3, 14.9, 14.8. IR (KBr, cm^{-1}): 3056, 2930, 1434, 1406. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{28}N$, 294.2216; found, 294.2215.

*3-Methyl-2,4-diphenyl-5,6,7,8-tetrahydroquinoline (**3ai**).*[8] The compound was prepared according to general procedure C. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh) giving **3ai** (13 mg) in 81% yield. Physical state: white solid. Mp: 106−109 °C. R_f: 0.48 (10% EtOAc/hexane). Mp: 103−105 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51−7.33 (m, 8H), 7.15−7.13 (m, 2H), 3.01 (t, J = 6.4 Hz, 2H), 2.36 (t, J = 6.4 Hz, 2H), 1.91−1.84 (m, 5H), 1.74−1.68 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.6, 154.5, 150.9, 141.9, 139.5, 129.4, 129.1, 128.5, 128.4, 127.8, 127.6, 126.2, 33.4, 28.1, 23.3, 18.0. IR (KBr, cm^{-1}): 3031, 1562, 1402, 1263. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{22}N$, 300.1747; found, 300.1763. The spectral data were in accordance with those reported in the literature.[8]

*3-Ethyl-2,4-diphenyl-5,6,7,8-tetrahydroquinoline (**3aj**).* The compound was prepared according to general procedure C. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh) giving **3aj** (9 mg) in 51% yield. Physical state: white solid. Mp: 125−127 °C. R_f: 0.75 (10% EtOAc/DCM). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47−7.33 (m, 8H), 7.18−7.16 (m, 2H), 2.99 (t, J = 6.4 Hz, 2H), 2.36−2.29 (m, 4H), 1.89−1.83 (m, 2H), 1.73−1.67 (m, 2H), 0.70 (t, J = 7.6 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.9, 154.3, 150.5, 142.0, 139.0, 132.6, 129.6, 129.1, 128.8, 128.5, 127.7, 127.6, 33.3, 28.1, 23.3, 23.1, 15.4. IR (KBr, cm^{-1}): 3059, 2872, 1557, 1441, 1401. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{24}N$, 314.1903; found, 314.1928.

2-Ethyl-3,4-diphenyl-5,6,7,8-tetrahydroquinoline (**3aj′**) The compound was prepared according to general procedure C. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh) giving **3aj′** (4 mg) in 23% yield. Physical state: colorless liquid. R_f: 0.5 (10% EtOAc/DCM). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17−7.07 (m, 6H), 6.98−6.96 (m, 2H), 6.91−6.89 (m, 2H), 3.03 (t, J = 6.4 Hz, 2H), 2.59 (q, J = 7.2 Hz, 2H), 2.37 (t, J = 6.4 Hz, 2H), 1.93−1.87 (m, 2H), 1.73−1.71 (m, 2H), 1.12 (t, J = 7.6 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.3, 156.1, 149.7, 139.0, 138.7, 133.3, 130.5, 129.3, 128.0, 127.8, 127.7, 126.9, 126.7, 33.4, 29.6, 28.0, 23.4, 23.4, 15.0. IR (KBr, cm^{-1}): 3059, 2932, 1492, 1432, 1401. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{24}N$, 314.1903; found, 314.1896.

*3-Butyl-2,4-diphenyl-5,6,7,8-tetrahydroquinoline and 2-Butyl-3,4-diphenyl-5,6,7,8-tetrahydroquinoline (**3ak** and **3ak′**).* The compound was prepared according to general procedure C. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh) giving **3ak** and **3ak′** as an inseparable regio-isomer (13 mg) in 70% yield. Physical state: colorless liquid. R_f: 0.45 (10% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46−7.33 (m, 8H), 7.17−7.15 (m, 2H), 2.99 (t, J = 6.8 Hz, 2H), 2.33−2.26 (m, 4H), 1.89−1.83 (m, 2H), 1.73−1.67 (m, 2H), 1.11−1.04 (m, 2H), 0.88−0.81 (m, 2H), 0.46 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.0, 154.2, 150.6, 142.0, 139.0, 131.5, 129.5, 129.2, 128.8, 128.7, 128.4, 127.7, 127.5, 33.3, 32.9, 29.4, 28.1, 23.3, 23.3, 22.8, 13.5. IR (KBr, cm^{-1}): 3055, 2931, 1556, 1492, 1431, 1400. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{25}H_{28}N$, 342.2216; found, 342.2235.

*3-Pentyl-2,4-diphenyl-5,6,7,8-tetrahydroquinoline (**3al**).* The compound was prepared according to general procedure C. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh) giving **3al** (9 mg) in 46% yield. Physical state: colorless liquid. R_f: 0.4 (10% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46−7.32 (m, 8H), 7.17−7.15 (m, 2H), 2.99 (t, J = 6.4 Hz, 2H), 2.34−2.26 (m, 4H), 1.89−1.83 (m, 2H), 1.74−1.68 (m, 2H), 1.14−1.07 (m, 2H), 0.89−0.80 (m, 4H), 0.60 (t, J = 6.8 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.1, 154.3, 150.6, 142.2, 139.1, 131.5, 129.4, 129.2, 128.8, 128.8, 128.4, 127.7, 127.5, 33.4, 32.0, 30.4, 29.8, 28.1, 23.4, 23.3, 22.0, 13.9. IR (KBr, cm^{-1}): 3057, 2928, 1556, 1431, 1401. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{26}H_{30}N$, 356.2373; found, 356.2387.

*2-Pentyl-3,4-diphenyl-5,6,7,8-tetrahydroquinoline (**3al′**).* The compound was prepared according to general procedure C. The

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crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh) giving **3al′** (6 mg) in 31% yield. Physical state: yellow liquid. R_f: 0.5 (10% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16−7.06 (m, 6H), 6.97−6.94 (m, 2H), 6.91−6.89 (m, 2H), 3.02 (t, J = 6.4 Hz, 2H), 2.57−2.53 (m, 2H), 2.36 (t, J = 6.4 Hz, 2H), 1.92−1.86 (m, 2H), 1.73−1.68 (m, 2H), 1.60−1.52 (m, 2H), 1.17−1.14 (m, 4H), 0.79−0.75 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.4, 156.0, 149.6, 139.0, 138.8, 133.5, 130.6, 129.3, 128.0, 127.8, 127.6, 126.9, 126.6, 36.5, 33.5, 32.2, 30.4, 28.0, 23.4, 22.6, 14.2. IR (KBr, cm^{-1}): 3059, 2929, 1555, 1442, 1400. HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{26}H_{30}N$, 356.2373; found, 356.2370.

*3-Hexyl-2,4-diphenyl-5,6,7,8-tetrahydroquinoline (**3am**).* The compound was prepared according to general procedure C. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh) giving **3am** (11 mg) in 55% yield. Physical state: yellow liquid. R_f: 0.4 (10% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47−7.34 (m, 8H), 7.17−7.15 (m, 2H), 3.03 (t, J = 6.4 Hz, 2H), 2.34−2.26 (m, 4H), 1.87−1.83 (m, 2H), 1.73−1.69 (m, 2H), 1.11−1.07 (m, 2H), 0.98−0.95 (m, 2H), 0.83−0.79 (m, 4H), 0.69 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.0, 154.2, 150.6, 142.0, 139.0, 131.5, 129.5, 129.2, 128.8, 128.7, 128.4, 127.7, 127.5, 33.3, 31.1, 30.6, 29.7, 29.3, 28.1, 23.3, 23.3, 22.5, 14.2. IR (KBr, cm^{-1}): 3062, 2928, 1545, 1441, 1431, 1400. HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{27}H_{32}N$, 370.2529; found, 370.2548.

*2-Hexyl-3,4-diphenyl-5,6,7,8-tetrahydroquinoline (**3am′**).* The compound was prepared according to general procedure C. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh) giving **3am′** (4 mg) in 20% yield. Physical state: yellow liquid. R_f: 0.5 (10% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17−7.06 (m, 6H), 6.97−6.95 (m, 2H), 6.91−6.89 (m, 2H), 3.03 (t, J = 6.8 Hz, 2H), 2.57−2.53 (m, 2H), 2.36 (t, J = 6.4 Hz, 2H), 1.93−1.86 (m, 2H), 1.74−1.73 (m, 2H), 1.58−1.50 (m, 2H), 1.19−1.09 (m, 6H), 0.79 (t, J = 6.8 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.4, 155.9, 149.7, 138.9, 138.8, 133.5, 130.6, 129.3, 128.0, 127.8, 127.6, 126.9, 126.6, 36.4, 33.4, 31.8, 30.7, 29.6, 28.0, 23.3, 23.4, 22.8, 14.4. IR (KBr, cm^{-1}): 3062, 2929, 1555, 1442, 1431, 1400. HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{27}H_{32}N$, 370.2529; found, 370.2521.

*(4S,6aR,6bS,8aS,13aS,13bR)-6a,8a,9-Trimethyl-11,12-diphenyl-3,4,5,6,6a,6b,7,8,8a,13,13a,13b-dodecahydro-1H-naphtho-[2′,1′:4,5]indeno[1,2-c]pyridin-4-yl Acetate (**3na**).* The compound was prepared according to general procedure C. The crude reaction mixture was purified by column chromatography using silica gel (230−400 mesh) giving **3na** (14 mg) in 46% yield. Physical state: white solid. Mp: 208−210 °C. R_f: 0.2 (10% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28−7.21 (m, 5H), 7.16−7.14 (m, 3H), 7.06 (d, J = 7.6 Hz, 2H), 5.36 (d, J = 4.8 Hz, 1H), 4.64−4.57 (m, 1H), 2.64 (s, 3H), 2.53−2.40 (m, 3H), 2.34 (d, J = 6.8 Hz, 2H), 2.03 (s, 3H), 1.99−1.88 (m, 3H), 1.82−1.70 (m, 4H), 1.67−1.57 (m, 3H), 1.28−1.16 (m, 2H), 1.13 (s, 3H), 1.10 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 170.9, 154.8, 152.5, 151.3, 145.2, 141.1, 140.3, 139.0, 131.4, 130.4, 130.3, 128.3, 127.9, 127.4, 127.0, 122.4, 74.1, 57.3, 50.5, 46.2, 38.4, 37.2, 37.1, 36.3, 32.5, 31.9, 31.0, 28.1, 22.7, 21.8, 21.2, 19.6, 17.0. IR (KBr, cm^{-1}): 3056, 2956, 1730, 1562, 1378, 1244, 1034. HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{37}H_{42}NO_2$, 532.3210; found, 532.3192.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02558.

Optimization studies; mechanistic studies; copies of NMR spectra for the starting materials, products (^{1}H NMR and ^{13}C NMR); X-ray crystallography data (PDF)

FAIR data, including the primary NMR FID files, for compounds **1a**, **1b**, **1c**, **1d**, **1e**, **1f**, **1g**, **1h**, **1i**, **1j**, **1k**, **1l**, **1m**, **1o**, **1p**, **3aa**, **3ba**, **3ca**, **3da**, **3ea**, **3fa**, **3ga**, **3ha**, **3ja**, **3ka**, **3ab**, **3ac**, **3ae**, **3af**, **3ag**, **3ah**, **3ai**, **3aj**, **3aj′**, **3ak**, **3ak′**, **3al**, **3al′**, **3am**, **3am′**, and **3na** (ZIP)

Accession Codes

CCDC 2011120 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

Ponneri Chandrababu Ravikumar − *School of Chemical Sciences, National Institute of Science Education and Research (NISER) Bhubaneswar, HBNI, Khurda, Odisha 752050, India;* orcid.org/0000-0002-5264-820X; Email: pcr@niser.ac.in

Authors

Smruti Ranjan Mohanty − *School of Chemical Sciences, National Institute of Science Education and Research (NISER) Bhubaneswar, HBNI, Khurda, Odisha 752050, India*

Bedadyuti Vedvyas Pati − *School of Chemical Sciences, National Institute of Science Education and Research (NISER) Bhubaneswar, HBNI, Khurda, Odisha 752050, India*

Shyam Kumar Banjare − *School of Chemical Sciences, National Institute of Science Education and Research (NISER) Bhubaneswar, HBNI, Khurda, Odisha 752050, India*

Gopal Krushna Das Adhikari − *School of Chemical Sciences, National Institute of Science Education and Research (NISER) Bhubaneswar, HBNI, Khurda, Odisha 752050, India*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.joc.0c02558

Notes

The authors declare no competing financial interest.

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