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Rhodium-Catalyzed Synthesis of Isoquinolines and Indenes from Benzylidenehydrazones and Internal Alkynes

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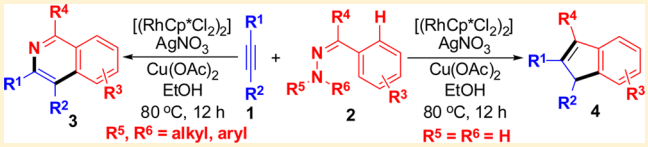
Supporting Information

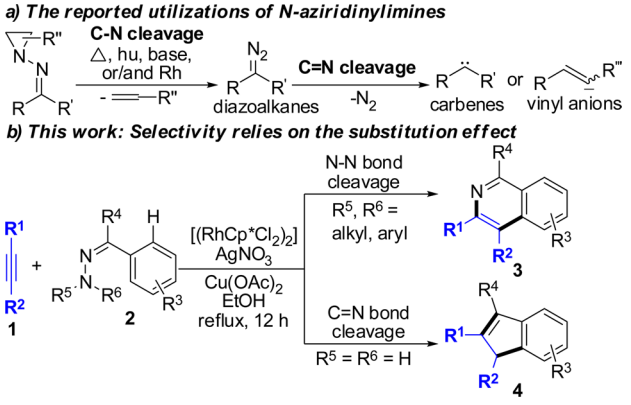
ABSTRACT: A new route is presented for the selective assembly of isoquinolines and indenes by rhodium-catalyzed tandem cyclization of benzylidenehydrazones with internal alkynes. This method involves the selective cleavage of the N−N bond and the C═N bonds and is dependent on the substituents of the benzylidenehydrazone.



INTRODUCTION

N-Aziridinylimines have emerged as an important class of synthetic building blocks in organic synthesis since Eschenmoser first reported the thermal fragmentation of *N*-aziridinylimines from α,β-epoxy ketones in 1967.[1] Generally, labile *N*-aziridinylimines can be readily converted into different reactive intermediates, such as diazoalkane, carbene, and vinyl anion intermediates, by the use of different reaction conditions (heat, light, strong bases and/or transition metals; Scheme 1a)

Scheme 1. Utilizations of *N*-Aziridinylimines



and can be used as radical acceptors.[1−4] Despite impressive progress in this field, *N*-aziridinylimines often have poor selectivity, and stabilizing groups (often carbonyl groups) are required. For nonstabilized intermediates of *N*-aziridinylimines, transition metals are necessary to stabilize them in situ by generating nonstabilized metallocarbenoids, thereby introducing new functional groups on the molecules and leading to new functionalized complex compounds. However, to our knowledge, these transition-metal-catalyzed transforms are quite rare and limited to the intramolecular manner.[4] Thus, it is highly desirable to develop new transition-metal-catalyzed strategies involving intermolecular processes to expand the applications of *N*-aziridinylimines in organic synthesis.

In light of the above findings and the desire to expand the applications of *N*-aziridinylimines,[1−4] we investigated the reaction of benzylidenehydrazones with alkynes.[5] After a series of trials, we found that benzylidenehydrazones can undergo an oxidative tandem reaction with alkynes using the $[(RhCp^*Cl_2)_2]/AgNO_3/Cu(OAc)_2$ catalytic system and that the chemoselectivity is dependent on the substitution at the 1-position of the benzylidenehydrazone (Scheme 1b): isoquinolines are selectively assembled via cleavage of the N−N and C(sp^2)−H bonds with benzylidenehydrazones bearing two substituents at the 1-position, whereas indenes are formed from benzylidenehydrazones with two free N−H bonds through cleavage of the C═N and C(sp^2)−H bonds. Herein we report the Rh(III)-catalyzed oxidative tandem reaction between benzylidenehydrazones and internal alkynes to give isoquinolines and indenes. This reaction is catalyzed by a catalytic amount of $[(RhCp^*Cl_2)_2]$ combined with a catalytic amount of $AgNO_3$ and involves the use of $Cu(OAc)_2$ as a promoter (Scheme 1b).[6−8] Notably, the products, isoquinolines and indenes, are ubiquitous structural components of multitudinous natural products and biomolecules.[9,10]

RESULTS AND DISCUSSION

Our initial investigation was performed with 1,2-diphenylethyne (**1a**) and *N*-(1-phenylethylidene)aziridinylimine (**2a**) in the presence of a Rh catalyst (Table 1).[4] In the presence of 5 mol % $[(RhCp^*Cl_2)_2]$, a trace amount of isoquinoline **3aa** was observed by GC−MS analysis (entry 1). The yield of **3aa** markedly increased to 72% with the addition of 1 equiv of $Cu(OAc)_2$ (entry 2). Unfortunately, two other Cu catalysts,

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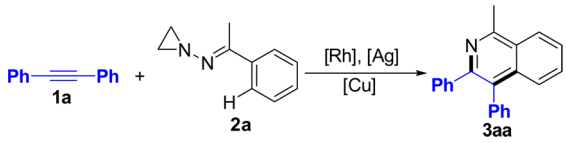
Table 1. Screening for Optimal Conditions[a]



entry	[Rh] (mol %)	[Ag]	[Cu]	solvent	yield (%)
1	$[(RhCp^*Cl_2)_2]$ (5)	—	—	EtOH	trace
2	$[(RhCp^*Cl_2)_2]$ (5)	—	$Cu(OAc)_2$	EtOH	72
3	$[(RhCp^*Cl_2)_2]$ (5)	—	$CuCl_2$	EtOH	trace
4	$[(RhCp^*Cl_2)_2]$ (5)	—	$Cu(OTf)_2$	EtOH	<5
5	$[(RhCp^*Cl_2)_2]$ (5)	—	CuO	EtOH	23
6	$[(RhCp^*Cl_2)_2]$ (5)	$AgSbF_6$	$Cu(OAc)_2$	EtOH	72
7	$[(RhCp^*Cl_2)_2]$ (5)	$AgNO_3$	$Cu(OAc)_2$	EtOH	85
8	$[(RhCp^*Cl_2)_2]$ (5)	AgOAc	$Cu(OAc)_2$	EtOH	79
9	$[(RhCp^*Cl_2)_2]$ (5)	Ag_2CO_3	$Cu(OAc)_2$	EtOH	84
10	$[(RhCp^*Cl_2)_2]$ (5)	Ag_2O	$Cu(OAc)_2$	EtOH	56
11[b]	$[(RhCp^*Cl_2)_2]$ (5)	$AgNO_3$	$Cu(OAc)_2$	EtOH	54
12	$[(RhCp^*Cl_2)_2]$ (2)	$AgNO_3$	$Cu(OAc)_2$	EtOH	60
13	$RhCl_3$ (5)	$AgNO_3$	$Cu(OAc)_2$	EtOH	trace
14	$[RhCp^*(NCMe)_3]^{2+}$ (5)	$AgNO_3$	$Cu(OAc)_2$	EtOH	trace
15	—	$AgNO_3$	$Cu(OAc)_2$	EtOH	0
16	$[(RhCp^*Cl_2)_2]$ (5)	$AgNO_3$	$Cu(OAc)_2$	MeOH	73
17[c]	$[(RhCp^*Cl_2)_2]$ (5)	$AgNO_3$	$Cu(OAc)_2$	*t*-AmOH	72
18[c]	$[(RhCp^*Cl_2)_2]$ (5)	$AgNO_3$	$Cu(OAc)_2$	toluene	trace
19[c]	$[(RhCp^*Cl_2)_2]$ (5)	$AgNO_3$	$Cu(OAc)_2$	DMSO	16
20[d]	$[(RhCp^*Cl_2)_2]$ (5)	$AgNO_3$	$Cu(OAc)_2$	EtOH	48
21	$[(RhCp^*Cl_2)_2]$ (5)	$AgNO_3$	—	EtOH	38
22[e]	$[(RhCp^*Cl_2)_2]$ (5)	$AgNO_3$	—	EtOH	46
23[f]	$[(RhCp^*Cl_2)_2]$ (5)	$AgNO_3$	—	EtOH	trace
24[g]	$[(RhCp^*Cl_2)_2]$ (5)	$AgNO_3$	—	EtOH	33
25[e]	$[(RhCp^*Cl_2)_2]$ (5)	—	—	EtOH	36
26[g]	$[(RhCp^*Cl_2)_2]$ (5)	—	—	EtOH	49
27[h]	$[(RhCp^*Cl_2)_2]$ (5)	$AgNO_3$	$Cu(OAc)_2$	EtOH	82

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), [Rh], [Ag] (20 mol %), and [Cu] (1 equiv) in the solvent (2 mL) at reflux under an argon atmosphere for 12 h, unless otherwise noted. [b]At 60 °C for 24 h. [c]At 80 °C. [d]$Cu(OAc)_2$ (20 mol %). [e]CsOAc (1 equiv) instead of $Cu(OAc)_2$. [f]NaOAc (1 equiv) instead of $Cu(OAc)_2$ (>95% of **2a** was recovered). [g]HOAc (1 equiv) instead of $Cu(OAc)_2$. [h]**1a** (2 mmol, 0.365 g) and **2a** (2.5 mmol, 0.4 g) for 48 h.

$CuCl_2$ and $Cu(OTf)_2$, had no effect on the reaction (entries 3 and 4). When CuO was used, isoquinoline **3aa** was obtained in 23% yield (entry 5). It has been reported that Ag salts, particularly $AgSbF_6$, promote C−H activation/carbocyclization transformations.[6−8] Thus, a series of Ag salts were examined as catalysts for the reaction (entries 6−10). $AgSbF_6$, the reported efficient silver salt, had no effect on the reaction (entry 6), and Ag_2O disfavored the reaction (entry 10). However, $AgNO_3$, AgOAc, and $AgCO_3$ promoted the reaction (entries 7−9). For example, the addition of 20 mol % $AgNO_3$ increased the yield from 72% to 85% (entry 2 vs entry 7). Subsequent investigation of the effect of temperature showed that the reaction at reflux gave the best results (entries 7 and 11). Notably, the reaction was successful with 2 mol % Rh, albeit with a moderate yield (entry 12). However, neither $RhCl_3$ nor $[RhCp^*(NCMe)_3]^{2+}$ catalyzed the reaction (entries 13 and 14). It is noteworthy that the reaction cannot take place in the absence of the Rh catalyst (entry 15). Among the solvents investigated, the reaction in EtOH gave the highest yield (entries 7 and 16−19). To understand the role of $Cu(OAc)_2$, some control experiments were carried out (entries 20−26). The results showed that the yield significantly decreased from 85% to 48% in the presence of 20 mol % $Cu(OAc)_2$ (entry 7 vs entry 20), and to 38% without Cu catalysts (entry 7 vs entry 21). It has been reported that the presence of either CsOAc or HOAc promotes some C−H activation/carbocyclization transformations.[6,7] Thus, the use of CsOAc or HOAc instead of $Cu(OAc)_2$ was tested (entries 22 and 24): the presence of CsOAc decreased the yield from 85% to 46% (entry 7 vs entry 22), and the presence of HOAc decreased the yield from 85% to 33% (entry 7 vs entry 24). However, the presence of NaOAc instead of $Cu(OAc)_2$ resulted in no detectable isoquinoline **3aa** (entry 23). The use of CsOAc or HOAc was also examined without both the Ag salt and the Cu salt (entries 25 and 26): the Rh-catalyzed annulation reaction gave isoquinoline **3aa** in 36% yield using CsOAc and in 49% yield using HOAc. These results suggest that $Cu(OAc)_2$ may serve as both a base and an oxidant to promote the reaction and that the N═N bond of **2a** can be cleaved by bases or acids, such as $Cu(OAc)_2$, CsOAc, and HOAc. Finally, the reaction of 2 mmol of alkyne **1a** with 2.5 mmol of aziridinylimine **2a** gave isoquinoline **3aa** in good yield (entry 27).

After the optimal reaction conditions had been determined, a variety of hydrazones **2** were reacted with **1a** to investigate viable hydrazone substrates (Scheme 2). In the presence of $[(RhCp^*Cl_2)_2]$, $AgNO_3$, and $Cu(OAc)_2$, 1,1-dialkyl-substituted

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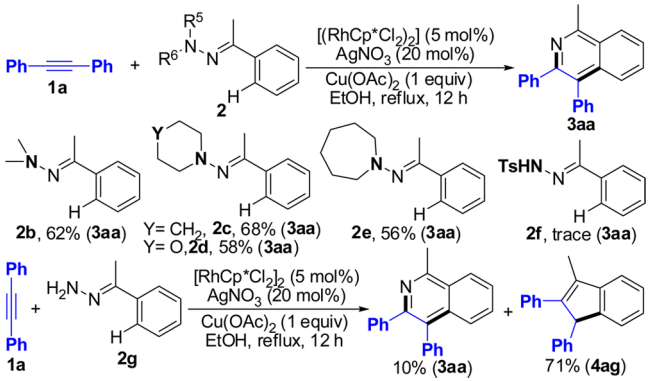
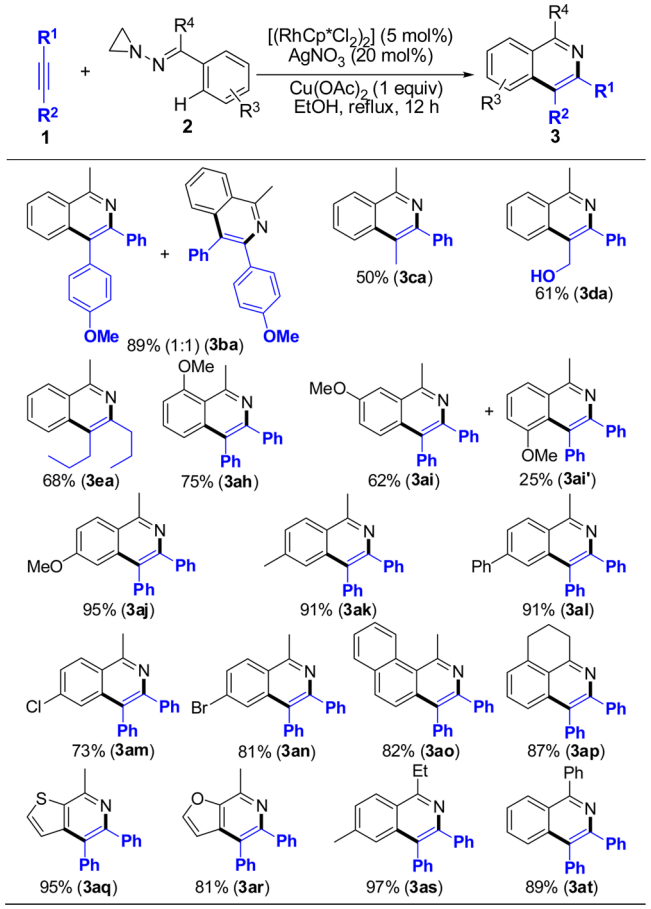
Scheme 2. Screening of the Effect of Substitution at the 1-Position of the Benzylidenehydrazone



hydrazones **2b–e** gave isoquinoline **3aa**, although their reactivities were lower than that of aziridinylimine **2a**. However, hydrazone **2f**, which has a Ts group at the 1-position, was unreactive. To our surprise, (1-phenylethylidene)hydrazone (**2g**) with two free N–H bonds gave indene **4ag** as the major product (71% yield) together with isoquinoline **3aa** as a side product (10% yield).

As shown in Table 2, we applied the Rh-catalyzed tandem approach to the synthesis of various functionalized isoquinolines **3**. Initially, a variety of internal alkynes **1b–e** were investigated for the reaction with aziridinylimine **2a**, and they gave the expected products **3ba–ea** under the optimal conditions. For example, unsymmetric diarylalkyne **1b** underwent the reaction with aziridinylimine **2a**, $[(RhCp^*Cl_2)_2]$, $AgNO_3$, and $Cu(OAc)_2$ to afford a 1:1 mixture of two regioselective isoquinolines **3ba** in 89% total yield. The reaction of prop-1-ynylbenzene (**1c**) with aziridinylimine **2a** regiospecifically gave only isoquinoline **3ca** in moderate yield. Alkyne **1d**, which has a free OH group, was also found to be suitable for producing isoquinoline **3da** in 61% yield. The optimal conditions were compatible with aliphatic alkyne **1e** (product **3ea**). Therefore, we decided to explore the scope of *N*-(1-arylethylidene)hydrazones **2** in the presence of alkyne **1a**, $[(RhCp^*Cl_2)_2]$, $AgNO_3$, and $Cu(OAc)_2$ (products **3ah–at**). Extensive screening revealed that several substituents, including MeO, Me, Ph, Cl, and Br groups, on the aromatic ring of the *N*-(1-arylethylidene) moiety were well-tolerated (products **3ah–an**), and the reactivity order was *para* > *meta* > *ortho*. While *o*-MeO-substituted substrate **2h** reacted with alkyne **1a** to give isoquinoline **3ah** in 75% yield, *m*- and *p*-MeO-substituted substrates **2i** and **2j** provided isoquinolines **3ai** and **3aj** in 87% and 95% yield, respectively. Notably, *m*-MeO-substituted substrate **2i** gave a mixture of regioselective isomers. Both Cl- and Br-substituted isoquinolines **3am** and **3an** were successfully formed, thereby facilitating possible additional modifications at the halogenated position. Importantly, this current reaction could be applied to prepare complex heterocycles **3ao–ar**, which makes this methodology more useful in organic synthesis. For example, the reaction provides a facile route to benzo[*h*]isoquinoline **3ao** and 8,9-dihydro-7*H*-benzo[*de*]-quinoline **3ap**. Interestingly, both thieno[2,3-*c*]pyridine **3aq** and furo[2,3-c]pyridine **3ar** were also formed in good yields. It is noteworthy that 1-ethyl- and 1-phenyl-substituted isoquinolines **3as** and **3at** were easily prepared.

Table 2. Rh-Catalyzed Synthesis of Isoquinolines 3[a]



[a]Reaction conditions: **1** (0.2 mmol), **2** (0.3 mmol), $[(RhCp^*Cl_2)_2]$ (5 mol %), $AgNO_3$ (20 mol %), and $Cu(OAc)_2$ (1 equiv) in EtOH (2 mL) at reflux for 12 h.

We next turned our attention to the preparation of indenes from (1-phenylethylidene)hydrazone (**2g**) and its derivatives **2u–z** (Table 3). In the presence of $[(RhCp^*Cl_2)_2]$, $AgNO_3$, and $Cu(OAc)_2$, hydrazone **2g** showed high reactivity with various alkynes to give indenes **4cg–gg** in satisfactory yields. For example, the reaction of hydrazone **2g** with 1-phenylpropyne (**1c**) afforded indene **4cg** in good yield, albeit with only a 5% yield of isoquinoline **3aa**. When alkynols **1d** and **1f** were used, the corresponding indenes **4dg** and **4fg** together with the dehydrated indenes **5dg** and **5fg** were isolated.[8h] The current reaction could be readily used for the synthesis of 1,2,3-trialkyl-substituted indene **4eg**, although isoquinoline **3ea** was also formed. Notably, electron-poor alkyne **1g** under the optimal conditions gave only indene **4gg** in moderate yield. Furthermore, other hydrazones **2u–z** with substituents such as MeO, Me, Cl, and NO_2 groups on the aromatic ring successfully reacted with alkyne **1a** to provide the corresponding indenes **4au–az** in moderate to good yields.

Table 1 shows that isoquinoline **3aa** was obtained in 72% yield without Ag salt (entry 2) and that the yield increased to 85% in the presence of $AgNO_3$ (entry 7), suggesting that $AgNO_3$ only activates $[(RhCp^*Cl_2)_2]$. The reaction of alkyne **1a** with aziridinylimine **2a** in the presence of $[(RhCp^*Cl_2)_2]$, $AgNO_3$, and $Cu(OAc)_2$ was monitored in situ by GC–MS analysis, which showed that some byproducts were formed, including bis(1-phenylethylidene)hydrazone (**6aa**) and acetophenone (**7aa**) (eq 1 in Scheme 3). Further experiments showed that the reaction of 0.15 mmol of hydrazone **6aa** with

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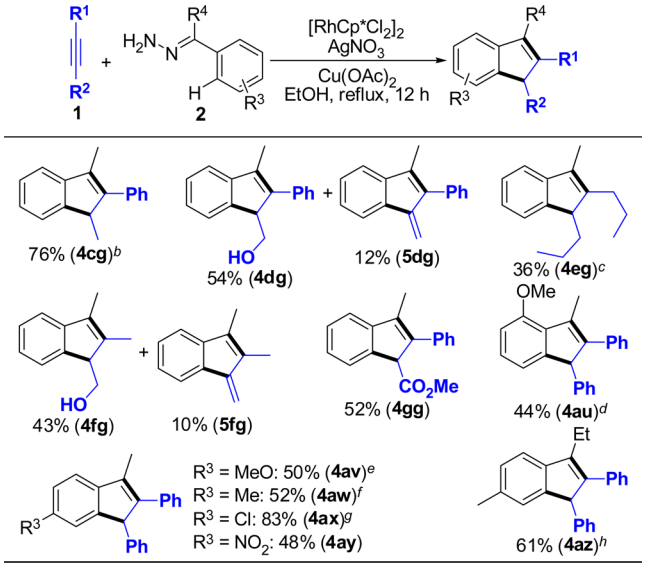
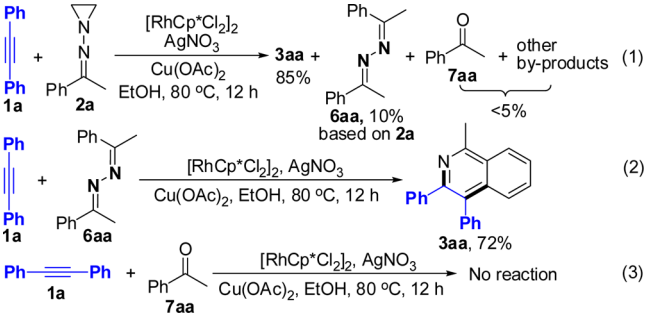
Table 3. Rh-Catalyzed Synthesis of Indenes 4 and 5[a]



[a]Reaction conditions: **1** (0.2 mmol), **2** (0.3 mmol), $[(RhCp^*Cl_2)_2]$ (5 mol %), $AgNO_3$ (20 mol %), and $Cu(OAc)_2$ (1 equiv) in EtOH (2 mL) at reflux for 12 h. [b]Isoquinoline **3ca** was isolated in 5% yield. [c]Isoquinoline **3ea** was isolated in 48% yield. [d]Isoquinoline **3ah** was isolated in 46% yield. [e]Isoquinoline **3aj** was isolated in 22% yield. [f]Isoquinoline **3ak** was isolated in 22% yield. [g]Isoquinoline **3am** was isolated in 15% yield. [h]Isoquinoline **3as** was isolated in 17% yield.

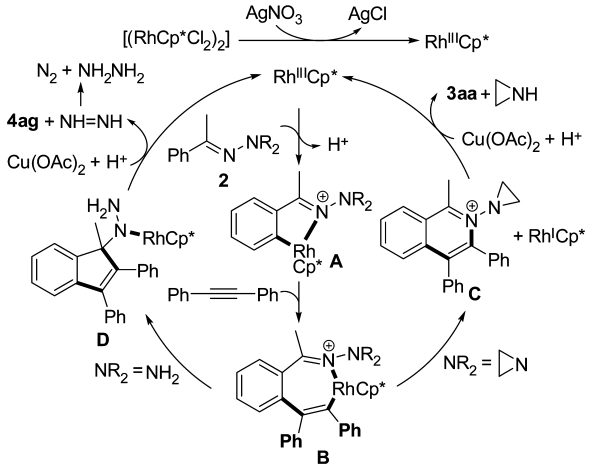
Scheme 3. Control Experiments



0.2 mmol of alkyne **1a** gave isoquinoline **3aa** in 72% yield (eq 2) but that ketone **7aa** was unreactive (eq 3). Compared with the yield of the reaction under the optimized reaction conditions (entry 7 in Table 1), these results indicate that hydrazone **6aa** might be involved in this process but is probably not an intermediate in the main pathway of the reaction.

Consequently, mechanisms for the selective syntheses of isoquinolines and indenes are proposed on the basis of the present results and previously reported mechanisms[4−8] (Scheme 4). Initially, $[(RhCp^*Cl_2)_2]$ is easily converted to the active $Rh^{III}Cp^*$ species by $AgNO_3$.[6−8] Subsequently, $Rh^{III}Cp^*$ treated with benzylidenehydrazone **2** gives a new Rh intermediate **A** via cleavage of the $C(sp^2)$−H bond and formation of the C−Rh and Rh−N bonds, which is supported by the results of in situ HRMS analysis (see Figure S1 in the Supporting Information). Insertion of alkyne **1a** into the $C(sp^2)$−Rh bond of Rh intermediate **A** offers intermediate **B**, which can follow one of two pathways depending on the substitution of benzylidenehydrazone **2**: either (1) direct reductive elimination of intermediate **B** to give intermediate **C** and the Rh^ICp^* species or (2) addition of the carbon atom

Scheme 4. Possible Mechanisms



of the C=N bond in intermediate **B**, leading to intermediate **D**. Finally, N−N bond cleavage of either intermediate **C** or intermediate **D** takes place to yield the corresponding product **3aa** or **4ag** with the aid of $Cu(OAc)_2$.

CONCLUSIONS

In summary, we have illustrated a novel Rh-catalyzed tandem reaction for the selective synthesis of isoquinolines and indenes. This method is realized through selective cleavage of the N−N bond or the C=N bond followed by sequential C−H activation and cyclization with internal alkynes. The mechanism has been discussed according to kinetic isotope effect experiments and in situ HRMS analysis.

EXPERIMENTAL SECTION

General Considerations. The ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solvent on an NMR spectrometer using TMS as an internal standard. LRMS was performed on a GC−MS instrument and HRMS was measured on an electrospray ionization (ESI) apparatus using time-of-flight (TOF) mass spectrometry. Melting points are uncorrected.

Preparation of Benzylidenehydrazones 2. All of the benzylidenehydrazones **2** were synthesized according to known methods.[3]

Typical Experimental Procedure for the Rh-Catalyzed Synthesis of Isoquinolines and Indenes. To a Schlenk tube were added alkyne **1** (0.2 mmol), benzylidenehydrazone **2** (0.3 mmol), $[(RhCp^*Cl_2)_2]$ (5 mol %), $AgNO_3$ (20 mol %), $Cu(OAc)_2$ (0.2 mmol), and anhydrous EtOH (2 mL). Then the tube was charged with argon, and the reaction mixture was stirred under reflux (oil bath temperature of about 80 °C) for the indicated time until complete consumption of the starting material was achieved as monitored by TLC and/or GC−MS analysis. After the reaction was finished, the reaction mixture was cooled to room temperature, diluted with diethyl ether (5 mL), and washed with brine (3 × 1 mL). The aqueous phase was re-extracted with diethyl ether (3 × 2 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate = 20:1) to afford the desired product.

*1-Methyl-3,4-diphenylisoquinoline (**3aa**).*[7q] Yellow solid (50.2 mg, 85% yield), mp 104.8−106.6 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 3.07 (s, 3H), 7.15−7.23 (m, 5H), 7.30−7.37 (m, 5H), 7.56−7.58 (m, 2H), 7.64−7.66 (m, 1H), 8.17−8.20 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.7, 125.5, 126.1, 126.2, 126.5, 126.9, 127.1, 127.6, 128.1, 129.1, 129.9, 130.2, 131.4, 135.9, 137.5, 141.0, 149.4, 157.7; LRMS (EI 70 eV) *m*/*z* (%) 295 (M^+, 52), 294 (100).

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*4-(4-Methoxyphenyl)-1-methyl-3-phenylisoquinoline (**3ba**).* Yellow solid (28.9 mg, 44.5% yield), mp 152.4−153.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.06 (s, 3H), 3.82 (s, 3H), 6.86−6.89 (m, 2H), 7.12−7.22 (m, 5H), 7.36−7.40 (m, 2H), 7.55−7.59 (m, 2H), 7.68−7.70 (m, 1H), 8.17−8.19 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.7, 55.2, 113.6, 125.5, 126.2 (126.2), 126.4, 126.8, 127.6, 128.8, 129.6, 129.8, 130.2, 132.4, 136.3, 141.1, 149.5, 157.4, 158.6; LRMS (EI 70 eV) *m*/*z* (%) 325 (M^+, 69), 324 (100); HRMS (ESI) calcd for $C_{23}H_{19}NO$ $[M + H]^+$ 326.1539, found 326.1554.

*3-(4-Methoxyphenyl)-1-methyl-4-phenylisoquinoline (**3ba′**).*[11] Yellow solid (28.9 mg, 44.5% yield), mp 161.7−163.6 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.06 (s, 3H), 3.74 (s, 3H), 6.71−6.74 (m, 2H), 7.22−7.24 (m, 2H), 7.31−7.38 (m, 5H), 7.55−7.57 (m, 2H), 7.62−7.64 (m, 1H), 8.16−8.18 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.7, 55.1, 113.1, 125.5, 125.9, 126.1, 126.2 (2C), 127.0, 128.3, 128.6, 129.8, 131.3, 131.5, 133.5, 136.1, 137.8, 148.9, 157.6, 158.6; LRMS (EI 70 eV) *m*/*z* (%) 325 (M^+, 67), 324 (100); HRMS (EI) calcd for $C_{23}H_{19}NO$ $[M + H]^+$ 326.1539, found 326.1574.

*1,4-Dimethyl-3-phenylisoquinoline (**3ca**).*[7q] Yellow solid (23.3 mg, 50% yield), mp 88.5−90.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.59 (s, 3H), 2.98 (s, 3H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.56−7.62 (m, 3H), 7.74 (t, *J* = 7.5 Hz, 1H), 8.05 (d, *J* = 8.5 Hz, 1H), 8.16 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.4, 22.5, 122.2, 124.1, 126.0, 126.1, 126.2, 127.4, 128.1, 129.8, 136.2, 141.6, 150.6, 155.9; LRMS (EI 70 eV) *m*/*z* (%) 233 (M^+, 47), 232 (100).

*(1-Methyl-3-phenylisoquinolin-4-yl)methanol (**3da**).*[7p] Yellow solid (30.4 mg, 61% yield), mp 151.8−153.6 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.02 (s, 2H), 7.40−7.43 (m, 1H), 7.47 (t, *J* = 7.0 Hz, 2H), 7.62−7.66 (m, 3H), 7.79 (t, *J* = 8.0 Hz, 1H), 8.19 (d, *J* = 8.5 Hz, 1H), 8.29 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.7, 59.4, 124.1, 124.4, 126.1, 126.7 (2C), 128.0, 128.2, 129.6, 130.6, 135.7, 140.4, 151.8, 158.6; LRMS (EI 70 eV) *m*/*z* (%) 249 (M^+, 95), 248 (100).

*1-Methyl-3,4-dipropylisoquinoline (**3ea**).*[7q] Yellow oil (30.9 mg, 68% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.03−1.10 (m, 6H), 1.63−1.71 (m, 2H), 1.75−1.83 (m, 2H), 2.89−2.92 (m, 5H), 2.96−2.99 (m, 2H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.95 (d, *J* = 8.5 Hz, 1H), 8.07 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.4, 14.6, 22.3, 23.8, 24.2, 29.8, 37.4, 123.5, 125.2, 125.9, 126.0, 126.1, 129.4, 135.4, 151.6, 155.6; LRMS (EI 70 eV) *m*/*z* (%) 227 (M^+, 53), 226 (41), 212 (80), 198 (100).

*8-Methoxy-1-methyl-3,4-diphenylisoquinoline (**3ah**).*[7p] Yellow solid (48.8 mg, 75% yield), mp 139.4−141.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.21 (s, 3H), 3.99 (s, 3H), 6.88 (d, *J* = 8.0 Hz, 1H), 7.14−7.23 (m, 6H), 7.28−7.36 (m, 5H), 7.42 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.2, 55.5, 105.9, 118.3, 119.0, 126.9, 127.0, 127.5, 128.1, 128.3, 130.0, 130.2, 131.4, 138.2, 138.8, 140.9, 149.5, 157.4, 158.1; LRMS (EI 70 eV) *m*/*z* (%) 325 (M^+, 70), 324 (100).

*7-Methoxy-1-methyl-3,4-diphenylisoquinoline (**3ai**).*[7p] Yellow solid (40.3 mg, 62% yield), mp 128.2−130.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.03 (s, 3H), 3.40 (s, 3H), 6.95 (d, *J* = 7.5 Hz, 1H), 7.09−7.17 (m, 8H), 7.21−7.23 (m, 2H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.4, 55.5, 110.0, 118.0, 125.6, 126.4, 127.1, 127.3, 127.7, 130.2, 130.3, 141.4, 151.0, 156.8; LRMS (EI 70 eV) *m*/*z* (%) 325 (M^+, 84), 324 (100).

*5-Methoxy-1-methyl-3,4-diphenylisoquinoline (**3ai′**).*[3] Yellow solid (16.3 mg, 25% yield), mp 146.5−149.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.02 (s, 3H), 3.96 (s, 3H), 7.13−7.24 (m, 6H), 7.29−7.37 (m, 6H), 7.57 (d, *J* = 9.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.8, 55.4, 103.4, 122.2, 126.7, 127.0, 127.2, 127.5, 127.9, 128.1, 129.1, 130.2, 131.3 (2C), 137.7, 141.0, 147.6, 155.9, 157.8; LRMS (EI 70 eV) *m*/*z* (%) 325 (M^+, 76), 324 (100).

*6-Methoxy-1-methyl-3,4-diphenylisoquinoline (**3aj**).*[7q] Yellow solid (61.8 mg, 95% yield), mp 181.0−182.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.02 (s, 3H), 3.72 (s, 3H), 6.91 (s, 1H), 7.15−7.23 (m, 6H), 7.30−7.35 (m, 5H), 8.11 (d, *J* = 9.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.6, 55.2, 104.5, 118.7, 121.9, 126.8, 127.1, 127.4, 127.5, 128.2, 128.6, 130.2, 131.3, 137.9, 138.1, 141.2, 150.1, 157.0, 160.5; LRMS (EI 70 eV) *m*/*z* (%) 325 (M^+, 63), 324 (100).

*1,6-Dimethyl-3,4-diphenylisoquinoline (**3ak**).*[7q] Yellow solid (56.2 mg, 91% yield), mp 165.4−166.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.41 (s, 3H), 3.03 (s, 3H), 7.13−7.21 (m, 5H), 7.29−7.35 (m, 5H), 7.38−7.40 (m, 2H), 8.06 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.1, 22.6, 124.5, 125.0, 125.4, 126.8, 126.9, 127.5, 128.1, 128.6, 128.7, 130.2, 131.4, 136.1, 137.7, 140.1, 141.1, 149.5, 157.3; LRMS (EI 70 eV) *m*/*z* (%) 309 (M^+, 57), 308 (100).

*1-Methyl-3,4,6-triphenylisoquinoline (**3al**).*[7p] Yellow solid (67.5 mg, 91% yield), mp 176.5−178.1 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.08 (s, 3H), 7.16−7.19 (m, 3H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.30−7.41 (m, 8H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.81 (d, *J* = 8.5 Hz, 1H), 7.85 (s, 1H), 8.23 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.6, 123.9, 125.1, 126.1, 126.9, 127.1, 127.2, 127.4, 127.5, 127.9, 128.2, 128.8, 129.3, 130.2, 131.4, 136.3, 137.4, 140.4, 141.0, 142.4, 149.9, 157.5; LRMS (EI 70 eV) *m*/*z* (%) 371 (M^+, 63), 370 (100).

*6-Chloro-1-methyl-3,4-diphenylisoquinoline (**3am**).*[7r] Yellow solid (48.0 mg, 73% yield), mp 175.6−177.4 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.04 (s, 3H), 7.16−7.20 (m, 5H), 7.32−7.36 (m, 5H), 7.50 (d, *J* = 9.0 Hz, 1H), 7.62 (s, 1H), 8.11 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.7, 124.3, 125.0, 127.1, 127.3, 127.4, 127.6, 128.4 (2C), 130.1, 131.2, 136.3, 136.8, 137.0, 140.5, 150.5, 157.6; LRMS (EI 70 eV) *m*/*z* (%) 331 (M^+ + 2, 19), 329 (M^+, 51), 330 (40), 328 (100).

*6-Bromo-1-methyl-3,4-diphenylisoquinoline (**3an**).*[7q] Yellow solid (60.4 mg, 81% yield), mp 190.2−191.6 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.03 (s, 3H), 7.17−7.20 (m, 5H), 7.33−7.35 (m, 5H), 7.63 (d, *J* = 9.0 Hz, 1H), 7.80 (s, 1H), 8.02 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.6, 124.5, 125.0, 127.1, 127.2, 127.4, 127.6, 128.2, 128.3, 128.4, 129.9, 130.1, 131.2, 136.7, 137.3, 140.5, 150.5, 157.7; LRMS (EI 70 eV) *m*/*z* (%) 375 (M^+ + 2, 53), 373 (M^+, 55), 372 (100), 374 (100).

*1-Methyl-3,4-diphenylbenzo[h]isoquinoline (**3ao**).*[7q] Yellow solid (56.6 mg, 82% yield), mp 140.9−142.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.43 (s, 3H), 7.18−7.25 (m, 5H), 7.32−7.37 (m, 3H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 9.0 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.70−7.73 (m, 1H), 7.76 (d, *J* = 9.0 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 8.89 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.5, 123.9, 124.2, 126.6, 126.8, 127.1, 127.2, 127.3, 127.6, 128.2, 128.7, 129.6, 130.2, 131.1, 131.6, 132.9, 137.2, 138.0, 140.6, 150.9, 155.4; LRMS (EI 70 eV) *m*/*z* (%) 345 (M^+, 78), 344 (100).

*2,3-Diphenyl-8,9-dihydro-7H-benzo[de]quinoline (**3ap**).*[7p] Yellow solid (55.9 mg, 87% yield), mp 158.6−160.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.21−2.26 (m, 2H), 3.15 (t, *J* = 6.0 Hz, 2H), 3.35−3.37 (m, 2H), 7.11−7.21 (m, 5H), 7.27−7.36 (m, 6H), 7.42−7.46 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.3, 30.6, 34.7, 123.4, 123.8, 124.6, 126.8, 126.9, 127.5, 128.9, 129.9, 130.2, 131.3, 136.1, 137.7, 138.4, 141.1, 149.3, 159.2; LRMS (EI 70 eV) *m*/*z* (%) 321 (M^+, 62), 320 (100).

*7-Methyl-4,5-diphenylthieno[2,3-c]pyridine (**3aq**).*[7p] Yellow solid (57.2 mg, 95% yield), mp 148.5−149.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.90 (s, 3H), 7.17−7.23 (m, 6H), 7.27−7.31 (m, 3H), 7.35 (d, *J* = 7.5 Hz, 2H), 7.58 (d, *J* = 5.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.6, 124.2, 127.0, 127.1, 127.7, 128.2 (2C), 130.3, 130.5, 130.9, 134.2, 138.2, 140.4, 145.6, 150.9, 151.3; LRMS (EI 70 eV) *m*/*z* (%) 301 (M^+, 56), 300 (100).

*7-Methyl-4,5-diphenylfuro[2,3-c]pyridine (**3ar**).*[7n] Yellow solid (46.2 mg, 81% yield), mp 107.9−108.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.85 (s, 3H), 6.72 (s, 1H), 7.19−7.35 (m, 10H), 7.73 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.7, 106.4, 126.7, 127.0 (2C), 127.7, 128.3, 130.2, 130.3, 134.2, 137.6, 140.5, 141.3, 147.8, 149.6, 149.9; LRMS (EI 70 eV) *m*/*z* (%) 285 (M^+, 54), 284 (100).

*1-Ethyl-6-methyl-3,4-diphenylisoquinoline (**3as**).* Yellow solid (62.7 mg, 97% yield), mp 138.8−140.7 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.52 (t, *J* = 7.5 Hz, 3H), 2.42 (s, 3H), 3.38−3.43 (m, 2H), 7.13−7.23 (m, 5H), 7.32−7.41 (m, 7H), 8.14 (d, *J* = 9.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 22.0, 28.7, 123.6, 125.0, 125.1, 126.7, 126.9, 127.4, 128.0, 128.1, 128.4, 128.5, 129.1, 130.2, 131.3, 136.8, 137.8, 139.8, 141.2, 149.3, 161.8; LRMS (EI 70 eV) *m*/*z* (%) 323 (M^+, 59), 322 (100); HRMS (EI) calcd for $C_{24}H_{22}N$ $[M + H]^+$ 324.1747, found 324.1745.

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*1,3,4-Triphenylisoquinoline (**3at**).*[12] Yellow solid (63.5 mg, 89% yield), mp 171.6−173.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14−7.19 (m, 3H), 7.28−7.30 (m, 2H), 7.33−7.38 (m, 3H), 7.42−7.58 (m, 7H), 7.71 (d, J = 8.5 Hz, 1H), 7.81−7.83 (m, 2H), 8.17 (d, J = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 125.4, 126.0, 126.5, 126.9, 127.2, 127.4, 127.5, 128.2, 128.3 (2C), 128.5, 129.9, 130.0, 130.2, 130.4, 136.9, 137.5, 139.8, 140.8, 149.6, 159.7; LRMS (EI 70 eV) m/z (%) 357 (M^+, 63), 356 (100).

*3-Methyl-1,2-diphenyl-1H-indene (**4ag**).*[13] White solid (40.0 mg, 71% yield), mp 89.3−90.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.33 (s, 3H), 4.93 (s, 1H), 7.02 (d, J = 8.0 Hz, 2H), 7.07−7.19 (m, 6H), 7.24−7.33 (m, 5H), 7.39 (d, J = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.9, 57.8, 119.1, 123.6, 125.4, 126.4, 126.5, 126.8, 128.1 (2C), 128.4, 129.0, 135.5, 136.3, 140.0, 145.0, 145.9, 148.0; LRMS (EI 70 eV) m/z (%) 282 (M^+, 100), 267 (64).

*1,3-Dimethyl-2-phenyl-1H-indene (**4cg**).*[14] White solid (33.4 mg, 76% yield), mp 74.2−75.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.19 (d, J = 7.5 Hz, 3H), 2.24 (s, 3H), 3.85−3.89 (m, 1H), 7.21−7.49 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.6, 16.3, 45.7, 119.1, 122.5, 124.9, 126.6 (2C), 128.3, 128.5, 129.0, 133.2, 136.5, 145.8, 146.7, 148.3; LRMS (EI 70 eV) m/z (%) 220 (M^+, 100), 205 (94).

*(3-Methyl-2-phenyl-1H-inden-1-yl)methanol (**4dg**).* Yellow oil (25.5 mg, 54% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.24 (s, 3H), 3.63−3.66 (m, 1H), 3.98−4.01 (m, 1H), 4.05−4.06 (m, 1H), 7.23−7.44 (m, 8H), 7.57 (d, J = 7.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.6, 53.8, 63.4, 119.4, 123.0, 125.1, 127.0, 127.3, 128.5, 128.9, 135.9, 136.1, 141.9, 144.0, 146.8; LRMS (EI 70 eV) m/z (%) 236 (M^+, 67), 206 (98), 205 (100); HRMS (ESI) calcd for $C_{17}H_{17}O$ $[M + H]^+$ 237.1274, found 237.1286.

*3-Methyl-1-methylene-2-phenyl-1H-indene (**5dg**).*[15] Colorless oil (5.2 mg, 12% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.19 (s, 3H), 5.56 (s, 1H), 6.07 (s, 1H), 7.23−7.26 (m, 1H), 7.29 (d, J = 7.0 Hz, 1H), 7.33−7.36 (m, 4H), 7.44 (t, J = 7.5 Hz, 2H), 7.63 (d, J = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.4, 111.7, 118.6, 119.3, 125.4, 126.9, 128.1, 128.2, 130.3, 134.9, 135.9, 137.1, 138.4, 143.8, 147.4; LRMS (EI 70 eV) m/z (%) 218 (M^+, 86), 203 (100).

*3-Methyl-1,2-dipropyl-1H-indene (**4eg**).*[13] Colorless oil (15.4 mg, 36% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.82 (t, J = 7.0 Hz, 3H), 0.92−0.96 (m, 4H), 1.06−1.16 (m, 1H), 1.39−1.48 (m, 1H), 1.56−1.67 (m, 2H), 1.89−1.96 (m, 1H), 2.02 (s, 3H), 2.21−2.26 (m, 1H), 2.44−2.50 (m, 1H), 3.37 (s, 1H), 7.12 (t, J = 7.0 Hz, 1H), 7.20−7.26 (m, 2H), 7.36 (d, J = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.2, 14.1, 14.5, 18.1, 23.0, 28.6, 32.3, 49.3, 117.9, 122.4, 123.6, 126.1, 132.1, 146.0, 146.8, 146.9; LRMS (EI 70 eV) m/z (%) 214 (M^+, 44), 185 (54), 143 (100).

*(2,3-Dimethyl-1H-inden-1-yl)methanol (**4fg**).* Colorless oil (15.0 mg, 43% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.03 (s, 3H), 2.04 (s, 3H), 3.38 (s, 1H), 3.84−3.87 (m, 1H), 4.14−4.17 (m, 1H), 7.15 (t, J = 7.0 Hz, 1H), 7.21 (d, J = 7.5 Hz, 1H), 7.29 (t, J = 7.5 Hz, 1H), 7.44 (d, J = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.2, 12.4, 54.8, 62.7, 118.2, 122.5, 124.1, 127.0, 134.0, 138.4, 143.5, 147.3; LRMS (EI 70 eV) m/z (%) 174 (M^+, 70), 129 (99), 128 (100); HRMS (ESI) calcd for $C_{12}H_{15}O$ $[M + H]^+$ 175.1117, found 175.1130.

*2,3-Dimethyl-1-methylene-1H-indene (**5fg**).* Colorless oil (3.1 mg, 10% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.06 (s, 3H), 2.09 (s, 3H), 5.57 (s, 1H), 5.89 (s, 1H), 7.10−7.13 (m, 2H), 7.23 (t, J = 7.0 Hz, 1H), 7.50 (d, J = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 9.6, 10.5, 108.2, 117.5, 118.8, 124.6, 127.9, 131.8, 135.9, 137.1, 144.5, 148.5; LRMS (EI 70 eV) m/z (%) 156 (M^+, 65), 141 (100); HRMS (ESI) calcd for $C_{12}H_{13}$ $[M + H]^+$ 157.1012, found 157.1020.

*Methyl 3-Methyl-2-phenyl-1H-indene-1-carboxylate (**4gg**).* White solid (27.5 mg, 52% yield), mp 85.8−87.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.61 (s, 3H), 3.65 (s, 3H), 4.83 (s, 1H), 7.05 (t, J = 8.0 Hz, 2H), 7.17−7.29 (m, 4H), 7.35 (t, J = 7.5 Hz, 1H), 7.51 (d, J = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.5, 51.0, 55.9, 121.2, 124.2, 126.6, 127.1, 127.7, 128.4 (2C), 134.5, 139.5, 143.8, 149.0, 151.9, 165.8; LRMS (EI 70 eV) m/z (%) 264 (M^+, 62), 205 (100); HRMS (ESI) calcd for $C_{18}H_{17}O_2$ $[M + H]^+$ 265.1223, found 265.1236.

*4-Methoxy-3-methyl-1,2-diphenyl-1H-indene (**4au**).* White solid (27.5 mg, 44% yield%), mp 104.8−106.6 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.48 (s, 3H), 3.88 (s, 3H), 4.87 (s, 1H), 6.79 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 7.5 Hz, 2H), 7.05−7.14 (m, 5H), 7.22−7.26 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.9, 55.4, 58.2, 109.5, 116.8, 126.3, 126.4, 126.5, 127.9, 128.2, 128.4, 129.2, 133.2, 136.0, 136.6, 140.1, 143.7, 150.4, 154.7; LRMS (EI 70 eV) m/z (%) 313 (26), 312 (M^+, 100), 297 (50); HRMS (ESI) calcd for $C_{23}H_{21}O$ $[M + H]^+$ 313.1587, found 313.1599.

*6-Methoxy-3-methyl-1,2-diphenyl-1H-indene (**4av**).* White solid (31.2 mg, 50% yield), mp 98.6−100.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.30 (s, 3H), 3.73 (s, 3H), 4.90 (s, 1H), 6.77 (s, 1H), 6.86 (d, J = 8.0 Hz, 1H), 7.03 (d, J = 8.0 Hz, 2H), 7.08 (t, J = 7.5 Hz, 1H), 7.11−7.15 (m, 3H), 7.22−7.28 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.0, 55.5, 57.7, 110.2, 112.2, 119.6, 126.2, 126.4, 128.1, 128.5, 128.6, 135.2, 136.5, 139.1, 140.2, 143.0, 149.8, 158.4; LRMS (EI 70 eV) m/z (%) 313 (27), 312 (M^+, 100), 297 (49); HRMS (EI) calcd for $C_{23}H_{21}O$ $[M + H]^+$ 313.1587, found 313.1599.

*3,6-Dimethyl-1,2-diphenyl-1H-indene (**4aw**).*[13] Yellow solid (30.8 mg, 52% yield), mp 167.8−169.6 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.31 (s, 3H), 2.32 (s, 3H), 4.90 (s, 1H), 7.00−7.04 (m, 3H), 7.07−7.16 (m, 5H), 7.23−7.29 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.9, 21.5, 57.6, 118.9, 124.5, 126.3, 126.4, 127.5, 128.0, 128.2, 128.4, 128.9, 135.2, 135.5, 136.5, 140.3, 143.3, 144.0, 147.3; LRMS (EI 70 eV) m/z (%) 296 (M^+, 100), 281 (69).

*6-Chloro-3-methyl-1,2-diphenyl-1H-indene (**4ax**).* Yellow oil (52.5 mg, 83% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.30 (s, 3H), 4.91 (s, 1H), 7.01 (d, J = 7.5 Hz, 2H), 7.10 (t, J = 7.5 Hz, 1H), 7.13−7.17 (m, 4H), 7.21−7.27 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.9, 57.6, 120.0, 124.1, 126.7, 126.8, 127.1, 128.1 (2C), 128.6, 128.9, 131.3, 134.8, 135.9, 139.1, 144.4, 145.4, 149.6; LRMS (EI 70 eV) m/z (%) 318 (M^+ + 2, 18), 316 (M^+, 59), 281 (100); HRMS (ESI) calcd for $C_{22}H_{18}Cl$ $[M + H]^+$ 317.1091, found 317.1104.

*3-Methyl-6-nitro-1,2-diphenyl-1H-indene (**4ay**).* Yellow solid (31.4 mg, 48% yield), mp 153.8−155.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.38 (s, 3H), 5.03 (s, 1H), 7.02 (d, J = 7.5 Hz, 2H), 7.13−7.24 (m, 4H), 7.30−7.31 (m, 4H), 7.46 (d, J = 8.0 Hz, 1H), 8.01 (s, 1H), 8.25 (d, J = 8.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.9, 57.9, 118.9, 119.1, 123.5, 127.2, 127.6, 128.0, 128.3 (2C), 128.9 (2C), 129.3, 134.8, 135.2, 137.7, 146.0, 148.6, 151.2, 152.4; LRMS (EI 70 eV) m/z (%) 328 (25), 327 (M^+, 100), 310 (28); HRMS (ESI) calcd for $C_{22}H_{18}NO_2$ $[M + H]^+$ 328.1332, found 328.1343.

*3-Ethyl-6-methyl-1,2-diphenyl-1H-indene (**4az**).* White solid (37.8 mg, 61% yield), mp 119.6−120.6 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.34 (t, J = 7.0 Hz, 3H), 2.30 (s, 3H), 2.69−2.78 (m, 2H), 4.87 (s, 1H), 7.01−7.02 (m, 3H), 7.07 (t, J = 7.5 Hz, 1H), 7.11−7.15 (m, 4H), 7.23−7.24 (m, 4H), 7.31 (d, J = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 19.4, 21.4, 57.9, 119.2, 124.7, 126.4, 126.5, 127.5, 128.1, 128.2, 128.4, 128.7, 135.0, 136.6, 140.2, 141.6, 142.2, 143.6, 148.7; LRMS (EI 70 eV) m/z (%) 310 (M^+, 65), 281 (100); HRMS (EI) calcd for $C_{24}H_{23}$ $[M + H]^+$ 311.1794, found 311.1805.

*1,2-Bis(1-phenylethylidene)hydrazone (**6aa**).*[16] Yellow solid (7.1 mg, 10% yield), mp 122.8−124.7 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.32 (s, 6H), 7.40−7.44 (m, 6H), 7.90−7.92 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.0, 126.6, 128.3, 129.6, 138.4, 157.7; LRMS (EI 70 eV) m/z (%) 236 (M^+, 43), 221 (100).

■ ASSOCIATED CONTENT

Supporting Information

The reaction determined in situ by HRMS analysis, kinetic isotope effect experiments, and copies of spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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