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Ruthenium(II)-Catalyzed C–H Bond Activation: An Efficient Route toward Indenamines

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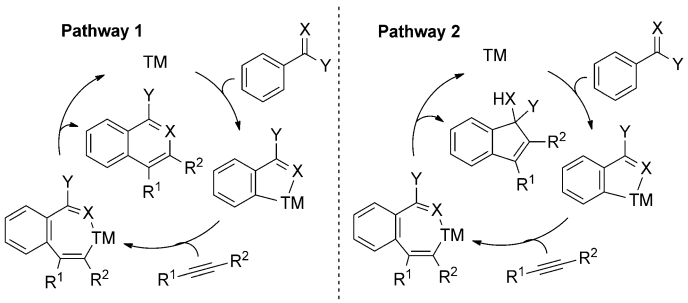
An efficient and atom-economical method for the synthesis of substituted indenamines from *N*-tosylarylimines and alkynes via ruthenium(II)-catalyzed C–H bond activation and annulation is described. The catalytic reaction proceeds well with a broad substrate scope and in good yields. A possible mechanism is proposed that involves imine nitrogen chelation-assisted *ortho*-C–H bond activation of the substrate, alkyne insertion, and intramolecular insertion of the C=NTs group into the C–Ru bond. Isotope-labeling experiments are performed to understand the underlying mechanism of the reaction.

Introduction

Transition-metal-catalyzed C–H bond functionalization has emerged as a prevailing method for the construction of C–C and C–heteroatom bonds.[1] Various chelating functional groups have been used to control the site selectivity of C–H bond functionalization owing to their ubiquitous nature. The chelating groups are usually nitrogen- or oxygen-containing functional groups.[2] The installation and removal of these functional groups often limit the applicability of the C–H bond activation methodology in the synthesis of complex organic molecules. Therefore, the development of reactions that involve the transformation of chelating groups into other functional groups is highly desirable.

The transition-metal-catalyzed, directing group-assisted *ortho*-C–H bond activation and annulation reactions with alkynes have recently been reported to play an indispensable role in the synthesis of heterocyclic and carbocyclic compounds.[3] These reactions involve directed C–H bond activation and metallacycle formation, alkyne insertion into organometallic intermediates, and reductive elimination to form final products. However, a similar strategy to perform the nucleophilic addition of organometallic intermediates to the directing functional groups instead of reductive elimination is less explored (Scheme 1). There are only a few examples of reactions involving C–H activation and [3+2] annulation via nucleophilic addition of organometallic intermediates to the directing functional groups (e.g., ketone, imine, and amide).[4–8] Our group[6d] and others[6] previously reported a [3+2]-type annulation reaction to form substituted indenols via transition-metal-catalyzed C–H activation and carbocyclization of aryl ketones with alkynes. Similarly, the [3+2] annulation of aromatic imines with alkynes via C–H bond activation was reported to be effective in forming various cyclic amines.[4] Mostly, rhenium[4a,5a,7] and rhodium[4b,c,5b,6c,d,8] complexes were found to be efficient catalyst systems for these types of C–H activation and [3+2] annulation reactions. The less expensive ruthenium complexes demonstrated better catalytic activity in C–H bond activation reactions,[3f,9] which provides an opportunity to explore the possibility of using them in the [3+2] annulation reaction of aryl imines with alkynes to form indenamine derivatives.[4d,e] As an extension of our effort in the development of new organic transformations through C–H bond activation,[10] herein we report an efficient method for the synthesis of *N*-tosylindenamines through the ruthenium(II)-catalyzed C–H activation reactions.



Scheme 1. Transition-metal-catalyzed C–H activation and annulation pathways. TM = transition metal. X = O or NR; Y, R^1, and R^2 = alkyl or aryl.

Results and Discussion

The reaction of *N*-tosylbenzaldimine **1a** with diphenylacetylene **2a** in the presence of 2 mol% $[RuCl_2(p\text{-cymene})]_2$, 20 mol%

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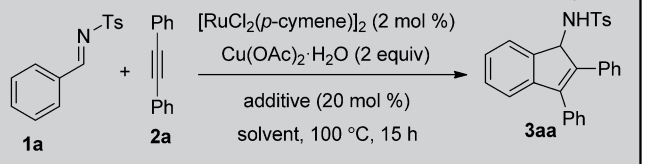
Table 1. Optimization studies for the annulation of imines with alkynes.[a]



Entry	Additive	Solvent	Yield[b] [%]
1	–	DCE	–
2	**$AgSbF_6$**	**DCE**	**93 (90)**[c]
3	$AgBF_4$	DCE	57
4	AgOAc	DCE	–
5	Ag_2O	DCE	–
6	KPF_6	DCE	8
7	$NaBF_4$	DCE	9
8	$AgSbF_6$	*t*-amyl alcohol	–
9	$AgSbF_6$	1,2-dimethoxyethane	–
10	$AgSbF_6$	toluene	32
11	$AgSbF_6$	THF	25
12	$AgSbF_6$	1,4-dioxane	26
13	$AgSbF_6$	ethyl acetate	27
14	$AgSbF_6$	DCE	42[d]
15	$AgSbF_6$	DCE	54[e]

[a] Unless otherwise stated, all reactions were performed with **1a** (0.20 mmol), **2a** (0.24 mmol), $[RuCl_2(p\text{-cymene})]_2$ (0.004 mmol), $Cu(OAc)_2{\cdot}H_2O$ (0.40 mmol), and an additive (0.04 mmol) in a solvent (1 mL) at 100 °C for 15 h; [b] Yields were determined from ^1H NMR analysis with 1,2-dimethoxyethane as the internal standard; [c] Isolated yield; [d] 10 mol% $AgSbF_6$ was used; [e] 1 equiv. of $Cu(OAc)_2{\cdot}H_2O$ was used.

$AgSbF_6$, and 2 equiv. of $Cu(OAc)_2{\cdot}H_2O$ in 1,2-dichloroethane (DCE) at 100 °C for 15 h gave *N*-tosylindenamine **3aa** in 90% isolated yield (Table 1, entry 2). The structure of **3aa** was confirmed by its ^1H and ^{13}C NMR and HRMS data. The choice of the oxidant, silver additive, and solvent is vital to the catalytic reaction. The reaction did not proceed smoothly in the absence of $Cu(OAc)_2{\cdot}H_2O$. We tested various other metal additives in the formation of **3aa**, and none of them was found to be superior to $AgSbF_6$ (Table 1, entries 3–7). We also examined the reaction by replacing DCE with other solvents, and most of them were less effective or ineffective (Table 1, entries 8–13). Finally, lowering the amount of $AgSbF_6$ or $Cu(OAc)_2{\cdot}H_2O$ suppressed the yield of **3aa** (Figure 1).

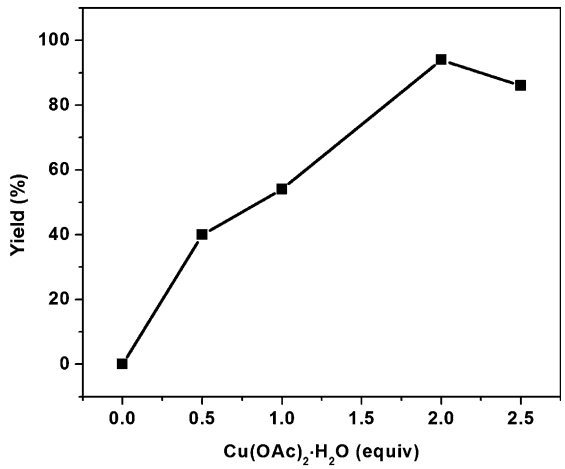
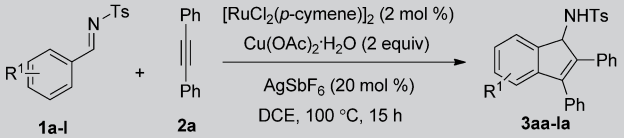


Figure 1. Effect of $Cu(OAc)_2{\cdot}H_2O$ on indenamine formation.

Under the optimized reaction conditions described above, several substituted *N*-tosylbenzaldimines **1b–l** were tested with diphenylacetylene **2a** to understand the scope of the reaction (Table 2). The 4-F-, 4-Cl-, and 4-Br-substituted aldimines **1b–d** underwent C–H activation and annulation smoothly with **2a** to give the corresponding indenamine derivatives **3ba–da** in 93, 84, and 95% yields, respectively (Table 2, entries 2–4). Similarly, aldimines substituted with 4-Ph and 4-CF_3 groups effectively reacted with **2a** under standard conditions to afford **3ea–fa** in excellent yields. The 4-Me- and 4-OMe-substituted substrates **1h** and **i** reacted in a less effective manner with **2a** to give **3ha** and **ia** in 50 and 39% yields, respectively. In addition, 3-bromobenzaldimine **1j** reacted with **2a** to give **3ja** in 82% yield (Table 2, entry 10). In the reaction, despite the presence of two possible C–H bond activation sites at C2 and C6 of **1j**, the C–H activation occurred only at C6, likely owing to the steric effect of the bromo group at C3. Similarly, 3-iodo

Table 2. Results of the reaction of *N*-tosylaldimines **1** with diphenylacetylene **2a**.[a]



1a: R^1 = H
1b: R^1 = 4-F
1c: R^1 = 4-Cl
1d: R^1 = 4-Br
1e: R^1 = 4-Ph
1f: R^1 = 4-CF_3
1g: R^1 = 4-$C(CH_3)_3$
1h: R^1 = 4-Me
1i: R^1 = 4-OMe
1j: R^1 = 3-Br
1k: R^1 = 3-I
1l: R^1 = 2-Br

Entry	1	Product 3	Yield[b] [%]
1	**1a**	**3aa**; R^1 = H	90
2	**1b**	**3ba**; R^1 = F	93
3	**1c**	**3ca**; R^1 = Cl	84
4	**1d**	**3da**; R^1 = Br	95
5	**1e**	**3ea**; R^1 = Ph	70
6	**1f**	**3fa**; R^1 = CF_3	97
7	**1g**	**3ga**; R^1 = 4-$C(CH_3)_3$	93
8	**1h**	**3ha**; R^1 = Me	50
9	**1i**	**3ia**; R^1 = OMe	39
10	**1j**	**3ja**; R^1 = Br	82
11	**1k**	**3ka**; R^1 = I	42
12	**1l**	**3la**	48

[a] Unless otherwise stated, all reactions were performed with **1** (0.40 mmol), **2a** (0.480 mmol), $[RuCl_2(p\text{-cymene})]_2$ (0.008 mmol), $Cu(OAc)_2{\cdot}H_2O$ (0.80 mmol), and $AgSbF_6$ (0.080 mmol) in DCE (2 mL) at 100 °C for 15 h; [b] Isolated yield.

aldimine **1k** gave **3ka** in moderate yield. The reaction worked well for 2-bromo aldimine **1l** to form the corresponding product **3la** in moderate yield (Table 2, entry 12). The substrates **1c**, **d**, **j**, and **k** produced halogen-substituted indenamine derivatives in good to excellent yields, which were set aside for further transformations.[11]

In addition to that of **2a**, we examined the scope of various symmetrical and unsymmetrical alkynes in the present reaction (Table 3). 4-Methyl (**2b**)- and 3-methyl (**2c**)-substituted diphenylacetylenes reacted with **1c** to give the corresponding products in excellent yields (Table 3, entries 1 and 2). Similarly, 4-F-, 4-Cl-, 4-Br-, and 4-CF_3-containing diarylacetylenes **2d**–**g** produced respective indenamine products in excellent yields at a slightly higher reaction temperature and longer reaction time (Table 3, entries 3–6).

To probe the regioselectivity of the catalytic reaction, the unsymmetrical alkynes **2h**–**j** were investigated. 1-Phenyl-1-propyne (**2h**), but-1-yn-1-ylbenzene (**2i**), and hex-1-yn-1-ylbenzene (**2j**) reacted efficiently with **1a** to give two regioisomeric products in high yields and with high regioselectivity (Table 3, entries 7–9). Similarly, prop-1-yne-1,3-diyldibenzene (**2k**) reacted with **1c** to give **3ck** in good yield and with excellent regioselectivity (95:5). We also tested the reaction of the enyne substrate **2l** with **1a**, which afforded **3al** in 73% yield and with high regioselectivity (Table 3, entry 11).

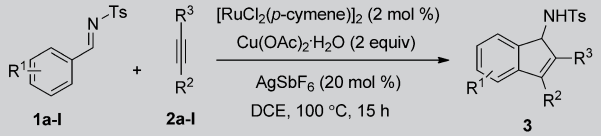
In addition to *N*-tosylaldimines, we investigated other imine substrates under our reaction conditions (Table 4). Aldimine (**1m**) derived from benzenesulfonamide reacted with **2a** to afford **3ma** in 76% yield (Table 4, entry 1). Similarly, the reaction of substrates **1n** and **o** with **2a** gave the corresponding products in moderate yields. *N*-Tosylketimine (**1p**) also underwent C–H activation and [3+2] carbocyclization with **2a** to furnish the tertiary carbinamine product **3pa** in moderate yield (Table 4, entry 4). Notably, the reaction did not proceed with *N*-aryl or *N*-H imines of aldehyde or ketone instead of *N*-tosylimines (Table 4, entries 5 and 6).

To elucidate the mechanism of the present catalytic reaction, we first performed an intermolecular competition reaction of imine substrates with different substitutions (Scheme 2). In the three sets of reactions, the nucleophilicity of the substrate had no effect on their relative reactivity, which indicates that the C–H bond ruthenation unlikely follows an electrophilic aromatic substitution mechanism.

To understand the mechanism of this catalytic reaction in detail, we treated **1a** with 10 equiv. of D_2O under standard reaction conditions at the end of the reaction; 75% hydrogen–deuterium–exchanged **1a** was recovered in 83% yield. This result indicates reversible C–H bond ruthenation with *N*-tosylimine (Scheme 3). To further understand the underlying nature of the mechanism of the present reaction, we measured inter- and intramolecular kinetic isotopic effects (KIEs) of the catalytic reaction of **1a** with **2a**. An intermolecular KIE of $k_H/k_D = 1.08$ was observed for the competition reaction of **1a** and deuterium-labeled **[D_5]-1a** with **2a**. Similarly, an intramolecular competition experiment of **[D_1]-1a** with **2a** revealed a KIE of $k_H/k_D = 1.27$ (Scheme 3). These small KIE values indicate that the C–H bond activation step may not be the rate-limiting step.[10d–f,12]

Based on our experimental results and the known metal-catalyzed, directing group-assisted C–H bond activation and [3+2] annulation reactions,[4–8,10] a possible mechanism of the present ruthenium(II)-catalyzed C–H activation and annulation is proposed in Scheme 4. The catalytic cycle is probably initiated by the removal of chloride by Ag^+ in $[RuCl_2(p\text{-cymene})]_2$ to form a coordinatively unsaturated ruthenium monomer followed by the coordination of imine nitrogen to the ruthenium complex and subsequent *ortho*-C–H bond activation to form five-membered ruthenacycle **A**. The coordination of alkyne **2a** to ruthenium complex **A** and the regioselective inser-

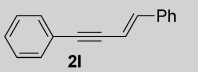
Table 3. Scope of alkynes in ruthenium(II)-catalyzed C–H activation and annulation.[a]



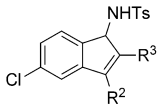
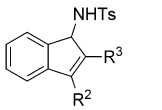
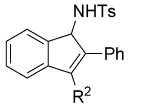
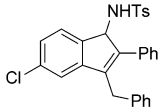
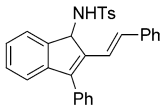
1a-l 2a-l 3

2a: R^2, R^3 = Ph
2b: R^2, R^3 = 4-MeC_6H_4
2c: R^2, R^3 = 3-MeC_6H_4
2d: R^2, R^3 = 4-FC_6H_4
2e: R^2, R^3 = 4-ClC_6H_4
2f: R^2, R^3 = 4-BrC_6H_4
2g: R^2, R^3 = 4-$CF_3C_6H_4$

2h: R^2 = Me, R^3 = Ph
2i: R^2 = Et, R^3 = Ph
2j: R^2 = $(CH_2)_3Me$, R^3 = Ph
2k: R^2 = CH_2Ph, R^3 = Ph

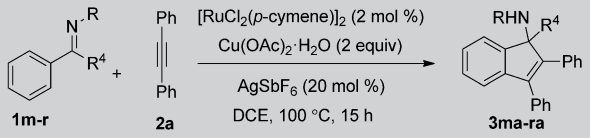


2l

Entry	1	2	Product 3		Yield[b] [%]
1	**1c**	**2b**		**3cb**; R^2, R^3 = 4-MeC_6H_4	90
2	**1c**	**2c**		**3cc**; R^2, R^3 = 3-MeC_6H_4	97
3	**1c**	**2d**		**3cd**; R^2, R^3 = 4-FC_6H_4	83[c]
4	**1c**	**2e**		**3ce**; R^2, R^3 = 4-ClC_6H_4	89[c]
5	**1c**	**2f**		**3cf**; R^2, R^3 = 4-BrC_6H_4	86[c]
6	**1a**	**2g**		**3ag**; R^2, R^3 = 4-$CF_3C_6H_4$	63[c]
7	**1a**	**2h**		**3ah**; R^2 = Me	91 (7:1)[d]
8	**1a**	**2i**		**3ai**; R^2 = Et	90 (10:1)[d]
9	**1a**	**2j**		**3aj**; R^2 = $(CH_2)_3CH_3$	58 (7:1)[d]
10	**1c**	**2k**		**3ck**	66 (95:5)[d]
11	**1a**	**2l**		**3al**	73 (7:1)[d]

[a] Unless otherwise stated, all reactions were performed with **1** (0.40 mmol), **2** (0.48 mmol), $[RuCl_2(p\text{-cymene})]_2$ (0.008 mmol), $Cu(OAc)_2{\cdot}H_2O$ (0.80 mmol), and $AgSbF_6$ (0.08 mmol) in DCE (2 mL) at 100 °C for 15 h; [b] Isolated yield; [c] 120 °C, 24 h; [d] Ratios of regioisomers are given in parentheses and were determined from ^1H NMR analysis; major isomers are shown.

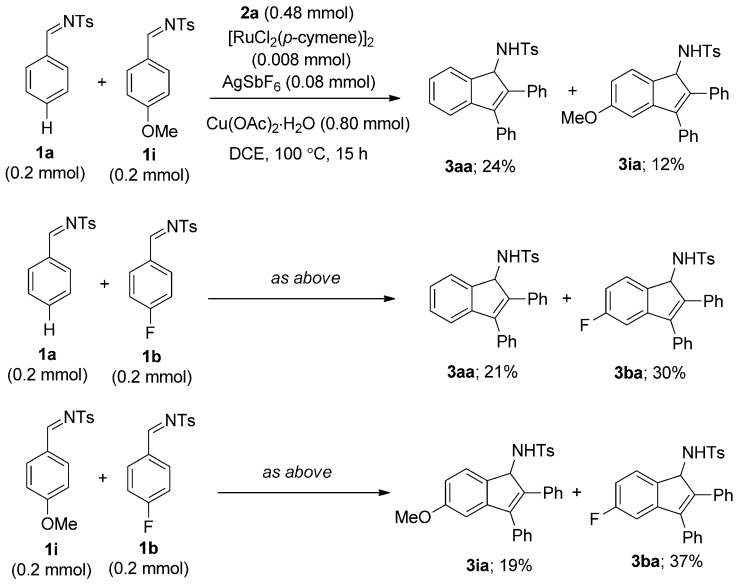
Table 4. Scope of imines in ruthenium(II)-catalyzed C–H activation and annulation.[a]



1m: R = SO_2Ph, R^4 = H; **1n**: R = $SO_2$4-ClC_6H_4, R^4 = H; **1o**: R = SO_2Et, R^4 = H; **1p**: R = Ts, R^4 = Ph; **1q**: R = Ph, R^4 = H; **1r**: R = H, R^4 = Ph

Entry	1	Product 3	Yield[b] [%]
1	**1m**	**3ma**; R = SO_2Ph, R^4 = H	76
2	**1n**	**3na**; R = $SO_2$4-ClC_6H_4, R^4 = H	31
3	**1o**	**3oa**; R = SO_2Et, R^4 = H	35
4	**1p**	**3pa**; R = Ts, R^4 = Ph	57
5	**1q**	**3qa**; R = Ph, R^4 = H	–
6	**1r**	**3ra**; R = H, R^4 = Ph	–

[a] Unless otherwise stated, all reactions were performed with **1** (0.40 mmol), **2a** (0.48 mmol), $[RuCl_2(p\text{-cymene})]_2$ (0.008 mmol), $Cu(OAc)_2{\cdot}H_2O$ (0.80 mmol), and $AgSbF_6$ (0.08 mmol) in DCE (2 mL) at 100 °C for 15 h; [b] Isolated yield.



Scheme 2. Intermolecular competition studies.

tion of alkyne into the C–Ru bond gives the seven-membered ruthenacycle **B** with the *N*-tosylimine group π-coordinated to the ruthenium center.[4,5,6c,d,10g] The subsequent intramolecular insertion of the C=NTs group into the Ru–alkenyl bond affords the ruthenium amido intermediate **C**. Active ruthenium(II) is released likely through protonation. The reaction does not proceed without $Cu(OAc)_2{\cdot}H_2O$, and the yield was low with use of a small amount of copper salt. Therefore, $Cu(OAc)_2$ could be an acetate source for acetate-assisted cyclometalation.[9c]

The *N*-tosylindenamines prepared by using this method can be readily unprotected by treating them with SmI_2.[13] Similarly, these *N*-tosylindenamines are easily converted into the corresponding indenones with tetrabutylammonium fluoride (Scheme 5).[14]

Conclusions

We developed an efficient ruthenium-catalyzed, chelation-assisted *ortho*-C–H bond activation of *N*-tosylbenzaldimines and [3+2] annulation with alkynes to afford substituted indenamine derivatives in good to excellent yields. A possible mechanism is proposed for the catalytic reaction. The kinetic isotope labeling studies suggest that C–H activation follows reversible cyclometalation and that an initial C–H activation step may not be the rate-limiting step. Further studies on the intramolecular C–H activation and related transformations are ongoing in our laboratory.

Experimental Section

General information

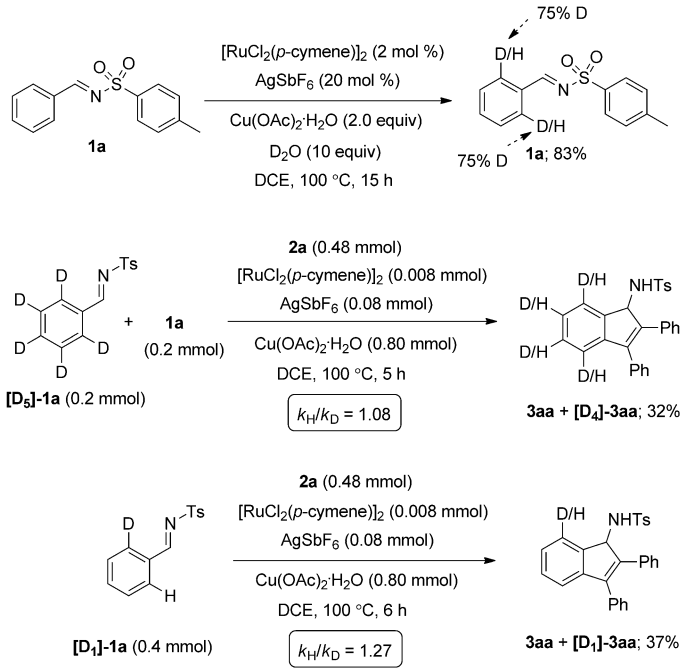
Unless otherwise stated, all reactions were performed under a nitrogen atmosphere on a dual-manifold Schlenk line and in oven-dried glassware. All solvents were dried according to known methods and distilled before use.[15]

General method for the synthesis of *N*-tosylindenamines

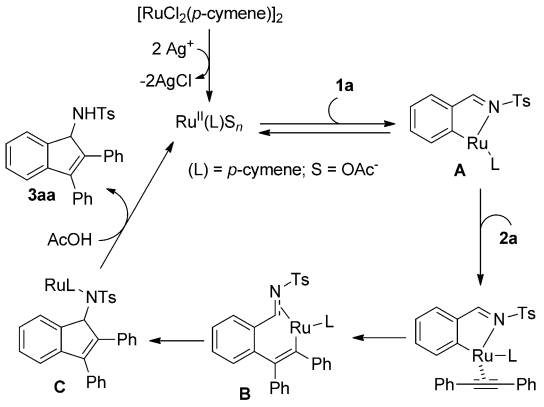
A sealed tube containing $[RuCl_2(p\text{-cymene})]_2$ (5.0 mg, 0.008 mmol), $AgSbF_6$ (27.0 mg, 0.08 mmol), $Cu(OAc)_2{\cdot}H_2O$ (160.0 mg, 0.80 mmol), *N*-tosylimines **1** (0.4 mmol), and alkyne **2** (0.48 mmol) was evacuated and purged thrice with nitrogen gas. Then, DCE (2.0 mL) was added to the system with a syringe under a nitrogen atmosphere and the reaction mixture was stirred at 100 °C for 15 h. After the completion of the reaction, the mixture was cooled and diluted with CH_2Cl_2 (10 mL). The mixture was filtered through a Celite pad (Celite 545, Showa Chemical Industry Co.) , and the Celite pad was washed several times with CH_2Cl_2 (50 mL). The combined filtrate was concentrated in vacuo, and the residue was purified by column chromatography using ethyl acetate/*n*-hexane (1:4) to afford the desired product **3**.

N-(2,3-Diphenyl-1*H*-inden-1-yl)-4-methylbenzenesulfonamide (3aa)

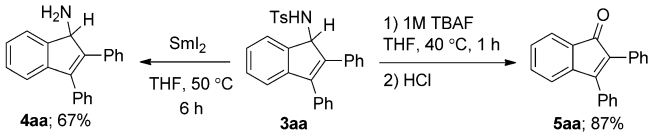
White solid; m.p. 181–183 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 7.2 Hz, 1H), 7.36–7.30 (m, 3H), 7.28–7.20 (m, 6H), 7.19–7.16 (m, 1H), 7.09 (t, *J* = 7.2 Hz, 1H), 6.97 (t, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 7.6 Hz, 2H), 5.50 (d, *J* = 8.8 Hz, 1H), 4.52 (d, *J* = 8.4 Hz, 1H), 2.47 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.7 (C), 143.4 (C), 143.3 (C), 141.2 (C), 141.0 (C), 138.0 (C), 134.1 (C), 133.1 (C), 129.6 (2 *C*H), 129.3 (2 *C*H), 129.1 (2 *C*H), 128.6 (2 *C*H), 128.4 (*C*H), 128.0 (2 *C*H), 127.8 (*C*H), 127.4 (2 *C*H), 127.1 (*C*H), 126.5 (*C*H), 124.8 (*C*H), 120.7 (2 *C*H), 61.0 (*C*H), 21.5 ppm (CH_3); IR (neat): $\tilde{\nu}$ = 3301, 1596, 1157 cm^{-1}; HRMS (EI^+): *m/z*: calcd for $C_{28}H_{23}NO_2S$: 437.1449; found: 437.1444.



Scheme 3. Isotope-labeling studies. D = deuterium; H = hydrogen.



Scheme 4. Proposed reaction mechanism.



Scheme 5. Synthesis of indenamine and indenone. TBAF = tetrabutylammonium fluoride.

4-Methyl-*N*-(2-methyl-3-phenyl-1*H*-inden-1-yl)benzenesulfonamide (3 ah)

Brown solid; m.p. 119–121 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 7.6 Hz, 1H), 7.36–7.30 (m, 2H), 7.24–7.14 (m, 6H), 7.01 (d, J = 6.8 Hz, 2H), 5.31 (d, J = 8.8 Hz, 1H), 4.47 (d, J = 8.4 Hz, 1H), 2.44 (s, 3H), 2.12 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.5 (C), 143.2 (C), 143.2 (C), 140.4 (C), 138.1 (C), 136.7 (C), 133.9 (C), 129.5 (2 *C*H), 129.0 (2 *C*H), 128.4 (*C*H), 128.1 (2 *C*H), 127.3 (2 *C*H), 126.9 (*C*H), 126.3 (*C*H), 124.3 (*C*H), 119.2 (*C*H), 61.0 (*C*H), 21.5 (CH_3), 11.6 ppm (CH_3); ; IR (neat): $\tilde{\nu}$ = 3062, 2923, 1596, 1326, 1157 cm^{-1}; HRMS (EI$^+$): *m/z*: calcd for $C_{23}H_{21}NO_2S$: 375.1293; found: 375.1294.

N-(3-Benzyl-5-chloro-2-phenyl-1*H*-inden-1-yl)-4-methylbenzenesulfonamide (3 ck)

White solid; m.p. 144–146 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.0 Hz, 1H), 7.26–7.17 (m, 5H), 7.15–7.08 (m, 6H), 7.01–6.96 (m, 3H), 5.35 (d, J = 8.4 Hz, 1H), 4.84 (d, J = 8.8 Hz, 1H), 3.89 (s, 2H), 2.44 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.3 (C), 144.4 (C), 143.3 (C), 141.7 (C), 137.9 (C), 137.7 (C), 137.7 (C), 134.4 (C), 133.1 (C), 129.5 (2 *C*H), 128.7 (2 *C*H), 128.7 (2 *C*H), 128.4 (2 *C*H), 128.0 (2 *C*H), 127.6 (*C*H), 127.2 (2 *C*H), 126.4 (*C*H), 126.1 (*C*H), 125.4 (*C*H), 120.7 (*C*H), 60.8 (*C*H), 31.8 (CH_2), 21.5 ppm (CH_3); IR (neat): $\tilde{\nu}$ = 3262, 2923, 1596, 1434, 1326, 1157 cm^{-1}; HRMS (EI$^+$): *m/z*: calcd for $C_{29}H_{24}ClNO_2S$: 485.1216; found: 485.1219.

N-(2,3-Diphenyl-1*H*-inden-1-yl)benzenesulfonamide (3 ma)

White solid; m.p. 169–171 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, J = 7.6 Hz, 2H), 7.60 (t, J = 7.2 Hz, 1H), 7.51–7.44 (m, 3H), 7.35–7.20 (m, 6H), 7.17 (t, J = 6.4 Hz, 2H), 7.08 (t, J = 7.6 Hz, 1H), 6.97 (t, J = 7.6 Hz, 2H), 6.84 (d, J = 7.2 Hz, 2H), 5.51 (d, J = 7.6 Hz, 1H), 4.60 ppm (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.7 (C), 143.3 (C), 141.2 (C), 141.1 (C), 141.1 (C), 134.1 (C), 133.1 (C), 132.6 (*C*H), 129.3 (2 *C*H), 129.1 (2 *C*H), 129.0 (2 *C*H), 128.6 (2 *C*H), 128.5 (*C*H), 128.0 (2 *C*H), 127.8 (*C*H), 127.3 (2 *C*H), 127.2 (*C*H), 126.6 (*C*H), 124.8 (*C*H), 120.7 (*C*H), 61.2 ppm (*C*H); IR (neat): $\tilde{\nu}$ = 3301, 1596, 1157 cm^{-1}; HRMS (EI$^+$): *m/z*: calcd for $C_{27}H_{21}NO_2S$: 423.1293; found: 423.1289.

N-(2,3-Diphenyl-1*H*-inden-1-yl)ethanesulfonamide (3 oa)

White solid; m.p. 147–149 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, J = 6.4 Hz, 1H), 7.37–7.27 (m, 8H), 7.25–7.19 (m, 5H), 5.64 (d, J = 9.2 Hz, 1H), 4.18 (d, J = 9.2 Hz, 1H), 2.91 (sxt, J = 7.2 Hz, 1H), 2.79 (sxt, J = 6.8 Hz, 1H), 1.00 ppm (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.7 (C), 143.4 (C), 142.0 (C), 140.6 (C), 134.1 (C), 133.8 (C), 129.5 (2 *C*H), 129.1 (2 *C*H), 128.5 (3 *C*H), 128.2 (2 *C*H), 127.7 (*C*H), 127.5 (*C*H), 126.5 (*C*H), 124.5 (*C*H), 120.7 (*C*H), 61.7 (*C*H), 49.0 (CH_2), 8.0 ppm (CH_3); IR (neat): $\tilde{\nu}$ = 3278, 3054, 1319, 1141 cm^{-1}; HRMS (EI$^+$): *m/z*: calcd for $C_{23}H_{21}NO_2S$: 375.1293; found: 375.1297.

4-Methyl-*N*-(1,2,3-triphenyl-1*H*-inden-1-yl)benzenesulfonamide (3 pa)

White solid; m.p. 203–205 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (d, J = 7.2 Hz, 2H), 7.33–7.29 (m, 5H), 7.28–7.26 (m, 1H), 7.19–7.09 (m, 6H), 7.05–7.00 (m, 7H), 6.68 (d, J = 7.2 Hz, 2H), 5.36 (s, 1H), 2.39 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.5 (C), 144.3 (C), 143.3 (C), 142.8 (C), 141.7 (C), 141.7 (C), 137.6 (C), 134.1 (C), 132.8 (C), 129.6 (2 *C*H), 129.1 (*C*H), 129.1 (3 *C*H), 128.7 (2 *C*H), 128.5 (2 *C*H), 128.2 (2 *C*H), 128.2 (*C*H), 127.8 (*C*H), 127.8 (*C*H), 127.7 (*C*H), 127.7 (*C*H), 127.7 (*C*H), 127.6 (*C*H), 126.1 (*C*H), 124.9 (2 *C*H), 120.5 (*C*H), 73.8 (C), 21.4 ppm (CH_3); IR (neat): $\tilde{\nu}$ = 3054, 1596, 1326, 1157 cm^{-1}; HRMS (EI$^+$): *m/z*: calcd for $C_{34}H_{27}NO_2S$: 513.1762; found: 513.1771.

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