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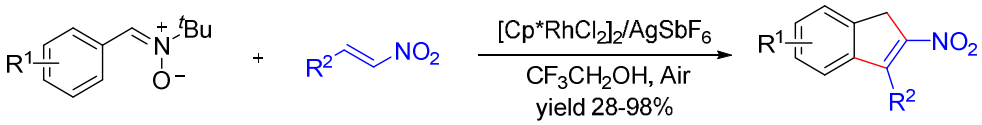
Rhodium(III)-Catalyzed C-H Activation of Nitrones and Annulative Coupling with Nitroalkenes

Dachang Bai,[†] Qingqian Jia,[†] Teng Xu, [†] Qiuqiu Zhang,[†] Fen Wu,[†] Chaorui Ma,[†] Bingxian Liu,[†] Junbiao Chang,*[,†] Xingwei Li*[,†,‡]

[†]Henan Key Laboratory of Organic Functional Molecule and Drug Innovation, School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang 453007, China

[‡]Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

Abstract: Rh(III)-catalyzed synthesis of nitro-functionalized indenes has been realized via C-H activation of arylnitrones and annulation with nitroolefins. The reaction proceeded in moderate to high yields with good functional group tolerance under ambient atmosphere.



Transition metal-catalyzed C-H bond activation has proven to be a powerful strategy for the step-economical construction of C-C bonds and has become an increasingly important tool in organic syntheses.[1] In particular, Rh(III)-catalyzed systems have stood out with high efficiency, good selectivity, functional group compatibility, and diverse synthetic applicability.[2] In these systems, a directing group is almost inevitably required to ensure activity and selectivity of the C-H bond. Importantly, the development of mild, straightforward, and eco-friendly processes assisted by a multifunctional directing group is especially attractive, which allows realization of molecular diversity and synthetic versatility.[3] A variety of nitrogen and oxygen directing group such as amide, imine, ester, and ketone have been developed.[2,4] However, benzaldehydes are generally

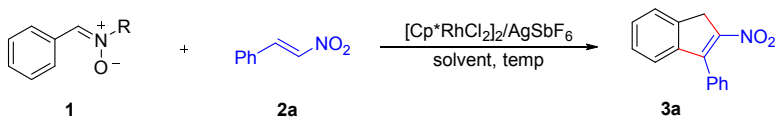
challenging as arene substrates because of the low ligating ability of the aldehyde oxygen and related competitive side reactions.[5] Instead, they are often viable as a coupling partner.[6] A strategy to enhance the directing effect of aldehyde carbonyl is to convert it to an imine,[7] hydrazine,[8] nitrone,[9] or azomethine imine,[10] which has exhibited high reactivity although lower electrophilicity in the coupling with alkynes, alkenes, and diazo compounds. Among these electrophilic DGs, imines have shown unique reactivity, and many [3+2] annulative coupling reactions with alkynes,[7a-d] and alkylation/olefination with alkenes have been reported.[7e-7f]

As a special imine, nitrones have played a vital role in C-H activation reactions due to the polar nature of N−O bond and the electrophilicity of the imine moiety.[9] [3+2] and even [3+3] annulative coupling systems have been developed using nitrone as an efficient directing group. Although coupling of nitrones with olefins has been reported, the reaction is generally limited to olefination using a terminal olefin.[9c, 9g] On the other hand, although disubstituted activated olefins have been employed as a coupling partner,[11] applications of substituted nitroalkenes still lag behind. Very recently, Ellman reported Rh(III)-catalyzed C−H activation of benzamides and insertion into nitroalkenes.[12] In only one example, the authors reported synthesis of a nitroindene using acetophenone as a substrate. To further apply nitroalkenes in useful cyclization reactions, we now report Rh(III)-catalyzed efficient synthesis of nitroindenes via C-H activation of arylnitrones under operationally simple conditions.

We commenced our studies by examining the reaction parameters of the coupling of *N*-*tert*-butyl-*α*-phenylnitrone (**1a**) with (*E*)-2-nitroethenylbenzene (**2a**, Table 1). Our initial attempts using a Rh(III) catalyst in CF_3CH_2OH afforded the [3+2] addition product **3a** in 21% yield at 120 ^oC (entry 1). Increasing the amount of $AgSbF_6$ improved the yield to 46% (entry 2), while addition of PivOH and AgOAc significantly decreased the catalytic efficiency, and bases such as

CsOAc, K_2CO_3, and $Cu(OAc)_2$ also inhibited the reaction (entries 3-7). To our delight, using two equiv of **1a** boosted the yield to 82% (entry 8), and this reaction even occurred efficiently under ambient air (entry 9). The reaction was sensitive to the solvent, and the yield of **3a** drastically decreased when DCE, THF, HFIP or dioxane was used (entries 10-15). The product was obtained in 83% yield at 80 ^oC, but further decreased the temperature to 60 ^oC resulted in lower yield (entries 16-17). Decreasing the catalyst loading to 2.5 mol % also significantly reduced the yield (entry 18). Our control experiments confirmed that both the rhodium(III) catalyst and $AgSbF_6$ were necessary (entries 19-20). Further studies revealed other Rh catalysts, such as $Cp^*Rh(CH_3CN)_3(SbF_6)_2$, $[RhCl(cod)]_2$, and $RhCl(PPh_3)_3$ were totally ineffective for the annulation reaction (entries 21, 23 and 24), and only 19% yield was obtained for $Cp^*Rh(CH_3CN)_3(SbF_6)_2/AgSbF_6$ (entry 22). With *N*-phenyl nitrone (**1a`**), only starting material was recovered (entry 25), and *N*-benzyl nitrone (**1a``**) afforded the product in 17% yield (entry 26). Furthermore, no product was observed when benzaldehyde was used instead of the arylnitrone.

Table 1. Control Reactions [a]



1 **2a** **3a**

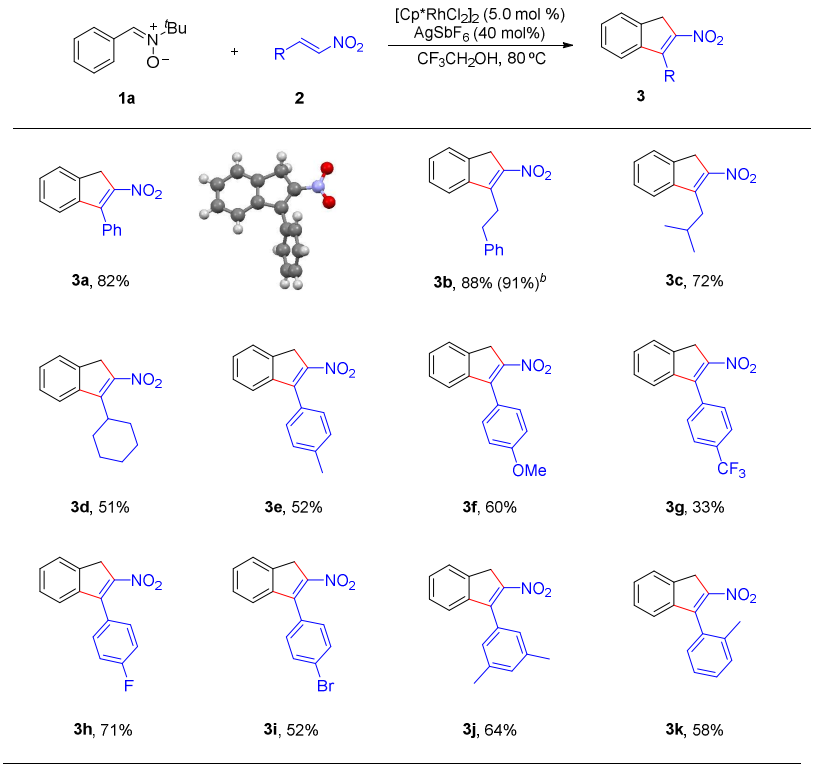
entry	R	catalyst (mol %)	additive	solvent	*T* (°C)	yield[b] (%)
1[c]	^{t}Bu (**1a**)	$[Cp^*RhCl_2]_2$(5.0)/ $AgSbF_6$(20)	--	CF_3CH_2OH	120	21
2[c]	^{t}Bu (**1a**)	$[Cp^*RhCl_2]_2$(5.0)/ $AgSbF_6$(40)	--	CF_3CH_2OH	120	46
3[c]	^{t}Bu (**1a**)	$[Cp^*RhCl_2]_2$(5.0)/ $AgSbF_6$(40)	PivOH	CF_3CH_2OH	120	31
4[c]	^{t}Bu (**1a**)	$[Cp^*RhCl_2]_2$(5.0)/ $AgSbF_6$(40)	CsOAc	CF_3CH_2OH	120	trace
5[c]	^{t}Bu (**1a**)	$[Cp^*RhCl_2]_2$(5.0)/ $AgSbF_6$(40)	K_2CO_3	CF_3CH_2OH	120	trace
6[c]	^{t}Bu (**1a**)	$[Cp^*RhCl_2]_2$(5.0)/ $AgSbF_6$(40)	$Cu(OAc)_2$	CF_3CH_2OH	120	trace
7[c]	^{t}Bu (**1a**)	$[Cp^*RhCl_2]_2$(5.0)/ $AgSbF_6$(40)	AgOAc	CF_3CH_2OH	120	20
8[d]	^{t}Bu (**1a**)	$[Cp^*RhCl_2]_2$(5.0)/ $AgSbF_6$(40)	--	CF_3CH_2OH	120	82
9[d]	^{t}Bu (**1a**)	$[Cp^*RhCl_2]_2$(5.0)/ $AgSbF_6$(40)	--	CF_3CH_2OH	120	80
10[d]	^{t}Bu (**1a**)	$[Cp^*RhCl_2]_2$ (5.0)/ $AgSbF_6$(40)	--	DCE	120	17
11[d]	^{t}Bu (**1a**)	$[Cp^*RhCl_2]_2$(5.0)/ $AgSbF_6$(40)	--	THF	120	6
12[d]	^{t}Bu (**1a**)	$[Cp^*RhCl_2]_2$ (5.0)/ $AgSbF_6$(40)	--	HFIP	120	28
13[d]	^{t}Bu (**1a**)	$[Cp^*RhCl_2]_2$(5.0)/ $AgSbF_6$(40)	--	Dioxane	120	16
14[d]	^{t}Bu (**1a**)	$[Cp^*RhCl_2]_2$(5.0)/ $AgSbF_6$(40)	--	Toluene	120	trace
15[d]	^{t}Bu (**1a**)	$[Cp^*RhCl_2]_2$(5.0)/ $AgSbF_6$(40)	--	EtOH	120	trace
16[d]	^{t}Bu (**1a**)	$[Cp^*RhCl_2]_2$(5.0)/ $AgSbF_6$(40)	--	CF_3CH_2OH	80	83
17[d]	^{t}Bu (**1a**)	$[Cp^*RhCl_2]_2$(5.0)/ $AgSbF_6$(40)	--	CF_3CH_2OH	60	75
18[d]	^{t}Bu (**1a**)	$[Cp^*RhCl_2]_2$(2.5)/ $AgSbF_6$(20)	--	CF_3CH_2OH	120	56
19[d]	^{t}Bu (**1a**)	$[Cp^*RhCl_2]_2$(5.0)/--	--	CF_3CH_2OH	120	--
20[d]	^{t}Bu (**1a**)	--/$AgSbF_6$(40)	--	CF_3CH_2OH	120	--
21[d]	^{t}Bu (**1a**)	$Cp^*Rh(CH_3CN)_3(SbF_6)_2$(10.0)/--	--	CF_3CH_2OH	80	--
22[d]	^{t}Bu (**1a**)	$Cp^*Rh(CH_3CN)_3(SbF_6)_2$(10.0)/$AgSbF_6$(40)	--	CF_3CH_2OH	80	19
23[d]	^{t}Bu (**1a**)	$[RhCl(cod)]_2$(5.0)/ $AgSbF_6$(40)	--	CF_3CH_2OH	80	--
24[d]	^{t}Bu (**1a**)	$RhCl(PPh_3)_3$(10.0)/ $AgSbF_6$(40)	--	CF_3CH_2OH	80	--
25[d]	Ph (**1a'**)	$[Cp^*RhCl_2]_2$(5.0)/ $AgSbF_6$(40)	--	CF_3CH_2OH	80	--
26[d]	Bn (**1a''**)	$[Cp^*RhCl_2]_2$(5.0)/ $AgSbF_6$(40)	--	CF_3CH_2OH	80	17

[a]Reaction conditions: **2a** (0.2 mmol), additive (1.0 equiv), solvent (2.0 mL), 24h, entries 1-8 under the argon, entries 9-26 under the air. [b]isolated yields. [c]**1a** (0.2 mmol). [d]**1** (0.4 mmol).

With the optimized conditions in hand, we first examined the scope of the nitroalkene (Scheme 1). A variety of alkyl and aryl-substituted nitroalkenes proved to be effective coupling partners under the standard conditions.[13] Aliphatic nitroalkenes afforded products **3b-3d** in good to high

yields, and **3b** was isolated in 91% yields when a 4.0 mmol scale reaction was carried out. Introduction of various electron-donating, -withdrawing or halogen groups (**3e-3i**) into the *para* position of the aromatic *β*-nitrostyrenes ring was fully tolerated (30-71%). The reaction efficiency is related to the electronic effect of the *para* substituent, electron-rich groups on the aromatic ring gave products (**3e** and **3f**) in moderate yield, probably due to the lower activity of the nitroalkenes bearing electron-rich substituents. While the electron-withdrawing group afforded the nitroindene product (**3g**) in 33% yield, accompanying by the formation of multiple unassigned products. Methyl group at the *meta* or *ortho* position was also tolerated, as in the formation of desired products **3j** and **3k** in moderate yields.

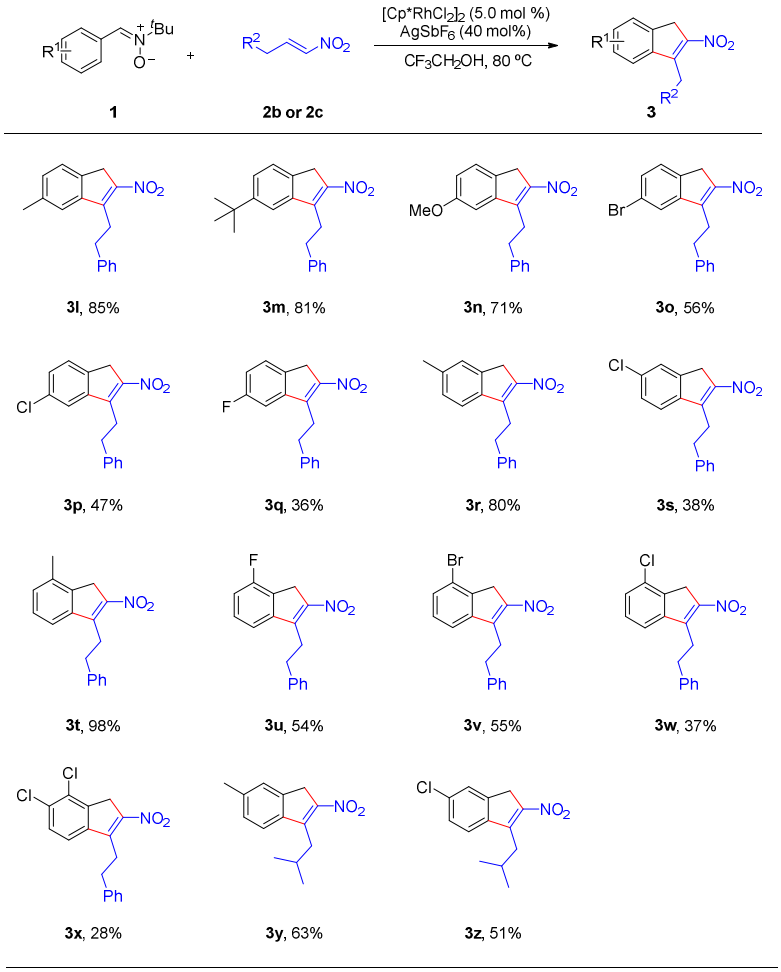
Scheme 1. Scope of Nitroalkenes.[a]



[a]Reaction conditions: $[Cp^*RhCl_2]_2$ (5.0 mol %), $AgSbF_6$ (40 mol%), **1a** (0.4 mmol), **2** (0.2 mmol), CF_3CH_2OH (2.0 mL), 24h, air, isolated yields. [b]4.0 mmol of **1a** was used.

We next explored the scope of the aryl nitrone substrate with nitroalkenes **2b** and **2c** (Scheme 2). Nitrones bearing Me-, ^{t}Bu- and MeO- and halogens at *para* position coupled with **2b** to afford the nitroindene in moderate to good yields (**3l-3q**). Products **3r** and **3s** were obtained in 80% and 38% yields for *meta* Me- and Cl-substituted nitrone, respectively. Introduction of an *ortho* methyl group is well-tolerated (**3t**), although coupling of *ortho* F-, Br- and Cl-substituted nitrones afforded relatively lower yields (**3u-3x**). With nitroalkene **2c** being a coupling partner, products **3y** and **3z** were also obtained in comparable yield.

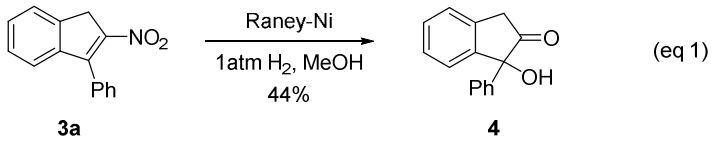
Scheme 2. Scope of Arylnitrons.[a]



[a]Reaction conditions: $[Cp^*RhCl_2]_2$ (5.0 mol %), $AgSbF_6$ (40 mol%), **1** (0.4 mmol), **2** (0.2 mmol), CF_3CH_2OH (2.0 mL), 24h, air, isolated yields.

To demonstrate the synthetic utility of the annulated products, a derivatization reaction has been carried out. The nitroindene was reduced by H_2 in the presence of Raney-Ni,[14] affording ketone **4** in 44% yield (Scheme 3, eq 1).

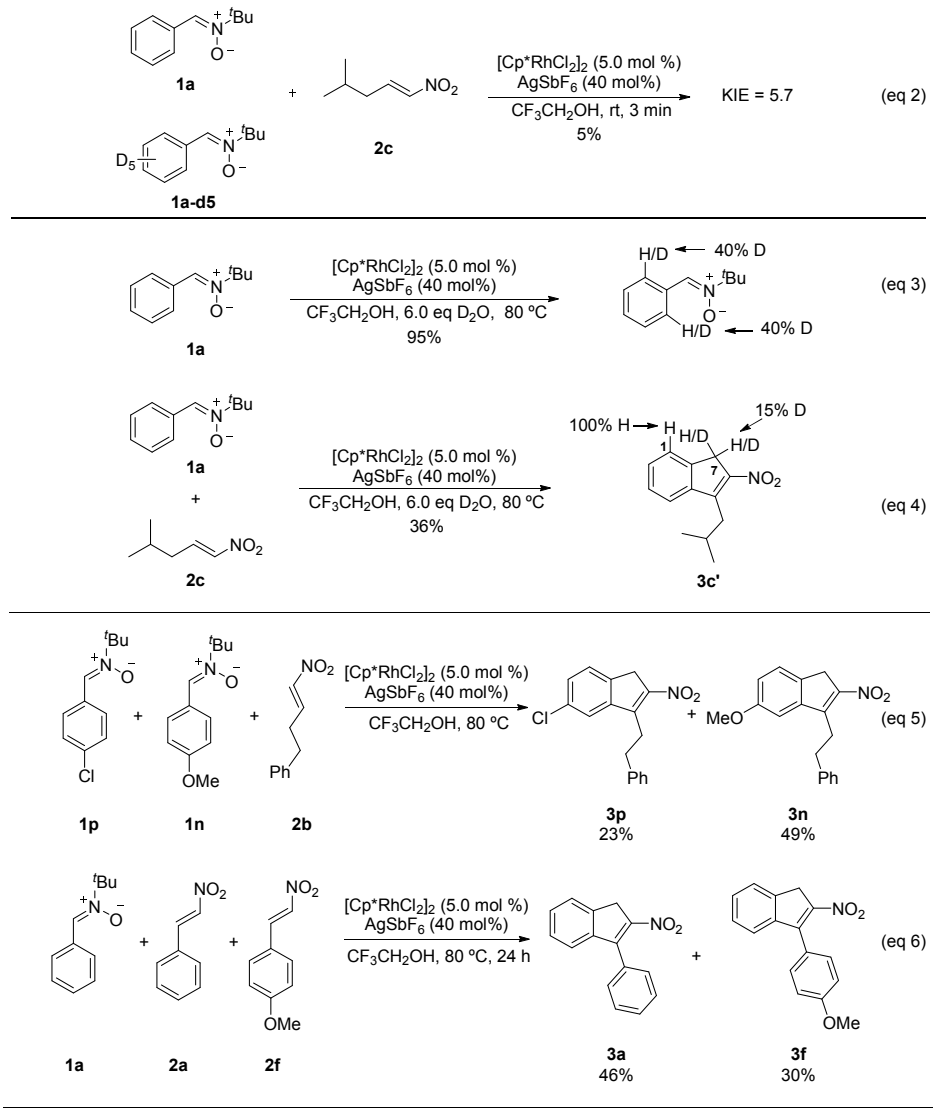
Scheme 3. Derivatization Reactions.



3a **4** (eq 1)

We next performed several experiments to gain mechanistic insight (Scheme 4). A kinetic isotope effect (KIE) value of 5.7 was obtained for the competitive coupling of a mixture of **1a** and **1a-**d_5 with **2c** at a low conversion under the standard conditions (Scheme 4, eq 2). This result indicated that cleavage of the C-H bond activation was likely involved in the turnover-limiting step. Moreover, H/D exchange between nitrone **1a** and D_2O was performed, and the nitrone starting material was recovered with 40% deuteration at the *ortho* positions, indicating reversibility of C-H activation in the absence of the nitroalkene (Scheme 4, eq 3). When D_2O was added into the reaction of **1a** with **2c**, no H/D exchanged at the ortho position of the nitroindene product, indicative of irreversibility of the C-H under the catalytic conditions. In addition, H/D exchanged was observed at the acidic methylene position of the indene (Scheme 4, eq 4). When an equimolar mixture of **1p** and **1n** was allowed to competitively couple with olefin **2b**, two nitroindene were obtained in 23% and 49% yield, where the electron-rich nitrone reacted preferentially (Scheme 4, eq 5). In another competitive reaction using two electronically different olefins **2a** and **2f**, the products **3a** and **3f** were obtained in 1.5:1 ratio, where the electron-poor olefin only exhibited slightly higher reactivity (Scheme 4, eq 6).

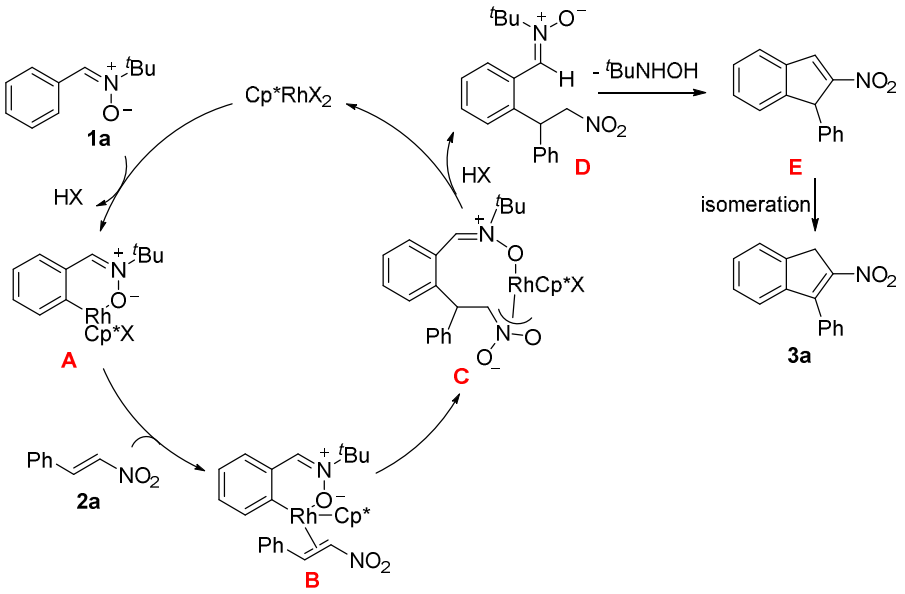
Scheme 4. Mechanistic Studies



On the basis of our preliminary experiments and related literature reports, a proposed mechanism is given in Scheme 5. An active catalyst [Cp*RhX_2] (X = SbF_6) was generated via halide abstraction. C-H activation of **1a** produced an rhodacyclic intermediate **A**, and coordination of the nitroalkene **2a** provides an olefin intermediate **B**, which undergoes migratory insertion to provide a Rh(III) alkyl species **C**. Protonolysis of **C** affords an alkylated nitrone intermediate **D** and regenerates the active rhodium species. The nitrone species **D** is proposed to undergo

intramolecular Henry-type reaction to release the ^{t}BuNHOH afforded nitroindene **E**, which eventually isomerizes to the thermodynamically more stable product **3a**.

Scheme 5. Proposed Mechanism



In summary, we have demonstrated an easy handling approach to access nitroindenes through Rh(III)-catalyzed C-H activation/annulation of arylnitrons with nitroalkenes. This reaction occurred smoothly under air atmosphere. The scope of the arylnitrone and nitroalkene substrates have been defined, and good functional groups tolerance has been achieved. Mechanistic studies have been performed using H/D exchange and competition experiments. Further studies on the synthesis of other carbocycles via C-H activation and functionalization are underway in our laboratories.

EXPERIMENTAL SECTION

General Information: All chemicals were obtained from commercial sources and were used as received unless otherwise noted. All the reactions were carried out under argon atmosphere using

standard Schlenk technique. The ^{1}H NMR spectra were recorded on a 400 MHz or 600 MHz NMR spectrometer. The ^{13}C NMR spectra were recorded at 100 MHz or 150 MHz. The ^{19}F NMR spectra were recorded at 565 MHz. Chemical shifts were expressed in parts per million (δ) down field from the internal standard tetramethylsilane, and were reported as s (singlet), d (doublet), t (triplet), dd (doublet of doublet), dt (doublet of triplet), m (multiplet), brs (broad singlet), etc. The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale. High resolution mass spectra were obtained on an Agilent Q-TOF 6540 spectrometer. Column chromatography was performed on silica gel (300-400 mesh) using petroleum ether (PE)/dichloromathane (DCM). Thin layer chromatography was performed on pre-coated glassback plates and visualized with UV light at 254 nm. Flash column chromatography was performed on silica gel. The arylnitrone **1a** was purchased from commercial sources, other arylnitrones were prepared by using literature procedures.[15] The nitroalkenes were prepared according the literature report. [12]

General procedure for Rhodium(III)-Catalyzed C-H Activation/annulation of Arylnitrons with Nitroalkenes: Arylnitrone (0.400 mmol, 2.00 equiv) and nitroalkene (0.200 mmol, 1.00 equiv), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.010 mmol, 0.050 equiv), $AgSbF_6$ (27.5 mg, 0.080 mmol, 0.200 equiv) in CF_3CH_2OH (2.0 mL) were charged into a 50 mL pressure tube under the air atmosphere. The tube was then sealed and placed in a preheated oil bath at 80 °C. After the reaction was complete, the reaction vial was removed from the oil bath and cooled to ambient temperature. The reaction mixture was filtered through a pad of celite eluting with ethyl acetate, concentrated and purified by silica gel chromatography (PE : DCM = 2:1) to give the indicated product.

The following products were obtained under air atmosphere procedure.

2-nitro-3-phenyl-1H-indene (**3a**); a yellow solid (mp = 104-106 °C); (39 mg, 83% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.58–7.41 (m, 7H), 7.36 (m, 2H), 4.16 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 148.4, 146.8, 142.4, 140.2, 131.4, 130.1, 129.3, 128.8, 128.5, 127.8, 124.8, 124.5, 38.0. HRMS (ESI): $[M + Na]^+$ calculated for $C_{15}H_{11}NNaO_2$: 260.0682, found:260.0685.

2-nitro-3-phenethyl-1H-indene (**3b**); a yellow solid (mp = 68-71°C); (47 mg, 88% yield); ^{1}H NMR (600 MHz, $CDCl_3$):δ 7.56 (d, J = 7.6 Hz, 1H), 7.51 (d, J = 7.3 Hz, 1H), 7.48 (d, J = 7.2 Hz, 1H), 7.42 (d, J = 7.4 Hz, 1H), 7.30 (m, 2H), 7.24-7.18 (m, 1H), 4.00 (s, 2H), 3.47-3.33 (t, J = 8.2 Hz, 2H), 3.07-2.91 (t, J = 8.2 Hz, 1H, 2H).^{13}C NMR (151 MHz, $CDCl_3$): δ 151.2, 147.4, 141.6, 140.8, 140.3, 130.1, 128.6, 128.5, 127.6, 126.5, 124.5, 122.9, 37.4, 34.5, 28.8. HRMS (ESI): $[M + Na]^+$ calculated for $C_{17}H_{15}NNaO_2$: 288.0995, found:288.1002.

3-isobutyl-2-nitro-1H-indene (**3c**); a yellow solid (mp = 49-52 °C); (31 mg, 72% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.61 (d, J = 7.4 Hz, 1H), 7.55–7.38 (m, 3H), 4.02 (s, 2H), 3.06 (d, J = 7.0 Hz, 2H), 2.25–2.10 (m, 1H), 1.02 (d, J = 6.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 151.8, 147.7, 142.6, 140.3, 130.1, 127.6, 124.5, 123.6, 37.6, 35.1, 29.3, 23.16. HRMS (ESI): $[M+Na]^+$ calculated for $C_{13}H_{15}NNaO_2$: 240.0995, found:240.1003.

3-cyclohexyl-2-nitro-1H-indene (**3d**); yellow solid (mp = 66-68 °C); (21 mg, 43% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.91 (d, J = 7.5 Hz, 1H), 7.49 (d, J = 7.1 Hz, 1H), 7.44 (d, J = 6.9 Hz, 1H), 7.39 (d, J = 7.4 Hz, 1H), 4.09 (s, 2H), 3.96–3.86 (m, 1H), 2.00 (dd, J = 25.0, 12.5 Hz, 2H), 1.86-1.81 (m, 5H), 1.52-1.31 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 155.0, 146.9, 141.1, 140.8, 129.4, 127.1, 125.6, 124.7, 38.0, 37.7, 30.1, 26.5, 26.2. HRMS (ESI): $[M+Na]^+$ calculated for $C_{15}H_{17}NNaO_2$: 266.1151, found:266.1154.

2-nitro-3-(p-tolyl)-1H-indene (**3e**); a yellow oil; (26 mg, 52% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.3 Hz, 1H), 7.49 (s, 1H), 7.37 (m, 4H), 7.33 (d, *J* = 7.4 Hz, 1H), 4.17 (s, 2H), 2.46 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 148.6, 146.5, 142.6, 140.2, 139.6, 130.1, 129.3, 128.9, 128.4, 127.8, 124.9, 124.5, 38.0, 21.7. HRMS (ESI): $[M + Na]^+$ calculated for $C_{16}H_{13}NNaO_2$: 274.0838, found:274.0838.

3-(4-methoxyphenyl)-2-nitro-1H-indene (**3f**); a yellow solid (mp = 141-142°C); (27 mg, 50% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.4 Hz, 1H), 7.51–7.42 (m, 3H), 7.40 (m, 2H), 7.05 (d, *J* = 8.1 Hz, 2H), 4.17 (s, 2H), 3.90 (s, 3H).^{13}C NMR: (151 MHz, $CDCl_3$): δ 160.6, 148.3, 146.3, 142.6, 140.3, 130.8, 130.1, 127.7, 125.0, 124.5, 123.3, 114.0, 55.5, 38.1. HRMS (ESI): $[M + Na]^+$ calculated for $C_{16}H_{13}NNaO_3$: 290.0788, found:290.0791.

2-nitro-3-(4-(trifluoromethyl)phenyl)-1H-indene (**3g**); a yellow oil; (15 mg, 24% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.79 (d, *J* = 7.7 Hz, 2H), 7.58 (t, *J* = 9.0 Hz, 3H), 7.52 (m, 1H), 7.40 (d, *J* = 6.2 Hz, 1H), 7.26 (d, *J* = 7.3 Hz, 1H), 4.21 (s, 2H). ^{19}F NMR (565 MHz, $CDCl_3$):δ -63.53. ^{13}C NMR (151 MHz, $CDCl_3$): δ 147.6, 146.9, 141.9, 140.1, 135.3, 131.3 (q, *J* = 32.5 Hz), 130.5, 129.3, 128.1, 125.7, 125.6, 124.7, 124.5, 38.0. HRMS (ESI): $[M+Na]^+$ calculated for$C_{16}H_{10}F_3NaNO_2$:328.0556, found:328.0566.

3-(4-fluorophenyl)-2-nitro-1H-indene (**3h**); a yellow solid (mp = 178-180 °C); (26 mg, 52% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.57 (d, *J* = 7.3 Hz, 1H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.47 (s, 2H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.32 (d, *J* = 7.4 Hz, 1H), 7.22 (t, *J* = 8.2 Hz, 2H), 4.18 (s, 2H). ^{19}F NMR (565 MHz, $CDCl_3$): δ -111.93. ^{13}C NMR (151 MHz, $CDCl_3$): δ 163.3 (d, *J* = 249.5 Hz), 147.4, 147.0, 142.3, 140.1, 131.1, 131.0, 130.3, 127.9, 127.2, 124.7(d, *J* = 6.7 Hz, 1H), 115.8 (d,

J = 21.8 Hz, 1H), 38.0. HRMS (ESI): $[M + Na]^+$ calculated for $C_{15}H_{10}FNaNO_2$: 278.0588, found:278.0592.

3-(4-bromophenyl)-2-nitro-1H-indene (**3i**); yellow solid (mp =110-113 °C); (33 mg, yield 52%); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.1 Hz, 2H), 7.54 (dd, *J* = 22.4, 7.4 Hz, 2H), 7.34 (m, 4H), 4.17 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 147.2, 142.0, 140.1, 131.9, 130.6, 130.4, 130.3, 128.0, 124.7, 124.6, 123.8, 38.0. HRMS (EI) Calcd. for $C_{15}H_{10}BrNO_2$ (M^+): 314.9895; Found: 314.9897.

3-(3,5-dimethylphenyl)-2-nitro-1H-indene (**3j**); yellow solid (mp = 73-75 °C); (34 mg, 64% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.55 (d, *J* = 7.3 Hz, 1H), 7.49 (d, *J* = 7.0 Hz, 1H), 7.35 (t, *J* = 10.1 Hz, 2H), 7.12 (s, 1H), 7.05 (s, 2H), 4.16 (s, 2H), 2.39 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 148.9, 146.6, 142.7, 140.2, 138.2, 131.4, 131.1, 130.0, 127.7, 126.3, 125.0, 124.5, 38.0, 21.5. HRMS (ESI): $[M+Na]^+$ calculated for $C_{17}H_{15}NNaO_2$: 288.0995, found:288.0997.

2-nitro-3-(o-tolyl)-1H-indene (**3k**); a yellow solid (mp = 111-114 °C); (29 mg, 58% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.56 (t, *J* = 14.6 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.42–7.28 (m, 4H), 7.15 (dd, *J* = 20.1, 7.6 Hz, 2H), 4.21 (s, 2H), 2.16 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 148.9, 147.7, 142.5, 140.2, 136.1, 131.6, 130.4, 130.2, 129.0, 127.9, 127.8, 126.0, 124.8, 124.5, 37.7, 19.8. HRMS (ESI): $[M+Na]^+$ calculated for $C_{16}H_{13}NNaO_2$: 274.0838, found:274.0839.

5-methyl-2-nitro-3-phenethyl-1H-indene (**3l**); a yellow solid (mp = 72-74°C); (47 mg, 85% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (m, *J* = 7.6 Hz, 1H), 7.30 (m, 6H), 7.26-7.18 (m, 1H), 3.95 (s, 2H), 3.47-3.32 (t, *J* = 8.0 Hz, 2H), 3.03-2.92 (t, *J* = 8.0Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.4, 147.6, 141.8, 141.0, 137.6, 137.5, 131.3, 128.7, 128.6, 126.5, 124.3,

123.5, 37.1, 34.6, 28.9, 21.7. HRMS (ESI): $[M + Na]^+$ calculated for $C_{18}H_{17}NNaO_2$: 302.1151, found:302.1152.

5-(*tert*-butyl)-2-nitro-3-phenethyl-1H-indene (**3m**); a yellow solid (mp = 91-93 °C); (52 mg, 81% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 7.9 Hz, 1H), 7.47-7.40 (m, 2H), 7.29-7.25 (m, 4H), 7.21 (d, *J* = 6.6 Hz, 1H), 3.96 (s, 2H), 3.42 (t, *J* = 7.9 Hz, 2H), 3.01 (t, *J* = 7.9 Hz, 2H), 1.33 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.0, 151.1, 147.6, 141.6, 141.0, 137.6, 128.7, 128.6, 127.8, 126.5, 124.1, 119.6, 37.0, 35.0, 34.7, 31.6, 28.8. HRMS (ESI): $[M + Na]^+$ calculated for $C_{21}H_{23}NNaO_2$: 344.1621, found:344.1621.

5-methoxy-2-nitro-3-phenethyl-1H-indene (**3n**); a yellow solid (mp = 73-74 °C); (42 mg, 71% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.39 (d, *J* = 8.2 Hz, 1H), 7.29 (m, 4H), 7.22 (m, 1H), 7.02 (d, *J* = 8.2 Hz, 1H), 6.98 (s, 1H), 3.94 (s, 2H), 3.82 (s, 3H), 3.37 (t, *J* = 7.8 Hz, 2H), 2.97 (t, *J* = 7.9 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 159.7, 151.2, 148.4, 143.0, 140.9, 132.5, 128.7, 128.6, 126.6, 125.3, 116.9, 107.8, 55.7, 36.8, 34.6, 28.9. HRMS (ESI): $[M + Na]^+$ calculated for $C_{18}H_{17}NNaO_3$: 318.1101, found:318.1103.

5-bromo-2-nitro-3-phenethyl-1H-indene (**3o**);a yellow solid (mp = 90-92 °C); (38 mg, 56% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.58 (m, 2H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.34–7.18 (m, 5H), 3.96 (s, 2H), 3.36 (t, *J* = 7.7 Hz, 2H), 2.97 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 149.9, 148.4, 143.7, 140.5, 138.7, 132.9, 128.7, 128.6, 126.7, 126.1, 126.0, 121.7, 37.2, 34.5, 28.8. HRMS (ESI): $[M + Na]^+$ calculated for $C_{17}H_{14}BrNNaO_2$: 366.0100, found:366.0099.

5-chloro-2-nitro-3-phenethyl-1H-indene (**3p**); a yellow solid (mp = 73-75 °C); (28 mg, 47% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.45 (s, 1H), 7.43 (s, 2H), 7.34–7.25 (m, 4H), 7.23 (d, *J* = 6.9 Hz, 1H), 3.98 (s, 2H), 3.36 (t, *J* = 7.8 Hz, 2H), 2.96 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR (151 MHz,

$CDCl_3$): δ 150.0, 148.5, 143.4, 140.5, 138.2, 133.9, 130.1, 128.7, 128.6, 126.7, 125.7, 123.1, 37.2, 34.5, 28.8. HRMS (ESI): $[M + Na]^+$ calculated for $C_{17}H_{14}ClNNaO_2$: 322.0605, found:322.0605.

5-fluoro-2-nitro-3-phenethyl-1H-indene (**3q**); as a yellow oil; (20 mg, 36% yield); ^1H NMR (600 MHz, $CDCl_3$): δ 7.45 (m, 1H), 7.33-7.25 (m, 5H), 7.23 (m, 1H), 7.18 (m, 1H), 3.98 (s, 2H), 3.36 (t, *J* = 8.0 Hz, 2H), 2.97 (t, *J* = 8.0 Hz, 2H). ^{19}F NMR (565 MHz, $CDCl_3$): δ -114.27. ^{13}C NMR (151 MHz, $CDCl_3$): δ 162.8 (d, *J* = 245.5 Hz), 150.2, 148.9, 143.6 (d, *J* = 8.6 Hz), 140.6, 135.6, 128.8, 128.6, 126.7, 125.9 (d, *J* = 8.7 Hz), 117.4(d, *J* = 23.2 Hz), 109.9 (d, *J* = 23.6 Hz), 37.0, 34.6, 29.0. HRMS (ESI): $[M + Na]^+$ calculated for $C_{17}H_{14}FNNaO_2$: 306.0901, found: 306.0906.

6-methyl-2-nitro-3-phenethyl-1H-indene (**3r**); a yellow solid (mp = 86-88°C); (45 mg, 80% yield); ^1H NMR (600 MHz, $CDCl_3$): δ 7.44 (d, *J* = 7.8 Hz, 1H), 7.31 (m, 5H), 7.23 (m, 2H), 3.96 (s, 2H), 3.42 (t, *J* = 7.9 Hz, 2H), 3.01 (t, *J* = 7.9 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 151.7, 146.7, 141.0, 141.0, 140.8, 139.1, 128.7, 128.6, 126.5, 125.4, 122.8, 77.4, 77.2, 77.0, 37.3, 34.6, 29.0, 22.1. HRMS (ESI): $[M + H]^+$ calculated for $C_{18}H_{18}NO_2$: 280.1338, found:280.1336.

6-chloro-2-nitro-3-phenethyl-1H-indene (**3s**); a yellow solid (mp = 67-70 °C); (23 mg, 38% yield); ^1H NMR (600 MHz, $CDCl_3$):δ 7.50 (s, 1H), 7.40 (m, 2H), 7.28 (m, 4H), 7.22 (m, 1H), 4.00 (s, 2H), 3.38 (t, *J* = 7.7 Hz, 2H), 2.96 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 150.5, 147.4, 141.7, 140.6, 140.3, 136.5, 128.7, 128.6, 128.2, 126.7, 125.1, 124.0, 77.4, 77.2, 77.0, 37.3, 34.6, 28.9. HRMS (ESI): $[M + Na]^+$ calculated for $C_{17}H_{14}ClNNaO_2$: 322.0605, found:322.0607.

7-methyl-2-nitro-3-phenethyl-1H-indene (**3t**); a yellow solid (mp = 55-57°C); (55 mg, 98% yield). ^1H NMR (600 MHz, $CDCl_3$): δ 7.41 (d, *J* = 7.4 Hz, 1H), 7.36–7.26 (m, 6H), 7.22 (d, *J* =

8.8 Hz, 1H), 3.87 (s, 2H), 3.36 (t, *J* = 7.7 Hz, 2H), 2.97 (t, *J* = 7.6 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 151.7, 147.3, 141.4, 140.9, 139.2, 134.0, 131.4, 128.7, 128.6, 128.0, 126.5, 120.7, 36.5, 34.67, 29.0, 18.5. HRMS (ESI): $[M + Na]^+$ calculated for $C_{18}H_{17}NNaO_2$: 302.1151, found:302.1158.

7-fluoro-2-nitro-3-phenethyl-1H-indene (**3u**)**;** a yellow solid (mp = 80-81 °C); (31 mg, 54% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.43–7.37 (m, 1H), 7.34 (d, *J* = 7.5 Hz, 1H), 7.32–7.24 (m, 4H), 7.22 (t, *J* = 6.8 Hz, 1H), 7.16 (t, *J* = 8.4 Hz, 1H), 4.04 (s, 2H), 3.36 (t, *J* = 7.6 Hz, 2H), 2.96 (t, *J* = 7.6 Hz, 2H). ^{19}F NMR (565 MHz, $CDCl_3$): δ -118.30. ^{13}C NMR (151 MHz, $CDCl_3$): δ 158.6 (d, *J* = 249.9 Hz), 150.4 (d, *J* = 2.4 Hz), 147.9, 144.6 (d, *J* = 6.1 Hz), 140.6, 129.8 (d, *J* = 6.9 Hz), 128.7, 128.6, 126.6, 125.6 (d, *J* = 18.4 Hz), 119.1 (d, *J* = 3.3 Hz), 117.0 (d, *J* = 20.2 Hz), 34.6, 34.3, 29.0. HRMS (ESI): $[M + Na]^+$ calculated for $C_{17}H_{14}FNNaO_2$: 306.0901, found:306.0896.

7-bromo-2-nitro-3-phenethyl-1H-indene (**3v**); a yellow solid (mp = 129-131 °C); (38 mg, 55% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.60 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.40–7.14 (m, 6H), 3.99 (s, 2H), 3.36 (t, *J* = 7.6 Hz, 2H), 2.96 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 150.5, 143.1, 140.7, 133.1, 129.5, 128.8, 128.6, 126.7, 122.1, 119.4, 39.1, 34.7, 29.1. HRMS (ESI): $[M + Na]^+$ calculated for $C_{17}H_{14}BrNNaO_2$: 366.0100, found:366.0099.

7-chloro-2-nitro-3-phenethyl-1H-indene (**3w**); a yellow solid (mp = 121-123°C); (22 mg, 37% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.44 (t, *J* = 8.1 Hz, 1H), 7.37 (d, *J* = 7.7 Hz, 1H), 7.32-7.24 (m, 5H), 7.22 (d, *J* = 6.7 Hz, 1H), 4.02 (s, 2H), 3.39 (t, *J* = 7.7 Hz, 2H), 2.97 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 150.5, 147.8, 143.2, 140.6, 138.2, 130.7, 130.1, 129.3,

128.7, 128.6, 126.7, 121.5, 37.2, 34.7, 29.1. HRMS (ESI): $[M + Na]^+$ calculated for $C_{17}H_{14}ClNNaO_2$: 322.0605, found:322.0600.

6,7-dichloro-2-nitro-3-phenethyl-1H-indene (**3x**); a yellow solid (mp = 111-113 °C); (19 mg, 28% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.2 Hz, 1H), 7.34-7.14 (m, 6H), 4.04 (s, 2H), 3.36 (t, *J* = 7.6 Hz, 2H), 2.96 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 150.0, 147.8, 141.3, 140.4, 140.0, 134.5, 130.2, 129.3, 128.8, 128.6, 126.7, 122.0, 37.9, 34.6, 29.0. HRMS (ESI): $[M + Na]^+$ calculated for $C_{17}H_{13}C_{l2}NNaO_2$: 356.0216, found:356.0216.

3-isobutyl-6-methyl-2-nitro-1H-indene (**3y**); as a yellow solid (mp = 107-109°C); (29 mg, 63% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.49 (d, *J* = 7.9 Hz, 1H), 7.31 (s, 1H), 7.23 (d, *J* = 7.8 Hz, 1H), 3.96 (s, 2H), 3.04 (d, *J* = 7.3 Hz, 2H), 2.45 (s, 3H), 2.26–2.05 (m, 1H), 1.01 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 152.2, 146.9, 140.8, 140.7, 140.0, 128.5, 125.2, 123.5, 37.4, 35.2, 29.3, 23.1, 22.0. HRMS (ESI): $[M+Na]^+$ calculated for $C_{14}H_{17}NNaO_2$: 254.1151, found:254.1155.

6-chloro-3-isobutyl-2-nitro-1H-indene (**3z**); a yellow oil，(26 mg, 51% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.53 (d, *J* = 8.3 Hz, 1H), 7.49 (s, 1H), 7.41 (dd, *J* = 8.2, 1.6 Hz, 1H), 4.01 (s, 2H), 3.03 (d, *J* = 7.3 Hz, 2H), 2.14 (m, 1H), 1.01 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 150.9, 147.6, 141.7, 141.1, 136.3, 128.1, 125.0, 124.6, 37.5, 35.1, 29.3, 23.1. HRMS (ESI): $[M+Na]^+$calculated for$C_{13}H_{14}ClNNaO_2$: 274.0605, found:274.0609.

Derivatization Reactions:

1-hydroxy-1-phenyl-1,3-dihydro-2H-inden-2-one (4): **3a** (125.0 mg, 0.53 mmol) was dissolved in methanol (2.0 mL) and Raney-Ni (30 mg) was added, The reaction vessel was then pressurized with hydrogen at 1 atm and vigorously stirred at room temperature. After complete

conversion (TLC), The heterogeneous mixture was then filtered through a bed of celite and the celite subsequently washed with CH_2Cl_2, The filtrate was concentrated (rotary evaporator) to remove the solvent, concentrated and purified by silica gel chromatography (PE :EA = 2:1) to give the product **4** (50.9 mg, yield 44%); (mp = 100-103 °C). ^{1}H NMR (600 MHz, Acetone): δ 7.47 (d, *J* = 7.0 Hz, 1H), 7.46-7.36 (m, 2H), 7.36-7.28 (m, 5H), 7.28-7.22 (m, 1H), 5.46 (s, 1H), 3.73 (d, *J* = 21.8 Hz, 1H), 3.54 (d, *J* = 21.9 Hz, 1H). ^{13}C NMR (151 MHz, Acetone): δ 214.00, 145.8, 142.8, 137.7, 129.9, 129.1, 129.0, 128.4, 127.00, 126.5, 125.9, 82.8, 40.9. HRMS (ESI): $[M+Na]^+$calculated for $C_{15}H_{12}NaO_2$: 247.0730, found: 247.0739.

KIE measurements of reaction for 3c:

An equimolar mixture of **1a** (36.0 mg, 0.2mmol) and **1a-d5** (37.0 mg, 0.2 mmol), **2c** (26.0 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.010 mmol, 0.050 equiv), $AgSbF_6$ (27.5 mg, 0.080 mmol, 0.200 equiv) in CF_3CH_2OH (2.0 mL) were charged into a pressure tube under the air atmosphere. The reaction mixture was stirred at room temperature for 3 min. then filtered through a 0.5 inch plug of silica gel (eluting with EtOAc) to remove the solid and the residue was purified by silica gel chromatography,using PE/EA (10:1) to afford the mixed product **3c**. KIE value (k_H/k_D = 5.7) was determined on the basis of ^{1}HNMR analysis.

H/D exchange:

For **1a**: Arylnitron **1a** (69.0 mg, 0.400 mmol, 2.00 equiv), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.010 mmol, 0.050 equiv), $AgSbF_6$ (27.5 mg, 0.080 mmol, 0.200 equiv) and D_2O (22 mg, 1.20 mol) in CF_3CH_2OH (2.0 mL) were charged into a 50 mL pressure tube under the air atmosphere. The tube was then sealed and placed in a preheated oil bath at 80 °C for 24 h, then reaction vial was removed from the oil bath and cooled to ambient temperature. The reaction mixture was filtered

through a pad of celite eluting with ethyl acetate, concentrated and purified by silica gel chromatography (PE : DCM = 1:2) to give the product. H/D exchange at the 2-position was detected on the basis of ^{1}H NMR analysis.

For **3c'**: Arylnitron **1a** (69.0 mg, 0.400 mmol, 2.00 equiv) and nitroalkene **2c** (26.0 mg, 0.200 mmol, 1.00 equiv), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.010 mmol, 0.050 equiv), $AgSbF_6$ (27.5 mg, 0.080 mmol, 0.200 equiv) and D_2O (22 mg, 1.2 mol) in CF_3CH_2OH (2.0 mL) were charged into a 50 mL pressure tube under the air atmosphere. The tube was then sealed and placed in a preheated oil bath at 80 °C under the air for 3 min. then reaction vial was removed from the oil bath and cooled to ambient temperature. The reaction mixture was filtered through a pad of celite eluting with ethyl acetate, concentrated and purified by silica gel chromatography (PE : DCM = 2:1) to give the product. For the product **3c**', only H/D exchange at the 7-position was detected, no H/D exchange at the 2-position was detected on the basis of ^{1}H NMR analysis.

Competitive Experiment:

For **3p/3n**: An equimolar mixture of **1p** (42.2 mg, 0.2 mmol), **1n** (41.4 mg, 0.2 mmol), **2b** (36.0 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.010 mmol, 0.050 equiv), $AgSbF_6$ (27.5 mg, 0.080 mmol, 0.200 equiv) in CF_3CH_2OH (2.0 mL) were charged into a pressure tube under the air atmosphere. The reaction mixture was stirred at room temperature for 24h. then filtered through a 0.5 inch plug of silica gel (eluting with EtOAc) to remove the solid and the residue was purified by silica gel chromatography, using PE/EA (10:1) to afford the mixed product. The yield ratio (**3p/3n**= 1:2.1) was determined on the basis of ^{1}H NMR analysis.

For **3a/3f**: An equimolar mixture of **1a** (35.0 mg, 0.2 mmol), **2a** (30.0 mg, 0.2 mmol), **2b** (36.0 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.010 mmol, 0.050 equiv), $AgSbF_6$ (27.5 mg, 0.080 mmol,

0.200 equiv) in CF_3CH_2OH (2.0 mL) were charged into a pressure tube under the air atmosphere. The reaction mixture was stirred at room temperature for 24h. then filtered through a 0.5 inch plug of silica gel (eluting with EtOAc) to remove the solid and the residue was purified by silica gel chromatography, using PE/EA (10:1) to afford the mixed product. The yield ratio (**3a/3f** = 1.5:1) was determined on the basis of ^{1}H NMR analysis.

AUTHOR INFORMATION

Corresponding Author

xwli@dicp.ac.cn

changjunbiao@zzu.edu.cn

Notes

The authors declare no competing financial interests.

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Supporting Information

Copies of ^{1}H NMR and ^{13}C NMR spectra for all new compounds, deuterium-labelling experiments, competitive experiment, This material is available free of charge via the Internet at http://pubs.acs.org.

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