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Transition metal-catalyzed pentannulation of propargyl acetates via styrylcarbene intermediates

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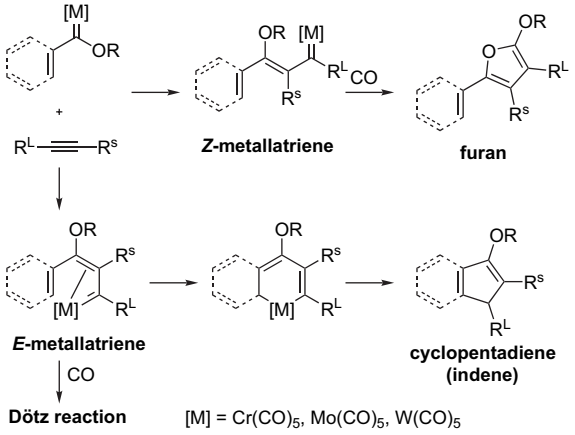
Dedicated to the heartfelt memory of late Professor Yoshihiko Ito

Abstract—The indene formation from phenyl-substituted *sec*- and *tert*-propargyl esters (*terminal alkynes*) was achieved by platinum or ruthenium catalysis via *E*-vinylcarbenoid intermediate. Considering the competitive reactions of pentannulation versus cyclopropanation, the equilibrium ratios of *E* and *Z* vinylcarbenoid intermediates from *sec*- and *tert*-propargyl esters are estimated at ca. 10:90 and 40:60, respectively. Two reaction pathways, Nazarov-type cyclization and/or metallacycle from styrylcarbenoid species, are proposed by considering ratios of products in the control experiment.

1. Introduction

Vinylcarbene complexes are versatile intermediates in organic synthesis and widely applicable to stoichiometric and catalytic annulations.[1] Metallatrienes[2] including a vinylcarbene moiety are the key intermediates for benzannulation reactions (Dötz reactions) based on a pentacarbonylchromium template. Meanwhile, the unique benzannulations are known to compete with non-CO-incorporated cyclization of intermediary vinylcarbene complexes to give five-membered rings such as cyclopentadiene or indene derivatives (Scheme 1).[3]

We have previously developed catalytic reactions via vinylcarbene complexes generated from *sec*- and *tert*-propargyl carboxylates with a wide range of transition metals.[4] We reported that the intermolecular cyclopropanation and intramolecular pentannulation reactions (indene formation) via vinylcarbene complexes as intermediates are effectively catalyzed by $[RuCl_2(CO)_3]_2$.[4b] The reactions of 1-phenyl-2-propynyl acetate with several alkenes afforded (*Z*)-1-acetoxy-2-phenylvinyl cyclopropanes exclusively, while 1,1-diphenyl-2-propynyl acetate gave 3-phenyl-1*H*-inden-2-yl acetate as a major product (Scheme 2). Thus, the distribution of products was influenced by substituents at a propargyl position. The proposed mechanism for the generation of vinylcarbene complexes from propargyl acetates is illustrated in Scheme 3. The ruthenium vinylcarbene complex generated from *sec*-propargyl ester (R^L=Ph, R^S=H) favors a



Scheme 1. Non-CO-incorporated cyclization or pentannulation of metallatrienes.

(*Z*)-structure **A** that minimizes sterical repulsion, and thus the intermolecular cyclopropanation occurs preferentially rather than pentannulation (indene formation) (Scheme 2). On the other hand, a *tert*-propargyl ester (R^S=R^L=Ph) affords a single intermediate (**A**=**B**), and the carbene center undergoes a formal insertion into a C–H bond of a proximal phenyl ring to give 3-phenyl-1*H*-inden-2-yl acetate. Sarpong et al. reported that the $PtCl_2(PPh_3)_2$/PhIO-catalyzed pentannulation of *tert*-propargyl ester having an electron-withdrawing group at the alkyne terminus (*internal alkynes*) affords indenes (Scheme 4).[5] Most recently, Wang et al. developed the Au-catalyzed synthesis of indene derivatives

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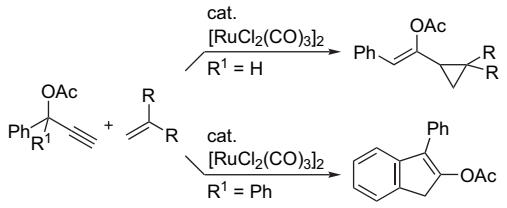
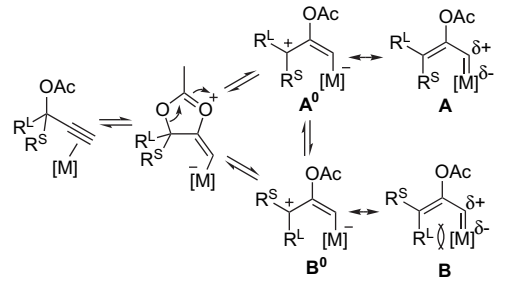
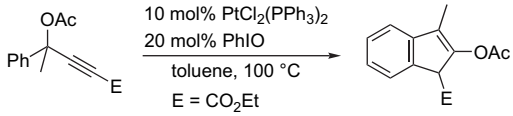
from propargyl sulfides and related dithioacetals (Scheme 5).[6] When we reinvestigated pentannulation of several propargyl esters under transition metal catalysis, we found that steric and electronic modification of propargyl esters affect the intermediacy, followed by indene formation. We wish to report herein the scope and limitation of transition metal-catalyzed indene synthesis using *sec*- and *tert*-propargyl acetates (*terminal alkynes*).



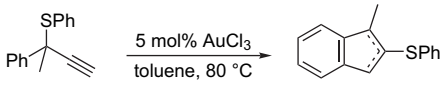
Scheme 2. Ru-catalyzed transformation of propargyl acetates.



Scheme 3. Generation of vinylcarbene complexes **A** and **B**.



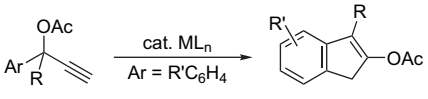
Scheme 4. Sarpong's indene synthesis.



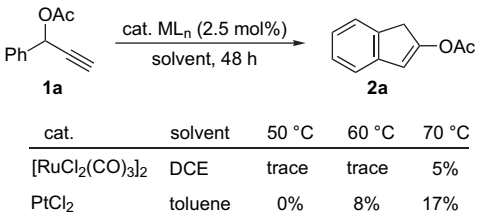
Scheme 5. Wang's indene synthesis.

2. Results and discussion

Because we had noticed that ruthenium and platinum complexes were effective catalysts for the carbene transfer reactions using propargyl acetates as a carbene source,[4] we reinvestigated indene synthesis using $[RuCl_2(CO)_3]_2$ or $PtCl_2$ and several types of propargyl acetates (Eq. 1). We began with *sec*-propargyl esters as the carbene precursor (R=H). The reaction of 1-phenyl-2-propynyl acetate (**1a**) with 2.5 mol % $[RuCl_2(CO)_3]_2$ in dichloroethane (DCE) at 50, 60, or 70 °C was almost sluggish, giving 1*H*-inden-2-yl acetate (**2a**) in up to 5% yield after 48 h (Scheme 6).[7]



(1)



cat.	solvent	50 °C	60 °C	70 °C
$[RuCl_2(CO)_3]_2$	DCE	trace	trace	5%
$PtCl_2$	toluene	0%	8%	17%

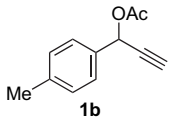
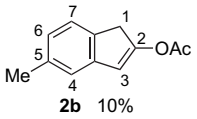
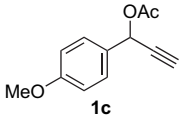
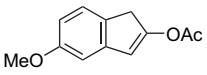
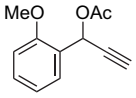
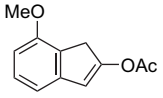
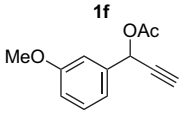
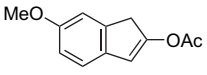
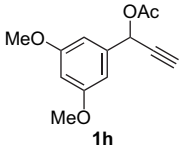
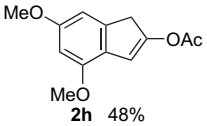
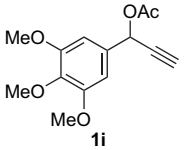
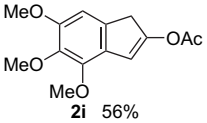
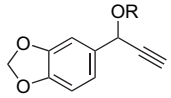
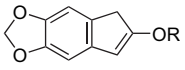
Scheme 6. Ru- and Pt-catalyzed indene formation from **1a**.

On the other hand, $PtCl_2$-catalyzed pentannulation of **1a** at 60 and 70 °C gave **2a** in 8% and 17% yields, respectively, although it was still sluggish at 50 °C. In the same reaction of **1a**, $PtCl_2(PPh_3)_2$/PhIO[5] as well as $AuCl(PPh_3)$ with/without $AgSbF_6$[2b] exhibited marginal catalytic activity, yielding **2a** up to 9% at 70 °C. Based on these preliminary results, we further investigated the $PtCl_2$-catalyzed pentannulation of *sec*-propargyl esters **1b–l** having several substituents on a phenyl ring. Results are summarized in Table 1. *sec*-Propargyl acetates having *para*-tolyl or *ortho*- and *para*-anisyl substituents gave low yields of the corresponding indenes (entries 1–3). In each case, major products were 5- or 7-substituted 1*H*-inden-2-yl acetates. *meta*-Anisyl-substituted ester **1g** gave 6-methoxy-1*H*-inden-2-yl acetate **2g** in 45% yield (entry 4). As the number of methoxy substituents at *meta*- and *para*-positions increased, yields of indenes were increased (entries 5 and 6). The reaction of 3,4-methylenedioxyphenyl-substituted ester **1j–l** resulted in the highest yield of an indene, giving **2j** in 64% yield (entry 7). 3,4-Methylenedioxyphenyl-substituted benzoic and pivalic esters also gave indenes in excellent yields (entries 8 and 9). Meanwhile, $[RuCl_2(CO)_3]_2$ as a catalyst was rather ineffective for **1j**, the yield of **2j** being 15%. *sec*-Propargyl acetates **1d** and **1e** having a *para*-chloro and a bromophenyl group (not shown) were much less reactive under platinum-catalyzed conditions, giving the 5-halogenated 1*H*-inden-2-yl acetates in up to 10% yield. These results indicate that substituents on a phenyl ring influence the nucleophilicity of a reaction site on the phenyl ring toward a positively charged carbene carbon more strongly than does the stability of the allyl cationic intermediates $\mathbf{A^0}$ and $\mathbf{B^0}$ that participate in the isomerization of vinylcarbenoids **A** and **B**, as shown in Scheme 3. It is noted that 5-substituted indenes[8] obtained from *sec*-propargyl esters are different from 6-substituted indenes obtained in the $PtCl_2(PPh_3)_2$/PhIO-catalyzed pentannulation reported by Sarpong et al.[5]

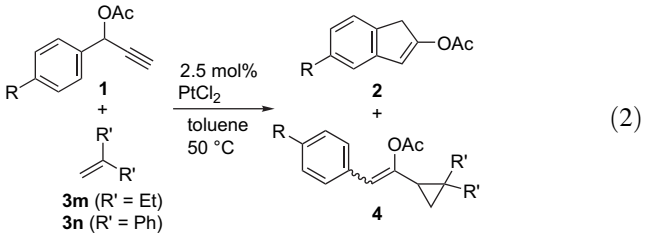
Because pentannulation was assumed to require the intervention of the sterically less favored (*E*)-carbenoids **B**, a controlled experiment to intercept the intermediates was attempted by using cyclopropanation reactions with alkenes.

In the presence of a catalytic amount of $PtCl_2$, reactions of *sec*-propargyl esters, **1a–e** and **1j** with 2-ethyl-1-butene **3m** (20 equiv) or 1,1-diphenylethene **3n** (5 equiv) were carried out in toluene at 50 °C (Eq. 2).[9] The results are shown in Table 2. In most cases, *Z*-alkene-enriched cyclopropanes were obtained as major products together with trace amounts of indenes **2**.[10] These results indicate that vinylcarbene intermediates can be formed from *sec*-propargyl esters even at 50 °C, and the *Z*-vinylcarbene complex **A** mainly contributes to the equilibrium between **A** and **B**.

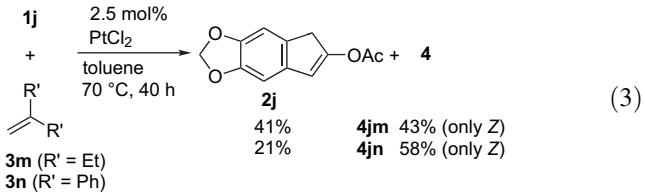
Table 1. Formation of indenes from *sec*-propargyl esters **1**[a]

Entry	1	Indene **2** and yield[b]
1	 **1b**	 **2b** 10%
2	 **1c**	 **2c** 16%
3	 **1f**	 **2f** 9%
4	 **1g**	 **2g** 45%
5	 **1h**	 **2h** 48%
6	 **1i**	 **2i** 56%
7	 **1j**	 R=Ac **2j** 64% (15%)[c]
8	**1k**	R=Bz **2k** 81%[d]
9	**1l**	R=Piv **2l** 65%[d]

[a] Reaction conditions: **1** (0.5 mmol), $PtCl_2$ (2.5 mol %) in toluene (2.5 mL) at 70 °C for 48 h.
[b] In some cases, <5% of an inseparable indene isomer was detected.
[c] $[RuCl_2(CO)_3]_2$ (2.5 mol %) in DCE at 50 °C for 72 h.
[d] For 18 h.



(2)



(3)

In contrast, reactions of 3,4-methylenedioxyphenyl-substituted ester **1j** with the same alkenes gave a discernible amount of an indene **2j** in 41% and 21% yields together with (*Z*)-vinylcyclopropanes as major products (Eq. 3). These results imply that both *para*- and *meta*-substituents promote isomerization between (*Z*)- and (*E*)-vinylcarbenoids followed by the pentannulation, but the equilibrium is otherwise very slow. We can estimate that the equilibrium ratios of (*Z*)- and (*E*)-vinylcarbenoids from **1** are ca. 9:1 except for **1j**. However, electron-donating *para*-substituents on phenyl rings, which should be responsible for the stabilization of cationic intermediates, are less effective for indene formation than *meta*-substituents.

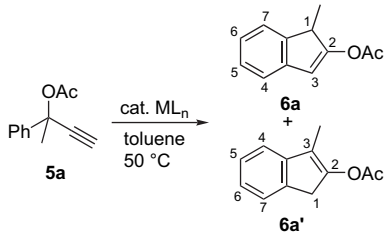
Table 2. Cyclopropanation versus indene formation using *sec*-propargyl ester **1** and alkenes **3m** or **3n**

R in **1**	Alkene **3**	Time (h)	Product and yield (*Z*/*E*)[a]
H (**1a**)	**3m**	24	**4am** 64% (88:12)
Me (**1b**)		24	**4bm** 75% (94:6)
MeO (**1c**)		8	**4cm** 69% (96:4)
Cl (**1d**)		16	**4dm** 74% (92:8)
Br (**1e**)		12	**4em** 73% (94:6)
H (**1a**)	**3n**	48	**4an** 82% (91:9)
Me (**1b**)		24	**4bn** 64% (93:7)
MeO (**1c**)		24	**4cn** 80% (89:11)
Cl (**1d**)		40	**4dn** 75% (90:10)
Br (**1e**)		24	**4en** 65% (92:8)

[a] Ratios of *Z* and *E* were determined by ^1H NMR.

Next, we examined indene formation from *tert*-propargyl ester **5a** having methyl and phenyl groups at a propargyl position. Typical results using several catalysts are summarized in Table 3. $[RuCl_2(CO)_3]_2$ as a catalyst promoted the pentannulation of **5a** at 50 °C to give a mixture of 1-methyl-2-indene **6a** and 3-methyl-2-indene **6a′** in 35% yield with an 83:17 ratio. $PtCl_2$ exhibited prominent catalytic activity in indene formation from *tert*-propargyl ester **5a** even at 50 °C, giving **6a** and **6a′** in 85% yield with a 72:28 ratio. Under Sarpong's catalytic conditions ($PtCl_2(PPh_3)_2$/PhIO)[5]a mixture of **6a** and **6a′** was obtained from **5a** in 73% yield with a 79:21 ratio, while under Toste's catalytic conditions ($AuCl(PPh_3)/AgSbF_6$),[2b] the total yield of **6a** and **6a′** was only 9% with reversed selectivity (**6a**/**6a′**=26:74).[11] Reactions of *tert*-propargyl ester **5** having several substituents on a phenyl ring were carried out under $PtCl_2$ catalysis, which led to the highest yield of indenes. Results are summarized in Table 4.

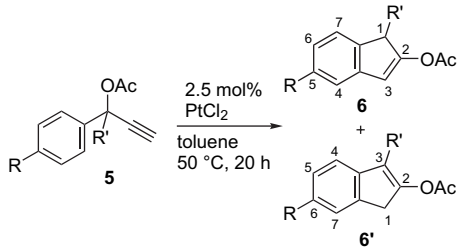
Table 3. Transition metal-catalyzed formation of indene from *tert*-propargyl ester **5**[a]



ML_n (2.5 mol %)	Time (h)	Yield of indenes (**6a**/**6a′**)
$[RuCl_2(CO_3)]_2$	20	35% (83:17)
$PtCl_2$	14	85% (72:28)
$PtCl_2(PPh_3)_2$/PhIO (1/8)	20	73% (79:21)
$AuCl(PPh_3)/AgSbF_6$ (1/1)	20	9% (26:74)

[a] Ratios of indenes were determined by ^1H NMR.

Table 4. $PtCl_2$-catalyzed formation of indenes from *tert*-propargyl esters **5**



Entry	5	R	R′	Yield of indenes (**6**/**6′**)[a]
1	**5a**	H	Me	85% (72:28)
2	**5b**	Me	Me	78% (67:33)
3	**5c**	MeO	Me	85% (53:47)
4	**5d**	Cl	Me	82% (49:51)
5	**5e**	Br	Me	85% (50:50)
6	**5f**	CF_3	Me	66% (56:44)
7[b]	**5g**	H	Et	86% (78:22)

[a] Ratios of indenes were determined by ^{1}H NMR.
[b] Reaction time: 16 h.

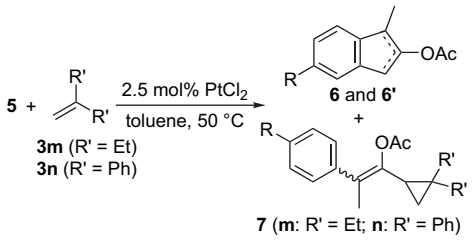
In most cases, high yields of indenes were obtained, except with CF_3-substituent (entries 1–6). Irrespective of electron-donating and electron-withdrawing *para*-substituents of **5**, a mixture of **6** and **6′** was obtained more efficiently than was the case for *sec*-propargyl esters **1** (vide supra). The reaction of 3-phenylpent-1-yn-3-yl acetate **5g** (R=H, R′=Et) was complete within 16 h, giving a mixture of **6g** and **6g′** in 86% yield (78:22) (entry 7). The slight rate enhancement, which leads to rapid indene formation, is probably caused by the predominance of *E*-vinylcarbenoid resulting from an ethyl group. Platinum-catalyzed reactions of **5** afforded 1-alkyl-2-acetoxyindenes **6** predominantly with the same selectivity for *sec*-propargyl esters **1**. The present $PtCl_2$-catalyzed reaction shows the reverse selectivity in indene formation reported by Sarpong et al.[5]

To gain an insight into indene formation, we again carried out the competitive reactions of *tert*-propargyl esters **5** in the presence of alkenes. The reactions of **5** with 2-ethyl-1-butene **3m** (20 equiv) or 1,1-diphenylethene **3n** (5 equiv) afforded a mixture of indenes **6**/**6′** and vinylcyclopropanes **7**. The results are summarized in Table 5, and were completely different from those of *sec*-propargyl esters **1** (see Table 2).[12]

Electron-donating substituents (R=Me, MeO) on a phenyl ring led to the predominant formation of indenes **6**/**6′**, while halogenated phenyl rings (R=Cl, Br) afforded cyclopropanes **7** predominantly. Ratios of *Z* and *E* in vinylcyclopropanes **7** ranged from ca. 50:50 to 60:40, which were completely different from ca. 90:10 for *sec*-propargyl esters.[10] This indicates that the higher ratio of an *E*-vinylcarbene intermediate in equilibrium can facilitate the formation of indenes. The ratios of **6** and **6′** were similar to those for the noncompetitive reactions using **5** (see Table 4). Accordingly, indene formation strongly depends on the rapid equilibrium as well as the ratio between intermediates **A** and **B**.

The $PtCl_2$-catalyzed reaction of diphenyl-substituted *tert*-propargyl ester **5h** afforded a mixture of 1-phenyl-2-acetoxyindene **6h** and 2-phenyl-2-acetoxyindene **6h′** in 84% yield (**6h**/**6h′**=61:39) (Eq. 4).

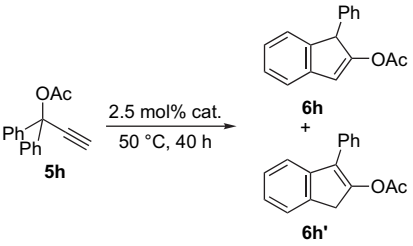
Table 5. Cyclopropanation versus indene formation using *tert*-propargyl esters **5** and alkenes **3m** or **3n**



R in **5**	Alkene **3**	Products and yields	
		6+**6′** (ratio)[a]	**7** (*Z*/*E*)[b]
H (**5a**)	**3m**[c]	43% (70:30)	**7am** 40% (58:42)
Me (**5b**)		52% (68:32)	**7bm** 31% (52:48)
MeO (**5c**)		67% (50:50)	**7cm** 25% (57:43)
Cl (**5d**)		22% (50:50)	**7dm** 68% (58:42)
Br (**5e**)		25% (44:56)	**7em** 65% (55:45)
H (**5a**)	**3n**[d]	41% (71:29)	**7an** 53% (55:45)
Me (**5b**)		45% (67:33)	**7bn** 43% (55:45)
MeO (**5c**)		43% (53:47)	**7cn** 38% (53:47)
Cl (**5d**)		14% (50:50)	**7dn** 74% (58:42)
Br (**5e**)		18% (44:56)	**7en** 75% (52:48)

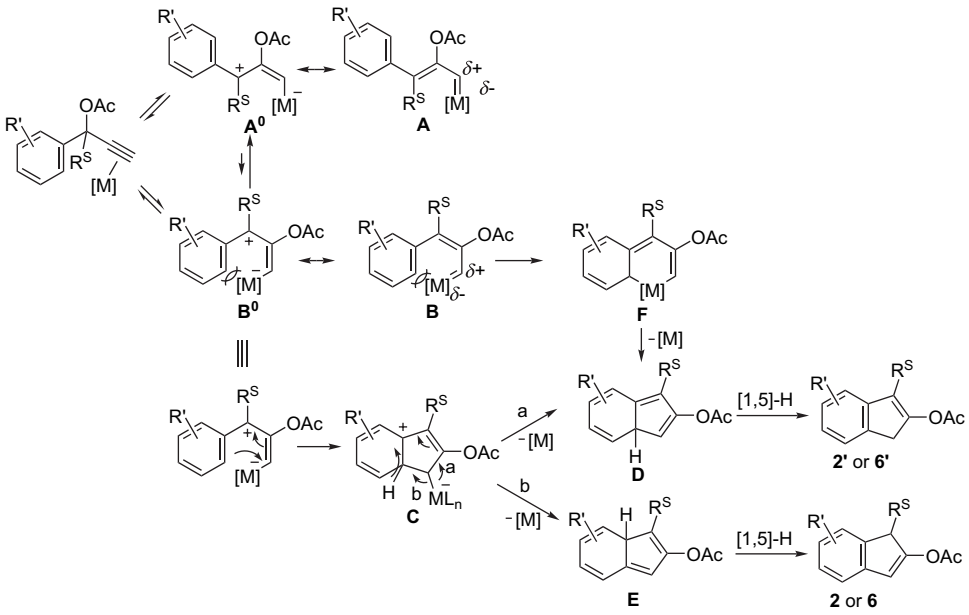
[a] Ratios of **6** and **6′** were determined by ^{1}H NMR.
[b] Ratios of *Z* and *E* in **7** were determined by ^{1}H NMR.
[c] For 2 h.
[d] For 5 h.

In contrast, the $[RuCl_2(CO)_3]_2$-catalyzed reaction of **5h** gave **6h′** predominantly (**6h**/**6h′**=4:96). Because we observed that no isomerization of indene **6h′** (96% enriched) into **6h** occurred under the platinum- or ruthenium-catalyzed conditions, each indene isomer must be produced via different pathways. Several plausible mechanisms for pentannulation via vinylcarbenoids or styrylcarbenoids have been postulated.[2,5,6,13,14] Because the substituted patterns of indenes reported in this article and our previous paper are completely different from those reported by Nolan et al.,[13b] mechanisms via allene complexes can be excluded. The most plausible mechanism is shown in Scheme 7.



(4)

As we mentioned above, *E*-vinylcarbene complexes in equilibrium through an allyl cationic intermediate are the first structural requisite for indene formation. Considering the competitive reactions of pentannulation versus cyclopropanation, we can estimate that the equilibrium ratios of *E* and *Z* from *sec*- and *tert*-propargyl esters **1** and **5** are ca. 10:90 and 40:60, respectively. The enhancement of indene formation by both *para*- and *meta*-substituents in *sec*-propargyl esters **1** suggests that a *Z*-platinum–carbene complex **A** isomerizes to *E*-carbene complex **B** via cationic species



Scheme 7. Plausible mechanism of Ru- and Pt-catalyzed indene formation.

$\mathbf{A^0}$ and $\mathbf{B^0}$, followed by Nazarov-type cyclization (pentannulation)[15] involving an *ortho*-aromatic carbon and a positively charged carbene center to give intermediate **C**. Subsequently, elimination of platinum from **C** affords the intermediate **D** or **E**, followed by a 1,5-hydrogen shift to give 2-acetoxyindenes. In contrast, low yields of indenes in ruthenium-catalyzed reactions of **1a**, **1j**, and **5a** are probably caused by the overwhelming sterical requirement that disfavors isomerization from **A** to **B**. In the indene formation from **5h**, Ru catalysis gave 2-phenyl-2-acetoxyindene **6h′** predominantly, while Pt catalysis favors the formation of 1-phenyl-2-acetoxyindene **6h**. However, the absence of isomerization of the isolated indene and the catalyst-dependent selectivity of indenes cannot be explained by only Nazarov-type cyclization mechanism for indene formation. The absence of enhancement with the *meta*-substituent of **1j** suggests that the nucleophilicity of an *ortho*-aromatic carbon is not a crucial factor in ruthenium-catalyzed indene formation. We therefore propose the reaction pathway via metallacycle **F** as an alternative pentannulation mechanism, particularly in Ru catalysis. Closely related pentannulation of styrylcarbene complexes has been proposed for the byproduct formation in the Dötz reaction.[3]

3. Conclusion

We have demonstrated indene formation from phenyl-substituted *sec*- and *tert*-propargyl esters (*terminal alkynes*) in the presence of platinum or ruthenium catalysts. The efficiency of indene formation in platinum catalysis was affected by electron-donating substituents in propargyl acetates, which can stabilize the intermediary cationic species required for indene formation, although the selectivity for indenes from *tert*-propargyl acetates was not high. In contrast, ruthenium catalysis can provide high selectivity for indene in the reaction of diphenyl-substituted *tert*-propargyl acetate, probably because of facile metallacycle formation. Because the sterically demanding $RuCl_2(CO)_3$ moiety having three additional carbonyl ligands compared with $PtCl_2$ prefers the sterical stabilization in intermediates, electronic tuning by substituents is not effective for indene formation.

4. Experimental

4.1. General

All solvents were dried by the usual methods and distilled before use. Organic reagents were used as purchased. All catalytic reactions were carried out under an inert gas atmosphere using standard Schlenk techniques and a glovebox. Column chromatographies were performed on silica gel (230–400 mesh). Analytical TLC was performed on ready-made plates coated with silica gel on glass. The NMR spectra (^1H and ^{13}C) were measured for solutions in $CDCl_3$ with Me_4Si as an internal standard at 25 °C.

Preparation of propargyl esters **1** and **5**, NOE experiments to determine the regiochemistry of major products of **2**, NOE experiments to determine the olefin regioisomers of vinylcyclopropanes **4** and **7**, and NMR Spectra of **2f**, **2h**, **2i**, **4jm**, **4cn**, **4jn**, **5f**, **5g**, **6c**, **6d**, **6f**, **6g**, and **7cn** are provided in Supplementary data.

4.2. Typical procedure for synthesis of indenes 2 and 6

A catalytic amount of $PtCl_2$ (0.013 mmol) was placed in a flame-dried Schlenk flask under N_2. A solution of **1** or **5** (0.50 mmol) in anhydrous toluene (2.5 mL) was added to the flask at room temperature. After the mixture was stirred at 50 or 70 °C for each appropriate time, the reaction mixture was cooled to room temperature and then diluted with EtOAc. The resulting organic solution was filtered through a short silica gel pad. The filtrate was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel (hexane/EtOAc=10/1) to give indene **2** or **6**. Indene **2a** is a known compound.

4.2.1. 5-Methyl-2-indenyl acetate (2b). A colorless oil (10% yield). IR (neat) ν_{max} cm^{-1}: 2924, 1765 (C=O), 1619, 1371, 1233, 1049, 887. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.21 (d, J=7.2 Hz, 1H), 7.11 (s, 1H), 6.96 (d, J=7.2 Hz, 1H), 6.55 (s, 1H), 3.52 (s, 2H), 2.36 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 168.0, 155.7, 142.8, 136.2, 134.1, 125.0, 123.0, 121.7, 114.7, 37.5, 21.6, 21.3. Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.85; H, 6.64.

4.2.2. 5-Methoxy-2-indenyl acetate (2c). A colorless oil (16% yield) (ca. 5% of regioisomeric indene **2g** was detected by ^{1}H NMR). IR (neat) ν_{max} cm^{-1}: 2947, 1748 (C=O), 1610, 1478, 1033, 872, 593, 467. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.23 (d, J=8.1 Hz, 1H), 6.86 (d, J=2.4 Hz, 1H), 6.69 (dd, J=8.1, 2.4 Hz, 1H), 6.56 (s, 1H), 3.80 (s, 3H), 3.50 (s, 2H), 2.24 (s, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 168.0, 159.0, 156.7, 144.1, 129.1, 123.9, 114.8, 110.0, 107.0, 55.4, 37.1, 21.2. Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.50; H, 6.00.

4.2.3. 7-Methoxy-2-indenyl acetate (2f). A colorless oil (9% yield) (a trace amount of regioisomeric indene was detected). IR (neat) ν_{max} cm^{-1}: 2936, 1763 (C=O), 1614, 1484, 1263, 1200, 1086, 772. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.23 (dd, J=8.2, 8.2 Hz, 1H), 6.94 (d, J=8.2 Hz, 1H), 6.72 (d, J=8.2 Hz, 1H), 6.58 (s, 1H), 3.87 (s, 3H), 3.51 (s, 2H), 2.25 (s, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 168.1, 156.0, 154.8, 144.5, 128.2, 123.7, 114.6, 114.3, 107.2, 55.2, 35.4, 21.2. HRMS (FAB) m/z: Calcd for $C_{12}H_{12}O_3$ (M^+) 204.0786. Found: 204.0786.

4.2.4. 6-Methoxy-2-indenyl acetate (2g). A colorless oil (45% yield) (ca. 5% of regioisomeric indene **2c** was detected by ^{1}H NMR). IR (neat) ν_{max} cm^{-1}: 2939, 2936, 1765 (C=O), 1611, 1479, 1370, 1199, 1030, 858, 712, 521. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.17 (d, J=8.2 Hz, 1H), 6.95 (s, 1H), 6.79 (d, J=8.2 Hz, 1H), 6.52 (s, 1H), 3.80 (s, 3H), 3.54 (s, 2H), 2.23 (s, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 168.2, 157.5, 153.7, 139.0, 135.5, 121.3, 114.4, 111.9, 110.4, 55.5, 37.9, 21.1. Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.30; H, 5.80.

4.2.5. 4,6-Dimethoxy-2-indenyl acetate (2h) and 5,7-dimethoxy-2-indenyl acetate (2h′). A colorless oil (48% yield) (9% of regioisomeric indene **2h′** was detected by ^{1}H NMR). IR (neat) ν_{max} cm^{-1}: 2943, 1749 (C=O), 1598, 1457, 1373, 1227, 1078, 856, 721, 560. **2h** (major): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.60 (s, 1H), 6.58 (d, J=1.6 Hz, 1H), 6.39 (d, J=1.6 Hz, 1H), 3.83 (s, 3H), 3.81 (s, 3H), 3.55 (s, 2H), 2.22 (s, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 168.2, 158.9, 153.4, 151.8, 139.8, 123.9, 111.2, 101.5, 97.1, 55.7, 55.5, 38.4, 21.2. **2h′** (minor): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.54 (s, 1H), 6.52 (d, J=1.8 Hz, 1H), 6.31 (d, J=1.8 Hz, 1H), 3.84 (s, 3H), 3.81 (s, 3H), 3.45 (s, 2H), 2.24 (s, 3H). HRMS (FAB) m/z: Calcd for $C_{13}H_{14}O_4$ (M^+) 234.0892. Found: 234.0882.

4.2.6. 4,5,6-Trimethoxy-2-indenyl acetate (2i). A colorless oil (56% yield) (ca. 5% of regioisomeric indene was detected by ^{1}H NMR). IR (KBr) ν_{max} cm^{-1}: 2940, 1764 (C=O), 1601, 1472, 1201, 1115, 1032, 875, 719, 601. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.75 (s, 1H), 6.64 (s, 1H), 3.93 (s, 3H), 3.87 (s, 3H), 3.85 (s, 3H), 3.53 (s, 2H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.0, 153.0, 151.5, 146.9, 140.8, 133.1, 128.0, 111.4, 104.3, 61.2, 61.1, 56.4, 38.1, 21.2. HRMS (FAB) m/z: Calcd for $C_{14}H_{16}O_5$ (M^+) 264.0998. Found: 264.0991.

4.2.7. 5*H*-Indeno[5,6-*d*][1,3]dioxol-6-yl acetate (2j). A white solid (64% yield), mp 79.8–80.3 °C. IR (KBr) ν_{max} cm^{-1}: 3119, 2905, 1761 (C=O), 1618, 1468, 1290, 1199, 1032, 795, 583. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.84 (s, 1H), 6.78 (s, 1H), 6.47 (s, 1H), 5.91 (s, 2H), 3.46 (s, 2H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.0, 154.3, 146.3, 145.0, 136.1, 130.3, 114.6, 105.1, 102.3, 100.6, 37.7, 21.2. Anal. Calcd for $C_{12}H_{10}O_4$: C, 66.05; H, 4.62. Found: C, 66.18; H, 4.57.

4.2.8. 5*H*-Indeno[5,6-*d*][1,3]dioxol-6-yl benzoate (2k). A white solid (81% yield), mp 87.8–88.1 °C. IR (KBr) ν_{max} cm^{-1}: 2890, 2366, 1730 (C=O), 1621, 1468, 1259, 1120, 1056, 7867, 705. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.14 (d, J=7.8 Hz, 2H), 7.62 (dd, J=7.8, 7.8 Hz, 1H), 7.50 (dd, J=7.8, 7.8 Hz, 2H), 6.90 (s, 1H), 6.84 (s, 1H), 6.65 (s, 1H), 5.94 (s, 2H), 3.63 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.9, 154.6, 146.5, 145.2, 136.3, 133.6, 130.6, 130.0, 129.4, 128.6, 115.1, 105.3, 102.5, 100.7, 37.9. HRMS (FAB) m/z: Calcd for $C_{17}H_{12}O_4$ (M^+) 280.0736. Found: 280.0728.

4.2.9. 5*H*-Indeno[5,6-*d*][1,3]dioxol-6-yl pivalate (2l). A white solid (65% yield), mp 150.0–150.7 °C. IR (KBr) ν_{max} cm^{-1}: 2977, 2355, 1743 (C=O), 1467, 1278, 1128, 857, 671. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.85 (s, 1H), 6.78 (s, 1H), 6.46 (s, 1H), 5.91 (s, 2H), 3.47 (s, 2H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.8, 154.9, 146.5, 145.0, 136.4, 130.4, 114.4, 105.2, 102.3, 100.6, 39.2, 37.7, 27.1. HRMS (FAB) m/z: Calcd for $C_{15}H_{16}O_4$ (M^+) 260.1049. Found: 260.1051.

4.2.10. 1-Methyl-2-indenyl acetate (6a) and 3-methyl-2-indenyl acetate (6a′). A colorless oil (85% yield, **6a**/**6a′**=72:28) (a mixture of regioisomers). IR (neat) ν_{max} cm^{-1}: 2973, 1762 (C=O), 1462, 1200, 755. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33–7.13 (m, 8H, **6a**+**6a′**), 6.61 (s, 1H, **6a**), 3.56 (s, 2H, **6a′**), 3.56 (q, J=7.2 Hz, 1H, **6a**), 2.24 (s, 3H, **6a′**), 2.23 (s, 3H, **6a**), 1.97 (t, J=2.2 Hz, 3H, **6a′**), 1.31 (d, J=7.2 Hz, 3H, **6a**). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.5, 167.8, 159.5, 150.0, 143.8, 142.6, 141.6, 138.0, 126.7, 126.2, 124.4, 124.3, 123.4, 123.2, 122.2, 120.1, 118.7, 112.9, 43.1, 36.7, 21.2, 20.8, 14.8, 8.5. Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.76; H, 6.52.

4.2.11. 1,5-Dimethyl-2-indenyl acetate (6b) and 3,6-dimethyl-2-indenyl acetate (6b′). A colorless oil (78% yield, **6b**/**6b′**=67:33) (a mixture of regioisomers). IR (neat) ν_{max} cm^{-1}: 2971, 1764 (C=O), 1619, 1370, 1201, 1052, 889, 815, 586. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.23–6.95 (m, 6H, **6b**+**6b′**), 6.56 (s, 1H, **6b**), 3.54 (q, J=7.2 Hz, 1H, **6b**), 3.52 (s, 2H, **6b′**), 2.36 (s, 3H, **6b′**), 2.35 (s, 3H, **6b**), 2.24 (s, 6H, **6b**+**6b′**), 1.96 (s, 3H, **6b′**), 1.30 (d, J=7.2 Hz, 3H, **6b**). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 168.8, 168.0, 159.8, 149.3, 141.8, 141.2, 139.9, 138.3, 136.4, 134.2, 126.9, 125.1, 124.2, 123.4, 122.0, 121.8, 118.5, 113.0, 42.8, 36.6, 21.5, 21.4, 21.2, 20.8, 15.0, 8.5. Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.11; H, 6.99.

4.2.12. 5-Methoxy-1-methyl-2-indenyl acetate (6c) and 6-methoxy-3-methyl-2-indenyl acetate (6c′). A colorless oil (85% yield, **6c/6c′**=53:47) (a mixture of regioisomers). IR (neat) ν_{max} cm^{-1}: 2935, 1763 (C=O), 1615, 1474, 1370, 1118, 1030, 818, 589. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.23–6.95 (m, 2H, **6c+6c′**), 6.95–6.94 (m, 1H, **6c**), 6.84–6.80 (m, 2H, **6c**), 6.70–6.67 (m, 1H, **6c**), 6.57 (s, 1H, **6c**), 3.79 (s, 3H, **6c**), 3.79 (s, 3H, **6c′**), 3.53 (s, 2H, **6c′**), 3.50 (q, J=7.2 Hz, 1H, **6c**), 2.25 (s, 3H, **6c**), 2.24 (s, 3H, **6c′**), 1.94 (t, J=2.0 Hz, 3H, **6c′**), 1.29 (d, J=7.2 Hz, 3H, **6c**). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 168.9, 167.9, 160.6, 159.1, 157.8, 148.1, 143.0, 139.8, 136.9, 134.9, 123.1, 122.8, 119.2, 113.0, 111.5, 110.4, 109.8, 107.4, 55.5, 55.3, 42.5, 36.8, 21.1, 20.8, 15.1, 8.5. HRMS (FAB) m/z: Calcd for $C_{13}H_{14}O_3$ (M^+) 218.0943. Found: 218.0937.

4.2.13. 5-Chloro-1-methyl-2-indenyl acetate (6d) and 6-chloro-3-methyl-2-indenyl acetate (6d′). A colorless oil (82% yield, **6d/6d′**=49:51) (a mixture of regioisomers). IR (neat) ν_{max} cm^{-1}: 2977, 1766 (C=O), 1606, 1371, 1196, 1074, 883, 821, 582. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.30–7.10 (m, 6H, **6d+6d′**), 6.58 (s, 1H, **6d**), 3.57 (s, 2H, **6d′**), 3.54 (q, J=7.5 Hz, 1H, **6d**), 2.27 (s, 6H, **6d+6d′**), 1.96 (t, J=2.0 Hz, 3H, **6d′**), 1.31 (d, J=7.5 Hz, 3H, **6d**). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 168.6, 167.8, 160.8, 150.2, 143.5, 142.5, 140.8, 139.7, 132.6, 130.4, 126.6, 124.3, 123.8, 123.3, 123.1, 121.2, 119.7, 112.3, 42.9, 36.7, 21.2, 20.8, 14.8, 8.5. HRMS (FAB) m/z: Calcd for $C_{12}H_{11}ClO_2$ (M^+) 222.0448. Found: 222.0455.

4.2.14. 5-Bromo-1-methyl-2-indenyl acetate (6e) and 6-bromo-3-methyl-2-indenyl acetate (6e′). A colorless oil (85% yield, **6e/6e′**=50:50) (a mixture of regioisomers). IR (neat) ν_{max} cm^{-1}: 2976, 1765 (C=O), 1600, 1370, 1071, 885, 818, 577. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.44–7.38 (m, 3H, **6e+6e′**), 7.26 (dd, J=7.8, 1.8 Hz, 1H, **6e**), 7.13 (d, J=7.8 Hz, 1H, **6e**), 7.09 (d, J=7.8 Hz, 1H, **6e**), 6.57 (s, 1H, **6e**), 3.55 (s, 2H, **6e′**), 3.51 (q, J=7.5 Hz, 1H, **6e**), 2.26 (s, 6H, **6e+6e′**), 1.95 (t, J=1.8 Hz, 3H, **6e′**), 1.30 (d, J=7.5 Hz, 3H, **6e**). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 168.5, 167.8, 160.6, 150.2, 143.9, 142.9, 141.3, 140.0, 129.4, 127.2, 126.5, 124.0, 123.7, 123.1, 120.6, 120.1, 118.2, 112.1, 42.9, 36.7, 21.2, 20.8, 14.7, 8.4. Anal. Calcd for $C_{12}H_{11}BrO_2$: C, 53.96; H, 4.15. Found: C, 54.13; H, 4.29.

4.2.15. 1-Methyl-5-trifluoromethyl-2-indenyl acetate (6f) and 3-methyl-6-trifluoromethyl-2-indenyl acetate (6f′). A colorless oil (66% yield, **6f/6f′**=56:44) (a mixture of regioisomers). IR (neat) ν_{max} cm^{-1}: 2976, 1767 (C=O), 1438, 1322, 1198, 891, 831, 585. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58–7.28 (m, 6H), 6.56 (s, 1H), 3.64 (s, 2H), 3.61 (q, J=7.3 Hz, 1H), 2.28 (s, 3H), 2.28 (s, 3H), 2.00 (t, J=2.0 Hz, 3H), 1.34 (d, J=7.3 Hz, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 168.5, 167.8, 160.7, 152.4, 147.5, 146.2, 142.5, 142.5, 138.4, 129.4 (q, J=31.7 Hz), 126.5 (q, J=40.7 Hz), 125.0 (q, J=277.3 Hz), 124.5 (q, J=266.1 Hz), 123.8 (q, J=4.1 Hz), 122.5, 121.5 (q, J=4.1 Hz), 120.1 (q, J=3.7 Hz), 118.7, 117.6 (q, J=3.7 Hz), 112.3, 43.3, 36.9, 21.2, 20.8, 14.5, 8.4. HRMS (FAB) m/z: Calcd for $C_{13}H_{11}F_3O_2$ (M^+) 256.0711. Found: 256.0713.

4.2.16. 1-Ethyl-2-indenyl acetate (6g) and 3-ethyl-2-indenyl acetate (6g′). A colorless oil (86% yield, **6g/6g′**=78:22) (a mixture of regioisomers). IR (neat) ν_{max} cm^{-1}: 2967, 1766 (C=O), 1461, 1370, 1195, 1010, 899, 753. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36–7.13 (m, 8H), 6.64 (s, 1H), 3.60 (t, J=5.4 Hz, 1H), 3.57 (s, 2H), 2.48 (q, J=7.7 Hz, 2H), 2.26 (s, 3H), 2.26 (s, 3H) 2.02–1.78 (m, 2H), 1.18 (t, J=7.7 Hz, 3H), 0.76 (t, J=7.3 Hz, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 168.0, 162.6, 158.0, 149.6, 142.5, 141.0, 129.3, 128.1, 127.3, 126.7, 126.3, 124.4, 124.3, 123.5, 122.6, 120.9, 119.1, 114.3, 48.9, 36.8, 22.4, 21.3, 20.9, 17.0, 12.5, 9.3. HRMS (FAB) m/z: Calcd for $C_{13}H_{14}O_2$ (M^+) 202.0994. Found: 202.0995.

4.2.17. 1-Phenyl-2-indenyl acetate (6h) and 3-phenyl-2-indenyl acetate (6h′). A yellow solid (84% yield, **6h/6h′**=61:39) (a mixture of regioisomers). IR (KBr) ν_{max} cm^{-1}: 3021, 1762 (C=O), 1597, 1455, 1368, 1217, 752, 698, 535. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48–7.07 (m, 18H, **6h+6h′**), 6.70 (d, J=1.8 Hz, 1H, **6h**), 4.75 (s, 1H, **6h**), 3.77 (s, 2H, **6h′**), 2.16 (s, 3H, **6h′**), 2.06 (s, 3H, **6h**). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 168.9, 168.0, 157.9, 150.7, 142.5, 142.5, 141.8, 138.2, 137.4, 132.2, 128.7, 128.5, 128.5, 128.2, 128.1, 127.6, 127.1, 127.1, 126.4, 125.0, 124.9, 123.7, 123.5, 121.1, 120.1, 115.0, 54.7, 37.3, 21.0, 20.9. Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.76; H, 5.72.

4.3. Typical procedure for synthesis of styrylcyclopropanes

The reactions were carried out with 2-ethylbut-1-ene (**3m**) (20 equiv) and 1,1-diphenylethene (**3n**) (5 equiv) under the same conditions for the catalytic indene synthesis. A catalytic amount of $PtCl_2$ (0.013 mmol) was placed in a flame-dried Schlenk flask under N_2. A solution of **1** or **5** (0.50 mmol) with alkene in anhydrous toluene (2.5 mL) was added to the flask at room temperature. After the mixture was stirred at 50 or 70 °C for 2–48 h, the reaction mixture was cooled to room temperature and then diluted with EtOAc. The resulting organic solution was filtered through a short silica gel pad. The filtrate was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel (hexane/EtOAc=10/1) to give styrylcyclopropane **4** or **7** with the corresponding indene.

4.3.1. 1-(2,2-Diethylcyclopropyl)-2-phenylvinyl acetate (4am). A colorless oil (64% yield, Z/E=88:12). IR (neat) ν_{max} cm^{-1}: 2963, 1758 (C=O), 1671, 1204, 1065, 750, 695, 520. *E*-**4am**: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40–7.17 (m, 5H), 5.95 (s, 1H), 2.19 (s, 3H), 1.70 (dd, J=7.4, 5.4 Hz, 1H), 1.59–1.50 (m, 2H), 1.41–1.18 (m, 1H), 1.12–1.05 (m, 1H), 0.93 (t, J=7.3 Hz, 3H), 0.90 (t, J=7.3 Hz, 3H), 0.74 (dd, J=7.4, 5.4 Hz, 1H), 0.61 (dd, J=5.4, 5.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.4, 149.0, 134.3, 128.2, 128.1, 126.8, 116.9, 29.9, 28.8, 28.0, 22.8, 21.2, 18.1, 10.8, 10.7. *Z*-**4am**: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.33 (s, 1H) 2.16 (s, 3H), 1.86 (dd, J=7.4, 5.4 Hz, 1H), 0.31 (dd, J=5.4, 5.4 Hz, 1H). (Other peaks cannot be distinguished from major peaks.) Anal. Calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 78.92; H, 8.41.

4.3.2. 1-(2,2-Diethylcyclopropyl)-2-(4-methylphenyl)-vinyl acetate (4bm). A colorless oil (75% yield, Z/E=94:6). IR (neat) ν_{max} cm^{-1}: 2963, 2934, 1758 (C=O),

1369, 1204, 872, 590. *E*-**4bm**: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.24 (d, J=7.9 Hz, 2H), 7.09 (d, J=7.9 Hz, 2H), 5.91 (s, 1H), 2.31 (s, 3H), 2.18 (s, 3H), 1.68 (dd, J=8.4, 5.2 Hz, 1H), 1.56–1.50 (m, 2H), 1.25–1.18 (m, 1H), 1.12–1.05 (m, 1H), 0.93 (t, J=7.2 Hz, 3H), 0.90 (t, J=7.2 Hz, 3H), 0.73 (dd, J=8.4, 5.2 Hz, 1H), 0.60 (dd, J=5.2, 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.5, 148.3, 136.6, 131.4, 128.9, 128.0, 116.7, 29.8, 28.8, 28.0, 22.8, 21.2, 21.2, 18.1, 10.8, 10.6. *Z*-**4bm**: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27 (d, J=7.9 Hz, 2H), 7.12 (d, J=7.9 Hz, 1H), 5.91 (s, 1H), 2.33 (s, 3H), 2.15 (s, 3H), 1.83 (dd, J=8.4, 5.2 Hz, 1H), 0.31 (dd, J=5.2, 5.2 Hz, 1H). (Other peaks cannot be distinguished from major peaks.) Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found: C, 79.10; H, 8.72.

4.3.3. 1-(2,2-Diethylcyclopropyl)-2-(4-methoxyphenyl)-vinyl acetate (4cm). A colorless oil (69% yield, *Z*/*E*=96:4). IR (neat) ν_{max} cm^{-1}: 2962, 1752 (C=O), 1608, 1206, 1036, 1036, 871, 830, 538. *E*-**4cm**: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31 (d, J=8.8 Hz, 2H), 6.82 (d, J=8.8 Hz, 2H), 5.88 (s, 1H), 3.77 (s, 3H), 2.19 (s, 3H), 1.68 (dd, J=8.3, 5.2 Hz, 1H), 1.56–1.51 (m, 2H), 1.22–1.18 (m, 1H), 1.09–1.05 (m, 1H), 0.93 (t, J=5.2, 5.2 Hz, 3H), 0.90 (t, J=7.4 Hz, 3H), 0.72 (dd, J=8.3, 5.2 Hz, 1H), 0.59 (dd, J=7.4 Hz, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 168.6, 158.4, 147.6, 129.4, 127.0, 116.3, 113.7, 55.1, 29.6, 28.7, 27.8, 22.7, 21.1, 18.0, 10.7, 10.5. *Z*-**4cm**: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32 (d, J=8.8 Hz, 2H), 6.84 (d, J=8.8 Hz, 2H), 6.27 (s, 1H), 3.79 (s, 3H), 0.30 (dd, J=5.2, 5.2 Hz, 1H). (Other peaks cannot be distinguished from major peaks.) Anal. Calcd for $C_{18}H_{24}O_3$: C, 74.97; H, 8.39. Found: C, 74.81; H, 8.27.

4.3.4. 1-(2,2-Diethylcyclopropyl)-2-(4-chlorophenyl)-vinyl acetate (4dm). A colorless oil (74% yield, *Z*/*E*=92:8). IR (neat) ν_{max} cm^{-1}: 2963, 2934, 1759 (C=O), 1492, 1370, 1201, 1013, 870, 589. *E*-**4dm**: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31–7.23 (m, 4H), 5.90 (s, 1H), 2.18 (s, 3H), 1.68 (dd, J=8.3, 5.4 Hz, 1H), 1.57–1.50 (m, 2H), 1.25–1.17 (m, 1H), 1.12–1.05 (m, 1H), 0.93 (t, J=7.2 Hz, 3H), 0.90 (t, J=7.2 Hz, 3H), 0.74 (dd, J=8.3, 5.4 Hz, 1H), 0.60 (dd, J=5.4, 5.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.2, 149.7, 132.8, 132.3, 129.3, 128.4, 115.7, 30.0, 28.8, 27.9, 22.8, 21.1, 18.1, 10.8, 10.8. *Z*-**4dm**: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.28 (s, 1H), 0.29 (dd, J=5.4, 5.4 Hz, 1H). (Other peaks cannot be distinguished from major peaks.) Anal. Calcd for $C_{17}H_{21}ClO_2$: C, 69.73; H, 7.23. Found: C, 70.02; H, 7.31.

4.3.5. 1-(2,2-Diethylcyclopropyl)-2-(4-bromophenyl)-vinyl acetate (4em). A colorless oil (73% yield, *Z*/*E*=94:6). IR (neat) ν_{max} cm^{-1}: 2963, 1759 (C=O), 1488, 1201, 1010, 870, 708, 589. *E*-**4em**: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32 (d, J=8.3 Hz, 2H), 7.14 (d, J=8.3 Hz, 2H), 5.80 (s, 1H), 2.09 (s, 3H), 1.59 (dd, J=8.5, 5.4 Hz, 1H), 1.49–1.41 (m, 2H), 1.15–1.09 (m, 1H), 1.04–0.98 (m, 1H), 0.85 (t, J=7.4 Hz, 3H), 0.81 (t, J=7.4 Hz, 3H), 0.67 (dd, J=8.5, 5.4 Hz, 1H), 0.52 (dd, J=5.4, 5.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.1, 149.8, 133.2, 131.3, 129.6, 120.5, 115.8, 30.0, 28.7, 28.0, 22.8, 21.1, 18.1, 10.8, 10.6. *Z*-**4em**: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34 (d, J=8.3 Hz, 2H), 7.17 (d, J=8.3 Hz, 1H), 6.18 (s, 1H), 1.61 (dd, J=8.5, 5.4 Hz, 1H), 0.22 (dd, J=5.4, 5.4 Hz, 1H). (Other peaks cannot be distinguished from major peaks.) Anal. Calcd for $C_{17}H_{21}BrO_2$: C, 60.54; H, 6.28. Found: C, 60.81; H, 6.36.

4.3.6. 2-(Benzo[*d*][1,3]dioxol-5-yl)-1-(2,2-diethylcyclopropyl)vinyl acetate (4jm). A colorless oil (43% yield, *Z* only). IR (neat) ν_{max} cm^{-1}: 2963, 1756 (C=O), 1622, 1470, 1208, 1039, 876, 590. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.96 (d, J=1.2 Hz, 1H), 6.79 (dd, J=8.4, 1.2 Hz, 1H), 6.73 (d, J=8.4 Hz, 1H), 5.93 (s, 2H), 5.85 (s, 1H), 2.21 (s, 3H), 1.67 (dd, J=7.8, 4.8 Hz, 1H), 1.58–1.48 (m, 2H) 1.19 (dq, J=14.0, 7.6 Hz, 1H), 1.08 (dq, J=14.0, 7.6 Hz, 1H), 0.93 (t, J=7.6 Hz, 3H), 0.89 (t, J=7.6 Hz, 3H), 0.72 (dd, J=7.8, 4.8 Hz, 1H), 0.58 (dd, J=4.8, 4.8 Hz, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 168.4, 147.8, 147.5, 146.3, 128.4, 122.4, 116.5, 108.1, 108.1, 100.9, 29.8, 28.8, 27.9, 22.8, 21.3, 18.1, 10.8, 10.7. HRMS (FAB) *m*/*z*: Calcd for $C_{18}H_{22}O_4$ (M^+) 302.1518. Found: 302.1518.

4.3.7. 1-(2,2-Diphenylcyclopropyl)-2-phenylvinyl acetate (4an). A white solid (82% yield, *Z*/*E*=91:9). IR (KBr) ν_{max} cm^{-1}: 3024, 1748 (C=O), 1493, 1375, 1204, 1155, 754, 705, 597. *E*-**4an**: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41–7.09 (m, 15H), 5.82 (s, 1H), 2.63 (dd, J=8.4, 6.0 Hz, 1H), 2.03 (s, 3H), 1.82 (dd, J=6.0, 6.0 Hz, 1H), 1.66 (dd, J=8.4, 6.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.4, 146.5, 145.6, 140.3, 134.1, 130.2, 128.3, 128.1, 128.0, 127.9, 127.4, 126.8, 126.5, 126.1, 117.3, 38.3, 30.7, 21.0, 19.9. *Z*-**4an**: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.41 (s, 1H), 2.89 (dd, J=8.4, 6.0 Hz, 1H), 1.58 (dd, J=8.4, 6.0 Hz, 1H). (Other peaks cannot be distinguished from major peaks.) Anal. Calcd for $C_{25}H_{22}O_2$: C, 84.72; H, 6.26. Found: C, 84.79; H, 6.32.

4.3.8. 1-(2,2-Diphenylcyclopropyl)-2-(4-methylphenyl)-vinyl acetate (4bn). A white solid (64% yield, *Z*/*E*=93:7). IR (KBr) ν_{max} cm^{-1}: 3022, 1748 (C=O), 1494, 1204, 1151, 701, 550. *E*-**4bn**: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39–7.00 (m, 14H), 5.78 (s, 1H), 2.60 (dd, J=8.8, 5.9 Hz, 1H), 2.25 (s, 3H), 2.03 (s, 3H), 1.79 (dd, J=5.9, 5.9 Hz, 1H), 1.64 (dd, J=8.8, 5.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.4, 145.9, 145.6, 140.4, 136.5, 131.2, 130.2, 128.9, 128.8, 128.2, 127.9, 127.4, 126.5, 126.0, 117.1, 38.1, 30.8, 21.2, 21.0, 19.9. *Z*-**4bn**: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.35 (s, 1H), 2.87 (dd, J=8.8, 5.9 Hz, 1H), 2.30 (s, 3H), 2.01 (s, 3H). (Other peaks cannot be distinguished from major peaks.) Anal. Calcd for $C_{26}H_{24}O_2$: C, 84.75; H, 6.57. Found: C, 84.55; H, 6.67.

4.3.9. 1-(2,2-Diphenylcyclopropyl)-2-(4-methoxyphenyl)-vinyl acetate (4cn). A white solid (80% yield, *Z*/*E*=89:11). IR (KBr) ν_{max} cm^{-1}: 3064, 1749 (C=O), 1509, 1204, 1154, 1026, 702, 591. *E*-**4cn**: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39–7.37 (m, 2H), 7.25–7.21 (m, 6H), 7.15–7.10 (m, 2H), 7.05–7.03 (m, 2H), 6.74–6.72 (m, 2H), 5.76 (s, 1H), 3.87 (s, 3H), 2.61 (dd, J=8.0, 5.6 Hz, 1H), 2.03 (s, 3H), 1.78 (dd, J=5.6, 5.6 Hz, 1H), 1.63 (dd, J=8.0, 5.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.4, 158.2, 145.6, 145.1, 140.4, 130.2, 129.2, 128.2, 127.8, 127.4, 126.7, 126.4, 126.0, 116.8, 113.5, 55.0, 38.1, 30.7, 21.0, 19.8. *Z*-**4cn**: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.33 (s, 1H), 3.70 (s, 1H), 1.98 (s, 3H), 0.88 (dd, J=8.0, 5.6 Hz, 1H). (Other peaks cannot be distinguished from major peaks.) HRMS (FAB) *m*/*z*: Calcd for $C_{26}H_{24}O_3$ (M^+) 384.1725. Found: 384.1720.

4.3.10. 1-(2,2-Diphenylcyclopropyl)-2-(4-chlorophenyl)-vinyl acetate (4dn). A white solid (75% yield, *Z*/*E*=90:10). IR (KBr) ν_{max} cm^{-1}: 3030, 1755 (C=O), 1492, 1198, 1013, 876, 748, 703, 551. *E*-**4dn**: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38–7.36 (m, 2H), 7.29–7.14 (m, 10H), 7.01–6.99 (m, 2H), 5.74 (s, 1H), 2.59 (dd, *J*=8.9, 5.9 Hz, 1H), 2.03 (s, 3H), 1.80 (dd, *J*=5.9, 5.9 Hz, 1H), 1.66 (dd, *J*=8.9, 5.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.2, 147.2, 145.4, 140.2, 132.6, 132.4, 130.2, 129.2, 128.3, 128.3, 127.9, 127.4, 126.6, 126.1, 116.1, 38.5, 30.6, 21.0, 19.9. *Z*-**4dn**: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.34 (s, 1H), 2.79 (dd, *J*=8.9, 5.9 Hz, 1H). (Other peaks cannot be distinguished from major peaks.) Anal. Calcd for $C_{25}H_{21}ClO_2$: C, 77.21; H, 5.44. Found: C, 77.07; H, 5.57.

4.3.11. 1-(2,2-Diphenylcyclopropyl)-2-(4-bromophenyl)-vinyl acetate (4en). A white solid, (65% yield, *Z*/*E*=92:8). IR (KBr) ν_{max} cm^{-1}: 3026, 1750 (C=O), 1487, 1200, 1151, 1011, 853, 705, 547. *E*-**4en**: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38–7.36 (m, 2H), 7.31–7.21 (m, 8H), 7.18–7.13 (m, 2H), 6.94–6.92 (m, 2H), 5.71 (s, 1H), 2.59 (dd, *J*=9.0, 5.8 Hz, 1H), 2.02 (s, 3H), 1.80 (dd, *J*=5.8, 5.8 Hz, 1H), 1.65 (dd, *J*=9.0, 5.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.1, 147.3, 145.3, 140.2, 133.0, 131.2, 130.2, 129.5, 128.4, 127.9, 127.4, 126.6, 126.1, 120.5, 116.1, 38.5, 30.6, 21.0, 19.9. *Z*-**4en**: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.31 (s, 1H), 2.78 (dd, *J*=9.0, 5.8 Hz, 1H). (Other peaks cannot be distinguished from major peaks.) Anal. Calcd for $C_{25}H_{21}BrO_2$: C, 69.29; H, 4.88. Found: C, 68.99; H, 4.95.

4.3.12. 2-(Benzo[*d*][1,3]dioxol-5-yl)-1-(2,2-diphenylcyclopropyl)vinyl acetate (4jn). A white solid (58% yield, *Z* only), mp 113.2–113.6 °C. IR (KBr) ν_{max} cm^{-1}: 3025, 1749 (C=O), 1490, 1160, 1038, 842, 734, 698. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38–7.36 (m, 2H), 7.28–7.16 (m, 8H), 6.67–6.64 (m, 2H), 6.55 (d, *J*=8.4 Hz, 1H), 5.88 (s, 2H), 5.73 (s, 1H), 2.58 (dd, *J*=8.8, 6.4 Hz, 1H), 2.07 (s, 3H), 1.79 (dd, *J*=6.4, 6.4 Hz, 1H), 1.65 (dd, *J*=8.8, 6.4 Hz, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 168.5, 147.3, 146.3, 145.6, 145.4, 140.4, 130.3, 128.3, 128.2, 128.0, 127.5, 126.5, 126.1, 122.3, 117.0, 108.1, 108.0, 100.8, 38.2, 30.8, 21.2, 19.9. HRMS (FAB) *m*/*z*: Calcd for $C_{18}H_{22}O_4$ (M^+) 398.1518. Found: 398.1518.

4.3.13. 1-(2,2-Diethylcyclopropyl)-2-phenylprop-1-enyl acetate (7am). A colorless oil (40% yield, dr=58:42) (a mixture of *E* and *Z* isomers). IR (neat) ν_{max} cm^{-1}: 2963, 2934, 1755 (C=O), 1223, 1191, 1056, 766, 701. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.32–7.17 (m, 10H), 2.19 (s, 3H), 2.10 (s, 3H), 1.91 (s, 3H), 1.87 (s, 3H), 1.76 (dd, *J*=8.4, 4.6 Hz, 1H), 1.61–1.03 (m, 9H), 0.96 (t, *J*=7.2 Hz, 3H), 0.88 (t, *J*=7.2 Hz, 3H), 0.88 (t, *J*=7.2 Hz, 3H), 0.70 (dd, *J*=8.4, 4.6 Hz, 1H), 0.62 (t, *J*=7.2 Hz, 3H), 0.43 (dd, *J*=4.6, 4.6 Hz, 1H), 0.42 (dd, *J*=8.4, 4.6 Hz, 1H), 0.04 (dd, *J*=4.6, 4.6 Hz, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 169.2, 168.6, 143.8, 142.1, 140.7, 140.6, 128.6, 128.2, 127.9, 127.8, 127.4, 126.6, 126.5, 126.5, 29.5, 29.4, 28.7, 28.5, 25.7, 25.5, 23.9, 23.7, 20.8, 20.6, 19.2, 18.6, 18.5, 17.7, 10.9, 10.7, 10.6, 10.0. Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found: C, 79.27; H, 8.84.

4.3.14. 1-(2,2-Diethylcyclopropyl)-2-(4-methylphenyl)-prop-1-enyl acetate (7bm). A colorless oil (31% yield, dr=52:48) (a mixture of *E* and *Z* isomers). IR (neat) ν_{max} cm^{-1}: 2963, 1753 (C=O), 1513, 1458, 1367, 1223, 1191, 1055, 819. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.25–7.08 (m, 8H), 2.34 (s, 3H), 2.31 (s, 3H), 2.18 (s, 3H), 2.08 (s, 3H), 1.89 (s, 3H), 1.89 (s, 3H), 1.76 (dd, *J*=5.3, 8.8 Hz, 1H), 1.62–1.01 (m, 9H), 0.94 (t, *J*=7.9 Hz, 3H), 0.93 (t, *J*=7.9 Hz, 3H), 0.88 (t, *J*=7.9 Hz, 3H), 0.68 (dd, *J*=5.3, 8.8 Hz, 1H), 0.65 (t, *J*=7.9 Hz, 3H), 0.43 (dd, *J*=5.3, 8.8 Hz, 1H), 0.42 (dd, *J*=5.3, 5.3 Hz, 1H), 0.04 (dd, *J*=5.3, 5.3 Hz, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 169.4, 168.7, 143.7, 141.9, 137.8, 137.6, 136.2, 136.1, 128.6, 128.5, 128.5, 127.4, 126.4, 125.9, 29.4, 29.3, 28.6, 28.4, 25.7, 25.5, 23.8, 23.6, 21.1, 21.1, 20.8, 20.6, 19.1, 18.6, 18.4, 17.6, 10.8, 10.6, 10.5, 10.0. Anal. Calcd for $C_{19}H_{26}O_2$: C, 79.68; H, 9.15. Found: C, 79.67; H, 9.11.

4.3.15. 1-(2,2-Diethylcyclopropyl)-2-(4-methoxyphenyl)-prop-1-enyl acetate (7cm). A colorless oil (25% yield, dr=57:43) (a mixture of *E* and *Z* isomers). IR (neat) ν_{max} cm^{-1}: 2962, 1752 (C=O), 1609, 1511, 1246, 1193, 1036, 833, 556. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.25 (d, *J*=8.8 Hz, 2H), 7.13 (d, *J*=8.8 Hz, 2H), 6.85 (d, *J*=8.8 Hz, 2H), 6.82 (d, *J*=8.8 Hz, 2H), 3.81 (s, 3H), 3.79 (s, 3H), 2.18 (s, 3H), 2.08 (s, 3H), 1.90 (s, 3H), 1.89 (s, 3H), 1.75 (dd, *J*=8.7, 5.4 Hz, 1H), 1.60–1.00 (m, 9H), 0.96 (t, *J*=7.5 Hz, 3H), 0.94 (t, *J*=7.5 Hz, 3H), 0.88 (t, *J*=7.5 Hz, 3H), 0.69 (dd, *J*=8.7, 5.4 Hz, 1H), 0.67 (t, *J*=7.5 Hz, 3H), 0.43 (dd, *J*=8.7, 5.4 Hz, 1H), 0.42 (dd, *J*=5.4, 5.4 Hz, 1H), 0.04 (dd, *J*=5.4, 5.4 Hz, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 169.3, 168.8, 158.3, 158.2, 143.6, 141.8, 133.1, 132.9, 129.7, 128.7, 126.0, 125.6, 113.3, 113.3, 55.2, 55.2, 29.5, 29.3, 28.6, 28.4, 25.7, 25.5, 23.8, 23.7, 20.8, 20.6, 19.2, 18.6, 18.4, 17.7, 10.8, 10.6, 10.5, 10.0. Anal. Calcd for $C_{19}H_{26}O_3$: C, 75.46; H, 8.67. Found: C, 75.42; H, 8.67.

4.3.16. 1-(2,2-Diethylcyclopropyl)-2-(4-chlorophenyl)-prop-1-enyl acetate (7dm). A colorless oil (68% yield, dr=58:42) (a mixture of *E* and *Z* mixture). IR (neat) ν_{max} cm^{-1}: 2963, 2934, 1756 (C=O), 1490, 1368, 1222, 1192, 832, 597. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.30–7.23 (m, 6H), 7.14–7.11 (m, 2H), 2.19 (s, 3H), 2.07 (s, 3H), 2.07 (s, 3H), 1.89 (s, 3H), 1.74 (dd, *J*=8.7, 5.4 Hz, 1H), 1.60–1.01 (m, 9H), 0.96 (t, *J*=7.5 Hz, 3H), 0.95 (t, *J*=7.5 Hz, 3H), 0.85 (t, *J*=7.5 Hz, 3H), 0.70 (dd, *J*=8.7, 5.4 Hz, 1H), 0.66 (t, *J*=7.5 Hz, 3H), 0.45 (dd, *J*=8.7, 5.4 Hz, 1H), 0.43 (dd, *J*=5.4, 5.4 Hz, 1H), 0.03 (dd, *J*=5.4, 5.4 Hz, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 169.1, 168.6, 144.5, 142.8, 139.2, 139.0, 132.5, 132.3, 130.0, 129.0, 128.1, 128.1, 125.5, 125.0, 29.7, 29.5, 28.6, 28.4, 25.6, 25.4, 23.8, 23.7, 20.7, 20.5, 19.0, 18.8, 18.2, 17.7, 10.8, 10.6, 10.4, 10.0. Anal. Calcd for $C_{18}H_{23}ClO_2$: C, 70.46; H, 7.56. Found: C, 70.27; H, 7.57.

4.3.17. 1-(2,2-Diethylcyclopropyl)-2-(4-bromophenyl)-prop-1-enyl acetate (7em). A colorless oil (65% yield, dr=55:45) (a mixture of *E* and *Z* isomers). IR (neat) ν_{max} cm^{-1}: 2963, 1754 (C=O), 1668, 1487, 1368, 1220, 1192, 1071, 827, 597. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.44 (d, *J*=8.0 Hz, 2H), 7.40 (d, *J*=8.0 Hz, 2H), 7.19 (d, *J*=8.0 Hz, 2H), 7.06 (d, *J*=8.0 Hz, 2H), 2.18 (s, 3H), 2.07 (s, 3H), 1.89 (s, 3H), 1.88 (s, 3H), 1.73 (dd, *J*=7.4, 5.2 Hz, 1H), 1.59–1.02 (m, 9H), 0.95 (t, *J*=7.0 Hz, 3H), 0.93 (t, *J*=7.0 Hz, 3H), 0.87 (t, *J*=7.0 Hz, 3H), 0.70 (dd, *J*=7.4,

5.2 Hz, 1H), 0.66 (t, *J*=7.0 Hz, 3H), 0.45 (dd, *J*=7.4, 5.2 Hz, 1H), 0.44 (dd, *J*=5.2, 5.2 Hz, 1H), 0.03 (dd, *J*=5.2, 5.2 Hz, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 168.9, 168.3, 144.4, 142.6, 139.6, 139.4, 131.0, 130.9, 130.3, 129.2, 125.4, 124.9, 120.5, 120.3, 29.7, 29.5, 28.6, 28.4, 25.6, 25.5, 23.9, 23.7, 20.7, 20.6, 18.9, 18.9, 18.2, 17.7, 10.8, 10.6, 10.5, 10.1. Anal. Calcd for $C_{18}H_{23}BrO_2$: C, 61.54; H, 6.60. Found: C, 61.30; H, 6.55.

4.3.18. 1-(2,2-Diphenylcyclopropyl)-2-phenylprop-1-enyl acetate (7an). A colorless oil (53% yield, dr=55:45) (a mixture of *E* and *Z* isomers). IR (neat) ν_{max} cm^{-1}: 3057, 3024, 1753 (C=O), 1495, 1195, 1067, 766, 701, 550. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34–7.07 (m, 26H), 6.96–6.91 (m, 4H), 2.86 (dd, *J*=9.2, 5.6 Hz, 1H), 2.63 (dd, *J*=9.2, 5.6 Hz, 1H), 2.16 (s, 3H), 1.90 (s, 3H), 1.78 (s, 3H), 1.71 (dd, *J*=5.6, 5.6 Hz, 1H), 1.65 (s, 3H), 1.57 (dd, *J*=9.2, 5.6 Hz, 1H), 1.47 (dd, *J*=5.6, 5.6 Hz, 1H), 1.32 (dd, *J*=9.2, 5.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.0, 168.1, 145.6, 145.5, 141.4, 141.2, 140.7, 140.6, 140.3, 140.0, 129.5, 129.4, 128.6, 128.4, 128.2, 128.1, 127.9, 127.8, 127.8, 127.6, 127.4, 127.1, 126.9, 126.5, 126.4, 126.1, 125.9, 37.2, 37.1, 28.2, 28.2, 20.4, 20.3, 20.1, 20.0, 19.5, 18.9. (Three peaks (Ar or vinyl) are included in others.) Anal. Calcd for $C_{26}H_{24}O_2$: C, 84.75; H, 6.57. Found: C, 84.84; H, 6.50.

4.3.19. 1-(2,2-Diphenylcyclopropyl)-2-(4-methylphenyl)-prop-1-enyl acetate (7bn). A colorless oil (43% yield, dr=55:45) (a mixture of *E* and *Z* isomers). IR (neat) ν_{max} cm^{-1}: 3024, 2919, 1754 (C=O), 1663, 1195, 1061, 701, 548. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.29–7.08 (m, 22H), 7.02–7.00 (m, 2H), 6.95–6.93 (m, 2H), 6.87–6.84 (m, 2H), 2.86 (dd, *J*=9.3, 6.3 Hz, 1H), 2.64 (dd, *J*=9.3, 6.3 Hz, 1H), 2.36 (s, 3H), 2.27 (s, 3H), 2.15 (s, 3H), 1.89 (s, 3H), 1.77 (s, 3H), 1.71 (dd, *J*=6.3, 6.3 Hz, 1H), 1.68 (s, 3H), 1.56 (dd, *J*=9.3, 6.3 Hz, 1H), 1.47 (dd, *J*=6.3, 6.3 Hz, 1H), 1.33 (dd, *J*=9.3, 6.3 Hz, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 169.1, 168.3, 145.7, 145.6, 141.4, 141.2, 140.9, 139.8, 137.7, 137.4, 136.6, 136.2, 129.6, 129.5, 128.9, 128.6, 128.5, 128.5, 128.4, 128.1, 128.0, 128.0, 127.9, 127.8, 127.7, 127.3, 126.7, 126.4, 126.1, 125.9, 37.1, 37.0, 28.3, 28.2, 21.1, 21.1, 20.3, 20.3, 20.1, 20.0, 19.4, 18.8. Anal. Calcd for $C_{27}H_{26}O_2$: C, 84.78; H, 6.85. Found: C, 85.04; H, 6.98.

4.3.20. 1-(2,2-Diphenylcyclopropyl)-2-(4-methoxyphenyl)prop-1-enyl acetate (7cn). A colorless oil (38% yield, dr=53:47) (a mixture of *E* and *Z* isomers). IR (neat) ν_{max} cm^{-1}: 3025, 1752 (C=O), 1510, 1245, 1032, 910, 833, 701, 587. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.29–7.09 (m, 20H), 6.97–6.86 (m, 6H), 6.76–6.73 (m, 2H), 3.82 (s, 3H), 3.75 (s, 3H), 2.85 (dd, *J*=9.0, 6.3 Hz, 1H), 2.65 (dd, *J*=9.0, 6.3 Hz, 1H), 2.15 (s, 3H), 1.90 (s, 3H), 1.76 (s, 3H), 1.71 (dd, *J*=6.3, 6.3 Hz, 1H), 1.69 (s, 3H), 1.56 (dd, *J*=9.0, 6.3 Hz, 1H), 1.47 (dd, *J*=6.3, 6.3 Hz, 1H), 1.34 (dd, *J*=9.0, 6.3 Hz, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 169.1, 168.4, 158.6, 158.1, 145.7, 145.7, 141.3, 141.2, 140.9, 139.8, 132.9, 132.7, 129.8, 129.6, 129.5, 128.6, 128.4, 128.2, 127.9, 127.9, 127.9, 127.7, 127.3, 126.6, 126.4, 126.2, 126.1, 125.9, 113.6, 113.3, 55.3, 55.1, 37.1, 37.0, 28.4, 28.2, 20.4, 20.3, 20.2, 20.0, 19.4, 18.8. HRMS (FAB) *m/z*: Calcd for $C_{27}H_{26}O_3$ (M^+) 398.1882. Found: 398.1873.

4.3.21. 1-(2,2-Diphenylcyclopropyl)-2-(4-chlorophenyl)-prop-1-enyl acetate (7dn). A colorless oil (74% yield, dr=58:42) (a mixture of *E* and *Z* isomers). IR (neat) ν_{max} cm^{-1}: 2963, 2934, 1756 (C=O), 1490, 1368, 1222, 1192, 832, 597. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.32–7.07 (m, 24H), 6.94–6.84 (m, 4H), 2.84 (dd, *J*=8.7, 6.3 Hz, 1H), 2.59 (dd, *J*=8.7, 6.3 Hz, 1H), 2.14 (s, 3H), 1.90 (s, 3H), 1.75 (s, 3H), 1.72 (dd, *J*=6.3, 6.3 Hz, 1H), 1.67 (s, 3H), 1.56 (dd, *J*=8.7, 6.3 Hz, 1H), 1.47 (dd, *J*=6.3, 6.3 Hz, 1H), 1.35 (dd, *J*=8.7, 6.3 Hz, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 168.8, 168.2, 145.4, 145.4, 142.0, 141.1, 140.7, 140.7, 139.1, 138.7, 132.8, 132.3, 130.0, 129.5, 129.4, 128.8, 128.4, 128.4, 128.2, 128.0, 127.9, 127.9, 127.8, 127.6, 126.7, 126.5, 126.2, 126.2, 126.0, 126.0, 37.2, 37.2, 28.4, 28.0, 20.3, 20.2, 20.2, 20.0, 19.2, 18.6. Anal. Calcd for $C_{26}H_{23}ClO_2$: C, 77.51; H, 5.75. Found: C, 77.47; H, 5.75.

4.3.22. 1-(2,2-Diphenylcyclopropyl)-2-(4-bromophenyl)-prop-1-enyl acetate (7en). A colorless oil (75% yield, dr=52:48) (a mixture of *E* and *Z* isomers). IR (neat) ν_{max} cm^{-1}: 3025, 1748 (C=O), 1488, 1368, 1224, 1071, 828, 698, 548. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.46–7.42 (m, 2H), 7.33–7.06 (m, 22H), 6.93–6.90 (m, 2H), 6.83–6.78 (m, 2H), 2.84 (dd, *J*=9.3, 6.3 Hz, 1H), 2.58 (dd, *J*=9.3, 6.3 Hz, 1H), 2.13 (s, 3H), 1.89 (s, 3H), 1.75 (s, 3H), 1.72 (dd, *J*=6.3, 6.3 Hz, 1H), 1.66 (s, 3H), 1.56 (dd, *J*=9.3, 6.3 Hz, 1H), 1.47 (dd, *J*=6.3, 6.3 Hz, 1H), 1.35 (dd, *J*=9.3, 6.3 Hz, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 168.7, 168.1, 145.3, 145.3, 141.9, 141.0, 140.6, 140.6, 139.5, 139.2, 131.3, 131.0, 130.3, 129.5, 129.3, 129.2, 128.4, 128.2, 127.9, 127.8, 127.8, 127.6, 126.7, 126.4, 126.2, 126.2, 126.0, 126.0, 120.9, 120.4, 37.2, 27.2, 28.3, 28.0, 20.3, 20.2, 20.1, 19.9, 19.1, 18.5. Anal. Calcd for $C_{26}H_{23}BrO_2$: C, 69.80; H, 5.18. Found: C, 69.59; H, 5.27.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.09.064.

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7. Starting material **1a** was fully consumed, however only indene **2a** could be determined.
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9. When the platinum-catalyzed reaction of **1a** with **3n** was carried out at 70 °C for 14 h, **4an** was obtained in 70% yield (*Z*/*E*=91:9), with a trace amount of **2a**. Since no significant difference in selectivity of products and an isomeric ratio of cyclopropanes was observed, we employed the milder reaction conditions.
10. *E* and *Z* structures of vinylcyclopropanes **4** and **7** were determined by NOE studies (see Supplementary data).
11. Comparing these results with Sarpong's shown in Scheme 4,[5] the terminal substituents might play one of the most important roles affecting the olefin regioselectivity in platinum catalysis. However, the difference in selectivity of indenes resulting from terminal alkynes is not clear at present.
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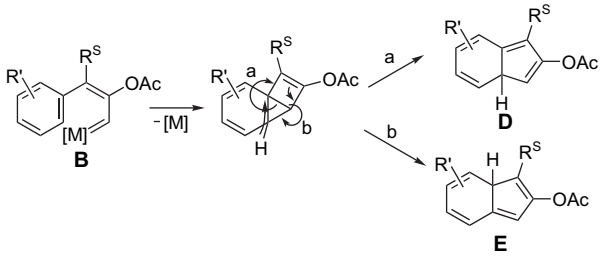

Alternative reaction pathway via Buchner mechanism.

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