

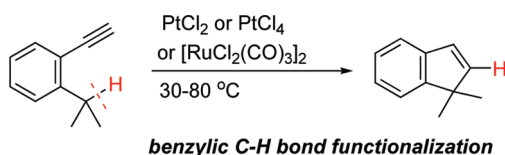
Platinum and Ruthenium Chloride-Catalyzed Cycloisomerization of 1-Alkyl-2-ethynylbenzenes: Interception of π -Activated Alkynes with a Benzylic C–H Bond

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Received May 24, 2009



Air-stable and commercially available alkynophilic metal salts, such as PtCl₂, PtCl₄, and [RuCl₂(CO)₃]₂, catalyze the cycloisomerization of 1-alkyl-2-ethynylbenzenes to produce substituted indenenes even at an ambient temperature. Electrophilically activated alkynes can be intercepted by simple benzylic C–H bonds at primary, secondary, and tertiary carbon centers. Mechanistic studies, such as labeling studies and kinetic isotope and substituent effects, indicate that the cycloisomerization proceeds through the formation of a vinylidene intermediate and turnover-limiting 1,5-shift of benzylic hydrogen.

Introduction

The development of new catalytic reactions triggered by π -activation of alkynes using electrophilic metal salts,

especially gold and platinum, is a rapidly evolving area of research.¹ To date, this alkyne activation strategy has been applied to a diverse range of transformations, the mechanism of which can be well-rationalized, in most cases, on the basis of two limited resonance structures resulting from π -alkyne complex **I** (Scheme 1). One form is a vinyl cation species **II**, which is susceptible to nucleophilic attack by lone-pair electrons of heteroatoms and π -electrons of arenes.^{1,2} The other form is a carbene–carbenoid species **III**, which can be intercepted by unsaturated bonds via cyclopropanation.^{1,3} Apart from these typical reaction modes via **II** and **III**, involvement of a vinylidene intermediate **IV** has also been suggested in several Pt- and Au-catalyzed reactions,⁴ as is frequently proposed for other metals.⁵ Regardless of the intermediate involved, the electrophilically activated alkyne moiety is trapped, in most cases, by electron-rich functionalities, including heteroatoms, stabilized carbanions, and unsaturated bonds. A few notable exceptions exist, however,

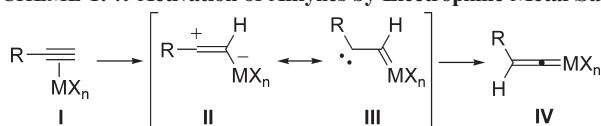
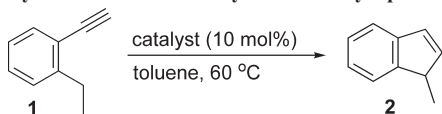
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SCHEME 1. π -Activation of Alkynes by Electrophilic Metal SaltsTABLE 1. Cycloisomerization of **1** by Various Alkynophilic Metals^a

entry	catalyst	time (h) ^b	GC yield (%)
1	PtCl ₂	22	> 99
2	PtCl ₄	1	87
3 ^c	PtCl ₄	12	51
4	PtBr ₂	15	72
5	AuCl ₃	5	0 ^d
6 ^e	AuCl[P(4-CF ₃ C ₆ H ₄) ₃]/AgSbF ₆	22	0 ^d
7	[RuCl ₂ (CO) ₃] ₂	24	86
8	[IrCl(CO) ₃] _n	29	44
9	Rh ₂ (O ₂ CCF ₃) ₄	22	0 ^d

^a Reaction conditions: **1** (0.1 mmol), catalyst (0.01 mmol) in toluene (0.5 mL) at 60 °C. ^b The approximate time required for complete consumption of **1**. ^c Run at 30 °C. ^d Complicated mixture. ^e 1,2-Dichloroethane was used as a solvent.

in which an inert C(sp³)-H bond participates in the reaction involving activated alkynes. Yamamoto reported the Pt-catalyzed cycloisomerization reaction of 1-ethynyl-2-(1-alkoxybut-3-enyl)benzenes through a vinylidene intermediate, as in **IV**.^{4d} In the reaction, a benzylic C-H bond adjacent to both allyl and methoxy groups is added across a terminal alkyne moiety to afford indenenes. However, a benzylic C-H bond of simple alkyl groups is inapplicable, and the reaction requires heating at an elevated temperature (120 °C). Liu reported that a similar transformation can be accomplished with simple allylic^{6a} and benzylic^{6b} C-H bonds by using [TpRu(PPh₃)(CH₃CN)₂]⁺ which is a typical vinylidene generator. However, even with this elaborate catalyst, the benzylic C-H bonds in secondary alkyl groups cannot be functionalized. Quite recently, Urabe reported a rhodium-catalyzed cycloisomerization reaction, in which benzylic C-H bonds of benzyl ethers react with a vinyl cation intermediate, as in **II**, to form dihydropyrans.⁷ However, the substrates require highly electron-deficient sulfonyl alkynes and benzylic C-H bonds adjacent to an oxygen atom. Herein, we report that commonly used alkynophilic metal salts, such as PtCl₂ and [RuCl₂(CO)₃]₂, serve as the general catalyst for the cycloisomerization of 1-alkyl-2-ethynylbenzenes under relatively mild reaction conditions (30–80 °C), leading to benzylic C-H bond functionalization of simple alkyl groups. It is demonstrated, for the first time, that simple tertiary C-H bonds can participate in this type of catalytic cycloisomerization reaction to form all-carbon quaternary centers. The mechanistic aspect of this intriguing cycloisomerization is thoroughly discussed.

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Results and Discussion

We initially examined the cycloisomerization of ethynylbenzene derivative **1**, since prior to this study, no effective catalysts were identified for a cycloisomerization of this type of simple substrate (Table 1).⁸ To our delight, the use of commercially available platinum salts, PtCl₂ and PtCl₄, furnished the desired indene **2** at 60 °C in good yield (entries 1 and 2). Notably, with a PtCl₄ catalyst, the reaction proceeded at ambient temperature, although it was accompanied by an undesired decomposition of **1** (entry 3). Interestingly, PtBr₂, which was reportedly inactive for cycloisomerization in the absence of olefinic moiety,^{4d} worked well under the present conditions (entry 4).⁹ Whereas the use of other alkynophilic metal salts, including gold complexes, led to a complicated mixture (entries 5, 6, and 9), [RuCl₂(CO)₃]₂ exhibited a catalytic activity comparable to that for platinum salts (entry 7).¹⁰ It should be noted that isomerization of the double bond in **2** to a more substituted isomer did not occur under these conditions.

With several effective catalysts in hand, we next examined the scope of this intriguing cycloisomerization reaction (Table 2). The benzylic C-H bond of a methyl group can participate in this reaction to afford indene in modest yield (entry 3). Introduction of sterically demanding polyaromatic groups at the homobenzylic position successfully furnished the corresponding indene derivatives, which are potentially useful for the synthesis of extended indenyl systems (entries 4–9). The cycloisomerization took place smoothly in the presence of relatively acidic protons, such as those in diphenylmethyl (entries 4 and 5) and fluorenyl (entries 6 and 7) groups. Most notably, tertiary C-H bonds could be annulated efficiently with platinum and ruthenium catalysts (entries 10–17, 21–23, and 27–29). Moreover, cycloisomerization proceeded even at 30 °C, when PtCl₄ was used as a catalyst (entries 12, 15, 20, 23, 26, and 29). This tertiary C-H bond functionalization can successfully be applied to the synthesis of spirocyclic indenenes (entries 13–17). These reactions demonstrate the potential power of this π -activation approach, whereby a tertiary C-H bond is directly transformed into an all-carbon quaternary center in a catalytic manner at room temperature. Ethynylbenzenes bearing the benzylic C-H bonds adjacent to heteroatoms, such as oxygen (entries 18–29) and nitrogen (entries 30 and 31), also serve as good substrates, furnishing heteroatom-substituted indenenes. In the case of substrates bearing secondary benzylic C-H bonds, the formation of enol ethers or enamines via double-bond isomerization was not observed.¹¹ In addition, we detected no byproducts formed through carbon-heteroatom bond fission, which has been known to occur in the reactions of alkynophilic metal salts with similar substrates.¹²

To gain insight into the reaction mechanism, we next investigated the reaction of deuterated alkyne **3** in the

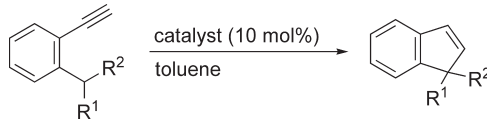
(8) With a similar substrate, 38% yield after 100 h of stirring at 105 °C was obtained with a Ru catalyst. See ref 6b.

(9) The reaction did not proceed under conditions similar to that reported by Yamamoto (10 mol % PtBr₂ in CH₃CN at 60 °C). See ref 4d.

(10) Alkynophilic Lewis acids, such as GaCl₃ and InCl₃, afforded no desired product.

(11) With a TpRu catalyst, isomerization to silyl enol ether occurred predominantly. See ref 6b.

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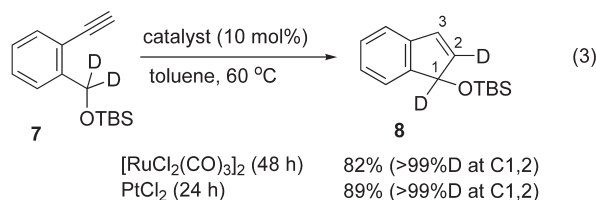
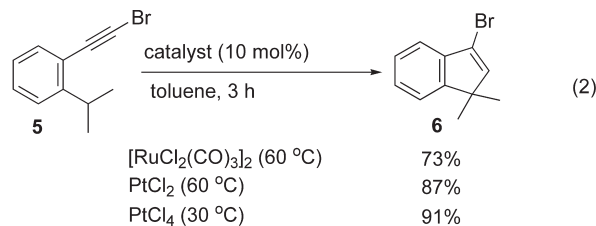
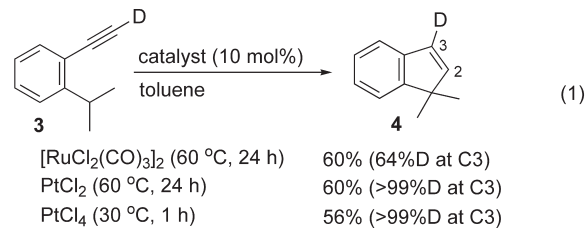
TABLE 2. Catalytic Cycloisomerization of 1-Alkyl-2-ethynylbenzenes^a


entry	R ¹	R ²	cat ^b	T (°C) ^c	time (h)	product	yield (%) ^d
1	Me	H	A	80	24		86 (R = Me) ^e
2	Me	H	B	80	22		>99 (R = Me) ^e
3	H	H	A	80	24		44 (R = H) ^e
4	CHPh ₂	H	A	80	24		80
5	CHPh ₂	H	B	80	18		43
6	9-Flu ^f	H	A	80	24		84 (R = H)
7	9-Flu ^f	H	B	80	16		78 (R = H)
8	9-MeFlu ^g	H	A	80	24		55 (R = Me)
9	9-MeFlu ^g	H	B	80	24		61 (R = Me)
10	Me	Me	A	60	24		72 ^e
11	Me	Me	B	60	2		56 ^e
12	Me	Me	C	30	1		60 ^e
13	-(CH ₂) ₄ -	A	60	24		84	
14	-(CH ₂) ₄ -	B	60	24		88	
15	-(CH ₂) ₄ -	C	30	24		82	
16	-(CH ₂) ₅ -	A	60	24		69	
17	-(CH ₂) ₅ -	B	60	20		78	
18	OC ₈ H ₁₈	H	A	60	18		94
19	OC ₈ H ₁₈	H	B	60	20		83
20	OC ₈ H ₁₈	H	C	30	20		76
21 ^h	OMe	Me	A	60	24		80 ^e
22 ^h	OMe	Me	B	60	20		>99 ^e
23 ^h	OMe	Me	C	30	2		84 ^e
24	OTBS	H	A	60	48		76
25	OTBS	H	B	80	22		93
26	OTBS	H	C	30	6		87
27	OTBS	Me	A	60	24		35
28	OTBS	Me	B	60	8		82
29	OTBS	Me	C	30	24		99
30	9-Carb ⁱ	H	A	80	24		99
31	9-Carb ⁱ	H	B	80	24		91

^a Reaction conditions: substrate (0.5 mmol), catalyst (0.05 mmol) in toluene (2.5 mL). ^b A: [RuCl₂(CO)₃]₂; B: PtCl₂; C: PtCl₄. ^c Oil bath temperature. ^d Isolated yields unless otherwise noted. ^e GC yields. ^f 9-Fluorenyl. ^g 9-Methyl-9-fluorenyl. ^h Run in THF as a solvent. ⁱ 9-Carbazolyl.

presence of ruthenium and platinum salts used in this study (eq 1). As a result, indene **4**, in which a deuterium atom is selectively incorporated at the 3-position, was obtained exclusively with all catalysts, although, in the case of a ruthenium catalyst, the deuterium content was decreased to 64% probably due to a H/D exchange with the residual

water.¹³ Furthermore, the cycloisomerization of bromoalkyne **5** furnished 3-bromoindene **6** as a sole product (eq 2), while other internal alkynes afforded no indenenes under these conditions. These results clearly indicate the intermediacy of a vinylidene complex.⁵ The catalytic cycloisomerization of the substrate labeled at the benzylic position, as in **7**, afforded indene **8**, in which the cleaved deuterium atom was incorporated at the C2 position (eq 3).

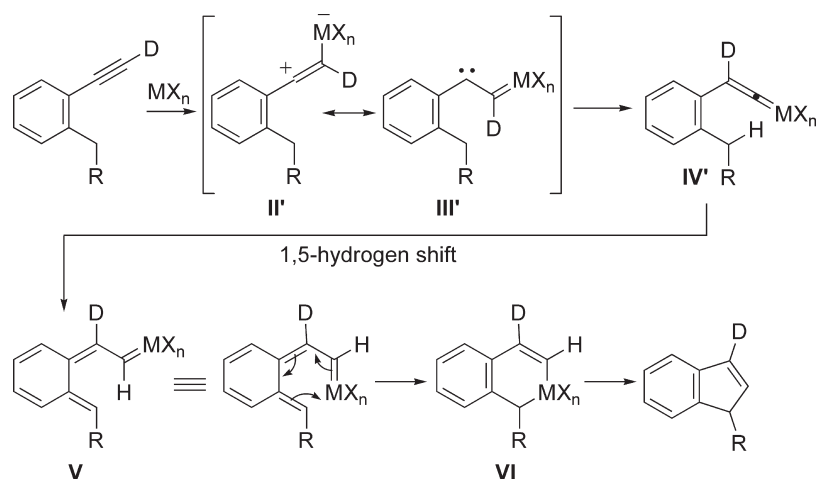


The possible mechanisms that can rationalize both the hydrogen shift events observed above are provided in Scheme 2. The vinylidene complex **IV'** is formed via π -activation of an alkyne moiety under the influence of alkynophilic metal salts. The 1,5-hydrogen shift through a conjugated system in **IV'** then forms metal-carbenoid **V**. The intermediate **V** can be viewed as a metallocyclohexatriene, thus electrocyclicization of **V** would form the metallacycle **VI**. Subsequent reductive elimination of **VI** leads to the final product. As an alternate pathway, the direct insertion of metal vinylidene **IV'** into a benzylic C–H bond nearby would also afford the indene product.^{4d}

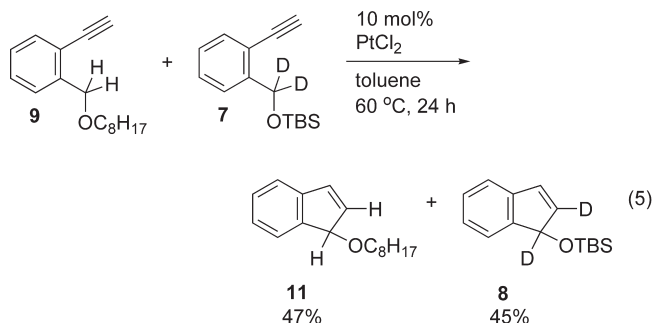
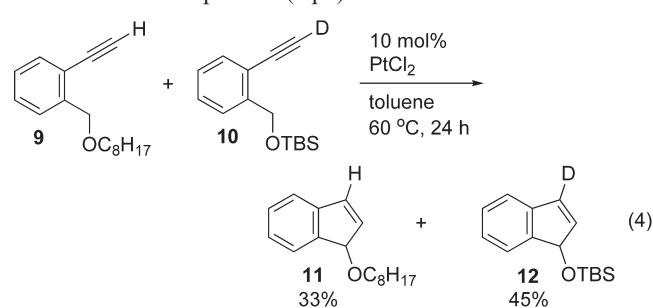
The present catalytic cycloisomerization involved the migration of two hydrogen atoms, one at the alkyne terminus and the other at the benzylic position. To obtain a more detailed description of these hydrogen shifts, additional labeling experiments were conducted. A crossover experiment using a pair of substrates, **9** and **10**, afforded indenenes **11** and **12**, and no exchange of the deuterium label was observed by ¹H NMR analysis, indicating that the 1,2-shift of the alkynyl hydrogen proceeded through an intramolecular pathway (eq 4). Similar crossover experiments using a substrate

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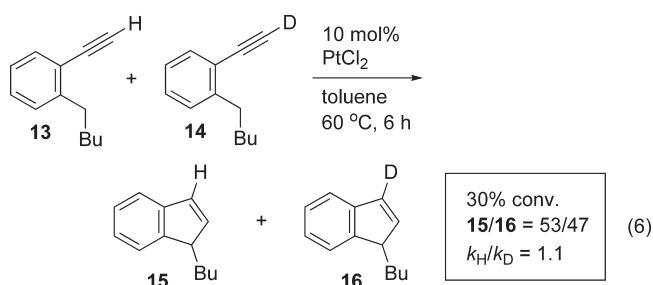
SCHEME 2. Possible Mechanisms



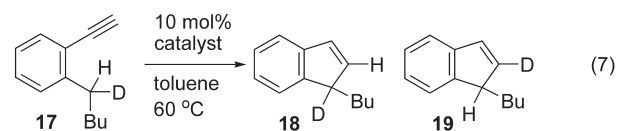
set of **7** and **9** revealed that the benzylic hydrogen shift was also an intramolecular process (eq 5).



The effect of these two hydrogen shifts on the overall reaction rate was next investigated. The intermolecular competition reaction of labeled (**14**) and unlabeled (**13**) alkynes resulted in the formation of indene containing 47% deuterium at low conversion (30%) (eq 6). The kinetic isotope effect of the alkyne hydrogen was estimated to be 1.1, indicating that the 1,2-hydrogen shift was a relatively facile process in this catalysis.



On the other hand, the kinetic isotope effect of the benzylic hydrogen was examined by an intramolecular competition reaction using the monodeuterated substrate **17** (eq 7). As a result, k_H/k_D was determined to be 1.9 based on the ratio of **18/19**, which was estimated by ^1H NMR of the isolated products.



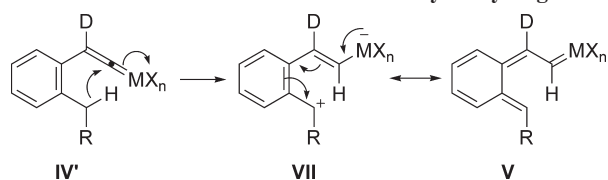
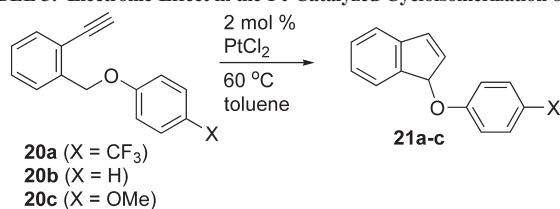
catalyst	time	conv.	18/19	k_H/k_D
$[\text{RuCl}_2(\text{CO})_3]_2$	48 h	>99%	66/34	1.9
PtCl_2	44 h	>99%	65/35	1.9

The electronic effect of the benzylic C–H bond on the reaction rate was also examined using aromatic alkynes bearing electronically different aryloxy groups (Table 3). Although the cycloisomerization of **20a–c** proceeded smoothly under the optimized conditions to furnish 1-aryloxyindenes **21a–c** in good yields, the difference in reactivity between these substrates was clearly observed under conditions where a reduced amount of catalyst (2 mol %) was used. Under these conditions, the substrate bearing an electron-donating group (**20c**) afforded the product at a higher rate than **20b**, whereas introduction of an electron-withdrawing group (**20a**) significantly retarded the cycloisomerization reaction. Based on the kinetic isotope effect experiments (eqs 6 and 7), the observed electronic effect presumably reflected the electronic sensitivity of the benzylic hydrogen shift.

To obtain further insight into the benzylic hydrogen shift, we next examined a cycloisomerization reaction of chiral substrate **22**. Under Pt-catalyzed conditions, a nearly racemic product was obtained (eq 8). If the benzylic hydrogen shift proceeds in a concerted manner, which is expected in a direct vinylidene insertion process, the configuration of the benzylic carbon should be retained on the basis of an analogy to metal–carbenoid insertion reactions into C–H bonds.¹⁴

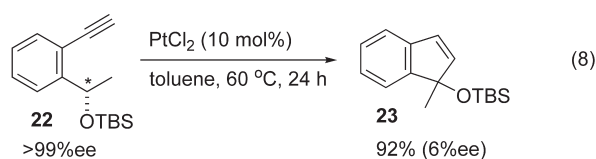
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SCHEME 3. Possible Mechanism for a Benzylic Hydrogen Shift

TABLE 3. Electronic Effect in the Pt-Catalyzed Cycloisomerization of **20**^a

X	isolated yield of 21 (%)		
	2 h	6 h	under optimized conditions
CF ₃	trace	trace	77 (10 mol % of PtCl ₂ , 80 °C, 24 h)
H	7	25	82 (10 mol % of PtCl ₂ , 60 °C, 3.5 h)
OMe	19	44	66 (10 mol % of PtCl ₂ , 60 °C, 2 h)

^a Reaction conditions: substrate **20** (0.5 mmol), catalyst (0.01 mmol) in toluene (2.5 mL) at 60 °C.



The mechanism that can accommodate all the experimental observations is depicted in Scheme 3. The benzylic hydrogen is transferred as a hydride to the most electrophilic vinylidene α -carbon, resulting in the formation of benzyl cation intermediate **VII**. Since the resonance structure of benzyl cation intermediate **VII** is carbene intermediate **V**, which will lead to the indene product as shown in Scheme 2. Although the observed kinetic isotope effect was relatively small (eq 7), all of the experimental data can be rationalized with certainty by assuming a 1,5-hydride shift (**IV'** \rightarrow **VII**) as the turnover-limiting step of this catalytic cycloisomerization. Thus, the introduction of electron-donating groups to stabilize the benzylic cation **VII** should accelerate the overall reaction, which was indeed observed experimentally (Table 3). The lifetime of the benzylic cation **VII** is likely to be long enough to allow the rotation around the C(aryl)–C(benzylic) axis, which leads to complete racemization of the benzylic stereocenter.¹⁵

(15) Chirality transfer is accomplished in some gold-catalyzed cycloisomerizations, in which carbocationic intermediates are involved. Nakamura, I.; Sato, T.; Terada, M.; Yamamoto, Y. *Org. Lett.* **2008**, *10*, 2649. See also ref 12.

Conclusion

In summary, we have identified commonly used alkynophilic metal salts, such as PtCl₂, PtCl₄, and [RuCl₂(CO)₃]₂, as versatile catalysts for the cycloisomerization of 1-alkyl-2-ethynylbenzenes to afford substituted indenenes. The scope of substrates have been significantly expanded compared to related catalytic systems,^{4d,6b,7} especially noteworthy are the applicability of tertiary C–H bonds and the achievement of a room-temperature reaction. This reaction enables a direct functionalization of the benzylic C–H bond in simple alkyl groups with electrophilically activated alkynes.¹⁶ Labeling studies and substituent effect and chirality transfer experiments revealed that the reaction proceeds through the formation of a vinylidene intermediate via a 1,2-hydrogen shift of the alkyne hydrogen and a 1,5-shift of benzylic hydrogen. Studies aimed at expanding the scope of this π -activation-triggered C–H bond functionalization are ongoing in our laboratory.

Experimental Section

PtCl₂-Catalyzed Cycloisomerization of *tert*-Butyl(2-ethynylbenzyloxy)dimethylsilane (Table 2, Entry 25). To a flame-dried, 10-mL, two-necked flask equipped with a reflux condenser were added *tert*-butyl(2-ethynylbenzyloxy)dimethylsilane (123 mg, 0.5 mmol), PtCl₂ (13 mg, 0.05 mmol), and toluene (2.5 mL) under nitrogen atmosphere. After the mixture was stirred at 60 °C for 22 h, it was cooled to room temperature. The volatiles were removed in vacuo, and the residue was purified by column chromatography on silica gel (hexane/EtOAc = 20:1) to give (1*H*-inden-1-yl)oxy(*tert*-butyl)dimethylsilane as a colorless oil (116 mg, 93%); *R*_f 0.20 (hexane/EtOAc = 20/1); ¹H NMR (CDCl₃) δ 0.08 (s, 3H), 0.17 (s, 3H), 0.95 (s, 9H), 5.25 (s, 1H), 6.35 (dd, *J* = 5.7, 1.8 Hz, 1H), 6.71 (d, *J* = 5.7 Hz, 1H), 7.17–7.26 (m, 3H), 7.42 (d, *J* = 6.8 Hz, 1H); ¹³C NMR (CDCl₃) δ -4.2, 18.3, 25.9, 78.0, 121.3, 123.3, 125.8, 128.0, 131.8, 138.1, 142.1, 146.08; IR (neat) 3068 s, 2929 s, 2856 s, 1558 m, 1469 s, 1389 m, 1360 s, 1333 s, 1255 s, 1171 s, 1120 s, 1092 s, 1009 s; MS *m/z* (relative intensity) 246 (M⁺, 5), 190 (19), 189 (40), 116 (12), 115 (100), 75 (21); exact mass calcd for C₁₅H₂₂OSi 246.1440, found 246.1435.

Acknowledgment. This work was carried out, in part, by the Program of Promotion of Environmental Improvement to Enhance Young Researchers' Independence, the Special Coordination Funds for Promoting Science and Technology, Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. We also thank the Instrumental Analysis Center, Faculty of Engineering, Osaka University, for assistance with the MS, HRMS, and elemental analyses.

Supporting Information Available: Detailed experimental procedures and characterization of products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(16) On the submission of this manuscript, a similar transformation using internal alkynes has been reported: Yang, S.; Li, Z.; Jian, X.; He, C. *Angew. Chem., Int. Ed.* **2009**, *48*, 3999.