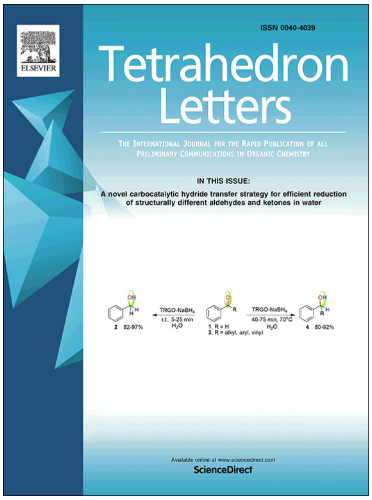

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Cascade reaction including a formal [5+2] cycloaddition by use of alkyne-$Co_2(CO)_6$ complex

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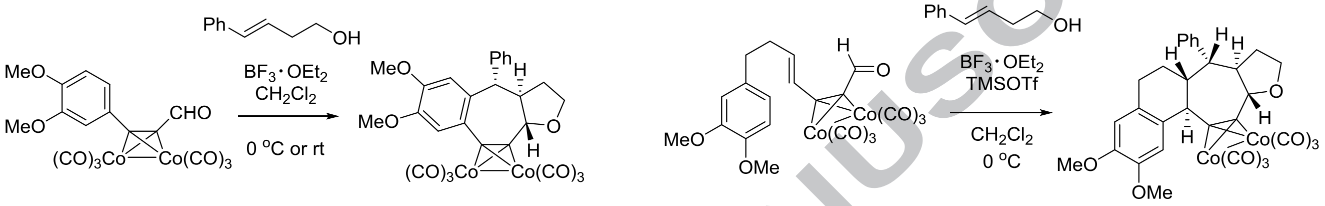
Yuki Sakata[a] , Eiko Yasui[a] , Megumi Mizukami[b] and Shinji Nagumo[a]*



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Cascade reaction including a formal [5+2] cycloaddition by use of alkyne-$Co_2(CO)_6$ complex

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ABSTRACT

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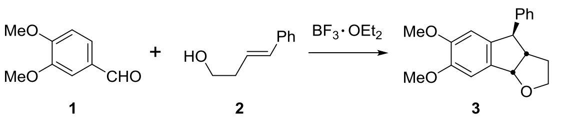
A new cascade reaction including formal [5+2] cycloaddition was developed. Treatment of homocinnamyl alcohol and $Co_2(CO)_6$-complexed arylpropynal with $BF_3 \cdot OEt_2$ resulted in the generation of hydrobenzocycloheptafuran having an alkyne-$Co_2(CO)_6$ complex. The reaction consists of 5-membered ring selective Prins cyclization and subsequent Friedel-Crafts cyclization. The cascade reaction was applied to a further multi-step cascade cyclization, which resulted in the formation of more complex polycyclic hydrofurans.

Since new two bonds are formed in one operation, cycloaddition reactions continue to attract much interest as a method for rapid construction of highly substituted cyclic molecules. Notably, a [5+2] cycloaddition has the potential for synthesis of cycloheptane derivatives found in a number of natural products.[1] This type of cycloaddition necessitates an elaborate design of C_5-component. In pioneer works in this field, pentadienyl cation derived from some kind of quinone (perezone type)[2] and oxidopyrylium ylide[3] were utilized as the coupling partner. The reactions generate bridgehead skeleton involving a seven-membered carbocycle. Thereafter, Wender *et al.* developed a transition-metal catalyzed [5+2] cycloaddition using vinylcyclopropane and π-systems.[4] The cycloaddition proceeds concomitantly with ring cleavage of a cyclopropane to afford a non-bridgehead-type polysubstituted cycloheptane molecules. Tanino *et al.* reported a more straightforward construction of non-bridgehead-type cycloheptanes on the basis of a formal [5+2] cycloaddition utilizing the characteristics of alkyne-$Co_2(CO)_6$ complex.[5] The cobalt complex fits the cyclization of a medium-membered ring due to the large bond angle[6] and stabilizes the neighboring carbocation.[7] We also reported aromatic cyclizations of an iminium ion and a vinylepoxide to generate molecules containing medium rings with the aid of alkyne-$Co_2(CO)_6$ complex.[8,9] Incidentally, we recently reported a novel cascade reaction consisting of a five-membered selective Prins cyclization of benzaldehydes with a homocinnamyl alcohol and subsequent intramolecular Friedel-Crafts reaction (Scheme 1).[10,11] Based on the characteristic feature of two C-C bonds being formed in one operation, this reaction can be categorized as a formal [3+2] cycloaddition. We then expected as an extension of the cascade reaction that arylpropanals might react with homocinnamyl alcohol to afford furans fused with a cycloheptane ring. However, it was thought that the planning would not be so easy because an intramolecular Friedel-Crafts reaction of arylpropanal might occur alone to give indanol. It should be possible to avoid such a five-membered ring formation by using the substrates with alkyne-$Co_2(CO)_6$ complex. We report here a new cascade reaction involving formal [5+2] cycloaddition of $Co_2(CO)_6$-complexed propynals linked to a benzene ring and/or alkene and homocinnamyl alcohol



Scheme 1. Cascade reaction consisting of 5-membered selective Prins cyclization and intramolecular Friedel-Crafts reaction.

Prior to cascade reaction utilizing alkyne-$Co_2(CO)_6$ complex, we investigated the reaction of arylpropanals **4** with **2** (Table 1). Treatment of phenylpropanal **4a** with $BF_3 \cdot OEt_2$ at 0 °C in CH_2Cl_2 resulted in complex mixture. Aldehyde **4b** having 3,5-dimethylbenzene reacted well with **2** to generate *cis*-benzocycloheptafuran **6b** (62%) and its *trans*-isomer **5b** (26%) after separation by column chromatography with silica gel. The cascade reaction of **4c** and **2** proceeded more smoothly to afford a mixture of *cis*-isomer **6c** and its *trans*-isomer **5c** with a ratio of

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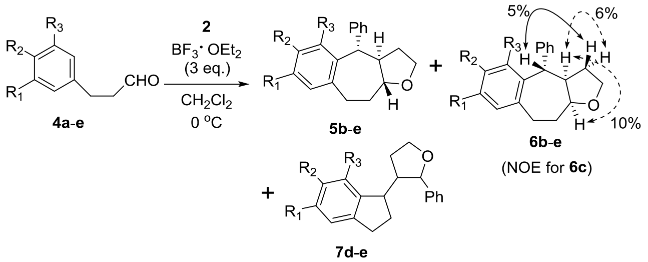
2.3 : 1 in 91% yield after 30 min. The reaction of **4d** having 3,4,5-trimethoxybenzene under the same conditions resulted in the generation of tetrahydrofuranyl indane **7d** (20%) in addition to a mixture of **6d** and **5d** (64%, **6d** : **5d** = 2.6 : 1). Compound **7d** was a mixture of two stereo isomers, but their relative configurations have not been determined yet. In the case of **4e** having 3,5-dimethoxybenzene, the combined yield of **6e** and **5e** was very low and **7e** became the main product. Formation of **7** seems to increase as reactivity of the aromatic ring increases. The stereochemistry of major stereo isomer **6c** was determined by NOE NMR measurement of a mixture with **5c** as shown in Table 1. On the other hand, the stereochemistry of minor isomer **5c** was determined by synthetic transformation from **17c** and the details are to be mentioned later (Scheme 5).

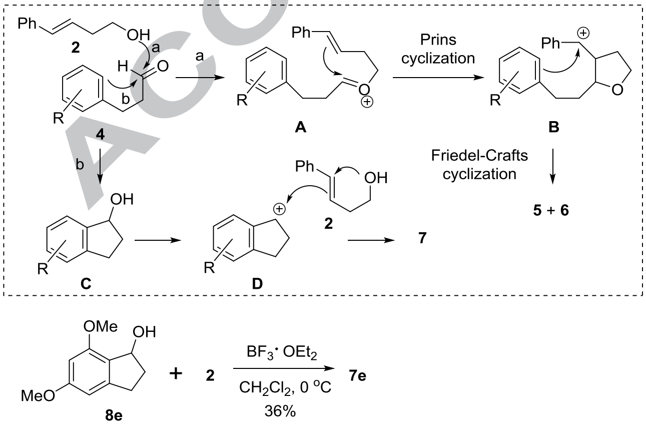
Table 1. Reaction of arylpropanal with homocinnamyl alcohol



Entry	Sub.	Time	Prod. (yield, ratio in mixture)	
1	**4a** (R_1=R_2=R_3=H)		complex mixture	
2	**4b** (R_1=R_3=Me, R_2=H)	1 h	**5b** (26%), **6b** (62%)	
3	**4c** (R_1=R_2=OMe, R_3=H)	30 min	**5c** + **6c** (91%, 1 : 2.3)	
4	**4d** (R_1=R_2=R_3=OMe)	15 min	**5d** + **6d** (64%, 1 : 2.6)	**7d** (20%, 2 : 1)*
5	**4e** (R_1=R_3=OMe, R_2=H)	15 min	**5e** + **6e** (16%, 1 : 3.3)	**7e** (44%, 1 : 1)*

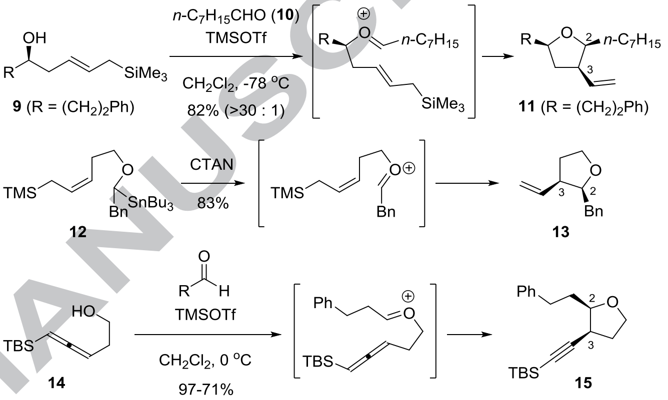
* Ratios in parentheses indicate them of the two stereo isomers.

The formation of **5** and **6** should start with the occurrence of oxonium ion **A** by condensation of **2** and **4** (Scheme 2, route **a**). Subsequently, 5-ring selective Prins cyclization of **A** proceeds to give hydrofuranyl-benzyl cation **B**, which is further converted to two isomeric products **5** and **6**. On the other hand, the formation of **7** should start with intramolecular Friedel-Crafts reaction of **4** as we anticipated in advance (Scheme 2, route **b**). Subsequently, dehydroxylation of the resulting **C** occurs to generate benzylic cation **D**, which is further converted to **7** by alkene attack of **2** concomitant with hydrofuran ring formation. In fact, separately synthesized indanol **8e** was confirmed to react with **2** to give **7e** under the same acidic conditions.



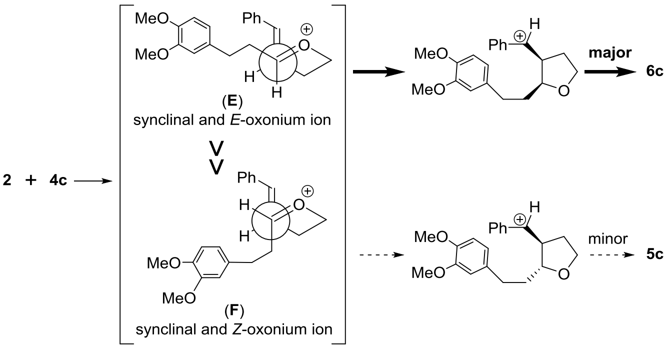
Scheme 2. Tentative mechanism for the formation of **5**-**7**

It should be noted that somewhat preferential formation of *cis*-fused products **6** was observed in all cascade reactions. The stereochemical trend is attributed to the *cis*/*trans* selectivity of Prins cyclization. A general stereochemical trend of 5-membered ring selective Prins cyclization of disubstituted homoallyl alcohol can be ascertained by several silyl-Prins reactions. Silyl-Prins reaction of allylsilane **9** generates tetrahydrofuran **11** with 2,3-*cis*-selectivity (Scheme 3).[12] Also, oxidative silyl-Prins reaction of allylsilane **12** proceeds *cis*-selectively to afford **13**.[13] Incidentally, Sakaguchi and Ohfune *et al.* reported that also silyl-Prins cyclization of allenylsilane **14** with several aldehydes including **4a** proceeded *cis*-selectively in most cases.[14] The stereoselection in the last example was explained by a plausible mechanism through a synclinal transition state model in which an oxonium ion takes a thermodynamically stable *E*-configuration.[15] We adapted their explanation to the stereochemical trend observed in the cascade reaction of **4** and **2** including 5-membered selective Prins cyclization as shown in Scheme 4. Thus, cyclization of an oxonium ion formed by condensation of **4** and **2** favors a transition state (**E**) with an *E*-form oxonium ion over another one (**F**).



R = PhCH$_2$CH$_2$, (CH$_3$)$_2$CH, 3-MeOPh (*cis* : *trans* = >20 : 1)
R = 3,4-(MeO)$_2$Ph (*cis* : *trans* = 2 : 1)

Scheme 3. Several silyl Prins cyclizations generating hydrofuran

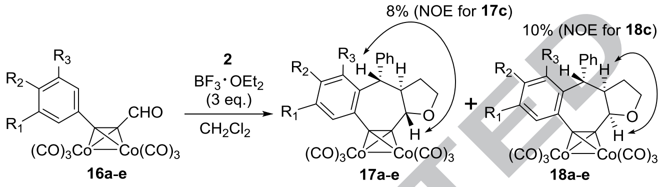


Scheme 4. Stereochemical consideration for reaction of **2** and **4c**

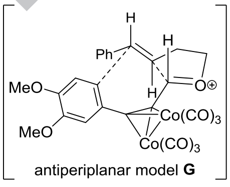
The side reaction triggered by intramolecular Friedel-Crafts reaction of arylpropanals **4d** and **4e** was a serious problem of the cascade reaction. We thus tried the cascade reaction using cobalt-complexed arylpropynals **16** because alkyne-Co$_2$(CO)$_6$ complex was known to resist a five-membered ring formation due to its wide bond angle of ca. 140° (Table 2).[16] Treatment of **16a** and **2** with BF$_3$·OEt$_2$ at 0 °C resulted in the formation of a complex mixture (Entry 1). However, the cascade reaction of **16b** and **2** proceeded gradually under the same conditions to give a mixture of **17b** and **18b** in 39% yield with a ratio of 30 : 1 after 3 h (Entry 2). Furthermore, when the reaction was performed at room temperature, the mixture was obtained in 62% yield with a ratio of 7 : 1 (Entry 3). Aldehyde **16c** reacted smoothly with **2** under the same conditions to give *trans*-Co$_2$(CO)$_6$-complexed cycloheptafuran **17c** and *cis*-one **18c** in 92% as a mixture with a ratio of 3 : 1 (at 0 °C, 1.5 h) or 4 : 1 (at rt, 0.5 h) (Entry 4 and 5). These stereo isomers were separated by careful column chromatography, and their relative configurations were determined by NOE correlations as shown in Table 2.

Interestingly, the formation of **17c** seemed to be more selective at the early stage according to careful TLC monitoring of the reaction mixture. We thus quenched the reaction mixture of **16c** and **2** after being stirred in the presence of $BF_3 \cdot OEt_2$ at 0 ^oC for 3 min, at which time much aldehyde and homocinnamyl alcohol remained. The ratio of **17c** and **18c** at that time was 5 : 1. This finding indicated that the Prins cyclization at the first step kinetically favored *trans*-formation over *cis*-one with a ratio of >5 : 1 and then *trans*-product **17c** was gradually isomerized to *cis*-one **18c** *via* a $Co_2(CO)_6$-complexed propargyl cation formed by C-O bond cleavage of the hydrofuran ring.[17] In order to confirm such an isomerization, isolated **17c** was treated with $BF_3 \cdot OEt_2$ in CH_2Cl_2 at room temperature for 3 h. As a result, **17c** and **18c** were obtained as a mixture with a ratio of ca. 2.5 : 1. On the other hand, isomerization of **18c** proceeded gradually to afford a mixture of **17c** and **18c** with the same ratio after 12 h. The cascade reaction of **16d** and **16e** having more reactive benzene rings proceeded smoothly at 0 ^oC to generate mixtures of **17d-e** and **18d-e** with ratios of 7 : 1 and 4 :1 (Entry 6 and 7). It should be noted that the cascade reaction of **16** shows the opposite stereochemical preference from that of **4**. Sakaguchi and Ohfune *et al.* mentioned their silyl-Prins reaction would take also antiperiplanar transition state to give a mixture of the *cis*- and *trans*-isomers in the case of using 3,4-dimethoxybenzaldehyde which has an electron donating group (Scheme 3).[14] In the cascade cyclization of **16**, alkyne-$Co_2(CO)_6$ complex would guide antiperiplanar transition state (**G**) shown in right side of Table 2 to afford *trans*-isomer **17**. Two C-C bond formations might occur almost simultaneously since the hydrogen at the benzyl position and the neighboring hydrogen remained *trans* configuration.

Table 2. Reaction of **16** with homocinnamyl alcohol **2**



Entry	Substrate	Temp.	Time	**17** + **18** (%)	**17** : **18**
1	**16a** (R_1=R_2=R_3=H)	0 ^oC		complex mixture	
2	**16b** (R_1=R_3=Me, R_2=H)	0 ^oC	3 h	39*	30 : 1
3	**16b** (R_1=R_3=Me, R_2=H)	rt	3 h	62**	7 : 1
4	**16c** (R_1=R_2=OMe, R_3=H)	0 ^oC	1.5 h	92	3 : 1
5	**16c** (R_1=R_2=OMe, R_3=H)	rt	0.5 h	92	4 : 1
6	**16d** (R_1=R_2=R_3=OMe)	0 ^oC	1 h	97	7 : 1
7	**16e** (R_1=R_3=OMe, R_2=H)	0 ^oC	0.5 h	97	4 : 1

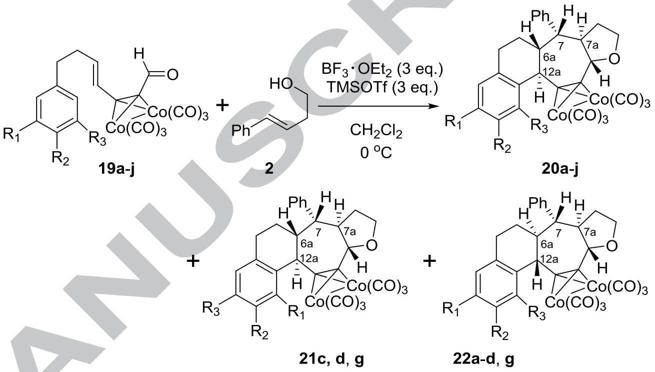


antiperiplanar model **G**

* Substrate was recovered in 30% yield.
** Substrate was recovered in 10% yield.

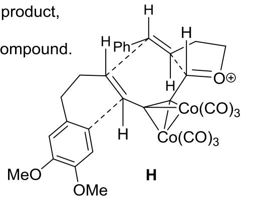
It is well known that the cobalt complex activates neighboring alkenes.[18] With the expectation of establishing a new method for construction of a polycyclic framework by a single operation, we tried a more multi-step cascade cyclization of aldehydes **19** having an internal alkene linked to alkyne-$Co_2(CO)_6$ complex and a terminal benzene ring. A survey of optimized conditions was first carried out using **19h**. Treatment of **19h** with $BF_3 \cdot OEt_2$ (3 eq. or 6 eq.) in CH_2Cl_2 at 0 ^oC afforded **20h** in 37% or 36% yield with recovery of starting materials after 3 hours. Meanwhile, the reaction with TMSOTf (3 eq. or 6 eq.) proceeded more rapidly to give **20h** in 51% or 49% yield after 20 min. Interestingly, maximum yield was obtained by using TMSOTf (3 eq.) and $BF_3 \cdot OEt_2$ (3 eq.) (Table 3, entry 8).[19] With the best conditions in hand, the scope of the cacade reactions was examined using various aldehydes (Table 3). The reaction of **19a** with **2** afforded polycyclic furan **20a** (41%) and **22a** (8%). It was confirmed from observation of NOE correlations that major product **20a** has *trans-cis-trans* configurations for hydrogens at the sequential 12a-6a-7-7a bonds, whereas **22a** has *trans-trans-trans* configurations. These results indicate that both double bonds in **19a** and **2** connect with other parts in an anti-parallel fashion in the formation of both **20a** and **22a**. Also aldehydes **19b-j** having various substituted benzene rings reacted with **2** to generate trans-cis-trans products **20b-j** in 40-70% yields. The reactions of **19c**, **19d** and **19g** afforded slight amounts of regional isomers **21c**, **21d** and **21g**. The preferential formation of **20** might be explained by a nearly concerted mechanism through a transition state **H** involving antiperiplanar coformation between an oxonium ion and a styrene double bond.

Table 3. Further multi-step cascade reaction of **19**

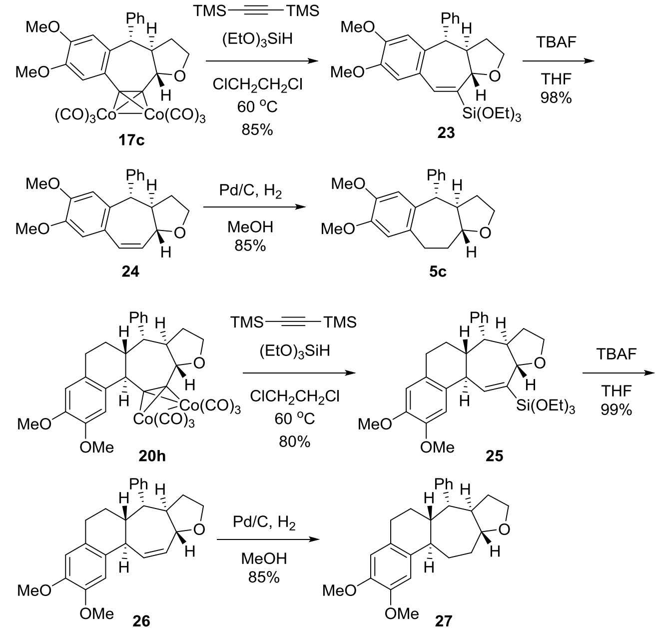


Entry	Substrate	R_1	R_2	R_3	Products (Yield, Ratio in mixture)		
1	**19a**	H	H	H	**20a** (41%)		**22a** (8%)
2	**19b**	H	Me	H	**20b** (57%)		**22b** (9%)
3	**19c**	Me	H	H	**20c** + **21c** (61%, 5 : 1)		**22c** (12%)*
4	**19d**	Me	Me	H	**20d** + **21d** (51%, 7 : 1)		**22d** (8%)
5	**19e**	Me	H	Me	**20e** (56%)**		
6	**19f**	H	OMe	H	**20f** (67%)		
7	**19g**	OMe	H	H	**20g** (47%)	**21g** (6%)	**22g** (6%)
8	**19h**	OMe	OMe	H	**20h** (70%)		
9	**19i**	OMe	OMe	OMe	**20i** (46%)		
10	**19j**	OMe	H	OMe	**20j** (40%)		

* The product includes a structurally unidentified minor product, which is probably stereoisomer. The ratio is ca. 2 : 1.
** The product includes a trace amount of unidentified compound.



Finally, we transformed $Co_2(CO)_6$-complexed polycyclic hydrofuran **17c** to the saturated cycloheptafuran **5c** in order to confirm the relative configuration of **5c** that had not been detected by NOE correlation (Table 1). Treatment of **17c** with $(EtO)_3SiH$ in the presence of bis(trimethylsilyl)acetylene at 60 ^oC resulted in decomplexation of $Co_2(CO)_6$-complex concomitant with regioselective hydrosilylation to give vinylsilane **23** in 85% yield.[20] Desilylation of **23** with TBAF proceeded smoothly to afford **24** in 98% yield. Catalytic hydrogenation of **24** with Pd/C in MeOH afforded **5c** in 85% yield, of which ^1H and ^{13}C NMR spectroscopic data accorded with those of minor product obtained in the cascade reaction of **4c** and **2**. Also decomplexation of 20h concomitant with hydrosilylation gave vinylsilane **25** in 80% yield upon treatment with $(EtO)_3SiH$ and bis(trimethylsilyl)acetylene at 60 ^oC. Compound **25** was efficiently transformed to **27** through a removal of silyl group and the subsequent catalytic hydrogenation.



Scheme 5. Synthetic transformation of Alkyne-$Co_2(CO)_6$ Complex

In conclusion, we developed several cascade reactions including formal [5+2] cycloaddition. These reactions consist of 5-membered ring selective Prins cyclization and subsequent seven-membered ring formation by nucleophilic attack of benzene rings or alkene. In the case of using arylpropanal, whether the reaction goes well or not was found to depend on the reactivity of the benzene ring. 3,5-Dimethoxyphenylpropanal **4e** mainly underwent intramolecular Friedel-Crafts reaction prior to attack by homocinnamyl alcohol **2**. The resulting intermediate **8e** immediately reacted with **2** to give an unexpected product **7e**. Alkyne-$Co_2(CO)_6$ complex was useful for solving the serious problem. The cascade reaction of **16e** resulted in the generation of benzocycloheptafuran **17e** and **18e** in an excellent combined yield. The reaction of **16** selectively formed *trans*-fused isomers **17** unlike the cycloheptafuran formation of **4** that proceeded *cis*-selectively. A more multi-step cascade cyclization of **19** expectedly proceeded to afford polycyclic furans **20** as major products in moderate to good yields in total. These new cascade cyclizations including formal [5+2] cycloaddition would be applicable to target-oriented synthesis.

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Supplementary Material

Supplementary data to this article can be found online at

Highlights

・Cascade cyclization of $Co_2(CO)_6$-complexed arylpropynal gave benzocycloheptafuran.

・It consists of 5-menbered ring selective Prins and Friedel-Crafts cyclizations.

・The $Co_2(CO)_6$-complex suppresses a ring formation of aldehyde itself.

・Polycyclic furans are obtained by using Cobalt-complexed alkynal linked to alkene.