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Rh(I)-catalyzed allenic Pauson–Khand reaction: first construction of the bicyclo[6.3.0]undecadienone ring system

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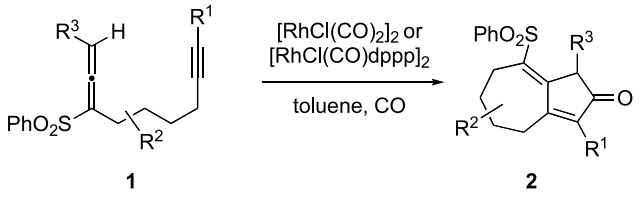
Abstract—The Rh(I)-catalyzed Pauson–Khand reaction of allenynes afforded the bicyclo[6.3.0]undecadienones as well as their benzo and furo derivatives. In addition, a novel $[RhCl(CO)_2]_2$-catalyzed [2,3]-sigmatropic rearrangement of the sulfinic ester species of propargyl alcohols was developed.

1. Introduction

The $Co_2(CO)_6$-mediated Pauson–Khand reaction (PKR)[1] of enynes is well recognized as one of the most convenient and straightforward methods for the construction of the bicyclo[3.3.0]octenone as well as bicyclo[4.3.0]nonenone ring systems. However, this attractive ring-closing reaction could not be generally used for the preparation of the C_1-carbon homologated bicyclic framework, namely a bicyclo[5.3.0]decenone skeleton.[2,3] Recent efforts from this laboratory[4] have led to the development of an effective method for the construction of bicyclo[5.3.0] ring system based on the Rh(I)-catalyzed PKR of allenynes.[5] Thus, a solution of 3-(phenylsulfonyl)octa-1,2-dien-7-yne derivatives **1** was heated in the presence of a catalytic amount of $[RhCl(CO)_2]_2$ or $Rh[Cl(CO)dppp]_2$ in toluene under CO pressure to produce the corresponding 2-phenylsulfonylbicyclo[5.3.0]deca-1,7-dien-9-ones **2** in high to reasonable yields (Scheme 1).[6] Our endeavors were then directed towards confirming the limitations of this newly developed Rh(I)-catalyzed ring-closing reactions. In particular, we were interested in the preparation of the bicyclo[6.3.0]-undecadienone skeleton,[7] because to our best knowledge no reports on the synthesis of the bicyclo[6.3.0] ring system by PKR is so far available. We now describe the first example of PKR for the preparation of bicyclo[6.3.0]undeca-1,8-dien-10-ones, and their benzo and furo congeners.



1 2

Scheme 1.

2. Results and discussion

The simple linear allenyne **7** was chosen as a first starting material for Rh(I)-catalyzed PKR and prepared as follows (Scheme 2). Treatment of 7-iodo-1-(trimethylsilyl)hept-1-yne (**3**)[8] with the acetylide, derived from 3-(*tert*-butyldiphenylsiloxy)prop-1-yne, afforded the coupled product **4** in 51% yield, the desilylation of which was subsequently carried out by exposure to tetrabutylammonium fluoride (TBAF) to provide the propargyl alcohol derivative **5** in 93% yield. The Sonogashira reaction of **5** with iodobenzene furnished the phenylacetylene derivative **6** in 79% yield, and this compound was transformed into the desired allenyne **7** in a 68% overall yield by successive exposure to benzenesulfenyl chloride (PhSCl) and *m*-chloroperbenzoic acid (*m*CPBA).[4] With the required allenyne **7** in hand, this compound was used for the ring-closing reaction in the presence of a catalytic amount (5 mol%) of $[RhCl(CO)dppp]_2$ in refluxing toluene for 7 h under an atmosphere of CO, that had been established for the preparation of bicyclo[4.3.0]nona-1,6-dien-8-ones and bicyclo[5.3.0]deca-1,7-dien-9-ones.[4] However, no eight-membered bicyclic compounds could be detected in the reaction mixture. Changing the catalyst from $[RhCl(CO)dppp]_2$ to $[RhCl(CO)_2]_2$ (5 mol%) in refluxing

Keywords: Pauson–Khand reaction; Allenyne; Bicyclo[6.3.0]undecadienone; [2,3]-Sigmatropic rearrangement; $[RhCl(CO)_2]_2$; $[RhCl(CO)dppp]_2$.
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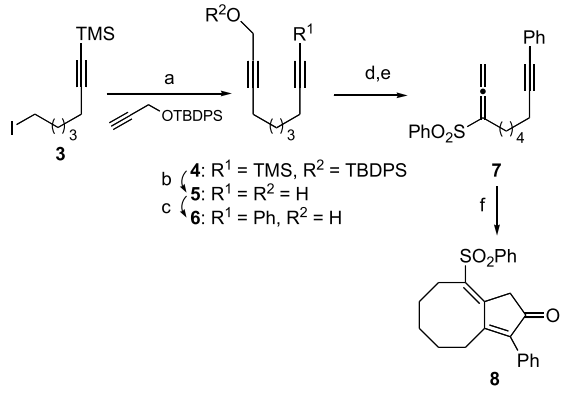
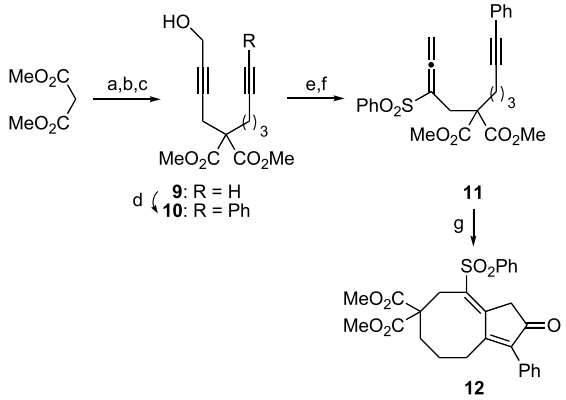


Scheme 2. Reagents and conditions: (a) ^{n}BuLi, THF–DMPU, −78 °C to rt, (51%); (b) TBAF, THF, rt, (93%); (c) PhI, $Pd(PPh_3)_2Cl_2$, CuI, $^{i}Pr_2NH$, THF, rt, (79%); (d) PhSCl, Et_3N, THF, −78 °C; (e) *m*CPBA, CH_2Cl_2, 0 °C, (68%); (f) 20 mol% of $[RhCl(CO)_2]_2$, 1 atm of CO, refluxing xylene, (23%).

toluene for 96 h led to the isolation of the desired bicyclo[6.3.0]undeca-1,8-dien-10-one **8** in a low yield (11%). When the ring-closing reaction was carried out in the presence of 10 mol% of $[RhCl(CO)_2]_2$ in refluxing xylene, compound **8** was obtained in 18% yield. Although the increasing load of the catalyst (20 mol%) with a higher reaction temperature (in refluxing xylene for 0.5 h) brought about further improvement of the chemical yield (23%), a satisfactory chemical yield of **8** has not yet been attained. The other catalysts were examined, but the chemical yields were much less than 23%. For instance, the allenyne **7** was exposed to 10 mol% of $(PPh_3)_3RhCl$ in refluxing xylene to furnish **8** in 14% yield.

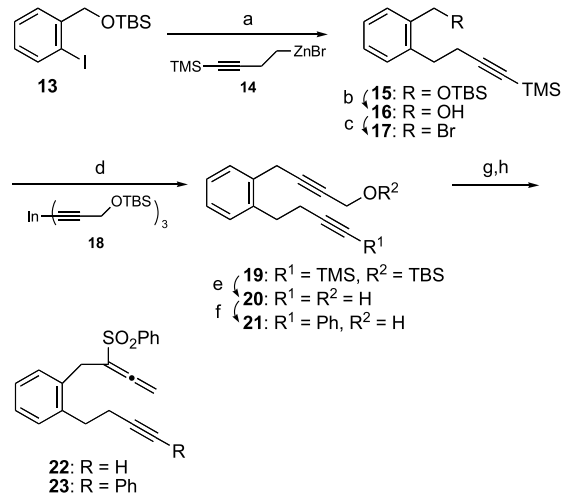
We next investigated the Rh(I)-catalyzed PKR of the allenyne **11** possessing a *gem*-bis(methoxycarbonyl) functionality on the carbon appendage hoping for the Thorpe-Ingold-type effect[9] in the ring-closing step. Thus, the dimethyl malonate was successively alkylated with 5-iodopent-1-yne[10] and 4-iodo-1-(*tert*-butyldiphenylsiloxy)but-2-yne[4b] to afford the dialkylated product, which was subsequently desilylated with TBAF to produce **9** in a 44% overall yield. Conversion of **9** into the allenyne **11** via **10** (71 and 77%, respectively) was realized according to the procedure described for the preparation of **7** from **5**. Upon exposure to 10 mol% of $[RhCl(CO)_2]_2$ in refluxing xylene for 2.5 h, the allenyne **11** underwent the ring-closing reaction to furnish the bicyclo[6.3.0] derivative **12** in 43% yield. When a similar reaction was performed in the presence of $[RhCl(CO)dppp]_2$ instead of $[RhCl(CO)_2]_2$, the desired compound **12** was also obtained, but the yield was much lower (29%) compared to $[RhCl(CO)_2]_2$ (Scheme 3). As a result, the introduction of a *gem*-bis(methoxycarbonyl) group on the carbon appendage of the allenynes made significant improvement in the chemical yield of the cyclized products (23–43%).



Scheme 3. Reagents and conditions: (a) 5-iodopent-1-yne, NaH, THF, 0 °C to rt; (b) 4-iodo-1-(TBDPSO)but-2-yne, NaH, THF, 0 °C to rt; (c) TBAF, THF, rt, (44%); (d) PhI, $Pd(PPh_3)_2Cl_2$, CuI, $^{i}Pr_2NH$, THF, rt, (77%); (e) PhSCl, Et_3N, THF, −78 °C; (f) *m*CPBA, CH_2Cl_2, 0 °C, (71%); (g) 10 mol% of $[RhCl(CO)_2]_2$, 1 atm of CO, refluxing xylene, (43%).

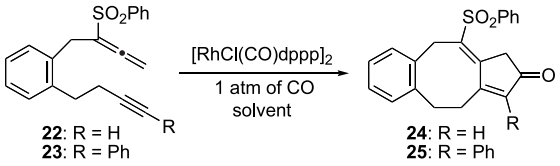
Our endeavors then turned to application of this Rh(I)-catalyzed PKR to the 1,2-disubstituted-aromatic substrates bearing a butyne as well as a buta-1,2-diene residue in which the template effect of the aromatic ring would be expected to facilitate the ring-closing step like the *gem*-bis(methoxycarbonyl) moiety of **11**. According to the literature procedure,[11] 4-bromo-1-(trimethylsilyl)but-1-yne[12] was transformed into the corresponding zinc reagent **14** in situ, which was then coupled with the iodobenzene derivative **13**[13] under the Negishi coupling conditions[14] to provide **15**. A *tert*-butyldimethylsilyl (TBS) group on the primary hydroxyl moiety of **15** was removed by acid treatment to furnish **16** in a 62% overall yield. The second coupling reaction between the benzyl bromide derivative **17**, derived from **16** using a conventional procedure in 99%, and the indium species **18**, prepared in situ from the reaction of 3-(*tert*-butyldimethylsiloxy)prop-1-yne with ^{n}BuLi and $InCl_3$,[15] under the palladium coupling conditions gave **19**, which was subsequently desilylated by TBAF to produce **20** in a 65% overall yield. Compound **20** was converted into the phenylacetylene derivative **21** under the Sonogashira conditions (73%) and two compounds, **20** and **21**, were then transformed into the corresponding allenynes **22** (50%) and **23** (43%) by the standard method (Scheme 4).

A solution of **22** and 10 mol% of $[RhCl(CO)_2]_2$ in xylene was refluxed for 0.5 h (disappearance of the starting material was



Scheme 4. Reagents and conditions: (a) $Pd(PPh_3)_4$, DMA, 80 °C; (b) TsOH, THF, rt, (62%); (c) CBr_4, PPh_3, CH_2Cl_2, 0 °C to rt, (99%); (d) $Pd(dppf)Cl_2$, THF, reflux; (e) TBAF, THF, 0 °C, (65%); (f) PhI, $Pd(PPh_3)_2Cl_2$, CuI, $^{i}Pr_2NH$, THF, rt, (73%); (g) PhSCl, Et_3N, THF, −78 °C; (h) *m*CPBA, CH_2Cl_2, 0 °C, **22** (50%), **23** (43%).

Table 1. Rh(I)-catalyzed ring-closing reaction of compounds **22** and **23**



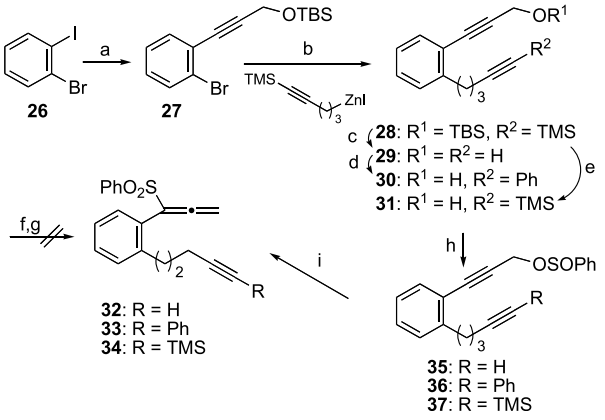
Entry	Substrate	R	Rh (mol%)	Solvent	Temperature	Time (h)	Product	Yield (%)
1	**22**	H	10[a]	Xylene	Reflux	0.5	**24**	63
2	**22**	H	10	Toluene	80 °C	1	**24**	87
3	**22**	H	5[b]	Toluene	80 °C	4	**24**	90
4	**23**	Ph	10[c]	Xylene	Reflux	2	**25**	83
5	**23**	Ph	5	Xylene	Reflux	2	**25**	76

[a] Compound **24** was isolated in 35% yield when $[RhCl(CO)_2]_2$ was used.
[b] When 2.5 mol% of $[RhCl(CO)dppp]_2$ was employed in toluene at 80 °C for 24 h, **24** was obtained in 66% yield along with the recovery of compound **22** in 4% yield.
[c] No reaction took place in toluene at 80 °C for 24 h.

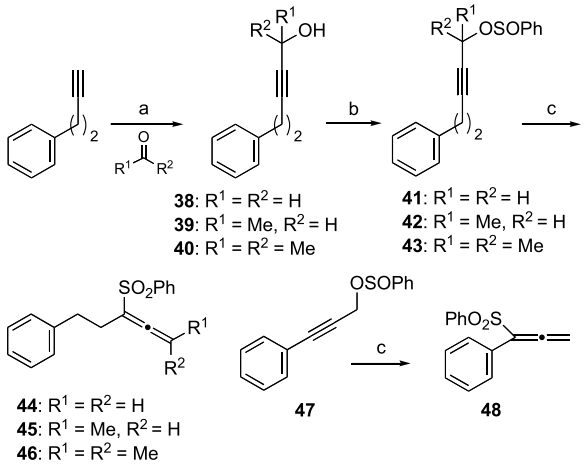
monitored by TLC) to produce the cyclized product **24** in 35% yield. Upon exposure to $[RhCl(CO)dppp]_2$ instead of $[RhCl(CO)_2]_2$ under the same conditions, **22** produced **24** in a significantly improved yield (63%) (Table 1, entry 1). The best result (90%) was obtained when **22** was treated with 5 mol% of $[RhCl(CO)dppp]_2$ in toluene at 80 °C for 4 h (entry 3). A similar result was observed when 10 mol% of $[RhCl(CO)dppp]_2$ was used (entry 2). Interestingly, the optimized conditions for the preparation of **24** (5 or 10 mol% of $[RhCl(CO)dppp]_2$ in toluene at 80 °C) was found to be no longer effective for the phenyl congener **23** resulting in no reaction. The desired phenyl derivative **25** was constructed in 83 and 76% yields when **23** was heated in refluxing xylene (entries 4 and 5). Thus, we have succeeded in the synthesis of the benzene ring-fused bicyclo[6.3.0]undecadienone frameworks in high yields by taking advantage of the template effect of the aromatic ring.

Investigation of the Rh(I)-catalyzed PKR of the regioisomers **32–34** regarding the benzene ring of allenynes **22** and **23** was the next objective of this program. Three propargyl alcohol derivatives **29–31** were prepared by conventional means as depicted in Scheme 5. Unexpectedly, the direct transformation of the propargyl alcohols **29–31** into the allenyl sulfones **32–34** by the standard two-step procedure was troublesome. In fact, compound **29** was successively exposed to PhSCl and *m*CPBA, however, the desired allenyl sulfone **32** could not be isolated in more than trace quantities. Thus, an alternative method for the preparation of the allenyl sulfones **32–34** was necessary. One of the possible solutions for this issue would involve the consecutive formation of benzene sulfinic ester derivatives from the propargyl alcohol derivatives and their thermal [2,3]-sigmatropic rearrangement.[16] Treatment of the propargyl alcohols **29–31** with benenesulfinyl chloride[17] in THF in the presence of $^{i}Pr_2NEt$ at −78 °C provided the corresponding sulfinic ester derivatives **35–37** without any difficulties. The thermal [2,3]-sigmatropic rearrangement of compounds **35** was attempted under several conditions, but the desired **32** was obtained only in trace quantities. The major product isolated from the reaction mixture was the hydrolyzed product **29** (15–33%).

Hiroi and co-workers[18] reported the efficient Pd-catalyzed [2,3]-sigmatropic rearrangement of the sulfinic esters of propargyl alcohols resulting in the formation of the corresponding allenyl sulfones. Thus, we became interested in determining if the Rh(I) catalyst would be able to catalyze the [2,3]-sigmatropic rearrangement of sulfinic esters **35–37**. To this end, the simpler sulfinic ester **41**, derived from the propargyl alcohol **38**, was treated with 5 mol% of $[RhCl(CO)_2]_2$ in toluene at 80 °C for 0.5 h under an atmosphere of N_2 to give the rearranged product **44** in 57% yield (Scheme 6). It should be noted that **44** was obtained in 28% yield when heated at 80 °C in toluene in the absence of $[RhCl(CO)_2]_2$ for 36 h. This result was different from the case of **35**, having a more sterically congested framework (1,2-disubstituted benzene ring), where no rearranged product could be isolated (Scheme 5). $[RhCl(CO)_2]_2$ was found to accelerate the transformation of **41** into **44** more effectively even at room temperature. As a matter of fact, **44** was formed in 82% yield upon exposure of **41** to 5 mol% of $[RhCl(CO)_2]_2$ in toluene at room temperature for 0.5 h. Neither $[RhCl(CO)dppp]_2$ nor $RhCl(PPh_3)_3$ was active for this transformation at room temperature leading to the complete recovery of the starting material. $[RhCl(COD)]_2$ and $[IrCl(COD)]_2$ furnished the desired product **44** at room temperature in the respective



Scheme 5. Reagents and conditions: (a) 3-(*tert*-butyldimethylsiloxy)prop-1-yne, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, THF, rt, (85%); (b) $Pd(PPh_3)_4$, DMA, 80 °C; (c) TBAF, THF, 0 °C, (74%); (d) PhI, $Pd(PPh_3)_2Cl_2$, CuI, $^{i}Pr_2NH$, THF, rt, (73%); (e) 10% aqueous HCl, THF, rt, (78% from **27**); (f) PhSCl, Et_3N, THF, −78 °C; (g) *m*CPBA, CH_2Cl_2, 0 °C; (h) PhSOCl, $^{i}Pr_2NEt$, THF, −78 °C, **35** (94%), **36** (93%), **37** (86%); (i) 5 mol% of $[RhCl(CO_2)]_2$, toluene, rt, **32** (26%), **33** (56%), **34** (75%) and recovery of **37** (16%).

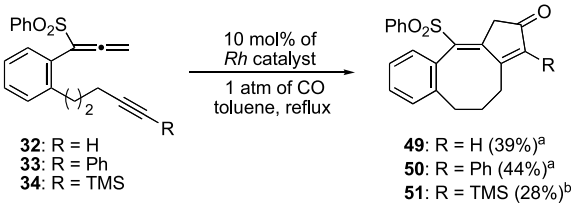


Scheme 6. Reagents and conditions: (a) ^{n}BuLi, THF, −78 °C, **38** (97%), **39** (94%), **40** (79%); (b) PhSOCl, $^{i}Pr_2NEt$, THF, −78 °C, **41** (75%), **42** (90%), **43** (65%); (c) 5 mol% of $[RhCl(CO_2)]_2$, toluene, rt, **44** (82%), **45** (86%), **46** (78%), **48** (63%).

yields of 58 and 74%, although a prolonged reaction time was necessary for complete consumption of the starting material (24 h in both cases). Toluene has so far provided the best result (82%) compared to other solvents like CH_2Cl_2, acetonitrile, DMF, and 1,4-dioxane (11–64%). The secondary and tertiary propargyl alcohols **42** and **43**, derived from the corresponding alcohols **39** and **40**,[19] respectively, were then submitted to the best conditions (5 mol% of $[RhCl(CO)_2]_2$ in toluene at room temperature for 0.25–1 h) to afford the corresponding allenyl sulfones **45** and **46** in the respective yields of 86 and 78%. The phenylacetylene derivative **47**, which was prepared by the reaction of 2-phenylprop-2-yn-1-ol with benzenesulfinyl chloride[17] and has a structure similar to **35**, was chosen as the next substrate. Compound **47** was treated with 5 mol% of $[RhCl(CO)_2]_2$ in toluene at room temperature for 2 h to provide the rearranged product **48** in a slightly lower yield (63%) compared to those of **44**–**46**. Thus, it became evident that $[RhCl(CO)_2]_2$ was effective for our purpose under mild conditions.

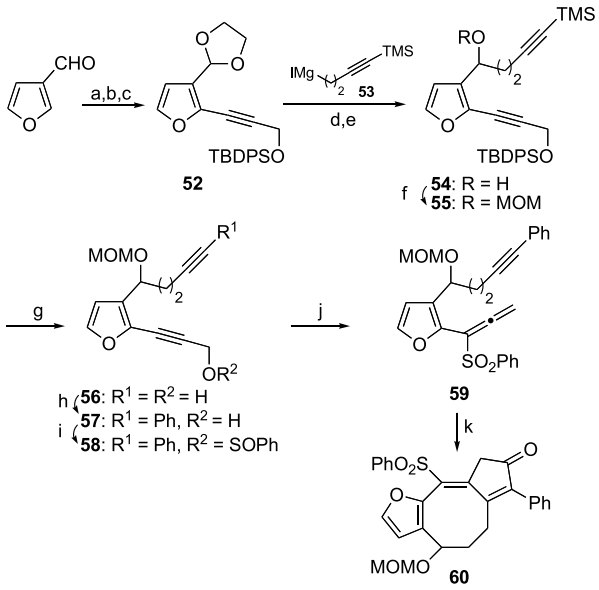
With these results available, we examined the Rh(I)-catalyzed synthesis of the allenyl sulfones **32**–**34** from **35**–**37** (Scheme 5). It took a prolonged reaction time (70 h) for consumption of the starting material, but gave the desired product **32** in 26% yield when the sulfinic ester **35** was exposed to the best conditions (5 mol% of $[RhCl(CO)_2]_2$ in toluene at room temperature). Heating the reaction mixture in toluene at 80 °C did not produce any improvement in the chemical yield (27%). The similar reaction was carried out under an atmosphere CO instead of N_2, hoping for spontaneous PKR, to afford the allenyl sulfone **32** in 30% yield as the sole isolatable product. The bicyclo[6.3.0] derivative (PKR product) could not be observed in the reaction mixture. In contrast to the case of **35** into **32**, the transformation of the TMS and phenyl congeners **36** and **37** into the corresponding allenyl sulones **33** and **34** smoothly proceeded at room temperature in the respective yields of 56 and 75%.

According to the procedure described for the conversion of **22** into **24** (Table 1, entry 3), the prepared allenyl sulfone **32** was exposed to a catalytic amount of $[RhCl(CO)dppp]_2$ in refluxing toluene under an atmosphere of CO to give the ring-closed product **49** in 39% yield. The phenyl congener **33** provided the bicyclo[6.3.0] derivative **50** in a higher yield (44%) under typical ring-closing conditions. For the TMS derivative **34**, $[RhCl(CO)_2]_2$ was found to be superior to $[RhCl(CO)dppp]_2$ furnishing **51** in 28% yield ($[RhCl(CO)dppp]_2$ gave **51** in 5% yield). Although the ring-closed products **49**–**51** could be constructed by the Rh(I)-catalyzed PKR irrespective of the substituent at the triple bond terminus, the yields of which were much less than those of their regioisomers **24** and **25** (see Table 1, Scheme 7).



Scheme 7. Reagents and conditions: (a) $[RhCl(CO)dppp]_2$ was used. (b) $[RhCl(CO_2)]_2$, was used.

By taking application of this method to total synthesis of natural products into account, we next investigated the Rh(I)-catalyzed PKR of the furan derivative **59** as a preliminary examination, because a 1,2-disubstituted furan moiety would not only serve as the template in the ring-closing step, but also provide some opportunities for further chemical elaboration leading to more complex functionalities. Thus, the substrate **59** for the ring-closing reaction was prepared as depicted in Scheme 8.



Scheme 8. Reagents and conditions: (a) LiTMEDA, ^{n}BuLi, then I_2, THF, −78 °C; (b) ethylene glycol, TsOH, benzene, reflux; (c) 3-(*tert*-butyldiphenylsiloxy)prop-1-yne, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, THF, rt, (52%); (d) 10% aqueous HCl, THF, rt; (e) **53**, Et_2O, 0 °C to rt, (85%); (f) MOMCl, $^{i}Pr_2NEt$, CH_2Cl_2, 0 °C to rt, (95%); (g) TBAF, THF, rt, (90%); (h) PhI, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, THF, rt, (91%); (i) PhSOCl, $^{i}Pr_2NEt$, THF, −78 °C, (98%); (j) 5 mol% of $[RhCl(CO_2)]_2$, toluene, rt, (55%); (k) 10 mol% of $[RhCl(CO)dppp]_2$, CO, toluene, reflux, (39%).

3-Furaldehyde was iodinated by the literature procedure[20] to afford 2-iodo-3-furaldehyde, the acetalization of which with ethylene glycol was followed by the Sonogashira coupling reaction with 3-(*tert*-butyldiphenylsiloxy)prop-1-yne providing **52** in a 52% overall yield. The carbon-homologation of **52** was performed by consecutive acid hydrolysis and the Grignard reaction with **53** to produce **54** in 85% yield, and the resulting secondary hydroxyl group of **54** was subsequently protected with a methoxymethyl (MOM) group to furnish **55** in 95% yield. Conversion of **55** into the target molecule **59** (55% from **58**) was easily achieved by the aforementioned procedures via compounds **56** (90%), **57** (91%), and **58** (98%). The Rh(I)-catalyzed PKR of compound **59** carried out in refluxing toluene in the presence of 10 mol% of $[RhCl(CO)dppp]_2$ under an atmosphere of CO for 2 h to furnish the desired bicyclo[6.3.0] skeleton **60** in 39% yield. Several different conditions were examined, but found to be inferior to the above result. It is noteworthy that compound **60** was directly prepared in 16% yield from the sulfinic ester derivative **58** by refluxing in toluene in the presence of 10 mol% of $[RhCl(CO)_2]_2$ under an atmosphere of CO. Compound **60** has a furan ring as well as a protected hydroxyl group, both of which would provide the foothold for further chemical modification of the functionalities.

3. Conclusions

In summary, we have shown that the Rh(I)-catalyzed PKR of allenynes can be applicable for constructing medium-sized bicyclo[6.3.0] frameworks. In fact, the bicylo[6.3.0] undecadienones as well as their benzo and furo derivatives could be formed in reasonable yields. In addition, the $[RhCl(CO)_2]_2$-catalyzed [2,3]-sigmatropic rearrangement of the sulfinic ester species of propargyl alcohols was developed. This procedure proceeds at room temperature to afford the allenyl sulfone derivatives in high yield. Thus, it would become a useful method when the thermal [2,3]-sigmatropic rearrangement of the sulfinic ester species of propargyl alcohols is troublesome.

4. Experimental

Melting points are uncorrected. Infrared spectra were measured in $CHCl_3$. ^1H NMR spectra were taken in chloroform-*d* ($CDCl_3$). $CHCl_3$ (7.26 ppm) for silyl compounds and tetramethylsilane (0.00 ppm) for compounds without a silyl group was used as an internal standard. ^{13}C NMR spectra were recorded in $CDCl_3$ with $CDCl_3$ (77.0 ppm) as an internal standard. All reactions were carried out under N_2 atmosphere unless otherwise stated. Silica gel (Silica gel 60, 40–50 μm) was used for chromatography. Organic extracts were dried over anhydrous Na_2SO_4.

4.1. General procedure for preparation of allenyl sulfones with PhSCl and *m*CPBA

To a solution of propargyl alcohol in THF (0.1 M) were added successively Et_3N (3.0 equiv) and PhSCl (1.5 equiv) at −78 °C. The reaction mixture was stirred until complete disappearance of the starting material monitored by TLC. The reaction mixture was quenched by addition of water and extracted with AcOEt. The extract was washed with water and brine, dried and concentrated to dryness. The residue was passed through a short pad of silica gel with hexane–AcOEt to afford the crude sulfoxide. To a solution of the crude sulfoxide in CH_2Cl_2 (0.1 M) was added a solution of *m*CPBA (1.5 equiv) in CH_2Cl_2 at 0 °C. The reaction mixture was stirred until complete disappearance of the starting material monitored by TLC. The reaction mixture was quenched by addition of saturated aqueous $Na_2S_2O_3$ and saturated aqueous $NaHCO_3$, and extracted with CH_2Cl_2. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was chromatographed with hexane–AcOEt to afford allenyl sulfones. Chemical yields were summarized in Schemes.

4.1.1. 10-Phenyl-3-(phenylsulfonyl)deca-1,2-dien-9-yne (7). A colorless oil: IR 2253, 1971, 1940, 1308, 1150 cm^{-1}; ^1H NMR δ 7.93–7.86 (m, 2H), 7.66–7.47 (m, 3H), 7.40–7.23 (m, 5H), 5.34 (t, 2H, J=3.6 Hz), 2.35 (t, 2H, J=6.6 Hz), 2.31–2.21 (m, 2H), 1.62–1.35 (m, 6H); ^{13}C NMR δ 207.7, 140.1, 133.4, 131.4, 129.0, 128.1, 128.0, 127.5, 123.9, 113.2, 89.9, 84.4, 80.8, 28.2, 27.9, 26.8, 26.5, 19.2; MS *m*/*z* 350 (M^+, 0.5); HRMS calcd for $C_{22}H_{22}O_2S$ 350.1340, found 350.1336.

4.1.2. 5,5-Bis(methoxycarbonyl)-10-phenyl-3-(phenylsulfonyl)deca-1,2-dien-9-yne (11). A colorless oil: IR 1967, 1936, 1732, 1308, 1153 cm^{-1}; ^1H NMR δ 7.93–7.84 (m, 2H), 7.66–7.47 (m, 3H), 7.31–7.23 (m, 5H), 5.32 (t, 2H, J=3.3 Hz), 3.65 (s, 6H), 2.93 (t, 2H, J=3.3 Hz), 2.32 (t, 2H, J=6.9 Hz), 2.12–2.01 (m, 2H), 1.43–1.20 (m, 2H); ^{13}C NMR δ 208.1, 170.4, 139.7, 133.6, 131.5, 129.1, 128.2, 127.6, 123.8, 108.9, 89.1, 85.5, 81.1, 56.6, 52.6, 31.1, 28.5, 23.4, 19.4; MS *m*/*z* 466 (M^+, 1.9); HRMS calcd for $C_{26}H_{26}O_6S$ 466.1450, found 466.1445.

4.1.3. 1-(But-3-ynyl)-2-[2-(phenylsulfonyl)buta-2,3-dienyl]benzene (22). A colorless oil: IR 3308, 2118, 1967, 1935, 1308, 1151 cm^{-1}; ^1H NMR δ 7.92–7.82 (m, 2H), 7.66–7.57 (m, 1H), 7.56–7.47 (m, 2H), 7.19–6.99 (m, 4H), 5.17 (t, 2H, J=3.6 Hz), 3.62 (t, 2H, J=3.6 Hz), 2.62 (t, 2H, J=7.6 Hz), 2.28 (td, 2H, J=7.6, 2.6 Hz), 1.94 (t, 1H, J=2.6 Hz); ^{13}C NMR δ 208.3, 139.9, 138.5, 133.8, 133.5, 130.4, 129.2, 129.0, 127.9, 127.3, 126.5, 113.2, 84.7, 83.3, 69.1, 31.0, 30.8, 19.6; MS *m*/*z* 322 (M^+, 0.5). Anal. Calcd for $C_{20}H_{18}O_2S$: C, 74.50; H, 5.63. Found: C, 74.30; H, 5.65.

4.1.4. 1-(4-Phenylbut-3-ynyl)-2-[2-(phenylsulfonyl)buta-2,3-dienyl]benzene (23). A colorless oil: IR 1967, 1935, 1308, 1151 cm^{-1}; ^1H NMR δ 7.92–7.84 (m, 2H), 7.62–7.44 (m, 3H), 7.38–7.00 (m, 9H), 5.18 (t, 2H, J=4.0 Hz), 3.67 (t, 2H, J=4.0 Hz), 2.69 (t, 2H, J=7.3 Hz), 2.50 (t, 2H, J=7.3 Hz); ^{13}C NMR δ 208.4, 140.1, 138.9, 133.9, 133.5, 131.4, 130.5, 129.6, 129.1, 128.2, 128.1, 127.7, 127.3, 126.6, 123.7, 113.4, 89.1, 84.7, 81.5, 31.4, 30.9, 20.8; MS *m*/*z* 399 (M^+, 0.3). Anal. Calcd for $C_{26}H_{22}O_2S$: C, 78.36; H, 5.56. Found: C, 78.02; H, 5.60.

4.2. General procedure for preparation of propargyl sulphinates

To a solution of propargyl alcohol in THF (0.1 M) were added successively $^{i}Pr_2NEt$ (3.0 equiv) and PhSOCl (1.5 equiv) at −78 °C. After stirring for 1.5 h, the reaction mixture was quenched by addition of water and extracted with AcOEt. The extract was washed with water and brine, dried and concentrated to dryness. The residue was chromatographed with hexane–AcOEt to afford propargyl sulfinate. Chemical yields were summarized in Schemes.

4.2.1. 5-Phenylpent-2-yn-1-yl benzenesulfinate (41). A colorless oil: ^{1}H NMR δ 7.74–7.71 (m, 2H), 7.56–7.53 (m, 3H), 7.31–7.17 (m, 5H), 4.62 (dt, 1H, J=15, 2.2 Hz), 4.33 (dt, 1H, J=15, 2.2 Hz), 2.79 (t, 2H, J=7.6 Hz), 2.48 (tt, 2H, J=7.6, 2.2 Hz); ^{13}C NMR δ 144.4, 140.3, 132.3, 129.0, 128.4, 128.3, 126.3, 125.3, 88.5, 74.6, 52.9, 34.6, 20.9; MS m/z 284 (M^+, 3.6); HRMS calcd for $C_{17}H_{16}O_2S$ 284.0871, found 284.0870.

4.2.2. 6-Phenylhex-3-yn-2-yl benzenesulfinate (42). As a mixture of diastereomers. Compound **42** was a colorless oil: IR 2245 cm^{-1}; ^{1}H NMR for one isomer δ 7.72–7.69 (m, 2H), 7.55–7.49 (m, 3H), 7.32–7.20 (m, 5H), 5.04 (qt, 1H, J=6.6, 2.0 Hz), 2.86 (t, 2H, J=7.6 Hz), 2.56 (td, 2H, J=7.6, 2.0 Hz), 1.49 (d, 3H, J=6.6 Hz); ^{13}C NMR for one isomer δ 145.6, 140.3, 132.1, 128.9, 128.5, 128.4, 126.4, 125.1, 87.5, 79.4, 65.4, 34.7, 23.3, 20.9; ^{1}H NMR data for the other isomer δ 7.74–7.71 (m, 2H), 7.54–7.47 (m, 3H), 7.31–7.15 (m, 5H), 5.00 (qt, 1H, J=6.6, 2.0 Hz), 2.71 (t, 2H, J=7.6 Hz), 2.37 (td, 2H, J=7.6, 2.0 Hz), 1.55 (d, 3H, J=6.6 Hz); ^{13}C NMR data for the other isomer δ 144.8, 140.4, 132.0, 128.8, 128.4, 128.3, 126.3, 125.4, 86.9, 79.2, 63.3, 34.6, 24.1, 20.8; MS m/z 298 (M^+, 2.7); HRMS calcd for $C_{18}H_{18}O_2S$ 298.1027, found 298.1025.

4.2.3. 2-Methyl-6-phenylhex-3-yn-2-yl benzenesulfinate (43). A colorless oil: IR 2241 cm^{-1}; ^{1}H NMR δ 7.70–7.65 (m, 2H), 7.52–7.48 (m, 3H), 7.35–7.17 (m, 5H), 2.88 (t, 2H, J=7.4 Hz), 2.60 (t, 2H, J=7.4 Hz), 1.74 (s, 3H), 1.62 (s, 3H); ^{13}C NMR δ 146.6, 140.3, 131.5, 128.8, 128.5, 128.3, 126.3, 125.0, 88.0, 82.0, 76.4, 34.7, 31.2, 31.0, 20.9; MS m/z 312 (M^+, 11.3); HRMS calcd for $C_{19}H_{20}O_2S$ 312.1184, found 312.1190.

4.2.4. 3-Phenylprop-2-ynyl benzenesulfinate (47). A colorless oil: IR 2228 cm^{-1}; ^{1}H NMR δ 7.83–7.76 (m, 2H), 7.62–7.53 (m, 3H), 7.42–7.26 (m, 5H), 4.84, 4.58 (AB-q, 2H, J=5.6 Hz); ^{13}C NMR δ 144.2, 144.1, 132.4, 131.8, 129.1, 128.8, 128.2, 125.3, 87.9, 82.8, 52.5; MS m/z 256 (M^+, 1.2); HRMS calcd for $C_{15}H_{12}O_2S$ 256.0558, found 256.0565.

4.2.5. 1-(Pent-4-ynyl)-2-[3-(phenylsulfinyloxy)prop-1-ynyl]benzene (35). A pale yellow oil: IR 3308, 2224, 2116 cm^{-1}; ^{1}H NMR δ 7.81–7.77 (m, 2H), 7.59–7.53 (m, 3H), 7.38–7.11 (m, 4H), 4.89, 4.61 (AB-q, 2H, J=16 Hz), 2.85 (t, 2H, J=7.6 Hz), 2.20 (td, 2H, J=6.9, 2.6 Hz), 1.97 (t, 1H, J=2.6 Hz), 1.83 (quin, 2H, J=6.9 Hz); ^{13}C NMR δ 144.0, 132.7, 132.4, 129.1, 129.0, 128.9, 125.9, 125.4, 125.3, 121.4, 86.6, 86.3, 84.2, 68.7, 52.9, 33.3, 29.3, 18.0; MS m/z 322 (M^+, 0.4); HRMS calcd for $C_{20}H_{18}O_2S$ 322.1027, found 322.1023.

4.2.6. 1-(5-Phenylpent-4-ynyl)-2-[3-(phenylsulfinyloxy)prop-1-ynyl]benzene (36). A colorless oil: IR 2224 cm^{-1}; ^{1}H NMR δ 7.78–7.75 (m, 2H), 7.55–7.51 (m, 3H), 7.41–7.36 (m, 3H), 7.31–7.22 (m, 5H), 7.19–7.12 (m, 1H), 4.85, 4.58 (AB-q, 2H, J=16 Hz), 2.90 (t, 2H, J=7.6 Hz), 2.41 (t, 2H, J=7.3 Hz), 1.92 (quin, 2H, J=7.3 Hz); ^{13}C NMR δ 144.3, 144.0, 132.7, 132.4, 131.5, 129.1, 129.0, 128.2, 127.6, 125.9, 125.3, 123.9, 121.4, 89.8, 86.7, 86.3, 81.1, 53.0, 33.5, 29.4, 19.0; FABMS m/z 399 (M^++1, 3.3); FABHRMS calcd for $C_{26}H_{23}O_2S$ 399.1419, found 399.1428.

4.2.7. 1-[3-(Phenylsulfinyloxy)prop-1-ynyl]-2-[5-(trimethylsilyl)pent-4-ynyl]benzene (37). A pale yellow oil: IR 2224, 2172 cm^{-1}; ^{1}H NMR δ 7.81–7.77 (m, 2H), 7.59–7.53 (m, 3H), 7.38–7.35 (m, 1H), 7.29–7.11 (m, 3H), 4.89, 4.62 (AB-q, 2H, J=16 Hz), 2.82 (t, 2H, J=7.3 Hz), 2.23 (t, 2H, J=7.3 Hz), 1.83 (quin, 2H, J=7.3 Hz), 0.15 (s, 9H); ^{13}C NMR δ 144.3, 144.0, 132.7, 132.4, 129.1, 129.0, 125.9, 125.3, 121.3, 107.0, 86.7, 86.3, 84.9, 52.9, 33.4, 29.3, 19.4, 0.1; FABMS m/z 395 (M^++1, 2.2); FABHRMS calcd for $C_{23}H_{27}O_2SiS$ 395.1501, found 395.1509.

4.2.8. 3-[1-(Methoxymethoxy)-5-phenylpent-4-ynyl]-2-[3-(phenylsulfinyloxy)prop-1-ynyl]furan (58). As a mixture of diastereomers. Compound **58** was a colorless oil: IR 2230 cm^{-1}; ^{1}H NMR δ 7.75–7.71 (m, 2H), 7.55–7.49 (m, 3H), 7.41–7.35 (m, 2H), 7.33 (d, 1H, J=2.0 Hz), 7.28–7.23 (m, 3H), 6.42 (d, 1H, J=2.0 Hz), 4.92–4.86 (m, 1H), 4.80–4.74 (m, 1H), 4.59–4.45 (m, 3H), 3.37 (m, 3H), 2.59–2.43 (m, 2H), 2.18–2.09 (m, 1H), 1.96–1.87 (m, 1H); ^{13}C NMR δ 144.3, 144.1, 144.1, 133.8, 133.7, 132.4, 131.7, 131.7, 131.4, 129.0, 128.2, 127.6, 125.3, 125.2, 123.7, 109.7, 94.2, 90.4, 88.9, 88.9, 81.2, 76.7, 68.6, 55.6, 52.3, 52.3, 35.0, 35.0, 15.8, 15.8; FABMS m/z 449 (M^++1, 13.7); FABHRMS calcd for $C_{26}H_{25}O_5S$ 449.1422, found 449.1415.

4.3. General procedure for Rh(I)-catalyzed synthesis of allenyl sulfones from propargyl sulfinates

To a solution of sulfinates (0.1 mmol) in toluene (1 mL) was added 5 mol% of $[RhCl(CO)_2]_2$. Then the reaction mixture was stirred at room temperature for several hours. The solvent was evaporated off, and the residue was chromatographed to afford allenyl sulfones. Chemical yields were summarized in Schemes.

4.3.1. 5-Phenyl-3-(phenylsulfonyl)penta-1,2-diene (44). A colorless oil: IR 1969, 1940, 1317, 1150 cm^{-1}; ^{1}H NMR δ 7.89–7.86 (m, 2H), 7.63–7.50 (m, 3H), 7.26–7.06 (m, 5H), 5.31 (t, 2H, J=3.3 Hz), 2.74 (t, 2H, J=7.2 Hz), 2.58–2.50 (m, 2H); ^{13}C NMR δ 208.0, 140.2, 140.1, 133.4, 129.1, 128.4, 128.3, 128.1, 126.2, 112.4, 84.5, 33.6, 28.4; MS m/z 284 (M^+, 8.3); FABHRMS calcd for $C_{17}H_{17}O_2S$ 285.0949, found 285.0952 (M^++1).

4.3.2. 6-Phenyl-4-(phenylsulfonyl)hexa-2,3-diene (45). A colorless oil: IR 1963, 1315, 1148 cm^{-1}; ^{1}H NMR δ 7.87–7.84 (m, 2H), 7.61–7.51 (m, 3H), 7.26–7.05 (m, 5H), 5.66

(qt, 1H, J=7.4, 2.8 Hz), 2.76–2.71 (m, 2H), 2.58 (qd, 2H, J=8.1, 2.8 Hz), 1.60 (d, 3H, J=7.4 Hz); ^{13}C NMR δ 204.8, 140.3, 140.1, 133.2, 129.0, 128.4, 128.3, 128.0, 126.1, 111.9, 96.4, 33.5, 28.3, 13.2; MS *m/z* 298 (M^+, 5.3); FABHRMS calcd for $C_{18}H_{19}O_2S$ 299.1106, found 299.1104 ($M^+ + 1$).

4.3.3. 2-Methyl-6-phenyl-4-(phenylsulfonyl)hexa-2,3-diene (46). A colorless oil: IR 1963, 1313, 1148 cm^{-1}; ^{1}H NMR δ 7.86–7.82 (m, 2H), 7.62–7.47 (m, 3H), 7.26–7.06 (m, 5H), 2.75 (t, 2H, J=6.9 Hz), 2.61 (t, 2H, J=6.9 Hz), 1.58 (s, 6H); ^{13}C NMR δ 202.2, 140.6, 140.3, 133.0, 128.9, 128.3, 128.2, 127.9, 126.0, 110.2, 107.3, 33.6, 28.1, 19.5; MS *m/z* 312 (M^+, 10.8); FABHRMS calcd for $C_{19}H_{21}O_2S$ 313.1262, found 313.1264 ($M^+ + 1$).

4.3.4. 1-Phenyl-1-(phenylsulfonyl)propa-1,2-diene (48). A colorless oil: IR 1963, 1927, 1321, 1153 cm^{-1}; ^{1}H NMR δ 7.82–7.79 (m, 2H), 7.56–7.26 (m, 8H), 5.55 (s, 2H); ^{13}C NMR δ 209.1, 140.3, 140.2, 133.4, 128.9, 128.8, 128.6, 128.5, 128.2, 115.2, 83.9; MS *m/z* 256 (M^+, 7.2); FABHRMS calcd for $C_{15}H_{13}O_2S$ 257.0637, found 257.0657 ($M^+ + 1$).

4.3.5. 1-(Pent-4-ynyl)-2-[1-(phenylsulfonyl)propa-1,2-dienyl]benzene (32). A pale yellow oil: IR 3308, 1967, 1931, 1321, 1153 cm^{-1}; ^{1}H NMR δ 7.71–7.12 (m, 9H), 5.47 (s, 2H), 2.45 (t, 2H, J=7.9 Hz), 2.10 (td, 2H, J=6.9, 2.6 Hz), 1.98 (t, 1H, J=2.6 Hz), 1.57 (quin, 2H, J=6.9 Hz); ^{13}C NMR δ 208.2, 141.7, 139.6, 133.5, 131.1, 129.6, 129.4, 128.8, 128.7, 127.5, 125.9, 112.5, 84.0, 82.9, 68.8, 31.8, 29.5, 18.3; MS *m/z* 322 (M^+, 0.4); HRMS calcd for $C_{20}H_{18}O_2S$ 322.1028, found 322.1024.

4.3.6. 1-(5-Phenylpent-4-ynyl)-2-[1-(phenylsulfonyl)propa-1,2-dienyl]benzene (33). A colorless oil: IR 2232, 1967, 1931, 1321, 1153 cm^{-1}; ^{1}H NMR δ 7.68–7.66 (m, 2H), 7.58–7.54 (m, 1H), 7.44–7.34 (m, 4H), 7.32–7.28 (m, 4H), 7.26–7.15 (m, 3H), 5.46 (s, 2H), 2.51 (t, 2H, J=7.9 Hz), 2.33 (t, 2H, J=6.9 Hz), 1.64 (quin, 2H, J=6.9 Hz); ^{13}C NMR δ 208.1, 141.9, 139.4, 133.5, 131.5, 131.1, 129.6, 129.4, 128.8, 128.6, 128.3, 127.7, 127.5, 125.9, 123.7, 112.4, 89.6, 82.9, 81.2, 32.0, 29.8, 19.2; MS *m/z* 398 (M^+, 24.9); HRMS calcd for $C_{26}H_{22}O_2S$ 398.1341, found 398.1342.

4.3.7. 1-[1-(Phenylsulfonyl)propa-1,2-dienyl]-2-[5-(trimethylsilyl)pent-4-ynyl]benzene (34). A pale yellow oil: IR 2170, 1967, 1931, 1321, 1153 cm^{-1}; ^{1}H NMR δ 7.70–7.56 (m, 3H), 7.47–7.41 (m, 2H), 7.30–7.14 (m, 4H), 5.50 (s, 2H), 2.44 (t, 2H, J=7.9 Hz), 2.14 (t, 2H, J=6.9 Hz), 1.55 (quin, 2H, J=6.9 Hz), 0.18 (s, 9H); ^{13}C NMR δ 208.2, 141.9, 139.6, 133.5, 131.0, 129.6, 129.4, 128.8, 128.6, 127.5, 125.9, 112.4, 106.9, 85.1, 82.9, 32.0, 29.7, 19.7, 0.2; MS *m/z* 394 (M^+, 1.6). Anal. Calcd for $C_{23}H_{26}OSSi$: C, 70.01; H, 6.64. Found: C, 69.99; H, 6.96.

4.3.8. 3-[1-(Methoxymethoxy)-5-phenylpent-4-ynyl]-2-[1-(phenylsulfonyl)propa-1,2-dienyl]furan (59). A colorless oil: IR 1965, 1917, 1325, 1153 cm^{-1}; ^{1}H NMR δ 7.86 (d, 2H, J=7.3 Hz), 7.58 (t, 1H, J=7.3 Hz), 7.50–7.43 (m, 3H), 7.42–7.38 (m, 2H), 7.34–7.28 (m, 3H), 6.40 (d, 1H, J=1.7 Hz), 5.56 (s, 2H), 4.69 (dd, 1H, J=9.3, 4.4 Hz), 4.34, 4.28 (AB-q, 2H, J=6.9 Hz), 3.33 (s, 3H), 2.54–2.33 (m, 2H), 1.99–1.87 (m, 1H), 1.60–1.50 (m, 1H); ^{13}C NMR δ 209.4, 144.3, 140.2, 138.0, 133.6, 131.4, 128.9, 128.3, 128.2, 127.7, 127.3, 123.7, 109.9, 106.5, 93.6, 89.1, 84.4, 81.2, 67.2, 55.5, 34.9, 15.8; MS *m/z* 448 (M^+, 22.1); FABHRMS calcd for $C_{26}H_{25}O_5S$ 449.1422, found 449.1435 ($M^+ + 1$).

4.4. General procedure for Rh(I)-catalyzed PKR

To a solution of allenylalkyne (0.1 mmol) in solvent (1 mL) was added Rh(I) catalyst (5, 10 or 20 mol%). Then the reaction mixture was warmed to the temperature shown in text under CO atmosphere until complete disappearance of the starting material monitored by TLC. The solvent was evaporated off, and the residue was chromatographed to afford cyclized products. Chemical yields were summarized in Schemes.

4.4.1. 9-Phenyl-2-(phenylsulfonyl)bicyclo[6.3.0]undeca-1,8-dien-10-one (8). Colorless needles: mp 184.5–187 °C ($CHCl_3$–hexane); IR 1707, 1306, 1150 cm^{-1}; ^{1}H NMR δ 7.93–7.89 (m, 2H), 7.64 (t, 1H, J=7.3 Hz), 7.57 (t, 2H, J=7.3 Hz), 7.46–7.35 (m, 3H), 7.25–7.19 (m, 2H), 3.79 (s, 2H), 3.07 (t, 2H, J=6.8 Hz), 2.93 (t, 2H, J=7.1 Hz), 1.78 (quin, 2H, J=7.1 Hz), 1.66–1.49 (m, 4H); ^{13}C NMR δ 201.6, 164.9, 148.6, 147.0, 140.7, 134.7, 133.5, 130.6, 129.3, 129.1, 128.8, 128.4, 127.6, 40.9, 28.3, 27.6, 27.4, 26.1, 21.5; MS *m/z* 378 (M^+, 64.5); HRMS calcd for $C_{23}H_{22}O_3S$ 378.1289, found 378.1288.

4.4.2. 4,4-Bis(methoxycarbonyl)-9-phenyl-2-(phenylsulfonyl)bicyclo[6.3.0]undeca-1,8-dien-10-one (12). Colorless powders: mp 254–256 °C ($CHCl_3$–hexane); IR 1730, 1709, 1308, 1150 cm^{-1}; ^{1}H NMR δ 7.94–7.86 (m, 2H), 7.69–7.52 (m, 3H), 7.46–7.34 (m, 3H), 7.22–7.14 (m, 2H), 3.94–3.71 (m, 8H), 3.61 (d, 1H, J=17 Hz), 3.34 (d, 1H, J=22 Hz), 3.00–2.70 (m, 2H), 2.36–2.12 (m, 2H), 1.85–1.60 (m, 2H); ^{13}C NMR δ 200.6, 171.3, 170.8, 163.2, 149.7, 149.2, 141.1, 133.6, 133.4, 130.2, 129.5, 129.1, 128.5, 127.6, 56.7, 53.1, 40.8, 32.2, 27.5, 26.8, 24.0; MS *m/z* 494 (M^+, 16.3); FABHRMS calcd for $C_{27}H_{27}O_7S$ 495.1477, found 495.1488 ($M^+ + 1$).

4.4.3. 11-(Phenylsulfonyl)-1,4,5,10-tetrahydro-2*H*-benzo[*g*]cyclopentacycloocten-2-one (24). Colorless powders: mp 155–157 °C (hexane–AcOEt); IR 1701, 1308, 1150 cm^{-1}; ^{1}H NMR δ 7.81–7.75 (m, 2H), 7.66–7.57 (m, 1H), 7.55–7.45 (m, 2H), 7.17–6.98 (m, 4H), 6.33 (s, 1H), 4.23 (br s, 2H), 3.45–3.14 (m, 6H); ^{13}C NMR δ 202.2, 171.7, 146.4, 140.6, 138.8, 137.9, 136.2, 135.6, 133.6, 131.5, 131.3, 129.3, 127.7, 127.2, 126.6, 41.9, 34.0, 32.6, 29.7; MS *m/z* 350 (M^+, 43.3); HRMS calcd for $C_{21}H_{18}O_3S$ 350.0977, found 350.0975.

4.4.4. 3-Phenyl-11-(phenylsulfonyl)-1,4,5,10-tetrahydro-2*H*-benzo[*g*]cyclopentacycloocten-2-one (25). Pale yellow powders: mp 227–229 °C ($CHCl_3$–hexane); IR 1709, 1308, 1148 cm^{-1}; ^{1}H NMR δ 7.87–7.79 (m, 2H), 7.67–7.37 (m, 6H), 7.33–7.24 (m, 2H), 7.15–7.01 (m, 3H), 6.96–6.89 (m, 1H), 4.25 (br s, 2H), 3.59 (br s, 2H), 3.24 (s, 4H); ^{13}C NMR δ 200.8, 164.7, 148.8, 146.8, 140.7, 136.9, 136.6, 136.6, 133.5, 130.9, 130.8, 130.3, 129.3, 129.3, 129.2, 128.5,

127.8, 127.3, 127.0, 41.8, 34.8, 33.0, 28.3; MS *m/z* 426 (M^+, 29.6); FABHRMS calcd for $C_{27}H_{23}O_3S$ 427.1368, found 427.1368 ($M^+ + 1$).

4.4.5. 11-(Phenylsulfonyl)-1,4,5,6-tetrahydro-2*H*-benzo[*f*]cyclopentacycloocten-2-one (49). Colorless powders: mp 126–129 °C ($CHCl_3$–hexane); IR 1701, 1321, 1150 cm^{-1}; ^1H NMR δ 7.79–7.72 (m, 1H), 7.48–7.45 (m, 3H), 7.33–7.25 (m, 4H), 6.96–6.95 (m, 1H), 6.27 (s, 1H), 3.85, 3.80 (AB-q, 2H, $J=22$ Hz), 2.46–2.38 (m, 2H), 2.26 (td, 1H, $J=13$, 5.9 Hz), 1.85–1.70 (m, 2H), 1.66–1.57 (m, 1H); ^{13}C NMR δ 202.7, 171.9, 146.3, 139.9, 139.7, 138.2, 138.1, 135.3, 133.2, 131.2, 131.0, 130.3, 128.6, 127.8, 125.9, 41.6, 31.2, 30.2, 27.2; MS *m/z* 350 (M^+, 100); HRMS calcd for $C_{21}H_{18}O_3S$ 350.0977, found 350.0979.

4.4.6. 3-Phenyl-11-(phenylsulfonyl)-1,4,5,6-tetrahydro-2*H*-benzo[*f*]cyclopentacycloocten-2-one (50). Pale yellow plates: mp 219–221.5 °C ($CHCl_3$–hexane); IR 1707, 1321, 1150 cm^{-1}; ^1H NMR δ 7.76–7.74 (m, 1H), 7.52–7.20 (m, 12H), 6.97–6.95 (m, 1H), 4.01, 3.92 (AB-q, 2H, $J=22$ Hz), 2.63–2.58 (m, 1H), 2.49–2.41 (m, 1H), 2.37 (td, 1H, $J=13$, 4.9 Hz), 1.80–1.75 (m, 2H), 1.60–1.56 (m, 1H); ^{13}C NMR δ 201.2, 164.9, 147.7, 146.1, 140.2, 140.0, 135.0, 133.1, 131.4, 131.2, 130.5, 130.3, 129.1, 128.8, 128.6, 128.4, 127.8, 127.6, 125.9, 40.8, 31.3, 30.4, 24.2; MS *m/z* 426 (M^+, 60.1); FABHRMS calcd for $C_{27}H_{23}O_3S$ 427.1368, found 427.1357 ($M^+ + 1$).

4.4.7. 11-(Phenylsulfonyl)-3-(trimethylsilyl)-1,4,5,6-tetrahydro-2*H*-benzo[*f*]cyclopentacycloocten-2-one (51). Pale yellow needles: mp 153.5–156 °C (hexane–THF); IR 1695, 1317, 1148 cm^{-1}; ^1H NMR δ 7.75–7.68 (m, 1H), 7.50–7.42 (m, 3H), 7.35–7.20 (m, 4H), 6.98–6.90 (m, 1H), 3.81, 3.70 (AB-q, 2H, $J=22$ Hz), 2.61 (dt, 1H, $J=13$, 2.8 Hz), 2.45–2.34 (m, 1H), 2.27 (td, 1H, $J=13$, 5.9 Hz), 1.82 (td, 1H, $J=13$, 4.6 Hz), 1.75–1.50 (m, 2H), 0.23 (s, 9H); ^{13}C NMR δ 207.2, 177.4, 150.6, 147.7, 140.2, 140.1, 134.0, 133.5, 131.2, 131.1, 130.2, 128.6, 127.8, 127.6, 125.8, 42.0, 31.6, 30.3, 26.4, −0.3; MS *m/z* 422 (M^+, 1.9). Anal. Calcd for $C_{24}H_{26}O_3SSi$: C, 68.21; H, 6.20. Found: C, 68.25; H, 6.49.

4.4.8. 4-(Methoxymethoxy)-7-phenyl-10-(phenylsulfonyl)-4,5,6,9-tetrahydro-8*H*-cyclopentacycloocta[5,6-*b*]furan-8-one (60). Pale yellow powders: mp 219–221 °C ($CHCl_3$–hexane); IR 1710, 1310, 1151 cm^{-1}; ^1H NMR δ 7.89 (d, 2H, $J=7.6$ Hz), 7.56–7.38 (m, 7H), 7.30–7.20 (m, 2H), 6.39 (d, 1H, $J=1.7$ Hz), 4.59 (dd, 1H, $J=12$, 6.1 Hz), 4.51, 4.39 (AB-q, 2H, $J=6.8$ Hz), 3.97, 3.85 (AB-q, 2H, $J=23$ Hz), 3.33 (s, 3H), 2.76 (d, 1H, $J=13$ Hz), 2.22–2.10 (m, 1H), 1.91 (td, 1H, $J=13$, 5.1 Hz), 1.86–1.76 (m, 1H); ^{13}C NMR δ 200.7, 163.2, 149.6, 141.7, 141.0, 133.4, 130.4, 129.4, 129.1, 129.0, 128.9, 128.6, 127.5, 127.0, 108.6, 94.9, 69.3, 55.8, 40.5, 37.2, 25.0; MS *m/z* 476 (M^+, 37.9); FABHRMS calcd for $C_{27}H_{25}O_6S$ 477.1372, found 477.1371 ($M^+ + 1$).

4.5. Preparation of propargyl alcohol derivatives

4.5.1. 10-(*tert*-Butyldiphenylsiloxy)-1-(trimethylsilyl) deca-1,8-diyne (4). To a solution of 3-(*tert*-butyldiphenylsiloxy)prop-1-yne (2.96 g, 10.0 mmol) in THF–DMPU (5/1, 90 mL) was added ^{n}BuLi (1.38 M in hexane solution, 8.40 mL, 11.6 mmol) at −78 °C. After stirring for 30 min, a solution of **3** (2.28 g, 7.73 mmol) in THF–DMPU (5/1, 10 mL) was gradually added to the reaction mixture, which was stirred at room temperature for 14 h. The reaction mixture was quenched by addition of saturated aqueous NH_4Cl and extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was chromatographed with hexane–AcOEt (10/1) to afford **4** (2.33 g, 51%) as a colorless oil: IR 2170 cm^{-1}; ^1H NMR δ 7.78–7.69 (m, 4H), 7.46–7.34 (m, 6H), 4.32 (t, 2H, $J=2.0$ Hz), 2.27–2.10 (m, 4H), 1.60–1.37 (m, 6H), 1.07 (s, 9H), 0.16 (s, 9H); ^{13}C NMR δ 135.6, 133.4, 129.7, 127.6, 107.4, 85.5, 84.4, 78.6, 53.0, 28.2, 28.0, 27.9, 26.7, 19.8, 19.2, 18.7, 0.2; FABMS *m/z* 461 ($M^+ + 1$, 3.3). Anal. Calcd for $C_{29}H_{40}OSi$: C, 75.59; H, 8.75. Found: C, 75.67; H, 8.75.

4.5.2. Deca-2,9-diyn-1-ol (5). To a solution of **4** (2.33 g, 5.06 mmol) in THF (50 mL) was added TBAF (1.0 M in THF solution, 12 mL, 12 mmol) at room temperature. After stirring for 30 min, THF was evaporated off, and the residue was chromatographed with hexane–AcOEt (5/1) to afford **5** (0.710 g, 93%) as a colorless oil: IR 3609, 3441, 2226 cm^{-1}; ^1H NMR δ 4.23 (t, 2H, $J=2.3$ Hz), 2.28–2.13 (m, 4H), 1.94 (t, 1H, $J=2.6$ Hz), 1.72 (br s, 1H), 1.59–1.42 (m, 6H); ^{13}C NMR δ 86.3, 84.4, 78.5, 68.3, 51.4, 28.0, 27.9, 27.9, 18.6, 18.3; MS *m/z* 150 (M^+, 3.6); HRMS calcd for $C_{10}H_{14}O$ 150.1044, found 150.1053.

4.5.3. 10-Phenyldeca-2,9-diyn-1-ol (6). To a solution of **5** (580 mg, 3.83 mmol) in THF (38 mL) were added $Pd(PPh_3)_2Cl_2$ (26.9 mg, 3.83×10^{-2} mmol) and CuI (14.6 mg, 7.66×10^{-2} mmol) at room temperature. Iodobenzene (0.85 mL, 7.7 mmol) and $^i Pr_2NH$ (5.02 mL, 38.3 mmol) were then added dropwise to the reaction mixture. After being stirred for 24 h, the reaction mixture was filtered by suction. The filtrate was concentrated, and the residue was chromatographed with hexane–AcOEt (5/1) to afford **6** (688 mg, 79%) as a colorless oil: IR 3609, 3445, 2253, 2226 cm^{-1}; ^1H NMR δ 7.42–7.36 (m, 2H), 7.30–7.24 (m, 3H), 4.23 (s, 2H), 2.41 (t, 2H, $J=6.8$ Hz), 2.28–2.20 (m, 2H), 1.70 (br s, 1H), 1.66–1.52 (m, 6H); ^{13}C NMR δ 131.5, 128.1, 127.5, 124.0, 90.0, 86.2, 80.8, 78.5, 51.3, 28.2, 28.1, 28.0, 19.2, 18.6; MS *m/z* 226 (M^+, 4.3); HRMS calcd for $C_{16}H_{18}O$ 226.1358, found 226.1354.

4.5.4. 5,5-Bis(methoxycarbonyl)deca-2,9-diyn-1-ol (9). To a solution of dimethyl malonate (1.14 mL, 10.0 mmol) in THF (70 mL) was added NaH (60% in mineral oil, 520 mg, 13.0 mmol) at 0 °C. After stirring for 30 min, a solution of 5-iodopent-1-yne (3.19 g, 12.0 mmol) in THF (30 mL) was gradually added to the reaction mixture, which was stirred at room temperature for 36 h. The reaction mixture was quenched by addition of saturated aqueous NH_4Cl and extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was passed through a short pad of silica gel with hexane–AcOEt (4/1) to afford the crude alkyne. To a solution of the crude alkyne in THF (70 mL) was added NaH (60% in mineral oil, 416 mg, 10.4 mmol) at 0 °C. After stirring for 10 min, a solution of 4-iodo-1-(*tert*-butyldiphenylsiloxy)but-2-yne (3.16 g, 7.27 mmol) in THF (17 mL) was gradually added to the reaction mixture, which was

stirred at room temperature for 1.5 h. The reaction mixture was quenched by addition of saturated aqueous NH_4Cl and extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was passed through a short pad of silica gel with hexane–AcOEt (6/1) to afford the crude diyne. To a solution of the crude diyne in THF (44 mL) was added TBAF (1.0 M in THF solution, 4.9 mL, 4.9 mmol) at room temperature. After stirring for 1.5 h, THF was evaporated off, and the residue was chromatographed with hexane–AcOEt (3/1) to afford **9** (1.17 g, 44%) as a colorless oil: IR 3607, 3508, 3308, 2118, 1726 cm^{-1}; ^1H NMR δ 4.19 (br s, 2H), 3.73 (s, 6H), 2.84 (t, 2H, $J=2.0$ Hz), 2.21 (td, 2H, $J=6.9$, 2.6 Hz), 2.17–2.07 (m, 2H), 1.96 (t, 1H, $J=2.6$ Hz), 1.93 (br s, 1H), 1.50–1.33 (m, 2H); ^{13}C NMR δ 170.5, 83.3, 81.7, 79.6, 68.7, 56.5, 52.6, 50.5, 31.2, 23.1, 23.0, 18.3; MS *m/z* 266 (M^+, 0.7); HRMS calcd for $C_{14}H_{18}O_5$ 266.1155, found 266.1161.

4.5.5. 5,5-Bis(methoxycarbonyl)-10-phenyldeca-2,9-diyn-1-ol (10). According to the procedure for preparation of **6** from **5**, **10** (530 mg, 77%) was obtained from **9** (532 mg, 2.00 mmol) as a colorless oil: IR 3607, 3471, 1732 cm^{-1}; ^1H NMR δ 7.43–7.33 (m, 2H), 7.31–7.24 (m, 3H), 4.20–4.10 (m, 2H), 3.74 (s, 6H), 2.88 (t, 2H, $J=2.3$ Hz), 2.44 (t, 2H, $J=7.3$ Hz), 2.26–2.16 (m, 2H), 1.95–1.81 (m, 1H), 1.60–1.42 (m, 2H); ^{13}C NMR δ 170.7, 131.5, 128.2, 127.6, 123.8, 89.2, 81.7, 81.2, 80.3, 56.9, 52.7, 51.0, 31.5, 23.6, 23.3, 19.5; MS *m/z* 342 (M^+, 2.4); HRMS calcd for $C_{20}H_{22}O_5$ 342.1467, found 342.1465.

4.5.6. 2-(Hydroxymethyl)-1-[4-(trimethylsilyl)but-3-ynyl]benzene (16). To a suspension of zinc powder (1.31 g, 20.0 mmol) in DMA (8.0 mL) was added I_2 (254 mg, 1.00 mmol) at room temperature. The reaction mixture was stirred until the red color of I_2 disappeared. Then a solution of 4-bromo-1-(trimethylsilyl)but-1-yne (2.05 g, 10.0 mmol) in DMA (2.0 mL) was added and the reaction mixture was warmed to 80 °C. After stirring for 3 h, a solution of **13** (1.76 g, 5.05 mmol) in DMA (1.0 mL) and $Pd(PPh_3)_4$ (289 mg, 0.250 mmol) were added to the reaction mixture, which was stirred at 80 °C for 1 h. The reaction mixture was filtered through a Celite pad, and the filtrate was diluted with 10% aqueous HCl and extracted with Et_2O. The extract was washed with water and brine, dried and concentrated to dryness. The residue was passed through a short pad of silica gel with hexane–AcOEt (20/1) to afford the crude **15**. To a solution of the crude **15** in THF (50 mL) was added TsOH–H_2O (476 mg, 2.50 mmol) at room temperature. After being stirred for 13 h, the reaction mixture was quenched by addition of saturated aqueous $NaHCO_3$ and extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was chromatographed with hexane–AcOEt (4/1) to afford **16** (727 mg, 62%) as a colorless oil: IR 3609, 3503, 2170 cm^{-1}; ^1H NMR δ 7.40–7.20 (m, 4H), 4.74 (s, 2H), 2.94 (t, 2H, $J=7.6$ Hz), 2.55 (t, 2H, $J=7.6$ Hz), 1.71 (s, 1H), 0.14 (s, 9H); ^{13}C NMR δ 138.8, 138.5, 129.7, 128.6, 128.0, 126.7, 106.7, 85.6, 63.1, 31.1, 21.9, 0.0; MS *m/z* 232 (M^+, 4.5). Anal. Calcd for $C_{14}H_{20}OSi$: C, 72.36; H, 8.67. Found: C, 72.11; H, 8.95.

4.5.7. 2-(Bromomethyl)-1-[4-(trimethylsilyl)but-3-ynyl]benzene (17). To a solution **16** (349 mg, 1.50 mmol) in CH_2Cl_2 (15 mL) were added PPh_3 (637 mg, 3.00 mmol) and CBr_4 (746 mg, 2.25 mmol) at 0 °C, and the reaction mixture was stirred at room temperature for 1 h. CH_2Cl_2 was evaporated off, and the residue was chromatographed with hexane–AcOEt (30/1) to afford **17** (438 mg, 99%) as a colorless oil: IR 2172 cm^{-1}; ^1H NMR δ 7.38–7.15 (m, 4H), 4.59 (s, 2H), 2.98 (t, 2H, $J=7.6$ Hz), 2.59 (t, 2H, $J=7.6$ Hz), 0.15 (s, 9H); ^{13}C NMR δ 139.4, 135.7, 130.5, 130.1, 129.0, 127.0, 106.1, 85.7, 31.6, 31.1, 21.4, 0.0; MS *m/z* 294 (M^+, 1.2), 296 (M^+, 1.2). Anal. Calcd for $C_{14}H_{19}BrSi$: C, 56.94; H, 6.49. Found: C, 56.77; H, 6.56.

4.5.8. 2-(But-3-ynyl)-1-(4-hydroxybut-2-ynyl)benzene (20). Lithium acetylide, prepared from 1-(*tert*-butyldimethylsiloxy)prop-2-yne (766 mg, 4.50 mmol) and ^{n}BuLi (1.42 M in hexane, 3.24 mL, 4.60 mmol), in THF (1.3 mL) was added to a suspension of $InCl_3$ (354 mg, 1.60 mmol) in THF (10 mL) at −78 °C. After being stirred for 30 min, the resulting solution was then added to a solution of **17** (809 mg, 2.74 mmol) and $Pd(dppf)Cl_2$ (CH_2Cl_2 complex, 22.4 mg, 2.70×10^{-2} mmol) in THF (12 mL). The reaction mixture was refluxed for 18.5 h, quenched by addition of MeOH and 10% aqueous HCl, and extracted with Et_2O. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was passed through a short pad of silica gel with hexane–AcOEt (50/1) to afford the crude diyne **19**. To a solution of the crude **19** in THF (23 mL) was added TBAF (1.0 M in THF solution, 7.0 mL, 7.0 mmol) at 0 °C, and the reaction mixture was stirred for 1 h. THF was evaporated off, and the residue was chromatographed with hexane–AcOEt (4/1) to afford **20** (354 mg, 65%) as a colorless oil: IR 3606, 3439, 3306, 2118 cm^{-1}; ^1H NMR δ 7.42–7.36 (m, 1H), 7.22–7.16 (m, 3H), 4.25 (t, 2H, $J=2.4$ Hz), 3.61 (t, 2H, $J=2.4$ Hz), 2.89 (t, 2H, $J=7.8$ Hz), 2.48 (td, 2H, $J=7.8$, 2.4 Hz), 2.10 (br s, 1H), 1.99 (t, 1H, $J=2.4$ Hz); ^{13}C NMR δ 138.1, 134.4, 129.2, 129.0, 127.1, 126.8, 83.7, 83.6, 80.6, 69.1, 51.2, 31.3, 22.8, 19.6; MS *m/z* 198 (M^+, 2.4); HRMS calcd for $C_{14}H_{14}O$ 198.1044, found 198.1042.

4.5.9. 1-(4-Hydroxybut-2-ynyl)-2-(4-phenylbut-3-ynyl)benzene (21). According to the procedure for preparation of **6** from **5**, **21** (301 mg, 73%) was obtained from **20** (297 mg, 1.50 mmol) as a colorless oil: IR 3607, 3383, 2226 cm^{-1}; ^1H NMR δ 7.44–7.34 (m, 3H), 7.30–7.18 (m, 6H), 4.26 (t, 2H, $J=2.0$ Hz), 3.66 (t, 2H, $J=2.0$ Hz), 2.97 (t, 2H, $J=7.8$ Hz), 2.70 (t, 2H, $J=7.8$ Hz), 1.83 (br s, 1H); ^{13}C NMR δ 138.3, 134.5, 131.5, 129.4, 129.0, 128.2, 127.7, 127.2, 126.8, 123.6, 89.3, 83.8, 81.4, 80.6, 51.3, 31.7, 22.9, 20.8; MS *m/z* 274 (M^+, 2.1); HRMS calcd for $C_{20}H_{18}O$ 274.1357, found 274.1349.

4.5.10. 1-Bromo-2-[3-(*tert*-butyldimethylsiloxy)prop-1-ynyl]benzene (27). According to the procedure for preparation of **6** from **5**, **27** (552 mg, 85%) was obtained from **26** (0.25 mL, 2.00 mmol) as a colorless oil: ^1H NMR δ 7.57 (dd, 1H, $J=7.9$, 1.3 Hz), 7.46 (dd, 1H, $J=7.9$, 1.7 Hz), 7.25 (td, 1H, $J=7.6$, 1.3 Hz), 7.15 (td, 1H, $J=7.6$, 1.7 Hz), 4.59 (s, 2H), 0.94 (s, 9H), 0.18 (s, 6H); ^{13}C NMR δ 133.6, 132.4, 129.4, 126.9, 125.4, 125.1, 92.5, 83.2, 52.3, 25.8, 18.3, −5.0; MS *m/z* 323 (M^+, 2.5), 325 (M^+, 2.6). Anal. Calcd for $C_{15}H_{21}OBrSi$: C, 55.38; H, 6.51. Found: C, 55.06; H, 6.45.

4.5.11. 1-(3-Hydroxyprop-1-ynyl)-2-(pent-4-ynyl)benzene (29). According to the procedure for preparation of **15** from **13**, the crude **28** was obtained from **27** (975 mg, 3.00 mmol). To a solution of the crude **28** in THF (20 mL) was added TBAF (1.0 M in THF solution, 5.0 mL, 5.0 mmol) at 0 °C. After stirring for 10 min, THF was evaporated off, and the residue was chromatographed with hexane–AcOEt (4/1) to afford **29** (438 mg, 74%) as a colorless oil: IR 3607, 3431, 3306, 2233, 2116 cm^{-1}; ^1H NMR δ 7.43–7.40 (m, 1H), 7.29–7.13 (m, 3H), 4.53 (d, 2H, J=6.0 Hz), 2.90 (t, 2H, J=7.6 Hz), 2.24 (td, 2H, J=6.9, 2.6 Hz), 2.01 (t, 1H, J=2.6 Hz), 1.87 (quin, 2H, J=7.0 Hz), 1.71 (t, 1H, J=6.0 Hz); ^{13}C NMR δ 143.7, 132.4, 129.0, 128.6, 126.0, 122.0, 90.8, 84.5, 84.3, 68.6, 51.8, 33.3, 29.2, 18.1; MS m/z 198 (M^+, 2.5); FABHRMS calcd for $C_{14}H_{14}ONa$ 221.0943, found 221.0954 (M^++23).

4.5.12. 1-(3-Hydroxyprop-1-ynyl)-2-(5-phenylpent-4-ynyl)benzene (30). According to the procedure for preparation of **6** from **5**, **30** (120 mg, 73%) was obtained from **29** (118 mg, 0.600 mmol) as a colorless oil: IR 3607, 3425, 2232 cm^{-1}; ^1H NMR δ 7.44–7.39 (m, 3H), 7.31–7.13 (m, 6H), 4.46 (d, 2H, J=6.3 Hz), 2.96 (t, 2H, J=7.9 Hz), 2.46 (t, 2H, J=6.9 Hz), 1.96 (quin, 2H, J=6.9 Hz), 1.63 (t, 1H, J=6.3 Hz); ^{13}C NMR δ 143.8, 132.5, 131.5, 129.0, 128.6, 128.3, 127.7, 125.9, 123.9, 122.0, 90.8, 90.0, 84.3, 81.1, 51.7, 33.5, 29.4, 19.1; MS m/z 274 (M^+, 4.7); FABHRMS calcd for $C_{20}H_{18}ONa$ 297.1256, found 297.1246 (M^++23).

4.5.13. 1-(3-Hydroxyprop-1-ynyl)-2-[5-(trimethylsilyl)pent-4-ynyl]benzene (31). According to the procedure for preparation of **15** from **13**, the crude **28** was obtained from **27** (846 mg, 2.60 mmol). To a solution of the crude **28** in THF (20 mL) was added 10% aqueous HCl (5.0 mL) at room temperature. After being stirred for 1 h, the reaction mixture was quenched by addition of saturated aqueous $NaHCO_3$ and extracted with AcOEt. The extract was washed with water and brine, dried and concentrated to dryness. The residue was chromatographed with hexane–AcOEt (3/1) to afford **31** (557 mg, 78%) as a colorless oil: IR 3607, 3454, 2233, 2170 cm^{-1}; ^1H NMR δ 7.42–7.39 (m, 1H), 7.28–7.11 (m, 3H), 4.52 (s, 2H), 2.87 (t, 2H, J=7.6 Hz), 2.27 (t, 2H, J=7.3 Hz), 1.95 (s, 1H), 1.87 (quin, 2H, J=7.3 Hz), 0.17 (s, 9H); ^{13}C NMR δ 143.7, 132.4, 129.0, 128.6, 125.9, 122.0, 107.3, 90.8, 85.0, 84.3, 51.6, 33.5, 29.2, 19.5, 0.2; MS m/z 270 (M^+, 0.2). Anal. Calcd for $C_{17}H_{22}OSi$: C, 75.50; H, 8.20. Found: C, 75.23; H, 8.58.

4.5.14. 5-Phenylpent-2-yn-1-ol (38). To a solution of 4-phenylbut-1-yne (1.36 g, 10.5 mmol) in THF (100 mL) was added ^{n}BuLi (1.47 M in hexane solution, 10.7 mL, 15.8 mmol) at −78 °C. After stirring for 1 h, $(HCHO)_n$ (1.58 g, 52.5 mmol) was added to the reaction mixture, which was stirred for 2 h. The reaction mixture was quenched by addition of saturated aqueous NH_4Cl and extracted with AcOEt. The extract was washed with water and brine, dried and concentrated to dryness. The residue was chromatographed with hexane–AcOEt (2/1) to afford **38** (1.64 g, 97%) as a colorless oil: IR 3609, 3427, 2222 cm^{-1}; ^1H NMR δ 7.33–7.20 (m, 5H), 4.23 (dt, 2H, J=5.9, 2.1 Hz), 2.83 (t, 2H, J=7.6 Hz), 2.51 (tt, 2H, J=7.6, 2.1 Hz), 1.53 (t, 1H, J=5.9 Hz); ^{13}C NMR δ 140.5, 128.3, 128.2, 126.3, 87.9, 85.6, 51.2, 34.9, 20.8; MS m/z 160 (M^+, 3.7); FABHRMS calcd for $C_{11}H_{12}ONa$ 183.0786, found 183.0794 (M^++23).

4.5.15. 6-Phenylhex-3-yn-2-ol (39). To a solution of 4-phenylbut-1-yne (421 mg, 3.23 mmol) in THF (32 mL) was added ^{n}BuLi (1.47 M in hexane solution, 3.30 mL, 4.85 mmol) at −78 °C. After stirring for 1 h, CH_3CHO (0.91 mL, 16 mmol) was added to the reaction mixture, which was stirred for 1 h. The reaction mixture was quenched by addition of saturated aqueous NH_4Cl and extracted with AcOEt. The extract was washed with water and brine, dried and concentrated to dryness. The residue was chromatographed with hexane–AcOEt (5/1) to afford **39** (529 mg, 94%) as a colorless oil: IR 3603, 3420, 2241 cm^{-1}; ^1H NMR δ 7.33–7.20 (m, 5H), 4.64–4.55 (m, 1H), 2.82 (t, 2H, J=7.6 Hz), 2.49 (td, 2H, J=7.6, 1.8 Hz), 1.70 (d, 1H, J=5.1 Hz), 1.41 (d, 3H, J=6.4 Hz); ^{13}C NMR δ 140.6, 128.4, 128.3, 126.3, 83.9, 83.1, 58.5, 35.0, 24.6, 20.8; MS m/z 174 (M^+, 2.8); FABHRMS calcd for $C_{12}H_{14}ONa$ 197.0942, found 197.0951 (M^++23).

4.5.16. 2-Methyl-6-phenylhex-3-yn-2-ol (40).[19] According to the procedure for preparation of **39**, **40** (495 mg, 79%) was obtained from 4-phenylbut-1-yne (435 mg, 3.34 mmol) and CH_3COCH_3 (1.20 mL, 16.7 mmol) as a colorless oil: IR 3599, 3431, 2235 cm^{-1}; ^1H NMR δ 7.33–7.20 (m, 5H), 2.81 (t, 2H, J=7.6 Hz), 2.47 (t, 2H, J=7.6 Hz), 1.84 (s, 1H), 1.47 (s, 6H).

4.5.17. 2-[3-(*tert*-Butyldiphenylsiloxy)prop-1-ynyl]-3-(2,5-dioxolanyl)furan (52). To a solution of *N*,*N*,*N*′-trimethylethylenediamine (3.40 mL, 26.0 mmol) in THF (40 mL) was added ^{n}BuLi (1.46 M in hexane solution, 16.8 mL, 24.0 mmol) at −78 °C. After stirring for 10 min, 3-furaldehyde (1.73 mL, 20.0 mmol) was gradually added, and the reaction mixture was stirred for 20 min. Then ^{n}BuLi (35.0 mL, 50.0 mmol) was added dropwise to the reaction mixture, which was stirred for 2 h. A solution of I_2 (25.4 g, 100 mmol) in THF (10 mL) was added to the reaction mixture. After being stirred for 1 h, the reaction mixture was quenched by addition of saturated aqueous $Na_2S_2O_3$ and extracted with AcOEt. The extract was washed with water and brine, dried and concentrated to dryness. The residue was passed through a short pad of silica gel with hexane–AcOEt (5/1) to afford the crude iodide. To a solution of the crude iodide in benzene (31 mL) were added ethylene glycol (2.09 mL, 37.5 mmol) and TsOH–H_2O (476 mg, 2.50 mmol), and the reaction mixture was refluxed for 1.5 h under azeotropic removal of water. The reaction mixture was quenched by addition of Et_3N and extracted with AcOEt. The extract was washed with water and brine, dried and concentrated to dryness. The residue was passed through a short pad of silica gel with hexane–AcOEt (5/1) to afford the crude acetal. According to the procedure for preparation of **6** from **5**, **52** (4.49 g, 52%) was obtained from the crude acetal as a pale yellow oil: ^1H NMR δ 7.76–7.68 (m, 4H), 7.48–7.35 (m, 6H), 7.32 (d, 1H, J=2.0 Hz), 6.47 (d, 1H, J=2.0 Hz), 5.79 (s, 1H), 4.56 (s, 2H), 4.18–3.91 (m, 4H), 1.07 (s, 9H); ^{13}C NMR δ 143.4, 135.7, 135.5, 132.8, 129.8, 127.7, 109.1, 97.8, 94.9, 73.6, 65.1, 53.0, 26.6, 19.1; MS m/z 432 (M^+, 2.2). Anal. Calcd for $C_{26}H_{28}O_4Si$: C, 72.19; H, 6.52. Found: C, 71.95; H, 6.58.

4.5.18. 2-[3-(*tert*-Butyldiphenylsiloxy)prop-1-ynyl]-3-[1-hydroxy-5-(trimethylsilyl)pent-4-ynyl]furan (54). To a solution of **52** (433 mg, 1.00 mmol) in THF (10 mL) was added 10% aqueous HCl (3.0 mL) at room temperature. After being stirred for 1 h, the reaction mixture was quenched by addition of saturated aqueous $NaHCO_3$, and extracted with AcOEt. The extract was washed with water and brine, dried and concentrated to dryness. The residue was passed through a short pad of silica gel with hexane–AcOEt (10/1) to afford the crude aldehyde. To a solution of **53** (1.0 M in Et_2O solution, 9.9 mL, 9.9 mmol) was added crude aldehyde in Et_2O (10 mL) at 0 °C, and the reaction mixture was stirred at room temperature for 1 h. The reaction mixture was quenched by addition of 10% aqueous HCl and extracted with AcOEt. The extract was washed with water and brine, dried and concentrated to dryness. The residue was chromatographed with hexane–AcOEt (8/1) to afford **54** (868 mg, 85%) as a pale yellow oil: IR 3599, 3524, 2172 cm^{-1}; ^1H NMR δ 7.75–7.71 (m, 4H), 7.48–7.37 (m, 6H), 7.31 (d, 1H, $J=2.0$ Hz), 6.44 (d, 1H, $J=2.0$ Hz), 4.78 (dd, 1H, $J=7.8$, 5.1 Hz), 4.57 (s, 2H), 2.32 (td, 2H, $J=7.3$, 1.0 Hz), 2.05 (br s, 1H), 2.04–1.94 (m, 1H), 1.92–1.83 (m, 1H), 1.08 (s, 9H), 0.14 (s, 9H); ^{13}C NMR δ 143.6, 135.6, 133.2, 132.9, 132.9, 129.8, 127.7, 109.3, 106.5, 95.2, 85.3, 74.1, 65.9, 53.1, 36.1, 26.7, 19.2, 16.4, 0.1; MS *m/z* 514 (M^+, 0.8). Anal. Calcd for $C_{31}H_{38}O_3Si_2$: C, 72.33; H, 7.44. Found: C, 71.97; H, 7.46.

4.5.19. 2-[3-(*tert*-Butyldiphenylsiloxy)prop-1-ynyl]-3-[1-(methoxymethoxy)-5-(trimethylsilyl)pent-4-ynyl]furan (55). To a solution of **54** (419 mg, 0.814 mmol) in CH_2Cl_2 (8.1 mL) were added $^iPr_2NEt$ (0.28 mL, 1.6 mmol) and MOMCl (0.12 mL, 1.63 mmol) at 0 °C, and the reaction mixture was stirred at room temperature for 9 h. The reaction mixture was quenched by addition of water, and extracted with CH_2Cl_2. The extract was washed with water and brine, dried and concentrated to dryness. The residue was chromatographed with hexane–AcOEt (8/1) to afford **55** (432 mg, 95%) as a pale yellow oil: IR 2172 cm^{-1}; ^1H NMR δ 7.79–7.74 (m, 4H), 7.49–7.41 (m, 6H), 7.33 (d, 1H, $J=2.0$ Hz), 6.41 (d, 1H, $J=2.0$ Hz), 4.78 (dd, 1H, $J=8.1$, 5.4 Hz), 4.62–4.56 (m, 3H), 4.53 (d, 1H, $J=6.6$ Hz), 3.38 (s, 3H), 2.36 (td, 2H, $J=7.8$, 2.0 Hz), 2.13–2.04 (m, 1H), 1.95–1.86 (m, 1H), 1.12 (s, 9H), 0.17 (s, 9H); ^{13}C NMR δ 143.6, 135.6, 134.5, 132.9, 132.9, 130.2, 129.8, 127.7, 109.7, 106.4, 94.9, 94.3, 84.9, 73.9, 68.9, 55.6, 53.1, 35.2, 26.7, 19.2, 16.4, 0.1; MS *m/z* 558 (M^+, 0.4). Anal. Calcd for $C_{33}H_{42}O_4Si_2$: C, 70.92; H, 7.58. Found: C, 70.55; H, 7.72.

4.5.20. 2-(3-Hydroxyprop-1-ynyl)-3-[1-(methoxymethoxy)pent-4-ynyl]furan (56). According to the procedure for preparation of **5** from **4**, **56** (28.5 mg, 90%) was obtained from **55** (71.4 mg, 0.128 mmol) as a colorless oil: IR 3603, 3420, 3308, 2118 cm^{-1}; ^1H NMR δ 7.33 (d, 1H, $J=2.0$ Hz), 6.40 (d, 1H, $J=2.0$ Hz), 4.83 (dd, 1H, $J=8.3$, 5.9 Hz), 4.64–4.46 (m, 4H), 3.39 (s, 3H), 2.61 (br s, 1H), 2.37–2.25 (m, 2H), 2.17–2.01 (m, 1H), 1.99 (t, 1H, $J=$ 2.6 Hz), 1.95–1.79 (m, 1H); ^{13}C NMR δ 143.9, 134.7, 130.4, 109.5, 95.1, 93.9, 83.5, 74.7, 68.8, 68.2, 55.7, 51.4, 34.6, 15.0; MS *m/z* 248 (M^+, 1.2); FABHRMS calcd for $C_{14}H_{17}O_4$ 249.1126, found 249.1112 ($M^+ + 1$).

4.5.21. 2-(3-Hydroxyprop-1-ynyl)-3-[1-(methoxymethoxy)-5-phenylpent-4-ynyl]furan (57). According to the procedure for preparation of **6** from **5**, **57** (369 mg, 91%) was obtained from **56** (310 mg, 1.25 mmol) as a pale yellow oil: IR 3601, 3422, 2230 cm^{-1}; ^1H NMR δ 7.43–7.39 (m, 2H), 7.33 (d, 1H, $J=2.0$ Hz), 7.31–7.24 (m, 3H), 6.42 (d, 1H, $J=2.0$ Hz), 4.95 (dd, 1H, $J=8.3$, 5.6 Hz), 4.63, 4.53 (AB-q, 2H, $J=6.8$ Hz), 4.37 (s, 2H), 3.41 (s, 3H), 2.65–2.42 (m, 3H), 2.22–2.12 (m, 1H), 1.99–1.89 (m, 1H); ^{13}C NMR δ 143.9, 134.8, 131.4, 130.3, 128.2, 127.7, 123.8, 109.5, 95.1, 93.8, 89.0, 81.3, 74.5, 68.2, 55.6, 51.2, 34.7, 16.0; MS *m/z* 324 (M^+, 0.5). Anal. Calcd for $C_{20}H_{20}O_4$: C, 74.06; H, 6.21. Found: C, 73.85; H, 6.52.

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