JOC The Journal of Organic Chemistry

Article

pubs.acs.org/joc

Domino Cyclization of 1,*n*-Enynes (*n* = 7, 8, 9) Giving Derivatives of Pyrane, Chromene, Fluorene, Phenanthrene and Dibenzo[7]annulene by Ruthenium Complexes

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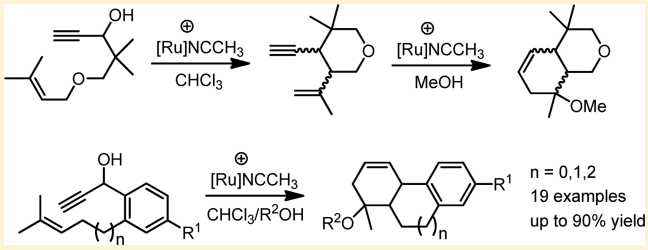
Supporting Information

ABSTRACT: Cyclization of the ether enyne **1** catalyzed by $[Ru]NCCH_3^+$ ($[Ru] = Cp(PPh_3)_2Ru$) in $CHCl_3$ generates a diastereomeric mixture of the substituted tetrahydropyran **11**. Presumably, formation of an allenylidene complex is followed by a cyclization by nucleophilic addition of the olefinic group to Cγ of the ligand giving a boat-like six-membered ring. The diastereoselectivity is controlled by the 1,3-diaxial interaction. The vinylidene complex **7**, a precursor of **11**, is obtained from **1** and [Ru]Cl. In a mixture of MeOH/$CHCl_3$, the domino cyclization of **1** further affords **14a**, a chromene product catalytically. The second cyclization proceeds via nucleophilic addition of the resulting olefinic unit to Cα of **7**. But the ether enyne **3** with a cyclopentyl ring on the olefinic unit undergoes only single cyclization due to steric effect. The propargyl alcohol and the two terminal methyl groups on the olefinic unit shape the cyclization. Thus, similar all-carbon 1,*n*-enynes (*n* = 7, 8, 9) **4**–**6** each with an aromatic linker undergo direct domino cyclization catalyzed by $[Ru]NCCH_3^+$, to give derivatives of tricyclic fluorene, phenanthrene and dibenzo[7]annulene, respectively, with no intermediate observed.

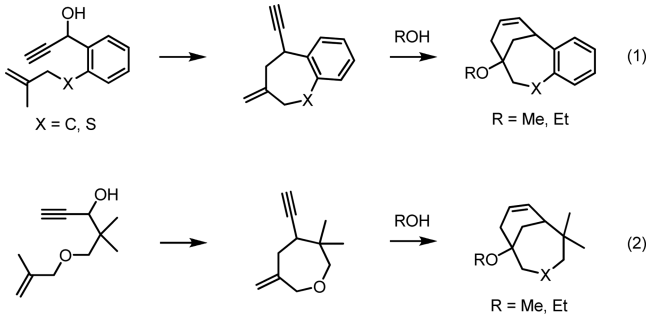


INTRODUCTION

Synthetic and natural heterocyclic compounds have attracted a great deal of attention due to their biological activities.[1] Transition-metal-catalyzed cycloisomerization and olefin metathesis are now regularly employed for preparations of these heterocycles.[2] It is well-documented that various ruthenium complexes could readily activate carbon−carbon triple bond of enynes inducing intra- or intermolecular carbon−carbon bond formation.[3] For many of these alkyne transformations, various metal vinylidene and allenylidene complexes have been considered as important key intermediates.[4] Therefore, widespread explorations have been carried out on various metal vinylidene complexes because of their versatile reactivity, and, using such strategies, a variety of complicated products have been readily obtained from simple substrates.[5] These results have encouraged the development of new types of metal-catalyzed reactions and the design of efficient synthetic approaches to heterocyclic compounds with bioactivities.[6]

Previously, we reported the Ru-mediated cyclization, skeletal rearrangement and cycloisomerization of enynes with propargylic functionality.[7] For example, cyclization of several 1,8-enynes (Scheme 1) consisting of the propargylic alcohol and the olefinic part containing an internal methyl group was studied.[8] The two unsaturated functional groups are linked either by an aromatic or by a more flexible carbon chain. Ruthenium-induced intramolecular cyclization reaction of these enynes is found to proceed via a sequential allenylidene/vinylidene ligands affording the product with a newly formed bridged bicyclic rings. Presumably, using this strategy, a simple fused, instead of bridged, bicyclic-ring system could be achieved if the olefinic part contains two terminal methyl groups without the internal one.

Scheme 1. Cascade Cyclization of 1,8-Enynes Tethering Propargylic Alcohol[8]



Indeed, we did investigate ruthenium-mediated cyclization reactions of an aromatic propargylic alcohol, with an *ortho*-substituted allyl sulfide containing two geminal methyl groups at the olefinic part.[8c] However, complex mixtures including a fused cyclic organic compound, a carbene complex and a

Received: February 4, 2016
Published: April 30, 2016

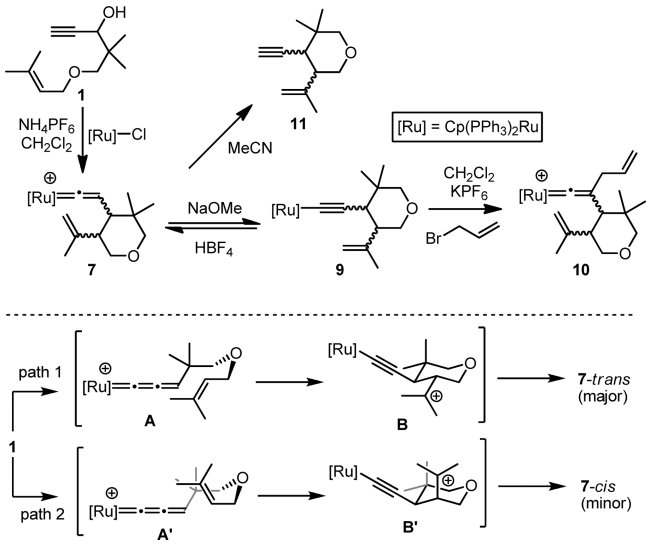
DOI: 10.1021/acs.joc.6b00260
J. Org. Chem. 2016, 81, 4494−4505

metallacyclic complex were formed in moderate yield. In order to improve the process with an aim to obtain a single product in high yield, we explore the ruthenium catalyzed reactions of 1,*n*-enynes bearing either an ether linkage with sp^3 carbon chain or a more rigid aromatic linker. Herein, we report high yield preparation of derivatives of hydropyran, hydroisochromene from ether linked 1,8-enynes and fluorene, phenanthrene and dibenzo[7]annulene derivatives from aromatic all carbon 1,7-, 1,8- and 1,9-enynes, respectively. The cationic ruthenium acetonitrile complex is found to serve as an efficient catalyst for domino cyclization of 1,*n*-enynes with an aromatic linker. In addition, for the ether linked 1,8-enynes, the solvent used in the reaction is found to control the sequence of domino cyclization.

RESULTS AND DISCUSSION

First Cyclization of 1,8-Enynes Leading to Hydropyran Derivatives. The ether linked 1,8-enyne **1**, where the triple bond is part of a propargyl alcohol and the double bond contains two geminal methyl groups, is prepared in high yield. Treatment of **1** with [Ru]Cl ([Ru] = $Cp(PPh_3)_2Ru$) in the presence of NH_4PF_6 in CH_2Cl_2 at room temperature affords the vinylidene complex **7** containing a newly formed oxane moiety as a mixture of two diastereomers in a ratio of 2:1, see Scheme 2 (upper). The reaction of a similar enyne **2** (see Table 1 for structure), containing a cyclopropyl group replacing the two methyl groups at C_4 in **1**, with [Ru]Cl also yields a mixture of diastereomeric vinylidene complex **8** containing a six-membered ring in a ratio of ca. 10:1, along with other side products. Purification by passing the crude mixture through a neutral-Al_2O_3 column gives a yellow powder, identified as the ruthenium acetylide complex similar to **9**, which, by protonation with HBF_4 at 0 °C, regenerates only the *trans*-isomer of **8**. Attempts to isolate the minor isomer failed.

Scheme 2. Cyclization Reactions of 1 and Disteroselectivity



The structure and configuration of **7** is determined by NMR spectroscopy. The ^{31}P NMR spectrum of diastereomers of **7**, with two stereogenic centers, displays two sets of two doublets at δ 43.75, 43.12 and 45.22, 43.50 with $^2J_{PP}$ = 26.5 and 26.8 Hz for the major and minor products, respectively. In the ^1H NMR spectrum of the major isomer of **7**, the coupling constant of 11.2 Hz between CγH and CδH is within the range of that of two *trans* vicinal protons at axial positions.[9]

The corresponding coupling constant of the minor *cis*-isomer is 3.6 Hz. In the 2D-HMBC NMR spectrum of **7**, the multiplet ^1H resonance at δ 2.96 assign to CδH displays correlation with the ^{13}C resonance at δ 42.2 assigned to Cγ, confirming the C–C bond formation between the terminal allyl unit and Cγ. The *trans*-configuration of the major isomer of **8**, prepared from **2**, is revealed by a similar coupling constant of 11.3 Hz between CγH and CδH.

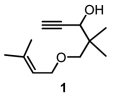
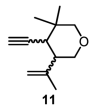
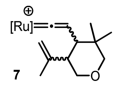
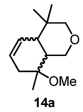
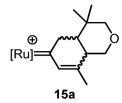
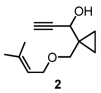
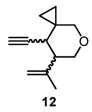
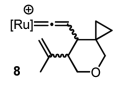
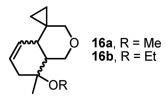
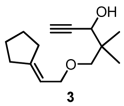
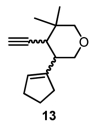
The cyclization of both **1** and **2** is believed to proceed via the formation of a γ-hydroxyvinylidene intermediate followed by a dehydration to give two kinds of allenylidene intermediates **A** and **A′** with different conformations (lower part of Scheme 2). Subsequently, an intramolecular addition of the terminal alkene to Cγ in **A** (path 1) gives the acetylide intermediate **B** with the tertiary cationic substituent at equatorial position. This is followed by an 1,5-hydrogen shift of the methyl group to Cβ of the acetylide ligand to give a less hindered product *trans*-**7**. In path 2, the intramolecular addition of the olefinic moiety to Cγ in **A′** similarly affords the corresponding **B′**. The steric repulsion of the two *cis*-groups in the cyclohexyl ring elevates the energy of intermediate **B′**. As a result, *trans*-**7** was obtained as the major product. An alternative pathway for the cyclization from **A**/**A′** to **B**/**B′** is the direct allenylidene-ene process.[10] For the formation of **7** from **B**/**B′**, the deprotonation/protonation sequence is also an option.

Deprotonation of **7** gives the ruthenium acetylide complex **9**. Protonation of **9** with HBF_4 at 0 °C quantitatively yields **7** maintaining the same isomer ratio (*trans*:*cis* = 2:1). Treatment of **9** with allyl bromide gives the cationic vinylidene complex **10** (*trans*:*cis* = 3:1). After the reaction, small amount of phosphine oxide is produced which may relate to the decreased yield of the *cis*-isomer. Complex **10** is stable under thermolytic condition. Single crystals of the *trans*-**10** are obtained at ambient temperature in toluene/CH_2Cl_2 solution and the structure is determined by a single crystal X-ray diffraction study (see Supporting Information for an ORTEP drawing of *trans*-**10**).

The cyclized organic product **11** is readily obtained when **7** is treated with CH_3CN. Also, heating *trans*-**8** in a cosolvent of $CH_3CN/CHCl_3$ at 60 °C for 16 h generates similar terminal enyne *trans*-**12** with a 5-oxaspiro moiety in good yield. Therefore, a catalytic reaction is attempted by thermolysis of **1** at 50 °C in the presence of 30 mol % of $[Ru]NCCH_3^+$ in $CHCl_3$ for 12 h. The diastereomeric mixture of **11** in a ratio of 2:1 is isolated in 80% yield. (Table 1, entry 1). Use of complexes bearing optically active phosphine ligands such as *S*- and *R*-BINAP does not result in better selectivity (Table 1, entry 2–3). Similarly, treatment of **2** with $[Ru]NCCH_3^+$ affords a diastereomeric mixture of **12** in a *trans*:*cis* ratio of 3:1 (Table 1, entry 5). Lower the catalyst loading to 20 mol % gives **12** in comparable yield (Table. 1, entry 6). The diastereoselectivity is believed to relate to the steric hindrance of the 1,3-diaxial interaction. Hence, **3** with a bulkier cyclopentyl ring on the olefinic tether is synthesized (see Table 1). The catalytic reaction of **3** and $[Ru]NCCH_3^+$ is performed in CH_2Cl_2 to yield **13** and the *trans*/*cis* ratio is improved to 5.7:1. (Table 1, entry 9) The structures of **11**, **12** and **13** are determined by NMR spectra. In the ^1H NMR spectrum of **11**, two singlet resonances at δ 4.93 and 4.84 are assigned to two olefinic methylene protons and, for **13**, a singlet resonance at δ 5.52 is assigned to the unique olefinic proton of the five-membered cyclopentene ring. The two broad resonances at δ 2.53 and 2.15 in the ^1H NMR spectrum of *trans*-**12** are assigned to two

DOI: 10.1021/acs.joc.6b00260
J. Org. Chem. 2016, 81, 4494–4505

Table 1. Formation of the Tetrahydropyran Derivatives from 1−3 by $CpL_2Ru(NCMe)^+$[a]

Entry	Starting material	L_2	Solvent	Yield (%)[b]	Ratio[c]	Organic products	Metal complex
1	 **1**	2 PPh_3	$CHCl_3$	**11** (80)	2:1 (trans:cis)	 **11**	 **7**
2		*S*-BINAP	$CHCl_3$	**11** (80)	2:1 (trans:cis)		
3		*R*-BINAP	$CHCl_3$	**11** (80)	2:1 (trans:cis)		
4		2 PPh_3	MeOH	**14a**, **15a** (90)[d]	1:2 (**14a**:**15a**)	 **14a**	 **15a**
5[e]	 **2**	2 PPh_3	$CHCl_3$	**12** (85)	3:1 (trans:cis)	 **12**	 **8**
6[e]		2 PPh_3	$CHCl_3$	**12** (86)	3:1 (trans:cis)		
7		2 PPh_3	MeOH	**16a** (75)	5:1 (trans:cis)	 **16a**, R = Me **16b**, R = Et	
8		2 PPh_3	EtOH	**16b** (71)	3:1 (trans:cis)		
9	 **3**	2 PPh_3	$CHCl_3$	**13** (45)	17:3 (trans:cis)	 **13**	[f]
10		2 PPh_3	MeOH	**13** (45)	17:3 (trans:cis)		

[a]All of the reactions are carried out at 50 °C for 12 h in the presence of 30 mol % $CpL_2RuNCCH_3^+$ except for entry 4, 7, and 8 with 50 mol %. [b]The yields are total yield of a mixture of *trans*- and *cis*-isomers after column chromatography. [c]The ratio of two stereoisomers was determined by ^1H NMR. [d]Total yield of **14a** and **15a**. [e]The reaction is carried out at 60 °C. [f]No vinylidene intermediate is isolated and no domino cyclization.

neighboring CH groups on the six-membered ring. These broad peaks are possibly due to the flexible six-membered ring. The *trans*-diastereomer is the major product for **12**. In the ^1H NMR spectrum of *cis*-**12**, the coupling constant $^3J_{HH}$ between the CH next to the OCH_2 group and the CH neighboring to the triple bond is 4.2 Hz due to an eclipsed conformation of the two neighboring CH.

The reaction of **1**−**3** to give **11**−**13** is proposed to proceed via formation of the vinylidene intermediate **7**, as described in Scheme 2 above.[7] Then, isomerization of the vinylidene ligand gives the π-coordinated alkynyl ligand, which is replaced by the incoming substrate **1**−**3**, producing **11**−**13**, to finish the catalytic cycle.

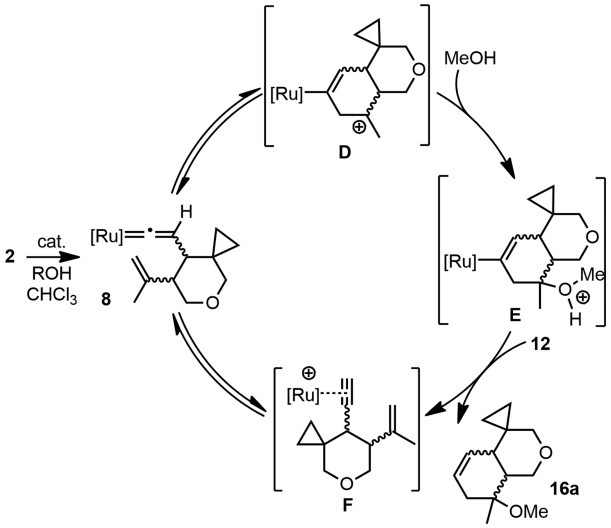
Domino Cyclization of 1,8-Enynes Leading to Isochromene Derivatives. As shown in Scheme 1, for some special enynes, particularly, with a methyl group on the olefinic unit, the first cyclization would afford yet another enyne product which could undergo further cyclization under proper condition. Previously, in a few Ru catalyzed reactions of such enynes, we have isolated the metal vinylidene complex also containing a nearby olefinic group. Then, by using different solvent further cyclization could be readily achieved.[11(a)] Since **11**, prepared from **1**, contains both an olefinic and a terminal triple bonds, a further cyclization is thus expected. Indeed, treatment of **1** with 20 mol % of $[Ru]NCCH_3^+$ in MeOH at 60 °C afforded the organic product **14a** and the carbene complex **15a**, both containing a new fused bicyclic ring by a domino cyclization, as shown in entry 4 of Table 1. The ratio of **14a** and **15a** is 1:2 as determined by the ^1H NMR spectrum. The reaction of **2** with 20 mol % of $[Ru]NCCH_3^+$ in MeOH at 60 °C, interestingly, yields only the domino cyclization product **16a**. Analogous compound **16b** is catalytically obtained in EtOH in 71% yield (Table 1, entry 7, 8).

The structures of **14a**, **15a**, **16a** and **16b** are determined by NMR spectra. For **14a**, the overlapped multiplet resonances at δ 5.62, assigned to two =CHs, show correlations with the neighboring methylene group in the COSY spectrum, clearly revealing the C−C bond formation. In the ^1H NMR spectrum of **16a**, the doublet of a triplet resonance at δ 2.30, with $^3J_{HH}$ = 11.7 and 4.7 Hz, and the broad resonance at δ 2.04 are assigned to the two bridgehead CH groups. The coupling constant of these two proton resonances is 11.7 Hz, indicating a *trans*-form of the two bridgehead CH groups. The configuration of both **16a** and **16b** is thus consistent with that in *trans*-**8**. However, treatment of **3** with $[Ru]NCCH_3^+$ in MeOH affords only **13** with the oxane moiety, no domino cyclization product is obtained (Table 1, entry 10). This is probably due to the steric hindrance when the bulkier five-membered cyclopentyl ring approaches Cα of the vinylidene ligand.

DOI: 10.1021/acs.joc.6b00260
J. Org. Chem. 2016, 81, 4494−4505

The plausible mechanism of the sequential cyclization of **2** is shown in Scheme 3. Formation of **8** proceeds via a similar

Scheme 3. Proposed Mechanism for Second Cyclization

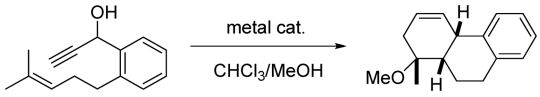


process for that of **7** mentioned above. Then, the nucleophilic addition of the olefinic group to Cα of the vinylidene ligand giving **D** is assisted by the formation of a tertiary carbocation. Addition of an alkoxide at the cationic carbon affords **E**, which then gives **16a**. Coordination of the triple bond of **12** to the ruthenium center is followed by 1,2-hydrogen shift to give **8** completing the catalytic cycle. Complex **15a** is presumably formed via an intermediate analogous to **D**, see Scheme 3,[8c] followed by a hydrogen migration.[11]

Similar domino cyclization for the formation of fused polycyclic compounds has been reported by Nishibayashi et al. in two separated experiments.[10] In the first step, the cyclization process was promoted by an optically active thiolate-bridged diruthenium complex. Then a Pt complex was required to serve as a catalyst for the second cyclization. In contrast, our ruthenium complex catalyzes the domino cyclization in alcohol and the intermediate of the reaction could be isolated in CH_2Cl_2.

Domino Cyclization of Enyne with Two Geminal Methyl Groups on the Olefin. To further explore the cyclization, the phenyl propargyl alcohol **4**, with an olefinic chain tethering at the *ortho* position of the aromatic ring was prepared.[12d] To check the validity of our proposal we intentionally put two geminal methyl groups at the olefinic unit. In the stoichiometric reaction of **4** with [Ru]Cl in MeOH in the presence of KPF_6, the domino cyclization product **17b** was isolated with quantitative recovery of [Ru]Cl (Table 2, entry 1). In the absence of metal complex, substrate **4** was recovered (Table 2, entry 2). When the loading of [Ru]Cl was reduced to 20 mol % without addition of salt, the reaction for 4 h gave **17b** in 56% yield with other side products (Table 2, entry 3). The reaction using 20 mol % of $[Ru]NCCH_3^+$ generates **17b** with 90% yield in 12 h (Table 2, entry 4). Further lowering the catalyst loading with a longer reaction time diminish the yield albeit with conservation of the domino cyclization (Table 2, entry 5). Treatment of **4** with $[Ru]NCCH_3^+$ in three other alcohols ROH (R = Et, ^{i}Pr, Bn) also affords **17c–17e**, respectively (see Table 3). We also introduced a methoxy group on the *para* positon of the

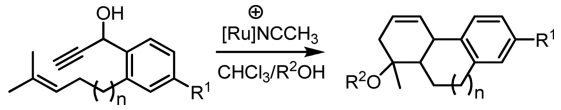
Table 2. Conditions for Catalytic Cyclization of 4

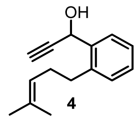
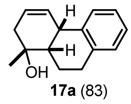
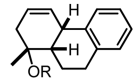
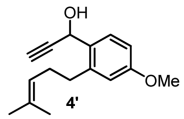
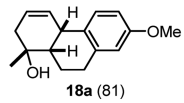
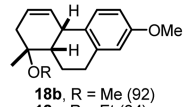
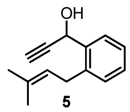
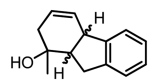
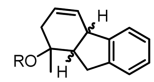
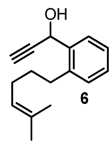
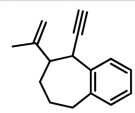
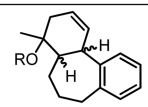


4 17b

entry	catalyst	mol %	time (h)	conversion (%)	yield (%)
1	[Ru]Cl/KPF_6	100	18	99	91
2	No catalyst	–	24	0	0
3	[Ru]Cl	20	4	93	56
4	$[Ru]NCCH_3^+$	20	12	97	90
5	$[Ru]NCCH_3^+$	10	31	95	75

Table 3. Preparations of the Tricyclic Compounds 17–21[a]



Starting material	Product	
	In Acetone	In Alcohol
 4	 **17a** (83)	 **17b**, R = Me (90) **17c**, R = Et (81) **17d**, R = *i*-Pr (79) **17e**, R = Bn (70)
 4′	 **18a** (81)	 **18b**, R = Me (92) **18c**, R = Et (84) **18d**, R = *i*-Pr (76) **18e**, R = Bn (76)
 5	 **19a** (87)	 **19b**, R = Me (95) **19c**, R = Et (90) **19d**, R = *i*-Pr (83) **19e**, R = Bn (75)
 6	 **21** (79)	 **20b**, R = Me (85) **20c**, R = Et (77)[b] **20d**, R = *i*-Pr (73)[b] **20e**, R = Bn (75)[b]

[a]The number in parentheses is yield (%). [b]Cyclizations of **6** to yield **20c–e** are all accompanied by **21**. Yields of **20c–e** contain its diastereomers and **21**.

aromatic propargyl alcohol to give **4′**. The catalytic domino cyclization of **4′** afforded the corresponding tricyclic product **18b** in $CHCl_3$/MeOH only in 8 h.

With the protocol to prepare benzo-fused tricyclic ring via metal-catalyzed cyclizations of 1,*n*-enynes with two olefinic terminal methyl groups, we reasoned that the chain length could be modified to vary the ring size in the product. The optimized condition for the catalytic domino cyclization reaction of **4** (Table 2, entry 4) was used to carry out the cyclizations of **5** and **6** in MeOH giving the tricyclic organic

DOI: 10.1021/acs.joc.6b00260
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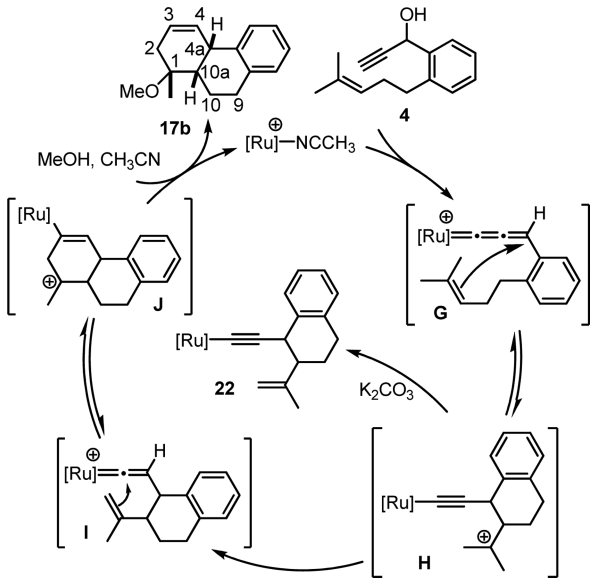
products **19b** and **20b**, respectively (see Table 3). The domino cyclization of **5** gave **19b** as a mixture of two diastereomers in a ratio of 1:1. Product **20b** with a seven-membered ring and with the diastereomeric ratio of 1:0.1 was isolated in 85% yield.

A plausible mechanism for the domino cyclization of **4** is shown in Scheme 4. After formation of **G** with the allenylidene

Scheme 4. Putative Mechanism for the Formation of 17b



ligand, the reaction might proceed via addition of the unsaturated group to the electrophilic Cγ of the ligand or by a concerted allenylidene-ene reaction pathway. The intramolecular addition results in a C–C bond formation, giving the acetylide complex **H** bearing a cationic charge at dimethyl-substituted tertiary carbon. Then transfer of one of the methyl protons to Cβ of the acetylide ligand yields the vinylidene intermediate **I**. Subsequently, the second nucleophilic addition of the olefinic moiety to Cα in **I** gives the cationic species **J**. Both cyclization processes yielding **H** and **J** are assisted by formation a tertiary carbocation. Then, addition of a methoxide at the cationic carbon is followed by protonation to yield **17b**.

Yields of **17b–e** decrease as the steric bulk of the alcohol increases (see Table 3). Interestingly, when acetone, instead of alcohol, is used, water molecule, freed at the formation of allenylidene, serves as a nucleophile to give the tricyclic product **17a**. This is different from our earlier works, where the second cyclization proceeds only when alcohol was used in the system.[8a] We previously reported isolation of intermediate analogous to **I** in the cyclization of two O- or S-containing enynes catalyzed by [Ru]Cl. However, the intermediate **I** is not observed during the catalytic cyclization reaction of all-carbon-chain aromatic enyne **4**. We suggest that the formation of six-membered ring transition state in the intermediate **I** accelerates the addition of the terminal olefinic segment to Cα. But the acetylide complex **22** (see Scheme 4), derived from deprotonation of **H** is obtained from a stoichiometric reaction of **4** and [Ru]Cl in CH_2Cl_2 in the presence of K_2CO_3 and KPF_6. This indicates that the first and second C–C bond formations take place at Cγ and Cα, respectively. Previously we have reported the reaction of [Ru]Cl with 4,4-disubstituted-1,6-enyne, which also has two methyl groups on the terminal carbon of the tethering allyl group, giving a carbene complex with a cyclopentenyl ring.[7] The C–C bond formation via a 5-*exo-dig* cyclization was proposed to occur while the triple bond is π-coordinated to the metal center. Here, however, formation of the hydroxyvinylidene intermediate and subsequent dehydration to yield the intermediate **G** is fast. Attempts to use coupling constants to determine the conformation of **17b** failed, due to complicated overlapped multiplet, thus, a 2D NOESY spectrum is used. In the NOESY spectrum of **17b** (see Supporting Information), cross peaks between the resonances of the methyl group and H^{10a}/H^{4a} (see Scheme 4 for numbering), reveal that the latter two protons are in *cis* conformation.

As the tether olefinic chain is made longer, cyclization also takes place. The catalytic domino cyclization of **6** with $[Ru]NCCH_3^+$ in MeOH leads to **20b**, with a benzo-fused seven-membered ring. Flexible tether made it more difficult to sustain the diastereoselectivity. Because of higher degree of freedoms resulted from more flexible linear tether, formation of all possible diasteromers of **20b–e** is inevitable.

For **6**, however, a mixture of products is obtained in alcohol other than MeOH. For example, the catalytic reaction of **6** in $CHCl_3$/EtOH, generates a mixture of diastereomers of **20c** and **21** in a ratio of 1:0.3:0.3. In addition, in $CHCl_3$/IPA or $CHCl_3$/BnOH, **21** is obtained as a minor product, and in acetone, **21** is produced exclusively (Table 3). This is presumably due to a more flexible seven-membered ring which hinders the approach of incoming alcohol to proceed the second cyclization for the vinylidene intermediate **I**. While the specific role of alcohol is unclear, it is assumed that a bulkier alcohol may suppress the formation of domino cyclization products **20c–e**.

CONCLUSIONS

Cyclization of enynes consisting of a propargylic alcohol and the olefinic portion containing two geminal methyl groups that are connected via an aliphatic or an aromatic linker is developed. Rapid and efficient domino cyclizations of these enynes are catalyzed by the cationic complex $Cp(PPh_3)_2Ru(CH_3CN)^+$ in MeOH with a methoxide added to the products all in high yields. The presence of two terminal methyl substituents on the olefinic part of these enynes assists their domino cyclization. For the enynes with aliphatic linker, the intermediate is isolated from the reaction in $CHCl_3$ and replacing the two geminal methyl groups with a cyclopentyl ring causes inhibition of the second cyclization giving the product with only one cyclization. For those enynes with more rigid aromatic linker, no intermediate is isolated, and by varying the length of the tethering chain, preparations of products with five- six- and seven-membered ring could be achieved in the first cyclization process. In the absence of alcohol, the reaction in acetone also gives the desired domino cyclization product, but with a hydroxyl group replacing the added methoxide.

EXPERIMENTAL SECTION

General Procedures. The manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. Complex $Cp(PPh_3)_2RuCl$[12a] and new compounds **1–3** and **4–6** were prepared by following the method reported in the literatures.[12b–d] The C and H analyses were carried out with an elemental microanalyzer and for some products the mixture of the diastereomers was used. Mass spectra were recorded using ESI-HRMS and FAB techniques. X-ray diffraction studies were carried out using instrument equipped with CCD detector. NMR spectra were recorded on a 400 or a 500 MHz FT-NMR spectrometer

DOI: 10.1021/acs.joc.6b00260
J. Org. Chem. 2016, 81, 4494–4505

at room temperature (unless stated otherwise). Chemical shifts are given in ppm. ^{1}H NMR chemical shifts were referenced to the residual solvent signal[13] and ^{13}C NMR chemical shifts were referenced to the deuterated solvent signal. The peak assignments have been achieved by 2D-COSY, HSQC, HMBC as well as NOESY spectra. The structures of **S1a**, **S1b**, **S2a**, **S2b**, **S3a**, **S3b**, **S4**, **S4′**, **S5**, **S6** and their corresponding schemes are shown in the Supporting Information.

Synthesis of ***1***. At room temperature, to a suspension of NaH (1.48 g, 37.2 mmol) in THF (10 mL) was added dropwise a THF solution (30 mL) of 2,2-dimethyl-1,3-propandiol (5.00 g, 33.8 mmol) with stirring for 30 min, and the resulting mixture was then heated to reflux for 1h. After cooling to room temperature, to this solution was added 1-bromo-3-methyl-2-butene (4.7 mL, 40.5 mmol) slowly in 1 h, and the mixture was heated to reflux for 8 h. The resulting solution was treated with water and extracted with ethyl acetate. The organic layer was washed with brine, dried over sodium sulfate and concentrated under reduced pressure to afford crude product 2,2-dimethyl-3-((3-methylbut-2-en-1-yl)oxy)propan-1-ol, **S1a** (3.49 g, 60%, see SI for structure) that was purified by chromatography through a silica column (hexane/EA: 4/1). Spectroscopic data of **S1a**: ^{1}H NMR (δ, $CDCl_3$, 400 MHz) 5.28 (t, 1H, $^3J_{HH}$ = 6.79 Hz, HC═); 3.91 (d, 2H, $^3J_{HH}$ = 6.79 Hz, OCH_2); 3.42 (d, 2H, $^3J_{HH}$ = 5.47 Hz, OCH_2); 3.24 (s, 2H, OCH_2); 2.81 (t, 1H, $^3J_{HH}$ = 5.47 Hz, OH); 1.71, 1.63, 0.88 (s, 12H, 4 CH_3). ^{13}C{^{1}H}NMR (δ, $CDCl_3$, 100 MHz) 137.0 (C═); 120.9 (HC═); 79.7, 72.2, 68.0 (OCH_2); 36.0 (C); 25.7, 21.9, 18.0 (4 CH_3). HRMS (ESI) m/z [M + H]$^+$ Calcd for $C_{10}H_{21}O_2^+$: 173.1536; Found: 173.1531. Compound **S1a** (3.49 g, 20.3 mmol) was dissolved in CH_2Cl_2 (50 mL) and to this solution was slowly added pyridinium chlorochromate/Celite (1:1 w/w, 6.51 g, 30.4 mmol). The mixture was stirred for 3 h, and solvent of the resulting solution was reduced under a vacuum and the residue purified by flash column to give 2,2-dimethyl-3-((3-methylbut-2-en-1-yl)oxy)propanal **S1b** (3.28 g, 95%.) Spectroscopic data of **S1b**: ^{1}H NMR (δ, $CDCl_3$, 400 MHz) 9.51 (s, 1H, CHO); 5.24 (m, 1H, HC═); 3.90 (d, 2H, $^3J_{HH}$ = 7.07 Hz, OCH_2); 3.36 (s, 2H, OCH_2); 1.69, 1.60, 1.03 (s, 12H, 4 CH_3). ^{13}C{^{1}H}NMR (δ, $CDCl_3$, 100 MHz) 205.5 (CH═O); 136.9 (C═); 120.9 (CH═); 74.9, 67.9 (2 OCH_2); 47.0 (C); 25.7, 19.0, 18.0 (4 CH_3). HRMS (ESI) m/z [M + H]$^+$ Calcd for $C_{10}H_{19}O_2^+$: 171.1380; Found: 171.1375. To a solution of **S1b** (3.28 g, 19.3 mmol) in THF (30 mL), was added ethynylmagnesium bromide (46.2 mL, 23.1 mmol) at room temperature under nitrogen. The solution was stirred for 14 h. After quenching by aqueous NH_4Cl solution (30 mL), the solution was extracted with ether (3 × 20 mL), then the mixture dried over sodium sulfate and after filtration, the filtrate was concentrated under reduced pressure and the residue eluted through a silica column (hexane/EA: 4/1) to give compound **1** (3.39 g, 90% yield). Spectroscopic data of **1**: ^{1}H NMR (δ, $CDCl_3$, 400 MHz) 5.29 (m, 1H, HC═); 4.14 (dd, 1H, $^3J_{HH}$ = 7.11 Hz, $^4J_{HH}$ = 1.96 Hz, CH); 3.94 (m, 2H, OCH_2); 3.77 (d, 1H, $^3J_{HH}$ = 7.11 Hz, OH); 3.58, 3.20 (2d, 2H, $^2J_{HH}$ = 8.93 Hz, OCH2); 2.41 (d, 1H, $^4J_{HH}$ = 1.96 Hz, ≡CH); 1.71, 1.64, 1.06, 0.94 (s, 12H, 4 CH_3). ^{13}C{^{1}H}NMR (δ, $CDCl_3$, 100 MHz) 137.4 (═C); 120.6 (HC═); 83.5 (≡C); 77.9 (HC≡); 73.3, 70.8 (2 OCH_2); 68.0 (CH); 38.7 (C); 25.7, 22.2, 21.0, 18.0 (4 CH_3). HRMS (ESI) m/z [M + Na]$^+$ Calcd for $C_{12}H_{20}NaO_2^+$: 219.1356; Found: 219.1359.

Synthesis of ***2***. At room temperature, to a suspension of 60% of NaH (0.78 g, 32.3 mmol) in THF (10 mL) is added dropwise a THF solution (30 mL) of 1,1-bis(hydroxymethyl)cyclopropane (3.00 g, 29.4 mmol) with stirring for 30 min, and the resulting mixture is then heated to reflux for 1h. After cooling to room temperature, to this solution is added 1-bromo-3-methyl-2-butene (4.13 mL, 35.3 mmol) slowly in 1 h, and the mixture is heated to reflux for 8 h. The resulting solution is treated with water (50 mL) and extracted with ethyl acetate (2 × 100 mL). The organic layer is washed with brine, dried over magnesium sulfate and concentrated under reduced pressure to afford crude product (1-(((3-methylbut-2-en-1-yl)oxy)methyl)cyclopropyl)-methanol **S2a** (3.05 g, 63%) that is purified by chromatography through a silica gel column (hexane/EA: 4/1). Spectroscopic data of **S2a**: ^{1}H NMR (δ, $CDCl_3$, 400 MHz) 5.31 (m, 1H, HC═); 3.96 (d, 2H, $^3J_{HH}$ = 6.8 Hz, OCH_2); 3.52 (s, 2H, OCH_2); 3.38 (s, 2H, OCH_2); 2.64 (br, 1H, OH); 1.72, 1.64 (s, 6H, 2 CH_3); 0.51 (m, 2H, CH_2); 0.46 (m, 2H, CH_2). ^{13}C{^{1}H}NMR (δ, $CDCl_3$, 100 MHz) 136.2 (C═); 120.1 (HC═); 75.6, 68.3, 66.7 (OCH_2); 21.6 (C); 24.9, 17.1, (2 CH_3); 7.9 (2 CH_2). HRMS (ESI) m/z [M + Na]$^+$ Calcd for $C_{10}H_{18}NaO_2^+$: 193.1204; Found: 193.1212. To a solution of **S2a** (3.05 g, 20.3 mmol) in CH_2Cl_2 (50 mL), was slowly added pyridinium chlorochromate/Celite (1:1 w/w, 5.8 g, 30.4 mmol). The resulting mixture was stirred for 3 h, and the resulting solution was filtered through a bed of Celite and dried. The residue was purified by flash column to give 1-(((3-methylbut-2-en-1-yl)oxy)methyl)-cyclopropanecarbaldehyde **S2b** (2.83 g, 94% yield). Spectroscopic data of **S2b**: ^{1}H NMR (δ, $CDCl_3$, 400 MHz) 9.04 (s, 1H, CHO); 5.31 (m, 1H, HC═); 3.97 (d, 2H, $^3J_{HH}$ = 6.9 Hz, OCH_2); 3.62 (s, 2H, OCH_2); 1.72, 1.65 (s, 6H, 2 CH_3); 1.20 (m, 2H, CH_2); 1.09 (m, 2H, CH_2). ^{13}C{^{1}H}NMR (δ, $CDCl_3$, 100 MHz) 200.2 (CH = O); 136.3 (C═); 112.0 (CH =); 68.5, 66.6 (2 OCH_2); 31.4 (C); 24.9, 17.1 (2 CH_3); 12.0 (2 CH_2). HRMS (ESI) m/z [M + Na]$^+$ Calcd for $C_{10}H_{16}NaO_2^+$: 191.1043; Found: 191.1054. To a solution of **S2b** (2.83 g, 16.8 mmol) in THF (30 mL), is added ethynylmagnesium bromide (42 mL, 20.2 mmol) at 0 °C under nitrogen. The solution is stirred for 12 h. After quenching by aqueous NH_4Cl solution (30 mL), the solution is extracted with ethyl acetate (3 × 20 mL), then the organic portion is dried over magnesium sulfate and concentrated under reduced pressure and eluted through a silica gel column (hexane/EA: 4/1) to give **2** (2.50 g, 91% yield). Spectroscopic data of **2**: ^{1}H NMR (δ, $CDCl_3$, 400 MHz) 5.31 (m, 1H, HC═); 4.04, 3.78 (2 d, 2H, $^3J_{HH}$ = 7.4 Hz, OCH_2); 4.01 (dd, 1H, $^3J_{HH}$ = 9.7 Hz, $^4J_{HH}$ = 2.3 Hz, CH); 3.98 (s, 2H, OCH_2); 3.05 (d, 1H, $^3J_{HH}$ = 9.7 Hz, OH); 2.43 (d, 1H, $^4J_{HH}$ = 2.3 Hz, ≡CH); 1.72, 1.65 (s, 6H, 2 CH_3); 0.63 (m, 4H, 2 CH_2). ^{13}C{^{1}H}NMR (δ, $CDCl_3$, 100 MHz) 137.6 (═C); 120.7 (HC═); 83.1 (≡C); 75.5 (HC≡); 73.0, 68.5 (2 OCH_2); 67.7 (CH); 25.8 (CH_3); 24.8 (C) 18.1 (CH_3); 10.9, 7.5 ($2CH_2$). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.26; H, 9.57. HRMS (ESI) m/z [M + Na]$^+$ Calcd for $C_{12}H_{18}NaO_2^+$: 217.1199; Found: 217.1227.

Synthesis of ***3***. To a suspension of NaH (1.18 g, 18.6 mmol) in THF (10 mL) was added at room temperature, dropwise a THF solution (30 mL) of 2,2-dimethyl-1,3-propandiol (2.79 g, 26.8 mmol) with stirring for 30 min, and the resulting mixture was then heated to reflux for 1h. After cooling to room temperature, to this solution was added (2-bromoethylidene)cyclopentane (3.5 mL, 29.5 mmol) slowly in 1 h, and the mixture was heated to reflux for 8 h. The resulting solution was treated with water and extracted with ethyl acetate. The organic layer was washed with brine, dried over sodium sulfate and after filtration dried under reduced pressure to afford the crude product 3-(2-cyclopentylideneethoxy)-2,2-dimethylpropan-1-ol **S3a** (3.18 g, 60%) that was purified by chromatography through a silica column (hexane/EA: 4/1). Spectroscopic data of **S3a**: ^{1}H NMR (δ, $CDCl_3$, 400 MHz) 5.38 (m, 1H, HC═); 3.91 (m, 2H, OCH_2); 3.47 (s, 1H, OH); 3.41 (d, 2H, $^2J_{HH}$ = 5.84 Hz, OCH_2); 3.25 (s, 2H, OCH_2); 2.22, 1.62 (m, 8H, 4 CH_2); 0.89 (s, 6H, 2 CH_3). ^{13}C{^{1}H}-NMR (δ, $CDCl_3$, 100 MHz) 139.7 (═C); 119.8 (HC═); 77.5, 72.2, 69.3 (3 OCH_2); 39.6 (C); 33.5, 26.1, 25.8 (4 CH_2); 22.6 (2 CH_3). HRMS (ESI) m/z [M + Na]$^+$ Calcd for $C_{12}H_{22}NaO_2^+$: 221.1512; Found: 221.1522. To a solution of **S3a** (3.18 g, 16.1 mmol) in CH_2Cl_2 (50 mL), was slowly added pyridinium chlorochromate/Celite (1:1 w/w, 6.91 g, 32.1 mmol). The resulting mixture was stirred for 3 h, and the resulting solution was dried under a vacuum and the residue was purified by flash column to give 3-(2-cyclopentylideneethoxy)-2,2-dimethylpropanal **S3b** (2.99 g, 95%.) Spectroscopic data of **S3b**: ^{1}H NMR (δ, $CDCl_3$, 400 MHz) 9.53 (s, 1H, CHO); 5.36 (m, 1H, HC═); 3.90 (m, 2H, OCH_2): 3.38 (s, 2H, OCH_2); 2.22, 1.61 (m, 8H, 4 CH_2); 1.05 (s, 6H, 2 CH_3). ^{13}C{^{1}H}NMR (δ, $CDCl_3$, 100 MHz) 206.42 (CHO); 142.36 (═C); 123.54 (HC═); 77.52, 68.15 (2 OCH_2); 42.13 (C); 33.49, 28.62, 25.82 (4 CH_2); 18.62 (2 CH_3). HRMS (ESI) m/z [M + Na]$^+$ Calcd for $C_{12}H_{20}NaO_2^+$: 219.1356; Found: 219.1362. To a solution of **S3b** (2.99 g, 15.2 mmol) in THF (30 mL), was added ethynylmagnesium bromide (38.4 mL, 19.2 mmol) at room temperature under nitrogen. The solution was stirred for 14 h. After quenching by aqueous NH_4Cl solution (30 mL), the solution was extracted with ether (3 × 20 mL), then dried over sodium

DOI: 10.1021/acs.joc.6b00260
J. Org. Chem. 2016, 81, 4494−4505

sulfate and concentrated under reduced pressure and the residue eluted through a silica column (hexane/EA: 4/1) to give **3** (3.04 g, 90% yield). Spectroscopic data of **3**: ^{1}H NMR (δ, $CDCl_3$, 400 MHz) 5.36−5.42 (m, 1H, HC═); 4.15 (dd, 1H, $^3J_{HH}$ = 7.10 Hz, $^4J_{HH}$ = 2.00 Hz, CH); 3.93 (m, 2H, OCH_2); 3.74 (d, 1H, $^3J_{HH}$ = 7.10 Hz, OH); 3.58, 3.21 (2d, 2H, $^2J_{HH}$ = 9.09 Hz, OCH_2); 4.15 (d, 1H, $^4J_{HH}$ = 2.00 Hz, ≡CH); 2.22 (dt, 4H, $^3J_{HH}$ = 19.12 Hz, $^4J_{HH}$ = 6.67 Hz, 2 CH_2); 1.63 (m, 4H, 2 CH_2). $^{13}C\{^1H\}$NMR (δ, $CDCl_3$, 100 MHz) 148.4 (═C); 116.0 (HC═); 83.3 (≡C); 77.5, 69.3 (2 OCH_2); 73.1 (≡CH); 70.3 (CH); 38.6 (C); 33.5, 28.6, 26.1, 25.8 (4 CH_2); 21.9, 20.7 (2 CH_3). HRMS (ESI) m/z $[M + Na]^+$ Calcd for $C_{14}H_{22}NaO_2^+$: 245,1512; Found: 245.1508.

Synthesis of ***4***. Compound **4** (1.4 g, 92%) as a clear liquid was prepared from 2-(4-methylpent-3-en-1-yl)benzaldehyde **S4** (1.3 g, 6.9 mmol) by a similar method mentioned below for **5**. Product **4** was purified by flash chromatography (SiO_2, 4:1 hexanes/EtOAc). Spectroscopic data of **4**: ^{1}H NMR (δ, $CDCl_3$, 400 MHz) 7.70 (d, 1H, $^3J_{HH}$ = 7.5 Hz, Ph); 7.30−7.20 (m, 3H, Ph); 5.68 (d, 1H, $^4J_{HH}$ = 2.3 Hz, CH); 5.20 (t, 1H, $^3J_{HH}$ = 7.1 Hz, ═CH); 2.75 (m, 2H, CH_2); 2.63 (d, 1H, $^4J_{HH}$ = 2.3 Hz, ≡CH); 2.43 (br, 1H, OH); 2.34, 2.30 (2 d, 2H, $^2J_{HH}$ = 7.5 Hz, CH_2); 1.70 (s, 3H, CH_3); 1.55 (s, 3H, CH_3). $^{13}C\{^1H\}$NMR (δ, $CDCl_3$, 100 MHz) 139.9; 137.7; 132.7; 129.8; 128.6; 126.8; 126.4 (Ph, ═C); 123.4 (═CH); 83.8 (≡C); 74.6 (≡CH); 61.5 (CH); 32.3; 29.9 (2 CH_2); 25.6; 17.6 (2 CH_3). Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 84.06; H, 8.43. HRMS (ESI) m/z $[M + Na]^+$ Calcd for $C_{15}H_{18}NaO^+$: 237.1250; Found: 237.1257.

Synthesis of ***4′***. Compound **4′** (2.2 g, 88%) as a clear liquid after flash chromatography (SiO_2, 4:1 hexanes/EtOAc) was similarly prepared from 4-methoxy-2-(4-methylpent-3-en-1-yl)benzaldehyde **S4′** (2.2 g, 10 mmol) by the method described below for **5**. Spectroscopic data of **4′**: ^{1}H NMR (δ, $CDCl_3$, 400 MHz) 7.62 (d, 1H, $^3J_{HH}$ = 8.0 Hz, Ph); 6.77−6.73 (m, 2H, Ph); 5.61 (dd, 1H, $^3J_{HH}$ = 5.5 Hz, $^4J_{HH}$ = 2.2 Hz, CH); 5.18 (septet of triplets, 1H, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.5 Hz, ═CH); 3.79 (s, 3H, OCH_3); 2.73 (m, 2H, CH_2); 2.62 (d, 1H, $^4J_{HH}$ = 2.2 Hz, ≡CH); 2.32, 2.28 (2 d, 2H, $^2J_{HH}$ = 7.8 Hz, CH_2); 2.14 (br, 1H, OH); 1.68 (s, 3H, CH_3); 1.53 (s, 3H, CH_3). $^{13}C\{^1H\}$NMR (δ, $CDCl_3$, 100 MHz) 159.7; 141.7; 132.7; 130.3; 128.5; 123.4; 115.4 (Ph, ═C); 111.5 (═CH); 84.0 (≡C); 74.4 (≡CH); 61.3 (CH); 55.2 (OCH_3); 32.5; 29.8 (2 CH_2); 25.7; 17.6 (2 CH_3). Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.60; H, 8.26. HRMS (ESI) m/z $[M + Na]^+$ Calcd for $C_{16}H_{20}NaO_2^+$: 267.1356; Found: 267.1360.

Synthesis of ***5***. To a Schlenk flask charged with 2-(3-methylbut-2-en-1-yl)benzaldehyde **S5** (1.7 g, 9.8 mmol) and 20 mL of dry THF at −78 °C was slowly added ethynylmagnesium bromide (29 mL, 15 mmol) under nitrogen and the solution was slowly warmed to room temperature. Then the solution was stirred for 12 h. The reaction was quenched with aqueous sat. NH_4Cl solution (30 mL), then extracted by diethyl ether (3 × 20 mL), and the combined organic layers were dried with $MgSO_4$ and after filtration concentrated under reduced pressure. The crude product was purified by flash chromatography (SiO_2, 4:1 hexanes/EtOAc) to yield **5** (1.7 g, 85%) as a yellow oil. Spectroscopic data of **5**: ^{1}H NMR (δ, $CDCl_3$, 400 MHz) 7.67 (m, 1H, Ph); 7.27−7.17 (m, 3H, Ph); 5.63 (dd, 1H, $^3J_{HH}$ = 5.7 Hz, $^4J_{HH}$ = 2.2 Hz, CH); 5.24 (septet of triplets, 1H, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.5 Hz, ═CH); 3.51, 3.44 (2 dd, 2H, $^2J_{HH}$ = 15.7 Hz, $^3J_{HH}$ = 7.5 Hz, CH_2); 2.62 (d, 1H, $^4J_{HH}$ = 2.2 Hz, ≡CH); 2.21 (d, 1H, $^3J_{HH}$ = 5.7 Hz, OH); 1.72 (br, 6H, 2 CH_3). $^{13}C\{^1H\}$NMR (δ, $CDCl_3$, 100 MHz) 139.4; 137.7; 133.1; 129.7; 128.8; 126.8; 126.5 (Ph, ═C); 122.8 (═CH); 83.5 (≡C); 74.7 (≡CH); 61.8 (CH); 31.2 (CH_2); 25.7, 17.9 (2 CH_3). Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 84.01; H, 8.09. HRMS (ESI) m/z $[M + Na]^+$ Calcd for $C_{14}H_{16}NaO$: 223.1094; Found: 223.1097.

Synthesis of ***6***. Compound **6** (0.81 g, 90%) was similarly prepared from 2-(5-methylhex-4-en-1-yl)benzaldehyde **S6** (0.80 g, 4.0 mmol) by the method described above for **5** to yield the product as a clear liquid after flash chromatography (SiO_2, 4:1 hexanes/EtOAc). Spectroscopic data of **6**: ^{1}H NMR (δ, $CDCl_3$, 400 MHz) 7.67 (dd, 1H, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 2.0 Hz, Ph); 7.28−7.17 (m, 3H, Ph); 5.65 (d, 1H, $^3J_{HH}$ = 5.1 Hz, $^4J_{HH}$ = 2.1 Hz, CH); 5.15 (septet of triplets, 1H, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.3 Hz, ═CH); 2.73 (m, 2H, CH_2); 2.62 (d, 1H, $^4J_{HH}$ = 2.1 Hz, ≡CH); 2.20 (br, 1H, $^3J_{HH}$ = 5.1 Hz, OH); 2.08, 2.04 (2 d, 2H, $^2J_{HH}$ = 7.0 Hz, CH_2); 1.70 (s, 3H, CH_3); 1.66 (t, 2H, $^4J_{HH}$ = 7.6 Hz, CH_2); 1.60 (s, 3H, CH_3). $^{13}C\{^1H\}$NMR (δ, $CDCl_3$, 100 MHz) 140.3; 137.6; 132.1; 129.7; 128.6; 126.8; 126.3 (Ph, ═C); 124.1 (═CH); 83.8 (≡C); 74.6 (≡CH); 61.5 (CH); 31.8; 31.5; 27.9 (3 CH_2); 25.7; 17.8 (2 CH_3). Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.13; H, 8.83. HRMS (ESI) m/z $[M + Na]^+$ Calcd for $C_{16}H_{20}NaO$: 251.1407; Found: 251.1415.

Synthesis of ***7***. A mixture of [Ru]Cl (148 mg, 0.21 mmol), **1** (50 mg, 0.25 mmol), and NH_4PF_6 (85 mg, 0.32 mmol), in CH_2Cl_2 (20 mL) was stirred at ambient temperature for 1 day. The resulting brown solution was filtered through a bed of Celite to remove the insoluble salts, and the pad was eluted with CH_2Cl_2 until the eluent was colorless, then the solvent of the filtrate were removed under a vacuum and the solid residue was extracted with a small volume of CH_2Cl_2 followed by reprecipitation by a 50 mL of stirred diethyl ether. Precipitates thus formed were collected in a glass frit, washed with diethyl ether/hexane 1:1 and dried under a vacuum. The product was obtained as a deep yellow powder identified as **7** (147 mg, 68% yield). The ratio of *trans*- and *cis*-isomers is 2:1. Spectroscopic data for the *trans*-isomers: ^{1}H NMR (δ, CD_2Cl_2, 400 MHz) 7.42−6.91 (m, 70H, Ph); 5.06 (s, 5H, Cp); 5.01 (s, 1H, HC═); 4.82 (s, 1H, HC═); 4.07 (dt, 1H, $^3J_{HH}$ = 9.8 Hz, $^4J_{HP}$ = 2.5 Hz, CβH); 3.85 (m, 1H, OCH_2); 3.50 (m, 1H, OCH_2); 3.07 (m, 1H, OCH_2); 3.02 (m, 1H, OCH_2); 2.62 (t, 1H, $^3J_{HH}$ = 10.3 Hz, CH); 2.09 (dt, 1H, $^3J_{HH}$ = 11.4 Hz, $^3J_{HH}$ = 4.2 Hz, CH); 1.73, 0.97, 0.82 (s, 9H, 3 CH_3). $^{13}C\{^1H\}$NMR (δ, CD_2Cl_2, 100 MHz) 343.7 (t, $^2J_{CP}$ = 14.9 Hz, Cα); 145.3 (═C); 135.4−128.3 (Ph); 114.3 (Cβ); 113.1 (CH_2 =); 94.7 (Cp); 78.7, 72.3 (2 OCH_2); 47.6, 45.7 (2 CH); 35.3 (C); 26.0, 22.7, 19.3 (3 CH_3). $^{31}P\{^1H\}$NMR (δ, CD_2Cl_2, 162 MHz) 43.75, 43.12 (2d, $^2J_{PP}$ = 26.5 Hz, PPh_3). Spectroscopic data for the *cis*-isomer: ^{1}H NMR (δ, CD_2Cl_2, 400 MHz) 7.93−6.99 (m, 70H, Ph); 5.12 (s, 5H, Cp); 5.10 (s, 1H, ═CH_2); 4.68 (s, 1H, ═CH_2); 4.44 (d, 1H, $^3J_{HH}$ = 10.5 Hz, CβH); 3.80 (dd, 1H, $^2J_{HH}$ = 11.9 Hz, $^3J_{HH}$ = 3.4 Hz, OCH_2); 3.43 (t, 1H, $^2J_{HH}$ = 11.9 Hz, OCH_2); 3.25 (m, 1H, OCH_2); 3.09 (2d, 1H, $^2J_{HH}$ = 12.0 Hz, OCH_2); 2.96 (dd, 1H, $^3J_{HH}$ = 10.5 Hz, $^3J_{HH}$ = 3.6 Hz, CH); 2.79 (br, 1H, CH); 1.80, 1.21, 0.86 (s, 9H, 3 CH_3). $^{13}C\{^1H\}$NMR (δ, CD_2Cl_2, 100 MHz) 342.7 (t, $^2J_{CP}$ = 15.1 Hz, Cα); 145.3 (═C); 135.4−128.3 (Ph); 111.2 (Cβ); 111.0 (CH_2 =); 94.6 (Cp); 72.5, 65.9 (2 OCH_2); 43.1, 42.2 (2 CH); 34.4 (C); 26.3, 24.4, 23.2 (3 CH_3). $^{31}P\{^1H\}$NMR (δ, CD_2Cl_2, 162 MHz) 45.22, 43.50 (2d, $^2J_{PP}$ = 26.8 Hz, PPh_3). Anal. Calcd for $C_{53}H_{53}F_6OP_3Ru$: C, 62.78; H, 5.27. Found: C, 62.37; H, 5.14. HRMS (ESI) m/z $[M]^+$ Calcd for $C_{53}H_{53}OP_2Ru^+$: 869.2610; Found: 869.2624.

Synthesis of ***8***. A mixture of [Ru]Cl (200 mg, 0.28 mmol), **2** (64 mg, 0.34 mmol), and NH_4PF_6 (90 mg, 0.64 mmol), in CH_2Cl_2 (20 mL) was stirred at ambient temperature for 18 h. The resulting brown solution was filtered through a bed of Celite to remove the insoluble salts, and the pad was eluted with CH_2Cl_2 until the eluent was colorless, then solvent of the filtrate was removed under a vacuum and the solid residue was extracted with a small volume of CH_2Cl_2 followed by reprecipitation by a 50 mL of stirred diethyl ether. Precipitates thus formed were collected in a glass frit, and then were dissolved by CH_2Cl_2 and passed through a bed of neutral-Al_2O_3 column with hexane as eluent. Collecting the yellow band followed by drying under a vacuum resulted in the yellow oil. Then a solution of $HBF_4{\cdot}Et_2O$ (48%, 0.02 mL, 0.11 mmol) in diethyl ether (20 mL) was added dropwise at 0 °C to a stirred solution of the yellow oil in 10 mL of ether. Immediately, insoluble solid precipitated but the addition was continued until no further solid was formed. The solution was then decanted, and the yellow solid was washed with diethyl ether and dried under a vacuum to give the deep yellow powder identified as *trans*-**8** (118 mg, 50% yield). Spectroscopic data of *trans*-**8**: ^{1}H NMR (δ, $CDCl_3$, 400 MHz) 7.93−6.99 (m, 30H, Ph); 5.11 (s, 5H, Cp); 5.08 (s, 1H, ═CH_2); 4.85 (s, 1H, ═CH_2); 3.93 (dd, 1H, $^2J_{HH}$ = 11.5 Hz, $^3J_{HH}$ = 4.0 Hz, OCH_2); 3.77 (m, 2H, CβH, OCH_2); 3.40 (t, 1H, $^2J_{HH}$ = 11.5 Hz, OCH_2); 3.09 (m, 2H, CγH, OCH_2); 2.09 (dt, 1H, $^3J_{HH}$ = 11.3 Hz,

DOI: 10.1021/acs.joc.6b00260
J. Org. Chem. 2016, 81, 4494−4505

$^{3}J_{HH}$ = 4.0 Hz, CH); 1.80 (s, 3H, CH_3); 0.52, 0.23 (m, 4H, 2 CH_2). $^{13}C\{^1H\}$NMR (δ, $CDCl_3$, 100 MHz) 344.3 (t, $^{2}J_{CP}$ = 14.2 Hz, Cα); 145.5 (=C); 134.9−128.6 (Ph); 112.8 (Cβ, $=CH_2$); 95.0 (Cp); 76.4, 72.3 (2 OCH_2); 51.7, 40.2 (2 CH); 29.8 (C); 23.6 (CH_3); 6.72, 6.6 (2 CH_2). $^{31}P\{^1H\}$NMR (δ, $CDCl_3$, 162 MHz) 44.76, 42.89 (2d, $^{2}J_{PP}$ = 27.3 Hz, PPh_3). Anal. Calcd for $C_{53}H_{51}F_6OP_3Ru$: C, 62.90; H, 5.08. Found: C, 63.07; H, 5.24. HRMS (ESI) m/z $[M]^+$ Calcd for $C_{53}H_{51}OP_2Ru^+$: 867.2454; Found: 867.2449.

*Synthesis of **9** and **10**.* The mixture of **7** (75 mg, 0.086 mmol) and NaOMe (6 mg, 0.11 mmol) in MeOH (30 mL) was stirred for 5 min at room temperature. After that, solvent of the solution was removed under a vacuum and then 20 mL of diethyl ether was added and the mixture was stirred using an ultrasonic cleaner. The solution was filtered through neutral Al_2O_3 to remove the insoluble salts, and then solvent of the filtrate was removed under a vacuum. The yellow final product was obtained by chromatography identified as **9** (67 mg, 90% yield). Spectroscopic data of **9**: The ratio of *trans*- and *cis*-isomers is 2:1. Spectroscopic data for the *trans*-isomer: ^1H NMR (δ, C_6D_6, 400 MHz) 7.56−7.65 (m, 20H, Ph); 6.95−6.96 (m, 30H, Ph); 4.96 (s, 1H, $=CH_2$); 4.93 (s, 1H, $=CH_2$); 4.40 (s, 5H, Cp); 4.11,3.35 (dd, 2H, $^{2}J_{HH}$ = 11.4 Hz, $^{3}J_{HH}$ = 4.6 Hz, OCH_2); 3.70, 3.16 (2d, 2H, $^{2}J_{HH}$ = 10.8 Hz, OCH_2); 2.81 (m, 1H, CH); 2.69 (d, 1H, $^{3}J_{HH}$ = 11.4 Hz, CH); 1.79 (s, 3H, CH_3); 1.43 (s, 3H, CH_3); 1.07 (s, 3H, CH_3). $^{13}C\{^1H\}$-NMR (δ, C_6D_6, 100 MHz) 146.2 (=C); 127.5−140.5 (Ph); 112.7 ($=CH_2$); 110.6 (Cβ); 92.2 (t, $^{2}J_{CP}$ = 25.0 Hz, Cα); 85.7 (Cp); 79.1 (OCH_2); 73.5 (OCH_2); 48.7 (CH); 46.2 (CH); 35.6 (C); 26.3, 20.9, 20.7 (3 CH_3). $^{31}P\{^1H\}$NMR (δ, C_6D_6, 162 MHz) 51.22 (s, PPh_3). Spectroscopic data for the *cis*-isomer: ^1H NMR (δ, C_6D_6, 400 MHz) 7.56−7.65 (m, 20H, Ph); 6.95−6.96 (m, 30H, Ph); 4.93 (s, 1H, $=CH_2$); 4.66 (s, 1H, $=CH_2$); 4.41 (s, 5H, Cp); 4.37 (m, 1H, OCH_2), 4.28 (dd, 1H, $^{2}J_{HH}$ = 10.6 Hz, $^{3}J_{HH}$ = 3.3 Hz, OCH_2); 4.03, 3.41 (2d, 2H, $^{2}J_{HH}$ = 10.8 Hz, OCH_2); 3.05 (br, 1H, CH); 2.81 (m, 1H, CH); 1.91 (s, 3H,CH_3); 1.29 (s, 3H, CH_3); 1.01 (s, 3H, CH_3). $^{13}C\{^1H\}$-NMR (δ, C_6D_6, 100 MHz) 146.7 (=C); 127.5−140.5 (Ph); 109.1 ($=CH_2$); 108.5 (Cβ); 93.8 (t, $^{2}J_{CP}$ = 25.0 Hz, Cα); 85.7 (Cp); 74.1 (OCH_2); 67.8 (OCH_2); 44.8 (CH); 42.6 (CH); 35.2 (C); 26.7, 25.6, 22.6 (3 CH_3). $^{31}P\{^1H\}$NMR (δ, C_6D_6, 162 MHz) 52.16, 50.34 (2d, $^{2}J_{PP}$ = 38.0 Hz, PPh_3). Anal. Calcd for $C_{53}H_{52}OP_2Ru$: C, 73.34; H, 6.04. Found: C, 73.27; H, 6.14. HRMS (ESI) m/z $[M + H]^+$ Calcd for $C_{53}H_{53}OP_2Ru^+$: 869.2610; Found: 869.2634.

To a mixture of **9** (165 mg, 0.19 mmol) and KPF_6 (39 mg, 0.21 mmol) in CH_2Cl_2 (20 mL) in a Schlenk flask under nitrogen, was added allyl bromide (26 mg, 0.21 mmol). The resulting solution was stirred for 8 h. After that, the solution was filtered through a bed of Celite to remove the insoluble salts, then the solvent of the filtrate was removed under a vacuum and the solid residue was extracted with a small volume of CH_2Cl_2 followed by reprecipitation by adding to a 50 mL of stirred ethyl ether solution. Precipitates thus formed were collected in a glass frit, washed with ethyl ether/hexane 1:1 and dried under a vacuum. The final product was obtained as a light pink powder identified as **10** (160 mg, 93% yield). Spectroscopic data of **10**: The ratio of *trans*- and *cis*-isomers is 3:1. Spectroscopic data for the *trans*-isomer: ^1H NMR (δ, $CDCl_3$, 400 MHz) 6.68−7.75 (m, 50H, Ph); 6.09 (m, 1H, =C(C)H); 5.13 (s, 5H, Cp); 5.28−4.91 (m, 4H, 2 $=CH_2$); 3.90, 2.86 (2d, 2H, $^{2}J_{HH}$ = 10.3 Hz, OCH_2); 3.27, 2.69 (2d, 2H, $^{2}J_{HH}$ = 10.9 Hz, OCH_2); 2.44 (br, 2H, 2 CH); 1.81, 1.10, 0.63 (s, 9H, 3 CH_3). $^{13}C\{^1H\}$NMR (δ, $CDCl_3$, 100 MHz) 349.9 (t, $^{3}J_{CP}$ = 12.2 Hz, Cα); 144.2 (=C); 139.2(=C(C)H); 122.4−135.1 (Ph, Cβ, =C); 116.5, 113.7 (2 $=CH_2$); 94.4 (Cp); 80.6, 73.9 (2 OCH_2); 42.9, 42.9 (2 CH); 36.7 (C); 28.4 (CH_2); 26.5, 23.6, 22.1 (3 CH_3). $^{31}P\{^1H\}$NMR (δ, $CDCl_3$, 162 MHz) 40.56 (br, PPh_3). Spectroscopic data for the *cis*-isomer: ^1H NMR (δ, $CDCl_3$, 400 MHz) 6.68−7.75 (m, 50H, Ph); 5.95 (m, 1H, =C(C)H); 5.38, 5.04 (m, 4H, 2 $=CH_2$); 5.17 (s, 5H, Cp); 3.79−3.04 (m, 6H, CH_2, 2 OCH_2); 2.67, 2.50 (m, 2H, 2 CH); 1.81, 0.96, 0.92 (s, 9H, 3 CH_3). $^{13}C\{^1H\}$NMR (δ, $CDCl_3$, 100 MHz) 351.0 (m, Cα); 145.6 (=C); 137.8 (=C(C)H); 122.4−135.1 (Ph, Cβ, =C); 94.1 (Cp); 73.9, 69.6 (2 OCH_2); 45.0, 39.6 (2 CH); 35.9 (C); 29.7 (CH_2); 28.1, 24.9, 24.1 (3 CH_3). $^{31}P\{^1H\}$NMR (δ, $CDCl_3$, 162 MHz) 40.91 (br, PPh_3). Anal. Calcd for $C_{56}H_{57}F_6OP_3Ru$: C, 63.81; H, 5.45. Found: C, 63.61; H, 5.34. HRMS (ESI) m/z $[M]^+$ Calcd for $C_{56}H_{57}OP_2Ru^+$: 909.2923; Found: 909.2948.

*Synthesis of **11**.* A solution of **7** (150 mg, 0.16 mmol) in $CDCl_3$ (1.5 mL) and CH_3CN (97 mg, 2.4 mmol, 0.12 mL) in an NMR tube was heated at 50 °C for 24 h. Then the solvent was removed in vacuo and CH_2Cl_2 (1 mL) was used to extract the product and diethyl ether (6 mL) was then added. The pale-orange precipitates thus formed was filtered and washed with diethyl ether and dried under a vacuum to give $[Ru]NCCH_3^+$. The filtrate was evaporated to dryness under a vacuum and the crude product was purified by flash chromatography (silica gel, hexanes/EtOAc = 10/1) to afford **11** (26 mg, 93%). Spectroscopic data of **11**: The ratio of *trans*- and *cis*-isomers is 2:1. Spectroscopic data for the *trans*-isomer: ^1H NMR (δ, $CDCl_3$, 400 MHz) 4.93 (s, 1H, $=CH_2$); 4.84 (s, 1H, $=CH_2$); 3.86 (m, 1H, OCH_2); 3.53, 3.07 (2d, 2H, $^{2}J_{HH}$ = 11.4 Hz, OCH_2); 3.12 (t, 1H, $^{2}J_{HH}$ = 11.4 Hz, OCH_2); 2.47 (td, 1H, $^{2}J_{HH}$ = 11.4 Hz, $^{3}J_{HH}$ = 4.5 Hz, CH); 2.28 (dd, 1H, $^{2}J_{HH}$ = 11.4 Hz, $^{4}J_{HH}$ = 2.4 Hz, CH); 2.08 (d, 1H, $^{4}J_{HH}$ = 2.4 Hz, ≡CH); 1.75, 1.13, 0.97 (s, 9H, 3 CH_3). $^{13}C\{^1H\}$NMR (δ, $CDCl_3$, 100 MHz) 143.4 (=C); 113.2 ($=CH_2$); 83.3 (≡C); 78.0, 72.2 (2 OCH_2); 71.1 (≡CH); 45.2, 42.5 (2 CH); 33.7 (C); 25.2, 21.1, 19.8 (3 CH_3). Spectroscopic data for the *cis*-isomer: ^1H NMR (δ, $CDCl_3$): 4.86 (s, 1H, $=CH_2$); 4.54 (s, 1H, $=CH_2$); 3.86 (m, 1H, OCH_2); 3.64 (t, 1H, $^{2}J_{HH}$ = 11.0 Hz, OCH_2); 3.48, 3.25 (2d, 2H, $^{2}J_{HH}$ = 11.5 Hz, OCH_2); 2.60 (br, 2H, 2 CH); 2.13 (d, 1H, $^{4}J_{HH}$ = 2.4 Hz, ≡CH); 1.74, 1.16, 1.01 (s, 9H, 3 CH_3). ^{13}C NMR (δ, $CDCl_3$): 143.6 (=C); 110.6 ($=CH_2$); 81.9 (≡C); 73.3, 73.3 (2 OCH_2); 66.8 (≡CH); 40.8, 40.2 (2 CH); 33.4 (C); 24.8, 22.0, 21.1 (3 CH_3). Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.77; H, 10.24. HRMS (ESI) m/z $[M + H]^+$ Calcd for $C_{12}H_{19}O^+$: 179.1431; Found: 179.1422.

*Synthesis of **12**.* A mixture of $[Ru]NCCH_3^+$ (55 mg, 0.06 mmol), **2** (60 mg, 0.31 mmol), in $CHCl_3$ (10 mL) was heated to 60 °C for 24 h. Then the solvent was removed in vacuo and CH_2Cl_2 (1 mL) was used to extract the product and after filtration, *n*-hexane (60 mL) was then added. The pale-orange precipitates thus formed was filtered and washed with diethyl ether and dried under a vacuum to give $[Ru]NCCH_3^+$ PF_6^-. The filtrate was evaporated to dryness under a vacuum and the crude product purified by flash chromatography (silica gel, hexane/EtOAc = 10/1) to afford **12** (47 mg, 86%). The product consists of *trans*- and *cis*-isomers in a ratio of 3:1. Spectroscopic data for the *trans*-**12**: ^1H NMR (δ, $CDCl_3$, 400 MHz) 4.87 (s, 1H, $=CH_2$); 4.64 (s, 1H, $=CH_2$); 4.11 (dd, 1H, $^{2}J_{HH}$ = 11.2 Hz, $^{4}J_{HH}$ = 1.8 Hz, OCH_2); 3.93, (dd, 1H, $^{2}J_{HH}$ = 11.2 Hz, $^{4}J_{HH}$ = 3.8 Hz, OCH_2); 3.78 (t, 1H, $^{2}J_{HH}$ = 11.2 Hz, OCH_2); 2.88 (d, 1H, $^{2}J_{HH}$ = 11.6 Hz, OCH_2); 2.53 (td, 1H, $^{3}J_{HH}$ = 11.2 Hz, $^{3}J_{HH}$ = 2.1 Hz, CH); 2.17 (d, 1H, $^{4}J_{HH}$ = 2.1 Hz, ≡CH); 2.15 (br, 1H, CH); 1.74 (s, 3H, CH_3); 0.71, 0.56, 0.46 (m, 4H, 2 CH_2). $^{13}C\{^1H\}$NMR (δ, $CDCl_3$, 100 MHz) 143.3 (=C); 111.2 ($=CH_2$); 82.7 (≡C); 72.4 (OCH_2); 71.5 (≡CH); 66.9 (OCH_2); 44.7, 39.0 (2 CH); 23.0 (C); 22.3 (CH_3); 14.3, 8.7 (2 CH_2). Spectroscopic data for the *cis*-**12**: ^1H NMR (δ, $CDCl_3$, 400 MHz) 4.94, 4.86 (s, 2H, $=CH_2$); 3.91, 3.08 (2d, 2H, $^{2}J_{HH}$ = 11.6 Hz, OCH_2); 3.73 (dd, 1H, $^{2}J_{HH}$ = 11.6 Hz, $^{3}J_{HH}$ = 2.2 Hz, OCH_2); 3.31 (t, 1H, $^{3}J_{HH}$ = 11.3 Hz, OCH_2); 2.96 (dd, 1H, $^{3}J_{HH}$ = 10.9 Hz, $^{4}J_{HH}$ = 2.3 Hz, CH); 2.46 (dt, 1H, $^{3}J_{HH}$ = 11.3 Hz, $^{3}J_{HH}$ = 4.2 Hz, CH); 1.95 (d, 1H, $^{4}J_{HH}$ = 2.3 Hz, ≡CH); 1.77 (s, 3H, CH_3); 0.87, 0.76, 0.27 (m, 4H, 2 CH_2). $^{13}C\{^1H\}$NMR (δ, $CDCl_3$, 100 MHz) 143.6 (=C); 113.2 ($=CH_2$); 81.5 (≡C); 75.4 (≡CH); 72.1 (OCH_2); 70.6 (OCH_2); 49.4, 37.5 (2 CH); 21.6 (CH_3); 19.7 (C); 8.5, 6.3 (2 CH_2). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.57; H, 9.21. HRMS (ESI) m/z $[M + H]^+$ Calcd for $C_{12}H_{17}O^+$: 177.1274; Found: 177.1272.

*Synthesis of **13**.* A solution of **3** (55 mg, 0.24 mmol) and $[Ru]NCCH_3^+$ (55 mg, 0.07 mmol) in cosolvent of $CHCl_3$/MeOH in an NMR tube was heated at 60 °C for 24 h. Then the solvent was removed in vacuo and CH_2Cl_2 (1.0 mL) was used to extract the product and diethyl ether (6.0 mL) was then added. After filtration, the filtrate was evaporated to dryness under a vacuum and the crude product was purified by flash chromatography (silica gel, hexanes/EtOAc = 10/1) to afford **13** (22 mg, 45%). Spectroscopic data of **13**: The ratio of *trans*- and *cis*-isomers is 17:3. Spectroscopic data for the *trans*-isomer: ^1H NMR (δ, $CDCl_3$, 500 MHz) 5.52 (s, 1H, =CH);

DOI: 10.1021/acs.joc.6b00260
J. Org. Chem. 2016, 81, 4494−4505

3.84 (dd, 1H, $^2J_{HH}$ = 11.5 Hz, $^3J_{HH}$ = 4.6 Hz, OCH_2); 3.08 (t, 1H, $^2J_{HH}$ = 11.5 Hz, OCH_2); 3.50, 3.04 (2d, 2H, $^2J_{HH}$ = 11.3 Hz, OCH_2); 2.62 (td, 1H, $^3J_{HH}$ = 11.5 Hz, $^3J_{HH}$ = 4.6 Hz, CH); 2.29 (br, 4H, 2 CH_2); 2.24 (dd, 1H, $^3J_{HH}$ = 11.5 Hz, $^4J_{HH}$ = 2.1 Hz, CH); 2.04 (d, 1H, $^4J_{HH}$ = 2.1 Hz, ≡CH); 1.82 (quintet, 2H, $^3J_{HH}$ = 7.4 Hz, CH_2); 1.11, 0.93 (s, 6H, 2 CH_3). $^{13}C\{^1H\}$NMR (δ, $CDCl_3$, 125 MHz) 142.1 (C═); 126.8 (═CH); 83.7 (≡C); 78.0, 72.0 (2 OCH_2); 71.0 (HC≡); 43.0, 39.9 (2 CH); 33.7 (C); 33.1, 32.3, 23.2 (3 CH_2); 25.1, 19.7 (2 CH_3). Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.41; H, 9.88. HRMS (ESI) m/z $[M + Na]^+$ Calcd for $C_{14}H_{20}NaO^+$: 227.1407; Found: 227.1406.

*Synthesis of **14a** and **15a**.* A mixture of [Ru]Cl (230 mg, 0.32 mmol), **1** (62 mg, 0.32 mmol), and KPF_6 (77 mg, 0.42 mmol), in MeOH (30 mL) was stirred at 50 °C for 1 day. After that, the solvent was removed under reduced pressure and then 20 mL of CH_2Cl_2 was added. The solution was filtered through a bed of Celite to remove the insoluble salts, and the pad was eluted with CH_2Cl_2 until the eluent was colorless, then the solvent of the filtrate were removed under a vacuum and the solid residue was extracted with a small volume of CH_2Cl_2 followed by reprecipitation by a 50 mL of stirred diethyl ether. Precipitates thus formed were collected in a glass frit and dried under a vacuum to give the final as a deep red powder identified as **15a** (167 mg, 60% yield). The filtrate was evaporated to dryness under a vacuum and the crude product purified by chromatography (silica gel, hexanes/EtOAc = 10/1) to afford **14a** (20 mg, 30% yield). Spectroscopic data for the major diastereomer **14a**: ^1H NMR (δ, $CDCl_3$, 400 MHz) 5.62 (m, 2H, 2 ═CH); 3.86 (dd, 1H, $^2J_{HH}$ = 11.4 Hz, $^3J_{HH}$ = 4.6 Hz, OCH_2); 3.20 (s, 3H, OCH_3); 3.15−3.04 (m, 3H, 2 OCH_2); 2.32 (m, 1H, CH); 1.97 (m, 2H, CH_2); 1.93 (m, 1H, CH); 1.12, 1.10, 0.89 (s, 9H, 3 CH_3). $^{13}C\{^1H\}$NMR (δ, $CDCl_3$, 100 MHz) 126.6, 124.8 (2 ═CH); 74.9 (C); 74.0, 65.3 (2 OCH_2); 48.1 (OCH_3); 43.5, 36.8 (2 CH); 35.0 (CH_2); 33.3 (C); 26.2, 24.0, 21.4 (3 CH_3). Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.21; H, 10.68. HRMS (ESI) m/z $[M + Na]^+$ Calcd for $C_{13}H_{22}NaO_2^+$: 233.1517; Found: 223.1507. Spectroscopic data of **15a**: The ratio of *trans*- and *cis*-isomers is 3:1. Spectroscopic data for the *trans*-isomer: ^1H NMR (δ, $CDCl_3$, 400 MHz) 6.89−7.49 (m, 40H, Ph); 6.73 (s, 1H, HC(C) =); 4.86 (s, 5H, Cp); 4.41 (d, 1H, $^2J_{HH}$ = 16.5 Hz, CH_2); 4.01 (dd, 1H, $^2J_{HH}$ = 10.9 Hz, $^3J_{HH}$ = 4.4 Hz, OCH_2); 2.72 (t, 1H, $^2J_{HH}$ = 10.9 Hz, OCH_2); 3.43, 2.97 (2d, 2H, $^2J_{HH}$ = 11.3 Hz, OCH_2); 2.27 (dd, 1H, $^2J_{HH}$ = 16.5 Hz, $^3J_{HH}$ = 13.7 Hz, CH_2); 1.71 (br, 1H, CH); 1.34 (t, 1H, $^3J_{HH}$ = 11.1 Hz, CH_2); 0.99, 0.91, 0.81 (s, 9H, 3 CH_3). $^{13}C\{^1H\}$NMR (δ, $CDCl_3$, 100 MHz) 317.6 (t, $^2J_{CP}$ = 9.7 Hz, Cα); 151.5 (HC═); 148.2 (C═); 128.2−135.8 (Ph); 94.5 (Cp); 79.3 (OCH_2); 69.0 (OCH_2); 59.7 (CH_2); 48.4 (CH); 41.1 (CH); 32.9 (C); 23.3, 20.6, 18.9 (3 CH_3). $^{31}P\{^1H\}$NMR (δ, $CDCl_3$, 162 MHz) 45.26, 45.02 (2d, $^2J_{PP}$ = 29.1 Hz, PPh_3). Spectroscopic data for the *cis*-isomer: ^1H NMR (δ, $CDCl_3$, 400 MHz) 6.89−7.49 (m, 40H, Ph, HC(C) =); 4.86 (s, 5H, Cp); 4.17 (dd, 1H, $^2J_{HH}$ = 18.5 Hz, $^3J_{HH}$ = 3.4 Hz, CH_2); 3.61 (dd, 1H, $^2J_{HH}$ = 11.2 Hz, $^3J_{HH}$ = 4.8 Hz, OCH_2); 3.03 (t, 1H, $^2J_{HH}$ = 11.2 Hz, OCH_2); 3.43, 3.24 (2d, 2H, $^2J_{HH}$ = 12.5 Hz, OCH_2); 2.80 (m, 1H, CH_2); 2.34 (m, 1H, CH); 1.71 (br, 1H, CH); 1.07, 0.95, 0.87 (s, 9H, 3 CH_3). $^{13}C\{^1H\}$NMR (δ, $CDCl_3$, 100 MHz) 316.7 (t, $^2J_{CP}$ = 9.7 Hz, Cα); 151.5 (═CH); 148.4 (═C); 128.2−135.8 (Ph); 94.8 (Cp); 72.4 (OCH_2); 63.2 (OCH_2); 54.6 (CH_2); 42.0 (CH); 39.5 (CH); 31.3 (C); 26.2, 23.6, 23.1 (3 CH_3). $^{31}P\{^1H\}$NMR (δ, $CDCl_3$): 46.63, 44.56 (2d, $^2J_{PP}$ = 29.1 Hz, 2 PPh_3). Anal. Calcd for $C_{53}H_{53}F_6OP_3Ru$: C, 62.78; H, 5.27. Found: C, 62.71; H, 5.30. HRMS (ESI) m/z $[M]^+$ Calcd for $C_{53}H_{53}OP_2Ru^+$: 869.2610; Found: 869.2615.

*Synthesis of **16a**.* The solution of **2** (27 mg, 0.14 mmol) and [Ru]Cl (50 mg, 0.07 mmol) in a cosolvent of $CHCl_3$/MeOH (2:1) was heated to 60 °C for 1 day. Then the solvent was removed under a vacuum and 1 mL of CH_2Cl_2 was used to extract the crude product. This is followed by reprecipitation by a 50 mL of stirred *n*-hexane. The deep brown precipitates thus formed were filtered and washed with *n*-hexane and dried under a vacuum to give [Ru]Cl. The filtrate was evaporated to dryness under a vacuum and the crude product purified by flash chromatography (silica gel, hexane/EtOAc = 4/1) to afford **16a** (22 mg, 75%). The ratio of *trans*- and *cis*- isomers of **16a** is 5:1. Only the major diasteromer is assignable. Spectroscopic data for the major diastereomer **16a**: ^1H NMR (δ, $CDCl_3$, 400 MHz) 5.68 (m, 1H, ═C(C)H); 5.54 (m, 1H, ═C(C)H); 3.93 (dd, 1H, $^2J_{HH}$ = 11.6 Hz, $^3J_{HH}$ = 4.7 Hz, OCH_2) 3.65, 2.77 (2d, 2H, $^2J_{HH}$ = 11.7 Hz, OCH_2); 3.26 (d, 1H, $^2J_{HH}$ = 11.6 Hz, OCH_2); 3.23 (s, 3H, OCH_3); 2.30 (dt, 1H, $^3J_{HH}$ = 11.7 Hz, $^3J_{HH}$ = 4.7 Hz, CH); 2.03 (br, 2H, CH, CH_2); 1.12 (s, 3H, CH_3); 0.61, 0.38 (m, 4H, 2CH_2). $^{13}C\{^1H\}$NMR (δ, $CDCl_3$): 127.3, 126.5 (2 ═C); 74.8 (C), 72.0, 65.2 (2 OCH_2); 48.3 (OCH_3); 42.3, 39.7 (2 CH); 35.9 (CH_2); 29.8 (C); 21.8 (CH_3); 13.8, 7.2 (2 CH_2). Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.75; H, 9.61. HRMS (ESI) m/z $[M + H]^+$ Calcd for $C_{13}H_{21}O_2^+$: 209.1537; Found: 209.1547.

*Synthesis of **16b**.* Compound **16b** (24 mg, 71%) was similarly prepared from the reaction of **2** (30 mg, 0.15 mmol) and [Ru]Cl (56 mg, 0.08 mmol) in a cosolvent of $CHCl_3$/MeOH (2:1) was heated to 60 °C for 1 day. The product consists of *trans*- and *cis*- isomers in a ratio of 3:1. Only the major diasteromer is assignable. Spectroscopic data for the major diastereomer **16b**: ^1H NMR (δ, $CDCl_3$, 400 MHz) 5.68 (m, 1H, ═C(C)H); 5.55 (m, 1H, ═C(C)H); 3.94 (dd, 1H, $^2J_{HH}$ = 11.7 Hz, $^3J_{HH}$ = 4.7 Hz, OCH_2) 3.66, 2.77 (2d, 2H, $^2J_{HH}$ = 11.4 Hz, OCH_2); 3.46 (m, 2H, OCH_2); 3.29 (t, 2H, $^2J_{HH}$ = 11.7 Hz, OCH_2); 2.31 (m, 1H, CH); 2.05 (m, 2H, CH_2); 1.47 (br, 1H, CH); 1.16 (t, 3H, $^3J_{HH}$ = 7.0 Hz, CH_3); 1.13 (s, 3H, CH_3); 0.61, 0.38 (m, 4H, 2CH_2). $^{13}C\{^1H\}$NMR (δ, $CDCl_3$, 100 MHz) 127.3, 126.6 (2 ═C); 74.5 (C), 72.1, 65.4, 55.5 (3 OCH_2); 42.3, 40.1 (2 CH); 36.3 (CH_2); 22.5 (CH_3); 22.3 (C); 16.1 (CH_3); 13.8, 7.2 (2 CH_2). Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.66; H, 9.98. HRMS (ESI) m/z $[M + H]^+$ Calcd for $C_{14}H_{23}O_2^+$: 223.1693; Found: 223.1689.

*Synthesis of **17a**.* To a mixture of **4** (0.040 g, 0.19 mmol) and $[Ru]NCCH_3^+$ (0.033 g, 0.037 mmol) was added acetone (10 mL), and the solution was heated to 60 °C for 12 h. Then the solvent was removed under a vacuum and 1 mL of CH_2Cl_2 was used to extract the product and diethyl ether (ca. 6 mL) was then added. The pale-orange precipitates thus formed was filtered and washed with diethyl ether and dried under a vacuum to give $[Ru]NCCH_3^+$. The filtrate was evaporated to dryness under a vacuum and the crude product purified by flash chromatography (silica gel, hexanes/EtOAc = 8/1) to afford **17a** (0.033 g, 83%). Spectroscopic data of **17a**: ^1H NMR (δ, $CDCl_3$, 400 MHz) 7.20−7.06 (m, 4H, Ph); 5.57−5.52 (m, 2H, ═CH, ═CH); 3.52 (br, 1H, CH); 2.86−2.69 (m, 2H, CH_2); 2.21−2.15 (m, 1H, CH_2); 2.08−2.01 (m, 2H, CH_2, CH); 1.86−1.84 (m, 1H, CH_2); 1.49−1.40 (m, 1H, CH_2); 1.38 (br, 1H, OH); 1.34 (s, 3H, CH_3). $^{13}C\{^1H\}$NMR (δ, $CDCl_3$, 100 MHz) 138.9 (Ph); 137.2 (Ph); 130.4 (═CH); 129.1; 128.8; 126.1; 125.9 (Ph); 123.8 (═CH); 71.5 (C); 44.6 (CH); 40.7 (CH); 36.3 (CH_2); 29.6 (CH_2); 27.8 (CH_3); 19.6 (CH_2). Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 84.12; H, 8.53. HRMS (ESI) m/z $[M + H]^+$ Calcd for $C_{15}H_{19}O^+$: 215.1431; Found: 215.1399.

*Synthesis of **17b**.* Compound **17b** (0.050 g, 90%) was similarly prepared from the reaction of **4** (0.052 g, 0.24 mmol) and $[Ru]NCCH_3^+$ (0.043 g, 0.049 mmol) in a cosolvent of $CHCl_3$/MeOH (2:1). Spectroscopic data of **17b**: ^1H NMR (δ, $CDCl_3$, 400 MHz) 7.20−7.06 (m, 4H, Ph); 5.55−5.48 (m, 2H, ═CH, ═CH); 3.45 (br, 1H, CH); 3.25 (s, 3H, OMe); 2.83−2.69 (m, 2H, CH_2); 2.17−1.95 (m, 4H, CH_2; CH_2; CH); 1.44−1.31 (m, 1H, CH_2); 1.29 (s, 3H, CH_3). $^{13}C\{^1H\}$NMR (δ, $CDCl_3$, 100 MHz) 139.1 (Ph); 137.26 (Ph); 130.6 (═CH); 129.2; 128.9; 126.0; 125.8 (Ph); 123.5 (═CH); 75.3 (C); 48.2 (OMe); 40.5 (CH); 40.3 (CH); 34.1 (CH_2); 29.6 (CH_2); 21.4 (CH_3); 19.2 (CH_2). Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.10; H, 8.89. HRMS (ESI) m/z $[M + H]^+$ Calcd for $C_{16}H_{21}O^+$: 229.1587; Found: 229.1553.

*Synthesis of **17c**.* Compound **17c** (0.045 g, 81%) was similarly prepared from the reaction of **4** (0.049 g, 0.23 mmol) and $[Ru]NCCH_3^+$ (0.041 g, 0.047 mmol) in a cosolvent of $CHCl_3$/EtOH (2:1). Spectroscopic data of **17c**: ^1H NMR (δ, $CDCl_3$, 400 MHz) 7.20−7.06 (m, 4H, Ph); 5.54−5.47 (m, 2H, ═CH, ═CH); 3.46 (q, $^3J_{HH}$ = 7.0 Hz, 3H, OCH_2, CH); 2.82−2.68 (m, 2H, CH_2); 2.20−1.97 (m, 4H, CH_2; CH_2; CH); 1.44−1.34 (m, 1H, CH_2); 1.29 (s, 3H, CH_3); 1.20 (t, $^3J_{HH}$ = 7.0 Hz, 3H, CH_3). $^{13}C\{^1H\}$NMR (δ, $CDCl_3$, 100 MHz) 139.2 (Ph); 137.3 (Ph); 130.5 (═CH); 129.2;

DOI: 10.1021/acs.joc.6b00260
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128.92; 125.9; 125.8 (Ph); 123.6 (=CH); 75.1 (C); 55.4 (OCH_2); 40.8 (CH); 40.3 (CH); 34.6 (CH_2); 29.6 (CH_2); 22.2 (CH_3); 19.3 (CH_2); 16.2 (CH_3). Anal. Calcd for $C_{17}H_{22}O$: C, 84.25; H, 9.15. Found: C, 84.33; H, 9.20.

Synthesis of ***17d***. Compound **17d** (0.068 g, 79%) was similarly prepared from the reaction of **4** (0.072 g, 0.34 mmol) and $[Ru]NCCH_3^+$ (0.059 g, 0.067 mmol) in a 2:1 cosolvent of $CHCl_3$/IPA (2:1). Spectroscopic data of **17d**: ^{1}H NMR (δ, $CDCl_3$, 400 MHz) 7.19−7.06 (m, 4H, Ph); 5.55−5.46 (m, 2H, =CH, =CH); 3.93 (septet, $^3J_{HH}$ = 6.2 Hz, 1H, OCH); 3.46 (br, 1H, CH); 2.82−2.69 (m, 2H, CH_2); 2.20−1.92 (m, 4H, CH_2; CH_2; CH); 1.44−1.34 (m, 1H, CH_2); 1.29 (s, 3H, CH_3); 1.17 (d, 3H, $^3J_{HH}$ = 6.2 Hz, CH_3); 1.16 (d, 3H, $^3J_{HH}$ = 6.2 Hz, CH_3). $^{13}C\{^1H\}$NMR (δ, $CDCl_3$, 100 MHz) 139.3 (Ph); 137.5 (Ph); 130.7 (=CH); 129.2; 128.9; 125.9; 125.8 (Ph); 123.7 (=CH); 75.9 (C); 62.7 (OCH); 42.5 (CH); 40.6 (CH); 34.3 (CH_2); 29.6 (CH_2); 25.4 (CH_3); 25.1 (CH_3); 23.1 (CH_3); 19.7 (CH_2). Anal. Calcd for $C_{18}H_{24}O$: C, 84.32; H, 9.44. Found: C, 84.26; H, 9.38.

Synthesis of ***17e***. Compound **17e** (0.086 g, 70%) was similarly prepared from the reaction of **4** (0.088 g, 0.41 mmol) and $[Ru]NCCH_3^+$ (0.072 g, 0.082 mmol) in a cosolvent of $CHCl_3$/Benzyl alcohol (10:1). Spectroscopic data of **17e**: ^{1}H NMR (δ, $CDCl_3$, 400 MHz) 7.40−7.07 (m, 9H, Ph); 5.58−5.51 (m, 2H, =CH, =CH); 4.51 (s, 2H, OCH_2); 3.51 (br, 1H, CH); 2.84−2.69 (m, 2H, CH_2); 2.30−2.09 (m, 4H, CH_2; CH_2; CH); 1.48−1.44 (m, 1H, CH_2); 1.42 (s, 3H, CH_3). $^{13}C\{^1H\}$NMR (δ, $CDCl_3$, 100 MHz) 139.6 (Ph); 139.1 (Ph); 137.3 (Ph); 130.6 (=CH); 129.3; 128.9; 128.4; 127.4; 127.2; 126.0; 125.9 (Ph); 123.6 (=CH); 75.9 (C); 62.8 (OCH_2); 41.2 (CH); 40.4 (CH); 34.4 (CH_2); 29.6 (CH_2); 22.3 (CH_3); 19.4 (CH_2). Anal. Calcd for $C_{22}H_{24}O$: C, 86.80; H, 7.95. Found: C, 86.85; H, 8.00.

Synthesis of ***18a***. Compound **18a** (silica gel, hexanes/EtOAc = 2/1, 0.045 g, 81%) was similarly prepared from the reaction of **4′** (0.055 g, 0.23 mmol) and $[Ru]NCCH_3^+$ (0.039 g, 0.045 mmol) in acetone for 8 h. Spectroscopic data for **18a**: ^{1}H NMR (δ, $CDCl_3$, 400 MHz) 7.11 (d, $^3J_{HH}$ = 8.5 Hz, 1H, Ph); 6.75 (dd, 1H, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 2.8 Hz, Ph); 6.61 (d, 1H, $^4J_{HH}$ = 2.8 Hz, Ph); 5.51 (m, 2H, =CH, =CH); 3.76 (s, OCH_3, 3H); 3.47 (br, 1H, CH); 2.76 (m, 2H, CH_2); 2.20−1.82 (m, 4H, CH_2, CH_2, CH); 1.47−1.36 (m, 2H, OH, CH_2); 1.34 (s, 3H, CH_3). $^{13}C\{^1H\}$NMR (δ, $CDCl_3$, 100 MHz) 157.6; 138.3; 131.1 (Ph); 130.6 (=CH); 130.0 (Ph); 123.5 (=CH); 113.1; 112.7 (Ph); 71.5 (C); 55.2 (OCH_3); 44.8; 39.9 (2 CH); 36.2; 29.9 (2 CH_2); 27.8 (CH_3); 19.6 (CH_2). Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.60; H, 8.27. HRMS (ESI) m/z $[M + Na]^+$ Calcd for $C_{16}H_{20}NaO_2^+$: 267.1356; Found: 267.1364.

Synthesis of ***18b***. Compound **18b** (silica gel, hexanes/EtOAc = 10/1, 0.042 g, 92%) was similarly prepared from the reaction of **4′** (0.043 g, 0.18 mmol) and $[Ru]NCCH_3^+$ (0.031 g, 0.035 mmol) in a cosolvent of $CHCl_3$/MeOH (2:1) for 8 h. Spectroscopic data of **18b**: ^{1}H NMR (δ, $CDCl_3$, 400 MHz) 7.11 (d, 1H, $^3J_{HH}$ = 8.4 Hz, Ph); 6.74 (dd, 1H, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 3.0 Hz, Ph); 6.61 (d, 1H, $^4J_{HH}$ = 3.0 Hz, Ph); 5.50 (m, 2H, =CH, =CH); 3.76 (s, 3H, OCH_3); 3.40 (br, 1H, CH); 3.25 (s, 3H, OCH_3); 2.74 (m, 2H, CH_2); 2.17−1.89 (m, 4H, CH_2, CH_2, CH); 1.42−1.35 (m, 1H, CH_2); 1.28 (s, 3H, CH_3). $^{13}C\{^1H\}$-NMR (δ, $CDCl_3$, 100 MHz) 157.6; 138.4; 131.3 (Ph); 130.7 (=CH); 130.1 (Ph); 123.2 (=CH); 113.2; 112.6 (Ph); 75.3 (C); 55.2; 48.2 (2 OCH_3); 40.7; 39.5 (2 CH); 34.1; 29.9 (2 CH_2); 21.4 (CH_3); 19.2 (CH_2). Anal. Calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 79.09; H, 8.53. HRMS (ESI) m/z $[M + Na]^+$ Calcd for $C_{17}H_{22}NaO_2^+$: 281.1512; Found: 281.1507.

Synthesis of ***18c***. Compound **18c** (silica gel, hexanes/EtOAc = 10/1, 0.043 g, 84%) was similarly prepared from the reaction of **4′** (0.046 g, 0.19 mmol) and $[Ru]NCCH_3^+$ (0.033 g, 0.038 mmol) in a cosolvent of $CHCl_3$/EtOH (2:1) for 8 h. Spectroscopic data of **18c**: ^{1}H NMR (δ, $CDCl_3$, 400 MHz) 7.10 (d, 1H, $^3J_{HH}$ = 8.9 Hz, Ph); 6.74 (dd, 1H, $^3J_{HH}$ = 8.9 Hz, $^4J_{HH}$ = 2.8 Hz, Ph); 6.60 (d, 1H, $^4J_{HH}$ = 2.8 Hz, Ph); 5.49 (m, 2H, =CH, =CH); 3.76 (s, 3H, OCH_3); 3.46 (q, 2H, $^3J_{HH}$ = 7.5 Hz, OCH_2); 3.39 (br, 1H, CH); 2.73 (m, 2H, CH_2); 2.18−1.97 (m, 4H, CH_2, CH_2, CH); 1.43−1.32 (m, 1H, CH_2); 1.28 (s, 3H, CH_3); 1.20 (t, 3H, $^3J_{HH}$ = 7.5 Hz, CH_3). $^{13}C\{^1H\}$NMR (δ, $CDCl_3$, 100 MHz) 157.6; 138.4; 131.4 (Ph); 130.7 (=CH); 130.1 (Ph); 123.3 (=CH); 113.2; 112.6 (Ph); 75.2 (C); 55.3 (OCH_2); 55.2 (OCH_3); 41.0; 39.5 (2 CH); 34.6; 30.0 (2 CH_2); 22.2 (CH_3); 19.3 (CH_2); 16.2 (CH_3). Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found: C, 79.39; H, 8.92. HRMS (ESI) m/z $[M + Na]^+$ Calcd for $C_{18}H_{24}NaO_2^+$: 295.1669; Found: 295.1666.

Synthesis of ***18d***. Compound **18d** (silica gel, hexanes/EtOAc = 10/1, 0.044 g, 76%) was similarly prepared from the reaction of **4′** (0.049 g, 0.20 mmol) and $[Ru]NCCH_3^+$ (0.035 g, 0.040 mmol) in a cosolvent of $CHCl_3$/IPA (2:1) for 8 h. Spectroscopic data of **18d**: ^{1}H NMR (δ, $CDCl_3$, 400 MHz) 7.09 (d, 1H, $^3J_{HH}$ = 8.7 Hz, Ph); 6.74 (dd, 1H, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 2.7 Hz, Ph); 6.60 (d, 1H, $^4J_{HH}$ = 2.7 Hz, Ph); 5.48 (m, 2H, =CH, =CH); 3.93 (septet, 1H, $^3J_{HH}$ = 6.2 Hz, OCH); 3.76 (s, OCH_3, 3H); 3.40 (br, 1H, CH); 2.74 (m, 2H, CH_2); 2.18−1.89 (m, 4H, CH_2, CH_2, CH); 1.42−1.32 (m, 1H, CH_2); 1.28 (s, 3H, CH_3); 1.17 (d, 3H, $^3J_{HH}$ = 6.2 Hz, CH_3); 1.16 (d, 3H, $^3J_{HH}$ = 6.2 Hz, CH_3). $^{13}C\{^1H\}$NMR (δ, $CDCl_3$, 100 MHz) 157.6; 138.6; 131.5 (Ph); 130.8 (=CH); 130.1 (Ph); 123.4 (=CH); 113.2; 112.6 (Ph); 76.0 (C); 62.7 (OCH); 55.2 (OCH_3); 42.6; 39.8 (2 CH); 34.3; 29.9 (2 CH_2); 25.4 (2 CH_3); 23.1 (CH_3); 19.6 (CH_2). Anal. Calcd for $C_{19}H_{26}O_2$: C, 79.68; H, 9.15. Found: C, 79.60; H, 9.20. HRMS (ESI) m/z $[M + Na]^+$ Calcd for $C_{19}H_{26}NaO_2^+$: 309.1826; Found: 309.1828.

Synthesis of ***18e***. Compound **18e** (silica gel, hexanes/EtOAc = 10/1, 0.069 g, 76%) was similarly prepared from the reaction of **4′** (0.066 g, 0.27 mmol) and $[Ru]NCCH_3^+$ (0.047 g, 0.054 mmol) in a cosolvent of $CHCl_3$/BnOH (2:1) for 8 h. Spectroscopic data of **18e**: ^{1}H NMR (δ, $CDCl_3$, 400 MHz) 7.39−7.26 (m, 5H, Ph); 7.13 (d, 1H, $^3J_{HH}$ = 8.7 Hz, Ph); 6.76 (dd, 1H, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 2.7 Hz, Ph); 6.61 (d, 1H, $^4J_{HH}$ = 2.7 Hz, Ph); 5.53 (m, 2H, =CH, =CH); 4.51 (s, 2H, OCH_2); 3.77 (s, 3H, OCH_3); 3.46 (br, 1H, CH); 2.75 (m, 2H, CH_2); 2.30−2.09 (m, 4H, CH_2, CH_2, CH); 1.46−1.42 (m, 1H, CH_2); 1.41 (s, 3H, CH_3). $^{13}C\{^1H\}$NMR (δ, $CDCl_3$, 100 MHz) 157.2; 139.6; 138.4; 131.3 (Ph); 130.8 (=CH); 130.1; 128.3; 127.4; 127.2 (Ph); 123.2 (=CH); 113.2; 112.7 (Ph); 76.0 (C); 62.8 (OCH_2); 55.2 (OCH_3); 41.4; 39.6 (2 CH); 34.4; 29.9 (2 CH_2); 22.3 (CH_3); 19.3 (CH_2). Anal. Calcd for $C_{23}H_{26}O_2$: C, 82.60; H, 7.84. Found: C, 82.68; H, 7.88. HRMS (ESI) m/z $[M + Na]^+$ Calcd for $C_{23}H_{26}NaO_2^+$: 357.1825; Found: 357.1834.

Synthesis of ***19a***. To a mixture of **5** (0.042 g, 0.21 mmol) and $[Ru]NCCH_3^+$ (0.037 g, 0.042 mmol) was added dry acetone (10 mL), and the solution was heated to 55 °C for 12 h. Then the solution was removed under a vacuum and 1 mL of CH_2Cl_2 was used to extract the product and diethyl ether (ca. 6 mL) was then added. The pale-orange precipitates thus formed was filtered and washed with diethyl ether and dried under a vacuum to give $[Ru]NCCH_3^+$. The filtrate was evaporated to dryness under a vacuum and the crude product purified by flash chromatography (silica gel, hexanes/EtOAc = 2/1) to afford the diastereomer mixture of **19a** in a ratio of 1.8:1 (0.037 g, 87%). Spectroscopic data for major diastereomer: ^{1}H NMR (δ, $CDCl_3$, 400 MHz) 7.25−7.11 (m, 4H, Ph); 5.71 (m, 1H, =CH); 5.58 (m, 1H, =CH); 3.74 (br, 1H, CH); 2.96 (d, 2H, $^3J_{HH}$ = 9.1 Hz, CH_2); 2.65 (m, 1H, CH); 2.32 (m, 1H, CH_2); 2.10 (m, 1H, CH_2); 1.57 (br, 1H, OH); 1.36 (s, 3H, CH_3). $^{13}C\{^1H\}$NMR (δ, $CDCl_3$, 100 MHz) 144.9; 142.4 (Ph); 128.5 (=CH); 126.8; 126.5; 124.9 (Ph); 123.7 (=CH); 123.6 (Ph); 71.0 (C); 49.2; 46.5 (2 CH); 36.3; 32.9 (2 CH_2); 28.2 (CH_3). Spectroscopic data for minor diastereomer: ^{1}H NMR (δ, $CDCl_3$, 400 MHz) 7.25−7.11 (m, 4H, Ph); 5.74 (m, 1H, =CH); 5.56 (m, 1H, =CH); 3.84 (br, 1H, CH); 2.90 (dd, 1H, $^2J_{HH}$ = 13.7 Hz, $^3J_{HH}$ = 6.9 Hz, CH_2); 2.71 (m, 1H, CH); 2.65 (m, 1H, CH_2); 2.32 (m, 1H, CH_2); 2.10 (m, 1H, CH_2); 1.57 (br, 1H, OH); 1.29 (s, 3H, CH_3). $^{13}C\{^1H\}$NMR (δ, $CDCl_3$, 100 MHz) 145.2; 142.0 (Ph); 129.5 (=CH); 126.7 124.8; 124.2 (Ph); 122.6 (=CH); 70.7 (C); 49.5; 44.3 (2 CH); 35.2; 34.8 (2 CH_2); 27.7 (CH_3). HRMS (ESI) m/z $[M + Na]^+$ Calcd for $C_{14}H_{16}NaO^+$: 223.1094; Found: 223.1099.

Synthesis of ***19b***. The diastereomer **19b** in a ratio of 1:1 (silica gel, hexanes/EtOAc = 20/1, 0.054 g, 95%) was similarly prepared from the reaction of **5** (0.053 g, 0.26 mmol) and $[Ru]NCCH_3^+$ (0.046 g, 0.053 mmol) in a cosolvent of $CHCl_3$/MeOH (2:1) for 8 h. Spectroscopic data for major diastereomer: ^{1}H NMR (δ, $CDCl_3$, 400 MHz) 7.23−7.11 (m, 4H, Ph); 5.51 (m, 2H, =CH, =CH); 3.66 (br, 1H, CH); 3.29 (s, 3H, OCH_3); 2.83 (m, 3H, CH, CH_2); 2.31 (m, 1H, CH_2); 2.09 (m, 1H, CH_2); 1.34 (s, 3H, CH_3). $^{13}C\{^1H\}$NMR (δ, $CDCl_3$, 100

DOI: 10.1021/acs.joc.6b00260
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MHz) 145.1; 142.5 (Ph); 128.5 (=CH); 126.8; 126.4; 125.1; 123.8 (Ph); 123.4 (=CH); 75.1 (C); 48.6 (OCH_3); 46.7; 46.6 (2 CH); 33.5; 32.9 (2 CH_2); 22.5 (CH_3). Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 84.11; H, 8.45. HRMS (ESI) m/z $[M + Na]^+$ Calcd for $C_{15}H_{18}NaO^+$: 237.1250; Found: 237.1248. Spectroscopic data for minor diastereomer: ^{1}H NMR (δ, $CDCl_3$, 400 MHz) 7.23−7.10 (m, 4H, Ph); 5.67 (m, 1H, =CH); 5.50 (m, 1H, =CH); 3.78 (br, 1H, CH); 3.25 (s, 3H, OCH_3); 2.83 (m, 2H, CH, CH_2); 2.71 (m, 1H, CH_2); 2.34 (m, 1H, CH_2); 2.10 (m, 1H, CH_2); 1.21 (s, 3H, CH_3). $^{13}C\{^1H\}$NMR (δ, $CDCl_3$, 100 MHz) 145.7; 142.0 (Ph); 129.4 (=CH); 126.6; 126.6; 124.7; 124.1 (Ph); 121.9 (=CH); 74.7 (C); 48.9 (OCH_3); 46.2; 44.5 (2 CH); 34.4; 31.3 (2 CH_2); 22.6 (CH_3). HRMS (ESI) m/z $[M + Na]^+$ Calcd for $C_{15}H_{18}NaO^+$: 237.1250; Found: 237.1243.

Synthesis of ***19c***. The diastereomer **19c** in a ratio of 1:1 (silica gel, hexanes/EtOAc = 20/1, 0.049 g, 90%) was similarly prepared from the reaction of **5** (0.048 g, 0.24 mmol) and $[Ru]NCCH_3^+$ (0.042 g, 0.048 mmol) in a 2:1 cosolvent of $CHCl_3$/EtOH for 8 h. Spectroscopic data for major diastereomer: ^{1}H NMR (δ, $CDCl_3$, 400 MHz) 7.23−7.11 (m, 4H, Ph); 5.50 (m, 2H, =CH, =CH); 3.64 (br, 1H, CH); 3.54−3.38 (m, 2H, OCH_2); 2.84 (m, 3H, CH, CH_2); 2.33 (m, 1H, CH_2); 2.09 (m, 1H, CH_2); 1.34 (s, 3H, CH_3); 1.17 (t, 3H, $^3J_{HH}$ = 7.3 Hz, CH_3). $^{13}C\{^1H\}$NMR (δ, $CDCl_3$, 100 MHz) 145.3; 142.6 (Ph); 128.4 (=CH); 126.7; 126.4; 125.1; 123.8 (Ph); 123.5 (=CH); 74.8 (C); 55.7 (OCH_2); 46.6; 46.6 (2 CH); 34.0; 33.0 (2 CH_2); 23.3; 16.4 (2 CH_3). Spectroscopic data for minor diastereomer: ^{1}H NMR (δ, $CDCl_3$, 400 MHz) 7.23−7.10 (m, 4H, Ph); 5.66 (m, 1H, =CH); 5.49 (m, 1H, =CH); 3.78 (br, 1H, CH); 3.54−3.38 (m, 2H, OCH_2); 2.81 (m, 2H, CH, CH_2); 2.70 (m, 1H, CH_2); 2.23 (m, 1H, CH_2); 2.10 (m, 1H, CH_2); 1.20 (s, 3H, CH_3); 1.20 (t, 3H, $^3J_{HH}$ = 6.8 Hz, CH_3). $^{13}C\{^1H\}$NMR (δ, $CDCl_3$, 100 MHz) 145.9; 142.2 (Ph); 129.3 (=CH); 126.5; 126.5; 124.7; 124.0 (Ph); 122.0 (=CH); 74.5 (C); 56.3 (OCH_2); 46.9; 44.7 (2 CH); 33.0; 32.0 (2 CH_2); 23.3; 16.1 (2 CH_3). HRMS (ESI) m/z $[M + Na]^+$ Calcd for $C_{16}H_{20}NaO^+$: 251.1407; Found: 251.1403.

Synthesis of ***19d***. The diastereomer mixture of **19d** in a ratio of 1.6:1 (silica gel, hexanes/EtOAc = 20/1, 0.065 g, 83%) was similarly prepared from the reaction of **5** (0.065 g, 0.32 mmol) and $[Ru]NCCH_3^+$ (0.057 g, 0.065 mmol) in a cosolvent of $CHCl_3$/IPA (5:1) for 7 h. Spectroscopic data for major diastereomer: ^{1}H NMR (δ, $CDCl_3$, 400 MHz) 7.24−7.10 (m, 4H, Ph); 5.50 (m, 2H, =CH, =CH); 3.97 (septet, 1H, $^3J_{HH}$ = 6.1 Hz, OCH); 3.64 (br, 1H, CH); 2.94−2.66 (m, 3H, CH, CH_2); 2.35 (m, 1H, CH_2); 2.10 (m, 1H, CH_2); 1.36 (s, 3H, CH_3); 1.19 (d, 3H, $^3J_{HH}$ = 6.1 Hz, CH_3); 1.17 (d, 3H, $^3J_{HH}$ = 6.1 Hz, CH_3). $^{13}C\{^1H\}$NMR (δ, $CDCl_3$, 100 MHz) 145.2; 142.8 (Ph); 128.5 (=CH); 126.7; 126.3; 125.0; 123.8 (Ph); 123.6 (=CH); 75.5 (C); 62.8 (OCH); 48.4; 46.8 (2 CH); 34.0; 33.4 (2 CH_2); 25.5; 25.1; 24.5 (3 CH_3). Spectroscopic data for minor diastereomer: ^{1}H NMR (δ, $CDCl_3$, 400 MHz) 7.24−7.10 (m, 4H, Ph); 5.67 (m, 1H, =CH); 5.50 (m, 1H, =CH); 3.87 (septet, 1H, $^3J_{HH}$ = 6.3 Hz, OCH); 3.82 (br, 1H, CH); 2.94−2.66 (m, 3H, CH, CH_2); 2.24 (m, 1H, CH_2); 2.10 (m, 1H, CH_2); 1.20 (s, 3H, CH_3); 1.15 (d, 3H, $^3J_{HH}$ = 6.2 Hz, CH_3); 1.11 (d, 3H, $^3J_{HH}$ = 6.2 Hz, CH_3). $^{13}C\{^1H\}$NMR (δ, $CDCl_3$, 100 MHz) 146.0; 142.2 (Ph); 129.1 (=CH); 126.5; 126.4; 124.7; 124.0 (Ph); 122.3 (=CH); 74.9 (C); 63.0 (OCH); 47.5; 44.9 (2 CH); 34.3; 32.3 (2 CH_2); 25.3; 24.8; 24.3 (3 CH_3). HRMS (ESI) m/z $[M + Na]^+$ Calcd for $C_{17}H_{22}NaO^+$: 265.1563; Found: 265.1565.

Synthesis of ***19e***. The diastereomer mixture **19e** in a ratio of 1.6:1 (silica gel, hexanes/EtOAc = 20/1, 0.063 g, 75%) was similarly prepared from the reaction of **5** (0.058 g, 0.29 mmol) and $[Ru]NCCH_3^+$ (0.051 g, 0.058 mmol) in a cosolvent of $CHCl_3$/BnOH (5:1) for 9 h. Spectroscopic data for major diastereomer: ^{1}H NMR (δ, $CDCl_3$, 400 MHz) 7.39−7.13 (m, 9H, Ph); 5.56 (m, 2H, =CH, =CH); 4.57 (m, 2H, OCH_2); 3.71 (br, 1H, CH); 2.95 (m, 3H, CH, CH_2); 2.45 (m, 1H, CH_2); 2.19 (m, 1H, CH_2); 1.46 (s, 3H, CH_3). $^{13}C\{^1H\}$NMR (δ, $CDCl_3$, 100 MHz) 145.2; 142.6; 139.6 (Ph); 128.5 (=CH); 128.3; 127.2; 127.2; 126.8; 126.4; 125.1; 123.8 (Ph); 123.4 (=CH); 75.6 (C); 62.9 (OCH_2); 47.3; 46.7 (2 CH); 33.8; 33.1 (2 CH_2); 23.4 (CH_3). Spectroscopic data for minor diastereomer: ^{1}H NMR (δ, $CDCl_3$, 400 MHz) 7.39−7.13 (m, 9H, Ph); 5.71 (m, 1H, =CH); 5.54 (m, 1H, =CH); 4.53, 4.48 (2 d, 2H, $^1J_{HH}$ = 11.2 Hz, OCH_2); 3.88 (br, 1H, CH); 2.91 (m, 2H, CH, CH_2); 2.77 (m, 1H, CH_2); 2.38 (m, 1H, CH_2); 2.19 (m, 1H, CH_2); 1.32 (s, 3H, CH_3). $^{13}C\{^1H\}$NMR (δ, $CDCl_3$, 100 MHz) 145.8; 142.0; 139.9 (Ph); 129.6 (=CH); 128.2; 127.2; 127.1; 126.6; 126.5; 124.7; 124.1 (Ph); 121.9 (=CH); 75.3 (C); 63.4 (OCH_2); 47.1; 44.8 (2 CH); 34.3; 31.4 (2 CH_2); 23.4 (CH_3). HRMS (ESI) m/z $[M + Na]^+$ Calcd for $C_{21}H_{22}NaO^+$: 313.1563; Found: 313.1560.

Synthesis of ***20b***. The diastereomers mixture of **20b** in a ratio of 1:0.1 (silica gel, hexanes/EtOAc = 10/1, 0.047 g, total yield 85%) were similarly prepared from the reaction of **6** (0.052 g, 0.23 mmol) and $[Ru]NCCH_3^+$ (0.040 g, 0.046 mmol) in a 2:1 cosolvent of $CHCl_3$/MeOH (2:1) for 8 h. Only the major diastereomer of **20b** is assignable. Spectroscopic data for major diastereomer of **20b**: ^{1}H NMR (δ, $CDCl_3$, 500 MHz) 7.17−7.05 (m, 4H, Ph); 5.69 (m, 2H, =CH, =CH); 3.98 (m, 1H, CH); 3.22 (s, 3H, OCH_3); 2.77 (t, 2H, $^3J_{HH}$ = 6.4 Hz, CH_2); 2.22 (m, 1H, CH_2); 2.13 (m, 1H, CH_2); 2.07 (m, 1H, CH); 1.90 (m, 1H, CH_2); 1.76 (m, 1H, CH_2); 1.47 (m, 1H, CH_2); 1.24 (m, 1H, CH_2); 1.07 (s, 3H, CH_3). $^{13}C\{^1H\}$NMR (δ, $CDCl_3$, 125 MHz) 142.4; 141.6; 129.7 (Ph); 128.9 (=CH); 128.8; 126.5; 126.0 (Ph); 124.7 (=CH); 76.2 (C); 48.2 (OCH_3); 42.9; 41.6 (2 CH); 36.2; 33.7; 25.9; 25.7 (4 CH_2); 20.7 (CH_3). HRMS (ESI) m/z $[M + Na]^+$ Calcd for $C_{17}H_{22}NaO^+$: 265.1563; Found: 265.1558.

Synthesis of ***20c***. The diastereomers mixture of **20c** and **21** in a ratio of 1:0.3:0.3 (silica gel, hexanes/EtOAc = 10/1, 0.049 g, total yield 77%) were similarly prepared from the reaction of **6** (0.057 g, 0.25 mmol) and $[Ru]NCCH_3^+$ (0.044 g, 0.050 mmol) in a cosolvent of $CHCl_3$/EtOH (2:1) for 8 h. Only the major diastereomer of **20c** is assignable. Spectroscopic data for major diastereomer of **20c**: ^{1}H NMR (δ, $CDCl_3$, 400 MHz) 7.14−7.04 (m, 4H, Ph); 5.68 (m, 2H, =CH, =CH); 4.01 (m, 1H, CH); 3.32 (s, 2H, OCH_2); 2.77 (t, 2H, $^3J_{HH}$ = 6.0 Hz, CH_2); 2.24 (m, 1H, CH_2); 2.12 (m, 1H, CH_2); 2.06 (m, 1H, CH); 1.89 (m, 1H, CH_2); 1.76 (m, 1H, CH_2); 1.47 (m, 1H, CH_2); 1.24 (m, 1H, CH_2); 1.19 (t, 3H, $^3J_{HH}$ = 7.1 Hz, CH_3); 1.08 (s, 3H, CH_3). $^{13}C\{^1H\}$NMR (δ, $CDCl_3$, 100 MHz) 142.4; 141.7; 129.7; 128.8 (Ph); 128.7 (=CH); 126.5; 126.0 (Ph); 124.9 (=CH); 76.1 (C); 55.5 (OCH_2); 43.0; 42.0 (2 CH); 36.8; 33.7; 25.9; 25.7 (4 CH_2); 21.4; 16.4 (2 CH_3). HRMS (ESI) m/z $[M + Na]^+$ Calcd for $C_{18}H_{24}NaO^+$: 279.1720; Found: 279.1719.

Synthesis of ***20d***. The diastereomers mixture of **20d** and **21** in a ratio of 1:1.6:0.4 (silica gel, hexanes/EtOAc = 10/1, 0.040 g, total yield 73%) were similarly prepared from the reaction of **6** (0.046 g, 0.20 mmol) and $[Ru]NCCH_3^+$ (0.035 g, 0.040 mmol) in a cosolvent of $CHCl_3$/IPA (2:1) for 8 h. Only the major diastereomer of **20d** is assignable. Spectroscopic data for major diastereomer of **20d**: ^{1}H NMR (δ, $CDCl_3$, 500 MHz) 7.20−7.06 (m, 4H, Ph); 5.70 (m, 2H, =CH, =CH); 4.12 (m, 1H, CH); 3.86 (m, 1H, OCH); 2.78 (m, 2H, CH_2); 2.25 (m, 1H, CH_2); 2.15 (m, 1H, CH_2); 1.97 (m, 1H, CH); 1.86 (m, 2H, CH_2, CH_2); 1.52 (m, 2H, CH_2, CH_2); 1.13 (t, 3H, $^3J_{HH}$ = 6.4 Hz, CH_3); 1.12 (t, 3H, $^3J_{HH}$ = 6.4 Hz, CH_3); 1.05 (s, 3H, CH_3). $^{13}C\{^1H\}$NMR (δ, $CDCl_3$, 125 MHz) 142.1; 141.5; 129.3 (Ph); 128.9 (=CH); 128.7; 126.4; 126.0 (Ph); 125.0 (=CH); 76.6 (C); 62.9 (OCH); 43.6; 42.6 (2 CH); 37.2; 33.4 (2 CH_2); 25.4; 25.2 (2 CH_2, 2 CH_3); 21.6 (CH_3). HRMS (ESI) m/z $[M + Na]^+$ Calcd for $C_{19}H_{26}NaO^+$: 293.1876; Found: 293.1876.

Synthesis of ***20e***. The diastereomers mixture of **20e** and **21** in a ratio of 1:0.6:0.4 (silica gel, hexanes/EtOAc = 10/1, 0.062 g, total yield 75%) were similarly prepared from the reaction of **6** (0.059 g, 0.26 mmol) and $[Ru]NCCH_3^+$ (0.045 g, 0.052 mmol) in a cosolvent of $CHCl_3$/BnOH (2:1) for 8 h. Only the major diastereomer of **20e** is assignable. Spectroscopic data for major diastereomer of **20e**: ^{1}H NMR (δ, $CDCl_3$, 500 MHz) 7.36−6.99 (m, 9H, Ph); 5.71 (m, 2H, =CH, =CH); 4.50, 4.45 (2 d, 2H, $^2J_{HH}$ = 12.0 Hz, OCH_2); 4.09 (m, 1H, CH); 2.78 (m, 2H, CH_2); 2.22 (m, 1H, CH_2); 2.13 (m, 1H, CH_2); 2.09 (m, 1H, CH); 1.90 (m, 1H, CH_2); 1.70 (m, 1H, CH_2); 1.56 (m, 1H, CH_2); 1.24 (m, 1H, CH_2); 1.16 (s, 3H, CH_3). $^{13}C\{^1H\}$NMR (δ, $CDCl_3$, 125 MHz) 142.2; 141.4; 129.5; 129.0 (Ph); 128.8 (=CH); 128.8; 126.5; 126.0 (Ph); 124.9 (=CH); 76.0 (C); 62.7 (OCH_2); 42.8; 42.5 (2 CH); 36.7; 33.5; 25.6; 25.4 (4 CH_2); 21.2

DOI: 10.1021/acs.joc.6b00260
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(CH_3). HRMS (ESI) m/z $[M + Na]^+$ Calcd for $C_{23}H_{26}NaO^+$: 341.1876; Found: 341.1874.

Synthesis of ***21***. Compound **21** (silica gel, hexanes/EtOAc = 10/1, 0.030 g, 79%) was similarly prepared from the reaction of **6** (0.041 g, 0.18 mmol) and $[Ru]NCCH_3^+$ (0.031 g, 0.036 mmol) in acetone for 8 h. Spectroscopic data for **21**: ^1H NMR (δ, $CDCl_3$, 400 MHz) 7.13−7.08 (m, 4H, Ph); 4.90 (m, 1H, $=CH_2$); 4.79 (m, 1H, $=CH_2$); 3.85 (br, 1H, CH); 3.43 (td, 1H, $^2J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 1.5 Hz, CH_2); 2.65 (dd, 1H, $^2J_{HH}$ = 14.4 Hz, $^3J_{HH}$ = 6.6 Hz, CH_2); 2.35 (m, 1H, CH_2); 2.34 (d, 1H, $^2J_{HH}$ = 2.7 Hz, $\equiv$CH); 2.18 (d, 1H, $^3J_{HH}$ = 12.1 Hz, CH); 2.04 (m, 1H, CH_2); 1.86 (br, 1H, CH_2); 1.83 (s, 3H, CH_3); 1.38 (m, 1H, CH_2). $^{13}C\{^1H\}$NMR (δ, $CDCl_3$, 100 MHz) 149.5 ($=$C); 142.9; 140.7; 130.5; 129.0; 127.2; 126.3 (Ph); 110.3 ($=CH_2$); 83.1 ($\equiv$C); 74.0 ($\equiv$CH); 48.8 (CH); 43.7 (CH); 34.7; 31.9; 28.1 (3 CH_2); 22.1 (CH_3). Anal. Calcd for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.33; H, 8.59. HRMS (ESI) m/z $[M + Na]^+$ Calcd for $C_{16}H_{18}Na^+$: 233.1301; Found: 233.1306.

Synthesis of ***22***. To a Schlenk flask charged with [Ru]Cl (0.19 g, 0.26 mmol), KPF_6 (0.058 g, 0.31 mmol) and K_2CO_3 (0.72 g, 0.52 mmol) was added 1,8-enyne **4** (0.073 g, 0.34 mmol) and 10 mL of CH_2Cl_2 under nitrogen. The resulting solution was stirred at room temperature for 15 h. The solvent was removed under a vacuum, and the residue dissolved in 1.0 mL of ether was passed through a neutral Al_2O_3 column eluted with diethyl ether. Collecting the solution of the yellow band followed by drying under a vacuum resulted in the yellow acetylide product **22** (0.16 g, 70%). Spectroscopic data for **22**: ^1H NMR (δ, C_6D_6, 400 MHz) 7.61−7.55 (m, 12H, Ph); 7.40−7.36 (m, 1H, Ph); 7.24−7.22 (m, 1H, Ph); 7.11−6.85 (m, 20H, Ph); 5.19 (s, 1H, $=CH_2$); 5.15 (m, 1H, $=CH_2$); 4.38 (s, 5H, Cp); 4.37 (br, 1H, CHβ); 2.96 (m, 1H, CH_2); 2.78 (m, 1H, CH_2); 2.78 (m, 1H, CH_2); 2.33 (m, 1H, CH); 2.08 (s, 3H, CH_3); 1.98 (m, 1H, CH_2). $^{13}C\{^1H\}$NMR (δ, C_6D_6, 100 MHz) 148.9−126.0 (Ph, $=$C, Cβ); 109.8 ($=CH_2$); 95.2 (t, $^2J_{CP}$ = 24.6 Hz, Cα); 85.7 (Cp); 46.4 (CH); 39.5 (Cγ); 30.1 (CH_2); 23.6 (CH_2); 22.8 (CH_3). $^{31}P\{^1H\}$NMR (δ, C_6D_6, 162 MHz) 52.33, 50.75 (2 d, $^2J_{PP}$ = 37.8 Hz, 2 PPh_3). Anal. Calcd for $C_{56}H_{50}P_2Ru$: C, 75.91; H, 5.69. Found: C, 75.83; H, 5.74. HRMS (ESI) m/z $[M + H]^+$ Calcd for $C_{56}H_{51}P_2Ru^+$: 887.2504; Found: 887.2501.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00260.

Compound characterization data and NMR peak assignments. (PDF)

Complete crystallographic data for *trans*-**10**. (CIF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the Ministry of Science and Technology of Taiwan ROC, for financial support under the grant number of MOST 103-2113-M-002-004.

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DOI: 10.1021/acs.joc.6b00260
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