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Palladium-catalyzed hydrogenolysis of 2-alkynyl formates and elimination of 2-alkynyl carbonates. 2-Alkynylpalladium complex *vs.* allenylpalladium complex as intermediates

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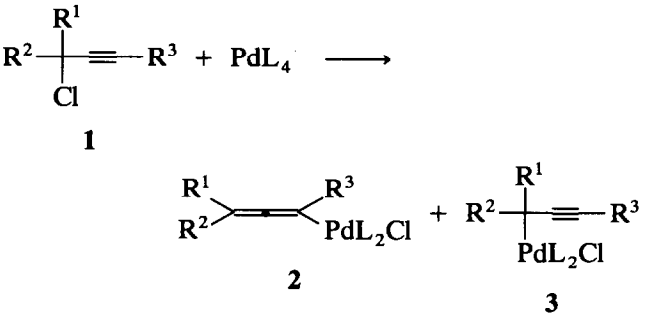
Abstract

Examples of palladium-catalyzed reactions of 2-alkynyl esters *via* the 2-alkynylpalladium intermediates are presented. The palladium-catalyzed hydrogenolysis of 2-alkynyl formates, which have internal triple bonds, affords alkynes *via* the 2-alkynylpalladium as an intermediate. The elimination reaction of 2-alkynyl carbonates yields conjugated enynes *via* the 2-alkynylpalladium intermediates.

Key words: Palladium; Catalysis; 2-Alkynyl carbonate; 2-Alkynyl formate; Conjugated enyne; Disubstituted alkyne

1. Introduction

Various allylic compounds, particularly allylic acetates, undergo several palladium-catalyzed transformations *via* π-allylpalladium complexes, and these reactions are useful in organic synthesis [1]. We found that allylic carbonates have higher reactivity than allylic acetates, and undergo several transformations which are not possible with the corresponding acetates, particularly under mild neutral conditions [2]. In contrast to the extensive research carried out on the palladium-catalyzed reactions of allylic compounds, only a few studies have been carried out on the reactions of 2-alkynyl (or propargyl) compounds, which have a triple bond instead of a double bond. 2-Alkynyl compounds seem to be less reactive than allylic compounds towards palladium catalysts. In view of the high reactivity of allylic carbonates, we have initiated systematic studies on the palladium-catalyzed transformations of 2-alkynyl carbonates and found several smooth reactions, such as carbonylation [3], hydrogenolysis [4], nucleophilic substitution [5], coupling with alkenes [6] and alkynes [7]. These reactions can be explained by the formation of allenylpalladium complexes as intermediates. Elsevier and co-workers studied the complex formation of 2-alkynyl halides **1** (propargylic halides) with $Pd(PPh_3)_4$ and found that two complexes are formed depending on their structures. Namely, *trans*-(σ-allenyl)bis-(triphenylphosphine)palladium halides **2** (allenyl complex) is formed when R^3 is hydrogen. On the other hand, the 2-alkynylpalladium complexes **3** (propargylic complexes) are obtained when R^3 is a bulky group, such as t-butyl and trimethylsilyl, and R^1 and R^2 are both hydrogen. A mixture of both isomers is formed when R^3 is methyl and R^1 and R^2 are both hydrogen. The same complex formation from 2-alkynyl acetates takes place in the presence of zinc or lithium chloride [8].



1 **2** **3**

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It is expected that similar complex formation should take place as an intermediate in the palladium-catalyzed reactions of other 2-alkynyl compounds. All the products we have obtained so far by the palladium-catalyzed reactions of 2-alkynyl carbonates with various substrates can be explained by the formation of the allenyl complexes. Products of the reaction of 2-alkynyl halides and acetates with organometallic compounds of zinc and magnesium obtained by other workers are also explained by the allenyl intermediates [9]. An example of the palladium-catalyzed reaction *via* the 2-alkynylpalladium intermediate is the formation of a mixture of allenes and alkynes by hydrogenolysis with various metal hydrides [10].

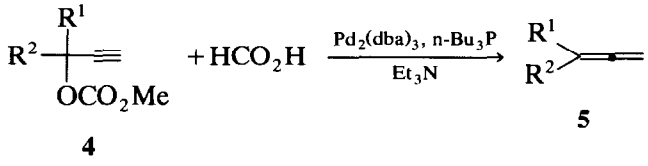
We were interested in the possibility of obtaining the products which are derived from 2-alkynyl complexes **3**. In the course of our studies along this direction, we found that the palladium-catalyzed hydrogenolysis of certain 2-alkynyl formates affords alkynes selectively, rather than allenes. Also the palladium-catalyzed elimination of 2-alkynyl carbonates affords conjugated enynes. The formation of these products can be clearly explained by the formation of 2-alkynyl complex **3** as intermediate. In this paper, details of these studies on the catalytic reactions *via* the 2-alkynyl intermediates are presented. Brief accounts of these studies have been given [11,12].

2. Results and discussion

2.1. Palladium-catalyzed hydrogenolysis of 2-alkynyl formates

We reported that terminal allylic compounds are converted regioselectively to 1-alkenes by palladium-catalyzed hydrogenolysis with ammonium formate [13], and we have carried out extensive studies on this useful palladium-catalyzed regioselective hydrogenolysis of various allylic substrates with ammonium formate, or triethylammonium formate [14]. As a further extension, we applied the hydrogenolysis to 2-alkynyl carbonates. In the literature, a clean allene formation by the palladium-catalyzed reaction of 2-alkynyl acetates with SmI_2 was reported [15].

In previous papers, we reported that 2-alkynyl carbonates are converted to allenes by palladium-catalyzed hydrogenolysis with ammonium formate by using $Pd_2(dba)_3$ combined with an excess of $^nBu_3P$ as a catalyst [16]. We found that the structure of 2-alkynyl carbonates has a crucial effect on the reaction, and we observed that a clean reaction proceeded only with 2-alkynyl carbonates **4** which have a terminal acetylenic bond (3-methoxycarbonyloxy-1-alkynes) to give terminal allenes **5**.



4 **5**

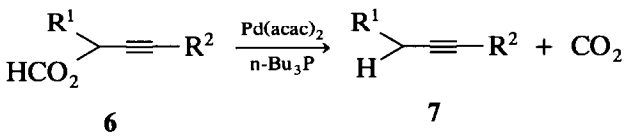
Otherwise the reaction was not selective. For example, we reported briefly on the formation of a mixture (5 : 1) of the allene and the alkynes from 2-undecynyl methyl carbonate which has an internal acetylenic bond. Gore and co-workers reported that the palladium-catalyzed reaction of various 2-alkynyl bromides, mesylates, and phosphates, which have internal acetylenic bonds, with $LiAlH_4$ and Et_3BHLi gave mixtures of allenes and alkynes [10]. The selectivity is dependent on the nature of the hydride sources and the leaving groups.

Another complication observed in the hydrogenolysis of 2-alkynyl compounds is that the allenes produced are reduced further to alkenes with an excess of ammonium formate [4]. In addition, it is known that alkynes are reduced to alkenes with triethylammonium formate [17]. Therefore it is important to suppress these over-reductions. In our studies on hydrogenolysis of allylic compounds, we found that clean hydrogenolysis is observed by use of allylic formates without addition of triethylammonium formate. Thus, we expected that the reaction of 2-alkynyl formates without addition of ammonium formate, instead of 2-alkynyl carbonates, would suppress the over-reduction of the products completely.

We found that the preparative method of the palladium catalyst is crucial for obtaining satisfactory results. Recently, we have found that $Pd(OAc)_2$ or $Pd(acac)_2$ is reduced easily to Pd^0 with $^nBu_3P$, and the Pd^0 species coordinated by a weak ligand of tributylphosphine oxide is formed [18]. We observed that the catalyst prepared *in situ* from equimolar amounts of $Pd(OAc)_2$ or $Pd(acac)_2$ and $^nBu_3P$ is more active for the hydrogenolysis than the Pd^0 catalyst prepared from $Pd_2(dba)_3$ and an excess of $^nBu_3P$ and used in the previous studies. With these considerations in mind, we have reinvestigated the hydrogenolysis of 2-alkynyl (propargylic) formates in order to clarify the scope of the reaction by using the above mentioned active catalyst. Particularly we gave our attention to the palladium-catalyzed reaction of 2-alkynyl compounds which have internal acetylenic bonds.

We studied the decarboxylation-hydrogenolysis of 2-alkynyl formates **6** which have internal acetylenic bonds and various functional groups, and observed smooth hydrogenolysis at room temperature by using the catalyst prepared by mixing equimolar amounts of Pd(acac)**2** and $^nBu_3P$ in THF or benzene. The use of this catalyst is essential and other catalysts such as

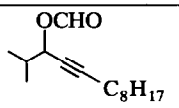
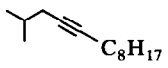
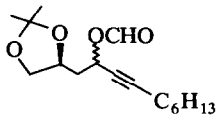
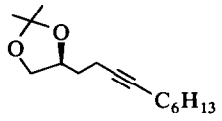
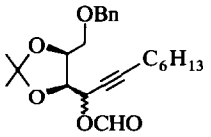
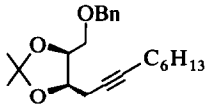
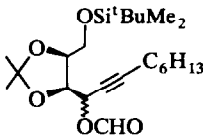
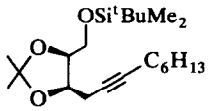
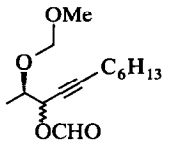
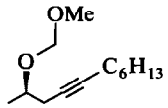
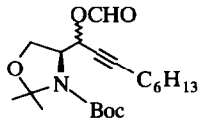
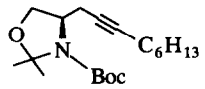
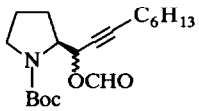
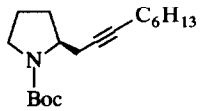
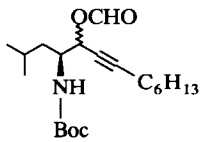
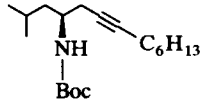
$Pd_2(dba)_3$ and Bu_3P do not give satisfactory results. The products we obtained were not allenes. Instead, alkynes **7** were obtained cleanly by displacement of the formate group with the hydride. Only a small amount of allenes was detected.



6 **7**

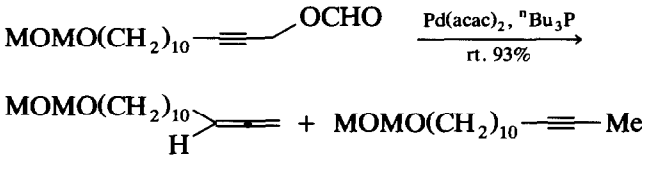
The reaction was carried out in the following way. THF or benzene are good solvents. $Pd(acac)_2$ and $^nBu_3P$ (10 mol%) were mixed in a 1:1 ratio in these solvents to form a pale yellow solution in a few minutes. Then 2-alkynyl formate **6** was added and the mixture was stirred at room temperature. Disappearance of the formate was confirmed by TLC, and the alkynes **7** were isolated in high yield after the usual workup. Representative results of the reaction of various 2-alkynyl formates are shown in Table 1. The reaction tolerates other functional groups; the reaction of 2-alkynyl formate with various oxygen and nitrogen

TABLE 1. Palladium-catalyzed hydrogenolysis of 2-alkynyl formates [a]

Entry	2-Alkynyl formates	Solvent	Time (h)	Acetylenes	Yield (%) [b]	Acetylene/allene [c]
1		PhH	3		92	99/1
2		PhH	3		97	97/3
3		THF	19		95	98/2
4		THF	19		97	96/4
5		PhH	16		85	96/4
6		THF	15		89	98/2
7		PhH	20		87	99/1
8		THF	5		93	97/3

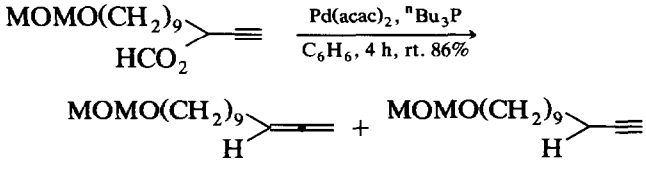
[a] Reactions were carried out using $Pd(acac)_2$ (10 mol%) and $^nBu_3P$ (10 mol%) at room temperature. [b] Isolated yields by flash column chromatography on SiO_2. [c] Determined by ^1H NMR (400 MHz) and/or GLC (capillary column 25 m × 0.3 mm).

functional groups proceeded smoothly as shown by the examples in Table 1. As one exception, we observed the formation of the terminal allene as a major product from the following 2-alkynyl formate [13-(methoxymethyloxy)-2-tridecynyl formate] which has an internal acetylenic bond and a primary formate.



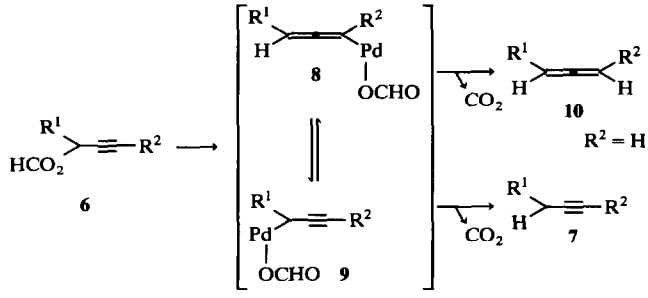
allene/acetylene = 91/9

2-Alkynyl formates which have terminal acetylenic bonds were converted cleanly to allenes with this palladium catalyst at room temperature. This procedure is superior in yield and selectivity to the procedure reported in previous papers, in which 2-alkynyl carbonates were treated with ammonium formate using $Pd_2(dba)_3$ and $^nBu_3P$ in DMF at 100°C [4]. These results show that either allenes or alkynes are prepared chemoselectively from the 2-alkynyl esters depending on the structure.



allene/acetylene = 99/1

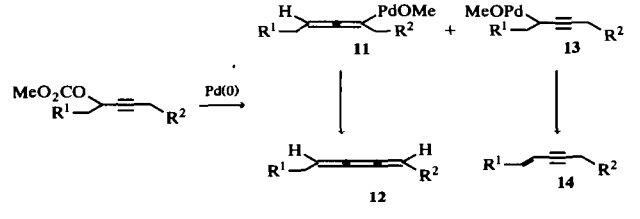
The formation of alkynes from 2-alkynyl compounds is interesting from a mechanistic viewpoint. The σ-allenylpalladium formate complex **8** is formed from 2-alkynyl formate **6**. The complex **8** is a precursor of allenes **10**. On the other hand, the formation of alkynes **7** can be explained by the σ-2-alkynylpalladium complex **9** as a precursor. Formation of either the allenes **10** or the alkynes **7** by hydrogenolysis of 2-alkynyl compounds **6**, depending on their structure and ligand effect, suggests that these two intermediate complexes are involved. The allenylpalladium complex **8** should be in an equilibrium with the 2-alkynylpalladium complex **9**. At first the 2-alkynylpalladium complex **9** is formed from **6**, which undergoes rapid decarboxylation to afford the alkynes **7** in the absence of phosphine and when R^2 is not hydrogen. When R^2 is hydrogen, the equilibrium may be shifted to the more stable allenylpalladium complex **8**. The decarboxylation of **8** affords the allenylpalladium hydride, which undergoes reductive elimination to form the allenes **10**. So far, all the palladium-catalyzed reactions of 2-alkynyl compounds are explained by the formation of the allenylpalladium complex **8** as the intermediate. But the formation of alkynes **7** clearly shows that the products are derived from the 2-alkynylpalladium complex **9**.



This selective formation of alkynes **7** from 2-alkynyl formates **6** has considerable synthetic importance for the preparation of dialkylated alkynes. Direct introduction of an alkyl group to terminal alkynes by S_N2 type alkylation with alkyl halides is not easy because of the extensive elimination reaction of the alkyl halides. On the other hand, the reaction of metal acetylides with aldehydes or ketones proceeds under milder conditions to give good yields of 2-alkynyl (propargyl) alcohols. Then the alcohol group can be removed easily by palladium-catalyzed hydrogenolysis after converting them to formates as described in this paper.

2.2. *Palladium-catalyzed elimination of 2-alkynyl carbonates*

We have reported that the palladium-catalyzed elimination of allylic compounds *via* π-allylpalladium complexes affords conjugated dienes, which are formed by the elimination of β-hydrogen *via* σ-allylpalladium intermediates [19]. Then we were interested in the palladium-catalyzed elimination reaction of 2-alkynyl compounds. Two reaction paths are expected. As one possibility, we assumed that 1,2,3-trienes **12** may be formed by β-elimination *via* the allenylpalladium intermediate **11**, which is the main contributing intermediate in the palladium-catalyzed reaction of 2-alkynyl carbonates. On the other hand, conjugated enynes **14** should be formed by β-elimination, if the 2-alkynyl intermediate **13** is an intermediate. Actually we observed the exclusive formation of the conjugated enynes **14** by the elimination, offering another example of the intermediacy of the 2-alkynylpalladium complex **13**.



The elimination reaction proceeded with a variety of 2-alkynyl carbonates under mild and neutral condi-

TABLE 2. Palladium-catalyzed elimination of 2-alkynyl carbonates

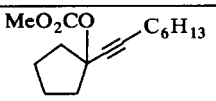
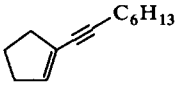
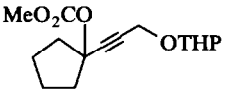
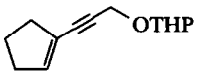
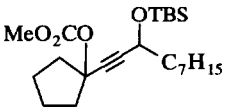
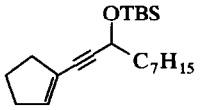
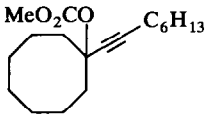
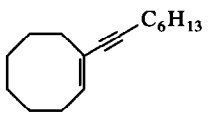
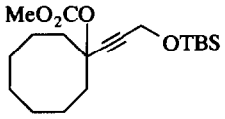
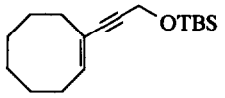
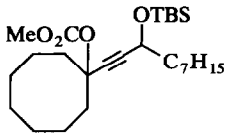
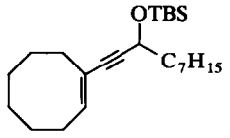
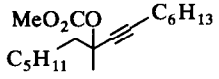
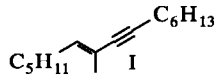
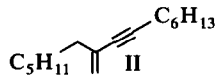
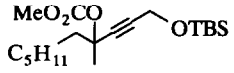
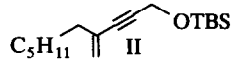
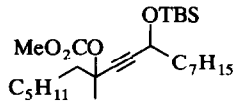
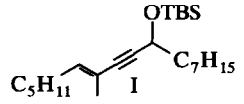
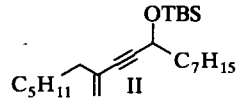
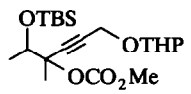
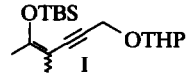
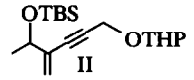
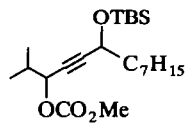
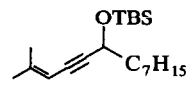
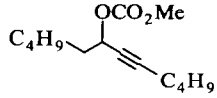
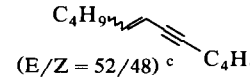
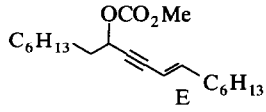
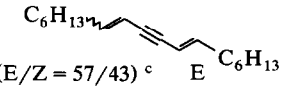
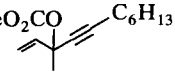
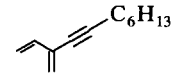
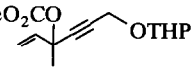
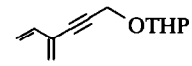
Entry	2-Alkynyl carbonates	Pd catalyst [a]	Time (h)	Enynes	Yield (%) [b]	Ratio I/II [c]
1		A-1 B	1 1		93 96	
2		A-2 B	2 3		98 71	
3		A-2 B	3 2		90 85	
4		A-1 B	2 2		90 85	
5		A-1	2		98	
6		A-2	2		94	
7		A-2	2.5		98	86/14
		B	1		95	28/72
8		A-1	2		93	83/17
		B	2.5		64	32/68
9		A-2	2.5		97	72/28
		B	2		85	22/78
10		A-1	3		76	28/72
		B	4		70	0/100
11		B	8		83	

TABLE 2 (continued)

Entry	2-Alkynyl carbonates	Pd catalyst [a]	Time (h)	Enynes	Yield (%) [b]	Ratio I/II [a]
12		B	1.5	 (E/Z = 52/48) [c]	99	
13		B	1.5	 (E/Z = 57/43) [c]	96	
14		A-1	0.5		79	
15		A-1	0.5		68	

[a] Catalysts: (A-1): $Pd_2(dba)_3$ (5 mol%), dppf (10 mol%), (A-2) $Pd_2(dba)_3$ (2.5 mol%), dppf (5 mol%) (B) $Pd(OAc)_2$ (10 mol%), PPh_3 (30 mol%). [b] Isolated yields by flash column chromatography on SiO_2. [c] Determined by ^1H NMR (400 MHz) and GLC (capillary column: 25 m × 0.3 mm). Geometry of the trisubstituted olefins is tentatively assigned as *E*.

tions; the results are listed in Table 2. The reaction with tertiary 2-alkynyl carbonates derived from cyclic ketones proceeded smoothly to give the conjugated enynes in good yields as shown in Table 2. As an exception, only poor results were obtained from the reaction of the 2-alkynyl carbonates derived from cyclohexanones. It may be difficult for the palladium catalyst to take a smooth eclipsed form required for β-elimination in the transition state. On the other hand, the reactions of the tertiary carbonates derived from 2-octanone, which should provide two regioisomeric olefins, were significantly affected by the palladium catalysts used (entries 7, 8 and 9). That is, 1,1-disubstituted alkenes **II** were formed by $Pd(OAc)_2/PPh_3$ in a highly regioselective manner. In sharp contrast, trisubstituted alkenes **I** were afforded selectively by the action of $Pd_2(dba)_3$ and dppf. Bidentate phosphines are suitable for the selective formation of the trisubstituted alkenes; dppf [1,1'-bis(diphenylphosphino)ferrocene] being much superior to dppe [1,2-bis(diphenylphosphino)-ethane], dppp [1,3-bis(diphenylphosphino)-propane], and dppb [1,4-bis(diphenylphosphino)butane]. Interestingly, the adjacent oxygen functionality has a large influence on the regioselectivity, 1,1-disubstituted alkene **II** being afforded with high regioselectivity (entry 10). In particular, the reaction with $Pd(OAc)_2$ and PPh_3 showed perfect regioselectivity.

Then, secondary 2-alkynyl carbonates were subjected to this elimination reaction, giving rise to the conjugated enynes by the action of $Pd(OAc)_2$ and PPh_3 (entries 11–13), but with poor stereoselectivity, giving nearly equal amounts of *E* and *Z* isomers (entries 12 and 13). The reaction with $Pd_2(dba)_3/dppf$ was sluggish for these carbonates. By this reaction, labile 2-(alkynyl)butadienes, not easily available by conventional methods [20], were also obtained in satisfactory yields (entries 14 and 15).

As a synthetic method of the conjugated enynes, the coupling reaction of terminal alkynes with alkenyl halides using Pd^0 and Cu^I as the catalysts is well known [21]. However, preparation of alkenyl halides with functional groups is not always easy. On the other hand, the reaction reported in this paper offers a convenient synthetic method for conjugated enynes. The method is particularly useful because the 2-alkyl carbonates are prepared easily by the reaction of terminal alkynes with ketones or aldehydes.

3. Experimental details

3.1. General

^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were taken in $CDCl_3$ as solvent. Chemical shifts are given in δ units relative to tetramethylsilane as an internal standard. High resolution mass spectra (HRMS) were recorded on Jeol-JMS-DX 303 HF. The elemental analyses were carried out with a Perkin Elmer 2400 CHN Elemental Analyzer.

3.2. Preparation of 2-alkynyl formates for hydrogenolysis

All 2-alkynyl alcohols were prepared by the reaction of ketones or aldehydes with magnesium or lithium acetylides. The 2-alkynyl alcohols thus prepared were treated with a mixture of formic acid and acetic anhydride to give 2-alkynyl formates. A typical procedure

for the preparation of formate of 2-methyl-4-tridecyn-3-ol is the following (Table 1, entry 1). A mixture of pyridine (4.04 ml, 50 mmol) and 2-methyl-4-tridecyn-3-ol (1.05 g, 5 mmol) was cooled to 0°C, and a mixture of Ac_2O (2.36 ml, 25 mmol) and HCO_2H (0.94 ml, 25 mmol) was added; the mixture was stirred at room temperature for 1 h. Benzene (20 ml) and ethyl acetate (20 ml) were added to the reaction mixture, which was treated with water (40 ml) and 1 N HCl (40 ml). The organic layer was washed with aq. $NaHCO_3$ and dried ($MgSO_4$). The solvent was evaporated to afford a yellowish oil, which was purified by column chromatography. The formate was obtained as a pale yellow oil (1.07 g, 90%).

3.3. Hydrogenolysis of formate (entry 1)

To a mixture of $Pd(acac)_2$ (30.4 mg, 0.1 mmol) and benzene (1.5 ml), $^nBu_3P$ (0.025 ml, 0.1 mmol) was added dropwise with stirring. A brown mixture rapidly turned to a clear pale yellow solution. A benzene (3 ml) solution of the formate (238 mg, 1 mmol), obtained in the above, was added to the catalyst solution and the mixture was stirred at room temperature for 3 h. The mixture was diluted with ether (20 ml) and passed through Florisil. A crude oil was obtained after evaporation of the solvent, and purified by column chromatography to afford 2-methyl-4-tridecyne as an oil (178.8 mg, 92%).

Hydrogenolysis of other formates were carried out similarly and the physical data for the allene and alkynes are as follows.

13-Methoxymethyloxy-1,2-tridecadiene. ^{1}H NMR: δ 1.27–1.50 (m, 14H, CH_2); 1.52–1.63 (m, 2H, CH_2); 1.93–2.03 (m, 2H, CH_2); 3.35 (s, 3H, OCH_3); 3.50 (t, J = 6.62 Hz, 2H, OCH_2); 4.61 (s, 2H, OCH_2O); 4.63 (dt, J = 6.60, 3.30 Hz, 2H, CH_2=C); 5.08 (t, t, J = 6.60, 6.70 Hz, 1H, CH=C). ^{13}C NMR: δ 18.7, 26.2, 28.2, 28.9, 29.0, 29.1, 29.2, 29.5, 29.7, 55.0, 67.8, 74.5, 90.0, 92.9, 96.3, 208.4. MS: *m/e* 240 (M^+). HRMS: ($M^+ - C_2H_6O$) $C_{13}H_{22}O$ calcd.: 194.1671. Found: 194.1617.

The following alkynes are shown in Table 1.

2-Methyl-4-tridecyne (entry 1). ^{1}H NMR: δ 0.88 (t, J = 6.60 Hz, 3H, CH_3); 0.95 (d, J = 6.96 Hz, 6H, CH_3); 1.20–1.52 (m, 12H, CH_2); 1.70–1.81 (m, 1H, CH); 2.0–2.50 (m, 2H, CH_2); 2.12–2.18 (m, 2H, CH_2). ^{13}C NMR: δ 14.1, 18.7, 21.9, 22.6, 28.0, 28.3, 28.8, 29.1, 29.2, 31.8, 79.0, 81.1. HRMS: $C_{14}H_{26}$ calcd.: 194.2034. Found: 194. 1959.

1,2-Dimethylmethylenedioxy-5-dodecyne (entry 2). ^{1}H NMR: δ 0.87 (t, J = 6.66 Hz, 3H, CH_3); 1.22–1.50 (m, 8H, CH_2); 1.34 (s, 3H, CH_3); 1.39 (s, 3H, CH_3); 1.60–1.85 (m, 2H, CH_2); 2.08–2.16 (m, 2H, CH_2); 2.20–2.30 (m, 2H, CH_2); 3.57 (dd, J = 7.80, 7.48 Hz, 1H, OCH); 4.08 (dd, J = 7.80, 6.00 Hz, 1H, OCH); 4.15–4.24 (m, 1H, OCH). ^{13}C NMR: δ 14.0, 15.3, 22.5, 25.6, 25.7, 26.9, 28.5, 28.7, 29.0, 31.3, 33.1, 69.2, 75.0, 78.9, 80.9, 108.6. Anal. Found: C, 75.72; H, 11.39.$C_{15}H_{26}O_2$ calcd.: C, 75.58; H, 11.00%.

1-Benzyloxy-2,3-dimethylmethylenedioxy-5-dodecyne (entry 3). ^{1}H NMR; δ 0.89 (t, J = 6.96 Hz, 3H, CH_3); 1.20–1.48 (m, 8H, CH_2); 1.43 (s, 3H, CH_3); 2.04–2.10 (m, 2H, CH_2); 2.45–2.60 (m, 2H, CH_2); 3.55–3.72 (m, 2H, OCH_2); 3.85–4.10 (m, 2H, OCH); 4.58 (d, J = 12.09 Hz, 1H, OCH); 4.63 (d, J = 12.9 Hz, 1H, OCH); 7.26–7.35 (m, 5H, aromatic protons). ^{13}C NMR: δ 13.7,14.0, 18.6, 22.5, 23.2, 27.0, 27.06, 27.09, 28.4, 28.6, 28.7, 28.8, 31.3, 31.6, 70.7, 73.5, 74.8, 76.1, 79.7, 80.3, 82.9, 109.2, 127.6, 128.3, 138.0. Anal. Found: C, 76.83; H, 9.63. $C_{22}H_{32}O_3$ calcd.: C, 76.70; H, 9.36%.

1-t-Butyldimethylsiloxy-2,3-dimethylmethylenedioxy-5-dodecyne (entry 4). ^{1}H NMR: δ 0.073 (s, 6H, $SiCH_3$); 0.89 (t, J = 5.86 Hz, 3H, CH_3); 0.90 (s, 9H, CH_3); 1.20–1.52 (m, 8H, CH_2); 1.39 (s, 3H, CH_3); 1.42 (s, 3H, CH_3); 2.12–2.18 (m, 2H, CH_2); 2.50–2.55 (m, 2H, CH_2); 3.79 (d, J = 4.03 Hz, 2H, OCH_2); 3.85–4.01 (m, 2H, OCH). ^{13}C NMR: -5.48, -5.39, 14.0, 18.3, 18.8, 22.5, 23.3, 25.9, 27.0, 27.2, 28.6, 28.9, 31.3, 63.6, 75.2, 76.2, 80.6, 82.5, 108.8. Anal. Found: C, 68.56; H, 11.27. $C_{21}H_{40}O_3Si$ calcd.: C, 68.42; H, 10.94%.

2-Methoxymethyloxy-4-undecyne (entry 5). ^{1}H NMR: δ 0.87 (t, J = 6.59 Hz, 3H, CH_3); 1.25 (d, J = 6.23 Hz, 3H, CH_3); 1.20–1.50 (m, 8H, CH_2); 2.10–2.16 (m, 2H, CH_2); 2.26–2.45 (m, 2H, CH_2); 3.36 (s, 3H, OCH_3); 3.75–3.84 (m, 1H, OCH); 4.67 (s, 2H, OCH_2O). ^{13}C NMR: δ 14.0, 18.7, 19.9, 22.5, 26.9, 28.5, 28.9, 29.0, 31.3, 31.6, 55.2, 70.9, 72.0, 76.5, 82.0, 93.5, 95.0. Anal. Found: C, 73.72; H, 11.71. $C_{13}H_{24}O_2$ calcd.: C, 73.53; H, 11.39%.

N-Boc-2,2-dimethyl-5-(2-nonynyl)oxazolidine (entry 6). ^{1}H NMR: δ 0.87 (t, J = 6.60 Hz, 3H, CH_3); 1.20–1.60 (m, 8H, CH_2); 1.46 (s, 15H, CH_3); 2.08–2.68 (m, 4H, CH_2); 3.80–4.02 (m, 3H, NCH, OCH). ^{13}C NMR: δ 14.0, 18.7, 22.5, 23.3, 23.4, 24.6, 26.6, 27.5, 28.4, 28.5, 28.9, 31.3, 56.8, 57.0, 66.6, 66.8, 76.4, 79.8, 80.2, 81.9, 82.2, 93.6, 94.2, 151.6, 152.1. Anal. Found: C, 70.55; H, 10.59; N, 4.16. $C_{19}H_{33}NO_3$ calcd.: C, 70.55; H, 10.28; N, 4.33%.

1-(2-N-Boc-pyrrolidyl)-2-nonyne (entry 7). ^{1}H NMR: δ 0.89 (t, J = 6.59 Hz, 3H, CH_3); 1.20–1.40 (m, 8H, CH_2); 1.44 (s, 9H, CH_3); 1.70–2.0 (m, 4H, CH_2);

2.05–2.06 (m, 4H, CH_2); 3.25–3.43 (m, 2H, NCH_2); 3.72–3.91 (m, 1H, NCH). ^{13}C NMR: δ 14.0, 18.7, 22.5, 22.8, 23.6, 24.2, 28.5, 28.9, 29.7, 30.5, 31.3, 46.6, 47.0, 56.4, 79.2, 154.4. Anal. Found: C, 73.82; H, 11.01; N, 4.56. $C_{18}H_{31}NO_2$ calcd.: C, 73.67; H, 10.65; N, 4.77%.

2-Methyl-4-N-Boc-amino-6-tridecyne (entry 8). ^1H NMR: δ 0.87–0.95 (m, 9H, CH_3); 1.25–1.51 (m, 10H, CH_2); 1.45 (s, 9H, CH_3); 1.58–1.65 (m, 1H, CH); 2.12–2.18 (m, 2H, CH_2); 2.25–2.44 (m, 2H, CH_2); 3.70–3.80 (m, 1H, NCH); 4.50–4.60 (m, 1H, NH). ^{13}C NMR: δ 13.8, 14.0, 18.7, 21.1, 22.5, 22.8, 24.4, 24.8, 25.2, 26.1, 28.4, 28.5, 29.0, 31.4, 43.2, 47.1, 75.8, 79.1, 82.8, 155.3. Anal. Found: C, 73.93; H, 11.88; N, 4.36. $C_{19}H_{35}NO_2$ calcd.: C, 73.73; H, 11.40; N, 4.53%.

3.4. Preparation of 2-alkynyl carbonates for the elimination

The 2-alkynyl alcohols prepared as described above were treated with methyl chloroformate to give 2-alkynyl carbonates. A typical example of the preparation is as follows (Table 2, entry 1). To a THF (7 ml) solution of 1-(1-octynyl)cyclopentanol (1.54 g, 7.96 mmol) was added ^{n}BuLi (6.13 ml, 9.56 mmol) dropwise at −78°C and the mixture was stirred for 1 h. Then methyl chloroformate (0.93 ml, 11.94 mmol) was added dropwise at −78°C. The solution was gradually warmed to room temperature and stirred for 15 h. The reaction was quenched by the addition of a saturated $NaHCO_3$ solution (30 ml) and extracted with ethyl acetate (35 ml). The extract was dried over $MgSO_4$. The solvents were evaporated under a vacuum to give an oily product, which was purified by column chromatography (silica gel, hexane/ethyl acetate/triethylamine, 100:6:1) and pure 1-(1-octynyl)cyclopentyl methyl carbonate was obtained as a colorless oil (1.92 g, 96%).

3.5. The elimination reaction

A typical example of the elimination is as follows (Table 2, entry 1). To a mixture of $Pd_2(dba)_3$ (45.8 mg, 0.05 mmol) and dppf (55.4 mg, 0.10 mmol) in THF (2 ml), a solution of 1-(1-octynyl)cyclopentyl methyl carbonate (252 mg, 1.0 mmol) in THF (2 ml) was added. The solution was heated at 60°C for 1 h. The mixture was cooled to room temperature, ether was added, and filtered through Florisil. A brown oil was obtained after evaporation of the solvent, purified by column chromatography on silica gel (hexane), affording pure 1-(1-octynyl)cyclopentene as a pale yellow oil (164 mg, 93.2%).

The elimination of other carbonates was carried out similarly and the physical data for the enynes shown in Table 2 are as follows.

1-(1-Cyclopentenyl)octyne (entry 1). ^1H NMR: δ 0.88 (t, $J = 6.60$ Hz, 3H, CH_3); 1.22–1.43 (m, 6H, CH_3); 1.46–1.59 (m, 2H, CH_2); 1.83–1.91 (m, 2H, CH_2); 2.31 (t, $J = 6.96$ Hz, 2H, CH_2); 2.35–2.45 (m, 4H, $CH_2C{=}C$) 5.92 (bs, 1H, C=CH). ^{13}C NMR: δ 14.0, 14.1, 19.41, 19.47, 22.5, 23.2, 28.6, 28.8, 31.3, 33.0, 36.6, 77.7, 91.5, 125.0, 135.8, 135.9. HRMS: $C_{13}H_{20}$ calcd.: 176.1565. Found: 176.1618.

1-(1-Cyclopentenyl)-3-(tetrahydropyranyloxy)propyne (entry 2). ^1H NMR: δ 1.49–1.92 (m, 8H, CH_2); 2.36–2.48 (m, 4H, CH_2); 3.48–3.56 (m, 1H, OCH); 3.79–3.89 (m, 1H, OCH); 4.33 (d, $J = 15.7$ Hz, 1H, OCH); 4.42 (d, $J = 15.7$ Hz, 1H, OCH); 4.81 (t, $J = 3.23$ Hz, 1H, OCHO); 6.02–6.07 (m, 1H, C=CH). ^{13}C NMR: δ 19.0, 23.2, 25.3, 30.2, 33.1, 36.2, 54.8, 61.9, 83.1, 86.1, 96.6, 124.0, 138.3. HRMS: $C_{13}H_{18}O_2$ calcd.: 206.1292. Found: 206.1345.

1-(1-Cyclopentenyl)-3-(t-butyldimethylsiloxy)decyne (entry 3). ^1H NMR: δ 0.11, (s, 3H, $SiCH_3$); 0.13 (s, 3H, $SiCH_3$); 0.89 (t, $J = 6.96$ Hz, 3H, CH_3); 0.90 (s, 9H, Si^tBu); 1.20–1.45 (m, 10H, CH_2); 1.60–1.72 (m, 2H, CH_2); 1.83–1.94 (m, 2H, CH_2); 2.36–2.47 (m, 4H, CH_2); 4.46 (t, $J = 6.59$ Hz, 1H, OCH); 5.07–6.01 (m, 1H, C=CH). ^{13}C NMR: δ −4.93, −4.39, 14.1, 18.3, 22.7, 23.2, 25.3, 25.82, 25.87, 29.2, 31.8, 33.2, 36.3, 38.7, 63.5, 81.4, 92.4, 124.4, 137.0. MS: *m/e* 334 (M^+). HRMS: ($M^+ - C_4H_8$) $C_{17}H_{30}OSi$ calcd.: 278.2066. Found: 278.2059.

1-(1-Cycloоctenyl)octyne (entry 4). ^1H NMR: δ 0.89 (t, $J = 6.71$ Hz, 3H, CH_3); 1.24–1.64 (m, 16H, CH_2); 2.10–2.20 (m, 2H, CH_2); 2.24–2.32 (m, 4H, CH_2); 5.97 (t, $J = 8.36$ Hz, 1H, C=CH). ^{13}C NMR: δ 14.1, 19.4, 22.6, 25.8, 26.5, 26.9, 28.4, 28.6, 29.0, 29.8, 30.3, 31.4, 82.9, 87.0, 124.2, 135.8. HRMS: $C_{16}H_{26}$ calcd.: 218.2034. Found: 218.2030.

1-(1-Cyclooctenyl)-3-(t-butyldimethylsiloxy)propyne (entry 5). ^1H NMR: δ 0.13 (s, 6H, $SiCH_3$); 0.91 (s, 9H, CH_3); 1.45–1.63 (m, 8H, CH_2); 2.10–2.20 (m, 2H, CH_2); 2.25–2.32 (m, 2H, CH_2); 4.43 (s, 2H, OCH_2); 6.06 (t, $J = 8.31$ Hz, 1H, C=CH). ^{13}C NMR: δ −5.0, 18.3, 25.69, 25.76, 25.8, 26.3, 26.9, 28.4, 29.6, 29.7, 52.3, 84.7, 87.3, 123.4, 137.6. HRMS: $C_{17}H_{30}OSi$ calcd.: 278.2066. Found: 278.1994.

1-(1-Cycloocenyl)-3-(t-butyldimethylsiloxy)decyne (entry 6). ^1H NMR: δ 0.11 (s, 3H, $SiCH_3$); 0.13 (s, 3H, $SiCH_3$); 0.88 (t, $J = 6.83$ Hz, 3H, CH_3); 1.20–1.70 (m, 20H, CH_2); 2.10–2.20 (m, 2H, CH_2); 2.24-02.38 (m, 2H, CH_2); 4.42 (t, $J = 6.53$ Hz, 1H, OCH); 6.02 (t,

J = 8.36 Hz, C=CH). ^{13}C NMR: δ −4.90, −4.40, 14.1, 18.3, 22.7, 25.4, 25.8, 25.9, 26.4, 26.9, 28.4, 29.2, 29.7, 29.9, 31.8, 38.8, 63.5, 86.5, 88.1, 123.5, 137.0. MS: *m/e* 376 (M^+). HRMS: ($M^+ - C_4H_8$) $C_{20}H_{36}OSi$ calcd.: 320.2536. Found: 320.2527.

7-Methylpenta-6-decen-8-yne (I) and 2-hexyl-1-decen-3-yne (II) (entry 7). ^{1}H NMR (**I:II** = 86:14): δ 0.89 (m, 6H, CH_3); 1.20–1.61 (m, 14H, CH_2); 1.81 (s, 2.58H, CH_3); 2.08–2.26 (m, 2H, CH_2); 2.34 (t, J = 6.77 Hz, 2H, CH_2); 5.11 (bs, 0.14H, C=CH); 5.20 (bs, 0.14H, C=CH); 5.57 (t, J = 7.27 Hz, 0.86H, C=CH). ^{13}C NMR: δ 14.1, 19.5, 22.5, 23.4, 28.1, 28.5, 28.6, 28.9, 30.5, 31.4, 31.5, 31.7, 80.0, 93.6, 118.0, 136.7. HRMS: $C_{16}H_{28}$ calcd.: 220.2191. Found: 220.2195.

1-t-Butyldimethylsiloxy-4-methyl-4-decen-2-yne (I) and 5-(t-butyldimethylsiloxy)-2-hexyl-1-penten-3-yne (II) (entry 8). ^{1}H NMR (**I:II** = 83:17): δ 0.13 (s, 3H, $SiCH_3$); 0.14 (s, 3H, $SiCH_3$); 0.88 (t, J = 6.72 Hz, 3H, CH_3); 0.93 (s, 9H, Si^{t}Bu); 1.24–1.38 (m, 6H, CH_2); 1.82 (s, 2.49H, CH_3); 2.10–2.25 (m, 2H, CH_2); 4.43 (s, 0.34H, OCH_2O); 4.47 (s, 1.66H, OCH_2); 5.20 (bs, 0.17H, C=CH); 5.29 (bs, 0.17H, C=CH); 5.65 (t, J = 7.33 Hz, 0.83H, C=CH). ^{13}C NMR: δ −5.10, 14.1, 18.3, 22.6, 22.61, 25.8, 28.9, 30.6, 31.5, 52.3, 84.3, 91.1, 117.3, 138.3. MS: *m/e* 280 (M^+). HRMS: ($M^+ - C_4H_8$) $C_{17}H_{24}OSi$ calcd.: 224.1597. Found: 224.1568.

7-Methyl-10-t-butyldimethylsiloxyhepta-6-decen-8-yne (I) and 5-t-butyldimethylsiloxy-2-hexyl-1-dodecen-3-yne (II) (entry 9). ^{1}H NMR (**I:II** = 72:28): δ 0.12 (s, 3H, $SiCH_3$); 0.14 (s, 3H, $SiCH_3$); 0.88 (t, J = 6.84 Hz, 3H, CH_3); 0.91 (s, 9H, Si^{t}Bu); 1.20–1.55 (m, 16H, CH_2); 1.64–1.75 (m, 2H, CH_2); 1.82 (s, 2.16H, CH_3); 2.10–2.25 (m, 2H, CH_2); 4.49 (t, J = 6.53 Hz, 1H, OCH); 5.18 (bs, 0.28H, C=CH); 5.26 (bs, 0.28H, C=CH); 5.62 (t, J = 7.20 Hz, 0.72H, C=CH). ^{13}C NMR: δ −5.0, −4.4, 14.1, 18.3, 22.7, 23.1, 25.4, 25.9, 28.6, 28.9, 29.3, 30.6, 31.7, 31.8, 37.3, 38.7, 38.9, 63.6, 83.4, 94.5, 117.5, 137.8. HRMS: $C_{24}H_{46}OSi$ calcd.: 378.3318. Found: 378.3372.

2-(t-butyldimethylsiloxy)-6-(tetrahydropyranyloxy)-2-hexen-4-yne (I) and 1-tetrahydropyranyloxy-4-(1-t-butyldimethylsiloxyethyl)-4-penten-2-yne (II) (entry 10). ^{1}H NMR (**I:II** = 0:100): δ 0.05 (s, 3H, $SiCH_3$); 0.06 (s, 3H, $SiCH_3$); 0.90 (s, 9H, Si^{t}Bu); 1.30 (d, J = 6.35 Hz, 3H, CH_3); 1.45–1.88 (m, 6H, CH_2); 3.50–3.58 (m, 1H, OCH), 3.80–3.90 (m, 1H, OCH); 4.26 (q, J = 6.35 Hz, 1H, OCH); 4.36 (d, J = 15.8 Hz, 1H, OCH); 4.42 (d, J = 15.8 Hz, 1H, OCH); 4.82–4.86 (m, 1H, OCHO); 5.39 (bs, 1H, C=CH); 5.58 (bs, 1H, C=CH). ^{13}C NMR: δ −5.0, −4.9, 18.2, 19.0, 23.8, 25.4, 25.8, 30.2, 54.6, 62.0, 70.5, 84.4, 86.5, 96.7, 119.5, 135.7. HRMS: $C_{18}H_{32}O_3Si$ calcd.: 324.2122. Found: 324.2128.

^{1}H NMR (**I:II** = 28:72): δ 0.05 (s, 2.16H, $SiCH_3$); 0.06 (s, 2.16H, $SiCH_3$); 0.13 (s, 0.84H, $SiCH_3$); 0.17 (s, 0.84H, $SiCH_3$); 0.90 (s, 6.48H, Si^{t}Bu); 0.94 (s, 2.52H, Si^{t}Bu); 1.30 (d, J = 6.35 Hz, 2.16H, CH_3); 1.46–1.90 (m, 6H, CH_2); 1.70 (s, 0.84H, CH_3); 1.80 (s, 0.84H, CH_3); 3.49–3.58 (m, 1H, OCH); 3.80–3.90 (m, 1H, OCH); 4.26 (q, J = 6.35 Hz, 2.16H, OCH); 4.35 (d, J = 15.8 Hz, 1H, OCH); 4.42 (d, J = 15.8 Hz, 1H, OCH); 4.82–4.86 (m, 1H, OCHO); 5.38 (bs, 0.72H, C=CH); 5.58 (bs, 0.72H, C=CH). ^{13}C NMR: δ −5.0, −4.9, −4.5, 17.0, 18.2, 19.0, 23.8, 25.4, 25.8, 30.2, 31.0, 54.6, 62.0, 70.5, 84.4, 86.5, 96.7, 119.5, 135.7. HRMS: $C_{18}H_{32}O_3Si$ calcd.: 324.2122. Found: 324.2131.

2-Methyl-6-t-butyldimethylsilyloxy-2-tridecen-4-yne (entry 11). ^{1}H NMR: δ 0.11 (s, 3H, $SiCH_3$); 0.13 (s, 3H, $SiCH_3$); 0.88 (t, J = 6.77 Hz, 3H, CH_3); 0.91 (s, 9H, Si^{t}Bu); 1.20–1.50 (m, 10H, CH_2); 1.63–1.74 (m, 2H, CH_2); 1.79 (s, 3H, CH_3); 1.88 (s, 3H, CH_3); 4.49 (t, J = 6.54 Hz, 1H, OCH); 5.27 (bs, 1H, C=CH). ^{13}C NMR: δ −5.0, −4.4, 14.1, 18.3, 20.8, 22.7, 24.7, 25.4, 25.8, 29.3, 31.8, 39.0, 63.6, 82.0, 93.2, 105.1, 147.9. HRMS: $C_{20}H_{38}OSi$ calcd.: 322.2614. Found: 322.2645.

5-Dodecen-7-yne (entry 12). ^{1}H NMR: δ 0.83–0.96 (m, 6H, CH_3); 1.22–1.58 (m, 8H, CH_2); 2.03–2.12 (m, 1.16H, CH_2); 2.22–2.38 (m, 2.84H, CH_2); 5.38–5.49 (m, 1H, C=CH); 5.79 (dt, J = 10.40, 7.38 Hz, 0.48H, C=CH); 6.03 (dt, J = 15.80, 7.08 Hz, 0.52H, C=CH). ^{13}C NMR: δ 14.11, 14.14, 14.4, 14.6, 19.6, 19.7, 22.49, 22.53, 22.7, 22.8, 23.2, 30.2, 31.50, 31,54, 31.6, 33.2, 77.9, 79.7, 89.1, 94.9, 109.9, 110.4, 143.0, 143.8. HRMS: $C_{12}H_{20}$ calcd.: 164.1566. Found: 164.1570.

7,11-Octadecadien-9-yne (entry 13). ^{1}H NMR: δ 0.80–0.97 (m, 6H, CH_3); 1.18–1.47 (m, 16H, CH_2); 2.04–2.16 (m, 3.10H, CH_2); 2.26–2.35 (m, 0.90H, CH_2); 5.52–6.17 (m, 4H, C=CH). ^{13}C NMR: δ 14.1, 22.6, 22.7, 28.77, 28.8, 30.2, 31.6, 31.7, 33.1, 84.9, 86.8, 92.4, 109.1, 109.7, 109.8, 143.3, 144.3. HRMS: $C_{18}H_{30}$ calcd.: 246.2349. Found: 246.2354.

3-Methylene-1-undecen-4-yne (entry 14). ^{1}H NMR: δ 0.80–0.98 (m, 3H, CH_3); 1.19–1.64 (m, 8H, CH_2); 2.37 (t, J = 7.02 Hz, 2H, CH_2); 5.22 (d, J = 10.50 Hz, 1H, C=CH); 5.35 (s, 1H, C=CH); 5.44 (s, 1H, C=CH); 5.63 (d, J = 17.3 Hz, 1H, C=CH); 6.35 (dd, J = 17.3, 10.11 Hz, 1H, C=CH). ^{13}C NMR: δ 14.1, 19.3 22.6, 28.6, 31.3, 31.6, 76.9, 92.9, 117.3, 122.6, 130.5, 136.7. HRMS: $C_{12}H_{18}$ calcd.: 162.1409. Found: 162.1412.

6-Tetrahydropyranyloxy-3-methylene-1-hexen-4-yne (entry 15). ^{1}H NMR: δ 1.42–1.91 (m, 6H, CH_2); 3.46–3.57 (m, 1H, OCH); 3.78–3.91 (m, 1H, OCH);

4.41 (d, $J = 15.84$ Hz, 1H, OCH); 4.47 (d, $J = 15.84$ Hz, 1H, OCH); 4.86 (t, $J = 3.30$ Hz, 1H, OCHO); 5.34 (d, $J = 10.00$ Hz, 1H, C=CH); 5.43 (s, 1H, C=CH); 5.52 (s, 1H, C=CH); 5.62 (d, $J = 17.03$ Hz, 1H, C=CH); 6.33 (dd, $J = 17.03$, 10.00 Hz, 1H, C= CH). ^{13}C NMR: δ 19.0, 25.3, 30.3, 54.5, 62.0, 82.2, 87.5, 96.7, 117.8, 124.2, 129.6, 135.9. HRMS: $C_{12}H_{16}O_2$ calcd.: 192.1151. Found: 192.1160.

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