Pergamon

Tetrahedron 55 (1999) 8155–8167

TETRAHEDRON

Novel 1,3-Diene Synthesis from Alkyne and Ethylene by Ruthenium-Catalyzed Enyne Metathesis

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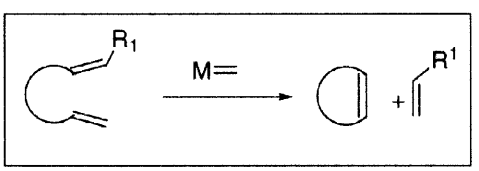
Received 1 March 1998; accepted 10 December 1998

Abstract:
A novel 1,3-diene synthetic method from alkyne and ethylene was developed using ruthenium-catalyzed enyne metathesis. The reaction procedure is very simple: A CH_2Cl_2 solution of alkyne was stirred at room temperature under ethylene gas (1 atm.) in the presence of a catalytic amount of ruthenium benzylidene complex. The yield was good and the conversion yield was high. Dienes having functional groups such as a keto-carbonyl group, silyloxy group, ester, and ketal were synthesized from the corresponding alkynes and ethylene. In this reaction, the alkyne having a hetero atom at the propargylic position gave a good result and ether oxygen or amine nitrogen that coordinate strongly to the ruthenium catalyst prevents the reaction.

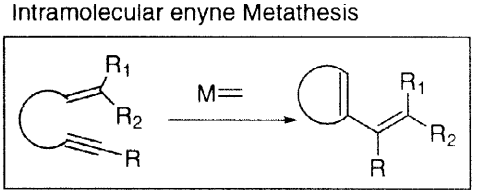
Key Words: *Enyne Metathesis; Diene; Ruthenium; Metathesis; Alkyne Metathesis; Ethylene;*

Metathesis reaction is a powerful strategy in synthetic organic chemistry,[1] and it is generally accepted that this reaction is catalyzed by transition metal alkylidenes.[2] Intermolecular-diene metathesis produces many olefins and it is difficult to synthesize the desired olefin selectively by diene metathesis although these reactions are dependent on the steric and electronic nature of the substituents on the alkene.[3] Recently, some intermolecular diene metathesis reactions have been reported.[3] Diene-metathesis has usually been used as intramolecular-diene metathesis,[4] and it provides a cyclized product and alkylidenes. Intramolecular-enyne metathesis is a very unique reaction.[5] It seems likely that the alkylidene part of the alkene migrates to the alkyne carbon. Thus, the resultant cyclized product has the diene moiety.

Intramolecular Diene Metathesis



Intramolecular enyne Metathesis

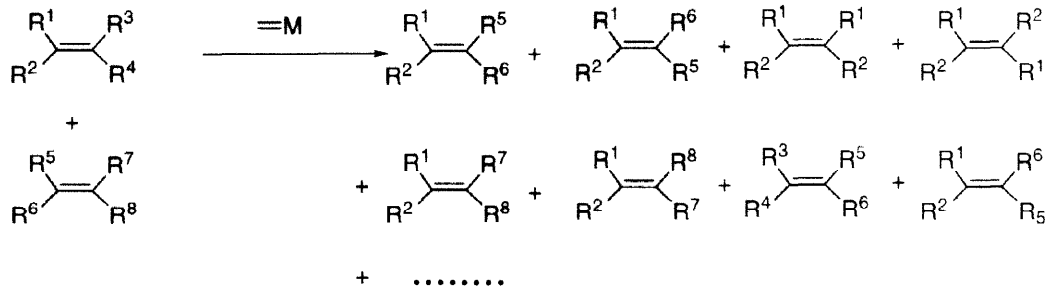


However, intermolecular enyne metathesis is more complicated than intermolecular diene metathesis, because three kinds of metatheses, intermolecular diene metathesis, intermolecular alkyne metathesis, and intermolecular enyne metathesis, are included in this reaction and they produce many olefins, dienes, and polymers as shown in Scheme 2. Moreover, these products are further metathesized by carbene complex to give a complicated mixture. Thus, it seems that it is impossible to use this reaction for the

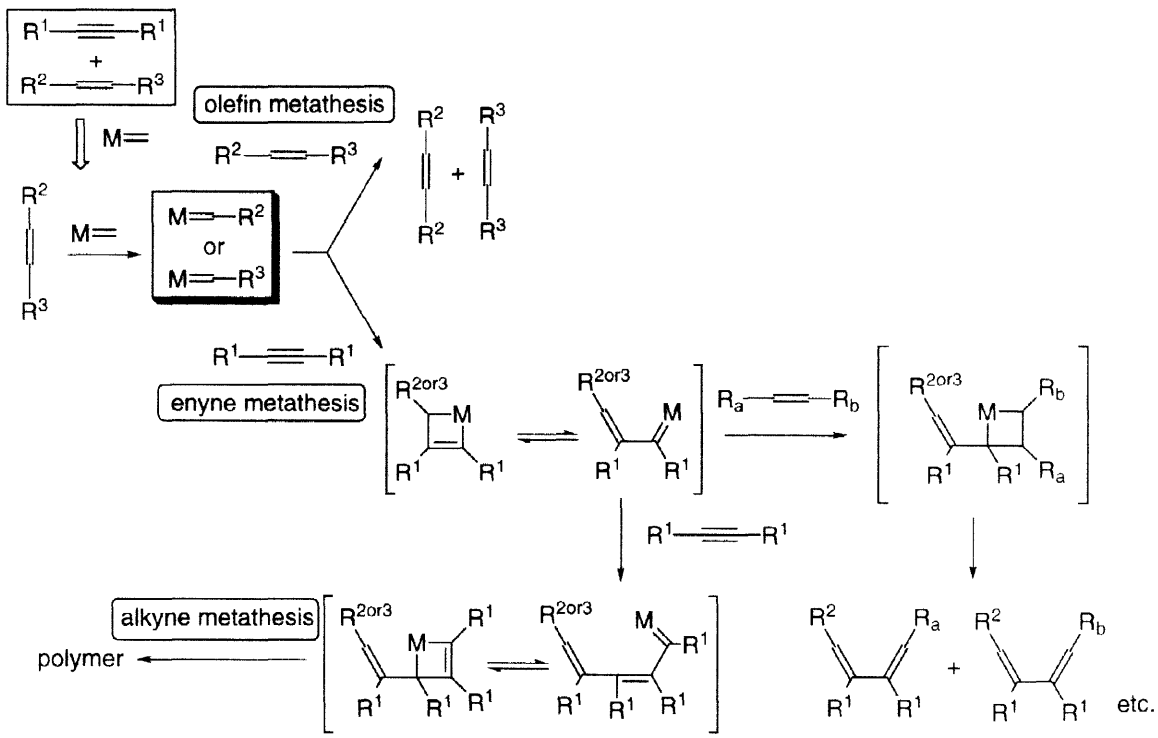
PII: S0040-4020(99)00297-5

synthesis of desired diene selectively.

Scheme 1 Intermolecular-Diene Metathesis

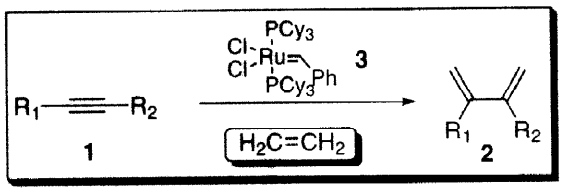


Scheme 2 Reaction Course of Intermolecular Enyne Metathesis

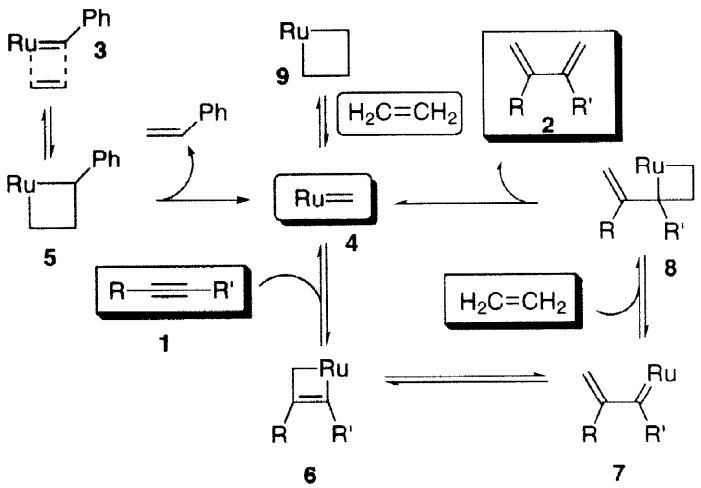


1,3-Diene is useful in synthetic organic chemistry, and many synthetic procedures are known[6,7]: elimination from allyl bromide, allyl alcohol, 1,4- or 2,3-dihalogenated compound by a base or Zn, or ring opening of cyclobutene, and symmetrical or unsymmetrical coupling reactions of vinylic compounds using organometallic complexes. We planned 1,3-diene synthesis by intermolecular ruthenium-catalyzed enyne metathesis.[8] Our plan is shown in Scheme 3. In this reaction, we used ethylene gas as the alkene. Reaction of ethylene with ruthenium carbene complex **3** produces ruthenacyclobutane **5**, which converts into the real catalyst **4** and styrene.[9] It reacts with alkyne **1** to produce ruthenacyclobutene **6**, which converts into ruthenium vinylmethylidene complex **7**. It should react with ethylene, not alkyne **1**, to produce diene **2** *via* ruthenacyclobutane **8**, and ruthenium methylidene complex **4** would be regenerated. If ruthenium methylidene complex **4** reacts with ethylene, ruthenacyclobutane **9** is produced. However, this process is a so-called *non-productive process*, and ethylene and ruthenium methylidene complex **4** are reproduced. Thus, the desired diene **2** should be obtained.

Scheme 3 Our Plan for 1,3-Diene Synthesis Using Intermolecular-Enyne Metathesis

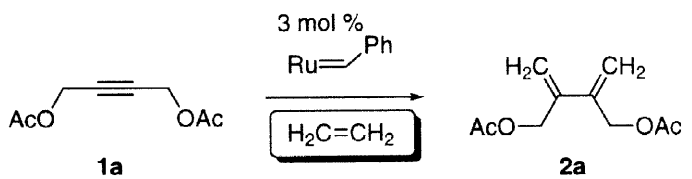


Pathway for Intermolecular Enyne Metathesis



When a CH_2Cl_2 solution of symmetrical alkyne **1a** and ruthenium carbene complex **3** (3 mol %) was stirred at room temperature for 45 h under ethylene gas, the desired diene was obtained in 66% yield (conversion yield, 89%). The use of 10 mol% of ruthenium complex **3** slightly improved the yield of the diene.

Scheme 4 Reaction of alkyne **1a** with **3** under ethylene gas

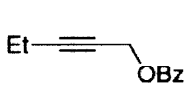
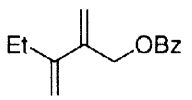
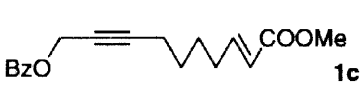
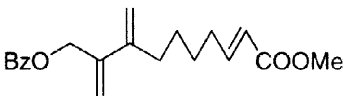
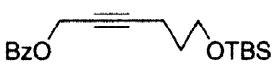
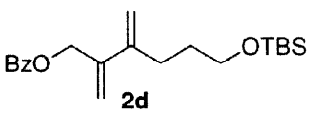
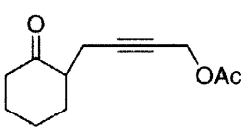
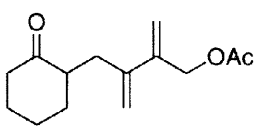
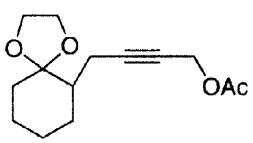
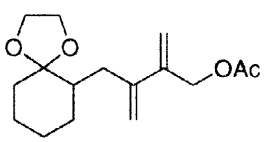
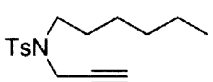
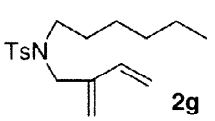
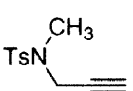
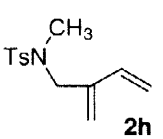


3 (mol %)	yield (%)	conversion yield (%)
3	66	89
10	71	90

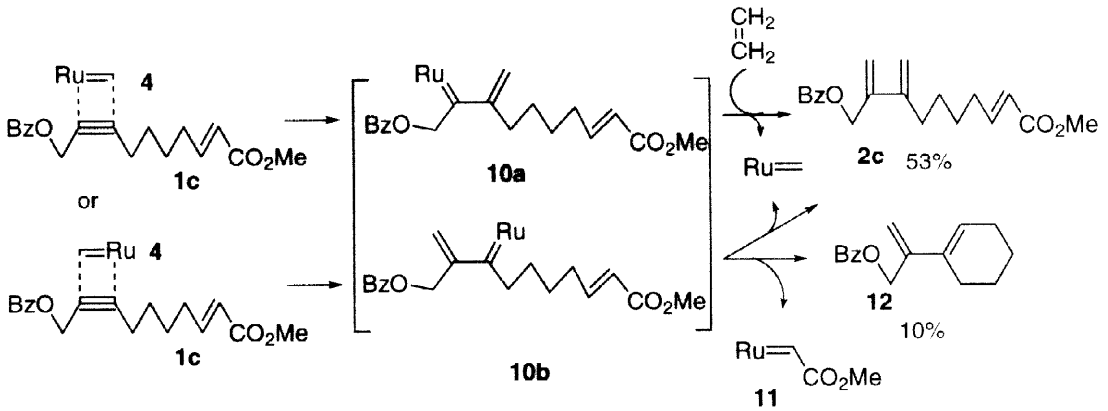
In a similar manner, the reactions of various alkynes **1** with ruthenium carbene complex **3** under ethylene gas were carried out, and the results are shown in Table 1. Dienes having functional groups such as a keto-carbonyl group, silyloxy group, ester, and ketal were synthesized from the corresponding alkynes and ethylene. It was quite interesting that the terminal alkyne could be converted into diene in high yield (Run 6). The yields were good to moderate, and the conversion yields were high.

In the reaction of **1c** with ethylene, cyclized product **12** was obtained as a by-product in 10% yield. Presumably, ruthenium carbene complex **4** reacts with **1c** to give **10a** and/or **10b**, and then it reacts with ethylene to give the desired diene **2c**. On the other hand, ruthenium carbene complex **10b** reacts with internal olefin to give the 6-membered cyclized diene **12** and ruthenium carbene complex **11**.

Table 1 1,3-Diene Synthesis of Intermolecular Enyne Metathesis

Run	Substrate	Ru (mol %)	Product	Yield [a]
1	 **1b**	3	 **2b**	62% (100%)
2	 **1c**	10 [b]	 **2c**	53% (82%)
3	 **1d**	10 [b]	 **2d**	60% (86%)
4	 **1e**	3	 **2e**	74% (89%)
5	 **1f**	3	 **2f**	48% (84%)
6	 **1g**	5	 **2g**	81% (100%)[c]
7	 **1h**	10 [b]	 **2h**	45% (65%)[d]

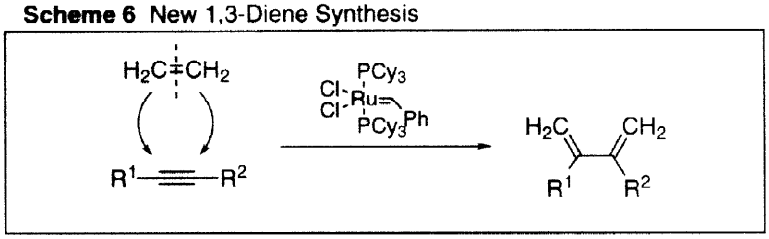
All reactions were carried out in CH_2Cl_2 (0.1 M solution) under ethylene gas using ruthenium catalyst at room temperature for 45 h. a) Yields in parenthesis are conversion yields. b) 5 mol % of ruthenium catalyst **3** was used. After 40 h, 5 mol % of **3** was readded. c) 0.03 M solution, Reaction time, 22h. d) Reaction time, 22 h.



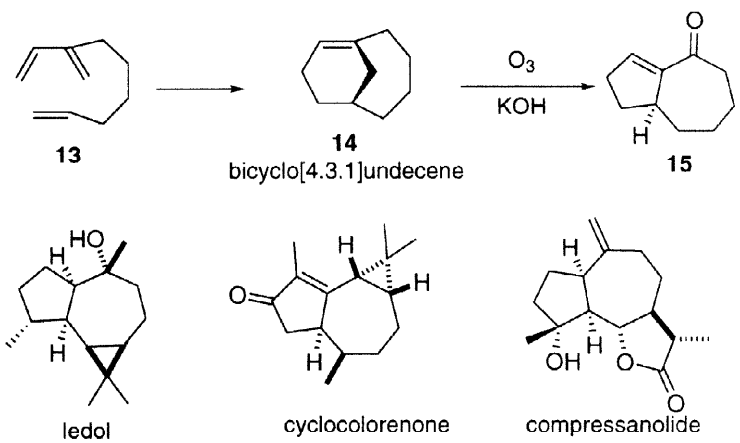
Scheme 5

The results indicate that a novel synthetic method of 1,3-diene from alkyne and ethylene could be developed using ruthenium-catalyzed enyne metathesis. The remarkable characteristic for this procedure is that the synthetic procedure is very simple, namely, the CH_2Cl_2 solution of alkyne was stirred at room temperature under ethylene gas (1 atm.) in the presence of a catalytic amount of ruthenium benzylidene catalyst (3-10 mol %).

Scheme 6 New 1,3-Diene Synthesis

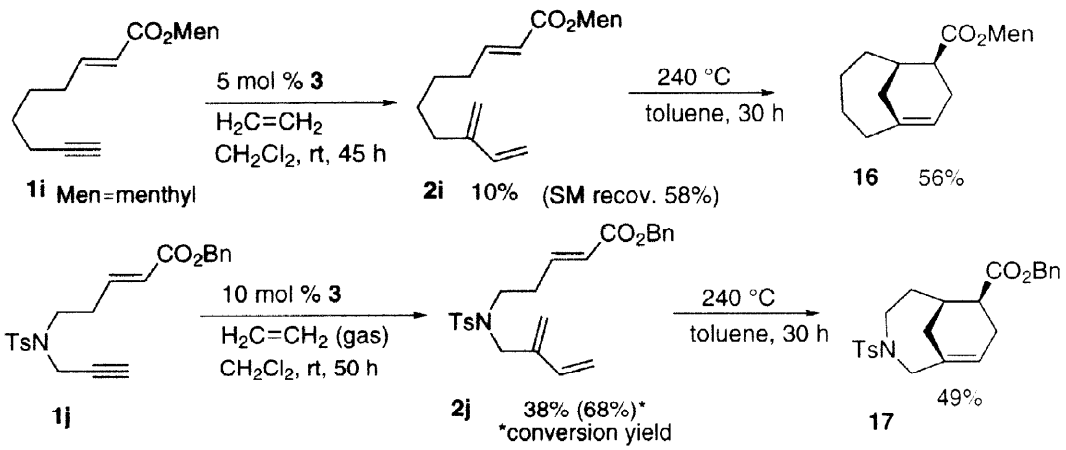


Recently, a very efficient method of synthesizing bicyclo[5.3.0]undecene skeleton from bicyclo[4.3.1]undecene by intramolecular Diels-Alder reaction was reported.[10] These skeletons are widely found in natural products; for example, ledol, cyclocolorenone, and compressanolide. If the present method can be used for the synthesis of the starting triene, a short synthetic pathway could be developed for the synthesis of these natural products.



Scheme 7

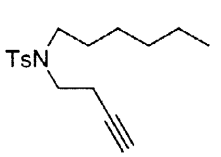
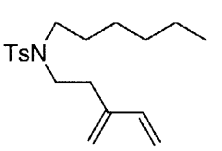
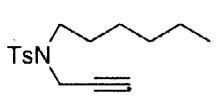
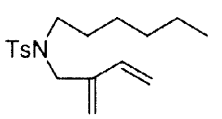
Scheme 8 Synthesis of bicyclo[4.3.1]undecene



When enyne **1i** was treated with 5 mol % of ruthenium carbene complex **3** in CH_2Cl_2 at room temperature for 45 h under ethylene gas, the desired diene **2i** was obtained although the yield was low. A toluene solution of triene **2i** was heated at 240 °C for 30 h to give bicyclo[4.3.1]undecene **16** in 56% yield. In a similar manner, alkyne **1j** was treated with **3** under ethylene gas to provide triene **2j** in 38% yield (conversion yield, 68%). These results indicate that bicyclo[4.3.1]undecene skeletons are easily obtained from trienes **2i** and **2j**, which were obtained from alkynes **1i** and **1j**, respectively. However, the yield of triene **2i** was low. Although the reason why the enyne metathesis product was obtained in low yield in this case is not clear, we noticed that all of the alkynes, except **1i**, used in this diene synthesis have a hetero atom such as amide nitrogen or ester oxygen at the propargylic position.

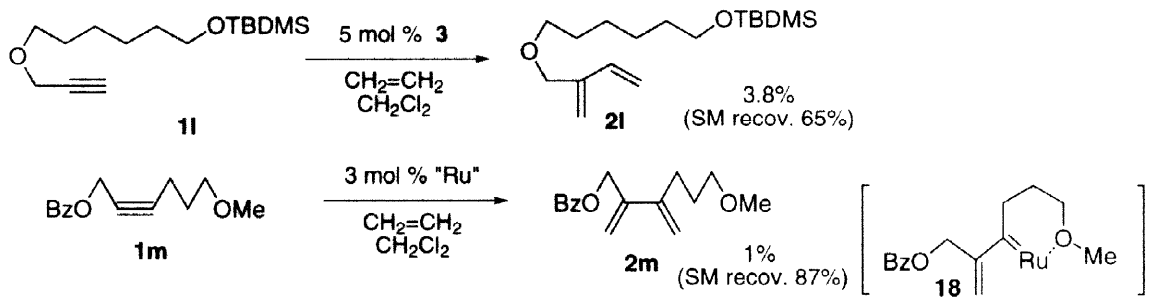
Thus, we reinvestigated this diene synthesis. When alkyne **1k**, whose methylene is elongated compared with that of **1g**, was treated with **3** in a similar manner under ethylene gas, the desired diene was obtained in only 11% yield, although **1g** gave **2g** in high yield (Table 2). Moreover, alkynes **1l** and **1m** gave only trace amounts of the desired dienes, **2l** and **2m**. In the former case, ether oxygen at the propargylic position would strongly coordinate with the ruthenium carbene complex, and catalytic activity of the ruthenium complex would decrease. The latter result compared with that of **1d** (Table 1, run 3) is quite interesting because alkyne **1d** having silyl ether gave **2d** in good yield, while alkyne **1m** having methyl ether provided the desired diene **2m** in only 1% yield. Probably, the methyl ether oxygen strongly coordinated to ruthenium carbene complex and the catalytic activity would decrease.

Table 2 Enyne Metathesis of alkyne having tosyl amide group under ethylene gas

run	substrate		product		yield (conversion yield)
1		**1k**		**2k**	11 (46%)
2		**1g**		**2g**	81 (100%)

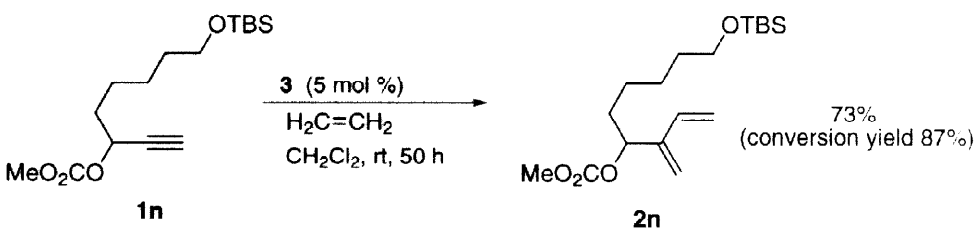
All reactions were carried out using 5 mol % of ruthenium catalyst in CH_2Cl_2 under ethylene gas.

Scheme 9 Reaction of alkyne having various substituent



Based on the above results, we attempted to react alkyne **1n** having the methoxycarbonyloxy group at the propargylic position with ethylene in the presence of **3** in a similar manner, because the ester oxygen at the propargylic position gave the good results (Table 1, runs, 2, 3, 4, and 5) and the silyl ether did not disturb this reaction. As the result, the desired diene **2n** was obtained in good yield.

Scheme 10



In conclusion, we have developed a new synthetic method of 1,3-diene from alkyne and ethylene gas using ruthenium carbene complex **3**. The reaction procedure is very simple, and the reaction proceeds smoothly at room temperature. In this reaction, the alkynes having a hetero atom such as amide nitrogen or ester oxygen at the propargylic position gave the good results, although the reactions were prevented by a hetero atom such as ether oxygen or amine nitrogen in a tether, which is strongly coordinated to the ruthenium catalyst. Since the produced diene is useful for the Diels-Alder reaction, the present diene synthesis would be useful for the synthesis of natural products.

Acknowledgment

This work was supported by Research Fellowships for Young Scientists (to A. K.) from the Japan Society for the Promotion of Science (JSPS).

EXPERIMENTAL

All manipulations were performed under an argon atmosphere using standard Schlenk techniques, and the solution of the catalytic reaction was degassed through freeze-pump-thaw cycle. Solvents were distilled under an argon atmosphere from sodium benzophenone ketyl (THF) or CaH_2 (CH_2Cl_2). All other reagents and solvents were purified when necessary using standard procedures. Column chromatography was performed on silica gel 60 (70-230 mesh, 60 Å), and flash chromatography was performed on silica gel 60 (230-400 mesh, 60 Å) using the indicated solvent.

1-Benzoyl-2-pentyne (1b). ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.16 (t, J = 7.5 Hz, 3 H), 2.26 (tq, J = 7.5, 2.2 Hz, 2 H), 4.91 (t, J = 2.2 Hz, 2 H), 7.41~7.47 (m, 2 H), 7.57 (m,

1 H), 8.05~8.11 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.4, 13.5, 53.3, 73.4, 88.9, 128.3 (2 C), 129.7 (2 C), 133.0 (2 C), 165.9; IR (neat) ν 3065, 2242, 1725, 1601, 1269, 1107 cm^{-1}; LRMS (EI) *m/z* 188 (M^+), 173, 159, 105, 77; HRMS (EI) *m/z* calcd for $C_{12}H_{12}O_2$ 188.0980, found 188.0850.

Methyl 10-benzoyloxy-2-decen-8ynoate (1c). ^{1}H NMR (270 MHz, $CDCl_3$) δ1.50~1.65 (m, 4 H), 2.18~2.35 (m, 4 H), 3.72 (s, 3 H), 4.91 (t, *J* = 2.2 Hz, 1 H), 5.83 (dt, *J* =1.6, 15.6 Hz, 1 H), 6.95 (dt, *J* = 15.6, 6.9 Hz, 1 H), 7.41~7.48 (m, 2 H), 7.57 (m, 1 H), 8.05~8.10 (m, 2 H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ18.5, 27.0, 27.7, 31.6, 51.3, 53.2, 74.5, 87.0, 121.2, 128.3 (2 C), 129.7 (2 C), 133.1, 148.9, 165.9, 167.0; IR(neat) ν 2234, 1722, 1654, 1602, 1268, 1176, 1152 cm^{-1}; LRMS (EI) *m/z* 299 (M^+-1), 241, 195, 105, 77; HRMS (EI) *m/z* calcd for $C_{18}H_{18}O_4$ (M^+-1) 299.1373, found 299.1273.

1-Benzoyloxy-6-tert-butyldimethylsiloxy2-hexyne (1d). ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.65 (s, 6 H), 0.89 (s, 9 H), 1.67~1.78 (m, 2 H), 1.67~1.78 (m, 2 H), 2.33 (tt, *J* = 7.1, 2.2 Hz, 2 H), 4.91 (t, *J* = 2.2 Hz, 2 H), 7.40~7.47 (m, 2 H), 7.52~7.59 (m, 1 H), 8.03~8.10 (m, 2 H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 15.2, 18.3, 25.9 (5 C), 31.4, 53.2, 61.4, 71.2, 87.3, 128.3 (2 C), 129.7 (3 C), 133.1, 165.9; IR(neat) ν 2238, 1726, 1268, 1106 cm^{-1}; LRMS (EI) *m/z* 333 (M^+), 275, 179, 105, 77; HRMS (EI) *m/z* calcd for $C_{19}H_{28}O_3Si$ (M^+) 333.1841, found 333.1891.

1-Acetoxy-4-(2-oxo)cyclohexenyl-2-butyne (1e). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.40 (dt, *J* = 12.8, 3.7 Hz, 1 H), 1.60~1.75 (m, 2 H), 1.92 (m, 1 H), 2.09 (s, 3 H), 2.11 (m, 1 H), 2.22 (dddd, *J* = 2.0, 2.3, 8.5, 17.4 Hz, 1 H), 2.31 (m, 1 H), 2.38 (m, 1 H), 2.42 (m, 1 H), 2.49 (m, 1 H), 2.66 (dddd, *J* = 2.1, 2.3, 4.5, 17.4 Hz, 1 H), 4.65 (dd, *J* = 2.3, 2.1 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.0, 20.6, 25.0, 27.7, 33.2, 41.8, 49.3, 52.6, 75.1, 85.4, 170.2, 210.7; IR (neat) ν 2940, 2862, 2240, 1746, 1711, 1227, 1026 cm^{-1}; LRMS (EI) *m/z* 208 (M^+), 180, 166, 148, 43; HRMS (EI) *m/z* calcd for $C_{12}H_{16}O_3$ 208.1261, found 208.1081.

1-Acetoxy-4-(2,2-ethylenedioxy)cyclohexenyl-2-butyne (1f). ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.23~1.85 (m, 8 H), 2.00~2.10 (m, 2 H), 2.08 (s, 3 H), 2.53 (ddt, *J* = 2.2, 3.6, 16.6 Hz, 1 H), 3.86~3.98 (m, 4 H), 4.65 (t, *J* = 2.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.4, 20.9, 23.9, 24.6, 29.1, 34.6, 44.0, 53.0, 64.7, 64.8, 74.2, 87.0, 109.8, 170.3; IR (neat) ν 2238, 1746, 1226 cm^{-1}.; LRMS (EI) *m/z* 252 (M^+), 224, 209, 193; HRMS (EI) *m/z* calcd for $C_{14}H_{20}O_4$ 252.1508, found 252.1358.

***N*-2-propynyl-*N*-(*p*-toluenesulfonyl)pentylamine (1g).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 6.8 Hz, 3 H), 1.28(m, 6 H), 1.55 (m, 2 H), 2.01 (t, *J* = 2.4 Hz, 1 H), 2.42 (s, 3 H), 3.18 (t, *J* = 7.3 Hz, 2 H), 4.13 (d, *J* = 2.4 Hz, 2 H), 7.29 (d, *J* = 8.3 Hz, 2 H), 7.73 (d, *J* = 8.3 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ14.0, 21.5, 22.5, 26.2, 27.4, 31.4, 36.1, 46.3, 73.5, 76.6, 127.5 (2 C), 129.3 (2 C), 135.8, 143.2; IR(neat) ν 3274, 2118, 1348, 1162 cm^{-1}; LRMS (EI) *m/z* 293 (M^+), 292, 269, 222, 155, 91, 40; HRMS (EI) *m/z* calcd for $C_{16}H_{23}NO_2S$ 293.1216, found 293.1476.

Menthyl 2-nonen-8-ynoate (1i). To a solution of 7,7-dibromo-6-hepten-1-ol (1.14 g, 4.19 mmol) in THF (28 mL) was added BuLi (1.55 M Hexane solution 8.2 mL, 12.7 mmol) at -78 °C and the solution was stirred at the same temperature for 20 min. To this solution was added aqueous sat. NH_4Cl solution and the solution was stirred at room temperature. THF was removed and the aqueous layer was extracted with ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The organic layer was purified by column chromatography on silica gel (hexane/acetone, 2:1) to give a colorless alcohol (330 mg, 70%, 2.94 mmol), which was dissolved in CH_2Cl_2 (29 mL). To this solution was added MS 4A (6.3 g) and PCC (1.58 g, 7.35 mmol) and the solution was stirred at 0°C for 30 min. Ether was added and the solution was passed

through the short Florisil tube and the solution was concentrated. The residue was dissolved in CH_2Cl_2 (15 mL) and menthyl (triphenylphosphoranylidene)acetate (1.60 g, 3.90 mmol) was added and the solution was stirred at room temperature for 11 h. The solution was concentrated and the residue was purified by column chromatography on silica gel (hexane/acetone, 5:1) to give a colorless oil of **1i** (402 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82 (d, J= 6.7 Hz, 3 H), 0.82 (d, J= 7.0 Hz, 3 H), 0.84 (m, 1 H), 0.92 (m, 1 H), 0.98 (m, 1 H), 1.38-1.28 (m, 1 H), 1.50-1.38 (m, 1 H), 1.68-1.59 (m, 4 H), 1.80 (m, 1 H), 1.90 (t, J= 2.6 Hz, 1 H), 1.95 (bd, J= 17.3 Hz, 1 H), 2.16 (ddd, J= 7.0, 6.7, 4.4 Hz, 2 H), 2.29-2.23 (m, 2 H), 4.66 (dt, J= 10.8, 4.4 Hz, 1 H), 5.77 (d, J= 15.5 Hz, 1 H), 6.85 (dt, J= 15.5, 7.0 Hz, 1 H), ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.4, 17.8, 20.7, 22.0, 23.5, 24.7, 26.3, 26.7, 30.9, 31.3, 34.3, 40.9, 47.1, 68.9, 73.9, 83.5, 122.4, 147.6, 166.0; IR (neat) ν 2955, 2361, 1714, 1655, 1456, 1194, 1149 cm^{-1}; LRMS (EI) *m/z* 275 (M^+-Me), 181, 177, 152, 138, 95, 79, 55; HRMS (EI) *m/z* calcd for $C_{18}H_{27}O_2$ 275.2011, found 275.2291.

Benzyl 6-(*p*-toluenesulfonyl)-6-azanon-2-en-8-ynoate (1j). A solution of 2-propynyl-4-(*p*-toluenesulfonyl)amine (1.68 g, 8.03 mmol) and NaH (60% oil dispersion 385 mg, 9.63 mmol) in DMF (22 mL) was stirred at room temperature for 30 min. To this solution was added 3-tetrahydropyranyloxypropyl bromide in DMF (10 mL) and the solution was stirred at room temperature for 1 h. To this solution was added aqueous sat. NH_4Cl solution and the aqueous layer was extracted with ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (hexane/AcOEt, 2:1) to give a colorless oil of *N*-2-propynyl-*N*-(*p*-toluenesulfonyl)-3-tetrahydropyranyloxybutylamine (2.34 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.59-1.43(m, 4 H), 1.86-1.74 (m, 4 H), 2.01 (t, J= 2.4 Hz, 1 H), 2.39 (s, 3 H), 3.38-3.18 (m, 2 H), 3.74-3.39 (m, 2 H), 3.76 (dt, J= 10.3, 5.9, Hz, 1 H), 3.80 (m, 1 H), 4.12 (t, J= 2.4 Hz, 2 H), 4.53 (m, 1 H), 7.25 (d, J = 8.3 Hz, 2 H), 7.70 (d, J= 8.3 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.6, 21.4, 25.3, 27.9, 30.6, 36.5, 43.8, 62.3, 64.4, 76.5, 98.6, 127.6 (2C), 129.3 (2C), 135.8, 143.3; IR (neat) ν 2238, 1356, 1181, 1050 cm^{-1}; LRMS (EI) *m/z* 337 (M^+), 246, 182, 155, 91, 41; HRMS (EI) *m/z* calcd for $C_{18}H_{25}O_4S$ (M^+) 337.1473, found 337.1475. A solution of *N*-2-propynyl-*N*-(*p*-toluenesulfonyl)-3-tetrahydropyranyloxybutylamine (1.79 g, 5.10 mmol) and TsOH·H_2O (97.0 mg, 0.510 mmol) in MeOH (20 mL) was stirred at room temperature for 12 h. To this solution, water was added and the aqueous layer was extracted with ethyl acetate. The organic layer was washed with aqueous sat. $NaHCO_3$ solution and brine, dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (hexane/AcOEt, 1:1) to give a colorless oil of alcohol (1.36 g, quant.). A solution of alcohol (1.37 g, 5.12 mmol), MS 4A (16.5 g), and PCC (3.30 g, 15.3 mmol) in CH_2Cl_2 (34 mL) and the solution was stirred at 0 °C for 30 min. To this solution was added ether and the solution was passed through the Florisil tube and the solution was concentrated. The residue was dissolved in CH_2Cl_2 (20 mL) and benzyl (triphenylphosphoranylidene)acetate (2.10 g, 5.12 mmol) was added and the whole mixture was stirred at room temperature for 11 h. The solution was concentrated and the residue was purified by column chromatography on silica gel (hexane/acetone, 5:1) to give a colorless oil of **1j** (1.21 g, 59%). ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.06 (t, J= 2.4 Hz, 1 H), 2.41 (s, 3 H), 2.51 (m, 2 H), 3.31 (dd, J= 6.4, 6.1 Hz, 2 H), 4.11 (d, J= 2.4 Hz, 2 H), 5.17 (s, 2 H), 5.93 (d, J= 15.4 Hz, 1 H), 6.93 (dt, J= 15.4, 7.1 Hz, 1 H), 7.27 (d, J= 8.3 Hz, 2 H), 7.27-7.31 (m, 5 H), 7.70 (d, J= 8.3 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.2, 21.5, 30.9, 36.8, 45.0, 60.3, 66.1, 74.0, 76.3, 123.1, 127.5 (3C), 128.1(2 C), 129.4 (3 C), 135.3, 135.8, 143.6, 144.8, 165.6; IR (neat) ν 3286,

2117, 1720, 1654, 1598, 1496, 1348, 1266, 1162, 1091 cm^{-1}; LRMS (EI) *m/z* 397 (M^+), 290, 262, 242, 155, 91, 41; HRMS (EI) *m/z* calcd for $C_{22}H_{23}NO_4S$ 397.1347, found 397.1349.

***N*-3-Butynyl-*N*-(*p*-toluenesulfonyl)hexylamine(1k).** ^1H NMR (270 MHz, $CDCl_3$) δ 0.86 (t, *J* = 6.6 Hz, 3 H), 1.18–1.35 (m, 6 H), 1.46–1.60 (m, 2 H), 1.98 (t, *J* = 2.6 Hz, 1 H), 2.42 (s, 3 H), 2.46 (dt, *J* = 7.9, 2.6 Hz, 2 H), 3.14 (t, *J* = 7.6 Hz, 2 H), 3.28 (t, *J* = 7.3 Hz, 2 H), 7.30 (d, *J* = 8.2 Hz, 2 H), 7.69 (d, *J* = 8.2 Hz, 2 H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 13.9, 19.6, 21.4, 22.5, 26.2, 28.5, 31.3, 46.9, 48.9, 70.1, 80.9, 127.0, 129.6, 136.7, 143.2; IR ν (neat) 2120, 1346, 1158 cm^{-1}; MS m/z 307 (M^+), 268, 213, 198, 184, 155, 91; EI-HRMS m/z calcd for $C_{17}H_{25}NO_4S$ (M^+) 307.1604, found 307.1605.

6-(*tert*-Butyldimethylsilyloxy)-1-ethynylhexyl methyl carbonate (1n). ^1H NMR (400 MHz, $CDCl_3$) δ 0.00 (S, 6 H), 0.85 (s, 9 H), 1.29-1.39 (m, 2 H), 1.40-1.54 (m, 4 H), 1.72-1.85 (m, 2 H), 2.49 (d, *J* = 2.4 Hz, 1 H), 3.59 (t, *J* = 6.5 Hz, 2 H), 3.75 (s, 3 H), 5.15 (dt, *J* = 6.7, 2.4 Hz, 1 H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 18.3, 24.5, 25.3, 25.9, 25.9, 32.5, 34.5, 54.8, 62.9, 67.8, 74.3, 80.5, 154.9; IR (neat) ν 2124, 1754, 1100 cm^{-1}; LRMS (EI) *m/z* 314 (M^+), 257, 239, 183, 155; HRMS (EI) *m/z* calcd for $C_{16}H_{30}O_4Si$ (M^+) 314.1923, found 314.1934.

Typical Procedure for the Synthesis of Diene 2a. A solution of alkyne **1a** (60.7 mg, 0.357 mmol) was stirred in the presence of ruthenium catalyst **3** (6.4 mg, 2.2 mol%) in CH_2Cl_2 (3.5 mL) and the solution was stirred at room temperature for 45 h. The solution was stirred under air for several hours. The solvent was removed and the residue was purified by column chromatography on silica gel (hexane/AcOEt, 2:1) to give a colorless oil of **2a** (40 mg, 66%) along with **1a** (15.8 mg, 26%). ^1H NMR (270 MHz, $CDCl_3$) δ 2.10 (s, 6 H) 4.78 (s, 4 H), 5.31 (bs, 2 H), 5.33 (bs, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2 (2 C), 65.2 (2 C), 116.1 (2 C), 139.6 (2 C), 170.8 (2 C); IR (neat) ν 1032, 1231, 1605, 1742, 3102 cm^{-1}; LRMS (EI) *m/z* 198 (M^+), 156, 138, 123, 43 (bp); HRMS (EI) *m/z* calcd for $C_{10}H_{14}O_4$ 198.0847, found 198.0897.

1-Benzoyloxy-2,3-dimethylenepentane (2b). ^1H NMR (270 MHz, $CDCl_3$) δ 1.11 (t, *J* = 7.3 Hz, 3 H), 2.32 (d, *J* = 7.3 Hz, 2 H), 5.02 (bs, 1 H), 5.03 (bs, 1 H), 5.06 (bs, 1 H), 5.16 (bs, 1 H), 5.36 (bs, 2 H), 7.40~7.48 (m, 2 H), 7.56 (m, 1 H), 8.04~8.11(m, 2 H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 12.9, 26.6, 65.7, 111.5, 114.3, 128.3 (2C), 129.6 (2 C), 130.2, 132.9, 141.8, 146.6; IR (neat) ν 1722, 1600, 1584, 1270, 1110 cm^{-1}; LRMS (EI) *m/z* 216 (M^+), 187, 161, 111, 105, 77; HRMS (EI) *m/z* calcd for $C_{14}H_{16}O_2$ 216.1079, found 216.1159.

Methyl 10-benzoyloxy-8,9-dimethylene-2-decenoate (2c). ^1H NMR (270 MHz, $CDCl_3$) δ 1.49~1.52 (m, 4 H), 2.20~2.25 (m, 2 H), 2.29~2.34 (m, 2 H), 3.72 (s, 3 H), 5.01 (s, 2 H), 5.04 (s, 1 H), 5.17 (s, 1 H), 5.33 (s, 1 H), 5.35 (s, 1 H), 5.82 (dt, *J* = 1.6, 15.6 Hz, 1 H), 6.96 (dt, *J* = 6.9, 15.6 Hz, 1 H), 7.42~7.47 (m, 2 H), 7.56 (m,1 H), 8.04~8.07 (m, 2 H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 27.7, 27.8, 32.0, 33.8, 51.4, 65.7, 112.9, 114.7, 121.0, 128.4 (2 C), 129.6 (3 C), 133.0, 141.6, 144.7, 149.3, 166.2, 167.1; IR (neat) ν 1722, 1601, 1271, 1111 cm^{-1}; LRMS (EI) *m/z* 329, 328 (M^+), 296, 223, 206, 191, 174, 105 (bp), 77; HRMS (EI) *m/z* calcd for $C_{20}H_{24}O_4$ 328.1504, found 328.1694.

1-Benzoyloxy-6-*tert*-butyldimethylsilyloxy-2-hexyne (2d). ^1H NMR (270 MHz, $CDCl_3$) δ 0.05 (s, 6 H), 0.90 (s, 9 H), 1.66~1.78 (m, 2 H), 2.33~2.42 (m, 2 H), 3.64 (t, *J* = 6.3 Hz, 2 H), 5.02 (d, *J* = 0.7 Hz, 2 H), 5.07 (bs, 1 H), 5.18 (bs, 1 H), 5.36 (bs, 1 H), 5.39 (bs, 1 H), 7.41~7.48 (m, 2 H), 7.56 (m, 1 H), 8.04~8.10 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.3, 26.0, 30.3, 31.6, 62.6, 65.8, 112.8, 114.8, 128.4 (2 C), 129.7 (2 C), 130.5, 133.0, 144.8, 166.2; IR (neat) ν 1746, 1601, 1226, 1024 cm^{-1}; LRMS (EI) *m/z* 252 (M^+), 224, 209, 193; HRMS (EI) *m/z* calcd for $C_{14}H_{20}O_4$ (M^+-Bu) 252.1508, found

252.1358.

1-Acetoxy-4-(2-oxo)cyclohexenyl-2,3-dimethylenebutane (2e). ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.29 (m, 1 H), 1.53~1.76 (m, 2 H), 1.85 (m, 1 H), 2.09 (s, 3 H), 1.96~2.16 (m, 3 H), 2.20~2.50 (m, 3 H), 3.01 (ddd, J= 1.0, 4.2, 14.5 Hz, 1 H), 4.75 (bs, 2 H), 5.00 (bs, 1 H), 5.11 (bs, 1 H), 5.23 (bs, 1 H), 5.25 (bs, 1 H); ^{13}C NMR δ 20.8, 24.9, 27.8, 33.5, 33.7, 42.0, 48.7, 65.0, 114.4, 114.8, 141.2, 142.7, 170.5, 212.2; IR (neat) ν 2936, 2860, 1742, 1710, 1600, 1448, 1232, 1046 cm^{-1}; LRMS (EI) *m/z* 236 (M^+), 222, 194, 176; HRMS (EI) *m/z* calcd for $C_{14}H_{20}O_3$ 236.1090, found 236.1420.

1-Acetoxy-4-(2,2-ethylenedioxy)cyclohexenyl-2,3-dimethylenebutane (2f). ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.18~1.49 (m, 4 H), 1.62~1.81 (m, 5 H), 1.92 (dd, J= 10.5, 13.3 Hz, 1 H), 2.09 (s, 3 H), 2.75 (bd, J= 13.3 Hz, 1 H), 3.93~4.04 (m, 4 H), 4.76 (bs, 2 H), 4.97 (bs, 1 H), 5.08 (bs, 1 H), 5.27 (bs, 1 H), 5.42 (bs, 1 H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 21.0, 23.9, 24.6, 28.9, 33.3, 34.8, 42.7, 64.7, 64.8, 65.3, 110.7, 114.2, 115.5, 141.2, 143.5, 170.7; IR(neat) ν 3090, 2936, 1743, 1599, 1232, 1047 cm^{-1}; LRMS (EI) *m/z* 280 (M^+), 237, 221, 99 (bp); HRMS (EI) *m/z* calcd for $C_{16}H_{24}O_4$ 280.1612, found 280.1682.

***N*-(2-Methylene-4-propenyl)-*N*-(*p*-toluenesulfonyl)pentylamine (2g).** ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.85 (t, J= 6.9 Hz, 3 H), 1.19 (m, 6 H), 1.41 (m, 2 H), 2.43 (s, 3 H), 3.05 (t, J= 7.7 Hz, 2 H), 3.91 (s, 2 H), 5.14 (s, 1 H), 5.14 (bd, J= 11.3 Hz, 1 H), 5.19 (s, 1 H), 5.46 (bd, J= 17.8 Hz, 1 H), 6.36 (dd, J= 11.3 Hz, 1 H), 7.31 (d, J= 8.3 Hz, 2H), 7.71 (d, J= 8.3 Hz, 2 H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 14.0, 21.5, 22.5, 26.5, 28.1, 31.4, 48.3, 49.9, 115.3, 118.4, 127.1 (2 C), 129.5 (2 C), 136.1, 136.5, 140.7, 143.0; IR (neat) ν 1596, 1340, 1160 cm^{-1}; LRMS (EI) *m/z* 321 (M^+), 268, 166, 155, 139, 91, 41; HRMS (EI) *m/z* calcd for $C_{18}H_{27}NO_2S$ 321.1762, found 321.1762.

***N*-Methyl-*N*-(*p*-toluenesulfonyl)-2-methylene-3-butenylamine (2h)** ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.45 (s, 3 H), 2.60 (s, 3 H), 3.74 (s, 2 H), 5.11 (s, 1 H), 5.18 (d, J= 10.9 Hz, 1H), 5.21 (s, 1 H), 5.77 (bd, J= 17.6 Hz, 1 H), 6.36 (dd, J= 17.6, 10.9 Hz, 1 H), 7.34 (bd, J= 8.1 Hz, 2 H), 7.70 (bd, J= 8.1 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) d 21.6, 31.2, 52.0, 116.0, 119.0, 127.4, 129.6, 133.6, 135.6, 139.9, 143.3; IR (neat) 1596, 1338, 1162 cm^{-1}; GCMS m/z 251 (M^+), 198, 187, 155, 96, 91, 53; HRMS (EI) m/z calcd for $C_{13}H_{17}NO_2S$ (M^+) 251.1026, found 251.1003.

Menthyl 8-methylene-2,9-nonadienoate (2i). A crude product which was obtained from **1i** (153 mg, 0.527 mmol) and **3** (23.5 mg, 5.0 mol %) under ethylene was purified by column chromatography on silica gel (hexane/benzene, 4:1) to give a colorless oil of **2i** (31.9 mg, 10%) and **1i** (88.7 mg, 58%). ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.76 (d, J= 6.7 Hz, 3 H), 0.88 (d, J= 7.0 Hz, 3 H), 0.89 (d, J= 6.4 Hz, 3 H), 1.14-0.80 (m, 1 H), 1.41 (m, 1 H), 1.50 (m, 1 H), 1.62-1.73 (m, 4 H), 1.87, (m, 1 H), 2.02 (m, 1 H), 2.34-2.17 (m, 4 H), 4.71 (dt, J= 10.8, 4.4 Hz, 1 H), 4.98 (bs, 1 H), 5.03 (bs, 1 H), 5.06 (d, J= 10.8 Hz, 1 H), 5.20 (d, J= 17.6 Hz, 1 H), 5.81 (d, J=15.8 Hz, 1 H), 6.36 (dd, J= 10.8, 1.5 Hz, 1 H), 6.95 (dt, J= 15.8, 6.7 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.4, 20.7, 22.0, 23.6, 26.3, 27.6, 27.8, 31.1, 31.4, 32.0, 34.3, 40.9, 47.1, 73.8, 113.1, 115.7, 121.7, 138.8, 146.0, 148.8, 166.3; IR (neat) ν 3056, 2932, 1712, 1598, 1490, 1252, 1176, 1128, 1070 cm^{-1}; LRMS (EI) *m/z* 303 (M^+-Me), 214, 179, 138, 83, 95, 55; HRMS (EI) *m/z* calcd for $C_{20}H_{31}O_2$ (M^+-Me) 303.2324, found 303.2564.

Benzyl 8-methylene-6-(*p*-toluenesulfonyl)-6-aza-2,9-decadienoate (2j).

A solution of **1j** (117 mg, 0.294 mmol) and **3** (13.1 mg, 5.0 mol %) in CH_2Cl_2 (4.4 mL) was stirred under ethylene gas for 40 h. The solution was concentrated and the residue was purified by column chromatography on silica gel (Hexane/AcOEt 10:1) to give a colorless oil of **2j** (45.2 mg, 36%) and **1j**(17.9 mg, 15%). ^{1}H NMR (270 MHz,

$CDCl_3$) δ 2.42-2.38 (m, 2 H), 2.42 (s, 3 H), 3.12 (dd, J = 7.9, 7.5 Hz, 2 H), 3.90 (s, 2 H), 5.19-5.10 (m, 5 H), 5.51 (d, J = 17.8 Hz, 1 H), 5.79 (d, J = 15.6 Hz, 1 H), 6.32 (dd, J = 17.8, 15.6 Hz, 1 H), 6.81 (dt, J = 15.6, 7.1 Hz, 1 H), 7.37-7.30 (m, 7 H), 7.70 (d, J = 8.1 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.5, 31.8, 46.5, 50.8, 66.2, 116.2, 119.2, 122.8, 127.2 (3 C), 128.2 (3 C), 129.8 (3 C), 135.8, 135.9, 140.6, 143.5, 145.4, 165.8; IR (neat) ν 1716, 1654, 1598, 1496, 1456, 1340, 1266, 1162 cm^{-1}; LRMS (EI) *m/z* 425 (M^+), 397, 369, 270, 155, 121, 91; HRMS (EI) *m/z* calcd for $C_{24}H_{27}NO_4S$ 425.1660, found 425.1670.

***N*-Hexyl-*N*-(*p*-toluenesulfonyl)-3-methylene-4-pentenylamine (2k).** ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.80 (t, J = 6.9 Hz, 3 H), 1.09–1.30 (m, 6 H), 1.40–1.53 (m, 2 H), 2.35 (s, 3 H), 2.42 (t, J = 7.7 Hz, 2 H), 3.07 (t, J = 7.7 Hz, 2 H), 3.09–3.18 (m, 2 H), 4.93 (brs, 1 H), 4.98 (brs, 1 H), 5.03 (d, J = 10.7 Hz, 1 H), 5.22 (d, J = 17.6 Hz, 1 H), 6.25 (dt, J = 17.6, 10.7 Hz, 1 H), 7.22 (d, J = 8.3 Hz, 2 H), 7.62 (d, J = 8.3 Hz, 2 H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 14.0, 21.5, 22.5, 26.4, 28.7, 31.4, 31.7, 47.6, 48.7, 52.7, 114.0, 117.6, 127.2, 129.6, 137.2, 138.2, 143.0, 143.3; IR (neat) 1654, 1596, 1342, 1158 cm^{-1}; MS m/z 335 (M^+), 268, 180, 155, 91; EI-HRMS m/z calcd for $C_{19}H_{29}NO_2S$ (M^+) 335.1955, found 335.1937.

6-(*tert*-Butyldimethylsilyloxy)-1-(1-methylene-2-propenyl)-hexyl methyl carbonate (2n). ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.01 (s, 6 H), 0.85 (s, 9 H), 1.23-1.39 (m, 4 H), 1.41-1.53 (m, 2 H), 1.65-1.78 (m, 2 H), 3.56 (t, J = 6.5 Hz, 2 H), 3.74 (s, 3 H), 5.11 (d, J = 11.3 Hz, 1 H), 5.16 (s, 1 H), 5.18 (s, 1 H), 5.27 (t, J = 6.3 Hz, 1 H), 5.33 (d, J = 18.0 Hz, 1 H), 6.29 (dd, J = 18.0, 11.3 Hz,, 1 H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 18.3, 25.2, 25.4, 25.9, 25.9, 32.6, 34.1, 54.6, 63.0, 77.6, 114.8, 115.3, 135.4, 145.0, 155.2; IR (neat) ν 1752, 1594, 1100 cm^{-1}; MS *m/z* 342 (M^+), 289, 285, 211, 155; HRMS (EI) *m/z* calcd for $C_{18}H_{34}O_4Si$ (M^+) 342.2227, found 342.2253.

Synthesis of [4.3.1]Undecene Skeleton by Diels-Alder Reaction

1α-H-9β-(Menthyloxycarbonyl)bicyclo[4.3.0]undec-6-ene (16). A solution of **2i** (29.8 mg, 97.2 mmol) in toluene (3.0 mL) was heated at 150 °C for 30 h. The solution was concentrated and the residue was purified by column chromatography on silica gel (hexane/benzene, 3:1) to give a colorless oil of **16** (16.8 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.76 (d, J = 6.7 Hz, 3 H), 0.88 (d, J = 7.0 Hz, 3 H), 0.89 (d, J = 6.4 Hz, 3 H), 1.30-0.80 (m, 4 H), 1.60-1.31 (m, 9 H), 1.65-1.60 (m, 2 H), 2.18-2.74 (m, 7 H), 2.50-2.26 (m, 3 H), 4.66 (dt, J = 10.8, 4.4 Hz, 1 H), 5.59 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.2, 20.8, 21.9, 22.0, 23.4, 25.8, 26.3, 27.5, 31.2, 31.4, 33.9, 34.3, 35.3, 35.5, 38.7, 41.0, 47.1, 47.6, 73.8, 123.5, 142.2, 142.3, 176.3; IR (neat) ν 2955, 1734, 1599, 1456, 1191, 1050 cm^{-1}; LRMS (EI) *m/z* 318 (M^+), 303, 196, 180, 167, 151, 135, 138, 83, 69, 55; HRMS (EI) *m/z* calcd for $C_{21}H_{34}O_2$ (M^+) 318.2558, found 318.2559.

6α-H-7β-(Benzyloxycarbonyl)-3-aza-3-(*p*-toluenesulfonyl)-bicyclo[4.3.0]undec-1-(9)-ene (17). A solution of **2j** (40.5 mg, 85.2 mmol) in toluene (2.0 mL) was heated at 230 °C for 30 h. The solution was concentrated and the residue was purified by preparative thin layer chromatography on silica gel (hexane/AcOEt, 3:1) to give a colorless oil of **17** (47.0 mg, 49%). ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.17 (d, J = 10.3 Hz, 1 H), 3.53 (dt, J = 14.6, 3.6 Hz, 1 H), 4.34 (bd, J = 10.3 Hz, 1 H), 5.13 (s, 2 H), 5.82 (bs, 1 H), 7.36-7.26 (m, 7 H), 7.69-7.66 (bd, J = 8.3 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.5, 27.2, 30.1, 34.4, 38.1, 42.1, 46.3, 53.6, 66.4, 126.9 (2 C), 128.0 (2 C), 128.2, 128.6 (2 C), 129.7 (2 C), 130.8, 135.9, 136.5, 138.2, 143.1, 175.4; IR (neat) ν 1732, 1598, 1496, 1332, 1160, 1094 cm^{-1}; LRMS (EI) *m/z* 270 (M^+-Ts), 163, 155, 135, 107, 91, 77; HRMS (EI) *m/z* calcd for $C_{17}H_{20}NO_2$ (M^+-Ts) 270.1494, found 270.1504.

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