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Nickel-Catalyzed Tandem Coupling of Allyl Electrophiles, Alkynes, and Alkynyltins

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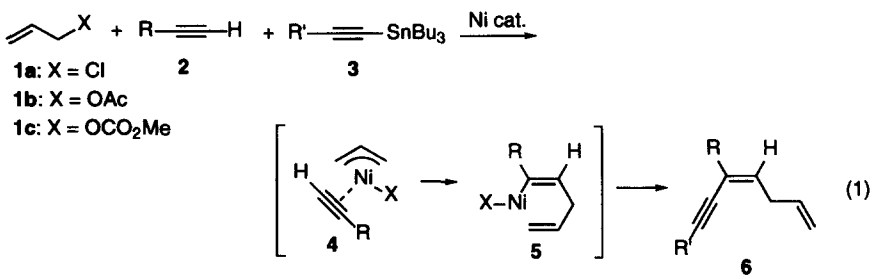
Abstract: The nickel-catalyzed intermolecular coupling of allyl acetate or allyl carbonate with alkynes and alkynyltins was carried out in the presence of LiCl to give 3,6-dien-1-yne regio- and stereoselectively. On the other hand, the intramolecular cyclization and coupling of ω-alkynyl electrophiles with alkynyltins gave five-membered cyclic products.

INTRODUCTION

Tandem reactions, which permit complex molecules to be reasonably well constructed in a few steps, are an important topic in organic synthesis.[1] We recently investigated the successive introduction of carbon units into alkyne based on a nickel-catalyzed coupling reaction with organometallics[2] and found a nickel-catalyzed three-component coupling reaction of allyl chloride (**1a**) with 1-alkyne **2** and alkynyltin **3** to regio- and stereoselectively provide 3,6-dien-1-yne **6** (Eq. 1).[3] This reaction may proceed via insertion of **2** to π-allylnickel(II) intermediate **4**,[4] which was generated from nickel(0) and **1a**,[5] to yield intermediate **5**, followed by transmetalation of **3** and then reductive elimination. These results prompted us to further survey whether this method could be extended to the reaction of allyl acetate (**1b**) or allyl carbonate (**1c**) instead of **1a** with **2** and **3**. In this paper, we describe the tandem coupling of some allyl electrophiles **1** with **2** and **3** in the presence of nickel catalyst.



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RESULTS AND DISCUSSION

Intermolecular coupling of allyl acetate or carbonate with alkyne and alkynyltin

The reaction of **1b** (1.0 equiv) with 1-hexyne (**2a**, R = Bu) (1.1 equiv) and **3a** (R' = Ph) (1.1 equiv) in the presence of 10 mol % $Ni(acac)_2$ and DIBALH in THF at reflux did not give the reaction product **6** (R = Bu, R' = Ph) (run 2 in Table 1). However, when LiCl (1.0 equiv vs. **1b**) was added to the reaction system, **6** was obtained regio- and stereoselectively in 30 % yield (run 3). The acetoxy group on the generated intermediate **4** or **5** (X = OAc) was substituted for the chloride of LiCl and the resulting intermediate **5** (X = Cl) reacted with **3a**.[6] However, the yield of **6** was not improved by the further addition of LiCl (3.0 equiv) (run 4). Similar results were observed in the reaction with **1c** (runs 5 and 6). The substrates **1b** and **1c** were less effective than **1a** in this three-component coupling (vs. run 1).[3]

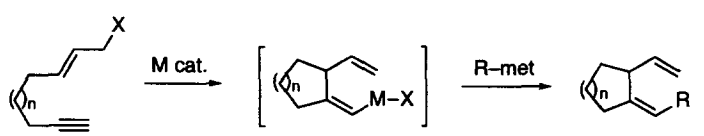
Table 1. Nickel-Catalyzed Tandem Coupling of **1**, **2a** (R = Bu), and **3a** (R' = Ph)[a]

Run	1	LiCl, equiv vs. **1**	Time, h	**6**, %[b]
1[c]	**1a**	0	1	70
2	**1b**	0	20	0
3		1.0	5	30
4		3.0	5	22
5	**1c**	0	20	0
6		3.0	5	35

[a] Reaction conditions: $Ni(acac)_2$ (0.1 mmol), DIBALH (1.0 M hexane, 0.1 mL), **1** (1.0 mmol), **2a** (1.1 mmol), and **3a** (1.1 mmol) with THF under N_2 at reflux. [b] Isolated yield. [c] See ref 3.

Intramolecular cyclization and coupling of ω-alkynyl electrophile with alkynyltin

Next, we applied this tandem reaction to the intramolecular cyclization depicted in Eq. 2. Oppolzer's group developed the cyclization of an ω-alkynyl electrophile, the so-called "metallo-ene" reaction, using a nickel or palladium catalyst.[7] Recently, the palladium-catalyzed reaction (M = Pd) of the ω-alkynyl electrophile with organometallics (R–met) was also reported.[7c] We investigated intramolecular cyclization and coupling with organotin in the presence of nickel catalyst (M = Ni).

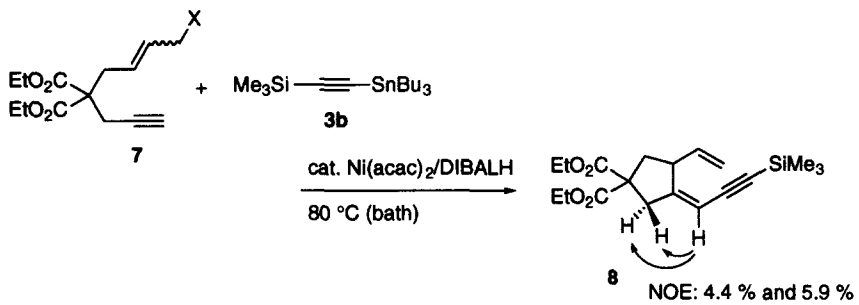


(2)

The nickel-catalyzed (10 mol %) reaction of **7a** (1.0 equiv, X = OAc) with **3b** (1.1 equiv) proceeded in the presence of LiCl (1.0 equiv) to give a cyclic compound **8** in a moderate yield (run 2 in Table 2). The yield of **8**

was increased to 51 % when 3.0 equiv of LiCl was used (run 3). The selection of solvent was important in the intramolecular cyclization and coupling. A mixture of THF and DMF (1:4) was a more efficient solvent than THF alone (run 4, **8**: 60 % yield). The reaction of **7b** (X = Cl) instead of acetate **7a** also gave the desired product **8** in the absence of LiCl (run 5). The reactivity of **7** was not dependent on the stereochemistry of the carbon-carbon double bond (run 6). The structure of **8** was assigned based on the ^{1}H NMR spectra and a NOE experiment.

Table 2. Nickel-Catalyzed Cyclization and Coupling of **7** and **3b**[a]



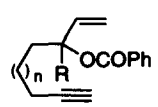
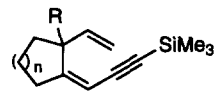
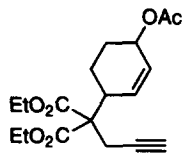
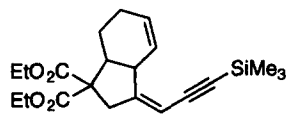
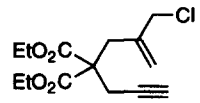
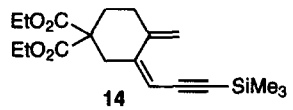
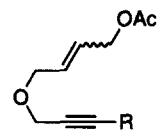
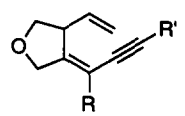
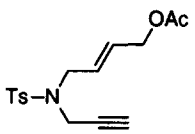
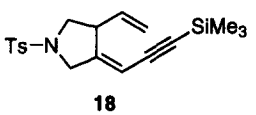
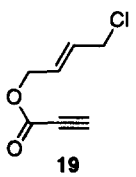
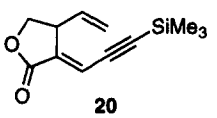
Run	**7** (*E*/*Z*)	X	Solvent	LiCl, equiv vs. **7**	**8**, %[b]
1	**7a** (100:0)	OAc	THF	0	0
2	**7a** (100:0)	OAc	THF	1.0	44
3	**7a** (100:0)	OAc	THF	3.0	51
4	**7a** (100:0)	OAc	THF/DMF (1:4)	3.0	60
5	**7b** (100:0)	Cl	THF/DMF (1:4)	0	50
6	**7c** (50:50)	Cl	THF/DMF (1:4)	0	47

[a] Reaction conditions: Ni(acac)$_2$ (0.1 mmol), DIBALH (1.0 M hexane, 0.1 mL), **7** (1.0 mmol), and **3b** (1.1 mmol) in solvent (5 mL) at 80 °C for 2 h. [b] Isolated yield.

The results of intramolecular cyclization and coupling with various ω-alkynyl electrophiles are summarized in Table 3. Each reaction produced a five-membered cyclic compound in good yield. The yield of **10b** was lower than that of **10a** because of the steric effect of the methyl group at the allylic position of the starting material **9b** (entries 1 and 2). Cyclic acetate **11** could also be applied to this reaction (entry 4). However, neither **9c** nor **13** gave the corresponding six-membered ring product **10c** or **14**, respectively (entries 3 and 5).[8] The reactions of ether **15** and amide **17** gave the corresponding heterocyclic compounds **16** and **18**, respectively (entries 6–8). We previously observed that the three-component coupling of **1a** with methyl propynoate and **3** did not proceed. Lactone **20** also could not be synthesized from the reaction of ester **19** (entry 10).

In summary, the nickel-catalyzed three-component coupling of allyl acetate (**1b**) or carbonate (**1c**) with **2** and **3** was carried out in the presence of LiCl to give product **6** regio- and stereoselectively. However, the coupling reaction with **1b** or **1c** was less effective than that with allyl chloride (**1a**). On the other hand, ω-

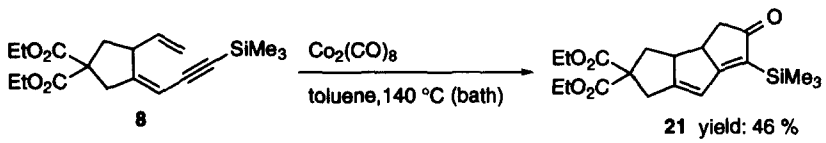
Table 3. Nickel-Catalyzed Cyclization and Coupling of ω-Alkynyl Electrophiles and **3**[a]

Entry	ω-Alkynyl electrophile	3	Product	Yield, %[b]
		**3b**		
1	**9a** R = H, n = 1		**10a** R = H, n = 1	50
2	**9b** R = Me, n = 2		**10b** R = Me, n = 1	36
3	**9c** R = H, n = 2		**10c** R = H, n = 2	0
4	 **11**	**3b**	 **12**	55
5	 **13**	**3b**	 **14**	0[c]
				
6	**15a** R = H[d]	**3a**	**16a** R = H, R' = Ph	46
7	**15b** R = Et[d]	**3b**	**16b** R = Et, R' = $SiMe_3$	71
8	 **17**	**3b**	 **18**	49
9	 **19**	**3b**	 **20**	0[c]

[a] Reaction conditions: $Ni(acac)_2$ (0.1 mmol), DIBALH (1.0 M hexane, 0.1 mL), ω-alkynyl electrophile (1.0 mmol), **3** (1.1 mmol), and LiCl (3.0 mmol) in THF/DMF (1 mL:4 mL) at 80 °C (bath) for 2 h. [b] Isolated yield. [c] Yield in the absence of LiCl. [d] *E*/*Z* = 50:50 mixture.

alkynyl acetate and benzoate could be applied to this nickel-catalyzed cyclization and reacted with **3** in the

presence of LiCl to give the corresponding five-membered compounds. These coupling products could be converted to a triquinane structure by Pauson-Khand reaction.[9] For example, compound **21** was synthesized by treating **8** with $Co_2(CO)_8$ in toluene at 140 °C (Eq. 3).



8 **21** yield: 46 % (3)

EXPERIMENTAL

General Procedures. All reactions were carried out under dry N_2 atmosphere. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ using Me_4Si as internal standard. Unless otherwise noted, the starting material was obtained from commercial suppliers and used without further purification. THF was distilled from sodium benzophenone. Toluene was dried by distillation from CaH_2. DMF was dried by distillation from BaO under reduced pressure. Oct-1-en-7-yn-3-yl benzoate (**9a**),[10] 3-methyloct-1-en-7-yn-3-yl benzoate (**9b**),[10] *N*-(4-acetoxybut-2-enyl)-*N*-(prop-2-ynyl)-*p*-toluenesulfon-amide (**17**),[7] 4'-chloro-2'-(*E*)-butenyl prop-2-ynoate (**19**),[11] (phenylethynyl)tributyltin (**3a**),[12] and [(trimethyl-silyl)ethynyl]tributyltin (**3b**)[12] were prepared as described in the literature.

Ethyl (*E*)-6-Acetoxy-2-(ethoxycarbonyl)-2-(prop-2-ynyl)hex-4-enoate (7a). In the same way as described for methyl (*E*)-6-acetoxy-2-(ethoxycarbonyl)-2-(prop-2-ynyl)hex-4-enoate,[10] a mixture of diethyl 2-(prop-2-ynyl)malonate, which was pepared from diethyl malonate and 3-bromopropyne, (1.03 g, 5.17 mmol) and 1-acetoxy-4-chlorobut-2-ene[13] (0.82 g, 5.51 mmol) was treated with 0.22 g of NaH (60 % oil dispersion; 5.78 mmol of NaH) in THF to give the titled **7a** (1.35 g, 84 %); bp 120 °C (1.2 mmHg); R_f = 0.29 (hexane/EtOAc = 5:1); ^1H NMR (270 MHz, $CDCl_3$): δ 1.25 (t, *J* = 7.3 Hz, 6 H), 2.01 (t, *J* = 2.4 Hz, 1 H), 2.04 (s, 3 H), 2.77 (d, *J* = 2.4 Hz, 2 H), 2.80 (d, *J* = 7.3 Hz, 2 H), 4.20 (q, *J* = 7.3 Hz, 4 H), 4.49 (d, *J* = 6.0 Hz, 2 H), 5.55–5.77 (m, 2 H); IR (neat): 3283, 2984, 1736, 1444, 1367, 1240, 1207, 1028, 858 cm^{-1}; GC/MS (EI, 70 eV): *m/z* (rel. int., %) 310 (M^+, 0), 198 (55), 177 (100), 176 (58), 149 (56), 131 (47), 105 (82), 96 (50), 91 (45), 79 (50), 77 (49). Anal. Calcd for $C_{16}H_{22}O_6$: C, 61.92; H, 7.15. Found: C, 61.71; H, 7.24.

Ethyl (*E*)-6-Chloro-2-(ethoxycarbonyl)-2-(prop-2-ynyl)hex-4-enoate (7b). In a manner similar to that described for (*E*)-6-chloro–2-(methoxycarbonyl)-2-(4-tetrahydropyranoxybut-2-enyl)hex-4-enoate,[14] a mixture of diethyl 2-(prop-2-ynyl)malonate (2.12 g, 10.7 mmol) and 1,4-dichlorobut-2-ene (3.82 g, 30.4 mmol) was treated with K_2CO_3 (1.51 g, 10.9 mmol) in DMF to give the titled **7b** (2.38 g, 78 %); bp 160 °C (4 mmHg); R_f = 0.35 (hexane/EtOAc = 10:1); ^1H NMR (270 MHz, $CDCl_3$): δ 1.25 (t, *J* = 7.3 Hz, 6 H), 2.02 (t, *J* = 2.6 Hz, 1 H), 2.78 (d, *J* = 2.6 Hz, 2 H), 2.80 (d, *J* = 7.3 Hz, 2 H), 3.99 (d, *J* = 6.6 Hz, 2 H), 4.21 (q, *J* =

7.3 Hz, 4 H), 5.65 (dt, J = 15.1, 7.3 Hz, 1 H), 5.78 (dt, J = 15.1, 6.6 Hz, 1 H); IR (neat): 2982, 1736, 1288, 1211, 1059, 858 cm^{-1}; GC/MS (EI, 70 eV): *m/z* (rel. int., %) 286 (M^+, 0), 251 (M^+ – Cl, 100), 177 (70), 105 (45). Anal. Calcd for $C_{14}H_{19}O_4Cl$: C, 58.64; H, 6.68. Found: C, 58.63; H, 6.79.

Ethyl 2-(4-Acetoxycyclohex-2-en-1-yl)-2-(ethoxycarbonyl)pent-4-ynoate (11). In a manner similar to that described for **7b**, a mixture of diethyl 2-(prop-2-ynyl)malonate (1.47 g, 7.40 mmol) and 1-acetoxy-4-chlorocyclohex-2-ene[13] (1.33 g, 7.6 mmol) was treated with 0.35 g of NaH (60 % oil dispersion; 9.01 mmol of NaH) in DMF to give the titled **11** (1.98 g, 79 %); bp 155 °C (0.5 mmHg); R_f = 0.26 (hexane/EtOAc = 5:1); ^1H NMR (270 MHz, $CDCl_3$); δ 1.24 (t, J = 7.3 Hz, 3 H), 1.27 (t, J = 7.3 Hz, 3 H), 1.46–1.64 (m, 2 H), 1.92–1.97 (m, 1 H), 2.02 (t, J = 2.4 Hz, 1 H), 2.05 (s, 3 H), 2.14–2.19 (m, 1 H), 2.81 (dd, J = 17.1, 2.4 Hz, 1 H), 2.87 (dd, J = 17.1, 2.4 Hz, 1 H), 3.19–3.23 (m, 1 H), 4.18 (q, J = 7.3 Hz, 2 H), 4.24 (q, J = 7.3 Hz, 2 H), 5.25–5.30 (m, 1 H), 5.65 (ddd, J = 10.4, 3.6, 1.8 Hz, 1 H), 5.97 (ddd, J = 10.4, 3.6, 1.8 Hz, 1 H); GC/MS (EI, 70 eV): *m/z* (rel. int., %) 336 (M^+, 0), 129 (74), 96 (100), 79 (57). Anal. Calcd for $C_{18}H_{24}O_6$: C, 64.27; H, 7.19. Found: C, 63.99; H, 7.19.

Ethyl 4-Chloromethyl-2-(ethoxylcarbonyl)-2-(prop-2-ynyl)pent-4-enoate (13). In a manner similar to that described for **7b**, a mixture of diethyl 2-(prop-2-ynyl)malonate (1.60 g, 8.01 mmol) and 3-chloro-2-chloromethylprop-1-ene (2.83 g, 22.7 mmol) was treated with K_2CO_3 (1.16 g, 8.38 mmol) in DMF/THF mixture to give the titled **13** (1.94 g, 84%); bp 110 °C (0.3 mmHg); R_f = 0.33 (hexane/EtOAc = 7:1); ^1H NMR (270 MHz, $CDCl_3$): δ 1.27 (t, J = 7.2 Hz, 6 H), 2.06 (t, J = 2.6 Hz, 1 H), 2.81 (d, J = 2.6 Hz, 2 H), 3.01 (s, 2 H), 3.97 (d, J = 1.0 Hz, 2 H), 4.17–4.38 (m, 4 H), 5.14 (s, 1 H), 5.33 (d, J = 1.0 Hz, 1 H); GC/MS (EI, 70 eV): *m/z* (rel. int., %) 286 (M^+, 0), 251 (M^+ – Cl, 49), 177 (59), 149 (53), 105 (100), 103 (50), 91 (42), 77 (45). HRMS for $C_{14}H_{19}O_4Cl$ ($M^+ - {}^{35}Cl$): Calcd, 251.1283; Found, 251.1279.

Non-1-en-8-yn-3-yl Benzoate (9c). In a manner similar to that described for **9a**,[10,15] a mixture of hept-6-ynal (1.00 g, 9.09 mmol) and vinylmagnesium chloride (1.0 M in THF, 20 mL) was treated with benzoyl chloride (2.38 g, 16.9 mmol) in THF to give the titled **9c** (1.21 g, 55%); bp 125 °C (2 mmHg); R_f = 0.43 (hexane/EtOAc = 10:1); ^1H NMR (500 MHz, $CDCl_3$): δ 1.50–1.62 (m, 4 H), 1.71–1.85 (m, 2 H), 1.92 (t, J = 3.0 H, 1 H), 2.21 (td, J = 6.7, 3.0 Hz, 2 H), 5.21 (dt, J = 10.4, 1.2 Hz, 1 H), 5.33 (dt, J = 17.1, 1.2 Hz, 1 H), 5.50 (td, J = 6.1, 6.1 Hz, 1 H), 5.90 (ddd, J = 17.1, 10.4, 6.1 Hz, 1 H), 7.41–8.08 (m, 5 H); IR (neat): 2941, 1718, 1271, 1113, 713 cm^{-1}; GC/MS (EI, 70 eV): *m/z* (rel. int., %) 242 (M^+, 1), 105 (100), 77 (53). Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.22; H, 7.54.

1-(Prop-2-yn-1-oxy)but-2-en-4-ol. To a stirred solution of 782 mg of sodium hydride (60 % in oil, 20.4 mmol) in DMF (20 mL) was added but-2-ene-1,4-diol (2.43 g, 20.5 mmol) at 0 °C. After 10 min the mixture warmed to room temperature and kept at this temperature for 1 h. Then, 3-bromopropyne was added dropwise and the reaction mixture was stirred at this temperature overnight. The reaction mixture was quenched and extracted four times with ether. The combined organic layers were washed with brine, dried (Na_2SO_4), filtered, and evaporated in vacuo. The residue was purified by column chromatography on silica gel to give the

titled product (1.24 g, 48 %) as a colorless oil: R_f = 0.33; cis and trans mixture of ^{1}H NMR (500 Hz, $CDCl_3$); δ 2.43 (t, J = 2.5 Hz, 1 H), 2.45 (t, J = 2.5 Hz, 1 H), 4.03–4.24 (m, 14 H), 5.65–5.96 (m, 4 H).

1-(Prop-2-yn-1-oxy)but-2-en-4-yl Acetate (15a). To a solution of 1-(prop-2-yn-1-oxy)but-2-ene-4-ol (1.30 g, 10.2 mmol) and pyridine (1.12 g, 14.1 mmol) in THF (20 mL) was added acetyl chloride (1.23 g, 15.5 mmol) at 0 °C. The reaction mixture was stirred at room temperature. After 3 h, the reaction was quenched and extracted four times with ether. The combined organic layers were washed with brine, dried ($MgSO_4$), filtered, and evaporated in vacuo. The residue was distilled to give **15a** (1.58 g, 92 %) as a colorless oil: bp 75 °C (3 mmHg); the cis and trans mixture of ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.05 (s, 3 H), 2.06 (s, 3 H), 2.43 (t, J = 2.6 Hz, 1 H), 2.44 (t, J = 2.6 Hz, 1 H), 4.07–4.08 (m, 2 H), 4.14 (d, J = 2.6 Hz, 4 H), 4.17 (d, J = 5.1 Hz, 2 H), 4.56 (d, J = 5.4 Hz, 2 H), 4.65 (d, J = 5.1 Hz, 2 H), 4.71–4.75 (m, 2 H), 5.82–5.85 (m, 2 H); IR (neat): 3293, 2857, 1740, 1578, 1444, 1375, 1240, 1092, 1030, 970, 667 cm^{-1}; GC/MS (EI, 70 eV): *m/z* (rel. int., %) 168 (M^+, 1), 79 (81), 71 (100), 69 (69). Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 63.93; H, 7.22.

1-(Pent-2-yn-1-oxy)but-2-ene-4-yl Acetate (15b). In a manner similar to that described **15a**, a mixture of 1-(pent-2-yn-1-oxy)but-2-ene-4-ol (1.26 g, 8.2 mmol) and acetyl chloride (0.79 g, 10.1 mmol) was treated to give **15b** (1.36 g, 85%) as a colorless oil; bp 130 °C (2.5 mmHg); the cis and trans mixture of ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.15 (t, J = 7.6 Hz, 6 H), 2.06 (s, 3 H), 2.07 (s, 3 H), 2.21-2.27 (m, 4 H), 4.05–4.06 (m, 2 H), 4.13 (t, J = 2.2 Hz, 4 H), 4.15–4.17 (m, 2 H), 4.57–4.58 (m, 2 H), 4.67 (d, J = 5.9 Hz, 2 H), 5.72–5.78 (m, 2 H), 5.84–5.86 (m, 2 H); IR (neat): 2939, 1741, 1375, 1234, 1084, 1028, 970 cm^{-1}; GC/MS (EI, 70 eV): *m/z* (rel. int., %) 196 (M^+, 2), 108 (41), 96 (45), 79 (94), 70 (100), 69 (90). Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.19; H, 8.23.

Typical Procedure of Nickel-Catalyzed Three Component Coupling of 1b with 2a and 3a (Run 2 in Table 1). To a solution of $Ni(acac)_2$ (26 mg, 0.1 mmol) in THF (5 mL) were added DIBALH in a 1.0 M toluene solution (0.1 mL) at 0 °C, and the mixture was stirred for 5 min. To this black solution were then added **3a** (410 mg, 1.05 mmol), **2a** (90 mg, 1.1 mmol), **1b** (100 mg, 1.0 mmol), and LiCl (145 mg, 3.45 mmol) at 0 °C, and then the mixture was stirred at reflux for 5 h. To this was added aqueous NH_4F (30 mL), and stirring continued for 30 min to remove the tributyltin chloride. After filtration through Celite, the aqueous layer was extracted four times with ether. The combined organic layers were washed with brine, dried over $MgSO_4$ for 30 min, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to yield (Z)-3-Butyl-1-phenyhept-3,6-dien-1-yne (**6**) (67 mg, 30 %). The spectral data and elemental analysis have already been reported, see ref 3.

Typical Procedure of Nickel-Catalyzed Intramolecular Cyclization and Coupling of 7a with 3b (Run 3 in Table 2). To a solution of $Ni(acac)_2$ (26 mg, 0.1 mmol) in THF (1 mL) were added DIBALH in a 1.0 M toluene solution (0.1 mL) at 0 °C, and the mixture was stirred for 5 min. To this black

solution were then added DMF (4 mL), **3b** (387 mg, 1.00 mmol), **7a** (307 mg, 0.99 mmol), and LiCl (145 mg, 3.45 mmol) at 0 °C, and then the mixture was stirred at reflux for 2 h. To this was added aqueous NH_4F (30 mL), and stirring continued for 30 min to remove the tributyltin chloride. After filtration through Celite, the aqueous layer was extracted four times with ether. The combined organic layers were washed with brine, dried over $MgSO_4$ for 30 min, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to yield Diethyl 3-Ethenyl-4-[[3-(trimethylsilyl)prop-2-yn]ylidene]cyclopentan-1,1-dicarboxylate (**8**) (206 mg, 60 %). An analytical sample was obtained by bulb-to-bulb distillation, bp 150 °C (1.8 mmHg); R_f = 0.37 (hexane/AcOEt = 10:1); ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.15 (s, 9 H), 1.23 (t, J = 7.3 Hz, 3 H), 1.24 (t, J = 7.3 Hz, 3 H), 2.09 (dd, J = 13.2, 7.6 Hz, 1 H), 2.70 (ddd, J = 13.2, 8.3, 1.3 Hz, 1 H), 2.92 (dt, J = 16.8, 1.3 Hz, 1 H), 3.09 (dt, J = 16.8, 2.6 Hz, 1 H), 3.53 (m, 1 H), 4.19 (q, J = 7.3 Hz, 4 H), 5.05 (m, 2 H), 5.54 (dd, J = 2.6, 1.3 Hz, 1 H), 5.78 (ddd, J = 17.2, 10.2, 7.6 Hz, 1 H). NOE (270 MHz) irradiated at 5.54 ppm, observed 2.92 ppm (4.4 %) and 3.09 ppm (5.9 %); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ –0.07, 13.98, 39.66, 41.64, 46.09, 58.89, 61.62, 99.46, 101.85, 104.37, 115.27, 137.65, 157.18, 171.03; IR (neat): 2980, 2123, 1743, 1448, 1367, 1286, 1249, 1249, 1176, 1066, 846 cm^{-1}; MS (EI, 70 eV): *m/z* (rel. int., %) 348 (M^+, 7), 274 (55), 201 (100), 75 (40). Anal. Calcd for $C_{19}H_{28}O_4Si$: C, 65.48; H, 8.10. Found: C, 65.23; H, 8.01.

1-Ethenyl-2-[[3-(trimethylsilyl)prop-2-yn]ylidene]cyclopentane (10a). bp 85 °C (0.9 mmHg); R_f = 0.45 (hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.16 (s, 9 H), 1.54–2.44 (m, 6 H), 3.35–3.49 (m, 1 H), 5.00 (d, J = 9.8 Hz, 1 H), 5.05 (d, J = 17.0 Hz, 1 H), 5.50 (s, 1 H), 5.75–5.82 (m, 1 H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 0.04, 24.24, 32.70, 33.79, 47.42, 96.65, 102.37, 103.07, 113.98, 138.44, 162.89; IR (neat): 2959, 2123, 1635, 1248, 1076, 842, 760 cm^{-1}; GC/MS (EI, 70eV): *m/z* (rel. int., %) 204 (M^+, 50), 189 (85), 161 (41), 145 (43), 130 (44), 73 (100), 59 (68). Anal. Calcd for $C_{13}H_{20}Si$: C, 76.40; H, 9.86. Found: C, 76.10; H, 10.11.

1-Ethenyl-1-methyl-2-[[3-(trimethylsilyl)prop-2-yn]ylidene]cyclopentane (10b). bp 95 °C (1 mmHg); R_f = 0.5 (hexane); ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.61 (s, 9 H), 1.41 (s, 3 H), 1.59–1.86 (m, 4 H), 2.42–2.49 (m, 2 H), 4.98–5.05 (m, 2 H), 5.51 (t, J = 1.9 Hz, 1 H), 6.01 (dd, J = 17.5, 10.5 Hz, 1 H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ –0.14, 23.00, 23.27, 36.08, 42.15, 48.94, 99.05, 101.64, 102.78, 111.04, 143.31, 165.74; IR (neat): 2959, 2123, 1635, 1249, 844, 760 cm^{-1}; GC/MS (EI, 70eV): *m/z* (rel. int., %) 218 (M^+, 11), 203 (100), 73 (64). Anal. Calcd for $C_{14}H_{22}Si$: C, 76.99; H, 10.15. Found: C, 76.71; H, 10.18.

Diethyl 9-[[3-(trimethylsilyl)prop-2-yn]ylidene]bicyclo[4.3.0]non-2-en-7,7-dicarboxylate (12). mp 75–75.5 °C (from ethnol); R_f = 0.4 (hexane/AcOEt = 10:1); ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.19 (s, 9 H), 1.20–1.29 (m, 6 H), 1.41–1.45 (m, 1 H), 1.15 (s, 1 H), 1.90–2.05 (m, 2 H), 2.78–3.02 (m, 2 H), 3.30–3.60 (m, 2 H), 4.15–4.33 (m, 4 H), 5.50 (s, 1 H), 5.70–5.90 (m, 1 H), 6.30–6.50 (m, 1 H); ^{13}C NMR (67.8 MHz): δ –0.11, 14.00, 14.13, 22.00, 23.78, 39.19, 42.68, 43.04, 61.46, 61.57, 62.72, 99.03, 102.71, 103.20, 125.34, 126.60, 157.57, 169.31, 170.98; IR (disk): 2961, 2121, 1734, 1251,

1068, 1041, 864, 692 cm^{-1}; GC/MS (EI, 70eV): *m/z* (rel. int., %) 374 (M^+, 57), 227 (68), 153 (52), 73 (100). Anal. Calcd for $C_{21}H_{30}O_4Si$: C, 67.34; H, 8.07. Found: C, 67.42; H, 7.99.

3-Ethenyl-4-[[3-(trimethylsilyl)prop-2-yn]ylidene]tetrahydrofurane (16a). bp 80 °C (5 mmHg); R_f = 0.3 (hexane/AcOEt = 10:1); ^1H NMR (500 MHz, $CDCl_3$) δ 3.64–3.72 (m, 1 H), 3.83 (dd, *J* = 9.2, 4.2 Hz, 1 H), 4.04 (dd, *J* = 9.2, 6.7 Hz, 1 H), 4.40 (dd, *J* = 14.7, 1.8 Hz, 1 H), 4.44 (dt, *J* = 14.7, 1.8 Hz, 1 H), 5.17 (dd, *J* = 10.4, 1.2 Hz, 1 H), 5.26 (dd, *J* = 17.7, 1.2 Hz, 1 H), 5.71–5.73 (m, 1 H), 5.89 (ddd, *J* = 17.7, 10.4, 7.9 Hz, 1 H), 7.27–7.42 (m, 5 H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 48.14, 71.55, 73.86, 86.11, 94.00, 101.34, 116.20, 123.55, 128.11, 128.32, 131.22, 136.04, 155.44; IR (neat): 2976, 2951, 1489, 1313, 1070, 920, 756, 690 cm^{-1}; GC/MS (EI, 70eV): *m/z* (rel.int., %) 210 (M^+, 43), 180 (58), 179 (63), 178 (61), 165 (69), 128 (100), 115 (48). Anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.37; H, 6.78.

3-Ethenyl-4-[[3-(trimethylsilyl)pent-2-yn]ylidene]tetrahydrofurane (16b). bp 100 °C (1 mmHg); R_f = 0.44 (hexane/AcOEt = 15:1); ^1H NMR (270 MHz, $CDCl_3$): δ 0.19 (s, 9 H), 1.09 (t, *J* = 7.3 Hz, 3 H), 2.00 (q, *J* = 7.3 Hz, 2 H), 3.46–3.58 (m, 1 H), 3.81–3.96 (m, 2 H), 4.26–4.48 (m, 2 H), 5.06–5.19 (m, 2 H), 5.72–5.87 (m, 1 H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 0.09, 12.51, 26.60, 48.66, 69.51, 73.60, 97.75. 103.77, 115.18, 117.07, 136.35, 148.72; IR (neat): 2966, 2139, 1249, 1066, 842, 760 cm^{-1}; GC/MS (EI, 70eV): *m/z* (rel.int., %) 234 (M^+, 13), 205 (57), 73 (100). HRMS for $C_{14}H_{22}OSi$ (M^+): Calcd, 234.1440; Found, 234.1445.

3-Ethenyl-2-[[3-(trimethylsilyl)prop-2-yn]ylidene]-1-(4-toluenesulfonyl)pyrrolidine (18). mp 82–84 °C; R_f = 0.29 (hexane/AcOEt = 10:1); ^1H NMR (500 MHz, $CDCl_3$): δ 0.15 (s, 9 H), 2.44 (s, 3 H), 3.26 (dd, *J* = 9.8, 7.1 Hz, 1 H), 3.34 (dd, *J* = 9.8, 3.1 Hz), 3.52–3.62 (m, 1 H), 3.74 (dd, *J* = 15.3, 1.8 Hz, 1 H), 3.99 (dt, *J* = 15.3, 2.5 Hz 1 H), 5.06–5.14 (m, 2 H), 5.46 (dd, *J* = 2.5, 1.8 Hz, 1 H), 5.69 (ddd, *J* = 17.1, 9.8, 7.3 Hz, 1 H), 7.33 (d, *J* = 8.5 Hz, 2 H), 7.70 (d, *J* = 8.5 Hz, 2 H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ –0.17, 21.54, 46.46, 51.79, 53.08, 100.65, 100.78, 104.24, 116.36, 127.89, 129.73, 132.33, 135.02, 143.91, 152.47; IR (dish): 2957, 1345, 1248, 1159, 1090, 1042, 845 cm^{-1}; GC/MS (EI, 70eV): *m/z* (rel.int., %) 360 (M^+, 16), 359 (58), 204 (100), 161 (49), 91 (74), 73 (86). Anal. Calcd for $C_{19}H_{25}O_2NSSi$: C, 63.47; H, 7.01; N, 3.90. Found: C, 63.34; H, 7.03; N, 4.06.

The Pauson-Khand reaction of 8.[10] In a 50 mL-stainless steel autoclave were placed **8** (288 mg, 0.826 mmol), $Co_2(CO)_8$ (440 mg, 1.287 mmol), and toluene (10 mL). The autoclave was heated with stirring at 140 °C for 48 h. After the autoclave was cooled to room temperature, the content filtered, the residue washed with ether, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography on silica gel (ether/petrol = 10:1~100:0) to give **21** as a white solid (143 mg, 46%); mp 96.5–97 °C (recrystalization from H_2O/MeOH); ^1H NMR (500 MHz, $CDCl_3$): δ 0.19 (s, 9 H), 1.26 (t, *J* = 7.3 Hz, 3 H), 1.27 (t, *J* = 7.3 Hz, 3 H), 1.91 (dd, *J* = 12.8, 11.6 Hz, 1 H), 2.30 (dd, *J* = 17.1, 6.1 Hz, 1 H), 2.51 (dd, *J* = 17.1, 6.7 Hz, 1 H),

2.68 (dd, J = 12.8, 7.9 Hz, 1 H), 2.84–2.92 (m, 1 H), 3.02–3.20 (m, 3 H), 4.22 (q, J = 7.3 Hz, 4 H), 6.35 (s, 1 H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ −1.04, 14.04, 33.97, 37.69, 41.56, 54.31, 56.77, 61.89, 62.01, 63.07, 119.86, 129.19, 170.21, 171.06, 171.59, 198.11, 213.04; IR (nujol): 1728, 1676, 1367, 1271, 1211, 1068, 841 cm^{-1}; GC/MS (EI, 70eV): *m/z* (rel.int., %) 376 (M^+, 100). Anal. Calcd for $C_{20}H_{28}O_5Si$: C, 63.80; H, 7.50. Found: C, 63.67; H, 7.33.

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