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Selected Paper

Nickel-Catalyzed [4 + 2 + 2]-Type Annulation Reaction of Cyclobutanones with Diynes and Enynes

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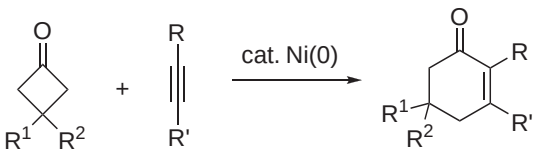
In the presence of a nickel(0) catalyst, cyclobutanones reacted with diynes to produce bicyclic eight-membered ring ketones. Cyclobutanones acted as a C4 unit in the formal [4 + 2 + 2]-type annulation reaction, which proceeded through a ring-expansion of a spirocyclic seven-membered oxanickelacycle to a nine-membered nickelacycle via β-carbon elimination. A similar annulation reaction was also examined with enynes.

Transition-metal-catalyzed multi-component annulation reactions[1] have been one of the most attractive research topics in synthetic organic chemistry. Multiple carbon–carbon bond formations occur in a single chemical operation with good atom economy, providing a powerful method for the construction of cyclic carbon frameworks. A number of carbon units and reaction modes have been developed to expand the range of accessible carbocycles. For example, $[5 + 2 + 1]$[2] and $[4 + 2 + 2]$[3] annulation reactions have enabled a direct synthesis of eight-membered carbocycles, which are an important structural feature often found in biologically active compounds. Further exploration of new reaction modes is desired to expand the utility of multi-component annulation reactions.

We have reported a nickel-catalyzed intermolecular alkyne insertion reaction of cyclobutanones which forms six-membered carbocycles (Scheme 1).[4] An alkyne was formally inserted between the carbonyl carbon and the α-carbon through the initial formation of an oxanickelacycle intermediate by oxidative cyclization of an alkyne and the carbonyl group of a cyclobutanone with nickel(0), which was followed by β-carbon elimination and reductive elimination. This result presented an example of a $[4 + 2]$ annulation reaction, in which cyclobutanones act as a C4 unit. We next envisaged that incorporation of another unsaturated carbon–carbon bond into the initially formed oxanickelacycle could extend this protocol even further to a three-component annulation reaction to construct medium-sized carbocycles. In this article, we describe the details of our study on the nickel-catalyzed $[4 + 2 + 2]$ annulation reaction of cyclobutanones with diynes and enynes.[5]



Scheme 1.

Results and Discussion

A solution of dimethyl 2,2-bis(but-2-ynyl)malonate (**1a**, 1.5 molar equivalents) in toluene was added dropwise to a mixture of 3-methyl-3-phenylcyclobutanone (**2a**), bis(1,5-cyclooctadiene)nickel(0) (10 mol %), and tricyclohexylphosphine (20 mol %) in toluene at 100 °C. The reaction mixture was stirred at that temperature for 3 h. A formal $[4 + 2 + 2]$ annulation reaction took place to give bicyclo[6.3.0]undecadienone **3a** in 83% yield (Table 1, Entry 1). The structure of **3a** was unambiguously assigned by NMR spectroscopy (^{1}H, ^{13}C, NOESY, HMQC, and HMBC). No formation of a six-membered ketone that might have arisen from a $[4 + 2]$ annulation reaction of **2a** with the alkyne moiety was observed. Several phosphine ligands were examined under otherwise identical conditions (Table 1). Whereas triphenylphosphine and tri-*t*-butylphosphine showed low reactivities, tri-*n*-butylphosphine worked efficiently at 100 °C to give **3a** in 92% (Entries 3–5). Self-oligomerization of the diyne **1a** was a major side-reaction, which was partially suppressed by slow addition of **1a**. Ligands other than phosphines were also examined to reveal that the use of N-heterocyclic carbene ligands[6] improved the catalyst activity of nickel(0) so that the $[4 + 2 + 2]$ annulation occurred even at room temperature. In particular IPr (10 mol %) gave **3a** in the best yield of 91% with the use of 1.2 mol equiv of **2a** (Entry 8).

The structure of alkyne **4** is given by substraction of one of two alkyne moieties from diyne **1a** with the sterically demanding malonate moiety being retained. For comparison with diyne **1a**, alkyne **4** was subjected to reaction with cyclobutanone **2a** (Scheme 2). The formal insertion reaction failed to occur, suggesting that simultaneous coordination of the two alkyne moieties is required for the initial oxidative cyclization to proceed.

We postulate the mechanism shown in Scheme 3. The diyne and cyclobutanone initially bind to nickel(0) to form **5**. Subsequent oxidative cyclization leads to the formation of spirocyclic oxanickelacycloheptadiene **7**. There are two species **6** and **6′** conceivable as the intermediate between **5** and **7**. Nickelacyclopentadiene **6**[7] can occur through oxidative cyclization

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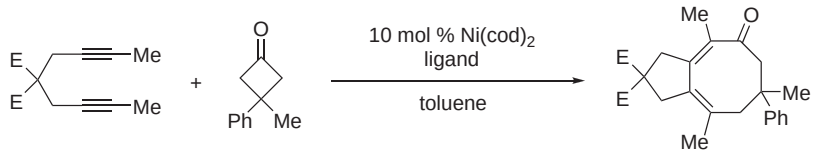
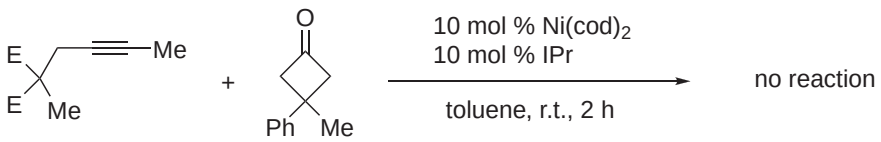
Table 1. Optimization of Reaction Conditions[a)]



1a (E = CO_2Me) **2a** **3a**

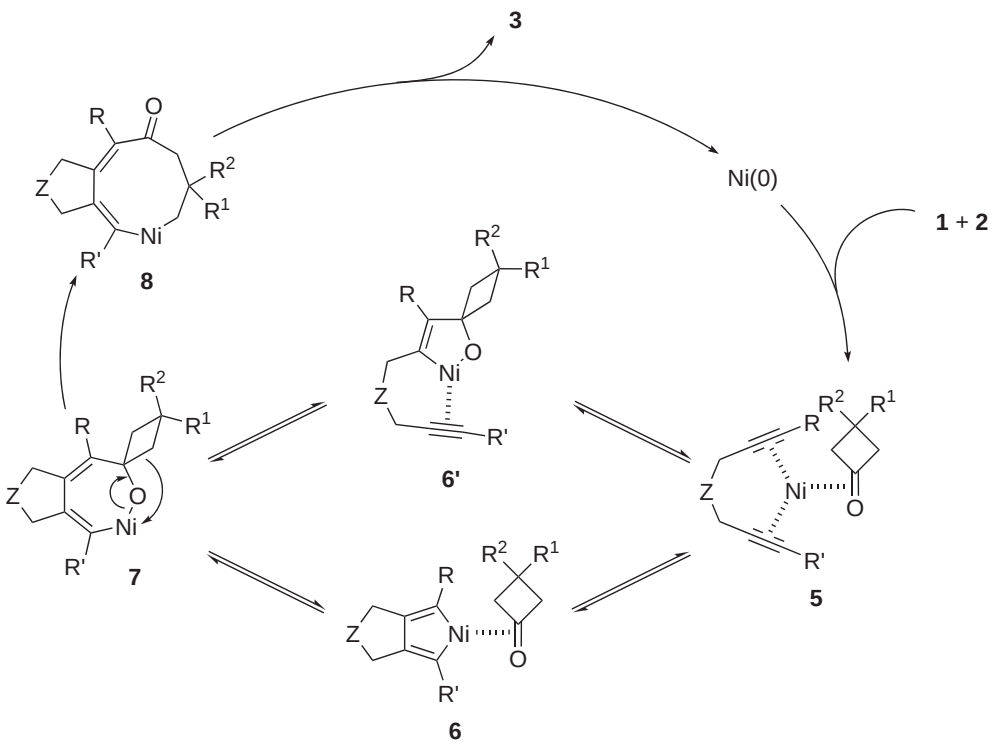
Entry	**2a**/mol equiv	Ligand	Temp/°C	Time/h	Yield/%[b)]
1	1.5	20 mol % P(*c*-Hex)$_3$	100	3	83
2	1.5	none	100	3	0
3	1.5	20 mol % PPh_3	100	3	8
4	1.5	20 mol % PBu_3	100	3	92
5	1.5	20 mol % P(*t*-Bu)$_3$	100	3	0
6	1.5	10 mol % IPr	100	1	93
7	1.5	10 mol % IPr	rt	1	94
8	1.2	10 mol % IPr	rt	1	91
9	1.2	10 mol % IMes	rt	12	30
10	1.2	10 mol % SIPr	rt	12	76
11	1.2	10 mol % I*t*Bu	rt	1	0

a) A solution of diyne **1a** in toluene was added dropwise to the reaction mixture (Entries 1–5).
b) Isolated yield.



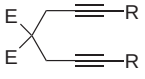
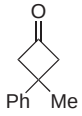
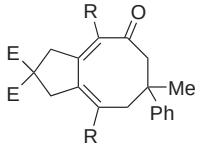
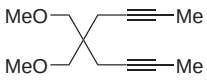
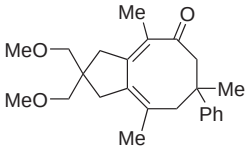
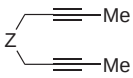
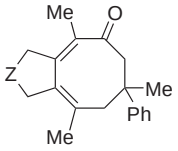
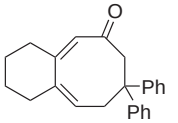
4 (E = CO_2Me) **2a**

Scheme 2.



Scheme 3.

Table 2. Screening of Diynes **1**[a)]

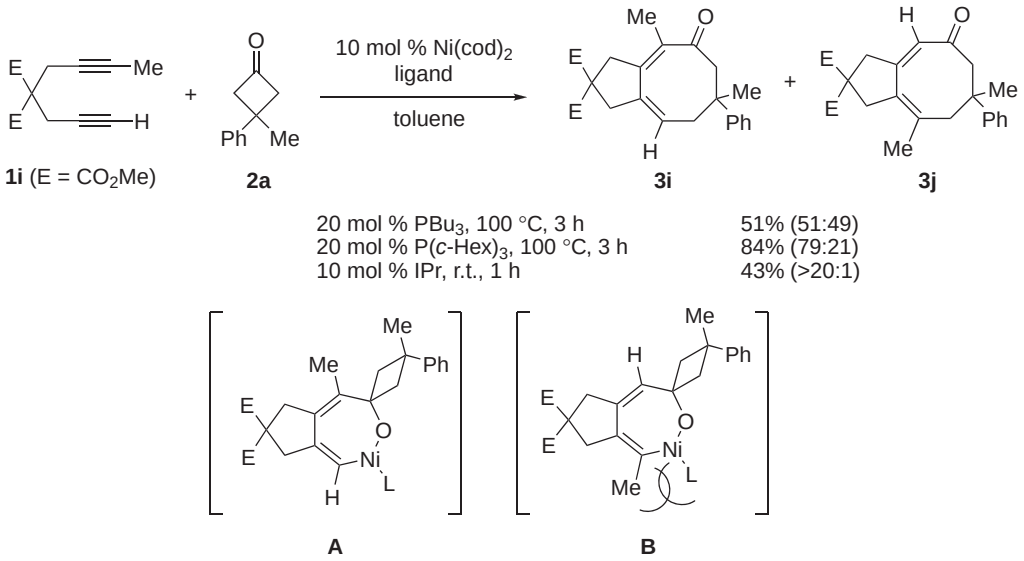
Entry	Diyne **1**	Cyclobutanone **2**	Condition	Product **3**, Yield/%[b)]
	 (E = CO_2Me)	 **2a**		
1	**1b** (R = H)		A[c),d)]	**3b**, 68
2	**1c** (R = Et)		A	**3c**, 85
				
3	**1d**		A	**3d**, 88
4	**1d**		B	**3d**, 91
				
5	**1e** (Z = CH_2)		A	**3e**, 78
6	**1e** (Z = CH_2)		B	**3e**, 87
7	**1f** (Z = O)		A	**3f**, 61
8	**1g** (Z = NTs)		A	**3g**, 32
9	**1g** (Z = NTs)		B	**3g**, 71
				
10	**1h**	**2b**	A[d),e)]	**3h**, 46

a) Condition A: Cyclobutanone **2**, diyne **1** (1.5 mol equiv to **2**), $Ni(cod)_2$ (10 mol %), and PBu_3 (20 mol %) in toluene at 100 °C for 3 h. Condition B: Cyclobutanone **2**, diyne **1** (1.2 mol equiv to **2**), $Ni(cod)_2$ (10 mol %), and IPr (10 mol %) in toluene at room temperature for 1–3 h. b) Isolated yield. c) P(*c*-Hex)$_3$ was used. d) 3.0 mol equiv of diyne was used. e) 20 mol % $Ni(cod)_2$ and 40 mol % P(*c*-Hex)$_3$ were used.

of the two alkyne moieties on nickel(0), whereas hetero-type oxidative cyclization of the carbonyl group and one of the alkyne moieties would form another possible five-membered cyclic intermediate **6′**.[8] Subsequent incorporation of the third unsaturated functionality into the Ni–C bond of either five-membered nickelacycle **6** or **6′** leads to the formation of spirocyclic oxanickelacycloheptadiene **7**.[9,10] Then, the four-membered ring of the spiro nickelacycle **7** is opened by β-carbon elimination[11] to expand the seven-membered nickelacycle to the nine-membered nickelacycle **8**. This ring-expanding process is promoted presumably by release of the ring strain of the four-membered carbocycle of the nickel(II) tertiary cyclobutanolate. Finally, reductive elimination gives the product **3** with nickel(0) regenerated.

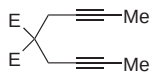
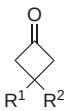
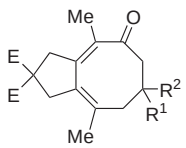
Next, various diynes **1** were subjected to the annulation reaction under the reaction conditions A (Ni–phosphine) and B (Ni–IPr) (Table 2). The reaction of diyne **1b**, possessing terminal alkyne moieties, suffered from its rapid self-oligomerization, and required the use of tricyclohexylphosphine as ligand and 3.0 molar equivalents of **1b** to attain 68% yield of **3b**, whereas diethyl-substituted diyne **1c** showed reactivity similar to **1a** and gave product **3c** in 85% yield (Entries 1 and 2). However, diynes having either isopropyl or phenyl substituents at the alkyne terminus failed to undergo the reaction, presumably due to steric reasons. The reaction worked well with diynes having various tethers under appropriate conditions. Diyne **1e** linked by a trimethylene tether produced **3e** in 87% yield under condition B (Entry 6). The reaction of oxa-1,6-diyne **1f** with **2a** afforded **3f** containing an ether linkage in its framework in 61% yield under condition A (Entry 7). Whereas aza-1,6-diyne **1g** afforded product **3g** in 32% yield under condition A, condition B improved the yield to 71% (Entries 8 and 9). Although octa-1,7-diyne (**1h**) whose linker was longer by one carbon could also join the [4 + 2 + 2] annulation reaction, it was less reactive than **1b** and **1d** to produce **3h** in 46% yield under the fortified condition A (Entry 10).

The reaction of unsymmetrical diyne **1i** was examined in terms of the regiochemical selectivity (Scheme 4). Whereas the tri-*n*-butylphosphine ligand showed no selectivity, moderate selectivity was observed with the sterically bulkier tricyclohexylphosphine ligand to give a 4:1 mixture of regioisomers **3i** and **3j**. Thus, the regioselectivity varied depending on the



Scheme 4.

Table 3. Screening of Cyclobutanones **2**[a)]

Entry	Diyne **1a**	Cyclobutanone **2**	Condition	Product **3**, Yield/%[b)]
	 **1a** (E = CO_2Me)			
1	**2b** ($R^1 = R^2$ = Ph)		A	**3k**, 84
2	**2c** ($R^1 = R^2$ = Et)		A	**3l**, 70
3	**2d** (R^1 = Ph, R^2 = H)		A	**3m**, 83
4	**2d** (R^1 = Ph, R^2 = H)		B	**3m**, 84
5	**2e** (R^1 = Oct, R^2 = H)		A	**3n**, 84
6	**2e** (R^1 = Oct, R^2 = H)		B	**3n**, 91

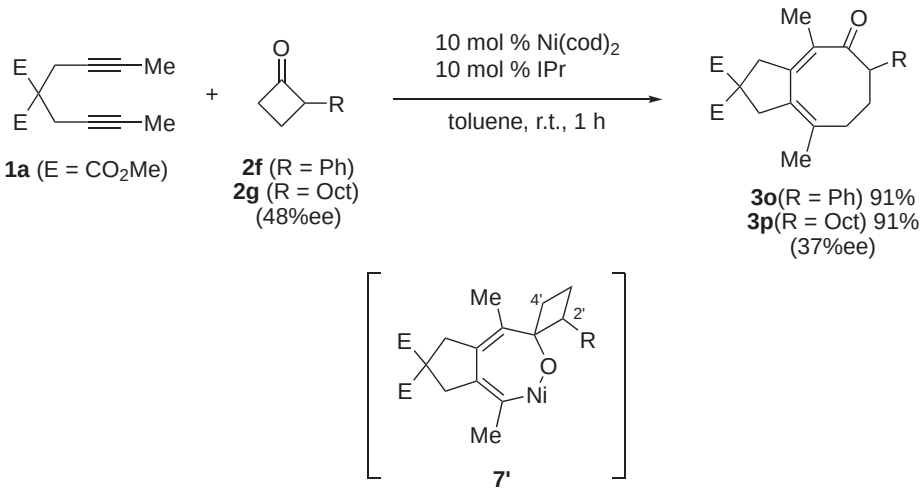
a) Condition A: Cyclobutanone **2**, diyne **1** (1.5 mol equiv to **2**), $Ni(cod)_2$ (10 mol %), and PBu_3 (20 mol %) in toluene at 100 °C for 3 h. Condition B: Cyclobutanone **2**, diyne **1** (1.2 mol equiv to **2**), $Ni(cod)_2$ (10 mol %), and IPr (10 mol %) in toluene at room temperature for 1–3 h. b) Isolated yield.

ligands, which were accounted for in terms of bulkiness. There are two regioisomeric intermediates **A** and **B** conceivable for **7** in Scheme 3. When a ligand is bulky enough, intermediate **A** would be favored over **B** because intermediate **B** would suffer from unfavorable steric repulsion between the methyl group at the alkyne terminus and the ligand (L). The IPr ligand would be bulkier than tricyclohexylphosphine, and therefore, produced **3i** in a more selective manner, although the chemical yield was moderate.

Cyclobutanones **2b** and **2c** possessing two substituents at the 3-position reacted with **1a** to give bicyclo[6.3.0]undecane derivatives **3k** and **3l**, respectively, in good yield (Table 3, Entries 1 and 2). With cyclobutanones **2d** and **2e**, the hydrogen at the 3-position of the cyclobutanone might have caused β-hydride elimination with intermediate **8**. The following reductive elimination could form a monocyclic product.[4] To our delight, however, cyclobutanones **2d** and **2e** afforded the corresponding eight-membered ring products selectively without formation of such a side product (Entries 3–6).

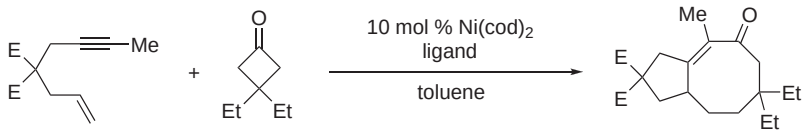
The use of unsymmetrical 2-substituted cyclobutanones **2f** and **2g** was also examined under the catalysis of Ni–IPr (Scheme 5). A high regioselectivity of >20:1 was observed for the β-carbon elimination step. We assume that, with intermediate **7′**, migration of the methylene carbon (C4′) is preferred over that of the methyne carbon (C2′), probably due to steric reasons. In the case of the enantiomerically enriched substrate **2g** (48% ee), the enantiopurity decreased to 37% with the product **3p**, which might be a result of enolization partially occurring with the carbonyl-containing compounds involved, e.g. **2g**, **3p**, and/or **8**.

We next examined an analogous nickel-catalyzed [4 + 2 + 2] annulation of enynes[3c] with cyclobutanones. Good regioselectivity could be expected for the three-component assembly because the alkene and alkyne moieties would possess different reactivities. The reaction of **2c** with dimethyl 2-allyl-2-(but-2-ynyl)malonate (**9a**, 1.5 molar equivalents) was carried out using the three typical ligands, tri-*n*-butylphosphine, tricyclohexylphophine, and IPr (Table 4). A slow addition proce-



Scheme 5.

Table 4. Optimization of Reaction Conditions[a)]



Entry	Ligand	Temp/°C	Time/h	Yield/%[b)]
1	20 mol % PBu_3	100	3	63
2	20 mol % P(*c*-Hex)$_3$	100	3	81
3	10 mol % IPr	rt	3	14
4	10 mol % IPr	60	3	59
5	10 mol % IPr	100	3	63

a) A solution of enyne **9a** in toluene was added dropwise to the reaction mixture (Entries1 and 2).
b) Isolated yield.

dure using tricyclohexylphosphine as ligand worked well at 100 °C to give the bicyclo[6.3.0]undecenone **10a** in 81% yield (Entry 2). The structure of **10a** was unambiguously assigned by NMR spectroscopy (^{1}H, ^{13}C, NOESY, HMQC, and HMBC), and only one regioisomer in which the external alkyne carbon of enyne **9a** was connected to the carbonyl carbon of **2c** was detected. The enyne **9a** was less reactive toward the [4 + 2 + 2] annulation reaction than the diyne **1a**, and the use of the IPr ligand gave a lower yield at both 60 and 100 °C due to concomitant occurrence of self-oligomerization of **9a** (Entries 3–5).

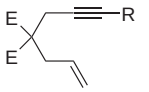
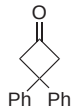
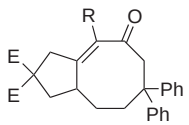
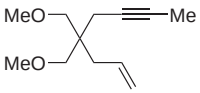
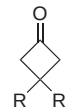
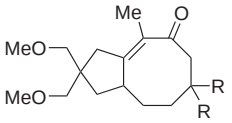
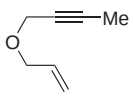
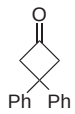
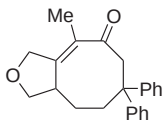
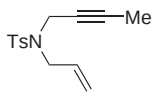
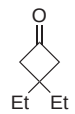
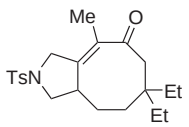
Under the optimized conditions, various bicyclo[6.3.0]-undecenones were synthesized by [4 + 2 + 2] annulation of enynes **9** with cyclobutanones **2** (Table 5). Cyclobutanone **2b** possessing two substituents at the 3-position reacted with enyne **9a** to give the product in good yield (Entry 1). The enyne **9b** having an ethyl substituent at the alkyne terminus afforded the product in 86% yield, whereas an enyne with a terminal alkyne moiety failed to participate in the annulation reaction due to rapid oligomerization at the terminal alkyne moiety (Entry 2). The enyne having a 2-methyl-2-propenyl group failed to undergo the reaction, presumably due to steric reasons. A tosylamide linker as well as an ether linker could be included in the skeleton, although the yield was less than those with malonate based linkers (Entries 5 and 6).

The mechanism of the annulation reaction of enynes would be similar to that of diynes. We assume that the intermediate **12** is more likely to occur in order to explain the good regioselectivity observed. The higher reactivity of the alkyne moiety relative to the alkene moiety for the initial hetero-type oxidative cyclization could be the reason of the selective formation of the intermediate **12** (Scheme 6).

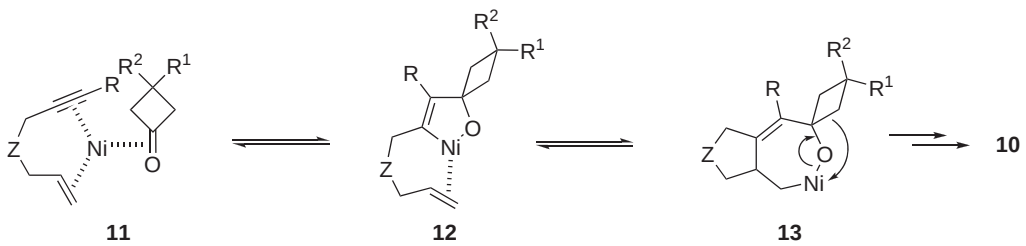
Conclusion

In summary, we have developed a nickel-catalyzed [4 + 2 + 2]-type annulation reaction of cyclobutanones with diynes/enynes, in which a spirocyclic intermediate was expanded through β-carbon elimination. In the multi-component annulation reaction, cyclobutanones acted as a useful C4 unit in combination with alkyne and alkene units. This method provides a new direct access to bicyclic eight-membered ring ketones.

Table 5. Reaction of Cyclobutanones **2** and Enynes **9** Forming Bicyclo[6.3.0]undecenone **10**[a)]

Entry	Enyne **9**	Cyclobutanone **2**	Product **10**, Yield/%[b)]
	 (E = CO_2Me)		
1	**9a** (R = Me)	**2b**	**10b** (R = Me), 87
2	**9b** (R = Et)	**2b**	**10c** (R = Et), 86
			
3	**9c**	**2b** (R = Ph)	**10d** (R = Ph), 87
4	**9c**	**2c** (R = Et)	**10e** (R = Et), 74
			
5	**9d**	**2b**	**10f**, 32
			
6	**9e**	**2c**	**10g**, 41

a) Cyclobutanone **2**, enyne **9** (1.5 mol equiv to **2**), $Ni(cod)_2$ (10 mol %), and P(*c*-Hex)$_3$ (20 mol %) in toluene at 100 °C for 3 h. b) Isolated yield.



11 **12** **13**

Scheme 6.

Experimental

General. All reactions were carried out with standard Schlenk and glove box techniques under a nitrogen atmosphere. Preparative thin-layer chromatography was performed with silica gel 60 PF_{254} (Merck). ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 2000 (^1H at 300.07 MHz and ^{13}C at 75.46 MHz) spectrometer or a JEOL JNM-A400 (^1H at 399.65 MHz and ^{13}C at 100.40 MHz) spectrometer. Proton chemical shifts were referenced to residual solvent signals in $CDCl_3$ (δ 7.26). Carbon chemical shifts were referenced to the deuterated solvent signals in $CDCl_3$ (δ 77.00) and C_6D_6 (δ 128.00). High-resolution mass spectra were recorded on a JOEL JMS-SX102A spectrometer.

Materials. Diynes **1a**,[12] **1b**,[12] **1c**,[13] **1d**,[13] **1e**,[14] **1f**,[15] **1g**,[16] **1i**,[17] and enynes **9a**,[18] **9b**,[19] **9c**,[20] **9d**,[21] **9e**,[22] and N-heterocyclic carbenes IPr,[23] SIPr,[23] IMes,[23] I*t*Bu[24] were prepared according to the literature methods. Cyclobutanones **2a**–**2e** were prepared by [2 + 2] cycloaddition of the corresponding olefins with dichloroketene and subsequent dechlorination with zinc dust in acetic acid.[25] Cyclobutanones **2f** and **2g** were prepared from cyclopropylidenation of benzaldehyde[26] and subsequent *m*CPBA oxidation.[27] Toluene was distilled over sodium/benzophenone ketyl prior to use. All other commercially available chemical resources were used without further purifications.

General Procedure A. A toluene solution (0.80 mL) of $Ni(cod)_2$ (5.5 mg, 0.020 mmol), PBu_3 (8.1 mg, 0.040 mmol), and cyclobutanone **2** (0.20 mmol) was stirred at 100 °C for a few minutes. To the solution was added dropwise a toluene solution (0.20 mL) of diyne **1** (0.30 mmol) via syringe over 2.5 h. After being stirred for a further 0.5 h, the reaction mixture was concentrated. The residue was purified by preparative thin-layer chromatography on silica gel to afford product **3**.

General Procedure B. A toluene solution (0.50 mL) of $Ni(cod)_2$ (5.5 mg, 0.020 mmol) and IPr (7.8 mg, 0.020 mmol) was stirred for at least 6 h and added to a mixture of cyclobutanone **2** (0.20 mmol) and diyne **1** (0.24 mmol) in toluene (1.50 mL). After being stirred for 1–3 h at room temperature, the reaction mixture was filtered through a pad of Florisil®. The filtrate was con-

centrated, and the residue was purified by preparative thin-layer chromatography on silica gel to afford product **3**.

Dimethyl 2,5,7-Trimethyl-5-phenylbicyclo[6.3.0]undeca-1,7-dien-3-one-10,10-dicarboxylate (3a): ^{1}H NMR δ 1.18 (s, 3H), 1.41 (s, 3H), 1.96 (s, 3H), 2.31–2.42 (m, 3H), 2.96 (d, J = 15.3 Hz, 1H), 3.11–3.17 (m, 3H), 3.54 (d, J = 9.9 Hz, 1H), 3.72 (s, 3H), 3.75 (s, 3H), 7.20–7.34 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 16.0, 23.0, 29.0, 38.9, 42.0, 47.4, 49.6, 50.4, 52.9, 53.0, 55.7, 125.4, 126.2, 128.2, 131.8, 135.3, 141.3, 147.1, 148.8, 171.6, 171.7, 201.7; HRMS (EI) calcd for $C_{24}H_{28}O_5$ (M^+) 396.1937, found 396.1938.

Dimethyl 5-Methyl-5-phenylbicyclo[6.3.0]undeca-1,7-dien-3-one-10,10-dicarboxylate (3b): ^{1}H NMR δ 1.38 (s, 3H), 2.26–2.33 (m, 1H), 2.61 (br s, 1H), 2.71 (dd, J = 12.8, 8.0 Hz, 1H), 2.98–3.36 (m, 5H), 3.73 (s, 3H), 3.74 (s, 3H), 6.00 (s, 1H), 6.08 (br t, 1H), 7.19–7.26 (m, 1H), 7.31–7.34 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 30.0, 40.8, 41.7, 42.2, 49.4, 51.6, 53.0 [two carbons], 56.2, 125.2, 126.3, 126.8, 128.4, 133.4, 140.2, 146.4, 150.7, 171.1, 171.2, 202.2; HRMS (EI) calcd for $C_{22}H_{24}O_5$ (M^+) 368.1624, found 368.1628.

Dimethyl 2,7-Diethyl-5-methyl-5-phenylbicyclo[6.3.0]undeca-1,7-dien-3-one-10,10-dicarboxylate (3c): ^{1}H NMR δ 0.50–0.75 (m, 3H), 0.80–1.20 (m, 3H), 1.41 (s, 3H), 1.74–1.93 (m, 1H), 2.18–2.56 (m, 6H), 3.06–3.29 (m, 4H), 3.52 (d, J = 10.8 Hz, 1H), 3.72 (s, 3H), 3.75 (s, 3H), 7.17–7.33 (m, 5H); ^{13}C NMR (C_6D_6) δ 11.5, 13.7, 24.2, 29.0, 29.6, 38.7, 41.5, 46.4, 48.0, 50.0, 52.4, 52.5, 55.9, 125.7, 126.4, 128.5, 135.5, 138.9, 146.7, 147.6, 147.7, 171.5, 171.6, 200.1; HRMS (EI) calcd for $C_{26}H_{32}O_5$ (M^+) 424.2250, found 424.2253.

10,10-Bis(methoxymethyl)-2,5,7-trimethyl-5-phenylbicyclo-[6.3.0]undeca-1,7-dien-3-one (3d): ^{1}H NMR δ 1.14 (s, 3H), 1.42 (s, 3H), 1.93 (s, 3H), 2.20–2.57 (m, 7H), 3.20–3.35 (m, 10H), 3.54 (d, J = 9.9 Hz, 1H), 7.18–7.34 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 16.1, 23.2, 29.0, 37.3, 41.0, 43.0, 47.6, 49.7, 50.5, 59.26, 59.32, 75.7, 76.1, 125.4, 126.1, 128.2, 131.8, 137.8, 140.6, 147.4, 152.6, 201.9; HRMS (EI) calcd for $C_{24}H_{32}O_3$ (M^+) 368.2351, found 368.2354.

2,5,7-Trimethyl-5-phenylbicyclo[6.3.0]undeca-1,7-dien-3-one (3e): ^{1}H NMR δ 1.17 (s, 3H), 1.43 (s, 3H), 1.70–1.78 (m, 2H), 1.97 (s, 3H), 2.31–2.70 (m, 7H), 3.59 (d, J = 9.6 Hz, 1H), 7.19–7.23 (m, 1H), 7.30–7.35 (m, 4H); ^{13}C NMR (C_6D_6) δ 16.7, 22.0, 23.3, 29.4, 31.9, 35.4, 47.8, 49.9, 50.2, 125.8, 126.3, 128.4, 131.4, 138.9, 139.5, 148.1, 152.6, 200.8; HRMS (EI) calcd for $C_{20}H_{24}O$ (M^+) 280.1827, found 280.1827.

2,5,7-Trimethyl-5-phenyl-10-oxabicyclo[6.3.0]undeca-1,7-dien-3-one (3f): ^{1}H NMR δ 1.18 (br s, 3H), 1.47 (s, 3H), 1.86 (s, 3H), 2.30–2.49 (m, 3H), 3.61 (br s, 1H), 4.51–4.66 (m, 4H), 7.20–7.37 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 15.5, 23.4, 29.2, 47.5, 49.9, 51.7, 71.9, 73.4, 125.3, 126.4, 128.4, 129.4, 134.9, 141.0, 146.7, 147.3, 202.2; HRMS (EI) calcd for $C_{19}H_{22}O_2$ (M^+) 282.1620, found 282.1617.

10-(4-Tolylsulfonyl)-2,5,7-trimethyl-5-phenyl-10-azabicyclo-[6.3.0]undeca-1,7-dien-3-one (3g): ^{1}H NMR δ 1.11 (s, 3H), 1.44 (s, 3H), 1.86 (s, 3H), 2.15–2.42 (m, 3H), 2.43 (s, 3H), 3.27 (br s, 1H), 3.99–4.28 (m, 4H), 7.20–7.35 (m, 7H), 7.72 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 16.0, 21.5, 23.4, 29.0, 47.2, 49.7, 51.1, 52.0, 54.1, 125.2, 126.5, 127.7, 128.4, 129.8, 131.4, 132.0, 133.1, 143.0, 144.0, 144.1, 146.4, 201.2; HRMS (EI) calcd for $C_{26}H_{29}NO_3S$ (M^+) 435.1868, found 435.1868.

5,5-Diphenylbicyclo[6.4.0]dodeca-1,7-dien-3-one (3h): ^{1}H NMR δ 1.45–1.71 (m, 2H), 1.86–1.99 (m, 2H), 2.25–2.46 (m, 4H), 2.79 (dd, J = 12.3, 6.5 Hz, 1H), 2.91 (d, J = 10.7 Hz, 1H), 3.21 (dd, J = 12.3, 9.9 Hz, 1H), 3.79 (d, J = 10.7 Hz, 1H), 5.56 (ddd, J = 9.9, 6.5, 1.5 Hz, 1H), 5.91 (s, 1H), 7.15–7.32 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 26.9, 27.2, 36.7, 37.7, 38.6, 49.5, 54.9, 126.1, 126.3, 126.9, 127.0, 127.2, 128.0, 128.2, 129.1, 141.4, 146.3, 146.7, 152.9, 200.7; HRMS (EI) calcd for $C_{24}H_{24}O$ (M^+) 328.1827, found 328.1828.

Dimethyl 2,5-Dimethyl-5-phenylbicyclo[6.3.0]undeca-1,7-dien-3-one-10,10-dicarboxylate (3i): ^{1}H NMR δ 1.37 (s, 3H), 1.92 (s, 3H), 2.17 (br s, 1H), 2.62 (dd, J = 12.1, 8.0 Hz, 2H), 2.98–3.33 (m, 5H), 3.72 (s, 3H), 3.74 (s, 3H), 5.97 (s, 1H), 7.19–7.35 (m, 5H); ^{13}C NMR δ 15.9, 30.0, 39.8, 41.6, 43.0, 48.7, 52.3, 53.0 [two carbons], 55.7, 125.3, 126.1, 128.2, 131.0, 133.1, 140.8, 146.0, 146.5, 171.3, 171.5, 202.3; HRMS (EI) calcd for $C_{23}H_{26}O_5$ (M^+) 382.1780, found 382.1780.

Dimethyl 5,7-Dimethyl-5-phenylbicyclo[6.3.0]undeca-1,7-dien-3-one-10,10-dicarboxylate (3j): ^{1}H NMR δ 1.19 (br s, 3H), 1.42 (s, 3H), 2.34–2.60 (m, 3H), 2.90–3.30 (m, 4H), 3.46 (br s, 1H), 3.73 (s, 3H), 3.76 (s, 3H), 5.99 (s, 1H), 7.20–7.36 (m, 5H); ^{13}C NMR δ 23.1, 29.0, 38.8, 43.6, 48.1, 50.1, 50.3, 53.0, 53.1, 56.1, 125.3, 126.1, 126.4, 128.3, 134.2, 144.1, 146.8, 152.8, 171.3, 171.4, 202.5; HRMS (EI) calcd for $C_{23}H_{26}O_5$ (M^+) 382.1780, found 382.1784.

Dimethyl 2,7-Dimethyl-5,5-diphenylbicyclo[6.3.0]undeca-1,7-dien-3-one-10,10-dicarboxylate (3k): ^{1}H NMR δ 1.16 (s, 3H), 1.85 (s, 3H), 2.71–2.77 (m, 2H), 3.03 (d, J = 15.6 Hz, 1H), 3.16–3.23 (m, 4H), 3.75 (s, 3H), 3.77 (s, 3H), 3.92 (d, J = 9.9 Hz, 1H), 7.10–7.30 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 15.9, 23.0, 39.1, 41.9, 46.6, 47.8, 53.0, 55.7, 58.2, 126.3, 127.1, 127.9, 128.2, 132.1, 136.0, 140.6, 147.0, 147.2, 148.1, 171.6, 171.7, 199.9 [Some sp^2 carbon chemical shifts are observed as nonequivalent signals due to barrier to inversion of the cyclooctadienone ring]; HRMS (EI) calcd for $C_{29}H_{30}O_5$ (M^+) 458.2093, found 458.2097. Anal. Calcd for $C_{29}H_{30}O_5$: C, 75.96; H, 6.59. Found: C, 75.72; H, 6.71.

Dimethyl 5,5-Diethyl-2,7-dimethylbicyclo[6.3.0]undeca-1,7-dien-3-one-10,10-dicarboxylate (3l): ^{1}H NMR δ 0.82 (t, J = 7.1 Hz, 6H), 1.27 (br s, 4H), 1.77–2.08 (m, 3H), 1.87 (s, 3H), 1.95 (s, 3H), 2.54 (br s, 1H), 3.05–3.21 (m, 4H), 3.73 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 7.4, 16.0, 24.4, 27.9, 39.2, 42.1, 44.7, 47.5, 51.3, 53.0, 55.7, 131.8, 135.4, 140.8, 148.4, 171.6, 201.7; HRMS (EI) calcd for $C_{21}H_{30}O_5$ (M^+) 362.2093, found 362.2094.

Dimethyl 2,7-Dimethyl-5-phenylbicyclo[6.3.0]undeca-1,7-dien-3-one-10,10-dicarboxylate (3m): ^{1}H NMR δ 1.51 (br s, 3H), 1.93 (s, 3H), 2.38 (br s, 1H), 2.56 (br s, 2H), 3.10–3.24 (m, 5H), 3.65 (br s, 1H), 3.72 (s, 3H), 3.75 (s, 3H), 7.12–7.30 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 16.0, 23.5, 39.0, 41.9 [two carbons], 42.4, 50.4, 52.98, 53.04, 55.7, 126.6, 126.8, 128.3, 131.1, 135.1, 139.5, 143.4, 148.4, 171.6, 171.7, 203.5; HRMS (EI) calcd for $C_{23}H_{26}O_5$ (M^+) 382.1780, found 382.1773.

Dimethyl 2,7-Dimethyl-5-octylbicyclo[6.3.0]undeca-1,7-dien-3-one-10,10-dicarboxylate (3n): ^{1}H NMR δ 0.84 (t, J = 6.6 Hz, 3H), 1.23–1.40 (m, 14H), 1.85 (s, 3H), 1.91 (s, 3H), 1.96–2.85 (m, 5H), 3.11 (dd, J = 21.9, 17.4 Hz, 4H), 3.71 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 14.0, 15.8, 22.6, 23.2, 27.4, 29.2, 29.5, 29.6, 31.8, 34.7, 38.9, 40.3, 41.8, 43.2, 46.2, 52.9 [two carbons], 55.7, 131.3, 134.4, 140.2, 148.2, 171.6 [two carbons], 203.5; HRMS (EI) calcd for $C_{25}H_{38}O_5$ (M^+) 418.2719, found 418.2721.

Dimethyl 2,7-Dimethyl-4-phenylbicyclo[6.3.0]undeca-1,7-dien-3-one-10,10-dicarboxylate (3o): ^{1}H NMR δ 1.89 (s, 3H), 1.96 (s, 3H), 2.06–2.19 (m, 2H), 2.45–2.63 (m, 2H), 3.14 (d, J = 15.6 Hz, 1H), 3.19 (d, J = 1.2 Hz, 2H), 3.29 (d, J = 15.3 Hz, 1H),

3.77 (s, 3H), 3.79 (s, 3H), 4.46 (dd, $J = 13.1$, 4.1 Hz, 1H), 7.19–7.29 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 16.3, 21.8, 34.5, 39.0, 41.0, 41.8, 51.5, 52.98, 53.04, 56.0, 126.7, 127.9, 129.1, 131.9, 134.0, 139.6, 140.4, 147.3, 171.5, 171.7, 206.1; HRMS calcd (EI) for $C_{23}H_{26}O_5$ (M^+) 382.1780, found 382.1779.

Dimethyl 2,7-Dimethyl-4-octylbicyclo[6.3.0]undeca-1,7-dien-3-one-10,10-dicarboxylate (3p): ^{1}H NMR δ 0.83 (t, $J =$ 6.6 Hz, 3H), 1.16–1.30 (m, 14H), 1.63–1.80 (m, 1H), 1.80–1.94 (m, 2H), 1.85 (s, 3H), 1.89 (s, 3H), 2.22–2.36 (m, 1H), 2.99–3.12 (m, 1H), 3.00 (d, $J = 15.3$ Hz, 1H), 3.10 (d, $J = 0.6$ Hz, 2H), 3.20 (d, $J = 15.0$ Hz, 1H), 3.71 (s, 3H), 3.72 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 14.1, 16.0, 21.6, 22.6, 28.1, 29.2, 29.4, 29.8, 31.3, 31.8, 34.4, 38.9, 41.1, 41.6, 46.5, 52.9 [two carbons], 55.9, 131.5, 133.3, 140.2, 146.5, 171.6, 171.7, 209.3; HRMS (EI) calcd for $C_{25}H_{38}O_5$ (M^+) 418.2719, found 418.2720.

General Procedure for Enynes. A toluene solution (0.80 mL) of $Ni(cod)_2$ (5.5 mg, 0.020 mmol), P(*c*-Hex)$_3$ (11.2 mg, 0.040 mmol), and cyclobutanone **2** (0.20 mmol) was stirred at 100 °C for a few minutes. To the solution was added dropwise a toluene solution (0.20 mL) of enyne **9** (0.30 mmol) via syringe over 2.5 h. After being stirred for a further 0.5 h, the reaction mixture was concentrated. The residue was purified by preparative thin-layer chromatography on silica gel to afford product **10**.

Dimethyl 5,5-Diethyl-2-methylbicyclo[6.3.0]undeca-1-en-3-one-10,10-dicarboxylate (10a): ^{1}H NMR δ 0.75 (q, $J =$ 6.9 Hz, 6H), 1.01–1.38 (m, 7H), 1.78–1.90 (m, 1H) 1.82 (s, 3H), 2.00 (dd, $J = 16.5$, 5.4 Hz, 1H), 2.32 (d, $J = 12.0$ Hz, 1H), 2.68 (d, $J = 12.0$ Hz, 1H), 2.81 (dd, $J = 13.1$, 8.6 Hz, 1H), 3.05 (d, $J = 18.0$ Hz, 1H), 3.22 (d, $J = 18.0$ Hz, 1H), 3.50–3.66 (m, 1H), 3.71 (s, 3H), 3.72 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 7.2, 7.3, 15.7, 26.6, 28.9, 29.5, 31.7, 36.8, 40.9, 42.57, 42.63, 49.8, 52.88, 52.95, 58.0, 134.6, 154.0, 171.7, 171.8, 200.7; HRMS (CI) calcd for $C_{20}H_{30}O_5$ (M^+) 350.2093, found 350.2089.

Dimethyl 2-Methyl-5,5-diphenylbicyclo[6.3.0]undeca-1-en-3-one-10,10-dicarboxylate (10b): ^{1}H NMR δ 1.14–1.27 (m, 1H), 1.49–1.63 (m, 1H), 1.87 (d, $J = 1.2$ Hz, 3H), 1.97 (dd, $J = 13.5$, 5.1 Hz, 1H), 2.23 (d, $J = 14.4$ Hz, 1H), 2.35–2.46 (m, 1H), 2.78 (dd, $J = 13.4$, 8.3 Hz, 1H), 2.99 (dd, $J = 11.4$, 1.2 Hz, 1H), 3.10 (d, $J = 18.0$ Hz, 1H), 3.32 (d, $J = 18.0$ Hz, 1H), 3.50–3.65 (m, 1H), 3.74 (s, 6H), 4.06 (d, $J = 11.7$ Hz, 1H), 7.04–7.17 (m, 3H), 7.18–7.27 (m, 5H), 7.29–7.37 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 15.8, 29.3, 33.4, 41.0, 42.80, 42.83, 47.0, 51.2, 52.9, 53.0, 58.0, 125.9, 126.1, 127.2, 127.8, 128.3, 135.2, 146.1, 148.4, 154.0, 171.6, 171.8, 198.4 [one carbon missing]; HRMS (CI) calcd for $C_{28}H_{30}O_5$ (M^+) 446.2093, found 446.2093.

Dimethyl 2-Ethyl-5,5-diphenylbicyclo[6.3.0]undeca-1-en-3-one-10,10-dicarboxylate (10c): ^{1}H NMR δ 0.94 (t, $J =$ 7.4 Hz, 3H), 1.15–1.27 (m, 1H), 1.51–1.65 (m, 1H), 1.91 (dd, $J = 13.5$, 5.7 Hz, 1H), 2.19–2.50 (m, 4H), 2.79 (dd, $J = 12.5$, 8.3 Hz, 1H), 2.99 (d, $J = 11.1$ Hz, 1H), 3.15 (d, $J = 17.7$ Hz, 1H), 3.33 (d, $J = 18.0$ Hz, 1H), 3.50–3.65 (m, 1H), 3.75 (s, 6H), 4.03 (d, $J = 11.4$ Hz, 1H), 7.05–7.17 (m, 3H), 7.18–7.26 (m, 5H), 7.30–7.36 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.2, 23.4, 29.4, 33.4, 40.8, 41.9, 42.7, 47.0, 51.4, 52.90, 52.93, 58.0, 126.0, 126.1, 127.2, 127.8, 128.3, 141.7, 146.2, 148.2, 153.4, 171.5, 171.7, 197.8; HRMS (CI) calcd for $C_{29}H_{32}O_5$ (M^+) 460.2250, found 460.2254.

10,10-Bis(methoxymethyl)-2-methyl-5,5-diphenylbicyclo[6.3.0]undeca-1-en-3-one (10d): ^{1}H NMR δ 1.26–1.40 (m, 2H), 1.54–1.68 (m, 1H), 1.85 (s, 3H), 2.03 (dd, $J = 13.1$, 8.6 Hz, 1H), 2.25 (d, $J = 14.4$ Hz, 1H), 2.38–2.65 (m, 3H), 3.00 (d, $J =$ 11.1 Hz, 1H), 3.14–3.23 (m, 2H), 3.28–3.40 (m, 8H), 3.43–3.56 (m, 1H), 4.11 (d, $J = 11.7$ Hz, 1H), 7.06–7.38 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 15.9, 30.6, 33.5, 40.8, 41.1, 42.0, 46.0, 47.0, 51.3, 59.2, 59.3, 75.5, 76.3, 125.9, 126.0, 127.2, 127.8, 128.3, 134.9, 146.4, 148.6, 158.4, 198.8 [one carbon missing]; HRMS (CI) calcd for $C_{28}H_{34}O_3$ (M^+) 418.2508, found 418.2503.

10,10-Bis(methoxymethyl)-5,5-diethyl-2-methylbicyclo[6.3.0]undeca-1-en-3-one (10e): ^{1}H NMR δ 0.77 (q, $J = 7.4$ Hz, 6H), 1.06–1.40 (m, 8H), 1.80 (s, 3H), 1.81–1.94 (m, 1H), 2.09 (ddd, $J = 12.8$, 8.9, 1.1 Hz, 1H), 2.30–2.43 (m, 2H), 2.53 (d, $J = 17.7$ Hz, 1H), 2.73 (d, $J = 11.7$ Hz, 1H), 3.11–3.18 (m, 2H), 3.27–3.31 (m, 5H), 3.33 (s, 3H), 3.41–3.54 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 7.3, 7.4, 15.9, 26.6, 29.0, 30.9, 31.9, 36.8, 40.6, 40.9, 41.7, 45.9, 49.9, 59.2, 59.3, 75.4, 76.6, 134.4, 158.4, 201.2; HRMS (CI) calcd for $C_{20}H_{34}O_3$ (M^+) 322.2508, found 322.2502.

2-Methyl-5,5-diphenyl-10-oxabicyclo[6.3.0]undeca-1-en-3-one (10f): ^{1}H NMR δ 1.41–1.63 (m, 2H), 1.78 (d, $J = 1.2$ Hz, 3H), 2.23–2.33 (m, 1H), 2.26–2.47 (m, 1H), 3.02 (dd, $J = 12.0$, 1.5 Hz, 1H), 3.47–3.55 (m, 1H), 3.69 (d, $J = 8.7$ Hz, 1H), 3.95 (dd, $J = 8.7$, 6.0 Hz, 1H), 4.17 (d, $J = 11.4$ Hz, 1H), 4.40 (d, $J = 15.6$ Hz, 1H), 4.65 (d, $J = 15.9$ Hz, 1H), 7.03–7.09 (m, 2H), 7.12–7.18 (m, 1H), 7.19–7.30 (m, 5H), 7.31–7.38 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.6, 26.7, 33.2, 42.3, 47.4, 51.4, 73.1, 76.3, 126.1, 126.2, 127.2, 127.3, 127.9, 128.4, 132.1, 146.1, 148.4, 153.3, 198.2; HRMS (CI) calcd for $C_{23}H_{24}O_2$ (M^+) 332.1776, found 332.1779.

10-(4-Tolylsulfonyl)-5,5-diethyl-2-methyl-10-azabicyclo[6.3.0]-undeca-1-en-3-one (10g): ^{1}H NMR δ 0.73–0.80 (m, 6H), 1.01–1.55 (m, 7H), 1.72 (s, 3H), 1.78–1.95 (m, 1H), 2.39 (d, $J =$ 13.2 Hz, 1H), 2.43 (s, 3H), 2.61 (d, $J = 12.6$ Hz, 1H), 3.11 (dd, $J = 9.0$, 6.6 Hz, 1H), 3.34 (d, $J = 9.0$ Hz, 1H), 3.46–3.59 (m, 2H), 4.17 (d, $J = 16.2$ Hz, 1H), 7.35 (d, $J = 8.4$ Hz, 2H), 7.71 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 7.26, 7.33, 14.9, 21.6, 27.0, 27.1, 29.4, 31.1, 37.3, 41.1, 50.4, 53.7, 55.4, 128.0, 129.7, 131.3, 133.9, 144.0, 149.0, 199.4; HRMS (CI) calcd for $C_{22}H_{31}NO_3S$ (M^+) 389.2025, found 389.2028.

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