Cross [2 + 2] Cycloaddition of Bicyclic Alkenes with Alkynes Mediated by Cobalt Complexes: A Facile Synthesis of Cyclobutene Derivatives

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Bicyclic alkenes **1a**−**e** and **5** undergo [2 + 2] cycloaddition with a variety of alkynes PhC≡CPh, (TMS)C≡CH, HC≡C(CH$_3$)$_2$OH, (TMS)C≡CCO$_2$Et, PhC≡CCH$_3$, C$_2$H$_5$C≡CC$_2$H$_5$, CH$_3$C≡CC$_3$H$_7$, and CH$_3$C≡CC$_2$H$_5$ in the presence of Co(PPh$_3$)$_2$I$_2$, PPh$_3$, and Zn powder in toluene to afford the corresponding *exo*-cyclobutene derivatives **3a**−**m**, **6**, and **8a**−**g** in fair to excellent yields. The yield of this cycloaddition is highly sensitive to the cobalt catalyst, solvent, ligand, and temperature used. A mechanism involving a metallacyclopentene intermediate is proposed to account for this cobalt-catalyzed cyclization.

Introduction

The [2 + 2] cycloaddition of alkenes and alkynes, a powerful method for the construction of four-membered rings,[1,2] is thermally forbidden[3] but can be achieved photochemically,[4] by thermal reactions via biradical intermediates,[5]with the assistance of Lewis acids[6] or transition metal catalysts.[1c,d] Although cycloaddition reactions such as [2 + 2 + 2], [3 + 2], [4 + 2], [5 + 2], and [5 + 3] catalyzed by transition metal complexes are well-documented, only a few reports have appeared in the literature on the metal-promoted [2 + 2] cycloaddition.[7,8] Recently, we reported a nickel-catalyzed [2 + 2][9] cycloaddition of norbornadienes with disubstituted alkynes to give cyclobutene derivatives and [2 + 2 + 2] cycloaddition of norbornadienes with monosubstituted alkynes[10,11] to give cyclohexadiene products. Furthermore, we observed the ring expansion of the cyclobutene products from [2 + 2] cycloaddition to give cyclooctadiene moiety in high yields. The results of nickel-catalyzed [2 + 2] enyne cycloaddition prompted us to investigate the catalytic activity of other metal complexes. Herein, we report that cobalt complexes are also active catalysts for the [2 + 2] cycloaddition of bicyclic olefins and acetylenes. The alkynes that are active in this cobalt-catalyzed reaction are different from those of the previous nickel-promoted reaction. Both monosubstituted and dialkyl acetylenes undergo the cycloaddition smoothly. In addition, highly substituted oxabenzonorbornadienes are effective for the reaction.

Results and Discussion

Treatment of oxabenzonorbornadiene (**1a**) with diphenylacetylene (**2a**) in the presence of CoI$_2$(PPh$_3$)$_2$, PPh$_3$, and Zn powder in toluene under nitrogen atmosphere at 90 °C gave an *exo*-cyclobutene derivative **3a** (Scheme 1). Control reactions indicate that, in the absence of either cobalt complex or zinc powder, no **3a** was formed. The

(1) (a) *Comprehensive Organic Synthesis*; Trost, B. M., Flemming, I., Paquette, L. A., Eds.; Pergamon: Oxford, U.K., 1991; Vol. 5, Chapters 1−9. (b) *Advances in Cycloaddition*; JAI Press: Greenwich, U.K., 1988−1999; Vols. 1−6. (c) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081. (d) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 59. (e) Wender, P. A.; Husfeld, C. O.; Langkopf, E.; Love, J. A. *J. Am. Chem. Soc.* **1998**, *120*, 1940, and references therein.

(2) (a) *Comprehensive Organic Synthesis*; Trost, B. M., Flemming, I., Paquette, L. A., Eds.; Pergamon: Oxford, 1991; Vol. 5, Chapter 2. (b) Bird, C. W.; Cookson, R. C.; Hudec, J. *Chem. Ind.* (*London*) **1960**, 20. (b) Jolly, P. W.; Stone, F. G. A.; Mackenzie, K. *J. Chem. Soc.* **1965**, 6416. (c) Schrauzer, G. N. *Adv. Catal.* **1968**, *18*, 373. (d) Weigert, F. J.; Baird, R. L.; Shapley, J. R. *J. Am. Chem. Soc.* **1970**, *92*, 6630. (e) Binger, P. *Angew. Chem.* **1972**, *84*, 352. (f) Greco, A.; Carbonaro, A.; Dollasta, G. *J. Org. Chem.* **1970**, *35*, 271. (g) Coulson, D. R. *J. Org. Chem.* **1972**, *37*, 1253. (h) Cannell, L. G. *J. Am. Chem. Soc.* **1972**, *94*, 6867. (i) Noyori, R.; Ishigami, T.; Hayashi, N.; Takaya, H. *J. Am. Chem. Soc.* **1973**, *95*, 1674.

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(7) (a) Trost, B. M.; Yanai, M.; Hoogsteen, K. *J. Am. Chem. Soc.* **1993**, *115*, 5294. (b) Jordan, R. W.; Tam, W. *Org. Lett.* **2000**, *2*, 3031. (c) Winling, A.; Russell, R. A. *J. Chem. Soc., Perkin Trans. 1* **1998**, 3921. (d) Warrener, R. N.; Schultz, A. C.; Johnston, M. R.; Gunter, M. J. *J. Org. Chem.* **1999**, *64*, 4218. (e) Yi, C. S.; Lee, D. W.; Chen, Y. *Organometallics* **1999**, *18*, 2043. (f) Rosenblum, M.; Scheck, D. *Organometallics* **1982**, *1*, 397.

(8) (a) Mitsudo, T.; Kokuryo, K.; Takegami, Y.*J. Chem. Soc., Chem. Comm.* **1976**, 722. (b) Mitsudo, T.; Kokuryo, K.; Shinsugi, T.; Nakagawa, Y.; Watanabe, Y.; Takegami, Y. Suzuki, H.; Itoh, K.; Ishii, Y.; Simon, K.; Ibers, J. A. *J. Org. Chem.* **1979**, *44*, 4492. (c) Mitsudo, T.; Naruse, H.; Kondo, T.; Ozaki, Y.; Watanabe, Y. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 580.

(9) Huang, D. J.; Rayabarapu, D. K.; Li, L. P.; Sambaiah, T.; Cheng, C. H. *Chem. Eur. J.* **2000**, *6*, 3706.

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(11) (a) Sambaiah, T.; Li, L.-P.; Huang, D.-J.; Lin, C.-H.; Rayabarapu, D. K.; Cheng, C.-H. *J. Org. Chem.* **1999**, *64*, 36. (b) Hsiao, T.-Y.; Santhosh, K. C.; Liou, K.-F.; Cheng, C.-H. *J. Am. Chem. Soc.* **1998**, *120*, 12232.

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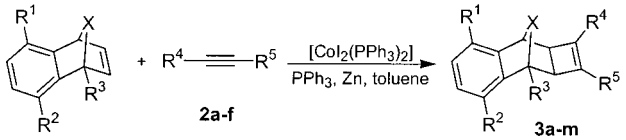
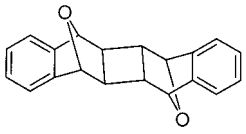
Scheme 1



1a X = O, $R^1 = R^2 = R^3 = H$
1b X = O, $R^1 = OCH_3$, $R^2 = R^3 = H$
1c X = O, $R^1 = OCH_3$, $R^2 = OCH_3$, $R^3 = H$
1d X = O, $R^1 = OCH_3$, $R^2 = OCH_3$, $R^3 = CH_3$
1e X = NCO_2Me, $R^1 = R^2 = R^3 = H$

stereochemistry of **3a** was established based on the coupling constants in its proton NMR spectrum: the protons at the 4/6 ring junction appear as a singlet showing no coupling with the bridgehead protons. The results strongly support that the protons at the ring junction occupy the endo position.[12,13] A coupling constant of 3−6 Hz for the bridgehead and a proton at the 4/6 ring junction is expected if the latter is at an exo position.[13] Product **3a** was further characterized by comparison of its NMR spectra with those of an authentic sample prepared from a nickel-catalyzed reaction.[9]

In addition to **3a**, a side product **4** from dimerization of 7-oxabenzonorbornadiene (**1a**) and other unknown species were also observed in this cobalt-catalyzed reaction. There are two types of [2 + 2] cycloaddition

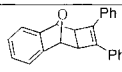
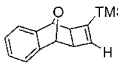
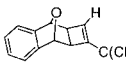
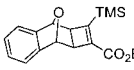
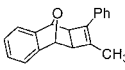
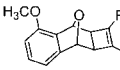
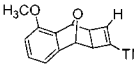
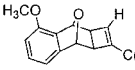
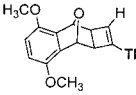
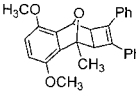
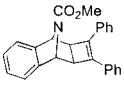
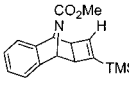
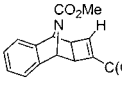


4

catalyzed by the cobalt system. One is the cycloaddition of **1a** with **2a** and the other is the homo [2 + 2] cycloaddition of **1a**. When both **1a** and **2a** are at ca. the same concentration, the reaction gave substantial amount of side products and low yield of the cross [2 + 2] cycloadduct **3a**. For example, the reaction of **1a** (1.00 mmol) with diphenylacetylene (2.00 mmol) in the presence of $CoI_2(PPh_3)_2$ (0.020 mmol), PPh_3 (0.160 mmol), and Zn (2.00 mmol) powder in toluene (2.0 mL) under nitrogen atmosphere at 90 °C gave products **3a** and **4** in 36 and 10% yields, respectively. The yield of **3a** increased greatly to 78% and dimer **4** to 7%, if 2 mmol of THF was also added to the above solution (method A). Another way to increase the yield of **3a** is to reduce the amount of **1a**. Thus, when 0.200 instead of 1.00 mmol of **1a** was employed (method B), the reaction afforded **3a** in 88% yield and dimer **4** in trace amount. Both methods were employed for the synthesis of cross [2 + 2] cycloaddition products. The results are listed in Tables 1 and 2. While method A gave lower yield of cross [2 + 2] cycloaddition product in most cases compared with method B, the former requires less cobalt catalyst and acetylene relative to benzonorbornadiene derivative **1**.

This catalytic reaction requires excess PPh_3 in order for the reaction to proceed smoothly. In the absence of extra PPh_3, the cobalt complex decomposed readily under the reaction conditions and no catalytic activity was observed. Addition of PPh_3 to the solution improved the stability of the catalyst and increased the yields of product **3a**. The optimal value of PPh_3 relative to cobalt

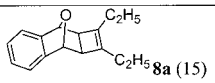
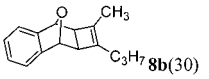
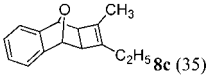
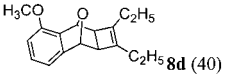
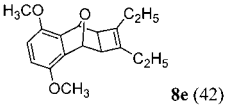
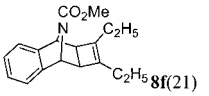
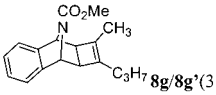
Table 1. [2 + 2] Cycloaddition of 7-Oxa- and 7-Azabenzonorbornadienes with Alkynes[a]

Entry	Alkene	Method[a]	Alkyne (mmol)	Product (yield %)[b]
1	**1a**	A	Ph—≡—Ph **(2a)**	 **3a** (78)
2	**1a**	B	**2a**	**3a** (88)
3	**1a**	A	TMS—≡—H **(2b)**	 **3b** (15)
4	**1a**	B	**2b**	**3b** (85)
5	**1a**	B	H—≡—$C(CH_3)_2OH$ **(2c)**	 **3c** (83)
6	**1a**	A	TMS—≡—CO_2Et **(2d)**	 **3d** (77)
7	**1a**	B	**2d**	**3d** (90)
8	**1a**	B	Ph—≡—CH_3 **(2e)**	 **3e** (60)
9	**1b**	B	Ph—≡—Ph **(2a)**	 **3f** (71)
10	**1b**	B	TMS—≡—H **(2b)**	 **3g/3g'** (38/46)
11	**1b**	B	H—≡—$C(CH_3)_2OH$ **(2c)**	 **3h/3h'** (43/33)
12	**1c**	B	TMS—≡—H **(2b)**	 **3i**(46)
13	**1d**	B	Ph—≡—Ph **(2a)**	 **3j**(60)
14	**1e**	A	Ph—≡—Ph **(2a)**	 **3k**(87)
15	**1e**	B	**2a**	**3k** (86)
16	**1e**	B	TMS—≡—H **(2b)**	 **3l/3l'** (42/29)
17	**1e**	B	H—≡—$C(CH_3)_2OH$ **(2c)**	 **3m/3m'** (95)

[a] Reaction conditions for method A: benzonorbornadiene (1.00 mmol), alkyne (2.00 mmol), $CoI_2(PPh_3)_2$ (0.0500 mmol), PPh_3 (0.320 mmol), Zn (2.00 mmol), toluene (2.00 mL), and THF (2.0 mmol); temperature, 90 °C; time, 48 h. Reaction conditions for method B: benzonorbornadiene (0.200 mmol), alkyne (2.00 mmol), $CoI_2(PPh_3)_2$ (0.0200 mmol), PPh_3 (0.160 mmol), Zn (2.00 mmol), and toluene (2.00 mL); temperature, 90 °C; time, 24 h. [b] Isolated yields are based on the benzonorbornadiene derivative used.

(12) (a) Smith, C. D. *J. Am. Chem. Soc.* **1966**, *88*, 4273. (b) Meinwald, J.; Meinwald, Y. C.; Baker, T. N. *J. Am. Chem. Soc.* **1964**, *86*, 4074.
(13) For similar exo selectivity see: (a) Duan, J.-P.; Cheng, C.-H. *Tetrahedron Lett.* **1993**, *34*, 4019. (b) Duan, J.-P.; Cheng, C.-H. *Organometallics* **1995**, *14*, 1608. (c) Feng, C.-C.; Nandi, M.; Sambaiah, T.; Cheng, C.-H. *J. Org. Chem.* **1999**, *64*, 3538.

Table 2. [2 + 2] Cycloaddition of 7-Oxa- and 7-Azabenzonorbornadienes with Alkynes[a]

Entry	Alkene	Method	Alkyne (mmol)	Product (yield %)[b]
1	**1a**	A	$C_2H_5{-}{\equiv}{-}C_2H_5$ **(7a)**	 **8a** (15)
2	**1a**	B	**7a**	**8a** (40)
3	**1a**	B	$H_3C{-}{\equiv}{-}C_3H_7$ **(7b)**	 **8b**(30)
4	**1a**	B	$C_2H_5{-}{\equiv}{-}CH_3$ **(7c)**	 **8c** (35)
5	**1b**	B	$C_2H_5{-}{\equiv}{-}C_2H_5$ **(7a)**	 **8d** (40)
6	**1c**	B	$C_2H_5{-}{\equiv}{-}C_2H_5$ **(7a)**	 **8e** (42)
7	**1e**	A	$C_2H_5{-}{\equiv}{-}C_2H_5$ **(7a)**	 **8f**(21)
8	**1e**	B	**7a**	**8f** (55)
9	**1e**	B	$H_3C{-}{\equiv}{-}C_3H_7$ **(7b)**	 **8g/8g'**(31/32)

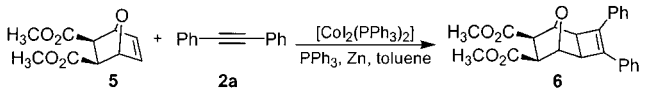
[a] The reaction conditions for methods A and B are similar to those shown in Table 1. [b] Isolated yields are based on the benzonorbornadiene derivative used.

metal is ca. 8 equiv; further increase of PPh_3 concentration retards the catalytic reaction. Several cobalt complexes $CoCl_2(PPh_3)_2$, $CoCl_2$(dppe), CoI_2(dppm), CoI_2(dppe), CoI_2, and $CoI_2(PPh_3)_2$ were also tested for the catalytic activity. Among these complexes, $CoI_2(PPh_3)_2$ is the most active giving product **3a** in the highest yield. To further understand the nature of [2 + 2] cycloaddition, the effect of solvent on the product yield was studied. Of the solvents, toluene, acetonitrile, tetrahydrofuran (THF), dichloromethane, and dimethylformamide (DMF) employed, only toluene gave high yield of product **3a**. Acetonitrile at 80 °C, THF at 60 °C, DMF at 90 °C, and dichloromethane at 35 °C all afforded no or trace of the cross [2 + 2] cycloaddition product. Homo [2 + 2] cycloaddition product **4** in substantial amount as well as unidentified products was also observed. The structure of **4** was characterized by ^{1}H NMR spectrum and by comparison of the spectrum with that of an authentic sample prepared by using a nickel complex as the catalyst.[14]

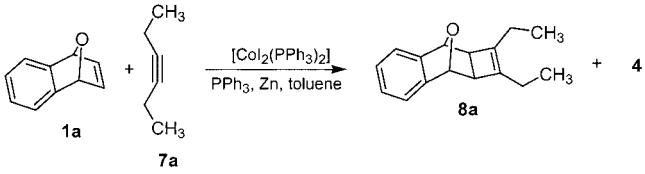
This cobalt-catalyzed cross [2 + 2] cycloaddition reaction is successfully extended to other internal acetylenes and terminal acetylenes. Thus, (TMS)C≡CH (**2b**), HC≡C(CH_3)$_2$OH (**2c**), (TMS)C≡CCO_2Et (**2d**), and PhC≡CCH_3 (**2e**) underwent cross [2 + 2] cycloaddition with **1a** in the presence of cobalt catalyst to give the corresponding cyclobutene derivatives **3b**−**e** in 85, 83, 90, and 60% yields, respectively (entries 2−5, Table 1).

Two regioisomers were formed as anticipated for the cross [2 + 2] cycloaddition of unsymmetrical oxanorbornadienes with unsymmetrical alkynes. Thus, the reaction of **1b** with **2b** and **2c** afforded **3g/3g′** and **3h/3h′** in 38/42 and 44/33% yields, respectively (entries 10 and 11). The low regioselectivity likely reflects the fact that the methoxy substituent on **1b** is far away from the reaction center. Similarly, highly substituted oxabenzonorbornadienes **1c** underwent cross [2 + 2] cycloaddition with HC≡C(TMS) to give **3i** in 46% yield, while **1d** reacted with PhC≡CPh affording **3j** in 60% yield (entries 12 and 13).

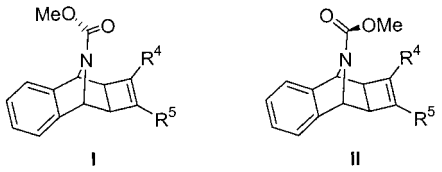
Scheme 2



Scheme 3



The alkenes used in the [2 + 2] cycloaddition can be further extended to azabenzonorbornadienes. Treatment of **1e** with **2a** gave cyclobutene derivative **3k** in 86% yield. The reaction of **1e** with unsymmetrical alkynes **2c** and **2f** requires special attention. Two products were observed for each reaction (Table 1, entries 16 and 17). The products of each reaction exhibit similar NMR spectra and the same molecular weight. On the basis of these observations, we assign the products to be stereoisomers arising from the orientation of the carbamate group. It is known that an amide or carbamate with two different substituents at the nitrogen atom exist as two stereoisomers **I** and **II** due to the fact that the atoms around

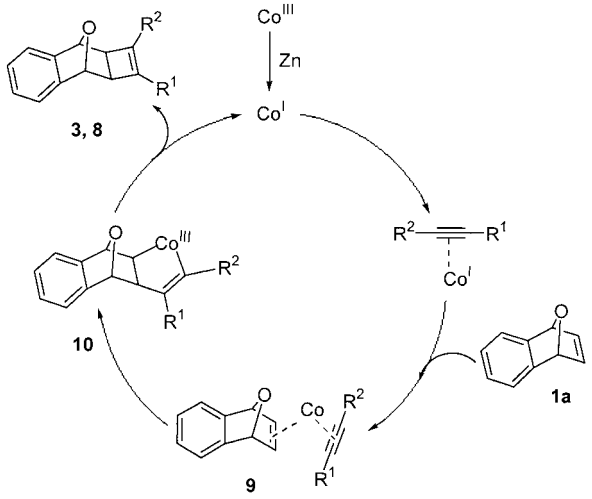


the carbon center of the amide or carbamate moieties are coplanar. In addition to oxa- and azabenzonorbornadienes, bicyclic oxanorbornene **5** also underwent facile cross [2 + 2] cycloaddition with diphenylacetylene under the standard reaction conditions to give cyclobutene derivative **6** in 90% yield (Scheme 2). Again, the cycloaddition is completely stereoselective affording only exo adduct **6**.

Dialkylacetylenes **7** also react with bicyclic alkenes **1** in the presence of $CoI_2(PPh_3)_2$, PPh_3, and Zn powder in toluene at 90 °C to give the corresponding cyclobutenes, albeit in lower yields. Table 2 summarizes the results of the cross [2 + 2] cycloaddition reactions of dialkylacetylenes. Treatment of **1a** with diethylacetylene (**7a**) in the presence of $CoI_2(PPh_3)_2$, PPh_3, and Zn powder gave cyclobutene derivative **8a** in 35% yield along with homo dimerization product **4**[14] in 35% yield and other unknown products (Scheme 3). The poor reactivity of dialkyl acetylenes compared with other acetylenes allows oxan-

(14) Huang, D.-J.; Cheng, C.-H. *J. Organomet. Chem.* **1995**, *490*, C1.

Scheme 4

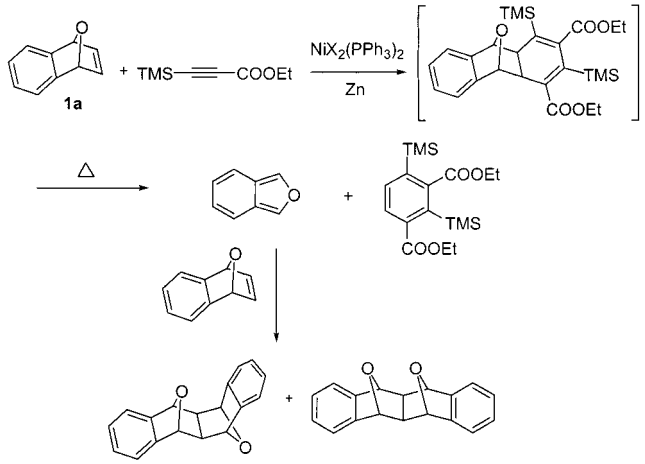


orbornadiene **1a** to undergo self-dimerization readily. Under similar reaction conditions, **1a** reacts with $CH_3C{\equiv}C(n\text{-}C_3H_7)$ (**7b**) and $CH_3C{\equiv}CC_2H_5$ (**7c**) to give the corresponding cyclobutene derivatives **8b** and **8c** in 30 and 35% yields, respectively (Table 2, entries 1−3). For substituted oxabenzonorbornadienes **1b** and **1c**, the [2 + 2] cycloaddition with **7a** also proceeds smoothly to give **8d** and **8e** in 40 and 42% yields, respectively. Similarly, azanorbornadiene **1e** reacts with symmetrical dialkylalkyne **7a** providing cyclobutene derivative **8f** in fair yield, and with unsymmetrical **7b** giving stereoisomers **8g** and **8g′** in 31 and 32% yields, respectively. In all these cases, for cross [2 + 2] cycloaddition involving dialkylacetylenes, the dimers of the corresponding norbornadiene derivatives were also observed.

On the basis of the known organometallic chemistry and the product formation, we propose a mechanism as depicted in Scheme 4 to account for the present cobalt-catalyzed [2 + 2] cycloaddition. Reduction of $Co(PPh_3)_2X_2$ to a Co(I) species by zinc metal initiates the catalytic reaction. Coordination of an alkyne and 7-oxabenzonorbornadiene (**1**) to the cobalt center followed by oxidative cyclometalation affords cobaltacyclopentene intermediate **10**. Subsequent reductive elimination of **10** gives the cyclobutene product and regenerates the Co(I) species. Similar mechanism can also explain the formation of self-dimerization product **4** of oxabenzonorbornadienes. The formation of intermediate cobaltacyclopentane from two norbornadiene molecules should be the key step in the self-dimerization. In view of the requirement of excess acetylenes relative to oxa- or azanorbornadienes, it is clear that coordination of oxa- or azanorbornadienes to the cobalt center is favorable over acetylenes.

Since both $Ni(PPh_3)_2X_2/PPh_3$ and $Co(PPh_3)_2I_2/PPh_3$ systems are all able to catalyze [2 + 2] cycloaddition of alkynes and oxabenzonorbornadienes, it is interesting to compare their catalytic properties. For $Ni(PPh_3)_2X_2/PPh_3$, in addition to cross [2 + 2] cycloaddition, endiyne cocyclotrimerization of alkenes and alkynes is also reported.[11] However, for the present $Co(PPh_3)_2I_2/PPh_3$ system, the tendency to promote endiyne cocyclotrimerization appears low, and no such product was observed in the reactions shown in Tables 1 and 2. An example of drastic difference of the catalytic activity is shown by the results of the reaction of oxabenzonorbornadiene (**1a**) with $(TMS)C{\equiv}CCO_2Et$ (**2d**) catalyzed by these two

Scheme 5



systems. The cobalt system gave only [2 + 2] cycloaddition product **3d** in excellent yield (Table 1, entry 7), while for the nickel-catalyzed reaction, entirely different products were obtained and were resulted from cocyclotrimerization of oxabenzonorbornadiene and **2d** (Scheme 5). It should be noted that the trend to catalyze cross [2 + 2] cycloaddition might not be followed by other cobalt complexes. For example, $CpCo(CO)_2$ are well-known for catalyzing cyclotrimerization of alkynes and in some cases intramolecular cocyclotrimerization of alkenes and alkynes.[15]

In conclusion, we have demonstrated that a cobalt phosphine system catalyzes cross [2 + 2] cycloaddition of bicyclic alkenes with a variety of alkynes including monosubstituted acetylenes and dialkylacetylenes to give cyclobutene derivatives in fair to good yields. The alkynes can be used in the present catalytic reaction are very different from those in the previous nickel-catalyzed cross [2 + 2] cycloaddition. Unlike the nickel catalysts, the cobalt system has little tendency, if it exists, to undergo endiyne cocyclotrimerization. These two systems appear to complement each other.

Experimental Section

All reactions were conducted under nitrogen atmosphere on a dual-manifold Schlenk line by using purified deoxygenated solvents and standard inert atmosphere techniques, unless otherwise stated. Reagents and chemicals were used as purchased without further purification. Oxa- and azabenzonorbornadienes were prepared following literature procedures.[16] $Co(PPh_3)_2I_2$, $CoCl_2(PPh_3)_2$, $CoCl_2$(dppe), CoI_2(dppm), and CoI_2(dppe) were synthesized according to reported procedures. The purity of each product was checked by NMR analysis.

General Procedure for the [2 + 2] Cycloaddition of Oxa- and Azabenzonorbornadienes with Alkynes (Method B). A round-bottom sidearm flask (25 mL) containing oxa- or azabenzonorbornadiene (0.200 mmol), $Co(PPh_3)_2I_2$ (0.0166 g, 0.0200 mmol), PPh_3 (0.0420 g, 0.160 mmol), and zinc powder (0.126 g, 2.00 mmol) was evacuated and purged with nitrogen gas three times. Freshly distilled dry toluene (2.0 mL) and an alkyne (2.0 mmol) were added. The reaction mixture was heated with stirring 90 °C for 24 h. The reaction mixture was then cooled and stirred under air for 15 min at room

(15) (a) Wakatsuki, Y.; Yamazaki, H. *J. Organomet. Chem.* **1977**, *139*, 169. (b) Grotjahn, D. B.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1986**, *108*, 2091. (c) Butenschon, H.; Winkler, M.; Vollhardt, K. P. C. *Chem. Commun.* **1986**, 388. (d) Johnson, E. P.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1991**, *113*, 381.

(16) Cragg, G. M. L.; Giles, R. G. F.; Roos, G. H. P. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1339.

temperature, filtered through Celite and silica gel, and eluted with dichloromethane. The filtrate was concentrated, and the residue was purified on a silica gel column using hexane as eluent first to remove nonpolar components such as PPh_3 and then with hexanes−ethyl acetate as eluent to afford the desired products.

Important spectral data for new compounds **3a**−**m, 6**, and **8a**−**g** follow.

3,4-Diphenyl-7,8-oxatricyclo[4.2.1.0^{2,5}]non-3-ene (3a). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65 (d t, J = 7.1 Hz, J = 1.4 Hz, 4 H, Ph), 7.32 (m, 8 H, Ph), 7.21 (m, 2 H, Ph), 5.18 (s, 2 H, O−CH, bridgehead), 3.02 (s, CH, endo-cyclobutene). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 144.96 (s), 138.69 (s), 134.64 (s), 128.49 (d), 128.04 (d), 126.65 (d), 126.46 (d), 119.66 (d), 76.43 (d, O−C, bridgehead), 45.44 (d). MS (*m*/*z* (%)): 322 ([*M*]$^+$, 100), 294 (24.8), 279 (12.6). HRMS (*m*/*z*). Calcd for $C_{24}H_{18}O$: 322.1359; Found: 322.1358. Anal. Calcd for $C_{24}H_{18}O$: C, 89.44; H, 5.59; O, 4.97. Found: C, 89.24; H, 5.70; O, 5.06.

3-Trimethylsilyl-7,8-benzo-9-oxatricyclo[4.2.1.0^{2,5}]non-3-ene (3b). ^{1}H NMR (300 MHz, $CDC1_3$): δ 7.26−7.30 (m, 2 H, benzo), 7.15−7.18 (m, 2 H, benzo), 6.68 (s, 1H, ═C−H), 4.94 (s, 1H, O−CH, bridgehead), 4.91(s, 1H, O−CH, bridgehead), 2.80 (d, J = 3.3 Hz, 1H, C−H, endo-cyclobutene), 2.72 (d, J = 3.3 Hz, 1H, C−H, *endo*-cyclobutene), 0.19 (s, 9 H, trimethylsilyl). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 155.43 (s), 146.99 (d), 144.46 (s), 126.32 (d), 126.29 (d), 119.47(d), 76.36 (d, O−C, bridgehead), 75.73 (d, O−C, bridgehead), 48.71 (d, *endo*-cyclobutene), 48.39 (d, *endo*-cyclobutene), −1.90 (q, trimethyl). MS (*m*/*z* (%)): 242 (M$^+$,3.6), 227 ([M − CH_3]$^+$, 4.3); HRMS (*m*/*z*): Calcd for $C_{15}H_{18}$0Si: 242.1127. Found: 242.1122. Anal. Calcd for $C_{15}H_{18}$0Si: C, 74.33; H, 7.48. Found: C, 73.90; H, 7.50.

3-(2-(2-Hydroxypropyl))-7,8-benzo-9-oxatricyclo[4.2.1.0^{2,5}]non-3-ene (3c). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.24−7.29 (m, 2H, benzo), 7.14−7.18 (m, 2H, benzo), 6.00 (s, 1 H, ═C−H, cyclobutene), 5.10 (s, 1H, O−CH, bridgehead), 4.94 (s, 1 H, O−CH, bridgehead), 2.79 (d, J = 3.2 Hz, 1H, C−H, *endo*-cyclobutene), 2.53 (d, J = 3.3 Hz, 1H, O−CH, *endo*-cyclobutene), 1.79 (b, −OH), 1.44 (s, 3H, methyl), 1.41 (s, 3H, methyl). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 156.08 (s), 145.00 (s), 144.31 (s), 126.59 (d), 126.55 (d), 126.16 (d), 119.75 (d), 119.48 (d), 76.58 (d, O−CH, bridgehead), 76.28 (d, O−CH, bridgehead), 69.88 (s, C−OH), 46.68 (d, C−H, *endo*-cyclobutene), 43.40 (d, C−H, *endo*-cyclobutene), 27.94 (q, $-CH_3$, methyl), 27.87 (q, $-CH_3$, methyl). MS (*m*/*z* (%)): 228 (M$^+$, 14.0), 213 ([M − CH_3]$^+$, 21.2), 195 (100.0). HRMS (*m*/*z*): Calcd for $C_{15}H_{16}$0: 228.1150. Found: 228.1152;

Ethyl 4-(Trimethylsilyl)-7,8-benzo-9-oxatricyclo[4.2.1.0^{2,5}]non-3-ene-3-carboxylate (3d). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31 (m, 2 H, benzo), 6.92 (m, 2H, benzo), 5.12 (s, 1H, bridgehead), 4.94 (s, 1H, bridgehead), 4.27 (q, J = 7.1 Hz, 2H, $-OCH_{2-}$), 2.97 (d, J = 3.4 Hz, 1H, *endo*-cyclobutene), 2.62 (d, J = 3.4 Hz, 1H, *endo*-cyclobutene), 1.37 (t, J = 7.1 Hz, 3H, $-CH_3$), 0.28 (s, 9H, $-Si(CH_3)_3$). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 166.61(s, C═O), 162.32 (s), 146.94 (s), 143.94 (s), 143.94 (s), 143.71 (s), 126.15 (d),119.52 (d), 119.11(d), 75.75 (d, O−C, bridgehead), 74.99 (d, O−C, bridgehead), 59.81(t), 47.17 (d), 45.69 (d), 13.88 (q), −2.00 (q, $Si(CH_3)_3$). MS (*m*/*z* (%)): 314 (M$^+$, 3.6), 299 ([M − CH_3]$^+$, 11.8), 241 ([M − $Si(CH_3)_3$]$^+$, 15.6), 196 (8.5), 168 (49.0), 73 ($Si(CH_3)_3$, 100.0). HRMS (*m*/*z*). Calcd for $C_{18}H_{22}0_3$: 314.1336. Found: 314.1335.

3-Phenyl-4-methyl-7,8-benzo-9-oxatricycl[4.2.1.0^{2,5}]non-3-ene (3e). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45 (d, J = 7.0 Hz, 2H, Ph), 7.36 (t, J = 7.0 Hz, 3H, Ph), 7.25 (m, 4H, Ph), 5.08 (s,1H, O−CH, bridgehead), 5.03 (s, 1H, O−CH, bridgehead), 2.90 (dq, J = 2.6 Hz, J = 1.8 Hz, 1H,C−H, *endo*-cyclobutene), 2.60 (d, J = 2.6 Hz, 1H, C−H, *endo*-cyclobutene), 2.11 (d, J = 1.8 Hz, 3H, $-CH_3$). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 145.17 (s), 144.95 (s), 138.63 (s), 137.87 (s), 134.52 (s), 128.46 (d), 127.03 (d), 126.50 (d), 126.47 (d), 125.82 (d), 119.59 (d), 119.49 (d), 76.26 (d, O−C, bridgehead), 75.43 (d, O−C, bridgehead), 47.42 (d), 44.61(d), 14.45 (q). MS (*m*/*z* (%)): 260 (M$^+$, 100.0), 245 ([M − CH_3]$^+$, 42.3), 217 (75.3), 292 (36.1), 115 (59.8). HRMS (*m*/*z*). Calcd for $C_{19}H_{16}O$: 260.1202. Found: 260.1198.

3,4-Diphenyl-7,8-(4-methoxylbenzo)-9-oxatricyclo[4.2.1.0^{2,5}]non-3-ene (3f). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.63 (t, J = 6.6 Hz, 4H, phenyl), 7.25 (m, 6H, phenyl), 7.16 (t, J = 7.4 Hz, 1H, benzo), 6.95 (d, J = 7.2 Hz, 1H, benzo), 6.25 (d, J = 8.2 Hz, 1H, benzo), 5.39 (s, 1H, bridgehead), 5.15 (s, 1H, bridgehead), 3.87 (s, 3 H, OCH_3), 3.38 (d, J = 3.5 Hz, 1H, *endo*-cyclobutene), 3.30 (d, J = 3.5 Hz, 1H, *endo*-cyclobutene). ^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$): δ 152.97 (s), 147.27 (s), 138.93 (s), 138.74 (s), 134.70 (s), 134.65 (s), 131.83 (s), 128.45 (d), 127.97 (d), 126.47 (d), 112.39 (d), 100.25 (d), 74.57 (d), 74.27 (d), 55.51(q), 45.41 (d), 44.99 (d). MS (*m*/*z* (%)): 352 (M$^+$, 100.0), 323 ([M − OCH_3]$^+$, 22.4), 291 (15.9), 275 (4.9), 102 (40.9). HRMS (*m*/*z*). Calcd for $C_{25}H_{20}O_2$: 352.1465. Found: 352.1461.

3-Trimethylsilyl-7,8-(4-methoxylbenzo)-9-oxatricyclo[4.2.1.0^{2,5}]non-3-ene (3g) and 3-Trimethylsilyl-7,8-(l-methoxylbenzo)-9-oxatricyclo[4.2.1.0^{2,5}]non-3-ene (3g′). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.11 (t, J = 7.6 Hz, 2H, benzo), 6.88 (t, J = 7.4 Hz, 2 H, benzo), 6.69 (d, J = 8.3 Hz, 2H, benzo), 6.63 (d, J = 5.4 Hz, 2H, benzo), 5.10 (s, 1H, bridgehead), 5.07 (s, 1H, bridgehead), 4.88 (s, 1H, bridgehead), 4.86 (s, 1H, bridgehead), 3.83 (s, 3H, O−CH_3), 3.82 (s, 3H, O−CH_3), 2.79 (d, J = 2.8 Hz, 1H, *endo*-cyclobutene), 2.74 (d, J = 3.2 Hz, 1H, *endo*-cyclobutene), 2.72 (d, J = 3.2 Hz, 1H, *endo*-cyclobutene), 2.65 (d, J = 3.1 Hz, 1H, *endo*-cyclobutene), 0.13 (s, 18H, $Si(CH_3)_3$). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 155.80 (s), 155.46 (s), 152.96 (s), 152.91 (s), 131.47 (s), 131.40 (s), 128.19 (d), 128.14 (d), 112.39 (d), 109.99 (d), 109.94 (d), 76.69 (d), 76.06 (d), 74.23 (d), 73.65 (d), 5.48 (q), 48.65 (d), 45.31(d), 47.96 (d), −1.84 (q, $Si(CH_3)_3$). MS (*m*/*z* (%)): 271 ([M − 1]$^+$, 19.4), 199 ([M − $Si(CH_3)_3$]$^+$, 100.0). HRMS (*m*/*z*). Calcd for $C_{16}H_{20}$Osi: 272.1233. Found: 272.1233.

3-(2-(2-Hydroxypropy1))-7,8-(4-methoxylbenzo)-9-oxatricyclo[4.2.1.0^{2,5}]non-3-ene (3h) and 4-(2-(2-Hydroxypropy1))-7,8-(4-methoxylbenzo)-9-oxatricyclo[4.2.1.0^{2,5}]non-3-ene (3h′). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.12 (t, J = 8.1 Hz, 1H, benzo), 6.88 (d, J = 7.1 Hz, 1H, benzo), 6.71 (d, J = 8.1 Hz, 1H, benzo), 5.99 (s, 1H, ═C−H), 5.12 (s, 1H, bridgehead), 5.07 (s, 1H, bridgehead), 3.82 (s, 3H, OCH_3), 2.75 (d, J = 3.4 Hz, 1H, *endo*-cyclobutene), 2.54 (d, J = 3.3 Hz, 1H, *endo*-cyclobutene), 1.41 (s, 3H, $-CH_3$), 1.38 (s, 3H, $-CH_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.14 (t, J = 8.1 Hz, 1H, benzo), 6.90 (d, J = 7.7 Hz, 1 H, benzo), 6.72 (d, J = 8.3 Hz, 1H, benzo), 6.01(s, 1H, ═C−H), 5.29 (s, lH, bridgehead), 4.93 (s, 1H, bridgehead), 3.84 (s, 3 H, $-OCH_3$), 2.81 (d, J = 3.3 Hz, 1H, *endo*-cyclobutene), 2.51 (d, J = 3.3 Hz, 1H, *endo*-cyclobutene), 1.43 (s, 3H, $-CH_3$). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 156.41 (s), 156.09 (s), 153.09 (s), 152.82 (s), 147.39 (s), 146.67 (s), 128.37 (s), 128.33 (s), 126.35 (d), 126.06 (d), 112.56 (d), 112.23 (d), 110.17 (d), 110.11 (d), 76.99 (d), 76.51 (d), 74.57 (d), 74.06 (d), 55.45 (q), 46.50 (d), 46.19 (d), 43.27 (d), 42.92 (d), 27.90 (q), 27.85 (q), 27.80 (q). MS (*m*/*z* (%)): 258 (M$^+$, 4.1), 243 ([M − CH_3]$^+$, 3.6), 148 (100.0). HRMS (*m*/*z*). Calcd for $C_{16}H_{18}O_3$: 258.1256. Found: 258.1241.

3-Trimethylsilyl-7,8-(1,4-dimethoxylbenzo)-9-oxatricyclo[4.2.1.0^{2,5}]non-3-ene (3i). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.63 (s, 2H, benzo), 5.07 (s, 1H, O−C, bridgehead), 5.05 (s, 1H, O−C, bridgehead), 3.78 (s, 3H, O−CH_3), 3.77 (s, 3H, O−CH_3), 2.78 (d, J = 3.2 Hz, 1H, *endo*-cyclobutene), 2.69 (d, J = 3.0 Hz, 1H, C−H, *endo*-cyclobutene), 0.13 (s, 9 H, −Si-$(CH_3)_3$). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 133.68 (s), 131.53 (s), 131.48 (s), 111.18 (d, benzo), 111.09 (d, benzo), 74.57 (d, O− C, bridgehead), 73.97 (d, O−C, bridgehead), 56.12 (q, O−CH_3), 56.09 (q, O−CH_3), 48.11 (d, C−H, *endo*-cyclobutene), 47.77 (d, *endo*-cyclobutene), −1.82 (q, $-Si(CH_3)_3$). HRMS (*m*/*z*). Calcd for $C_{17}H_{22}O_3Si$: 302.1338. Found: 302.1358.

3,4-Diphenyl-6-methyl-7,8-(1,4-dimethoxylbenzo)-9-oxatricyclo[4.2.1.0^{2,5}]non-3-ene (3j). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.62−7.65 (m, 4H, Ph), 7.34−7.61 (m, 4H, Ph), 7.26−7.34 (m, 4H, Ph), 6.71 (s, 2H, benzo), 5.40 (s, 1H, bridgehead), 3.85 (s, 3 H, $-OCH_3$), 3.81 (s, 3 H, O−CH_3), 3.08(d, J = 3.6 Hz, 1H, *endo*-cyclobutene), 3.01 (d, J = 3.6 Hz, 1H, *endo*-cyclobutene), 1.67 (s, 3H, methyl). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 148.07 (s), 147.00 (s), 139.32(s), 138.95 (s), 135.68 (s), 135.40 (s), 134.88 (s), 135.34 (s), 128.39 (d), 128.28 (d), 127.88 (d), 127.76 (d), 126.98 (d), 126.38 (d), 111.40 (d), 111.20

(d), 84,37 (s), 74.49 (d, bridgehead), 56.12 (q, $-OCH_3$), 56.09 (q, $-OCH_3$), 47.65 (d, *endo*-cyclobutene), 47.36 (d, *endo*-cyclobutene), 16.69 (q, methyl). MS (*m*/*z* (%)): 396 (M^+, 100.0), 381 ([M − CH_3]$^+$, 39.3). HRMS (*m*/*z*). Calcd for $C_{27}H_{24}O_3$: 396.1725. Found: 396.1698.

Methyl (3,4-Diphenyl-7,8-benzo-9-azatricyclo[4.2.1.0^{2,5}]-non-3-ene)-9-carboxylate (3k). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59 (t, J = 7.5 Hz, 4H, phenyl), 7.32 (m, 8H, phenylbenzo), 7.21(d, J = 3.1 Hz, 1H, benzo), 7.20 (d, J = 5.3 Hz, 1H, benzo), 5.28 (brs, 1H, bridgehead), 5.15 (brs, 1H, bridgehead), 3.29 (s, 3 H, $COOCH_3$), 2.96 (d, J = 3.2 Hz, 1H, *endo*-cyclobutene), 2.92 (d, J = 3.2 Hz, 1H, *endo*-cyclobutene). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 155.72 (s), 143.92 (s), 143.62 (s), 139.23 (s), 134.65 (s), 134.28 (s), 128.40 (s), 128.32 (d), 128.1 (d), *128.05* (d), 126.72 (d), 126.57 (d), 126.51 (d), 126.26 (d), 120.14 (d), 119.94 (d), 60.21(d), 60.06 (d), 51.67 (d), 46.20 (d), 45.87 (d). MS (*m*/*z* (%)): 379 (M^+, 100.0), 319 ([M − $COOCH_3$]$^+$, 5.0), 201 (25.0). HRMS (*m*/*z*). Calcd for $C_{26}H_{21}N$: 379.1547. Found: 379.1584. Anal. Calcd for $C_{26}H_{21}N$: C, 87.02; H, 6.87. Found: C, 87.44; H, 6.15.

Methyl (3-(Trimethylsilyl)-7,8-benzo-9-azatricyclo-[4.2.1.0^{2,5}]non-3-ene)-9-carboxylate (3l) and Methyl (3-(Trimethylsilyl)-7,8-benzo-9-azatricyclo[4.2.1.0^{2,5}]non-3-ene)-9-carboxylate (3l′). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27 (m, 4H, benzo), 7.15 (m, 4H, benzo), 6.64(s, 1H, =C−H), 6.58 (s, 1H, =C−H), 4.99 (s, 1H, bridgehead), 4.97 (s, 1H, bridgehead), 4.89 (s, 1H, bridgehead), 4.87 (s, 1H, bridgehead), 3.62 (s, 6H, $NCOOCH_3$), 2.74 (d, J = 2.9 Hz, 1H, *endo*-cyclobutene), 2.70 (d, J = 2.9 Hz, 1H, cyclobutene), 2.65 (d, J = 2.8 Hz, 1H, *endo*-cyclobutene), 2.61 (d, J = 3.0 Hz, 1H, cyclobutene), 0.16 (s, 3H, $Si(CH_3)_3$), 0.14 (s, 3H, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 157.49 (s), 155.99 (s), 155.85 (s), 155.75 (s), 149.11-(d), 147.62 (d), 143.61 (s), 143.47 (s), 126.28 (d), 120.15 (d), 120.07 (d), 119.78 (d), 119.72 (d), 60.09 (d), 59.96 (d), 59.63 (d), 59.97 (d), 51.89 (q), 51.83 (q), 49.43 (d), 49.32 (d), 48.99 (d), -1.96 (q, $Si(CH_3)_3$). HRMS (*m*/*z*). Calcd for $C_{17}H_{21}O_2Nsi$: 299.1342. Found: 299.134. Anal. Calcd for $C_{17}H_{21}O_2NSi$: C, 68.19; H, 7.07; N, 4.68. Found: C, 67.77; H, 7.13; N, 4.75.

Methyl (2-(2-Hydroxypropyl)-7,8-benzo-9-azatricyclo-[4.2.1.0^{2,5}]non-3-ene)-9-carboxylate (3m). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.20−7.29 (m, 2H, benzo), 7.13−7.17 (m, 2H, benzo), 5.85 (s, 1H, = C−H), 5.19 (s, 1H, bridgehead), 4.59 (s, 1H, bridgehead), 3.66 (s, 3H, $NCOOCH_3$), 2.75 (d, J = 2.8 Hz, 1H, *endo*-cyclobutene), 2.47 (d, J = 3.2 Hz, 1H, *endo*-cyclobutene), 1.32 (s, 3H, $-CH_3$), 1.25 (s, 3H, -CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 158.59 (s, N−C=O), 158.42(s), 143.06 (s), 142.55 (s), 127.62 (d), 126.71(d), 126.53 (d), 120.29 (d), 119.50 (d), 68.65 (s), 60.84 (d, bridgehead), 60.52 (d, bridgehead), 52.35 (q, $-OCH_3$), 46.17 (d, *endo*-cyclobutene), 44.51 (d, *endo*-cyclobutene), 27.36 (q, $-CH_3$), 25.26 (q, $-CH_3$). MS (*m*/*z* (%)): (M^+, 14.8), 192 (100.0). HRMS (*m*/*z*). Calcd for $C_{17}H_{19}O_3N$: 285.1365. Found: 285.1370.

3,4-Diphenyl-7,8-dicarbomethoxy-9-oxatricyclo[4.2.1.0^{2,5}]-non-3-ene (6). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49 (d, J = 8.2 Hz, 4H, Ph), 7.26−7.35 (m, 6H, Ph), 4.75 (s, 2H, O−C, bridgehead), 3.69 (s, 6H, O−CH_3), 3.11(s, 2H, *endo*-cyclobutene), 2.99 (s, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 171.35 (s), 138.30 (s), 134.28 (s), 128.48 (d), 128.14 (d), 126.41 (d), 76.07 (d, O−C, bridgehead), 52.13 (q, O−CH_3), 51.41 (d, *endo*-cyclobutene), 46.54 (d). MS (*m*/*z* (%)) 390 (M^+, 100.0), 331 ([M − $COOCH_3$]$^+$, 4.9). HRMS (*m*/*z*). Calcd for $C_{24}H_{22}O_5$: 390.1467. Found: 390.1452.

3,4-Diethyl-7,8-benzo-9-oxatricyclo[4.2.1.0^{2,5}]non-3-ene (8a). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.23−7.25 (m, 2 H, benzo), 7.12−7.15 (m, 2 H, benzo), 4.92 (s, 2H, O−CH, brigehead), 2.48 (s, 2H, *endo*-cyclobutene), 2.18 (q, J = 5.9 Hz, 2H, $-CH_2-$, methylene), 1.09 (t, J = 7.6 Hz, 3H, −CH3, methyl). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 145.23 (s), 141.36 (s), 126.23 (d, benzo), 119.34 (d, benzo), 76.02 (d, O−C, bridgehead), 45.16 (d, O−C, bridgehead), 20.50 (t, $-CH_2-$, ethyl), 12.28 (q, $-CH_3$, methyl). MS (*m*/*z* (%)): 226 (M^+, 12.0), 197 ([M − C_2H_5]$^+$, 25.6), 18 (100.0). HRMS (*m*/*z*). Calcd for $C_{16}H_{18}O$: 226 1358. Found: 226.1351.

3-Methyl-4-propyl-7,8-benzo-9-oxatricyclo [4.2.1.0^{2,5}]-non-3-ene (8b). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.21−7.26 (m, 2H, benzo), 7.12−7.16 (m, 2H, benzo), 4.93 (s, 1H, O−CH, bridgehead), 4.90 (s, 1H, O−CH, bridgehead), 2.49 (d, J = 1.7 Hz, 1H, *endo*-cyclobutene), 2.44 (d, J = 2.1 Hz, 1H, *endo*-cyclobutene), 2.10 (t, J = 7.4 Hz, 2H, $-CH_2-$, methylene), 1.72 (s, 3H, $-CH_3$, methyl), 1.47−1.50 (m, 2H, $-CH_2-$, methylene), 0.95 (t, J = 7.3 Hz, 3 H, $-CH_3$, methyl). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 145.27 (s), 145.19 (s), 141.36 (s), 136.81 (s), 126.22 (d), 119.36 (d), 75.98 (d, O−C, bridgehead), 75.41 (d, O−C, bridgehead), 47.06 (d, C−H, cyclobutene), 46.01 (d, cyclobutene), 29.24 (t, $-CH_2-$, methylene), 20.85 (t, $-CH_2-$, methylene), 14.15 (q, $-CH_3$, methyl), 12.12 (q, $-CH_3$, methyl). MS (*m*/*z* (%)): 226 (M^+, 18.0), 197 ([M − C_2H_5]$^+$, 91.7), 179 (100.0). HRMS (*m*/*z*). Calcd for $C_{16}H_{18}O$: 226.1358. Found: 226.1364.

3-Ethyl-4-methyl-7,8-benzo-9-oxatricycl[4.2.1.0^{2,5}]non-3-ene (8c). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.23−7.26 (m, 2H, benzo), 7.12−7.15 (m, 2H, benzo) 4.92 (s, 1H, O−CH, bridgehead), 4.91 (s, 1H, O−CH, bridgehead), 2.51 (s, 1H, C−H, *endo*-cyclobutene), 2.43 (s, 1H, C−H, *endo*-cyclobutene), 2.16 (q, J = 9.4 Hz, 2H, $-CH_2-$, ethyl), 1.74 (s, 3H, $-CH_3$, methyl), 1.09 (t, J = 7.6 Hz, 3H, $-CH_3$, methyl). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 145.3 (s), 146.22 (s), 142.62 (s), 135.91(d), 126.26 (d), 119.39 (d),119.36 (d), 76.02 (d, O−C, bridgehead, 75.45 (d, O−C, bridgehead), 46.98 (d, C−H, *endo*-cyclobutene), 45.72 (d, C−H, *endo*-cyclobutene), 20.46 (t, $-CH_2-$, methylene), 12.17 (q, $-CH_3$, methyl), 12.04 (q, $-CH_3$, methyl). MS (*m*/*z* (%)): 212 (M^+, 64.0), 197 ([M − CH_3]$^+$, 39.5), 183 ([M − C_2H_5]$^+$, 81.4], 118 (100). HRMS (*m*/*z*). Calcd for $C_{15}H_{16}O$: 212.1201. Found: 212.1193.

3,4-Diethyl-7,8-(4-methoxylbenzo)-9-oxatricyclo[4.2.1.0^{2,5}]-non-3-ene (8d). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.11 (t, J = 7.7 Hz, 1H, benzo), 6.87 (d, J = 7.2 Hz, 1 H, benzo), 6.71(d, J = 8.2 Hz, 1H, benzo), 5.13 (s, 1H, O−CH, bridgehead), 4.91(s, 1 H, O−CH, bridgehead), 3.85 (s, 3H, OCH3), 2.52 (s, 1H, C−H, *endo*-cyclobutene), 2.48 (s, 1H, C−H, *endo*-cyclobutene), 2.17 (q, J = 7.7 Hz, 4H, $-CH_2-$, methylene), 1.08 (m, 6H, $-CH_3$, methyl). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 152.79 (s), 147.65 (s), 146.40 (s), 141.65 (s), 141.36 (s), 128.00 (d), 112.27 (d), 110.00 (d), 76.32 (d, O−C, bridgehead), 73.88 (d, O−C, bridgehead), 55.51 (q, O−CH3), 45.12 (d, C−H, *endo*-cyclobutene), 44.75 (d, C−H, *endo*-cyclobutene), 20.55 (t, $-CH_2-$), 20.52 (t, $-CH_2-$), 12.35 (q, $-CH_3$), 12.29 (q, $-CH_3$). HRMS (*m*/*z*). Calcd for $C_{17}H_{20}O_2$: 256.1463. Found: 256.1464.

3,4-Diethyl-7-8-(1,4-dimethoxylbenzo)-9-oxatricyclo-[4.2.1.0^{2,5}]non-3-ene (8e). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.62 (s, 2H, benzo), 5.09 (s, 2H, O−C, bridgehead), 3.78 (s, 6H, O−CH_3), 2.50 (s, 2H, C−H, *endo*-cyclobutene), 2.15 (q, J = 7.6 Hz, 4H, $-CH_2-$, methylene), 1.07 (t, J = 7.7 Hz, 6H, $-CH_3$, methyl). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 147.27 (s), 141.59 (s), 134.35 (s), 111.13 (d, benzo), 74.22 (d, O−C, bridgehead), 56.15 (q, O−CH_3), 44.61(d, C−H, *endo*-cyclobutene), 20.56 (t, $-CH_2-$), 12.37 (q, $-CH_3$). HRMS (*m*/*z*). Calcd for $C_{18}H_{22}O_3$: 286.1569. Found: 286.1592.

Methyl (3,4-Diethyl-7,8-benzo-9-azatricyclo[4.2.1.0^{2,5}]-non-3-ene)-9-carboxylate (8f). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.24 (m, 2H, benzo), 7.13 (m, 2H, benzo), 4.93 (s, 1H, bridgehead), 4.86 (s, 1H, ridgehead), 3.62 (s, 3H, O−CH_3, 2.41 s, 1H, *endo*-cyclobutene), 2.40 (s, 1H, *endo*-cyclobutene), 2.02−2.20 (m, 4H, $-CH_2-$), 1.06 (t, J = 7.4 Hz, 6H, $-CH_3$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 155.74 (s, C=O), 144.00 (s), 143.86 (s), 143.67 (s), 142.48 (s), 126.23 (d, benzo), 126.14 (d, benzo), 119.93 (d, benzo), 119.65 (d, benzo), 60.19 (d), 59.45 (d), 51.89 (q, O−CH_3), 45.55 (d), 45.36 (d), 20.61(t, $-CH_2-$), 20.43 (t, $-CH_2-$), 11.86 (q, $-CH_3$), 11.74 (q, $-CH_3$). MS (*m*/*z* (%)): 283 (M^+, 5.2), 175 (100.0). HRMS (*m*/*z*). Calcd for $C_{18}H_{21}O_2N$: 283.1572. Found: 283.1588.

Methyl (3-Methyl-4-propyl-7,8-benzo-9-azatricyclo [4.2.1.0^{2,5}]non-3-ene)-9-carboxylate (8g) and Methyl (3-Propyl-4-methyl-7,8-benzo-9-azatricyclo[4.2.1.0^{2,5}]non-3-ene)-9-carboxylate (8g′). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.23 (m, 4H, benzo), 7.12 (m, 4 H, benzo), 4.94 (s, 1H, bridgehead), 4.92 (s, 1H, bridgehead), 4.87 (s, 1H, bridgehead), 4.85 (s, 1 H, bridgehead), 3.61(s, 6H, $NCOOCH_3$), 2.43 (s, 2H, *endo*-cyclobutene), 2.36 (S, 2H, *endo*-cyclobutene), 2.03 (m, 4H, $-CH_2-$), 1.65 (s, 3H, $-CH_3$), 1.63 (s, 3H, $-CH_3$), 1.47 (m, 4H,

$-CH_{2-}$), 0.92 (t, J = 7.4 Hz, 6H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 155.77 (s, C═O), 144.02 (s), 143.92 (s), 143.82 (s), 143.73 (s), 142.61(s), 139.45 (s), 138.04 (s), 126.21(d), 126.12 (d), 119.89 (d), 119.65 (d), 60.23 (d), 59.84 (d), 59.50 (d), 59.10 (d), 51.87 (q, $-CH_3$), 47.67 (d), 47.55 (d), 46.47 (d), 46.28 (d), 29.20 (t, $-CH_{2-}$), 29.01 (t, $-CH_{2-}$), 20.49 (t, $-CH_{2-}$), 20.34 (t, $-CH_{2-}$), 14.18 (q, $-CH_3$), 12.42 (q), 12.09 (q). MS (*m*/*z* (%)): 283 (M^+, 43.1), 254 ([M − C_2H_5]$^+$, 6.8), 176 (100.0). HRMS (*m*/*z*). Calcd for $C_{18}H_{21}O_2N$: 283.1592. Found: 283.1567.

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Supporting Information Available: ^1H and ^{13}C NMR spectra for **3a**−**m, 6,** and **8a**−**g**. This material is available free of charge via the Internet at http://pubs.acs.org.

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