Nickel-Catalyzed [2+2] Cycloaddition of Alkynes with Activated Cyclic Alkenes: Synthesis and Novel Ring Expansion Studies of Cyclobutene Products

Daw-Jen Huang, Dinesh Kumar Rayabarapu, Lih-Ping Li, Thota Sambaiah, and Chien-Hong Cheng*[a]

Abstract: Oxabenzonorbornadienes **1** and **2** and azabenzonorbornadiene **3** undergo [2+2] cycloaddition with alkynes (PhC≡CPh, PhC≡CMe, PhC≡CCO_2Et, PhC≡CCH$(OEt)_2$, and HC≡C$(CH_2)_4$Me) in the presence of $[Ni(PPh_3)_2Cl_2]$, PPh_3, and Zn powder in toluene to afford the corresponding *exo*-cyclobutene derivatives **4a–e**, **5a–e**, and **6** in fair to excellent yields. Under similar conditions, $EtCO_2C{\equiv}CCO_2Et$ does not react with **1** in toluene to give the [2+2] cycloaddition product, but in acetonitrile, the catalytic [2+2] cycloaddition proceeds and cycloadduct **4f** is isolated in 83% yield. At high temperature, these cyclobutene derivatives readily undergo ring expansion to yield the corresponding 8-membered carbocyclic dienes. Thus, flash vacuum pyrolysis of **4a**, **4d**, **4f**, **6**, and **14** at 500 °C affords dienes **13a–d** and **15** in 70–96% yields. This interesting ring expansion may be viewed as the insertion of an alkyne moiety into the carbon–carbon double bond of a cyclic olefin resulting in the enlargement of the ring by two carbons. Compound **13a** is readily deoxygenated by $TiCl_4$ and Zn in THF to give a cyclooctatetraene derivative **16** in 89% yield.

Keywords: alkynes · cycloadditions · cyclobutenes · norbornadienes · ring expansions

Introduction

Transition metal-mediated [*m*+*n*] cycloadditions are powerful methods for the synthesis of cyclic compounds and have continued to attract great attention.[1] The [2+2] cycloaddition of alkenes and alkynes, a convenient route to the synthesis of 4-membered rings,[2] is intriguing in view of the fact that the reaction is thermally forbidden[3] in the absence of a metal catalyst. Only scattered reports on this cycloaddition have appeared in the literature.[4–7] Moreover, applications of the cyclobutene products in organic synthesis have not been explored.

Recently, we observed that, in the presence of Zn powder, nickel phosphine complexes catalyzed the [2+2+2] cocyclotrimerization of fullerene, oxa- and azabenzonorbornadienes, and various α, β-unsaturated ketones and esters with alkynes to give multiple-ring products.[8] Ikeda and his co-workers also reported the [2+2+2] cocyclotrimerization of α, β-unsaturated ketones with alkynes using a nickel halide and zinc halide as the catalyst system.[9] In this paper, we wish to report that nickel phosphine complexes also catalyze stereoselectively the [2+2] cycloaddition of oxa- or azabenzonorbornadienes with various alkynes to give *exo*-cyclobutene derivatives. In addition, these cyclobutene derivatives undergo a novel ring expansion, converting the fused 4/6-rings into a cyclooctadiene moiety in high yields. A large number of important biologically active natural products consisting of cyclooctane derivatives are known,[10, 11] but the construction of 8-membered carbocyclic rings remains a challenge to synthetic chemists.[12–16] The present nickel-catalyzed [2+2] cycloaddition and the subsequent ring expansion provide a quick and efficient method for the construction of 8-membered rings bearing various functional groups.

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Results and Discussion

Treatment of oxabenzonorbornadiene (**1**) with diphenylacetylene in the presence of $[Ni(PPh_3)_2Cl_2]$, PPh_3, and Zn powder in toluene under a nitrogen atmosphere at 90 °C gives an *exo*-cyclobutene derivative **4a** in 85% yield (Scheme 1). Control reactions indicate that in the absence of either nickel complex or zinc powder, no **4a** is formed. Extra PPh_3 stabilizes the nickel catalyst system. If the $PPh_3/[Ni(PPh_3)_2Cl_2]$ ratio is lower than 8:1 under these reaction conditions, the nickel catalyst

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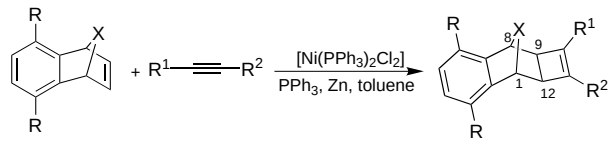


1 X = O, R = H
2 X = O, R = OCH_3
3 X = NCO_2Me, R = H

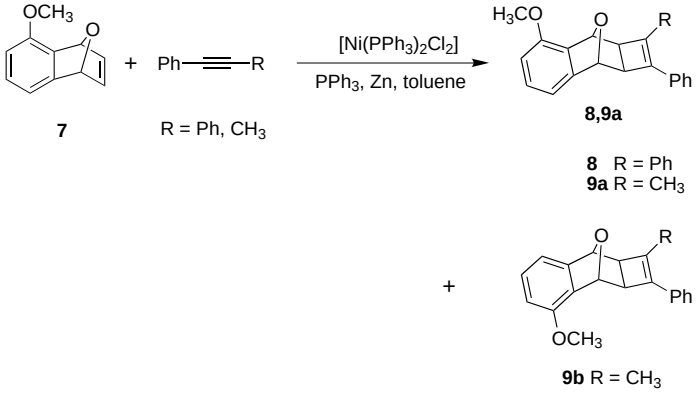
4
5
6

Scheme 1. Oxa- and azabenzonorbornadienes react with diphenylacetylene in the presence of $[Ni(PPh_3)_2Cl_2]$, PPh_3, and Zn powder to give *exo*-cyclobutene derivatives.

readily decomposes and the catalytic activity decreases rapidly.

This $[Ni(PPh_3)_2Cl_2]/PPh_3/Zn$ system in toluene also efficiently catalyzes the cycloaddition of **1** with other internal and terminal acetylenes including PhC≡CMe, PhC≡CCO_2Et, PhC≡$CCH(OEt)_2$, and HC≡$C(CH_2)_4$Me to afford the corresponding *exo*-cyclobutene derivatives **4b**–**e** in fair to excellent yields (Table 1). It is noteworthy that the reaction of **1** with PhC≡$CCH(OEt)_2$ gave formyl derivative **4e** in 90% yield. No corresponding diethyl acetal derivative was isolated, presumably owing to hydrolysis during the work-up process. The same nickel catalyst system, however, is inactive for the [2+2] cycloaddition of diethylacetylene and bis(trimethylsilyl)acetylene. The reaction of diethyl acetylenedicarboxylate with **1** depends greatly on the solvent. There is no [2+2] cycloaddition product observed in toluene, but when the catalytic reaction was carried out in acetonitrile, the [2+2] cycloadducts **4f** was isolated in 83% yield.

Similarly, 2,5-dimethoxy-7-oxabenzonorbornadiene (**2**) undergoes cross-[2+2] cycloaddition with PhC≡CPh, PhC≡CMe, PhC≡CCO_2Et, PhC≡$CCH(OEt)_2$, and HC≡$C(CH_2)_4$Me in the presence of $[Ni(PPh_3)_2Cl_2]/PPh_3/Zn$ catalyst system to afford the corresponding *exo*-cyclobutenes **5a**–**e** in good to excellent yields (Scheme 1, Table 1). The reaction of **2** with PhC≡$CCH(OEt)_2$ also gave formyl derivative **5e** in 96% yield. The reaction of 2-methoxy-7-oxabenzonorbornadiene (**7**) with diphenylacetylene gave [2+2] cycloadduct **8** in 96% yield. On the other hand, when **7** was treated with methylphenylacetylene, two regioisomers **9a** and **9b** were obtained in 40 and 41% yield (Scheme 2). The alkenes used in the



7 R = Ph, CH_3

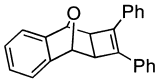
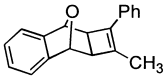
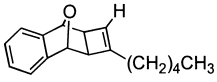
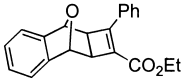
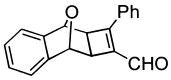
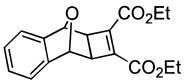
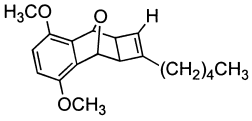
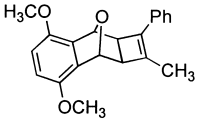
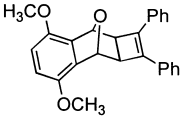
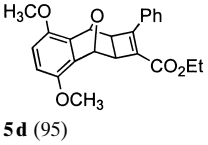
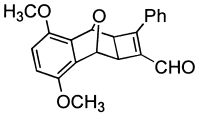
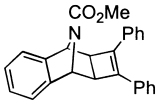
8,9a

8 R = Ph
9a R = CH_3

9b R = CH_3

Scheme 2. Oxabenzonorbornadiene **7** reacts with methylphenylacetylene to furnish two regioisomers **9a** and **9b**.

Table 1. [2+2] Cycloaddition of 7-oxa- and 7-azabenzonorbornadienes with alkynes.[a]

Entry	Norbornadiene	T[°C]	Alkyne ([mmol])	Product (yield [%])[b]
1	**1**	90	Ph—≡—Ph (2.0)	 **4a** (85)
2	**1**	85	Ph—≡—CH_3 (2.0)	 **4b** (82)
3	**1**	80	H—≡—$(CH_2)_4CH_3$ (2.0)	 **4c** (55)
4	**1**	30	Ph—≡—CO_2Et (1.2)	 **4d** (64)
5	**1**	90	Ph—≡—$CH(OEt)_2$ (2.0)	 **4e** (90)
6[c]	**1**	80	EtO_2C—≡—CO_2Et (1.2)	 **4f** (83)
7	**2**	52	H—≡—$(CH_2)_4CH_3$ (2.0)	 **5a** (42)
8	**2**	90	Ph—≡—CH_3 (3.0)	 **5b** (86)
9	**2**	95	Ph—≡—Ph (2.0)	 **5c** (76)
10	**2**	90	Ph—≡—CO_2Et (2.0)	 **5d** (95)
11	**2**	90	Ph—≡—$CH(OEt)_2$ (2.0)	 **5e** (96)
12	**3**	95	Ph—≡—Ph (2.5)	 **6** (98)

[a] Reaction conditions: benzonorbornadiene (1.00 mmol), $[NiCl_2(PPh_3)_2]$ (0.0500 mmol), PPh_3 (0.800 mmol), Zn (2.75 mmol), and toluene (2.00 mL). [b] Isolated yields based on the benzonorbornadiene derivative used. [c] CH_3CN was used instead of toluene.

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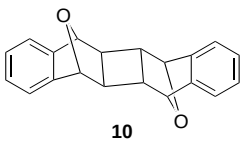
[2+2] cycloaddition can be extended to azabenzonorbornadiene. Thus, in the presence of the $[Ni(PPh_3)_2Cl_2]/PPh_3/Zn$ system, **3** reacts with diphenylacetylene to give the corresponding cyclobutene derivative **6** in 98% yield (Table 1, entry 12).

For all reactions of **1**–**3** and **7** with different alkynes to give the cyclobutene derivatives, only the *exo* isomers were observed. *Exo* stereochemistry of these products was established on the basis of the coupling constant of the protons H-9 and H-12 on the 4/6-ring junction and the bridgehead protons H-1 and H-8 (see Scheme 1). It is well known that for a norbornadiene derivative, the coupling constant between an *exo* and a bridgehead proton is 3 to 6 Hz, but is essentially zero for an *endo* and a bridgehead proton. For all cyclobutene derivatives synthesized by the present method, the protons H-9 and H-12 on the 4/6-ring junction appear as singlets and show no sign of coupling with the bridgehead protons. These results indicate that H-9 and H-12 occupy the *endo* positions.[17] Similar *exo* selectivity was observed for palladium or nickel-catalyzed addition of aryl groups to oxa- and azabenzonorbornadienes.[18]

To enable us to understand the scope of catalysts, we tested several nickel complexes with different ligands for catalytic activity in the [2+2] cycloaddition of 7-oxabenzonorbornadiene (**1**) with diphenylacetylene. As shown in Table 2, nickel systems $[Ni(PPh_3)_4]$, $[NiCl_2(P\text{-}nBu_3)_2]/Zn$, and $[Ni(PPh_3)_2Cl_2]/PPh_3/Zn$ revealed high catalytic activity for the cross-[2+2] cycloaddition. On the other hand, $NiBr_2/Zn$ and $[Ni(cod)_2]$ (cod = cycloocta-1,5-diene) gave not only the cross-[2+2] cycloadduct, but also the product (**10**) from homo-[2+2] cycloaddition of oxabenzonorbornadiene.[19] No homocycloaddition product was observed when nickel phosphine systems were used.



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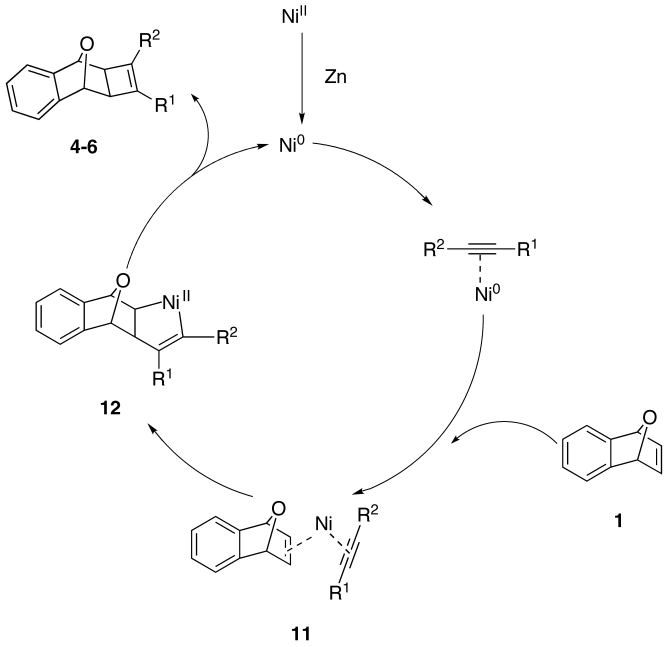
Given the known organometallic chemistry of nickel and the structure of the products observed, we propose the mechanism depicted in Scheme 3 to account for the present nickel-catalyzed [2+2] cycloaddition. Reduction of $[Ni(PPh_3)_2X_2]$ to a Ni^0 species by zinc metal initiates the catalytic reaction. Coordination of an alkyne and 7-oxabenzonorbornadiene (**1**) to the nickel center followed by oxidative cyclometallation affords a nickelacyclopentene intermediate, **12**. Subsequent reductive elimination of the metallacycle **12** gives the cyclobutene product and regenerates the Ni^0 species.



Scheme 3. Proposed mechanism of the nickel-catalyzed [2+2] cycloaddition.

Table 2. Effect of nickel catalysts on the [2+2] cycloaddition of 7-oxabenzonorbornadiene with diphenylacetylene.[a]

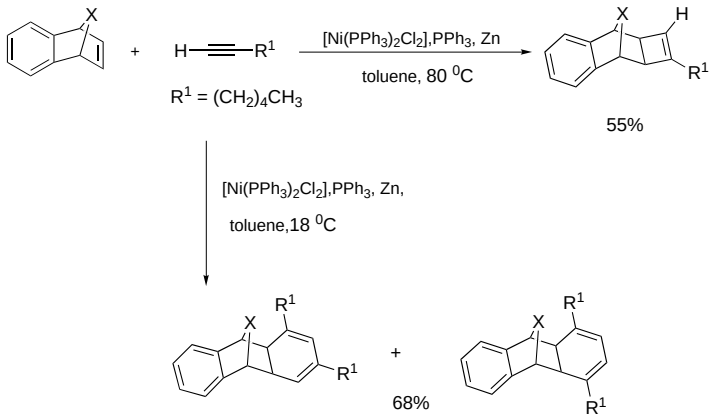
Entry	Solvent	NBE (**1**)/alkyne [mmol]	Ni catalyst [mmol]	Yield [%][b]	
				4a	**10**
1	THF	1.0/2.0	$NiBr_2$ (0.10), Zn (3.0)	65	32
2	toluene	0.5/1.0	$[Ni(cod)_2]$ (0.10)	63	36
3	toluene	0.5/1.0	$[Ni(PPh_3)_4]$ (0.050)	76	–
4	toluene	0.5/1.0	$[NiCl_2(P^nBu_3)_2]$ (0.05), Zn(3.0)	84	–
5	toluene	1.0/2.0	$[NiCl_2(PPh_3)_2]$ (0.05), PPh_3 (0.8), Zn (3.0)	85	–

[a] Reaction conditions: for THF (2.0 mL) at 62 °C and for toluene (1.0 mL) at 80 °C for 24 h. [b] Isolated yields.

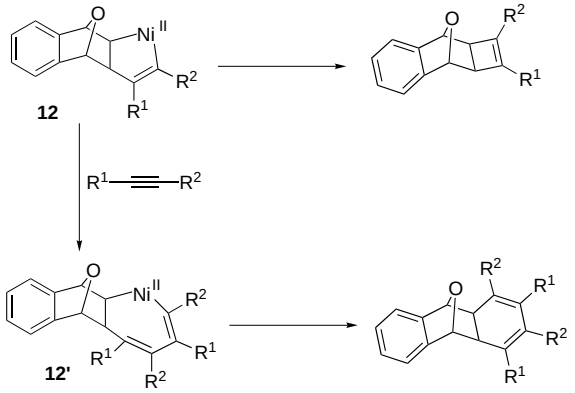
The products of the cycloaddition of oxa- and azabenzonorbornadienes with alkynes catalyzed by the $[Ni(PPh_3)_2Cl_2]/PPh_3/Zn$ system depend greatly on the reaction conditions and the alkynes employed. For disubstituted alkynes PhC≡CPh, PhC≡CMe, $PhC{\equiv}CCO_2Et$, $PhC{\equiv}CCH(OEt)_2$, and $EtO_2CC{\equiv}CCO_2Et$, the reaction with oxa- and azabenzonorbornadienes strongly favors cross-[2+2] cycloaddition. Nonetheless, for $MeC{\equiv}CCO_2Me$ and most monosubstituted alkynes such as PhC≡CH and $HC{\equiv}C(CH_2)_4Me$, [2+2+2] cocyclotrimerization of an oxa- or azabenzonorbornadiene with two alkynes dominates.[8b] Competition between the [2+2+2] and [2+2] cycloadditions can be clearly seen in the reaction of $HC{\equiv}C(CH_2)_4Me$ with oxabenzonorbornadiene (**1**). At ambient temperature, the reaction gives mainly the [2+2+2] cycloaddition products in 68% yield,[8c] but as the reaction temperature increases to 80 °C, the [2+2] cycloaddition dominates, giving **4c** in 55% yield (Scheme 4).

The observed selectivity for [2+2] and [2+2+2] cycloaddition of alkynes may be explained by the competition reactions shown in Scheme 5. For disubstituted alkynes, further insertion of the alkyne into **12** to give **12′** is generally unfavorable due to the strong steric repulsion among the four substituents on the two coplanar alkyne moieties in **12′**. Thus, the reductive elimination process to give the cross-[2+2] cycloaddition product dominates. On the other hand, reduc-

0947-6539/00/0620-3708 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 20



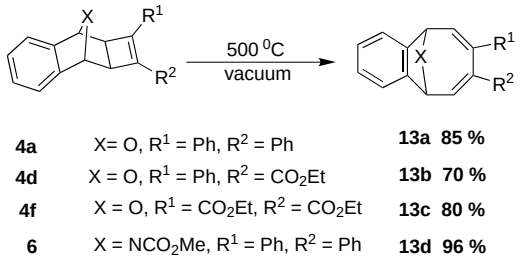
Scheme 4. Competition between [2+2+2] and [2+2] cycloadditions in the reaction of $HCC(CH_2)_4Me$ with **1**.



Scheme 5. Competing reactions behind the observed selectivity for [2+2] and [2+2+2] cycloaddition of alkynes.

tive elimination of **12** (a five-membered-ring metallacycle) to give a four-membered-ring product is expected to have higher activation energy than that of the reductive elimination of **12′** (a seven-membered-ring metallacycle) to afford a six-membered ring cocyclotrimerization product. As a result, the tendency to form cyclobutenes relative to cyclohexadienes increases as the reaction temperature raises.

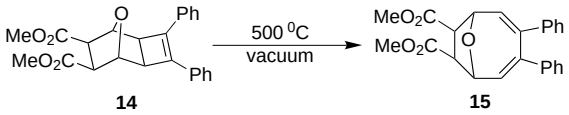
Ring expansion of cyclobutene derivatives: The cyclobutene derivatives prepared by the present nickel-catalyzed [2+2] cycloaddition method are quite stable at ambient temperature. However, heating these [2+2] cycloaddition products at high temperature leads to ring expansion and the formation of 8-membered carbocyclic dienes. Thus, flash vacuum pyrolysis of **4a** at 500 °C readily affords diene **13a** in 85% yield and 99% selectivity (Scheme 6). Compound **13a** is fully characterized by MS, NMR, and IR spectral data. The mass spectrum showing a molecular ion at m/z 322 indicates that **13a** has the same molecular formula as that of starting compound **4a**. In the ^{1}H NMR spectrum of **13a**, the bridgehead and olefin protons appear at $\delta = 5.82$ (d, $J = 5.7$ Hz) and 6.41 (d, $J = 5.7$ Hz), respectively. The observation of only two resonances with coupling constant of 5.7 Hz in the non-aromatic region of the ^{1}H NMR spectrum is in agreement with the proposed symmetrical ring structure. The observed



Scheme 6. Ring expansion of cyclobutenes **4d**, **4f**, and **6** to give **13b–d**.

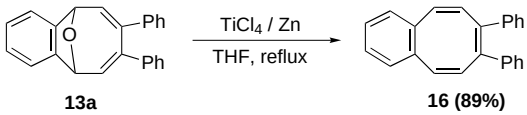
number of ^{13}C NMR signals and the coupling patterns also support the proposed ring-expansion structure.

Similarly, cyclobutenes **4d**, **4f**, **6**, and **14**[20] also underwent ring expansion smoothly at 500 °C and gave **13b–d** and **15** in 70, 80, 96, and 92% yields, respectively (Schemes 6 and 7). The spectral data of these compounds clearly show that their structures are similar to that of **13a**.



Scheme 7. Ring expansion of cyclobutene **14** to give **15**.

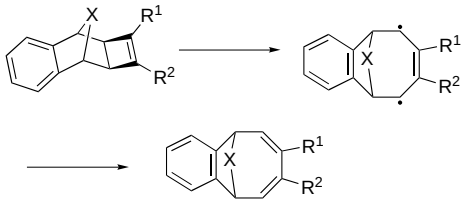
Deoxygenation of **13a** with $TiCl_4$ and Zn[21] in THF affords the corresponding cyclooctatetraene derivative **16** in 89% yield (Scheme 8). The ^{1}H NMR spectrum of this product



Scheme 8. Deoxygenation of **13a** with $TiCl_4$ and Zn to afford the corresponding cyclooctatetraene derivative **16**.

shows two resonances at $\delta = 6.36$ and 6.56 for the olefinic protons with a coupling constant of 11 Hz in addition to the signals in the aromatic region. This observed coupling constant strongly suggests *cis* stereochemistry for the olefinic double bonds consistent with the proposed cyclooctatetraene structure. The ^{13}C NMR and MS data also confirm the deoxygenated 8-membered-ring structure.

The results of high-temperature thermal ring opening of cyclobutene derivatives **4a**, **4d**, **4f**, and **6** is surprising in view of the *cis* stereochemistry of products **13a–d**. Cyclobutene derivatives are known to undergo ring-opening reactions thermally[22, 23] by a conrotatory process and photochemically[24] by a disrotatory pathway to give diene products. A thermally allowed conrotatory process clearly cannot explain the observed *cis* structure of products **13a–d** in the present high-temperature ring-opening reaction. While the mechanism is still not known, a simple diradical process involving homoleptic scission of the carbon–carbon single bond between the two fused carbons of the cyclobutene moiety followed by the required disrotatory process and bond rearrangement explains satisfactorily the present ring-opening results (Scheme 9).[25]



Scheme 9. Proposed diradical mechanism explaining the ring-opening results.

Conclusion

We have demonstrated that nickel complexes catalyze [2+2] cycloaddition of activated alkenes and alkynes in addition to the previously reported [2+2+2] cycloaddition of an alkene and two alkyne molecules. The [2+2] cycloaddition is a convenient method for the preparation of *exo*-cyclobutene derivatives of oxa- and azabenzonorbornadienes. These cyclobutene derivatives undergo high-temperature thermal ring expansion to give substituted cyclooctadienes. The result of ring expansion is equivalent to insertion of an alkyne moiety into the carbon–carbon double bond of a cyclic olefin leading to enlargement of the ring by two carbons. The present new methodology provides a quick and efficient alternative for constructing 8-membered rings bearing various functional groups. Application in natural product synthesis is currently in progress.

Experimental Section

All reactions were conducted under nitrogen on a dual-manifold Schlenk line with purified deoxygenated solvents and standard inert-atmosphere techniques, unless otherwise stated. Reagents and chemicals were used as purchased without further purification. Oxa- and azabenzonorbornadienes (**1**–**3**, **7**) were prepared following literature procedures.[26] Catalyst $[Ni(PPh_3)_2Cl_2]$ was synthesized according to a reported procedure.[27] The purity of each product was checked by NMR analysis.

General procedure for the [2+2] cycloaddition of oxa- and azabenzonorbornadienes with alkynes: A round-bottom side-arm flask (50 mL) containing oxa- or azabenzonorbornadiene (1.00 mmol), $[Ni(PPh_3)_2Cl_2]$ (0.0500 mmol), PPh_3 (0.210 g, 0.800 mmol), and zinc powder (0.180 g, 2.75 mmol) was evacuated and purged with nitrogen gas three times. Freshly distilled dry toluene (2.0 mL) and an alkyne (1.2–3.0 mmol) were added. The reaction mixture was heated and stirred at the appropriate temperature (shown in Table 1) for 24 h. The reaction mixture was then cooled and stirred in the air for 15 min at room 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 with hexane/ethyl acetate as eluent to afford the desired products.

Compound **10** was characterized by comparison of its spectral data with those reported earlier.[19] Important spectral data for new compounds **4a**–**f**, **5a**–**e**, **6**, **8**, and **9a**–**b**, follow.

(1*S,8*R**,9*S**,12*R**)-10,11-Phenyl-13-oxatetracyclo[6.4.1.0^{2,7}.0^{9,12}]trideca-2,4,6,10-tetraene (4a)**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.65$ (dt, $J = 7.1$ Hz, $J = 1.4$ Hz, 4H, Ph), 7.32 (m, 8H, Ph), 7.21 (m, 2H, Ph), 5.18 (s, 2H, O–CH, bridgehead), 3.02 (s, CH, *endo*-cyclobutene); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta = 144.96$ (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 $C_{24}H_{18}0$ 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.

(1*S,8*R**,9*S**,12*R**)-10-Methyl-11-phenyl-13-oxatetracyclo[6.4.1.0^{2,7}.0^{9,12}]-trideca-2,4,6,10-tetraene (4b)**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.45$ (d, $J =$ 7.0 Hz, 2H, Ph), 7.36 (t, $J = 7.0$ Hz, 3H, Ph), 7.32–7.15 (m, 4H, Ph), 5.08 (s, 1H, O–CH, bridgehead), 5.02 (s, 1H, O–CH, bridgehead), 2.90 (dq, $J =$ 2.6 Hz, $J = 1.8$ Hz, 1H, CH, *endo*-cyclobutene), 2.60 (d, $J = 2.6$ Hz, CH, *endo*-cyclobutene), 2.11 (d, $J = 1.8$ Hz, CH_3); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta = 145.17$ (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), 76.20 (d, O–C, bridgehead), 75.43 (d, O–C, bridgehead), 47.41 (d), 44.61 (d), 14.45 (q); MS: *m*/*z* (%): 260 ([*M*]$^+$, 100), 245 ([*M* – CH_3]$^+$, 42.3); HRMS: *m*/*z*: calcd for $C_{19}H_{16}O$ 260.1202, found 260.1198.

(1*S,8*R**,9*S**,12*S**)-10-Pentyl-13-oxatetracyclo[6.4.1.0^{2,7}.0^{9,12}]trideca-2,4,6,10-tetraene (4c)**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.24$ (m, 2H, benzo), 7.15 (m, 2H, benzo), 5.89 (brs, 1H, =C–H, cyclobutene), 4.94 (s, 1H, O–CH, bridgehead), 4.89 (s, 1H, O–CH, bridgehead), 2.62 (d, $J = 3.2$ Hz, 1H, CH, *endo*-cyclobutene), 2.55 (d, $J = 3.2$ Hz, 1H, CH, *endo*-cyclobutene), 2.11 (m, 2H, CH_2, pentyl), 1.55 (m, 2H, CH_2, pentyl), 1.36 (m, 4H, CH_2, pentyl), 0.89 (t, $J = 6.9$ Hz, CH_3); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta = 151.57$ (s), 145.23 (s), 144.56 (s), 132.13 (d), 128.55 (d), 127.06 (d), 126.35 (d), 119.50 (d), 76.37 (d, O–C, bridgehead), 75.42 (d, O–C, bridgehead), 48.65 (d), 44.39 (d), 31.69 (t), 29.51 (t), 26.43 (t), 22.49 (t), 14.02 (q); MS: *m*/*z* (%): 240 ([*M*]$^+$, 51.7), 183 ([*M* – C_4H_9]$^+$, 100); HRMS: *m*/*z*: calcd for $C_{17}H_{20}O$ 240.1515, found 240.1509.

Ethyl(1*S,8*R**,9*S**,12*R**)-11-Phenyl-13-oxatetracyclo[6.4.1.0^{2,7}.0^{9,12}]trideca-2,4,6,10-tetraene-10-carboxylate (4d)**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 8.13 (dd, $J = 7.6$ Hz, $J = 1.9$ Hz, 2H, Ph), 7.49–7.36 (m, 5H, Ph), 7.21 (dd, $J = 5.3$ Hz, $J = 3.1$ Hz, 2H, Ph), 5.22 (s, 1H, O–CH, bridgehead), 5.17 (s, 1H, O–CH, bridgehead), 4.33 (q, 2H, $J = 7.1$ Hz, O–CH_2), 3.05 (AB d, $J_{AB} = 3.7$ Hz, CH, *endo*-cyclobutene), 2.93 (AB d, $J_{AB} = 3.7$ Hz, CH, *endo*-cyclobutene), 1.41 (t, J = 7.1 Hz, CH_3); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta = 162.55$ (s, C=O), 154.60 (s), 144.59 (s), 144.21 (s), 131.80 (s), 130.37 (d), 128.84 (d), 128.40 (d), 128.19 (d), 126.83 (d), 126.69 (d), 119.91 (d), 119.61 (d), 76.12 (d, O–C, bridgehead), 76.08 (d, O–C, bridgehead), 60.32 (t), 44.83 (d), 44.52 (d), 14.33 (q); MS: *m*/*z* (%): 318 ([*M*]$^+$, 16.0), 290 ([*M* – C_2H_4]$^+$, 4.0), 272 ([*M* – OC_2H_5]$^+$, 25.2), 244 ([*M* – COOEt]$^+$, 100); HRMS: *m*/*z*: calcd for $C_{21}H_{18}O_3$ 318.1257; found 318.1251; anal. calcd for $C_{21}H_{18}O_3$: C 79.24, H 5.66, O 15.10; found: C 78.85, H 5.715, O 15.44.

(1*S,8*R**,9*S**,12*R**)-11-Phenyl-13-oxatetracyclo[6.4.1.0^{2,7}.0^{9,12}]trideca-2,4,6,10-tetraene-10-carbaldehyde (4e)**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 10.22 (s, 1H, CHO), 7.77 (m, 2H, Ph), 7.50 (m, 3H, Ph), 7.36 (m, 2H, Ph), 7.23(m, 2H, Ph), 5.25 (s, 1H, O–CH, bridgehead), 5.22 (s, 1H, O–CH, bridgehead), 3.14 (d, $J = 3.7$ Hz, 1H, CH, *endo*-cyclobutene), 3.04 (d, $J =$ 3.7 Hz, 1H, CH, *endo*-cyclobutene); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta =$ 185.49 (d, CHO), 157.31 (s), 144.54 (s), 143.83 (s), 137.00 (s), 131.99 (s), 131.19 (d), 129.07 (d), 128.56 (d), 127.09 (d), 126.86 (d), 120.05 (d), 119.69 (d), 76.29 (d, O–C, bridgehead), 76.17 (d, O–C, bridgehead), 45.87 (d), 43.26 (d); MS: *m*/*z* (%): 274 ([*M*]$^+$, 68.4), 245 (55.9); HRMS: *m*/*z*: calcd for $C_{19}H_{14}O_2$ 274.0995, found 274.0980.

Synthesis of diethyl (1*S,8*R**,9*S**,12*R**)-13-oxatetracyclo[6.4.1.0^{2,7}.0^{9,12}]-trideca-2,4,6,10-tetraene-10,11-dicarboxylate (4f)**: A round-bottom side-arm flask (25 mL) containing oxabenzonorbornadiene **1** (1.00 mmol), $[Ni(PPh_3)_2Cl_2]$ (0.0500 mmol), and zinc powder (0.180 g, 2.75 mmol) was evacuated and purged with nitrogen gas three times. Freshly distilled dry CH_3CN (3.0 mL) and diethyl acetylenedicarboxylate (0.19 mL, 1.2 mmol) were added to this system. The reaction mixture was heated and stirred at 80 °C for 24 h; it was then cooled and stirred in the air for 15 min at room 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 with hexane/ethyl acetate (*v*/*v* = 9/1) as eluent to afford the title compound (0.26 g, 0.83 mmol) in 83% yield. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.28$ (dd, $J = 5.3$ Hz, $J = 3.0$ Hz, 2H, Ph), 7.15 (dd, $J = 5.3$ Hz, $J = 3.0$ Hz, 2H, Ph), 5.16 (s, 2H, O–CH, bridgehead), 4.26 (q, 4H, $J = 7.1$ Hz, O–CH_2), 2.86 (s, 2H, =CH, *endo*-cyclobutene), 1.32 (t, 6H, $J = 7.1$ Hz, CH_3); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta = 160.83$ (s, C=O), 143.65 (s), 142.19 (s), 126.88 (d), 119.85 (d), 75.41 (d), 60.98 (t), 45.70 (d), 14.03 (q); MS: *m*/*z* (%): 314 ([*M*]$^+$, 19.0), 286 ([*M* – C_2H_4]$^+$, 8.4), 268 ([*M* – OC_2H_5]$^+$, 32.2), 240 ([*M* – COOEt]$^+$, 100); HRMS: *m*/*z*: calcd for $C_{18}H_{18}O_5$ 314.1154, found 314.1159.

(1*S,8*R**,9*S**,12*S**)-3,6-Dimethoxy-10-pentyl-13-oxatetracyclo[6.4.1.0^{2,7}.0^{9,12}]trideca-2,4,6,10-tetraene (5a)**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.69$ (s, 2H, dimethoxybenzo), 5.90 (brs, 1H, =CH, cyclobutene), 5.13 (s, 1H, O–CH, bridgehead), 5.09 (s, 1H, O–CH, bridgehead), 3.81 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 2.66 (d, $J = 3.2$ Hz, 1H, CH, *endo*-cyclobutene), 2.59

  0947-6539/00/0620-3710 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 20

(br d, $J = 3.2$ Hz, CH, *endo*-cyclobutene), 2.11 (m, 2H, CH_2, pentyl), 1.55 (m, 2H, CH_2, pentyl), 1.32 (m, 4H, CH_2, pentyl), 0.90 (br t, 3H, $J = 6.8$ Hz, CH_3, pentyl); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 151.79$ (s), 147.33 (s), 134.40 (s), 133.70 (s), 127.19 (d), 111.23 (d), 111.18 (d), 74.78 (d, O–C, bridgehead), 73.59 (d, O–C, bridgehead), 56.10 (q, OCH_3), 48.06 (d), 43.80 (d), 31.69 (t), 29.51 (t), 26.42 (t), 22.45 (t), 13.97 (q); MS: *m*/*z* (%): 300 ($[M]^+$, 49.4), 271 ($[M - C_2H_5]^+$, 49.4); HRMS: *m*/*z*: cacld for $C_{19}H_{24}O_3$ 300.1727, found 300.1728.

(1*S,8*R**,9*S**,12*R**)-3,6-Dimethoxy-10-methyl-11-phenyl-13-oxatetracyclo[6.4.1.0^{2,7}.0^{9,12}]trideca-2,4,6,10-tetraene (5b)**: ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.46$ (d, $J = 8.2$ Hz, 2H, Ph), 7.36 (br t, $J = 8.0$ Hz, 2H, Ph), 7.24 (m, 1H, Ph), 6.67 (s, 2H, 1,4-dimethoxybenzo), 5.28 (s, 1H, O–CH, bridgehead), 5.21 (s, 1H, O–CH, bridgehead), 3.83 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 2.93 (dq, $J = 3.6$ Hz, $J = 1.4$ Hz, 1H, CH, *endo*-cyclobutene), 2.64 (d, $J = 3.6$ Hz, 1H, CH, *endo*-cyclobutene), 2.11 (d, $J = 1.4$ Hz, 3H, CH_3); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 147.38$ (s), 147.21 (s), 138.82 (s), 138.01 (s), 134.50 (s), 134.19 (s), 133.98 (s), 128.43 (d), 126.98 (d), 125.84 (d), 111.23 (d), 111.17 (d), 74.39 (d, O–C, bridgehead), 73.60 (d, O–C, bridgehead), 56.13 (q, OCH_3), 46.78 (d), 44.00 (d), 14.45 (q); MS: *m*/*z* (%): 320 ($[M]^+$, 100), 305 ($[M - CH_3]^+$, 41.1); HRMS: *m*/*z*: calcd for $C_{12}H_{20}O_3$ 320.1414, found 320.1408.

(1*S,8*R**,9*S**,12*R**)-3,6-Dimethoxy-10,11-diphenyl-13-oxatetracyclo[6.4.1.0^{2,7}.0^{9,12}]trideca-2,4,6,10-tetraene (5c)**: ^1H NMR (300 MHz, $CDCl_3$): $\delta =$ 7.65 (d, $J = 7.1$ Hz, 4H, Ph), 7.37 (t, $J = 7.1$ Hz, 4H, Ph), 7.31 (t, $J = 7.1$ Hz, 2H, Ph), 6.70 (s, 2H, 1,4-dimethoxybenzo), 5.36 (s, 2H, O–CH, bridgehead), 3.84 (s, 6H, OCH_3), 3.05 (s, 2H, CH, *endo*-cyclobutene); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 147.35$ (s), 138.88 (s), 134.65 (s), 133.99 (s), 128.46 (d), 127.97 (d), 126.50 (d), 111.34 (d), 74.60 (d, O–C, bridgehead), 56.13 (q, OCH_3), 44.85 (d); MS: *m*/*z* (%): 382 ($[M]^+$, 100), 353 ($[M - OCH_3]^+$; HRMS: *m*/*z*: calcd for $C_{26}H_{22}O_3$ 382.1571, found 382.1572.

Ethyl(1*S,8*R**,9*S**,12*R**)-3,6-Dimethoxy-11-phenyl-13-oxatetracyclo[6.4.1.0^{2,7}.0^{9,12}]trideca-2,4,6,10-tetraene-10-carboxylate (5d)**: ^1H NMR (300 MHz, $CDCl_3$): $\delta = 8.15$ (dd, $J = 7.4$ Hz, $J = 2.1$ Hz, 2H, Ph), 7.44 (m, 3H, Ph), 6.71 (s, 2H, 1,4-dimethoxybenzo), 5.40 (s, 1H, O–CH, bridgehead), 5.34 (s, 1H, O–CH, bridgehead), 4.36 (q AB d, $J = 7.1$ Hz, $J_{AB} =$ 2.5 Hz, 1H, O–CH_2), 4.32 (q AB d, $J = 7.1$ Hz, $J_{AB} = 2.5$ Hz, 1H, OCH_2), 3.85 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 3.07 (d, $J = 3.6$ Hz, 1H, CH, *endo*-cyclobutene), 2.97 (d, $J = 3.6$ Hz, 1H, CH, *endo*-cyclobutene), 1.40 (t, $J =$ 7.1 Hz, 3H, CH_3); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 162.65$ (s, C=O), 154.82 (s), 147.46 (s), 147.29 (s), 133.66 (s), 133.32 (s), 131.88 (s), 130.39 (d), 128.93 (d), 128.45 (d), 111.86 (d), 111.31 (d), 74.50 (d, O–C, bridgehead), 74.29 (d, O–C, bridgehead), 60.34 (t), 56.22 (q, OCH_3), 56.03 (q, OCH_3), 44.31 (d), 44.14 (d), 14.39 (q); MS: *m*/*z* (%): 378 ($[M]^+$, 59.3), 332 ($[M - C_2H_4]^+$, 5.8), 304 ($[M - COOEt]^+$, 100); HRMS: *m*/*z*: calcd for $C_{23}H_{22}O_5$ 378.1469, found 378.1443.

(1*S,8*R**,9*S**,12*R**)-3,6-Dimethoxy-11-phenyl-13-oxatetracyclo[6.4.1.0^{2,7}.0^{9,12}]trideca-2,4,6,10-tetraene-10-carbaldehyde (5e)**: ^1H NMR (300 MHz, $CDCl_3$): $\delta = 10.17$ (s, 1H, CHO), 7.77 (m, 2H, Ph), 7.46 (m, 3H, Ph), 6.69 (s, 2H, 1,4-dimethoxybenzo), 5.39 (s, 1H, O–CH, bridgehead), 5.36 (s, 1H, O–CH, bridgehead), 3.83 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 3.14 (d, $J =$ 3.6 Hz, 1H, CH, *endo*-cyclobutene), 3.05 (d, $J = 3.6$ Hz, 1H, CH, *endo*-cyclobutene); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 185.42$ (d, CHO), 157.44 (s), 147.47 (s), 147.21 (s), 137.17 (s), 133.63 (s), 132.92 (s), 132.05 (s), 131.14 (d), 129.04 (d), 128.65 (d), 111.77 (d), 111.31 (d), 74.66 (d, O–C, bridgehead), 74.40 (d, O–C, bridgehead), 56.08 (q, OCH_3), 56.04 (q, OCH_3), 45.32 (d), 42.86 (d); MS: *m*/*z* (%): 334 ($[M]^+$, 39.4), 305 ($[M - CHO]^+$, 21.5); HRMS: *m*/*z*: calcd for $C_{21}H_{18}O_4$ 334.1206, found 334.1205.

Methyl(1*S,8*R**,9*S**,12*R**)-10,11-diphenyl-13-azatetracyclo[6.4.1.0^{2,7}.0^{9,12}]-trideca-2,4,6,10-tetraene-10-carboxylate (6)**: ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.59$ (t, $J = 7.5$ Hz, 4H, phenyl), 7.32 (m, 8H, phenyl, benzo), 7.21 (d, $J =$ 3.1 Hz, 1H, benzo), 7.20 (d, $J = 5.3$ Hz, 1H, benzo), 5.28 (br s, 1H, N–CH, bridgehead), 5.15 (br s, 1H, N–CH, bridgehead), 3.29 (s, 3H, OCH_3), 2.96 (d, $J = 3.2$ Hz, 1H, CH, *endo*-cyclobutene), 2.92 (d, $J = 3.2$ Hz, 1H, CH, *endo*-cyclobutene); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 155.72$ (s, C=O), 143.92 (s), 143.62 (s), 140.42 (s), 139.23 (s), 134.65 (s), 134.28 (s), 128.40 (d), 128.32 (d), 128.14 (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 (q), 46.20 (d), 45.87 (d); MS: *m*/*z* (%): 379 (M^+, 100), 319 ($[M - COOCH_3]^+$, 5.0); HRMS: *m*/*z*: calcd for $C_{26}H_{21}NO_2$ 379.1574, found 379.1584.

(1*S,8*R**,9*S**,12*R**)-3-Methoxy-10,11-diphenyl-13-oxatetracyclo[6.4.1.0^{2,7}.0^{9,12}]trideca-2,4,6,10-tetraene (8)**: ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.63$ (t, $J = 6.6$ Hz, 4H, phenyl), 7.37–7.25 (m, 6H, phenyl), 7.16 (t, $J = 7.4$ Hz, 1H, benzo), 6.95 (d, $J = 7.2$ Hz, 1H, benzo), 6.75 (d, $J = 8.2$ Hz, 1H, benzo), 5.39 (s, 1H, O–CH, bridgehead), 5.14 (s, 1H, O–CH, bridgehead), 3.86 (s, 3H, OCH_3), 3.04 (d, $J = 3.5$ Hz, 1H, CH, *endo*-cyclobutene), 3.00 (d, $J = 3.5$ Hz, 1H, CH, *endo*-cyclobutene); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 152.97$ (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), 110.25 (d), 76.66 (d), 74.27 (d), 55.51 (q), 45.41 (d), 44.99 (d); MS: *m*/*z* (%): 352 ($[M]^+$, 100), 323 ($[M - OCH_3]^+$, 22.4); HRMS: *m*/*z*: calcd for $C_{25}H_{20}O_2$ 352.1465, found 352.1461.

(1*S,8*R**,9*S**,12*R**)-3-Methoxy-11-methyl-10-phenyl-13-oxatetracyclo-[6.4.1.0^{2,7}.0^{9,12}]trideca-2,4,6,10-tetraene (9a)**: ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.48$ (t, $J = 7.1$ Hz, 2H, phenyl), 7.38 (t, $J = 7.1$ Hz, 2H, phenyl), 7.25 (t, $J = 7.1$ Hz, 1H, phenyl), 7.17 (t, $J = 7.1$ Hz, 1H, benzo), 6.97 (d, $J =$ 7.1 Hz, 1H, benzo), 6.76 (d, $J = 7.1$ Hz, 1H, benzo), 5.26 (s, 1H, O–CH, bridgehead), 5.10 (s, 1H, O–CH, bridgehead), 3.88 (s, 3H, OCH_3), 2.96 (dd, $J = 3.4$ Hz, $J = 1.8$ Hz, 1H, CH, *endo*-cyclobutene), 2.62 (d, $J = 3.4$ Hz, 1H, CH, *endo*-cyclobutene), 2.13 (br s, 3H, CH_3); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 152.79$ (s), 147.23 (s), 138.55 (s), 137.83 (s), 134.48 (s), 131.93 (s), 128.23 (d), 126.95 (d), 125.76 (d), 112.24 (d), 110.10 (d), 75.64 (d), 74.00 (d), 55.45 (d), 55.45 (q), 46.88 (d), 14.39 (q); MS: *m*/*z* (%): 290 ($[M]^+$, 50.2), 275 ($[M - CH_3]^+$, 100); HRMS: *m*/*z*: calcd for $C_{20}H_{18}O_2$ 290.1308, found 290.1276.

(1*R,8*S**,9*R**,12*S**)-3-Methoxy-10-methyl-11-phenyl-13-oxatetracyclo-[6.4.1.0^{2,7}.0^{9,12}]trideca-2,4,6,10-tetraene (9b)**: ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.48$ (t, $J = 7.1$ Hz, 2H, phenyl), 7.38 (t, $J = 7.1$ Hz, 2H, phenyl), 7.25 (t, $J = 7.1$ Hz, 1H, phenyl), 7.16 (t, $J = 7.1$ Hz, 1H, benzo), 6.92 (d, $J = 7.1$ Hz, 1H, benzo), 6.76 (d, $J = 8.3$ Hz, 1H, benzo), 5.32 (s, 1H, O–CH, bridgehead), 5.04 (s, 1H, O–CH, bridgehead), 3.89 (s, 3H, OCH_3), 2.92 (d d, $J =$ 3.2 Hz, $J = 1.8$ Hz, 1H, CH, *endo*-cyclobutene), 2.66 (d, $J = 3.2$ Hz, 1H, CH, *endo*-cyclobutene), 2.13 (br s, 3H, CH_3); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 152.89$ (s), 147.46 (s), 138.88 (s), 138.04 (s), 134.48 (s), 131.74 (s), 128.40 (d), 126.95 (d), 125.81 (d), 112.40 (d), 110.04 (d), 76.44 (d), 73.21 (d), 55.45 (q), 47.32 (d), 44.11 (d), 14.39 (q); MS: *m*/*z* (%): 290 ($[M]^+$, 50.2), 275 ($[M - CH_3]^+$, 100); HRMS: *m*/*z*: calcd for $C_{20}H_{18}O_2$ 290.1308, found 290.1296.

General procedure for flash vacuum pyrolysis of 4a, 4d, 4f, and 6: A cyclobutene derivative (**4a, 4d, 4f**, or **6**) (0.270 mmol) in a sample boat (5 mL) was inserted into one end of a glass (quartz or pyrex) tube. The other end of the tube was connected to a stopcock. This glass tube, longer than the furnace used for heating by ca 15 cm, was then placed in the furnace but with the sample end kept outside of the furnace. The glass tube was evacuated through the stopcock for about 20 min until the vacuum in the tube reached $\approx 10^{-1}$ Torr. The furnace was then heated to 500 °C and was kept at the same temperature for 30 min. The sample end of the glass tube was then inserted into the furnace and the reaction mixture started to condense at the other end of the tube. When all the reactants shifted from one end to the other of the tube (≤ 1 min), the glass tube was cooled to room temperature. The crude product was extracted with dichloromethane, concentrated, and separated on a silica gel column with hexane/ethyl acetate mixture as eluent to provide the desired products.

Important spectral data for compounds **13a-d** follow.

(1*R,8*S**)-10,11-Diphenyl-13-oxatricyclo[6.4.1.0^{2,7}]trideca-2,4,6,9,11-pentaene (13a)**: ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.00–6.98$ (m, 9H), 6.81–6.84 (m, 5H), 6.41 (d, $J = 5.6$ Hz, 2H), 5.82 (d, $J = 5.7$ Hz, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 144.13$ (s), 140.35 (s), 139.63 (s), 138.60 (d), 129.05 (d), 127.67 (d), 127.10 (d), 127.05 (d), 125.85 (d), 125.80 (d), 119.44 (d), 80.72 (d); MS: *m*/*z* (%): 322 ($[M]^+$, 24), 293 (100); HRMS: *m*/*z*: calcd for $C_{24}H_{18}O$ 322.1358, found 322.1350.

Ethyl(1*R,8*S**)-11-phenyl-13-oxatricyclo[6.4.1.0^{2,7}]trideca-2,4,6,9,11-pentaene-10-carboxylate (13b)**: ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.38–7.18$ (m, 5H), 7.07–7.05 (m, 4H), 6.92 (d, $J = 5.7$ Hz, 1H), 6.34 (d, $J = 5.7$ Hz, 1H), 5.75 (t, $J = 5.7$ Hz, 2H), 3.71 (q, $J = 7.1$ Hz, 2H), 0.73 (t, $J = 7.1$ Hz, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 169.41$ (s), 143.89 (s), 142.07 (d), 140.41 (s), 139.61 (d), 139.30 (s), 136.12 (s), 133.85 (s), 128.50 (d), 128.12 (d), 127.92 (d), 126.84 (d), 126.68 (d), 119.79 (d), 119.60 (d), 80.61 (d), 80.22 (d), 60.84 (t), 13.34 (q); IR (neat): 2936, 1718 cm^{-1}; MS: *m*/*z* (%): 318 ($[M]^+$, 6), 305 (100); HRMS: *m*/*z*: calcd for $C_{21}H_{18}O_3$ 318.1256, found 318.1259.

Diethyl(1*R,8*S**)-13-Oxatricyclo[6.4.1.0^{2,7}]trideca-2,4,6,9,11-pentaene-10,11-dicarboxylate (13c)**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.25 - 7.24$ (m, 4H), 7.08 (d, $J = 5.4$ Hz, 2H), 5.73 (d, $J = 5.6$ Hz, 2H), 4.12 (q, $J = 7.2$ Hz, 4H, O–CH_2), 1.22 (t, $J = 7.2$ Hz, 6H, CH_3); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta = 168.04$ (s, C=O), 144.09 (d), 139.43 (s), 129.49 (s), 119.93(d), 79.97 (d), 61.26 (t), 13.93 (q); IR (neat): 2986, 1726 cm^{-1}; MS: *m*/*z* (%): 314 ([*M*]$^+$, 6), 285 (100); HRMS: *m*/*z*: calcd for $C_{18}H_{18}O_5$ 314.1154, found 314.1156.

Methyl(1*R,8*S**)-10,11-diphenyl-13-azatricyclo[6.4.1.0^{2,7}]trideca-2,4,6,9,11-pentaene-13-carboxylate (13d)**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.37 - 7.24$ (m, 4H), 6.95 – 6.92 (m, 6H), 6.76 – 6.73 (m, 4H), 6.45 (t, $J = 6.4$ Hz, 2H), 5.72 (d, $J = 6.4$ Hz, 1H), 5.63 (d, $J = 6.4$ Hz, 1H), 3.77 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta = 154.35$ (s), 144.29 (s), 139.43 (s), 139.30 (s), 139.13 (s), 138.83 (d), 138.64 (d), 129.11 (d), 129.01 (d), 127.69 (d), 127.05 (d), 126.99 (d), 125.70 (d), 120.48 (d), 60.81 (d), 60.43 (d), 52.63 (q); IR (neat): 1704 cm^{-1}; MS: *m*/*z* (%): 379 ([*M*]$^+$, 72), 320 ([*M* – COOEt]$^+$, 29); HRMS: *m*/*z*: calcd for $C_{26}H_{21}O_2N$ 379.1573, found 379.1570.

Dimethyl(1*R,6*S**,7*R**,8*S**)-3,4-diphenyl-9-oxabicyclo[4.2.1]nona-2,4-diene-7,8-dicarboxylate (15)**: [2+2] cycloadduct **14** (0.0104 g, 0.0266 mmoL) underwent ring opening to give product **15** (0.0096 g) in 92% yield. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.74$ (s, 6H), 3.78 (s, 2H), 5.21 (d, $J =$ 5.5 Hz, 2H), 6.38 (d, $J = 5.4$ Hz, 2H), 6.93 – 6.96 (m, 4H), 7.03 – 7.06 (m, 6H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta = 52.25$ (q), 57.28 (d), 79.30 (d), 126.27 (d), 127.45 (d), 128.42 (d), 137.72 (d), 141.09 (s), 142.89 (s), 170.92 (s); IR (neat): 2948, 1736, 1439, 1222, 1015, 929, 761 cm^{-1}; EI-MS: *m*/*z* (rel intensity): 390 ([*M*]$^+$, 11), 359 ([*M* – OCH_3]$^+$, 100), 331 ([*M* – COOMe]$^+$, 46); HRMS: *m*/*z*: calcd for $C_{24}H_{22}O_5$: 390.1467; found 390.1452.

Synthesis of 7,8-diphenylbenzo[*a*]cyclooctene (16): A round-bottom side-arm flask (50 mL) was charged with zinc powder (0.500 g, 7.65 mmol) and the system was evacuated and purged with nitrogen gas three times. Freshly distilled dry THF (10.0 mL) and $TiCl_4$ (0.33 mL, 3.00 mmol) were added to the system. The solution was stirred at room temperature for a few minutes and cooled to 0 °C. A THF solution of **13a** (0.194 g, 0.600 mmol in 5.0 mL THF) was added to the solution and the system was then refluxed for 16 h. On cooling to room temperature, the solution was quenched with water (15.0 mL) and filtered. The filtrate was extracted with ether (60 mL). The ether layer was washed with brine (40 mL), dried ($MgSO_4$), filtered, and concentrated. The residue was separated on a silica gel column with hexane as eluent to afford **16** in 89% yield (0.164 g). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.15 - 7.17$ (m, 4H), 7.02 – 7.06 (m, 2H), 6.99 (d, $J = 1.8$ Hz, 2H), 6.98 (d, $J = 1.8$ Hz, 2H), 6.83 – 6.86 (m, 4H), 6.56 (d, $J = 11.0$ Hz, 2H), 6.36 (d, $J =$ 11.0 Hz, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta = 140.30$ (s), 138.41 (s), 137.90 (s), 135.59 (d), 131.22 (d), 129.35 (d), 128.81 (d), 127.74 (d), 126.73 (d), 126.47 (d); IR (neat): 2932 cm^{-1}; MS: *m*/*z* (%): 306 ([*M*]$^+$, 100), 237; HRMS: *m*/*z*: calcd for $C_{24}H_{18}$ 306.1409, found 306.1397.

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[20] Compound **14** was prepared in 90% from dimethyl acetylenedicarboxylate and dimethyl (2*R*,3*S*)-7-oxabicyclo[2.2.1]hep-5-ene-2,3-dicarboxylate in toluene in the presence of $[Co(PPh_3)_2I_2]$, PPh_3, and Zn powder. The results will be published in a separate paper. Important spectral data of **14**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.49$ (d, $J =$ 8.2 Hz, 4H, Ph), 7.26 – 7.35 (m, 6H, Ph), 4.75 (s, 2H, bridgehead), 3.69 (s, 6H, O–CH_3), 3.11 (s, 2H, *endo*-cyclobutene), 2.99 (s, 2H); HRMS calcd for $C_{24}H_{22}O_5$ 390.1467, found 390.1452.

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