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Diels−Alder Approach to Biaryls: Elucidation of Competing Tandem [2+2] Cycloaddition/[1,3] Sigmatropic Shift Pathway

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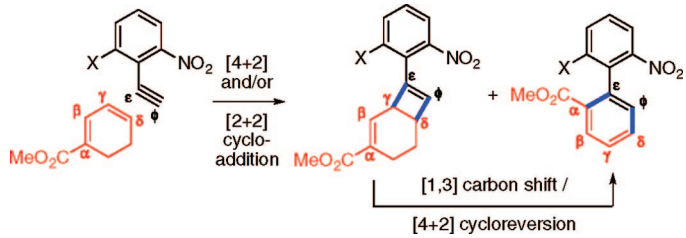
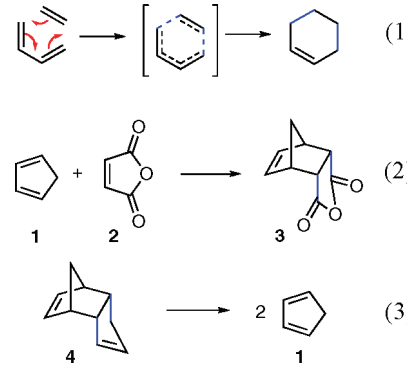


Reaction of 2-halo-6-nitrophenylacetylene with an electron deficient diene gives rise to a [4+2] cycloaddition/cycloreversion biaryl product and a bicyclo[4.2.0]octadiene resulting from a competing [2+2] cycloaddition pathway. The cyclobutene can be opened to give a mixture of cyclooctatriene and biaryl in varying amounts depending on heat and light exposure. The conversion of the cyclobutene into biaryl occurs through a [1,3] sigmatropic carbon shift followed by [4+2] cycloextrusion of ethylene gas.

Introduction

Since its discovery 80 years ago by Diels and Alder,[1] the [4+2] cycloaddition has proven to be a powerful tool for the construction of complex molecular architectures. The widely accepted mechanism for this transformation involves a cyclic concerted reorganization of the electrons between a diene (4π electrons) and a dienophile (2π electrons).[2] Analysis of the molecular orbitals for this transformation has shown that the highest occupied molecular orbital (HOMO) from the diene typically interacts with the lowest unoccupied molecular orbital (LUMO) of the diene.[3] Inverse demand Diels−Alder processes have also been utilized in which an electron-rich dienophile and an electron-poor diene are employed.[4] While the parent reaction between 1,3-butadiene and ethylene requires forcing conditions to proceed (eq 1),[2,5] systems in which the diene contains an electron donating group(s) and/or the dienophile contains an electron withdrawing group(s) have been shown to progress under much more reasonable conditions. Additionally, rigidifying the conformation of the diene has also been shown to have a dramatic effect on the rate of the reaction by keeping the diene in the reactive *s*-cis conformation.[6] A classical example employed in undergraduate organic laboratories is the reaction of maleic anhydride (**2**) with cyclopentadiene (**1**) (eq 2).[7] Cyclopentadiene (**1**) is commonly prepared via retro-Diels−Alder cycloaddition (often called a cycloreversion) of dicyclopentadiene (**4**) (eq 3).[8] Both forward and reverse cycloadditions have found considerable use in organic synthesis.[9]



Our laboratory has utilized the combination of a Diels−Alder cycloaddition and a cycloreversion to provide access to a wide

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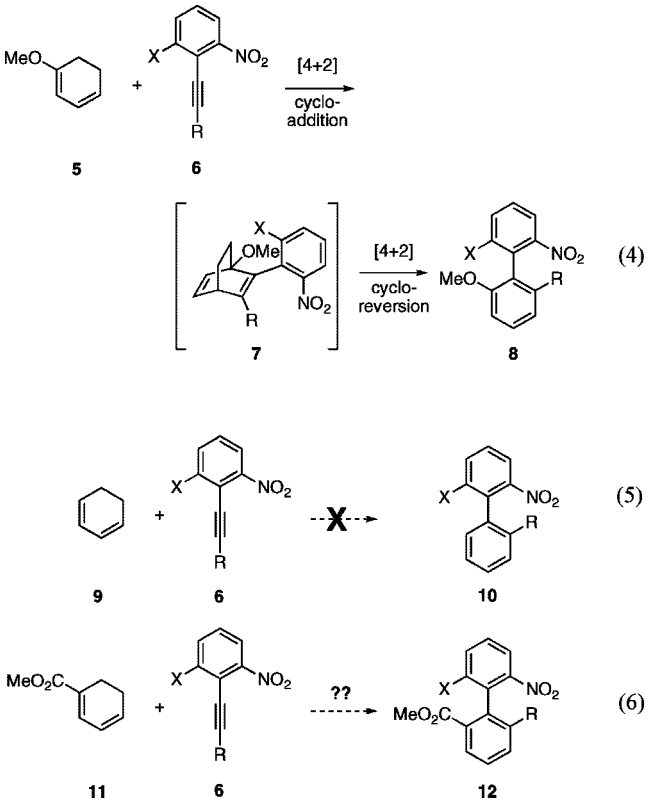
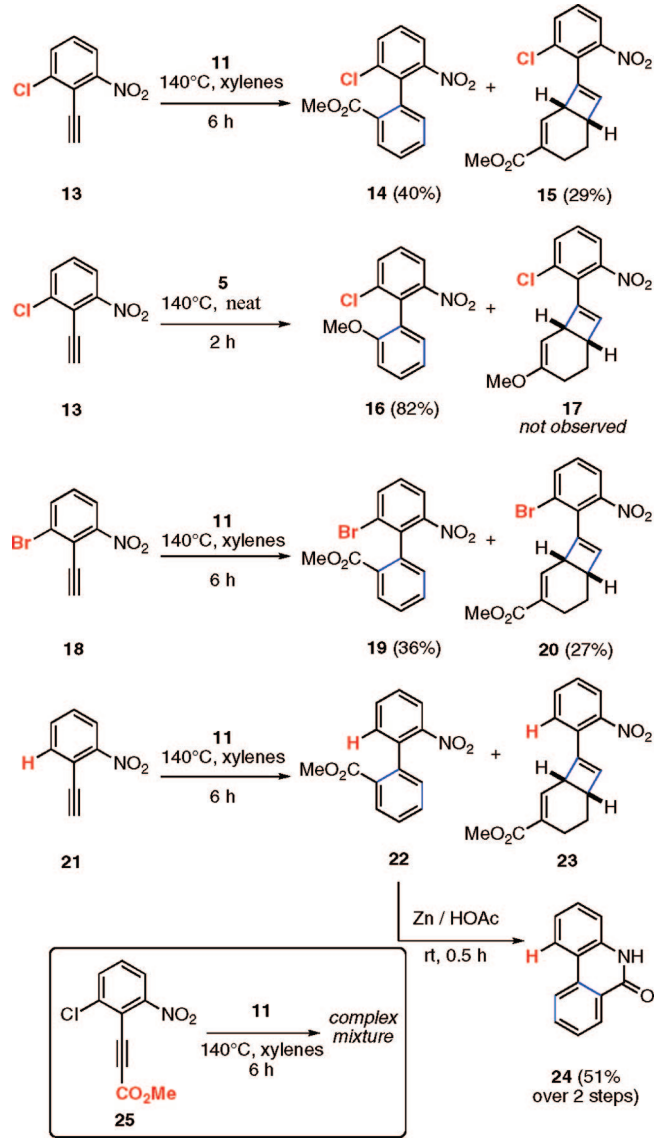
range of highly substituted biaryl compounds.[10,11] We have primarily exploited the use of *o*-nitrophenyl-substituted alkynes **6** as our dienophile component and oxygenated dienes (e.g., **5**) for the 4π component in this Diels−Alder approach to biaryls (DAB) (eq 1).[10] These substrates have shown a remarkable ability to construct highly congested biaryl linkages **8**—many of which possess four ortho substitutents with respect to the central biaryl bond. We have presumed that this transformation proceeded through an initial [4+2] cycloaddition to generate the [2.2.2] bicycle **7** followed by [4+2] cycloreversion to provide the biaryl **8**. We have isolated what we believe to be the [2.2.2] bicyclic intermediate **7** and shown that heating of this intermediate does cleanly generate the biaryl **8**. Interestingly, our attempts to induce cycloaddition reactions with the parent 1,3-cyclohexadiene (**9**) have not met with success to date (eq 5). We are unsure at this juncture as to the exact rationale for lack of clean cycloaddition using diene **9**. In an effort to explore the scope of our DAB strategy, the extension of our DAB strategy to electron-deficient dienes such as 1-carbomethoxy-cyclohexadiene (**11**)[12] seemed like a logical step (eq 6). This diene has been shown to undergo [4+2] cycloadditions with electron rich dienophiles such as ynamine[13a,b] in an inverse electron demand Diels−Alder process. Herein, we disclose an account of the reactivity and mechanistic underpinings of diene **11** with our *o*-nitrophenyl alkynes **6**.



Results and Discussion

We first elected to explore the initial reactivity of diene **11** with our chloro alkyne **13** (Scheme 1). The diene **11** can be prepared in two steps from methyl 4-bromocrotonate.[12] Our group has previously reported the one-step synthesis of alkyne **13** from the commercially available 2-chloro-6-nitrobenzaldehyde.[10c] Heating a mixture of the two reagents **11** and **13** at 140 °C in xylenes for 6 h resulted in the consumption of starting materials and the formation of two products as a 1.3:1 mixture (**14**:**15**) based on crude ^{1}H NMR analysis. The compounds proved quite challenging to separate by standard chromatographic techniques on a small scale; however, this mixture could be purified via recrystallization from diethyl ether/petroleum ether. On a large scale (>2 g), reasonable separation

SCHEME 1. Cycloaddition Reactions of Acetylenes 13, 18, and 21 with Dienes 11 and 5



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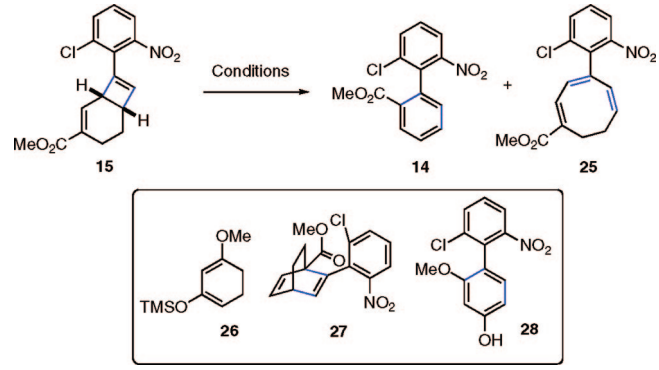
could be achieved via careful silica gel chromatography with use of a CH_2Cl_2/hexanes gradient. We initially hypothesized that compound **15** might be the [2.2.2] bicyclic adduct as shown in eq 1; however, the ^1H and ^{13}C NMR did not support that assignment. Fortunately, we were able to unambiguously establish the structure of compound **15** by X-ray crystallographic analysis.[14] While this example represents the first reported case from our laboratory of isolating a cyclobutene from our DAB protocols, we have previously observed products that would appear to have been constructed from a [2+2] cycloaddition followed by electrocyclic ring opening.[10b,c] To the best of our knowledge, there is only one previous report of a formal [2+2] byproduct being formed with the diene **11**.[13a] It should be noted that no other regioisomers of either biaryl **14** or bicycle **15** were isolated from the reaction. This selectivity speaks once again to the powerful directing ability of the *o*-nitrophenyl moiety.[10f] Our traditional DAB strategy has employed electron rich dienes such as 1-methoxy-1,3-cyclohexadiene (**5**). This diene reacts cleanly with alkyne **13** to provide solely biaryl **16** in excellent yield (82%). None of the cyclobutene product **17** was observed under these conditions. We have also explored the reactivity of other alkynes with the diene **11**. In the case of the analogous 2-bromo series (compound **18**), we found a similar reactivity pattern to the chloro alkyne **13**. This result was somewhat surprising, as we have previously observed divergent reactivity between these two alkynes **13** and **18** with Brassard's diene.[10c] We also screened the non-halogenated alkene **21**. Unfortunately, purification of the products **22** and **23** from this reaction has proven quite challenging. We can confirm the presence of the key signals in the crude ^1H NMR spectrum from this transformation for both the biaryl **22**[15] and the cyclobutene **23**; however, we have been unable to effectively purify these two compounds. Fortunately, treatment of the mixture with Zn/AcOH affected reduction of the nitro moiety with in situ cyclization to form the known lactam **24**.[16] Finally, we investigated the performance of the acetylenic ester **25**[10b] in the cycloaddition process with diene **11**; however, a complex mixture of products was observed.

TABLE 1. Thermolysis and/or Photolysis of Cyclobutene 15



entry	conditions	ratio of biaryl **14**:cyclooctatriene **25**
a	xylenes (0.5 M), xylenes, 160 °C, 6 h	1.1:1 (42% **14**, 37% **25**)
b	**26** (3 equiv), xylenes (0.5 M), 160 °C, 6 h	1.1:1 (no other products formed)
c	xylenes (0.5 M), 160 °C, 6 h (no light)	1.8:1 (47% **14**, 26% **25**)
d	xylenes (0.5 M), 140 °C, 40 h	no reaction
e	xylenes (0.5 M), 140 °C, 6 h (120W light bulb)	0:1 (83% **25**)

To further probe this reaction pathway, we studied the thermolysis and photolysis of cyclobutene **15** (Table 1). Interestingly, treatment of cyclobutene **15** at more elevated temperatures (160 °C, 6 h) resulted in the formation of two products: the biaryl **14** and the 8-membered cyclooctatriene **25** (entry a). The structure of cyclooctatriene **25** was conclusively established via X-ray crystallographic analysis.[17] It is important to note that all of the cyclobutene **15** is consumed under these conditions. One explanation for the formation of biaryl **14** could be a retro [2+2] cycloaddition, which produces the initial starting materials **11** and **13** that could then recombine to form the [2.2.2] bicycle **27** (as well as the cyclobutene **15**) followed by [4+2] cycloreversion to yield the biaryl **14**. To probe the validity of this mechanism, the cyclobutene **15** was heated under identical conditions except for the presence of the 1,3-bisoxygenated diene **26** (entry b). Interestingly, these conditions produced biaryl **14** and cyclooctatriene **25** as the only observable products after 6 h at 160 °C. Diene **26** has been shown to react readily with the alkyne **13**[10c] and formation of the alternate biaryl **28** should be observed if a cycloreversion of cyclobutene **15** to alkyne **13** is an active reaction pathway. This result would appear to rule out the [2+2] cycloreversion of **15** under the reaction conditions. Alternatively, a recent report of thermal [1,3] carbon shifts by Baldwin[18] led us to suspect that a [1,3] sigmatropic carbon shift could also be an active pathway that would lead to biaryl **14**. These types of [1,3] shifts are common in rigid systems and proceed via symmetry allowed suprafacial inversion of configuration.[16] The inversion of configuration would not be noticed in our case as the product is biaryl **14**, which has all sp^2 hybridized carbons. Inspection of the X-ray and DFT-level geometry optimized[19] structures shows that the orbitals in **15** are well-aligned to undergo a [1,3] carbon shift. We were also intrigued to explore if the divergent pathways that were being observed (biaryl formation and cyclooctatriene formation) could be related to a photochemical process. Repeating the same initial experiment (entry a) in the absence of light did improve the

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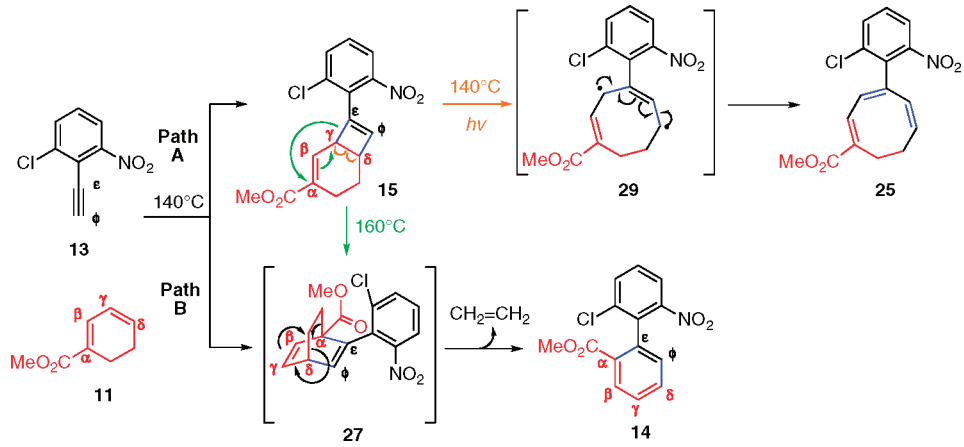
SCHEME 2. Proposed Mechanistic Pathway



ratio of biaryl to cyclooctatriene (1.8:1, **14**:**25**) (entry c). Since excluding light favored formation of the biaryl **14**, the irradiation with light might favor the cyclooctatriene **25**.[20] As was expected, lowering the reaction temperature to 140 °C gave no reaction as previously shown since none of cyclooctatriene **25** was formed.[21] Interestingly, exposure of cyclobutene **15** to a 120 W halogen bulb at the same temperature (140 °C) led to the formation of the cyclooctatriaene **18** as the *sole product* in good yield (83%) (entry e). It should be noted that variation of light exposure on the initial reaction between acetylene **13** and diene **11** appeared to have no effect on the course of the reaction as similar distributions (**14**:**15**) of products (ca. 1.3−1.5:1) were found.

A proposed mechanistic pathway for the formation of these products is shown in Scheme 2. The initial reaction at 140 °C proceeds through at least two competing pathways (Paths A and B). Path A involves a net [2+2] cycloaddition at the γ and δ atoms of the diene **11** with the alkyne **13**. While thermal [2+2] cycloadditions are normally forbidden based on the Woodward−Hoffmann rules,[22] alkyne **13** does possess sets of orthogonally disposed p orbitals, which could participate in a concerted [2+2] pathway. The thermal [2+2] cycloadditions of ketenes are thought to proceed through a similar pathway.[23] The fact that variation in exposure to light on the initial reaction between **11** and **13** has no impact on the product distribution does indirectly support the concerted [2+2] pathway. Path B would proceed through a normal [4+2] cycloaddition to yield the bicyclo[2.2.2] octadiene **27**, which rapidly extrudes ethylene to give biaryl **14**. The rate of the [4+2] cycloreversion is thought to be driven, in part, by the relief of steric compression (along with the aromaticity produced in the new benzene ring in **14**). Although we did not isolate this bicycle **27**, we have documented its existence in previous work at lower temperatures.[10b] Upon thermolysis of cyclobutene **15**, a [1,3] sigmatropic carbon shift of the γ, ϵ bond would lead to the [2.2.2] bicycle **27**. This pathway could proceed via a concerted manifold or a diradical intermediate. Support for at least a predominance of the concerted [1,3] sigmatropic pathway can be found in the observation that exclusion of light led to an augmentation of the biaryl **14** (Table 1, entry c). Subsequent extrusion of ethylene via the [4+2] cycloreversion reveals the biaryl **14**. Alternatively, photolysis of cyclobutene **15** would induce homolytic cleavage of the γ, δ bond to form the diradical intermediate **29**. Subsequent spin flip and recombination would produce the triene **25**. Thermal 4π electrocyclic opening of the cyclobutene **15** is also a possibility as these reactions are thermally allowed; however, this concerted pathway would produce a trans double bond in the 8-membered ring. Support for the diradical or stepwise process is found in the exclusive formation of cyclooctatriene **25** under photolysis (Table 1, entry e).

In conclusion, the use of the electron deficient diene **11** in the DAB strategy has led to the elucidation of a competing [2+2] cycloaddition reaction to give a cyclobutene **15** along with the normally observed [4+2] cycloaddition which leads to biaryl **14**. Heating of the cyclobutene **15** at elevated temperature results in the formation of biaryl **14** via a [1,3] sigmatropic carbon shift and a cyclooctatriene **25** resulting from opening of the highly strained bicycle. Variation of heat and light exposure led to changes in product distribution. On the basis of the findings described within, an alternate mechanism for biaryl formation in our DAB chemistry may be operable: namely, an initial [2+2] cycloaddition followed by [1,3] sigmatropic carbon shift. It is unclear at this juncture if this competitive [2+2] cycloaddition/[1,3] shift pathway is only accessible with electron deficient dienes such as **11** or is more broadly applied to electron rich dienes. Further detailed studies into the nature of our DAB strategy will be reported in due course.

Experimental Section

Biaryl 14 and Cyclobutene 15. To a pressure vessel containing acetylene **13** (105 mg, 0.564 mmol) was added diene **11** (234 mg, 1.69 mmol) and xylenes (1.1 mL) at rt. The mixture was heated at 140 °C for 6 h then allowed to cool to rt. The mixture was loaded directly onto silica gel and purified by chromatography over silica gel, eluting with 10% EtOAc/hexanes, and recrystallized from Et_2O/petroleum ether to give **14** (66.1 mg, 0.227 mmol, 40%) as a yellow crystalline solid and bicyclo[4.2.0]octadiene **15** (52.8 mg, 0.166 mmol, 29%) as a yellow crystalline solid. **Biaryl 14:** Mp 72−73 °C; IR (neat) 2958, 1722, 1528, 1350, 1264 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (dd, J = 7.8, 1.4 Hz, 1H), 8.00 (dd, J = 8.3,

(19) The molecular modelling program Spartan '06 was used to carry out the Density Functional B3LYP calculations. The 6-31G** basis set was chosen to perform the geometry optimization. Computations were performed with a Linux workstation running Spartan version '06.
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1.1 Hz, 1H), 7.75 (dd, $J = 8.0$, 1.1 Hz, 1H), 7.65 (td, $J = 7.5$, 1.4 Hz, 1H), 7.56 (td, $J = 7.8$, 1.4 Hz, 1H), 7.51 (t, $J = 8.2$ Hz, 1H), 7.19 (dd, $J = 7.6$, 1.0 Hz, 1H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 149.3, 136.6, 136.1, 135.4, 133.6, 132.6, 130.8, 129.7, 129.0, 128.7, 128.6, 122.5, 52.2; HRMS (CI^+) calcd for $C_{14}H_{11}NO_4Cl$ (M + H) 292.0377, found 292.0382. **Cyclobutene 15:** Mp 94−95 °C; IR (neat) 2928, 1711, 1532, 1435, 1368, 1250 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, $J = 8.2$, 1.2 Hz, 1H), 7.56 (dd, $J = 8.2$, 1.2 Hz, 1H), 7.33 (t, $J = 8.1$ Hz, 1H), 6.98 (dd, $J = 5.8$, 2.8 Hz, 1H), 6.51 (s, 1H), 4.06 (ddd, $J = 5.6$, 4.1, 1.4 Hz, 1H), 3.73 (s, 3H), 2.67−3.25 (m, 1H), 2.06−2.15 (m, 1H), 1.98−2.03 (m, 1H), 1.48 (dddd, $J = 12.3$, 9.6, 5.4, 4.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 150.5, 140.9, 137.7, 137.2, 135.1, 133.3, 133.28, 128.7, 127.0, 121.6, 51.7, 44.1, 39.7, 25.2, 20.8; HRMS (CI^+) calcd for $C_{16}H_{15}NO_4Cl$ (M +H) 320.06896, found 320.06881.

Biaryl 16. To a pressure vessel containing acetylene **13** (47.2 mg, 0.258 mmol) was added diene **5** (85.8 mg, 92.3 μL, 0.775 mmol) at rt. After heating at 140 °C for 2 h, the crude mixture was cooled to rt and purified by chromatography over silica gel, eluting with 10% EtOAc/hexanes to give biaryl **16** (56.0 mg, 0.212 mmol, 82%) as a crystalline solid. Mp 69−70 °C; IR (neat) 2944, 1530, 1358, 1261 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (dd, $J = 8.2$, 1.3 Hz, 1H), 7.73 (dd, $J = 8.0$, 1.2 Hz, 1H), 7.45 (t, $J = 8.1$ Hz, 1H), 7.44 (ddd, $J = 7.3$, 6.4, 1.7 Hz, 1H), 7.19 (dd, $J = 7.5$, 1.8 Hz, 1H), 7.07 (td, $J = 7.5$, 1.0 Hz, 1H), 7.00 (dd, $J = 8.4$, 1.0 Hz, 1H), 3.76 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.3, 151.1, 136.3, 133.6, 132.1, 130.4, 130.2, 128.7, 123.3, 122.3, 120.7, 111.0, 55.6; HRMS (CI^+) calcd for $C_{13}H_{10}NO_3Cl$ (M + H) 263.03492, found 263.03508.

Biaryl 19 and Cyclobutene 20. To a pressure vessel containing acetylene **18** (61.7 mg, 0.273 mmol) was added diene **11** (113 mg, 0.819 mmol) and xylenes (0.55 mL). After heating at 140 °C for 6 h, the mixture was cooled to rt, loaded directly onto silica gel, and purified via silica gel chromatography, eluting with 75−100% hexanes/PhMe to give biaryl **19** (33.0 mg, 0.0981 mmol, 36%) as a yellow oil and cyclobutene **20** (26.8 mg, 0.0737 mmol, 27%) as a yellow oil. **Biaryl 19:** IR (neat) 2952, 1723, 1528, 1434, 1350, 1265 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (dd, $J = 7.8$, 1.3 Hz, 1H), 8.03 (dd, $J = 8.2$, 1.2 Hz, 1H), 7.93 (dd, $J = 8.0$, 1.0 Hz, 1H), 7.64 (td, $J = 7.6$, 1.4 Hz, 1H), 7.56 (td, $J = 7.8$, 1.4 Hz, 1H), 7.42 (t, $J = 8.2$ Hz, 1H), 7.16 (dd, $J = 7.6$, 1.2 Hz, 1H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 149.2, 138.6, 137.8, 136.8, 132.6, 130.8, 129.7, 129.2, 128.9, 128.7, 125.5, 123.1, 52.2; HRMS (EI^+) calcd for $C_{14}H_{10}NO_4Br$ (M^+) 334.97931, found 334.97775. **Cyclobutene 20:** IR (neat) 2919, 1716, 1525, 1438, 1371, 1248 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, $J = 8.0$, 1.0 Hz, 1H), 7.61 (dd, $J = 8.1$, 1.1 Hz, 1H), 7.26 (t, $J = 8.0$ Hz, 1H), 6.97 (dd, $J = 5.8$, 2.8 Hz, 1H), 6.48 (s, 1H), 4.08 (t, $J = 4.0$ Hz, 1H), 3.73 (s, 3H), 3.23 (s, 1H), 2.69 (d, $J = 16$ Hz, 1H), 2.09−2.18 (m, 1H), 1.97−2.03 (m, 1H), 1.44−1.51 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 150.5, 140.7, 138.9, 137.6, 136.6, 133.3, 129.2, 129.0, 124.6, 122.2, 51.7, 44.2, 39.5, 25.2, 20.9; HRMS (EI^+) calcd for $C_{16}H_{14}NO_4Br$ (M + Na) 386.0004, found 386.0009.

Lactam 24. To a pressure vessel containing acetylene **21** (52.6 mg, 0.358 mmol) was added diene **11** (148 mg, 1.07 mmol) at rt. The mixture was heated at 140 °C for 6 h then allowed to cool to rt. The crude mixture was loaded directly on silica gel and purified by chromatography over silica gel, eluting with 10% EtOAc/hexanes, to give a mixture of two compounds as determined by crude ^{1}H NMR analysis that were consistent with biaryl **22** and cyclobutene **23**. To this mixture (0.358 mmol) was added Zn dust (117 mg, 1.79 mmol) and AcOH (1.79 mmol) at rt. After 30 min, the reaction was filtered over celite, eluting with EtOAc (20 mL). The organic phase was basified with saturated aq $NaHCO_3$ and washed with H_2O (15 mL) and saturated aq NaCl (15 mL). The dried extract ($MgSO_4$) was purified by chromatography over silica gel, eluting with 0−50% EtOAc/CH_2Cl_2, to give **24**[15] (35.2 mg, 0.180 mmol, 51%) as a white crystalline solid. ^{1}H NMR (400 MHz, d_6-DMSO) δ 11.7 (s, 1H), 8.52 (d, $J = 8.2$ Hz, 1H), 8.40 (d, $J = 7.8$ Hz, 1H), 8.34 (dd, $J = 7.4$, 1.3 Hz, 1H), 7.87 (td, $J = 7.2$, 1.4 Hz, 1H), 7.66 (td, $J = 8.0$, 1.1 Hz, 1H), 7.50 (td, $J = 8.3$, 1.2 Hz, 1H), 7.38 (d, $J = 8.1$, 1.0 Hz, 1H), 7.28 (td, $J = 8.2$, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 161.3, 137.0, 134.7, 133.3, 130.1, 128.4, 127.9, 126.2, 123.7, 123.1, 122.7, 118.0, 116.6.

Cyclooctatriene 25. To a pressure vessel containing cyclobutene **15** (16.9 mg, 0.0529 mmol) was added xylenes (0.2 mL). The solution was irradiated (120 W halogen bulb) with heating at 140 °C. After 40 h, the solution was cooled to rt and loaded directly onto silica gel. The reaction was purified by chromatography over silica gel, eluting with 10−20% EtOAc/hexanes to give cyclooctatriene **25** (14.0 mg, 0.0438 mmol, 83%) as a yellow solid. Mp 86−87 °C; IR (neat) 2952, 1711, 1532, 1434, 1357 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, $J = 8.2$, 1.2 Hz, 1H), 7.67 (dd, $J = 8.1$, 1.3 Hz, 1H), 7.22 (d, $J = 4.8$ Hz, 1H), 6.03 (dt, $J = 9.9$, 5.0 Hz, 1H), 5.78−5.83 (m, 2H), 3.80 (s, 3H), 2.65−2.91 (m, 2H), 2.61−2.66 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 150.6, 137.5, 136.4, 136.12, 136.11, 135.5, 135.3, 133.8, 128.8, 126.5, 124.9, 122.4, 52.0, 28.7, 25.7; HRMS (EI^+) calcd for $C_{16}H_{14}NO_4Cl$ (M^+) 319.06113, found 319.06050.

Biaryl 14 and Cyclooctatriene 25. Procedure A. To a pressure vessel was added cyclobutene **15** (174 mg, 0.544 mmol) and xylenes (1.09 mL) and the solution was heated at 160 °C for 6 h. The mixture was cooled to rt then purified by chromatography over silica gel, eluting with 5−10% EtOAc/hexanes, to give biaryl **14** (66.8 mg, 0.229 mmol, 42%) and cyclooctatriene **25** (65.2 mg, 0.204 mmol, 37%) as yellow crystalline solids.

Procedure B. To a pressure vessel was added cyclobutene **15** (48.3 mg, 0.151 mmol) and xylenes (0.30 mL). After heating at 160 °C for 6 h in the absence of light, the mixture was cooled to rt, loaded directly onto silica gel, and purified via silica gel chromatography, eluting with 5−10% EtOAc/hexanes to give biaryl **14** (20.7 mg, 0.0709 mmol, 47%) and cyclooctatriene **25** (12.6 mg, 0.0393 mmol, 26%).

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Supporting Information Available: ^{1}H and ^{13}C spectra for all new compounds and X-ray crystallographic data for compounds **15** (CCDC 686300) and **25** (CCDC 686299). This material is available free of charge via the Internet at http://pubs.acs.org.

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