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Ruthenium-Catalyzed Homo Diels−Alder [2 + 2 + 2] Cycloadditions of Alkynyl Phosphonates with Bicyclo[2.2.1]hepta-2,5-diene

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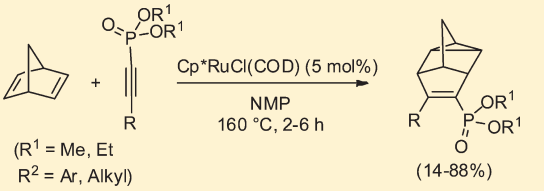
Supporting Information

ABSTRACT: Ruthenium-catalyzed homo Diels−Alder [2 + 2 + 2] cycloadditions between alkynyl phosphonates and bicyclo[2.2.1]hepta-2,5-diene were studied. The observed reactivity was found to be dependent on the presence of the phosphonate moiety. The Ru-catalyzed cycloaddition was compatible with a variety of aromatic and aliphatic substituted alkynyl phosphonates, providing the corresponding phosphonate substituted deltacyclenes in low to good yields (up to 88%).

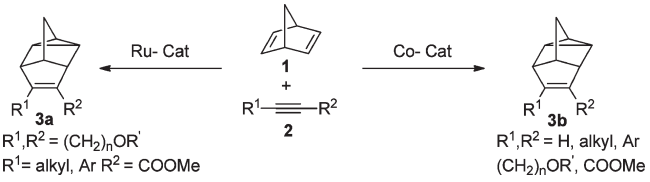


The homo-Diels−Alder (HDA) cycloaddition is described as [2 + 2 + 2] cycloaddition resulting in the formation of tetracyclic structures of considerable strain known as deltacyclanes. These reactions have been reported to occur both thermally and with transition-metal catalysis.[1] Typically, the HDA cycloaddition between bicyclic alkenes and alkynes has been explored en route to highly substituted fused polycyclic intermediates in natural product synthesis.[2] The use of transition metals to catalyze this reaction has been well documented, and cycloadditions involving alkynyl dienophiles have been promoted by cobalt,[3] cobalt−zinc,[4] and ruthenium[5] catalysts, Scheme 1. For example, using the Ru(II) catalyst (NBD)$RuCl_2(PPh_3)_2$, Tenaglia performed the HDA cycloaddition between norbornadiene and a variety of symmetrical and unsymmetrical disubstituted alkynes, and good yields at 90 °C for 5−60 h were achieved.[5a]

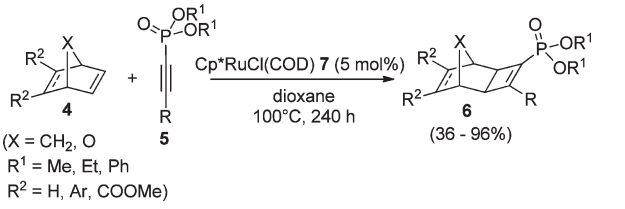
In the past decade our research group has extensively investigated ruthenium catalyzed [2 + 2] cycloadditions between bicyclic alkenes and a wide range of alkynes yielding a variety of cyclobutene adducts.[6,7] Recently we reported on [2 + 2] cycloadditions between bicyclic alkenes and electron deficient alkynyl phosphonates catalyzed by Cp*RuCl(COD), these substrates were found to be less reactive than other heteroatom containing alkynes, requiring relatively long reaction time and a higher reaction temperature, Scheme 2.[8]

To achieve a faster rate of reaction, optimization studies of the various reactions parameters were undertaken, including screening of a variety of solvents. When polar aprotic NMP was used as a solvent it was found that the expected [2 + 2] cycloadduct was not formed; instead, only the [2 + 2 + 2] HDA cycloadduct was observed. This is the first example of a homo-Diels−Alder cycloaddition involving alkynyl phosphonates and the only heteroatom-substituted alkyne other than silicon to undergo this mode of reaction.[3f,4a,4b] In this paper, we report our studies of the homo-Diels−Alder [2 + 2 + 2] cycloadditions between alkynyl phosphonates and bicyclo[2.2.1]hepta-2,5-diene (norbornadiene) catalyzed by Cp*RuCl(COD).

Scheme 1. Literature Examples of Transition-Metal-Catalyzed HDA Cycloaddition of Alkynes



Scheme 2. Ruthenium-Catalyzed [2 + 2] Cycloadditions between Bicyclic Alkenes and Alkynyl Phosphonates



Vinyl phosphonates have been found to be important biomolecules in metabolic processes, as anticancer and antiviral drugs, and as antibacterial and antifungal compounds.[9] The phosphonate group can also be modified by established procedures to a wide variety of other phosphorus groups including phosphines.[10] The selective fragmentation of homo-Diels−Alder cycloadducts into diquinanes is also well established.[2] The formation of a HDA cycloadduct containing a vinyl phosphonate is thus desirable, and investigations into the observed ruthenium catalyzed [2 + 2 + 2] HDA cycloaddition were further pursued.

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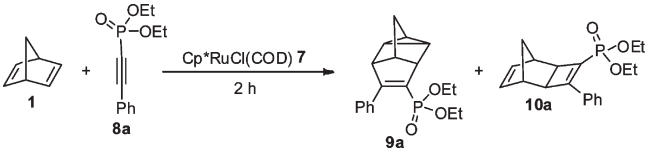
Table 1. Optimization of Solvent and Temperature for Ru-Catalyzed HDA [2 + 2 + 2] Cycloaddtions of Norbornadiene 1 with 1-Phenylethynyl Phosphonate 8a



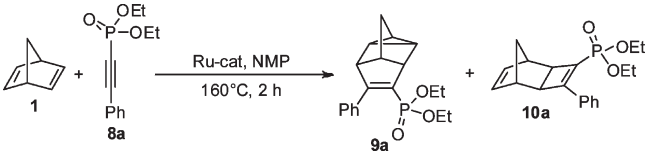
			yield[a] (%)	
entry	T (°C)	solvent	**9a**	**10a**
1	100	NMP	0[b]	0
2	150	NMP	70[b]	0
3	160	NMP	92	0
4	160	DMF	53	12
5	160	mesitylene	69	12
6	160	diglyme	0[b]	9
7	160	DMSO	0[c]	0
8	160	ethylene glycol	0[c]	0
9	100	dioxane	0	60[d]
10	100	neat	0	71[d]

[a] Yield by quantitative ^{31}P NMR with internal P(OMe)$_3$. [b] Starting alkyne observed in ^{31}P NMR spectrum. [c] Starting alkyne and decomposition of alkyne observed in ^{31}P NMR spectrum. [d] The reaction mixture was stirred for 240 h, see ref 8.

The observed HDA [2 + 2 + 2] cycloaddition between alkynyl phosphonate **8a**, synthesized by our previously reported method,[8] and norbornadiene **1** was optimized. The optimization experiments were performed with a 2 h reaction time and were monitored by ^{31}P NMP. Initially a series of solvents and temperatures were screened for their ability to promote the previously described HDA [2 + 2 + 2] cycloaddition, table 1. No evidence of any reaction was observed at temperatures below 100 °C; however, once the temperature was elevated to 150 °C the homo-Diels−Alder cycloadduct was observed, though some starting alkyne was still present (entries 1 and 2). The desired cycloadduct was achieved in 92% yield, and complete consumption of starting alkyne was observed at 160 °C with NMP (entry 3). To evaluate the effect of solvent, a variety of other high-boiling solvents were screened at 160 °C (entries 3−8). Both DMF and mesitylene yielded the HDA adduct **9a** in lower yields and reduced selectivity with the observation of 12% [2 + 2] adduct **10a** (entries 4 and 5). Diglyme, DMSO, and ethylene glycol (entries 6−8) were all noneffect. Using dioxane as solvent or running the reaction neat in norbornadiene **1**, only [2 + 2] cycloadduct **10a** was formed.[8] NMP was found to be the optimal solvent to promote the formation of homo-Diels−Alder adduct **9a** in high yield.

A variety of ruthenium catalysts were screened and the results are shown in table 2. Entry 2 shows that addition of silver triflate to Cp*RuCl(COD) (to generate a cationic active ruthenium species) greatly reduced the yield of HDA adduct **9a**. Another cationic Ru species examined (entry 3) was able to exclusively generate the desired HDA adduct **9a** in moderate yield but still was less effective than Ru catalyst **7**. Entry 4, a ruthenium dimer, achieved exclusive formation of the HDA adduct **9a**, however, in only 7% yield. Replacing the Cp* ligand of Ru catalyst **7** with Cp

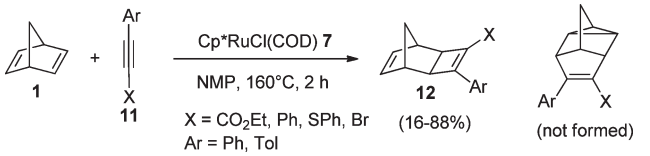
Table 2. Screening of Ruthenium Catalysts for HDA [2 + 2 + 2] Cycloaddtions of Norbornadiene 1 with 1-Phenylethynyl Phosphonate 8a



		yield[a] (%)	
entry	catalyst	**9a**	**10a**
1	Cp*RuCl(COD), **7**	92	0
2	Cp*RuCl(COD), AgOTf	5[b]	0
3	$[Cp^*Ru(CH_3CN)_3]^+ PF_6^-$	55[b]	0
4	$[RuCl_2(CO)_3]_2$	7[b]	0
5	CpRuCl(COD)	0[b]	25
6	$RuCl_2$(COD)	0[b]	8
7	$RuCl_2(PPh_3)_3$	0[c]	0
8	$CpRuCl(PPh_3)_2$	0[c]	0
9	no catalyst	0[c]	0

[a] Yield by quantitative ^{31}P NMR with internal P(OMe)$_3$. [b] Starting alkyne observed in the ^{31}P NMR spectrum. [c] Only starting alkyne observed in the ^{31}P NMR spectrum.

Scheme 3. Attempted Cycloadditions of Substituted Acetylenes without a Phosphonate Functionality



(entry 5) interestingly led to the observation of only [2 + 2] cycloadduct **10a** in 25%; similarly, replacing the Cp* ligand with Cl (entry 6) yielded **10a** as the sole adduct in 8%. The replacement of the COD ligand with phosphine (entries 7 and 8) eliminated reactivity toward either cycloadduct, and only unreacted starting alkyne was observed; these systems are most similar to the (NBD)$RuCl_2(PPh_3)_2$ catalyst used by Tenaglia for HDA reaction of disubstituted alkenes and norbornadiene.[5a] A control experiment with no catalyst was also conducted (entry 9), and only unreacted alkynyl phosphonate was observed.

After initial optimization studies, the reaction conditions were applied to other alkynes to demonstrate whether the phosphonate functionality was a necessity to achieve the observed HDA cycloaddition, Scheme 3. A quick screen of substituted acetylenes resulted in the exclusive formation of [2 + 2] cycloadducts,[8] suggesting that the HDA [2 + 2 + 2] cycloaddition is unique to the electronics of phosphonate-substituted alkynes when Cp*RuCl(COD) is used as the catalyst.

A variety of alkynyl phosphonates were prepared to better understand the electronic and steric factors influencing the observed ruthenium-catalyzed HDA [2 + 2 + 2] cycloadditions between alkynyl phosphonates and bicyclic alkenes. All alkynes

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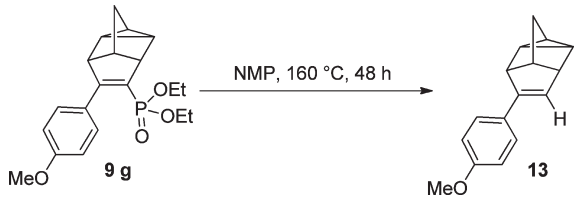
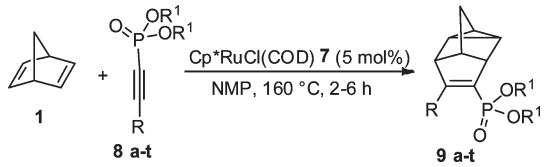
Scheme 4. Thermal Decomposition of Homo-Diels–Alder Cycloadduct 9g



were readily prepared from deprotonation of commercially available terminal alkynes using LDA or LHMDS followed by trapping the resulting carbanion with a chlorophosphonate.[8] The following examples of Ru-catalyzed HDA [2 + 2 + 2] cycloadditions of both aliphatic and aromatic substituted alkynyl phosphonates were heated for no longer than 6 h, even if not all starting alkynyl phosphonate had been consumed. It was found that prolonged heating could lead to decomposition of both the starting alkynyl phosphonate and the HDA adduct. The decomposition involved removal of the phosphonate moiety; this was observed most readily with alkyne **8g** (R = *p*-MeO-C_6H_4). A series of degradation studies in which alkyne **8g** and HDA cycloadduct **9g** were heated separately at 160 °C for 2 days both in the presence and absence of ruthenium catalyst **7** were carried out. In all cases, the alkynes and cycloadducts showed decomposition; the phosphonate-free HDA cycloadduct **13** was isolated from the decomposition of the HDA cycloadduct **9g**, Scheme 4. To confirm the observed degradation product **13** is from HDA cycloadduct **9g** and not produced by the HDA [2 + 2 + 2] cycloaddition of a degraded alkyne, the terminal acetylene analogue of alkynyl phosphonate **8g** was exposed to the optimized reaction conditions, and no reaction was observed. On the basis of these observations, reaction time was limited to no more than 6 h to limit any degradation of substrates.

Alkynyl phosphonates **8a**–**t** were subjected to optimal conditions in the presence of norbornadiene **1**, and the outcomes of the attempted cycloadditions are presented in Table 3. The first few substrates presented in Table 3 examine the effect of changing the substituents of the phosphonate moiety, R^1 (entries 1–3). Decreasing the size of R^1 led to a decreased yield and increased reaction time, and dimethyl phosphonate (R^1 = Me, entry 2) produced the desired HDA adduct **9b** in 73% over 4.5 h compared to 88% of **9a** in 2 h (R^1 = Et, entry 1). The effect of increasing steric bulk and replacing an aliphatic group with an aromatic functionality on the phosphonate is demonstrated by diphenyl phosphonate **8c** (R^1 = Ph, entry 3). The resulting cycloadduct of the diphenyl phosphonate **8c** was not the homo-Diels–Alder cycloadduct; instead, 24% of the corresponding [2 + 2] cycloadduct was isolated. The effects of alkyne substitution were examined with several examples of aromatic alkynyl phosphonates, and these were found to be compatible with the optimized reaction conditions. However, all reactions required increased reaction times and achieved lower yields than diethyl 1-phenylethynyl phosphonate, **8b** (entry 2). Examining the effects of aromatic substituents, a series *ortho*-, *meta*-, and *para*-substituted diethyl 1-phenylethynyl phosphonates were synthesized, including methyl-substituted (R = CH_3-C_6H_4, entries 4–6), methoxy-substituted (R = MeO-C_6H_4, entries 7–9), and trifluoromethyl-substituted (R = CF_3-C_6H_4, entries 10–12). The biggest degree of variation in yield within a series

Table 3. Ru-Catalyzed HDA [2 + 2 + 2] Cycloadditions of Norbornadiene 1 with Alkynyl Phosphonates 8a–s



entry	alkyne	R^1	R	time (h)	yield[a] (%)
1	**8a**	Et	Ph	2	88
2	**8b**	Me	Ph	4.5	73
3	**8c**	Ph	Ph	2	0 (24)[b]
4	**8d**	Et	*p*-Tol	5	60
5	**8e**	Et	*m*-Tol	6	37
6	**8f**	Et	*o*-Tol	5	71
7	**8g**	Et	*p*-MeO-C_6H_4	5	64
8	**8h**	Et	*m*-MeO-C_6H_4	5	74
9	**8i**	Et	*o*-MeO-C_6H_4	4.5	61
10	**8j**	Et	*p*-CF_3-C_6H_4	5	57
11	**8k**	Et	*m*-CF_3-C_6H_4	5	57
12	**8l**	Et	*o*- CF_3-C_6H_4	5	53
13	**8m**	Et	3-thiophene	4	48
14	**8n**	Et	H	5.5	0 (29)[b]
15	**8o**	Et	^{n}Bu	6	64
16	**8p**	Et	Cy	5	36
17	**8q**	Et	^{t}Bu	6	14[c]
18	**8r**	Et	CH_2OH	4	0 (15)[b]
19	**8s**	Et	CH_2CH_2OH	5	0[d]

[a] Yield of isolated cycloadduct after column chromatography. [b] Isolated yield of [2 + 2] adduct; no HDA cycloadduct observed. [c] Cycloadduct isolated as inseparable mixture with unreacted alkyne. [d] No reaction was observed.

was seen with the methyl-substituted compounds **8d**–**f**. Substitution at the *para* position produced a 60% yield (entry 4), a *meta* methyl group yielded only 37% isolated product (entry 5), and an *ortho* substituent gave a good yield of 71% (entry 6). These are interesting results compared to our previous studies of the [2 + 2] cycloadditions between alkynyl phosphonates and bicyclic alkenes in which it was observed that a *p*-methyl substituent produced an 83% yield, whereas an *o*-methyl substituent gave a much lower yield of 8%.[8] Methoxy-substituted phenylethynyl phosphonates **8g**–**i** (entries 7–9) gave comparable yields as the methyl-substituted substrates **8d**–**f**; however, the relative reactivity of *ortho, meta, para* substitution appears to follow an opposite trend. The highest yield was observed with a *m*-methoxy substituent (74%, entry 8), the *para* (entry 7) and *ortho* (entry 9) gave slightly lower yields of 64% and 61%, respectively. Finally, the effects of a strong electron-withdrawing group, trifluoromethyl, on the phenylethynyl phosphonate were examined. Yields were comparable but in general slightly lower than was observed for both methyl and methoxy substituents; furthermore, the location of substitution had minimal effect on the observed reactivity. Yields of 57%, 57%, and 53% were achieved with *p*-, *m*-, and *o*-trifluoromethyl-substituted phenylethynyl phosphonates **8j**–**l** (entries 10–12), respectively. A heteroatom-containing aromatic alkynyl phosphonate **8m** was synthesized and subjected to the HDA cycloaddition conditions

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(R = 3-thiophene, entry 13). Diethyl 3-thiophene-ylethynyl phosphonate **8m** underwent the desired HDA [2 + 2 + 2] cycloaddition with norbornadiene in moderate yield, 48%; in our [2 + 2] studies, this alkynyl phosphonate also showed reduced reactivity relative to phenyl-substituted alkynyl phosphonates as well.[8]

With a number of aromatic substituted alkynyl phosphonates found to be compatible with the optimized reaction conditions, a variety of aliphatic substrates were prepared to further expand the scope of the reaction. Terminal diethyl ethynyl phosphonate **8n** (R = H, entry 14) was found to exclusively produce the [2 + 2] cycloadduct in 29%; this demonstrates an important difference from the cobalt catalyzed HDA [2 + 2 + 2] cycloadditions between alkynes and bicyclic alkenes, developed by Lautens, which demonstrated high yields of HDA adducts from terminal alkynes.[3f] Alkynyl phosphonates **8o**−**q** are representative of aliphatic substituents possessing primary, secondary, and tertiary carbons at the propargylic position of the alkynyl phosphonates (entries 15−17). The highest yield was obtained with a primary aliphatic group **8o** (R = ^{n}Bu, entry 15), 64%, which was comparable to the substituted aromatics (entries 3−12) but still less than diethyl 1-phenylethynyl phosphonate **8a** (entry 1). Increasing substitution of the aliphatic center to a secondary carbon **8p** (R = Cy, entry 16) lowered the yield to 36%; in contrast, during our [2 + 2] studies this alkynyl phosphonate did not proceed to react at all, whereas the primary alkynyl phosphonate (R = ^{n}Bu) provided a moderate yield of the respective cycloadduct.[8] Continuing with this trend, a tertiary alkynyl phosphonate **8q** (R = ^{t}Bu, entry 17) was found also to exclusively undergo the HDA [2 + 2 + 2] cycloaddition, though the highest yield achieved was only 14%. Furthermore, the product could not be separated from unreacted starting alkynyl phosphonate, and attempts to consume all alkyne through prolonged heating or adjusting reactant equivalents were unsuccessful. The observed trend of decreasing reactivity with increasing propargylic substitution was also observed in studies of cobalt-catalyzed HDA [2 + 2 + 2] cycloadditions between norbornadiene and acetylenes.[3b]

Finally, the reaction conditions were applied to alkynyl phosphonates containing propargylic and homopropargylic alcohols **8r,s** (entries 18,19). These substrates were found to be quite incompatible with the optimized reaction conditions; for example, propargylic alcohol **8r** gave the [2 + 2] cycloadduct exclusively in 15% yield (entry 18). Increasing the chain length by a carbon to produce homopropargylic alkynyl phosphonate **8r** gave no evidence of reaction by ^{31}P NMR (entry 19).

In conclusion, we have demonstrated the first examples of ruthenium-catalyzed homo-Diels−Alder [2 + 2 + 2] cycloadditions between alkynyl phosphonates and bicyclic alkenes. The reaction was found to be dependent on the phosphonate present; dimethyl and diethyl phosphonates underwent the desired HDA cycloaddition, whereas diphenyl phosphonates only achieved the [2 + 2] mode of cycloaddition. Furthermore, our reaction conditions were compatible with a variety of aromatic and aliphatic substituents in low to good yields. Investigations with substituted bicyclic alkenes in addition to the exploration of the intramolecular variant of this reaction are currently underway in our laboratory. Finally, exploration of cyclopropane ring-openings toward phosphonate substituted deltacyclenes could further enhance the scope and applicability of this reaction.

EXPERIMENTAL SECTION

General Information. All reactions were carried out in an atmosphere of dry nitrogen or argon. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a 400 MHz spectrometer. Chemical shifts for ^{31}P NMR spectra are reported in parts per million (ppm) from phosphoric acid with trimethylphosphite as the external standard (trimethylphosphite: δ 141.0 ppm). Alkynyl phosphonates **8a**−**t** were prepared by our previously reported method.[8]

General Procedure for Ruthenium-Catalyzed Homo-Diels−Alder [2 + 2 + 2] Cycloadditions with Norbornadiene (Table 3, Entry 1). A mixture of alkynyl phosphonate **8a** (46.2 mg, 0.194 mmol) and norbornadiene (61.7 mg, 0.700 mmol) was prepared in an oven-dried screw-cap vial. The vial was purged with nitrogen and taken into the drybox where Cp*RuCl(COD) (4.8 mg, 0.013 mmol) and NMP (0.8 mL) were added, and the vial was sealed. The reaction mixture was stirred outside the glovebox at 160 °C for 2−6 h. The crude product was purified by flash chromatography to yield the corresponding cycloadduct (ethyl acetate/hexanes mixture).

Deltacyclene 9a (Table 3, Entry 1). The crude product was purified by column chromatography (EtOAc/hexanes 1:1) to provide cycloadduct **9a** (56.6 mg, 0.171 mmol, 88%) as a yellow oil: R_f 0.15 (EtOAc/hexanes 1:1); IR (CH_2Cl_2, NaCl) 2974 (m), 2931 (m), 1492 (w), 1266 (m), 1164 (w), 1029 (s), 964 (m), 738(m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.55−7.53 (m, 2H), 7.36−7.28 (m, 3H), 4.00−3.84 (m, 4H), 3.11 (br d, 1H, J = 1.4 Hz), 3.01 (br d, 1H, J = 1.4 Hz), 2.26 (s, 1H), 1.81 (td, 1H, J = 4.7, 1.0 Hz), 1.64−1.59 (m, 4H), 1.15 (t, 3H, J = 7.1 Hz), 1.10 (t, 3H, J = 7.1 Hz); ^{13}C NMR (APT, $CDCl_3$,100 MHz) δ 163.0 (d, J = 10.7 Hz), 136.3 (d, J = 4.3 Hz), 128.3 (d, J = 193.6 Hz), 128.2, 128.1, 127.8, 61.4 (d, J = 5.8 Hz), 61.2 (d, J = 5.5 Hz), 56.3, 56.1, 53.4 (d, J = 11.8 Hz), 32.6, 25.7, 23.8, 23.3 (d, J = 3.4 Hz), 16.1 (m, 2C); ^{31}P NMR ($CDCl_3$, 160 MHz) δ 17.36; HRMS (EI) calcd [M$^+$] for $C_{19}H_{23}O_3P$ m/z 330.1385, found 330.1391.

Deltacyclene 9b (Table 3, Entry 2). The crude product was purified by column chromatography (EtOAc/hexanes 1:1) to provide cycloadduct **9b** (45.9 mg, 0.152 mmol, 73%) as a pale yellow crystalline solid: R_f 0.14 (EtOAc/hexanes 1:1); IR (CH_2Cl_2, NaCl) 2951 (m), 1491 (w), 1244 (m), 1182 (w), 1030 (s), 944 (m), 766 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.55−7.53 (m, 2H), 7.36−7.30 (m, 3H), 3.58 (d, 3H, J = 11.2 Hz), 3.51 (d, 3H, J = 11.3 Hz) 3.09 (br d, 1H, J = 1.5 Hz), 3.02 (br d, 1H, J = 1.5 Hz), 2.27 (s, 1H), 1.82 (td, 1H, J = 4.7, 1.2 Hz), 1.64−1.60 (m, 4H); ^{13}C NMR (APT, $CDCl_3$, 100 MHz) δ 163.9 (d, J = 10.8 Hz), 136.1 (d, J = 4.1 Hz), 128.4, 127.9, 127.8, 127.0 (d, J = 194.7 Hz), 56.3 (d, J = 6.5 hz), 56.1, 53.3 (d, J = 11.6 Hz), 52.1 (d, J = 5.8 Hz), 51.8 (d, J = 5.6 Hz), 32.6, 25.7, 23.7, 23.3 (d, J = 3.4 Hz); ^{31}P NMR ($CDCl_3$, 160 MHz) δ 20.37; HRMS (EI) calcd [M$^+$] for $C_{17}H_{19}O_3P$ m/z 302.1072, found 302.1071.

Cycloadduct 10c (Table 3, Entry 3). The crude product was purified by column chromatography (EtOAc/hexanes 1:1) to provide cycloadduct **10c** (19.4 mg, 0.046 mmol, 24%) as a pale brown solid: R_f 0.64 (EtOAc/hexanes 1:1); IR (CH_2Cl_2, NaCl) 3060 (m), 2976 (m), 2937 (m), 1591 (s), 1489 (s), 1189 (s), 1071 (m), 966 (s), 738 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.96 (dd, 2H, J = 7.9, 2.4 Hz), 7.44−7.19 (m, 11H), 7.16−7.12 (m, 2H), 6.19 (br t, 2H, J = 1.64 Hz), 2.83−2.81 (m, 1H), 2.71 (br d, 2H, J = 1.52 Hz), 2.57 (d, 1H, J = 3.72 Hz), 1.33 (d, 1H, J = 9.6 Hz), 1.27 (d, 1H, J = 10.1 Hz); ^{13}C NMR (APT, $CDCl_3$,100 MHz) δ 164.6, 150.5 (d, J = 4.8 Hz), 150.3 (d, J = 4.8 Hz), 136.1, 135.4, 132.1, 130.3, 129.8 (2), 129.7, 128.6, 128.2, 126.5 (d, J = 181.9 Hz), 125.0 (d, J = 5.0 Hz), 120.6 (d, J = 4.5 Hz), 120.4 (d, J = 4.8 Hz), 45.6 (d, J = 33.3 Hz), 43.8 (d, J = 9.63 Hz), 39.7, 39.3, 39.1; ^{31}P NMR ($CDCl_3$, 160 MHz) δ 3.11 HRMS (EI) m/z calcd for $C_{27}H_{23}O_3P$ [M$^+$] 426.1385, found 426.1391.

Deltacyclene 9d (Table 3, Entry 4). The crude product was purified by column chromatography (EtOAc/hexanes 1:1) to provide cycloadduct **9d** (38.9 mg, 0.113 mmol, 60%) as an amber-yellow oil: R_f 0.27 (EtOAc/hexanes 3:2); IR (CH_2Cl_2, NaCl) 2954 (m), 2925 (m), 1492 (w), 1244 (m), 1026 (s), 961 (m), 765 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.54 (d, 2H, J = 8.1 Hz), 7.14 (d, 2H, J = 7.9 Hz),

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4.01−3.85 (m, 4H), 3.09 (br d, 1H, J = 1.8 Hz), 3.00 (s, 1H), 2.34 (s, 3H), 2.24 (s, 1H), 1.80 (td, 1H, J = 4.7, 1.0 Hz), 1.63−1.57 (m, 4H), 1.17 (t, 3H, J = 7.1 Hz), 1.12 (t, 3H, J = 7.1 Hz); ^{13}C NMR (APT, $CDCl_3$,100 MHz) δ 163.1 (d, J = 10.9 Hz), 138.2, 133.3 (d, J = 4.4 Hz), 128.4, 128.0 (d, J = 1.3 Hz), 127.2 (d, J = 193.7 Hz), 61.3 (d, J = 5.4 Hz), 61.1 (d, J = 5.4 Hz), 56.1 (d, J = 12.7 Hz), 56.0 (d, J = 2.6 Hz), 53.3 (d, J = 12.0 Hz), 32.6, 25.5, 23.7, 23.1 (d, J = 3.5 Hz), 21.2, 16.1 (t, 2C, J = 6.7 Hz); ^{31}P NMR ($CDCl_3$, 160 MHz) δ 17.662 Hz; HRMS (EI) calcd [M^+] for $C_{20}H_{25}O_3P$ m/z 344.1541, found 344.1549.

Deltacyclene 9e (Table 3, Entry 5). The crude product was purified by column chromatography (EtOAc/hexanes 1:1) to provide cycloadduct **9e** (26.6 mg, 0.077 mmol, 37%) as an amber-yellow oil: R_f 0.26 (EtOAc/hexanes 3:2); IR (CH_2Cl_2, NaCl) 2980 (m), 2929 (m), 1481 (w), 1238 (m), 1027 (s), 962 (s), 788 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.34 (br s, 2H), 7.22 (t, 1H, J = 7.7 Hz), 7.10 (d, 1H, J = 7.6 Hz), 4.01−3.85 (m, 4H), 3.09 (br d, 1H, J = 1.3 Hz), 2.99 (s, 1H), 2.35 (s, 3H), 2.24 (s, 1H), 1.80 (br td, 1H, J = 3.5 Hz, 0.9 Hz), 1.63−1.59 (m, 4H), 1.15 (t, 3H, J = 7.1 Hz), 1.11 (t, 3H, J = 7.1 Hz); ^{13}C NMR (APT, $CDCl_3$,100 MHz) δ 163.2 (d, J = 10.8 Hz), 137.2, 136.2 (d, J = 4.3 Hz), 128.9, 128.7 (d, J = 1.3 Hz), 127.7, 127.0, 125.2 (d, J = 1.3 Hz), 61.4 (d, J = 5.8 Hz), 61.1 (d, J = 5.7 Hz), 56.2 (d, J = 8.1 Hz), 56.1 (d, J = 1.4 Hz), 53.3 (d, J = 12.0 Hz), 32.6, 25.6, 23.7, 23.2 (d, J = 3.5 Hz), 21.3, 16.1 (t, 2C, J = 6.7 Hz); ^{31}P NMR ($CDCl_3$, 160 MHz) δ 17.890; HRMS (EI) calcd [M^+] for $C_{20}H_{25}O_3P$ m/z 344.1541, found 344.1549.

Deltacyclene 9f (Table 3, Entry 6). The crude product was purified by column chromatography (EtOAc/hexanes 1:1) to provide cycloadduct **9f** (45.6 mg, 0.132 mmol, 71%) as an amber-yellow oil: R_f 0.27 (EtOAc/hexanes 3:2); IR (CH_2Cl_2, NaCl) 2980 (m), 2930 (m), 1484 (w), 1236 (m), 1028 (s), 963 (s), 735 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.21−7.09 (m, 4H), 3.93−3.65 (m, 4H), 3.08 (d, 1H, J = 1.9 Hz), 2.80 (d, 1H, J = 2.1 Hz), 2.35 (s, 1H), 2.30 (s, 3H), 1.80 (br td, 1H, J = 4.7, 1.2 Hz), 1.68−1.52 (m, 4H), 1.09 (t, 3H, J = 7.0 Hz), 1.05 (t, 3H, J = 7.1 Hz); ^{13}C NMR (APT, $CDCl_3$,100 MHz) δ 163.6 (d, J = 10.6 Hz), 137.4, 135.2, 130.8 (d, J = 194.5 Hz), 129.6, 128.2, 127.6, 125.1, 61.2 (d, 2C, J = 5.9 Hz), 57.4 (m), 56.9 (m), 52.6 (d, J = 12.9 Hz), 32.5, 25.5, 23.4, 22.7 (d, J = 3.56 Hz), 20.1, 16.0 (m, 2C); ^{31}P NMR ($CDCl_3$, 160 MHz) δ 17.079; HRMS (EI) calcd [M^+] for $C_{20}H_{25}O_3P$ m/z 344.1541, found 344.1549.

Deltacyclene 9g (Table 3, Entry 7). The crude product was purified by column chromatography (EtOAc/hexanes 1:1) to provide cycloadduct **9g** (53.0 mg, 0.148 mmol, 64%) as a yellow oil: R_f 0.33 (EtOAc/hexanes 3:2); IR (CH_2Cl_2, NaCl) 2983 (s), 2925 (m), 1608 (m), 1508 (s), 1443 (w), 1266 (s), 1032 (s), 962 (s), 742 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.55−7.52 (m, 2H), 6.88−6.85 (m, 2H), 4.02−3.87 (m, 4H), 3.81 (s, 3H), 3.08 (br d, 1H, J = 1.9 Hz), 3.00 (br d, 1H, J = 1.9 Hz), 2.22 (s, 1H), 1.78 (td, 1H, J = 4.7, 1.1 Hz), 1.62−1.53 (m, 4H), 1.18 (t, 3H, J = 7.1 Hz), 1.14 (t, 3H, J = 7.1 Hz); ^{13}C NMR (APT, $CDCl_3$,100 MHz) δ 162.7 (d, J = 11.0 Hz), 159.7, 129.7, 128.7 (d, J = 4.4 Hz), 126.0 (d, J = 193.9 Hz), 113.2, 61.4 (d, J = 5.5 Hz), 61.1 (d, J = 5.4 Hz), 56.1−55.9 (m, 2C), 55.3, 53.4 (d, J = 11.8 Hz), 32.7, 25.4, 23.8, 23.0 (d, J = 3.4 Hz), 16.2 (t, 2C, J = 6.7 Hz); ^{31}P NMR ($CDCl_3$, 160 MHz) δ 18.335; HRMS (EI) calcd [M^+] for $C_{20}H_{25}O_4P$ m/z 360.1490, found 360.1501.

Deltacyclene 9h (Table 3, Entry 8). The crude product was purified by column chromatography (EtOAc/hexanes 1:1) to provide cycloadduct **9h** (51.9 mg, 0.144 mmol, 74%) as a yellow oil: R_f 0.34 (EtOAc/hexanes 3:2); IR (CH_2Cl_2, NaCl) 2980 (s), 2932 (s), 1600 (m), 1488 (m), 1243 (s), 1162 (m), 1027 (s), 964 (s), 789 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.30−7.24 (m, 2H), 7.14 (d, 1H, J = 7.6 Hz), 6.88 (dd, 1H, J = 2.0, 8.2 Hz), 4.06−3.90 (m, 4H), 3.87 (s, 3H), 3.14 (s, 1H), 3.05 (s, 1H), 2.29 (s, 1H), 1.85 (br t, 1H, J = 4.2 Hz), 1.67−1.62 (m, 4H), 1.21 (t, 3H, J = 7.1 Hz), 1.15 (t, 3H, J = 7.1 Hz); ^{13}C NMR (APT, $CDCl_3$,100 MHz) δ 162.9 (d, J = 10.6 Hz), 159.1, 137.6 (d, J = 4.2 Hz), 128.8, 128.5 (d, J = 193.4 Hz), 120.4, 114.5, 113.4 (d, J = 6.7 Hz), 61.5 (d, J = 5.8 Hz), 61.2 (d, J = 5.5 Hz), 56.2, 56.1, 55.3 (d, J = 8.6 Hz), 53.6 (d, J = 11.6 Hz) 32.7, 25.7, 23.8, 23.3 (d, J = 3.4 Hz), 16.2 (m, 2C); ^{31}P NMR ($CDCl_3$, 160 MHz) δ 17.753; HRMS (EI) calcd [M^+] for $C_{20}H_{25}O_4P$ m/z 360.1490, found 360.1497.

Deltacyclene 9i (Table 3, Entry 9). The crude product was purified by column chromatography (EtOAc/hexanes 1:1) to provide cycloadduct **9i** (41.3 mg, 0.115 mmol, 61%) as a yellow oil: R_f 0.22 (EtOAc/hexanes 3:2); IR (CH_2Cl_2, NaCl) 2978 (m), 2931 (m), 1587 (w), 1486 (w), 1246 (s), 1164 (w), 1028 (s), 962 (m), 753 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.34 (dd, 1H, J = 7.5, 1.7 Hz), 7.28−7.24 (m, 1H), 6.91 (td, 1H, J = 7.5, 0.9 Hz), 6.86 (d, 1H, J = 8.2 Hz), 3.96−3.78 (m, 7H), 3.03 (br d, 1H, J = 1.8 Hz), 2.92 (br d, 1H, J = 2.0 Hz), 2.24 (s, 1H), 1.74 (td, 1H, J = 4.7, 1.1 Hz), 1.64−1.56 (m, 4H), 1.11 (t, 3H, J = 7.1 Hz), 1.06 (t, 3H, J = 7.0 Hz); ^{13}C NMR (APT, $CDCl_3$,100 MHz) δ 162.2 (d, J = 10.0 Hz), 156.5, 130.9, 129.6 (d, J = 195.3 Hz), 129.4, 126.2 (d, J = 4.0 Hz), 120.0, 110.2, 61.3 (d, J = 5.8 Hz), 61.0 (d, J = 5.5 Hz), 56.7−56.1 (m, 2C), 55.2 (d, J = 8.9 Hz), 52.1 (d, J = 12.4 Hz), 32.7, 25.1, 23.4, 23.0 (d, J = 3.4 Hz), 16.1 (d, 2C, J = 3.4 Hz); ^{31}P NMR ($CDCl_3$, 160 MHz) δ 17.717; HRMS (EI) calcd [M^+] for $C_{20}H_{25}O_4P$ m/z 360.1490, found 360.1502.

Deltacyclene 9j (Table 3, Entry 10). The crude product was purified by column chromatography (EtOAc/hexanes 1:1) to provide cycloadduct **9j** (42.1 mg, 0.106 mmol, 57%) as a light amber oil: R_f 0.33 (EtOAc/hexanes 3:2); IR (CH_2Cl_2, NaCl) 2982 (m), 2942 (m), 1445 (w), 1325 (s), 1243 (m), 1025 (s), 963 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.64 (d, 2H, J = 8.3 Hz), 7.58 (d, 2H, J = 8.3 Hz), 4.04−3.83 (m, 4H), 3.12 (br d, 1H, J = 1.4 Hz), 3.00 (s, 1H), 2.28 (s, 1H), 1.85 (td, 1H, J = 4.7, 1.1 Hz), 1.65−1.61 (m, 4H), 1.18 (t, 3H, J = 7.0 Hz), 1.13 (t, 3H, J = 7.1 Hz); ^{13}C NMR (APT, $CDCl_3$,100 MHz) δ 161.3 (d, J = 10.4 Hz), 139.9, 131.0 (d, J = 193.1 Hz), 129.8, 128.4 (d, J = 1.7 Hz), 124.7 (q, J = 3.8 Hz), 124.1 (d, J = 272.0 Hz) 61.6 (d, J = 5.1 Hz), 61.4 (d, J = 5.5 Hz), 56.5 (d, J = 7.2 Hz), 56.2 (d, J = 16.8 Hz), 53.6 (d, J = 11.4 Hz), 32.6, 26.0, 23.9, 23.4 (d, J = 3.4 Hz), 16.2 (t, 2C, J = 7.0 Hz); ^{31}P NMR ($CDCl_3$, 160 MHz) δ 16.54; HRMS (EI) calcd [M^+] for $C_{20}H_{22}O_3F_3P$ m/z 398.1259, found 398.1250.

Deltacyclene 9k (Table 3, Entry 11). The crude product was purified by column chromatography (EtOAc/hexanes 1:1) to provide cycloadduct **9k** (44.3 mg, 0.111 mmol, 57%) as a light amber oil: R_f 0.28 (EtOAc/hexanes 3:2); IR (CH_2Cl_2, NaCl) 2982 (m), 2942 (m), 1445 (w), 1325 (s), 1243 (m), 1025 (s), 963 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.76−7.74 (m, 2H), 7.54 (d, 1H, J = 7.9 Hz), 7.46 (t, 1H, J = 7.7 Hz), 4.03−3.89 (m, 4H), 3.13 (br d, 1H, J = 1.4 Hz), 3.01 (br s, 1H), 2.29 (s, 1H), 1.85 (td, 1H, J = 3.7, 0.9 Hz), 1.66−1.62 (m, 4H), 1.15 (q, 6H, J = 7.0 Hz); ^{13}C NMR (APT, $CDCl_3$,100 MHz) δ 161.1, 137.0 (d, J = 4.3 Hz), 131.5, 130.7 (d, J = 197.0 Hz), 128.3 (2), 124.7 (m, 2C), 124.2, 61.5 (d, J = 5.7 Hz), 61.3 (d, J = 5.7 Hz), 56.5 (d, J =7.2 Hz), 56.1 (d, J = 16.7 Hz), 53.5 (d, J = 11.5 Hz), 32.6, 25.1, 23.8, 23.4, 16.0 (m, 2C); ^{31}P NMR ($CDCl_3$, 160 MHz) δ 16.66; HRMS (EI) calcd [M^+] for $C_{20}H_{22}O_3F_3P$ m/z 398.1259, found 398.1255.

Deltacyclene 9l (Table 3, Entry 12). The crude product was purified by column chromatography (EtOAc/hexanes 7:3) to provide cycloadduct **9l** (40.8 mg, 0.102 mmol, 53%) as a light amber oil: R_f 0.29 (EtOAc/hexanes 3:2); IR (CH_2Cl_2, NaCl) 2984 (m), 2933 (m), 1446 (w), 1317 (s), 1264 (m), 1034 (m), 962 (m), 734 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.65 (d, 1H, J = 7.8 Hz), 7.48 (t, 1H, J = 7.3 Hz), 7.39 (t, 1H, J = 7.6 Hz), 7.21 (d, 1H, J = 7.5 Hz), 3.94−3.73 (m, 4H), 3.04 (br d, 1H, J = 1.7 Hz), 2.85 (s, 1H), 2.38 (s, 1H), 1.81 (br t, 1H, J = 4.3 Hz), 1.66−1.45 (m, 4H), 1.11 (t, 3H, J = 7.0 Hz), 1.02 (t, 3H, J = 7.0 Hz); ^{13}C NMR (APT, $CDCl_3$,100 MHz) δ 161.1, 136.6, 132.4 (d, J = 196.0 Hz), 131.1, 128.3, 127.2, 125.9 (2), 124.2 (d, J = 273.8 Hz), 61.2 (d, J = 5.8 Hz), 61.1 (d, J = 6.0 Hz), 57.8 (m, 2C), 51.7 (d, J = 12.7 Hz), 32.4, 25.8, 23.4, 22.6 (d, J = 3.5 Hz), 16.1 (m, 2C); ^{31}P NMR ($CDCl_3$, 160 MHz) δ 15.80; HRMS (EI) calcd [M^+] for $C_{20}H_{22}O_3F_3P$ m/z 398.1259, found 398.1267.

Deltacyclene 9m (Table 3, Entry 13). The crude product was purified by column chromatography (EtOAc/hexanes 7:3) to provide cycloadduct **9m** (43.7 mg, 0.130 mmol, 48%) as a yellow crystalline solid: R_f 0.28 (EtOAc/hexanes 7:3); IR (CH_2Cl_2, NaCl) 3054 (m), 2985 (m), 1492 (w), 1265 (s), 1164 (w), 1025 (s), 966 (m), 738 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.68 (br d, 1H, J = 1.96 Hz), 7.50 (dd, 1H, J = 1.04, 5.08 Hz), 7.21−7.19 (1H, m), 4.03−3.86 (m, 4H), 3.02 (s, 2H), 2.14 (s, 1H), 1.72 (br t, 1H, J = 4.66 Hz), 1.57 (s, 2H), 1.52 (br t, 1H, J = 4.56 Hz), 1.46 (br t, 1H, J = 4.65 Hz), 1.16 (dt, 6H, J = 7.04, 11.3 Hz); ^{13}C NMR (APT, $CDCl_3$,100 MHz) δ 160.6, 131.7 (d, J = 196.2 Hz), 128.6, 128.3, 125.5, 124.9, 61.4 (d, J = 5.4 Hz), 61.3 (d, J = 5.4 Hz), 55.9, 55.7 (m), 53.4 (d, J = 11.4 Hz), 32.7, 25.3, 24.1, 22.6, 16.2 (m, 2C); ^{31}P NMR ($CDCl_3$, 160 MHz) δ 18.04; HRMS (EI) calcd [M^+] for $C_{17}H_{21}O_3PS$ m/z 336.0949, found 336.0939.

Cycloadduct 10n (Table 3, Entry 14). The crude product was purified by column chromatography (EtOAc/hexanes 7:3) to provide cycloadduct **10n** (28.4 mg, 0.123 mmol, 29%) as a pale yellow oil: R_f 0.23 (EtOAc/hexanes 7:3); IR (CH_2Cl_2, NaCl) 3053(m), 2983 (m), 1448(w), 1264 (s), 1026 (s), 968 (m), 896 (w), 738 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.06 (d, 1H, J = 4.6 Hz), 6.13 (t, 2H, J = 5.5 Hz), 4.09 (dquin, 4H, J = 2.5, 7.2 Hz), 2.59 (s, 2H), 2.48−2.46(m, 2H), 1.45 (d, 1H, J = 9.2 Hz), 1.36 (s, 1H), 1.33 (t, 6H, J = 7.1 Hz); ^{13}C NMR (APT, $CDCl_3$,100 MHz) δ 153.8 (d, J = 7.4 Hz), 140.5 (d, J= 180.3 Hz), 135.9, 135.5, 61.7 (t, 2C, J = 5.3 Hz), 46.7 (d, J = 9.5 Hz), 46.1 (d, J = 31.8 Hz), 39.5, 38.4, 38.1, 16.5 (dd, 2C, J = 2.4, 6.3 Hz); ^{31}P NMR ($CDCl_3$, 160 MHz) δ 9.843; HRMS (EI) calcd [M^+] for $C_{13}H_{19}O_3P$ m/z 254.1072, found 254.1066.

Deltacyclene 9o (Table 3, Entry 15). The crude product was purified by column chromatography (EtOAc/hexanes 7:3) to provide cycloadduct **9o** (43.7 mg, 0.141 mmol, 64%) as a light yellow oil: R_f 0.40 (EtOAc/hexanes 7:3); IR (CH_2Cl_2, NaCl) 2963(m), 2930 (m), 1445 (w), 1243 (m), 1057 (s), 1029 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 4.07−3.93 (m, 4H), 2.78 (br d, 1H, J = 1.52 Hz), 2.62 (br d, 1H, J = 1.92 Hz), 2.60−2.45 (m, 2H), 1.99 (s, 1H), 1.67 (td, 1H, J = 4.6, 0.8 Hz), 1.56−1.50 (m, 2H), 1.47−1.39 (m, 2H), 1.37−1.32 (m, 4H), 1.28 (td, 6H, J = 1.9, 7.0 Hz), 0.89 (t, 3H, J = 7.2 Hz); ^{13}C NMR (APT, $CDCl_3$,100 MHz) δ 169.3 (d, J = 13.6 Hz), 126.2 (d, J = 195.1 Hz), 61.0 (d, 2C, J = 4.5 Hz), 56.5 (d, J = 7.0 Hz), 54.0 (d, J = 18.5 Hz), 51.3 (d, J = 12.7 Hz), 32.5, 30.9 (d, J = 2.2 Hz), 30.1 (d, J = 3.2 Hz), 25.0, 23.2, 22.7, 22.5 (d, J = 3.5 Hz), 16.4 (d, 2C, J = 6.2 Hz), 14.0; ^{31}P NMR ($CDCl_3$, 160 MHz) δ 18.48; HRMS (EI) calcd [M^+] for $C_{17}H_{27}O_3P$ m/z 310.1698, found 310.1703.

Deltacyclene 9p (Table 3, Entry 16). The crude product was purified by column chromatography (EtOAc/hexanes 7:3) to provide cycloadduct **9p** (39.9 mg, 0.191 mmol, 36%) as a yellow oil: R_f 0.28 (EtOAc/hexanes 7:3); IR (CH_2Cl_2, NaCl): 2930 (m), 2856 (m), 1266 (s), 1166 (w), 1027 (s), 962 (m), 735 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 4.06−3.94 (m, 4H), 3.04 (br td, 1H, J = 11.1, 2.8 Hz), 2.78 (br d, 2H, J = 2.2 Hz), 1.92 (s, 1H), 1.72−1.61 (m, 4H), 1.60−1.56 (m, 2H), 1.52 (d, 2H, J = 5.8 Hz), 1.41−1.37 (m, 1H), 1.31−1.24 (m, 12H); ^{13}C NMR (APT, $CDCl_3$,100 MHz) δ 173.5, 123.6, 61.0 (m, 2C), 56.4 (d, J = 6.9 Hz), 51.0 (d, J = 12.7 Hz), 50.7, 39.0 (d, J = 3.0 Hz), 32.6, 31.8, 26.1, 25.9, 25.1, 23.1, 22.9 (d, J = 3.6 Hz), 16.4 (d, 2C, J = 6.6 Hz); ^{31}P NMR ($CDCl_3$, 160 MHz) δ 18.83; HRMS (EI) calcd [M^+] for $C_{19}H_{29}O_3P$ m/z 336.1854, found 336.1850.

Deltacyclene 9q (Table 3, Entry 17). The crude product was purified by column chromatography (EtOAc/hexanes 7:3) to provide cycloadduct **9q** (8.9 mg, 0.028 mmol, 14%) as a yellow oil: R_f 0.38 (EtOAc/hexanes 7:3). Isolated as an impure product (~3:1 starting alkyne **8q**/HDA adduct **9q**) from ^1H NMR: IR (CH_2Cl_2, NaCl) 2982 (m), 1458 (w), 1266 (s), 1028 (s), 970 (m), 735 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 4.08−4.00 (m, 4H), 2.93 (br d, 1H, J = 1.8 Hz), 2.88 (br d, 1H, J = 1.7 Hz), 1.90 (br s, 1H), 1.73 (br s, 1H), 1.66 (td, 1H, J = 4.6, 1.0 Hz), 1.55−1.5 (m, 2H), 1.43 (td, 1H, J = 4.5, 1.8 Hz), 1.31 (t, 6H, J = 7.0 Hz), 1.26 (s, 9H); ^{13}C NMR (APT, $CDCl_3$,100 MHz) δ 175.5, 124.3 (d, J = 191.9 Hz), 61.0 (d, 2C, J = 5.5 Hz), 53.1, 53.7, 53.5, 35.3, 32.5, 30.2, 24.8, 23.1, 22.7, 16.4 (m, 2C); ^{31}P NMR ($CDCl_3$, 160 MHz) δ 18.997; HRMS (EI) calcd [M^+] for $C_{17}H_{27}O_3P$ m/z 310.1698, found 310.1692.

Cycloadduct 10r (Table 3, Entry 18). The crude product was purified by column chromatography (EtOAc/hexanes 7:3) to provide cycloadduct **10r** (13.6 mg, 0.048 mmol, 15%) as a light yellow oil: R_f 0.19 (EtOAc/hexanes 7:3); IR (CH_2Cl_2, NaCl) 3386 (s), 2979 (m), 1628 (m), 1444 (w), 1231 (m), 1163 (s), 1024 (s), 968 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.08 (t, 2H, J = 2.7 Hz), 5.24 (t, 1H, J = 5.6 Hz), 4.36−4.32 (m, 2H), 4.16−4.04 (m, 4H), 2.39 (s, 1H), 2.51 (s, 1H), 2.40 (s, 2H), 1.44 (d, 1H, J = 9.3 Hz), 1.38 (d, 1H, J = 9.3 Hz), 1.33 (t, 6H, J = 7.1 Hz); ^{13}C NMR (APT, $CDCl_3$, 100 MHz) δ 171.3 (d, J = 11.2 Hz), 135.7, 135.3, 129.3 (d, J = 197.1 Hz), 62.1 (d, J = 5.7 Hz), 62.0 (d, J = 5.8 Hz), 61.4, 45.9 (d, J = 31.3 Hz), 43.0 (d, J = 8.1 Hz), 39.5, 38.9, 37.8, 16.4 (d, J = 6.3 Hz), 16.3 (d, J = 6.4 Hz); ^{31}P NMR ($CDCl_3$, 160 MHz) δ 12.38; HRMS (CI) calcd for $C_{14}H_{21}O_4P$ [M + H]$^+$ 285.1256 m/z, found 285.1261 m/z.

Deltacyclene 13 (Scheme 4). Deltacyclene **9g** (28.1 mg, 0.078 mmol) and NMP (1.0 mL) were added to a screw cap vial in the glovebox and sealed. The mixture was stirred outside of the glovebox at 160 °C for 48 h. The crude product was purified by column chromatography (EtOAc/hexanes 7:3) to provide deltacyclene **13** (2.4 mg, 0.011 mmol, 14%) as a light yellow crystalline solid: R_f 0.78 (EtOAc/hexanes 7:3); IR (CH_2Cl_2, NaCl) 2926 (m), 2855 (m), 1597 (w), 1492 (w), 1175 (w), 913 (s) cm^{-1}, ^1H NMR ($CDCl_3$, 400 MHz) δ 7.37−7.35 (m, 2H), 6.86−6.84 (m, 2H), 6.23 (d, 1H, J = 2.8 Hz), 3.80 (s, 3H), 3.02 (s, 1H), 2.69 (s, 1H), 2.08 (s, 1H), 1.75−1.72 (m, 1H), 1.60−1.59 (m, 2H), 1.40−1.39 (m, 2H); ^{13}C NMR (APT, $CDCl_3$,100 MHz) δ 158.5, 147.7, 129.6, 127.2, 126.0, 125.9, 113.9, 113.8, 56.5, 55.3, 50.0, 49.3, 32.7, 25.4, 24.2, 22.2; HRMS (EI) calcd [M^+] for $C_{16}H_{16}O$ m/z 224.1201, found 224.1209.

■ ASSOCIATED CONTENT

Supporting Information. ^1H and ^{13}C NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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