Cobalt-Catalyzed [2π + 2π + 2π] (Homo Diels−Alder) and [2π + 2π + 4π] Cycloadditions of Bicyclo[2.2.1]hepta-2,5-dienes

Mark Lautens,* William Tam, Julia Craig Lautens, Louise G. Edwards, Cathleen M. Crudden, and A. Catherine Smith

Contribution from the Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1

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Abstract: The scope of the cobalt-catalyzed [2π + 2π + 2π] (homo Diels−Alder, HDA) and [2π + 2π + 4π] cycloaddition reactions with norbornadienes has been investigated. Cobalt acetylacetonate, $Co(acac)_3$ or $Co(acac)_2$, upon reduction by diethylaluminum chloride (Et_2AlCl) in the presence of 1,2-bis(diphenylphosphino)ethane (dppe), is very effective in promoting the HDA reaction between norbornadiene and a variety of unactivated acetylenes to yield deltacyclenes. Azeotropic drying of the cobalt compound before use is found to increase the reactivity of the catalyst. Moderate to excellent enantioselectivity of these [2π + 2π + 2π] (up to 91% ee) and [2π + 2π + 4π] (up to 79% ee) cycloadditions can be achieved by the use of a chiral phosphine. 7-Substituted norbornadienes are also found to be reactive in the cobalt-catalyzed HDA reactions, affording the corresponding deltacyclenes in good yields. However, low *anti/syn* selectivities are observed, in contrast with the corresponding nickel-catalyzed HDA reaction with electron-deficient dienophiles. 2-Substituted norbornadienes are found to be less reactive in the cobalt-catalyzed HDA reactions, and the regio- and stereoselectivities are only moderate. The intramolecular versions of these [2π + 2π + 2π] and [2π + 2π + 4π] cycloadditions have also been investigated and provide efficient methods for the construction of highly strained pentacyclic frameworks from norbornadiene.

Introduction

The discovery and development of novel cycloaddition reactions continues to attract considerable attention. Metal-catalyzed cycloaddition reactions are of particular interest due to the mild reaction conditions and unique reactivity and selectivity imparted by the metal and its ligands. Four-, six-, and eight-electron processes have been studied from the methodological and synthetic perspective.[1−3]

The homo Diels−Alder (HDA) reaction is a six-electron [2π + 2π + 2π] process which occurs under thermal and metal-catalyzed conditions and generates novel, strained polycyclic compounds. Discovered nearly 40 years ago, it has not yet been applied in natural product synthesis. The thermal HDA process is applicable to a limited range of substrates which are activated, whereas transition metal catalysts were investigated and found to have a broader scope.[4−7] The vast majority of previous studies were carried out using bicyclo[2.2.1]hepta-2,5-diene (norbornadiene, NBD) and various dienophiles. In addition to the HDA process, NBD undergoes several other competing cycloaddition reactions (Scheme 1).[8−14] Unfortunately cycloaddition reactions of NBD often yield a mixture of cycloadducts.

It was essential to find catalysts, or modify known catalysts, to selectively generate single cycloadducts in high yield. In addition, control over the regio-, stereo-, and enantioselectivity

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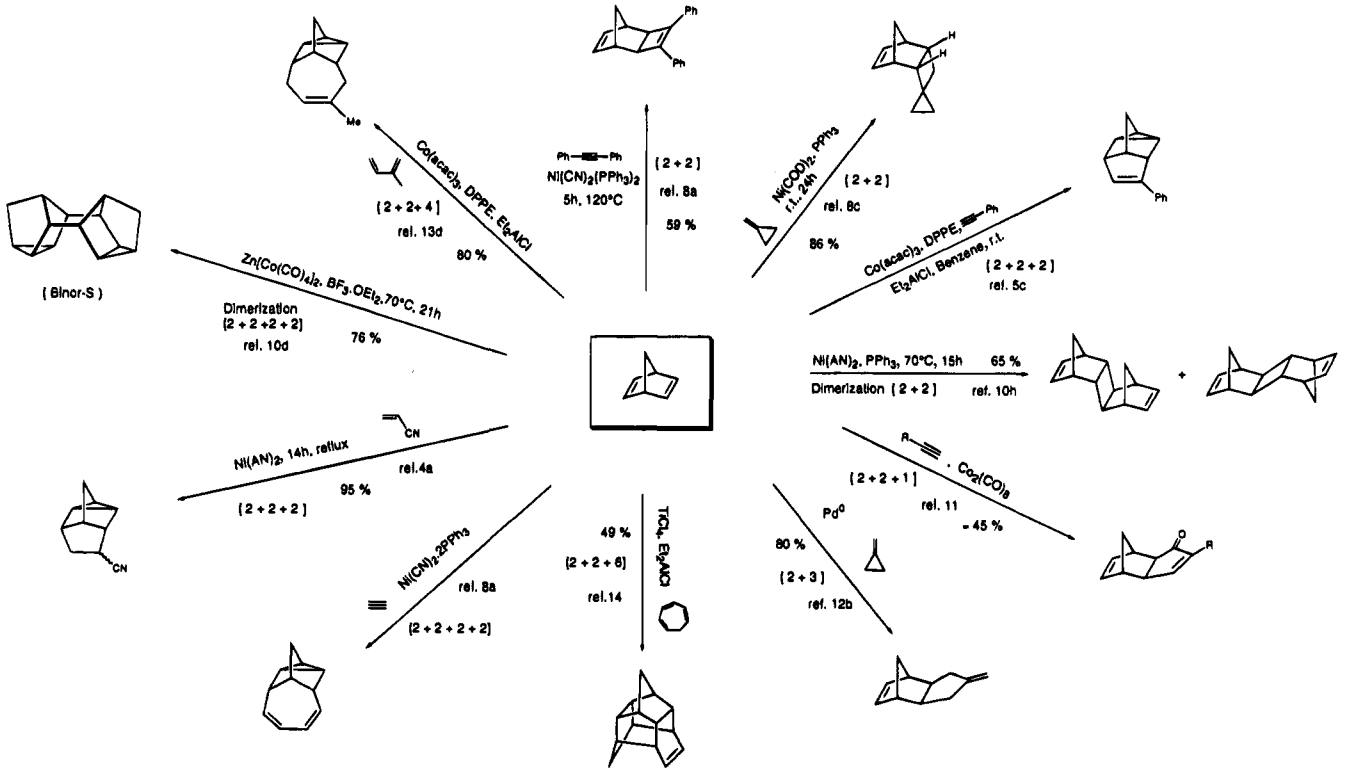
Scheme 1. Various Modes of Metal-Catalyzed Cycloadditions of Norbornadiene

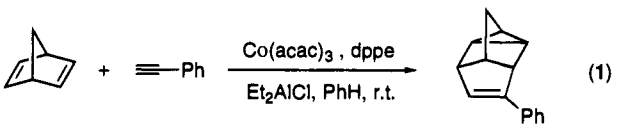


was necessary and experiments to this end are described herein. Our long-term goal is the synthesis of polycycles including triquinanes via a cycloaddition–fragmentation sequence, *vide infra*.

Cobalt-Catalyzed HDA Reaction of Norbornadiene with Alkyl- and Arylacetylenes

Unactivated acetylenes are poor dienophiles in Diels–Alder cycloadditions which severely limits their use in synthesis.[15] Several imaginative, albeit indirect, alternatives employing activated alkyne equivalents have been developed.[16] Metal-catalyzed inter- and intramolecular Diels–Alder reactions of dienes with unactivated alkynes represent a significant breakthrough with tremendous synthetic potential.[2a–d]

Similarly, the report by Lyons that unactivated acetylenes react with norbornadiene in the presence of low-valent cobalt complexes to yield [2π + 2π + 2π] cycloadducts was an important advance (eq 1).[5a,b] Unfortunately, substitution of the



aryl group in the acetylene for an alkyl group resulted in low yields of the desired coupling products. Instead the major adducts were those from the homocoupling of two norbornadienes.[5a,b,10]

Lyons' observations were the starting point for our investigation. Deltacyclene **3a** was isolated in 75–80% yield when we treated a benzene solution of norbornadiene and phenylacetylene (1 equiv with respect to NBD) under the conditions described by Lyons (1–5 mol % of commercially available $Co(acac)_3$ and 1,2-bis(diphenylphosphino)ethane (dppe) (1:1 with respect to Co), which was reduced with excess Et_2AlCl) (eq 2).[5a] Any change in solvent, ligand, or the use of other acetylenes led to unacceptable yields and very slow reactions. For example, 1-hexyne gave less than 10% of the desired HDA adduct even after prolonged heating.

(8) For metal-catalyzed [2π + 2π] cycloadditions of NBD with enophiles, see: (a) Schrauzer, G. N.; Glockner, P. *Chem. Ber.* **1964**, *97*, 2451. (b) Schrauzer, G. N. *Adv. Catal.* **1968**, *18*, 373. (c) Noyori, R.; Ishigumi, T.; Hayashi, N.; Takaya, H. *J. Am. Chem. Soc.* **1973**, *95*, 1674. (d) Mitsudo, T.; Naruse, H.; Kondo, T.; Ozaki, Y.; Watanabe, Y. *Angew. Chem., Int. Ed, Engl.* **1994**, *33*, 580.

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(11) For Pauson–Khand-type [2 + 2 + 1] cycloadditions of NBD, see: Pauson, P. L. *Tetrahedron* **1985**, *41*, 5885 and references therein.

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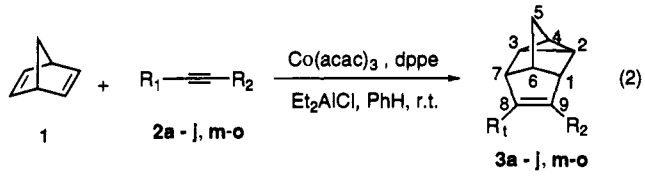


(2)

We reasoned that adventitious moisture might interfere with the reduction step since the reported preparation of $Ni(COD)_2$ indicates that drying commercially available "anhydrous" $Ni(acac)_2$ before the reduction step is necessary.[17] After azeotropic drying of $Co(acac)_3$, a dramatic improvement was noted in both the yield and range of substrates which participated in the cycloaddition (Table 1). Acetylenes bearing a branched or

Table 1. Cobalt-Catalyzed HDA Reaction of NBD with Unactivated Alkynes

entry	deltacyclene	R_1	R_2	yield (%)
1	**3a**	Ph	H	quantitative
2	**3b**	^{n}Bu	H	91
3	**3c**	^{i}Pr	H	58
4	**3d**	^{t}Bu	H	50
5	**3e**	$(CH_2)_4OPMB$	H	74
6	**3f**	$(CH_2)_3OTBS$	H	90
7	**3g**	$CH_2CH(OAc)C_2H_5$	H	82
8	**3h**	CH_2OR	H	N.R.[a]
9	**3i**	$SiMe_3$	H	50[b]
10	**3j**	CH_2SiMe_3	H	75
11	**3m**	Et	Et	55
12	**3m**	Et	Et	65[c]
13	**3n**	Ph	Ph	*d*
14	**3n**	Ph	Ph	58[c,e]
15	**3o**	$SiMe_3$	$SiMe_3$	*d*
16	**3o**	$SiMe_3$	$SiMe_3$	*c, d*

[a] R = Me, TBS. [b] Another product **3i'** (Figure 1) was isolated (10%) along with deltacyclene **3i**. [c] Reaction run at 60 °C. [d] Only NBD dimers were obtained. [e] 15% of NBD dimers were obtained along with **3n**.

n-alkyl chain gave good to excellent yields as did alkyl chains bearing silyl or aryl ethers. The only monosubstituted acetylene which failed to react was a propargyl ether (R = Me, TBDMS) (entry 8). In fact it is a poison in an otherwise successful cycloaddition with other acetylenes.

The cycloadditions with terminal acetylenes **2a−j** tend to be very clean processes yielding a single $[2\pi + 2\pi + 2\pi]$ product (except in the case of **2i**, where a tricyclo[2.2.1.$0^{3,5}$]heptane **3i'** (Figure 1) was isolated (10%) along with the expected deltacyclene **3i**). Internal acetylenes (**2m−o**) tended to be less reactive than terminal acetylenes and in some cases gave norbornadiene dimers as the major products. Diphenylacetylene reacted at 60 °C rather than room temperature. The case of bis(trimethylsilyl)acetylene, no desired HDA adduct was obtained even on prolonged heating at 60 °C.

A comparison was also made between $Co(acac)_2$ and $Co(acac)_3$ in the cycloaddition of several acetylenes. Empirically we observed that the rates of cycloadditions with $Co(acac)_3$ were faster than with $Co(acac)_2$ but the yields of deltacyclenes were similar. Another Co(II) source was reported by Cheng and coworkers who showed that reduction of CoI_2 yielded an active catalyst in the HDA reaction.[5e] Similar reactivity was noted by these authors.

In the absence of alkyne, a >60% yield of NBD dimers was obtained using cobalt catalysts, in keeping with previous reports.[10d,e] Slow trimerization of alkynes to the corresponding benzene derivatives was also observed under the same conditions

(17) For preparation of $Ni(COD)_2$, see: (a) Schunn, R. A.; Ittel, S. D.; Cushing, M. A. *Inorg. Synth.* **1990**, *28*, 94. (b) Schunn, R. A. *Inorg. Synth.* **1974**, *15*, 5.

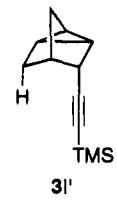
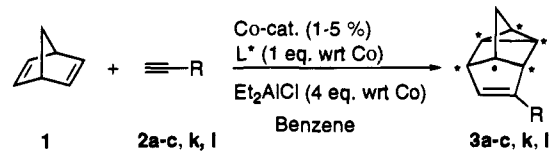


Figure 1.

in the absence of NBD.[18] These results, as well as the high yields of deltacyclenes in the presence of an acetylene, suggest that the coordination of a NBD and an alkyne is greatly favored over the coordination of two NBD or two alkyne units to the same metal species. Further discussion on the mechanistic aspects of the cycloaddition is presented in a later section.

Asymmetric Induction Studies

The development of an enantioselective process would considerably broaden the utility of this reaction which generates six stereocenters and two rings in a single reaction. This possibility was probed by adding a chiral phosphine ligand to the cobalt complex prior to the reducing agent (eq 3).[6a,19]



(3)

a: R = Ph
b: R = ^{n}Bu
c: R = ^{i}Pr
k: R = $(CH_2)_4OAc$
l: R = $(CH_2)_4OTBS$

Various chiral phosphines were studied in the reaction between NBD and several acetylenes (Figure 2, Table 2).[20,21] (*S,S*)-Chiraphos and (*R*)-prophos typically gave the best yields and enantioselectivities with the acetylenes studied. BPE and duphos ligands were shown to be less selective, and (*R*)-BINAP and (+)-DIOP gave no cycloadduct.

Phenylacetylene was the exception to this general trend since (*S,S*)-Me-BPE gave the highest ee among the phosphines studied (Table 2, entries 1−15). At −2 to 6 °C, the ee of **3a** was 82%, while at higher temperature, the yield increased but the ee decreased. At lower temperature (<−15 °C), no reaction was observed. For other ligands in the BPE series (entries 4−11),

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(20) Abbreviations: prophos, 1,2-bis(diphenylphosphino)propane; chiraphos, 2,3-bis(diphenylphosphino)butane; DIOP, 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane; BPE, 1,2-bis(phospholano)-ethane;[21c] duphos, 1,2-bis(phospholano)benzene;[21c] BINAP, 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl.

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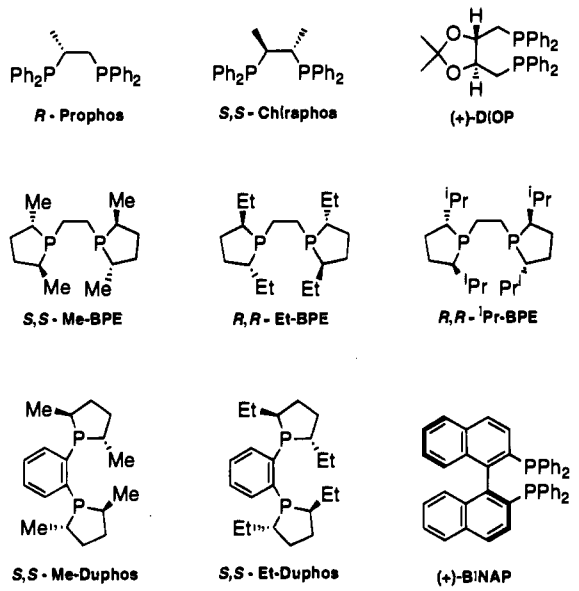


Figure 2. Structure of various chiral phosphines.

Table 2. Cobalt-Catalyzed Enantioselective HDA Reaction

entry	adduct	L*	Co cat.	t (°C)	yield (%)	de[a]
1	**3a**	dppe	$Co(acac)_3$	20–35	100	
2		(*S,S*)-chiraphos		25–27	37	69 (*R*)
3		(*R*)-prophos		25–32	93	48 (*S*)
4		(*S,S*)-Me-BPE	$Co(acac)_3$	20–27	91	65 (*S*)
5				−2 to 6	70	**82** (*S*)
6			$Co(acac)_2$	20–30	93	70 (*S*)
7				−5 to 0	78	77 (*S*)
8		(*R,R*)-Et-BPE	$Co(acac)_3$	19–28	30	44 (*R*)
9			$Co(acac)_2$	20–26	86	60 (*R*)
10		(*R,R*)-^{i}Pr-BPE	$Co(acac)_3$	19–24	28	7 (*R*)
11			$Co(acac)_2$	18–24	42	20 (*R*)
12		(*S,S*)-Me-duphos	$Co(acac)_3$	22–30	12	63 (*S*)
13			$Co(acac)_2$	18–25	28	47 (*S*)
14		(*S,S*)-Et-duphos	$Co(acac)_3$	20–30	33	16 (*S*)
15			$Co(acac)_2$	22–30	18	14 (*S*)
16[b]	**3b**	(*S,S*)-chiraphos	$Co(acac)_3$	25–28	64	80 (*R*)
17		(*S,S*)-chiraphos		25–26	83	**91** (*R*)
18		(*R*)-prophos		25–27	87	78 (*S*)
19		(*S,S*)-Me-BPE		20–27	87	12 (*S*)
20		(*R,R*)-Et-BPE		4–29	10	11 (*R*)
21	**3c**	(*S,S*)-chiraphos	$Co(acac)_3$	25–33	75	36 (*R*)
22		(*R*)-prophos		30–40	33	**55** (*S*)
23	**3k**	(*S,S*)-chiraphos	$Co(acac)_3$	28–32	85	**85** (*R*)
24	**3l**	(*S,S*)-chiraphos	$Co(acac)_3$	28–32	67	18 (*S*)
25[b]	**3l**	(*S,S*)-chiraphos	$Co(acac)_3$	28–30	60	**80** (*R*)

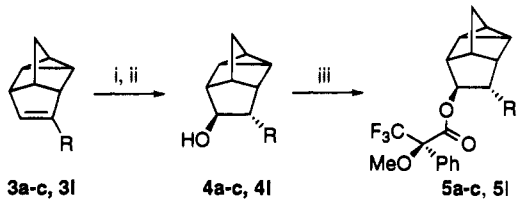
[a] de of **5** = ee of **3**. (*R*) or (*S*) refers to the stereochemistry of the carbon bearing the ester group in Mosher ester **5** (eq 4). [b] Reaction run in THF/toluene (3:1) instead of in benzene.

the use of $Co(acac)_2$ instead of $Co(acac)_3$ at room temperature usually gave higher yields and higher ee's. But at a lower temperature (−5 to 6 °C), $Co(acac)_3$ gave a higher ee with a lower yield than $Co(acac)_2$ (entries 5 and 7). (*R*)-Prophos also gave a high yield but the ee was only moderate. (*S,S*)-Chiraphos gave a higher ee than (*R*)-prophos, but the yield was rather low, Duphos ligands usually gave unacceptable yields and ee's (entries 12–15). It is difficult to discern any clear trend from these results.

(*S,S*)-Chiraphos was the most effective ligand with 1-hexyne (Table 2, entries 16–20). Use of (*R*)-prophos gave a high yield of cycloadduct but with a lower ee than with (*S,S*)-chiraphos. BPE ligands gave low enantioselectivity for alkyl-substituted acetylenes. Unfortunately no clear trend emerged from the studies of ligands, initial oxidation state of the catalyst, or temperature.

An acetylene bearing a remote oxygen also reacted with high enantioselectivity, but the choice of protecting group and solvent had a significant influence on the ee (Table 2, entries 23–25). When acetylene **2l** was reacted under the standard conditions, the enantioselectivity was very low and favored the enantiomeric cycloadduct opposite to that obtained with other alkynes. However, when the solvent was changed to THF/toluene (3/1) rather than neat benzene, the ee improved to 80% and the "usual" enantiomer was formed. It is tempting to speculate that THF competes with the silyl ether for a binding site on the cobalt and that intramolecular complexation in **2l** leads to little difference in energy in the diastereomeric transition states leading to product. While it may be a coincidence, the 80% ee obtained is identical to reactions with 1-hexyne when THF/toluene is used (entry 16). The ee also improved when the protecting group was changed from a silyl ether to an acetate ester. The oxygen is now less Lewis basic due to the electron-withdrawing ester function.

To determine the degree and sense of induction we used a combination of spectroscopic and chemical techniques. A standard protocol was developed: racemic and chiral deltacyclenes **3a–c,l** were subjected to hydroboration–oxidation to give single regio- and stereoisomeric alcohols **4a–c,l**, and the resulting alcohols were converted to Mosher esters **5a–c,l** (eq 4).[22] For **3k**, the ester was treated with K_2CO_3/MeOH and the



(4)

Key: i. BH_3 or 9-BBN; ii. H_2O_2/NaOH, EtOH; iii. Mosher acid chloride, Et_3N, DMAP,CH_2Cl_2

resulting alcohol was protected (TBDMSCl, DMF, imidazole) to give silyl ether **3l**, which was compared with **3l** formed from reaction of **2l** with NBD.

The ee's of deltacyclenes **3a–c,l** were determined by measuring the de's of the Mosher esters **5a–c,l** by ^{19}F and/or ^1H NMR. The absolute stereochemistry of **5a** was initially assigned by using the Mosher method.[22,23] The absolute stereochemistry of **5a** was confirmed using X-ray crystallography, and all other substrates were then assigned using the Mosher method (Figure 3).[24]

A chiral binding pocket must be generated in the reactive catalyst–ligand complex, and a best fit which minimizes steric interactions between the substituent on the acetylene and the aryl groups of the phosphine is responsible for the selectivity. Lewis acid–Lewis base interactions cannot be important since most of the acetylenes studied lack Lewis basic sites.

(22) For the use of Mosher ester, see: (a) Dale, J. E.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543. (b) Dale, J. E.; Mosher, H. S. *J. Am. Chem. Soc.* **1973**, *95*, 512.

(23) For the use of *O*-methyl mandelate ester, see: (a) Trost, B. M.; Belletire, J. L.; Godleski, S.; McDougal, P. G.; Balkovec, J. M.; Baldwin, J. J.; Christy, M. E.; Ponticello, G. S.; Varga, S. L.; Springer, J. P. *J. Org. Chem.* **1986**, *51*, 2370. (b) Roy, B.; Deslongchamps, P. *Can. J. Chem.* **1985**, *63*, 651.

(24) Lautens, J. C.; Lautens, M.; Lough, A. J. *Acta Crystallogr.* **1991**, *C47*, 2725. This is the only report which confirms the absolute stereochemistry of a deltacyclene from the enantioselective HDA reaction. The crystal used for the structure determination was obtained by crystallization of a diastereomeric mixture of **5a** and *enant*-**5a** from pentane. *enant*-**5a** crystallized selectively as colorless needles. ^1H NMR showed that the crystals had the sense of induction that is predominant from reactions with (*R*)-prophos.

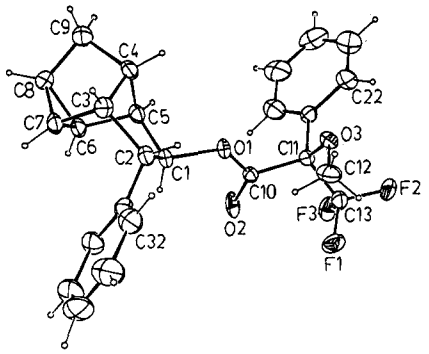


Figure 3. X-ray structure of Mosher ester *enant*-**5a**.[24]

Brunner's group has also independently investigated the enantioselective HDA reaction between NBD and phenylacetylene with the use of the chiral bidentate phosphine norphos.[6b] Up to 98.4% ee was obtained, but the absolute stereochemistry was not proven but predicted on the basis of GC retention times and is in agreement with our results. Brunner and Prester have extended these studies to include a variety of other bidentate phosphines.[6c] High enantioselectivities were obtained with phenylacetylene (>99.4% ee with norphos or BDPP) and 1-hexyne (>98% with norphos).

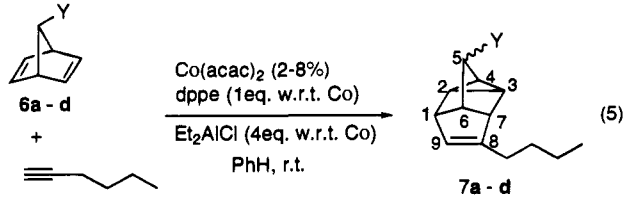
More recently, Buono and Pardigon showed that a cobalt(II) iodide complex with an amino acid based chiral phosphine gives a highly enantioselective HDA reaction (with phenylacetylene and 1-hexyne, up to 97% ee were achieved).[6d]

Cobalt-Catalyzed HDA Reactions of Substituted Norbornadienes

Since our overall objective was to investigate the HDA reaction as a route to polycyclic natural products by a cycloaddition–fragmentation sequence, it was necessary to develop efficient routes to cycloadducts bearing functionalities on or near the cyclopropane moieties in order to assist the cleavage reactions. Various substituted norbornadienes were prepared and subjected to the HDA reaction.

Unlike the Diels–Alder reaction (where predictable and high regioselectivity is expected in a cycloaddition between an electron-rich diene and an electron-poor dienophile), little is known about the regiochemical outcome of an analogous unsymmetrical HDA reaction. Prior to our studies, reports of successful cycloadditions using substituted norbornadienes were rare in the literature.[7f,i] Recently, the effect of a 2-substituent or a 7-substituent on the regio- and stereoselectivity in the nickel-catalyzed HDA reaction with electron-deficient dienophiles was reported.[4e-g] High levels of selectivities as well as good yields were observed.

Similar studies were carried out in the cobalt-catalyzed HDA reaction of 7- or 2-substituted norbornadienes with unactivated acetylenes. The effect of the 7-substituent on the norbornadiene in the cobalt-catalyzed HDA reaction is shown in eq 5 and Table



(5)

3. 7-Hexyl-NBD (**6a**) and 7-Ph-NBD (**6b**) showed no *anti/syn* selectivity in the HDA reaction with 1-hexyne. The *anti/syn* selectivity increased slightly when Y = OCOPh (**7c**) and OTIPS (**7d**). Although the yields in these HDA reactions are very high,

Table 3. Effect of the 7-Substituent on Cobalt-Catalyzed HDA Reaction with 1-Hexyne

entry	Y	yield (%)	cycloadduct	*anti:syn*
1	hexyl	80	**7a**	50:50
2	Ph	94	**7b**	50:50
3	OCOPh	96	**7c**	59:41
4	OTIPS	84	**7d**	65:35

Scheme 2

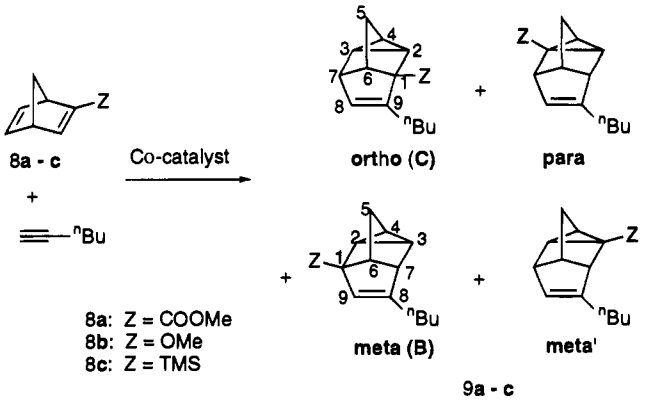


Table 4. HDA Reaction between 2-TMS-NBD and 1-Hexyne

entry	Co cat.[a]	*t* (°C)	recovered **8c** (%)	total isolated yield of HDA adducts, **9c** (%)	ratio[b] **A**:**B**:**C**
1	$Co(acac)_2$	r.t.	28	42	1:3.5:23.3
2		70	30	50	1.7:1:3.7
3		r.t.[c]	60	<10	0:2.1:1
4	$Co(acac)_3$	r.t.	28	30	0:1:11.3
5		70	47	21	1:7:11
6		r.t.[c]	60	<10	0:4.6:1
7	$Co(acac)_3$[d]	r.t.	42	37	1:1.2:8.3

[a] 5% of Co catalyst (with 1 equiv of dppe and 4 equiv of Et_2AlCl with respect to Co). [b] Isomers **C** and **B** were identified as the *ortho* and *meta* adducts, respectively, but isomer **A** was not identified. [c] Using (1:1) THF/PhH as solvent instead of PhH alone. [d] Another 5% of Co catalyst was added after 24 h.

the *anti/syn* selectivities were much lower than those of the corresponding nickel-catalyzed reactions with electron-deficient olefins.[4f] The lack of selectivity may be due to the similarity in electron density of the acetylenic carbons since the 7-substituent clearly differentiates the electron density of the olefinic carbons in the NBD component.

Four different HDA adducts are possible in the reaction between a 2-substituted NBD and an unactivated terminal acetylene (Scheme 2). Norbornadienes bearing an electron-withdrawing group **8a** (Z = COOMe) or an electron-donating group **8b** (Z = OMe) at the 2-position did not afford any HDA adduct with 1-hexyne under the cobalt-catalyzed conditions. Instead, aromatic derivatives resulting from trimerization of 1-hexyne were isolated. With a silyl substituent **8c** (Z = TMS), low to moderate yields of HDA adducts were obtained (Table 4). The best regioselectivity obtained was 11.3:1 (Table 4, entry 4), but the isolated yield was only 30%.

The major regioisomer (**C**) was identified as the *ortho* isomer, and the minor isomer (**B**) was identified as the *meta* isomer by using ^{13}C (APT) NMR and ^1H NMR decoupling techniques. In the ^{13}C (APT) NMR, both isomeric products showed three cyclopropane carbons bearing hydrogens, thus the TMS group is not attached to the cyclopropane and therefore these isomers have to be the *ortho* and *meta* isomers. For the *ortho* isomer (**C**), H^7 coupled with H^3, H^6, and H^8, while in the *meta* isomer

(**B**), H^7 coupled with H^3 and H^6 but not with H^9. Reactions in a 1:1 mixture of THF and benzene led to an increase in the proportion of the *meta* isomer (**B**) (Table 4, entries 3 and 6). Other studies using phenylacetylene instead of 1-hexyne gave similar results, but once again the yields were never greater than 30%.

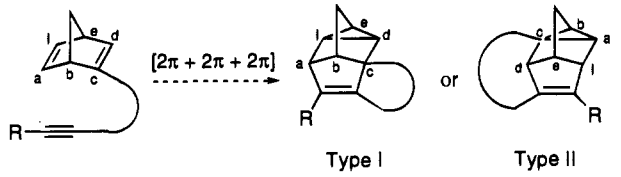
A 2-substituted NBD reacts much more slowly than NBD itself in the HDA cycloaddition.[4g] Low yields in the HDA reaction with 2-substituted norbornadienes and the isolation of acetylene trimers suggested that 2-substituted norbornadienes do not coordinate well to the active cobalt complex compared to the parent NBD. Thus, side reactions such as trimerization of the acetylene dominate.

Cobalt-Catalyzed Intramolecular HDA Reactions

The additional ring which arises from an intramolecular HDA reaction may be useful for the synthesis of triquinanes or other polycyclic compounds. The decrease in entropy associated with tethering the two reactive components suggests that the reaction would be significantly more facile than the intermolecular reaction.[25] However, this potential rate enhancement is compromised by the dramatic decrease in rate associated with intermolecular cycloadditions with substituted norbornadienes as described previously. There were no reported examples of successful intramolecular HDA reactions in the literature prior to 1992.[5d,26]

In an intramolecular reaction, there are two possible modes of $[2\pi + 2\pi + 2\pi]$ cycloaddition which have to be considered (Scheme 3). The dienophile in the tether can cyclize on C^a–C^b–C^c to give a cycloadduct of type I or it can cyclize on C^d–C^e–C^f to give a type II cycloadduct. Molecular models and MM2 calculations indicate that both products would be stable.

Scheme 3



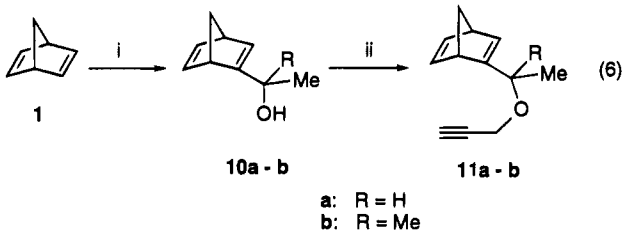
Efficient routes to the cycloaddition precursors were developed starting with norbornadiene. Deprotonation of norbornadiene with *n*-BuLi/KOBu^t occurred smoothly at −78 °C in THF.[27] Treatment of this anion with lithium bromide followed by acetaldehyde or acetone gave alcohols **10a** (R = H, 1.5:1 mixture of diastereomers) and **10b** (R = Me). Treatment with KH and THF −50 to 0 °C) and reaction of the alkoxide (in the presence of 18-crown-6) with propargyl bromide gave **11a** (R = H) and **11b** (R = Me) in 96% and 39% yields (eq 6).

While the thermal cycloaddition of **11a** (at 170 °C in mesitylene for 24 h) gave only 3% of the desired HDA adduct **12a**, the cobalt-catalyzed HDA reaction at *room temperature* increased the yield of the cycloadduct 5-fold to 15% (Table 5, entry 1). Dienyne **11b** under the same cobalt-catalyzed conditions afforded the corresponding HDA adduct **12b** in 22% yield.

(25) (a) Ciganek, E. *Org. React.* **1984**, *32*, 1. (b) Taber, D. F. *Intramolecular Diels-Alder and Alder Ene Reactions*; Springer-Verlag: Berlin, 1984. (c) Fallis, A. G. *Can. J. Chem.* **1984**, *62*, 183. (d) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 10.

(26) For an early attempt at an intramolecular HDA reaction, see: Kelly, T. R. *Tetrahedron Lett.* **1973**, *14*, 437. Instead of undergoing the HDA reaction, an intramolecular "ene" reaction was observed.

(27) For deprotonation of NBD, see: (a) Brandsma, L.; Verkruijsse, H. D. *Recl. Trav. Chim. Pays-Bas* **1986**, *105*, 66. (b) Wittig, G.; Otten, J. *Tetrahedron Lett.* **1963**, *10*, 601.

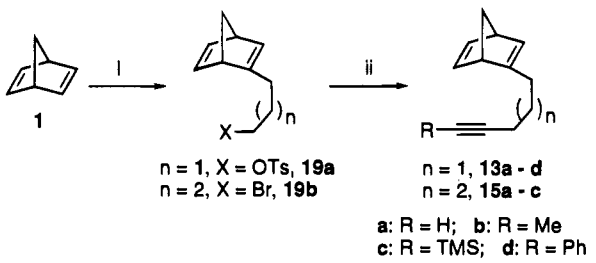


(6)

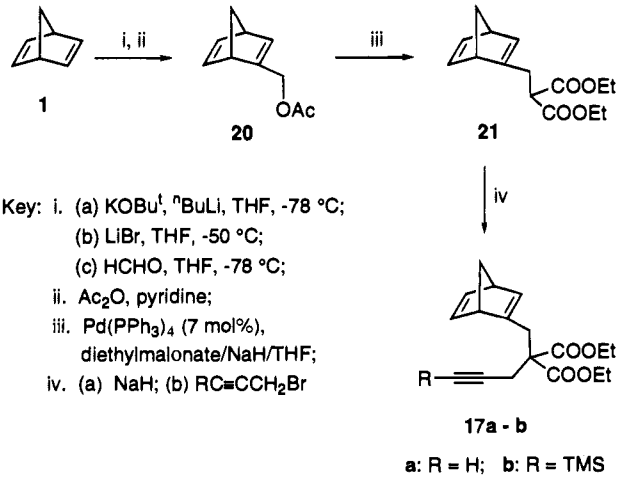
Key: i. (a) KOBu^t, ^{n}BuLi, THF, -78 °C;(b) LiBr, THF, -50 °C; (c) RCOMe, THF, -78 °C;
ii. (a) KH, 18-c-6; (b) propargyl bromide

Although the yields of the cycloadditions were modest, these initial results were encouraging since as shown previously, the *intermolecular* HDA reaction between NBD and propargyl ethers failed to give any cycloadduct. The Lewis acidic character of the reducing agent, Et_2AlCl, was also of concern since the starting materials **11** and the cycloadducts **12** contained sensitive functional groups (propargylic and allylic ethers). Furthermore, the *intermolecular* reactions of 2-substituted norbornadienes were generally very slow. A significant improvement in the yields of the cycloaddition was realized when the oxygen within the tether were replaced by a methylene unit. These results are described below.

Scheme 4. Preparation of Dienynes



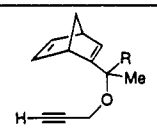
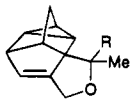
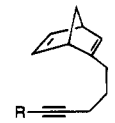
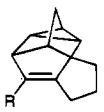
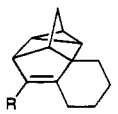
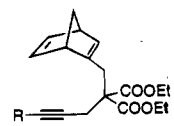
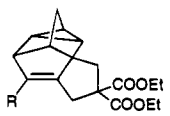
Key: i. (a) KOBu^t, ^{n}BuLi, THF, -78 °C;(b) For n = 2, $Br(CH_2)_4Br$; For n = 1, $Br(CH_2)_3OH$, then TsCl, pyridine;
ii. RC≡CLi, THF/DMSO



Key: i. (a) KOBu^t, ^{n}BuLi, THF, -78 °C; (b) LiBr, THF, -50 °C; (c) HCHO, THF, -78 °C;
ii. Ac_2O, pyridine;
iii. $Pd(PPh_3)_4$ (7 mol%), diethylmalonate/NaH/THF;
iv. (a) NaH; (b) $RC{\equiv}CCH_2Br$

The all-carbon dienynes **13a–d**, **15a–c**, and **17a,b** were prepared as shown in Scheme 4, and their intramolecular cycloadditions were studied (Table 5). No reaction was observed when **13a** was heated at 150 °C in the absence of the catalyst. However, under cobalt-catalyzed conditions, cycloadditions occurred smoothly. The cycloadditions were carried out at 0.15–1.0 M dienyne, thus avoiding the use of syringe pumps

Table 5. Intramolecular Cycloaddition of Dienynes using Cobalt Catalysts

Entry	Dienynes	Conditions[a] (% Co)	Cycloadducts	Yield[b]
1				
	11a (R=H)	A	**12a**	3%
	11a (R=H)	B (8%)	**12a**	15%[c]
	11b (R=Me)	B (8%)	**12b**	22%
2				
	13a (R=H)	A		N.R.
	13a (R=H)	B (7%)	**14a**	78%
	13a (R=H)	C (7%)	**14a**	64%
	13b (R=Me)	B (8%)	**14b**	69%
	13c (R=TMS)	B (10%)	**14c**	63%
	13d (R=Ph)	B (11%)	**14d**	70%
3				
	15a (R=H)	B (5%)	**16a**	64%
	15b (R=Me)	B (8%)	**16b**	43%
	15c (R=TMS)	B (10%)	**16c**	48%
4				
	17a (R=H)	B (7%)	**18a**	60%
	17b (R=TMS)	B (8%)	**18b**	39%[d]

[a] A = 140−170 °C. B = $Co(acac)_3$, dppe, 6 equiv of Et_2AlCl. C = $Co(acac)_2$, dppe, 3−4 equiv of Et_2AlCl. [b] Isolated yields of pure material. [c] The starting dienyne was a 1.5:1 mixture of diastereomers. The cycloadduct was 3.5:1 mixture of diastereomers. Unreacted starting material was recovered (22%). [d] 18% of dienyne **17b** was recovered.

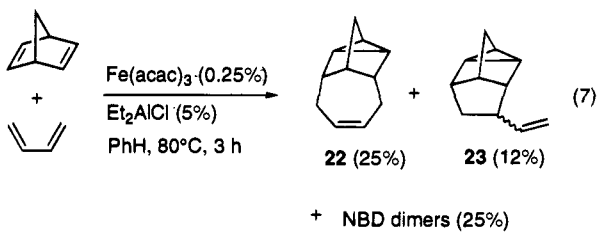
or high-dilution reaction conditions. This concentration is significantly higher than for many intramolecular reactions[25] and is feasible due to the sluggishness of the competing intermolecular coupling reactions.

All the intramolecular HDA adducts observed were the type I adducts (Scheme 3); no type II adduct was detected in any case. Higher yields were obtained with the dienynes with a three-carbon tether **13a−d** compared to the corresponding four-carbon tether **15a−c**. Attempted cycloadditions for the corresponding two-carbon and five-carbon tether dienynes were unsuccessful. While the use of $Co(acac)_2$ instead of $Co(acac)_3$ under the same conditions gave slightly lower yields, increasing the reaction temperature to 80 °C showed no improvement of the yields.

We have also attempted to use the asymmetric HDA reaction to effect a kinetic resolution of racemic dienyne **13a** using (*R*)-prophos as the ligand. Treatment of **13a** (with $Co(acac)_3$ (8%), (*R*)-prophos (8%), and Et_2AlCl (32%)) was monitored by capillary GC, and the reaction was quenched at 36% completion. The purified cycloadduct was analyzed by the hydroboration−Mosher ester protocol described earlier and found to be racemic.

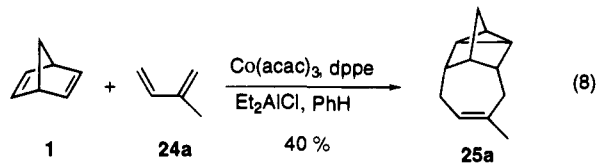
Cobalt-Catalyzed [2π + 2π + 4π] Cycloaddition Reactions

Metal-catalyzed [2π + 2π + 4π] cycloaddition between NBD and 1,3-butadienes was first reported by Carbonaro and co-workers using an iron catalyst in 1970 (eq 7).[13a] A [2π + 2π + 4π] cycloadduct **22** was formed (25%), accompanied by a [2π + 2π + 2π] adduct **23** (12%) and NBD dimers (25%). The use of another catalytic system ($CoCl_2$/dppe/Et_2AlCl, in toluene at 75 °C for 5 h) increased the yield of the [2π + 2π + 4π] cycloadduct **22** to 68% and avoided the formation of the [2π + 2π + 2π] adduct **23**.[13b]



(7)

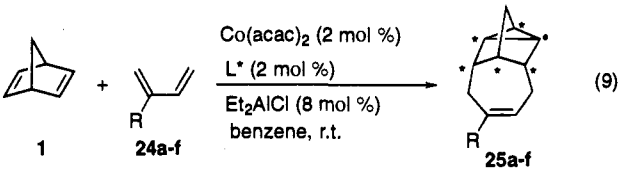
Lyons and co-workers extended these studies using $Co(acac)_3$/dppe/Et_2AlCl in benzene with NBD (**1**) and isoprene **24a** to give the corresponding [2π + 2π + 4π] cycloadduct, but the yield was modest (eq 8).[5b]



(8)

The cobalt catalyst system which had functioned well in the HDA reaction between NBD and unactivated acetylenes was also examined in the [2π + 2π + 4π] cycloadditions between NBD and 2-substituted 1,3-butadienes.

The initial studies focused on the cycloaddition between NBD (**1**) and isoprene **24a** (R = Me) (eq 9). The diene was used in excess (1.5−3 equiv) vs NBD to minimize the competitive homodimerization of NBD and to compensate for the loss of the diene due to polymerization. $Co(acac)_2$ and $Co(acac)_3$ gave similar ee's, but Co(II) gave the adduct in 5−10% higher yield and was used for the other dienes. The enantioselectivity was measured for a series of phosphines and (*R*)-prophos was found to be superior for the eight-electron reaction (Table 6). In addition, the yield of cycloadduct was generally higher than reported in the previous studies.[5b]



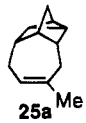
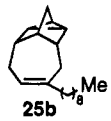
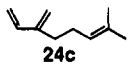
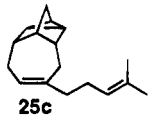
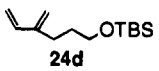
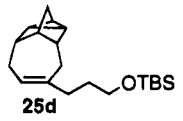
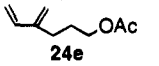
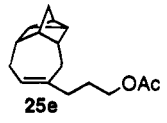
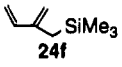
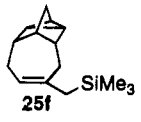
(9)

Table 6. Effect of Phosphines on Asymmetric [2π + 2π + 4π] Cycloadditions of NBD (1) with Isoprene **24a**

entry	ligand, L*	yield (%)	ee (%)
1	(*R*)-prophos	66	72 (*S*)
2[a]	(*R*)-prophos	57	74 (*S*)
3	(*S,S*)-chiraphos	25	40 (*R*)
4	(*S,S*)-Me-BPE	40	35 (*R*)
5	(*R,R*)-^{i}Pr-BPE	12	40 (*R*)
6	(*S,S*)-Me-duphos	18	9 (*S*)

[a] Using $Co(acac)_3$ instead of $Co(acac)_2$.

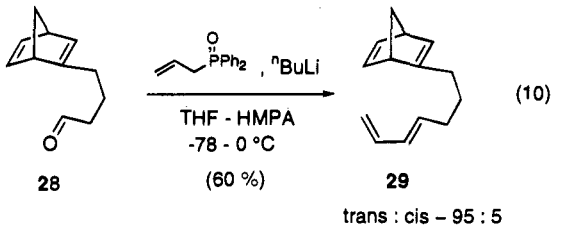
Table 7. Asymmetric [4π + 2π + 2π] Cycloaddition between NBD and Various 2-Substituted Buta-1,3-dienes

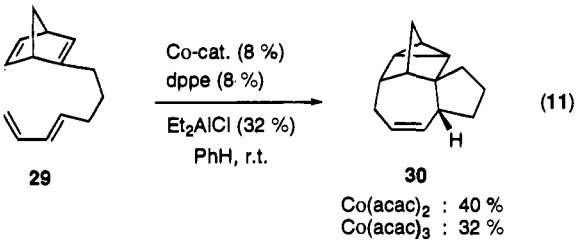
Entry	Diene	Cycloadduct	Yield	ee
1	 **24a**	 **25a**	66 %	72 %
2	 **24b**	 **25b**	40 %	74 %
3	 **24c**	 **25c**	49 %	79 %
4	 **24d**	 **25d**	40 %	73 %
5	 **24e**	 **25e**	52 %	73 %
6	 **24f**	 **25f**	49 %	71 %

In order to determine the generality of this reaction, other dienes were prepared[28] and subjected to the standard conditions ($Co(acac)_2$/(*R*)-prophos/Et_2AlCl) (Table 7). In contrast to the reaction of NBD and acetylenes, where significant effects were noted as R was varied, very little change in the ee was observed for the 2-substituted dienes studied. However, the yields were generally 40−65%, probably due to the competing polymerization of the dienes and dimerization of NBD under the reaction conditions. We did not observe formation of [2π + 2π + 2π] adducts analogous to **23**.

The ee's of the cycloadducts were determined using the same strategy as previously described for the HDA reaction. Hydroboration−oxidation of a [2π + 2π + 4π] adduct gave a single regio- and stereoisomeric alcohol (**26a**,**b**,**d**,**f**) which was esterified with Mosher acid chloride to provide the Mosher ester (**27a**,**b**,**d**,**f**). According to models, both faces of the alkene appeared to be accessible in the hydroboration, but only the *exo* isomer was formed. The diastereomeric excess was measured by ^1H and/or ^{19}F NMR. The absolute stereochemistry of the cycloadducts was assigned using Mosher's model.[22,23] (*R*)-Prophos gave the cycloadducts with absolute stereochemistry as depicted in eq 9. The same sense of asymmetric induction was observed in the homo-Diels−Alder reaction. The assignment of the absolute stereochemistry was supported by X-ray crystallography.[29]

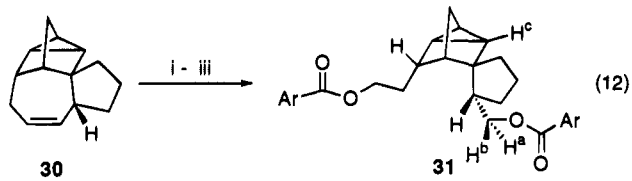
On the basis of the success of the intramolecular cobalt-catalyzed HDA reaction, the related intramolecular [2π + 2π + 4π] cycloaddition was examined. Diene **29** was prepared from readily available aldehyde **28**[4g] as shown in eq 10, and was subjected to the cycloaddition reaction conditions (eq 11).



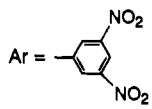


The rate of this cycloaddition was very slow and required 48−72 h for complete consumption of the starting material. Very little reaction was observed when less than 8 mol % of the catalyst was used. Larger amounts of catalyst (>15 mol %) led to decomposition of the starting material, and increasing the reaction temperature to 60 °C did not improve the yield of the cycloaddition.

The stereochemistry of the cycloaddition (*exo* or *endo*) was determined by ^1H NMR decoupling and NOE experiments on compound **31**, which was prepared from cycloadduct **30** (eq 12). On irradiation of **31** at δ 4.3 ppm (H^a), a 10% NOE was observed at δ 1.13 ppm (H^c) and a 21% NOE at δ 4.78 ppm (H^b).



Key: i. O_3, MeOH/CH_2Cl_2, – 78 °C
ii. $NaBH_4$
iii. 3,5-dinitrobenzoic acid, DCC, DMAP, CH_2Cl_2



Attempted reaction of diene **32** with a four-carbon tether and the type II[25b,30] dienes **33** and **34** (Figure 4) did not afford any of the desired cycloadducts; either no reaction or decomposition of the starting materials was observed.

Discussion

Low-valent cobalt [Co^{-1}, Co^0, and Co^{+1}] is known to complex with nonconjugated dienes (e.g., 1,5-COD, NBD, etc.) and acetylenes.[31] The Co^{+2} or Co^{+3} pre-catalyst used in this study is presumably reduced by Et_2AlCl to either Co^0 or Co^{+1}.

(28) (a) Deprotonation of isoprene (KO^{t}Bu, LiTMP, THF) and trapping with octyl bromide or ethylene oxide provided efficient synthesis of **24b**,**d**,**e**. For the direct metalation of isoprene, see: Brandsma, L.; Klusener, P. A. A.; Hommes, H. H.; Verkruijsse, H. D. *J. Chem. Soc., Chem. Commun.* **1985**, 1677. (b) **24f** was prepared by coupling reaction between 2-chlorobutadiene and (chloromethyl)trimethylsilane using $Ni(dppp)Cl_2$ as catalyst. For experimental details, see: Sakurai, H.; Hosomi, A.; Saito, M. *Tetrahedron Lett.* **1979**, *21*, 429.

(29) Cycloadduct **25f** was hydroborated, oxidized (BH_3, NaOH, H_2O_2), and esterified with *O*-methylmandelic acid/DCC. After isolation of the major diastereomer, treatment with NaOMe and MeOH gave the alcohol as a single enantiomer. Esterification with 3,5-dinitrobenzoyl chloride and recrystallization from methanol/pentane (1:1) gave suitable quality crystals. The absolute configuration proposed from the Mosher model was supported by X-ray crystallography of the 3,5-dinitrobenzoate ester. Details of the structure will be reported by Dr. Alan Lough.

(30) Shea, K. J.; Burke, L. D.; England, W. P. *J. Am. Chem. Soc.* **1988**, *110*, 860.

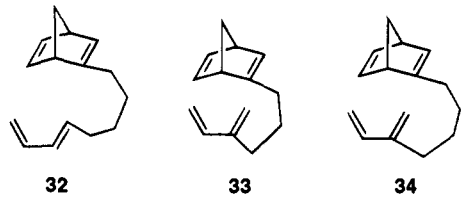


Figure 4.

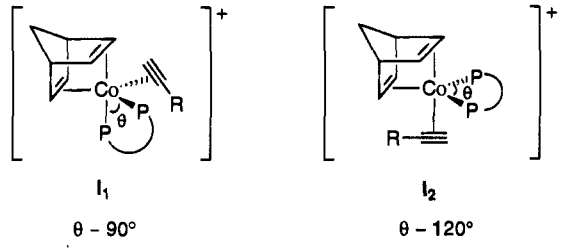


Figure 5. Possible intermediates.

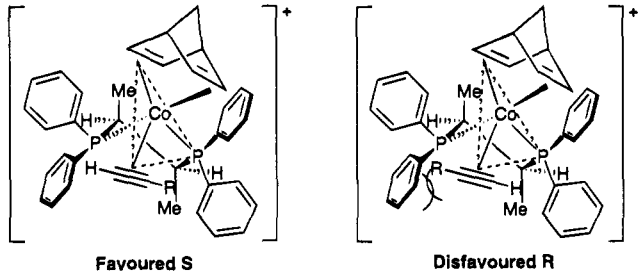


Figure 6. Proposed asymmetric complex with (*S,S*)-chiraphos.

Co^{+1}, which has the electronic configuration [Ar]$3d^8$, commonly forms five-coordinate complexes with trigonal bipyramidal geometry. Previous reports on some low-valent cobalt complexes with NBD indicate that the two olefins in NBD occupy one axial and one equatorial position (with bite angle ~ 90°) in the trigonal bipyramid.[31,32] Thus, although very little is known about the structure of the catalytically active complex, structures $\mathbf{I_1}$ and/or $\mathbf{I_2}$ are reasonable intermediates (Figure 5).

For chelating bidentate phosphine ligands, $R_2P(CH_2)_nPR_2$, the two phosphorus atoms can occupy either two equatorial positions (giving intermediate $\mathbf{I_2}$) or one equatorial and one axial position (giving intermediate $\mathbf{I_1}$), depending on the bite angle θ, and the chain length between the two phosphorus atoms.[21,31-35] Most of the bidentate phosphines shown in Figure 2 have a normal bite angle θ of approximately 85–95°,[21a] supporting the generation of intermediate $\mathbf{I_1}$ (with θ = 90°).

Asymmetric induction by a chiral phosphine on the reactive intermediate $\mathbf{I_1}$ leads to a preference for the formation of one enantiomer of deltacyclene. Figure 6 shows the proposed asymmetric complex with (*S,S*)-chiraphos. The prediction of the absolute configuration of the product from this complex is in agreement with the experimental results.

(31) Wilkinson, G.; Stone, F. G. A.; Abel, E. W. In *Comprehensive Organometallic Chemistry*; Kemmitt, R. D. W., Russell, D. R., Eds.; Pergamon Press: Toronto, 1982; Vol. 5, Chapter 34.

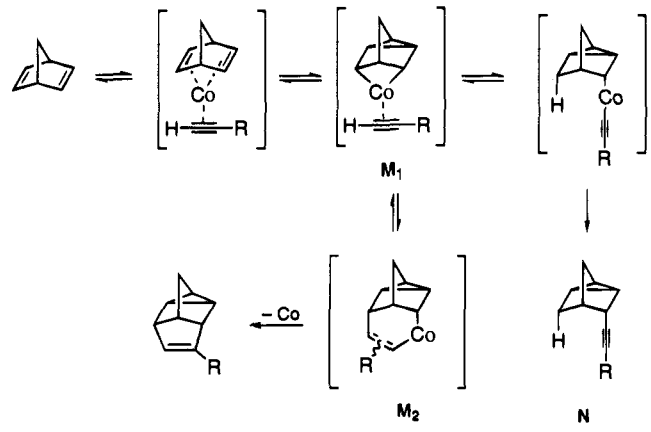
(32) (a) Swaminathan, S.; Lessinger, L. *Cryst. Struct. Commun.* **1978**, *7*, 621. (b) Stephens, F. S. *J. Chem. Soc., Dalton Trans.* **1972**, 1754. (c) Boer, F. P.; Flynn, J. J. *J. Am. Chem. Soc.* **1971**, *93*, 6495. (d) Langenbach, H. J.; Keller, E.; Vaherenkamp, H. *J. Organomet. Chem.* **1979**, *171*, 259. (e) Ng, Y. S.; Penfold, B. R. *Acta Crystallogr., Sect. B* **1978**, *34*, 1978.

(33) Wilkinson, G.; Stone, F. G. A.; Abel, E. W. In *Comprehensive Organometallic Chemistry*; Jolly, P. W., Ed.; Pergamon Press: Toronto, 1982; Vol. 6, Chapter 37.

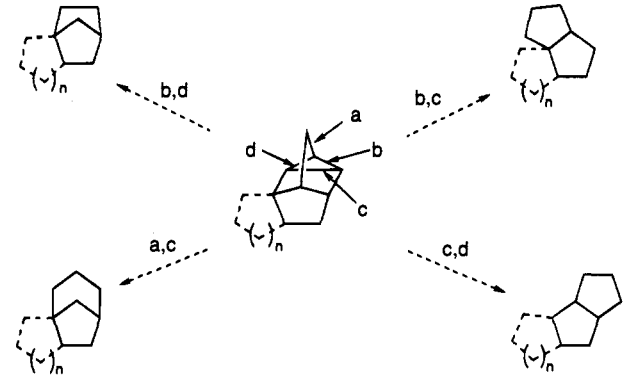
(34) Jolly, P. W.; Wilke, G. *The Organic Chemistry of Nickel*; Academic Press: New York, 1974; Vol. I.

(35) McAuliffe, C. A.; Levason, W. *Phosphine, Arsine and Stibine Complexes of the Transition Elements*; Elsevier Scientific Publishing Co.: New York, 1979.

Scheme 5. Proposed Mechanism for Cobalt-Catalyzed HDA Reaction



Scheme 6. Fragmentation Options



The individual steps in the cycloaddition are not known, but several proposals have been put forward.[4c,5b,36] Our results provide additional insight and support of these proposals. Following the complexation of NBD and the acetylene to the low-valent cobalt, formation of metallacycle $\mathbf{M_1}$ occurs (Scheme 5). This notion is supported by isolation of 5–10% of side product **N** (when R = TMS (**3i'**), Table 1), where formation of the metallacycle $\mathbf{M_1}$ has occurred but insertion into the terminal C–H bond, rather than carbometalation, follows. Carbometalation of the metallacycle–acetylene complex $\mathbf{M_1}$ would yield metallacycle $\mathbf{M_2}$, which undergoes reductive elimination to the final product. Further support for these intermediates arises from the isolation of related metallacycles ($\mathbf{M_1}$ and $\mathbf{M_2}$).[37]

Conclusions and Future Studies

We have investigated the scope of the cobalt-catalyzed [$2\pi + 2\pi + 2\pi$] (HDA) and [$2\pi + 2\pi + 4\pi$] cycloaddition reactions with norbornadienes. Moderate to excellent enantioselectivity of these cycloadditions can be achieved by the use of a catalytic amount a cobalt complex and a chiral phosphine. The regioselectivity of the cobalt-catalyzed HDA reaction of 7-substituted norbornadienes differs significantly from the related nickel-catalyzed reaction as does the reactivity of 2-substituted norbornadienes.

The intramolecular HDA reaction occurs in very good yield for a variety of substrates and provides a very powerful and

(36) For a theoretical study of proposed organometallic intermediates in metal-catalyzed HDA reaction, see: Gugelchuk, M. M.; Wisner, J. *Organometallics*, in press.

(37) (a) Halpern, J.; Cassar, L. *J. Chem. Soc., Chem. Commun.* **1970**, 1082. (b) Fraser, A. R.; Bird, P. H.; Beyman, S. A.; Shapley, J. R.; White, R.; Osborn, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 597. (c) Halpern, J. *Org. Synth. Met. Carbonyls* **1977**, 2, 705. (d) Evans, L.; Kemmit, R.; Kimura, B.; Russel, D. *J. Chem. Soc., Chem. Commun.* **1972**, 509.

efficient method for the construction of highly strained polycyclic molecules. The starting materials are readily assembled from norbornadiene.

The results presented herein lay the foundation for an efficient entry into linearly and angularly fused polycyclic natural products provided that methodology is developed for the selective cleavage of the cyclopropane carbon−carbon bonds in the cycloadducts (Scheme 6). Preliminary results in our laboratory indicate that selective cleavage is indeed possible. Details of these studies will follow shortly.

Experimental Section

General Procedure. Flash column chromatography was performed on 230−400 mesh silica gel using the method of Still.[43] Infrared spectra were taken on a Nicolet 8210E FTIR spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini-200 or VXR-400 spectrometer and are reported in parts per million from tetramethylsilane with the solvent resonance as the internal standard (chloroform, δ 7.24 ppm). ^{19}F NMR was recorded on a Varian Gemini-300 spectrometer. Chemical shifts for ^{13}C NMR spectra are reported in parts per million from tetramethylsilane with the solvent as the internal standard (deuterochloroform, δ 77.00 ppm). High-resolution mass spectra were recorded with a VG 70-250S spectrometer. Optical rotations were taken with a Perkin-Elmer 243B polarimeter. Capillary GC analyses were obtained from a Hewlett-Packard Model 5890A gas−liquid chromatography, using a HP 20M Carbowax column, equipped with a Hewlett-Packard Model 3396A digital integrator.

Unless stated otherwise commercial reagents were used without purification. Tetrahydrofuran and diethyl ether were distilled immediately prior to use from sodium wire/benzophenone. Pyridine and dichloromethane were distilled immediately prior to use from calcium hydride. BPE and duphos ligands were obtained from Professor Mark Burk (Duke University) as a gift and were used without purification. 7-Substituted norbornadienes (**7a−d**),[38] 2-substituted norbornadienes (**8a−c**),[27,39] 2-substituted-1,3-butadienes,[28] and allyldiphenylphosphine oxide[40] were prepared as described in the literature.

General Procedure for the Cobalt-Catalyzed [2π + 2π + 2π] Cycloaddition between Norbornadiene (1) and Various Acetylenes (2a−o). To a flame-dried flask equipped with a magnetic stir bar, a rubber septum, and a temperature probe were added $Co(acac)_3$ (1−2 mol %) and the phosphine ligand (1 equiv based on cobalt). The flask was flushed with argon. Benzene, norbornadiene (1 mmol), and the acetylene (1.5−2 mmol) were added. A solution of diethylaluminum chloride (DEAC) in toluene (4 equiv based on cobalt) was added dropwise, and the temperature was monitored using the internal temperature probe. The temperature was controlled by placing a water bath under the flask when necessary. It is important that the reaction temperature remain above 24−25 °C to promote the reaction but below 30−35 °C to optimize asymmetric induction. The reaction turned dark brownish-green upon addition of Et_2AlCl. The reaction was stirred at room temperature for 1−24 h as monitored by TLC. The workup consisted of removal of solvent *in vacuo* yielding dark green oils which were purified by bulb-to-bulb distillation or flash chromatography to obtain clear, colorless oils. Spectroscopic data for deltacyclenes **3b**−l are given below. The spectra of **3a,m,n** were in accord with those reported in the literature.[5b,e]

8-Butyltetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene (3b): ^1H NMR (400 MHz, $CDCl_3$) δ 5.62 (m, 1H), 2.46 (d, 1H, J = 2.2 Hz), 2.40 (br s, 1H,), 2.11 (d, 1H, J = 6.9 Hz), 2.09 (dd, 1H, J = 6.9, 1.5 Hz), 1.87 (s, 1H), 1.63 (dtt, 1H, J = 4.7, 1.6, 1.3 Hz), 1.46 (m, 2H), 1.38 (2H, m), 1.30 (h, 2H, J = 7.2 Hz), 1.23 (m, 2H), 1.21 (m, 2H), 0.87 (t, 3H, J = 7.1 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 151.3, 127.0, 57.4, 51.9, 48.7, 32.9, 31.1, 30.6, 25.6, 23.8, 22.7, 22.5, 14.1; IR (neat) 3053, 2955, 1600, 1270 cm^{-1}; HRMS calcd for $C_{13}H_{18}$ *m/e* 174.1404, found *m/e* 174.1414. With (*S,S*)-chiraphos $[\alpha]_D$ = −0.94° (*c* = 1.8, CH_2Cl_2), which corresponds to 91% ee; with (*R*)-prophos $[\alpha]_D$ = +0.4° (CH_2Cl_2), which corresponds to 78% ee.

8-(2-Propyl)tetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene (3c): ^1H NMR (400 MHz, $CDCl_3$) δ 5.61 (br s, 1H), 2.49 (m, 1H), 2.48 (m, 1H), 2.40 (h, 1H, J = 6.8 Hz), 1.86 (br s, 1H), 1.62 (m, 1H), 1.43 (m, 2H), 1.21 (m, 2H), 1.02 (d, 3H, J = 6.8 Hz), 1.01 (d, 3H, J = 6.8 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 157.6, 124.6, 57.4, 50.5, 48.4, 32.9, 30.1, 25.5, 23.7, 22.8, 22.0, 21.4; IR (neat) 3060, 2959, 1595, 1271 cm^{-1}; HRMS calcd for $C_{12}H_{16}$ *m/e* 160.1248, found *m/e* 160.1248. With (*S,S*)-chiraphos $[\alpha]_D$ = −1.9° (*c* = 1.53, CH_2Cl_2), which corresponds to 36% ee.

8-(2-Methyl-2-propyl)tetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene (3d): ^1H NMR (200 MHz, $CDCl_3$) δ 5.51 (m, 1H), 2.59 (s, 1H), 2.47 (s, 1H), 1.82 (m, 1H), 1.60 (m, 1H), 1.46 (m, 2H), 1.45−1.20 (m, 2H), 1.02 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 160.7, 123.5, 57.5, 49.3, 48.3, 40.2, 32.9, 29.3, 25.3, 23.7, 23.0; IR(neat) 3062, 2961, 1595, 1273 cm^{-1}; HRMS calcd for $C_{13}H_{18}$ *m/e* 174.1404, found *m/e* 174.1406.

Methoxybenzyl 4-(Tetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-enyl)-1-butyl Ether (3e): ^1H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, 2H, J = 8.6 Hz), 6.86 (d, 2H, J = 8.6), 5.57 (d, 1H, J = 1.3 Hz), 4.41 (s, 2H), 3.78 (s, 3H), 3.42 (d, 1H, J = 6.5 Hz), 3.41 (d, 1H, J = 6.5 Hz), 2.46 (br s, 1H), 2.39 (s, 1H), 2.12 (d, 1H, J = 7.1 Hz), 2.10 (d, 1H, J = 7.9 Hz), 1.87 (s, 1H), 1.68 (m, 3H), 1.45 (m, 2H), 1.21 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 159.9, 150.9, 131.4, 129.8, 127.7, 114.4, 72.9, 70.5, 57.6(2), 55.6, 52.1, 48.9, 33.1, 31.3, 29.9, 25.8, 25.2, 24.0, 22.8; IR (neat) 3054, 2951, 1471, 1254, 1100, 836 cm^{-1}; HRMS calcd for $C_{21}H_{26}O_2$ *m/e* 310.1926, found *m/e* 310.1928.

Dimethyl(1,1-dimethylethyl)[(3-(tetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-enyl)-1-propyl)oxy]silane (3f): ^1H NMR (200 MHz, $CDCl_3$) δ 5.58 (br s, 1H), 3.57 (t, 2H, J =7 Hz), 2.47 (br s, 1H), 2.40 (br s, 1H), 2.15 (d, 1H, J = 7.0 Hz), 2.14 (d, 1H, J = 7.1 Hz), 1.86 (br s, 1H), 1.62 (m, 2H), 1.43 (m, 2H), 1.21 (m, 1H), 0.85 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 150.7, 127.4, 63.2, 57.5, 51.9, 48.7, 40.2, 32.9, 31.6, 27.5, 26.2, 25.6, 23.8, 22.5, −5.1; IR (neat) 3060, 2961, 1737, 1595, 1472, 1101, 836 cm^{-1}. Anal. Calcd for $C_{18}H_{30}OSi$: C, 74.42; H, 10.41. Found: C, 74.60; H, 10.26.

1-(Tetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8′-enyl)-2-butyl Acetate (3g): ^1H NMR (400 MHz, $CDCl_3$) δ 5.67 (m, 1H), 4.90 (q, 0.5H, J = 7.2 Hz), 4.88 (q, 0.5H, J = 7.2 Hz), 2.47 (br s, 1H), 2.35 (m, 3H), 2.01 (s, 1.5H), 2.00 (s, 1.5H), 1.87 (m, 1H), 1.70−1.40 (m, 3H), 1.42 (m, 2H), 1.20 (m, 2H), 0.85 (t, 3H, J =7 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 171.3, 146.4, 146.2, 130.7, 130.6, 74.7, 74.5, 57.9, 57.7, 52.3, 52.0, 48.9, 48.8, 35.8, 35.4, 32.8, 26.9, 25.8, 25.6, 23.5, 23.4, 22.5, 21.4, 9.8, 9.7; IR (neat) 3062, 2961, 1737, 1595, 1372, 1269 cm^{-1}; HRMS calcd for $C_{15}H_{20}O_2$ *m/e* 232.1458 and fragment $C_{13}H_{16}$ *m/e* 172.1245, found for fragment $C_{13}H_{16}$ *m/e* 172.1235.

8-(Trimethylsilyl)tetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene (3i): ^1H NMR (400 MHz, $CDCl_3$) δ 6.30 (br d, 1H), 2.7 (s, 1H), 2.6 (dd, 1H, J = 2.7, 2.0 Hz), 1.85 (m, 1H), 1.65 (m, 1H), 1.55 (m, 2H), 1.19 (dddd, 1H, J = 6.1, 4.7, 2.0, 1.3 Hz),1.09 (dddd, 1H, J = 6.1, 4.7, 1.3, 1.3 Hz), 0.05 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 150.1, 146.1, 58.3, 52.1, 50.6, 33.6, 25.8, 23.3, 23.1, −1.2; IR (neat) 2940, 1270 cm^{-1}. Anal. Calcd for $C_{12}H_{18}Si$: C, 75.71; H, 9.53. Found: C, 75.72; H, 9.51.

2-((Trimethylsilyl)acetylene)tricyclo[2.2.1.0^{3,5}]heptane (3i′). The chemical shifts observed are similar to those reported by Lyons for 2-vinylnortricyclane.[5b] ^1H NMR (200 MHz, $CDCl_3$): δ 2.22 (s, 1H), 1.95 (br s, 1H), 1.78 (s, 1H), 1.33 (br s, 2H), 1.05−1.23 (m, 4H), 0.05 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 108.3, 85.9, 37, 36.4, 35.2, 33.1, 30.6, 31, 16.2, 11.0, 9.6, 0.1. IR (neat): 2950, 2120, 1270 cm^{-1}.

8-((Trimethylsilyl)methyl)tetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene (3j): ^1H NMR (200 MHz, $CDCl_3$) δ 5.40 (br s, 1H), 2.42 (br s, 1H), 2.29 (br s, 1H) 1.85 (br s, 1H), 1.60 (m, 3H), 1.55 (m, 1H), 1.43 (br s, 2H), 1.23 (d, 1H, J = 5.0 Hz), 1.21 (d, 1H, J = 4.8 Hz), −0.01 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 144.0, 122.2, 57.7, 54.4, 49.0, 33.0, 25.4, 23.8, 22.4, 22.0, −1.2; IR (neat) 3052, 2950, 1604, 1247 cm^{-1}; HRMS calcd for $C_{13}H_{20}Si$ *m/e* 203.1375, found *m/e* 203.1364.

8-(4-Acetoxybutyl)tetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene (3k): ^1H NMR (200 MHz, $CDCl_3$) δ 5.56 (s, 1H), 4.01 (t, 2H), 2.45 (s, 1H), 2.37 (s,

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1H), 2.12 (t, 2H), 2.08 (s, 1H), 1.85 (s, 1H), 1.61−1.43 (m, 7H), 1.21−1.17 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 171.1, 150.1, 127.3, 64.4, 57.1, 51.4, 48.3, 32.5, 30.4, 28.1, 25.2, 24.2, 23.3, 22.1, 20.7; IR (neat) 3050, 1742, 1670, 1240, 1268 cm^{-1}; HRMS calcd for $C_{15}H_{20}O_2$ *m/e* 232.1463, found *m/e* 232.1462; $[\alpha]_D = -0.25°$ ($c = 2.0$, CH_2Cl_2), which correspond to 85% ee.

8-(4-(*tert*-Butyldimethylsiloxy)butyl)tetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene (3l): ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.57 (s, 1H), 3.58 (t, 2H), 2.46 (s, 1H), 2.40 (s, 1H), 2.15 (t, 2H), 1.87 (s, 1H), 1.69−1.54 (m, 3H), 1.45 (s, 2H), 1.23 (d, 3H), 0.87 (m, 10H), 0.019 (m, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 150.4, 143.3, 127.0, 62.9, 61.5, 57.1, 51.6, 48.4, 32.6, 31.2, 27.2, 25.8, 25.3, 23.4, 22.2, −5.5; IR (neat) 3054, 1670, 1102, 1255, 812, 800 cm^{-1}; HRMS calcd for $C_{19}H_{32}SiO$ *m/e* 304.2222, found *m/e* 289.1977 (loss of CH_3); $[\alpha]_D = -0.324°$ (c = 1.5, CH_2Cl_2), which corresponds to 80% ee.

General Method for Determination of Enantiomeric Excess in the Cycloadducts. The cycloadducts prepared from the cobalt-catalyzed asymmetric cycloadditions were submitted to a hydroboration−oxidation and esterification sequence. In the hydroboration, 3 equiv of BH_3·SMe_2 were used to ensure that no resolution occurred in the reaction of a chiral monoalkylborane (generated by reaction of BH_3 with a chiral olefin) with a chiral olefin. The resulting alcohols were purified by flash chromatography and then esterified with (+)-Mosher acid chloride. The ^{19}F and ^{1}H NMR spectra were recorded for crude samples of racemic and optically enriched materials. The ratios and chemical shifts obtained were identical before and after column chromatography. The cycloadduct **3k** was converted into cycloadduct **3l** before analysis of the ee. The results obtained for **4l** were confirmed by a hydroboration of **3l** using 9-borabicyclo[3.3.1]nonane (9-BBN); this reagent was not used in all cases because of the difficulty encountered in separating cyclooctanediol from the desired product.

Alternatively, in the case of cycloadduct **3c**, it was possible to use a chiral shift reagent[41] to measure the ee directly for the olefin. This provided a third means to measure the asymmetric induction. The olefin was dissolved in $CDCl_3$, and aliquots of an *ca.* 3:1 mixture of Ag(fod):Eu(hfbc)$_3$ in $CDCl_3$ were added and spectra acquired. This process was continued until protons were clearly resolved for the racemic adduct. The process was repeated on enantiomerically enriched material and the ratio measured. The values obtained by this method were within 5% of the values obtained by the sequence described above.

General Procedure for Hydroboration−Oxidation of Deltacyclenes (3a−c,l). The cycloadduct was transferred to a flame-dried round bottom flask and either dissolved in THF (0.5 mL) or used neat (under Ar). BH_3·SMe_2 in THF (2 M) or in CH_2Cl_2 (1 M) (3 equiv based on boron) was added, and the reaction was stirred for 1 h at 0 °C and 1 h at room temperature until complete disappearance of starting material was noted as judged by TLC. The mixture was oxidized by the addition of absolute ethanol, NaOH (3 M), and H_2O_2 (30%) and heated to reflux for at least 1 h. The reaction was worked up by extracting the aqueous layer with CH_2Cl_2 (3×) and washing the combined organics with saturated NH_4Cl. The solvent was removed *in vacuo*, and the product was purified by flash chromatography (15% ethyl acetate in hexanes). Spectroscopic data for alcohols **4a−c**,l are given below.

Alcohol 4a: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.30−7.17 (m, 5H), 4.29 (d, 1H), 3.10 (t, 1H, J= 3.5 Hz), 2.27 (br s, 1H), 2.21 (br s, 1H), 2.10 (br s, 2H), 1.61−1.49 (m, 2H), 1.25 (m, 1H), 0.98−0.85 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 142.9, 128.1, 128.0, 126.0, 79.1, 58.6, 51.0, 48.5, 40.2, 30.7, 15.2, 12.8, 11.6; IR (CCl_4) 3610, 3530−3140, 3090, 3040, 3005, 2960, 2880, 2170−2400 cm^{-1}; HRMS calcd for $C_{15}H_{16}O$ *m/e* 212.1201, found *m/e* 212.1199. With (*S,S*)-chiraphos $[\alpha]_D$ = +99.4° (c = 1.23, CH_2Cl_2), and with (*R*)-prophos $[\alpha]_D = -86.5°$ (c = 1.20, CH_2Cl_2).

Alcohol 4b: ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.59 (s, 1H), 2.03 (s, 1H), 1.09 (m, 2H), 1.70−1.11 (m, 11H), 0.89−0.75 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 79.7, 53.2, 50.9, 45.9, 39.2, 32.0, 31.1, 30.9, 22.7, 14.6, 13.9, 12.6, 10.8 ppm; IR (neat) 3331, 3056 cm^{-1}; HRMS calcd for $C_{13}H_{20}O$ *m/e* 192.1514, found *m/e* 192.1516. With (*S,S*)-chiraphos $[\alpha]_D$ = +47.3° (c = 0.98, CH_2Cl_2).

Alcohol 4c: ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.71 (d, 1H), 2.05−1.94 (m, 3H), 1.70−1.41 (m, 4H), 1.41−1.25 (m, 1H), 1.17 (m, 1H), 1.11−0.98 (d, 3H), 0.98−0.87 (m, 4H), 0.82 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 78.6, 61.5, 50.8, 45.1, 39.3, 31.0, 30.7, 21.7, 21.6, 14.4, 12.6, 10.8; IR (CCl_4) 3610, 3530, 3130, 3070, 3005, 2780, 2385, 2180 cm^{-1}. With (*S,S*)-chiraphos $[\alpha]_D$ = +3.9 (c = 1.3, CH_2Cl_2), and with (*R*)-prophos $[\alpha]_D = -39.1$ (c = 0.97, CH_2Cl_2).

Alcohol 4l: ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.58 (t, 2H), 2.03 (s, 1H), 1.93 (m, 2H), 1.69 (m, 1H), 1.55−1.31 (m, 10H), 1.14 (t, 1H), 0.92−0.75 (m, 11H), 0.14 (m, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 79.6, 63.2, 53.1, 50.8, 45.8, 39.2, 32.8, 32.1, 31.1, 29.1, 25.8, 24.8, 18.2, 14.6, 12.6, 10.8, −5.5; IR (neat) 3347, 3055, 1254, 1097, 802, 812 cm^{-1}. Anal. Calcd for $C_{19}H_{34}SiO_2$: C, 70.74; H, 10.63. Found: C, 70.88; H, 10.71. With (*S,S*)-chiraphos $[\alpha]_D$ = +26.9° (c = 0.55, CH_2Cl_2).

Conversion of 3k to 3l. Direct hydroboration of **3k** gave a mixture of products; therefore, diastereomeric analysis of cycloadduct **3k** was accomplished by cleavage of the acetate and silylation of the primary alcohol to form cycloadduct **3l**.

Cycloadduct **3k** (0.7321 g, 3.16 mmol), K_2CO_3 (0.553 g, 4.0 mmol), and dry MeOH (4 mL) were stirred in a flame-dried flask under argon for 6 h, another 0.1 g of K_2CO_3 was added, and the reaction mixture was stirred overnight. The methanol was removed under reduced pressure and the resulting solid extracted into 1:1 CH_2Cl_2/H_2O with 3 × 10 mL of CH_2Cl_2. The volatiles were removed under reduced pressure, and the oil was used directly in the next step without further purification (0.605 g, 102%). A small aliquot was purified by flash chromatography (34% EtOAc/hexanes) for an optical rotation $[\alpha]_D$ = −0.38° (c = 2.4, CH_2Cl_2) (from (*S,S*)-chiraphos). ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.60 (s, 1H), 3.62 (t, 2H), 2.49 (s, 1H), 2.42 (s, 1H), 2.32 (s, 1H), 2.15 (t, 2H), 1.89 (s, 1H), 1.67−1.43 (m, 7H), 1.25 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 150.4, 127.0, 62.5, 57.0, 51.4, 48.3, 32.5, 32.2, 30.6, 25.2, 24.0, 23.3, 22.1. IR (neat): 3342, 3053, 1615, 1029, 1055 cm^{-1}. HRMS: calcd for $C_{13}H_{18}O$ *m/e* 109.1358, found *m/e* 190.1367.

Cycloadduct **3l** was prepared from the above alcohol by combining the alcohol (0.405 g, 2.13 mmol), TBDMSCl (0.375 g, 2.50 mmol), DMF (2.5 mL), and imidazole (200 mg, 2.9 mmol) in a flame-dried flask. After 3 h of stirring, the solution was poured into a separatory funnel containing 9:1 hexanes/CH_2Cl_2 and H_2O. The combined organic fractions were dried over $MgSO_4$ and the volatiles removed under reduced pressure. After flash chromatography with 2% EtOAc/hexanes, **3l** was isolated as a clear oil (0.648 g, 100%).

General Procedure for Mosher Ester Preparation. 4-(*N,N*-Dimethylamino) pyridine (DMAP) (1 equiv) was weighed into a flame-dried round bottom flask. The alcohol (1 equiv) derived from the hydroboration of the cycloaddition product was added into the flask along with triethylamine (100 μL) and 0.5 mL of CH_2Cl_2. (*R*)-(+)-Mosher acid chloride (2−3 equiv) was added with a pipette where upon the reaction changed from clear and colorless to yellow and cloudy. The reaction was stirred for 1−3 h. Workup consisted of extraction with CH_2Cl_2, washing with aqueous NH_4Cl, and drying over $MgSO_4$ followed by evaporation of solvent under reduced pressure. The product was purified by flash chromatography (or by passing through a silica plug), ensuring that all the product was recovered from the column. Comparison of the diastereomeric excesses between purified and crude esters (by ^{19}F and ^{1}H NMR) gave identical results. Yields were consistently >80%. Spectroscopic data for alcohols **5a−c**,l are given below.

Mosher Ester 5a: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.49−7.08 (m, 10H, $-CHC_6\mathbf{H}_5$ and Mosher $-C_6\mathbf{H}_5$), 5.45 (d, 1H, $-COOC\mathbf{H}-$), 3.48 (two s, 3H, $-OCH_3$), 3.33 and 3.22 (two t, 1H, $-C\mathbf{H}C_6H_5$), 2.30−0.76 (m, 8H). The $-C\mathbf{H}C_6C_5$ peaks at 3.33 and 3.22 ppm were used to determine the de and the values compared with the results of ^{19}F NMR. ^{19}F NMR (188 MHz, $CDCCl_3$): δ −72.04 and −72.10 (two s, $-CF_3$). Anal. Calcd for $C_{25}H_{23}F_3O_3$: C, 70.08; H, 5.41. Found: C, 69.77; H, 5.34.

Mosher Ester 5b: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.52−7.26 (m, 10H, Mosher $-C_6\mathbf{H}_5$), 4.77 (d, 1H, $-COOC\mathbf{H}-$), 3.46 (d, 3H, $-OCH_3$), 2.11 and 2.05 (two s, 1H, $-C\mathbf{H}C_4H_9$), 1.96−0.72 (m, 16H); de ((*S,S*)-chiraphos) 90%, ((*R*)-prophos) 78%; ^{19}F NMR (188 MHz, $CDCl_3$) δ −72.16 and −72.24 (two s, $-CF_3$), de ((*S,S*)-chiraphos) 87%, ((*R*)-prophos) 68%.

(41) Parker, D. *Chem. Rev.* **1991**, *91*, 1441.

Mosher Ester 5c: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.61−7.28 (m, 5H, Mosher $-C_6H_5$), 4.97 (s, 1H, $-COOCH-$), 3.59 (s, 3H, $-CH_3$), 2.08 (s, 1H, $-CHCH(CH_3)_2$), 2.01 and 1.88 (two s, 1H), 1.80−0.73 (m, 14H); ^{19}F NMR (188 MHz, $CDCl_3$) δ −72.05 and −72.10 (two s, 3F, $-CF_3$).

Mosher Ester 5l: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.115, 2.048 (two s, 1H; de (from acetate with (*S,S*)-chiraphos) 77%, (from **3l** prepared in benzene) 16%, (from **3l** prepared in THF/toluene) 79%; ^{19}F NMR (188 MHz, $CDCl_3$) δ −72.10, −72.08; de (from **3k**) 90%, (from **3l** prepared in benzene) 18%, (from **3l** prepared in THF/toluene) 79%.

General Procedure for the Cobalt-Catalyzed [2π + 2π + 2π] Cycloaddition between 7-Substituted Norbornadienes (6a−d) and 1-Hexyne. To a flame-dried flask equipped with a magnetic stir bar, a rubber septum, and a temperature probe, was added 7-substituted norbornadiene[38] (1 mmol), 1-hexyne (1.5−2 mmol), and benzene. The flask was flushed with argon. $Co(acac)_2$ (4−8 mol %) and dppe (1 equiv based on cobalt) were then added to yield a pink solution. A solution of diethylaluminum chloride (Et_2AlCl) in toluene (4 equiv based on cobalt) was added dropwise, and the temperature was monitored using the internal temperature probe. The temperature was controlled between 20 and 40 °C by the use of a water bath. The reaction turned dark brownish green upon addition of Et_2AlCl. The reaction was stirred at room temperature for 3−48 h. The reaction mixture was then filtered through a plug of silica (eluted with Et_2O/hexanes), and removal of the solvent *in vacuo* yielded a dark green oil which was purified by bulb-to-bulb distillation or flash chromatography to obtain clear, colorless oils. Spectroscopic data for cycloadducts **7a−d** are given below.

8-Butyl-5-hexyltetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene (7a): ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.56 (m, 1H), 2.61 (br s, 0.5H), 2.53 (br s, 0.5H), 2.47 (br s, 0.5H), 2.41 (br s, 0.5H), 2.10 (m, 2H), 1.72 (m, 2H), 1.56 (m, 1H), 1.38−1.20 (m, 16H), 0.92−0.82 (m, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 150.81, 150.60, 126.42, 126.30, 61.29, 52.08, 48.94, 48.81, 45.56, 45.13, 31.91, 31.02, 30.71, 30.38, 30.14, 30.02, 29.80, 29.66, 29.37, 28.49, 24.79, 23.55, 23.13, 22.68, 22.49, 21.88, 14.12, 13.99; IR (neat) 3051, 2959, 2924, 2854, 1616, 1462, 1377, 1265 cm^{-1}; HRMS calcd for $C_{19}H_{30}$ *m/e* 258.2347, found *m/e* 258.2344.

8-Butyl-5-phenyltetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene (7b): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.62−7.20 (m, 5H), 5.62 (m, 0.5H), 5.58 (m, 0.5H), 3.11 (br s, 1H), 2.74 (br s, 0.5H), 2.67 (br s, 0.5H), 2.55 (br s, 0.5H), 2.47 (br s, 0.5H), 2.11 (m, 2H), 1.98 (m, 1H), 1.93 (m, 1H), 1.56−1.20 (m, 6H), 0.90 (t, 1.5H, J = 6.8 Hz), 0.87 (t, 1.5H, J = 7.3 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 150.44, 150.40, 142.10, 141.95, 128.72, 127.97(2), 127.45, 127.22, 127.14, 126.18, 125.84, 63.04, 52.74, 49.48(2), 48.95, 45.73, 30.94, 30.69, 30.34, 30.28, 28.96, 24.39, 23.87, 23.15, 22.65, 22.46, 13.98, 13.95; IR (neat) 3058, 3230, 2959, 2924, 2875, 1602, 1497, 1455, 1377, 1272, 1209 cm^{-1}; HRMS calcd for $C_{19}H_{22}$ *m/e* 250.1721, found *m/e* 250.1731.

8-Butyltetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-en-5-yl Benzoate (7c): ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.07−8.00 (m, 2H), 7.58−7.37 (m, 3H), 5.66 (m, 0.41H), 5.56 (m, 0.59H), 5.07 (t, 1H, J = 1.85 Hz), 3.11 (m, 0.41H), 3.03 (br s, 0.59H), 2.74 (br s, 0.59H), 2.67 (br s, 0.41H), 2.55 (m, 0.59H), 2.20−2.06 (m, 2.41H), 1.96 (tt, 1H, J = 4.8, 1.6 Hz), 1.62−1.20 (m, 6.41H), 0.98−0.84 (m, 3.59H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 166.49, 150.59, 149.63, 132.71, 130.62, 129.52, 128.23, 126.39, 125.79, 125.57, 79.02, 58.59, 50.93, 48.79, 47.74, 35.64, 30.76, 30.32, 30.20, 30.16, 28.04, 27.93, 24.28, 23.76, 23.06, 22.51, 22.45, 22.40, 13.93; IR (neat) 3058, 2959, 2931, 2861, 1722, 1602, 1581, 1455, 1314, 1272, 1173, 1117 cm^{-1}; HRMS calcd for $C_{20}H_{22}O_2$ *m/e* 294.1620, found *m/e* 294.1639.

8-Butyl-5-(triisopropylsiloxy)tetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene (7d): ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.64 (m, 0.35H), 5.49 (m, 0.65H), 4.12−4.04 (m, 1H), 3.04 (m, 0.35H), 2.95 (br s, 0.65H), 2.60−2.48 (m, 1.3H), 2.45 (br s, 0.35H), 2.20−2.05 (m, 2.35H), 1.81 (br s, 1H), 1.64 (m, 1H), 1.50−1.22 (m, 4H), 0.94−0.85 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 151.26, 149.82, 126.83, 125.57, 76.70, 76.62, 62.54, 50.51, 48.53, 47.25, 45.23, 31.34, 31.24, 30.95, 30.45, 30.28, 24.28, 23.73, 23.05, 22.50, 22.46, 18.04, 14.04, 13.98, 12.22; IR (neat) 3058, 2956, 2868, 1465, 1362, 1257, 1109, 1073, 1014 cm^{-1}; HRMS calcd for $C_{22}H_{38}OSi$ *m/e* 346.2692, found *m/e* 346.2686.

Cobalt-Catalyzed [2π + 2π + 2π] Cycloaddition of 2-(Trimethylsilyl)norbornadiene (8c) and 1-Hexyne. To a flame-dried flask equipped with a magnetic stir bar, a rubber septum, and a temperature probe were added 2-TMS-NBD (**8c**) (200.0 mg, 1.22 mmol), 1-hexyne (0.20 mL, 1.83 mmol), and benzene (0.50 mL). $Co(acac)_3$ (21.7 mg, 5 mol %) and dppe (24.3 mg, 5 mol %) were added followed by addition of Et_2AlCl (1.8 M, 0.14 mL, 20 mol %). The reaction mixture was stirred for 3 days before being filtered through a plug of silica. Removal of the solvent *in vacuo* yielding an oil which was purified by bulb-to-bulb distillation provided the recovered starting material **8c** (56.3 mg, 28%; 60 °C at 10 mmHg) and the cycloadduct **9c** (88.0 mg, 30%, inseparable mixture of cycloadducts **B** (*meta* isomer) and **C** (*ortho* isomer) with ratio 1:11.3 (Table 4, entry 4) measured by ^{1}H NMR; 80 °C at 0.8 mmHg). Similar cycloadditions were carried out at different temperatures, with different solvent systems, and using $Co(acac)_2$ instead of $Co(acac)_3$, and the results are shown in Table 4. The ratios of cycloadducts **A**:**B**:**C** were measured by the integration in ^{1}H NMR at **A** (δ 5.68), **B** (δ 5.57), and **C** (δ 5.46). Cycloadducts **C** and **B** were identified as the *ortho* and *meta* isomers by using ^{13}C (APT) and ^{1}H NMR decoupling techniques as described in the text.

9-Butyl-1-(trimethylsilyl)tetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene (9c) (the Major *ortho* Isomer): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.46 (br s, 1H), 2.55 (m, 1H), 2.46 (br s, 1H), 2.12 (tm, 2H, J = 7.8 Hz), 1.84 (br s, 1H), 1.65 (tdd, 1H, J = 4.8, 2.9, 1.6 Hz), 1,57 (m, 1H), 1.48 (dt, 1H, J = 11.4, 1.5 Hz), 1.44−1.35 (m, 2H), 1.31 (p, 2H, J = 7.0 Hz), 1.25 (dd, 1H, J = 4.8, 1.9 Hz), 0.89 (t, 3H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.27, 129.38, 58.84, 54.24, 46.18, 32.37, 30.71, 30.40, 26.72, 25.65, 23.42, 22.41, 13.83, −2.30; IR (neat) 3064, 2934, 2875, 1710, 1463, 1407, 1381, 1249, 1086 cm^{-1}; HRMS calcd for $C_{16}H_{26}Si$ *m/e* 246.1804, found *m/e* 246.1810.

1-(2′-Norbornadienyl)ethanol (10a). Norbornadiene (23.4 mL, 217 mmol) was added to a flame-dried flask containing potassium *tert*-butoxide (13.5 g, 120 mmol) and THF (110 mL) at −70 °C (dry ice/acetone bath). *n*-Butyllithium (57.2 mL, 2.1 M, 120 mmol) was added dropwise to this solution, maintaining the temperature below −70 °C. This mixture was stirred for 30 min at −65 °C and then warmed to −35 °C over 30 min. After the mixture was cooled to −70 °C, a solution of lithium bromide (14.15 g, 163 mmol) in THF (50 mL) was added via cannula with vigorous stirring at −50 °C. After 30 min, acetaldehyde (9.1 mL, 163 mmol) in THF (20 mL) was added at −70 °C. After a further 30 min, water (300 mL) was added. The aqueous layer was extracted with ether (4 × 200 mL). The ether layer was washed with brine (1 × 250 mL) and dried over magnesium sulfate. After removal of the solvent *in vacuo*, the crude product was purified by bulb-to-bulb distillation (70 °C at 8 mmHg), providing the alcohol **10a** as a clear oil (12.3 g, 75%, ~2:1 of diastereomers): ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.71 (m, 2H), 6.30 (m, 1H), 4.46 (qd, 1H, J = 6.47, 1.51 Hz, major diastereomer), 4.42 (qd, 1H, J = 6.31, 1.26 Hz, minor diastereomer), 3.45 (m, 2H), 2.18 (s, 1H), 1.93 (m, 2H), 1.20 (d, 3H, J = 6.47 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) major diastereomer [minor diastereomer] δ 161.69, [161.42], 143.72, [143.35], [142.88], 142.60, [135.02], 134.52, 73.64, [73.50], 66.84, [66.80], 50.49, [50.34], 49.94, [49.85], 21.20, [21.05]; IR (neat) 3200−3600 (br s), 3121, 3065, 2973, 2931, 2868, 1708, 1652, 1623, 1553, 1448, 1370, 1300, 1131, 1089, 1061, 878, 808, 709 cm^{-1}; HRMS calcd for $C_9H_{12}O$ *m/e* 136.0888, found *m/e* 136.0890.

2-(2′-Norbornadienyl)propan-2-ol (10b). Norbornadiene (9.4 mL, 87 mmol) was added to a flame-dried flask containing potassium *tert*-butoxide (5.15 g, 46 mmol) and THF (47 mL) which was cooled in a dry ice/acetone bath. *n*-Butyllithium (17.4 mL, 2.5 M, 43.5 mmol) was added dropwise to this solution, maintaining the temperature below −70 °C. This mixture was stirred for 30 min at −65 °C and then warmed to −35 °C over 30 min. After cooling the mixture to −70 °C, a solution of lithium bromide (5.68 g, 66 mmol) in THF (22 mL) was added via cannula with vigorous stirring at −50 °C. After 15 min, acetone (4.8 mL, 65 mmol) in THF (8.8 mL) was added at −70 °C. After a further 20 min, water (120 mL) was added. The aqueous layer was extracted with ether (4 × 150 mL). The ether layer was washed with brine (1 × 150 mL) and dried over magnesium sulfate. After removal of the solvent *in vacuo*, the crude product was purified by bulb-to-bulb distillation (80 °C at 8 mmHg), providing the alcohol **10b** as a clear oil (3.94 g, 60%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.72 (m, 2H), 6.24 (m, 1H), 3.49 (m, 2H), 1.91 (t, 2H, J = 1.61 Hz), 1.65 (s, 1H), 1.27 (s, 3H), 1.26 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 164.61,

143.35, 142.83, 132.68, 73.27, 70.45, 50.58, 49.86, 27.95, 27.90; IR (neat) 3200−3600 (br s), 3121, 3064, 2981, 2931, 2868, 1701, 1616, 1553, 1462, 1363, 1300, 1159, 941, 808, 716, 646 cm^{-1}; HRMS calcd for $C_{10}H_{14}O$ *m/e* 150.1045, found *m/e* 150.1050.

Dienyne 11a. 18-Crown-6 (4.44 g, 16.8 mmol) in THF (15 mL) was added to a flame-dried flask containing potassium hydride (6.48 g, 162 mmol) which was cooled in a dry ice/acetone (−70 °C) bath. Alcohol **10a** (11.18 g, 82.1 mmol) in THF (25 mL) was added at −70 °C, and the resulting mixture was stirred for 30 min at −50 °C. Propargyl bromide (80% by weight in toluene, 36.1 mL, 242 mmol) was added at −70 °C, and the reaction mixture was stirred for 4 h at 0 °C. The reaction was worked up by adding saturated aqueous ammonium chloride (60 mL). The aqueous layer was extracted with ether (4 × 150 mL), and the combined ether layers were washed with brine (2 × 200 mL) and dried over magnesium sulfate. After removal of the solvent *in vacuo*, the crude product was purified by flash column chromatography (20% diethyl ether in hexanes) to provide dienyne **11a** as a mixture (1:1.5) of diastereomers (13.66 g, 96%): ^1H NMR (200 MHz, $CDCl_3$) δ 6.73 (m, 2H), 6.45 (m, 1H), 4.32 (q, 1H, $J = 6.4$ Hz), 4.10 (d_{AB}d, 1H [minor diastereomer], $J' = 15.6$, 2.3 Hz), 3.97 (d_{AB}d, 1H [minor diastereomer], $J' = 15.6$, 2.3 Hz), 3.92 (d_{AB}d, 1H [major diastereomer], $J = 15.7$, 2.3 Hz), 3.70 (d_{AB}d, 1H [major diastereomer], $J = 15.7$, 2.3 Hz), 3.50 (m, 2H), 2.35 (m, 1H), 1.96 (m, 2H), 1.29 (d, 3H [major diastereomer], $J = 6.4$ Hz), 1.16 (d, 3H [minor diastereomer], $J' = 6.4$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) major diastereomer [minor diastereomer] δ 157.74, [157.39], [143.02], 142.99, [142.95], 142.81, [139.39], 138.91, [122.26], 126.50, [80.40], 80.32, 73.00, [72.58], 72.55, 55.09, [55.03], [50.19], 49.92, 49.39, [49.18], 19.51, [18.36]; IR (neat) 3304, 3065, 2981, 2938, 2868, 1756, 1616, 1553, 1441, 1370, 1335, 1300, 1075, 808 cm^{-1}; HRMS calcd for $C_{12}H_{14}O$ 174.1045, found *m/e* 174.1050.

Dienyne 11b. 18-Crown-6 (220 mg, 0.73 mmol) in THF (4 mL) was added to a flame-dried flask containing potassium hydride (294 mg, 7.32 mmol) which was cooled in a dry ice/acetonitrile (−30 °C) bath. Alcohol **10b** (567 mg, 3.66 mmol) in THF (4 mL) was added at −30 °C, and the resulting mixture was stirred for 5 h at 0 °C. Propargyl bromide (80% by weight in toluene, 1.28 mL, 11 mmol) was added at −30 °C, and the mixture was stirred for 40 h at room temperature. The reaction mixture was then worked up by adding saturated aqueous ammonium chloride (10 mL). The aqueous layer was extracted with ether (4 × 30 mL). The ether layer was washed with brine (1 × 80 mL) and then dried over magnesium sulfate. After removal of the solvent *in vacuo*, the crude product was purified by flash column chromatography (50% diethyl ether in hexanes) to provide the dienyne **11b** (267 mg, 39%): ^1H NMR (200 MHz, $CDCl_3$) δ 6.73 (m, 2H), 6.37 (m, 1H), 3.83 (d_{AB}d, 1H, $J = 15.12$, 2.45 Hz), 3.74 (d_{AB}d, 1H, $J = 15.12$, 2.45 Hz), 3.54 (m, 2H), 2.33 (t, 1H, $J = 2.45$ Hz), 1.94 (t, 2H, $J = 1.64$ Hz), 1.31 (s, 3H), 1.20 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 161.32, 142.97, 142.82, 137.82, 81.59, 75.83, 73.10, 73.06, 51.48, 50.39, 50.22, 25.02; IR (neat) 3297, 3114, 3065, 2981, 2931, 2868, 2116, 1736, 1645, 1616, 1553, 1441, 1370, 1335, 1300, 1075, 1047, 878, 850, 808, 716, 653, 625 cm^{-1}; HRMS calcd for $C_{13}H_{16}O$ *m/e* 188.1201, found *m/e* 188.1192.

3-(2′-Norbornadienyl)propyl Tosylate (19a). Norbornadiene (6.0 mL, 56 mmol) was added to a flame-dried flask containing potassium *tert*-butoxide (5.77 g, 51 mmol) and THF (35 mL) which was cooled in a dry ice/acetone bath. *n*-Butyllithium (19.5 mL, 48.8 mmol) was added dropwise to this solution, maintaining the temperature below −50 °C. This mixture was stirred for 30 min at −65 °C and then warmed to −40 °C over 30 min. After the mixture was cooled to −70 °C, 3-bromopropan-1-ol (1.80 mL, 19.9 mmol) was added dropwise. The mixture was stirred for 1.5 h in the dry ice/acetone bath, with gradual warming to −35 °C, then to room temperature over 30 min. The reaction was quenched with aqueous $NaHSO_4$ (1 M, 100 mL), the aqueous layer was extracted with ether (3 × 200 mL), and the combined ether layer was washed sequentially with water (2 × 100 mL) and brine (1 × 100 mL) and dried over magnesium sulfate. After removal of the solvent *in vacuo*, the unreacted 3-bromopropan-1-ol was removed by bulb-to-bulb distillation. The product 3-(2′-norbornadienyl)propan-1-ol was then obtained by bulb-to-bulb distillation (80 °C at 0.25 mmHg, 2.25 g, 75%): ^1H NMR (200 MHz, $CDCl_3$) δ 6.73 (m, 2H), 6.14 (m, 1H), 3.59 (t, 2H, $J = 6.4$ Hz), 3.48 (br s, 1H), 3.27 (br s, 1H), 2.26 (m, 2H), 1.94 (m, 2H), 1.68 (m, 2H), 1.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.21, 143.74, 142.28, 133.75, 73.45, 62.54, 53.42, 49.99, 30.06, 27.77; IR (neat) 3300 (br s), 3064, 2968, 2933, 2865, 1622, 1556 cm^{-1}; HRMS calcd for $C_{10}H_{14}O$ *m/e* 150.1045, found *m/e* 150.1044. Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 78.89; H, 9.66.

The tosylate (**19a**) was prepared from the above alcohol (2.25 g, 15.0 mmol) using tosyl chloride (3.21 g, 16.8 mmol) and pyridine (3.2 mL, 40 mmol) in dichloromethane (20 mL). The mixture was stirred overnight, diluted with dichloromethane (350 mL) and extracted with $NaHSO_4$ (1 M, 2 × 150 mL) and brine (1 × 150 mL). The organic layer was dried over magnesium sulfate, the solvent was removed *in vacuo*, and the crude product (4.68 g, contains a trace of tosyl chloride) was used directly in the next reaction (synthesis of dienyne **13a−d**). A small sample was purified by flash chromatography (50% diethyl ether in hexanes) for characterization: ^1H NMR (200 MHz, $CDCl_3$) δ 7.75 (d_{AB}, 2H, $J = 8.4$ Hz), 7.32 (d_{AB}, 2H, $J = 8.4$ Hz), 6.65 (m, 2H), 6.00 (m, 1H), 3.93 (t, 2H, $J = 6.7$ Hz), 3.42 (br s, 1H), 3.16 (br s, 1H), 2.43 (s, 3H), 2.20 (m, 2H), 1.88 (t, 2H, $J = 1.6$ Hz), 1.74 (d_{AB}d, 1H, $J = 6.4$, 6.4 Hz), 1.67 (d_{AB}dd, 1H, $J = 6.4$, 6.4, 1.6 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 156.34, 144.48, 143.56, 141.86, 134.54, 132.93, 129.61, 127.68, 73.32, 69.87, 53.15, 49.92, 26.95, 26.24, 21.48; IR (neat) 3065, 2970, 2937, 2869, 1600, 1557, 1498, 1449, 1361, 1307, 1175, 1097 cm^{-1}; HRMS calcd for $C_{17}H_{20}O_3S$ *m/e* (M^+) 304.1133, *m/e* $(M - H)^-$ 303.1055, found *m/e* $(M - H)^-$ 303.1050.

4-(2′-Norbornadienyl)-1-bromobutane (19b). Norbornadiene (9.0 mL, 83 mmol) was added to a flame-dried flask containing potassium *tert*-butoxide (8.85 g, 79 mmol) and THF (30 mL) which was cooled in a dry ice/acetone bath. *n*-Butyllithium (30.0 mL, 2.5 M, 75 mmol) was added dropwise to this solution, maintaining the temperature below −50 °C. This mixture was stirred for 30 min at −65 °C and then warmed to −40 °C over 30 min. After cooling the mixture to −65 °C, it was added via cannula over 30 min to a cooled flask containing 1,4-dibromobutane (38.0 mL, 318 mmol) in THF (30 mL). The mixture was stirred for 3 h in the dry ice bath, with gradual warming to −40 °C. The reaction was then quenched with saturated ammonium chloride (100 mL). The aqueous layer was extracted with dichloromethane (5 × 100 mL). The organic layer was then washed sequentially with water (2 × 150 mL) and brine (1 × 150 mL) and dried over magnesium sulfate. After removal of the solvent *in vacuo*, the crude product was distilled to give three fractions: the first fraction contained recovered 1,4-dibromobutane, the second fraction consisted of a mixture of the product with 1,4-dibromobutane (4.96 g, ca. 90:10 starting material: product), and the third fraction contained the product (65−70 °C at 0.6 mmHg, 9.86 g, 58%, ca. 94:6 product:starting material). ^1H NMR (200 MHz, $CDCl_3$) δ 6.74 (m, 2H), 6.12 (m, 1H), 3.47 (br s, 1H), 3.38 (t, 2H, $J = 6.7$ Hz), 3.26 (br s, 1H), 2.20 (t, 2H, $J = 5.9$ Hz), 1.93 (m, 2H), 1.80 (m, 2H), 1.56 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.96, 143.81, 142.28, 133.97, 73.51, 53.37, 50.05, 33.81, 32.30, 30.48, 25.67. IR (neat): 3064, 2965, 2933, 2864, 2838, 1555, 1450 cm^{-1}. HRMS: calcd for $C_{11}H_{15}Br$ *m/e* 226.0358, found *m/e* 226.0346.

Dienyne 13a. Tosylate **19a** (4.68 g, 15.4 mmol) in THF (25 mL) was added to lithium acetylide ethylenediamine complex (5.70 g, 90% by weight, 56 mmol) in DMSO (25 mL). The reaction was stirred for 1 h and then quenched by the addition of water (150 mL). The product was extracted into pentane (3 × 250 mL), and the organic layer was washed sequentially with water (3 × 100 mL) and brine (1 × 100 mL) and then dried over magnesium sulfate. The solvent was removed *in vacuo*, and the crude product was purified by bulb-to-bulb distillation (80 °C at 5 mmHg) to provide dienyne **13a** as a clear oil (2.39 g, 78%): ^1H NMR (200 MHz, $CDCl_3$) δ 6.74 (m, 2H), 6.14 (m, 2H), 3.47 (br s, 1H), 3.25 (br s, 1H), 2.28 (m, 2H), 2.12 (m, 2H), 1.94 (m, 2H), 1.68 (d_{AB}, 1H, $J = 7.13$ Hz), 1.61 (d_{AB}, 1H, $J = 7.13$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.58, 143.83, 142.26, 134.23, 84.38, 73.52, 68.32, 53.43, 50.07, 30.39, 26.05, 17.92; IR (neat) 3307, 3313, 3064, 2970, 2934, 2865, 2835, 2118, 1555, 1452 cm^{-1}; HRMS calcd for $C_{12}H_{14}$ *m/e* 158.1095, found *m/e* 158.1088.

Dienyne 13b. *n*-Butyllithium (2.32 mL, 2.5 M, 5.79 mmol) was added to the dienyne **13a** (763 mg, 4.82 mmol) in THF (3 mL) at −70 °C (dry ice/acetone bath). After stirring for 30 min, methyl iodide (0.6 mL, 9.65 mmol) was added at −70 °C. The reaction mixture was warmed to room temperature, and DMSO (3 mL) was added. After

stirring for 3 h, the reaction mixture was quenched by the addition of water (80 mL). The aqueous layer was extracted with pentane (4 × 80 mL). The organic layer was washed with water (2 × 100 mL) and brine (1 × 80 mL) and then dried over magnesium sulfate. After removal of the solvent *in vacuo*, the crude product was purified by bulb-to-bulb distillation (70 °C at 1.5 mmHg) to provide dienyne **13b** as a clear oil (803 mg, 97%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.72 (m, 2H), 6.12 (m, 1H), 3.46 (m, 1H), 3.24 (m, 1H), 2.24 (m, 2H), 2.04 (m, 2H), 1.93 (m, 2H), 1.74 (t, 3H, J = 2.56 Hz), 1.56 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 158.15, 143.97, 142.46, 134.04, 78.99, 75.51, 73.44, 53.37, 49.95, 30.46, 26.48, 18.13, 3.19; IR (neat) 3114, 3065, 2973, 2938, 2868, 2362, 1631, 1553, 1455, 1434, 1307, 878, 688 cm^{-1}; HRMS calcd for $C_{13}H_{16}$ *m/e* 172.1252, found *m/e* 172.1247.

Dienyne 13c. *n*-Butyllithium (4.70 mL, 11.8 mmol) was added to a solution of trimethylsilylacetylene (1.70 mL, 12.0 mmol) in THF (9.0 mL) at −78 °C. The reaction was stirred for 1 h followed by the addition of the tosylate **19a** (2.83 g, 9.30 mmol) in THF (12 mL) at −78 °C. The reaction mixture was then warmed to 0 °C, and DMSO (18 mL) was added. The mixture was stirred at room temperature for 2.5 h before quenching with water (50 mL). The product was extracted into pentane (3 × 250 mL), and the organic layer was washed sequentially with water (3 × 100 mL) and brine (1 × 100 mL) and dried over magnesium sulfate. The solvent was removed *in vacuo*, and the product was purified twice by bulb-to-bulb distillation (80 °C at 0.5 mmHg) to provide dienyne **13c** as a clear oil (1.22 g, 79%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.75 (d_{AB}dd, 1H, J = 5.2, 2.7, 0.9 Hz), 6.72 (d_{AB}dd, 1H, J = 5.2, 2.6, 0.8 Hz), 6.14 (dtd, 1H, J = 3.1, 1.5, 0.8 Hz), 3.47 (br s, 1H), 3.26 (br s, 1H), 2.28 (d_{AB}dd, 1H, J = 14.9, 7.3, 1.5 Hz), 2.24 (d_{AB}dd, 1H, J = 14.9, 6.6, 1.5 Hz), 2.15 (t, 2H, J = 7.1 Hz), 1.97 (d_{AB}t, 1H, J = 5.74, 1.63 Hz), 1.93 (d_{AB}t, 1H, J = 5.74, 1.59 Hz), 1.61 (m, 2H), 0.13 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.72, 143.84, 142.31, 134.23, 107.31, 84.60, 73.55, 53.50, 50.12, 30.48, 26.29, 19.43, 0.19; IR (neat) 3113, 3065, 2964, 2934, 2901, 2865, 2844, 2838, 2174, 1620, 1556, 1450 cm^{-1}; HRMS calcd for $C_{15}H_{22}Si$ *m/e* 230.1490, found *m/e* 230.1478.

Dienyne 13d. *n*-Butyllithium (2.10 mL, 5.25 mmol) was added to a solution of phenyl acetylene (0.59 mL, 5.4 mmol) in THF (5.0 mL) at −78 °C. The reaction was stirred for 1 h followed by the addition of the tosylate **19a** (1.50 g, 4.93 mmol) in THF (7.0 mL). The reaction mixture was then warmed to 0 °C, and DMSO (10 mL) was added. The mixture was stirred at room temperature for 3 h before quenching with water (100 mL). The product was extracted into pentane (3 × 200 mL), and the organic layer was washed sequentially with water (3 × 100 mL) and brine (1 × 100 mL) and dried over magnesium sulfate. The solvent was removed *in vacuo*, and the product was purified by bulb-to-bulb distillation to give a forerun (60 °C at 0.1 mmHg, 38 mg) and the desired product **13d** (90−100 °C at 0.1 mmHg, 230 mg, 20%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.37 (m, 2H), 7.26 (m, 3H), 6.76 (m, 2H), 6.18 (m, 1H), 3.49 (br s, 1H), 3.30 (br s, 1H), 2.35 (t, 4H, J = 7.1 Hz), 1.97 (m, 2H), 1.77 (d_{AB}t, 1H, J = 7.02 Hz), 1.70 (d_{AB}t, 1H, J = 7.02 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.78, 143.86, 142.33, 134.19, 131.52, 128.15, 127.47, 124.02, 90.05, 80.82, 73.56, 53.50, 50.11, 30.61, 26.36, 18.97; IR (neat, cm^{-1}) 3063, 3019, 2970, 2932, 2864, 2839, 2200, 1598, 1490, 1450 cm^{-1}; HRMS calcd for $C_{18}H_{18}$ *m/e* 234.1408, found *m/e* 234.1397.

Dienyne 15a. 4-(2′-Norbornadienyl)-1-bromobutane (**19b**) (988 mg, 4.35 mmol) in DMSO (1.0 mL) was added to lithium acetylide ethylenediamine complex (1.14 g, 90% by weight, 11 mmol) in DMSO (2.0 mL) at ca. 10 °C. The reaction was stirred for 1 h and quenched carefully by the addition of water (25 mL). The product was extracted into pentane (4 × 40 mL), and the organic layer was washed sequentially with water (2 × 40 mL) and brine (1 × 40 mL) and then dried over magnesium sulfate. The solvent was removed *in vacuo*, and the product was purified by bulb-to-bulb distillation (80−90 °C at 5 mmHg) to provide dienyne **15a** as a clear oil (471 mg, 62%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.75 (m, 2H), 6.14 (m, 1H), 3.49 (br s, 1H), 3.28 (br s, 1H), 2.19 (m, 4H), 1.98 (dt, 1H), 1.94 (m, 2H), 1.51 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.34, 143.79, 142.32, 133.59, 84.53, 73.45, 68.17, 53.40, 50.01, 30.88, 28.05, 26.22, 18.22; IR (neat) 3307, 3116, 3064, 2970, 2934, 2863, 2840, 2118, 1555, 1459 cm^{-1}. Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.83; H, 9.01.

Dienyne 15b. *n*-Butyllithium (1.32 mL, 2.5 M, 3.3 mmol) was added to the dienyne **15a** (473 mg, 2.75 mmol) in THF (2 mL) at −70 °C (dry ice/acetone bath). After stirring for 30 min, methyl iodide (0.34 mL, 5.5 mmol) was added at −70 °C. The reaction mixture was warmed to room temperature and DMSO (2 mL) was added. After being stirred at room temperature for 5 h, the reaction mixture was quenched by the addition of water (60 mL). The aqueous layer was extracted with pentane (4 × 60 mL). The organic layer was washed with water (2 × 80 mL) and brine (1 × 60 mL) and then dried over magnesium sulfate. After removal of the solvent *in vacuo*, the crude product was purified by bulb-to-bulb distillation (85 °C at 2 mmHg) to provide dienyne **15b** as a clear oil (494 mg, 96%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.73 (m, 2H), 6.11 (m, 1H), 3.46 (m, 1H), 3.25 (m, 1H), 2.17 (m, 2H), 2.08 (m, 2H), 1.93 (m, 2H), 1.74 (t, 3H, J = 2.35 Hz), 1.45 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 158.62, 143.87, 142.41, 133.51, 79.30, 75.48, 73.53, 53.55, 50.13, 31.11, 28.83, 26.51, 18.69, 3.58; IR (neat, cm^{-1}) 3114, 3065, 2966, 2931, 2861, 2052, 1623, 1553, 1448, 1328, 1300, 1230, 1188 cm^{-1}; HRMS calcd for $C_{14}H_{18}$ *m/e* 186.1408, found *m/e* 186.1396.

Dienyne 15c. *n*-Butyllithium (2.20 mL, 5.50 mmol) was added to a solution of trimethylsilylacetylene (1.0 mL, 7.1 mmol) in THF (3.5 mL) at −78 °C. The reaction was stirred for 1 h before the addition of 4-(2′-norbornadienyl)-1-bromobutane (**19b**) (898 mg, 3.95 mmol) in DMSO (5.0 mL) at 0 °C. The mixture was then warmed to room temperature and stirred for 3.5 h before quenching with water (30 mL). The product was extracted into pentane (5 × 80 mL), and the organic layer was washed sequentially with water (2 × 40 mL) and brine (1 × 40 mL) and dried over magnesium sulfate. The solvent was removed *in vacuo*, and the product was purified by bulb-to-bulb distillation (80−90 °C at 0.5 mmHg) to provide dienyne **15c** as a clear oil (816 mg, 86%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.73 (m, 2H), 6.11 (br s, 1H), 3.47 (br s, 1H), 3.25 (br s, 1H), 2.19 (t, 4H, J = 6.70 Hz), 1.93 (m, 2H), 1.47 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.42, 143.78, 142.34, 133.52, 107.49, 84.36, 73.43, 53.39, 50.00, 30.88, 28.14, 26.27, 19.68, 0.16; IR (neat) 3116, 3065, 2961, 2934, 2900, 2863, 2840, 2175, 1621, 1556 cm^{-1}; HRMS calcd for $C_{16}H_{24}Si$ *m/e* 244.1647, found *m/e* 244.1638.

(2-Norbornadienyl)methyl Acetate (20). Acetic anhydride (4.2 mL, 44.5 mmol) was added to a flame-dried flask containing (2-norbornadienyl)methanol[27a] (3.40 g, 27.83 mmol), pyridine (7.0 mL, 86.6 mmol), and dichloromethane (60 mL), and the reaction was stirred overnight at room temperature. After being quenched with water, the product was extracted into dichloromethane and the organic layer was washed sequentially with saturated copper(II) sulphate, water, and brine and dried over magnesium sulfate. The solvent was removed *in vacuo*, and the product was purified by flash column chromatography (10% diethyl ether in hexanes) to provide acetate **20** as a clear oil (3.92 g, 86%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.73 (m, 2H), 6.48 (m, 1H), 4.67 (s, 2H), 3.53 (br s, 1H), 3.39 (br s, 1H), 2.02 (s, 3H), 2.00 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 170.63, 152.54, 143.27, 142.32, 139.43, 73.70, 62.98, 51.41, 50.20, 20.84; IR (neat) 3064, 2976, 2942, 2867, 1743, 1646, 1555, 1443, 1378, 1248, 1029 cm^{-1}. This acetate polymerized easily on standing and was used immediately (within a day) for the next step without further characterization.

Diethyl ((2-Norbornadienyl)methyl)malonate (21). (2-Norbornadienyl)methyl acetate (**20**) (2.00 g, 12.2 mmol) in THF (13 mL) was added to a flame-dried flask containing triphenylphosphine (0.32 g, 1.22 mmol) and tetrakis(triphenylphosphine)palladium (0.99 g, 0.86 mmol), and the mixture was stirred at room temperature for 1 h. In a separate flask, diethyl malonate (11.0 mL, 72.5 mmol) was added slowly to a slurry of pentane-washed sodium hydride (1.72 g, 71.7 mmol) in THF (42 mL) and stirred for 20 min. The resulting clear solution was added to the former via a cannula, and the combined reaction mixture was stirred at 65 °C for 24 h. After being quenched with water (100 mL), the product was extracted into Et_2O (3 × 100 mL) and the organic layer was washed brine and dried over magnesium sulfate. The solvent was removed *in vacuo*, the excess diethyl malonate was removed by vacuum distillation (50 °C at 0.25 mmHg), and the crude product was purified by flash column chromatography (20% diethyl ether in hexanes) to provide the malonate **21** as a clear oil (2.42 g, 75%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.60 (m, 2H), 6.19 (m, 2H), 4.17 (q, 4H, J = 7.1 Hz), 3.47 (t, 1H, J = 7.6 Hz), 3.45 (m, 1H), 3.26 (br s, 1H), 2.76 (d_{AB}d,

2H, J = 15.5, 7.6 Hz), 1.90 (m, 2H), 1.21 (t, 3H, J = 7.1 Hz), 1.20 (t, 3H, J = 7.1 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 169.03, 154.56, 143.52, 142.12, 136.09, 73.56, 61.26, 53.44, 50.60, 50.17, 30.65, 14.01; IR (neat) 3064, 2983, 2942, 2908, 2874, 1731, 1643, 1464, 1445, 1392, 1367, 1277, 1036 cm^{-1}; HRMS calcd for $C_{15}H_{20}O_4$ *m/e* 264.1361, found *m/e* 264.1355.

Dienyne 17a. Diethyl ((2-norbornadienyl)methyl)malonate (**21**) (500.2 mg, 1.89 mmol) in THF (9 mL) was added to a slurry of pentane-washed sodium hydride (80.0 mg, 3.33 mmol), and the mixture was stirred at room temperature for 2 h. Propargyl bromide (80 wt % in toluene, 0.70 mL, 6.26 mmol) was then added to the mixture at 0 °C. The combined reaction mixture was stirred overnight at room temperature. After being quenched with saturated ammonium chloride (50 mL), the product was extracted into Et_2O (3 × 50 mL) and the organic layer was washed brine and dried over magnesium sulfate. The solvent was removed *in vacuo*, and the crude product was purified by flash column chromatography (20% diethyl ether in hexanes) to provide the dienyne **17a** as a clear oil (538.4 mg, 94%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.70 (m, 2H), 6.38 (m, 1H), 4.21 (m, 4H), 3.47 (m, 1H), 3.22 (br s, 1H), 3.01 (br s, 2H), 2.70 (d_{AB}d, 2H, J = 17.1, 2,7 Hz), 2.06−1.90 (m, 3H), 1.25 (m, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 169.75, 169.65, 151.92, 143.14, 142.68, 140.12, 79.05, 74.22, 71.38, 61.41, 56.32, 53.97, 50.14, 33.11, 22.51, 13.87; IR (neat) 3288, 3065, 2984, 2937, 2867, 2124, 1734, 1618, 1558, 1468, 1448, 1369, 1289, 1233, 1199, 1098 cm^{-1}; HRMS calcd for $C_{18}H_{22}O_4$ *m/e* 302.1518, found *m/e* 302.1522.

Dienyne 17b. Diethyl ((2-norbornadienyl)methyl)malonate (**21**) (498.9 mg, 1.89 mmol) in THF (9 mL) was added to a slurry of pentane-washed sodium hydride (85.0 mg, 3.54 mmol), and the mixture was stirred at room temperature for 2 h. 3-Bromo-1-(trimethylsilyl)-1-propyne (0.80 mL, 5.65 mmol) was then added to the mixture at 0 °C. The combined reaction mixture was stirred overnight at room temperature. After being quenched with saturated ammonium chloride (50 mL), the product was extracted into Et_2O (3 × 50 mL) and the organic layer was washed brine and dried over magnesium sulfate. The solvent was removed *in vacuo*, and the crude product was purified by flash column chromatography (20% diethyl ether in hexanes) to provide the dienyne **17b** as a clear oil (648.9 mg, 92%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.67 (m, 2H), 6.33 (m, 1H), 4.16 (m, 4H), 3.44 (br s, 1H), 3.18 (br s, 1H), 2.96 (br s, 2H), 2.68 (d_{AB}, 2H, J = 17.2 Hz), 1.92 (m, 2H), 1.23 (t, 3H, J = 7.1 Hz), 1.22 (t, 3H, J = 7.1 Hz), 0.10 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 169.91, 169.83, 152.17, 143.28, 142.79, 140.13, 101.85, 88.12, 74.32, 61.46, 56.67, 54.10, 50.27, 33.25, 23.97, 14.01, −0.07; IR (neat) 3064, 2980, 2961, 2903, 2864, 2259, 2181, 1740, 1633, 1467, 1447, 1368, 1291, 1253, 1190, 1097, 1034 cm^{-1}; HRMS calcd for $C_{21}H_{30}O_4Si$ *m/e* 374.1913, found *m/e* 374.1920.

General Procedure for the Cobalt-Catalyzed Intramolecular [2π + 2π + 2π] Cycloaddition. $Co(acac)_3$ (2−10 mol %) and dppe (1.6−8 mol %) were added to a flame-dried flask equipped with a magnetic stir bar and a rubber septum. The dienyne (1 mmol) was added in benzene (6 mL), followed by Et_2AlCl (DEAC, 12 −60 mol %, 1.8 M in toluene). The mixture was stirred at room temperature under nitrogen for 3−36 h. The reaction was quenched by the addition of 20 drops of 2-propanol and 10 mL of hexanes to precipitate the inorganic material, and the resulting mixture was filtered through a plug of silica using hexanes or ether (100 mL). Evaporation of the solvent gave a crude product which was purified by bulb-to-bulb distillation or flash column chromatography on silica gel. Spectroscopic data for cycloadducts **12a,b**, **14a−d**, **16a−c**, and **18a,b** are given below.

Pentacyclene 12a. Pentacyclene **12a** was obtained as an inseparable mixture of diastereomers (~3.5:1): ^{1}H NMR (200 MHz, $CDCl_3$) major diastereomer [minor diastereomer] δ 5.58 (dt, 1H, J = 2.4, 2.4 Hz), [5.52 (dt, 1H, J' = 2.5, 2.5 Hz)], 4.25 (m, 2H), 4.18 (q, 1H, J = 6.4 Hz), [3.95 (q, 1H, J' = 6.4 Hz)], 2.82 (m, 1H), 2.10 (br s, 1H), 1.75 (m, 1H), 1.44 (m, 4H), [1.37 (m, 4H)], 1.10 (d, 3H, J = 6.4 Hz), [1.25 (d, 3H, J = 6.4 Hz)]; ^{13}C NMR (100 MHz, $CDCl_3$) major diastereomer [minor diastereomer] δ 155.31, [156.60], 119.31, [118.68], 74.99, [75.30], 70.55, 63.94, [64.68], 60.33, 54.88, [61.00], [55.03], 32.04, [31.93], 25.82, [25.47], 25.36, 25.32, 24.35, 21.61, [18.08], 16.92; IR (neat) 3065, 2978, 2931, 2861, 1652, 1455, 1377, 1272, 1251 cm^{-1}; HRMS calcd for $C_{12}H_{14}O$ *m/e* 174.1044, found *m/e* 174.1047.

Pentacyclene 12b: ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.51 (dt, 1H, J = 2.4, 2.3 Hz), 4.30 (m, 2H), 2.82 (br s, 1H), 1.97 (m, 1H), 1.79 (m, 1H), 1.43 (m, 4H), 1.29 (s, 3H), 1.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.50, 118.67, 78.34, 72.80, 62.68, 59.04, 55.09, 31.62, 25.63, 25.60, 25.44, 24.30, 23.34; IR (neat) 3065, 2966, 2931, 2861, 1462, 1384, 1363, 1328, 1258 cm^{-1}; HRMS calcd for $C_{13}H_{16}O$ *m/e* 188.1201, found *m/e* 188.1200.

Pentacyclene 14a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.50 (dt, 1H, J = 2.4, 2.4 Hz), 2.66 (dt, 1H, J = 2.4, 2.2 Hz), 2.22 (d_{AB}dd, 1H, J = 7.0, 2.2, 0.9 Hz), 2.20 (d_{AB}d, 1H, J = 7.0, 2.2 Hz), 1.96 (m, 2H), 1.75 (br s, 1H), 1.65 (m, 1H), 1.60 (d_{AB}t, 1H, J = 12.9, 6.9 Hz), 1.49 (d_{AB}t, 1H, J = 12.9, 7.4 Hz), 1.44 (m, 2H), 1.36 (ddd, 1H, J = 5.4, 5.4, 2.4 Hz), 1.13 (ddm, 1H, J = 5.4, 5.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.47, 119.37, 66.23, 63.27, 53.49, 32.24, 30.41, 27.45, 26.28, 26.17, 25.15, 24.81; IR (neat) 3059, 2950, 2879, 2855, 2837, 1640, 1445 cm^{-1}; HRMS calcd for $C_{12}H_{14}$ *m/e* 158.1095, found *m/e* 158.1101.

Pentacyclene 14b: ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.45 (t, 1H, J = 2.1 Hz), 2.11 (m, 2H), 1.95 (m, 2H), 1.72 (m, 1H), 1.69 (t, 3H, J = 1.7 Hz), 1.61 (m, 1H), 1.50 (m, 2H), 1.39 (m, 3H), 1.13 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 149.62, 129.05, 66.09, 62.04, 58.08, 32.03, 30.55, 28.09, 26.72, 24.65, 24.31, 24.18, 14.54; IR (neat) 3044, 2931, 2854, 2727, 1645, 1441, 1377, 1314, 1272, 1216, 1159 cm^{-1}; HRMS calcd for $C_{13}H_{16}$ *m/e* 172.1252, found *m/e* 172.1248.

Pentacyclene 14c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.75 (t, 1H, J = 2.1 Hz), 2.26 (m, 2H), 1.98 (m, 2H), 1.64 (br s, 1H), 1.60 (m, 2H), 1.53 (t, 1H, J = ca. 13 Hz), 1.46 (m, 2H), 1.23 (m, 1H), 1.10 (dd, 1H, J = 5.6, 5.3 Hz), 0.06 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.66, 130.70, 67.66, 61.85, 56.98, 32.34, 30.35, 27.20, 27.13, 26.12, 24.70, 24.11, −0.73; IR (neat) 3060, 3047, 3023, 2950, 2934, 2856, 2833, 1610, 1446 cm^{-1}; HRMS calcd for $C_{15}H_{22}Si$ *m/e* 230.1490, found *m/e* 230.1485.

Pentacyclene 14d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (m, 4H), 7.12 (tt, 1H, J = 7.2, 1.4 Hz), 3.22 (t, 1H, J = 2.2 Hz), 2.56 (m, 2H), 2.13 (m, 2H), 1.89 (br s, 1H), 1.72 (m, 2H), 1.57 (m, 4H), 1.31 (dd, 1H, J = 6.2, 4.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.49, 137.46, 132.02, 128.32, 125.57, 125.27, 68.03, 60.02, 54.86, 32.00, 30.58, 27.68, 27.49, 27.08, 24.31, 23.97; IR (neat) 3101, 3055, 2946, 2930, 2857, 2830, 1634, 1599, 1495, 1460, 1446 cm^{-1}; HRMS calcd for $C_{18}H_{18}$ *m/e* 234.1408, found *m/e* 234.1408.

Pentacyclene 16a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.56 (t, 1H, J = 2.9 Hz), 2.46 (m, 1H), 2.42 (dm, 1H, J = 16.4 Hz), 2.06 (dddd, 1H, J = 16.4, 13.4, 5.2, 2.9 Hz), 1.76 (m, 2H), 1.68 (dm, 1H, J = ca. 12 Hz), 1.63 (tdt, 1H, J = 4.7, 2.8, 1.4 Hz), 1.50 (m, 3H), 1.41−1.18 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.05, 124.97, 61.27, 56.23, 48.27, 30.89, 28.03, 28.01, 26.98, 26.39, 25.89, 24.84, 23.33; IR (neat) 3047, 3008, 2925, 2856, 2823, 1620 cm^{-1}; HRMS calcd for $C_{13}H_{16}$ *m/e* 172.1252, found *m/e* 172.1245.

Pentacyclene 16b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (m, 1H), 2.39 (m, 1H), 2.31 (t, 1H, J = 2.1 Hz), 2.12 (m, 1H), 1.84 (m, 2H), 1.64 (m, 3H), 1.58 (m, 1H), 1.44 (m, 4H), 1.30 (m, 2H), 1.23 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.89, 133.76, 59.56, 53.42, 56.46, 30.52, 26.85, 26.25, 24.86, 28.40, 24.91, 24.40, 23.36, 12.98; IR (neat) 3044, 2924, 2854, 2819, 1652, 1441, 1377, 1314, 1286, 1251 cm^{-1}; HRMS calcd for $C_{14}H_{18}$ *m/e* 186.1408, found *m/e* 186.1408.

Pentacyclene 16c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.57 (dm, 1H, J = 16.6 Hz), 2.56 (t, 1H, J = 2.1 Hz), 2.08 (ddd, 1H, J = 16.6, 12.9, 5.2 Hz), 1.74 (m, 2H), 1.65 (m, 1H), 1.56 (tdt, 1H, J = 4.7, 2.8, 1.4 Hz), 1.49 (t, 2H, J = 1.4 Hz), 1.38 (br s, 1H), 1.35−1.16 (m, 5H), 0.07 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.18, 135.49, 60.17, 58.15, 52.20, 31.04, 28.29, 28.03, 27.09, 26.58, 24.99, 23.01, −0.26; IR (neat) 3059, 3046, 2949, 2930, 2858, 2818, 1582, 1445 cm^{-1}; HRMS calcd for $C_{16}H_{24}Si$ *m/e* 244.1647, found *m/e* 244.1643.

Pentacyclene 18a: ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.58 (m, 1H), 4.16 (q, 2H, J = 7.0 Hz), 4.12 (q, 2H, J = 7.0 Hz), 2.95 (d_{AB}d, 1H, J = 16.7, 2.6 Hz), 2.81, (d_{AB}d, 1H, J = 16.7, 1.4 Hz), 2.61 (dd, 1H, J = 4.9, 2.3 Hz), 2.22 (d_{AB}, 2H, J = 14.0 Hz), 1.88 (br s, 1H), 1.63 (m, 1H), 1.41 (m, 2H), 1.36 (m, 1H), 1.25−1.15 (m, 7H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 171.78, 171.69, 154.37, 122.07, 65.24, 65.16, 64.52, 61.36, 61.30, 53.25, 35.06, 34.48, 32.07, 26.47, 25.46, 24.66, 13.96; IR (neat) 3057, 2977, 2938, 2858, 1729, 1465, 1446, 1365, 1256, 1227, 1177, 1094, 1058 cm^{-1}; HRMS calcd for $C_{18}H_{22}O_4$ *m/e* 302.1518, found *m/e* 302.1520.

Pentacyclene 18b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.19 (q, 2H, J = 7.0 Hz), 4.15 (q, 2H, J = 7.1 Hz), 2.95 (d_{AB}, 2H, J = 16.8 Hz), 2.72 (t, 1H, J = 2.2 Hz), 2.24 (d_{AB}, 2H, J = 13.9 Hz), 1.80 (m, 1H), 1.60 (dddd, 1H, J = 5.8, 4.7, 2.5, 1.4 Hz), 1.45 (d_{AB}m, 2H, J = 11.4 Hz), 1.25 (m, 1H), 1.24 (t, 3H, J = 7.2 Hz), 1.23 (t, 3H, J = 7.2 Hz), 1.14 (tm, 1H, J = 5.8 Hz), 0.09 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.94, 171.75, 165.12, 133.97, 66.58, 65.29, 63.52, 61.48, 61.38, 56.76, 35.45, 34.89, 32.26, 26.51, 25.12, 23.98, 14.12, 14.09, −0.83; IR (neat) 3051, 2955, 2873, 2182, 1736, 1620, 1464, 1445, 1368, 1254, 1224, 1180, 1098, 1062, 1030 cm^{-1}; HRMS calcd for $C_{21}H_{30}O_4Si$ *m/e* 374.1913, found *m/e* 374.1910.

General Procedure for the Enantioselective Cobalt-Catalyzed [2π + 2π + 4π] Cycloaddition between Norbornadiene (1) and Various 2-Substituted 1,3-Butadienes (24a−f). To a flame-dried flask equipped with a magnetic stir bar, a rubber septum, and a temperature probe were added $Co(acac)_3$ or $Co(acac)_2$ (1−2 mol %) and the chiral phosphine ligand (1 equiv based on cobalt). The flask was flushed with argon., then benzene, norbornadiene (1 mmol), and the 2-substituted buta-1,3-diene[28] (1.5−3 mmol) were added. A solution of diethylaluminum chloride (DEAC) in toluene (4 equiv based on cobalt) was added dropwise and the temperature was monitored using an internal temperature probe. The temperature was controlled by placing a cool water bath under the flask when necessary. It is important that the reaction temperature remain above 24−25 °C to promote the reaction, but below 30−35 °C to optimize asymmetric induction. The reaction turned brownish green upon addition of Et_2AlCl. The reaction was stirred at room temperature for 1−4 days. The workup consisted of passing the reaction mixture through a short plug of silica to remove the catalyst, removal of solvent *in vacuo* yielding dark green oils which were purified by bulb-to-bulb distillation or flash chromatography to obtain clear, colorless oils. Spectroscopic data for cycloadducts **25a−f** are given below.

9-Methyltetracyclo[5.4.0.0^{2,4}.0^{3,7}]undec-9-ene (25a). The spectra were in accord with those reported in the literature.[5b] With (*R*)-prophos, $[\alpha]_D$ = −20.6° (72% ee); with (*S,S*)-chiraphos, $[\alpha]_D$ = +11.5° (40% ee); with (*S,S*)-Me-BPE, $[\alpha]_D$ = +10.1° (35% ee); with (*R,R*)-^{i}Pr-BPE, $[\alpha]_D$ = +11.5° (40% ee); with (*S,S*)-Me-duphos, $[\alpha]_D$ = −2.4° (9% ee); with (*R*)-prophos and $Co(acac)_3$, $[\alpha]_D$ = −21.5° (74% ee).

9-Nonyltetracyclo[5.4.0.0^{2,4}.0^{3,7}]undec-9-ene (25b): $[\alpha]_D$ = −5.1° (74% ee); ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.26 (m, 1H), 2.15 (m, 4H), 1.91 (m, 2H), 1.70 (m, 2H), 1.55 (m, 1H), 1.24 (m, 16H), 0.98 (m, 1H), 0.83 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 139.24, 121.27, 41.50, 41.43, 41.09, 40.59, 36.08, 33.74, 32.17, 29.87, 29.61, 29.56, 28.56, 22.98, 14.42, 14.23, 14.16, 11.13; IR (neat) 3058, 2924, 2875, 2854, 1462, 1377, 1300, 1173, 1124, 1061 cm^{-1}; HRMS calcd for $C_{20}H_{32}$ *m/e* 272.2504, found *m/e* 272.2517.

9-(4-Methyl-3-pentenyl)tetracyclo[5.4.0.0^{2,4}.0^{3,7}]undec-9-ene (25c): $[\alpha]_D$ = −10.5° (79% ee); ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.28 (m, 1H), 5.09 (m, 1H) 2.05 (m, 8H), 1.62 (m, 9H), 1.23 (m, 2H), 0.98 (m, 1H), 0.80 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 138.84, 131.03, 124.52, 121.49, 41.48, 41.08, 40.58, 40.16, 36.07, 33.84, 33.73, 29.63, 27.38, 25.96, 14.22, 14.13, 11.12; IR (neat) 3051, 2966, 2931, 2875, 2833, 1673, 1448, 1377, 1321, 1300, 1103 cm^{-1}; HRMS calcd for $C_{17}H_{24}$ *m/e* 228.1878, found *m/e* 228.1866.

9-(3-(*tert*-Butyldimethylsiloxy)propyl)tetracyclo[5.4.0.0^{2,4}.0^{3,7}]undec-9-ene (25d): $[\alpha]_D$ = −5.4° (73% ee); ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.27 (m, 1H), 3.57 (t, 2H, J = 6.60 Hz), 2.18 (m, 4H), 1.95 (m, 2H), 1.69 (m, 2H), 1.58 (m, 2H), 1.56 (m, 1H), 1.22 (m, 2H), 0.98 (m, 1H), 0.87 (s, 9H), 0.80 (m, 1H), 0.77 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 138.58, 121.77, 62.97, 41.34, 40.93, 40.42, 37.37, 35.94, 33.63, 31.54, 29.47, 26.12, 18.50, 14.04, 13.94, 10.94, −5.10; IR (neat) 3051, 2931, 2875, 1462, 1432, 1384, 1251, 1103, 836 cm^{-1}; HRMS calcd for (M − H)$^+$ *m/e* 317.2301, found *m/e* 317.2311, for (M − CH_3)$^+$ *m/e* 303.2144, found *m/e* 303.2166.

3-(Tetracyclo[5.4.0.0^{2,4}.0^{3,7}]undec-9-enyl)propyl Acetate (25e): $[\alpha]_D$ = −6.3° (73% ee); ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.28 (m, 1H), 4.02 (t, 2H, J = 6.74 Hz), 2.20 (m, 4H), 2.01 (s, 3H), 1.96 (m, 2H), 1.69 (m, 4H), 1.54 (m, 1H), 1.22 (m, 2H), 0.98 (m, 1H), 0.78 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 170.96, 137.47, 122.47, 64.32, 41.43, 40.93, 40.42, 37.37, 36.01, 33.66, 29.56, 27.28, 21.24, 14.16, 14.05, 11.12; IR (neat) 3051, 2938, 2875, 2833, 1743, 1434, 1384, 1363, 1300, 1244, 1040 cm^{-1}; HRMS calcd for $C_{16}H_{22}O_2$ *m/e* 246.1620, found *m/e* 246.1610.

9-((Trimethylsilyl)methyl)tetracyclo[5.4.0.0^{2,4}.0^{3,7}]undec-9-ene (25f): $[\alpha]_D$ = −13.5° (71% ee); ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.08 (m, 1H), 2.20 (m, 4H), 1.69 (m, 2H), 1.54 (m, 1H), 1.43 (m, 2H), 1.22 (m, 2H), 0.99 (m, 1H), 0.83 (m, 2H), 0.00 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 136.25, 119.31, 43.03, 41.41, 40.86, 36.54, 36.02, 31.92, 29.92, 14.28, 13.41, 11.22, −0.77; IR (neat) 3058, 2952, 2931, 2875, 2833, 1667, 1462, 1413, 1321, 1244, 1159, 850 cm^{-1}; HRMS calcd for $C_{15}H_{24}Si$ *m/e* 232.1647, found *m/e* 232.1688.

General Method for Determination of Enantiomeric Excess in the Cycloadducts. The enantiomeric excess of cycloadducts **25a,b,d,f** were determined using the same strategy (hydroboration−oxidation followed by Mosher ester preparation) as previously described for the HDA reaction. The cycloadduct **25e** was converted into cycloadduct **25d** before analysis of the ee. This approach was not suitable for cycloadduct **25c** since selective hydroboration of the endocyclic olefin was not possible in the presence of the remote olefin. Instead, the ee was determined by conversion of **25e** into **25c** and comparison of the optical rotations. Spectroscopic data for alcohols **26a,b,d,f** are given below.

Alcohol 26a: ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.46 (ddd, 1H, J = 12.54, 10.67, 3.30 Hz), 2.06 (ddd, 1H, J = 13.38, 4.40, 3.34 Hz), 1.83 (ddd, 1H, J = 14.08, 9.16, 4.84 Hz), 1.76 (m, 1H), 1.72 (m, 3H), 1.52 (ddd, 1H, J = 13.63, 10.62, 3.29 Hz), 1.46 (m, 1H), 1.35−1.18 (m, 4H), 0.97 (m, 1H), 0.92 (d, 3H, J = 6.59 Hz), 0.89 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 73.22, 42.23, 41.74, 40.94, 40.42, 36.43, 36.09, 19.24, 18.01, 14.27, 11.36; IR (neat) 3374 (s, br), 3051, 2910, 2875, 2756, 2235, 1687, 1455, 1441, 1384, 1314, 1286, 1251, 1019, 998, 906, 794, 730 cm^{-1}; HRMS calcd for $C_{12}H_{18}O$ *m/e* 178.1358, found *m/e* 178.1358.

Alcohol 26b: ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.56 (m, 1H), 2.05 (dt, 1H, J = 13.39, 3.62 Hz), 1.85 (m, 1H), 1.77 (m, 1H), 1.72 (m, 2H), 1.53 (m, 2H), 1.23 (m, 20H), 0.98 (m, 1H), 0.88 (m, 2H), 0.85 (t, 3H, J = 6.68 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 72.27, 44.88, 42.18, 41.52, 40.85, 36.08, 35.87, 32.76, 32.51, 31.98, 30.28, 29.79, 29.72, 29.43, 26.93, 22.76, 17.65, 14.39, 14.19, 11.33; IR (neat) 3374 (s, br), 3065, 2924, 2875, 2854, 1638, 1462, 1441, 1377, 1307, 1026, 1005, 906 cm^{-1}. Anal. Calcd for $C_{20}H_{34}O$: C, 82.69; H, 11.80. Found: C, 82.61; H, 11.74.

Alcohol 26d: ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.57 (m, 3H), 2.05 (dt, 1H, J = 13.39, 3.87 Hz), 1.96 (m, 1H), 1.73 (m, 4H), 1.58−1.34 (m, 7H), 1.20 (m, 2H), 0.95 (m, 1H), 0.87 (m, 2H), 0.86 (s, 9H), 0.02 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 71.67, 63.80, 44.72, 42.24, 41.69, 40.67, 36.20, 36.04, 32.64, 29.47, 28.47, 26.24, 18.64, 17.89, 14.51, 11.50, −4.96; IR (neat) 3374 (s, br), 3051, 2952, 2931, 2875, 1462, 1441, 1384, 1363, 1251, 1096, 1033, 1005, 941, 836, 808, 780 cm^{-1}; HRMS calcd for $C_{20}H_{36}O_2Si$ *m/e* 336.2485, found *m/e* 336.2467.

Alcohol 26f: ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.43 (m, 1H), 2.07 (dt, 1H, J = 13.35, 4.07 Hz), 1.91 (ddd, 1H, J = 13.52, 8.79, 4.56 Hz), 1.72 (m, 3H), 1.49 (ddd, 1H, J = 13.63, 10.34, 3.50 Hz), 1.39 (m, 1H), 1.22 (m, 4H), 1.04−0.82 (m, 5H), −0.01 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 73.23, 42.46, 41.68, 40.53, 36.32, 36.12, 36.03, 20.41, 17.86, 14.55, 11.46, 0.02; IR (neat) 3381 (s, br), 3051, 2945, 2910, 2875, 1441, 1413, 1314, 1251, 1005, 906. 875, 836 cm^{-1}; HRMS calcd for $C_{15}H_{26}OSi$ *m/e* 250.1753, found *m/e* 250.1766.

Conversion of Deltacyclene 25e to 25d. Direct hydroboration of **25e** gave a mixture of products; therefore, diastereomeric analysis of cycloadduct **25e** was accomplished by cleavage of the acetate and silylation of the primary alcohol to form cycloadduct **25d**.

DIBAL-H (0.15 mL, 0.842 mmol) was added to a flame-dried flask containing the cycloadduct **25e** (100.0 mg, 0.406 mmol) and THF (0.5 mL) at −78 °C. The reaction mixture was stirred at −78 °C for 30 min before quenching with saturated ammonium chloride. The product was extracted into Et_2O, and the organic layer was washed brine and dried over magnesium sulfate. The solvent was removed *in vacuo* to provide 3-(tetracyclo[5.4.0.0^{2,4}.0^{3,7}]undec-9-enyl)propanol as a clear oil (78.4 mg, 95%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.33 (m, 1H), 3.63 (t, 2H, J = 6.2 Hz), 2.30−2.15 (m, 4H), 2.12−1.98 (m, 2H), 1.74−1.58 (m, 4H), 1.55 (br s, 1H), 1.45 (br s, 1H), 1.23 (t, 2H, J = 1.4 Hz), 0.99 (td, 1H, J = 5.8, 1.0 Hz), 0.79 (m, 2H). Without further purification

this alcohol was converted to **25d** by silylation with *tert*-butyldimethylsilyl chloride (58.0 mg, 0.385 mmol) and imidazole (31.0 mg, 0.455 mmol) in DMF (0.38 mL) to provide **25d** (122.2 mg, 99%). The spectral data were identical to those of the one that was made via the cobalt-catalyzed cycloaddition as reported above.

Conversion of Deltacyclene 25e to 25c. Selective hydroboration of the endocyclic olefin in **25c** was not possible in the presence of the remote olefin; therefore, diastereomeric analysis of cycloadduct **25c** was accomplished by conversion of **25e** into **25c** and comparison of the optical rotations. Cycloadduct **25e** {$[\alpha]_D = -6.3°$ (73% ee)} was first reduced to the 3-(tetracyclo[5.4.0.0^{2,4}.0^{3,7}]undec-9-enyl)propanol as mentioned above. This alcohol (109.3 mg, 0.535 mmol) was then oxidized under Swern oxidation conditions[42] to provide 3-(tetracyclo-[5.4.0.0^{2,4}.0^{3,7}]undec-9-enyl)propanal (79.1 mg, 73%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.72 (m, 1H), 5.31 (m, 1H), 2.47 (tm, 2H, J = 7.5 Hz), 2.37−2.01 (m, 6H), 1.68 (m, 2H), 1.54 (br s, 1H), 1.21 (br s, 2H), 0.98 (t, 1H, J = 5.3 Hz), 0.76 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 203.31, 136.94, 122.95, 42.24, 40.99, 40.44, 39.93, 35.60, 33.40, 33.23, 29.05, 13.60, 13.48, 10.58. This aldehyde was then converted to **25c** by Wittig olefination. Sodium bis(trimethylsilyl)amide (1 M in THF, 0.13 mL, 0.13 mmol) was added to a flame-dried flask containing isopropyltriphenylphosphonium iodide (58.1 mg, 0.134 mmol) and THF (0.15 mL) at −78 °C. After being stirred for 30 min, the above aldehyde, 3-(tetracyclo[5.4.0.0^{2,4}.0^{3,7}]undec-9-enyl)propanal (16 mg, 0.079 mmol), was added and the reaction mixture was stirred at room temperature overnight. After being quenched with saturated ammonium chloride (50 mL), the product was extracted into hexanes and the organic layer was washed dilute hydrochloric acid and brine and dried over magnesium sulfate. The solvent was removed *in vacuo*, and the crude product was purified by flash column chromatography (hexanes) to provide the product **25c** as a clear oil (2.8 mg, 23%, $[\alpha]_D = -8.6°$) and the recovered aldehyde (5.2 mg, 33%). The spectral data of this product were identical to those of the one that was made via the cobalt-catalyzed cycloaddition as reported above.

Spectroscopic Data for Mosher Esters 27a−f in Determining the Diastereomeric Excess (de). Mosher ester **27a** (de = 72%): ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.85 (d, 3H, 86.4%), −0.63 (d, 3H, 13.6%). Mosher ester **27b** (de = 74%): ^{19}F NMR (188 MHz, $CDCl_3$) δ −71.43 (86.9%), −71.52 (13.1%). Mosher ester **27d** (de = 73%): ^{19}F NMR (188 MHz, $CDCl_3$) δ −71.47 (86.4%), −71.42 (13.6%). Mosher ester **27d** (derived from cycloadduct **25e**) (de = 73%): ^{19}F NMR (188 MHz, $CDCl_3$) δ −71.47 (86.6%), −71.42 (13.4%). Mosher ester **27f** (de = 71%): ^{19}F NMR (188 MHz, $CDCl_3$) δ −71.29 (85.5%), −71.53 (14.5%).

Synthesis of Diene 29. *n*-Butyllithium (2.66 mL, 2.5 M, 6.65 mmol) was added dropwise to a flame-dried flask containing allyldiphenylphosphine oxide[40] (1.61 g, 6.65 mmol) THF (22 mL), and HMPA (2.73 g, 2.30 mL) at −78 °C. The resulting reddish-orange solution was stirred at −78 °C for 20 min. Aldehyde **28** (889 mg, 5.47 mmol, prepared from bromide **19b** in two steps)[6g] in THF (2 mL) was added over a period of 15 min, and the resulting solution was stirred at −78 °C for 10 min, at 0 °C for 30 min and finally at room temperature for 2 h. The reaction mixture was then poured into ice-cooled aqueous hydrochloric acid (1 M, 100 mL). The product was extracted into hexanes (4 × 100 mL), and the organic layer was washed sequentially with water (100 mL) and brine (2 × 100 mL) and then dried over magnesium sulfate. The solvent was removed *in vacuo*, and the crude product was purified by bulb-to-bulb distillation (80 °C at 15 mmHg) to yield a pale yellow oil which was then purified again by flash column chromatography (hexanes) to provide diene **29** (613.4 mg, 60%, contaminated with 5% of the *cis* isomer as determined by ^{1}H NMR): ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.74 (m, 2H), 6.30 (ddd, 1H, J = 16.8, 10.3, 10.2 Hz), 6.12 (m, 1H), 6.06 (dd, 1H, J = 15.1, 10.2 Hz), 5.68 (dt, 1H, J = 15.1, 7.2 Hz), 5.07 (dd, 1H, J = 16.8, 1.2 Hz), 4.94 (dd, 1H, J = 10.3, 1.2 Hz), 3.48 (m, 1H), 3.26 (br s, 1H), 2.19 (m, 2H), 2.04 (m, 2H), 1.94 (m, 2H), 1.51 (p, 2H, 7.5 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 158.69, 143.98, 142.51, 137.43, 135.25, 133.71, 131.27, 114.80, 73.42, 53.38, 49.93, 32.00, 30.81, 26.62; IR (neat) 3065, 2973, 2931, 2861, 1652, 1602, 1553, 1448, 1433, 1300, 1005 cm^{-1}; HRMS calcd for $C_{14}H_{18}$ *m/e* 186.1409, found *m/e* 186.1411.

Cobalt-Catalyzed Intramolecular [4π + 2π + 2π] Cycloaddition of Diene 29. Diene **29** (200.2 mg, 1.08 mmol) was dissolved in benzene (2.2 mL), and $Co(acac)_3$ (10%, 38.0 mg, 0.107 mmol) and dppe (8%, 34.2 mg, 0.086 mmol) were then added followed by DEAC (1.8 M, 0.24 mL, 0.43 mmol). After 48 h, the reaction mixture was filtered through a plug of silica using hexanes as the eluent and the resulting oil was purified by flash column chromatography (hexanes) to yield the cycloadduct pentacyclene **30** (63.3 mg, 32%). Similar cycloaddition was carried out by using $Co(acac)_2$ instead of $Co(acac)_3$ under the same conditions (the cycloaddition was completed after 20 h with $Co(acac)_2$) to provide the cycloadduct pentacyclene **30** (40%).

Pentacyclene 30: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.62−5.54 (m, 2H), 2.40 (m, 1H), 2.32 (br s, 1H), 2.30 (m, 1H), 1.93 (m, 1H), 1.74 (dd, 1H, J = 3.8, 1.4 Hz), 1.65−1.46 (m, 6H), 1.35 (br s, 1H), 1.16 (d, 1H, J = 10.1 Hz), 1.00 (td, 1H, J = 5.2, 1.2 Hz), 0.91 (t, 1H, J = 5.2 Hz), 0.83 (t, 1H, J = 5.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.03, 127.31, 53.47, 46.24, 45.07, 42.69, 34.56, 34.22, 34.17, 30.01, 22.40, 19.17, 17.16, 10.84; IR (neat) 3058, 3016, 2952, 2875, 2826, 1462, 1448, 1432, 1321 cm^{-1}; HRMS calcd for $C_{14}H_{18}$ *m/e* 186.1408, found *m/e* 186.1411.

Conversion of Pentacyclene 30 to Bis(3,5-dinitrobenzoyl ester) 31. Ozone was bubbled through a solution containing pentacyclene **30** (275.0 mg, 1.48 mmol), dichloromethane (5 mL), and absolute methanol (1 mL) at −78 °C. Ozonolysis was completed in 3 h as monitored by TLC. Sodium borohydride (300.0 mg, 7.93 mmol) was added slowly to the reaction mixture at −78 °C. The reaction mixture was then allowed to stir at room temperature overnight. After being quenched with water (20 mL) and aqueous hydrochloric acid (1 M, 2 mL), the product was extracted into ethyl acetate (6 × 50 mL) and dried over anhydrous sodium sulphate. The solvent was removed *in vacuo*, and the crude product diol was used without further purification and characterization. This diol was dissolved in dichloromethane (10 mL) and DCC (566.3, 2.74 mmol), and 3,5-dinitrobenzoic acid (570.2 mg, 2.68 mmol) and DMAP (30.1 mg, 0.25 mmol) were added sequentially. The reaction mixture was stirred at room temperature for 24 h before quenching with water. The product was extracted into dichloromethane, and the organic layer was washed sequentially with water and brine and dried over magnesium sulfate. The solvent was removed *in vacuo*, and the product was purified by flash column chromatography (50% Et_2O/hexanes) to yield the diester **31** as a white powder (677.6 mg, 75% overall yield from pentacyclene **30**). The stereochemistry of the diester **31** was verified by ^{1}H NMR decouplings and NOE experiments. On irradiation at δ 4.3 ppm (H^a) of compound **31**, enhancement was observed at δ 1.13 ppm (H^c) (10%) and at δ 4.78 ppm (H^b) (21%).

Bis(3,5-dinitrobenzoyl ester) 31: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (t, 2H, J = 2.2 Hz), 9.12 (m, 4H), 4.78 (dd, 1H, J = 11.0, 4.8 Hz), 4.53 (m, 2H), 4.30 (t, 1H, J = 11.0 Hz), 2.21 (p, 2H, J = 7.0 Hz), 1.84−1.56 (m, 9H), 1.32 (t, 1H, J = 5.1 Hz), 1.24 (d, 1H, J = 10.6 Hz), 1.18 (t, 1H, J = 5.1 Hz), 1.13 (t, 1H, J = 5.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.57, 162.49, 148.60(2), 134.00, 133.97, 129.29, 129.26, 122.32(2), 68.72, 67.00, 55.20, 45.49, 43.51, 39.96, 35.67, 33.61, 30.68, 29.33, 22.99, 18.80, 18.20, 12.00; IR (neat) 3105, 2954, 2881, 1725, 1629, 1547, 1462, 1344, 1284, 1169, 1076 cm^{-1}; HRMS calcd for $C_{28}H_{26}N_4O_{12}$ *m/e* 610.1547, found *m/e* 610.1567.

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