Development of a New Cobalt Catalyst System for the [4 + 2 + 2] Cycloadditions of Functionalized Norbornadienes and Butadiene

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The combination CoX_2/ligand/reducing agent/Lewis acid generates effective catalysts for the transition metal catalyzed [4 + 2 + 2] homo Diels−Alder reactions of norbornadienes with butadienes, leading to a new system which is highly effective at room temperature: CoI_2/dppe/Zn/ZnI_2. This catalyst shows broad functional group tolerance over a range of norbornadienes, and selectivity over other pathways such as butadiene polymerization and norbornadiene oligomerization. The Lewis acid effect in these cobalt-catalyzed [4 + 2 + 2] cycloadditions has also been probed.

Introduction

Metal-catalyzed cycloadditions are important, emerging synthetic procedures for the efficient assembly of complex molecules.[1] These multistep processes result in the production of at least two new carbon−carbon bonds, typically with excellent stereocontrol. The transition metal catalyzed homo Diels−Alder cycloaddition of norbornadiene and butadiene is an overall eight-electron [4π + 2π + 2π] process which occurs only under metal-catalyzed conditions (there are no thermally promoted versions) and results in the formation of highly caged polycyclic compounds.[2] Discovered more than 30 years ago,[3] it has not yet been well developed and applied in organic synthesis,[4] although Lautens has extensively probed features of both the [4 + 2 + 2][5] and [2 + 2 + 2][6] reactions. While the starting materials are readily available and inexpensive, two problems limit synthetic applications of this reaction. One is the existing catalysts for [4 + 2 + 2] reaction have a number of shortcomings including a limited scope, revealed in the lack of functional group tolerance, and a lack of selectivity for the desired cycloaddition over dimerization of norbornadiene or the polymerization of butadienes. The other drawback is the lack of an efficient method to open the cycloadduct to synthetically useful building blocks.

In earlier explorations of [4 + 2 + 2] cycloadditions between norbornadienes and 1,3-butadiene,[7] we reported a study of the cycloaddition followed by the Zeise's dimer opening/ozonolysis sequence to successfully unravel the highly caged cycloadducts to *cis*-fused bicyclo[5.3.0]decanes (Scheme 1), the core structure of numerous sesquiterpenes of biological interest.[8] In that work, the best catalysts found for the [4 + 2 + 2] cycloaddition of norbornadiene and butadiene were all cobalt-based systems modified from literature applications in both [2 + 2 + 2] and [4 + 2 + 2] homo Diels−Alder reactions of norbornadiene: (1) catalyst **A**, Co(acac)$_2$/dppe/Et_2AlCl (1:1.5:10)[3d,9] in toluene; (2) catalyst **B**, CoI_2/dppe/Zn (1:2:10)[10] in CH_2Cl_2; (3) catalyst **C**, CoI_2/

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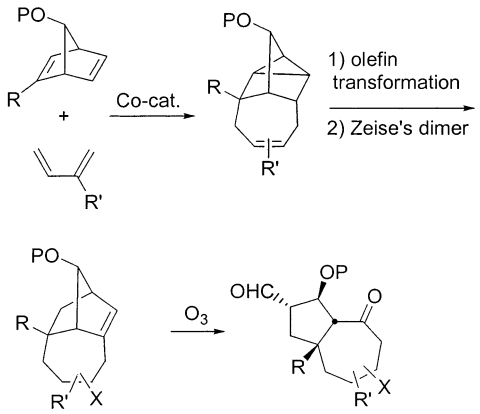
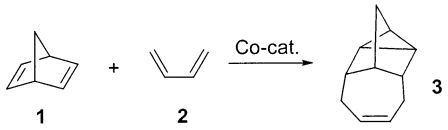
Scheme 1



dppe/ZnI_2 (1:2:5)[11] in CH_2Cl_2; and (4) catalyst **D**, CoI_2/dppe/$NaBH_4$/ZnI_2 (1:1:1:3)[12] in CH_2Cl_2. All promoted the cycloaddition of norbornadiene and 1,3-butadiene in over 80% yield. However, these catalytic systems were sensitive to the anhydrous character of the cobalt species, the identity of the solvent, and the presence and position of functionalized substituents on the norbornadiene and butadiene. For example, catalyst **A** proved to be less than optimal, to completely unsuitable, for norbornadienes substituted at C2 with ethers and esters.[13] The cycloadditions promoted by catalyst **B** and **C** occurred only under relatively harsh conditions (>80 °C), which always caused certain amounts of dimerization of norbornadiene and/or polymerization of butadiene. The Hilt catalyst **D** was unique in promoting the cycloaddition at room temperature, although the use of $NaBH_4$ as the reducing agent limits its applications. Lautens has successfully accomplished asymmetric [4 + 2 + 2] cycloadditions of norbornadiene using a Co(acac)$_2$/lig*/Et_2AlCl system with chiral, enantiopure bisphosphine ligands at temperatures slightly above room temperature.[5] However as noted above, Et_2AlCl cannot be used as the reducing agent with certain C-2-substituted norbornadienes due to the intervention of normal [4 + 2] cycloadditions. These limitations prompted us to develop a more active catalyst that would promote the [4 + 2 + 2] cycloaddition at room temperature or below in order to be more "functional group friendly", as well as to enhance the utility and generality of this method with a broader range of substituted norbornadienes. In this paper, we report the development of such a new catalyst system, which promotes the near quantitative cycloaddition of functionalized norbornadienes and butadiene at room temperature, and also probe the Lewis acid effect observed in the [4 + 2 + 2] cycloaddition process.

Table 1. Reducing Reagent Effect in the CoI_2/dppe (1:1) System for Cycloadditions of 1 with 2[a]



entry	red. agent	equiv of CoI_2	time (h)	yield of **3** (%)[b]
1	none		20	0
2	Zn	10	20	0
3	Mg	10	20	0
4	$LiBH_4$	4	20	0
5	$NaBH_4$	4	20	0
6	$Zn(BH_4)_2$	4	8	64
7	$ZnEt_2$	4	5	80
8	BEt_3	4	20	0

[a] All reactions were performed in CH_2Cl_2, 0.5 M of **1** with 5 mol % Co, 3 equiv of **2** at room temperature. [b] Isolated yields.

Results and Discussion

Optimization of the Catalyst. The investigation began with optimization experiments on the existing catalysts. Catalyst **A**, which uses Et_2AlCl as the reducing agent, was excluded from further work due to its propensity to promote [4 + 2] cycloadditions of norbornadienes bearing C-2 ester substituents (methyl norbornadiene-2-carboxylate). The remaining catalysts, **B**, **C**, and **D**, share common features: (1) all use CoI_2 as the cobalt source; (2) all use dppe as the ligand; (3) all succeed in CH_2Cl_2 as solvent; (4) all use zinc metal or a zinc salt as a cocatalyst. Success with catalyst **C** was somewhat confusing since there is no apparent reducing agent. Experiments designed to address this issue of the reducing agent were performed initially.

When norbornadiene and 1,3-butadiene were mixed in the presence of in situ generated Co(dppe)I_2, prepared from CoI_2 + dppe, 1:1, in CH_2Cl_2 at room temperature for 20 h, no reaction occurred, and the resulting purple solution maintained its color throughout (entry 1 in Table 1). The addition of reducing reagents such as Mg, $LiBH_4$, and $NaBH_4$ gave the same purple color and the same results. The use of zinc powder[10] produced a brown suspension with an induction period of about 1 h, but to our surprise, no cycloadduct could be detected at room temperature even after 20 h. When $Zn(BH_4)_2$ was used instead of Zn, the brown color formed immediately and the cycloadduct was isolated in 64% yield after 8 h. Better yields (80%) and shorter reaction times (5 h) were achieved when $ZnEt_2$ was used as the reducing agent.

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Table 2. Reducing Reagents in the CoI_2/dppe/ZnI_2 (1:1:3) System for Cycloadditions of 1 with 2[a]

entry	red. agent	eq. CoI_2	time (h)	yield of **3** (%)[b]
1	none		20	0
2	Mg	1	20	0
3	Zn	1	10	87
4	$LiAl(OEt)_3H$	1	20	0
5	$LiAl(OBu^t)_3H$	1	20	0
6	$NaBH_4$	1	10	80

[a] All reactions were performed in CH_2Cl_2, 0.5 M of **1** with 5 mol % Co, 3 equiv of **2** at room temperature. [b] Isolated yields.

The cloudy brown solution remained throughout when $Zn(BH_4)_2$ and $ZnEt_2$ were used. When the single-electron reagent BEt_3 was used, a blue solution formed with no cycloadduct detected.

The seemingly unique role of zinc reagents in the cycloaddition of norbornadiene and 1,3-butadiene was very interesting. It has been reported that in the presence of phosphine ligands, CoX_2 can be reduced to Co(I) by $NaBH_4$ in ethanol, by Mg in THF, by Na-Hg in Et_2O, and by Zn or DIBAL in CH_2Cl_2 at room temperature.[12a,14] The results in Table 1 therefore indicate that reduction of cobalt even in the presence of dppe is not a sufficient condition to achieve the [4 + 2 + 2] cycloaddition. Considering the different presentations of Zn, Zn-$(BH_4)_2$, and $ZnEt_2$, a Lewis acid effect rather than a reducing agent role is possible. Thus, the effect of different reducing agents on the Co(dppe)I_2/ZnI_2 system with Zn(II) as a Lewis acid was then examined. First, the same reaction was attempted using Co(dppe)I_2 with ZnI_2 in CH_2Cl_2 at room temperature with no reducing agent present. Not surprisingly, no cycloadduct could be detected (Table 2, entry 1). The addition of Mg powder as a reducing reagent still led to no reaction (Table 2, entry 2). Gratifyingly, the use of zinc powder or $NaBH_4$ as reducing reagent with Co(dppe)I_2/ZnI_2 successfully gave the cycloadduct **3** in 87% and 80% isolated yields, respectively (Table 2, entries 2 and 6). This suggested that *both a reducing agent and a Lewis acid are necessary for the reaction*. It has been reported that aluminum hydrides, $LiAl(OBu^t)_3H$ and $LiAl(OEt)_3H$, can also reduce Co(dppe)I_2 in the presence of ZnI_2.[12a] However, to our surprise, although a dark brown color did form suggesting an active catalyst, no cycloadduct was detected (Table 2, entries 4 and 5). This is particularly confusing since the modified Lyon system, $Co(acac)_2$/dppe/Et_2AlCl (1:1.5:5),[7d] and other Co/Al-based catalysts,[3b−f,5] can effectively promote the [4 + 2 + 2] cycloaddition between norbornadiene and butadiene to produce **3**.

The critical role of different Lewis acids was then thoroughly tested under the same reaction conditions (CH_2Cl_2, rt), using the Co(dppe)I_2/$NaBH_4$ system (Table 3). Quite encouragingly, group XIII metals $BF_3{\cdot}OEt_2$ (20%), $GaCl_3$ (47%), and $InCl_3$ (88%) were all effective to varying degrees in promoting the cycloaddition between **1** and **2**, with the exception of $AlCl_3$ and $AlBr_3$ (entries 2−6). Of the group XII metals, $ZnCl_2$ (90%) and ZnI_2 (80%) were very successful (entries 7 and 8), while $CdCl_2$ and $HgCl_2$ gave no product at all (entries 9 and 10). *meta*-Stable CuI (30%) was also marginally successful, while CuCl, CuBr, $CuCl_2$, and $Cu(OTf)_2$ all failed to give any cycloadduct (entries 11−15). Other metals such as $SnCl_4$, $SnBr_4$, $Ti(OPr^i)_4$, and $MnCl_2$ gave no product at all (entries 16−19). Very surprisingly, group II metals $CaCl_2$ (14%) and $BaCl_2$ (5%) and group I metals LiCl (23%), LiBr (25%), and CsCl (<5%) were also marginally successful in very slow reactions, although magnesium salts $MgCl_2$ and MgI_2 failed (entries 20−26). These results suggested that zinc is not essential but is perhaps the optimal Lewis acid. It also suggests that the *Lewis acid is not only helpful for the generation of effective catalyst species but is critical for the cycloaddition process*.

Table 3. Lewis Acid Effect in the CoI_2/dppe/$NaBH_4$/MX_n (1:1:1:3) System for Cycloadditions of 1 with 2[a]

entry	MX_n	time (h)	yield of **3** (%)[b]	entry	MX_n	time (h)	yield of **3** (%)[b]
1	none	20	0	14	$CuCl_2$	20	0
2	$BF_3{\cdot}Et_2O$	20	20	15	$Cu(OTf)_2$	20	0
3	$AlCl_3$	20	0	16	$SnCl_4$	20	0
4	$AlBr_3$	20	0	17	$SnBr_4$	20	0
5	$GaCl_3$	20	47	18	$Ti(OPr^i)_4$	20	0
6	$InCl_3$	20	87	19	$MnCl_2$	20	0
7	$ZnCl_2$	10	90	20	MgI_2	20	0
8	ZnI_2	10	80	21	$MgCl_2$	20	0
9	$CdCl_2$	20	0	22	$CaCl_2$	20	14
10	$HgCl_2$	20	0	23	$BaCl_2$	20	5
11	CuI	20	30	24	LiCl	20	23
12	CuCl	20	0	25	LiBr	20	25
13	CuBr	20	0	26	CsCl	20	<5

[a] All reactions were performed in CH_2Cl_2, 0.5 M of **1** with 5 mol % Co, 3 equiv of **2** at room temperature. [b] Isolated yields.

Table 4. Room Temperature Catalysts for the Cycloaddition of Norbornadiene (1) and Butadiene (2)[a]

entry	catalyst	time (h)	yield of **3** (%)[b]
1	CoI_2/dppe/$NaBH_4$/$InCl_3$ (1:1:1:3)	10	88
2	CoI_2/dppe/$NaBH_4$/ZnI_2 (1:1:1:3)	10	80
3	CoI_2/dppe/$NaBH_4$/$ZnCl_2$ (1:1:1:3)	10	90
4	CoI_2/dppe/$Zn(BH_4)_2$ (1:1:4)	8	64
5	CoI_2/dppe/$ZnEt_2$ (1:1:4)	5	80
6	CoI_2/dppe/Zn/ZnI_2 (1:1:1:3)	8	87

[a] All reactions were performed in CH_2Cl_2, 0.5 M of **1** with 5 mol % Co, 3 equiv of **2** at room temperature. [b] Isolated yields.

From these results, several catalysts that are quite effective at room temperature for promoting the [4 + 2 + 2] cycloaddition of norbornadiene and butadiene can be listed (Table 4). Among them, the new catalyst system CoI_2/dppe/Zn/ZnI_2 (1:1:1:3) in CH_2Cl_2 (catalyst **E**, entry 6) was the most reproducible and eventually proved to have the widest range of applications. Furthermore, when the temperature was lowered to 0 °C with catalyst **E**, an 84% yield of **3** was still obtained after 24 h, with the remaining 16% being account for as starting material. Several monodentate phosphine ligands (PPh_3, $PMePh_2$, Cy_2P-Biphenyl, PBu_3) were examined as replacements for dppe in this system, but all proved ineffective. Thus, a bidentate bisphosphine ligand is necessary, presumably to stabilize the reduced cobalt species as previously suggested.[7d] Previously we had reported that dppe was the best bidentate, bisphosphine ligand in a similar study,[7d] so no other bisphosphine ligands were examined.

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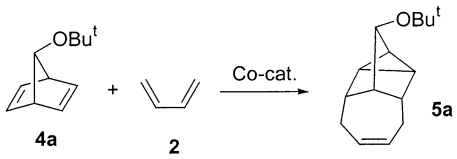
On the basis of this CoI_2/dppe/Zn/ZnI_2 (1:1:1:3) system, other transition metal halides in place of CoI_2 were tested in the same reaction. Of all the systems examined, only $FeCl_3$ gave cycloadduct, and a 45% isolated yield of **3** was obtained. All others, $Sc(OTf)_3$, $TiCl_4$, Cp_2TiCl_2, $Ti(OPr^i)_4$, $CrCl_2$, $MnCl_2$, $NiBr_2$, CuI, $NbCl_5$, $ClRu(PPh_3)_3$, $ClRh(PPh_3)_3$, $PdCl_2$, and $[Pt(C_2H_4)Cl_2]_2$, failed to give any cycloadduct. Other cobalt species such as $Co(acac)_2$, $CpCo(CO)_2$, and $Co_2(CO)_8$ were also ineffective at room temperature. Thus to date, only Co and Fe catalysts are able to promote [4 + 2 + 2] cycloadditions between homoconjugated dienes such as **1** and conjugated dienes such as **2** at room temperature.

Since the dimerization of **1**, along with the polymerization of **2** are pathways that compete with the transition metal catalyzed [4 + 2 + 2] homo Diels–Alder reaction with other catalysts, particularly at elevated temperatures, this new catalyst system [CoI_2/dppe/Zn/ZnI_2 (1:1:1:3)] was then examined for the production of these potential side products. A series of four parallel reactions were carried under the same conditions. After 20 h, the control reaction (**1**:**2**, 1:3, 0.5 M **1** in CH_2Cl_2 with 5 mol % Co catalyst based on **1**) gave an 87% isolated yield of cycloadduct **3** without any **1** remaining, although butadiene was still present. No norbornadiene dimers were detected, and only a minimal amount of butadiene polymerization was observed. When norbornadiene (**1**) was stirred with this catalyst under the same conditions, but without any butadiene added, 50% of **1** was recovered, with the remainder occurring as a mixture of dimers by weight.[15] To determine whether butadiene (**2**) polymerization was promoted by the catalyst under these conditions, **2** was also treated with CoI_2/dppe/Zn/ZnI_2 (1:1:1:3) at room temperature for 20 h in CH_2Cl_2. Only a trace amount of butadiene polymer was isolated (<5 wt %). When butadiene was replaced with isoprene under the same conditions, no polymer was formed and isoprene was completely recovered. No cycloaddition occurred between **1** and isoprene at room temperature. These experiments clearly indicate that the new catalyst greatly favors the [4 + 2 + 2] cycloaddition between **1** and **2**, with a minimum of butadiene polymerization and no dimerization of **1**. However, it is not an effective catalyst with isoprene as the homo dienophile at room temperature.

Cycloadditions of Substituted Norbornadienes. Expanding the scope of the transition metal catalyzed homo Diels–Alder reaction to include substituted norbornadienes is a critical goal if this chemistry is to be applied in organic synthesis. To this end, 7-*tert*-butoxynorbornadiene (**4a**)[16] was used to test the room-temperature catalysts from Table 4. Most encouragingly, the "all-zinc"-based catalyst **E** [CoI_2/dppe/Zn/ZnI_2 (1:1:1:3)] promoted the successful cycloaddition at room temperature in excellent yield (93%, Table 5, entry 1). In contrast, the systems employing $NaBH_4$ as the reducing agent were considerably less effective, giving lower yields in comparison with the reaction of norbornadiene (**1**), often with significant polymerization of butadiene (Table 5, entries 3 and 4). The reaction of **4a** using catalyst **E** could be accomplished on a gram scale in near quantitative yields.

Table 5. Comparison of Different Catalysts for the Cycloaddition of 4a and 2[a]



entry	catalyst	time (h)	yield of **5a** (%)[b]
1	CoI_2/dppe/Zn/ZnI_2 (1:1:1:3) − cat. **E**	20	93
2	CoI_2/dppe/$NaBH_4$/$InCl_3$ (1:1:1:3)	20	7
3	CoI_2/dppe/$NaBH_4$/ZnI_2 (1:1:1:3)	20	75
4	CoI_2/dppe/$NaBH_4$/$ZnCl_2$ (1:1:1:3)	20	55

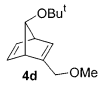
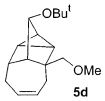
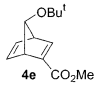
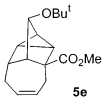
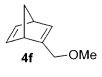
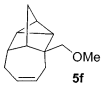
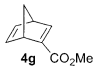
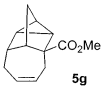
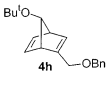
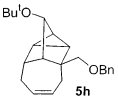
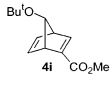
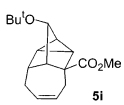
[a] All reactions were performed in CH_2Cl_2, 0.5 M of **1** with 5 mol % Co, 3 equiv of **2** at room temperature. [b] Isolated yields.

With the success of catalyst **E** in producing cycloadduct **5a**, other derivatized norbornadienes were then examined in cycloadditions with butadiene using this catalyst (Table 6). 7-Benzoyloxynorbornadiene (**4b**)[17] also gave an excellent yield of **5b** at room temperature (99%, entry 1), and the homo Diels–Alder reaction of *syn*-2-methyl-7-*tert*-butoxynorbornadiene (**4c**)[7b] to produce **5c** also proceeded smoothly (96%, entry 2). However, *syn*-7-*tert*-butoxy-2-methoxymethylnorbornadiene (**4d**) and methyl *syn*-7-*tert*-butoxynorbornadiene-2-carboxylate (**4e**) failed to give any cycloadducts, even under refluxing condition (entries 3 and 4). These failures were somewhat surprising since the corresponding norbornadienes lacking the 7-*tert*-butoxy group, **4f** and **4g** (entries 5 and 6), had previously been shown to be excellent homo dienes for the cobalt-catalyzed cycloaddition,[7d] while 7-*tert*-butoxynorbornadiene itself (**5a**) was also an excellent substrate, as demonstrated by the results in Table 5. It was surmised that the problem with **4d** and **4e** may originate in the potential chelation of the cobalt catalyst between the oxygen of the C-2 substituent and the *tert*-butoxyl oxygen away from the homo diene *endo* face. To test this, the corresponding *anti* ether **4h** and *anti* ester **4i** were routinely prepared (Scheme 2) and examined in the [4 + 2 + 2] cycloaddition with butadiene using catalyst **E**. Both gave satisfactory yields of cycloadducts **5h** and **5i**, respectively (61% and 84%, entries 7 and 8). Thus, the failure of the *syn* isomers **4d** and **4e** to participate in the cycloaddition was attributed to a chelation problem preventing complexation of the homoconjugated diene π-system with the cobalt catalyst.

Mechanism. Considerable speculation about the mechanism of both the transition metal catalyzed [2 + 2 + 2] and [4 + 2 + 2] homo Diels–Alder reactions has appeared.[18] As previously noted, sharp differences exist between these two reactions, which likely proceed by routes with distinctive features that differentiate them. Indeed to date, there is no confirmed example of a [2 + 2 + 2] adduct resulting from a cobalt-catalyzed homo Diels–Alder reaction of a butadiene with a norbornadiene.[19] Two key distinctive features of the [4 + 2 + 2] reaction that must be explained is the role of the Lewis

(15) For a review: Mango, F. D. *Coord. Chem. Rev.* **1975**, *15*, 109–205.
(16) (a) Story, P. R. *J. Org. Chem.* **1961**, *26*, 287–290. (b) Story, P. R.; Fahrenholtz, S. R. *Org. Synth., Coll. Vol. V* **1973**, 151–154.
(17) Tanida, H.; Tsuji, T. *J. Org. Chem.* **1964**, *29*, 849–852.
(18) See discussion in ref 7d.

Table 6. Cycloadditions of Substituted Norbornadienes with Butadiene Using Catalyst E[a]

Entry	Substrate	Product	Time (h)	Yield of 5 (%)[b]
1	 **4b**	 **5b**	24	99
2	 **4c**	 **5c**	24	96
3	 **4d**	 **5d**	24	0
4	 **4e**	 **5e**	24	0
5[c]	 **4f**	 **5f**	5[c]	59[c]
6[d]	 **4g**	 **5g**	31[d]	76[d]
7	 **4h**	 **5h**	24	61
8	 **4i**	 **5i**	24	84

[a] All reactions were performed in CH_2Cl_2 at room temperature, 0.5 M **4b**−**4i** with 3 equiv of butadiene using 5 mol % Co at room temperature unless otherwise noted. [b] Isolated yields. [c] From ref 7d. Reaction performed in $ClCH_2CH_2Cl$ at 80−90 °C, 1.6 M **4f**, 1.5 equiv of butadiene using CoI_2/dppe/Zn (1:2:10) as catalyst, 2.5 mol % in Co. [d] From ref 7d. Reaction performed in $ClCH_2CH_2Cl$ at 80 °C, 1.6 M **4g**, 1.5 equiv of butadiene using CoI_2/dppe/Zn (1:2:10) as catalyst, 1 mol % in Co.

acid and the strong preference (and in most cases, requirement) for a bidentate, bisphosphine ligand rather than monophosphines. The advantage of the bisphosphine over the monophosphine ligand most likely lies in the greater stabilization of the active, catalytic cobalt species, presumed to be Co(I). A plausible mechanism is presented in Scheme 3.

In this analysis, ZnI_2 accelerates the reduction of Co(dppe)I_2 by zinc metal through formation of a Co−Zn binuclear complex **6**, which has a weaker Co−I bond and thus is more vulnerable to reduction. This accounts for the more rapid formation of the characteristic brown color of the active catalyst when ZnI_2 is added. Thus, Co(I) dimer **7** becomes a prominent candidate as the active catalyst. Subsequent coordination of norbornadiene to form 18-electron complex **8**, which requires a bidentate bisphosphine ligand such as dppe for stabilization, then begins the catalytic cycle. It has been reported that norbornadiene forms stable square pyramidal complexes with $Co(PMe_3)_3^+$ with the double bonds of norbornadiene in the two basal positions.[20] Perhaps assisted by ZnI_2, one of the phosphine ligands of dppe dissociates from the cobalt, freeing a binding site for butadiene coordination **9**. Then, metallocyclization occurs forming six-coordinate bipyramidal complex **10**. Subsequent olefin insertion and reductive elimination with cyclopropane closure returns the active catalyst **7**, while producing cycloadduct **3**. The critical role of ZnI_2 in the room-temperature catalyst thus appears in assisting the initial reduction of Co(II) to Co(I), and more importantly, enabling the butadiene coordination in the presence of the bisphosphine ligand.[21]

Conclusions

A new cobalt catalyst system, CoI_2/dppe/Zn/ZnI_2 (1:1:1:3), has been discovered that promotes the [4 + 2 + 2] homo Diels−Alder cycloaddition of norbornadienes with butadiene at or below room temperature. The ability to achieve excellent yields at these lower temperatures bodes well for improving the enantioselectivity of these transition metal catalyzed homo Diels−Alder reactions using chiral ligands.[5] The role of the ZnI_2 may be to both promote the reduction of Co(II) to Co(I) and to assist in freeing a binding site on the active cobalt catalyst for coordination of the butadiene.

Experimental Section

General Methods. Melting points were determined in capillaries and are uncorrected; ^{1}H NMR and ^{13}C NMR spectra data were recorded at 93.94 kG (^{1}H 400 MHz) and 70.5 kG (^{1}H 300 MHz, ^{13}C 75 MHz) at ambient temperature in $CDCl_3$ (^{1}H and ^{13}C), benzene-d_6 (^{1}H), or CD_3CN (^{13}C). Chemical shifts (in ppm) are referenced to the residual $CHCl_3$ (δ 7.24) and C_6D_5H (δ 7.16) for the ^{1}H references and the center line of the solvent multiplet for the ^{13}C reference ($CDCl_3$ δ 77.0; CD_3CN δ 1.39). All hydroxyl resonances were confirmed by D_2O exchange. Unless otherwise noted, each carbon resonance represents a single carbon (relative intensity). Mass spectra (HRMS) were recorded in either CI (140 eV) or EI (70 eV) mode as noted. Infrared spectra were recorded on NaCl plates. Solid samples were prepared by depositing a solution of the sample (typically in $CDCl_3$) on the plate and allowing the solvent to evaporate prior to recording the IR spectra.

All reaction solvents were anhydrous and were distilled immediately prior to use (toluene, Et_2O, and THF from sodium, $ClCH_2CH_2Cl$ and CH_2Cl_2 from CaH_2);[22] chromatography solvents were distilled prior to use. Norbornadiene (**1**) was distilled prior to use and stored under argon; powdered zinc was activated prior to use by sequential washing with 5% aqueous HCl, EtOH, and Et_2O (twice with each solvent, with approximately twice the volume of the solid zinc) on a glass fritted funnel with vacuum filtration. Other commercially available reagents were used without further purification. All reactions were carried out in oven-dried (105 °C) glassware. The glass vessels used for the low boiling point reactants were heavy-walled tubes (25.4 × 102 mm) with Teflon plugs, designated as "pressure tubes" in the text. Reactions at −78

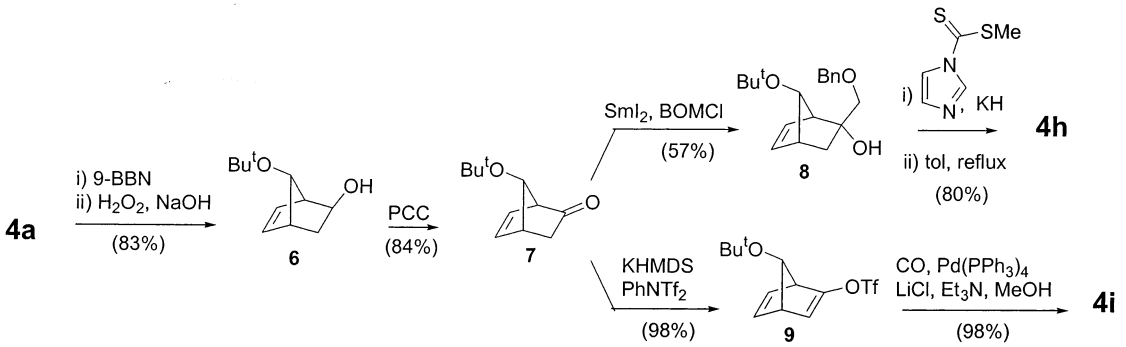
(19) Takahashi reported the formation of a [2 + 2 + 2] cycloadduct (ref 3b) from the cobalt-catalyzed reaction of butadiene with norbornadiene, and Lautens also mentioned this product forming in a communication footnote, ref 5a. However, in the subsequent full paper (ref 5b), he states that no such adducts were detected. We also could not detect any [2 + 2 + 2] cycloadduct (ref 7d). This cycloadduct has been reported in low yields with iron catalysts (ref 3a).

(20) Dartiguenave, M.; de Carvalho, L. C. A.; Dartiguenave, Y.; Bélanger-Gariépy, F.; Simard, M.; Beauchamp, A. L. *J. Organomet. Chem.* **1987**, *326*, 139−149.

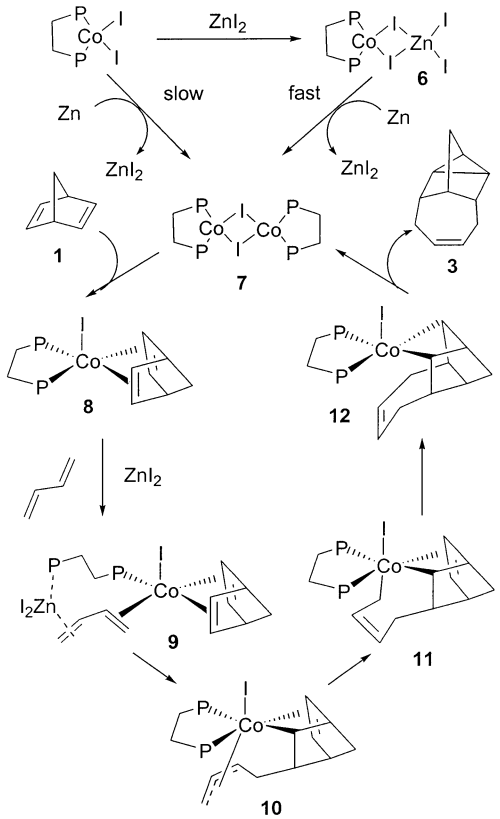
(21) (a) Trost, B. M.; Pinkerton, A. B. *J. Am. Chem. Soc.* **1999**, *121*, 1988−1989. (b) Trost, B. M.; Pinkerton, A. B.; Seidel, M. *J. Am. Chem. Soc.* **2001**, *123*, 12466−12476.

(22) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon: New York, 1980.

Scheme 2



Scheme 3



°C were maintained using dry ice−acetone baths; reactions at −30 °C were maintained using dry ice−50% aqueous acetone baths. Workup of the cycloadditions included passage through a silica gel plug, which is a disposable pipet filled with apporximately 3 cm of flash silica gel. Flash chromatography was performed using silica gel-60 (43−60 μm); TLC was performed on silica gel plates, and visualization was accomplished with ammonium molybdate stain: ammonium molybdate (4 g)/H_2O (60 mL)/H_2SO_4 (4 mL). Compounds **4a**,[16] **4b**,[17] and **4c**[7b] were prepared according to literature procedures without significant modification. Full characterizations of **3**,[7b] **5a**,[7b] **5b**,[7d] and **5c**[7b] have been reported in previous publications.

General Procedure for the [4 + 2 + 2] Cycloadditions of Norbornadienes. To a stirred, purple solution of CoI_2 (15.6 mg, 0.05 mol) and dppe (19.9 mg, 0.05 mmol) in CH_2Cl_2 (1.0 mL) in a pressure tube at 0 °C under Ar were added 1,3-butadiene (0.1 mL, 1.16 mmol) and 7-*tert*-butoxynorbornadiene (**4a**, 164 mg in 1 mL of CH_2Cl_2, 1 mmol), and then zinc powder (3.3 mg, 0.05 mmol) and ZnI_2 (47.9 mg, 0.15 mmol) were quickly added under Ar. The pressure tube was immediately capped and allowed to warm to room temperature. The dark brown cloudy solution was then stirred at room temperature for 20 h. The reaction mixture was passed through a silica gel plug to remove the catalyst, washing with CH_2Cl_2 (3 × 5 mL). The washings were collected, and the solvent removed in vacuo to give the crude product, which was purified by flash chromatography (hexanes/EtOAc, 20:1) to give pure **5a**[7b] (R_f = 0.3, 203 mg, 93%) as a colorless oil. Changing the order of addition did not effect the yield, but anything added after the formation of dark brown catalytic solution must be rigorously air-free. 1,3-Butadiene (bp −5 °C) was transferred via cannula as a liquid trapped at −78 °C.

***syn*-7-*tert*-Butoxy-2-methoxymethylbicyclo[2.2.1]hepta-2,5-diene (4d).**[23] To a suspension of $KOBu^t$ (143 mg, 1.3 mmol) and 7-*tert*-butoxynorbornadiene (**4a**, 164 mg, 1 mmol) in Et_2O (5 mL) at −50 °C under Ar was added dropwise *n*-BuLi (1.6 M in hexanes, 0.88 mL, 1.4 mmol), forming a brown suspension. The reaction mixture was maintained at −50 °C for 2 h, and then methoxymethyl chloride (106 μL, 1.4 mmol) was added in one drop, immediately forming a white suspension. The reaction mixture was allowed to warm to −30 °C and stirred for 45 min, then quenched with water (5 mL) at −30 °C. The organic layer was separated and washed with saturated aqueous $NaHCO_3$ (3 mL), H_2O (3 mL), and brine (3 mL), then dried over anhydrous Na_2SO_4. The solvent was removed in vacuo and the residue purified by flash chromatography (hexanes/EtOAc, 20:1) to give pure **4d** (R_f = 0.3, 170 mg, 82%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.09 (s, 9H), 3.25 (s, 3H), 3.27 (br s, 1H), 3.32 (br s, 1H), 3.75 (br s, 1H), 4.07 (AA′, 2H), 6.28 (dd, J = 2.8, 0.8 Hz, 1H), 6.58 (ddd, J = 4.8, 3.6, 1.2 Hz, 1H), 6.64 (ddd, J = 4.8, 3.6, 1.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 29.4 (3C), 56.5, 57.9, 58.4, 71.8, 74.5, 104.3, 134.2, 140.2, 140.8, 149.9. HRMS (EI, 70 eV): *m*/*z* 207.1381 ([M − 1]$^+$, 6.5%), calcd for $C_{13}H_{19}O_2$ 207.1384. The relative stereochemistry of **4d** was established by the observation of NOEs between H-7 and H-5 and H-6 (DNOE).

Methyl *syn*-7-*tert*-Butoxybicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (4e). 4e was prepared as described above for **4d** beginning with **4a** (164 mg, 1 mmol) and quenching the anion of **4a** with methyl chloroformate (155 μL, 2 mmol). After quenching the reaction with water, the organic layer was separated and treated by the same workup. Purification by flash chromatography (hexanes/EtOAc, 20:1) gave pure **4e** (R_f = 0.2, 200 mg, 90%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.10 (s, 9H), 3.51 (br s, 1H), 3.72 (s, 3H), 3.73 (br s, 1H), 3.88 (br s, 1H), 6.56 (dd, J = 4.4, 4.4 Hz, 1H), 6.73 (dd, J = 4.4, 4.4 Hz, 1H), 7.42 (d, J = 2.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 29.3 (3C), 52.3, 56.6, 58.1, 75.0, 106.0, 138.9, 140.9, 144.3, 150.8, 166.8. IR (NaCl): 1733 cm^{-1}. HRMS (EI, 140 eV): *m*/*z* 222.1243 ([M]$^+$, 7.6%), calcd for $C_{13}H_{18}O_3$ 222.1256. The relative stereochemistry of **4e** was established by the observation of NOEs between H-7 and H-5 and H-6.

(23) Adapted from: (a) Verkruijsse, H. D.; Brandsma, L. *Recl. Trav. Chim. Pays-Bas* **1986**, *105*, 66−68. (b) Brandsma, L.; Verkruijsse, H. D. *Prepr. Polar. Organomet. Chem.* **1987**, *1*, 52−53.

***anti*-7-*tert*-Butoxybicyclo[2.2.1]hept-2-en-*exo*-5-ol (6).**[24] To a solution of 7-*tert*-butoxynorbornadiene (**4a**, 8.2 g, 50 mmol) in THF (100 mL) under Ar was added 9-BBN (0.5 M in THF, 100 mL) via cannula at room temperature. The reaction solution was sonicated for 3 h at room temperature, then stirred for 2 days. After the solution was cooled to 0 °C, H_2O (50 mL) and aqueous NaOH (3 M, 75 mL) were added, then 30% H_2O_2 (75 mL) was added dropwise over 30 min. The mixture was allowed to warm to room temperature and stirred for 3 h, then neutralized with 3 M HCl. The mixture was extracted with Et_2O (3 × 200 mL), and the combined organic phase was washed with saturated aqueous Na_2SO_3 (50 mL), saturated aqueous $NaHCO_3$ (50 mL), H_2O (50 mL), and saturated brine (50 mL), then subsequently dried over anhydrous Na_2SO_4. After removing the solvent in vacuo, the residue was purified by flash chromatography (hexanes/EtOAc, 3:1) to give the known compound **6** (R_f = 0.26, 7.5 g, 83% yield) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.16 (s, 9H), 1.37 (ddd, J = 12.8, 3.0, 3.0 Hz, 1H), 1.56 (dd, J = 12.8, 8.0 Hz, 1H), 1.98 (br s, OH), 2.62 (br s, 1H), 2.68 (br s, 1H), 3.76 (ddd, J = 8.0, 2.2 Hz, 1H), 4.27 (br s, 1H), 5.89 (dd, J = 5.6, 3.0 Hz, 1H), 6.13 (dd, J = 5.6, 2.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.4 (3C), 34.5, 46.0, 55.5, 70.8, 73.6, 86.4, 129.3, 136.4. The relative stereochemistry of **6** was confirmed by the lack of coupling between H-5$_{endo}$ and H-4[25] and supported by the observation of an NOE between H-7 with *exo*-H-6 only (no NOE to a C-5 proton).

***anti*-7-*tert*-Butoxybicyclo[2.2.1]hept-5-en-2-one (7).** To a suspension of PCC (646.7 mg, 3 mmol) in CH_2Cl_2 (20 mL) was added **6** (364 mg, 2 mmol). The resulting dark brown suspension was stirred under Ar at room temperature for 6 h, then passed through a silica gel plug washing with CH_2Cl_2 (3 × 20 mL). The solvent was removed in vacuo and the residue purified by flash chromatography (hexanes/EtOAc, 8:1) to give **7** (R_f = 0.3, 302 mg, 84% yield) as a white solid. Mp: 77−78 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.17 (s, 9H), 1.97 (dd, J_{AB} = 17.2 Hz, J = 1.2 Hz, 1H), 2.01 (dd, J_{AB} = 17.2, J = 2.8, 0.8 Hz, 1H), 3.07−3.12 (2H), 4.22 (br s, 1H), 5.96 (m, 1H), 6.49 (dd, J = 5.6, 2.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.3 (3C), 38.2, 47.0, 62.7, 74.4, 89.5, 125.3, 139.4, 211.0. IR (NaCl): 2978, 1746 cm^{-1}. HRMS (EI, 70 eV): *m*/*z* 181.1221 ([M + 1]$^+$, 14.7%), calcd for $C_{11}H_{17}O_2$ 181.1228.

***anti*-5-*exo*-Benzyloxymethyl-7-*tert*-butoxybicyclo[2.2.1]-hepta-2-en-*exo*-5-ol (8).** A suspension of Sm (466.7 mg, 3.1 mmol) and ICH_2CH_2I (964.6 mg, 3.4 mmol) in THF (30 mL) was sonicated under Ar for 4 h until a deep blue color formed.[26] To this solution, **7** (141 mg, 0.778 mmol) and benzyloxymethyl chloride (99.2 uL, 0.86 mmol) in THF (2 mL) were added dropwise via syringe. The reaction mixture was stirred at room temperature for 18 h, during which time a yellow precipitate slowly formed, and then 1 M HCl was added until the precipitate dissolved. The reaction mixture was extracted with Et_2O (3 × 30 mL), and the combined organic layers were washed with saturated aqueous $NaHCO_3$ (20 mL), H_2O (20 mL), and saturated brine (20 mL), then dried over anhydrous Na_2SO_4. The solvent was removed in vacuo and the residue purified by flash chromatography (hexanes/EtOAc, 3:1) to give **8** (R_f = 0.15, 135 mg, 57% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.07 (s, 9H), 1.09 (d, J = 13.2 Hz, 1H), 1.75 (dd, J = 13.2, 3.4 Hz, 1H), 2.22 (br s, ex, OH), 2.71 (br s, 1H), 2.94 (br s, 1H), 3.60 (AB, J = 9.8 Hz, 2H), 3.73 (br s, 1H), 4.55 (d, J = 12 Hz, 1H), 4.66 (d, J = 12 Hz, 1H), 6.10 (dd, J = 6.0, 3.0 Hz, 1H), 6.33 (dd, J = 6.0, 2.8 Hz, 1H), 7.27−7.35 (5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.2 (3C), 38.6, 47.9, 55.4, 73.4, 73.6, 76.6 (overlapped with $CDCl_3$), 77.4, 87.1, 127.7 (3C), 128.4 (2C), 129.5, 135.1, 138.0. ^{13}C NMR (75 MHz, CD_3CN): δ 28.9 (3C), 39.3, 49.2, 56.7, 74.27, 74.34, 78.2, 78.5, 87.9, 128.9, 129.1 (2C), 129.7 (2C), 131.2, 135.4, 140.1. IR (neat): 3466, 3064, 2972, 1100 cm^{-1}. HRMS (CI, 140 eV): *m*/*z* 303.1941 ([M + 1]$^+$, 0.13%), calcd for $C_{19}H_{27}O_2$ 303.1960. The relative stereochemistry of **8** was established by the observation of NOEs of H-7 with *exo*-H-6 and the CH_2OBn methylene protons.

***anti*-2-Benzyloxymethyl-7-*tert*-butoxybicyclo[2.2.1]-hepta-2,5-diene (4h).** To a solution of **8** (130 mg, 0.43 mmol) and 1-(methyldithiocarbonyl)imidazole[27] (134 mg, 0.86 mmol) in THF (5 mL) was added KH (35% in mineral oil, 147.6 mg, 1.29 mmol) at 0 °C and the reaction mixture stirred at room temperature for 14 h. Aqueous saturated $NaHCO_3$ (5 mL) was added at 0 °C, and the mixture was allowed to warm to room temperature. The reaction mixture was extracted with Et_2O (3 × 10 mL), and the combined organic layers were dried over anhydrous Na_2SO_4. After removing the solvent in vacuo, the residue was dissolved in toluene (5 mL) and refluxed for 24 h.[28] The solution was cooled to room temperature, and the solvent was removed in vacuo. The residue was purified by flash chromatography (hexanes/EtOAc, 20:1) to give **4h** (R_f = 0.25, 97 mg, 80% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.12 (s, 9H), 3.35 (br s, 1H), 3.39 (br s, 1H), 3.84 (br s, 1H), 4.12 (J_{AB} = 13.2 Hz, J = 1.6 Hz, 1H), 4.15 (J_{AB} = 13.2 Hz, J = 1.6 Hz, 1H), 4.41 (AB-system, J_{AB} = 12.0, 2H), 6.40 (dd, J = 3.2, 1.6 Hz, 1H), 6.58 (m, 1H), 6.62 (m, 1H), 7.27 (m, 1H), 7.28−7.35 (5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.4 (3C), 55.6, 56.9, 68.9, 71.9, 73.7, 103.4, 127.6, 127.8 (2C), 128.4 (2C), 135.0, 136.8, 137.6, 138.6, 151.6. HRMS (EI, 70 eV): *m*/*z* 284.1756 ([M]$^+$, 0.3%), calcd for $C_{19}H_{24}O_2$ 284.1776.

***anti*-7-*tert*-Butoxybicyclo[2.2.1]hepta-2,5-dien-2-yl triflate (9).** To a solution of **7** (1.8 g, 10 mmol) in THF (50 mL) was added dropwise KHMDS (0.5 M in toluene, 30 mL, 15 mmol) at −78 °C under Ar. After stirring for 2 h, the solution was warmed to 0 °C for 10 min, and *N*-phenyltrifluoromethanesulfonimide ($PhNTf_2$, 5.12 g, 15 mmol) was added. The solution was stirred at room temperature for 8 h, and then aqueous saturated $NaHCO_3$ (5 mL) was added. Diethyl ether (200 mL) was added, and the separated organic layer was washed with aqueous saturated $NaHCO_3$ (30 mL), H_2O (30 mL), and saturated brine (30 mL) and then dried over anhydrous Na_2SO_4. After removing the solvent in vacuo, the residue was purified by flash chromatography (hexanes/EtOAc, 20:1) to give **9** (R_f = 0.33, 3.05 g, 98% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.14 (s, 9H), 3.34 (br s, 1H), 3.40 (br s, 1H), 4.12 (br s, 1H), 6.18 (dd, J = 4.0, 1.6 Hz, 1H), 6.65 (br s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.2 (3C), 54.1, 56.9, 74.6, 76.9, 104.0, 118.5 (q, $^1J_{CF}$ = 319 Hz), 122.8, 135.4, 138.3, 162.9. HRMS (CI, 140 eV, CH_4): *m*/*z* 313.0736 ([M + 1]$^+$, 1.3%), calcd for $C_{12}H_{16}SF_3O_4$ 313.0722.

Methyl *anti*-7-*tert*-Butoxybicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (4i). To a solution of **9** (3.05 g, 9.78 mmol) in MeOH (100 mL) was added LiCl (2.07 g, 48.8 mmol), NEt_3 (1.4 mL, 9.78 mmol), and $Pd(PPh_3)_4$ (333 mg, 0.33 mmol). The suspension was stirred under CO (1 atm, balloon) for 3 h. The suspension was filtered through a silica gel plug eluting with CH_2Cl_2 (3 × 20 mL). The solvent was removed in vacuo, and then Et_2O (200 mL) and water (50 mL) were added to the residue. The separated organic layer was dried over anhydrous Na_2SO_4. After removing the solvent in vacuo, the residue was purified by flash chromatography (hexanes/EtOAc, 20:1) to give **4i** (R_f = 0.26, 2.11 g, 98% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.12 (s, 9H), 3.53 (br s, 1H), 3.73 (s, 3H), 3.79 (br s, 1H), 3.86 (br s, 1H), 6.51 (dd, J = 6.0, 3.6 Hz, 1H), 6.67 (m, 1H), 7.47 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.3

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(3C), 51.4, 55.6, 57.1, 74.2, 104.8, 135.7, 137.6, 145.5, 150.7, 165.0. IR (NaCl): 1717 cm^{-1}. HRMS (EI, 70 eV): *m*/*z* 222.1271 ($[M]^+$, 1.2%), calcd for $C_{13}H_{18}O_3$ 222.1256.

***anti*-1-Benzyloxymethyl-5-*tert*-butoxytetracyclo-[5.4.0.0^{2,4}.0^{3,7}]undec-9-ene (5h). 5h** was prepared following the General Procedure, with **4h** (59 mg in 0.3 mL of CH_2Cl_2, 0.2 mmol) at room temperature for 24 h (Table 6, entry 7). Purification by flash chromatography (hexanes/EtOAc, 30:1) gave pure **5h** (R_f = 0.3, 43 mg, 61%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.84 (t, J = 5.2 Hz, 1H), 0.91 (t, J = 5.2 Hz, 1H), 1.05 (s, 9H), 1.05 (overlapped, 1H), 1.60 (s, 1H), 2.07 (dd, J = 16.8, 7.2 Hz, 1H), 2.20 (br d, J = 17.6 Hz, 1H), 2.30 (dd, J = 16.8, 6.4 Hz, 1H), 2.45 (dd, J = 17.6, 2.4 Hz, 1H), 2.56 (d, J = 5.6 Hz 1H), 3.18 (d, J = 9.2 Hz, 1H), 3.47 (d, J = 9.2 Hz, 1H), 3.89 (s, 1H), 4.32 (d, J_{AB} = 12.0 Hz, 1H), 4.58 (d, J_{AB} = 12.0 Hz, 1H), 5.50 (m, 2H), 7.19 (m, 1H), 7.20−7.25 (4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 17.2, 17.3, 21.1, 28.8 (3C), 29.7, 36.5, 37.8, 48.1, 48.3, 73.3, 73.8, 76.2, 77.3, 127.6, 127.8 (2C), 128.4 (2C), 128.58, 128.64, 138.8. HRMS (EI, 70 eV): *m*/*z* 338.2237 ($[M]^+$, 0.8%), calcd for $C_{23}H_{30}O_2$ 338.2246.

Methyl *anti*-5-*tert*-Butoxytetracyclo[5.4.0.0.^{2,4}0^{3,7}]undec-9-en-1-carboxylate (5i). 5i was prepared following the General Procedure with **4i** (183 mg in 0.8 mL of CH_2Cl_2, 0.82 mmol) at room temperature for 24 h (Table 6, entry 8). Purification by flash chromatography (hexanes/EtOAc, 20:1) gave pure **5i** (R_f = 0.3, 191 mg, 84%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.14 (s, 9H), 1.14 (overlapped, 2H), 1.31 (dd, J = 5.0, 5.0 Hz, 1H), 1.88 (br s, 1H), 2.23−2.30 (m, 2H), 2.39−2.47 (m, 2H), 2.59 (br d, J = 5.6 Hz, 1H), 3.57 (br s, 1H), 3.69 (s, 3H), 5.49−5.54 (m, 1H), 5.63−5.69 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 17.0, 17.3, 19.3, 28.5 (3C), 29.3, 34.2, 37.7, 49.6, 51.7, 54.6, 73.6, 77.0 (overlapped with $CDCl_3$), 126.1, 129.8, 177.8. IR (NaCl): 1723 cm^{-1}. HRMS (EI, 70 eV): *m*/*z* 276.1701 ($[M]^+$, 2.7%), calcd for $C_{17}H_{24}O_3$ 276.1725. The ^{1}H NMR spectrum was also recorded in benzene-d_6 to resolve the cyclopropyl resonances. ^{1}H NMR (400 MHz, C_6D_6): δ 1.07 (dd, J = 5.2, 5.2 Hz, 1H), 1.14 (s, 9H), 1.25 (dd, J = 5.2, 5.2 Hz, 1H), 1.46 (dd, J = 5.2, 5.2 Hz, 1H), 2.03 (br s, 1H), 2.17−2.33 (3H), 2.52 (dd, J = 17.0, 2.2 Hz, 1H), 2.86 (d, J = 5.6 Hz, 1H), 3.39 (s, 3H), 3.87 (br s, 1H), 5.46−5.52 (m, 1H), 5.59−5.64 (m, 1H). The ^{13}C NMR spectrum was also recorded in CD_3CN to observe the signal overlapped by the $CDCl_3$ solvent peak. ^{13}C NMR (75 MHz, CD_3CN): δ 18.3, 18.4, 20.6, 29.1 (3C), 30.2, 35.3, 39.0, 51.0, 52.7, 55.7, 74.5, 78.1, 127.6, 131.1, 178.6.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for all new compounds, **4d**, **4e**, **4h**, **4i**, **5h**, **5i**, **6**−**9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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