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Catalytic Cycloisomerization of Enynes by Using a Nickel-Zinc-Acid System

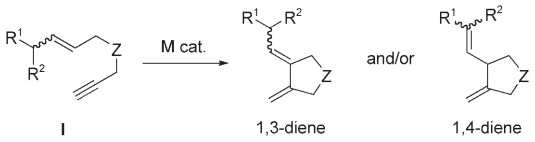
Shin-ichi Ikeda,* Natsuko Daimon, Reiko Sanuki, and Kazunori Odashima[a]

Abstract: Catalytic cycloisomerization of enynes has been accomplished in the presence of an Ni^0-PPh_3-Zn-carboxylic acid or -$ZnCl_2$ system. A nickel(I)–hydride complex, thought to be generated by reduction of the protonated nickel(II) complex with Zn, is proposed as the catalytic species. This cycloisomerization shows reactivity behavior that is different from that of a conventional metal-catalyzed reaction. In particular, in the reaction with (*E*)-enynes, the catalytic system has a selectivity that favors the formation of the 1,3-diene over the 1,4-diene. In addition, this catalytic system has been applied to the domino cyclization of dienynes for the construction of tricyclic compounds.

Keywords: cycloisomerizations · domino reactions · enynes · nickel · zinc

Introduction

The transition metal catalyzed cycloisomerization of enynes is an efficient method for the synthesis of various cyclic compounds.[1,2] Compared with the classical thermal Alder ene reaction, the catalytic reaction of enynes **I** with an *allylic methylene* group (R^1 and/or R^2 = H in Scheme 1) can provide not only 1,4-dienes, but also 1,3-dienes under mild conditions. Generally, various transition-metal complexes, such as those of Pd,[3] Ru,[4] Ti,[5] Rh,[6] and Ni-$CrCl_2$,[7] catalyze the ene-type reaction of **I** to furnish 1,4-dienes. As an exception, in the Pd-catalyzed reaction, the presence of branching or an oxygenated group at the allylic position of enynes can alter the regioselectivity.[8] The reaction of enynes tethered to a remote double bond also gives 1,3-dienes rather than 1,4-dienes.[8a] However, it is difficult to control the selective formation of 1,3-dienes, which are important building blocks in the Diels–Alder reaction.[9]



M cat. = Pd, Ru, Ti, Rh, Ni-$CrCl_2$
R^1 = H or alkyl, R^2 = H · · · · 1,4-diene selectivity
as exceptions,
in Pd-catalyzed reaction,
R^1–R^2= -$(CH_2)_5$-
R^1 = alkoxyl or hydroxyl, R^2 = H
R^1 = CH_2=$CH(CH_2)_2$-, R^2 = H
} 1,3-diene selectivity

Scheme 1. Selective cycloisomerization to 1,3- versus 1,4-dienes.

For this reaction, two principal possible mechanisms have been proposed (Scheme 2): a) a metallacycle process involving the oxidative cyclization of a transition-metal catalyst (M) with the enyne, and b) a hydrometalation/carbometalation process involving the addition of a metal–hydride species ($H–M^+$) generated by the in situ protonation of M.[1] Subsequent β-hydrogen elimination from **II** or **III**/**III′** leads to the formation of 1,3- and 1,4-dienes, respectively. This β-hydrogen elimination usually requires a *cis* relationship between the carbon–metal (C–M) and carbon–hydrogen (C–H) bonds, which have to be aligned to optimize the orbital overlap. At this point, **II** offers a better geometry for β-elimination of a $C–H^b$ bond leading to the 1,4-diene than for that of a $C–H^a$ bond leading to the 1,3-diene, since the dihedral angle between the C–M and $C–H^b$ bonds is close to 0°. In the reaction via a hydrometalation/carbometalation process, although the geometry of **III′** makes it possible to eliminate the β-$C–H^a$ bond leading to the 1,3-diene, since the $C–H^a$ bond has lower energy due to its allylic nature, it is still insufficient to achieve 1,3-diene selectivity.

We describe here in detail our studies on the nickel-catalyzed cycloisomerization of 1,6-enynes via hydrometalation. This reaction is carried out in the presence of a new catalytic system, in which Zn powder is added as a reducing agent

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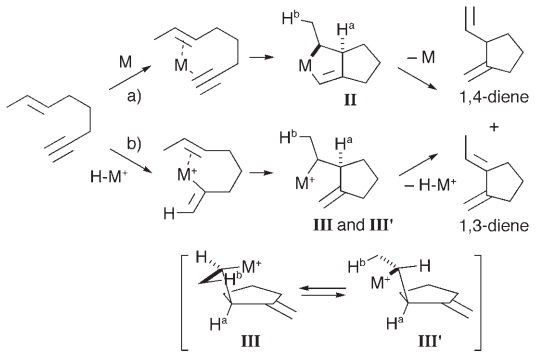


Scheme 2. Metal-catalyzed cycloisomerization of enynes.

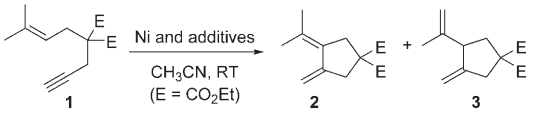
to a nickel hydride complex (H–Ni^+), and shows reactivity behavior that is different from that of a conventional metal-catalyzed reaction. In particular, the catalytic system has a selectivity that favors the formation of the 1,3-diene over the 1,4-diene. In addition, we envisage a process that involves the further interception of **III** or **III′** by a remote unsaturated substrate. This catalytic system can also be applied to the domino cyclization of dienynes for the construction of tricyclic compounds.

Results and Discussion

We initially investigated the reaction of **1** in the presence of $[Ni(cod)_2]$ (10 mol%), PPh_3 (20 mol%), and trifluoroacetic acid (CF_3CO_2H, 20 mol%) in CH_3CN. Although the formation of **2** and **3** was observed after 20 h (48% GC yield, **2**/**3** 9:91), some 46% of unreacted **1** was also recovered (run 1 in Table 1). When Zn powder (200 mol%) was added to the reaction mixture, the reaction proceeded efficiently for 2 h to give **2** and **3** in a combined yield of 70% (run 2). No reaction occurred in the absence of CF_3CO_2H (run 3). While the reaction using *p*-nitrophenol instead of CF_3CO_2H also failed (run 4), acetic acid (AcOH) proved to be moderately effective in the presence of Zn powder (run 6 vs run 5). Moreover, a system of $[NiCl_2(PPh_3)_2]$ and Zn was also found to catalyze the cycloisomerization (run 7). By comparison with run 3, this result suggests that zinc chloride ($ZnCl_2$), generated by the reduction of $[NiCl_2(PPh_3)_2]$ with Zn,[10] is involved in the reaction. When $ZnCl_2$ (20 mol%) was added to the reaction mixture from run 3, the yield of **2** and **3** increased to the level achieved in run 7 (run 8). The addition of Zn powder to the catalytic system promoted the reaction further (run 9). A further experiment revealed that PPh_3 could be omitted from the reaction mixture (run 10). When toluene or THF was used as a solvent, no reaction occurred.

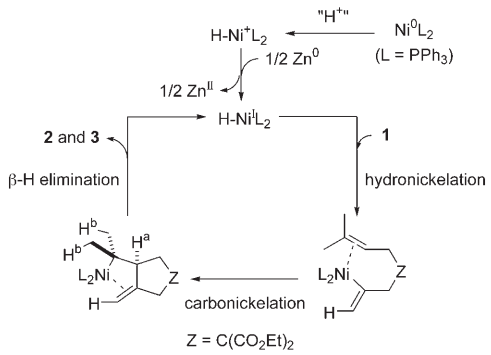
We believe that the present cycloisomerization involves hydrometalation by a nickel hydride species (Scheme 2b), as in the Pd^0-AcOH system (M = Pd) reported by Trost et al.[1b] The addition of Brønsted acids such as CF_3CO_2H, H_2SO_4, HCl, $HSnCl_3$ (HCl + $SnCl_2$), and HCN to Ni^0 complexes leads to the formation of nickel(II)–hydride complexes.[11] However, Barefield et al. reported that a protonated nickel(II) species, $HNi(PPh_3)_nX$ (X = Cl or $SnCl_3$), rapidly decomposed to generate a nickel(I) species, $NiX(PPh_3)_n$, with evolution of H_2 gas at room temperature.[12] On the other hand, an $NiX(PPh_3)_n$ complex, as well as a cationic nickel(II) hydride, $HNi[P(OEt)_3]_4^+$,[13] catalyzes the isomerization of alkenes.[14] A low concentration of $HNi(PPh_3)_nX$, generated from the reaction of $NiX(PPh_3)_n$ (2 equiv) with the alkene, was shown to be responsible for the catalytic activity.[12] In the present reaction, the nickel(II) hydride species (M = $Ni(PPh_3)_2$ in Scheme 2b) would be generated,[15] although no helpful information was obtained by NMR. In the reaction using $ZnCl_2$, a proton source would be generated by the treatment of $ZnCl_2$ with a small amount of water present in situ. Under these circumstances, $ZnCl_2$ would assist in the protonation of the Ni^0 species to more effectively give the nickel(II) hydride species.[16] Nevertheless, the role of Zn powder has yet to be accounted for (recall that the reaction did not proceed smoothly in the absence of Zn powder; compare runs 1, 5, and 8 in Table 1). We further propose an alternative pathway, in which half an equivalent of Zn reduces the nickel(II) hydride to the nickel(I) species, $[HNi(PPh_3)_2]$ (Scheme 3). The nickel(I) hydride would add to the alkyne part of **1** and subsequent carbonickelation would give an alkylnickel intermediate. Subsequent β-hydrogen (H^a or H^b) elimination would lead to the formation of **2** or **3**, respectively.

Table 1. Screening of catalysts and additives.[a]



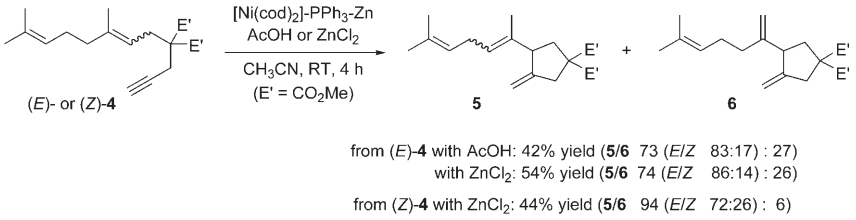
Run	Ni cat.	PPh_3 [mol%]	Zn [mol%]	Acid [mol%]	*t* [h]	Yield[b] [%]
1	$[Ni(cod)_2]$	20	0	CF_3CO_2H (20)	24	48[c]
2	$[Ni(cod)_2]$	20	200	CF_3CO_2H (20)	2	70
3	$[Ni(cod)_2]$	20	200	–	24	0
4	$[Ni(cod)_2]$	20	200	ArOH[d] (20)	24	0
5	$[Ni(cod)_2]$	20	0	AcOH (20)	24	<5
6	$[Ni(cod)_2]$	20	200	AcOH (20)	20	73
7	$[NiCl_2(PPh_3)_2]$	–	200	–	2	54
8	$[Ni(cod)_2]$	20	0	$ZnCl_2$ (20)	24	45[e]
9	$[Ni(cod)_2]$	20	200	$ZnCl_2$ (20)	2	73
10	$[Ni(cod)_2]$	0	200	$ZnCl_2$ (20)	24	0

[a] Reaction conditions: Ni cat. (10 mol%) in CH_3CN at room temperature. [b] Combined yield of **2** and **3**. [c] The starting **1** was recovered (46%). [d] ArOH = *p*-nitrophenol. [e] The starting **1** was recovered (14%).



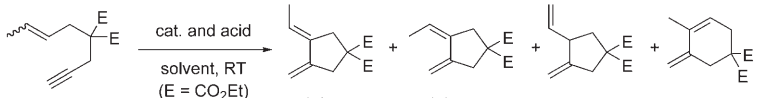
Scheme 3. Plausible catalytic cycle for cycloisomerization promoted by H–Ni^{I} species.

Enynes **4** bearing unsymmetrical trisubstituted alkene functions show an interesting switch in regioselectivity between the Ni^0-Zn-acid and Pd^0-AcOH systems. Thus, it has been established that the Pd-catalyzed reaction with the geranyl-based (*E*)-**4** gives mainly the less substituted 1,4-diene **6**.[3,17–19] In sharp contrast, when (*E*)-**4** was exposed to the Ni^0-Zn-acid catalytic system, the more substituted 1,4-diene **5** rather than **6** was produced (Scheme 4). The reaction with the neryl-based enyne (*Z*)-**4** also gives **5** with high regioselectivity.[20]



Scheme 4. Reactions of (*E*)- and (*Z*)-**4**.

Table 2. Cycloisomerizations of (*E*)- and (*Z*)-**7a**.

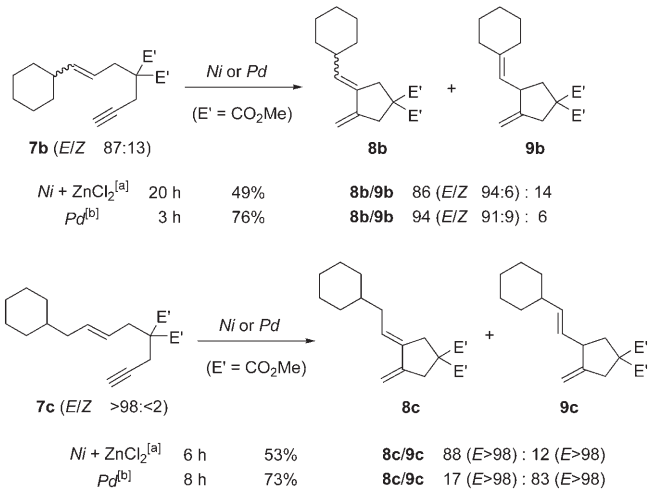


Run	**7a**	Cat.[a]	Acid [mol%]	Solvent	*t* [h]	Yield[b] [%]	Ratio[c]
1	(*E*)	*Ni*	AcOH (20)	CH_3CN	8	72	78:1:19:2
2		*Ni*	–	CH_3CN	48	0	–
3		*Ni*	$ZnCl_2$ (20)	CH_3CN	3	69	86:2:10:2
4		*Pd*	AcOH (10)	C_6H_6	6	75	50:2:48:0
5		*Pd*	AcOH (10)	CH_3CN	6	58	45:2:53:0
6		*Pd* + Zn[d]	AcOH (10)	CH_3CN	24	trace	–
7[e]		Ni-$CrCl_2$				75	1:3:0[f]
8	(*Z*)	*Ni*	AcOH (20)	CH_3CN	3	67	3:31:33:33
9		*Ni*	$ZnCl_2$ (20)	CH_3CN	1	67	2:31:33:34
10		*Pd*	AcOH (10)	C_6H_6	2	80	2:30:68:0
11[e]		Ni-$CrCl_2$				74	1:13:0[f]

[a] *Ni*: [Ni(cod)$_2$] (10 mol%), PPh_3 (20 mol%), and Zn (200 mol%). *Pd*: [$Pd_2(dba)_3$]·$CHCl_3$ (5 mol%) and PPh_3 (10 mol%). [b] Isolated yield. [c] Product ratio of (*E*)-**8a**/(*Z*)-**8a**/**9a**/**10a** determined by ^{1}H NMR. [d] Zn (200 mol%) was added. [e] A polymer (phosphinylated 2% cross-linked polystyrene)-supported catalytic system, see ref. [7]. [f] Product ratio of **8a**/**9a**/**10a**.

As mentioned above, the system consisting of a nickel hydride species and Zn shows reactivity behavior that is different from that of a conventional metal-catalyzed cycloisomerization. We next investigated the reaction with (*E*)- and (*Z*)-**7a** using our catalytic system. The results are summarized in Table 2. The addition of (*E*)-**7a** to a mixture of [Ni(cod)$_2$] (10 mol%), PPh_3 (20 mol%), Zn powder (200 mol%), and AcOH (20 mol%) in CH_3CN at room temperature and allowing the reaction to proceed for 8 h gave a mixture of cyclic compounds **8a**, **9a**, and **10a** in a combined yield of 72% (run 1). Remarkably, the 1,3-diene **8a** was observed as the major isomer by ^{1}H NMR (78% selectivity). The stereochemistry was confirmed to be (*E*) by means of a NOESY experiment. Using $ZnCl_2$ in place of AcOH also promoted cycloisomerization to give (*E*)-**8a**, and indeed the reaction was faster and more selective (3 h, 86% selectivity, run 3). In contrast, when the reaction was performed with a Pd^0-AcOH system, the selectivity in favor of (*E*)-**8a** was lower (run 4). When the reaction was carried out in CH_3CN instead of benzene, the selectivity for **8a** decreased further (run 5). The addition of Zn powder proved to be wholly ineffective (run 6). In a reaction using the polymer-supported Ni-$CrCl_2$ system reported by Trost, **9a** was obtained selectively (run 7).[7] The alkene geometry of **7a** determined that of **8a**; that is, the reaction with (*Z*)-**7a** provided (*Z*)-**8a**. However, the selective formation of **8a** was not observed in any of the reactions (runs 8–11).

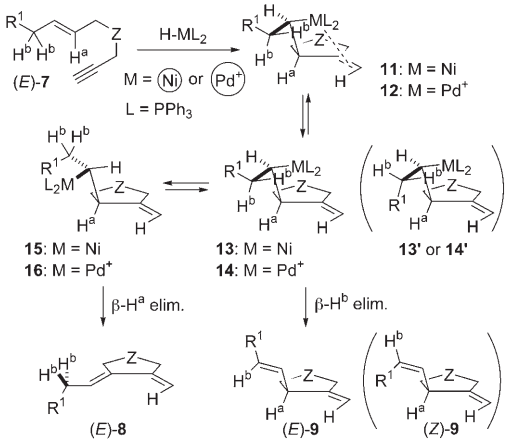
The results of cycloisomerizations with **7b–g** using an Ni^0-Zn-$ZnCl_2$ or -AcOH system are shown in Schemes 5 and 6, and are compared with those achieved using the Pd^0-AcOH system. In the presence of either catalytic system, the reaction of **7b** bearing a branched allylic substituent selectively afforded the corresponding 1,3-diene **8b**. On the other hand, in the reaction with the methylene-extended **7c**, a remarkable difference in regioselectivity was seen between the two catalytic systems. Thus, whereas the Pd-catalyzed reaction selectively gave the 1,4-diene **9c**, the 1,3-diene **8c** was predominantly obtained in the presence of the Ni^0-Zn-$ZnCl_2$ system (Scheme 5). The reactions of other (*E*)-alkene-substituted substrates **7d–g** in the presence of the Ni^0-Zn-$ZnCl_2$ or -AcOH system selectively afforded 1,3-dienes **8d–g**, respectively (Scheme 6). The reaction with



Scheme 5. Cycloisomerizations of **7b** and **7c**. [a] $[Ni(cod)_2]$ (10 mol%), PPh_3 (20 mol%), Zn (200 mol%), and $ZnCl_2$ (20 mol%) in CH_3CN at RT. [b] $[Pd_2(dba)_3]\cdot CHCl_3$ (5 mol%), PPh_3 (10 mol%), and AcOH (10 mol%) in C_6H_6 at RT.

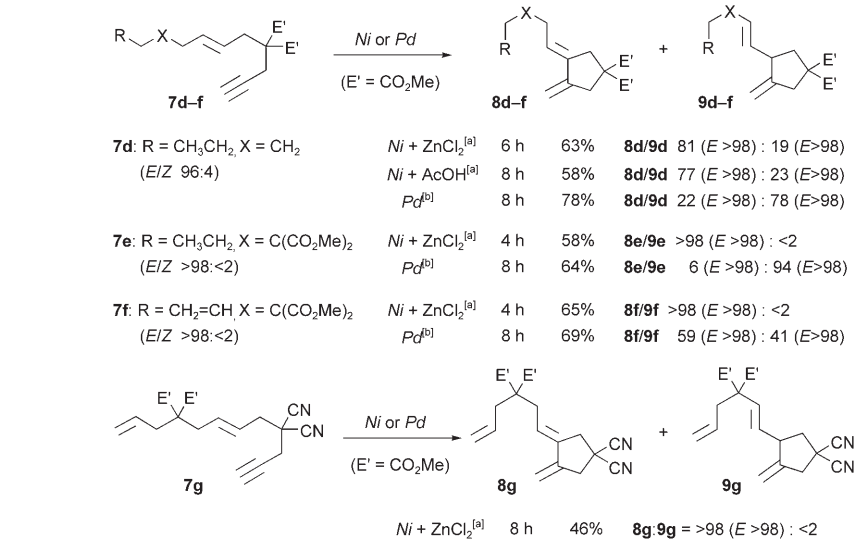
7d in the presence of $ZnCl_2$ gave **8d** more effectively than when AcOH was used. In all cases, even when the products provided by one catalytic system were exposed to another, isomerization between **8** and **9** was not observed.

The reaction of (*E*)-**7** with the H–M species (M = Ni or Pd^+) produces an alkylmetal intermediate **11** or **12**, respectively, via 5-*exo*-carbometalation (Scheme 7). Dissociation of the coordinated exocyclic alkene part from the metal center (M) would generate **13** or **14**, respectively. While the geometry is appropriate for β-hydrogen elimination of a C–H^b bond leading to (*E*)-1,4-dienes **9**,[21] the conformer **15** or **16** would undergo β-H^a elimination leading to 1,3-dienes **8**, since the C–H^a bond has lower energy due to its allylic nature. The intermediate **11** (M = Ni) should be readily converted to **13**, due to the weaker coordination of the exocyclic alkene part to the neutral Ni center as compared with the cationic Pd center. Therefore, the reaction of (*E*)-**7** in the presence of the Ni^0-Zn-$ZnCl_2$ or -AcOH system selectively affords (*E*)-1,3-dienes **8**. In the Pd-catalyzed reaction, the remote double bond of the starting **7f** controls the regioselectivity of **8f** and **9f** (see Scheme 6). Due to the coordination of the remote double bond (R^1 = CH_2=$CHCH_2C(CO_2Me)_2$) to the Pd center, the geometry of **16** is not ideal for the elimination of the C–H^b bond leading to **9f**.[8a] In contrast, in the reaction using the Ni^0-Zn-$ZnCl_2$ or -AcOH system, the selectivity in favor of **8e** and **8f** arising from **15** (M = Ni) is independent of the remote double bond of the starting **7e** and **7f**.



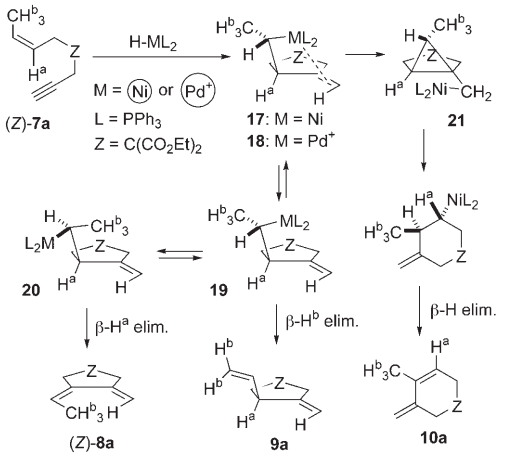
Scheme 7. Reaction with (*E*)-**7** leading to (*E*)-**8** and **9**.

The alkene geometry of the starting **7** affects not only the stereochemistry of **8**, but also the selective formation of **8** versus **9**. In the reaction with (*Z*)-**7a**, **19** would be derived from **17** (M = Ni) or **18** (M = Pd^+) (Scheme 8). Subsequent conformational rotation generates **20**, which enables β-elimination of the C–H^a bond to provide (*Z*)-**8a**. However, the formation of (*Z*)-**8a**, compared with that of (*E*)-**8a** arising from the β-H^a-elimination of **15**, would be a somewhat disfavorable path due to the steric configuration with the methyl group *syn* to the 1,3-diene part. As a result, **9a** is readily obtained by β-elimination of the C–H^b bond. In addition, there is also a cyclopropanation route to provide **21**, which would undergo



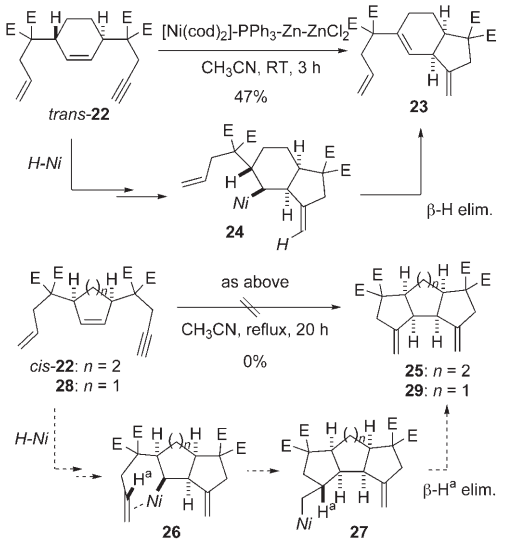
Scheme 6. Cycloisomerizations of **7d–g**. [a] $[Ni(cod)_2]$ (10 mol%), PPh_3 (20 mol%), Zn (200 mol%), and $ZnCl_2$ or AcOH (20 mol%) in CH_3CN at RT. [b] $[Pd_2(dba)_3]\cdot CHCl_3$ (5 mol%), PPh_3 (10 mol%), and AcOH (10 mol%) in C_6H_6 at RT.

β-carbon elimination followed by β-hydrogen elimination to give the six-membered **10a**.[22]



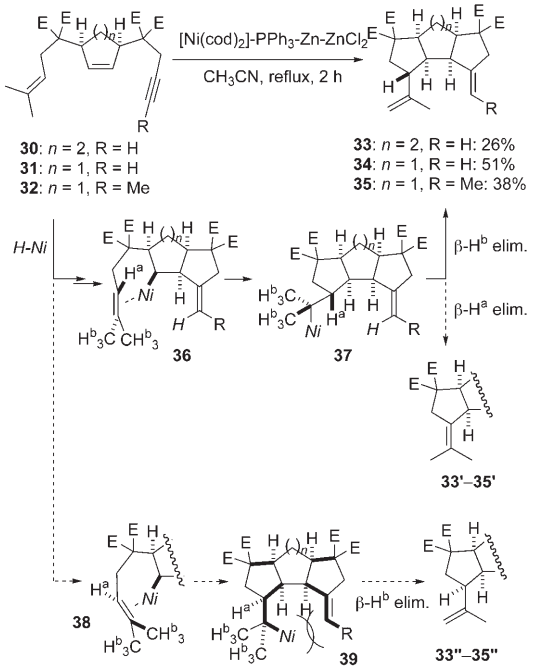
Scheme 8. Reaction with (*Z*)-**7a** leading to (*Z*)-**8a**, **9a**, and **10a**.

This catalytic system was applied to the reaction with dienynes **22** (Scheme 9). With *trans*-**22**, product **23** was obtained by the β-H elimination of **24**, which has a *cis*-β-hydrogen atom. In contrast, the reaction with *cis*-**22** gave complicated mixtures. If the expected intermediate **26**, which lacks *cis*-β-hydrogen atoms, had undergone insertion of the tethered *cis*-alkenyl part into the C–Ni bond to generate **27**, subsequent β-H elimination would have given the corresponding product **25**. Attempted reaction with the cyclopentene **28** did not give the corresponding **29** either.[23]



Scheme 9. Reactions with *trans*- and *cis*-**22** and **28** (E = CO_2Me).

Domino cyclization is achieved by the treatment of dienynes **30**–**32** bearing a prenyl group (Scheme 10). The reaction of **30** in the presence of the Ni^0-Zn-$ZnCl_2$ system gave the tricyclic product **33**. The cyclization of **31** proceeded efficiently to afford **34** in 51% yield. In the reaction with **32** having an internal alkyne function, the corresponding tricycle **35** was obtained. The stereochemistry of the ethylidene moiety of **35** indicates that hydronickelation occurs by *cis*-addition to the internal alkyne function. In these domino cyclizations, **36**, generated by hydronickelation/carbonickelation, is believed to undergo insertion of the adjacent alkene function into the C–Ni bond to produce **37**, which is followed by β-H^b elimination to give **33**–**35**. In contrast, the formation of **33′**–**35′** was not observed. The exocyclic alkylidene moiety is so close to another methylidene moiety that the β-H^a elimination of **37** does not occur. Similarly, the diastereomers **33″**–**35″** are not obtained due to the steric hindrance between the exocyclic methylidene group and the alkylnickel unit of **39** arising from insertion of the coordinating alkene function of **38**.



Scheme 10. Reactions with dienynes **30**–**32** (E = CO_2Me).

Conclusion

We have demonstrated that the catalytic cycloisomerization of enynes can be accomplished in the presence of an Ni^0-PPh_3-Zn-carboxylic acid or -$ZnCl_2$ system. A nickel(II)–hydride complex, believed to be generated by reduction of the protonated Ni^{II}–PPh_3 complex with Zn, is proposed as the catalytic species. The catalytic species is believed to undergo hydronickelation to the alkynyl function of the enyne, which is followed by carbonickelation to produce the alkylnickel intermediate. Subsequent β-H elimination then leads to the formation of a cycloisomeric product. The present cycloisomerization shows reactivity behavior that is different from that of a conventional metal-catalyzed reaction. In particular, in the reaction with an (*E*)-enyne, the catalytic system

shows a selectivity that favors the formation of the (*E*)-1,3-diene over the 1,4-diene. The alkylnickel intermediate can readily adopt a geometry such as **III′**, which is appropriate for β-hydrogen elimination of the β-C–H[a] bond. This catalytic system has been applied to the domino cyclization of dienynes for the construction of tricyclic compounds. The selectivity observed is dependent on the geometry of the intermediate at the β-hydrogen elimination stage.

Experimental Section

General: All reactions were carried out under a dry N_2 atmosphere. ^1H and ^{13}C NMR spectra were recorded from samples in $CDCl_3$ solution with Me_4Si as an internal standard. CH_3CN was distilled from P_2O_5. CF_3CO_2H and AcOH were used without further purification. $ZnCl_2$ was dried under reduced pressure at 150 °C. Enynes **1**,[24] **4**,[22] **7a**,[25] **7b**,[3] **7c**, and **7d** were prepared by reaction of the corresponding allyl halides with diethyl or dimethyl malonate followed by propargylation. In the case of **7c** and **7d**, the allylating agents were prepared by bromination of the corresponding alcohols according to the literature procedure.[26] Dienynes **28** and **31** were prepared according to literature procedures.[22]

Dimethyl 2-((*E*)-4-cyclohexylbut-2-enyl)-2-(prop-2-ynyl)malonate (7c): Pale-yellow oil; R_f = 0.49 (hexane/AcOEt 7:1); ^1H NMR (500 MHz, $CDCl_3$): δ = 0.81–0.91 (m, 2H; CH_2), 1.07–1.71 (m, 9H; CH_2, CH), 1.88 (t, J = 7.0 Hz, 2H; CH_2), 2.01 (t, J = 2.3 Hz, 1H; CH), 2.75 (d, J = 7.3 Hz, 2H; CH_2), 2.79 (d, J = 2.3 Hz, 2H; CH_2), 3.74 (s, 6H; OCH_3), 5.17 (dt, J = 15.4, 7.3 Hz, 1H; =CH), 5.57 (dt, J = 15.4, 7.3 Hz, 1H; =CH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 22.65, 26.32, 26.42, 33.03, 35.44 (CH_2), 37.93 (CH), 40.59 (CH_2), 52.70 (OCH_3), 57.14 (C), 71.38 (≡CH), 78.99 (≡C), 123.56, 134.95 (=CH), 170.34 (C=O); IR (neat): $\tilde{\nu}$ = 3300, 2960, 2875, 1740 (ν_{CO}), 1440, 1285, 1205 cm^{-1}; HRMS (70 eV, EI): m/z: calcd for $C_{18}H_{26}O_4$: 306.1831; found: 306.1820 [M^+].

Dimethyl 2-((*E*)-oct-2-enyl)-2-(prop-2-ynyl)malonate (7d): Colorless oil; R_f = 0.49 (hexane/AcOEt 7:1); ^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 7.1 Hz, 3H; CH_3), 1.23–1.36 (m, 6H; CH_2), 1.95 (q, J = 6.9 Hz, 2H; CH_2), 2.01 (t, J = 2.7 Hz, 1H; CH), 2.74 (d, J = 7.6 Hz, 2H; CH_2), 2.79 (d, J = 2.7 Hz, 2H; CH_2), 3.74 (s, 6H; OCH_3), 5.20 (dtt, J = 15.1, 7.6, 1.5 Hz, 1H; =CH), 5.56 (dt, J = 15.1, 6.9 Hz, 1H; =CH); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.05 (CH_3), 22.50, 22.60, 29.02, 31.30, 32.57, 35.37 (CH_2), 52.69 (OCH_3), 57.16 (C), 71.32 (≡CH), 78.98 (≡C), 122.57, 136.48 (=CH), 170.33 (C=O); IR (neat): $\tilde{\nu}$ = 3300, 2960, 2945, 1740 (ν_{CO}), 1440, 1215 cm^{-1}; HRMS (70 eV, EI): m/z: calcd for $C_{16}H_{24}O_4$: 280.2674; found: 280.1669 [M^+].

(*E*)-Tetramethyl dodec-6-en-1-yne-4,4,9,9-tetracarboxylate (7e): A solution of dimethyl 2-propylmalonate (900 mg, 5.17 mmol) in DMF (5 mL) was added dropwise to a suspension of NaH (60% in mineral oil, 352 mg, 8.8 mmol) in DMF (10 mL) at room temperature and the mixture was stirred for 30 min. A solution of dimethyl 2-((*E*)-4-chlorobut-2-enyl)-2-(prop-2-ynyl)malonate[27] (590 mg, 2.28 mmol) in DMF (15 mL) was then added dropwise and the reaction mixture was stirred at room temperature for 2 h. After treatment with aqueous HCl (5%, 50 mL), the aqueous layer was extracted with Et_2O (3×10 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ for 30 min, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give **7e** (489 mg, 54%). White powder; m.p. 71–73 °C; R_f = 0.12 (hexane/AcOEt 4:1); ^1H NMR (400 MHz, $CDCl_3$): δ = 0.92 (t, J = 7.3 Hz, 3H; CH_3), 1.12–1.22 (m, 2H; CH_2), 1.79–1.83 (m, 2H; CH_2), 2.02 (t, J = 2.7 Hz, 1H; CH), 2.59 (d, J = 7.3 Hz, 2H; CH_2), 2.75 (d, J = 7.3 Hz, 2H; CH_2), 2.76 (d, J = 2.7 Hz, 2H; CH_2), 3.71 (s, 6H; OCH_3), 3.74 (s, 6H; OCH_3), 5.31 (dt, J = 15.3, 7.1, 1H; =CH), 5.43 (dt, J = 15.3, 7.3 Hz, 1H; =CH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.28 (CH_3), 17.40, 22.59, 34.52, 35.27, 35.85 (CH_2), 52.35, 52.81 (OCH_3), 56.84, 57.69 (C), 71.51 (≡CH), 78.79 (≡C), 127.47, 129.64 (=CH), 170.10, 171.73 (C=O); IR (neat): $\tilde{\nu}$ = 3300, 2955, 1740, 1730 (ν_{CO}), 1435, 1290, 1250, 1220, 1200, 1175, 1125, 1060, 985 cm^{-1}; DIMS (70 eV, EI): m/z (%): 396 (1) [M^+], 365 (18) [M^+–OMe], 145 (100); HRMS (70 eV, EI): m/z: calcd for $C_{19}H_{25}O_7$: 365.1598; found: 365.1600 [M^+–OMe].

(*E*)-Tetramethyl dodeca-1,6-dien-11-yne-4,4,9,9-tetracarboxylate (7f): A solution of dimethyl 2-allylmalonate (850 mg, 5.0 mmol) in DMF (5 mL) was added dropwise to a suspension of NaH (60% in mineral oil, 260 mg, 6.5 mmol) in DMF (10 mL) at room temperature and the mixture was stirred for 30 min. A solution of dimethyl 2-((*E*)-4-chlorobut-2-enyl)-2-(prop-2-ynyl)malonate[27] (543 mg, 2.1 mmol) in DMF (15 mL) was then added dropwise and the reaction mixture was stirred at room temperature for 2 h. After treatment with aqueous HCl (5%, 50 mL), the aqueous layer was extracted with Et_2O (3×10 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ for 30 min, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give **7f** (709 mg, 86%). White powder; m.p. 71–72 °C; R_f = 0.12 (hexane/AcOEt 4:1); ^1H NMR (400 MHz, $CDCl_3$): δ = 2.01 (t, J = 2.6 Hz, 1H; CH), 2.58 (d, J = 7.3 Hz, 2H; CH_2), 2.60 (d, J = 7.3 Hz, 2H; CH_2), 2.75 (d, J = 7.1 Hz, 2H; CH_2), 2.76 (d, J = 2.6 Hz, 2H; CH_2), 3.71 (s, 6H; OCH_3), 3.74 (s, 6H; OCH_3), 5.09 (d, J = 11.0 Hz, 1H; =CH), 5.11 (d, J = 15.9 Hz, 1H; =CH), 5.32 (dt, J = 15.2, 7.3 Hz, 1H; =CH), 5.44 (dt, J = 15.2, 7.3 Hz, 1H; =CH), 5.56–5.67 (m, 1H; =CH); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 22.62, 35.31, 35.63, 36.83 (CH_2), 52.43, 52.83 (OCH_3), 56.81, 57.63 (C), 71.53 (≡CH), 78.77 (≡C), 119.27 (CH_2), 127.89, 129.32, 132.28 (=CH), 170.10, 171.11 (C=O); IR (neat): $\tilde{\nu}$ = 3300, 2955, 1740, 1730 (ν_{CO}), 1435, 1280, 1200, 1070, 995, 950, 875 cm^{-1}; DIMS (70 eV, EI): m/z (%): 394 (0) [M^+], 363 (26) [M^+–OMe], 59 (100); HRMS (70 eV, EI): m/z: calcd for $C_{19}H_{23}O_7$: 363.1470; found: 365.1444 [M^+–OMe].

2-((*E*)-5-Phenylpent-2-enyl)-2-(prop-2-ynyl)malononitrile (7g): A solution of dimethyl 2-allylmalonate (1.7 g, 10.0 mmol) in DMF (7 mL) was added dropwise to a suspension of NaH (60% in mineral oil, 520 mg, 13 mmol) in DMF (10 mL) at room temperature and the mixture was stirred for 30 min. A solution of *trans*-1,4-dichloro-2-butene (2.5 g, 20 mmol) in DMF (25 mL) was then added dropwise and the mixture was stirred at room temperature for 2 h. After treatment with aqueous HCl (5%, 50 mL), the aqueous layer was extracted with Et_2O (3× 20 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ for 30 min, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel [R_f = 0.44 (hexane/AcOEt 7:1)] to give dimethyl 2-allyl-2-((*E*)-4-chlorobut-2-enyl)malonate (1.09 g, 42%). This compound was immediately used in the next reaction. Thus, a solution of 2-(prop-2-ynyl)malononitrile (1.25 g, 12.0 mmol) in DMF (7 mL) was added dropwise to a suspension of NaH (60% in mineral oil, 280 mg, 7 mmol) in DMF (10 mL) at room temperature and the mixture was stirred for 1 h. A solution of dimethyl 2-allyl-2-((*E*)-4-chlorobut-2-enyl)malonate (1.09 g, 4.2 mmol) in DMF (25 mL) was then added dropwise and the mixture was stirred at room temperature for 20 h. After treatment with aqueous HCl (5%, 50 mL), the aqueous layer was extracted with Et_2O (3×20 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ for 30 min, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give **7g** (716 mg, 52%). Pale-yellow gum; R_f = 0.44 (hexane/AcOEt 2:1); ^1H NMR (500 MHz, $CDCl_3$): δ = 2.40 (t, J = 2.5 Hz, 1H; CH), 2.66 (d, J = 7.3 Hz, 2H; CH_2), 2.69 (d, J = 7.3 Hz, 2H; CH_2), 2.78 (d, J = 7.3 Hz, 2H; CH_2), 2.90 (d, J = 2.5 Hz, 2H; CH_2), 5.13 (d, J = 10.2 Hz, 1H; =CH), 5.14 (d, J = 15.6 Hz, 1H; =CH), 5.54–5.80 (m, 3H; =CH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.31, 35.65 (CH_2), 36.38 (C), 37.19, 39.05 (CH_2), 52.61 (OCH_3), 57.60 (C), 74.48 (≡C), 75.45 (≡CH), 114.23 (CN), 119.58 (=CH_2), 123.98, 131.94, 134.17 (=CH), 170.90 (C=O); IR (neat): $\tilde{\nu}$ = 3280, 2950, 1730 (ν_{CO}), 1435, 1285, 1215, 1145, 1055, 975, 925, 860 cm^{-1}; DIMS (70 eV, EI): m/z (%): 328 (0) [M^+], 287 (17) [M^+–C_3H_5], 225 (34) [M^+–$C_6H_3N_2$], 165 (100); HRMS (70 eV, EI): m/z: calcd for $C_{15}H_{15}N_2O_4$: 287.1032; found: 287.1031 [M^+–C_3H_5], 225.1128 [M^+–$C_6H_3N_2$].

Dimethyl 2-[*trans*-4-(1,1-bis(methoxycarbonyl)but-3-ynyl)cyclohex-2-enyl]malonate (*trans*-22): A solution of dimethyl 2-allyl-2-[*trans*-4-(bis(-methoxycarbonyl)methyl)cyclohex-2-en-1-yl]malonate[28] (1.18 g,

2.98 mmol) in DMF (20 mL) was added dropwise to a suspension of NaH (60% in mineral oil, 380 mg, 9.50 mmol) in DMF (15 mL). A solution of propargyl bromide (2.30 g, 19.3 mmol) in DMF (5 mL) was then added dropwise and the mixture was stirred at room temperature for 1 h. After treatment with aqueous HCl (5%, 30 mL), the aqueous layer was extracted with Et_2O (4×20 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ for 30 min, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give *trans*-**22** (1.98 g, 85%). Pale-yellow solid; m.p. 83–85 °C; R_f = 0.23 (hexane/AcOEt 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.38–1.43 (m, 2H; CH_2), 1.85–1.92 (m, 2H; CH_2), 2.01 (t, J = 2.7 Hz, 1H; CH), 2.62–2.72 (m, 2H; CH_2), 2.78–2.88 (m, 2H; CH_2), 2.81–3.09 (m, 2H; CH_2), 3.69 (s, 3H; CH_3), 3.71 (s, 6H; 2×CH_3), 3.75 (s, 3H; CH_3), 5.06 (dd, J = 10.1, 1.8 Hz, 1H; =CH), 5.08 (dd, J = 16.8, 1.8 Hz, 1H; =CH), 5.68–5.77 (m, 1H; =CH), 5.75 (s, 2H; 2×=CH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 22.4, 24.3, 37.1 (CH_2), 38.9, 39.4 (CH), 52.0, 52.2, 52.5, 52.6 (OCH_3), 60.1, 61.4 (C), 71.4 (≡CH), 79.2 (≡C), 118.6 (=CH_2), 128.6, 129.8, 133.0 (=CH), 169.9, 170.1, 170.6, 171.0 (O=C); IR (KBr disk): $\tilde{\nu}$ = 3280, 2950, 1730 (ν_{CO}), 1440, 1230, 1200, 1000, 940 cm^{-1}; DIMS (70 eV, EI): *m*/*z* (%): 420 (1) [M^+], 251 (40) [M^+−HCCCH$_2$C(CO$_2$Me)$_2$], 249 (53) [M^+−H$_2$C=CHCH$_2$C(CO$_2$Me)$_2$], 129 (100); HRMS (70 eV, EI): *m*/*z*: calcd for $C_{14}H_{19}O_4$: 251.1283; found: 251.1282 [M^+−HCCCH$_2$C(CO$_2$Me)$_2$], 249.1125 [M^+−H$_2$C=CHCH$_2$C(CO$_2$Me)$_2$)].

Dimethyl 2-[*cis*-4-(1,1-bis(methoxycarbonyl)but-3-ynyl)cyclohex-2-enyl]-malonate (*cis*-22): A solution of dimethyl allylmalonate (1.64 g, 9.55 mmol) in THF (5 mL) was added to a suspension of NaH (60% in mineral oil, 382 mg, 9.55 mmol) in THF (5 mL) at room temperature and the mixture was stirred for 30 min. This mixture was then added dropwise to a solution of [Pd(PPh$_3$)$_4$] (233 mg, 0.202 mmol) and dimethyl (*cis*-4-acetoxycyclohex-2-en-1-yl)malonate[29] (1.24 g, 4.61 mmol) in THF (10 mL) and the resulting mixture was stirred at 60 °C for 21 h. After treatment with aqueous HCl (5%, 30 mL), the aqueous layer was extracted with Et_2O (3×20 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ for 30 min, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel [R_f = 0.23 (hexane/AcOEt 4:1)] to give dimethyl 2-allyl-2-[*cis*-4-(bis(methoxycarbonyl)methyl)cyclohex-2-enyl]malonate (1.18 g, 67%). This compound was immediately used in the next reaction. Thus, a solution of dimethyl 2-allyl-2-[*cis*-4-(bis(methoxycarbonyl)methyl)cyclohex-2-enyl]malonate (1.18 g, 2.98 mmol) in DMF (20 mL) was added dropwise to a suspension of NaH (60% in mineral oil, 155 mg, 3.88 mmol) in DMF (20 mL). A solution of propargyl bromide (1.11 g, 9.34 mmol) in DMF (5 mL) was then added dropwise and the mixture was stirred at room temperature for 1 h. After treatment with aqueous HCl (5%, 30 mL), the aqueous layer was extracted with Et_2O (4×20 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ for 30 min, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give *cis*-**22** (882 mg, 82%). Pale-yellow gum; R_f = 0.23 (hexane/AcOEt 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.42–1.76 (m, 4H; 2×CH_2), 2.01 (t, J = 2.7 Hz, 1H; CH), 2.68 (d, J = 7.3 Hz, 2H; CH_2), 2.84 (dd, J = 10.4, 2.7 Hz, 2H; CH_2), 2.79–3.07 (m, 2H; 2×CH), 3.71 (s, 3H; CH_3), 3.73 (s, 3H; CH_3), 3.74 (s, 3H; CH_3), 5.06–5.10 (m, 2H; =CH_2), 5.65–5.73 (m, 1H; =CH), 5.79–5.89 (m, 2H; 2×=CH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 22.0, 22.2, 23.0 (CH_2), 36.7, 37.3 (CH), 37.6 (CH_2), 52.1, 52.2, 52.6, 52.7 (OCH_3), 60.1, 61.4 (C), 71.6 (≡CH), 79.1 (≡C), 118.7 (=CH_2), 128.3, 130.0, 132.8 (=CH), 170.0, 170.1, 170.8, 170.9 (O=C); IR (neat): $\tilde{\nu}$ = 3275, 2950, 1730 (ν_{CO}), 1440, 1220, 1060 cm^{-1}; DIMS (70 eV, EI): *m*/*z* (%): 420 (1) [M^+], 251 (43) [M^+−HCCCH$_2$C(CO$_2$Me)$_2$], 249 (54) [M^+−H$_2$C=CHCH$_2$C(CO$_2$Me)$_2$], 129 (100); HRMS (70 eV, EI): *m*/*z*: calcd for $C_{14}H_{19}O_4$: 251.1283; found: 251.1269 [M^+−HCCCH$_2$C(CO$_2$Me)$_2$], 249.1123 [M^+−H$_2$C=CHCH$_2$C(CO$_2$Me)$_2$)].

Dimethyl 2-prenyl-2-[*cis*-4-(1,1-bis(methoxycarbonyl)but-3-ynyl)cyclohex-2-enyl]malonate (30): A solution of dimethyl prenylmalonate (5.97 g, 29.9 mmol) in THF (20 mL) was added to a suspension of NaH (60% in mineral oil, 1.17 g, 29.3 mmol) in THF (20 mL) at room temperature and the mixture was stirred for 30 min. This mixture was then added dropwise to a solution of Pd(PPh$_3$)$_4$ (870 mg, 0.753 mmol) and dimethyl (*cis*-4-acetoxycyclohex-2-en-1-yl)malonate[29] (4.01 g, 14.8 mmol) in THF (20 mL) and the resulting mixture was stirred at 80 °C for 1.5 h. After treatment with aqueous HCl (5%, 30 mL), the aqueous layer was extracted with Et_2O (5×30 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ for 30 min, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel [R_f = 0.26 (hexane/AcOEt 4:1)] to give dimethyl 2-prenyl-2-[*cis*-4-(bis(methoxycarbonyl)methyl)cyclohex-2-enyl]malonate (4.10 g, 68%). This compound was immediately used in the next reaction. Thus, a solution of dimethyl 2-prenyl-2-[*cis*-4-(bis(methoxycarbonyl)methyl)cyclohex-2-enyl]malonate (3.98 g, 14.7 mmol) in DMF (20 mL) was added dropwise to a suspension of NaH (60% in mineral oil, 854 mg, 21.4 mmol) in DMF (15 mL). A solution of propargyl bromide (4.73 g, 39.8 mmol) in DMF (5 mL) was added dropwise and the resulting mixture was stirred at room temperature for 5 h. After treatment with aqueous HCl (5%, 30 mL), the aqueous layer was extracted with Et_2O (4×20 mL). The combined organic layers were washed with water and brine, dried over $MgSO_4$ for 30 min, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give **30** (2.44 g, 56%). White solid; m.p. 90–91 °C; R_f = 0.34 (hexane/AcOEt 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.43–1.56 (m, 4H; 2×CH_2), 1.60 (s, 3H; CH_3), 1.68 (s, 3H; CH_3), 1.66–1.77 (m, 2H; CH_2), 2.01 (t, J = 2.7 Hz, 1H; CH), 2.65 (d, J = 7.3 Hz, 2H; CH_2), 2.81 (dd, J = 17.3, 2.7 Hz, 1H; one of CH_2), 2.81 (ddd, J = 11.7, 5.8, 2.9 Hz, 1H; CH), 2.86 (dd, J = 17.3, 2.7 Hz, 1H; one of CH_2), 3.05 (ddd, J = 11.7, 6.1, and 2.8 Hz, 1H; CH), 3.69 (s, 3H; CH_3), 3.70 (s, 3H; CH_3), 3.74 (s, 3H; CH_3), 3.74 (s, 3H; CH_3), 4.98 (t, J = 7.3 Hz, 1H; =CH), 5.80 (dt, J = 10.7, 2.5 Hz, 1H; =CH), 5.87 (dt, J = 10.7, 2.5 Hz, 1H; =CH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.8 (CH_3), 22.1, 22.2, 22.9 (CH_2), 26.0 (CH_3), 31.8 (CH_2), 36.8, 36.9 (CH), 52.0, 52.2, 52.6, 52.7 (OCH_3), 60.1, 61.2 (C), 71.5 (≡CH), 79.1 (≡C), 117.8, 128.2, 130.2 (=CH), 135.4 (=C), 170.0, 170.1, 171.2, 171.3 (O=C); IR (KBr disk): $\tilde{\nu}$ = 3300, 2950, 1720 (ν_{CO}), 1440, 1230, 1060 cm^{-1}; DIMS (70 eV, EI): *m*/*z* (%): 448 (1) [M^+], 145 (100); elemental analysis calcd (%) for $C_{24}H_{32}O_8$: C 64.27, H 7.19; found: C 64.19, H 7.21.

***cis*-3-[1,1-Bis(methoxycarbonyl)-4-methyl-3-pentenyl]-5-[1,1-bis(methoxycarbonyl)-3-pentynyl]cyclopentene (32)**: A solution of *cis*-3-[1′,1′-bis-(methoxycarbonyl)methyl]-5-[1′,1′-bis(methoxycarbonyl)-3′-(4′-methyl-pentenyl)]cyclopentene[22] (800 mg, 2.02 mol) in DMF (15 mL) was added dropwise to a suspension of NaH (60% in mineral oil, 168 mg, 4.20 mmol) in DMF (10 mL). A solution of 1-bromo-2-butyne (1.34 g, 10.1 mmol) in DMF (5 mL) was then added dropwise and the mixture was stirred at room temperature for 1 h. After treatment with aqueous HCl (5%, 30 mL), the aqueous layer was extracted with Et_2O (4×20 mL). The combined organic layers were washed with water and brine, dried over $MgSO_4$ for 30 min, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/AcOEt 9:1, gradually increased to 6:1 to increase polarity) to give **32** (548 mg, 61%). White solid; m.p. 62–65 °C; R_f = 0.31 (hexane/AcOEt 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.37 (dt, J = 12.8, 10.2 Hz, 1H; one of CH_2), 1.61 (s, 3H; CH_3), 1.68 (s, 3H; CH_3), 1.74 (t, J = 2.4 Hz, 3H; CH_3), 2.15 (dt, J = 12.8, 7.7 Hz, 1H; one of CH_2), 2.57 (dd, J = 14.9, 7.3 Hz, 1H; one of CH_2), 2.63 (dd, J = 14.9, 7.8 Hz, 1H; one of CH_2), 2.72 (dq, J = 2.4, 17.1 Hz, 1H; one of CH_2), 2.76 (dq, J = 2.4, 17.1 Hz, 1H; one of CH_2), 3.33–3.39 (m, 1H; CH), 3.54–3.59 (m, 1H; CH), 3.66 (s, 3H; CH_3), 3.68 (s, 3H; CH_3), 3.70 (s, 3H; CH_3), 3.74 (s, 3H; CH_3), 4.95–5.05 (m, 1H; =CH), 5.75–5.90 (m, 2H; 2×=CH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 3.5, 17.8 (CH_3), 23.4 (CH_2), 26.0 (CH_3), 27.5, 31.8 (CH_2), 47.3, 47.4 (CH), 51.8, 52.1, 52.2, 52.5 (OCH_3), 59.9, 60.7 (C), 73.5, 78.8 (≡C), 117.8, 132.3, 132.7 (=CH), 135.4 (=CH), 170.0, 170.5, 170.9, 171.4 (O=C); IR (disk): $\tilde{\nu}$ = 2950, 1750 (ν_{CO}), 1730 (ν_{CO}), 1430, 1290, 1230, 1050, 750 cm^{-1}; DIMS (70 eV, EI): *m*/*z* (%): 448 (2) [M^+], 69 (100); elemental analysis calcd (%) for $C_{24}H_{32}O_8$: C 62.27, H 7.19; found: C 62.24, H 6.98.

General procedure for Ni- or Pd-catalyzed reactions with enynes and dienynes: In a 20 mL three-necked flask were placed [Ni(cod)$_2$] (0.05 mmol) or [Pd$_2$(dba)$_3$·CHCl$_3$] (0.025 mmol), PPh$_3$ (0.1 mmol), Zn dust (0 or 1.0 mmol), a carboxylic acid or $ZnCl_2$ (0.1 mmol), and CH_3CN or benzene (3 mL), and the mixture was stirred at 25 °C for 10 min. The requisite enyne or dienyne (0.5 mmol) was then added at 25 °C, and the

resulting mixture was stirred at the same temperature for 1–48 h. After the addition of aqueous HCl (5%, 30 mL), the aqueous layer was extracted with Et_2O (3×10 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ for 30 min, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel. An analytical sample was obtained by bulb-to-bulb distillation.

Diethyl 3-methylene-4-(prop-1-en-2-yl)cyclopentane-1,1-dicarboxylate (2): Colorless oil; b.p. 120°C (5 mm Hg); R_f = 0.50 (hexane/AcOEt 5:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.24–1.27 (m, 6H; CH_3), 1.66 (s, 3H; CH_3), 2.12 (dd, J = 13.0, 11.3 Hz, 1H; one of CH_2), 2.51 (ddd, J = 13.0, 7.8, 1.5 Hz, 1H; one of CH_2), 2.91 (dq, J = 16.8, 2.4 Hz, 1H; one of CH_2), 3.06 (dd, J = 16.8, 1.5 Hz, 1H; one of CH_2), 3.27–3.32 (m, 1H; CH), 4.17–4.23 (m, 4H; OCH_2), 4.81 (d, J = 2.4 Hz, 1H; one of =CH_2), 4.84 (d, J = 1.0 Hz, 2H; =CH_2), 5.01–5.02 (brs, 1H; one of =CH_2); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.03, 18.15 (CH_3), 38.48, 40.77 (CH_2), 51.09 (CH), 58.75 (C), 61.52 (OCH_2), 107.92, 113.36 (=CH_2), 144.80, 149.47 (=CH), 171.56, 171.65 (O=C); IR (neat): $\tilde{\nu}$ = 2990, 1730 (ν_{CO}), 1270, 1250, 1235, 1190, 1075, 890 cm^{-1}; GCMS (70 eV, EI): m/z (%): 266 (8) [M^+], 192 (70), 119 (100); elemental analysis calcd (%) for $C_{15}H_{22}O_4$: C 67.64, H 8.33; found: C 67.83, H 8.54.

A mixture of (*E*)- and (*Z*)-dimethyl 3-methylene-4-(6-methylhepta-2,5-dien-2-yl)cyclopentane-1,1-dicarboxylate (5) and dimethyl 3-methylene-4-(6-methylhepta-1,5-dien-2-yl)cyclopentane-1,1-dicarboxylate (6): Colorless oil; b.p. 145°C (2 mm Hg); R_f = 0.37 (hexane/AcOEt 4:1); ^{1}H NMR of (*E*)-**5** (500 MHz, $CDCl_3$): δ = 1.53 (s, 3H; CH_3), 1.63 (s, 3H; CH_3), 1.70 (s, 3H; CH_3), 2.12 (dd, J = 12.9, 11.9 Hz, 1H; one of CH_2), 2.46 (ddd, J = 12.9, 7.6, 1.7 Hz, 1H; one of CH_2), 2.71 (t, J = 7.0 Hz, 2H; CH_2), 2.91 (dq, J = 16.8, 2.6 Hz, 1H; one of CH_2), 3.08 (dd, J = 16.8, 1.2 Hz, 1H; one of CH_2), 3.16–3.23 (m, 1H; CH), 3.73 (s, 3H; OCH_3), 3.74 (s, 3H; OCH_3), 4.74 (d, J = 2.1 Hz, 1H; =CH), 4.98 (d, J = 2.1 Hz, 1H; =CH), 5.06–5.14 (m, 1H; =CH), 5.26 (t, J = 7.3 Hz, 1H; =CH); some protons of (*Z*)-**5** were also detected at δ = 1.53 (d, J = 1.2 Hz; CH_3), 1.63 (s; CH_3), 1.68 (s; CH_3), 2.11 (t, J = 12.9 Hz; one of CH_2), 3.76 (s; OCH_3), 4.72 (d, J = 2.1 Hz; =CH), 4.96 (d, J = 2.1 Hz; =CH), 5.32 (td, J = 7.3 Hz; =CH); ^{1}H NMR of **6** (500 MHz, $CDCl_3$): δ = 1.61 (s, 3H; CH_3), 1.67 (s, 3H; CH_3), 1.94–2.17 (m, 5H; CH_2 and one of CH_2), 2.56 (ddd, J = 13.1, 7.5, 2.0 Hz, 1H; one of CH_2), 2.91–3.13 (m, 2H; CH_2), 3.22–3.31 (m, 1H; CH), 3.73 (s, 3H; OCH_3), 3.75 (s, 3H; OCH_3), 4.81 (d, J = 2.0 Hz, 1H; =CH), 4.88 (d, J = 2.0 Hz, 1H; =CH), 4.91 (s, 1H; =CH), 5.02 (d, J = 2.0 Hz, 1H; =CH), 5.06–5.14 (m, 1H; =CH); ^{13}C NMR of **5** (125 MHz, $CDCl_3$): δ = 12.19, 17.73, 25.68 (CH_3), 27.06, 38.52, 40.88 (CH_2), 50.79 (CH), 52.74 (OCH_3), 58.57 (C), 107.73 (=CH_2), 122.91, 127.22 (=CH), 131.69, 133.67, 149.72 (=C), 172.18 (C=O); ^{13}C NMR of **6** (125 MHz, $CDCl_3$): δ = 12.19, 17.69 (CH_3), 26.61, 32.17, 39.14, 40.96 (CH_2), 50.79 (CH), 52.80 (OCH_3), 58.64 (C), 108.26, 111.58 (=CH_2), 124.10 (=CH), 131.73, 148.86, 149.59 (=C), 172.14 (C=O); IR of mixture (neat): $\tilde{\nu}$ = 2960, 2925, 1735 (ν_{CO}), 1435, 1270, 1250, 1200, 1165, 1075, 890 cm^{-1}; GCMS of **5** (70 eV, EI): m/z (%): 306 (43) [M^+], 246 (62), 231 (37), 203 (50), 177 (57), 109 (100); GCMS of **6** (70 eV, EI): m/z (%): 306 (8) [M^+], 263 (34), 246 (62), 231 (24), 203 (74), 69 (100); elemental analysis calcd (%) for $C_{18}H_{26}O_4$: C 70.56, H 8.55; found: C 70.68, H 8.66.

(*E*)-Diethyl 3-ethylidene-4-methylenecyclopentane-1,1-dicarboxylate [(*E*)-8a]: The product was obtained as a mixture with **9a** (see below) by the reaction with (*E*)-**7a** using the Ni^0-PPh_3-Zn-AcOH system; colorless oil; b.p. 90°C (2 mm Hg); R_f = 0.55 (hexane/AcOEt 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.23 (t, J = 7.1 Hz, 6H; CH_3), 1.71 (d, J = 7.1 Hz, 3H; CH_3), 2.96 (s, 2H; CH_2), 3.01 (s, 2H; CH_2), 4.20 (q, J = 7.1 Hz; OCH_2), 4.81 (s, 1H; =CH), 5.23 (s, 1H; =CH), 5.90–5.97 (m, 1H; =CH); NOESY cross-peaks were detected: δ = 1.71 ⇄ 2.96 ppm and 3.01 ⇄ 4.81 ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.03, 14.87 (CH_3), 37.38, 41.44 (CH_2), 57.60 (C), 61.54 (OCH_2), 102.46 (=CH_2), 116.72 (=CH), 137.01, 145.33 (=C), 171.45 (C=O); IR (neat): $\tilde{\nu}$ = 2990, 1730 (ν_{CO}), 1445, 1365, 1250, 1195, 1165, 1065, 870 cm^{-1}; GCMS (70 eV, EI): m/z (%): 252 (25) [M^+], 178 (100); HRMS (70 eV, EI): m/z: calcd for $C_{14}H_{20}O_4$: 252.1362; found 252.1349 [M^+]; elemental analysis calcd (%) for $C_{14}H_{20}O_4$: C 66.65, H 7.99; found: C 66.53, H 8.04.

A mixture of (*Z*)-diethyl 3-ethylidene-4-methylenecyclopentane-1,1-dicarboxylate [(*Z*)-8a], diethyl 3-methylene-4-vinylcyclopentane-1,1-dicarboxylate (9a), and diethyl 4-methyl-5-methylenecyclohex-3-ene-1,1-dicarboxylate (10a): These products were obtained by the reaction with (*Z*)-**7a** by using the Ni^0-PPh_3-Zn-AcOH system; pale-yellow oil; b.p. 90°C (2 mm Hg); R_f = 0.55 (hexane/AcOEt 4:1); ^{1}H NMR of (*Z*)-**8a** (400 MHz, $CDCl_3$): δ = 1.24 (t, J = 7.1 Hz, 6H; CH_3), 1.83 (dt, J = 7.3, 1.7 Hz, 3H; CH_3), 2.98 (s, 2H; CH_2), 3.04 (s, 2H; CH_2), 4.10–4.24 (m, 4H; OCH_2), 5.16 (s, 1H; =CH), 5.22 (s, 1H; =CH), 5.62–5.68 (m, 1H; =CH); ^{1}H NMR of **9a** (400 MHz, $CDCl_3$): δ = 1.26 (t, J = 7.1 Hz, 6H; CH_3), 2.01 (dd, J = 12.9, 11.6 Hz, 1H; one of CH_2), 2.57 (ddd, J = 12.9, 7.8, 1.2 Hz, 1H; one of CH_2), 2.95 (dq, J = 17.1, 2.5 Hz, 1H; one of CH_2), 3.07 (d, J = 17.1 Hz, 1H; one of CH_2), 3.11–3.22 (m, 1H; CH), 4.10–4.24 (m, 4H; OCH_2), 4.81 (q, J = 2.2 Hz, 1H; =CH), 4.98 (q, J = 2.2 Hz, 1H; =CH), 5.06 (d, J = 11.2 Hz, 1H; =CH), 5.07 (d, J = 15.8 Hz, 1H; =CH), 5.65 (ddd, J = 15.8, 11.2, 7.9 Hz, 1H; =CH); ^{1}H NMR of **10a** (400 MHz, $CDCl_3$): δ = 1.26 (t, J = 7.1 Hz, 6H; CH_3), 1.80 (d, J = 1.5 Hz, 3H; CH_3), 2.67 (d, J = 2.0 Hz, 2H; CH_2), 2.87 (s, 2H; CH_2), 4.10–4.24 (m, 4H; OCH_2), 4.79 (s, 1H; =CH), 4.99 (s, 1H; =CH), 5.61 (s, 1H; =CH); ^{13}C NMR of mixture (125 MHz, $CDCl_3$): δ = 14.03, 15.21, 19.11 (CH_3), 31.70, 37.12, 40.18, 40.19, 42.52, 42.94 (CH_2), 47.72 (CH), 54.17, 57.54, 58.58 (C), 61.37, 61.47, 61.55 (OCH_2), 107.97, 110.64, 110.87, 116.02 (=CH_2), 121.53, 124.24 (=CH), 132.55, 136.00 (=C), 139.17 (=CH), 140.34, 144.51, 150.62 (=C), 170.01, 171.39, 171.56, 171.75 (C=O); IR (neat): $\tilde{\nu}$ = 2990, 1730 (ν_{CO}), 1445, 1365, 1250, 1195, 1065 cm^{-1}; GCMS of **9a** (70 eV, EI): m/z (%): 252 (2) [M^+], 105 (100); GCMS of a mixture of (*Z*)-**8a** and **10a** (70 eV, EI): m/z (%): 252 (8) [M^+], 105 (100); elemental analysis calcd (%) for $C_{14}H_{20}O_4$: C 66.65, H 7.99; found: C 66.51, H 8.06.

A mixture of (*E*)- and (*Z*)-dimethyl 3-(cyclohexylmethylene)-4-methylenecyclopentane-1,1-dicarboxylate (8b) and dimethyl 3-(cyclohexylidenemethyl)-4-methylenecyclopentane-1,1-dicarboxylate (9b): These products have been reported previously.[4a,8a] Pale-yellow oil; R_f = 0.41 (hexane/AcOEt 4:1); ^{1}H NMR of (*E*)-**8b** (500 MHz, $CDCl_3$): δ = 1.00–1.76 (m, 10H; CH_2), 2.05–2.18 (m, 1H; CH), 3.00 (d, J = 2.4 Hz, 2H; CH_2), 3.01 (s, 2H; CH_2), 3.73 (s, 6H; OCH_3), 4.82 (s, 1H; =CH), 5.24 (s, 1H; =CH), 5.71 (dt, J = 9.1, 2.6 Hz, 1H; =CH); the vinylic protons of (*Z*)-**8b** were also detected at δ = 5.10 (s, 1H), 5.19 (s, 1H); ^{1}H NMR of **9b** (500 MHz, $CDCl_3$): δ = 1.61–1.76 (m, 6H; CH_2), 1.88 (dd, J = 12.8, 11.5 Hz, 1H; one of CH_2), 2.05–2.18 (m, 4H; CH_2), 2.57 (dd, J = 12.8, 7.7 Hz, 1H; one of CH_2), 3.00–3.13 (m, 1H; one of CH_2), 3.35–3.44 (m, 2H; one of CH_2 and CH), 3.74 (s, 3H; OCH_3), 3.77 (s, 3H; OCH_3), 4.74–4.77 (m, 1H; =CH), 4.88–4.92 (m, 2H; =CH_2).

(*E*)-Dimethyl 3-(2-cyclohexylethylidene)-4-methylenecyclopentane-1,1-dicarboxylate (8c): Pale-yellow oil; b.p. 150°C (2 mmHg); R_f = 0.55 (hexane/AcOEt 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.87–1.72 (m, 11H; CH_2 and CH), 1.97 (t, J = 7.3 Hz, 2H; CH_2), 2.97 (s, 2H; CH_2), 3.01 (s, 2H; CH_2), 3.73 (s, 6H; OCH_3), 4.82 (s, 1H; =CH), 5.25 (s, 1H; =CH), 5.87–5.95 (m, 1H; =CH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 26.31, 26.46, 33.20, 37.44, 37.83, 38.26, 41.38 (CH_2 and CH), 52.72, 52.74 (OCH_3), 57.58 (C), 102.58 (=CH_2), 121.35 (=CH), 136.31, 145.98 (=C), 171.80 (C=O); IR (neat): $\tilde{\nu}$ = 2930, 2855, 1740 (ν_{CO}), 1450, 1435, 1250, 1200, 1070 cm^{-1}; GCMS (70 eV, EI): m/z (%): 306 (42) [M^+], 246 (100); elemental analysis calcd (%) for $C_{18}H_{26}O_4$: C 70.56, H 8.55; found: C 70.53, H 8.63.

Dimethyl 3-((*E*)-2-cyclohexylvinyl)-4-methylenecyclopentane-1,1-dicarboxylate (9c): Colorless oil; b.p. 145°C (2 mm Hg); R_f = 0.55 (hexane/AcOEt 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.90–3.13 (m, 16H; CH_2 and CH), 3.72 (s, 6H; OCH_3), 4.78 (d, J = 2.2 Hz, 1H; =CH), 4.94 (d, J = 2.2 Hz, 1H; =CH), 5.18 (ddd, J = 15.3, 8.2, 1.2 Hz, 1H; =CH), 5.42 (dd, J = 15.3, 6.7 Hz, 1H; =CH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 26.01, 26.16, 33.08, 40.18, 40.55, 40.80, 40.83, 46.67 (CH_2 and CH), 52.71, 52.76 (OCH_3), 58.34 (C), 107.54 (=CH_2), 127.91 (=CH), 138.71, 151.29 (=C), 172.18, 172.27 (C=O); IR (neat): $\tilde{\nu}$ = 2950, 2850, 1735 (ν_{CO}), 1450, 1435, 1270, 1250, 1200, 1165, 1075, 940, 780 cm^{-1}; GCMS (70 eV, EI): m/z (%): 306 (43) [M^+], 246 (100); elemental analysis calcd (%) for $C_{18}H_{26}O_4$: C 70.56, H 8.55; found: C 70.49, H 8.58.

A mixture of (*E*)-dimethyl 3-hexylidene-4-methylenecyclopentane-1,1-dicarboxylate (8d) and (*E*)-dimethyl 3-(hex-1-enyl)-4-methylenecyclopentane-1,1-dicarboxylate (9d): Colorless oil; b.p. 140 °C (2 mmHg); R_f = 0.51 (hexane/AcOEt 4:1); ^{1}H NMR of **8d** (400 MHz, $CDCl_3$): δ = 0.89 (t, J = 6.8 Hz, 3H; CH_3), 1.26–1.42 (m, 6H; CH_2), 2.07 (q, J = 7.3 Hz, 2H; CH_2), 2.98 (s, 2H; CH_2), 3.01 (s, 2H; CH_2), 3.73 (s, 6H; OCH_2), 4.82 (s, 1H; =CH), 5.25 (s, 1H; =CH), 5.84–5.92 (m, 1H; =CH); ^{1}H NMR of **9d** (400 MHz, $CDCl_3$): δ = 0.89 (t, J = 6.8 Hz, 3H; CH_3), 1.26–1.42 (m, 4H; CH_2), 1.92–2.05 (m, 3H; CH_2 and one of CH_2), 2.55 (dd, J = 12.9, 7.9 Hz, 1H; one of CH_2), 2.94 (dq, J = 17.1, 2.5 Hz, 1H; one of CH_2), 3.08 (d, J = 17.1 Hz, 1H; one of CH_2), 3.06–3.14 (m, 1H; CH), 3.73 (s, 6H; OCH_2), 3.74 (s, 6H; OCH_2), 4.80 (d, J = 2.2 Hz, 1H; =CH), 4.95 (d, J = 2.2 Hz, 1H; =CH), 5.22 (dd, J = 15.2, 8.0 Hz, 1H; =CH), 5.48 (dt, J = 15.2, 6.8 Hz, 1H; =CH); ^{13}C NMR of the mixture (125 MHz, $CDCl_3$): δ = 13.92, 14.05 (CH_3), 22.16, 22.58, 28.90, 29.58, 31.57, 31.65, 32.13, 37.69, 40.24, 40.83, 41.51 (CH_2), 46.76 (CH), 52.81 (OCH_2), 57.67, 58.42 (C), 102.66, 107.38 (=CH_2), 122.76, 130.51, 132.74 (=CH), 135.81, 145.19, 151.26 (=C), 139.17 (=CH), 171.87 (C=O); IR (neat): $\tilde{\nu}$ = 2990, 1730 (ν_{CO}), 1445, 1195 cm^{-1}; GCMS of **8d** (70 eV, EI): m/z (%): 280 (13) [M^+], 220 (100); GCMS of **9d** (70 eV, EI): m/z (%): 280 (30) [M^+], 220 (100); elemental analysis calcd (%) for $C_{16}H_{24}O_4$: C 68.54, H 8.63; found: C 68.29, H 8.73.

(*E*)-Dimethyl 3-(3,3-di(methoxycarbonyl)hexylidene)-4-methylenecyclopentane-1,1-dicarboxylate (8e): Colorless gum; R_f = 0.21 (hexane/AcOEt 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.93 (t, J = 7.0 Hz, 3H; CH_3), 1.16–1.25 (m, 2H; CH_2), 1.84–1.88 (m, 2H; CH_2), 2.70 (d, J = 7.6 Hz, 2H; CH_2), 2.98–3.00 (m, 4H; CH_2), 3.72 (s, 6H; OCH_3), 3.73 (s, 6H; OCH_3), 4.86 (s, 1H; =CH), 5.26 (s, 1H; =CH), 5.65–5.70 (m, 1H; =CH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.36 (CH_3), 17.64, 33.01, 34.99, 37.78, 41.30 (CH_2), 52.44, 52.86 (OCH_3), 57.49, 57.65 (C), 104.17 (=CH_2), 115.53 (=CH), 139.25, 144.63 (=C), 171.64, 171.87 (C=O); IR (neat): $\tilde{\nu}$ = 2960, 1735 (ν_{CO}), 1435, 1290, 1240, 1200, 1160, 1120, 1075 cm^{-1}; DIMS (70 eV, EI): m/z (%): 396 (51) [M^+], 163 (100); FT-ICRMS: m/z: calcd for $C_{20}H_{28}O_8$ + Na: 419.1676; found: 419.1665 [M^++Na].

Dimethyl 3-((*E*)-3,3-di(methoxycarbonyl)hex-1-enyl)-4-methylenecyclopentane-1,1-dicarboxylate (9e): Colorless gum; R_f = 0.21 (hexane/AcOEt 2:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.92 (t, J = 7.3 Hz, 3H; CH_3), 1.20 (sextet, J = 7.3 Hz, 2H; CH_2), 1.95–2.03 (m, 3H; CH_2 and one of CH_2), 2.57 (dd, J = 17.1, 7.6 Hz, 1H; one of CH_2), 2.93 (dq, J = 17.2, 2.3 Hz, 1H; one of CH_2), 3.09 (d, J = 17.2 Hz, 1H; one of CH_2), 3.21 (q, J = 8.2 Hz, 1H; CH), 3.72 (s, 3H; OCH_3), 3.73 (s, 6H; OCH_3), 3.75 (s, 3H; OCH_3), 4.73 (q, J = 2.2 Hz, 1H; =CH), 4.97 (q, J = 2.2 Hz, 1H; =CH), 5.36 (dd, J = 15.9, 8.4 Hz, 1H; =CH), 6.03 (d, J = 15.9 Hz, 1H; =CH); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.36 (CH_3), 17.67, 37.60, 40.13, 40.35 (CH_2), 46.67 (CH), 52.57, 52.61, 52.82, 52.89 (OCH_3), 58.47, 59.37 (C), 108.37 (=CH_2), 128.67, 132.83 (=CH), 150.29 (=C), 171.16, 171.20, 171.90, 172.09 (C=O); IR (neat): $\tilde{\nu}$ = 2960, 1735 (ν_{CO}), 1435, 1235, 1205, 1160, 1120, 1075 cm^{-1}; DIMS (70 eV, EI): m/z (%): 396 (10) [M^+], 217 (100); HRMS (70 eV, EI): m/z: calcd for $C_{20}H_{28}O_8$: 396.1785; found: 396.1786 [M^+].

(*E*)-Dimethyl 3-(3,3-di(methoxycarbonyl)hex-5-enylidene)-4-methylene-cyclo-pentane-1,1-dicarboxylate (8f): Colorless gum; R_f = 0.21 (hexane/AcOEt 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.64 (d, J = 7.7 Hz, 2H; CH_2), 2.69 (d, J = 7.6 Hz, 2H; CH_2), 2.99 (d, J = 1.9 Hz, 4H; CH_2), 3.72 (s, 6H; OCH_3), 3.73 (s, 6H; OCH_3), 4.86 (s, 1H; =CH), 5.09 (d, J = 11.6 Hz, 1H; =CH), 5.10 (d, J = 15.0 Hz, 1H; =CH), 5.27 (s, 1H; =CH), 5.63–5.72 (m, 2H; =CH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 32.91, 37.39, 37.83, 41.31 (CH_2), 52.50, 52.84 (OCH_3), 57.50, 57.76 (C), 104.26 (=CH_2), 115.23 (=CH), 119.31 (=CH_2), 132.37 (=CH), 139.52, 144.64 (=C), 171.24, 171.63 (C=O); IR (neat): $\tilde{\nu}$ = 2960, 1740 (ν_{CO}), 1440, 1290, 1245, 1200, 1160, 1075 cm^{-1}; DIMS (70 eV, EI) m/z (%): 394 (27) [M^+], 274 (100); FT-ICRMS: m/z: calcd for $C_{20}H_{26}O_8$ + Na: 417.1512; found: 417.1520 [M^++Na].

A mixture of (*E*)-dimethyl 3-(3,3-di(methoxycarbonyl)hex-5-enylidene)-4-methylenecyclopentane-1,1-dicarboxylate (8f) and dimethyl 3-((*E*)-3,3-di(methoxycarbonyl)hexa-1,5-dienyl)-4-methylenecyclopentane-1,1-dicarboxylate (9f): These products were obtained by the reaction with **7f** by using the Pd^0-PPh_3-AcOH system; colorless gum; b.p. 200 °C (2 mm Hg); R_f = 0.21 (hexane/AcOEt 2:1); ^{1}H NMR of **9f** (500 MHz, $CDCl_3$): δ = 1.96–2.02 (m, 1H; one of CH_2), 2.54–2.63 (m, 1H; one of CH_2), 2.80 (d, J = 7.0 Hz, 2H; CH_2), 2.93 (dd, J = 17.2, 2.2 Hz, 1H; one of CH_2), 3.08 (d, J = 17.2 Hz, 1H; one of CH_2), 3.21 (q, J = 8.0 Hz, 1H; CH), 4.76 (d, J = 2.2 Hz, 1H; =CH), 4.97 (d, J = 2.2 Hz, 1H; =CH), 5.03–5.17 (m, 2H; 2×=CH), 5.41 (dd, J = 16.2, 8.2 Hz, 1H; =CH), 5.62–5.71 (m, 1H; =CH), 5.98 (d, J = 16.2 Hz, 1H; =CH); ^{13}C NMR of **9f** (125 MHz, $CDCl_3$): δ = 39.78, 40.07, 40.26 (CH_2), 46.58 (CH), 52.57, 52.60, 52.76, 52.82 (OCH_3), 58.42, 59.29 (C), 108.46 (=CH_2), 118.93, 128.08, 132.20, 133.41, 150.09 (=CH_2 and =CH), 170.49, 170.54, 171.02, 171.99 (C=O); IR of mixture (neat): $\tilde{\nu}$ = 2960, 1730 (ν_{CO}), 1430, 1295, 1245, 1200, 1075 cm^{-1}; DIMS (70 eV, EI): m/z (%): 394 (12) [M^+], 215 (100); elemental analysis calcd (%) for $C_{20}H_{26}O_8$: C 60.90, H 6.64; found: C 60.67, H 6.67.

Dimethyl 2-allyl-2-((*E*)-2-(4,4-dicyano-2-methylenecyclopentylidene)-ethyl)malonate (8g): Colorless gum; R_f = 0.48 (hexane/AcOEt 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.68 (t, J = 7.3 Hz, 4H; CH_2), 3.14 (s, 2H; CH_2), 3.17 (s, 2H; CH_2), 3.75 (s, 6H; OCH_3), 3.07 (d, J = 2.2 Hz, 2H; CH_2), 5.09 (s, 1H; =CH), 5.14 (d, J = 16.7 Hz, 1H; =CH), 5.15 (d, J = 10.0 Hz, 1H; =CH), 5.57–5.67 (m, 1H; =CH), 5.94 (tt, J = 7.6, 2.1 Hz, 1H; =CH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 31.79, 33.06, 37.62, 41.51, 44.76 (CH_2 and C), 52.71 (OCH_3), 57.42 (C), 107.98, 115.47, 119.35, 119.76, 131.90, 134.51 (=CH_2, =CH, and =C), 139.64 (CN), 170.87 (C=O); IR (neat): $\tilde{\nu}$ = 2950, 2250 (ν_{CN}), 1735 (ν_{CO}), 1640, 1435, 1290, 1220, 1145, 1100, 1050, 995, 925, 895, 860 cm^{-1}; DIMS (70 eV, EI): m/z (%): 328 (8) [M^+], 209 (100); HRMS (70 eV, EI): m/z: calcd for $C_{18}H_{20}N_2O_4$: 328.1423; found: 328.1419 [M^+].

(3a*S,7a*R**)-Dimethyl 5-(1,1-di(methoxycarbonyl)but-3-enyl)-3,3a,7,7a-tetrahydro-3-methylene-2*H*-indene-1,1(6*H*)-dicarboxylate (23)**: Colorless solid; m.p. 128–129 °C; R_f = 0.60 (hexane/AcOEt 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.09–1.16 (m, 1H; one of CH_2), 1.33–1.37 (m, 1H; one of CH_2), 2.03–2.12 (m, 2H; CH_2), 2.75–2.81 (m, 2H; CH_2), 2.83–2.88 (m, 2H; CH_2), 3.26–3.31 (m, 1H; CH), 3.32 (s, 1H; CH), 3.71 (s, 3H; CH_3), 3.72 (s, 3H; CH_3), 3.73 (s, 3H; CH_3), 3.73 (s, 3H; CH_3), 4.82 (q, J = 2.2 Hz, 1H; =CH), 4.98 (d, J = 2.2 Hz, 1H; =CH), 5.03 (dd, J = 10.1, 1.6 Hz, 1H; =CH), 5.05 (dd, J = 17.1, 1.6 Hz, 1H; =CH), 5.83 (ddt, J = 17.1, 10.1, 7.0 Hz, 1H; =CH), 5.86 (dt, J = 2.1, 2.3 Hz, 1H; =CH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 22.3, 26.5, 37.8, 38.6 (CH_2), 42.5, 43.4 (CH), 52.4, 52.4, 52.5, 52.8 (OCH_3), 62.3, 63.8 (C), 108.1, 118.2 (=CH_2), 125.8 (=CH), 133.4 (=C), 133.6 (=CH), 150.2 (=C), 170.2, 170.4, 170.5, 172.1 (O=C); IR (KBr disk): $\tilde{\nu}$ = 2950, 1730 (ν_{CO}), 1430, 1230, 1040 cm^{-1}; DIMS (70 eV, EI): m/z (%): 420 (13) [M^+], 389 (29) [M^+−OMe], 287 (100); elemental analysis calcd (%) for $C_{22}H_{28}O_8$: C 62.85, H 6.71; found: C 62.60, H 6.72.

(3a*R,5a*S**,8*R**,8a*S**,8b*S**)-Tetramethyl octahydro-1-methylene-8-(prop-1-en-2-yl)-indacene-3,3,6,6(7*H*,8b*H*)-tetracarboxylate (33)**: Colorless hard gum; b.p. 210 °C (2 mm Hg); R_f = 0.23 (hexane/AcOEt 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.98–1.06 (m, 1H; one of CH_2), 1.35–1.43 (m, 1H; one of CH_2), 1.46 (m, 2H; CH_2), 1.62 (s, 3H; CH_3), 1.78 (dd, J = 14.3, 6.7 Hz, 1H; one of CH_2), 2.59–2.65 (m, 2H; CH and one of CH_2), 2.73 (dd, J = 14.3, 10.2 Hz, 1H; one of CH_2), 2.81 (dd, J = 16.0, 7.6 Hz, 1H; CH), 2.87 (dt, J = 10.2, 6.7 Hz, 1H; CH), 3.00–3.09 (m, 2H; 2×CH), 3.40 (dd, J = 16.4, 1.8 Hz, 1H; one of CH_2), 3.68 (s, 3H; CH_3), 3.69 (s, 3H; CH_3), 3.70 (s, 3H; CH_3), 3.73 (s, 3H; CH_3), 4.65 (s, 1H; =CH), 4.81 (s, 1H; =CH), 4.82 (s, 1H; =CH), 4.84 (s, 1H; =CH); a NOESY cross-peak was detected: δ = 2.87 ⇄ 3.40 ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.7 (CH_3), 21.5, 23.1, 38.4 (CH_2), 41.5 (CH), 41.8 (CH_2), 42.1, 42.9, 43.6, 46.3 (CH), 52.3, 52.6, 52.7, 52.9 (OCH_3), 63.0, 63.6 (C), 109.9, 110.7 (=CH_2), 147.3, 148.7 (=C), 170.7, 171.1, 172.6, 172.7 (O=C); IR (neat): $\tilde{\nu}$ = 2950, 1730 (ν_{CO}), 1435, 1245, 1165, 1075 cm^{-1}; DIMS (70 eV, EI): m/z (%): 448 (3) [M^+], 417 (3) [M^+−OMe], 328 (100); elemental analysis calcd (%) for $C_{24}H_{32}O_8$: C 64.27, H 7.19; found: C 64.25, H 7.31.

Compound 34: A colorless hard gum; b.p. 190 °C (2 mm Hg); R_f = 0.23 (hexane/AcOEt 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.00 (q, J = 12.0 Hz, 1H; one of CH_2), 1.49 (dt, J = 12.0, 6.7 Hz, 1H; one of CH_2), 1.65 (s, 3H; CH_3), 1.75 (dd, J = 14.3, 8.8 Hz, 1H; one of CH_2), 2.52 (q, J

= 8.9 Hz, 1H; CH), 2.65 (d, J = 15.9 Hz, 1H; one of CH_2), 2.89–2.99 (m, 2H; CH and one of CH_2), 3.12 (dq, J = 15.9, 2.1 Hz, 1H; one of CH_2), 3.24–3.38 (m, 3H; 2×CH), 3.66 (s, 3H; CH_3), 3.69 (s, 6H; 2×CH_3), 3.70 (s, 3H; CH_3), 4.68 (s, 1H; =CH), 4.72 (s, 1H; =CH), 4.73 (s, 1H; =CH), 4.96 (s, 1H; =CH); NOESY cross-peaks were detected: δ = 3.12 ⇄ 1.00 and 2.52 ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.6 (CH_3), 30.7, 40.9, 41.0 (CH_2), 46.6, 49.1, 50.1, 51.4, 51.6 (CH), 52.2, 52.4, 52.7, 52.8 (OCH_3), 60.9, 61.1 (C), 109.8, 111.9 (=CH_2), 146.0, 146.8 (=C), 170.3, 171.0, 171.8, 172.8 (O=C); IR (neat): $\tilde{\nu}$ = 2955, 1730 (ν_{CO}), 1430, 1270, 1250, 1215, 1160, 1095, 890 cm^{-1}; DIMS (70 eV, EI): m/z (%): 434 (6) [M^+], 403 (8) [M^+−OMe], 374 (100); elemental analysis calcd (%) for $C_{23}H_{30}O_8$: C 63.58, H 6.96; found: C 63.59, H 6.99.

Compound 35: A colorless hard gum; 190 °C (2 mm Hg); R_f = 0.21 (hexane/AcOEt 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.98 (q, J = 12.2 Hz, 1H; one of CH_2), 1.46–1.52 (m, 1H; one of CH_2), 1.53 (d, J = 6.7 Hz, 3H; CH_3), 1.62 (s, 3H; CH_3), 1.73 (dd, J = 14.4, 9.0 Hz, 1H; one of CH_2), 2.50 (q, J = 9.0 Hz, 1H; CH), 2.79–2.85 (m, 2H; CH_2), 2.85–2.97 (m, 2H; one of CH_2 and CH), 3.19–3.28 (m, 2H; 2×CH), 3.33 (t, J = 9.1 Hz, 1H; CH), 3.67 (s, 3H; CH_3), 3.68 (s, 3H; CH_3), 3.69 (s, 6H; 2×CH_3), 4.66 (s, 1H; =CH), 4.68 (s, 1H; =CH), 5.10–5.16 (m, 1H; =CH); NOESY cross-peaks were detected: δ = 1.53 ⇄ 2.79–2.85 ppm, 2.50 ⇄ 0.98 and 2.75–2.85 ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.6, 20.8 (CH_3), 30.6, 35.7, 40.8 (CH_2), 46.9, 49.4, 50.4, 51.0, 51.6 (CH), 52.2, 52.3, 52.6, 52.7 (OCH_3), 60.8, 61.3 (C), 110.0 (=CH_2), 121.6 (=CH), 137.0, 146.7 (=C), 170.5, 171.0, 172.0, 172.9 (O=C); IR (neat): $\tilde{\nu}$ = 2955, 1735 (ν_{CO}), 1435, 1250, 1220, 1160, 1100, 1065 cm^{-1}; DIMS (70 eV, EI): m/z (%): 448 (12) [M^+], 417 (7) [M^+−OMe], 388 (100); elemental analysis calcd (%) for $C_{24}H_{32}O_8$: C 64.27, H 7.19; found: C 64.13, H 7.24.

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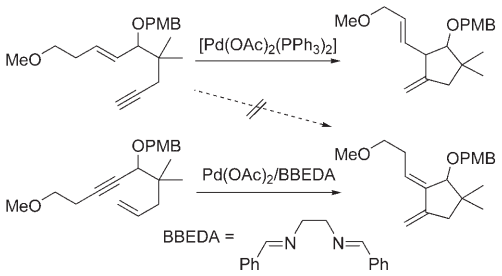
[9] By simply interchanging the positions of the alkyne and alkene functions, either type of diene can be obtained, as illustrated below.[8a] However, the selective transformation of **I** to 1,3-dienes remains unsolved.



[10] It is well known that Zn reduces NiX_2 complexes (X = Cl, Br, or I) to Ni^0 species, which are used as reagents and catalysts for various organic reactions, see: J.-L. Luche in *Encyclopedia of Reagents and Organic Synthesis, Vol. 8* (Ed.: L. A. Paquette), Wiley, Chichester, **1995**, pp. 5571–5573.

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[20] In the Ru-catalyzed reaction, while a geranyl-based enyne was selectively converted to the more substituted 1,4-diene, switching to the neryl-based enyne reversed the selectivity to give the less substituted 1,4-diene.[4]

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