Notes

Nickel-Catalyzed Coupling of Alkyne-Tethered Vinylcyclopropanes and Allyl Chloride

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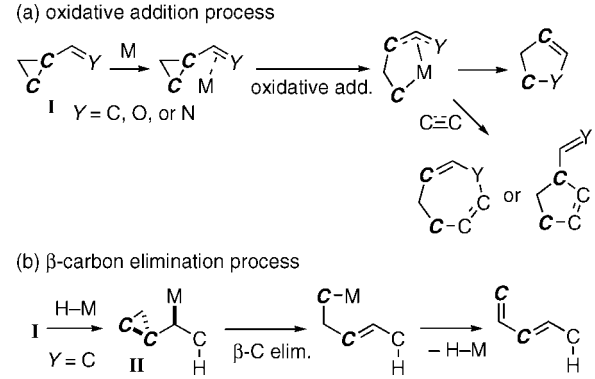
*Summary: A nickel-catalyzed coupling of the alkyne-tethered vinylcyclopropanes **1** (VCPs) with the allyl chloride **2** has been developed: the reaction proceeds via the addition of (π-allyl)nickel species to the alkyne moiety, the incorporation of the pendant VCP, and then β-syn elimination of the cyclopropyl carbon−carbon bond, to stereoselectively give **3** with an (E)-1,3-diene.*

Transition-metal-promoted transformations that include a ring-opening process of the cyclopropyl compounds **I** with an unsaturated bond, such as vinylcyclopropanes (VCPs), have attracted considerable attention.[1] In several cases, the reaction proceeds via coordination of the adjacent carbon−carbon double bond on the transition metal (M) and subsequent oxidative addition of the cyclopropyl moiety to M (Scheme 1a).[2] Recently, some research groups have reported that nickel complexes (M = Ni) effectively catalyzed the ring-opening reaction of **I** under mild conditions.[3,4] On the other hand, β-carbon elimination is another process that may enable cyclopropyl ring cleavage (Scheme 1b). Miller reported that the rearrangement of **I** to a 1,3-diene occurred via the β-carbon elimination of the (cyclopropylcarbinyl)nickel intermediate **II**,[5] which was generated by the addition of a nickel hydride (M = Ni) species to the adjacent carbon−carbon double bond of **I**. Inspired by the facile β-carbon elimination of **II**,[6–8] we have started to investigate our concept, depicted in Scheme 2. In this case, the reaction would undergo β-carbon elimination of **II′**, which is formed by the addition of a (π-allyl)nickel species to a carbon−carbon triple bond[6j,9] of the the alkyne-tethered VCPs **1** and subsequent incorporation of the pendant VCP moiety, to provide the 1,3-diene compounds **3**.

Scheme 1. Ring-Opening Reaction of Cyclopropyl Compounds I



Results and Discussion

The alkyne-tethered VCP **1a** was treated with allyl chloride (**2**; X = Cl) in the presence of Ni(cod)$_2$ (10 mol %), Zn powder

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(1) Khusnutdinov, R. I.; Dzhemilev, U. M. *J. Organomet. Chem.* **1994**, *471*, 1.

(2) Yu, Z.-X.; Wender, P. A.; Houk, K. N. *J. Am. Chem. Soc.* **2004**, *126*, 9154 and references therein.

(3) Reactions with VCPs (Y = C): (a) Zuo, G.; Louie, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 2277. (b) Zuo, G.; Louie, J. *J. Am. Chem. Soc.* **2005**, *127*, 5798. For other examples, see: (c) Suginome, M.; Matsuda, T.; Yoshimoto, T.; Ito, Y. *Organometallics* **2002**, *21*, 1537. (d) Bowman, R. K.; Johnson, J. S. *Org. Lett.* **2006**, *8*, 573.

(4) Reaction with cyclopropyl ketones and imines (Y = O, N): (a) Liu, L.; Montgomery, J. *J. Am. Chem. Soc.* **2006**, *128*, 5348. (b) Ogoshi, S.; Nagata, M.; Kurosawa, H. *J. Am. Chem. Soc.* **2006**, *128*, 5350. (c) Lloyd-Jones, G. C. *Angew. Chem., Int. Ed.* **2006**, *45*, 6788.

(5) (a) Pinke, P. A.; Stauffer, R. D.; Miller, R. G. *J. Am. Chem. Soc.* **1974**, *96*, 4229. Also see: (b) Miller, R. G.; Pinke, P. A.; Stauffer, R. D.; Golden, H. J.; Baker, D. J. *J. Am. Chem. Soc.* **1974**, *96*, 4211. (c) Pinke, P. A.; Miller, R. G. *J. Am. Chem. Soc.* **1974**, *96*, 4221.

(6) (a) Binger, P.; Doyle, M. J.; Benn, R. *Chem. Ber.* **1983**, *116*, 1. (b) Ng, D. K. P.; Luh, T.-Y. *J. Am. Chem. Soc.* **1989**, *111*, 9119. (c) Saito, S.; Masuda, M.; Komagawa, S. *J. Am. Chem. Soc.* **2004**, *126*, 10540. (d) Komagawa, S.; Saito, S. *Angew. Chem., Int Ed.* **2006**, *45*, 2446. (e) Murakami, M.; Ishida, N.; Murata, T. *Chem. Commun.* **2006**, 643. (f) Saito, S.; Takeuchi, K. *Tetrahedron Lett.* **2007**, *48*, 595. (g) Maeda, K.; Saito, S. *Tetrahedron Lett.* **2007**, *48*, 3173. (h) Ikeda, S.; Miyashita, H.; Taniguchi, M.; Kondo, H.; Okano, M.; Sato, Y.; Odashima, K. *J. Am. Chem. Soc.* **2002**, *124*, 12060. (i) Ikeda, S.; Sanuki, R.; Miyachi, H.; Miyashita, H.; Taniguchi, M.; Odashima, K. *J. Am. Chem. Soc.* **2004**, *126*, 10331. (j) Ikeda, S.; Suzuki, K.; Odashima, K. *Chem. Commun.* **2006**, 457.

(7) For a recent review on the catalytic cleavage of a carbon−carbon bond, including β-carbon eliminations, see: Jun, C.-H. *Chem. Soc. Rev.* **2004**, *33*, 610 and references therein.

(8) For other examples of the nickel-catalyzed reactions, including the β-carbon elimination process, see: (a) Necas, D.; Tursky, M.; Kotora, M. *J. Am. Chem. Soc.* **2004**, *126*, 10222. (b) Murakami, M.; Ashida, S.; Matsuda, T. *J. Am. Chem. Soc.* **2005**, *127*, 6932. (c) Murakami, M.; Ashida, S.; Matsuda, T. *J. Am. Chem. Soc.* **2006**, *128*, 2166. (d) Murakami, M.; Ashida, S. *Chem. Commun.* **2006**, 4599. (e) Mori, M.; Kimura, M.; Takahashi, Y.; Tamaru, Y. *Chem. Commun.* **2006**, 4303. (f) Shukla, P.; Cheng, C.-H. *Org. Lett.* **2006**, *8*, 2867. Also see: (g) Ogoshi, S.; Tonomori, K.; Oka, M.; Kurosawa, H. *J. Am. Chem. Soc.* **2006**, *128*, 7077.

(9) (a) Chiusoli, G. P.; Cassar, L. *Angew. Chem.* **1967**, *79*, 177. (b) Oppolzer, W. *Angew. Chem., Int. Ed.* **1989**, *28*, 38. (c) Llebaria, A.; Moretó, J. M. *J. Organomet. Chem.* **1993**, *451*, 1. (d) Garcia-Gómez, G.; Camps, X.; Cayuela, A. J.; Moretó, J. M. *Inorg. Chim. Acta* **1999**, *296*, 94. (e) Garcia-Gómez, G.; Moretó, J. M. *J. Am, Chem. Soc.* **1999**, *121*, 878. (f) Garcia-Gómez, G.; Moretó, J. M. *Chem. Eur. J.* **2001**, *7*, 1503. (g) Nadal, M. L.; Bosch, J.; Vila, J. M.; Klein, G.; Ricart, S.; Moretó, J. M. *J. Am. Chem. Soc.* **2005**, *127*, 10476. (h) Ikeda, S.; Cui, D.-M.; Sato, Y. *J. Org. Chem.* **1994**, *59*, 6877. (i) Cui, D.-M.; Tsuzuki, T.; Miyake, K.; Ikeda, S.; Sato, Y. *Tetrahedron* **1998**, *54*, 1063. (j) Ikeda, S.; Miyashita, H.; Sato, Y. *Organometallics* **1998**, *17*, 4316.

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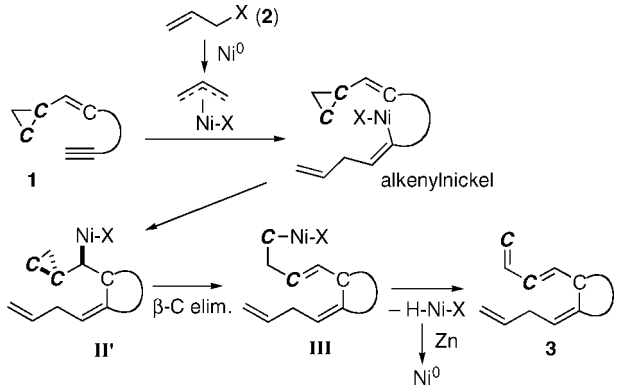
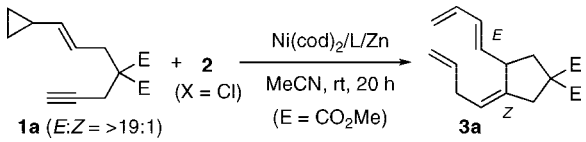
Scheme 2. Concept for the Reaction via β-Carbon Elimination



(300 mol %), and various phosphorus ligands in MeCN at room temperature for 20 h (eq 1). The results are shown in Table 1. When PPh_3 was added to the catalytic as a ligand, the desired coupling product **3a** was obtained (runs 1–3 vs run 4). In this reaction, β-hydrogen elimination of **III** would provide **3a**, along with the release of H−Ni−Cl (Scheme 2). Zinc powder reduces the species, due to regeneration of the Ni^0 species. Interestingly, the use of excess **2** (ca. 10 equiv) improved the yield of **3a** (run 3). This result suggests that the regeneration of the Ni^0 species requires **2** with Zn.[10] We further tried to improve the reaction yield by changing the phosphine ligands. However, while the reaction using P(*p*-tolyl)$_3$ also occurred (run 5), none of the phosphines with a large cone angle (run 6) or with electron-withdrawing (run 7) and -donating groups (runs 8 and 9) were suitable. Other allyl halides such as allyl bromide (X = Br), cinnamyl chloride, and ethyl 2-(chloromethyl)acrylate were not suitable for the reaction, since the corresponding allylzinc reagents would be derived from the reaction with Zn.[11] The stereochemistries of the 1,3-diene and alkylidene moieties of **3a** were determined to be *E* and *Z*, respectively, on the basis of ^{1}H NMR spectra and a NOESY experiment.



(1)

The results of the reaction of some alkyne-tethered VCPs **1b**−**f** with **2** (X = Cl) are summarized in Table 2. The reaction with the diacetoxymethyl-substituted species **1c** proceeded with an increase in the reaction temperature to 40 °C to give **3c** in 84% yield (entry 2). The trisubstituted alkene-tethered enyne **1d**, which was a mixture of *E* and *Z* isomers, also reacted to give **3d** as the sole product (entry 3). Even in the reactions with **1e** and **1f**, which have a methyl group at the alkenyl carbon atom adjacent to the cyclopropyl group, the products **3e** and **3f** were obtained, respectively (entries 4 and 5).

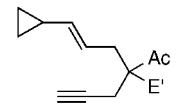
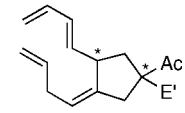
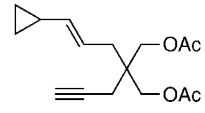
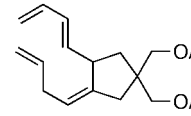
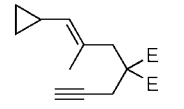
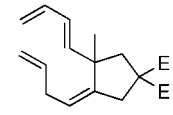
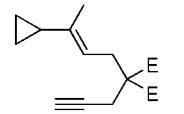
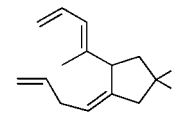
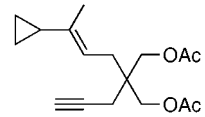
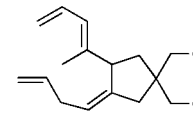
The stereochemistry of the alkylidene moiety of **3**, i.e., *Z* geometry, indicated that the reaction proceeded via a syn addition of (π-allyl)nickel species across the alkyne moiety of **1** to give the alkenylnickel species (Scheme 2). On the other hand, the stereochemistry of the 1,3-diene moiety of **3** showed an *E* geometry, even in reactions with *E*/*Z*-mixed **1d**−**f**. On the basis of the stereochemical outcome, plausible reaction paths from ***E*-1** and ***Z*-1** are proposed in Scheme 3. Thus, carbonickelation of the alkenylnickel species (depicted in Scheme 2) to the pendant VCP moiety in a 5-exo-trig mode would lead to the formation of **II′** and subsequent β-syn elimination of the cyclopropyl carbon−carbon bond to generate **III**. Regarding the conformation in the reaction of **II′**, **II′-*E*-*t*** and **II′-*E*-*c*** from ***E*-1** and **II′-*Z*-*t*** and **II′-*Z*-*c*** from ***Z*-1**are available, respectively. The cyclopropylcarbinylnickel species **II′-*E*-*t*** and **II′-*Z*-*t*** transform to ***trans*-III**, leading to **3** with an (*E*)-1,3-diene, whereas the conformers **II′-*E*-*c*** and **II′-*Z*-*c*** transform to ***cis*-III**, leading to **3** with a (*Z*)-1,3-diene. At this point, **II′-*E*-*c*** and **II′-*Z*-*c*** have

Table 1. Screening of Nickel-Catalyzed Coupling of 1a with 2 (X = Cl)[a]

run	**2** (equiv vs **1a**)	L	yield of **3a**,[b] %
1	2	PPh_3	9
2	5	PPh_3	12
3	10	PPh_3	63
4	10		0
5	10	P(C_6H_4Me-*p*)$_3$	42
6	10	P(C_6H_4Me-*o*)$_3$	0
7	10	P(C_6H_4F-*p*)$_3$	0
8	10	P(C_6H_4OMe-*p*)$_3$	0
9	10	P(*n*-Bu)$_3$	0

[a] The reaction was carried out in MeCN at room temperature for 20 h; molar ratio [**1a**]:[Ni(cod)$_2$]:[L]:[Zn] = 1: 0.1:0.2:3. [b] Isolated yield.

Table 2. Coupling of 1 with 2 (X = Cl)[a]

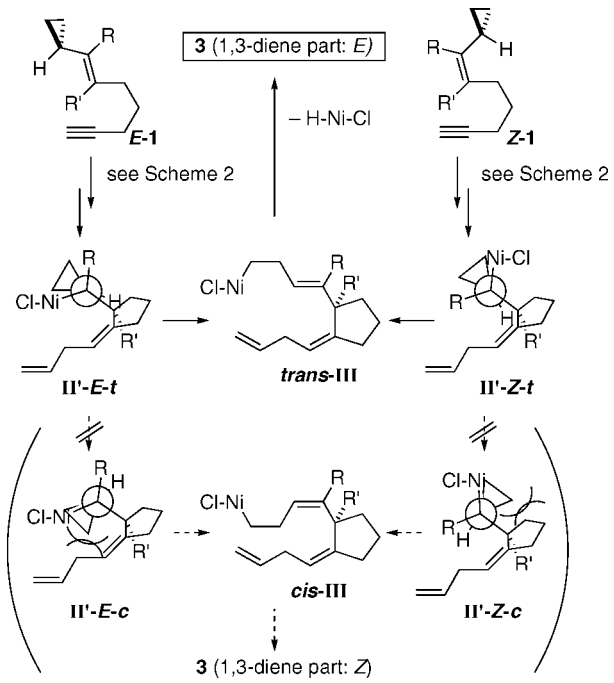
entry	1	3	yield (%)[b]
1	 **1b** (*E*/*Z* = >20:1)[c]	 **3b**	56 (dr = 2:1)[c]
2	 **1c** (*E*/*Z* = >20:1)[c]	 **3c**	trace 84[d]
3	 **1d** (*E*/*Z* = 6:1)[c]	 **3d**	51
4	 **1e** (*E*/*Z* = 3:1)[c]	 **3e**	53
5	 **1f** (*E*/*Z* mixture)	 **3f**	55[e]

[a] Unless stated otherwise, the reactions were carried out in MeCN at room temperature for 20 h; molar ratio: [**1**]:[**2**]:[Ni(cod)$_2$]:[PPh_3]:[Zn] = 1:10:0.1:0.2:2. E = CO_2Me and E′ = CO_2Et. [b] Isolated yield. [c] Determined by ^{1}H NMR. [d] The reaction was carried out at 40 °C for 5 h. [e] The reaction was carried out at 40 °C for 20 h.

(10) As one possibility, we suggest the following reduction process: (i) a hydronickelation of the H−Ni−Cl species to **2**, (ii) the β-elimination of the C−Cl bond to give a $NiCl_2$ species along with the release of propene, and (iii) the regeneration of the $NiCl_2$ species to the Ni^0 species by Zn powder. The nickel hydride species would catalyze the cycloisomerization of 1,6-enynes; see: Ikeda, S.; Daimon, N.; Sanuki, R.; Odashima, K. *Chem. Eur. J.* **2006**, *12*, 1797.

(11) Furukawa, J.; Kawabata, N. *Adv. Organomet. Chem.* **1974**, *12*, 83. On the other hand, **2** did not react with Zn powder in MeCN at room temperature to generate the allylzinc chloride.

Scheme 3. Occurrence of Stereoselectivity



sterically disfavorable conformations, while **II′-*E*-*t*** and **II′-*Z*-*t*** do not. Therefore, the reaction of ***E*-1**and ***Z*-1** proceeds through the more likely conformations **II′-*E*-*t*** and **II′-*Z*-*t*** to give **3** with an (*E*)-1,3-diene as a single product.

In the present reactions, **II′** has some β-hydrogen atoms. However, no product that results from β-elimination of the carbon−hydrogen bonds of **II′** was observed. This result indicates that the relief of ring strain in the cyclopropane moieties of **II′-*E*-*t*** and **II′-*Z*-*t***, causing the β-carbon elimination, is a more favorable process than β-hydrogen elimination.[5]

In summary, we have described a new nickel-catalyzed coupling of alkyne-tethered VCPs with allyl chloride. The reaction proceeds via syn addition of the (π-allyl)nickel species to the alkyne moiety and subsequent incorporation of the pendant VCP. β-Syn elimination of the cyclopropyl C−C bond followed by β-hydrogen elimination then stereoselectively gives **3** with an (*E*)-1,3-diene. Further studies on the reaction mechanism and the synthetic application are in progress in our laboratory.

Experimental Section

General Comments. All reactions were carried out under a dry N_2 atmosphere. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ with Me_4Si as an internal standard. MeCN was distilled from P_2O_5. $ZnCl_2$ was dried under reduced pressure at 150 °C.

Typical Experimental Pocedure (Run 3 in Table 1). In a 20 mL three-necked flask were placed $Ni(cod)_2$ (0.05 mmol), PPh_3 (0.1 mmol), Zn dust (1.5 mmol), and MeCN (3 mL), and the mixture was stirred at room temperature for 10 min. To this suspension was added **1a** (0.5 mmol) and **2** (5 mmol) at room temperature, and the mixture was then stirred at the same temperature for 20 h. After the addition of aqueous HCl (5%, 30 mL), the aqueous layer was extracted with Et_2O (10 mL × 3). 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 (7/1 hexane/AcOEt) to yield **3a** (63%) as a colorless oil.

(3*Z*)-Dimethyl 3-(But-3-enylidene)-4-((*E*)-buta-1,3-dienyl)cyclopentane-1,1-dicarboxylate (3a). Colorless oil. R_f = 0.36 (7/1 hexane/AcOEt). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.01 (dd, J = 13.1, 7.5 Hz, 1 H, one of CH_2), 2.67–2.74 (m, 3H, CH_2 and one of CH_2), 2.84 (d, J = 15.8 Hz, 1 H, one of CH_2), 3.05 (dt, J = 15.8. 2.1 Hz, 1 H, one of CH_2), 3.40 (q, J = 7.5 Hz, 1 H, CH), 3.71 (s, 3 H, OCH_3), 3.72 (s, 3 H, OCH_3), 4.92–5.04 (m, 3 H, =CH_2 and one of =CH_2), 5.12 (d, J = 17.1 Hz, 1 H, one of =CH_2), 5.42 (t, J = 7.4 Hz, 1 H, =CH), 5.57 (dd, J = 15.2, 7.5 Hz, 1 H, =CH), 5.74 (ddt, J = 17.1, 10.3, 6.1 Hz, 1 H, =CH), 6.05 (dd, J = 15.2, 10.2 Hz, 1 H, =CH), 6.28 (dt, J = 17.1, 10.2 Hz, 1 H, =CH); NOESY cross peaks were detected at δ 2.84 and 3.05 vs 5.42 ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 32.8, 41.0, 41.9 (CH_2), 42.7 (CH), 52.7 (CH_3), 59.0 (C), 114.7, 115.9 (=CH_2), 122.6, 130.8, 136.0, 136.6, 136.8 (=CH), 140.5 (=C), 171.8 (C=O); IR (neat): ν 2980, 2960, 1740 (ν_{CO}), 1440, 1260 cm^{-1}. DIMS (EI, 70 eV); *m*/*z* (%) 290 (12) [M^+], 129 (100). HRMS (70 eV, EI): *m*/*z* calcd for $C_{17}H_{22}O_4$ (M^+) 290.1518, found 290.1520.

(3*Z*)-Ethyl 1-Acetyl-3-(but-3-enylidene)-4-((*E*)-buta-1,3-dienyl)cyclopentanecarboxylate (3b, dr = ∼ 2:1). Colorless oil. R_f = 0.34 (9/1 hexane/AcOH). ^{1}H NMR of major isomer (500 MHz, $CDCl_3$): δ 1.25 (t, J = 7.0 Hz, 3 H, CH_3), 1.82 (dd, J = 13.4, 7.7 Hz, 1 H, one of CH_2), 2.17 (s, 3 H, CH_3), 2.62–2.82 (m, 4 H, CH_2 and one of CH_2 × 2), 2.94 (dt, J = 15.8, 2.1 Hz, 1 H, one of CH_2), 3.42 (q, J = 7.7 Hz, 1 H, CH), 4.14–4.24 (m, 2 H, OCH_2), 4.92–5.04 (m, 3 H, =CH_2 and one of =CH_2), 5.12 (d, J = 16.8 Hz, 1 H, one of =CH_2), 5.36–5.46 (m, 1 H, one of =CH_2), 5.52–5.60 (m, 1 H, =CH), 5.68–5.78 (m, 1 H, =CH), 6.00–6.09 (m, 1 H, =CH), 6.28 (dt, J = 16.8, 10.3 Hz, 1 H, =CH). ^{1}H NMR of minor isomer (500 MHz, $CDCl_3$): δ 1.24 (t, J = 7.0 Hz, 3 H, CH_3), 1.95 (dd, J = 13.4, 7.1 Hz, 1 H, one of CH_2), 2.17 (s, 3 H, CH_3), 2.62–2.82 (m, 4 H, CH_2 and one of CH_2 × 2), 3.07 (dt, J = 15.8, 2.0 Hz, 1 H, one of CH_2), 3.42 (q, J = 7.1 Hz, 1 H, CH), 4.14–4.24 (m, 2 H, OCH_2), 4.92–5.04 (m, 3 H, =CH_2 and one of =CH_2), 5.12 (d, J = 16.8 Hz, 1 H, one of =CH_2), 5.36–5.46 (m, 1 H, one of =CH_2), 5.52–5.60 (m, 1 H, =CH), 5.68–5.78 (m, 1 H, =CH), 6.00–6.09 (m, 1 H, =CH), 6.28 (dt, J = 16.8, 10.3 Hz, 1 H, =CH). ^{13}C NMR of diastereomer mixture (125 MHz, $CDCl_3$): δ [14.05, 14.13], [26.1. 26.5] (CH_3), [32.7, 32.8], [39.6, 40.0], [40.6, 40.7] (CH_2), [42.6, 42.7] (CH), 61.6 (OCH_3), [65.3, 65.9] (C), [114.7, 114.8], [115.87, 115.94] (=CH_2), [122.5, 122.6], [130.6, 130.7], [136.1, 136.2], [136.60, 136.65], [136.73, 136.75] (=CH), [140.6, 140.8] (=C), [172.0, 172.2], [203.5, 203.7] (C=O). IR (neat): ν 2980, 2930, 1715 (ν_{CO}), 1240, 1180 cm^{-1}. DIMS (EI, 70 eV): *m*/*z* (%) 288 (26) [M^+], 171 (100). HRMS (70 eV, EI): *m*/*z* calcd for $C_{18}H_{24}O_3$ (M^+) 288.1726, found 288.1723.

((3*Z*)-3-(But-3-enylidene)-4-((*E*)-buta-1,3-dienyl)-1-(acetoxymethyl)cyclopentyl)methyl Acetate (3c). Colorless oil. R_f = 0.17 (7/1 hexane/AcOEt). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.48 (dd, J = 13.1, 7.5 Hz, 1 H, one of CH_2), 1.95–2.00 (m, 1 H, one of CH_2), 2.06 (s, 3 H, CH_3), 2.07 (s, 3H, CH_3), 2.23 (d, J = 15.5 Hz, 1 H, one of CH_2), 2.34 (d, J = 15.5 Hz, 1 H, one of CH_2), 2.74 (t, J = 6.7 Hz, 2 H, CH_2), 3.34 (q, J = 7.5 Hz, 1 H, CH), 3.88 (d, J = 10.9 Hz, 1 H, one of OCH_2), 3.88 (d, J = 10.9 Hz, 1 H, one of OCH_2), 3.95 (d, J = 10.9 Hz, 1 H, one of OCH_2), 4.02 (s, 2 H, OCH_2), 4.92–5.01 (m, 3 H, =CH_2 and one of =CH_2), 5.12 (d, J = 17.1 Hz, 1 H, one of =CH_2), 5.40 (t, J = 6.7 Hz, 1 H, =CH), 5.59 (dd, J = 15.2, 7.4 Hz, 1 H, =CH), 5.75 (ddt, J = 17.1, 10.2, 6.7 Hz, 1 H, =CH), 6.04 (dd, J = 15.2, 10.2 Hz, 1 H, =CH), 6.29 (dt, J = 17.1, 10.2 Hz, 1 H, =CH). ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.8, 20.9 (CH_3), 32.8, 39.0, 40.3 (CH_2), 42.0 (C), 44.6 (CH), 65.5, 67.6 (OCH_2), 114.6, 115.7 (=CH_2), 122.8, 130.1, 136.7, 136.8, 137.0 (=CH), 141.8 (=C), 171.0, 171.1 (C=O). IR (neat): ν 2950, 1740 (ν_{CO}), 1380, 1240, 1040 cm^{-1}. DIMS (EI, 70 eV); *m*/*z* (%) 318 (2) [M^+], 143 (100). HRMS (70 eV, EI): *m*/*z* calcd for $C_{17}H_{22}O_2$ (M^+ - AcOH) 258.1619, found 258.1614.

(4*Z*)-Dimethyl 4-(But-3-enylidene)-3-((*E*)-buta-1,3-dienyl)-3-methylcyclopentane-1,1-dicarboxylate (3d). Colorless oil. R_f = 0.40 (7/1 hexane/AcOEt). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.29 (s, 3 H, CH_3), 2.32 (d, J = 13.7 Hz, 1 H, one of CH_2), 2.50 (d, J =

13.7 Hz, 1 H, one of CH_2), 2.74 (t, $J = 7.6$ Hz, 2 H, CH_2), 3.04 (s, 2 H, CH_2), 3.66 (s, 3 H, OCH_3), 3.69 (s, 3 H, OCH_3), 4.92–5.04 (m, 3 H, $=CH_2$ and one of $=CH_2$), 5.12 (d, $J = 17.0$ Hz, 1 H, one of $=CH_2$), 5.40 (tt, $J = 7.6$, 1.8 Hz, 1 H, =CH), 5.69 (d, $J = 15.2$ Hz, 1 H, =CH), 5.70–5.79 (m, 1 H, =CH), 6.00 (dd, $J = 15.2$, 10.4 Hz, 1 H, =CH), 6.30 (dt, $J = 17.0$, 10.4 Hz, 1 H, =CH). ^{13}C NMR (125 MHz, $CDCl_3$): δ 25.9 (CH_3), 32.6, 42.8 (CH_2), 46.3 (C), 50.0 (CH_2), 52.7 (CH_3), 58.1 (C), 114.81, 115.8 ($=CH_2$), 122.2, 128.0, 136.9, 137.0, 141.2 (=CH), 144.1 (=C), 171.7, 172.2 (C=O). IR (neat): ν 2950, 1740 (ν_{CO}), 1430, 1250, 1200, 1180 cm^{-1}. DIMS (EI, 70 eV): *m*/*z* (%) 304 (14) [M^+], 244 (54), 203 (97), 143 (100). HRMS (70 eV, EI): *m*/*z* calcd for $C_{18}H_{24}O_4$ (M^+) 304.1675, found 304.1671.

(3*Z*)-Dimethyl 3-(But-3-enylidene)-4-((*E*)-penta-2,4-dien-2-yl)cyclopentane-1,1-dicarboxylate (3e). Colorless oil. $R_f = 0.44$ (9/1 hexane/AcOEt). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.70 (s, 3 H, CH_3), 1.99 (dd, $J = 13.1$, 8.4 Hz, 1 H, one of CH_2), 2.62 (t, $J = 7.0$ Hz, 2 H, CH_2), 2.62–2.70 (m, 1 H, one of CH_2), 2.89 (d, $J = 15.5$ Hz, 1 H, one of CH_2), 3.01 (dt, $J = 15.5$, 2.1 Hz, 1 H, one of CH_2), 3.37 (t, $J = 8.4$ Hz, 1 H, CH), 3.71 (s, 3 H, OCH_3), 3.73 (s, 3 H, OCH_3), 4.90–4.96 (m, 2 H, $=CH_2$), 5.01 (dd, $J = 11.0$, 1.8 Hz, 1 H, one of $=CH_2$), 5.11 (dd, $J = 16.8$, 1.8 Hz, 1 H, one of $=CH_2$), 5.46 (t, $J = 7.0$ Hz, 1 H, =CH), 5.66–5.74 (m, 1 H, =CH), 5.93 (d, $J = 11.0$ Hz, 1 H, =CH), 6.53 (dt, $J = 16.8$, 11.0 Hz, 1 H, =CH). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.0 (CH_3), 32.6, 40.0, 43.1 (CH_2), 48.8 (CH), 52.7 (OCH_3), 59.1 (C), 114.6 ($=CH_2$), 115.8 ($=CH_2$), 123.1, 126.3, 133.1, 136.4 (=CH), 139.3, 139.8 (=C), 171.7 (C=O). IR (neat): ν 2970, 2950, 1730 (ν_{CO}), 1430, 1260, 1240 cm^{-1}. DIMS (EI, 70 eV): *m*/*z* (%) 304 (7) [M^+], 143 (100). HRMS (70 eV, EI): *m*/*z* calcd for $C_{18}H_{24}O_4$ (M^+) 304.1675, found 304.1677.

((3*Z*)-3-(But-3-enylidene)-1-(acetoxymethyl)-4-((*E*)-penta-2,4-dien-2-yl)cyclopentyl)methyl Acetate (3f). Colorless oil. $R_f = 0.43$ (4/1 hexane/AcOEt). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.49 (dd, $J = 13.1$, 8.2 Hz, 1 H, one of CH_2), 1.68 (s, 3 H, CH_3), 1.94–1.99 (m, 1 H, one of CH_2), 2.05 (s, 3 H, CH_3), 2.06 (s, 3 H, CH_3), 2.26 (d, $J = 15.5$ Hz, 1 H, one of CH_2), 2.32 (d, $J = 15.5$ Hz, 1 H, one of CH_2), 2.65 (t, $J = 7.3$ Hz, 2 H, CH_2), 3.32 (t, $J = 8.2$ Hz, 1 H, CH), 3.87 (d, $J = 11.0$ Hz, 1 H, one of OCH_2), 3.96 (d, $J = 11.0$ Hz, 1 H, one of OCH_2), 4.03 (s, 2 H, OCH_2), 4.91–4.98 (m, 2 H, $=CH_2$), 5.02 (d, $J = 10.4$ Hz, 1 H, one of $=CH_2$), 5.12 (dd, $J = 16.8$ Hz, 1 H, one of $=CH_2$), 5.44 (t, $J = 7.3$ Hz, 1 H, =CH), 5.67–5.75 (m, 1 H, =CH), 5.93 (d, $J = 10.4$ Hz, 1 H, =CH), 6.54 (dt, $J = 16.8$, 10.4 Hz, 1 H, =CH). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.8, 20.8, 20.9 (CH_3), 32.7, 37.9 (CH_2), 41.6 (C), 44.5 (CH_2), 48.3 (CH), 65.0, 67.8 (OCH_2), 114.6, 115.6 ($=CH_2$), 123.3, 125.8, 133.1, 136.5, 140.1 (=CH), 141.1 (=C), 171.0, 171.1 (C=O). IR (neat): ν 2950, 1740 (ν_{CO}), 1380, 1240, 1040 cm^{-1}. DIMS (EI, 70 eV): *m*/*z* (%) 332 (4) [M^+], 157 (100). HRMS (70 eV, EI): *m*/*z* calcd for $C_{20}H_{28}O_4$ (M^+) 332.1988, found 332.1987.

Supporting Information Available: Text giving experimental details for **1** and figures giving ^{1}H and ^{13}C NMR spectral data for **1**, **3**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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