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Intramolecular Pauson−Khand Reactions of α,β-Unsaturated Esters and Related Electron-Deficient Olefins

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Abstract: The intramolecular Pauson−Khand (PK) reaction of a variety of electron-poor enynes having an ester, cyano, or phosphonate group at the olefin terminus is described. Depending on the reaction conditions and substitution at the enyne, their dicobalthexacarbonyl complexes led preferentially to the exocyclic 1,3-diene or to the PK cyclopentenone product. In general, the 1,3-diene was obtained as the major product under *N*-oxide-promoted conditions, while the PK product was selectively formed in refluxing acetonitrile.

Today, the cobalt-mediated carbonylative cocyclization of an alkyne and an alkene, known as the Pauson−Khand (PK) reaction, has become one of the most powerful methods for the synthesis of cyclopentenones.[1] Concerning the structural scope of this reaction, although its high tolerance to electronically different functional groups at the alkyne moiety is well-known, this functional group compatibility has been much less studied in the case of the alkene partner. Particularly, since the pioneering work of Pauson and Khand,[2] it was generally assumed that π-conjugated electron-deficient olefins such as α,β-unsaturated esters and nitriles were not appropriate substrates in Pauson−Khand reactions because the key cobaltacycle intermediate underwent preferably an elimination process to give a conjugated 1,3-diene[3] rather than the carbonyl insertion step required in the formation of the cyclopentenone product. Unlike this belief, several cases of successful cobalt-mediated PK reactions of electron-poor olefins, without formation of 1,3-dienes, have been described in recent years.[4] Thus, Smit et al. reported some examples of intramolecular PK reactions of conformationally restricted enones,[5] Cazes et al. described that sterically uncongested electron-deficient olefins, like methyl acrylate and acrylonitrile, are suitable substrates in *N*-oxide-promoted intermolecular PK reaction,[6] and our group has recently reported the use of α,β-unsaturated sulfoxides[7] and sulfones[8] in intramolecular PK reactions. On the other hand, regarding the selectivity cyclopentenone vs diene formation in intramolecular PK reactions of unactivated enynes, Krafft et al. have reported that the thermolysis of their dicobalt hexacarbonyl complexes in refluxing toluene affords the exocyclic 1,3-dienes instead of the cyclopentenone products.[9]

In this context, we describe here the behavior of electron-deficient 1,6- (and 1,7-) enynes having an ester, cyano, or phosphonate function at the alkene terminus in cobalt-mediated cyclizations,[10] as well as the application of this process to the controlled formation of either the exocyclic 1,3-diene **2** or the PK bicyclo[3.3.0]octenone **3**.

First, to explore the viability of α,β-unsaturated esters in intramolecular PK reactions, the model 1,6-enynes **1a** and **1b**, readily prepared by Wadsworth−Emmons olefination of the corresponding alkynyl aldehyde, were converted into their hexacarbonyldicobalt complexes [$Co_2(CO)_8$, CH_2Cl_2] and treated under trimethylamine *N*-oxide (TMANO) promoted conditions[11] (conditions A or B) and thermal conditions (CH_3CN, 80 °C; conditions C), which proved to be the best experimental conditions in the case of the intramolecular PK reactions of α,β-unsaturated sulfones.[8] The results are summarized in Table 1.

Synthetically interesting, the outcome of the reaction of the enynes **1a**,**b** was very dependent on the reaction conditions. Thus, in refluxing acetonitrile, only the PK bicyclic product **3** could be detected and isolated (entries 3 and 6), whereas the use of *N*-oxide-promoted conditions in toluene or CH_2Cl_2 at room temperature led to the exocyclic 1,3-diene **2** as the major product[12] (entries 1, 2, and 5). A similar product selectivity was observed in the case of the α,β-unsaturated phosphonate ester **1c**: major formation of the 1,3-diene **2c** under *N*-oxide-promoted conditions A (entry 7) and exclusive formation of the PK product **3c** under thermal conditions (entry 9). This study was next applied to the 1,7-enyne **1d** (entries 10−12).

(1) For some reviews, see: (a) Sugihara, T.; Yamaguchi, M.; Nishizawa, M. *Chem. Eur. J.* **2001**, *7*, 3315−3318. (b) Brummond, K. M.; Kent, J. L. *Tetrahedron* **2000**, *56*, 3263−3283. (c) Chung, Y. K. *Coord. Chem. Rev.* **1999**, *188*, 297−341. (d) Schore, N. E. *Org. React.* **1991**, *40*, 1−90. (e) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081−1119.

(2) (a) Khand, I. U.; Pauson, P. L. *Heterocycles* **1978**, *11*, 59−67. (b) Khand, I. U.; Pauson, P. L. *J. Chem. Soc., Chem. Commun.* **1974**, 379.

(3) For a recent review on metal-mediated cyclization of enynes to give dienes, see: Aubert, C.; Buisine, O.; Malacria, M. *Chem. Rev.* **2002**, *102*, 813−834.

(4) For a review, see: Rodríguez Rivero, M.; Adrio, J.; Carretero, J. C. *Eur. J. Org. Chem.* **2002**, 2881−2889.

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(7) Carretero, J. C.; Adrio, J. *Synthesis* **2001**, 1888−1896.

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(10) For tungsten-mediated intramolecular PK reactions of α,β-unsaturated esters and nitriles, see: (a) Shiu, Y.-T.; Madhushaw, R. J.; Li, W.-T.; Lin, Y.-C.; Lee, G.-H.; Peng, S.-M.; Liao, F. L.; Wang, S.-L.; Liu, R. S. *J. Am. Chem. Soc.* **1999**, *121*, 4066−4067. (b) Hoye, T. R.; Suriano, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 1154−1156.

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(12) Unlike this behavior, Cazes et al. have reported some successful *N*-oxide-promoted intermolecular PK reactions (see ref 6a).

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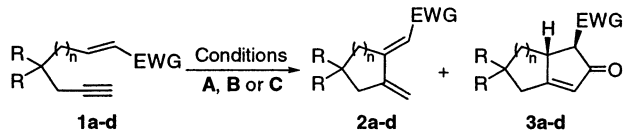
TABLE 1. Cobalt-Mediated Cyclization of Enynes 1a−d



1a-d **2a-d** **3a-d**

entry	enyne	*n*	EWG	R	conditions[a]	**2**:**3**[b]	yield(%)[c] **2**	**3**
1	**1a**	1	CO_2Et	H	A	84:16	45	8
2	**1a**	1	CO_2Et	H	B	67:33	27	13
3	**1a**	1	CO_2Et	H	C	<2:>98		31
4	**1b**	1	CO_2Et	Me	A	51:49	27	26
5	**1b**	1	CO_2Et	Me	B	82:18	41	9
6	**1b**	1	CO_2Et	Me	C	<2:>98		54
7	**1c**	1	$PO(OEt)_2$	H	A	66:34	40	18
8	**1c**	1	$PO(OEt)_2$	H	B	35:65	14	27
9	**1c**	1	$PO(OEt)_2$	H	C	<2:>98		37
10	**1d**	2	CO_2Et	CO_2Et	A	84:16	40	6
11	**1d**	2	CO_2Et	CO_2Et	B	>98:<2	57	
12	**1d**	2	CO_2Et	CO_2Et	C	34:66	13	25

[a] Conditions A: (i) $Co_2(CO)_8$, CH_2Cl_2, rt; (ii) $Me_3NO{\cdot}2H_2O$ (7 equiv). Conditions B: (i) $Co_2(CO)_8$, molecular sieves (4 Å), toluene, rt; (ii) $Me_3NO{\cdot}2H_2O$ (7 equiv). Conditions C: (i) $Co_2(CO)_8$, CH_2Cl_2, rt; (ii) CH_3CN, 80 °C. [b] Determined by ^1H NMR on the crude mixtures. [c] Yield after separation by silica gel chromatography.

This substrate proved to be more prone to giving the 1,3-diene than in the case of the 1,6-enynes **1a**−**c**, especially under conditions B (entry 11), which afforded exclusively the 1,3-diene **2d**. However, the PK bicyclic product **3d** could be again obtained as the major product under thermal conditions C, although with moderate chemoselectivity (entry 12, **2d**:**3d** = 34:66). In all cases, the products **2** and **3** were readily separated by silica gel chromatography.

To expand the scope of this process, the γ-oxygenated α,β-unsaturated esters **1e**−**j**, having different substitution at the γ-position, alkyne terminus, and ester moiety, were readily prepared by piperidine-promoted condensation of the corresponding aldehyde with ethyl *p*-tolylsulfinyl acetate[13] (SPAC condensation, 81−83% yield) and further hydroxyl protection.[14] Following the same procedure, but using *p*-tolylsulfinyl acetonitrile[15] in the SPAC condensation step, we also prepared the α,β-unsaturated nitrile **1k** (68% overall yield). The results obtained in the reaction of their dicobalt hexacarbonyl complexes under both refluxing acetonitrile (conditions C) and TMANO-promoted conditions (conditions B) are collected in Table 2.

Except for the free alcohol **1e**, which proved to be unreactive (entries 1 and 2), in every case, the selectivity of the reaction was generally high and again quite sensitive to the reaction conditions. Interestingly, in the case of the enynes **1g**,**i**−**k** a complete shift in the reaction selectivity was achieved. Thus, the 1,3-diene **2**[16] was the only product detected under conditions B (entries 5, 9, 11 and 13; 74−79% yield), while the PK product **3** was selectively formed under conditions C (entries 4, 6, 8, 10 and 14; 42−67% yield). In the latter cases, the PK products **3** were isolated as mixtures of epimers at C-6 (*endo*- + *exo*-isomers),[17] generally with low stereoselectivity, except the PK reactions of enynes **1h** (entry 8) and especially **1k** (entry 14), which occurred with high *endo*-selectivity.[18]

It is interesting to note that the chemoselectivity exhibited in the cyclization of the dicobalt hexacarbonyl complexes of the electron-poor enynes **1a**−**k** in refluxing acetonitrile (major formation of the cyclopentenone product) is in contrast to the results described by Krafft et al. in the thermolysis of the dicobalt hexacarbonyl complexes of unactivated enynes in refluxing toluene, which afforded selectively the 1,3-diene product.[9] To check if this different behavior was due to a solvent effect, we performed the reaction of the cobaltcarbonyl complexes of the enynes **1b** and **1g** in refluxing toluene. In the case of **1b**, we found effectively a reversal of the chemoselectivity with regard to the result obtained in refluxing acetonitrile, the diene **2b** now being the major product formed in the reaction, which shows that the solvent plays an important role in the selectivity of the thermally induced cyclization. However, the efficiency of this diene formation process in refluxing toluene was lower than using TMANO as a promoter in toluene at room temperature (conditions B) probably due to the relative instability of dienes **2** at high temperatures. In agreement with this belief, in the case of the thermally more unstable diene **2g**, the reaction of its precursor enyne **1g** in refluxing toluene only led to decomposition mixtures.

The reactivity and the potential synthetic interest of dienes **2** in Diels−Alder reactions were also briefly studied.[19] Due to the relative instability of dienes **2**, we found it more efficient to perform a one-pot cobalt cyclization/Diels−Alder process (Schemes 1 and 2). After *N*-oxide-promoted cyclization of the cobalt complexes of enynes **1g**,**i**,**j** (conditions B), the crude dienes **2** were treated in toluene at 100 °C with methyl maleimide as a dienophile. In all cases, the reaction was completely stereoselective, affording a single *endo*-cycloadduct **4**[20] (42−51% overall yield from enynes **1**). A similar result was obtained in the one-pot cobalt cyclization of the α,β-unsaturated nitrile **1k** and Diels−Alder reaction with methyl triazoline, which afforded the adduct **5k** as a single diastereomer in 39% overall yield.

(13) (a) Tanikaga, R.; Nozaki, Y.; Tamura, T.; Kaji, A. *Synthesis* **1983**, 134−135. (b) Tanikaga, R.; Nozaki, Y.; Tamura, T.; Kaji, A. *Chem. Lett.* **1980**, 781−784.

(14) Enyne **1j** was preferably prepared by Sonogashira reaction of the terminal alkyne **1e** [PhI, $Pd(OAc)_2$, CuI, PPh_3, Et_3N, C_6H_6, 80 °C; 72% yield] and further OH protection.

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(16) (*E*)-Configuration of dienes **2** was established by comparison with related compounds, see: Nishida, M.; Adachi, N.; Onozuka, K.; Matsumura, H.; Mori, M. *J. Org. Chem.* **1998**, *63*, 9158−9159.

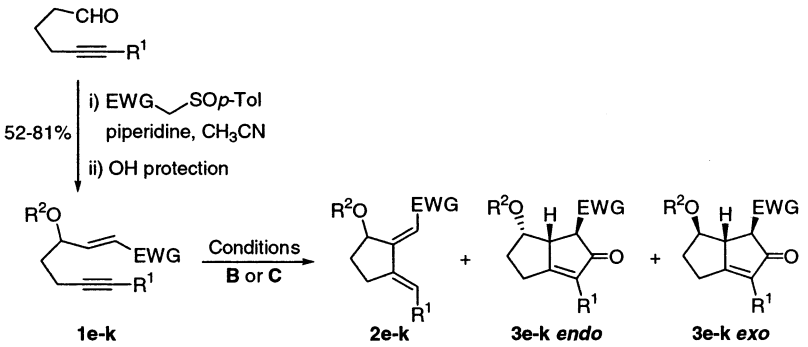
(17) In the stereochemical assignment of the *endo*/*exo* products **3f**−**k** the values of $J_{5,6}$ constitute a very useful diagnostic criteria: $J_{5,6}$ is significantly lower in the *endo* isomer ($J_{5,6}$ = 3.8−4.0 Hz, H_5/H_6 in cis arrangement) than in the *exo* isomer ($J_{5,6}$ = 8.9−9.3 Hz, H_5/H_6 in trans arrangement).

(18) Intramolecular PK reactions of enynes substituted at the allylic and propargylic position tend to be highly *exo*-selective. See, for instance: (a) Mukai, C.; Sonobe, H.; Kim, J. S.; Hanoka, M. *J. Org. Chem.* **2000**, *65*, 6654−6659. (b) Mukai, C.; Kim, J. S.; Sonobe, H.; Hanaoka, M. *J. Org. Chem.* **1999**, *64*, 6822−6832. (c) Magnus, P.; Principe, L. M.; Slater, M. J. *J. Org. Chem.* **1987**, *52*, 1483−1486. (d) Magnus, P.; Principe, L. M. *Tetrahedron Lett.* **1985**, *26*, 4851−4854. For *endo*-selective intramolecular PK reactions of α,β-unsaturated sulfones, see ref 8.

(19) For Diels−Alder reactions of related dienylesters, see: Grigg, R.; Stevenson, P.; Worakun, T. *Tetrahedron* **1988**, *44*, 2033−2048.

(20) Stereochemical assignment of products **4i**,**j** and **3j**,**n** was based on NMR spectroscopic analysis (NOESY experiments).

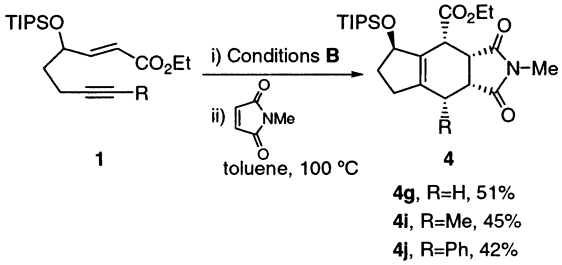
TABLE 2. Cobalt-Mediated Cyclization of Enynes 1e−k



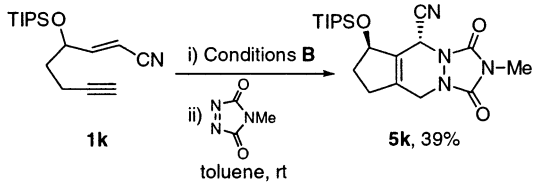
entry	enyne	EWG	R^1	R^2	conditions[a]	**2:3** (*endo:exo*)[b]	yield (%)[c]
1	**1e**	CO_2Et	H	H	B		d
2	**1e**	CO_2Et	H	H	C		d
3	**1f**	CO_2Et	H	CH_2OEt	B	64:36 (34:66)	59
4	**1f**	CO_2Et	H	CH_2OEt	C	<2:>98 (40:60)	61
5	**1g**	CO_2Et	H	TIPS	B	>98:<2	79
6	**1g**	CO_2Et	H	TIPS	C	<2:>98 (59:41)	66
7	**1h**	$CO_2{}^t$Bu	H	TIPS	B	26:74 (62:38)	54
8	**1h**	$CO_2{}^t$Bu	H	TIPS	C	<2:>98 (85:15)	67
9	**1i**	CO_2Et	Me	TIPS	B	>98:<2	79
10	**1i**	CO_2Et	Me	TIPS	C	<2:>98 (51:49)	61
11	**1j**	CO_2Et	Ph	TIPS	B	>98:<2	75
12	**1j**	CO_2Et	Ph	TIPS	C	55:45 (41:59)	85
13	**1k**	CN	H	TIPS	B	>98:<2	74
14	**1k**	CN	H	TIPS	C	<2:>98 (96:4)	42

[a] Conditions B and C as described in Table 1. [b] Determined by ^{1}H NMR on crude mixtures. [c] In isolated products after silica gel chromatography. [d] No reaction was observed.

SCHEME 1



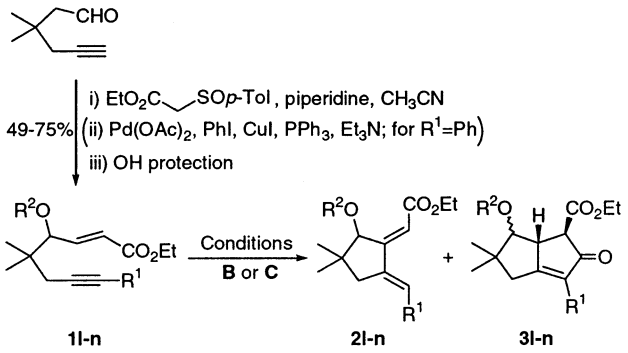
SCHEME 2



We next examined the effect of a higher substitution pattern at the enyne framework on the cyclization process. The α,β-unsaturated esters **1l**−**n**, having substitution at both γ- and δ-positions (Table 3), were prepared by SPAC condensation with 3,3-dimethyl-5-hexynal, eventual phenylation of the alkyne terminus in the case of enyne **1n** [PhI, $Pd(OAc)_2$, CuI, PPh_3, Et_3N], and hydroxyl protection.

Unlike the previous cases, the cyclization of enynes **1l**−**n** was much more selective, giving rise predominantly (entry 1) or exclusively to the PK product **3** regardless of the reaction conditions used (entries 2−6). In these cases, the difficulty in the formation of the exocyclic diene

TABLE 3. Cobalt-Mediated Cyclization of Enynes 1l−n

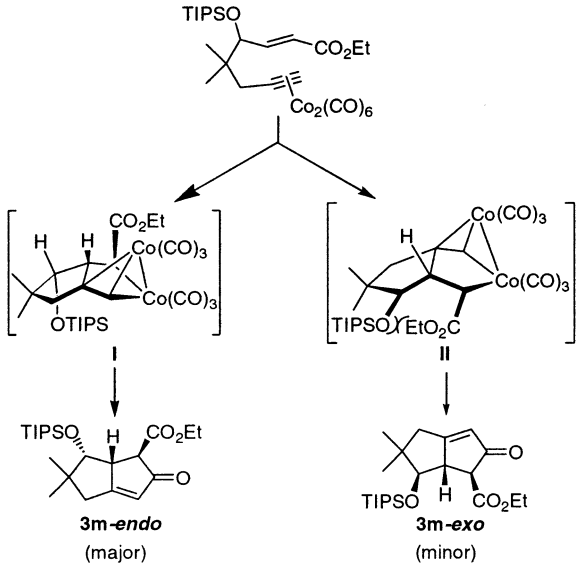


entry	**1**	R^1	R^2	conditions[a]	**2:3** (*endo:exo*)[b]	yield (%)[c]
1	**1l**	H	CH_2OEt	B	17:83 (85:15)	59
2	**1l**	H	CH_2OEt	C	<2:>98 (89:11)	60
3	**1m**	H	TIPS	B	<2:>98 (86:14)	80
4	**1m**	H	TIPS	C	<2:>98 (95:5)	88
5	**1n**	Ph	TIPS	B	<2:>98 (55:45)	62
6	**1n**	Ph	TIPS	C	<2:>98 (80:20)	82

[a] Conditions B and C as described in Table 1. [b] Determined by ^{1}H NMR on the crude mixtures. [c] In isolated products after silica gel chromatography.

product **2** may be attributed to its high steric congestion resulting from the hindrance between the *gem*-dimethyl group and the OTIPS, as well as the allylic OTIPS/CO_2-Et interaction. In agreement with the importance of minimizing the steric effects between the OR group and the *gem*-dimethyl and ester moieties, the PK reactions of the enynes **1l**−**n** occurred in most cases with a much higher *endo*-selectivity[17] (up to 95:5 *endo*/*exo* ratio, entry

SCHEME 3



4), likely due to the presumed higher stability of the cobaltacycle intermediate **I** (OTIPS and CO_2Et groups in an anti relationship) compared to the diastereomer **II** (Scheme 3).

In summary, electron-poor 1,6-enynes having an ester, cyano, or phosphonate moiety bonded to the alkene terminus are appropriate substrates in cobalt-mediated enyne cyclizations. Two competitive reaction pathways operate in the cyclization of their dicobalt hexacarbonyl complexes: the formation of the exocyclic 1,3-diene and the formation of the cyclopentenone PK product. The chemoselectivity of the reaction proved to be highly dependent on the substitution at the enyne and especially on the reaction conditions. In general, the PK product is selectively formed in refluxing acetonitrile, while in many cases the 1,3-diene can be isolated as the major product under TMANO-promoted conditions.

Experimental Section

Typical Procedures for Cobalt-Mediated Cyclizations: Cyclization of Enyne 1a. Amine *N*-Oxide-Promoted Reaction (Method A). A solution of **1a** (30 mg, 0.18 mmol) in CH_2Cl_2 (5 mL) was added to a flask containing solid $Co_2(CO)_8$ (80 mg, 0.23 mmol). The resulting solution was stirred until TLC analysis showed that formation of the complex was complete, and $Me_3NO{\cdot}2H_2O$ (140 mg, 1.26 mmol) was added in one portion. The resulting solution was stirred at room temperature until the complete disappearance of the complex. The solvent was evaporated, and the residue was diluted with ethyl ether and filtered through a pad of Celite. The combined solvents were evaporated, and the residue was purified by flash chromatography (hexane/ethyl acetate 10:1) to afford **2a** (13 mg, 45%, colorless oil) and **3a** (3 mg, 8%, colorless oil).

Amine *N*-Oxide/Molecular Sieves-Promoted Reaction (Method B). A solution of **1a** (30 mg, 0.18 mmol) in toluene (5 mL) was added to a flask containing solid $Co_2(CO)_8$ (80 mg, 0.23 mmol) and powdered molecular sieves (4 Å, oven dried at 80 °C for 4 h, 240 mg). The resulting solution was stirred until TLC analysis showed that formation of the complex was complete, and $Me_3NO{\cdot}2H_2O$ (140 mg, 1.26 mmol) was added in one portion. The resulting solution was stirred at room temperature until the complete disappearance of the complex and filtered through a pad of Celite. The combined solvents were evaporated, and the residue was purified by flash chromatography to afford **2a** (8 mg, 27%) and **3a** (5 mg, 13%).

Thermal Reaction in Acetonitrile (Method C). A solution of **1a** (30 mg, 0.18 mmol) in CH_2Cl_2 (5 mL) was added to a flask containing solid $Co_2(CO)_8$ (80 mg, 0.23 mmol). The resulting solution was stirred until TLC analysis showed that formation of the complex was complete, and the solvent was then removed under reduced pressure. The residue was diluted with CH_3CN (7 mL), and the resulting solution was heated at reflux until the complete disappearance of the complex. The solvent was evaporated, and the residue was diluted with ethyl ether and filtered through a pad of Celite. The combined solvents were evaporated, and the residue was purified by flash chromatography to afford **3a** (11 mg, 31%).

Ethyl (*E*)-2-(Methylidene)cyclopentylideneethanoate (2a): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.14 (t, J = 2.8 Hz, 1H), 5.57 (t, J = 2.4 Hz, 1H), 5.12 (t, J = 2.2 Hz, 1H), 4.17 (m, 2H), 2.93 (td, J = 2.4, 7.3 Hz, 2H), 2.43 (tt, J = 2.4, 7.3 Hz, 2H), 1.77 (m, 2H), 1.30 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.3, 160.2, 127.5, 109.0, 108.0, 59.4, 34.5, 33.1, 23.9, 14.4; HRMS (EI+) calcd for $(C_{10}H_{14}O_2)[M]^+$ 166.0994, found 166.0989.

4-(Ethoxycarbonyl)bicyclo[3.3.0]oct-1-en-3-one (3a): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.86 (m, 1H), 4.24 (q, J = 7.3 Hz, 2H), 3.33 (m, 1H), 3.08 (d, J = 4.1 Hz, 1H), 2.61 (m, 2H), 2.29−1.98 (m, 4H), 1.31 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.7, 190.4, 169.4, 122.6, 61.4, 59.4, 50.4, 30.2, 26.2, 25.3, 14.2; HRMS (EI+) calcd for $(C_{11}H_{14}O_3)[M]^+$ 194.0943, found 194.0936.

Typical Procedure for the One-Pot Cobalt Cyclization/Diels−Alder Reaction: Diels−Alder Adduct of Diene 2g and *N*-Methylmaleimide (4g). A solution of enyne **1g** (45 mg, 0.13 mmol) in toluene (8 mL) was added to a flask containing solid $Co_2(CO)_8$ (59 mg, 0.17 mmol) and molecular sieves (4 Å, 360 mg). The resulting solution was stirred for 30 min, and $Me_3NO{\cdot}2H_2O$ (103 mg, 0.93 mmol) was added in one portion. After the mixture was stirred at room temperature for 4 h, *N*-methylmaleimide (44 mg, 0.40 mmol) was added. The reaction mixture was stirred at reflux for 24 h and then filtered through a pad of Celite, which was washed with ethyl ether. The combined solvents were evaporated, and the residue was purified by flash chromatography (hexane/ethyl acetate 3:1) to afford **4g** (30 mg, 51%, white solid): mp 91−93 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.00 (m, 1H), 4.00 (m, 3H), 3.08 (m, 2H), 3.00 (s, 3H), 2.66 (dd, J = 8.1, 16.7 Hz, 1H), 2.42−2.23 (m, 4H), 1.75 (m, 1H), 1.16 (t, J = 7.3 Hz, 3H), 1.10 (m, 21H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.9, 178.6, 170.7, 141.9, 134.8, 77.6, 61.1, 41.7, 39.4, 38.5, 34.2, 33.2, 24.8, 23.8, 18.1, 14.0, 12.4. Anal. Calcd for $C_{24}H_{39}NO_5Si$ (449.6): C, 64.11; H, 8.74; N, 3.11. Found: C, 63.55; H, 9.07; N, 3.10.

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Supporting Information Available: Experimental procedures and characterization data of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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