Effect of Coordinating Ligands on the Pauson–Khand Cycloaddition: Trapping of an Intermediate

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Abstract: The Pauson–Khand cobalt-mediated cycloaddition has become a synthetically important reaction. Several modifications have increased the utility of the reaction, including reports that tertiary amine *N*-oxides greatly accelerate the rate of cycloaddition in both intra- and some intermolecular reactions. To date, there has been no direct evidence to support the mechanistic hypotheses for either the thermal or amine oxide promoted reactions beyond complete identification of the hexacarbonyl alkyne complex. While the amine oxide promoted reaction is normally greatly accelerated over the analogous thermal one, in the presence of amine oxides, the rate of cycloaddition of a 1,6-enyne may be enhanced even further by the presence of sulfur, nitrogen, or oxygen in the homopropargylic or bishomopropargylic position. A series of substrates were prepared in an attempt to identify the accelerating effect. Upon heating, these same heteroatom-substituted substrates reacted faster than those without coordinating heteroatoms. The rate-accelerating effects have been rationalized within the context of the proposed mechanism. During the course of studies with sulfur-substituted substrates, analysis by thin layer chromatography revealed the formation of a new complex which then appeared to be converted to the bicyclic cyclopentenone. Normally, under Pauson–Khand reaction conditions, no intermediates are observed. In the case of cobalt complex **1**, which required the longest reaction time for complete transformation to cyclopentenone, the intermediate complex was isolable, and its structure was verified by NMR spectroscopy.

Introduction

The Pauson–Khand cobalt-mediated cycloaddition has become a synthetically important reaction.[2] Several modifications have increased the utility of the reaction, including the discovery that tertiary amine *N*-oxides[3,4] greatly accelerate the rate of cycloaddition in both intra- and intermolecular reactions.[5] Other additives, i.e. DMSO and CH_3CN, have been shown to have a positive effect on the thermal reaction.[6] The ligand-directed variation provides regiocontrol over the intermolecular cycloaddition.[7] Recently, we have shown that the rate of the thermal intramolecular cycloaddition is greatly increased by the presence of a sulfur or oxygen atom in the homopropargylic or bishomopropargylic position of a 1,6-enyne.[8] To date, there has been no direct evidence to support the mechanistic hypotheses for either the thermal or amine oxide[9] promoted reactions beyond complete identification of the hexacarbonyl alkyne complex.[2,10,11] We now report that heteroatoms may also enhance the rate of the *N*-oxide-promoted intramolecular cycloaddition in some cases and retard the reaction when positioned in the homopropargylic site. This rate-retarding effect has allowed us to isolate an intermediate in the Pauson–Khand cycloaddition.

Results and Discussion

Initially, our investigations into the effect of ligands on the Pauson–Khand reaction centered around the thermal reaction (Table I). We found that, compared to the unsubstituted enyne, **2**, the presence of a ligand in the side chain resulted in an increase in both the reaction rate and yield in almost all of the cases. The greatest effect on the reaction rate was observed with sulfur and nitrogen ligands. Oxygen ligands were generally less effective. This trend matches that observed in the ligand-directed intermolecular Pauson–Khand reaction.[7] The position of the coordinating ligand was also important. Propargylic sulfide complex **15** reacted the fastest, although this may be due to polarization of the alkyne rather than coordination of the sulfur to cobalt. Substrates with homopropargylic ligands generally reacted more slowly than those with bishomopropargylic ligands, which were in turn slower than the trishomopropargylic example **14**. (In going from homo to bishomo to trishomo, the heterometallacycle formed by coordination of the ligand to cobalt is increasing in size and, perhaps, ease of formation.) The bishomopropargylic sulfide complex **1** is an exception to this rule; Pauson–Khand reaction of this substrate appeared to proceed through an intermediate complex (*vide infra*).

While the rate of the amine oxide promoted reaction is greatly accelerated over the analogous thermal one,[3,4] we have found

(1) NSF Summer Undergraduate Research Participants, Florida State University; R.H.R. (1991), S.F. (1992), C.V.P. (1992).

(2) For reviews on the Pauson–Khand reaction, see: Pauson, P. L.; Khand, I. U. *Ann. N. Y. Acad. Sci.* **1977**, *295*, 2. Pauson, P. L. *Tetrahedron* **1985**, *41*, 5855. Pauson, P. L. In *Organometallics in Organic Synthesis*; de Meijere, A., tom Dieck, H., Eds.; Springer-Verlag: Berlin, 1987, p 234. Schore, N. E. *Org. React. (N.Y.)* **1991**, *40*, 1. Schore, N. E. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed. Pergamon: Oxford, 1991; Vol. 5, p 1037.

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(7) Krafft, M. E.; Juliano, C. A.; Scott, I. L.; Wright, C.; McEachin, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 1693.

(8) Krafft, M. E.; Scott, I. L.; Romero, R. H. *Tetrahedron Lett.* **1992**, *33*, 3829.

(9) Tertiary amine *N*-oxides have been used to remove CO ligands from iron carbonyl complexes: Shuo, Y.; Hazum, E. *J. Chem. Soc., Chem. Commun.* **1974**, 336. Mechanistic information: Eekhof, J. H.; Hogeveen, H.; Kellogg, R. M. *J. Chem. Soc., Chem. Commun.* **1976**, 657. Albers, M. O.; Coville, N. J. *Coord. Chem. Rev.* **1984**, *53*, 227. Shen, J.-K.; Gao, Y.-C.; Shi, Q.-Z.; Basolo, F. *Organometallics* **1989**, *8*, 2144 and references cited therein.

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(11) (a) Exon, C.; Magnus, P. *J. Am. Chem. Soc.* **1983**, *105*, 2477. (b) Magnus, P.; Principe, L. M. *Tetrahedron Lett.* **1985**, *26*, 4851. (c) Magnus, P.; Principe, L. M.; Slater, M. J. *J. Org. Chem.* **1987**, *52*, 1483.

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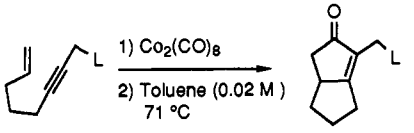
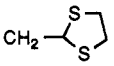
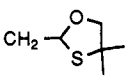
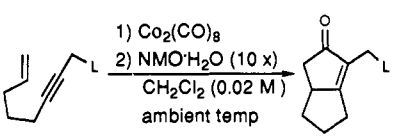
Table I. Pauson-Khand Reaction Under Thermal Conditions

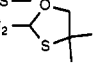


entry #			enone	time	yield
1	1	L = CH_2CH_2SMe	16	27 h	83%
2	2	L = $CH_2CH_2CH_3$	17	21 h	30%
3	3	L = 	18	7.5 h	67%
4	4	L = CH_2OEt	19	5.5 h	81%
5	5	L = 	20*	2.2 h	75%
6	6	L = 	21*	2.2 h	59%
7	7	L = 	22	2 h	60%
8	8	L = $CH_2CH_2NMe_2$	23	2 h	99%
9	9	L = CH_2NMe_2	24	2.2 h	80%
10	10	L = CH_2SEt	25	1.5 h	59%
11	11	L = 	26	1.5 h	58%
12	12	L = 	27	1.2 h	75%
13	13	L = 	28*	0.75 h	69%
14	14	L = $(CH_2)_3SEt$	29	0.5 h	91%
15	15	L = SEt	30	0.15 h	74%

* = 1:1 Mixture of Diastereomers

Table II. Pauson-Khand Reaction Under *N*-Oxide Conditions



entry #			enone	time	yield
1	1	L = $(CH_2)_2SMe$	16	5 d	35%[a]
2	12	L = 	27	27 h	74%
3	2	L = $CH_2CH_2CH_3$	17	7 h	46%
4	11	L = 	26	5.5 h	65%
5	13	L = 	28*	4 h	73%
6	8	L = $CH_2CH_2N(Me)_2$	23	3.25 h	96%
7	4	L = CH_2OEt	19	3 h	71%
8	7	L = 	22	3 h	67%
9	31	L = 	32	3 h	66%
10	10	L = CH_2SEt	25	2.5 h	74%
11	14	L = $(CH_2)_3SEt$	29	1.75 h	90%
12	3	L = 	18	1.5 h	60%
13	6	L = 	21*	1 h	76%
14	9	L = $CH_2N(Me)_2$	24	0.8 h	73%
15	5	L = 	20*	0.5 h	87%
16	15	L = SEt	30	0.13 h	39%

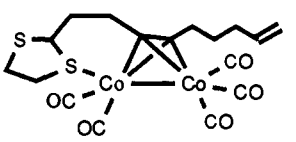
* = 1:1 mixture of diastereomers [a]48% of 1 recovered

that coordinating heteroatoms in the homo-, bishomo-, or trishomopropargylic position have a pronounced effect on the rate of cycloaddition.[8] Our results are listed in Table II.

The reactions were performed under the following conditions: the cobalt alkyne complexes were prepared from the alkyne and dicobalt octacarbonyl in the minimum amount of methylene chloride (0.1 M). After dilution to 0.02 M, *N*-methylmorpholine *N*-oxide monohydrate[12] (10 equiv) was added, as a solid, and the reaction was monitored by thin layer chromatography (TLC).

Unlike the thermal results, in which there were obvious trends, results from the amine oxide promoted reaction do not lend themselves to easy interpretation. As expected, the propargylic sulfide complex, **15**, again reacted most rapidly. Substrates bearing oxygen ligands, which previously gave only moderate rate enhancements under thermal conditions, now show strong rate-enhancing effects. Substrates that have ligands in the bishomopropargylic position, which previously were among the fastest substrates under thermal conditions, are now among the slowest, giving reaction times of, in some cases, days rather than minutes.

During the course of our studies of *N*-methylmorpholine *N*-oxide (NMO) promoted reactions with complexes of sulfur-substituted substrates, we noted, by thin layer chromatography, the formation of a new cobalt complex, which then appeared to be converted to the bicyclic cyclopentenone. Normally, under Pauson–Khand reaction conditions, no intermediates are observed. In the case of cobalt complex **12**, the new intermediate complex was isolable. Treatment of complex **12** with 10 equiv of *N*-methylmorpholine *N*-oxide monohydrate[12] (NMO·H_2O) in CH_2Cl_2 (0.02 M) at ambient temperature gave rise to complex **33** after 10 min. Silica gel chromatography yielded the pentacarbonyl complex **33** as a 2:1 mixture of diastereomers. Complex **33** represents a trapped form of the pentacarbonyl intermediate which is formed when the hexacarbonyl alkyne complex is treated with the amine oxide.[13a,b] Unfortunately, the decomposition of complex **33** apparently generates paramagnetic impurities which prevent lengthy NMR studies.



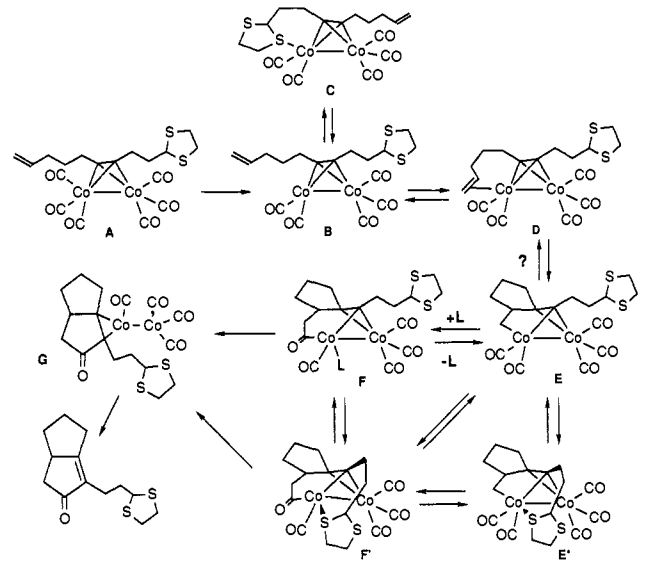
33

Treatment of **33** with carbon monoxide resulted in complete regeneration of the hexacarbonyl complex. Only 15 min at 71 °C

(12) NMO monohydrate is commercially available or may be prepared from *N*-methylmorpholine: VanRheenen, V.; Cha, D. Y.; Hartley, W. M. *Organic Syntheses*; Wiley: New York, 1988; Collect. Vol. VI, p 342. *N*-Methylmorpholine *N*-oxide monohydrate exhibits a sharp melting point at 75 °C. Purification of the *N*-oxide by precipitation from acetone (2×), as described in the *Organic Syntheses* procedure, gives highly crystalline monohydrate.

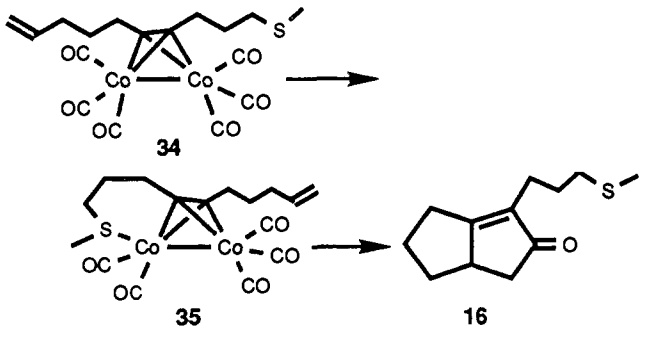
(13) (a) A complex prepared by substitution of one CO ligand for a phosphine has been reported and shown to undergo the thermal, intermolecular Pauson–Khand reaction: Bladon, P.; Pauson, P. L.; Brunner, H.; Eder, R. *J. Organomet. Chem.* **1988**, *355*, 449. (b) Very recently, Moretó et al. reported a special case of a carbene activated cobalt alkyne complex which undergoes a partial Pauson–Khand reaction to yield an interesting acyl cobaltacycle: Jordi, L.; Moretó, J. M.; Ricart, S.; Viñas, J. M.; Mejias, M.; Molins, E. *Organometallics* **1992**, *11*, 3507.

Scheme I



was necessary for the transformation of **33** to cyclopentenone **27**. The hexacarbonyl complex **12** required 1.5 h under identical conditions.[8] Complex **33**, when stirred at ambient temperature in CH_2Cl_2 under an atmosphere of nitrogen, required 27 h for complete conversion to a mixture of cyclopentenone **27** and hexacarbonyl complex **12**. The hexacarbonyl complex probably arises from reaction of **33** with carbon monoxide generated as the cobalt carbonyl residues decompose. This suggests that if **33** was not such a good carbon monoxide scavenger, less amine oxide would be needed for the cycloaddition to proceed to completion.

The bishomopropargylic sulfide cobalt complex **34**, upon treatment with $NMO{\cdot}H_2O$ in CH_2Cl_2, yielded the more stable pentacarbonyl complex **35** as a single isomer.[14a-c] Conversion of **34** to **16** required 5 days at ambient temperature in the presence of 10 equiv of $NMO{\cdot}H_2O$. The NMR spectra of both **33** and **35** clearly show the absence of alkene coordination and indicate the presence of coordinated sulfur (shift of the protons adjacent to sulfur and a nonequivalence of the methylene protons on the tether between the alkyne and sulfide). (See Table VII.)



These results can be rationalized within the context of the proposed mechanistic pathway,[11] which is illustrated in Scheme I. While a detailed mechanism has not been established, an approximation can be made based on the products obtained. Initial ligand exchange in the thermal process (**A** to **D**) is usually assumed to take place through a dissociative process via initial loss of carbon monoxide, although an associative process cannot be ruled out. In the amine oxide promoted reactions, CO_2 should be liberated in the first step.[9] The next step is metallacycle formation (**D** to **E**), which involves the insertion of the π-complexed alkene into one of the formal cobalt–carbon bonds. This step is proposed[2,11] to be rate limiting and product determining. Subsequent insertion of carbon monoxide into either of the cobalt–carbon bonds (**E** to **F**) and reductive coupling (**F** to **G**) gives the cobalt-complexed cyclopentenone.

Three steps in the proposed mechanism, **A** to **B**, **D** to **E**, and **E** to **F**, necessarily generate a vacant coordination site. Judicious placement of a coordinating ligand can be expected to lead to a stabilization of a coordinatively unsaturated complex by heteroatom complexation to the metal center. Stabilization of the pentacarbonyl complex **B** by formation of coordinatively saturated complex **C** may be considered as rate decelerating with increasing stability of **C**. Transformations **D** to **E** and **E** to **F** may be driven by heteroatom coordination to provide complexes **E′** or **F′**, respectively.[8,15] This acceleration may be a result of insertion of CO in complex **E′** occurring faster than in **E** as a result of heteroatom coordination. Alternatively, decarbonylation of **F** may be inhibited due to coordination of the heteroatom (**F′**). The bishomopropargylic ligands would be expected to provide a more stable complex (six-membered chelate ring) than the homopropargylic cases (five-membered chelate ring) due to the strain in a five-membered chelate ring caused by the bond angle at the carbon bound to cobalt. The increased stability of complex **C** can be used to account for the greatly reduced rate for the conversion of **1** to **16**. In most cases, though, the presence of a ligand in the homo- or bishomopropargylic position enhances the rate of cycloaddition, which suggests a dual role for the ligand. Interaction of the coordinating ligand in **E** or **F** could be viewed as a rate-accelerating role[8,15] which can compensate for the decrease in rate caused by the formation of complex **C**.

Incorporation of a chiral center adjacent to the coordinating ligand failed to provide any diastereocontrol (entries 5, 6, and 13, Table I, and entries 5, 13, and 15, Table II). Heteroatom coordination during the product-determining step, the cycloaddition, is expected to be an essential requirement for diastereocontrol over product formation. As indicated in Scheme I, this condition does not necessarily need to be met before cycloaddition may occur, thus providing an explanation for the lack of success.

In the amine oxide promoted reaction, the presence of a sulfur ligand, particularly in the bishomopropargylic position, leads to stabilization of a pentacarbonyl intermediate, whereas even the presence of ligands such as oxygen, that should bind only weakly to cobalt, results in increased reaction rates. Enyne **2** has no heteroatom ligands, yet might be expected to undergo reaction with the amine oxide at the same rate as those substrates which have heteroatom substitution. Attempts to identify or isolate an intermediate from the reaction of **2** with NMO were unsuccessful. The intermediate complex is apparently unstable to TLC and, due to the presence of paramagnetic impurities, could not be observed by NMR. Addition of an excess of trimethylphosphine to the reaction mixture 10 min after the addition of NMO resulted in the immediate formation of the corresponding monophosphine complex, as the major product, which was stable even in the presence of excess amine oxide. Analogous ligand exchange in the absence of NMO required several hours in refluxing CH_2Cl_2.

(14) (a) Due to the inherent instability of complex **35**, we were unable to obtain a mass spectrum. (b) For examples of substituted alkyne cobalt carbonyl complexes, see: Bonnet, J.-J.; Mathieu, R. *Inorg. Chem.* **1978**, *17*, 1973. Chia, L. S.; Culen, W. R.; Franklin, M.; Manning, A. R. *Inorg. Chem.* **1975**, *14*, 2521. Varadi, G.; Vizi-Orosz, A.; Vastag, S.; Palyi, G. *J. Organomet. Chem.* **1976**, *108*, 225. Bradley, D. H.; Khan, M. A.; Nicholas, K. M. *Organometallics* **1989**, *8*, 554. Bradley, D. H.; Khan, M. A.; Nicholas, K. M. *Organometallics* **1992**, *11*, 2598. (c) The position of substitution is not known; however, literature examples would suggest that substitution occurred in the apical position (trans to the Co–Co bond). See for example: Bonnet, J.-J.; Mathieu, R. *Inorg. Chem.* **1978**, *17*, 1973. Varadi, G.; Vizi-Orosz, A.; Vastag, S.; Palyi, G. *J. Organomet. Chem.* **1976**, *108*, 225. Chia, L. S.; Culen, W. R.; Franklin, M.; Manning, A. R. *Inorg. Chem.* **1975**, *14*, 2521.

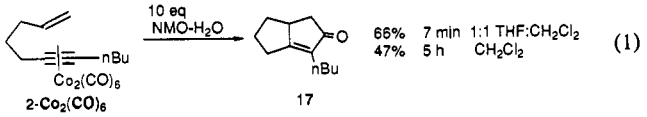
(15) Ligand accelerated insertions: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. Mawby, R. J.; Basolo, F.; Pearson, R. G. *J. Am. Chem. Soc.* **1964**, *86*, 3994. Wax, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 7028. Cotton, J. D.; Crisp, G. T.; Latif, L. *Inorg. Chim. Acta* **1981**, *47*, 171. Nicholas, K. M.; Raghu, S.; Rosenblum, M. *J. Organomet. Chem.* **1974**, *78*, 133. Wang, S.-J.; Angelici, R. J. *Inorg. Chem.* **1988**, *27*, 3233.

Table III. Decomplexation of Alkynes with NMO

alkyne–$Co_2(CO)_6$	yield (%)	conditions
1,7-cyclotridecadiyne	90	30 min, 1:1 THF/CH_2Cl_2
10-dodecyn-1-ol	90	10 min, 1:1 THF/CH_2Cl_2
1-phenyl-1-pentyne	92	10 min, 1:1 THF/CH_2Cl_2
1-phenyl-1-pentyne	91	35 min, CH_2Cl_2

Alkyne complexes that do not contain an olefin or a suitably placed ligand undergo very rapid decomplexation cleanly when treated with amine oxides (Table III).[16] Decomplexation is more rapid in a mixture of CH_2Cl_2 and THF than in CH_2Cl_2, as is frequently used. These rapid decomplexation results might suggest that, in the Pauson–Khand reaction, the alkene fills the vacant coordination site and stabilizes the pentacarbonyl intermediate, and subsequent cycloaddition is slow.

Since ligands tethered to the enyne were apparently playing a role in accelerating the *N*-oxide-promoted reaction, the use of ligating additives and coordinating solvents in the amine oxide promoted Pauson–Khand reaction was investigated. Addition of 10 equiv of oxathiolane or *N*-methylmorpholine resulted in no change in the overall reaction rate. However, use of a coordinating cosolvent, THF, provided encouraging results. Treatment of cobalt-complexed **2** with $NMO{\cdot}H_2O$ in a 1:1 CH_2Cl_2/THF mixture gave rise to a 66% yield of cyclopentenone **17** in 7 min (eq 1).



(1)

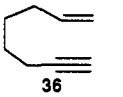
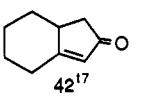
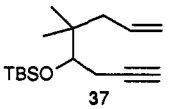
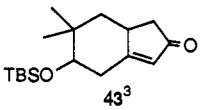
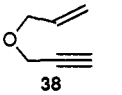
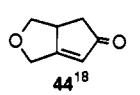
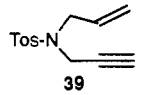
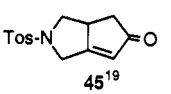
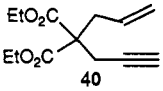
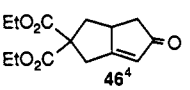
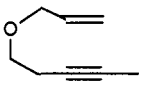
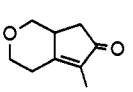
Table IV. Reaction of Cobalt-Complexed 2 with Different Amine Oxides in Different Solvents (Eq 1)

amine oxide	solvent	time	yield (%)
NMO (anhydrous)	CH_2Cl_2	5 h	41
NMO (anhydrous)	THF/CH_2Cl_2 (1:1)	7 min	68
NMO monohydrate[12]	CH_2Cl_2	5 h	47
NMO monohydrate[12]	THF/CH_2Cl_2 (1:1)	10 min	66
TMAO (anhydrous)	CH_2Cl_2	3.5 h	61
TMAO (anhydrous)	THF/CH_2Cl_2 (1:1)	8 min	62
TMAO dihydrate	CH_2Cl_2	5 h	32
TMAO dihydrate	THF/CH_2Cl_2 (1:1)	1.2 h	37

In contrast, reaction in CH_2Cl_2 required 5 h to give only 47% of the cycloadduct. A comparison of rates of reaction of cobalt-complexed enyne **2** with different forms of amine oxides is shown in Table IV. The best results (shortest reaction times and highest yields) were obtained with NMO, either the hydrate[12] or anhydrous form, or anhydrous trimethylamine *N*-oxide (TMAO) in the mixed solvent system.

However, during the course of this study we noted that, even in CH_2Cl_2 alone, some reactions were proceeding to completion in minutes, rather than hours as originally reported.[3] Examples are listed in Table V. We identified the quality of the $NMO{\cdot}H_2O$ as the factor responsible for the rate discrepancy. Freshly prepared $NMO{\cdot}H_2O$ gave the best results. Reactions with older bottles of $NMO{\cdot}H_2O$, which presumably contained substantial quantities of di- and trihydrates, required much longer reaction times.[12]

Table V

Entry #	Enyne	Cyclopentenone	Yield	Conditions
1	 36	 42[17]	52%	1.25 h CH_2Cl_2
2			41%	15 min T/M
3	 37	 43[3]	88%	12 min CH_2Cl_2
4			86%	9 min T/M
5	 38	 44[18]	62%	5 min CH_2Cl_2
6			76%	2 min T/M
7	 39	 45[19]	89%	3 min CH_2Cl_2
8			91%	1 min T/M
9	 40	 46[4]	95%	7 min CH_2Cl_2
10			92%	1 min T/M
11	 41	 47	81%	30 min CH_2Cl_2
12			73%	18 min T/M

T/M = 1:1 mixture of $THF:CH_2Cl_2$; $NMO{\cdot}H_2O$[12] was used for these reactions.

Table VI. Pauson-Khand Cycloaddition in Different Solvents (Eq 2)[a]

solvent	reaction time	yield (%)
CH_3CN	4 min	88
EtOAc	8 min	63
THF	10 min	72
acetone	10 min	78
THF/CH_2Cl_2 (1:1)	25 min	61
CH_2Cl_2	30 min	70
Et_2O	8 h	50
DMSO	14 h	71

[a] $NMO{\cdot}H_2O$[12] used for these reactions.

Most of the substrates reacted only moderately faster in THF/CH_2Cl_2 than CH_2Cl_2 alone. The effect does not appear to be as significant in these cases, but the influence of solvent is still evident. It is anticipated that the role of the coordinating solvent is similar to the role of the tethered heteroatoms (*vide supra*). A comparison of cycloaddition rates of **48** (eq 2) in other coordinating solvents is shown in Table VI. These results support the mechanistic role of ligating solvents. The extended time for reaction in DMSO may be due to the strength of DMSO as a ligand, which then becomes a rate-decelerating effect.

(2)

These results illustrate the substantial influence that coordinating heteroatoms exert over the Pauson–Khand cycloaddition. In addition, the trapping of the pentacarbonyl complexes provides direct experimental evidence for removal of carbon monoxide from the hexacarbonyl alkyne complex by amine oxides. Further work on the Pauson–Khand reaction is in progress, and the results will be reported in due course.

(16) Several reagents are normally used for alkyne decomplexation from cobalt carbonyl complexes. For example, Ce(4+): Seyferth, D.; Wehman, A. T. *J. Am. Chem. Soc.* **1970**, *92*, 5520. Schreiber, S. L.; Klimas, M. T.; Sammakia, T. *J. Am. Chem. Soc.* **1987**, *109*, 5749. Fe(3+): Pettit, R.; Nicholas, K. M. *Tetrahedron Lett.* **1971**, 3475. Lockwood, R. F.; Nicholas, K. M. *Tetrahedron Lett.* **1977**, 4163. NMO: Magnus, P.; Annoura, H.; Harling, J. *J. Org. Chem.* **1990**, *55*, 5749. Magnus, P.; Becker, D. P. *J. Chem. Soc., Chem. Commun.* **1985**, 640. TMAO: Schreiber, S. L.; Sammakia, T.; Crowe, W. E. *J. Am. Chem. Soc.* **1986**, *108*, 3128. Decomplexation by slow addition of $NMO{\cdot}H_2O$ to the cobalt complex at 0 °C results in oxidation of the alkyne to the 1,2-dicarbonyl compound in addition to yielding some of the decomplexed alkyne.

(17) Schore, N. E.; Croudace, M. C. *J. Org. Chem.* **1981**, *46*, 5436.

(18) Billington, D. C.; Willison, D. *Tetrahedron Lett.* **1984**, *25*, 4041.

(19) Jeong, N.; Yoo, S.-e.; Lee, S. J.; Lee, S. H.; Chung, Y. K. *Tetrahedron Lett.* **1991**, *32*, 2137.

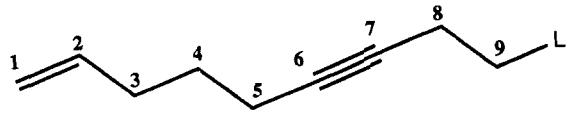


Figure 1. Numbering scheme for the alkynes.

Experimental Section

General. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from potassium prior to each use. Methylene chloride (CH_2Cl_2) and pyridine were distilled from calcium hydride. Hexane, chloroform ($CHCl_3$), methanol (MeOH), and ethyl acetate (EtOAc) were distilled prior to use. Toluene was distilled from sodium metal prior to use. All reactions were performed under an atmosphere of nitrogen. Infrared spectra (IR) were obtained on a Perkin-Elmer 1320 infrared spectrophotometer in $CHCl_3$ solutions. ^1H NMR spectra were obtained at 300 MHz on a Varian Gemini spectrometer or at 500 MHz on a Varian VXR500 spectrometer in $CDCl_3$ solutions unless otherwise noted. Carbon spectra were obtained at 75 MHz on a Varian Gemini 300 spectrometer in $CDCl_3$ solutions. Chemical shifts are reported in parts per million downfield relative to tetramethylsilane (δ 0.00); coupling constants are reported in hertz. Low-resolution mass spectra were obtained on a Finnigan 4510 GC/MS instrument. Mass spectral data is reported as *m/e* (relative intensity). Melting points were taken on a Meltemp and are uncorrected. Flash chromatography refers to that reported by Still.[20] Elemental analyses were performed by Atlantic Microlabs, Norcross, GA. The numbering scheme for the alkynes is shown in Figure 1.

Synthesis of 10-(Methylthio)-1-decen-6-yne (1). 10-(*tert*-Butyldimethylsiloxy)-1-decen-6-yne. To a solution of 1-(*tert*-butyldimethylsiloxy)-4-pentene (8.8 g, 44 mmol) in 4:1 THF/HMPA (250 mL) at −78 °C was added *sec*-butyllithium until a yellow color persisted. A solution of 4-pentenyl iodide (20 g, 100 mmol) in THF (50 mL) was added slowly, and the reaction mixture was warmed to ambient temperature and stirred for 2 h. After quenching with water, the THF was removed under reduced pressure. The resultant oil was partitioned between hexane and water. The aqueous layer was washed three times with hexane, and the combined organic layers were washed three times with water, dried over magnesium sulfate, and concentrated under reduced pressure. The resultant oil was used without further purification in the subsequent step. 300-MHz ^1H NMR: δ 0.04 (s, 6 H, $Si(CH_3)_2$), 0.89 (s, 9 H, $C(CH_3)_3$), 1.56 (tt, 2 H, J = 7.1, 7.1, 4-H), 1.67 (tt, 2 H, J = 7.1, 6.0, 9-H), 2.14 (obscured dtdd, 2 H, J = 7.1, 7.1, 2.2, 1.1, 3-H), 2.15 (obscured tt, 2 H, J = 7.1, 2.2, 5-H), 2.22 (tt, 2 H, J = 7.1, 2.2, 8-H), 3.68 (t, 2 H, J = 6.0, 10-H), 4.97 (ddt, 1 H, J = 10.4, 2.2, 1.1, 1-H), 5.03 (ddt, 1 H, J = 17, 2.2, 1.6, 1′-H), 5.80 (ddt, 1 H, J = 17, 10.4, 7.1, 2-H). 75-MHz ^{13}C NMR: δ 5.3, 15.3, 18.3, 18.5, 26.1, 28.5, 32.4, 33.0, 62.0, 80.3, 80.3, 115.4, 138.6. IR (cm^{-1}): 1634. Mass spectrum *m/e* (EI): 209 (M^+ −57).

10-Hydroxy-1-decen-6-yne. To a solution of 10-(*tert*-butyldimethylsiloxy)-1-decen-6-yne formed in the previous step in THF (100 mL) was added tetra-*n*-butylammonium fluoride [50 mL, 1 M (THF)], and the solution was stirred at room temperature for 1 h. The solution was then partitioned between chloroform and water. The organic layer was dried over magnesium sulfate and concentrated under reduced pressure. Flash chromatography (eluent 1:4 EtOAc/hexane) yielded 10-hydroxy-1-decen-6-yne (6.12 g) in 91% overall yield. 300-MHz ^1H NMR: δ 1.56 (br, 1 H, OH), 1.56 (tt, 2 H, J = 7.1, 7.1, 4-H), 1.74 (tt, 2 H, J = 7.1, 6.0, 9-H), 2.13 (obscured dtdd, 2 H, J = 7.1, 6.6, 1.6, 1.1, 3-H), 2.15 (obscured tt, 2 H, J = 7.1, 2.2, 5-H), 2.28 (tt, 2 H, J = 7.1, 2.2, 8-H), 3.75 (t, 2 H, J = 6.0, 10-H), 4.97 (ddt, 1 H, J = 9.9, 2.2, 1.1, 1-H), 5.02 (ddt, 1 H, J = 17, 2.2, 1.6, 1′-H), 5.79 (ddt, 1 H, J = 17, 9.9, 6.6, 2-H). 75-MHz ^{13}C NMR: δ 15.5, 18.3, 28.4, 31.9, 33.0, 62.2, 80.0, 80.9, 115.5, 138.6. IR (cm^{-1}): 3343. Mass spectrum *m/e* (CI: isobutane): 153 (M^+ + 1).

10-(Methylsulfonyloxy)-1-decen-6-yne. To an ice-cold solution of 10-hydroxy-1-decen-6-yne (0.512 g, 3.4 mmol) in methylene chloride (20 mL) were added triethylamine (0.7 mL, 5 mmol) and methanesulfonyl chloride (0.31 mL, 4 mmol). The reaction mixture was partitioned between chloroform and water. The organic layer was dried over magnesium sulfate and concentrated under reduced pressure. Filtration through a plug of silica gel (eluent 1:3 ethyl acetate/hexane) gave 10-(methylsulfonyloxy)-1-decen-6-yne (0.736 g, 95%) as a clear oil. 300-MHz ^1H NMR: δ 1.57 (tt, 2 H, J = 7.1, 7.1, 4-H), 1.90 (tt, 2 H, J = 6.6, 6.6, 9-H), 2.13 (m, 2 H, 3-H), 2.15 (obscured tt, 2 H, J = 7.1, 2.7, 5-H), 2.31 (tt, 2 H, J = 7.1, 2.2, 8-H), 3.01 (s, 3 H, SMe), 4.34 (t, 2 H, J = 6.6, 10-H), 4.97 (ddt, 1 H, J = 11, 2.2, 1.1, 1-H), 5.02 (ddt, 1 H, J = 17, 2.2, 1.6, 1′-H), 5.79 (ddt, 1 H, J = 17, 9.9, 6.6, 2-H). To a solution of 10-(methylsulfonyloxy)-1-decen-6-yne (1.26 g, 5.5 mmol) in 4:1 THF/HMPA (25 mL) was added lithium methylmercaptide (1.2 g, 22 mmol), and the reaction mixture was stirred at room temperature until the reaction was complete by TLC. The solution was diluted with hexane and extracted repeatedly with water. After drying over magnesium sulfate, the solution was concentrated under reduced pressure. Purification by Kugelrohr distillation gave 10-(methylthio)-1-decen-6-yne (**1**) (0.64 g, 64%). 300-MHz ^1H NMR ($CDCl_3$): δ 1.56 (tt, 2 H, J = 7.1, 7.1, 4-H), 1.76 (tt, 2 H, J = 7.1, 7.1, 9-H), 2.09 (s, 3 H, 11-H), 2.11–2.19 (m, 4 H, 3-H, 5-H), 2.27 (tt, 2 H, J = 7.1, 2.2, 8-H), 2.58 (t, 2 H, J = 7.1, 10-H), 4.97 (obscured dm, 1 H, J = 9.9, 1-H), 5.02 (obscured ddt, 1 H, J = 17, 1.65, 1.65, 1′-H), 5.79 (ddt, 1 H, J = 17, 9.9, 6.6, 2-H). 500-MHz ^1H NMR (C_6D_6): δ 1.46 (tt, 2 H, J = 7.3, 7.3, 4-H), 1.61 (tt, 2 H, J = 7.3, 6.9, 9-H), 1.73 (s, 3 H, 11-H), 2.04 (m, 4 H, 3-H, 5-H), 2.14 (tt, 2 H, J = 6.9, 2.75, 8-H), 2.38 (t, 2 H, J = 7.3, 10-H), 4.99 (ddt, 1 H, J = 10, 1.8, 1.4, 1-H), 5.01 (ddt, 1 H, J = 17, 1.8, 1.8, 1′-H), 5.67 (ddt, 1 H, J = 17, 10, 6.4, 2-H). 75-MHz ^{13}C NMR ($CDCl_3$): δ 15.6, 18.0, 18.3, 28.5, 28.7, 33.0, 33.4, 79.7, 80.9, 115.5, 138.6. 75-MHz ^{13}C NMR (C_6D_6): δ 15.0, 18.0, 18.4, 28.6, 28.8, 33.1, 33.3, 80.0, 80.8, 115.4, 138.5. IR (cm^{-1}): 1633. Mass spectrum *m/e* (EI): 167 (M^+ − 15). Anal. Calcd for $C_{11}H_{18}S$: C, 72.47; H, 9.95. Found: C, 72.32; H, 10.01.

Synthesis of 1-Undecen-6-yne (2). To a solution of 1-hexyne (2 mL, 17.4 mmol) in 4:1 THF/HMPA (50 mL) at −78 °C was added *sec*-butyllithium (13.5 mL, 17.55 mmol). A solution of 4-pentenyl iodide (3.3 g, 16.8 mmol) in THF (5 mL) was added slowly, and the reaction mixture was stirred at room temperature overnight. The reaction mixture was diluted with hexane and washed repeatedly with water. After drying over magnesium sulfate, the solvent was removed under reduced pressure. Purification by chromatography (eluent hexane) and distillation under reduced pressure (water aspirator) gave 1-undecen-6-yne (**2**) (1.73 g, 66%). 300-MHz ^1H NMR: δ 0.90 (t, 3 H, J = 7.1, 11-H), 1.33–1.49 (m, 4 H, 9-H, 10-H), 1.57 (tt, 2 H, J = 7.1, 7.1, 4-H), 2.14 (m, 6 H, 3-H, 5-H, 8-H), 4.97 (obscured dm, 1 H, J = 10, 1-H), 5.02 (obscured ddt, 1 H, J = 17, 1.65, 1.65, 1′-H), 5.80 (ddt, 1 H, J = 17, 10.4, 6.6, 2-H). 75-MHz ^{13}C NMR: δ 13.7, 18.3, 18.6, 22.1, 28.6, 31.5, 33.0, 80.1, 80.8, 115.4, 138.7. IR (cm^{-1}): 1632. Mass spectrum *m/e* (EI): 149 (M^+ − 1).

Synthesis of Dioxolane 3. To a solution of acetal **31** (1.528 g, 7.3 mmol) in benzene (36 mL) were added ethylene glycol (0.45 mL, 8.1 mmol) and *p*-toluenesulfonic acid (0.15 g). The mixture was then heated under reflux for 2 h. After cooling to room temperature, the solution was partitioned between chloroform and aqueous sodium hydroxide (2 M). The organic layer was washed once with water and once with saturated brine, dried over magnesium sulfate, and concentrated under reduced pressure. Chromatography (eluent 1:9 ethyl acetate/hexane) followed by Kugelrohr distillation yielded dioxolane **3** (0.704 g, 54%). 300-MHz ^1H NMR: δ 1.58 (tt, 2 H, J = 7.1, 7.1, 4-H), 2.14 (m, 2 H, 3-H), 2.18 (obscured tt, 2 H, J = 7.4, 2.2, 5-H), 2.52 (dt, 2 H, J = 5, 2.2, 8-H), 3.80–4.06 (m, 4 H, OCH_2CH_2O), 4.96 (obscured dm, 1 H, J = 10, 1-H), 5.01 (obscured dm, 1 H, J = 17, 1′-H), 5.02 (t, 1 H, J = 5, 9-H), 5.79 (ddt, 1 H, J = 17, 10.4, 7.1, 2-H). 75-MHz ^{13}C NMR: δ 18.4, 25.6, 28.2, 33.0, 65.6, 74.9, 82.5, 103.2, 115.4, 138.5. IR (cm^{-1}): 1632, 1130. Mass spectrum *m/e* (CI: isobutane): 181 (M^+ + 1).

Synthesis of 9-Ethoxy-1-nonen-6-yne (4). 9-(*tert*-Butyldimethylsiloxy)-1-nonen-6-yne. Alkylation of 1-(*tert*-butyldimethylsiloxy)-3-butyne with 4-pentenyl iodide following the same procedure as described for the synthesis of 10-(*tert*-butyldimethylsiloxy)-1-decen-6-yne or **2** gave 9-(*tert*-butyldimethylsiloxy)-1-nonen-6-yne in quantitative yield after chromatography (eluent 1:4 ethyl acetate/hexane). 300-MHz ^1H NMR: δ 0.07 (s, 6 H, $Si(CH_3)_2$), 0.89 (s, 9 H, $C(CH_3)_3$), 1.56 (tt, 2 H, J = 7.1, 7.1, 4-H), 2.12 (obscured dtdd, 2 H, J = 7.1, 6.6, 2.2, 1.1, 3-H), 2.15 (obscured tt, 2 H, J = 7.1, 2.2, 5-H), 2.36 (tt, 2 H, J = 7.1, 2.2, 8-H), 3.69 (t, 2 H, J = 7.1, 9-H), 4.97 (obscured ddt, 1 H, J = 10.4, 2.2, 1.1, 1-H), 5.02 (obscured ddt, 1 H, J = 17, 2.2, 1.6, 1′-H), 5.79 (ddt, 1 H, J = 17, 10.4, 6.6, 2-H). 75-MHz ^{13}C NMR: δ −5.2, 18.3, 18.5, 23.4, 26.1, 28.4, 33.0, 62.7, 77.6, 81.3, 115.41, 138.6. IR (cm^{-1}): 1634. Mass spectrum *m/e* (EI): 195 (M^+ − 57). Anal. Calcd for $C_{15}H_{28}OSi$: C, 71.36; H, 11.18. Found: C, 71.37; H, 11.16.

9-Hydroxy-1-nonen-6-yne. Removal of the TBS protecting group was achieved in 79% yield by following the procedure used to prepare 10-hydroxy-1-decen-6-yne. 300-MHz ^1H NMR: δ 1.59 (tt, 2 H, J = 7.1, 7.1, 4-H), 1.65 (s, 1 H, OH), 2.13 (obscured dtdd, 2 H, J = 7.1, 6.6, 1.6, 1.1, 3-H), 2.18 (obscured tt, 2 H, J = 7.1, 2.2, 5-H), 2.43 (tt, 2 H, J =

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6.0, 2.2, 8-H), 3.68 (t, 2 H, J = 6.0, 9-H), 4.98 (obscured ddt, 1 H, J = 10.4, 1.6, 1.1, 1-H), 5.03 (obscured ddt, 1 H, J = 17, 1.6, 1.6, 1'-H), 5.79 (ddt, 1 H, J = 17, 10.4, 6.6, 2-H). 75-MHz ^{13}C NMR: δ 18.3, 23.3, 28.3, 33.0, 61.7, 77.1, 82.4, 115.5, 138.5. IR (cm^{-1}): 3341. Mass spectrum m/e (CI: isobutane): 139 (M^+ + 1). Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.16; H, 10.23. Potassium hydride (1.8 g, 35% oil dispersion, 16 mmol) was washed three times with hexane, and then THF (10 mL) was added and the suspension was cooled to 0 °C. 9-Hydroxy-1-nonen-6-yne (1.436 g, 10.4 mmol) in THF (5 mL) was added, and the solution was warmed to room temperature. Iodoethane (2.5 mL, 31 mmol) was added slowly with ice cooling. After quenching with water, the solution was partitioned between ethyl acetate and water. The organic layer was washed once with saturated brine, dried over magnesium sulfate, and concentrated under reduced pressure. Kugelrohr distillation (aspirator) gave the ether **4** (1.575 g, 91%) as a colorless oil. 300-MHz ^{1}H NMR: δ 1.19 (t, 3 H, J = 7.1, 11-H), 1.57 (tt, 2 H, J = 7.1, 7.1, 4-H), 2.12 (obscured tddd, 2 H, J = 7.1, 7.1, 2.2, 1.6, 3-H), 2.14 (obscured tt, 2 H, J = 7.1, 2.2, 5-H), 2.37 (tt, 2 H, J = 7.1, 2.2, 8-H), 3.50 (t, 2 H, J = 7.1, 9-H), 3.51 (q, 2 H, J = 7.1, 10-H), 4.96 (obscured ddt, 1 H, J = 10.4, 2.2, 1.1, 1-H), 5.02 (obscured ddt, 1 H, J = 17, 2.2, 1.6, 1'-H), 5.79 (ddt, 1 H, J = 17, 10.4, 7.1, 2-H). 75-MHz ^{13}C NMR: δ 15.2, 18.3, 20.3, 28.4, 32.9, 66.5, 69.6, 77.4, 81.2, 115.4, 138.6. IR (cm^{-1}): 1630, 1109. Mass spectrum m/e (CI: isobutane): 167 (M^+ + 1). Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.26; H, 10.88.

Synthesis of Oxathiane 5. To a solution of acetal **31** (1.38 g, 6.6 mmol) in acetic acid (6 mL) were added 3-mercapto-1-propanol (0.57 g, 6.2 mmol) and boron trifluoride etherate (0.76 mL, 6.3 mmol), and the mixture was stirred at room temperature for 15 min, after which time TLC showed a trace amount of acetal **31**. Mercaptopropanol (2 × 3 drops) was added over 45 min to complete the formation of oxathiane **5**. The reaction mixture was diluted with methylene chloride and washed with water, aqueous sodium hydroxide (2 M), water, and dilute sodium chloride solution. After drying over magnesium sulfate, the organic layer was concentrated under reduced pressure. Purification by chromatography (eluent 1:30 ethyl acetate/hexane) followed by Kugelrohr distillation gave pure oxathiane **5** (0.737 g, 53%). 300-MHz ^{1}H NMR: δ 1.58 (tt, 2 H, J = 7.1, 7.1, 4-H), 1.68 (dm, 1 H, J = 13.7, 11_{eq}-H), 1.95 (ddddd, 1 H, J = 13.7, 13, 12, 4.4, 3.8, 11_{ax}-H), 2.14 (m, 2 H, 3-H), 2.17 (obscured tdd, 2 H, J = 7.1, 2.75, 2.2, 5-H), 2.55 (ABddd, 1 H, J_{AB} = 17, J = 6.6, 2.75, 2.2, 8-H), 2.66 (ABddd, 1 H, J_{AB} = 17, J = 6.0, 2.75, 2.2, 8'-H), 2.76 (dddd, 1 H, J = 13.7, 4.4, 2.2, 2.2, 10_{eq}-H), 3.04 (ddd, 1 H, J = 13.7, 13.2, 2.75, 10_{ax}-H), 3.61 (td, 1 H, J = 12, 2.2, 12_{ax}-H), 4.19 (dddd, 1 H, J = 12, 3.8, 2.2, 2.2, 12_{eq}-H), 4.83 (dd, 1 H, J = 6.6, 6.0, 9-H), 4.96 (ddt, 1 H, J = 9.9, 2.2, 1.1, 1-H), 5.02 (ddt, 1 H, J = 17, 2.2, 1.6, 1'-H), 5.79 (ddt, 1 H, J = 17, 10.4, 7.1, 2-H). 75-MHz ^{13}C NMR: δ 18.4, 25.8, 27.0, 28.1, 28.2, 32.9, 70.5, 75.4, 82.3, 83.0, 115.5, 138.6. IR (cm^{-1}): 1633. Mass spectrum m/e (EI): 210 (M^+), 103. Anal. Calcd for $C_{12}H_{18}OS$: C, 68.53; H, 8.63. Found: C, 68.31; H, 8.59.

Synthesis of Oxathiolane 6. Oxathiolane **6** was prepared in 77% yield from acetal **31** and mercaptoethanol following the same procedure as for oxathiane **5**. 300-MHz ^{1}H NMR: δ 1.58 (tt, 2 H, J = 7.4, 7.1, 4-H), 2.14 (m, 2 H, 3-H), 2.18 (obscured tt, 2 H, J = 7.1, 2.2, 5-H), 2.60 (ABdt, 1 H, J_{AB} = 16.5, J = 6.0, 2.2, 8-H), 2.76 (ABdt, 1 H, J_{AB} = 16.5, J = 6.0, 2.2, 8'-H), 3.02 (ABdd, 1 H, J_{AB} = 9.9, J = 6.0, 4.4, 10-H), 3.06 (ABdd, 1 H, J_{AB} = 9.9, J = 7.7, 5.5, 10'-H), 3.89 (ddd, 1 H, J = 9.4, 7.7, 6.0, 11-H), 4.32 (ddd, 1 H, J = 9.4, 7.7, 6.09, 11'-H), 4.97 (ddt, 1 H, J = 9.9, 2.2, 1.1, 1-H), 5.03 (ddt, 1 H, J = 17, 1.6, 1.6, 1'-H), 5.21 (t, 1 H, J = 6.0, 9-H), 5.79 (ddt, 1 H, J = 17, 10.4, 6.6, 2-H). 75-MHz ^{13}C NMR: δ 18.3, 27.8, 28.2, 32.9, 33.0, 72.1, 76.2, 82.6, 85.6, 115.5, 138.5. IR (cm^{-1}): 1633. Mass spectrum m/e (EI): 196 (M^+), 89. Anal. Calcd for $C_{11}H_{16}OS$: C, 67.30; H, 8.22. Found: C, 67.42; H, 8.21.

Synthesis of Dithiolane 7. Dithiolane **7** was prepared in 80% yield from acetal **31** and ethanedithiol following the same procedure as for oxathiane **5**. 300-MHz ^{1}H NMR: δ 1.59 (tt, 2 H, J = 7.1, 7.1, 4-H), 2.16 (obscured tdt, 2 H, J = 7.1, 6.6, 1.5, 3-H), 2.18 (obscured tt, 2 H, J = 7.1, 2.75, 5-H), 2.64 (dt, 2 H, J = 6.6, 2.75, 8-H), 3.22 (ABt, 2 H, J_{AB} = 7.7, J = 10.4, 10-H, 11-H), 3.28 (ABt, 2 H, J_{AB} = 7.7, J = 10.4, 10'-H, 11'-H), 4.61 (t, 1 H, J = 6.6, 9-H), 4.97 (ddt, 1 H, J = 9.9, 1.4, 1.5, 1-H), 5.04 (ddt, 1 H, J = 17, 1.5, 1.5, 1'-H), 5.80 (ddt, 1 H, J = 17, 9.9, 6.6, 2-H). 75-MHz ^{13}C NMR: δ 18.3, 28.2, 30.7, 33.0, 39.0, 52.9, 78.2, 82.3, 115.6, 138.6. IR (cm^{-1}): 1633. Mass spectrum m/e (EI): 212 (M^+), 184. Anal. Calcd for $C_{11}H_{16}S_2$: C, 62.21; H, 7.59. Found: C, 62.34; H, 7.60.

Synthesis of 10-(*N*,*N*-Dimethylamino)-1-decen-6-yne (8). To an ice-cold solution of 10-(methylsulfonyloxy)-1-decen-6-yne (0.853 g, 3.7 mmol) in ether (1 mL) in a resealable tube (Ace Glass) was added dimethylamine (5 mL). The sealed flask was stirred at room temperature overnight. After recooling, the flask was opened to the atmosphere and the excess amine allowed to evaporate. The product was dissolved in methylene chloride and washed with saturated sodium bicarbonate solution. The aqueous layer was extracted twice with methylene chloride, and the combined organic layers were dried over magnesium sulfate. Concentration under reduced pressure gave 10-(*N*,*N*-dimethylamino)-1-decen-6-yne (**8**) (0.556 g, 84%) as a clear oil. 300-MHz ^{1}H NMR: δ 1.57 (tt, 2 H, J = 7.1, 7.1, 4-H), 1.64 (tt, 2 H, J = 7.1, 7.1, 9-H), 2.14 (obscured dtt, 2 H, J = 7.1, 6.6, 1.6, 3-H), 2.18 (m, 4 H, 5-H, 8-H), 2.21 (s, 6 H, $N(Me)_2$), 2.33 (t, 2 H, J = 7.4, 10-H), 4.96 (obscured ddt, 1 H, J = 9.4, 1.6, 1.6, 1-H), 5.03 (obscured ddt, 1 H, J = 17, 1.6, 1.6, 1'-H), 5.80 (ddt, 1 H, J = 17, 9.4, 6.6, 2-H). 75-MHz ^{13}C NMR: δ 16.8, 18.3, 27.4, 28.5, 33.0, 45.7, 59.1, 80.3, 80.3, 115.4, 138.6. IR (cm^{-1}): 1634. Mass spectrum m/e (CI: isobutane): 180 (M^+ + 1, 100). Anal. Calcd for $C_{12}H_{21}N$: C, 80.83; H, 11.81. Found: C, 80.10; H, 11.77.

Synthesis of 9-(*N*,*N*-Dimethylamino)-1-nonen-6-yne (9). 9-(Methylsulfonyloxy)-1-nonen-6-yne. 9-(Methylsulfonyloxy)-1-nonen-6-yne was prepared in 94% yield after chromatography (eluent 1:3 ethyl acetate/hexane) following the procedure used to prepare 10-(methylsulfonyloxy)-1-decen-6-yne. 300-MHz ^{1}H NMR: δ 1.57 (tt, 2 H, J = 7.1, 7.1, 4-H), 2.13 (dtdd, 2 H, J = 7.1, 7.1, 1.6, 1.1, 3-H), 2.15 (tt, 2 H, J = 7.1, 2.3, 5-H), 2.62 (tt, 2 H, J = 7.1, 2.2, 5-H), 3.04 (s, 3 H, SCH_3), 4.26 (t, 2 H, J = 7.1, 9-H), 4.98 (ddt, 1 H, J = 10.4, 2.2, 1.1, 1-H), 5.03 (ddt, 1 H, J = 17, 2.2, 1.6, 1'-H), 5.78 (ddt, 1 H, J = 17, 10.4, 7.1, 2-H). 75-MHz ^{13}C NMR: δ 18.1, 20.2, 28.1, 32.9, 37.8, 68.3, 74.8, 83.1, 115.6, 138.4. IR (cm^{-1}): 1633, 1355, 1170. Mass spectrum m/e (EI): 137 (M^+ − 79).

9-(*N*,*N*-Dimethylamino)-1-nonen-6-yne (9) was prepared in 79% yield by following the procedure used to prepare 10-(*N*,*N*-dimethylamino)-1-decen-6-yne (**8**). 300-MHz ^{1}H NMR: δ 1.57 (tt, 2 H, J = 7.1, 7.1, 4-H), 2.13 (obscured dtm, 2 H, J = 7.1, 6.6, 3-H), 2.16 (obscured tt, 2 H, J = 7.1, 2.2, 5-H), 2.24 (s, 6 H, $N(Me)_2$), 2.30 (tt, 2 H, J = 7.1, 2.2, 8-H), 2.46 (tm, 2 H, J = 8, 9-H), 4.97 (obscured ddt, 1 H, J = 9.9, 1.6, 1.6, 1-H), 5.03 (obscured ddt, 1 H, J = 17, 1.6, 1.6, 1'-H), 5.79 (ddt, 1 H, J = 17, 9.9, 6.6, 2-H). 75-MHz ^{13}C NMR: δ 17.9, 18.3, 28.4, 33.0, 45.4, 59.2, 78.8, 80.8, 115.4, 138.6. IR (cm^{-1}): 1634. Mass spectrum m/e (CI: isobutane): 166 (M^+ + 1, 100).

Synthesis of 9-(Ethylthio)-1-nonen-6-yne (10). To an ice-cold solution of ethanethiol (2.1 mL, 28 mmol) in THF (50 mL) was added butyllithium (16.2 mL, 26 mmol) followed by a solution of 9-(methylsulfonyloxy)-1-nonen-6-yne (1.76 g, 8.4 mmol) in THF (20 mL). After heating under reflux for 1 h, the reaction mixture was cooled to room temperature, quenched with water, and partitioned between water and methylene chloride. The aqueous layer was extracted once with methylene chloride, and the combined organic layers were washed with saturated ammonium chloride solution and dried over magnesium sulfate. After removal of the solvent under reduced pressure, Kugelrohr distillation (aspirator) gave the thioether **10** (1.374 g, 93%) as a colorless oil. 300-MHz ^{1}H NMR: δ 1.26 (t, 3 H, J = 7.1, 11-H), 1.57 (tt, 2 H, J = 7.1, 7.1, 4-H), 2.13 (obscured dtdd, 2 H, J = 7.1, 6.6, 1.6, 1.1, 3-H), 2.17 (obscured tt, 2 H, J = 7.1, 2.2, 5-H), 2.44 (tt, 2 H, J = 7.1, 2.2, 8-H), 2.58 (q, 2 H, J = 7.1, 10-H), 2.66 (t, 2 H, J = 7.1, 9-H), 4.97 (obscured ddt, 1 H, J = 9.9, 2.2, 1.1, 1-H), 5.03 (obscured ddt, 1 H, J = 17, 2.2, 1.6, 1'-H), 5.80 (ddt, 1 H, J = 17, 9.9, 6.6, 2-H). 75-MHz ^{13}C NMR: δ 14.9, 18.3, 20.5, 26.2, 28.3, 31.4, 33.0, 79.1, 81.3, 115.5, 138.6. IR (cm^{-1}): 1630. Mass spectrum m/e (EI): 153 (M^+ − 29). Anal. Calcd for $C_{11}H_{18}S$: C, 72.47; H, 9.95. Found: C, 72.61; H, 9.98.

Synthesis of Dithiane 11. Dithiane **11** was prepared in 63% yield from acetal **31** and propanedithiol by following the same procedure as for oxathiane **5**. 300-MHz ^{1}H NMR: δ 1.59 (tt, 2 H, J = 7.1, 7.1, 4-H), 1.80 (dtt, 1 H, J = 13.7, 9, 6, 11_{ax}-H), 2.04–2.18 (m, 3 H, 11'-H, 3-H), 2.17 (t, 2 H, J = 7.1, 2.2, 5-H), 2.65 (dt, 2 H, J = 7.1, 2.2, 8-H), 2.87 (m, 4 H, 10-H, 12-H), 4.13 (t, 1 H, J = 7.1, 9-H), 4.96 (ddt, 1 H, J = 9.9, 2.2, 1.1, 1-H), 5.03 (ddt, 1 H, J = 17, 2.2, 1.6, 1'-H), 5.79 (ddt, 1 H, J = 17, 9.9, 6.6, 2-H). 75-MHz ^{13}C NMR: δ 18.4, 25.7, 26.2, 28.2, 30.3, 33.0, 46.5, 76.1, 83.5, 115.5, 138.6. IR (cm^{-1}): 1633, 1416, 907. Mass spectrum m/e (EI): 226 (M^+), 119. Anal. Calcd for $C_{12}H_{18}S_2$: C, 63.66; H, 8.01. Found: C, 63.78; H, 8.02.

Synthesis of Dithiolane 12. 1-Decen-6-yn-10-al. To a solution of 10-hydroxy-1-decen-6-yne (0.2 g, 1.3 mmol) in methylene chloride (20 mL) were added Celite (2 g) and pyridinium chlorochromate (0.57 g, 2.6 mmol). After stirring for 1 h at room temperature, the mixture was filtered through a silica gel plug and the product collected by eluting with 1:3 ethyl acetate/hexane. Concentration under reduced pressure yielded the aldehyde (194.2 mg, 98%). 300-MHz ^{1}H NMR: δ 1.56 (tt, 2 H, J

= 7.1, 7.1, 4-H), 2.11 (obscured tddd, 2 H, J = 7.1, 6.6, 1.6, 1.1, 3-H), 2.14 (obscured tt, 2 H, J = 7.1, 2.2, 5-H), 2.48 (m, 2 H, 9-H), 2.62 (m, 2 H, 8-H), 4.97 (obscured ddt, 1 H, J = 9.9, 2.2, 1.1, 1-H), 5.02 (obscured ddt, 1 H, J = 17, 2.2, 1.6, 1′-H), 5.78 (ddt, 1 H, J = 17, 9.9, 6.6, 2-H), 9.80 (t, 1 H, J = 1.6, 10-H). To a solution of 1-decen-6-yn-10-al (1.12 g, 7.5 mmol) in methylene chloride (20 mL) were added 1,2-ethanedithiol (0.75 mL, 9 mmol) and trifluoroacetic acid (10 drops). After stirring for 1 h at room temperature, the reaction was quenched with saturated sodium bicarbonate solution. The solution was partitioned between chloroform and aqueous sodium hydroxide (2 M). The aqueous layer was washed twice with chloroform. The combined organic layers were dried over magnesium sulfate and concentrated under reduced pressure. Flash chromatography (eluent 1:30 ethyl acetate/hexane) followed by Kugelrohr distillation yielded pure dithiolane **12** (1.252 g, 74%) as an oil. 300-MHz ^{1}H NMR: δ 1.57 (tt, 2 H, J = 7.1, 7.1, 4-H), 1.95 (dt, 2 H, J = 7.1, 7.1, 9-H), 2.13 (obscured tddd, 2 H, J = 7.1, 6.6, 1.6, 1.1, 3-H), 2.15 (obscured tt, 2 H, J = 7.1, 2.2, 5-H), 2.32 (tt, 2 H, J = 7.1, 2.2, 8-H), 3.15–3.28 (m, 4 H, SCH_2CH_2S), 4.62 (t, 1 H, J = 7.1, 10-H), 4.97 (obscured ddt, 1 H, J = 9.9, 2.2, 1.1, 1-H), 5.03 (obscured ddt, 1 H, J = 17, 2.2, 1.6, 1′-H), 5.79 (ddt, 1 H, J = 17, 9.9, 6.6, 2-H). 75-MHz ^{13}C NMR: δ 18.3, 18.5, 28.4, 33.0, 38.5, 39.1, 52.6, 79.0, 81.4, 115.5, 138.6. IR (cm^{-1}): 1633, 1426, 912. Mass spectrum m/e (EI): 198 (M^+ − 28). Anal. Calcd for $C_{12}H_{18}S_2$: C, 63.66; H, 8.01. Found: C, 63.59; H, 8.03.

Synthesis of Oxathiolane 13. Oxathiolane **13** was prepared from 1-decen-6-yl-10-al in 76% yield by following the same procedure used to prepare dithiolane **12** and 2-mercapto-2-methyl-1-propanol.[21] 300-MHz ^{1}H NMR: δ 1.45 and 1.46 both (s, 3 H, CH_3), 1.56 (tt, 2 H, J = 7.2, 7.2, 4-H), 1.94 (ABtd, 1 H, J_{AB} = 13.8, J = 7.2, 6, 9-H), 2.07 (obscured ABtd, 1 H, J_{AB} = 13.8, J = 7.2, 6, 9′-H), 2.11–2.19 (m, 4 H, 3-H, 3′-H, 5-H/8-H), 2.31 (tt, 2 H, J = 7.5, 2.4, 5-H/8-H), 3.57 (AB, 1 H, J = 9.5, OC*H*H), 3.83 (AB, 1 H, J = 9.5, OCH*H*), 4.97 (dm, 1 H, J = 9, 1-H), 5.02 (ddt, 1 H, J = 17, 1.5, 1.5, 1′-H), 5.40 (t, 1 H, J = 6.0, 10-H), 5.79 (ddt, 1 H, J = 17, 9.9, 7.2, 2-H). IR (cm^{-1}): 1634. Mass spectrum m/e (CI: isobutane): 253 (M^+ + 1). Anal. Calcd for $C_{14}H_{22}OS$: C, 70.54; H, 9.30. Found: C, 70.25; H, 9.29.

Synthesis of 11-(Ethylthio)-1-undecen-6-yne (14). Thioether **14** was prepared from 1-(*tert*-butyldimethylsiloxy)-5-hexyne and 4-pentenyl iodide following the same stepwise procedure used for the synthesis of 9-(ethylthio)-1-nonen-6-yne (**10**). 300-MHz ^{1}H NMR: δ 1.25 (t, 3 H, J = 7.1, CH_3), 1.58 (m, 4 H), 1.69 (m, 2 H), 2.16 (m, 6 H), 2.53 (q, 2 H, J = 7.1, CH_2CH_3), 2.53 (t, 2 H, J = 7.1, 11-H), 4.96 (obscured ddt, 1 H, J = 10.4, 2.2, 1.1, 1-H), 5.02 (obscured ddt, 1 H, J = 17, 2.2, 1.6, 1′-H), 5.80 (ddt, 1 H, J = 17, 10.4, 6.6, 2-H). 75-MHz ^{13}C NMR: δ 14.9, 18.3, 18.5, 28.3, 28.5, 28.8, 31.3, 33.0, 80.2, 80.5, 115.4, 138.5. IR (cm^{-1}): 1633. Mass spectrum m/e (CI: isobutane): 211 (M^+ + 1, 100).

Synthesis of 8-(Ethylthio)-1-octen-6-yne (15). Thioether **15** was prepared from 1-(*tert*-butyldimethylsiloxy)-2-propyne and 4-pentenyl iodide following the same stepwise procedure used for the synthesis of 9-(ethylthio)-1-nonen-6-yne (**10**). 300-MHz ^{1}H NMR: δ 1.29 (t, 3 H, J = 7.1, 10-H), 1.59 (tt, 2 H, J = 7.1, 7.1, 4-H), 2.14 (obscured dtm, 2 H, J = 7.1, 6.6, 3-H), 2.21 (obscured tt, 2 H, J = 7.1, 2.7, 5-H), 2.69 (q, 2 H, J = 7.1, 9-H), 3.27 (t, 2 H, J = 2.2, 8-H), 4.98 (obscured dm, 1 H, J = 9.9, 1-H), 5.04 (obscured ddt, 1 H, J = 17, 2.2, 1.6, 1′-H), 5.79 (ddt, 1 H, J = 17, 9.9, 6.6, 2-H). 75-MHz ^{13}C NMR: δ 14.4, 18.4, 19.5, 25.6, 28.2, 33.0, 76.4, 83.2, 115.6, 138.5. IR (cm^{-1}): 1633. Mass spectrum m/e (CI: isobutane): 169 (M^+ + 1, 100).

Synthesis of 1-Nonen-6-yn-9-al Diethyl Acetal (31). Alkylation of 3-butynal diethyl acetal (Aldrich Chemical Co.) with 4-pentenyl iodide following the same procedure as described for the synthesis of 1-undecen-6-yne (**2**) gave 1-nonen-6-yn-9-al diethyl acetal, (**31**), in 64% yield after chromatography (eluent 1:14 ethyl acetate/hexane) and Kugelrohr distillation. 300-MHz ^{1}H NMR: δ 1.21 (t, 6 H, J = 7.1, $(OCH_2CH_3)_2$), 1.57 (tt, 2 H, J = 7.1, 7.1, 4-H), 2.13 (m, 2 H, 3-H), 2.17 (obscured tt, 2 H, J = 7.1, 2.75, 5-H), 2.48 (dt, 2 H, J = 5.5, 2.75, 8-H), 3.56 (ABq, 2 H, J_{AB} = 9.9, J = 7.1, $(OCHHCH_3)_2$), 3.67 (ABq, 2 H, J_{AB} = 9.9, J = 7.1, $(OCHHCH_3)_2$), 4.61 (t, 1 H, J = 5.5, 9-H), 4.96 (obscured dm, 1 H, J = 10, 1-H), 5.02 (obscured ddt, 1 H, J = 17, 1.6, 1.6, 1′-H), 5.79 (ddt, 1 H, J = 17, 10.4, 6.6, 2-H). 75-MHz ^{13}C NMR: δ 15.3, 18.3, 25.2, 28.3, 32.9, 61.9, 75.9, 81.8, 101.7, 115.4, 138.5. IR (cm^{-1}): 1630. Mass spectrum m/e (EI): 103 (M^+ − 107). Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.11; H, 10.45.

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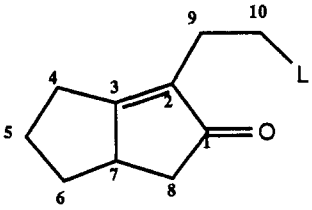


Figure 2. Numbering scheme for the cyclopentenones.

Data for Cyclopentenones 16–32. All enones with the exception of the amines **23** and **24** were prepared according to the general procedures listed below. Due to problems associated with the preparation of cobalt complexes bearing amine functionalities, the amines **23** and **24** were synthesized using preformed cobalt complexes which were prepared by the procedure described below. The numbering scheme for the cyclopentenones is shown in Figure 2.

Thermal Cyclizations (Table I): General Procedure. To a solution of alkyne **12** (105 mg, 0.47 mmol) in toluene (2 mL) was added dicobalt octacarbonyl (192 mg, 0.56 mmol), and the mixture was stirred at room temperature for 1 h (or until complex formation was complete by TLC). Toluene (21 mL) was added and the reaction mixture stirred at 71 °C (oil bath temperature) until the alkyne cobalt complex completely disappeared by TLC (1.2 h). Filtration through a silica gel plug (eluent 1:4 ethyl acetate/hexane) gave pure cyclopentenone **27** (87 mg, 75%).

Amine Oxide Promoted Cyclizations (Table II): General Procedure. To a solution of alkyne **12** (139 mg, 0.61 mmol) in methylene chloride (3 mL) was added dicobalt octacarbonyl (252 mg, 0.74 mmol), and the solution was stirred at room temperature for 1 h. The solution was diluted with methylene chloride (28 mL) and THF (31 mL). *N*-Methylmorpholine *N*-oxide monohydrate[12] (0.99 g, 7.3 mmol) was added, as a solid, and the reaction monitored by TLC. When no starting complex remained (27 h), the solution was filtered through a silica gel plug. This gave alkyne **12** (9 mg, 7%) and cyclopentenone **27** (115 mg, 74%).

Preparation of Amino Alkyne Complexes. Hydrogen chloride was bubbled through a solution of amine **23** (245 mg, 1.37 mmol) in ether (5 mL) in a centrifuge tube until the amine salt precipitated as an oil. The ether was decanted and the oil shaken with ether. The resultant solid was washed once with ether, the flask centrifuged, and the ether decanted. The solid was dissolved in methylene chloride (5 mL), and dicobalt octacarbonyl (515 mg, 1.5 mmol) was added. When complex formation was complete, the solution was diluted with methylene chloride and neutralized with aqueous sodium carbonate solution. The organic layer was washed once with water, dried over magnesium sulfate, and concentrated under reduced pressure without heat, leaving the alkyne complex (462 mg, 73%) as a bright red oil.

Cyclopentenone 16. 300-MHz ^{1}H NMR: δ 1.04 (dddd, 1 H, J = 11.5, 11.5, 11.5, 8.8, 6-H), 1.73 and 1.74 both (tt, 2 H, J = 7.1, 7.1, 10-H), 1.90–2.26 (m, 5 H), 2.06 (s, 3 H, SCH_3), 2.31 (ABt, 1 H, J_{AB} = 14.3, J = 7.1, 9-H), 2.40–2.56 (m, 4 H), 2.61 (dd, 1 H, J = 18, 6, 8-H), 2.74 (m, 1 H, 7-H). 75-MHz ^{13}C NMR: δ 15.5, 23.1, 25.4, 25.9, 27.5, 31.5, 34.1, 41.9, 44.7, 135.9, 185.1, 211.3. IR (cm^{-1}): 1694, 1652. Mass spectrum m/e (EI): 210 (M^+). Anal. Calcd for $C_{12}H_{18}OS$: C, 68.53; H, 8.63. Found: C, 68.28; H, 8.60.

Cyclopentenone 17. 300-MHz ^{1}H NMR: δ 0.88 (t, 3 H, J = 7.1, H-12), 1.04 (dddd, 1 H, J = 12.1, 12.1, 11, 8.3, 6-H), 1.29 (qt, 2 H, J = 7.1, 7.1, 11-H), 1.40 (m, 2 H, 10-H), 1.88–2.29 (m, 6 H), 2.50 (m, 2 H), 2.61 (dd, 1 H, J = 18.1, 6.6, 8-H), 2.73 (m, 1 H, 7-H). 75-MHz ^{13}C NMR: δ 14.0, 22.8, 23.8, 25.3, 25.9, 30.4, 31.6, 42.0, 44.7, 136.9, 184.4, 211.6. IR (cm^{-1}): 1697, 1653. Mass spectrum m/e (EI): 178 (M^+). Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.69; H, 10.25.

Cyclopentenone 18. 300-MHz ^{1}H NMR: δ 1.07 (dddd, 1 H, J = 12.1, 12.1, 11, 8.3, 6-H), 1.90–2.20 (m, 4 H), 2.41 (ABdddd, 1 H, J_{AB} = 14.8, J = 6.1, 1.1, 1.1, 1.1, 9-H), 2.54–2.70 (m, 4 H), 2.80 (m, 1 H, 7-H), 3.75–4.02 (m, 4 H, OCH_2CH_2O), 5.02 (dd, 1 H, J = 5.5, 5.0, 10-H). 75-MHz ^{13}C NMR: δ 25.7, 25.8, 29.2, 31.4, 41.8, 45.1, 65.2, 65.2, 103.2, 131.3, 187.8, 210.8. IR (cm^{-1}): 1694, 1651. Mass spectrum m/e (EI): 208 (M^+), 73.

Cyclopentenone 19. 300-MHz ^{1}H NMR ($CDCl_3$): δ 1.06 (dddd, 1 H, J = 11.5, 11.5, 11.5, 8.2, 6-H), 1.16 (dd, 3 H, J = 7.1, 6.6, 12-H), 1.89–2.20 (m, 4 H), 2.36 (ABt, 1 H, J_{AB} = 14, J = 7, 9-H), 2.46–2.59 (m, 3 H), 2.62 (dd, 1 H, J = 18, 6.6, 8-H), 2.76 (bm, 1 H, 7-H), 3.48 (t, 2 H, J = 7.1, 10-H), 3.40–3.55 (m, 2 H, 11-H). 500-MHz ^{1}H NMR (C_6D_6): δ 0.47 (dddd, 1 H, J = 11.45, 11.45, 11.45, 8.25), 1.01 (t, 3 H,

J = 6.9, 12-H), 1.38 (ABddd, 1 H, J_{AB} = 24.3, J = 11.0, 7.3, 7.3), 1.45–1.55 (m, 2 H), 1.70 (ABd, 1 H, J_{AB} = 17.9, J = 3.7, 8-H), 1.98–2.14 (m, 3 H), 2.32 (ABd, 1 H, J_{AB} = 17.4, J = 6.4, 8′-H), 2.37 (ABt, 1 H, J_{AB} = 14.1, J = 6.4, 9-H), 2.60 (ABt, 1 H, J_{AB} = 13.7, J = 6.4, 9′-H), 3.20 (q, 2 H, J = 6.8, 11-H), 3.42 (ABt, 1 H, J_{AB} = 9.1, J = 6.8, 10-H), 3.46 (ABt, 1 H, J_{AB} = 9.1, J = 6.4, 10′-H). 75-MHz ^{13}C NMR: δ 15.4, 24.9, 25.5, 25.9, 31.5, 41.9, 44.9, 66.3, 68.7, 133.6, 186.5, 211.3. IR (cm^{-1}): 1696, 1656. Mass spectrum m/e (EI): 194 (M^+).

Cyclopentenone 20: 1:1 isomer mixture. 300-MHz ^{1}H NMR: δ 1.04 and 1.08 both (dddd, 1 H, J = 11.5, 11.5, 11.5, 8.3, 6-H), 1.63 (ABtt, 1 H, J_{AB} = 14.3, J = 2.75, 2.2, 12_{eq}-H), 1.80–2.28 (m, 6 H), 2.39 (ABd, 1 H, J_{AB} = 13.7, J = 7.1, 8-H), 2.50–2.85 (m, 5 H), 2.95 (ddt, 1 H, J = 13.2, 12.6, 2.2, 11_{ax}-H), 3.54 and 3.56 both (ddd, 1 H, J = 12.6, 12.1, 2.2, 13_{ax}-H), 4.09 (ABm, 1 H, J = 12.1, 13_{eq}-H), 4.94 and 4.95 both (dd, 1 H, J = 7.7, 6.0, 10-H). 75-MHz ^{13}C NMR: δ 25.8, 26.0, 28.0, 28.1, 31.4, 31.4, 31.4, 31.4, 41.8, 41.9, 45.0, 70.4, 81.8, 82.1, 131.5, 131.7, 187.8, 188.1, 210.8, 210.9. IR (cm^{-1}): 1696, 1654. Mass spectrum m/e (EI): 238 (M^+). Anal. Calcd for $C_{13}H_{18}O_2S$: C, 65.51; H, 7.61. Found: C, 65.57; H, 7.65.

Cyclopentenone 21. 300-MHz ^{1}H NMR: δ 1.07 (dddd, 1 H, J = 11.5, 11.5, 11.5, 8.8, 6-H), 1.90–2.20 (m, 4 H), 2.45–2.72 (m, 4 H), 2.79 (m, 1 H, 7-H), 2.89 (dd, 1 H, J = 13.2, 5.5), 3.00 (m, 2 H), 3.78 (m, 1 H, 12-H), 4.29 (m, 1 H, 12′-H), 5.26 (m, 1 H, 10-H). 75-MHz ^{13}C NMR: δ 25.8, 25.9, 25.9, 31.4, 31.7, 31.7, 32.9, 33.0, 41.8, 41.8, 45.0, 71.5, 71.6, 85.3, 85.7, 132.6, 132.7, 187.6, 210.7. IR (cm^{-1}): 1696, 1653. Mass spectrum m/e (EI): 224 (M^+), 196. Anal. Calcd for $C_{12}H_{16}O_2S$: C, 64.25; H, 7.19. Found: C, 64.15; H, 7.20.

Cyclopentenone 22. 300-MHz ^{1}H NMR: δ 1.09 (dddd, 1 H, J = 11.5, 11.5, 11.5, 8.8, 6-H), 1.99–2.25 (m, 4 H), 2.50–2.70 (m, 4 H), 2.77 (dd, 1 H, J = 13.7, 7.1, 8-H), 2.81 (m, 1 H, 7-H), 3.14–3.30 (m, 4 H, SCH_2-CH_2S), 4.76 (t, 1 H, J = 7.14, 10-H). 75-MHz ^{13}C NMR: δ 25.8, 25.9, 31.5, 34.5, 38.6, 38.7, 41.9, 45.0, 52.4, 134.3, 187.4, 210.7. IR (cm^{-1}): 1691, 1652. Mass spectrum m/e (EI): 240 (M^+). Anal. Calcd for $C_{12}H_{16}OS_2$: C, 59.98; H, 6.72. Found: C, 59.94; H, 6.73.

Cyclopentenone 23. 500-MHz ^{1}H NMR ($CDCl_3$): δ 1.04 (dddd, 1 H, J = 11.8, 11.8, 11.8, 8.24, 6-H), 1.58 (ABtt, 1 H, J_{AB} = 8.7, J = 6.4, 6.4, 10-H), 1.97 (ddddd, 1 H, J = 12.8, 12.3, 10.5, 8.7, 6.9, 5-H), 2.02 (dd, 1 H, J = 17.9, 3.2, 8-H), 2.0–2.15 (m, 4 H), 2.19 (s, 6 H, $N(Me)_2$), 2.22 (m, 2 H), 2.51 (m, 2 H, 4-H), 2.60 (dd, 1 H, J = 17.9, 6.41, 8′-H), 2.73 (m, 1 H, 7-H). 75-MHz ^{13}C NMR: δ 21.8, 25.3, 25.9, 26.3, 31.5, 42.0, 44.7, 45.7, 59.8, 136.5, 184.6, 211.3. IR (cm^{-1}): 1696, 1652. Mass spectrum m/e (CI: isobutane): 208 (M^+ + 1, 100).

Cyclopentenone 24. 500-MHz ^{1}H NMR (C_6D_6): δ 0.68 (dddd, 1 H, J = 11.9, 11.9, 11.9, 7.8, 6-H), 1.59 (ddddd, 1 H, J = 12.8, 12.3, 10.5, 8.7, 6.9, 5-H), 1.69 (m, 1 H, 5′-H), 1.72 (m, 1 H, 6′-H), 1.92 (dd, 1 H, J = 17.4, 3.2, 8-H), 2.19 (m, 2 H, 4-H), 2.28 (s, 6 H, $N(Me)_2$), 2.30 (m, 1 H, 7-H), 2.43 (dtddd, 1 H, J = 14, 6.7, 2, 1, 1, 9-H), 2.58 (t, 2 H, J = 7.3, 10-H), 2.69 (dt, 1 H, J = 13.9, 6.9, 9′-H), 2.81 (dd, 1 H, J = 17.4, 6.4, 8′-H). 75-MHz ^{13}C NMR ($CDCl_3$): δ 22.1, 25.4, 25.9, 31.5, 41.9, 44.8, 45.5, 57.9, 134.8, 185.3, 211.1. IR (cm^{-1}): 1696, 1652. Mass spectrum m/e (CI: isobutane): 194 (M^+ + 1, 100).

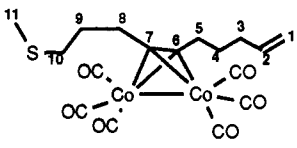
Cyclopentenone 25. 300-MHz ^{1}H NMR: δ 1.07 (dddd, 1 H, J = 11.5, 11.5, 11.5, 8.3, 6-H), 1.23 (t, 3 H, J = 7.7, 12-H), 1.90–2.20 (m, 5 H), 2.37 (ABt, 1 H, J_{AB} = 14.3, J = 7.1, 9-H), 2.45–2.70 (m, 7 H), 2.77 (m, 1 H, 7-H). 75-MHz ^{13}C NMR: δ 14.9, 24.5, 25.5, 25.8, 26.0, 30.1, 31.4, 41.9, 44.8, 134.9, 185.9, 210.9. IR (cm^{-1}): 1696, 1652. Mass spectrum m/e (EI): 210 (M^+). Anal. Calcd for $C_{12}H_{18}OS$: C, 68.53; H, 8.63. Found: C, 68.42; H, 8.63.

Cyclopentenone 26. 300-MHz ^{1}H NMR: δ 1.10 (dddd, 1 H, J = 11.5, 11.5, 11.5, 8.3, 6-H), 1.84 (dtt, 1 H, J = 14.8, 8.8, 5.5, 12-H), 1.90–2.17 (m, 5 H), 2.45–2.90 (m, 10 H), 4.32 (t, 1 H, J = 7.7, 10-H). 75-MHz ^{13}C NMR: δ 25.8, 24.8, 26.0, 30.2, 30.3, 30.3, 31.4, 41.9, 44.9, 45.9, 132.2, 187.6, 210.7. IR (cm^{-1}): 1696, 1653. Mass spectrum m/e (EI): 254 (M^+). Anal. Calcd for $C_{13}H_{18}OS_2$: C, 61.40; H, 7.14. Found: C, 61.49; H, 7.12.

Cyclopentenone 27. 300-MHz ^{1}H NMR: δ 1.06 (dddd, 1 H, J = 11.5, 11.5, 11.5, 8.3), 1.90–2.20 (m, 6 H), 2.26 (ABt, 1 H, J_{AB} = 14.3, J = 7.1, 9-H), 2.38 (ABt, 1 H, J_{AB} = 14.3, J = 7.1, 9′-H), 2.55 (m, 2 H), 2.62 (ABd, 1 H, J_{AB} = 17.5, J = 6, 8-H), 2.75 (m, 1 H, 7-H), 3.12–3.28 (m, 4 H, SCH_2CH_2S), 4.38 (t, 1 H, J = 7.1, 11-H). 75-MHz ^{13}C NMR: δ 23.8, 25.4, 25.9, 31.5, 37.6, 38.6, 42.0, 44.8, 53.5, 135.2, 185.3, 211.0. IR (cm^{-1}): 1691, 1651. Mass spectrum m/e (EI): 254 (M^+). Anal. Calcd for $C_{13}H_{18}OS_2$: C, 61.38; H, 7.13. Found: C, 61.48; H, 7.14.

Cyclopentenone 28: 1:1 isomer mixture. 500-MHz ^{1}H NMR: δ 1.07 and 1.08 both (dddd, 1 H, J = 11.8, 11.8, 11.8, 8), 1.46 (s, 6 H, $C(CH_3)_2$), 1.86–2.44 (m, 9 H), 2.54 (m, 1 H), 2.63 (dd, 1 H, J = 18, 6.5, 8-H), 2.76 (m, 1 H, 7-H), 3.55 (d, 1 H, J = 9, OC*H*H), 3.84 (d, 1 H, J = 9, OCH*H*), 5.21 and 5.22 both (t, 1 H, J = 6, 10-H). IR (cm^{-1}): 1696, 1652. Mass spectrum m/e (EI): 266 (M^+), 210.

Table VII



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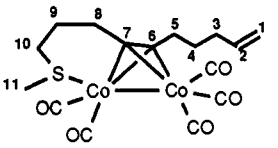

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	75-MHz ^{13}C NMR (C_6D_6)				500-MHz ^{1}H NMR (C_6D_6)				
	C-1	C-2	C-10	C-11	H-1	H-1′	H-2	H-10	H-11
1	115.4	138.5	33.3	15.0	4.99	5.01	5.67	2.38	1.73
34	115.7	138.2	33–34	14.8	4.95	5.00	5.66	2.21	1.75
35	115.4	138.8	38.1	25.5	4.99	5.07	5.77	1.3–1.9	1.40

Cyclopentenone 29. 500-MHz ^{1}H NMR (C_6D_6): δ 0.64 (dddd, 1 H, J = 11.7, 11.7, 11.7, 7.8, 6-H), 1.21 (t, 3 H, J = 7.3, 14-H), 1.58 (ddddd, 1 H, J = 12.8, 12.3, 10.5, 8.7, 6.9, 5-H), 1.65 (m, 1 H, 5′-H), 1.65 (tt, 2 H, J = 7.3, 7.3, 11-H), 1.67 (tt, 2 H, J = 7.3, 7.3, 10-H), 1.73 (m, 1 H, 6′-H), 1.88 (dd, 1 H, J = 17.9, 3.2, 8-H), 2.14 (m, 2 H, 4-H), 2.20 (dt broad, 1 H, J = 14.6, 8.2, 9-H), 2.26 (m, 1 H, 7-H), 2.42 (q, 2 H, J = 7.3, 13-H), 2.46 (dt, 1 H, J = 14.2, 7.3, 9′-H), 2.50 (t, 2 H, J = 7.3, 12-H), 2.52 (dd, 1 H, J = 17.4, 6.4, 8′-H). 75-MHz ^{13}C NMR ($CDCl_3$): δ 15.0, 23.6, 25.3, 25.9, 26.0, 27.4, 29.7, 31.5, 42.0, 44.7, 136.5, 184.6, 211.3. IR (cm^{-1}): 1695, 1652, 735. Mass spectrum m/e (CI: isobutane): 239 (M^+ + 1, 100). Anal. Calcd for $C_{14}H_{22}OS$: C, 70.54; H, 9.30. Found: C, 70.92; H, 9.48.

Cyclopentenone 30. 500-MHz ^{1}H NMR (C_6D_6): δ 0.62 (dddd, 1 H, J = 11.6, 11.6, 11.6, 8.3, 6-H), 1.29 (t, 3 H, J = 7.3, 11-H), 1.54 (m, 1 H, 5-H), 1.67 (m, 2 H, 5′-H, 6′-H), 1.86 (dd, 1 H, J = 17.4, 2.8, 8-H), 2.21 (m, 1 H, 7-H), 2.22 (m, 1 H, 4-H), 2.32 (ddd, 1 H, J = 18.9, 8.3, 8, 4′-H), 2.48 (dd, 1 H, J = 17.9, 6.4, 8′-H), 2.54 (m, 2 H, 10-H), 3.33 (ABm, 1 H, J = 13.3, 9-H), 3.49 (ABm, 1 H, J = 13.8, 9′-H). 75-MHz ^{13}C NMR ($CDCl_3$): δ 14.6, 23.9, 25.6, 25.9, 26.5, 31.4, 41.8, 44.9, 133.7, 186.6, 209.8. IR (cm^{-1}): 1695, 1651, 734. Mass spectrum m/e (CI: isobutane): 197 (M^+ + 1, 100). Anal. Calcd for $C_{11}H_{16}OS$: C, 67.30; H, 8.22. Found: C, 67.40; H, 8.16.

Cyclopentenone 32. 300-MHz ^{1}H NMR: δ 1.04 (dddd, 1 H, J = 11.5, 11.5, 11.5, 8.4, 6-H), 1.14 (t, 3 H, J = 7.1, CH_2CH_3), 1.15 (t, 3 H, J = 7.1, CH_2CH_3), 1.90–2.20 (m, 4 H), 2.39 (ABdm, 1 H, J_{AB} = 13.2, J = 6.6, 9-H), 2.50–2.68 (m, 4 H), 2.77 (m, 1 H, 7-H), 3.43 (ABq, 1 H, J_{AB} = 3.8, J = 7.1, $OCHHCH_3$), 3.47 (ABq, 1 H, J_{AB} = 3.8, J = 7.1, $OCHHCH_3$), 3.56 (ABq, 1 H, J_{AB} = 3.8, J = 7.1, $OCHHCH_3$), 3.66 (ABq, 1 H, J_{AB} = 3.8, J = 7.1, $OCHHCH_3$), 4.61 (t, 1 H, J = 5.5, 10-H).

Isolation of Complex 35. To a solution of alkyne **1** (31 mg, 0.17 mmol) in methylene chloride (8.4 mL) was added dicobalt octacarbonyl (63 mg, 0.18 mmol), and the solution was stirred at room temperature until complex formation was complete (15 min). *N*-Methylmorpholine *N*-oxide monohydrate[12] (0.2 g, 1.5 mmol) was added, and the solution was stirred for a further 5 min. TLC now showed almost complete formation of complex **35**. Filtration through an alumina plug, followed by concentration under reduced pressure, chromatography on silica gel (eluent 1:14 ethyl acetate/hexane), and concentration under reduced pressure, gave complex **35** (58 mg, 79%). NMR spectra of this complex were obtained only after filtration of a solution of complex **35** through alumina directly into an NMR tube containing a magnetic stir bar with the stir bar being removed just prior to inserting the tube into the NMR spectrometer. (The spectrum was recorded immediately.) (See Table VII.)

Complex 34. 300-MHz ^{1}H NMR ($CDCl_3$): δ 1.73 (tt, 2 H, J = 7.7, 7.7, 4-H), 1.93 (tt, 2 H, J = 7.7, 7.1, 9-H), 2.12 (s, 3 H, 11-H), 2.21 (tdm, 2 H, J = 7.1, 7.1, 3-H), 2.63 (t, 2 H, J = 7.1, 10-H), 2.82 (dd, 2 H, J = 7.7, 7.7, 5-H), 2.93 (dd, 2 H, J = 7.7, 7.7, 8-H), 5.01 (dm, 1 H, J = 9.9, 1-H), 5.06 (dm, 1 H, J = 17, 1′-H), 5.84 (ddt, 1 H, J = 17, 9.9, 7.1, 2-H). 500-MHz ^{1}H NMR (C_6D_6): δ 1.60 (tt, 2 H, J = 7.8, 7.3, 4-H),

1.73 (tt, 2 H, J = 7.5, 7.3, 9-H), 1.74 (s, 3 H, 11-H), 1.92 (tdm, 2 H, J = 7.3, 6.4, 3-H), 2.21 (t, 2 H, J = 6.9, 10-H), 2.57 (dd, 2 H, J = 8.3, 8.3, 5-H), 2.68 (dd, 2 H, J = 7.8, 7.8, 8-H), 4.95 (db, 1 H, J = 10, 1-H), 5.00 (db, 1 H, J = 17, 1'-H), 5.66 (ddt, 1 H, J = 17, 10, 6.9, 2-H). 75-MHz ^{13}C NMR ($CDCl_3$): δ 15.5, 30.9, 30.9, 33.0, 33.6, 33.7, 34.1, 99.1, 99.9, 115.8, 138.3, 201 (broad). 75-MHz ^{13}C NMR (C_6D_6): δ 14.8, 30.8, 31.0, 32.7, 33.4, 33.6, 33.7, 99.6, 100.1, 115.7, 138.2.

Complex 35. 500-MHz ^{1}H NMR ($CDCl_3$): δ 1.74 (m, 2 H), 2.10 (bs, 2 H), 2.20 (m, 2 H), 2.25 (s, 3 H, 11-H), 2.25 (m, 1 H), 2.40 (m, 1 H), 2.72 (m, 3 H), 2.94 (bs, 2 H), 4.99 (d, 1 H, J = 10, 1-H), 5.06 (d, 1 H, J = 17, 1'-H), 5.85 (m, 1 H, 2-H). 500-MHz ^{1}H NMR (C_6D_6): δ 1.36–1.87 (bm, 2 H, 9-H, 10-H), 1.40 (s, 3 H, 11-H), 1.46 (bm, 2 H, 9'-H, 10'-H), 1.77 (tt, 1 H, J = 7.3, 7.3, 4-H), 1.79 (tt, 1 H, J = 7.3, 7.3, 4'-H), 2.05 (dtm, 2 H, J = 7.3, 6.9, 3-H), 2.47 (ABm, 1 H, J = 15, 8-H), 2.50 (ABdd, 1 H, J_{AB} = 15, J = 7.3, 3.6, 8'-H), 2.63 (ABdd, 1 H, J_{AB} = 16, J = 9.1, 6.4, 5-H), 2.70 (ABdd, 1 H, J_{AB} = 15, J = 9.6, 5'-H), 4.99 (ddt, 1 H, J = 10, 2.3, 1.1, 1-H), 5.07 (ddt, 1 H, J = 17, 1.8, 1.8, 1'-H), 5.77 (ddt, 1 H, J = 17, 10, 6.4, 2-H). 75-MHz ^{13}C NMR ($CDCl_3$): δ 26.5, 27.4, 30.6, 33.4, 33.8, 38.8, 115.3, 139.0. 75-MHz ^{13}C NMR (C_6D_6): δ 25.5, 27.2, 30.8, 33.4, 33.8, 38.1, 115.4, 138.8. Due to the apparent instability of complex **35** in solution, high dilution was required in order to maintain the NMR spectrometer lock and obtain the carbon spectrum. As a result, only eight carbons could be observed.

Decomplexation of Alkynes (Table III): General Procedure. All of the alkynes were commercially available from Aldrich Chemical Company. To a solution of 10-dodecyn-1-ol dicobalt hexacarbonyl (0.573 g, 1.3 mmol) in a 1:1 mixture of THF/methylene chloride (24.4 mL) was added solid *N*-methylmorpholine *N*-oxide monohydrate[12] (1.65 g, 12 mmol), and the solution was stirred at room temperature. After 10 min, the solution had turned bright purple, and no starting cobalt complex was visible by TLC. Magnesium sulfate was added to the mixture, and after two minutes, filtration through a silica gel plug gave pure 10-dodecyn-1-ol (0.2 g, 90%).

Table IV. The reactions were carried out using the same procedure that was used for reactions in Table V.[12]

Table V: General Procedure. To a solution of alkyne **41** (124 mg, 1 mmol) in hexane (4 mL) was added dicobalt octacarbonyl (376 mg, 1.1 mmol), and the solution was stirred at room temperature until complex formation was complete (15 min). Filtration through a silica gel plug (eluent hexane) followed by concentration under reduced pressure gave the alkyne cobalt complex (402 mg, 98%). The cobalt complex was dissolved in 1:1 THF/methylene chloride (19.6 mL), and solid *N*-methylmorpholine *N*-oxide monohydrate[12] (1.32 g, 9.8 mmol) was added. The solution was stirred at room temperature until it turned bright purple and no starting cobalt complex was visible by TLC (18 min). Magnesium sulfate was added to the mixture, and after two minutes, filtration through a silica gel plug gave alkyne **41** (14 mg, 11%) and cyclopentenone **47** (109 mg, 73%).

Alkyne 41. 300-MHz ^{1}H NMR: δ 2.41 (tq, 2 H, J = 7.14, 2.75, 4-H), 2.78 (t, 3 H, J = 2.74, 1-H), 3.51 (t, 2 H, J = 7.14, 5-H), 4.00 (ddd, 2 H, J = 5.5, 1.65, 1.1, 6-H), 5.18 (ddt, 1 H, J = 10.45, 1.65, 1.1, 8-H), 5.27 (ddt, 1 H, J = 17.6, 1.65, 1.65, 8'-H), 5.91 (ddt, 1 H, J = 17.0, 10.45, 5.5, 7-H). 75-MHz ^{13}C NMR: δ 3.6, 20.3, 69.1, 72.2, 76.2, 117.5, 117.6, 135.3. IR (cm^{-1}): 1638. Mass spectrum m/e (EI): 109 (M^+ – 15). Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.45; H, 9.78.

Cyclopentenone 47. 300-MHz ^{1}H NMR: δ 1.71 (dd, 3 H, J = 1.65, 1.1, CH_3), 1.84 (ABd, 1 H, J_{AB} = 18.7, J = 2.2, OCH_2CHCHH), 2.44 (ABd, 1 H, J_{AB} = 18.7, J = 6.6, OCH_2CHCHH), 2.56 (ABdd, 1 H, J_{AB} = 13.7, J = 12, 6.6, $OCH_2CH_{ax}HC$), 2.72 (ABd, 1 H, J_{AB} = 13.7, J = 2.2, $OCH_2CHH_{eq}C$), 2.82–2.94 (m, 1 H, CH), 3.00 (dd, 1 H, J = 11.6, 9.9, $OCH_{ax}HCH$), 3.34 (ddd, 1 H, J = 12.1, 12.1, 2.8, $OCH_{ax}HCH_2C$), 4.21 (dd, 1 H, J = 11, 6.6, $OCHH_{eq}CH_2C$), 4.26 (dd, 1 H, J = 10, 6.0, $OCHH_{eq}CH$). 75-MHz ^{13}C NMR: δ 7.7, 30.1, 36.5, 40.1, 68.1, 74.4, 134.4, 171.3, 208.3. IR (cm^{-1}): 1696, 1652. Mass spectrum m/e (EI): 152 (M^+, 100). Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 71.17; H, 8.00.

Table VI: General Procedure. The reactions in Table VI were carried out using the procedure described for reactions in Table V (solid *N*-methylmorpholine *N*-oxide monohydrate[12]) except that (1) the cobalt alkyne complexes were isolated and purified prior to cycloaddition and (2) different solvents were used (0.02 M).

Enyne 48. 300-MHz ^{1}H NMR ($CDCl_3$): δ 0.98 (t, 3 H, J = 7.0, CH_2CH_3), 1.53 (tq, 2 H, J = 7.0, 7.0, $CH_2CH_2CH_3$), 2.19 (tt, 2 H, J = 7.0, 2.2, $CCH_2CH_2CH_3$), 4.05 (ddd, 2 H, J = 6.0, 1.6, 1.6, OCH_2CHCH_2), 4.14 (t, 2 H, J = 2.2, OCH_2CC), 5.2 (ddt, 1 H, J = 10.4, 1.6, 1.6, OCH_2CHCHH), 5.3 (ddt, 1 H, J = 17.0, 1.6, 1.6, OCH_2CHCHH), 5.91 (ddt, 1 H, J = 17.0, 10.4, 6.0, OCH_2CHCHH). 75-MHz ^{13}C NMR: δ 13.4, 20.8, 22.1, 57.8, 70.5, 76.3, 86.9, 117.6, 134.9. Anal. Calcd for $C_9H_{14}O$: C, 78.19; H, 10.23. Found: C, 78.02; H, 10.07.

Cyclopentenone 49. 500-MHz ^{1}H NMR (C_6D_6): δ 0.74 (t, 3 H, J = 7.3, CH_3), 1.30 (dtq, 1 H, J = 17.0, 7.8, 7.3, CH_3CHHCH_2), 1.34 (dtq, 1 H, J = 17.0, 7.8, 7.3, CH_3CHHCH_2), 1.52 (ABd, 1 H, J_{AB} = 17.4, J = 3.7, $CCHHCH$), 1.88 (ABtddd, 1 H, J_{AB} = 14.2, J = 7.8, 1.0, 1.0, 1.0, CH_3CH_2CHH), 2.12 (ABdd, 1 H, J_{AB} = 17.4, J = 6.8, 0.6, $CCHHCH$), 2.16 (partly obscured ABtddd, 1 H, J_{AB} = 14.2, J = 7.8, 1.0, 1.0, 1.0, CH_3CH_2CHH), 2.41 (m, 1 H, CH), 2.60 (ABd, 1 H, J_{AB} = 7.7, J = 11.0, $OCHHCH$), 3.76 (ABd, 1 H, J_{AB} = 7.7, J = 7.9, $OCHHCH$), 4.05 (ABm, 1 H, J_{AB} = 15.3, $OCHHC$), 4.13 (AB, 1 H, J_{AB} = 15.3, $OCHHC$). 75-MHz ^{13}C NMR: δ 14.0, 21.2, 26.4, 39.1, 43.6, 65.2, 72.1, 137.3, 176.7, 209.6. Mass spectrum m/e (CI: isobutane): 167 (M^+ + 1, 100).

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