cholesteryl skeleton), 2.6 (s, 3 H, CH_3S), 4.1 (m, 1 H, *H*COSOMe), 5.4 (broad signal, 1 H, HC=C-).

General Procedure for Preparation of Chiral Sulfoxides 11-27. Sulfoxides were obtained in quantitative yield by the addition of 1.2 equiv of RMgX or ArMgX to a solution of sulfinate in toluene at 0 °C. The mixture was then stirred for 1 h, quenched with saturated aqueous NH_4Cl solution, extracted with CH_2Cl_2, and purified by flash chromatography. Yields, ee's, specific rotations, absolute configurations, and comparison with literature data are collected in Tables IV and V.

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Supplementary Material Available: ^1H NMR spectra for compounds 1-10 and 30-32 (12 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Regioselectivity in the Reaction of Tantalum-Unsymmetrical Acetylene Complexes with Carbonyl Compounds. Stereoselective Preparation of 1-Alkenyl Sulfides, α,β-Unsaturated Esters, and Amides

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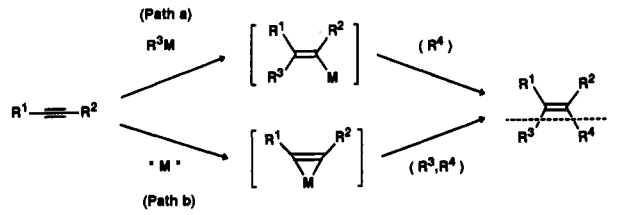
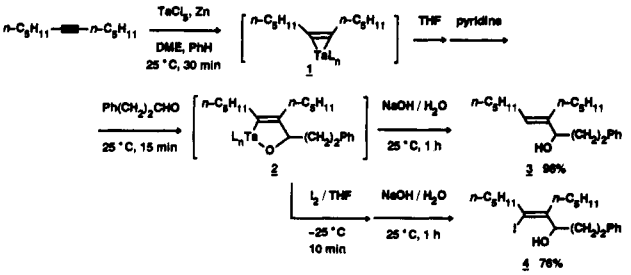
Tantalum-alkyne complexes, derived by treatment of alkynes with low-valent tantalum ($TaCl_5$ and zinc), react in situ with carbonyl compounds to give (*E*)-allylic alcohols stereoselectively. When unsymmetrical acetylenes are employed in the reaction, two regioisomeric allylic alcohols are produced. The regioselectivity of the reaction depends on the steric and electronic effects of the substituents on the acetylenes. For example, treatment of tantalum-alkyne complexes derived from methyl alkynyl sulfides with carbonyl compounds yields (*E*)-3-hydroxy-1-propenyl methyl sulfides in a regioselective manner. Tantalum-alkyne complexes derived from acetylenic esters react with carbonyl compounds regioselectively at the α-position of the esters to give *Z*-isomers of trisubstituted α,β-unsaturated esters. In contrast, tantalum-alkyne complexes derived from acetylenic amides react with carbonyl compounds predominantly at the β-position of the amides. The regioselectivity of the reaction between acetylenic amides and aldehydes, however, cannot be explained solely in terms of the steric and electronic effects of the substituents. Strong coordination of the amide group to the tantalum center could also be responsible for the observed selectivity, which is opposite to that observed with tantalum-acetylenic ester complexes.

The construction of carbon-carbon double bonds in a stereoselective manner is a fundamental but still challenging problem facing chemists, particularly in the case of tetra- and trisubstituted ethenes.[1] One attractive approach involves the introduction of two substituent units onto a readily accessible acetylene as shown in Scheme I. Carbometalation[2] or hydrometalation,[3] followed by treatment with electrophiles (path a), is a typical solution which uses this approach. Insertion of unsaturated compounds into a metal-carbon bond of a metallacyclopropene[4] (path b) provides another approach to substituted ethenes. In both cases, an unavoidable problem is control of the regiochemistry of the reaction when unsymmetrical alkynes ($R^1 \neq R^2$) are employed as starting materials. Electronic effects can be a controlling factor in the regioselectivity of the reaction. The carbometalation of acetylenic esters proceeds selectively to yield β-substituted α,β-unsaturated esters after aqueous workup.[5] Heteroatom substituents on acetylenic triple bonds can also play an important role in directing the regiochemistry. For example, hydroalumination of alkynyl sulfoxides produces α-aluminum-substituted alkenyl sulfoxides because of the strong electron-withdrawing effect of the sulfinyl group.[6] Similar effects are observed in analogous

Scheme I



Scheme II



(1) Arora, S. S.; Ugi, I. K. *Methoden der Organic Chemie*; Houben-Weyl: Stuttgart, 1972; Bd. V/1b.

(2) For reviews, see: (a) Normant, J. F.; Alexakis, A. *Synthesis* **1981**, 841. (b) Negishi, E. *Pure Appl. Chem.* **1981**, *53*, 2333. (c) Negishi, E.; Takahashi, T. *Synthesis* **1988**, 1.

(3) Davies, S. G. *Organotransition Metal Chemistry Applications To Organic Synthesis*, 1st ed.; Pergamon Press: Oxford, 1982. Mole, T.; Jeffery, E. A. *Organoaluminium Compounds*; Elsevier: Amsterdam, 1972.

(4) For representative reactions of metallacyclopropenes with unsaturated compounds, see: (a) Buchwald, S. L.; Lum, R. T.; Dewan, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7441. (b) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *Ibid.* **1987**, *109*, 2544. (c) Takahashi, T.; Swanson, D. R.; Negishi, E. *Chem. Lett.* **1987**, 623. (d) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047. (e) Hartung, J. B., Jr.; Pedersen, S. F. *J. Am. Chem. Soc.* **1989**, *111*, 5468. (f) Strickler, J. R.; Bruck, M. A.; Wexler, P. A.; Wigley, D. E. *Organometallics* **1990**, *9*, 266. (g) Strickler, J. R.; Wexler, P. A.; Wigley, D. E. *Organometallics* **1991**, *10*, 118. See also refs 7, 9, and 10.

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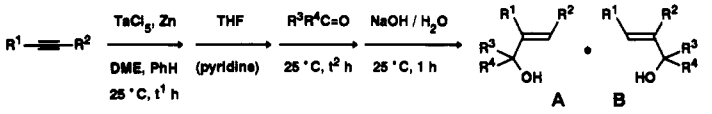
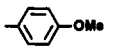
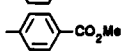
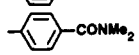
Table I. Regioselectivity of Reactions between Tantalum–Alkyne Complexes and Carbonyl Compounds[a]



run	R^1	R^2	carbonyl compds[b]	method[c]	t^1/h	t^2/h	yield[d]/%	A/B[e]
1	n-$C_{10}H_{21}$	H	A	a	0.7	0.75	48[f,g]	<1/>99
2	n-C_6H_{13}	c-C_6H_{11} (13)	C	d	1.5	0.25	80[g]	65/35 (14a)(14b)
3			D	d	1.5	0.25	73	68/32
4			E	d	1.5	0.25	83[g]	76/24
5	n-C_7H_{15}	t-Bu (6)	C	j	4.5	0.25	67[g,h]	>99/<1
6	n-C_6H_{13}	Ph (9)	C	d	1	0.25	73[g]	17/83
7	n-C_6H_{13}		C	d	0.7	0.3	84	34/66
8	n-C_6H_{13}		C	d	2	0.3	79	20/80
9	n-C_6H_{13}		C	e	0.7	2	64	25/75
10	n-C_6H_{13}		C	e	0.7	2	68	81/19
11	n-C_6H_{13}		C	e	0.5	2	62	55/45
12	n-$C_{10}H_{21}$	$SiMe_3$ (7)	C	g	1.5	0.5	77[g]	89/11
13	n-$C_{10}H_{21}$	$SiMe_2$-t-Bu (8)	C	k	3	0.5	68[g]	>99/<1
14	n-$C_{10}H_{21}$	SMe	C	e	0.2	0.5	73	>99/<1
15			E	e	0.2	0.5	77	>99/<1
16	n-$C_{10}H_{21}$	SPh (10)	C	e	0.5	0.5	85	77/23
17	c-C_6H_{11}	SMe	C	e	0.2	0.5	68	>99/<1
18	Ph	SMe	C	e	0.5	0.5	64	>99/<1
19	n-$C_{10}H_{21}$	SO_2Me	C	h	2.5	0.5	54[i]	54/46
20			E	i	2.5	0.5	62[i]	>99/<1
21	c-C_6H_{11}	SO_2Me	C	h	2.5	0.5	59[i]	39/61
22	n-$C_{10}H_{21}$	SO_2Ph	C	h	21	0.5	43[i]	28/72
23	n-$C_{10}H_{21}$	CO_2Et (11)	B	d	2[j]	0.5	76	5/95 (18a)(18b)
24			E	d	2[j]	0.5	72	3/97
25	c-C_6H_{11}	CO_2Et (12)	B	d	2[j]	0.5	76	2/98
26			E	f	2[j]	0.5	72	<1/>99
27	Ph	CO_2Et	B	d	1.5[j]	0.5	57	9/91
28	n-C_6H_{13}	$CONMe_2$	B	b	2	2[j]	79	90/10
29			E	c	2	3[j]	33	>98/<2
30	c-C_6H_{11}	$CONMe_2$	B	b	2	2[j]	73	76/24

[a] Reactions were performed on a 1.0 mmol scale at 25 °C. See Experimental Section. [b] Carbonyl compound: A, n-$C_8H_{17}CHO$; B, n-C_3H_7CHO; C, $Ph(CH_2)_2CHO$; D, c-$C_6H_{11}CHO$; E, cyclohexanone. [c] The following molar amounts of $TaCl_5$, zinc, pyridine, and a carbonyl compound were employed per mole of an acetylene. Method: a, 1.0, 1.5, 2.0, 1.2; b, 1.2, 1.8, 0, 2.0; c, 1.2, 1.8, 0, 3.0; d, 2.0, 3.0, 4.0, 1.2; e, 2.0, 3.0, 4.0, 2.0; f, 2.0, 3.0, 4.0, 2.4; g, 2.0, 3.0, 0, 1.2; h, 3.0, 4.5, 0, 2.0; i, 3.0, 4.5, 0, 4.0; j, 4.0, 6.0, 8.0, 1.2; k, 4.0, 6.0, 0, 1.2. [d] Isolated yields. [e] Regioisomeric ratios were determined by isolation, ^1H NMR, or ^{13}C NMR analysis. [f] Polymeric products of 1-dodecyne were produced in ca. 40% yield. [g] Reference 9f. [h] (Z)-2,2-Dimethyl-3-undecene was obtained in 24% yield. [i] Reduction of a sulfonyl gruop to a sulfide took place as a side reaction. [j] Reaction was conducted at 50 °C.

zirconocene reactions.[7] Alkylthio groups on the acetylenes stabilize the zirconocene–alkyne complexes and can be used to control the regiochemistry in subsequent coupling with other alkynes.

We chose the metallacyclopropene pathway (path b), focusing on tantalum–alkyne complexes[8] as a probe to carry out a detailed study of the factors which determine the regiochemical outcome of the reaction. The required tantalum–alkyne complexes can be obtained from a wide range of substituted acetylenes in a straightforward manner.[9] Typical reactions of the tantalum–alkyne complex are shown in Scheme II.[9b] Treatment of 6-dodecyne with low-valent tantalum, followed by addition of THF, pyridine, and 3-phenylpropanal, produced the oxatantalacyclopentene intermediate 2. Alkaline hydrolysis of 2 afforded the trisubstituted allylic alcohol 3 in 96% yield. The intermediate 2 was trapped with I_2 to give iodo alcohol 4 in 76% yield. Two substituent units were introduced exclusively at the cis vicinal positions, as would be expected from insertion of a carbonyl group into the tantalum–carbon bonds of complex 1.

Results and Discussion

In the case of unsymmetrical acetylenes, reactions of the tantalum–alkyne complexes with carbonyl compounds

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(9) (a) Kataoka, Y.; Takai, K.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1990**, *31*, 365. (b) Takai, K.; Kataoka, Y.; Utimoto, K. *J. Org. Chem.* **1990**, *55*, 1707. (c) Takai, K.; Miyai, J.; Kataoka, Y.; Utimoto, K. *Organometallics* **1990**, *9*, 3030. (d) Takai, K.; Tezuka, M.; Utimoto, K. *J. Org. Chem.* **1991**, *56*, 5980. (e) Kataoka, Y.; Takai, K.; Oshima, K.; Utimoto, K. *J. Org. Chem.* **1992**, *57*, 1615. (f) Kataoka, Y.; Miyai, J.; Oshima, K.; Takai, K.; Utimoto, K. *J. Org. Chem.* **1992**, *57*, 1973.

produce two regioisomeric allylic alcohols in varying ratios (Table I). The selectivity is determined by which tantalum–carbon bond of a tantalacyclopropene is subjected to insertion of a carbonyl compound. Although the tantalum–alkyne complexes derived using the $TaCl_5$–Zn system have not been characterized, the regioisomeric ratios are governed by the following factors:

Steric Effects of the Substituents on the Acetylenes. The size of the substituents on the acetylenes influences the regioselectivity of the reaction. For example, as R^2 becomes bulkier, higher regioselectivites (**A**/**B**) are obtained (runs 2 and 5). This effect appears to be the result of approach of the carbonyl compound from the less hindered side of the tantalacyclopropene.[9b,f] Tantalum complexes of 1-(trialkylsilyl)-1-alkynes reacted with aldehydes to give one of the regioisomers selectively (runs 12 and 13). Similar steric effects of the trimethylsilyl group on the regioselectivity were reported for the insertion of benzophenone into the tantalum complex, $(DIPP)_3Ta(Me_3SiC{\equiv}CMe)$ (DIPP = O-2,6-C_6H_3-*i*-Pr_2).[4f] With the sterically crowded alkynes **6**–**8**, both reactions, formation of tantalum complexes with the low-valent tantalum and insertion of aldehydes into the complexes, were retarded. Although a terminal alkyne produced significant amounts (ca. 40% yield) of polymer, insertion proceeded such that the hydrogen substituent was in the 4-position of the oxatantacyclopentene intermediate (run 1). The regioselectivities (**A**/**B**) of the insertion of carbonyl compounds into the tantalum–1-alkyne complexes are higher than those observed for insertion into the zirconocene–1-alkyne complexes.[10]

Electronic Effects of the Substituents. The reaction between 1-phenyl-1-alkyne **9** and 3-phenylpropanal took place primarily at the more sterically congested α-position of the phenyl group (run 6).[9b] This result suggests that the electronic effects of the substituents are also an important factor in determining the orientation. Although the ester and amide groups attached at the para positions of aromatic rings did not produce significant effects of the selectivities (runs 8 and 9), the ratio (**A**/**B**) increased when an electron-donating methoxy group was attached at the para position (run 7). The reactivities of acetylenes toward the low-valent tantalum in the formation of tantalum–alkyne complexes decreased in the following order: $R^1C{\equiv}CSR^2 > R^2C{\equiv}CR^2 > R^1C{\equiv}CSO_2R^2 \sim R^1C{\equiv}CCO_2R^2$. The rates of complexation decrease as the electron density of the C≡C group is decreased. In the case of an acetylene bearing and electron-donating MeS group, the reaction occurred at the β-position of the SMe group exclusively (run 14).[9c] This result stands in sharp contrast to the reaction between the zirconocene–1-(methylthio)-1-alkyne complex and carbonyl compounds, where two regioisomeric allylic alcohols are produced in approximately equal amounts.[7] Regioselectivities were also influenced by the substituent on the sulfur atom. Lower selectivities (**A**/**B**) were observed with 1-(phenylthio)-1-alkyne **10** (run 16). The resonance effect of the phenyl group weakens the effect of the sulfur.[9c] The ratios of α-adducts increased when sulfonyl-substituted acetylenes were employed (runs 19–22 except run 20 (vide infra)). When acetylenic esters were employed, one of the regioisomers **B**, generated by insertion of a carbonyl group into the tantalum–α-carbon bond of **1**, was produced with high regio- and stereocontrol (runs 23–27).[9d] The electronic effects of alkylthio and ester groups could be interpreted as indicating that new carbon–carbon bonds are formed between an electrophilic carbonyl carbon and the more "electron-rich" carbons of tantalacyclopropenes.

In contrast to the reactions of acetylenic esters, reactions of tantalum–acetylenic amide complexes with carbonyl compounds predominantly yielded regioisomers **A** (runs 28–30).[9d] The two factors mentioned above, steric and electronic effects of the substituents, are not in themselves enough to account for the observed regiochemistry (β-selectivity) in the reaction between tantalum–acetylenic amide complexes and aldehydes. Complexation of the acetylenic amides with the low-valent tantalum proceeded exceptionally fast, while reactivity of the tantalum–alkyne complexes toward aldehydes was low. These observations suggest that a strongly coordinating group on an acetylenic amide accelerates the approach of the triple bond toward the low-valent tantalum and then blocks the coordination of an aldehyde to the tantalum of the formed alkyne complex. When an acetylenic amide was added to the mixture of low-valent tantalum, the color of the mixture changed from greenish dark blue to ultramarine. A similar color change was observed after the addition of TMEDA to the mixture of low-valent tantalum. In order to test the hypothesis that the amide nitrogen located at an appropriate position of the acetylenic triple bond coordinates to tantalum, we compared the regioselectivities of reactions of two acetylenes having 2-pyridyl and 4-pyridyl groups (runs 10 and 11). Reaction at the β-position of the pyridyl group increased in both cases and a strong directing effect of the 2-pyridyl group was observed. The β-selectivity of the amide and 2-pyridyl groups could be attributed to strong coordination of the nitrogen to tantalum.[11]

The degree of regioselectivity is also dependent on the size of the substtiuents on the carbonyl groups.[12] When cyclohexanone was employed in place of aldehydes, the yields of the major isomers increased, especially in the case of sulfonyl- and amide-substituted acetylenes (runs 20 and 29). The increase in the steric interaction in these cases could be responsible for this regiochemical outcome.

Pyridine was added to the mixture of a tantalum–alkyne complex in order to prevent the formation of dehydration products, 1,3-dienes.[9b] Because the addition of pyridine reduces the reactivity of the tantalum–alkyne complex toward carbonyl compounds, we did not use pyridine with the less reactive complex. The addition of pyridine showed little effect on the regioisomer ratios. For example, reaction between acetylene **13** and 3-phenylpropanal with pyridine produced a 65/35 mixture of the two allylic alcohols **14a** and **14b** in 80% combined yield (run 2), while a 61/39 mixture of the two alcohols **14a** and **14b** was obtained in 55% combined yield, along with a mixture of conjugated dienes in 15% yield, in the absence of pyridine.

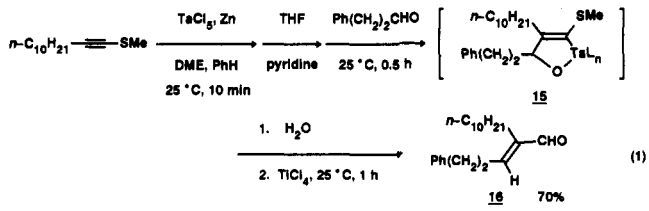
Reaction products from functionalized acetylenes are useful synthetic intermediates for further transformations. Acidic hydrolysis of oxatantalacyclopentene **15** derived from a tantalum–1-(methylthio)-1-dodecyne complex and 3-phenylpropanal preceeded smoothly with $TiCl_4$,[13] and an (*E*)-isomer of α,β-unsaturated aldehyde **16** was produced exclusively in 70% yield (eq 1). Quenching the reaction mixture of a tantalum–ethyl tridecenoate complex

(10) (a) Buchwald, S. L.; Lum, R. T.; Fisher, R. A.; Davis, W. M. *J. Am. Chem. Soc.* **1989**, *111*, 9113. (b) Buchwald, S. L.; Nielsen, R. B. *J. Am. Chem. Soc.* **1989**, *111*, 2870. (c) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 2544.

(11) The possibility of internal coordination of the nitrogen to the tantalum by aggregation of two or more tantalum–alkyne complexes can not be ruled out.

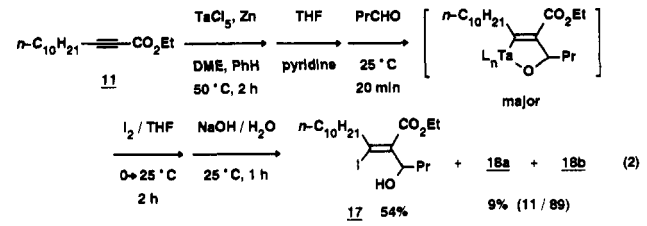
(12) For reactions for the tantalum-functionalized acetylene complexes with other unsaturated compounds, see: (a) Takai, K.; Kataoka, Y.; Yoshizumi, K.; Oguchi, Y.; Utimoto, K. *Chem. Lett.* **1991**, 1479. (b) Takai, K.; Miwatashi, S.; Kataoka, Y.; Utimoto, K. *Chem. Lett.* **1992**, 99.

(13) Trost, B. M.; Stanton, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 4018.



(1)

and butanal with iodine in THF at 0 °C for 15 min and 25 °C for 2 h afforded β-iodo-α,β-unsaturated ester **17** in 54% yield[14] along with untrapped allylic alcohols **18a** and **18b** in 9% combined yields (**18a**/**18b** = 11/89, eq 2). The



(2)

oxatantalacyclopentene intermediate is cleaved, with essentially complete retention of configuration, by iodinolysis to give the stereodefined iodo ester **17**. The carbon(sp²)–iodine bond of **17** provides a clue to the development of further transformations.[15]

Experimental Section

Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Benzene, tetrahydrofuran (THF), and 1,2-dimethoxyethane (DME) were distilled from sodium/benzophenone just before use. Zinc dust (GR grade) purchased from Wako Pure Chemical Industries, Ltd., was activated by washing several times with 5% hydrochloric acid, washing in turn with water, methanol, and ether, and drying in vacuo according to the literature.[16] Internal alkynes were prepared according to the standard procedure described in ref 17. Distillations of small amounts of products were performed with a Büchi Kugelrohr, and boiling points are indicated by an air bath temperature without correction. IR spectra were obtained on a JASCO IR-810 spectrometer. Mass spectra were obtained on a Hitachi M-80 mass spectrometer. ^1H and ^{13}C NMR spectra were determined with a Varian XL-200 spectrometer. Chemical shifts are expressed in ppm downfield from internal tetramethylsilane using the δ scale. Column chromatography was done with silica gel (200 mesh). Elemental analyses were performed by the staff at the Elemental Analyses Center of Kyoto University.

General Procedure for the Synthesis of Allylic Alcohols from Alkynes and Carbonyl Compounds. In a 50-mL reaction flask was placed $TaCl_5$ (0.72 g, 2.0 mmol) under an argon atmosphere. To the salt was added benzene (5 mL) and DME (5 mL) successively at 25 °C. Zinc (0.20 g, 3.0 mmol) was added at 25 °C to a pale yellow solution of $TaCl_5$, and the mixture was stirred at 25 °C for 40 min. The color of the mixture turned to greenish dark blue in a slightly exothermic process. To the mixture was added at 25 °C a solution of an alkyne (1.0 mmol) in DME and benzene (1:1, 2 mL), and the whole mixture was stirred at 25 °C. After consumption of the alkyne was confirmed by TLC, THF (6 mL) and pyridine (0.32 mL, 4.0 mmol) were added to the mixture, and then the mixture was stirred at 25 °C for an additional 15 min. A saturated carbonyl compound (1.2 mmol) was added to the mixture at 25 °C, and the mixture was stirred at 25 °C. Aqueous NaOH solution (15%, 2 mL) was added, and the mixture was stirred at 25 °C for an additional 1 h. The deposited white solid was removed by filtration with Hyflo-Super Cel and washed well with ethyl acetate (3 × 5 mL). Organic extracts were concentrated in vacuo and diluted with hexane (10 mL) or ethyl acetate (10 mL), dried over $MgSO_4$, and concentrated again in vacuo. Purification of the crude product by column chromatography on silica gel gave the desired allylic alcohols.

(*E*)-1,3-Dicyclohexyl-2-hexyl-2-propen-1-ol (A) and (*E*)-1,2-Dicyclohexyl-2-nonen-1-ol (B). Two regioisomers **A** and **B** could not be separated by column chromatography on silica gel. The regioisomeric ratio was determined by ^1H NMR analysis (**A**/**B** = 68/32): bp 118–119 °C (bath temp, 0.30 Torr); IR (neat, mixture of **A**/**B** = 68/32) 3402, 2916, 2848, 1448, 1080, 1008, 891 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–1.0 (m, 3 H), 1.0–1.9 (m, 29 H), 1.9–2.4 (m, 4 H), 3.64 (d, J = 7.0 Hz, 1 H, **A**), 3.67 (d, J = 7.4 Hz, 1 H, **B**), 5.14 (d, J = 9.8 Hz, 1 H, **A**), 5.34 (t, J = 7.3 Hz, 1 H, **B**); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.6, 26.0, 26.1, 26.3, 26.4, 26.6, 27.0, 27.8, 28.0, 28.7, 29.0, 30.0, 30.5, 30.7, 31.6, 31.7, 31.8, 31.9, 33.4, 33.5, 36.8, 39.2, 41.4, 41.9, 78.9, 80.2, 81.9, 127.1, 133.9, 133.9 (**A**) 145.4 (**B**). Anal. Calcd for $C_{21}H_{38}O$: C, 82.29; H, 12.50. Found: C, 82.11; H, 12.71.

(*E*)-2-Hexyl-1-(4-methoxyphenyl)-5-phenyl-1-penten-3-ol (A) and (*E*)-4-(4-Methoxyphenyl)-1-phenyl-4-undecen-3-ol (B). Two regioisomers **A** and **B** could not be separated by column chromatography on silica gel. The regioisomeric ratio was determined by ^1H NMR analysis (**A**/**B** = 34/66): bp 181–183 °C (bath temp, 0.30 Torr); IR (neat, mixture of **A**/**B** = 34/66) 3354, 2950, 2924, 2852, 1608, 1510, 1455, 1247, 1036, 834, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–1.0 (m, 3 H), 1.1–1.5 (m, 8 H), 2.70 (bs, 1 H), 1.7–1.8 (m, 2 H, **B**), 1.9–2.0 (m, 2 H, **B**), 2.1–2.4 (m, 4 H, **A**), 2.5–2.9 (m, 2 H), 3.81 (s, 3 H), 4.21 (t, J = 6.5 Hz, 1 H, **A**), 4.29 (t, J = 6.2 Hz, 1 H, **B**), 5.68 (t, J = 7.3 Hz, 1 H, **B**), 6.46 (s, 1 H, **A**), 6.8–7.0 (m, 2 H), 7.1–7.4 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.5, 28.4, 28.5, 28.9, 29.1, 29.7, 31.4, 31.6, 32.0, 32.2, 37.2, 37.5, 55.1, 75.9 (**A**), 76.2 (**B**), 113.5, 113.6, 125.0, 125.6, 125.7, 128.2, 128.3, 128.4, 129.2, 129.7, 130.1, 130.2, 142.0, 142.5, 143.7, 158.1, 158.4. Anal. Calcd for $C_{24}H_{32}O_2$: C, 81.77; H, 9.15. Found: C, 81.92; H, 9.45.

Methyl (*E*)-4-(2-Hexyl-3-hydroxy-5-phenyl-1-pentenyl)benzoate (A) and Methyl (*E*)-4-(1-Heptylidene-2-hydroxy-4-phenylbutyl)benzoate (B). Two regioisomers **A** and **B** could not be separated by column chromatography on silica gel. The regioisomeric ratio was determined by ^1H NMR analysis (**A**/**B** = 20/80): bp 195–197 °C (bath temp, 0.20 Torr); IR (neat, mixture of **A**/**B** = 20/80) 3402, 2950, 2922, 2852, 1724, 1607, 1437, 1279, 1114, 1105, 713, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.84 (t, J = 6.5 Hz, 3 H, **B**), 0.86 (t, J = 6.5 Hz, 3 H, **A**), 1.1–1.5 (m, 8 H), 1.90 (bs, 1 H), 1.6–1.8 (m, 2 H, **B**), 1.8–2.0 (m, 2 H, **B**), 2.1–2.3 (m, 2 H, **A**), 2.3–2.5 (m, 2 H, **A**), 2.6–2.9 (m, 2 H), 3.92 (s, 3 H, **A**), 3.93 (s, 3 H, **B**), 4.2–4.3 (m, 1 H, **A**), 4.3–4.4 (m, 1 H, **B**), 5.77 (t, J = 7.6 Hz, 1 H, **B**), 6.58 (s, 1 H, **A**), 7.1–7.4 (m, 7 H), 8.0–8.1 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.5, 28.5, 28.6, 28.8, 29.6, 31.6, 32.0, 32.1, 37.1, 37.5, 52.1, 75.2 (**A**), 75.9 (**B**), 124.4, 125.8, 125.9, 128.3, 128.7, 129.3, 129.5, 130.2, 141.5, 142.4. Anal. Calcd for $C_{25}H_{32}O_3$: C, 78.91; H, 8.48. Found: C, 78.74; H, 8.34.

(*E*)-*N*,*N*-Dimethyl-4-(2-hexyl-3-hydroxy-5-phenyl-1-pentenyl)benzamide (A) and (*E*)-*N*,*N*-Dimethyl-4-(1-heptylidene-2-hydroxy-4-phenylbutyl)benzamide (B). Two regioisomers **A** and **B** could not be separated by column chromatography on silica gel. The regioisomeric ratio was determined by ^1H NMR analysis (**A**/**B** = 25/75): bp 212–214 °C (bath temp, 0.20 Torr); IR (neat, mixture of **A**/**B** = 25/75) 3402, 2922, 2852, 1622, 1493, 1454, 1399, 1082, 786, 760, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85, (t, J = 6.6 Hz, 3 H, **B**), 0.86 (t, J = 6.6 Hz, 3 H, **A**), 1.1–1.5 (m, 8 H), 1.6–1.8 (m, 1 H + 2 H (**B**)), 1.8–2.0 (m, 2 H), 2.1–2.5 (m, 2 H, **A**), 2.5–2.9 (m, 2 H), 3.07 (bs, 3 H), 3.13 (bs, 3 H), 4.2–4.3 (m, 1 H, **A**), 4.3–4.4 (m, 1 H, **B**), 5.74 (t, J = 7.3 Hz, 1 H, **A**), 6.54 (s, 1 H, **B**), 7.1–7.4 (m, 7 H), 7.4–7.5 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 13.9, 22.4, 28.4, 28.7, 28.8, 29.5, 31.3, 31.5, 31.8, 32.0, 35.3, 37.0, 37.5, 39.5, 74.9 (**A**), 75.7 (**B**), 124.2, 125.5, 126.8, 127.0, 128.1, 128.2, 128.3, 129.1, 129.6, 134.2, 139.9, 141.8, 141.9, 142.3, 146.8, 171.5. Anal. Calcd for $C_{28}H_{35}NO_2$: C, 79.35; H, 8.96; N, 3.56. Found: C, 79.12; H, 9.08; N, 3.61.

(*E*)-2-(2-Hexyl-3-hydroxy-5-phenyl-1-pentenyl)pyridine: R_f = 0.57 (ethyl acetate:hexane = 1:1); bp 173–175 °C (bath temp, 0.20 Torr); IR (neat) 3274, 2950, 2922, 2852, 1586, 1468, 742, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.84 (t, J = 6.6 Hz, 3 H), 1.1–1.4 (m, 6 H), 1.3–1.6 (m, 2 H), 1.8–2.2 (m, 2 H), 2.3–2.5 (m, 2 H), 2.4–2.6

(14) None of the α-iodo unsaturated ester was obtained.

(15) For some examples, see: (a) Cowell, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4193. (b) Weir, J. R.; Patel, B. A.; Heck, R. F. *J. Org. Chem.* **1980**, *45*, 4926. (c) Jin, H.; Uenishi, J.; Christ, W. J.; Kishi, Y. *J. Am. Chem. Soc.* **1986**, *108*, 5644.

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(m, 1 H), 2.6–3.0 (m, 2 H), 4.2–4.3 (m, 1 H), 6.61 (s, 1 H), 7.1–7.2 (m, 1 H), 7.2–7.4 (m, 6 H), 7.63 (dt, J = 1.9, 7.7 Hz, 1 H), 8.6–8.7 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.5, 28.7, 29.0, 29.7, 31.4, 32.2, 37.4, 75.4, 121.0, 123.9, 124.0, 125.8, 128.3, 128.5, 136.1, 142.0, 148.9, 150.6, 156.6. Anal. Calcd for $C_{22}H_{29}NO$: C, 81.69; H, 9.04; N, 4.33. Found: C, 81.51; H 9.23; N, 4.48.

(*E*)-2-(1-Heptylidene-2-hydroxy-4-phenylbutyl)pyridine: R_f = 0.69 (ethyl acetate:hexane = 1:1); bp 173–175 °C (bath temp, 0.20 Torr); IR (neat) 3322, 2922, 2852, 1589, 1467, 749, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.86 (t, J = 6.5 Hz, 3 H), 1.1–1.4 (m, 7 H), 1.3–1.5 (m, 2 H), 1.6–1.8 (m, 1 H), 1.7–1.9 (m, 1 H), 2.11 (ddt, J = 2.2, 7.4, 7.4 Hz, 2 H), 2.60 (ddd, J = 6.2, 10.1, 13.9 Hz, 1 H), 2.68 (ddd, J = 6.2, 10.1, 13.9 Hz, 1 H), 4.28 (t, J = 6.9 Hz, 1 H), 5.85 (t, J = 7.4 Hz, 1 H), 7.1–7.4 (m, 7 H), 7.71 (dt, J = 1.8, 7.8 Hz, 1 H), 8.5–8.7 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.5, 28.7, 29.0, 29.6, 31.6, 32.5, 38.1, 78.1, 122.0, 124.8, 125.6, 128.2, 133.5, 136.4, 139.1, 142.2, 148.2. Anal. Calcd for $C_{22}H_{29}NO$: C, 81.69; H, 9.04; N, 4.33. Found: C, 81.76; H, 9.20; N, 4.38.

(*E*)-4-(2-Hexyl-3-hydroxy-5-phenyl-1-pentenyl)pyridine (A) and (*E*)-4-(1-Heptylidene-2-hydroxy-4-phenylbutyl)-pyridine (B). Two regioisomers **A** and **B** could not be separated by column chromatography on silica gel. The regioisomeric ratio was determined by ^{1}H NMR analysis (**A**/**B** = 55/45): bp 175–177 °C (bath temp, 0.20 Torr); IR (neat, mixture of **A**/**B** = 55/45) 3446, 2924, 2854, 1614, 1452, 1431, 1069, 1044, 786, 760, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.84 (t, J = 6.6 Hz, 3 H, **B**), 0.86 (t, J = 6.6 Hz, 3 H, **A**), 1.1–1.5 (m, 8 H), 1.6–1.8 (m, 1 H, **B**), 1.8–2.2 (m, 3 H), 2.3–2.5 (m, 1 H, **A**), 2.56 (bs, 1 H), 2.6–3.0 (m, 2 H), 4.2–4.4 (m, 1 H), 5.82 (t, J = 7.4 Hz, 1 H, **B**), 6.53 (s, 1 H, **A**), 7.1–7.4 (m, 7 H), 8.5–8.7 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.0, 14.6, 22.5, 28.5, 28.8, 29.0, 29.4, 29.5, 31.3, 31.5, 32.0, 37.1, 74.2 (**A**), 75.4 (**B**), 121.4, 124.3, 125.4, 125.9, 128.4, 140.2, 141.3, 141.6, 148.3, 148.5, 152.9. Anal. Calcd for $C_{22}H_{29}NO$: C, 81.69; H, 9.04; N, 4.33. Found: C, 81.64; H, 9.12; N, 4.35.

Typical Procedure for the Reaction between Tantalum-1-(Alkylthio)-1-alkyne Complexes with Aldehydes. Low-valent tantalum was prepared from $TaCl_5$ (0.72 g, 2.0 mmol) and zinc (0.20 g, 3.0 mmol) in DME–benzene (1:1, 10 mL) at 25 °C (vide supra). To the greenish dark blue mixture of the low-valent tantalum was added at 25 °C a solution of 1-(methylthio)-1-dodecyne (0.21 g, 1.0 mmol) in DME–benzene (1:1, 2 mL), and the whole mixture was stirred at 25 °C for 12 min. THF (6 mL) and pyridine (0.32 mL, 4.0 mmol) were added successively to the mixture. After the mixture was stirred at 25 °C for 20 min, 3-phenylpropanal (0.27 g, 2.0 mmol) was added, and the resulting mixture was stirred at 25 °C for 20 min, 3-phenylpropanal (0.27 g, 2.0 mmol) was added, and the resulting mixture was stirred at 25 °C for 30 min. Aqueous NaOH solution (15%, 2 mL) was added, and the mixture was stirred at 25 °C for an additional 1 h. The deposited brown solid was removed by filtration with Hyflo-Super Cel and washed well with ethyl acetate (3 × 5 mL). Organic extracts were dried over $MgSO_4$ and concentrated. Purification by column chromatography on silica gel (ethyl acetate–hexane (1:10)) gave (*E*)-2-decyl-1-(methylthio)-5-phenyl-1-penten-3-ol in 73% yield (0.25 g). **(*E*)-2-Decyl-1-(methylthio)-5-phenyl-1-penten-3-ol**: ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 5.0 Hz, 3 H), 1.17–1.50 (m, 17 H), 1.87 (ddd, J = 6.4, 7.8, 7.8 Hz, 2 H), 2.04–2.26 (m, 2 H), 2.27 (s, 3 H), 2.63 (dt, J = 7.8, 14.1 Hz, 1 H), 2.75 (dt, J = 7.8, 14.1 Hz, 1 H), 4.03–4.10 (m, 1 H), 5.95 (d, J = 0.8 Hz, 1 H), 7.12–7.33 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 14.1, 17.1, 22.3, 28.3, 29.3, 29.5, 29.6, 30.0, 31.9, 32.1, 37.1, 75.2, 123.8, 125.8, 128.4, 141.0, 141.8; IR (neat) 3360, 3024, 2920, 2852, 1456, 1378, 1276, 1031, 810, 744, 720, 697 cm^{-1}; MS m/z of the corresponding trimethylsilyl ether: 420 (M$^+$, 18), 373 (62), 316 (24), 315 (100); HRMS m/z of the trimethylsilyl ether, calcd for $C_{25}H_{44}OSSi$ (M$^+$) 420.2884, found 420.2859.

(*E*)-2-Decyl-5-phenyl-2-pentenal (16). When the reaction mixture of 1-(methylthio)-1-dodecyne (0.21 g, 1.0 mmol) and 3-phenylpropanal (0.27 g, 2.0 mmol) (vide supra) was treated with water (4.2 mL) and $TiCl_4$ (1.0 M of a CH_2Cl_2 solution, 2.1 mL, 2.1 mmol) at 25 °C for 2 h, (*E*)-2-decyl-1-(methylthio)-5-phenyl-1-penten-3-ol was hydrolyzed. After usual workup and purification by column chromatography on silica gel, (*E*)-2-decyl-5-phenyl-2-pentenal (16) was obtained in 70% yield (0.20 g). (*E*)-2-Decyl-5-phenyl-2-pentenal: bp 156 °C (bath temp, 0.22 Torr); ^{1}H NMR ($CDCl_3$) δ 0.87 (t, J = 6.3 Hz, 3 H), 1.25–1.38 (m, 16 H), 2.15–2.19 (m, 2 H), 2.67 (ddt, J = 2.2, 7.0, 7.0 Hz, 2 H), 2.82 (dt, J = 2.2, 7.0 Hz, 2 H), 6.45 (t, J = 7.0 Hz, 1 H), 7.20–7.43 (m, 5 H), 9.35 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.6, 24.0, 28.6, 29.3, 29.4, 29.5, 29.6, 30.6, 31.8, 34.7, 126.3, 128.3, 128.5, 140.5, 144.3, 153.2, 195.0; IR (neat) 3024, 2922, 2852, 2708, 1688, 1640, 1497, 1455, 1370, 1112, 1078, 746, 698, 434, 407 cm^{-1}; MS m/z 300 (M$^+$, 24), 159 (47), 117 (19), 116 (36), 104 (24), 91 (100). Anal. Calcd for $C_{21}H_{32}O$: C, 83.94; H, 10.73. Found: C, 84.10; H, 10.80.

1-((*E*)-1-Decyl-2-(methylthio)ethenyl)-1-cyclohexanol: ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.4 Hz, 3 H), 1.20–1.70 (m, 27 H), 2.09–2.18 (m, 2 H), 2.28 (s, 3 H), 6.04 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.1, 17.2, 21.9, 22.6, 25.5, 28.9, 29.3, 29.6, 30.0, 30.3, 31.9, 36.2, 74.5, 121.9, 145.2; IR (neat) 3428, 2920, 2854, 1464, 1447, 1377, 1255, 1129, 957, 808 cm^{-1}; MS m/s of the corresponding trimethylsilyl ether 384 (M$^+$, 15), 370 (35), 369 (100), 338 (30), 337 (93), 279 (94), 75 (51), 73 (76), 43 (40); HRMS m/z of the trimethylsilyl ether, calcd for $C_{22}H_{44}SSi$ (M$^+$) 384.2884, found 384.2868.

(*E*)-2-Decyl-5-phenyl-1-(phenylthio)-1-penten-3-ol: ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.0 Hz, 3 H), 1.25–1.60 (m, 17 H), 1.87–1.99 (m, 2 H), 2.11–2.34 (m, 2 H), 2.60–2.92 (m, 2 H), 4.11–4.24 (m, 1 H), 6.28 (s, 1 H), 7.23–7.40 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 14.2, 22.7, 28.9, 29.4, 29.6, 30.0, 31.9, 32.1, 37.3, 75.1, 119.9, 125.8, 125.9, 126.3, 128.3, 128.4, 128.7, 129.0, 141.7, 145.4; IR (neat) 3058, 3024, 2922, 2852, 1740, 1584, 1479, 1456, 1440, 1375, 1241, 1090, 1069, 1025, 737, 698 cm^{-1}; MS m/z of the corresponding trimethylsilyl ether 482 (M$^+$, 25), 379 (20), 378 (61), 377 (100), 374 (21), 373 (59); HRMS m/z of the trimethylsilyl ether ($C_{30}H_{46}OSSi$), calcd for $C_{27}H_{37}S$ (M$^+$ – $OSiMe_3$) 393.2618, found 393.2617.

(*Z*)-1-Phenyl-4-(phenylthio)-4-pentadecen-3-ol: ^{1}H NMR ($CDCl_3$) δ 0.87 (t, J = 6.4 Hz, 3 H), 1.23–1.45 (m, 16 H), 1.86–2.05 (m, 3 H), 2.27–2.39 (m, 2 H), 2.59–2.77 (m, 2 H), 4.10–4.21 (m, 1 H), 6.31 (t, J = 7.2 Hz, 1 H), 7.15–7.35 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 28.9, 29.3, 29.4, 29.6, 29.7, 31.9, 37.8, 75.0, 125.8, 128.1, 128.3, 128.4, 128.9, 135.1, 135.9, 139.7, 141.8; IR (neat) 3364, 3024, 2922, 2852, 1735, 1604, 1584, 1478, 1455, 1439, 1376, 1259, 1061, 1024, 737, 696 cm^{-1}; MS m/z of the corresponding trimethylsilyl ether 482 (M$^+$, 26), 393 (3), 379 (22), 378 (64), 377 (100), 374 (23), 373 (67); HRMS m/z of the trimethylsilyl ether ($C_{30}H_{46}OSSi$), calcd for $C_{27}H_{37}S$ (M$^+$ – $OSiMe_3$) 393.2618, found 393.2647.

(*E*)-2-Cyclohexyl-1-(methylthio)-5-phenyl-1-penten-3-ol: ^{1}H NMR ($CDCl_3$) δ 1.23–1.91 (m, 13 H), 2.21–2.41 (m, 1 H), 2.27 (s, 3 H), 2.63 (dt, J = 8.1, 14.1 Hz, 1 H), 2.79 (dt, J = 8.1, 14.1 Hz, 1 H), 4.09–4.15 (m, 1 H), 5.95 (d, J = 0.6 Hz, 1 H), 7.20–7.38 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 17.7, 26.0, 26.7, 30.1, 30.3, 32.4, 38.3, 40.7, 73.1, 123.2, 125.8, 128.3, 128.4, 142.0, 144.9; IR (neat) 3366, 3024, 2922, 2850, 1603, 1495, 1448, 1041, 1030, 819, 746, 697 cm^{-1}; MS m/z of the corresponding trimethylsilyl ether: 362 (M$^+$, 5), 315 (19), 259 (10), 258 (20), 257 (100), 91 (33), 75 (10), 73 (45); HRMS m/z of the trimethylsilyl ether, calcd for $C_{21}H_{34}OSSi$ (M$^+$) 362.2101, found 362.2098.

(*E*)-2,5-Diphenyl-1-(methylthio)-1-penten-3-ol: ^{1}H NMR ($CDCl_3$) δ 1.76–1.84 (m, 3 H), 2.26 (s, 3 H), 2.64 (ddt, J = 7.0, 7.0, 9.1 Hz, 1 H), 2.75 (ddt, J = 6.9, 6.9, 9.1 Hz, 1 H), 4.41–4.47 (m, 1 H), 6.29 (d, J = 1.0 Hz, 1 H), 7.15–7.45 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 17.5, 31.8, 37.5, 75.3, 125.7, 126.8, 127.5, 128.3, 128.3, 128.6, 137.6, 140.1, 141.7; IR (neat) 3360, 3022, 2918, 1492, 1454, 1440, 1072, 1047, 1030, 765, 747, 698, 668 cm^{-1}; MS m/z of the corresponding trimethylsilyl ethers 356 (M$^+$, 8), 310 (10), 309 (35), 252 (20), 251 (100), 91 (40), 73 (63); HRMS m/z of the trimethylsilyl ether calcd for $C_{21}H_{28}OSSi$ (M$^+$) 356.1631, found 356.1643.

(*E*)-2-Decyl-1-(methylsulfonyl)-5-phenyl-1-penten-3-ol: bp 215 °C (bath temp, 0.30 Torr); ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.4 Hz, 3 H), 1.23–1.58 (m, 16 H), 1.74 (dt, J = 5.4, 8.6 Hz, 1 H), 1.81 (dt, J = 5.4, 8.7 Hz, 1 H), 1.92–2.17 (m, 2 H), 2.64–3.00 (m, 3 H), 2.95 (s, 3 H), 4.17–4.23 (m, 1 H), 6.49 (s, 1 H), 7.23–7.40 (m, 5 H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.6, 28.8, 29.2, 29.3, 29.5, 30.0, 31.7, 31.8, 37.1, 44.0, 72.3, 123.5, 126.1, 128.4, 128.5, 141.0, 163.0; IR (neat) 3468, 3024, 2924, 2852, 1629, 1457, 1300, 1131, 1068, 965, 748. 698, 466, 429, 420 cm^{-1}. Anal. Calcd for $C_{22}H_{36}O_3S$: C, 69.43; H, 9.53. Found: C, 69.33; H, 9.79.

(*Z*)-4-(Methylsulfonyl)-1-phenyl-4-pentadecen-3-ol: bp 207 °C (bath temp, 0.2 Torr); ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.3 Hz, 3 H), 1.15–1.50 (m, 16 H), 2.03–2.18 (m, 2 H), 2.53–2.97 (m, 5 H),

2.99 (s, 3 H), 4.40–4.46 (m, 1 H), 6.31 (t, J = 7.7 Hz, 1 H), 7.18–7.38 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.6, 28.7, 29.0, 29.2, 29.3, 29.4, 29.5, 31.8, 32.2, 37.8, 45.0, 72.0, 126.0, 128.4, 128.5, 141.1, 142.5, 144.8; IR (neat) 3480, 2924, 2852, 1455, 1298, 1127, 1061, 748, 698, 462, 421, 415 cm^{-1}. Anal. Calcd for $C_{22}H_{36}O_3S$: C, 69.43; H, 9.53. Found: C, 69.42; H, 9.80.

1-((*E*)-1-Decyl-2-(methylsulfonyl)ethenyl)-1-cyclohexanol: bp 189 °C (bath temp, 0.20 Torr); ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.4 Hz, 3 H), 1.23–1.80 (m, 27 H), 2.50–2.58 (m, 2 H), 2.96 (s, 3 H), 6.58 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.9, 21.2, 22.5, 24.9, 28.2, 29.1, 29.2, 29.5, 30.4, 31.3, 31.7, 35.0, 43.9, 75.3, 122.9, 167.3; IR (neat) 3478, 2924, 2852, 1617, 1467, 1449, 1377, 1294, 1258, 1132, 1037, 964, 826, 771, 732, 424 cm^{-1}. Anal. Calcd for $C_{19}H_{36}O_3S$: C, 66.23; H, 10.53. Found: C, 66.14; H, 10.81.

(*E*)-2-Cyclohexyl-1-(methylsulfonyl)-5-phenyl-1-penten-3-ol: bp 195 °C (bath temp, 0.29 Torr); ^{1}H NMR ($CDCl_3$) δ 1.05–1.98 (m, 12 H), 2.25–2.35 (m, 1 H), 2.55–2.93 (m, 2 H), 2.88 (s, 3 H), 3.28–3.43 (m, 1 H), 4.22–4.28 (m, 1 H), 6.45 (s, 1 H), 7.20–7.33 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 25.6, 26.0, 30.7, 30.9, 32.2, 39.3, 44.3, 69.5, 124.7, 126.1, 128.5, 128.6, 141.1, 168.0; IR (neat) 3468, 2924, 2852, 1453, 1289, 1132, 1062, 963, 911, 732, 699, 433, 423, 415 cm^{-1}. Anal. Calcd for $C_{18}H_{26}O_3S$: C, 67.04; H, 8.13. Found: C, 67.32; H, 8.11.

(*Z*)-1-Cyclohexyl-2-(methylsulfonyl)-5-phenyl-1-penten-3-ol: bp 195 °C (bath temp, 0.29 Torr); ^{1}H NMR ($CDCl_3$) δ 1.02–1.50 (m, 5 H), 1.70–1.83 (m, 6 H), 2.01–2.15 (m, 2 H), 2.62–2.97 (m, 2 H), 3.00 (s, 3 H), 3.02–3.10 (m, 1 H), 4.38–4.42 (m, 1 H), 6.07 (d, J = 11 Hz, 1 H), 7.20–7.35 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 25.0, 25.5, 32.1, 32.2, 37.6, 37.8, 45.6, 72.0, 126.0, 128.4, 128.5, 140.5, 141.1, 149.2; IR (neat) 3478, 2924, 2850, 1636, 1496, 1451, 1305, 1286, 1155, 1129, 1064, 956, 767, 748, 699 cm^{-1}. Anal. Calcd for $C_{18}H_{26}O_3S$: C, 67.04; H, 8.13. Found: C, 67.17; H, 8.17.

(*E*)-2-Decyl-1-(phenylsulfonyl)-5-phenyl-1-penten-3-ol: bp 234 °C (bath temp, 0.21 Torr); ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J = 6.5 Hz, 3 H), 1.23–1.48 (m, 16 H), 1.63–2.02 (m, 4 H), 2.63–2.75 (m, 2 H), 2.88–3.03 (m, 1 H), 4.13–4.18 (m, 1 H), 6.52 (s, 1 H), 7.15–7.35 (m, 5 H), 7.50–7.68 (m, 3 H), 7.90–7.98 (m, 2 H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.7, 28.8, 29.2, 29.3, 29.4, 29.5, 29.6, 30.0, 31.6, 31.9, 37.1, 72.9, 124.9, 125.9, 126.1, 127.1, 128.4, 128.5, 129.1, 133.1, 141.0, 142.2, 162.7; IR (neat) 3486, 2924, 2852, 1625, 1448, 1304, 1146, 1085, 1071, 1029, 821, 733, 698, 687, 440 cm^{-1}. Anal. Calcd for $C_{27}H_{38}O_3S$: C, 73.26; H, 8.65. Found: C, 73.54; H, 8.82.

(*Z*)-1-Phenyl-4-(phenylsulfonyl)-4-pentadecen-3-ol: bp 234 °C (bath temp, 0.21 Torr); ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.5 Hz, 3H), 1.18–1.28 (m, 16 H), 2.00 (ddt, J = 3.8, 8.4, 12.7 Hz, 1 H), 2.12 (ddt, J = 5.6, 8.4, 14.4 Hz, 1 H), 2.46 (dt, J = 7.3, 7.5 Hz, 2 H), 2.59–2.84 (m, 2 H), 2.88–2.91 (m, 1 H), 4.38–4.48 (m, 1 H), 6.28 (t, J = 7.5 Hz, 1 H), 7.18–7.38 (m, 5 H), 7.53–7.70 (m, 3 H), 7.93–8.00 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.5, 28.4, 28.5, 29.0, 29.1, 29.3, 29.4, 31.7, 32.0, 38.0, 70.7, 125.5, 125.7, 127.0, 128.2, 128.3, 128.9, 133.0, 141.0, 141.7, 143.1, 144.6; IR (neat) 3488, 2922, 2852, 1736, 1637, 1497, 1447, 1304, 1145, 1083, 748, 727, 698, 688, 464, 406 cm^{-1}. Anal. Calcd for $C_{27}H_{38}O_3S$: C, 73.26; H, 8.65. Found: C, 73.19; H, 8.78.

Typical Procedure for the Reaction between Tantalum–Acetylenic Ester Complexes and Carbonyl Compounds. To the mixture of low-valent tantalum derived from $TaCl_5$ (0.72 g, 2.0 mmol) and zinc (0.20 g, 3.0 mmol) in DME–benzene (1:1, 10 mL) (vide supra) was added to 25 °C a solution of ethyl 2-tridecynoate (0.24 g, 1.0 mmol) in DME–benzene (1:1, 2 mL), and the whole mixture was stirred at 50 °C for 2 h. The reaction mixture was cooled to 25 °C; THF (6 mL) and pyridine (0.32 mL, 4.0 mmol) were added successively to the mixture. After the mixture was stirred at 25 °C for 15 min, butanal (86 mg, 1.2 mmol) was added and the resulting mixture was stirred at 25 °C for 30 min. Aqueous NaOH solution (15%, 2 mL) was added and the mixture was stirred at 25 °C for an additional 1 h. The deposited white solid was removed by filtration with Hyflo-Super Cel and washed with ethyl acetate (3 × 5 mL). Organic extracts were dried over $MgSO_4$ and concentrated. Purification by column chromatography on silica gel using ethyl acetate–hexane (1:10) as an eluent gave 0.24 g of a mixture of (*E*)-ethyl 3-decyl-4-hydroxy-2-heptenoate (**18a**) and (*Z*)-ethyl 2-(1-hydroxybutyl)-2-tridecenoate (**18b**) (75% combined yield, **16a**/**16b** = 5/95). **(*E*)-Ethyl 3-Decyl-4-hydroxy-2-heptenoate (18a,A) and (*Z*)-Ethyl 2-(1-Hydroxybutyl)-2-tridecenoate (18b, B).** Two regioisomers A and B were produced in 76% combined yields (**A**/**B** = 5/95). The isomers could not be separated by column chromatography on silica gel: bp 135 °C (bath temp, 0.2 Torr); ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.9 Hz, 3 H), 0.92 (t, J = 7.2 Hz, 3 H), 1.1–1.7 (m, 23 H), 2.41 (dt, J = 7.2, 7.2 Hz, 2 H), 2.64 (d, J = 7.6 Hz, 1 H), 4.1–4.2 (m, 1 H), 4.26 (q, J = 7.2 Hz, 2 H), 5.7–5.8 (m, 1 H(**A**)), 6.10 (t, J = 7.2 Hz, 1 H(**B**)); ^{13}C NMR ($CDCl_3$) δ 13.9, 14.1, 14.2, 19.2, 22.7, 29.2, 29.3, 29.4, 29.6, 31.9, 38.7, 60.4, 74.4, 134.0, 142.4, 167.8; IR (neat) 3426, 2954, 2922, 2854, 1707, 1466, 1378, 1209, 1094, 1028 cm^{-1}; MS m/z 294 ($M^+ - H_2O$, 8), 269 (100), 223 (55), 171 (15), 129 (13), 125 (19), 97 (18). Anal. Calcd for $C_{19}H_{36}O_3$: C, 73.03; H, 11.61. Found: C, 73.23; H, 11.88.

(*Z*)-Ethyl 3-(1-Hydroxycyclohexyl)-2-tridecenoate (A) and (*Z*)-Ethyl 2-(1-Hydroxycyclohexyl)-2-tridecenoate (B). Two regioisomers were produced in 72% combined yields (**A**/**B** = 3/97). The isomers could not be separated by column chromatography on silica gel: bp 137 °C (bath temp, 0.2 Torr); ^{1}H NMR ($CDCl_3$) δ 0.81 (t, J = 6.7 Hz, 3 H), 1.0–1.8 (m, 29 H), 2.10 (dt, J = 7.1, 7.6 Hz, 2 H), 2.82 (s, 1 H), 4.20 (q, J = 7.1 Hz, 2 H), 5.84 (t, J = 7.6 Hz, 1 H(**B**)), 5.97 (s, 1 H(**A**)); ^{13}C NMR ($CDCl_3$) δ 14.1, 14.2, 22.0, 22.6, 25.6, 29.2, 29.4, 29.5, 29.5, 31.8, 36.6, 60.5, 72.1, 134.0, 140.0, 169.7; IR (neat) 3426, 2924, 2852, 1720, 1459, 1374, 1265, 1186, 1030 cm^{-1}; MS m/z of the corresponding trimethylsilyl ether: 410 (M^+, 61), 395 (100), 339 (30), 269 (55), 171 (22). Anal. Calcd for $C_{21}H_{38}O_3$: C, 74.51; H, 11.31. Found: C, 74.66; H, 11.45.

(*E*)-Ethyl 3-Cyclohexyl-4-hydroxy-2-heptenoate (A) and (*Z*)-Ethyl 2-(Cyclohexylmethylene)-3-hydroxyhexanoate (B). Two regioisomers were produced in 76% combined yields (**A**/**B** = 2/98). The isomers could not be separated by column chromatography on silica gel: bp 110 °C (bath temp, 0.3 Torr); ^{1}H NMR ($CDCl_3$) δ 0.92 (t, J = 7.1 Hz, 3 H), 1.33 (t, J = 7.2 Hz, 3 H), 1.0–1.9 (m, 14 H), 2.62 (d, J = 7.7 Hz, 1 H), 2.7–2.8 (m, 1 H), 4.26 (q, J = 7.1 Hz, 2 H), 4.1–4.3 (m, 1 H), 5.74 (s, 1 H(**A**)), 5.89 (dd, J = 9.6, 0.6 Hz, 1 H(**B**)); ^{13}C NMR ($CDCl_3$) δ 13.9, 14.2, 19.2, 25.6, 25.9, 32.6, 38.1, 38.7, 60.4, 74.3, 132.2, 147.0, 167.8; IR (neat) 3424, 2954, 2926, 1702, 1449, 1251, 1207, 1178, 1157, 1028 cm^{-1}; MS m/z 236 ($M^+ - H_2O$, 12), 211 (100), 165 (80), 129 (23). Anal. Calcd for $C_{15}H_{26}O_3$: C, 70.83; H, 10.30. Found: C, 71.08; H, 10.51.

(*Z*)-Ethyl 3-cyclohexyl-2-(1-hydroxycyclohexyl)-2-propenoate: bp 120 °C (bath temp, 0.3 Torr); ^{1}H NMR ($CDCl_3$) δ 0.9–1.9 (m, 20 H), 1.26 (t, J = 7.3 Hz, 3 H), 2.1–2.3 (m, 1 H), 2.80 (s, 1 H), 4.20 (q, J = 7.3 Hz, 2 H), 5.63 (d, J = 9.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.2, 22.0, 25.6, 25.8, 32.8, 36.6, 38.8, 60.5, 72.0, 138.2, 138.8, 169.9; IR (neat) 3470, 2922, 2850, 1721, 1449, 1374, 1247, 1203, 1181, 1027, 967, 899 cm^{-1}; MS m/z 280 (M^+, 22), 234 (100), 191 (59), 151 (33). Anal. Calcd for $C_{17}H_{28}O_3$: C, 72.82; H, 10.06. Found: C, 72.88; H, 10.34.

(*E*)-Ethyl 4-hydroxy-3-phenyl-2-heptenoate: bp 120 °C (bath temp, 0.3 Torr); ^{1}H NMR ($CDCl_3$) δ 0.86 (m, 3 H), 1.05 (t, J = 7.1 Hz, 3 H), 1.3–1.7 (m, 4 H), 1.7–1.8 (m, 1 H), 3.99 (q, J = 7.1 Hz, 2 H), 4.4–4.5 (m, 1 H), 6.17 (d, J = 1.2 Hz, 1 H), 7.1–7.5 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 13.8, 13.9, 18.6, 37.2, 59.9, 75.5, 116.9, 127.7, 127.9, 128.0, 137.5, 160.4, 166.2; IR (neat) 3404, 2956, 2932, 1709, 1372, 1277, 1217, 1161, 1073, 1043 cm^{-1}; MS m/z of the corresponding trimethylsilyl ether 320 (M^+, 29), 277 (75), 145 (76), 73 (100). Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.63; H, 8.30.

(*Z*)-Ethyl 2-(1-hydroxybutyl)-3-phenyl-2-propenoate: bp 120 °C (bath temp, 0.3 Torr); ^{1}H NMR ($CDCl_3$) δ 0.95 (t, J = 7.0 Hz, 3 H), 1.09 (t, J = 7.1 Hz, 3 H), 1.2–1.8 (m, 4 H), 2.6–2.7 (m, 1 H), 4.14 (q, J = 7.1 Hz, 2 H), 4.4–4.5 (m, 1 H), 6.85 (s, 1 H), 7.2–7.4 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 13.6, 13.8, 18.9, 38.3, 60.6, 74.1, 127.9, 128.0, 128.2, 132.9, 135.5, 136.9, 169.0; IR (neat) 3404, 2958, 2932, 1712, 1379, 1226, 1141, 1088, 1066, 1027 cm^{-1}; MS m/z of the corresponding trimethylsilyl ether 320 (M^+, 2), 277 (100), 247 (28), 159 (54), 73 (36). Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.69; H, 8.34.

Iodinolysis of the Complex Derived from Tantalum–Ethyl 2-Tridecynoate Complex and Butanal. Tantalum–ethyl 2-tridecynoate complex derived from ethyl 2-tridecynoate (0.24 g, 1.0 mmol), $TaCl_5$ (0.72 g, 2.0 mmol), and zinc (0.20 g, 3.0 mmol) in DME–benzene (1:1, 12 mL) was treated with THF (6 mL), pyridine (0.32 mL, 4.0 mmol), and butanal (86 mg, 1.2 mmol) as described in the typical procedure (vide supra). To a stirred mixture of the oxatantalacyclopentene intermediate was added a solution of iodine (1.3 g, 5.0 mmol) in THF (6 mL) at 0 °C over

a period of 5 min. The resulting mixture was stirred at 25 °C for 2 h. Aqueous NaOH solution (15%, 2 mL) was added, and the mixture was stirred at 25 °C for an additional 1 h. The deposited white solid was removed by filtration with Hyflo-Super Cel and washed with ethyl acetate (3 × 5 mL). Organic extracts were dried over $MgSO_4$ and concentrated. Purification by preparative thin-layer chromatography using dichloromethane as an eluent gave 0.24 g of (*E*)-ethyl 2-(1-hydroxybutyl)-3-iodo-2-tridecenoate (17, 54% yield) and 28 mg of a mixture of (*E*)-ethyl 3-decyl-4-hydroxy-2-heptanoate (18a) and (*Z*)-ethyl 2-(1-hydroxybutyl)-2-tridecenoate (18b) (9% combined yield, 18a/18b = 11/89).

(*E*)-Ethyl 2-(1-hydroxybutyl)-3-iodo-2-tridecenoate (17): bp 140 °C (bath temp, 0.2 Torr); ^1H NMR ($CDCl_3$) δ 0.88 (t, *J* = 6.4 Hz, 3 H), 0.96 (t, *J* = 7.2 Hz, 3 H), 1.2–1.9 (m, 20 H), 1.31 (t, *J* = 7.2 Hz, 3 H), 2.40 (d, *J* = 7.0 Hz, 1 H), 2.6–2.8 (m, 2 H), 4.29 (q, *J* = 7.2 Hz, 2 H), 4.7–4.8 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.9, 14.1, 14.2, 19.0, 22.6, 28.4, 29.3, 29.3, 29.4, 29.5, 31.7, 37.6, 43.6, 61.4, 79.6, 116.4, 140.6, 165.3; IR (neat) 3444, 2954, 2952, 1725, 1620, 1460, 1367, 786 cm^{-1}; MS *m/z* 395 (M^+ – Pr, 100), 349 (28), 221 (25), 95 (20). Anal. Calcd for $C_{19}H_{35}IO_3$: C, 52.06; H, 8.05. Found: C, 52.20; H, 8.11. Treatment of the iodo ester 17 (88 mg, 0.20 mmol) with $Pd(PPh_3)_4$ (4.6 mg, 0.0040 mmol), Et_3N (61 mg, 0.60 mmol), and formic acid (18 mg, 0.40 mmol) in DMF (0.4 mL) at 60 °C for 1 h gave ester 18b in 87% yield (52 mg).[18]

Typical Procedure for the Reaction between Tantalum–Acetylenic Amide Complexes and Carbonyl Compounds. To the mixture of low-valent tantalum derived from $TaCl_5$ (0.72 g, 2.0 mmol) and zinc (0.20 g, 3.0 mmol) in DME–benzene (1:1, 10 mL) (vide supra) was added at 25 °C a solution of *N,N*-dimethyl-2-nonynamide (0.18 g, 1.0 mmol) in DME–benzene (1:1 2 mL), and the whole mixture was stirred at 25 °C for 2 h. THF (6 mL) was added to the mixture. After the mixture was stirred at 25 °C for 15 min, butanal (0.14 g, 2.0 mmol) was added at 25 °C and the resulting mixture was stirred at 50 °C for 2 h. The reaction mixture was cooled to 25 °C, aqueous NaOH solution (15%, 2 mL) was added, and the mixture was stirred at 25 °C for an additional 1 h. The deposited white solid was removed by filtration with Hyflo-Super Cel and washed with ethyl acetate (3 × 5 mL). Organic extracts were dried over $MgSO_4$ and concentrated. Purification by column chromatography on silica gel using ethyl acetate–hexane (1:10) as an eluent gave 0.18 g of (*E*)-*N,N*-dimethyl-3-hexyl-4-hydroxy-2-heptenamide (71% yield) and 20 mg of (*Z*)-*N,N*-dimethyl-2-heptylidene-3-hydroxyhexanamide (8% yield). **(*E*)-*N,N*-Dimethyl-3-hexyl-4-hydroxy-2-heptenamide**: bp 138 °C (bath temp, 0.2 Torr); ^1H NMR ($CDCl_3$) δ 0.87 (t, *J* = 6.6 Hz, 3 H), 0.95 (t, *J* = 6.8 Hz, 3 H), 1.2–1.7 (m, 12 H), 2.0–2.3 (m, 2 H), 2.4–2.5 (m, 1 H), 2.98 (s, 3 H), 3.01 (s, 3 H), 4.1–4.2 (m, 1 H), 6.12 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.9, 14.0, 18.9, 22.6, 29.0, 29.7, 29.7, 31.6, 34.6, 37.8, 37.9, 73.9, 117.0, 154.8, 168.8; IR (neat) 3386, 2954, 2928, 1648, 1611, 1459, 1397, 1265, 1148, 1064 cm^{-1}; MS *m/z* 255 (M^+, 9), 208 (38), 180 (100), 125 (18). Anal. Calcd for $C_{15}H_{29}NO_2$: C, 70.54; H, 11.44; N, 5.48. Found: C, 70.26; H, 11.45; N, 5.52. **(*Z*)-*N,N*-Dimethyl-2-heptylidene-3-hydroxyhexanamide**: bp 135 °C (bath temp, 0.2 Torr); ^1H NMR ($CDCl_3$) δ 0.88 (t, *J* = 6.7 Hz, 3 H), 0.93 (t, *J* = 6.6 Hz, 3 H), 1.2–1.8 (m, 12 H), 1.96 (dt, *J* = 7.3, 7.1 Hz, 2 H), 3.03 (s, 6 H), 3.5–3.7 (bm, 1 H), 4.0–4.2 (bm, 1 H), 5.64 (t, *J* = 7.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.1, 14.4, 19.1, 22.7, 28.8, 29.3, 29.5, 31.6, 34.2, 38.0, 38.3, 71.4, 131.2, 143.2, 170.7; IR (neat) 3394, 2954, 2926, 1612, 1501, 1459, 1400, 1266, 1128, 1071 cm^{-1}; MS *m/z* 255 (M^+, 3), 237 (7), 212 (100), 167 (11), 72 (33). Anal. Calcd for $C_{15}H_{29}NO_2$: C, 70.54; H, 11.44; N, 5.48. Found: C, 70.30; H, 11.55; N, 5.43.

(*E*)-*N,N*-Dimethyl-3-(1-hydroxycyclohexyl)-2-nonenamide: mp 105–106 °C (ethyl acetate–hexane); ^1H NMR ($CDCl_3$) δ 0.87 (t, *J* = 6.9 Hz, 3 H), 1.1–1.8 (m, 19 H), 2.2–2.3 (m, 2 H), 2.98 (s, 3 H), 3.00 (s, 3 H), 6.21 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.0, 21.7, 22.6, 25.3, 28.9, 30.0, 30.5, 31.5, 34.6, 35.8, 37.7, 74.6, 117.1, 157.6, 169.5; IR (Nujol) 3316, 1650, 1606, 1399, 1265, 1164, 1139, 987 cm^{-1}; MS *m/z* 281 (M^+, 3), 263 (27), 206 (100), 72 (17). Anal. Calcd for $C_{17}H_{31}NO_2$: C, 72.55; H, 11.10; N, 4.98. Found: C, 72.56; H, 11.24; N, 5.01.

(*E*)-*N,N*-Dimethyl-3-cyclohexyl-4-hydroxy-2-heptenamide: mp 49–50 °C (ethyl acetate–hexane); ^1H NMR ($CDCl_3$) δ 0.94 (t, *J* = 6.7 Hz, 3 H), 1.1–1.9 (m, 14 H), 2.3–2.6 (m, 2 H), 2.98 (s, 3 H), 3.00 (s, 3 H), 4.1–4.2 (m, 1 H), 6.08 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.0, 19.3, 25.9, 26.4, 26.6, 30.9, 31.3, 34.5, 38.0, 39.6, 41.0, 71.2, 117.7, 157.5, 169.4; IR (Nujol): 3294, 1654, 1647, 1597, 1307, 1267, 1148, 1066, 1017, 994 cm^{-1}; MS *m/z* 235 ($M^+ - H_2O$, 23), 206 (100), 109 (22), 72 (52). Anal. Calcd for $C_{15}H_{27}NO_2$: C, 71.10; H, 10.74; N, 5.53. Found: C, 70.98; H, 10.87; N, 5.53.

(*Z*)-*N,N*-Dimethyl-2-(cyclohexylmethylidene)-3-hydroxyhexanamide: bp 142 °C (bath temp, 0.2 Torr); ^1H NMR ($CDCl_3$) δ 0.93 (t, *J* = 6.9 Hz, 3 H), 1.0–2.1 (m, 15 H), 2.2–2.5 (bm, 1 H), 3.037 (s, 3 H), 3.041 (s, 3 H), 4.0–4.3 (bm, 1 H), 5.45 (d, *J* = 10.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.9, 19.1, 25.5, 25.8, 32.6, 32.7, 34.1, 38.2, 38.4, 38.7, 75.7, 136.2, 136.9, 169.8; IR (neat) 3358, 2918, 2850, 1599, 1501, 1448, 1261, 1142, 1060, 975, 899 cm^{-1}; MS *m/z* 253 (M^+, 2), 235 (10), 210 (100), 191 (22), 72 (19). Anal. Calcd for $C_{15}H_{27}NO_2$: C, 71.10; H, 10.74; N, 5.53. Found: C, 70.83; H, 11.01; N, 5.44.

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Supplementary Material Available: Spectroscopic data (IR, ^1H NMR, ^{13}C NMR, MS) for internal alkynes (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(18) The following method was modified: Cacchi, S.; Ciattini, P. G.; Morera, E.; Ortar, G. *Tetrahedron Lett.* **1986**, *27*, 5541.