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Reaction of Tantalum–Alkyne Complexes with Isocyanates or Acyl Cyanides. Stereoselective Functionalization of Carbon–Carbon Triple Bonds

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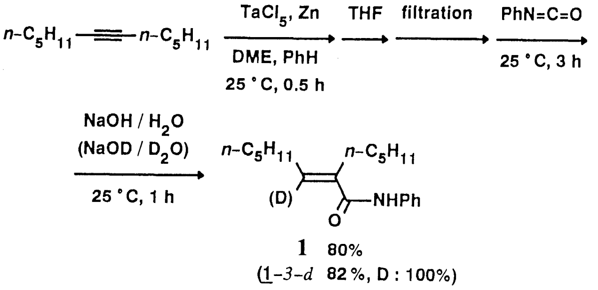
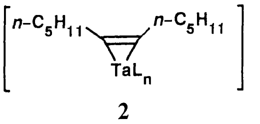
Treatment of alkynes with low-valent tantalum derived from $TiCl_5$ and zinc produces tantalum–alkyne complexes (not isolated), which react in situ with phenyl isocyanate (or butyl isocyanate) to give (*E*)-α,β-unsaturated amides stereoselectively. The tantalum–alkyne complexes also react with acyl cyanides in the presence of $BF_3 \cdot OEt_2$ to give α-cyanohydrins. In both reactions, filtration of the reaction mixture containing the tantalum–alkyne complexes before addition of isocyanates (or acyl cyanides) is indispensable to obtain good yields.

Insertion of unsaturated compounds into metal–carbon bonds is especially important as key steps of metal-mediated carbon–carbon bond formations.[1–4] We recently reported facile preparation of tantalum–alkyne complexes and utilized the complexes for the synthesis of (*E*)-allylic alcohols via insertion of carbonyl groups into tantalum–carbon(sp^2) bond.[4c] To explore the applicability of the tantalum–alkyne complexes, we chose isocyanates and acyl cyanides as the unsaturated compounds.

Stereoselecitve Formation of α,β-Unsaturated Amides from Alkynes and Isocyanates.[1f,2b,5,6b] Treatment of a tantalum–6-dodecyne complex **2**, derived from 6-dodecyne and a $TaCl_5$–Zn system,[4a] with phenyl isocyanate in a mixed solvent of DME–benzene–THF (1 : 1 : 1) at 25 °C gave a complex mixture; only 9% yield of the desired (*E*)-*N*-phenyl-2-pentyl-2-octenamide **1** could be obtained after workup. However, filtration of the reaction mixture containing the tantalum–alkyne complex under an argon atmosphere before addition of the isocyanate improved the reaction markedly and **1** was produced in 80% yield. Deuterated amide **1**-3-*d* was obtained in 82% yield (100% deuterated) by quenching the reaction mixture of **3** (or **4**) with alkaline D_2O.



(1)



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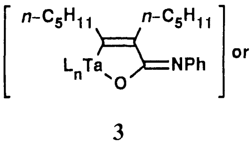

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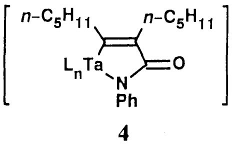
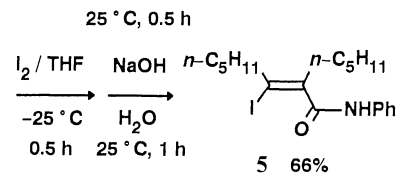


3 4

The results of the reactions between tantalum–alkyne complexes and isocyanates are summarized in Table 1. Reactions between the tantalum–alkyne complexes and butyl isocyanate took place at 25 °C and *N*-butyl-2-alkenamides were produced in good to excellent yields. In contrast, *t*-butyl and trimethylsilyl isocyanates were almost unreactive due to the bulkiness of the substituents (Runs 3 and 4). Reaction with *p*-toluenesulfonyl isocyanate proceeded slowly under the reaction conditions and the corresponding amide was obtained in 48% yield (Run 5).

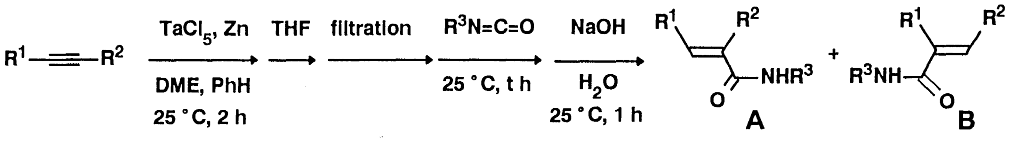
Tantalum–alkyne complexes derived from unsymmetrical alkynes produce two regioisomeric amides. Regioselectivities of the reactions between tantalum–alkyne complexes and isocyanates have the same tendency as those between the complexes and aldehydes.[4c] Insertion of isocyanates took place at the less hindered side of the tantalum–alkyne complexes (Runs 6—11). In the case of 1-methylthio-1-alkyne, regioisomer **A** was produced exclusively because of the electronic nature of the substituents (Runs 12 and 13).[4e]

Reaction of the tantalum–6-dodecyne complex **2** with phenyl isocyanate, followed by iodinolysis with 5 molar amounts of iodine at −25 °C produced (*Z*)-3-iodo-2-pentyl-2-octenamide (**5**) in 66% yield stereoselectively (Eq. 2). The structure of amide **5** was ascertained by deiodination of **5** with triethylammonium formate and $Pd(PPh_3)_4$ in DMF at 60 °C.[7]



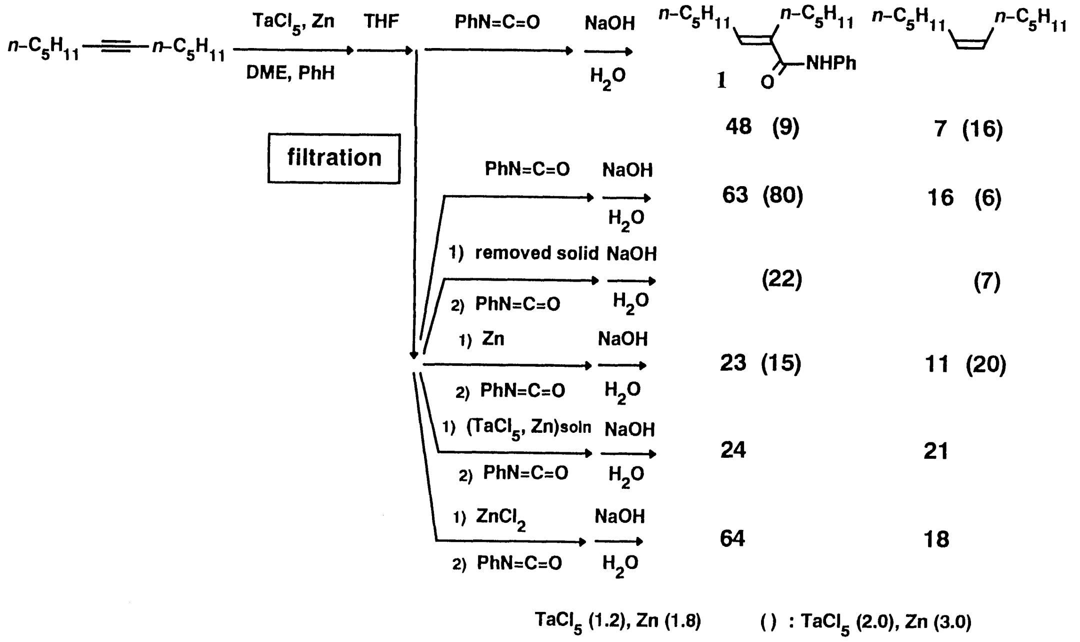
(2)

Table 1. Reactions between Alkynes and Isocyanates by Means of $TaCl_5$ and Zinc[a)]



Run	R^1	R^2	R^3	R^3NCO Molar amounts	t/h	Yield[b)] %	A/B[c)]
1	n-C_5H_{11}	n-C_5H_{11}	Ph	1.2	3	80 [**1**]	—
2			Bu	1.2	3	72	—
3			t-Bu	1.2	20	6 (79)	—
4			Me_3Si	1.2	20	<1 (63)	—
5			Ts	1.2	20	48 (29)	—
6	c-C_6H_{11}	n-C_6H_{13}	Ph	2.0	3	69	55/45
7			Bu	2.0	3	62	73/27
8	Ph	n-C_6H_{13}	Ph	4.0	3	51	60/40
9			Bu	4.0	3	74	72/28
10	Me_3Si	n-$C_{10}H_{21}$	Ph	4.0	3	60	84/16
11			Bu	1.2	3	33	82/18
12	MeS	n-$C_{10}H_{21}$	Ph	2.0	0.2	58	>99/<1
13			Bu	2.0	0.2	90	>99/<1

a) Reactions were conducted on 1.0 mmol scale. Two mole of $TaCl_5$ and 3.0 mol of zinc were employed per mole of an alkyne. b) Isolated yields. Yields of unreacted 6-dodecene are shown in parenthesis. c) Regioisomeric ratios (**A**/**B**) were determined by ^{1}H NMR analysis.

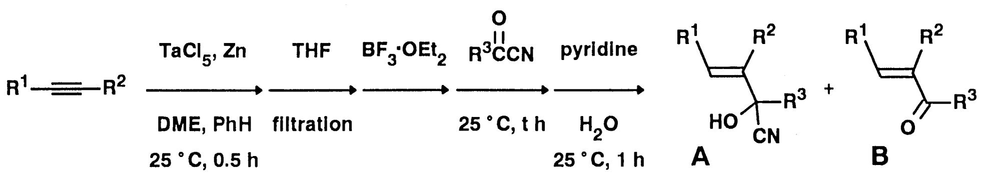


Scheme 1.

To clarify the effect of filtration, the following experiments were conducted (Scheme 1).[8)] (1) When the removed solid by filtration was put back to the reacted mixture of tantalum-alkyne complexes and isocyanates, many by-products appeared and the yield of the desired adduct **1** fell to 22%. (2) The following compounds were added into the filtered solution containing a tantalum-6-dodecyne complex before reaction with phenyl isocyanate. Yield of **1** is shown in parenthesis: Zinc, 1.8 molar amounts (23%); low-valent tantalum solution, 3 molar amounts (24%); zinc chloride, 1.8 molar amounts (64%); none (63%). α,β-Unsaturated amide **1** was obtained in 48% yield under the same conditions without filtration. These results suggest that excess amount of zinc or low-valent tantalum promotes further reactions which consume the initial adduct **3** (or **4**).

Reaction of the tantalum-6-dodecyne complex with phenyl thioisocynate resulted in recovery of (Z)-6-dodecene in 81% yield.[6a)] In contrast, tantalum-3-

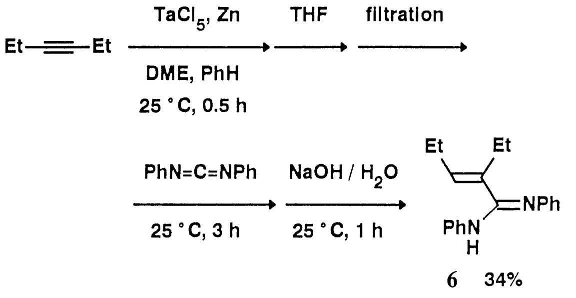
Table 2. Reactions between Alkynes and Acyl Cyanides by Means of $TaCl_5$ and Zinc[a)]



Run	R^1	R^2	R^3	t/h	Yield/%[b)] A	Yield/%[b)] B	$R^1CH=CHR^2$ %
1	n-C_5H_{11}	n-C_5H_{11}	$Ph(CH_2)_2$ **[7]**	3	60 **[8]**	7 **[9]**	11
2			c-C_6H_{11}	4	41	8	13
3			t-Bu **[10]**	5	<1	<1	83
4			Ph	4	<1[c)]	<1	21
5	Me_3Si	n-$C_{10}H_{21}$	$Ph(CH_2)_2$	3	70[d)]	8[d)]	4

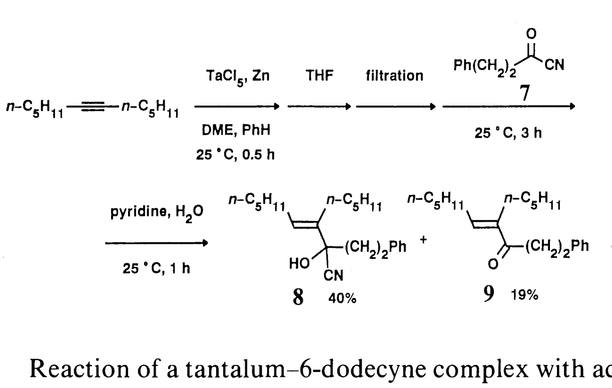
a) Reactions were conducted on 1.0 mmol scale. Two mole of $TaCl_5$, 3.0 mol of zinc, 1.0 mol of $BF_3\cdot OEt_2$, and 2.0 mol of acyl cyanide were employed per mole of an alkyne. b) Isolated yields. c) Many by-products appeared. d) The other regioisomer was not observed.

hexyne complex reacted with diphenylcarbodiimide to give (E)-α,β-unsaturated amidine **6** in 34% yield (Eq. 3).[6c)]



(3)

Reaction of Tantalum–Alkyne Complexes with Acyl Cyanides.[9,10)] While tantalum–alkyne complexes react with neither ester nor amide functional groups, insertion of a carbonyl group of acyl cyanide was found to take place to yield a mixture of an α-cyanohydrin and an α,β-unsaturated ketone after workup (Eq. 4).



(4)

Reaction of a tantalum–6-dodecyne complex with acyl cyanides **7**[10a)] proceeded slowly compared to that with ketone.[4c)] In addition, acyl cyanide **7** was consumed gradually by reaction with low-valent tantalum to yield a complex mixture. Thus, filtration of the reaction mixture of tantalum–6-dodecyne complex before addition with the acyl cyanide was indispensable to obtain adducts **8** and **9** in good combined yields. When the reaction mixture was quenched by addition of pyridine (8 molar amounts) and water, α-cyanohydrin **8** was produced as a main product. The reaction was accelerated by addition of Lewis acids (2 molar amounts);[4h)] yields of **8** and **9** are shown in parenthesis: $ZnCl_2$ (58%, 7%); $AlCl_3$ (17%, 18%); Me_3SiCl (42%, 11%); $BF_3\cdot OEt_2$ (63%, 16%); none (40%, 15%).

Reactivity of an acyl cyanide depends on bulkiness of a substituent of a carbonyl group. Acyl cyanide **10**[10b)] was recovered in 83% yield after exposure to a tantalum–6-dodecyne complex (Run 3). Reaction between a tantalum–6-dodecyne complex and benzoyl cyanide proceeded to give a complex mixture; the desired adducts were not obtained (Run 4). When trimethylsilyl-substituted alkyne was employed, insertion of acyl cyanide **7** proceeded regioselectively (Run 5).[4c)] Enone **9** was obtained selectively in 68% yield from 6-dodecyne by treatment of the crude mixture of Run 1 containing cyanohydrin **8** and enone **9** with a solution of sodium hydrogencarbonate.[11)]

Experimental

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 purchased from Wako Pure Chemical Industries, Ltd. (GR grade) was activated by washing several times with 5% hydrochloric acid, washing in turn with water, methanol, and ether, and drying in vacuo according to Fieser and Fieser.[12)] Internal alkynes were prepared according to the standard procedure described in Ref. 13. Distillation of small amounts of products was performed with a Büchi Kugelrohr, and boiling points are indicated by an air bath temperature without correction. All melting points were obtained on a Yanaco MP-50929 apparatus. 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 α,β-Unsaturated Amide. To a pale yellow solution of TaCl$_5$ (0.72 g, 2.0 mmol) in benzene (5 ml) and DME (5 ml) was added zinc dust (0.20 g, 3.0 mmol) at 25 °C under an argon atmosphere. The color of the solution turned greenish dark blue with slightly exothermic process. The resulting mixture was stirred at 25 °C for 40 min. To the mixture was added at 25 °C a solution of alkyne (1.0 mmol) in DME and benzene (1 : 1, 2 ml) and the whole mixture was stirred at 25 °C for 30 min. THF (5 ml) was added to the mixture. After being stirred at 25 °C for 15 min, the mixture was filtered under an argon atmosphere and the removed solid was washed with THF (2×3 ml). To the combined filtrates was added isocyanate (1.2 mmol) and the resulting mixture was stirred at 25 °C for 3 h. Aqueous NaOH solution (15%, 2 ml) was added and the mixture was stirred at 25 °C for 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 dried over MgSO$_4$ and concentrated in vacuo. Purification by column chromatography on silica gel gave α,β-unsaturated amide.

(*E*)-*N*-Phenyl-2-pentyl-2-octenamide (1): R_f=0.62 (ethyl acetate–hexane, 1 : 5); mp 54—56 °C; bp 130—132 °C (bath temp, 0.20 Torr, 1 Torr=133.322 Pa); IR (neat) 3296, 2924, 2854, 1653, 1598, 1539, 1439, 1324, 752, 689 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.88 (t, J=6.3 Hz, 3H), 0.90 (t, J=6.3 Hz, 3H), 1.2—1.6 (m, 12H), 2.16 (dt, J=7.3, 7.3 Hz, 2H), 2.37 (*t*, J=7.3 Hz, 2H), 6.26 (*t*, J=7.3 Hz, 1H), 7.07 (dd, J=7.6, 7.6 Hz, 1H), 7.29 (dd, J=7.6, 7.6 Hz, 2H), 7.57 (d, J=7.6 Hz, 2H), 7.7—7.8 (m, 1H); ^{13}C NMR (CDCl$_3$) δ=13.9, 22.4, 27.1, 28.1, 28.7, 31.5, 31.7, 119.9, 123.8, 128.7, 135.4, 137.7, 138.3, 168.0. Found: C, 79.62; H, 10.44; N, 4.84%. Calcd for $C_{19}H_{29}NO$: C, 79.39; H, 10.17; N, 4.87%.

(*E*)-*N*-Butyl-2-pentyl-2-octenamide: R_f=0.40 (ethyl acetate–hexane, 1 : 5); bp 139—141 °C (bath temp, 0.20 Torr); IR (neat) 3304, 2954, 2924, 2856, 1656, 1620, 1535, 1466, 1307 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.8—1.1 (m, 9H), 1.2—1.7 (m, 16H), 2.11 (dt, J=7.0, 7.3 Hz, 2H), 2.28 (t, J=7.3 Hz, 2H), 3.30 (dt, J=5.9, 6.9 2H), 5.6—5.8 (m, 1H), 6.12 (t, J=7.3 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ=13.7, 13.9, 20.1, 22.4, 27.1, 27.9, 28.7, 28.8, 31.5, 31.7, 39.3, 134.2, 137.2, 169.7. Found: C, 76.36; H, 12.64; N, 5.24%. Calcd for $C_{17}H_{33}NO$: C, 76.34; H, 12.44; N, 5.24%.

(*E*)-*N*-*t*-Butyl-2-pentyl-2-octenamide: R_f=0.41 (ethyl acetate–hexane, 1 : 10); bp 125—127 °C (bath temp, 0.16 Torr); IR (neat) 3314, 2924, 2856, 1657, 1624, 1529, 1453, 1363, 1223 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.8—1.0 (m, 6H), 1.2—1.6 (m, 12H), 1.31 (s, 9H), 2.0—2.2 (m, 2H), 2.2—2.4 (m, 2H), 5.4—5.7 (m, 1H), 6.03 (t, J=7.3 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ=14.0, 22.5, 27.2, 28.0, 28.7, 28.8, 29.6, 31.6, 31.8, 51.0, 133.6, 138.2, 169.6. Found: C, 12.43; H, 76.08; N, 5.21%. Calcd for $C_{17}H_{33}NO$: C, 76.34; H, 12.44; N, 5.24%.

(*E*)-*N*-*p*-Toluenesulfonyl-2-pentyl-2-octenamide: R_f=0.65 (ethyl acetate–hexane, 1 : 2); bp 188—190 °C (bath temp, 0.11 Torr); IR (neat) 3266, 2926, 2856, 1693, 1425, 1189, 812, 661 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.81 (t, J=6.5 Hz, 3H), 0.84 (t, J=6.5 Hz, 3H), 1.1—1.5 (m, 12H), 2.0—2.3 (m, 4H), 2.44 (s, 3H), 6.36 (t, J=7.3 Hz, 1H), 7.35 (d, J=8.5 Hz, 2H), 7.99 (d, J=8.5 Hz, 2H), 8.78 (bs, 1H); ^{13}C NMR (CDCl$_3$) δ=13.7, 13.8, 21.5, 22.3, 26.3, 28.1, 28.4, 28.5, 31.3, 31.4, 128.2, 129.3, 134.5, 135.7, 141.1, 144.6, 166.3. Found: C, 65.65; J, 8.75; N, 3.81%. Calcd for $C_{20}H_{31}NO_3S$: C, 65.72; H, 8.55; N, 3.83%.

(*E*)-*N*-Phenyl-3-cyclohexyl-2-hexyl-2-propenamide: R_f= 0.60 (ethyl acetate–hexane, 1 : 5); mp 138—140 °C; bp 198—200 °C (bath temp, 0.20 Torr); IR (Nujol) 3270, 1731, 1649, 1625, 1324, 694 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.88 (t, J=6.4 Hz, 3H), 1.0—1.5 (m, 12H), 1.6—1.9 (m, 6H), 2.3—2.5 (m, 3H), 6.05 (d, J=9.6 Hz, 1H), 7.10 (t, J=7.6 Hz, 1H), 7.33 (t, J=7.6 Hz, 2H), 7.44 (bs, 1H), 7.56 (d, J=7.6 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ=14.1, 22.6, 25.67, 25.73, 25.8, 27.5, 29.3, 29.5, 31.6, 32.7, 37.5, 119.8, 124.0, 128.9, 136.2, 138.2, 140.4, 168.1. Found: C, 80.56; H, 10.08; N, 4.43%. Calcd for $C_{21}H_{31}NO$: C, 80.46; H, 9.97; N, 4.47%.

(*E*)-*N*-Phenyl-2-cyclohexyl-2-nonenamide: R_f=0.64 (ethyl acetate–hexane, 1 : 5); mp 108—110 °C; bp 198—200 °C (bath temp, 0.20 Torr); IR (Nujol) 3216, 1731, 1648, 1628, 759, 694 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.90 (t, J=6.7 Hz, 3H), 1.1—1.6 (m, 12H), 1.6—1.9 (m, 6H), 2.1—2.3 (m, 2H), 2.4—2.6 (m, 1H), 5.88 (t, J=7.0 Hz, 1H), 7.10 (t, J=7.4 Hz, 1H), 7.27 (s, 1H), 7.33 (t, J=7.4 Hz, 2H), 7.54 (d, J=7.4 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ=14.1, 22.6, 25.8, 26.8, 27.5, 29.1, 29.3, 31.0, 31.1, 31.7, 39.0, 119.7, 124.1, 129.0, 132.4, 138.1, 143.9, 175.0. Found: C, 80.39; H, 10.17; N, 4.39%. Calcd for $C_{21}H_{31}NO$: C, 80.46; H, 9.97; N, 4.47%.

(*E*)-*N*-Butyl-3-cyclohexyl-2-cyclohexyl-2-propenamide: R_f= 0.33 (ethyl acetate–hexane, 1 : 5); bp 152—154 °C (bath temp, 0.30 Torr); IR (Nujol) 3298, 1655, 1618, 1541, 1535, 1230 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.9—1.0 (m, 6H), 1.1—1.5 (m, 12H), 1.4—1.9 (m, 10H), 2.2—2.4 (m, 3H), 3.30 (dt, J=6.3, 6.7 Hz, 2H), 5.7—5.8 (m, 1H), 5.90 (d, J=9.8 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ=13.8, 14.1, 20.1, 22.6, 25.7, 25.9, 27.4, 29.2, 29.4, 31.7, 31.8, 37.2, 39.4, 139.3. Found: C, 78.03; H, 12.21; N, 4.95%. Calcd for $C_{19}H_{35}NO$: C, 77.76; H, 12.12; N, 4,77%.

(*E*)-*N*-Butyl-2-cyclohexyl-2-nonenamide: R_f=0.41 (ethyl acetate–hexane, 1 : 5); bp 152—154 °C (bath temp, 0.30 Torr); IR (Nujol) 3290, 1649, 1618, 1523, 1237 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.8—1.0 (m, 6H), 1.1—1.5 (m, 12H), 1.4—1.9 (m, 10H), 2.10 (dt, J=7.2, 7.1 Hz, 2H), 2.3—2.5 (m, 1H), 3.25 (dt, J=6.3, 6.7 Hz, 2H), 5.4—5.6 (m, 1H), 5.65 (t, J=7.2 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ=13.8, 14.1, 20.1, 22.6, 25.8, 26.8, 27.3, 29.1, 29.4, 31.2, 31.7, 31.8, 38.8, 39.0, 130.9, 143.8, 169.7. Found: C, 77.53; H, 11.72; N, 4.82%. Calcd for $C_{19}H_{35}NO$: C, 77.76; H, 12.02; N, 4.77%.

(*E*)-*N*-Phenyl-2-hexyl-3-phenyl-2-propenamide: R_f=0.30 (ethyl acetate–hexane, 1 : 5); bp 194—196 °C (bath temp, 0.50 Torr); IR (Nujol) 3246, 1643, 1599, 1543, 1499, 751, 688 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.85 (t, J=6.0 Hz, 3H), 1.2—1.5 (m, 6H), 1.5—1.7 (m, 2H), 2.5—2.6 (m, 2H), 7.1—7.3 (m, 2H), 7.3—7.5 (m, 7H), 7.62 (d, J=7.6 Hz, 2H), 7.76 (bs, 1H); ^{13}C NMR (CDCl$_3$) δ=14.0, 22.5, 28.1, 28.9, 29.4, 31.5, 120.0, 124.3, 127.9, 128.4, 128.9, 129.0, 132.6, 135.8, 138.1, 139.8, 168.2. Found: C, 81.98; H, 8.23; N, 4.52%. Calcd for $C_{21}H_{25}NO$: C, 82.04; H, 8.20; N, 4.56%.

(*E*)-*N*-Phenyl-2-pheny-2-nonenamide: R_f=0.37 (ethyl acetate–hexane, 1 : 5); bp 194—196 °C (bath temp, 0.50 Torr); IR (neat) 3246, 3300, 2924, 2852, 1671, 1597, 1523, 1439, 1378, 752, 701 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.83 (t, J=7.0 Hz, 3H), 1.1—1.4 (m, 6H), 1.3—1.6 (m, 2H), 2.01 (dt, J=7.7, 7.3 Hz, 2H), 7.0—7.2 (m, 2H), 7.2—7.4 (m, 5H), 7.4—7.6 (m, 5H); ^{13}C NMR (CDCl$_3$) δ=14.0, 22.5, 28.8, 28.9, 29.4, 31.6, 119.8, 124.2, 128.4, 128.8, 129.1, 129.9, 135.4, 137.9, 143.0, 165.6. Found: C, 81.96; H, 8.30; N, 4.53%. Calcd for $C_{21}H_{25}NO$: C, 82.04; H, 8.20; N, 4.56%.

(*E*)-*N*-Butyl-2-hexyl-3-phenyl-2-propenamide (A) and (*E*)-*N*-Butyl-2-phenyl-2-nonenamide (B): The regioisomer ratio (**A**/**B**) was determined by ^{1}H NMR analysis (**A**/**B**=72/28). R_f=0.27 (ethyl acetate–hexane, 1 : 5); bp 175—177 °C (bath temp, 0.20 Torr); IR (neat, mixture of **A**/**B**=72/28) 3302, 2926, 2856, 1728, 1648, 1619, 1535, 1465, 1459, 1277, 699 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.86 (t, J=6.6 Hz, 3H), 0.95 (t, J=7.3 Hz, 3H), 1.1—1.7 (m, 12H), 1.9—2.0 (m, 2H, **B**), 2.50 (dd, J=7.4, 8.2 Hz, 2H, **A**), 3.2—3.3 (m, 2H, **B**), 3.3—3.4 (m, 2H, **A**), 5.3—5.4 (m, 1H, **B**), 6.1—6.2 (m, 1H, **A**), 7.0—7.5 (m, 6H); ^{13}C NMR (CDCl$_3$) δ=13.6, 13.8, 14.0, 19.9, 20.1, 22.5, 27.9, 28.6, 28.8, 29.0, 29.2, 31.5, 31.7, 39.5, 127.5 (**A**), 127.9 (**B**), 128.2 (**A**), 128.4 (**B**), 128.5 (**B**), 128.7 (**A**), 129.7 (**B**), 131.6 (**A**), 135.9 (**B**), 136.1 (**A**), 139.2 (**A**), 141.1 (**B**), 166.5 (**B**), 169.9 (**A**). Found: C, 79.35; H, 10.42; N, 4.90%. Calcd for $C_{19}H_{29}NO$: C, 79.39; H, 10.17; N, 4.87%.

(*Z*)-*N*-Phenyl-2-decyl-3-trimethylsilyl-2-propenamide: R_f=0.32 (ethyl acetate–hexane, 1 : 3); bp 167—169 °C (bath temp, 0.25 Torr); IR (neat) 3300, 2952, 2922, 1648, 1597, 1534, 1440, 1249, 858, 838, 734, 690 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.20 (s, 9H), 0.88 (t, J=6.8 Hz, 3H), 1.2—1.6 (m, 16H), 2.47 (dd, J=7.0, 8.0 Hz, 2H), 6.20 (s, 1H), 7.10 (t, J=7.7 Hz, 1H), 7.32 (t, J=7.7 Hz, 2H), 7.55 (bs, 1H), 7.59 (t, J=7.7 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ=−0.1, 14.1, 22.6, 29.3, 29.4, 29.5, 29.8, 31.9, 32.6, 119.8, 124.1, 128.9, 132.2, 138.1, 154.7, 168.1. Found: C, 73.19; H, 10.61; N, 3.83%. Calcd for $C_{22}H_{37}NOSi$: C, 73.48; H, 10.37; N, 3.89%.

(*Z*)-*N*-Phenyl-2-trimethylsilyl-2-tridecenamide: R_f=0.20 (ethyl acetate–hexane, 1 : 3); bp 167—169 °C (bath temp, 0.25 Torr); IR (Nujol) 3250, 1638, 1596, 1459, 840, 750, 690 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.26 (s, 9H), 0.90 (t, J=6 8 Hz, 3H), 1.2—1.6 (m, 16H), 2.23 (dt, J=7.6, 7.2 Hz, 2H), 6.59 (t, J=7.6 Hz, 1H), 7.09 (t, J=7.7 Hz, 1H), 7.13 (bs, 1H), 7.32 (t, J=7.7 Hz, 2H), 7.53 (d, J=7.7 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ=0.2, 14.1, 22.7, 29.3, 29.4, 29.5, 29.6, 31.9, 96.1, 119.7, 124.0, 129.0, 138.3, 148.3. Found: C, 73.28; H, 10.67; N, 3.82%. Calcd for $C_{22}H_{37}NOSi$: C, 73.48; H, 10.37; N, 3.89%.

(*Z*)-*N*-Butyl-2-decyl-3-trimethylsilyl-2-propenamide: R_f=0.50 (ethyl acetate–hexane, 1 : 5); bp 184—186 °C (bath temp, 0.30 Torr); IR (neat) 3298, 2922, 2852, 1636, 1595, 1534, 1466, 1249, 1123, 836, 691 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.16 (s, 9H), 0.88 (t, J=6.6 Hz, 3H), 0.94 (t, J=7.2 Hz, 3H), 1.2—1.6 (m, 18H), 2.3—2.4 (m, 2H), 3.30 (dt, J=6.3, 6.8 Hz, 2H), 3.2—3.3 (m, 2H), 5.9—6.0 (m, 1H), 6.00 (s, 1H); ^{13}C NMR (CDCl$_3$) δ=−0.1, 13.7, 14.1, 20.1, 22.6, 29.3, 29.46, 29.53, 29.8, 31.7, 31.9, 32.6, 39.3, 130.9, 154.5, 170.1. Found: C, 70.88; H, 12.42; N, 4.10%. Calcd for $C_{20}H_{41}NOSi$: C, 70.73; H, 12.17; N, 4.12%.

(*Z*)-*N*-Butyl-2-trimethylsilyl-2-tridecenamide: R_f=0.46 (ethyl acetate–hexane, 1 : 5); bp 184—186 °C (bath temp, 0.30 Torr); IR (neat) 3296, 2924, 2852, 1669, 1627, 1532, 1466, 1436, 1285, 1248, 841, 635 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.21 (s, 9H), 0.88 (t, J=6.8 Hz, 3H), 0.93 (t, J=7.0 Hz, 3H), 1.2—1.5 (m, 18H), 1.3—1.6 (m, 2H), 2.1—2.2 (m, 2H), 3.25 (dt, J=6.2, 6.8 Hz, 2H), 5.3—5.4 (m, 1H), 6.38 (t, J=7.5 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ=0.2, 13.8, 14.1, 20.1, 22.7, 28.2, 29.3, 29.4, 29.5, 31.8, 31.9, 39.2, 39.8, 141.2, 147.0, 173.7. Found: C, 70.60; H, 12.39; N, 4.17%. Calcd for $C_{20}H_{41}NOSi$: C, 70.73; H, 12.17; N, 4.12%.

(*E*)-*N*-Phenyl-2-decyl-3-methylthio-2-propenamide: R_f= 0.32 (ethyl acetate–hexane, 1 : 5); mp 54—56 °C; bp 214—216 °C (bath temp, 0.60 Torr); IR (Nujol) 3288, 1639, 1600, 1534, 1500, 1377, 1317, 754 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.88 (t, J=6.8 Hz, 3H), 1.2—1.5 (m, 14H), 1.3—1.6 (m, 2H), 2.41 (s, 3H), 2.4—2.5 (m, 2H), 7.10 (t, J=7.8 Hz, 1H), 7.22 (s, 1H), 7.33 (t, J=7.8 Hz, 2H), 7.3—7.4 (m, 1H), 7.42 (bs, 1H), 7.94 (d, J=7.8 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ=14.1, 17.3, 22.7, 27.9, 29.2, 29.3, 29.4, 29.6, 31.9, 120.0, 124.2, 129.0, 131.4, 138.0, 139.2, 164.5. Found: C, 72.02; H, 9.37; N, 4.20%. Calcd for $C_{20}H_{31}NOS$: C, 72.02; H, 9.37; N, 4.20%.

(*E*)-*N*-Butyl-2-decyl-3-methylthio-2-propenamide: R_f= 0.16 (ethyl acetate–hexane,1 : 3); bp 186—188 °C (bath temp, 0.50 Torr); IR (neat) 3310, 2922, 2852, 1734, 1624, 1533, 1466, 1377, 1288, 734 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.88 (t, J=6.8 Hz, 3H), 0.93 (t, J=7.1 Hz, 3H), 1.2—1.5 (m, 18H), 1.4—1.6 (m, 2H), 2.30 (t, J=7.4 Hz, 2H), 2.38 (s, 3H), 3.31 (dt, J=5.9, 5.9 Hz, 2H), 5.7—5.8 (m, 1H), 7.10 (s, 1H); ^{13}C NMR (CDCl$_3$) δ=13.7, 14.0, 17.1, 20.1, 22.6, 27.9, 28.9, 29.2, 29.4, 29.5, 31.7, 31.8, 39.5, 131.0, 137.5, 166.2. Found: C, 69.11; H, 11.50; N, 4.54%. Calcd for $C_{18}H_{35}NOS$: C, 68.95; H, 11.25; N, 4.47%.

(*Z*)-*N*-Phenyl-3-iodo-2-pentyl-2-octenamide (5): To a stirred solution of TaCl$_5$ (0.72 g, 2.0 mmol) in a mixed solvent of DME and benzene (1 : 1, 10 ml) at 25 °C under an argon atmosphere was added zinc (0.20 g, 3.0 mmol) and the mixture was stirred at 25 °C for 40 min. To the mixture was added at 25 °C a solution of 6-dodecyne (0.17 g, 1.0 mmol) in DME and benzene (1 : 1, 2 ml) and the whole mixture was stirred at 25 °C for 30 min. THF (5 ml) was added to the mixture. After being stirred at 25 °C for 15 min, the mixture was filtered under an argon atmosphere and the removed solid was washed with THF (2×3 ml). To the combined filtrates was added phenyl isocyanate (0.14 g, 1.2 mmol) and the resulting mixture was stirred at 25 °C for 3 h. To the mixture was added at −25 °C a solution of iodine (1.3 g, 5.0 mmol) in THF (6 ml) and the whole mixture was stirred at −25 °C for 30 min. Aqueous NaOH solution (15%, 2 ml) was added at 25 °C and the mixture was stirred at 25 °C for additional 1 h. The deposited white solid was removed by filtration with Hyflo-Super Cel® and washed with ethyl acetate (3×5 ml). The organic extracts were washed with saturated NaHSO$_3$ (10 ml) and brine, dried over MgSO$_4$, and concentrated in vacuo. Purification by column chromatography on silica gel with ethyl acetate–hexane (1 : 10) gave 0.27 g (66%) of (*Z*)-*N*-phenyl-3-iodo-2-pentyl-2-octenamide. R_f=0.62 (ethyl acetate–hexane, 1 : 5); bp 166—168 °C (bath temp, 0.18 Torr); IR (neat) 3274, 3130, 3056, 1653, 1599, 1540, 1441, 1328, 754, 690 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.87 (t, J=6.6 Hz, 3H), 0.91 (t, J=6.6 Hz, 3H), 1.2—1.5 (m, 8H), 1.4—1.8 (m, 4H), 2.42 (t, J=8.0 Hz, 2H), 2.54 (t, J=7.5 Hz, 2H), 7.12 (dd, J=7.4, 7.4 Hz, 1H), 7.32 (dd, J=7.4, 7.4 Hz, 2H), 7.4—7.6 (bs, 1H), 7.57 (d, J=7.4 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ=22.3, 22.4, 28.3, 28.9, 30.7, 31.5, 31.9, 40.5, 103.8, 120.1, 124.5, 128.9, 137.4, 144.9, 169.2. Found: C, 55.39; H, 6.82; N, 3.45%. Calcd for $C_{19}H_{28}INO$: C, 55.21; H, 6.83; N, 3.39%.

Procedure for Deiodination of 5:7) To a mixture of the α,β-unsaturated amide **5** (0.41 g, 1.0 mmol), Et$_3$N (0.42 ml, 3.0 mmol), and Pd(PPh$_3$)$_4$ (23 mg, 0.020 mmol) in DMF (2 ml) was added formic acid (0.075 ml, 2.0 ml). The mixture was stirred at 60 °C for 1 h under an argon atmosphere. The reaction mixture was poured into brine (15 ml) and extracted with ether (2×10 ml). The organic layer was washed with brine (10 ml) and dried over MgSO$_4$ and concentrated in vacuo. Purification by column chromatography on silica gel using ethyl acetate–hexane (1 : 20) as eluent gave 0.28 g (96%) of the amide **1**.

(*Z*)-*N*^{1},*N*^{2}-Diphenyl-2-ethyl-2-pentenamidine (6): To a stirred solution of TaCl$_5$ (0.72 g, 2.0 mmol) in a mixed solvent of DME and benzene (1 : 1, 10 ml) at 25 °C under an argon atmosphere was added zinc (0.20 g, 3.0 mmol) and the mixture was stirred at 25 °C for 40 min. To the mixture was added at 25 °C a solution of 3-hexyne (82 mg, 1.0 mmol) in DME and benzene (1 : 1, 2 ml) and the whole mixture was stirred at 25 °C for 30 min. THF (5 ml) was added to the mixture. After being stirred at 25 °C for 15 min, the mixture was filtered under an argon atmosphere and the removed solid was washed with THF (2×3 ml). To the combined filtrates was added diphenylcarbodiimide (0.24 g, 1.2 mmol)[14] and the resulting mixture was stirred at 25 °C for 3 h. Aqueous NaOH solution (15%, 2 ml) was added and the mixture was stirred at 25 °C for 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 layer was dried over MgSO$_4$ and concentrated in vacuo. Purification by column chromatography on silica gel with ethyl acetate–hexane (1 : 10) gave 94 mg (34%) of amidine **6**: R_f=0.45 (ethyl acetate–hexane, 1 : 5); mp 77—79 °C; bp 152—154 °C (bath temp, 0.20 Torr); IR (nujol) 3254, 1730, 1586, 1534, 1271, 1122, 1071, 754, 688 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.90 (t, J=7.4 Hz, 3H), 0.97 (t, J=7.5 Hz, 3H), 1.7—1.9 (m, 2H), 2.0—2.2 (m, 2H), 6.1—6.3 (m, 1H), 6.3—6.6 (m, 1H), 7.2—7.5 (m, 4H), 7.4—7.8 (m, 6H); ^{13}C NMR (CDCl$_3$) δ=12.7, 13.6, 20.7, 21.3, 120.2, 120.8, 121.38, 121.43, 121.5, 122.2, 128.6, 135.8, 137.9, 139.0, 155.8. Found: C, 81.68; H, 7.94; N, 10.00%. Calcd for C$_{19}$H$_{22}$N$_2$: C, 81.97; H, 7.97; N, 10.06%.

Typical Procedure for the Reaction of Tantalum–Alkyne Complexes with Acyl Cyanides: To a mixture of tantalum–6-dodecyne complex, derived from 6-dodecyne (0.17 g, 1.0 mmol), TaCl$_5$ (0.72 g, 2.0 mmol), and zinc (0.20 g, 3.0 mmol) in benzene (6 ml) and DME (6 ml) was added THF (3 ml) at 25 °C under an argon atmosphere. After being stirred at 25 °C for 15 min, the mixture was filtered under an argon atmosphere and the removed solid was washed with THF (2×1.5 ml). To the combined filtrates was added at 25 °C BF$_3$·OEt$_2$ (0.14 g, 1.0 mmol) and 2-oxo-4-phenylbutanenitrile (0.34 g, 2.0 mmol)[10a] and the resulting mixture was stirred at 25 °C for 3 h. Pyridine (0.65 ml, 8.0 mmol) and water (2.0 ml) was added successively to the resulting mixture at 25 °C. The deposited white 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 in vacuo. Purification by column chromatography on silica gel (ethyl acetate–hexane (1 : 30—1 : 10)) gave 0.20 g of α-cyanohydrin **8** (60% yield) and 21 mg of α,β-unsaturated ketone **9** (7% yield). When the crude mixture of **8** and **9** in ethyl acetate (10 ml) was treated with aq NaHCO$_3$ (1 M solution) at 25 °C for 24 h, **8** was converted to α,β-unsaturated ketone **9**. The reaction mixture was neutralized with aq NH$_4$Cl solution and extracted with ethyl acetate (3×20 ml). The organic extracts were washed with brine (40 ml), dried over anhydrous Na$_2$SO$_4$, and concentrated. Purification of the crude product by column chromatography on silica gel (ethyl acetate–hexane (1 : 30)) gave 0.20 g of **9** (68% yield).

(*E*)-2-Hydroxy-3-pentyl-2-(2-phenylethyl)-3-nonenenitrile (8): Dehydrocyanation of α-cyanohydrin **8** took place under distillation conditions. Mass spectral analysis and elemental analysis were conducted with the corresponding trimethylsilyl ether produced by treatment with trimethylsilylimidazole. IR (neat) 3410, 3024, 2952, 2926, 2856, 2225, 1498, 1457, 1379, 1059, 750, 698 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.90 (t, J=6.4 Hz, 6H), 1.2—1.6 (m, 12H), 2.1—2.3 (m, 6H), 2.42 (s, 1H), 2.7—3.0 (m, 2H), 5.91 (t, J=7.2 Hz, 1H), 7.2—7.5 (m, 5H); ^{13}C NMR (CDCl$_3$) δ=14.0, 22.3, 22.5, 27.1, 27.9, 29.0, 30.0, 30.7, 31.6, 32.4, 41.3, 76.2, 120.7, 126.2, 128.3, 130.3, 137.2, 140.5; MS (rel intensity) 399 (M$^+$+SiMe$_3$, 7), 342 (4), 295 (63), 294 (100), 195 (28), 105 (24), 91 (41). Found: C, 75.30; H, 10.60; N, 3.65%. Calcd for C$_{25}$H$_{41}$NOSi: C, 75.13; H, 10.34; N, 3.50%.

(*E*)-4-Pentyl-1-phenyl-4-decen-3-one (9): Bp 98—100 °C (bath temp, 0.25 Torr); IR (neat) 3024, 2952, 2924, 2854, 1670, 1466, 1455, 1111, 746, 698 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.88 (t, J=6.7 Hz, 3H), 0.90 (t, J=6.5 Hz, 3H), 1.2—1.6 (m, 12H), 2.1—2.4 (m, 4H), 2.94 (s, 4H), 6.55 (t, J=7.3 Hz, 1H), 7.2—7.4 (m, 5H); ^{13}C NMR (CDCl$_3$) δ=13.9, 14.0, 22.5, 25.7, 28.6, 28.8, 29.0, 30.8, 31.6, 31.9, 39.2, 125.9, 128.4, 141.6, 141.9, 142.8, 200.6; MS (rel intensity) 300 (M$^+$, 13), 229 (100), 91 (29), 69 (16), 55 (17). Found: C, 83.94; H, 10.82%. Calcd for C$_{21}$H$_{32}$O: C, 83.94; H, 10.73%.

(*E*)-2-Cyclohexyl-2-hydroxy-3-pentyl-3-nonenenitriie: Dehydrocyanation of the α-cyanohydrin took place under distillation conditions. Mass spectral analysis and elemental analysis were conducted with the corresponding trimethylsilyl ether produced by treatment with trimethylsilylimidazole. IR (neat) 3412, 2926, 2852, 1467, 1453, 1379, 1101, 1028 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.8—1.0 (m, 6H), 1.0—1.6 (m, 17H), 1.6—2.0 (m, 6H), 2.0—2.3 (m, 4H), 2.28 (s, 1H), 5.84 (t, J=7.2 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ=13.9, 22.2, 22.4, 25.7, 25.8, 25.9, 26.7, 27.9, 28.0, 29.0, 29.9, 31.5, 32.4, 44.2, 80.5, 120.0, 130.8, 136.5; MS (rel intensity) 377 (M$^+$+SiMe$_3$, 24), 295 (64), 294 (100), 239 (20), 238 (91), 195 (26), 168 (11), 73 (40). Found: C, 73.29; H, 11.77; N, 3.61%. Calcd for C$_{23}$H$_{43}$NOSi: C, 73.14; H, 11.48; N, 3.71%.

(*E*)-1-Cyclohexyl-2-pentyl-2-octen-1-one: Bp 92—93 °C (bath temp, 0.25 Torr); IR (neat) 2926, 2852, 1665, 1452, 1251, 1104 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.80 (t, J=7.0 Hz, 3H), 0.84 (t, J=6.4 Hz, 3H), 1.0—1.5 (m, 17H), 1.5—1.9 (m, 5H), 2.1—2.4 (m, 4H), 2.8—3.1 (m, 1H), 6.46 (t, J=7.3 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ=14.0, 22.5, 25.8, 25.9, 28.7, 28.8, 28.9, 29.8, 31.6, 44.3, 141.0, 141.3, 205.6; MS (rel intensity) 278 (M$^+$, 13), 207 (30), 195 (100), 83 (23), 55 (39). Found: C, 82.06; H, 12.51%. Calcd for C$_{19}$H$_{34}$O: C, 81.95; H, 12.31%.

(*E*)-3-Decyl-2-hydroxy-2-(2-phenylethyl)-4-trimethylsilyl-3-butenenitrile: Dehydrocyanation of the α-cyanohydrin took place under distillation conditions. Mass spectral analysis and elemental analysis were conducted with the corresponding trimethylsilyl ether produced by treatment with trimethylsilylimidazole. IR (neat) 3410, 3026, 2950, 2922, 2850, 1606, 1498, 1466, 1456, 1249, 1058, 858, 837, 748, 696 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.16 (s, 9H), 0.88 (t, J=6.3 Hz, 3H), 1.2—1.7 (m, 16H), 2.1—2.2 (m, 2H), 2.2—2.6 (m, 2H), 2.69 (s, 1H), 2.8—3.0 (m, 2H), 5.95 (s, 1H), 7.2—7.4 (m, 5H); ^{13}C NMR (CDCl$_3$) δ=−0.1, 14.1, 22.6, 29.27, 29.33, 29.5, 30.3, 30.7, 31.8, 31.96, 32.06, 42.3, 60.5, 76.7, 120.8, 126.2, 127.5, 128.4, 128.5, 140.5, 154.8; MS (rel intensity) 471 (M$^+$+SiMe$_3$, 2), 469 (2), 367 (36), 241 (15), 214 (27), 147 (10), 91 (28), 73 (100). Found: C, 71.11; H, 10.64; N, 2.86%. Calcd for C$_{28}$H$_{49}$NOSi$_2$: C, 71.27; H, 10.47; N, 2.97%.

(*E*)-4-Decyl-1-phenyl-5-trimethylsilyl-4-penten-3-one: Bp 123—125 °C (bath temp, 0.25 Torr); IR (neat) 3024, 2950, 2922, 2850, 1676, 1497, 1455, 1250, 855, 771, 748, 721, 697 cm^{-1};

^{1}H NMR ($CDCl_3$) δ=0.17 (s, 9H), 0.88 (t, J=6.7 Hz, 3H), 1.1—1.3 (m, 16H), 2.3—2.5 (m, 2H), 2.9—3.1 (m, 4H), 6.52 (s, 1H), 7.2—7.5 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=−0.3, 14.1, 22.7, 29.3, 29.5, 29.6, 30.0, 30.2, 31.4, 31.9, 39.5, 126.0, 128.4, 139.2, 141.6, 156.7, 201.5; MS (rel intensity) 372 (M^+, 21), 357 (11), 300 (11), 299 (31), 156 (18), 105 (17), 91 (43), 73 (100). Found: C, 77.32; H, 11.00%. Calcd for $C_{24}H_{40}OSi$: C, 77.35; H, 10.82%.

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