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Synthesis of Carbonyl Compounds via Ethynyl(*n*-butoxy or isopropoxy)dimethylsilane as a Reversely Polarized $^{+}CH_2CO^{-}$ Equivalent

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Regiospecific addition of organocopper reagents to ethynylalkoxydimethylsilane (**1**) followed by alkylation with alkyl halides gave 1,2-disubstituted vinylalkoxysilanes **3**. Oxidative cleavage of **3** provided ketones or aldehydes in good overall yields.

In the use of organosilicon compounds for organic synthesis, the substituents on silicon have been mainly alkyl or aryl groups (e.g. trimethyl- or *tert*-butyldimethylsilyl-).[1] More recently, it has been recognized that a functional substituent on silicon may modify the reactivity to confer novel synthetic utility.[2] Some examples include the control of regioselectivity in the alkylation of silylallyl carbanions,[3] and the control of stereoselectivity in the reactions of α-silylcarbanions.[4] Another important modification is the activation of a carbon silicon bond when the silicon moiety is substituted by electronegative groups such as fluorides or alkoxides. These activated organosilanes are more susceptible to reactions with electrophilic reagents such as peroxides,[5] halides,[6] and carbonyl compounds.[7]

We report here the overall conversion according to Scheme 1 in which the silicon reagent ethynylalkoxydimethylsilane **1** (**a**, R = *n*-Bu; **b**; R = i-Pr) can serve as a reversely polarized $^{+}CH_2CO^{-}$ equivalent[8] for the general synthesis of ketones and aldehydes. Organocopper reagents add regiospecifically[9] to the terminal carbon of the alkyne **1** to give the vinylcopper intermediate **2**. This is followed by reaction with alkyl halides or proton to give the vinylsilanes **3**. Due to the alkoxy substituent on silicon, vinylsilanes **3** can be oxidized readily by hydrogen peroxide/KF conditions[5] to the corresponding carbonyl compounds **4**.

Compound **1a** was prepared by the reaction of ethynylmagnesium bromide with *n*-butoxychlorodimethylsilane (**5**).[10] Alternatively, the alkoxy compound **1b** can be prepared in two steps via an aminosilane intermediate **6** (Scheme 2). Reaction of Bu_2CuLi, generated from butyllithium (2 mol) and copper iodide (1 mol), with **1** (2 mol) in ether at 20 °C gave the addition product **2** and then the vinylsilanes **3** in moderate yields (Table 1). It seemed that only half of the organocopper reagent was transferred to the alkynyl group. By reducing the amount of **1** to half that of the butylcopper reagent, the yield of **3** could be improved. However, this may not be synthetically desirable, especially in the case where the organolithium reagent is valuable. On the other hand, by using the reagent BuCu·LiI, generated from equal molar amounts of butyllithium and copper iodide, reacting with an equal number of moles of **1**, the yield was in the range of 70%. We found that the reaction yield could be improved further by adding 1 mol of trimethyl phosphite to the reaction mixture. An excess amount of trimethyl phosphite, on the other hand, reduced the yield of the reaction. Less reactive alkyl halides (e.g. *n*-BuBr) did not react under these conditions, but primary alkyl iodides did (as in compound **3g**, Table 2). In one particular case (compound **3c**, Table 1), the alkoxy group on silicon was hydrolyzed and the corresponding disiloxane was isolated as the product. The origin of the hydrolysis is not clear at this time, but may be due to the sensitivity of the siloxy ether to hydrolysis catalyzed by the metal salts.[11]

We have also explored the addition of organomagnesium–copper reagents to **1** since it is sometimes useful to generate organomagnesium compounds from the precursor organic halides. The reaction was found to be critically dependent on the choice of copper salt and the reaction temperature. Again, the use of equal numbers of moles of Grignard reagent, copper iodide, and trimethyl phosphite appeared to be optimal. The results are summarized in Table 2.

As expected, the stereochemistry of addition of the organocopper reagents to the triple bond is syn addition. This was evident when the vinylcopper intermediate **2** was quenched by a proton to give the product alkene with *E* stereochemistry.

The alkoxyvinylsilanes **3** can be oxidized efficiently and under mild reaction conditions (hydrogen peroxide/KF/

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(10) Wei, Z. Y.; Wang, D.; Li, J. S.; Chan, T. H. *J. Org. Chem.* **1989,** *54,* 5768.

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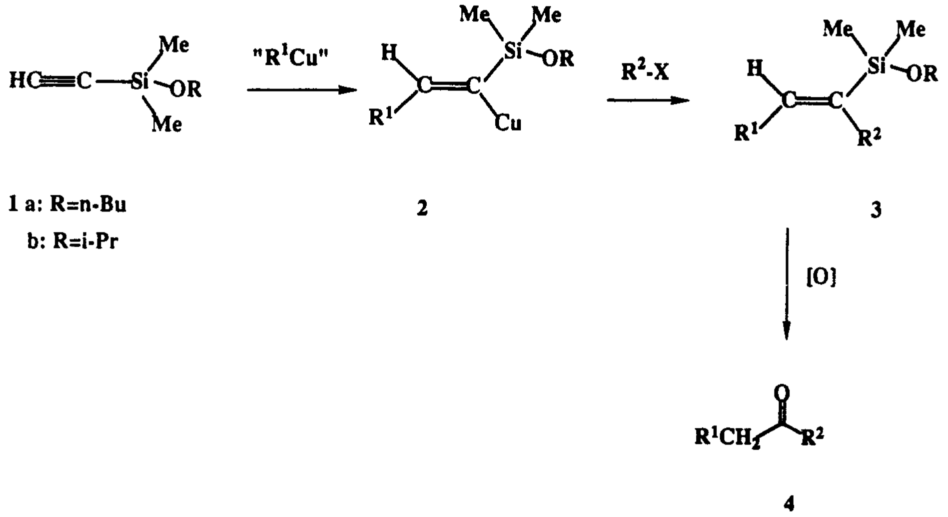
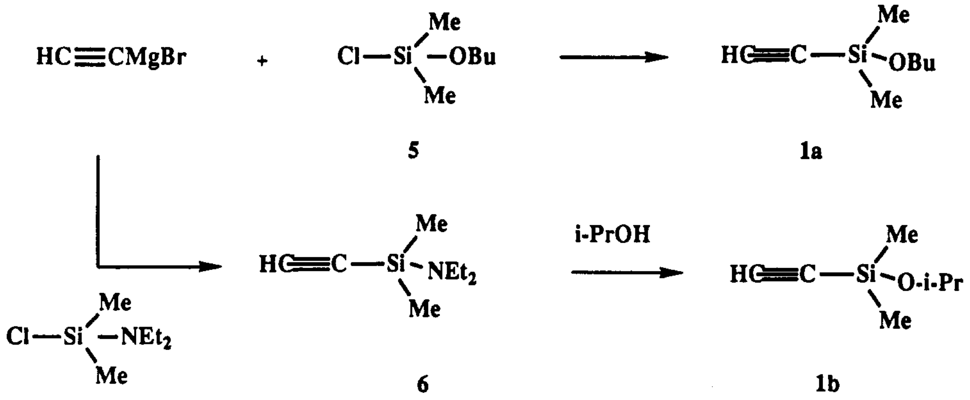
Scheme 1



Scheme 2



$KHCO_3$) to the corresponding ketones and aldehyes in good yields. In the case where there was a double bond at the β,γ-positions, the products obtained were the isomerized α,β-conjugated carbonyl compounds (examples **4a** and **4c**, Table 3).

Had the silyl group of **3** been trimethylsilyl or other alkyl(aryl)silyl groups, the oxidation of **3** would have required two steps, involving first epoxidation of the double bond by MCPBA followed by acid opening of the epoxysilane intermediate.[12] Such a sequence of steps would preclude the presence of a double bond or other acid sensitive groups in the carbonyl compounds. The overall reaction sequence in Scheme 1 therefore represents an efficient synthesis of carbonyl compounds in which compound **1** serves as a reversely polarized $^+CH_2CO^-$ equivalent.

Experimental Section

Boiling points are uncorrected. NMR spectra were run on a JEOL EX-100 or a Varian XL-200 or XL-400 spectrometer in $CDCl_3$ solutions with TMS as the internal standard. Mass spectra were determined on an AEI MS-50/PS-30 mass spectrometer. Infrared spectra were run on a PRE-780 or Carlzeiss specord 751 spectrometer. Final products were judged to be homogeneous by thin layer chromatography.

Ethynyl-*n*-butoxydimethylsilane (1a). To a solution of THF (250 mL) saturated with acetylene at room temperature was added dropwise a solution of ethylmagnesium bromide in THF (250 mL, 1 M, 0.25 mol). After addition, the solution was bubbled with additional acetylene for 0.5 h. The mixture was cooled to −78 °C. To the cooled mixture was added dropwise *n*-butoxychlorodimethylsilane (41.6 g, 0.25 mol) over 0.5 h. The mixture was allowed to warm to room temperature and then refluxed for 2 h. The mixture was evaporated to remove all the solvent. The solid residue was washed with petroleum ether (30–60 °C) several times and filtered. The washing and filtrate were combined and distilled to give compound **1a** as a colorless liquid, bp 142–3 °C/760 mmHg in 73% yield. ^1H NMR: δ 0.29 (6H, s), 0.95 (3H, t, J = 7.0 Hz), 1.28–1.46 (4H, m), 2.42 (1H, s), 3.7 (2H, t, J = 6.0 Hz). MS: m/z 141 ($M - 15^+$, 62), 131 (14), 113 (100), 83 (80). Exact mass calcd for $C_7H_{13}SiO$ ($M - 15^+$): 141.0735. Found: 141.0736.

Ethynyl(diethylamino)dimethylsilane (6). To a solution of THF (200 mL) saturated with acetylene was added dropwise a solution of ethylmagnesium bromide in THF (2.2 M, 50 mL, 0.11 mol). Acetylene was continuously bubbled through the reaction mixture until addition was complete, and the reaction mixture was cooled to −78 °C. To the mixture was added chloro(diethylamino)dimethylsilane (16.5 g, 0.10 mol). The mixture was warmed to room temperature, stirred for 2 h, and then refluxed for 3 h. The mixture was distilled to remove the solvents. The residue was washed with petroleum ether (30–60 °C) several times and filtered. The filtrates were distilled to give the product as a pale yellow liquid, bp 139–140 °C/760 mmHg in 70% (11-g) yield. ^1H NMR (CCl_4): δ 0.2 (6H, s), 0.9 (6H, t, J = 6.3 Hz), 2.0 (1H, s), 2.8 (4H, q, J = 6.3 Hz).

Ethynylisopropoxydimethylsilane (1b). To a flask equipped for distillation was added a mixture of compound **6** (15.7 g, 0.10 mol) and isopropanol (6.0 g, 0.10 mol). The mixture was heated to 80 °C, and the generated diethylamine was distilled off. After 2 h, the mixture was distilled to give **1b** as a colorless liquid, bp 98–99 °C/760 mmHg in 91% (13-g) yield. ^1H NMR:

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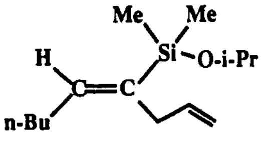
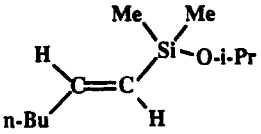
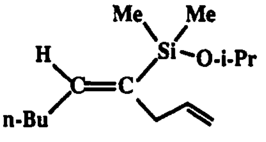
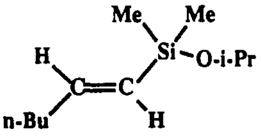
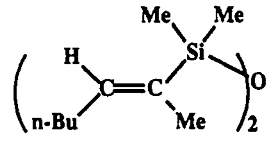
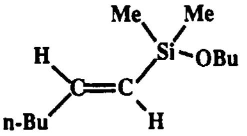
Table 1. Addition of Organocopper Reagents to 1

alkynylsilane	organocopper reagent	additive	R–X	product	yield, %
1b	Bu_2CuLi			 **3a**	45
1b	Bu_2CuLi		NH_4Cl	 **3b**	48
1b	BuCuLiI	$P(OMe)_3$		 **3a**	85
1b	BuCuLiI	$P(OMe)_3$	NH_4Cl	 **3b**	90
1b	BuCuLiI	$P(OMe)_3$	MeI	 **3c**	93
1a	BuCuLiI	$P(OMe)_3$	NH_4Cl	 **3d**	84

δ 0.26 (6H, s), 1.2 (6H, d, J = 5.6 Hz), 2.4 (1H, s), 4.16 (1H, h, J = 5.6 Hz). MS: m/z 127 (M − 15$^+$, 100), 117 (59), 83 (77). Exact mass calcd for $C_6H_{11}SiO$ (M − 15$^+$): 127.0579. Found: 127.0574.

General Procedures for the Addition of Butyllithium Copper Reagent to 1. To a solution of ether (30 mL) containing copper iodide (1.15 g, 6.0 mmol) at −25 °C was added a solution of BuLi in hexane (1.6 M, 3.5 mL, 5.6 mmol). The mixture was stirred for 30 min and cooled to −50 °C. A solution of compound 1 (5 mmol) and trimethyl phosphite (0.71 g, 5.7 mmol) in ether (5 mL) was added. The mixture was allowed to warm to 0 °C and left for 1 h. It was cooled back to −30 °C, and to it was added separately the electrophile (RX, 6 mmol), trimethyl phosphite (1.42 g, 11.4 mmol), and HMPA (2.2 g, 12.3 mmol). The mixture was stirred for 5 h at 20 °C. The reaction mixture was quenched with saturated aqueous NH_4Cl solution (20 mL). The organic phase was separated, and the aqueous phase was extracted with petroleum ether. The combined organic phase was dried ($MgSO_4$), filtered, and evaporated to dryness. The residue was purified by flash chromatography (eluent: petroleum ether).

(4-(1*E*,4*E*)-Nonadienyl)isopropoxydimethylsilane (3a). This compound was prepared from **1b** and allyl bromide as a colorless oil in 85% yield. ^{1}H NMR: δ 0.18 (6H, s), 0.9 (3H, t, J = 6.8 Hz), 1.15 (6H, d, J = 6.0 Hz), 1.2–1.5 (4H, m), 2.12 (2H, q, J = 7.6 Hz), 2.92 (2H, d, J = 6.8 Hz), 3.95 (1H, h, J = 6.0 Hz), 4.9–5.05 (2H, m), 5.6–5.9 (1H, m), 5.96 (1H, t, J = 7.6 Hz). IR (neat): 2940, 2910, 1620, 1600, 1240, 1140, 1040, 840, 775 cm^{-1}. MS: m/z 240 (6), 225 (30), 167 (100), 75 (38). Exact mass calcd for $C_{14}H_{28}SiO$: 240.1909. Found: 240.1907.

(1-(1*E*)-Hexenyl)isopropoxydimethylsilane (3b). This compound was prepared as a colorless oil from **1b** without the step of adding RX. The yield was 90%. ^{1}H NMR: δ 0.2 (6H, s), 0.9 (3H, t, J = 6.4 Hz), 1.17 (6H, d, J = 6.0 Hz), 1.2–1.5 (4H, m), 2.14 (2H, q, J = 6.4 Hz), 4.0 (1H, m), 5.65 (1H, d, J = 18.6 Hz), 6.15 (1H, dt, J = 18.6 Hz). IR (neat): 2940, 2905, 1608, 1240, 1040, 840, 790 cm^{-1}. MS: m/z 200 (1), 185 (100), 143 (74), 75 (37). Exact mass calcd for $C_{10}H_{21}SiO$ (M − 15$^+$): 185.1361. Found: 185.1364.

(2-(2*E*)-Heptenyl)isopropoxydimethyldisiloxane (3c). This compound was prepared from **1b** and methyl iodide as a colorless oil in 93% yield. ^{1}H NMR: δ 0.1 (12H, s), 0.9 (6H, t, J = 6.4 Hz), 1.15–1.5 (8H, m), 1.7 (6H, s), 2.0 (4H, q, J = 6.8 Hz), 5.9 (2H, t, J = 6.8 Hz). IR (neat): 2950, 2920, 1610, 1240, 1045, 820, 790, 780 cm^{-1}. MS: m/z 326 (15), 311 (8), 213 (25), 133 (100), 119 (38). Exact mass calcd for $C_{18}H_{38}Si_2O$: 326.2460. Found: 326.2447.

(1-(1*E*)-Hexenyl)butoxydimethylsilane (3d). This compound was prepared from **1a** without the step of adding RX. The yield was 84%. ^{1}H NMR: δ 0.17 (6H, s), 0.9 (3H, t, J = 6.3 Hz), 1.2–1.7 (8, m), 2.15 (2H, q, J = 6.6 Hz), 3.58 (2H, t, J = 6.3 Hz), 5.6 (1H, d, J = 18.6 Hz), 6.15 (1H, dt, J = 18.6 Hz). IR (neat): 2940, 2908, 1605, 1240, 1085, 840 cm^{-1}. MS: m/z 214 (1), 199 (100), 143 (20). Exact mass calcd for $C_{12}H_{26}Si$: 214.1752. Found: 214.1752.

General Procedures for the Addition of Organomagnesium Copper Reagent to Compound 1. To a solution of ether (15 mL) containing CuI (1.15 g, 6.0 mmol) at −30 °C, a solution of organomagnesium bromide in ether (1 M, 5.5 mL, 5.5 mmol) was added dropwise. The mixture was stirred at −20 °C for 1 h and then cooled to −50 °C. A solution of compound **1a** (0.76 g, 5.0 mmol) in ether (5 mL) and trimethyl phosphite (0.65 mL, 5.0 mmol) were added. The mixture was warmed to 0 °C, and stirred

Table 2. Addition of Organomagnesium-Copper Reagents to 1

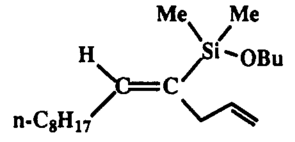
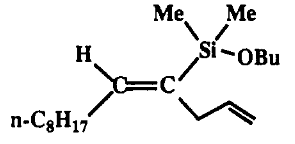
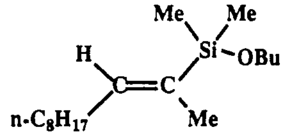
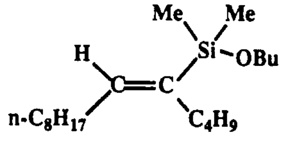
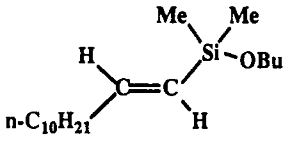
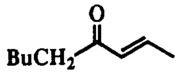
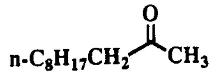
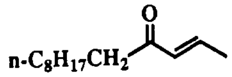
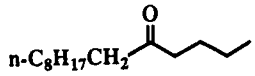
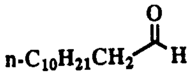
alkynylsilane	organocopper reagent	additive	R–X	product	yield, %
1a	*n*-$C_8H_{17}MgBr$ + CuBr	$P(OMe)_3$		 **3e**	61
1a	*n*-$C_8H_{17}MgBr$ + CuI	$P(OMe)_3$		 **3e**	65
1a	*n*-$C_8H_{17}MgBr$ + CuI	$P(OMe)_3$	MeI	 **3f**	64
1a	*n*-$C_8H_{17}MgBr$ + CuI	$P(OMe)_3$	*n*-BuI	 **3g**	56
1a	*n*-$C_{10}H_{21}MgBr$ + CuI	$P(OMe)_3$	NH_4Cl	 **3h**	61

Table 3. Oxidation of Vinylsilanes 3 to Carbonyl Compounds

vinylsilane	product 4	yield, %
3a	4a, 	89
3f	4b, 	87
3e	4c, 	85
3g	4d, 	90
3h	4e, 	51

for 2 h, and then cooled to −50 °C. A solution of RX (6 mmol) in ether (5 mL) was added, followed by trimethyl phosphite (1.3 mL, 10 mmol) and HMPA (1.8 mL, 10 mmol). The mixture was warmed to room temperature and stirred overnight. The mixture was cooled to −20 °C and quenched with saturated aqueous NH_4Cl solution (20 mL). The organic phase was separated, and the aqueous was washed three times (20 mL each) with petroleum ether (30–60 °C). The combined organic phase was dried ($MgSO_4$), filtered, and evaporated. The residue was purified by flash chromatography (eluent: petroleum ether).

(4-(1*E*,4*E*)-Tridecadienyl)-*n*-butoxydimethylsilane (3e). The compound was prepared from **1a**, octylmagnesium bromide, and allyl bromide as RX in 65% yield as a colorless oil. ^{1}H NMR: δ 0.2 (6H, s), 0.8–1.0 (6H, m), 1.2–1.6 (16H, m), 2.13 (2H, q, J = 7.8 Hz), 2.93 (2H, d, J = 7.2 Hz), 3.55 (2H, t, J = 6.8 Hz), 4.9–5.1 (2H, m), 5.6–5.9 (1H, m), 5.95 (1H, t, J = 7.8 Hz). IR (neat): 2940, 2910, 1620, 1600, 1240, 1020, 820, 775 cm^{-1}. MS: *m/z* 310 (1), 295 (7), 131 (100), 113 (27), 83 (41), 75 (56), 69 (40), 57 (43). Exact mass calcd for $C_{19}H_{38}SiO$: 310.2691. Found: 310.2705.

(2-(2*E*)-Undecenyl)-*n*-butoxydimethylsilane (3f). This compound was prepared from **1a** and octylmagnesium bromide with methyl iodide as RX as a colorless oil in 64% yield. ^{1}H NMR: δ 0.15 (6H, s), 0.8–1.0 (6H, m), 1.15–1.6 (16H, m), 1.68 (3H, s), 2.10 (2H, q, J = 6.8 Hz), 3.55 (2H, t, J = 6.4 Hz), 5.85 (1H, t, J = 6.8 Hz). IR (neat): 2943, 2910, 1610, 1245, 1050, 825, 780 cm^{-1}. MS: *m/z* 254 (2), 269 (100), 255 (22), 131 (83), 75 (70). Exact mass calcd for $C_{17}H_{36}SiO$: 284.2535. Found: 284.2539.

(5-(5*E*)-Tetradecenyl)-*n*-butoxydimethylsilane (3g). This compound was obtained from **1a**, octylmagnesium bromide, and butyl iodide as RX as a colorless in oil in 56% yield. ^{1}H NMR: δ 0.18 (6H, s), 0.8–1.0 (6H, m), 1.1–1.6 (20H, m), 2.0–2.2 (4H, m), 3.53 (2H, t, J = 6.4 Hz), 5.8 (1H, t, J = 6.8 Hz). IR (neat): 2940, 2910, 1605, 1460, 1370, 1240, 1030, 870, 775 cm^{-1}. MS: *m/z* 311 (M − 15$^+$, 62), 255 (100), 187 (47), 131 (41), 75 (49). Exact mass calcd for $C_{20}H_{42}SiO$: 326.3004. Found: 326.3010.

(1-(1*E*)-Dodecenyl)-*n*-butoxydimethylsilane (3h). This compound was prepared from **1a** and decylmagnesium bromide without the step of adding RX. The compound was obtained as a colorless oil in 61% yield. ^{1}H NMR: δ 0.20 (6H, s), 0.8–1.03 (6H, m), 1.2–1.6 (20H, m), 2.15 (2H, q, J = 6.5 Hz), 3.6 (2H, t, J = 6.3 Hz), 5.63 (1H, d, J = 18.6 Hz), 6.20 (1H, dt, J = 18.6, 6.5 Hz). IR (neat): 2940, 2910, 1610, 1240, 1030, 785 cm^{-1}. MS: *m/z* 298 (1), 283 (100), 131 (26), 75 (15). Exact mass calcd for $C_{18}H_{38}SiO$: 298.2691. Found: 298.2706.

General Procedures for the Oxidation of Compound 3. To a mixture of $KF{\cdot}H_2O$ (0.50 g, 5.1 mmol), $KHCO_3$ (0.25 g, 2.5 mmol), compound **3** (2 mmol) to be oxidized, methanol (2 mL), and THF (2 mL) at room temperature was added dropwise a solution of 30% hydrogen peroxide (0.75 mL, 6.6 mmol). After addition, the mixture was stirred overnight at 50 °C. To the mixture at 0 °C was added an aqueous solution of Na_2SO_3 (10%, 10 mL). The mixture was extracted with ether (2 × 20 mL). The organic phase was dried ($MgSO_4$), filtered, and evaporated. The residue was purified by column chromatography over silica gel (eluent: petroleum ether/ethyl acetate: 50/1) to give the product.

(2*E*)-Nonen-4-one (4a).[13] This compound was obtained by the oxidation of **3a** as a colorless oil in 89% yield. ^{1}H NMR: δ 0.90 (3H, t, J = 7.2 Hz), 1.15–1.5 (4H, m), 1.5–1.75 (2H, m), 1.95 (3H, d, J = 6.8 Hz), 2.55 (2H, t, J = 6.8 Hz), 6.18 (1H, d, J = 15.6 Hz), 6.87 (1H, dq, J = 15.6, 6.8 Hz). IR (neat): 2940, 2900, 1665 cm^{-1}. MS: *m/z* 140 (4), 125 (17), 99 (14), 84 (56), 69 (100). Exact mass calcd for $C_9H_{16}O$: 140.1201. Found: 140.1210.

(2*E*)-Tridecen-4-one (4c). This compound was prepared from **3e** as a colorless oil in 85% yield. ^{1}H NMR: δ 0.90 (3H, t, J = 7.2 Hz), 1.1–1.5 (12H, m), 1.5–1.75 (2H, m), 2.55 (2H, t, J = 7.0 Hz), 6.17 (1H, d, J = 15.6 Hz), 6.86 (1H, dq, J = 15.6, 6.8 Hz). IR (neat): 2940, 2910, 1695 cm^{-1}. MS: *m/z* 196 (1), 181 (4), 97 (11), 84 (81), 69 (100). Exact mass calcd for $C_{13}H_{24}O$: 196.1827. Found: 196.1824.

Tetradecan-5-one (4d).[14] This compound was prepared from **3g** as a white waxy solid in 90% yield. ^{1}H NMR: δ 0.85–1.0 (6H, m), 1.2–1.46 (14H, m), 1.46–1.7 (4H, m), 2.03 (4H, t, J = 7.0 Hz). IR (neat): 2940, 2910, 1700, 1455, 1370, 1130 cm^{-1}. MS: *m/z* 212 (6), 183 (4), 155 (40), 113 (15), 100 (26), 101 (17), 85 (78), 71 (45), 59 (11), 58 (100). Exact mass calcd for $C_{14}H_{28}O$: 212.2140. Found: 212.2156.

Undecan-2-one (4b).[15] This compound was prepared from **3f** as a colorless oil in 87% yield. ^{1}H NMR: δ 0.92 (3H, t, J = 6.0 Hz), 1.2–1.4 (12H, m), 1.5–1.7 (2H, m), 2.17 (3H, s), 2.44 (2H, t, J = 7.2 Hz). IR (neat): 2940, 2910, 1705, 1350, 1155 cm^{-1}. MS: *m/z* 170 (8), 155 (3), 71 (47), 58 (100), 43 (100). Exact mass calcd for $C_{11}H_{22}O$: 170.1670. Found: 170.1670.

Dodecanal (4e).[16] This compound was prepared from **3h** as a waxy solid in 51% yield. ^{1}H NMR: δ 0.93 (3H, t, J = 6.0 Hz), 1.2–1.5 (16H, m), 1.6–1.8 (2H, m), 2.45 (2H, t, J = 6.2 Hz), 9.8 (1H, s).

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