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A Straightforward Approach to Unsaturated Carboxylic Acid Derivatives Starting from Bis-Silylated Precursors

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Abstract

A new synthetic approach to substituted unsaturated carboxylic acid derivatives, such as amides, nitriles and esters, has been developed, starting from easily accessible bis-silylated precursors. The key step was based upon the reaction of a bis-silylated diene and a bis-silylated enyne with chlorosulphonyl isocyanate, which afforded mono-silylated amides, easily converted into substituted nitriles and esters.

Keywords
Silicon and Compounds; Carboxylic acids and derivatives

Introduction

In continuation of our studies on the synthesis of stereodefined conjugated polyenes [1-8], we recently reported that (all *E*) bis-silylated dienes and trienes can undergo a chemoselective and sequential electrophilic substitution of the trimethylsilyl group with acyl chlorides in the presence of $AlCl_3$ [2]. The sequence of reactions proved to be very useful for the ready synthesis of a series of natural compounds having a conjugated polyene structure [3-5,8].

In connection with this type of synthetic work, we have explored the possibility of a chemoselective substitution of the silyl group of bis-silylated systems, presenting different types of unsaturation, with other electrophiles, with the aim of synthesizing useful building blocks for the construction of polyunsaturated natural compounds.

In particular, vinyl [9] and alkynyl silanes [10] are known to undergo reaction with chlorosulphonyl isocyanate (CSI) to give, after acid work-up, α,β-unsaturated amides, with a

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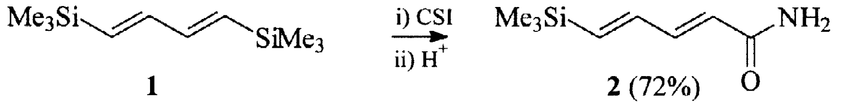
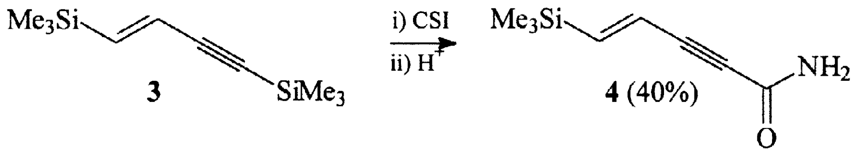
mechanism involving an electrophilic attack, followed by the silyl group migration. This result led us to attempt a similar reaction with our unsaturated bis-silylated systems, presenting both double and triple bonds, in the expectation of a chemoselective substitution of the silyl group. Indeed, we found that chlorosulphonyl isocyanate reacted selectively both with (all *E*) 1,4-bis-(trimethylsilyl)-1,3-butadiene **1** [11], and with (3*E*)-1,4-bis(trimethylsilyl)-3-buten-1-yne **3** [12] leading to the mono-silylated amides **2** and **4**, after acid work-up, in good yields (eqs 1 and 2):



(1)



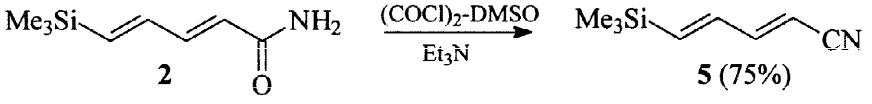
(2)

The presence of both the silyl and the amide group suggested the possibility of other useful and easy transformations of these functional groups. Consequently, in order to extend the synthetic utility of these amides, we started to perform the synthesis of a series of unsaturated carboxylic acid derivatives.

Results and Discussion

Many methods for the conversion of primary carboxamides into the related carboxylic acid derivatives, such as nitriles and esters, have been well documented in the literature [13-20]. In particular the conversion into nitriles by dehydration of carboxamides required, for example, $LiAlH_4$-$HgCl_2$ [13], $TiCl_4$ [14], $SOCl_2$ [15] or, more recently $(COCl)_2$-DMSO in the presence of triethylamine [16]. Furthermore, the conversion of amides into esters usually required conditions generally incompatible with sensitive substrates, such as treatment with the suitable alcohol in the presence of HCl [17], BF_3 [18] Amberlyst® 15 resin [19] or, more recently, dimethylformamide dimethyacetal [20]. Herein we describe the transformation of our silylated unsaturated amides into nitriles and into esters under mild condition reactions.

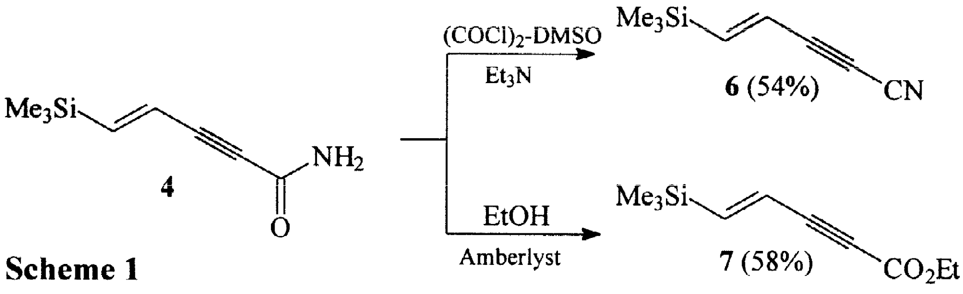
A first example is the easy conversion of amide **2** into the nitrile **5**, by employing oxalyl chloride and triethylamine (eq. 3):



(3)

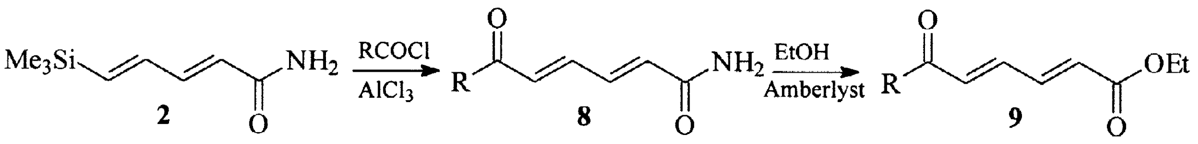
It is noteworthy that compound **5** was usually prepared, as reported in the literature [21,22], by the Wittig reaction, starting from a not readily available α,β-unsaturated mono-silylated aldehyde.

Under the same reaction conditions, the amide **4** also was readily transformed into the nitrile **6**. Furthermore, the amide **4** was converted into the ester **7** by treatment with ethanol in the presence of Amberlyst® 15 (Scheme 1).

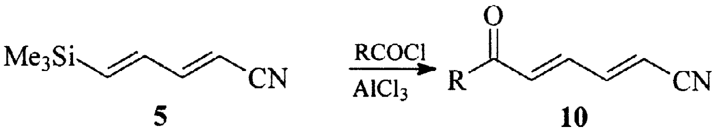


Scheme 1

All compounds **2** and **4-7** appeared to be useful synthetic intermediates, for the presence of different terminal functional groups and additional unsaturation. In particular, by electrophilic substitution with acyl chlorides in the presence of $AlCl_3$ of the remaining silyl group on compound **2** and on compound **5**, we synthesized respectively several dienic ketoamides **8**, further transformed into ketoesters **9**, and dienic ketonitriles **10** (eqs 4 and 5):



(4)



(5)

8a R = C_5H_{11} (92%)
8b R = C_7H_{15} (95%)
8c R = $MeO_2C(CH_2)_3$ (39%)

9a R = C_5H_{11} (80%)
9b R = C_7H_{15} (62%)

10a R = C_5H_{11} (67%)
10b R = C_7H_{15} (43%)

The ketoamides **8a-c** were obtained in fair to good yields with high retention of configuration, by employing appropriate acyl chlorides (92, 95 and 39% yield). The amides **8a** and **8b** were further converted into the respective ethyl esters **9a** and **9b** in good yields (80 and 62%). Likewise the ketonitriles **10a** and **10b** were obtained by acylation of the nitrile **5** (67 and 43% yield).

In conclusion, the procedure described here appears to be a useful route to stereodefined substituted carboxylic acid derivatives. Both mono-silylated derivatives and ketoamides, ketoesters or ketonitriles can be obtained, starting from readily available precursors. Moreover, the mild reaction conditions and the simplicity of the operations involved are additional features making the methodology very promising.

Experimental

Macherey-Nagel silica gel (60, particle size 0.040-0.063 mm) for flash column chromatography and Macherey-Nagel aluminum sheets with silica gel 60 F_{254} for TLC were used. GC analysis was performed on a Hewlett-Packard 5890 series II gas chromatograph equipped with a SE-30 (methylsilicone, 30 m x 0.25 mm id) capillary column. GC/mass-spectrometry analysis was performed on a Hewlett-Packard 5970A equipped with an HP-1 capillary column, 25 m, and HP MSD 5970B. ^{1}H-NMR spectra were recorded in deuterochloroform on a Bruker AM 500 spectrometer at 500 MHz and on a Bruker AM 300 spectrometer at 300 MHz. Elemental analyses were recorded on a Carlo Erba 1106 elemental analyzer. Commercial grade reagents and solvents were used as supplied. Amberlyst® 15 resin was purchased from Aldrich. The products were purified by flash chromatography or by crystallization. Petroleum ether 40 °C-70 °C was used as eluent for chromatography. Melting points (uncorrected) were determined on a Reichert Microscope.

Synthesis of products **2** *and* **4-7**

(2*E*,4*E*)-5-Trimethylsilyl-2,4-pentadienamide (2). Chlorosulphonyl isocyanate (0.48 mL, 5.55 mmol) was added, under nitrogen, to a CCl_4 solution (15 mL) of (1*E*,3*E*)-1,4-bis(trimethylsilyl)-1,3-butadiene **1** [11] (1 g, 5.04 mmol) cooled at 0 °C. After 0.5 h, the ice-bath was removed and the solution stirred at room temperature. After reaction completion (4 h), the solvent was removed under vacuum and the resulting mixture was dissolved in acetone (12 mL) and then HCl 0.1 N (8 mL) was added. The reaction mixture was refluxed for 5 min, then, after cooling at room temperature, an aqueous solution of NaOH (10%) was added, followed by extraction with ethyl acetate. The organic extracts were washed with water, separated and dried over Na_2SO_4. Crystallization from CH_2Cl_2/petroleum ether led to compound **2** (0.61 g, 72% yield) as a white solid, m.p. 148-149 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ 0.07 (s, 9H), 5.58-5.80 (br s, 1H), 5.81-6.02 (br s, 1H), 5.89 (d, J = 15.2 Hz, 1H), 6.28 (d, J = 18.3 Hz, 1H), 6.56 (dd, J = 18.3, 10.4 Hz, 1H), 7.12 (dd, J = 15.2, 10.4 Hz, 1H) ppm. MS m/e 169 (M^+, 4), 168 (13), 155 (13), 154 (100), 136 (12), 128 (8), 109 (7), 96 (7), 95 (8), 80 (12), 79 (12), 76 (8), 75 (69), 74 (40), 73 (12), 59 (18). IR: 3343, 3172, 1674, 1608, 1577, 1402, 1248, 1003, 864, 840 cm^{-1}. *Anal.* Calcd for $C_8H_{15}NOSi$: C, 56.76; H, 8.93; N, 8.27. Found: C, 56.65; H, 8.92; N, 8.11.

(4*E*)-5-Trimethylsilyl-4-buten-2-ynamide (4). Chlorosulphonyl isocyanate (1.06 mL, 12.2 mmol) was added, under nitrogen, to a $CHCl_3$ solution (17 mL) of (*E*)-1,4-bis(trimethylsilyl)-3-buten-1-yne **3** [12] (1 g, 5.09 mmol) cooled at 0 °C. After 1 h, the ice-bath was removed and the solution stirred at room temperature. After 24 h, the solvent was removed under vacuum and the mixture dissolved in acetone (17 mL) and then HCl 0.1 N (8.5 mL) was added. The reaction mixture was refluxed for 5 min, then, after cooling at room temperature, an aqueous solution of NaOH (10%) was added, followed by extraction with ethyl acetate. The organic extracts were washed with water and dried over Na_2SO_4. Crystallization from CH_2Cl_2/petroleum ether led to compound **4** (0.34 g, 40% yield) as a white solid, m.p. 159-160 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ 0.08 (s, 9H), 5.67-5.83 (br s, 1H), 5.96 (d, *J* = 19.4 Hz, 1H), 6.01-6.19 (br s, 1H), 6.73 (d, *J* = 19.4 Hz, 1H) ppm. MS m/e 167 (M^+, 7), 166 (44), 153 (8), 152 (57), 133 (12), 125 (9), 124 (42), 123 (34), 107 (20), 98 (19), 95 (10), 93 (9), 84 (17), 83 (27), 77 (25), 76 (11), 75 (26), 74 (100), 73 (18), 59 (35). IR: 3321, 3188, 2221, 1653, 1611, 1391, 1250, 976, 866, 840 cm^{-1}. *Anal.* Calcd for $C_8H_{13}NOSi$: C, 57.44; H, 7.83; N, 8.37. Found: C, 57.10; H, 7.95; N, 8.11.

(2*E*,4*E*)-5-Trimethylsilyl-2,4-pentadienenitrile (5). A CH_2Cl_2 solution (2.5 mL) of oxalyl chloride (0.22 mL, 2.5 mmol) was added, under nitrogen, to a solution of **2** (0.3 g, 1.77 mmol) and DMSO (0.25 mL, 3.55 mmol) in methylene chloride (7 mL) at -78 °C. After stirring for 15 min at -78 °C, Et_3N (0.74 mL, 5.3 mmol) was added dropwise to the mixture. After reaction completion (1 h), the mixture was quenched with water and extracted with ethyl acetate. The organic extracts were washed with brine, dried and evaporated. The residue was purified by flash column chromatography (silica gel, petroleum ether/EtOAc 9/1) leading to nitrile **5** [21,22] as a colorless oil (0.20 g, 75% yield).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.05 (s, 9H), 5.33 (d, *J* = 16.0 Hz, 1H), 6.33 (d, *J* = 18.3 Hz, 1H), 6.53 (dd, *J* = 18.3, 10.1 Hz, 1H), 6.93 (dd, *J* = 16.0, 10.1 Hz, 1H) ppm. MS m/e 151 (M^+, 16), 150 (14), 137 (8), 136 (61), 110 (5), 109 (21), 86 (9), 84 (9), 78 (5), 73 (12), 66 (29), 59 (100). IR: 2218, 1614, 1570, 1250, 1121, 1004, 863, 840 cm^{-1}.

(4*E*)-5-Trimethylsilyl-4-penten-2-ynenitrile (6). A CH_2Cl_2 solution (1.5 mL) of oxalyl chloride (0.15 mL, 1.68 mmol) was added, under nitrogen, to a solution of **4** (0.2 g, 1.20 mmol) and DMSO (0.17 mL, 2.41 mmol) in methylene chloride (3.5 mL) at -78 °C. After stirring for 15 min at -78 °C, Et_3N (0.50 mL, 3.60 mmol) was added dropwise to the mixture. After 24 h, the mixture was quenched with water and extracted with ethyl acetate. The organic extracts were washed with brine, dried and evaporated. The residue was purified by flash column chromatography (silica gel, EtOAc/petroleum ether 6/4) leading to nitrile **6** as a colorless oil (0.097 g, 54% yield).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.05 (s, 9H), 5.93 (d, J = 19.5 Hz, 1H), 7.05 (d, J = 19.5 Hz, 1H) ppm. MS m/e 149 (M^+, 1), 134 (57), 123 (9), 122 (79), 108 (16), 73 (9), 59 (100). IR: 2254, 1253, 1099, 1019, 976, 865, 846 cm^{-1}. *Anal.* Calcd for $C_8H_{11}NSi$: C, 64.37; H, 7.43; N, 9.38. Found: C, 64.12; H, 7.35; N, 9.21.

Ethyl (4*E*)-5-trimethylsilyl-4-penten-2-ynoate (7). 1.5 g of Amberlyst® 15 were added to an ethanol solution (4 mL) of compound **4** (0.1 g, 0.60 mmol). The mixture was warmed to the reflux temperature, in a sealed tube (reaction time 12 days). Removal of the resin by filtration and evaporation of the solvent provided the crude product **7**, which was purified by flash chromatography (silica gel, petroleum ether/EtOAc 9.5/0.5). 0.068 g (58% yield) of a colorless oil were obtained.

^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.07 (s, 9H), 1.28 (t, J = 7.1 Hz, 3H), 4.21 (q, J = 7.1 Hz, 2H), 5.96 (d, J = 19.7 Hz, 1H), 6.80 (d, J = 19.7 Hz, 1H) ppm. MS m/e 181 (55), 154 (10), 153 (77), 152 (10), 151 (36), 137 (14), 125 (36), 124 (27), 123 (100), 111(8), 110 (19), 109 (71), 108 (9), 107 (55), 103 (18), 99 (16), 95 (16), 93 (22), 83 (36), 77 (85), 75 (78), 73 (31). IR: 2212, 1713, 1252, 1086, 978, 864, 842 cm $^{-1}$. *Anal.* Calcd for $C_{10}H_{16}O_2Si$: C, 61.18; H, 8.21. Found: C, 61.05; H, 8.12.

General procedure for the synthesis of ketoamides 8, ketoesters 9 and ketonitriles 10.

A CH_2Cl_2 solution of freshly distilled acyl chloride (3 equiv.) was added, under nitrogen, to a cold (0 °C) suspension of anhydrous $AlCl_3$ (6 equiv.) in methylene chloride. The resulting mixture was allowed to stir at 0 °C for 20 min, then transferred via syringe to the addition funnel of a three-necked flask, cooled at 0 °C, which contained a CH_2Cl_2 solution of **2** or **5** (1 equiv.). After complete addition at 0 °C, the mixture was allowed to warm at room temperature. After reaction completion (1-10 h), the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted whit ethyl acetate. The organic extraxts were washed with water, dried over Na_2SO_4 and concentrated. Flash chromatography on silica gel of the residue afforded ketoamides **8** or ketonitriles **10**, which were purified by crystallization. The ketoesters **9** were easily prepared [19] by combining the amide **8** with sufficient solvent (EtOH) to cover the resin (Amberlyst® 15) and warming the mixture to the reflux temperature, in a tightly stoppered flask (reaction time 150 h). Removal of the resin by filtration and evaporation of the solvent provided the crude products **9**, which were isolated by flash chromatography and crystallized.

The spectral and physical data are as follows.

(2*E*,4*E*)-6-Oxo-2,4-undecadienamide (8a). Product **8a** was prepared from **2** (0.1 g, 0.59 mmol) in accordance with the general procedure and purified by flash chromatography (ethyl acetate as eluent) (0.106 g, 92% yield). The residual solid was crystallized from ethyl acetate giving white crystals of **8a**, m.p. 165-166 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ 0.87 (t, *J* = 7.0 Hz, 3H), 1.22-1.34 (m, 4H), 1.57-1.66 (m, 2H), 2.56 (t, *J* = 7.4 Hz, 2H), 5.55-5.70 (br s, 2H), 6.25 (d, *J* = 14.9 Hz, 1H), 6.44 (d, *J* = 15.2 Hz, 1H), 7.16 (dd, *J* = 15.2, 11.4 Hz, 1H), 7.28 (dd, *J* = 14.9, 11.4 Hz, 1H) ppm. MS m/e 195 (M^+, 3), 178 (9), 166 (6), 151 (6), 139 (20), 138 (8), 124 (16), 122 (21), 107 (7), 96 (100), 95 (24), 94 (10), 81 (25), 79 (14), 68 (8). IR: 3388, 3187, 1682, 1656, 1604, 998 cm^{-1}. *Anal.* Calcd for $C_{11}H_{17}NO_2$: C, 67.66; H, 8.78; N, 7.17. Found: C, 67.40; H, 8.92; N, 7.03.

(2*E*,4*E*)-6-Oxo-2,4-tridecadienamide (8b). Product **8b** was prepared from **2** (0.1 g, 0.59 mmol) in accordance with general procedure. Flash chromatography (ethyl acetate/methanol 9/1 as eluent) afforded 0.125 g (95% yield) of **8b**. The residue was crystallized from ethyl acetate giving white crystals of **8b**, m.p. 169-170 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ 0.86 (t, *J* = 7.0 Hz, 3H), 1.22-1.32 (m, 8H), 1.57-1.64 (m, 2H), 2.56 (t, *J* = 7.4 Hz, 2H); 5.47-5.61 (br s, 2H), 6.24 (d, *J* = 14.9 Hz, 1H), 6.44 (d, *J* = 15.3 Hz, 1H), 7.16 (dd, *J* = 15.3, 11.4 Hz 1H), 7.28 (dd, *J* = 14.9, 11.4 Hz, 1H) ppm. MS m/e 223 (M^+, 7), 206 (6), 179 (10), 166 (8), 152 (4), 149 (7), 139 (33), 138 (15), 124 (22), 122 (29), 107 (8), 96 (100), 95 (32), 94 (15), 81 (25), 79 (15), 68 (10). IR: 3388, 3189, 1682, 1656, 1604, 998 cm^{-1}. *Anal.* Calcd for $C_{13}H_{21}NO_2$: C, 69.92; H, 9.48; N, 6.27. Found: C, 69.62; H, 9.61; N, 6.21.

(2*E*,4*E*)-6-Oxo-9-carbomethoxy-2,4-nonadienamide (8c). 0.052 g (39% yield) of product **8c** were obtained from **2** (0.1 g, 0.59 mmol) after flash chromatography (EtOAc/petroleum ether 9/1 as eluent). White crystals of **8c**, m.p. 151-152 °C, were obtained by crystallization with ethyl acetate.

^{1}H-NMR (500 MHz, $CDCl_3$): δ 1.94 (quintet, *J* = 7.2 Hz, 2H), 2.36 (t, *J* = 7.2 Hz, 2H), 2.66 (t, *J* = 7.2 Hz, 2H), 3.65 (s, 3H), 5.60-5.71 (br s, 2H), 6.26 (d, *J* = 14.8 Hz, 1H), 6.41 (d, *J* = 15.2 Hz, 1H), 7.18 (dd, *J* = 15.2, 11.4 Hz, 1H), 7.27 (dd, *J* = 14.8, 11.4 Hz, 1H) ppm. MS m/e 209 (4), 208 (33), 194 (8), 193 (12), 181 (12), 177 (10), 149 (4), 138 (6), 135 (3), 124 (16), 121 (6), 107 (15), 96 (100), 81 (19), 79 (15), 68 (7). IR 3306, 3154, 1732, 1687, 1642, 1598, 1305, 1008 cm^{-1}. *Anal.* Calcd for $C_{11}H_{15}NO_4$: C, 58.66; H, 6.71; N, 6.22. Found: C, 58.81; H, 6.97; N, 6.16.

Ethyl (2*E*,4*E*)-6-oxo-2,4-undecadienoate (9a). Product **9a** was prepared by reaction of **8a** (0.1 g, 0.51 mmol) with EtOH (8 mL) in the presence of Amberlyst® 15 (1.5 g). Flash chromatography (petroleum ether/ethyl acetate 9/1) gave 0.092 g (80% yield) of **9a**. The residue was crystallized from petroleum ether affording white crystals of **9a**, m.p. 50-51 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ 0.87 (t, *J* = 7.1 Hz, 3H), 1.22-1.36 (m, 7H), 1.58-1.66 (m, 2H), 2.57 (t, *J* = 7.4 Hz, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 6.21 (d, *J* = 15.3 Hz, 1H), 6.43 (d, *J* = 15.4 Hz, 1H), 7.15 (dd, *J* = 15.4, 11.4 Hz, 1H), 7.30 (dd, *J* = 15.3, 11.4 Hz, 1H) ppm. MS m/e 224 (M^+, 10), 219 (12), 207 (17), 195 (56), 179 (35), 178 (31), 168 (68), 153 (61), 151 (27), 139 (30), 125 (39), 122 (22), 99 (14), 97 (100), 95 (88), 81 (27), 79 (24). IR: 1713, 1687, 1593, 1232, 1144, 1025 cm^{-1}. *Anal.* Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.40; H, 9.05.

Ethyl (2*E*,4*E*)-6-oxo-2,4-tridecadienoate (9b). Product **9b** was obtained from **8b** (0.05 g, 0.224 mmol) and EtOH (4 mL) in the presence of Amberlyst® 15 (0.75 g). Flash chromatography (petroleum ether/ethyl acetate 9/1) gave 0.035 g (62% yield) of **9b**. The residue was crystallized from petroleum ether affording white crystals of **9b**, m.p. 81-82 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ 0.86 (t, *J* = 7.0 Hz, 3H), 1.20-1.40 (m, 11H), 1.55-1.72 (m, 2H), 2.56 (t, *J* = 7.4 Hz, 2H), 4.09 (q, *J* = 7.2 Hz, 2H), 6.21 (d, *J* = 15.3 Hz, 1H), 6.42 (d, *J* = 15.4 Hz, 1H), 7.15 (dd, *J* = 15.4, 11.4 Hz, 1H), 7.29 (dd, *J* = 15.3, 11.4 Hz, 1H) ppm. MS m/e 252 (M^+, 3), 223 (12), 207 (12), 195 (11), 179 (15), 168 (40), 153 (30), 149 (9), 139 (16), 125 (32), 122 (14), 107 (13), 97 (100), 95 (85), 94 (19), 81 (28), 80 (16), 79 (23). IR: 1717, 1688, 1592, 1240, 1149, 1027 cm^{-1}. *Anal.* Calcd for $C_{15}H_{24}O_3$: C, 71.39; H, 9.59. Found: C, 71.60; H, 9.67.

(2*E*,4*E*)-6-Oxo-2,4-undecadienenitrile (10a). Product **10a** was prepared from **5** (0.1 g, 0.66 mmol) in accordance with general procedure. Flash chromatography (petroleum ether/ethyl acetate 9/1 as eluent) afforded 0.078 g (67% yield) of **10a**. The residue was crystallized from petroleum ether giving white crystals of **10a**, m.p. 58-59 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ 0.87 (t, *J* = 7.0 Hz, 3H), 1.18-1.35 (m, 4H), 1.55-1.68 (m, 2H), 2.56 (t, *J* = 7.4 Hz, 2H), 5.72 (d, *J* = 15.3 Hz, 1H), 6.42 (d, *J* = 14.8 Hz, 1H), 7.01-7.13 (m, 2H) ppm. MS m/e 177 (M^+, 1), 149 (4), 148 (12), 134 (4), 122 (5), 121 (51), 120 (9), 107 (10), 106 (100), 94 (25), 93 (27), 81 (16), 79 (20), 78 (44). IR: 2216, 1691, 1583, 1262, 1012 cm^{-1}. *Anal.* Calcd for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90. Found: C, 74.66; H, 8.62; N, 7.78.

(2*E*,4*E*)-6-Oxo-2,4-tridecadienenitrile (10b). Product **10b** was prepared from **5** (0.1 g, 0.66 mmol) in accordance with general procedure. 0.058 g (43% yield) were obtained after flash chromatography (petroleum ether/ethyl acetate 9/1). The residual solid was crystallized from petroleum ether affording white crystals of **10b**, m.p. 65-66 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ 0.86 (t, *J* = 7.0 Hz, 3H), 1.19-1.33 (m, 8H), 1.55-1.65 (m, 2H), 2.56 (t, *J* = 7.4 Hz, 2H), 5.72 (d, *J* = 15.3 Hz, 1H), 6.43 (d, *J* = 14.8 Hz, 1H), 7.01-7.13 (m, 2H) ppm. MS m/e 190 (2), 188 (2), 162 (6), 148 (14), 134 (7), 122 (10), 121 (87), 120 (14), 107 (15), 106 (100), 94 (42), 93 (47), 81 (32), 80 (14), 79 (28), 78 (58). IR: 2215, 1693, 1582, 1016 cm^{-1}. *Anal.* Calcd for $C_{13}H_{19}NO$: C, 76.06; H, 9.33; N, 6.82. Found: C, 75.98; H, 9.12; N, 6.75.

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