Tandem Silylformylation/Wittig Olefination of Terminal Alkynes: Stereoselective Synthesis of 2,4-Dienoic Esters

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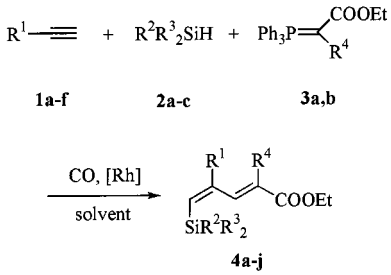
The rhodium(I)-catalysed sequential silylformylation/Wittig olefination of terminal alkynes with hydrosilanes and carbon monoxide in the presence of stabilised *P*-ylides leads to substituted 2,4-dienoic esters in a one-pot procedure. The α,β,γ,δ-unsaturated esters are generated with high (2*E*,4*Z*) stereoselectivity in good to excellent yields. Conversions of the products in [2+1] cycloaddition reactions are presented.

Introduction

The stereoselective formation and conversion of carbon–carbon double bonds ranks among the most important strategies in organic synthesis. Prominent examples of the former are various methods of alkyne addition[1] as well as carbonyl olefination.[2] Following our interest in the development of new tandem processes[3] we report here a novel sequential combination of both reaction types with a successive stereoselective formation of two double bonds in a one-pot procedure to form conjugated dienes. This is achieved by a combination of silylformylation of an alkyne followed by a Wittig olefination in a one-pot reaction.

The silylformylation of alkynes is an effective method for the stereoselective synthesis of highly functionalized double bonds.[4] We recently reported a sequential silylformylation/imine condensation reaction of terminal alkynes with hydrosilanes and carbon monoxide in the presence of primary amines leading to 4-silylated 1-aza-1,3-butadienes with high chemo-, regio- and stereoselectivity.[5] When the amine is replaced by a carbon nucleophile, such as an ylide, a new carbon–carbon double bond should be formed.

Breit and co-worker recently reported that stabilized phosphorous ylides do indeed undergo sequential Wittig reactions with aldehydes generated under hydroformylation conditions of alkenes.[6] Here, however, the newly generated double bond in most cases is hydrogenated under the hydroformylation conditions. Therefore, when this procedure is applied to alkynes, excessive hydrogenation leading to saturated products instead of the desired dienes has to be taken into account, not only because the final diene product can be hydrogenated but also because it is well-known that the hydroformylation of alkynes mainly leads to saturated monoaldehydes.[7] This loss of functionality, however, can be suppressed when hydrosilanes **2**, instead of hydrogen, are used as a hydrogen source. Thus we report here that stabilized phosphorous ylides **3** can trap β-silylated α,β-unsaturated aldehydes formed via silylformylation of various alkynes **1** in a one-pot procedure, without interfering with the catalytic cycle, to yield 1,3-dienes **4** as single stereoisomers (Scheme 1).



Scheme 1. Tandem silylformylation/Wittig olefination of terminal alkynes **1a–f** with hydrosilanes **2a–c** and carbon monoxide in the presence of *P*-ylides **3a,b**

Results and Discussion

The results of the silylformylation reaction of terminal alkynes in the presence of stabilized phosphorous ylides are compiled in Table 1. In general, the reactions were carried out with catalytic amounts of the zwitterionic $Rh(cod)BPh_4$ complex, as introduced for silylformylation by Zhou and Alper.[8] However, good results were also achieved using $Rh(CO)_2(acac)$ as the catalyst precursor and triphenylphosphite as additive (Entries 1, 5). The silylformylation step proceeds with high conversion rates when aliphatic hydrosilanes such as triethylsilane or *tert*-butyldimethylsilane are applied. In contrast, with both rhodium catalyst precursors no carbonylation was observed using the aromatic dimethylphenylsilane. From these reactions only the corresponding disilane was isolated as the major product (Entry 4). In our hands it was not possible to suppress this undesirable reaction.

The tandem reaction proceeds with high yields for both aliphatic and aromatic terminal alkynes. Propargylic alcohol was employed in protected forms (Entries 7–9), because Matsuda[9] has reported that propargyl alcohols or amines with protic hydrogen atoms undergo cyclization to β-lactones or β-lactams, respectively. While the propargyl ethers **1c–e** provide the 2,4-dienoic esters **4e–g** in good yields, the tertiary propargyl amine only reacts with low selectivity (Entry 10).

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Table 1. Tandem silylformylation/Wittig olefination of terminal alkynes **1a–f** with hydrosilanes **2a–c** and CO in the presence of *P*-ylides **3a,b**

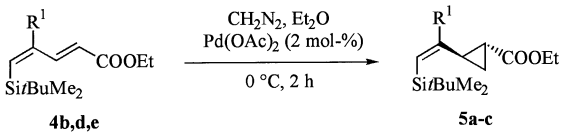
Entry	1	R^1	2	R^2	R^3	3	R^4	4[a]	Yield[b] [%]
1[c]	**1a**	Bu	**2a**	Et	Et	**3a**	H	**4a**	80
2	**1a**	Bu	**2a**	Et	Et	**3a**	H	**4a**	85
3	**1a**	Bu	**2b**	*t*Bu	Me	**3a**	H	**4b**	91
4	**1a**	Bu	**2c**	Ph	Me	**3a**	H	–	–[d]
5[c]	**1b**	Ph	**2a**	Et	Et	**3a**	H	**4c**	84
6	**1b**	Ph	**2b**	*t*Bu	Me	**3a**	H	**4d**	63
7	**1c**	CH_2OEt	**2b**	*t*Bu	Me	**3a**	H	**4e**	89
8	**1d**	CH_2OBzl	**2b**	*t*Bu	Me	**3a**	H	**4f**	71
9	**1e**	CH_2OTMS	**2b**	*t*Bu	Me	**3a**	H	**4g**	55
10	**1f**	CH_2NEt_2	**2b**	*t*Bu	Me	**3a**	H	**4h**	17
11	**1a**	Bu	**2a**	Et	Et	**3b**	Me	**4i**	28
12	**1b**	Ph	**2b**	*t*Bu	Me	**3b**	Me	**4j**	50[e]

[a] (2*E*,4*Z*) configuration for **4a,b,i**; (2*E*,4*E*) configuration for **4c–h,j**. – [b] Isolated yields. – The reactions were carried out using $Rh(cod)BPh_4$ (1 mol-% based on the amount of alkyne) in dichloromethane, a pressure of 50 bar CO at 75 °C for 40 h following the general procedure **A**. – [c] $Rh(CO)_2(acac)$ (1 mol-%), $P(OPh)_3$ (4 mol-%), toluene, 50 bar CO, 70 °C, 40 h. – [d] 71% of 1,1,2,2-tetramethyl-1,2-diphenyldisilane isolated. – [e] (4*E*:4*Z*) ratio = 5:1 (determined by NMR analysis of the crude product).

The application of ethyl 2-(triphenyl-λ^5-phosphanylidene)propanoate[10] (**3b**, Entries 11, 12) leads to the formation of trisubstituted double bonds in the Wittig reaction step. However, the yields are lower than with the *P*-ylide **3a**. In the case of the α,β,γ,δ-unsaturated ester **4j** a slight decrease of the selectivity at the γ,δ-double bond was observed [(4*E*)/(4*Z*) = 5:1]. It is reasonable to assume that the silylformylation step still occurs with high stereoselectivity and that a subsequent *cis*/*trans* isomerization takes place, since we observed an increased isomerization of the vinylsilane double bond during the tandem reaction on prolonged standing or, in some cases, at elevated temperatures.

A three step protocol for the synthesis of 5-silylated (2*E*,4*E*)-2,4-dienoic esters has previously been described by Jackson and co-workers.[11] However, our one-pot procedure offers a more effective and straightforward approach to the ε-silylated α,β,γ,δ-unsaturated esters with defined stereochemistry representing useful building blocks for further synthetic transformations. Above all, conversion of the vinylsilane moiety[12] and conjugate addition reactions, e.g. with organocuprates,[13] as well as cycloadditions, should provide interestingly functionalized products. As representative examples, applications in [2+1] cycloaddition reactions, e.g. cyclopropanation, are demonstrated.

The cyclopropanation was carried out according to the procedure of Vorbrüggen et al.[14] using diazomethane in the presence of catalytic amounts of $Pd(OAc)_2$. This reagent adds regio- and stereoselectively *cis* to the less substituted α,β-double bond of the dienoic acid ester (Scheme 2, Table 2).



4b,d,e **5a-c**

Scheme 2. Cyclopropanation of 5-silylated 2,4-dienoic esters **4b,d,e**

Table 2. Cyclopropanation of 5-silylated 2,4-dienoic esters **4b,d,e**

Entry	4	R^1	5	Yield[a] [%]
13	**b**	Bu	**a**	90
14	**d**	Ph	**b**	90
15	**e**	CH_2OEt	**c**	96

[a] Isolated yields.

The cyclopropane carboxylic acid esters were obtained in excellent yields with high stereoselectivity. These products are of interest for further transformations.[12,15]

Conclusion

The sequential silylformylation/Wittig reaction offers a novel approach for the stereoselective formation of two carbon–carbon double bonds in a one-pot procedure. 5-Silylated penta-2,4-dienoic acid derivatives can be obtained from easily available terminal alkynes, hydrosilanes and stabilized phosphorous ylides under carbonylative conditions in high yields. Application of the α,β,γ,δ-unsaturated esters in [2+1]-cycloaddition reactions leads to substituted vinylcyclopropanes with high stereoselectivity in excellent yields.

Experimental Section

General Remarks: 3-Ethoxypropyne[16] (**1c**), (prop-2-ynyloxymethyl)benzene[17] (**1d**), (trimethylprop-2-ynyloxy)silane[18] (**1e**), diethyl(prop-2-ynyl)amine[19] (**1f**), ethyl-2-(triphenyl-λ^5-phosphanylidene)propanoate[10] (**3b**) were prepared according to literature procedures. The catalyst precursor $Rh(cod)BPh_4$[20] was prepared as described previously. Diazomethane (***Caution!***) was prepared from *N*-methyl-*N*-nitrosourea according to a literature procedure.[21] All other chemicals were purchased from commercial sources. ^1H and ^{13}C NMR spectra were recorded with a Bruker DPX 300 or DRX 400 spectrometer using $CDCl_3$ as the solvent and CH_2Cl_2 as the internal standard. – IR spectra were performed with a Nicolet Impact 400 D, mass spectra with a Finnigan CA 5 and elemental analysis with a Leco CHNS-932. – Analytical gas chromatography was carried out with a Fisons 8130 gas chromatograph with 30-m CP sil-5 capillaries. – GC-MS spectra were obtained by using a comparable capillary and a Finnigan MAT 8320 (MS). – Pressure reactions were performed in autoclaves (type A, 250 mL, PTFE insert) from Berghof, Eningen. – Column chromatography was carried out with silica gel 60 from Merck, Darmstadt.

General Procedure A. – Preparation of 5-Silylated Penta-2,4-dienoic Acid Esters 4a–j: A mixture of the alkyne (4.0 mmol), silane (4.3 mmol), ylide (6.0 mmol) and Rh catalyst (1 mol-%, based on the amount of the alkyne) in 10 mL of dry dichloromethane was placed in an autoclave. After flushing the autoclave with argon the reactor was pressurized to 50 bar with CO. The reaction mixture was magnetically stirred at 75 °C for 40 h. Then the autoclave was allowed to cool to room temperature and the solvent was removed by rotary evaporation. The residue was dissolved in *n*-hexane/diethyl ether (2:1) and filtered through alumina. The products were then isolated by column chromatography with mixtures of *n*-hexane and *tert*-butyl methyl ether as eluent or by kugelrohr distillation.

Ethyl (2*E*,4*Z*)-4-Triethylsilylmethylene-2-octenoate (4a): Obtained from 1-hexyne (**1a**) (0.33 g, 4.0 mmol), triethylsilane (**2a**) (0.50 g, 4.3 mmol) and ylide **3a** (2.09 g, 6.0 mmol) after kugelrohr distillation (bp. 125 °C/0.2 mbar) in 85% (1.01 g) yield. – ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.69 (q, ^3J = 7.9 Hz, 6 H), 0.91 (t, ^3J = 7.2 Hz, 3 H), 0.94 (t, ^3J = 7.9 Hz, 9 H), 1.32 (t, ^3J = 7.2 Hz, 3 H), 1.30–1.51 (4 H), 2.31 (t, ^3J = 7.2 Hz, 2 H), 4.21 (q, ^3J = 7.2 Hz, 2 H), 5.92 (s, 1 H), 5.93 (d, ^3J = 15.5 Hz, 1 H), 7.52 (d, ^3J = 15.5 Hz, 1 H). – ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 4.9 (CH_2), 7.5 (CH_3), 13.9 (CH_3), 14.2 (CH_3), 22.5 (CH_2), 31.0 (CH_2), 35.4 (CH_2), 60.3 (CH_2), 118.2 (CH), 138.0 (CH), 145.6 (CH), 153.1 (Cq), 167.4 (Cq). – IR (neat): $\tilde{\nu}$ = 2955 s, 1716 s, 1623 m, 1565 m, 1272 s cm^{-1}. – GC-MS (EI, 70 eV): *m*/*z* (%) = 297 (29) [M$^+$ + 1], 267 (100), 251 (21), 131 (30), 117 (35), 103 (50), 75 (55), 59 (43). – $C_{17}H_{32}O_2Si$ (296.5): calcd. C 68.86, H 10.88; found C 68.8, H 10.9.

Ethyl (2*E*,4*Z*)-4-*tert*-Butyldimethylsilylmethylene-2-octenoate (4b): Obtained from 1-hexyne (**1a**) (0.33 g, 4.0 mmol), *tert*-butyldimethylsilane (**2b**) (0.50 g, 4.3 mmol) and ylide **3a** (2.09 g, 6.0 mmol) after kugelrohr distillation (bp. 130 °C/0.2 mbar) in 91% (1.08 g) yield. – ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.16 (s, 6 H), 0.87 (s, 9 H), 0.89 (t, ^3J = 7.0 Hz, 3 H), 1.28 (t, ^3J = 7.2 Hz, 3 H), 1.32 (m, 2 H), 1.44 (m, 2 H), 2.28 (t, ^3J = 7.0 Hz, 2 H), 4.19 (q, ^3J = 7.2 Hz, 2 H), 5.90 (d, ^3J = 15.8 Hz, 1 H), 5.93 (s, 1 H), 7.56 (d, ^3J = 15.8 Hz, 1 H). – ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = –3.8 (CH_3), 13.9 (CH_3), 14.3 (CH_3), 17.1 (Cq), 22.5 (CH_2), 26.5 (CH_3), 30.9 (CH_2), 35.6 (CH_2), 60.3 (CH_2), 118.4 (CH), 138.5 (CH), 145.5 (CH), 152.9 (Cq), 167.4 (Cq). – IR (neat): $\tilde{\nu}$ = 2955 s, 2930 s, 2858 s, 1718 vs, 1624 m, 1464 w, 1273 s, 1182 s, 839 s cm^{-1}. – MS (EI, 70 eV): *m*/*z* (%) = 296 (4) [M$^+$], 239 (87), 197 (24), 193 (9), 165 (23), 151 (8), 103 (52), 75 (100), 59 (14). – $C_{17}H_{32}O_2Si$ (296.5): calcd. C 68.86, H 10.88; found C 68.6, H 10.6.

Ethyl (2*E*,4*E*)-4-Phenyl-5-triethylsilylpenta-2,4-dienoate (4c): Obtained from phenylethyne (**1b**) (0.41 g, 4.0 mmol), triethylsilane (**2a**) (0.50 g, 4.3 mmol) and ylide **3a** (2.09 g, 6.0 mmol) after column chromatography (*n*-hexane/*tert*-butyl methyl ether = 40:1) in 84% (1.06 g) yield. – ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.79 (q, ^3J = 7.9 Hz, 6 H), 1.04 (t, ^3J = 7.9 Hz, 9 H), 1.30 (t, ^3J = 7.1 Hz, 3 H), 4.22 (q, ^3J = 7.1 Hz, 2 H), 5.78 (d, ^3J = 15.6 Hz, 1 H), 6.11 (s, 1 H), 7.26–7.38 (5 H), 7.78 (d, ^3J = 15.6 Hz, 1 H). – ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 4.8 (CH_2), 7.5 (CH_3), 14.2 (CH_3), 60.3 (CH_2), 122.5 (CH), 127.5 (CH), 128.1 (CH), 128.2 (CH), 141.0 (CH), 142.1 (Cq), 145.0 (CH), 154.4 (Cq), 167.2 (Cq). – IR (neat): $\tilde{\nu}$ = 3025 w, 1716 s, 1622 m, 1278 s, 1173 s, 701 m cm^{-1}. – GC-MS (EI, 70 eV): *m*/*z* (%) = 317 (33) [M$^+$ + 1], 287 (100), 271 (22), 243 (28), 185 (50), 103 (72).

Ethyl (2*E*,4*E*)-5-(*tert*-Butyldimethylsilyl)-4-phenylpenta-2,4-dienoate (4d): Obtained from phenylethyne (**1b**) (0.41 g, 4.0 mmol), *tert*-butyldimethylsilane (**2b**) (0.50 g, 4.3 mmol) and ylide **3a** (2.09 g, 6.0 mmol) after kugelrohr distillation (bp. 150 °C/0.1 mbar) in 63% (0.80 g) yield. – ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.25 (s, 6 H), 0.94 (s, 9 H), 1.27 (t, ^3J = 7.1 Hz, 3 H), 4.18 (q, ^3J = 7.1 Hz, 2 H), 5.73 (d, ^3J = 15.7 Hz, 1 H), 6.13 (s, 1 H), 7.21–7.33 (5 H), 7.81 (d, ^3J = 15.7 Hz, 1 H). – ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = –4.0 (CH_3), 14.2 (CH_3), 17.3 (Cq), 26.5 (CH_3), 60.4 (CH_2), 122.4 (CH), 127.6 (CH), 128.2 (CH), 128.2 (CH), 141.4 (CH), 142.2 (Cq), 144.9 (CH), 154.2 (Cq), 167.2 (Cq). – IR (neat): $\tilde{\nu}$ = 3025 w, 2953 s, 2929 s, 2857 m, 1717 vs, 1623 m, 1554 m, 1470 m, 1278 s, 1174 s, 825 s cm^{-1}. – MS (EI, 70 eV): *m*/*z* (%) = 316 (2) [M$^+$], 271 (5), 259 (100), 231 (14), 185 (47), 157 (23), 103 (28), 75 (59). – $C_{19}H_{28}O_2Si$ (316.5): calcd. C 72.10, H 8.92; found C 72.1, H 8.9.

Ethyl (2*E*,4*E*)-5-(*tert*-Butyldimethylsilyl)-4-(ethoxymethyl)penta-2,4-dienoate (4e): Obtained from 3-ethoxypropyne[16] (**1c**) (0.17 g, 2.0 mmol), *tert*-butyldimethylsilane (**2b**) (0.27 g, 2.3 mmol) and ylide **3a** (1.05 g, 3.0 mmol) after kugelrohr distillation (bp. 120 °C/0.1 mbar) in 89% (0.53 g) yield. – ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.17 (s, 6 H), 0.88 (s, 9 H), 1.19 (t, ^3J = 7.0 Hz, 3 H), 1.26 (t, ^3J = 7.2 Hz, 3 H), 3.45 (q, ^3J = 7.0 Hz, 2 H), 4.13 (s, 2 H), 4.18 (q, ^3J = 7.0 Hz, 2 H), 5.96 (d, ^3J = 15.9 Hz, 1 H), 6.24 (s, 1 H), 7.56 (d, ^3J = 15.9 Hz, 1 H). – ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = –4.0 (CH_3), 14.2 (CH_3), 15.1 (CH_3), 17.1 (Cq), 26.4 (CH_3), 60.3 (CH_2), 65.8 (CH_2), 72.7 (CH_2), 119.0 (CH), 139.2 (CH), 143.1 (CH), 148.2 (Cq), 167.1 (Cq). – IR (neat): $\tilde{\nu}$ = 2977 s, 2954 s, 2930 s, 2857 s, 1716 vs, 1626 s, 1575 m, 1471 s, 1446 m, 1365 s, 1275 vs, 1185 vs, 838 s cm^{-1}. – MS (EI, 70 eV): *m*/*z* (%) = 298 (2) [M$^+$], 241 (100), 197 (40), 167 (54), 139 (11), 123 (58), 103 (87), 94 (39), 75 (99), 59 (22). – $C_{16}H_{30}O_3Si$ (298.5): calcd. C 64.38, H 10.13; found C 64.4, H 10.1.

Ethyl (2*E*,4*E*)-4-Benzyloxymethyl-5-(*tert*-butyldimethylsilyl)penta-2,4-dienoate (4f): Obtained from (prop-2-ynyloxymethyl)benzene[17] (**1d**) (0.29 g, 2.0 mmol), *tert*-butyldimethylsilane (**2b**) (0.27 g, 2.3 mmol) and ylide **3a** (1.05 g, 3.0 mmol) after column chromatography (*n*-hexane/*tert*-butyl methyl ether = 10:1) in 71% (0.51 g) yield. – ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.21 (s, 6 H), 0.91 (s, 9 H), 1.29 (t, ^3J = 7.2 Hz, 3 H), 4.20 (q, ^3J = 7.2 Hz, 2 H), 4.21 (s, 2 H), 4.51 (s, 2 H), 6.00 (d, ^3J = 16.0 Hz, 1 H), 6.31 (s, 1 H), 7.33 (m, 5 H), 7.59 (d, ^3J = 16.0 Hz, 1 H). – ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = –4.0 (CH_3), 14.2 (CH_3), 17.1 (Cq), 26.5 (CH_3), 60.3 (CH_2), 72.2 (CH_2), 72.2 (CH_2), 119.3 (CH), 127.7 (CH), 127.8 (CH), 128.4 (CH), 137.9 (Cq), 139.9 (CH), 143.0 (CH), 147.9 (Cq), 167.1 (Cq). – IR (neat): $\tilde{\nu}$ = 3065 m, 3031 m, 2953 s, 2897 s, 2856 s, 1715 vs, 1626 s, 1575 s, 1470 s, 1365 s, 1274 s, 1185 s, 838 s cm^{-1}. – GC-MS (EI, 70 eV): *m*/*z* (%) = 361 (8) [M$^+$ + 1], 343 (90), 303 (10), 274 (7), 229 (15), 213 (26), 197 (42), 155 (34), 123 (30), 91 (100), 75 (28).

Ethyl (2*E*,4*E*)-5-(*tert*-Butyldimethylsilyl)-4-(trimethylsilyloxymethyl)penta-2,4-dienoate (4g): Obtained from (trimethylprop-2-ynyloxy)silane[18] (**1e**) (0.26 g, 2.0 mmol), *tert*-butyldimethylsilane (**2b**) (0.27 g, 2.3 mmol) and ylide **3a** (1.05 g, 3.0 mmol) after kugelrohr distillation (bp. 130 °C/ 0.1 mbar) in 55% (0.38 g) yield. – ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.09 (s, 9 H), 0.15 (s, 6 H), 0.87 (s, 9 H), 1.25 (t, ^3J = 7.1 Hz, 3 H), 4.16 (q, ^3J = 7.1 Hz, 2 H), 4.27 (s, 2 H), 5.84 (d, ^3J = 16.1 Hz, 1 H), 6.30 (s, 1 H), 7.57 (d, ^3J = 16.1 Hz, 1 H). – ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = –4.0 (CH_3), –0.5 (CH_3), 14.2 (CH_3), 17.0 (Cq), 26.4 (CH_3), 60.3 (CH_2), 63.6 (CH_2), 117.9 (CH), 136.2 (CH), 142.9 (CH), 149.9 (Cq), 167.0 (Cq). – IR (neat): $\tilde{\nu}$ = 2955 s, 2930 s, 2884 m, 2858 s, 1717 vs, 1626 m, 1578 m, 1471 m, 1311 m, 1252 s, 1184 s, 842 vs cm^{-1}. – MS (EI, 70 eV): *m*/*z* (%) = 342 (1) [M$^+$], 326 (13), 285 (100), 257 (22), 241 (13), 211 (11), 167 (22), 147 (52), 133 (19), 123 (48), 103 (35), 94 (35), 73 (99). – $C_{17}H_{34}O_3Si_2$ (342.6): calcd. C 59.59, H 10.00; found C 59.8, H 10.0.

Ethyl (2*E*,4*E*)-5-(*tert*-Butyldimethylsilyl)-4-(diethylaminomethyl)-penta-2,4-dienoate (4h): Obtained from diethyl(prop-2-ynyl)amine[19] (**1f**) (0.44 g, 4.0 mmol), *tert*-butyldimethylsilane (**2b**) (0.50 g, 4.3 mmol) and ylide **3a** (2.09 g, 6.0 mmol) after column chromatography (*n*-hexane/*tert*-butyl methyl ether = 5:1) in 17% (0.23 g) yield. – ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.16 (s, 6 H), 0.88 (s, 9 H), 0.97 (t, ^3J = 7.1 Hz, 6 H), 1.27 (t, ^3J = 7.2 Hz, 3 H), 2.45 (q, ^3J = 7.1 Hz, 4 H), 3.18 (s, 2 H), 4.17 (q, ^3J = 7.2 Hz, 2 H), 6.15 (d, ^3J = 15.8 Hz, 1 H), 6.25 (s, 1 H), 7.58 (d, ^3J = 15.8 Hz, 1 H). – ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = –3.9 (CH_3), 11.6 (CH_3), 14.3 (CH_3), 17.2 (Cq), 26.5 (CH_3), 46.9 (CH_2), 58.5 (CH_2),

60.2 (CH_2), 118.9 (CH), 139.9 (CH), 144.6 (CH), 149.8 (Cq), 167.5 (Cq). – IR (neat): $\tilde{\nu}$ = 2955 s, 2930 s, 2899 s, 2857 s, 1716 vs, 1624 s, 1569 m, 1471 s, 1367 s, 1275 s, 1182 s, 824 s cm^{-1}. – MS (EI, 70 eV): *m*/*z* (%) = 325 (7) [M^+], 310 (1), 280 (2), 86 (100), 75 (4), 58 (4). – $C_{18}H_{35}NO_2Si$ (325.6): calcd. C 66.41, H 10.84, N 4.30; found C 66.6, H 10.8, N 4.1.

Ethyl (2*E*,4*Z*)-2-Methyl-4-triethylsilylmethylene-2-octenoate (4i): Obtained from 1-hexyne (**1a**) (0.33 g, 4.0 mmol), triethylsilane (**2a**) (0.50 g, 4.3 mmol) and ylide **3b**[10] (2.17 g, 6.0 mmol) after column chromatography (*n*-hexane/*tert*-butyl methyl ether = 40:1) in 28% (0.35 g) yield. ^1H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.53 (q, ^3J = 7.8 Hz, 6 H), 0.85 (t, ^3J = 7.3 Hz, 3 H), 0.86 (t, ^3J = 7.8 Hz, 9 H), 1.27 (t, ^3J = 7.2 Hz, 3 H), 1.28 (m, 2 H), 1.37 (m, 2 H), 1.84 (s, 3 H), 2.24 (t, ^3J = 7.0 Hz, 2 H), 4.19 (q, ^3J = 7.2 Hz, 2 H), 5.52 (s, 1 H), 7.30 (s, 1 H). – ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 4.1 (CH_2), 7.4 (CH_3), 13.8 (CH_3), 13.9 (CH_3), 14.2 (CH_3), 22.4 (CH_2), 30.6 (CH_2), 40.1 (CH_2), 60.6 (CH_2), 127.3 (CH), 142.2 (CH), 148.8 (Cq), 154.9 (Cq), 168.4 (Cq). – IR (neat): $\tilde{\nu}$ = 2956 s, 2935 s, 2875 s, 1715 s, 1625 w, 1464 m, 1253 s, 1116 m, 832 m cm^{-1}. – MS (EI, 70 eV): *m*/*z* (%) = 310 (43) [M^+], 281 (100), 253 (28), 237 (31), 195 (28), 179 (48), 151 (16), 131 (84), 109 (17), 103 (64), 75 (56).

Ethyl (2*E*,4*E*)-5-(*tert*-Butyldimethylsilyl)-2-methyl-4-phenylpenta-2,4-dienoate (4j): Obtained from phenylethyne (**1b**) (0.20 g, 2.0 mmol), *tert*-butyldimethylsilane (**2b**) (0.25 g, 2.2 mmol) and ylide **3b**[10] (1.09 g, 3.0 mmol) after column chromatography (*n*-hexane/*tert*-butyl methyl ether = 20:1) in 50% (0.33 g) yield as a 5:1 mixture of the (4*E*) and (4*Z*) isomers. – Spectroscopic data only for the major isomer: ^1H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.13 (s, 6 H), 0.93 (s, 9 H), 1.33 (t, ^3J = 7.1 Hz, 3 H), 1.55 (s, 3 H), 4.25 (q, ^3J = 7.1 Hz, 2 H), 6.24 (s, 1 H), 7.32 (m, 5 H), 7.64 (s, 1 H). – ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = –4.9 (CH_3), 14.2 (CH_3), 14.5 (CH_3), 17.3 (Cq), 26.5 (CH_3), 60.7 (CH_2), 126.5 (CH), 127.7 (CH), 128.4 (CH), 130.6 (Cq), 131.6 (CH), 140.3 (CH), 142.2 (Cq), 152.5 (Cq), 168.2 (Cq). – IR (neat): $\tilde{\nu}$ = 3059 w, 3024 w, 2953 s, 2928 s, 2856 m, 1713 vs, 1556 w, 1470 m, 1365 m, 1249 vs, 1114 s, 825 s cm^{-1}. – GC-MS (EI, 70 eV): *m*/*z* (%) = 331 (58) [M^+ + 1], 315 (24), 285 (60), 229 (20), 199 (80), 171 (38), 107 (15), 89 (100), 75 (78). – $C_{20}H_{30}O_2Si$ (330.5): calcd. C 72.67, H 9.15; found C 72.4, H 9.2.

General Procedure B. – Preparation of Vinylcyclopropanecarboxylic Acid Esters 5a–c: Diazomethane (***Caution!***) was prepared from *N*-methyl-*N*-nitrosourea (5.0 mmol) and 2 mL of a 50% aqueous KOH solution in 30 mL diethyl ether at 0 °C following the procedure of Evans.[21] An excess of the ethereal diazomethane solution was added portionwise from a syringe to a suspension of the ethyl penta-2,4-dienoate (1.0 mmol) and $Pd(OAc)_2$ (2 mol-%) in dry diethyl ether (6 mL). The solution was stirred for 2 h at 0 °C. Excess diazomethane was quenched with a few drops of acetic acid. After filtration through alumina and concentration, the products were isolated by flash column chromatography with mixtures of *n*-hexane and *tert*-butyl methyl ether as eluent or by kugelrohr distillation.

Ethyl (1*S,2*S**)-2-[(1*Z*)-1-Butyl-2-(*tert*-butyldimethylsilyl)vinyl]cyclopropanecarboxylate (5a):** Obtained from **4b** (0.30 g, 1.0 mmol) after kugelrohr distillation (bp. 120 °C/0.1 mbar) in 90% (0.28 g) yield. – ^1H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.06 (s, 6 H), 0.85 (s, 9 H), 0.87 (t, ^3J = 7.0 Hz, 3 H), 1.12 (ddd, ^3J = 8.3 Hz, ^3J = 6.8 Hz, ^2J = 4.6 Hz, 1 H), 1.22 (t, ^3J = 7.0 Hz, 3 H), 1.27 (m, 5 H), 1.64 (t, ^3J = 6.8 Hz, 2 H), 1.71 (ddd, ^3J = 8.3 Hz,^3J = 5.2 Hz, ^3J = 4.4 Hz, 1 H), 2.27 (ddd, ^3J = 9.1 Hz, ^3J = 6.8 Hz, ^3J = 4.4 Hz, 1 H), 4.10 (q, ^3J = 7.0 Hz, 2 H), 5.33 (s, 1 H). – ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = –4.3 (CH_3), 14.0 (CH_3), 14.2 (CH_2), 14.3 (CH_3), 17.1 (Cq), 20.8 (CH), 22.5 (CH_2), 26.5 (CH_3), 28.0 (CH), 31.0 (CH_2), 33.4 (CH_2), 60.5 (CH_2), 123.4 (CH), 155.2 (Cq), 173.7 (Cq). – IR (neat): $\tilde{\nu}$ = 2955 s, 2929 s, 2899 s, 2857 s, 1728 s, 1601 m, 1464 s, 1365 m, 1257 s, 1179 s, 828 s cm^{-1}. – MS (EI, 70 eV): *m*/*z* (%) = 310 (1) [M^+], 253 (100), 241 (9), 207 (37), 179 (34), 151 (12), 103 (52), 75 (60). – $C_{18}H_{34}O_2Si$ (310.6): calcd. C 69.62, H 11.04; found C 69.5, H 11.0.

Ethyl (1*S,2*S**)-2-[(1*E*)-2-(*tert*-Butyldimethylsilyl)-1-phenylvinyl]-cyclopropanecarboxylate (5b):** Obtained from **4d** (0.32 g, 1.0 mmol) after flash column chromatography (*n*-hexane/*tert*-butyl methyl ether = 10:1) in 90% (0.30 g) yield. – ^1H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.16 (s, 3 H), 0.17 (s, 3 H), 0.92 (s, 9 H), 1.25 (t, ^3J = 7.2 Hz, 3 H), 1.26 (m, 1 H), 1.36 (ddd, ^3J = 9.1 Hz, ^3J = 5.3 Hz, ^2J = 4.4 Hz, 1 H), 1.53 (ddd, ^3J = 8.5 Hz, ^3J = 5.3 Hz, ^3J = 4.4 Hz, 1 H), 2.50 (ddd, ^3J = 9.1 Hz, ^3J = 6.7 Hz, ^3J = 4.4 Hz, 1 H), 4.13 (q, ^3J = 7.2 Hz, 2 H), 5.62 (s, 1 H), 7.11 (m, 2 H), 7.25 (m, 3 H). – ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = –4.4 (CH_3), 14.3 (CH_3), 15.4 (CH_2), 17.2 (Cq), 21.3 (CH), 26.5 (CH_3), 27.2 (CH), 60.5 (CH_2), 126.9 (CH), 127.8 (CH), 127.9 (CH), 129.6 (CH), 142.6 (Cq), 156.3 (Cq), 173.5 (Cq). – IR (neat): $\tilde{\nu}$ = 3078 w, 3057 w, 2954 s, 2929 s, 2856 m, 1728 vs, 1588 m, 1471 m, 1332 m, 1259 m, 1179 s, 825 s cm^{-1}. – MS (EI, 70 eV): *m*/*z* (%) = 330 (1) [M^+], 315 (1), 273 (100), 259 (10), 227 (23), 199 (27), 171 (11), 103 (34), 75 (50). – $C_{20}H_{30}O_2Si$ (330.5): calcd. C 72.67, H 9.15; found C 72.7, H 9.3.

Ethyl (1*S,2*S**)-2-[(1*E*)-2-(*tert*-Butyldimethylsilyl)-1-(ethoxymethyl)vinyl]cyclopropanecarboxylate (5c):** Obtained from **4e** (0.30 g, 1.0 mmol) after kugelrohr distillation (bp. 125 °C/0.2 mbar) in 96% (0.30 g) yield. – ^1H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.08 (s, 6 H), 0.86 (s, 9 H), 1.16 (t, ^3J = 7.0 Hz, 3 H), 1.22 (t, ^3J = 7.2 Hz, 3 H), 1.28 (m, 2 H), 1.90 (ddd, ^3J = 8.0 Hz, ^3J = 5.4 Hz, ^3J = 4.4 Hz, 1 H), 2.27 (ddd, ^3J = 9.0 Hz, ^3J = 7.2 Hz, ^3J = 4.4 Hz, 1 H), 3.37 (q, ^3J = 7.0 Hz, 2 H), 3.70 (s, 2 H), 4.10 (q, ^3J = 7.2 Hz, 2 H), 5.66 (s, 1 H). – ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = –4.5 (CH_3), 14.2 (CH_2), 14.3 (CH_3), 15.1 (CH_3), 17.0 (Cq), 20.9 (CH), 26.4 (CH_3), 26.6 (CH), 60.5 (CH_2), 65.3 (CH_2), 74.1 (CH_2), 128.2 (CH), 150.3 (Cq), 173.8 (Cq). – IR (neat): $\tilde{\nu}$ = 2977 s, 2954 s, 2930 s, 2857 s, 1728 vs, 1608 w, 1471 m, 1408 m, 1340 m, 1257 m, 1180 s, 832 s cm^{-1}. – MS (EI, 70 eV): *m*/*z* (%) = 312 (1) [M^+], 269 (12), 255 (100), 181 (25), 165 (19), 137 (16), 103 (50), 75 (52), 59 (32). – $C_{17}H_{32}O_3Si$ (312.5): calcd. C 65.33, H 10.32; found C 65.2, H 10.2.

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