Stereoselective Preparation of (Z)- γ -Silyl- γ , δ -Unsaturated Ketones and their Application in the Synthesis of 1,4-Diketones

Weixin Zheng,^a Xian Huang*a,^b

- ^a Department of Chemistry, Zhejiang University (Xixi Campus, Hangzhou 310028, P. R. China
- ^b The State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, P. R. China
- E-mail: huangx@mail.hz.zj.cn

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Abstract: Hydrozirconation reaction of alkynylsilanes 1 followed by Michael addition to α,β -unsaturated ketones in the presence of CuBr Me₂S complex produced (*Z*)- γ -silyl- γ,δ -unsaturated ketones 3 stereoselectively. 1,4-Diketones were prepared via epoxidation and hydrolysis of 3.

Key words: silicon, zirconium, Michael additions, ketones, enones, alkynes

Alkenylsilanes serve as important intermediates in organic synthesis.¹ It is well documented that the γ -silyl- γ , δ -unsaturated ketones are essentially used in the synthesis of jasmone.² However, only a few synthetic methods for γ silyl- γ , δ -unsaturated ketones have been published,^{3,4} which had the disadvantage of low stereoselectivity.³ In our preliminary work, the bifunctional ethenyl reagent containing silyl and zirconium moieties was obtained by the hydrozirconation reaction of alkynylsilanes.⁵ Based on the high reactivity of the zirconium group, the electrophilic substitution to the zirconated intermediate could produce the polysubstituted vinyl silanes with high regioand stereoselectivity. Owing to the silyl group, the vinyl silanes also have great potential to be converted to some useful compounds.

On the other hand, 1,4-diketones are widely used as building blocks for the preparation of five-membered carbocyclic and heterocyclic compounds.⁶A number of methods for the synthesis of 1,4-diketones have been developed.⁷⁻¹⁰ Among them, the Michael–Stetter addition of aldehydes to α , β -unsaturated ketones,⁷ cross aldol condensation of methyl ketones with α -bromo ketones followed by 1,3-dehydrobromination of the products and cleavage of cyclopropyl intermediates,⁸ the alkylation of stabilized alkaline metal enolates,⁹ enamines,^{9b} and tin enolates¹⁰ by α -halocarbonyl compounds are mainly described. Also, the conjugate acylation of an enone by an acyl anion equivalent is a very important process. Developing acyl anion equivalents and the resulting polarity umpolung of carbon atoms remain challenging problems.

Herein, we wish to report the synthesis of (Z)- γ -silyl γ , δ unsaturated ketones by hydrozirconation of alkynyl silanes followed by conjugate reaction to α , β -unsaturated

Synthesis 2002, No. 17, Print: 02 12 2002. Art Id.1437-210X,E;2002,0,17,2497,2502,ftx,en;F05602SS.pdf. © Georg Thieme Verlag Stuttgart · New York ISSN 0039-7881 ketones in the presence of copper (I) reagent and their utility in the synthesis of 1,4-diketones via epoxidation and hydrolysis.

Hydrozirconation of 1-alkynylsilanes **1** at room temperature in THF gave (*E*)- α -zirconated vinyl silanes **2**, which reacted conjugatively with α , β -unsaturated ketones in the presence of 15 mol% CuBr·Me₂S at 25 °C to yield (*Z*)- γ silyl- γ , δ -unsaturated ketones **3** predominately in moderate to good yields (Scheme 1). The results are listed in Table 1.



Scheme 1

The investigation of ¹H NMR spectra of the crude products showed the purity of *Z*-isomer was above 88%. When R was phenyl in compound **3** (Entry 1–5 in Table 1), the *Z*-configuration was verified by the X-ray diffraction study of compound **3d** (Figure 1).¹¹ It could be observed that the *syn*-addition of Cp₂Zr(H)Cl to phenylacetylenic silane led the zirconium atom occupying the carbon adjacent to the silyl group.

For compounds 3f-o as oils, ¹H NMR spectroscopy showed that the olefinic proton signal was characteristi-



Figure 1 ORTEP drawing of compound 3d.

Entry	R	R^1	R ²	Product ^a	Reaction conditions: Temp (°C)/time (h)	Yield (%) ^b (3/3') ^c
1	Ph	Ph	Ph	3a	25/4	63 (96/4)
2	Ph	Ph	<i>p</i> -CH ₃ OC ₆ H ₄	3b	25/4	66 (95/5)
3	Ph	Ph	$m-NO_2C_6H_4$	3c	25/5	68 (95/5)
4	Ph	$p-NO_2C_6H_4$	CH ₃	3d	25/5.5	70 (93/7)
5	Ph	(CH ₂) ₃		3e	25/5	66 (95/5)
6	n-C ₄ H ₉	Ph	Ph	3f	25/1.5	76 (90/10)
7	n-C ₄ H ₉	Ph	<i>p</i> -CH ₃ OC ₆ H ₄	3g	25/2.5	83 (90/10)
8	n-C ₄ H ₉	Ph	$m-NO_2C_6H_4$	3h	25/3	56 (88/12)
9	n-C ₄ H ₉	$p-NO_2C_6H_4$	CH ₃	3i	25/3	66 (89/11)
10	n-C ₄ H ₉	(CH ₂) ₃		3ј	25/4	60 (90/10)
11	$n-C_5H_{11}$	Ph	Ph	3k	25/2	72 (91/9)
12	$n-C_5H_{11}$	Ph	<i>p</i> -CH ₃ OC ₆ H ₄	31	25/2	80 (92/8)
13	$n-C_5H_{11}$	Ph	$m-NO_2C_6H_4$	3m	25/3	54 (92/8)
14	$n-C_5H_{11}$	$p-NO_2C_6H_4$	CH ₃	3n	25/3	59 (93/7)
15	$n-C_5H_{11}$	(CH ₂) ₃		30	25/4	60 (92/8)

Table 1 Synthesis of γ-Silynyl γ,δ-Unsaturated Ketones 3

^a All products were identified by ¹H NMR, IR, MS and elemental analyses.

^b Isolated yield of purified **3** was based on the alkynylsilanes used.

^c Percent ratio of 3/3' was determined by the integral value of the vinylic protons in the ¹H NMR spectra of the crude products.

cally split into a triplet with coupling constant ${}^{3}J$ (H,H) = 7.2 Hz, which indicated the zirconium moiety occupied the α -position carbon atom of the silyl group, which exhibited the same regioselectivity as that of the **3d**. The *Z*-olefin geometry was affirmed by ${}^{1}H{-}^{1}H$ 2D NOSEY spectra of **3l** (Figure 2).



Figure 2 The ${}^{1}H-{}^{1}H$ 2D NOESY correlation of compound 31.

Epoxidation of **3** with *m*-chloroperbenzoic acid occurred at the vinyl silanes to give epoxides **4**, which were treated with trifluoroacetic acid in refluxing methanol to afford **5** in good yields¹² (Scheme 2 and Table 2).

In conclusion, we have developed a novel route to the synthesis of (Z)- γ -silyl γ , δ -unsaturated ketones and studied their application in the synthesis of 1,4-diketones, which has the advantages of readily available materials, simple

procedures, mild reaction conditions and good yields. The polarity umpolung of the α -silyl vinylic carbon atom occurred in the synthesis of 1,4-diketones **5**, and the intermediate of the hydrozirconation reaction of alkynylsilane, (E)- α -zirconated vinyl silane, served as an acyl anion equivalent (Scheme 3).¹³ The investigation on the application of (Z)- γ -silyl γ , δ -unsaturated ketones in organic synthesis is still in progress.



Scheme 2





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Table 2	Synthesis	of 1.4-Diketones 5
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Entry	R	\mathbb{R}^1	R ²	Product ^a	Yield (%) ^b
1	Ph	Ph	Ph	5a	81
2	Ph	Ph	<i>p</i> -CH ₃ OC ₆ H ₄	5b	84
3	Ph	(CH ₂) ₃		5c	69
4	C_4H_9	Ph	Ph	5d	80
5	C_4H_9	(CH ₂) ₃		5e	85
6	$C_{5}H_{11}$	Ph	Ph	5f	88
7	C ₅ H ₁₁	Ph	<i>p</i> -CH ₃ OC ₆ H ₄	5g	75

^a All products were identified by ¹H NMR, IR, MS or elemental analyses.

^b Isolated yield based of the (Z)- γ -silyl γ , δ -ketones used.

The mps were uncorrected. ¹H NMR spectra were recorded on a Bruker Avance 400 (400 Hz) spectrometer in CDCl₃ with TMS as the internal standard; chemical shifts are quoted in ppm and J values are given in Hz. IR spectra were recorded on a Bruker Vector 22 spectrometer. EIMS was run on a HP 5989B mass spectrometer. Alkynyl silane,¹⁴ 1,3-diphenyl 2-propen-1-one,¹⁵ 1-(4'-methoxyphenyl)-3-phenyl-2-propen-1-one,15 1-(3'-nitrophenyl)-3-phe-2-propen-1-one,¹⁵ 4-(4'-nitrophenyl)-3-buten-2-one,¹⁶ nyl CuBr·Me₂S,¹⁷ and Schwartz's reagent [Cp₂Zr(H)Cl]¹⁸ were prepared according to the literature procedures. 2-Cyclohexen-1-one, MCPBA, TFA, MeOH (AR), CH₂Cl₂ (AR) were obtained commercially and used in reactions without any further purification. Petroleum ether with a bp 30-60 °C was used. THF was dried over sodium benzophenone ketyl and freshly distilled before use.

(Z)-γ-Silyl γ,δ-Unsaturated Ketones 3a-o; General Procedure

To a suspension of $Cp_2Zr(H)Cl$ (2 mmol) in THF (5 mL) in a Schlenk reaction tube, an alkynyl silane (1.0 mmol) was injected under nitrogen. The mixture was stirred at r.t. until a clear pale yellow solution of alkenylsilanes **2** was obtained.

To this pale yellow solution of 2, α , β -unsaturated ketone (1.2 mmol) and CuBr·Me₂S (0.15 mmol) were added under nitrogen and the mixture was stirred under the conditions listed in Table 1. The reaction was quenched by sat. aq NH₄Cl and extracted with Et₂O. The combined organic phase was dried (MgSO₄) and evaporated. A pure product was obtained by column chromatography (silica gel; petroleum ether–EtOAc, 40:1).

(Z)-1,3,5-Triphenyl-4-trimethylsilyl-4-penten-1-one (3a) Yield: 63%; pale yellow oil.

IR (neat): 3025, 2953, 1687, 1448, 1249, 755, 699 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): $\delta = 0.02$ (s, 9 H), ABX, $\delta_A = 3.25$, $\delta_B = 3.83$, $\delta_X = 5.12$ ($J_{AX} = 5.6$ Hz, $J_{BX} = 8.9$ Hz, $J_{AB} = 16.8$ Hz, 3 H), 7.01 (s, 1 H), 7.16–7.52 (m, 13 H), 7.82–7.83 (m, 2 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = 0.70, 40.87, 42.64, 126.19, 126.92, 127.83, 128.11, 128.28, 128.38, 128.39, 128.61, 128.72, 132.96, 138.43, 139.72, 142.56, 147.01, 198.31.

MS (EI): m/z (%) = 384 (M⁺, 4), 73 (100).

Anal. Calcd for $C_{26}H_{28}OSi: C$, 81.20; H, 7.34. Found: C, 81.16, H, 7.39.

(Z)-1-(4'-Methoxylphenyl)-3,5-diphenyl-4-trimethylsilyl-4penten-1-one (3b)

Yield: 66%; pale yellow oil.

IR (neat): 2955, 1676, 1600, 1510, 1492, 1257, 1218, 1169, 837, 734 $\rm cm^{-1}.$

¹H NMR (400 MHz, CDCl₃): $\delta = -0.01$ (s, 9 H), ABX, $\delta_A = 3.17$, $\delta_B = 3.76$, $\delta_X = 5.09$ ($J_{AX} = 5.6$ Hz, $J_{BX} = 8.8$ Hz, $J_{AB} = 16.4$ Hz, 3 H), 3.86 (s, 3 H), 6.83 (d, J = 8.8 Hz, 2 H), 6.99 (s, 1 H), 7.17–7.31 (m, 10 H), 7.79 (d, J = 8.8 Hz, 2 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = 0.56, 42.64, 42.76, 55.60, 114.43, 127.88, 128.13, 128.31, 128.53, 128.73, 128.81, 131.92, 145.19, 159.66, 197.01.

MS (EI): *m*/*z* (%) = 414 (M⁺, 5), 73 (100).

Anal. Calcd for $C_{27}H_{30}O_2Si$: C, 78.22; H, 7.29. Found: C, 78.18; H, 7.26.

(Z)-3,5-Diphenyl-(3'-nitrophenyl)-4-trimethylsiyl-4-penten-1- one (3c)

Yield: 68%; colorless crystals; mp 113–113.5°C (hexane).

IR (KBr): 3026, 2954, 1694, 1613, 1532, 1350, 1203, 838 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): $\delta = 0.01$ (s, 9 H), ABX, $\delta_A = 3.30$, $\delta_B = 3.73$, $\delta_X = 5.08$ ($J_{AX} = 7.6$ Hz, $J_{BX} = 6.0$ Hz, $J_{AB} = 16.0$ Hz, 3 H), 7.00 (s, 1 H), 7.11–7.31 (m, 10 H), 7.49 (t, J = 8.0 Hz, 1 H), 7.99 (d, J = 7.6 Hz, 1 H), 8.28 (d, J = 7.6 Hz, 1 H), 8.50 (s, 1 H).

¹³C NMR (100 MHz, CDCl₃): δ = 0.54, 41.04, 43.14, 122.93, 126.53, 126.91, 127.04, 127.62, 128.10, 128.21, 128.46, 129.61, 133.42, 137.83, 138.12, 140.13, 141.99, 146.03, 148.30, 196.46.

MS (EI): m/z (%) = 429 (M⁺, 4), 73 (100).

Anal. Calcd for $C_{26}H_{27}NO_3Si$: C, 72.69; H, 6.34. Found: C, 72.67; H, 6.37.

(Z)-[4-(4'-Nitrophenyl)]-6-phenyl-5-trimethylsilyl-5-hexen-2one (3d)

Yield: 70%; colorless crystals; mp 82.5-83 °C (hexane).

IR (KBr): 2954, 1718, 1519, 1491, 1346, 1249, 840 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): $\delta = -0.20$ (s, 9 H), 2.13 (s, 3 H), ABX, $\delta_A = 2.93$, $\delta_B = 3.11$, $\delta_X = 4.44$ ($J_{AX} = 8.3$ Hz, $J_{BX} = 6.3$ Hz, $J_{AB} = 16.9$ Hz, 3 H), 7.16 (d, J = 7.0 Hz, 2 H), 7.18–7.33 (m, 4 H), 7.47 (d, J = 8.7 Hz, 2 H), 8.17 (d, J = 8.7 Hz, 2 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = 0.08, 30.82, 45.13, 49.56, 123.76, 127.43, 128.06, 128.54, 129.45, 139.82, 142.02, 145.32, 146.72, 151.51, 206.04.

MS (EI): m/z (%) = 367 (M⁺, 3), 73 (100).

Anal. Calcd for $C_{21}H_{25}NO_3Si: C$, 68.63; H, 6.86. Found: C, 68.60; H, 6.84.

$(Z) \hbox{-} 1 \hbox{-} (Cyclohexanon \hbox{-} 3 \hbox{-} yl) \hbox{-} 2 \hbox{-} phenyl \hbox{-} 1 \hbox{-} trimethyle thene (3e)$

Yield: 66%; colorless crystals; mp 46–47 °C (hexane).

IR (neat): 2952, 1713, 1446, 1250, 837 cm⁻¹.

¹H NMR (400 MHz, $CDCl_3$): $\delta = -0.08$ (s, 9 H), 1.56–1.67 (m, 2 H), 2.00–2.03 (m, 1 H), 2.10–2.13 (m, 1 H), 2.32–2.48 (m, 4 H), 2.64–2.67 (m, 1 H), 7.14–7.31 (m, 6 H).

 ^{13}C NMR (100 MHz, CDCl_3): δ = 0.65, 25.58, 32.60, 41.40, 43.80, 48.54, 127.04, 127.90, 128.64, 140.26, 212.09.

MS (EI): m/z (%) = 272 (M⁺, 24), 73 (100).

Anal. Calcd for $C_{17}H_{24}OSi: C$, 74.94; H, 8.88. Found: C, 74.98; H, 8.94.

(Z)-1,3-Diphenyl-4-trimethylsilyl-4-nonen-1-one (3f) Yield: 76%; colorless oil.

IR (neat): 3061, 2956, 1599, 1248, 752 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 0.00 (s, 9 H), 0.88 (t, J = 7.1 Hz, 3 H), 1.26–1.31 (m, 4 H), 2.15–2.21 (m, 2 H), ABX, δ_A = 3.25, δ_B = 3.48, δ_X = 4.30 (J_{AX} = 6.9 Hz, J_{BX} = 7.8 Hz, J_{AB} = 16.2 Hz, 3 H), 6.04 (t, J = 7.6 Hz, 1 H), 7.15–7.25 (m, 5 H), 7.40–7.44 (m, 2 H), 7.50–7.54 (m, 1 H), 7.85–7.88 (m, 2 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = 0.57, 14.17, 22.56, 31.93, 32.38, 45.20, 45.93, 126.20, 128.08, 128.25, 128.45, 128.56, 132.83, 137.70, 140.21, 142.19, 144.34, 199.30.

MS (EI): m/z (%) = 364 (M⁺, 6), 73 (100).

Anal. Calcd for C₂₄H₃₂OSi: C, 79.06; H, 8.85. Found: C, 79.11; H, 8.89.

(Z)-1-(4'-Methoxyphenyl)-3-phenyl-4-trimethylsilyl-4-nonen-1one (3g)

Yield: 83%; colorless oil.

IR (neat): 2956, 1679, 1601, 1510, 1249, 1169, 1031, 837, 701 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): $\delta = 0.00$ (s, 9 H), 0.88 (t, J = 7.1 Hz, 3 H), 1.30–1.32 (m, 4 H), 2.15–2.19 (m, 2 H), 3,85 (s, 3 H), ABX, $\delta_A = 3.19$, $\delta_B = 3.42$, $\delta_X = 4.29$ ($J_{AX} = 7.1$ Hz, $J_{BX} = 7.6$ Hz, $J_{AB} = 15.9$ Hz, 3 H), 6.03 (t, J = 6.7 Hz, 1 H), 6.88 (d, J = 8.9 Hz, 2 H), 7.12–7.23 (m, 5 H), 7.85 (d, J = 8.9 Hz, 2 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = 0.59, 14.19, 22.56, 31.93, 32.41, 44.77, 46.05, 55.52, 113.68, 126.14, 128.47, 139.36, 130.79, 140.34, 142.08, 144.48, 163.30, 197.78.

MS (EI): m/z (%) = 394 (M⁺, 4), 73 (100).

Anal. Cald for $C_{25}H_{34}O_2Si$: C, 76.09; H, 8.68. Found: C, 76.11; H, 8.73.

(Z)-1-(3'-Nitrophenyl)-3-phenyl-4-trimethylsilyl-4-nonen-1-one (3h)

Yield: 56%; pale yellow oil.

IR (neat): 2958, 1697, 1543, 1352, 1249, 909, 734 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): $\delta = 0.01$ (s, 9 H), 0.89 (t, J = 7.3 Hz, 3 H), 1.31–1.33 (m, 4 H), 2.19–2.21 (m, 2 H), ABX, $\delta_A = 3.32$, $\delta_B = 3.48$, $\delta_X = 4.28$ ($J_{AX} = 7.1$ Hz, $J_{BX} = 7.7$ Hz, $J_{AB} = 16.2$ Hz, 3 H), 6.04 (t, J = 7.2 Hz, 1 H), 7.14–7.24 (m, 5 H), 7.61 (t, J = 8.0 Hz, 1 H), 8.16 (d, J = 7.8 Hz, 1 H), 8.37 (d, J = 8.1 Hz, 1 H), 8.62 (s, 1 H).

 ^{13}C NMR (100 MHz, CDCl₃): $\delta=0.54,$ 14.16, 22.59, 31.94, 32.41, 45.37, 46.09, 123.01, 126.53, 127.16, 128.43, 129.82, 133.60, 138.87, 140.14, 142.08, 143.65, 197.35.

MS (EI): m/z (%) = 409 (M⁺, 3), 73 (100).

Anal. Calcd for $C_{24}H_{31}NO_3Si: C$, 70.38; H, 7.63. Found: C, 70.39; H, 7.65.

(Z)-4-(4'-Nitrophenyl)-5-trimethylsilyl-5-decen-2-one (3i) Yield: 66%; pale yellow oil.

IR (neat): 2957, 1719, 1605, 1520, 1347, 1249, 840 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): $\delta = 0.02$ (s, 9 H), 0.93 (t, J = 7.2 Hz, 3 H), 1.36–1.41 (m, 2 H), 1.59–1.67 (m, 2 H), 2.07 (s, 3 H), 2.19– 2.22 (m, 2 H), ABX, $\delta_A = 2.78$, $\delta_B = 2.94$, $\delta_X = 4.21$ ($J_{AX} = 7.6$ Hz, $J_{BX} = 7.2$ Hz, $J_{AB} = 16.8$ Hz, 3 H), 6.06 (t, J = 7.6 Hz, 1 H), 7.34 (d, J = 8.8 Hz, 2 H), 8.13 (d, J = 8.8 Hz, 2 H).

 ^{13}C NMR (100 MHz, CDCl₃): $\delta = 0.48, 14.08, 22.54, 30.64, 31.93, 32.25, 45.06, 49.62, 123.51, 129.12, 139.71, 143.68, 146.50, 152.15, 206.36.$

MS (EI): m/z (%) = 347 (M⁺, 1), 73 (100).

Anal. Cald for $C_{19}H_{29}NO_3Si: C, 65.67; H, 8.41$. Found: C, 65.69; H, 8.46.

(Z)-1-(Cyclohexanon-3-yl)-1-trimethylsilyl-1-hexene (3j) Yield: 60%; colorless oil.

IR (neat): 2956, 2861, 1715, 1447, 1249, 837, 758 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): $\delta = 0.14$ (s, 9 H), 0.90 (t, J = 6.9 Hz, 3 H), 1.31–1.34 (m, 4 H), 1.36–1.48 (m, 1 H), 1.56–1.68 (m, 1 H), 1.76–1.86 (m, 1 H), 2.00–3.16 (m, 3 H), 2.26–2.42 (m, 5 H), 5.96 (t, J = 7.4 Hz, 1 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = –0.06, 13.50, 21.83, 24.89, 31.15, 31.73, 32.17, 40.70, 42.93, 140.53, 140.89, 211.96.

MS (EI): m/z (%) = 253 (M⁺ + 1, 3), 73 (100).

Anal. Calcd for C₁₅H₂₈OSi: C, 71.36; H, 11.18. Found: C, 71.35; H, 11.19.

(Z)-1,3-Diphenyl-4-trimethylsilyl-4-decen-1-one (3k)

Yield: 72%; colorless oil.

IR (neat): 2955, 2928, 1687, 1449, 1247, 838, 752 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): $\delta = 0.00$ (s, 9 H), 0.87 (t, J = 7.0 Hz, 3 H), 1.26–1.35 (m, 6 H), 2.15–2.20 (m, 2 H), ABX, $\delta_A = 3.25$, $\delta_B = 3.49$, $\delta_X = 4.31$ ($J_{AX} = 6.9$ Hz, $J_{BX} = 7.9$ Hz, $J_{AB} = 16.2$ Hz, 3 H), 6.05 (t, J = 7.3 Hz, 1 H), 7.15–7.54 (m, 8 H), 7.86–7.88 (m, 2 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = 0.49, 14.05, 22.64, 29.80, 31.62, 32.08, 45.12, 45.83, 126.12, 128.00, 128.17, 128.37, 128.48, 132.75, 137.61, 140.12, 142.15, 144.26, 199.21.

MS (EI): m/z (%) = 378 (M⁺, 4), 73 (100).

Anal. Calcd for $C_{25}H_{34}OSi: C$, 79.31; H, 9.05. Found: C, 79.20; H, 9.36.

(Z)-1-(4'-Methoxyphenyl)-3-phenyl-4-trimethylsilyl-4-decen-1one (3l)

Yield: 80%; colorless oil.

IR (neat): 2955, 1678, 1601, 1492, 1249, 1169, 837, 701 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): $\delta = 0.05$ (s, 9 H), 0.91 (t, J = 7.0 Hz, 3 H), 1.26–1.41 (m, 6 H), 2.19–2.24 (m, 2 H), 3.88 (s, 3 H), ABX, $\delta_A = 3.23$, $\delta_B = 3.46$, $\delta_X = 4.34$ ($J_{AX} = 7.0$ Hz, $J_{BX} = 7.7$ Hz, $J_{AB} = 16.1$ Hz, 3 H), 6.08 (t, J = 7.4 Hz, 1 H), 6.93 (d, J = 11.7 Hz, 2 H), 7.17–7.29 (m, 5 H), 7.90 (d, J = 11.7 Hz, 2 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = 0.58, 14.13, 22.71, 29.88, 31.68, 32.15, 44.74, 46.00, 55.48, 113.65, 126.12, 128.19, 128.45, 130.33, 130.75, 140.31, 142.09, 144.49, 163.29, 197.73.

MS (EI): m/z (%) = 408 (M⁺, 5), 73 (100).

Anal. Calcd for $C_{26}H_{36}O_2Si: C, 76.42; H, 8.88$. Found: C, 76.44; H, 8.92.

(Z)-(3'-Nitrophenyl)-3-phenyl-4-trimethylsilyl-4-decen-1-one (3m)

Yield: 54%; pale yellow oil.

IR (neat): 2955, 1696, 1533, 1491, 1451, 1350, 1248, 838, 702 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): $\delta = 0.02$ (s, 9 H), 0.88 (t, J = 6.8 Hz, 3 H), 1.27–1.38 (m, 6 H), 2.17–2.23 (m, 2 H), ABX, $\delta_A = 3.33$, $\delta_B = 3.49$, $\delta_X = 4.29$ ($J_{AX} = 7.2$ Hz, $J_{BX} = 7.6$ Hz, $J_{AB} = 16.0$ Hz, 3 H), 6.06 (t, J = 7.2 Hz, 1 H), 7.15–7.24 (m, 5 H), 7.62 (t, J = 8.0 Hz, 1 H), 8.16 (d, J = 8.0 Hz, 1 H), 8.37 (dd, J = 8.0, 1.2 Hz, 1 H), 8.63 (t, J = 2.0 Hz, 1 H).

 ^{13}C NMR (100 MHz, CDCl₃): $\delta=0.53,$ 14.11, 22.69, 29.90, 31.72, 32.17, 45.38, 46.07, 123.00, 126.52, 127.13, 128.42, 129.80, 133.58, 138.89, 140.17, 142.15, 143.66, 197.31.

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MS (EI): m/z (%) = 423 (M⁺, 2), 73 (100).

Anal. Calcd for $C_{25}H_{33}NO_3Si$: C, 70.88; H, 7.85. Found: C, 70.87; H, 7.88.

(Z)-4-(4'-Nitrophenyl)-5-trimethylsilyl-5-undecen-2-one (3n) Yield: 59%; pale yellow oil.

IR (neat): 2956, 1719, 1520, 1346, 839 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): $\delta = 0.02$ (s, 9 H), 0.91 (t, J = 7.1 Hz, 3 H), 1.29–1.42 (m, 6 H), 2.08 (s, 3 H), 2.17–2.23 (m, 2 H), ABX, $\delta_{\rm A} = 2.77$, $\delta_{\rm B} = 2.95$, $\delta_{\rm X} = 4.21$ ($J_{\rm AX} = 7.9$ Hz, $J_{\rm BX} = 6.8$ Hz, $J_{\rm AB} = 16.6$ Hz, 3 H), 6.06 (t, J = 7.4 Hz, 1 H), 7.34 (d, J = 8.8 Hz, 2 H), 8.12 (d, J = 8.8 Hz, 2 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = 0.55, 14.15, 22.69, 29.82, 30.72, 31.75, 32.24, 45.10, 49.68, 123.57, 129.20, 139.76, 143.79, 146.55, 152.22, 206.42.

MS (EI): m/z (%) = 361 (M⁺, 1), 73 (100).

Anal. Calcd for $C_{20}H_{31}NO_3Si$: C, 66.44; H, 8.64. Found: C, 66.45; H, 8.67.

(Z)-1-(Cyclohexanone-3-yl)-1-trimethylsilyl-1-heptene (30) Yield: 60%; colorless oil.

IR (neat): 2956, 2859, 1715, 1611, 1448, 1249, 837 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 0.14 (s, 9 H), 0.89 (t, *J* = 7.0 Hz, 3 H), 1.26–1.35 (m, 5 H), 1.36–1.56 (m, 1 H), 1.56–1.92 (m, 3 H), 2.00–2.20 (m, 3 H), 2.24–2.48 (m, 5 H), 5.97 (t, *J* = 7.2 Hz, 1 H).

 ^{13}C NMR (400 MHz, CDCl₃): δ = 0.52, 14.06, 22.64, 25.48, 29.81, 31.58, 31.99, 32.75, 41.28, 43.50, 48.56, 141.13, 141.43, 212.61.

MS (EI): m/z (%) = 266 (M⁺, 1), 73 (100).

Anal. Calcd for $C_{16}H_{30}OSi: C, 72.11; H, 11.35$. Found: C, 72.09; H, 11.36.

1,4-Diketones 5a-g; General Procedure

To the solution of MCPBA (0.3mmol) in CH_2Cl_2 (10mL) was added (*Z*)- γ -silyl γ , δ -unsaturated ketone **3** (0.3mmol). The mixture was stirred at r.t. until the vinylsilane disappeared. The mixture was washed in turn with sat. aq NaHCO₃, sat. brine and H₂O. CH₂Cl₂ was rotary evaporated and a solution of TFA (0.33 mmol) in MeOH (10mL) was added. After refluxing for 2 h, the reaction was worked up and a pure product was obtained by column chromatography (silica gel; light petroleum–EtOAc, 15:1).

1,3,5-triphenylpentane-1,4-dione (5a)

Yield: 81%; white solid; mp 78-80°C (hexane) (Lit.¹⁹ 79-80 °C).

IR (KBr): 3062, 2925, 1719, 1685, 1598, 1449, 788, 757, 700 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): $\delta = ABX$, $\delta_A = 3.15$, $\delta_B = 4.01$, $\delta_X = 4.53$ ($J_{AX} = 3.84$ Hz, $J_{BX} = 10.0$ Hz, $J_{AB} = 18.1$ Hz, 3 H), 3.85 (A'B', J = 10.8 Hz, 2 H), 7.05–7.52 (m, 13 H), 7.92–7.95 (m, 2 H). MS (EI): m/z (%) = 328 (M⁺, 1), 105 (100).

1-(4'-methoxylpenyl)-3,5-diphenylpentane-1,4-dione (5b) Yield: 84%; pale yellow oil.

IR (neat): 3028, 2926, 1719, 1674, 1601, 1510, 1249, 1169, 1031, 700 $\rm cm^{-1}$.

¹H NMR (400 MHz, CDCl₃): $\delta = ABX$, $\delta_A = 3.12$, $\delta_B = 3.96$, $\delta_X = 4.51$ ($J_{AX} = 3.8$ Hz, $J_{BX} = 10.0$ Hz, $J_{AB} = 17.9$ Hz, 3 H), 3.85 (s, 3 H), 3.85 (A'B', J = 6.8 Hz, 2 H), 6.89 (d, J = 8.9 Hz, 2 H), 7.22–7.33 (m, 5 H), 7.92 (d, J = 8.9 Hz, 2 H).

¹³C NMR (100 MHz, CDCl₃): δ = 39.5, 43.7, 46.9, 56.0, 114.0, 126.9, 127.1, 128.4, 128.6, 129.3, 129.4, 129.6, 129.7, 134.3, 134.5, 166.4, 197.6, 207.1.

MS (EI): m/z (%) = 359 (M⁺ + 1, 4), 135 (100).

Anal. Calcd for $C_{24}H_{22}O_3$: C, 80.42; H, 6.19. Found: C, 80.43; H, 6.21.

1-(Cyclohexanon-3-yl)-2-phenyl-1-acetone (5c)²⁰ Yield: 69%; colorless oil.

IR (neat): 3029, 2927, 1718, 1681, 1599, 1249, 1165, 788 cm⁻¹.

 ^1H NMR (400 MHz, CDCl_3): δ = 1.55–1.71 (m, 2 H), 1.84–2.01 (m, 2 H), 2.10–2.29 (m, 3 H), 2.36–2.51 (m, 1 H), 2.85–2.91 (m, 1 H), 3.63 (s, 2 H), 7.10–7.35 (m, 5 H).

MS (EI): m/z (%) = 216 (M⁺, 4), 105 (100).

1,3-Diphenylnonane-1,4-dione (5d)²¹

Yield: 80%; colorless oil.

IR (neat): 3054, 2931, 1715, 1685, 754, 701 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): $\delta = 0.82$ (t, J = 6.9 Hz, 3 H), 1.14– 1.22 (m, 2 H), 1.23–1.40 (m, 2 H), 1.51–1.63 (m, 2 H), 2.46–2.50 (m, 1 H), 2.56–2.60 (m, 1 H), ABX, $\delta_{\rm A} = 3.12$, $\delta_{\rm B} = 4.03$, $\delta_{\rm X} = 4.20$ ($J_{\rm AX} = 3.7$ Hz, $J_{\rm BX} = 10.1$ Hz, $J_{\rm AB} = 18.0$ Hz, 3 H), 7.27–7.53 (m, 8 H), 7.93–7.96 (m, 2 H).

MS (EI): m/z (%) = 309 (M⁺ + 1, 8), 105 (100).

1-(Cyclohexanon-3-yl)-1-hexanone (5e)²¹

Yield: 85%; colorless oil.

IR (neat): 2934, 2871, 1713, 1129, 733 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 0.89 (t, *J* = 7.2 Hz, 3 H), 1.20– 1.35 (m, 4 H), 1.56–1.63 (m, 2 H), 1.64–1.80 (m, 2 H), 2.05–2.15 (m, 2 H), 2.33–2.67 (m, 6 H), 2.88–2.92 (m, 1 H).

MS (EI): m/z (%) = 197 (M⁺ + 1, 15), 43 (100).

1,3-Diphenyldecane-1,4-dione (5f)

Colorless oil; yield: 88%.

IR (neat): 2929, 2857, 1715, 1685, 1494, 754, 701 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): $\delta = 0.83$ (t, J = 7.1 Hz, 3 H), 1.18– 1.25 (m, 6 H), 1.49–1.56 (m, 2 H), 2.47–2.51 (m, 1 H), 2.57–2.61 (m, 1 H), ABX, $\delta_A = 3.12$, $\delta_B = 4.04$, $\delta_X = 4.42$ ($J_{AX} = 3.6$ Hz, $J_{BX} = 10.2$ Hz, $J_{AB} = 18.0$ Hz, 3 H), 7.27–7.57 (m, 8 H), 7.95–7.97 (m, 2 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = 14.02, 22.48, 23.60, 28.69, 31.53, 41.86, 42.37, 53.32, 127.52, 128.10, 128.38, 128.56, 129.10, 133.20, 136.56, 138.25, 198.27, 209.49.

MS (EI): m/z (%) = 323 (M⁺ + 1, 23), 105 (100).

Anal. Calcd for $C_{22}H_{26}O_2$: C, 81.95; H, 8.13. Found: C, 81.90; H, 8.15.

1-(4'-Methoxylphenyl)-3-phenyldecane-1,4-dione (5g) Yield: 75%; colorless oil.

IR (neat): 2930, 1756, 1715, 1675, 1601, 1506, 1249, 1195, 701 $\rm cm^{-1}.$

¹H NMR (400 MHz, CDCl₃): $\delta = 0.81$ (t, J = 7.1 Hz, 3 H), 1.14– 1.21 (m, 6 H), 1.40–1.63 (m, 2 H), 2.39–2.47 (m, 2 H), ABX, $\delta_A = 2.78$, $\delta_B = 3.42$, $\delta_X = 4.25$ ($J_{AX} = 5.2$ Hz, $J_{BX} = 9.8$ Hz, $J_{AB} = 17.0$ Hz, 3 H), 3.77 (s, 3 H), 6.85 (d, J = 8.8 Hz, 2 H), 7.24– 7.36 (m, 5 H), 7.93 (d, J = 8.8 Hz, 2 H).

¹³C NMR (100 MHz, CDCl₃): δ = 14.0, 23.1, 32.2, 24.2, 29.5, 38.2, 39.5, 47.3, 56.0, 113.5, 126.9, 128.6, 129.3, 129.6, 129.7, 134.3, 166.4, 197.6, 208.2.

MS (EI): m/z (%) = 353 (M⁺ + 1, 4), 124 (100).

Anal. Calcd for $C_{23}H_{28}O_3$: C, 78.38; H, 8.01. Found: C, 78.32; H, 8.05.

X-Ray Crystal Data of 3d

The X-ray structural analysis of 3d (single crystal, Figure 1) crystallized from a hexane, colorless crystal, C21H25NO3Si (367.51); triclinic P – 1 with a = 7.6678(16), b = 11.185(2), c = 13.075(3) Å, $\alpha = 73.239(4)^{\circ}, \beta = 84.132(4)^{\circ}, \gamma = 80.324(4)^{\circ}, V = 1056.7(4) \text{ Å}^3,$ Z = 2, D = 1.155 Mg/m³, absorption coefficient 0.129 mm⁻¹ was performed at 293(2) K using graphite monochromated MoKa radiation ($\lambda = 0.71073$ Å, limiting indices $-10 \le h \le 7, -14 \le k \le 14, -16$ $\leq 1 \leq 17$, θ -range for data collection 1.63 to 28.29, reflections measured 6435, unique reflections 4657 ($R_{int} = 0.0614$). Completeness to $\theta = 28.29^{\circ} 88.6\%$, data/restraints/parameters = 4657/10/313. The structure was solved by direct methods and refined by full-matrix least-squares on F² using SHELXL-97 (Sheldrick, 1997) program system. All non-hydrogen atoms were refined anisotropically and the position of the hydrogen atoms was calculated as a riding model. The weighting scheme was $w^{-1} = s^2(F_0)^2 + (0.0785P)^2 + 0.0000P$ with $P = 1/3(F_o^2+2F_c^2)$. Goodness-of-fit on F^2 0.786; final R indices $[I > 2\sigma (I)], R1 = 0.0550, wR2 = 0.1195; R indices (all data)$ R1 = 0.1520, wR2 = 0.1812.

Selected bond distances [pm] and bond angles [°]: Si–C(8) 1.896(3), C(6)–C(7) 1.482(4), C(7)–C(8) 1.335(4), C(7)–H(6) 0.92(3), C(8)–C(9) 1.538(4), C(9)–C(10) 1.515(4), C(9)–C(16) 1.531(5), C(9)–H(7) 0.99(3), C(16)–C(17) 1.499(5), C(16)–H(12) 0.997(17), C(16)–H(13) 0.981(18), C(17)–C(18) 1.486(5), C(8)–C(7)–C(6) 127.0(4), C(8)–C(7)–H(6) 121.2(19), C(6)–C(7)–H(6) 111.4(19), C(7)–C(8)–C(9) 119.8(3), C(7)–C(8)–Si 124.0(3), C(9)–C(8)–Si 116.2(2), C(8)–C(9)–H(7) 105.5(15), C(17)–C(16)–C(9) 114.6(3), C(17)–C(16)–H(12) 104.2(17), C(9)–C(16)–H(12) 108.7(18), C(17)–C(16)–H(13) 109.4(19), C(9)–C(16)–H(13) 109.3(19), H(12)–C(16)–H(13) 110(3), O(1)–C(17)–C(18) 121.0(4), O(1)–C(17)–C(16) 122.1(4).

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