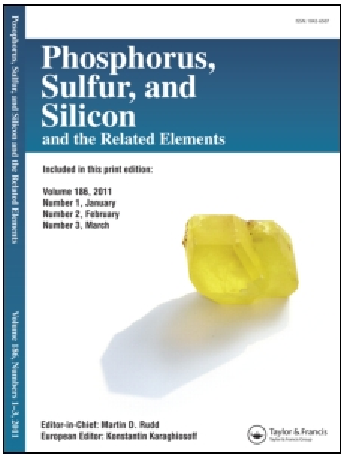


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

NEW AND CONVENIENT SYNTHESIS OF (*R*) AND (*S*) OF 2-METHYL-3-OXA-5-(TERT-BUTYLDIPHENYLSILYLOXYL) METHYLPENTANOATE AND 2-METHYL-3-OXA-5- (TERT-BUTYLDIMETHYLSILYLOXYL)METHYLPENTANOATE

Abdel-Sattar S. Hamad[a]; Dieter Schinzer[b]
[a] Department of Chemistry, Faculty of Science, University of Ain Shams, Cairo, Egypt [b] Chemisches Institut der Otto-von-Guericke-Universitat magdeburg, Universitatsplatz, Magdeburg, Germany

To cite this Article Hamad, Abdel-Sattar S. and Schinzer, Dieter(2000) 'NEW AND CONVENIENT SYNTHESIS OF (*R*) AND (*S*) OF 2-METHYL-3-OXA-5-(TERT-BUTYLDIPHENYLSILYLOXYL) METHYLPENTANOATE AND 2-METHYL-3-OXA-5- (TERT-BUTYLDIMETHYLSILYLOXYL)METHYLPENTANOATE', Phosphorus, Sulfur, and Silicon and the Related Elements, 158: 1, 187 — 199

To link to this Article: DOI: 10.1080/10426500008042086

URL: http://dx.doi.org/10.1080/10426500008042086

Phosphorus, Sulfur and Silicon, 2000, Vol. 158, pp. 187-199
Reprints available directly from the publisher
Photocopying permitted by license only

NEW AND CONVENIENT SYNTHESIS OF *(R)* AND *(S)* OF 2-METHYL-3-OXA-5-(TERT-BUTYLDIPHENYLSILYLOXYL) METHYLPENTANOATE AND 2-METHYL-3-OXA-5-(TERT-BUTYLDIMETHYLSILYL-OXYL)METHYLPENTANOATE

ABDEL-SATTAR S. HAMAD[a]* and DIETER SCHINZER[b]

[a]*Department of Chemistry, Faculty of Science, University of Ain Shams, Abbassia 11566, Cairo, Egypt and* [b]*Chemisches Institut der otto-von-Guericke-Universitat magdeburg, Universitatsplatz 2D-39106 magdeburg, Germany*

(Received May 26, 1999; In final form September, 1999)

(R) and *(S)* of 2-Methyl-3-oxa-5-(tert-butyldiphenylsilyloxyl)methylpentanoate (**4a**, **6a**) and *(R)* and *(S)* of 2-methyl-3-oxa-5-(tert-butyldimethylsilyloxyl)methylpentanoate (**4b**, **6b**) were synthesized by the reaction of the preparative compounds (**2a**, **2b**) with *(R)* and *(S)* methyl lactate (**3**, **4**) in the presence of a silver (I) oxide catalyst (Method B). The title compounds are useful for the synthesis of different natural products such as epothilones.

Keywords: Epothilones; Natural Products; silylation; Etherification; Organosilicon

Organosilicon compound have attracted considerable attention in several types of organic synthesis.[1,2] The silyl- substituted ones are expected to possess high potentials, but have not been prepared yet.[3] Here we report the preliminary results obtained in pursuit of this goal. In this paper our efforts focus on the synthesis of *(R)* 2-methyl-3-oxa-5-(tert-butyldiphenylsilyloxyl)methyl pentanoate **6a**, *(S)* 2-methyl-3-oxa-5-(tert-butyldiphenylsilyloxyl)methylpentanoate **4a**, *(R)* 2-methyl-3-oxa-5-(tert-butyldimethylsilyloxyl) methyl pentanoate **6b** and *(S)* 2-methyl-3-oxa-5-(tert-butyldimethylsilyloxyl)methyl pentanoate **4b** which are useful for the syn-

---

* Correspondence Author. Tel./Fax; (00)202–4831836; E-mail; hamad@asunet.shams.eun.eg

thesis of different natural products such as epothilones which were isolated by Hofle et al.[4,5]

2-Iodo-[(1-tert-butyldiphenylsilyloxy)]ethane **2a** was prepared in one step by silylation[6] of 2-iodoethanol with tert-butyldiphenylsilylchloride (1.3 equiv,) imidazole (3 equiv) in *N,N'*-dimethylformamide (DMF) at 23°C for 48 hours, as shown in (Scheme 1). 2-Iodo-[(1-tert-butyldimethylsilyloxy)]ethane **2b** was also prepared by following the procedure described in method (A), starting from commercially available iodoethanol **1** (Aldrich catalog). where the protecting group was replaced by tert-butyldimethylsilylchloride.

The ^1H NMR spectrum of **2a** exhibited signals for three non equivalent protons in phenyl rings corresponding to 10 hydrogen atoms. The down field signals are assigned to the six hydrogen protons for Ar-H_m and Ar-H_p which appear as multiplet at δ 7.42 and 7.39 ppm respectively and also show signals doublets of doublets for four protons of Ar-H_o at δ 7.68 and 7.67 ppm.

Moreover, in the ^{13}C-NMR spectrum, signals for 3 aromatic CH at $\delta = 135.56$, 129.82, 127.75, with the carbon (C^i) at $\delta = 133.32$. The sp^3-C atoms of two signals (two triplets) at $\delta = 64.65$ and 6.7 for CH_2O Si- and CH_2I respectively. There are also two signals at 26.79 and 19.25 for $3(CH_3)$ and Si-C^i.

Unfortunately, the unexpected correlation of ^{13}J (C,H) peaks to some of these C-atoms in the ^{13}C NMR for Si-O-CH_2-$C\underline{H}_2I$. The methylene group adjacent to iodide could be exhibiting unusual chemical shifts at δ 6.70 ppm in (DEPT-135) the NMR spectrum did not allow the structure to be established unambiguously. After purification via flash chromatography with pure pentane the product was obtained as a colorless viscous liquid in 79.5 % yield which solidified at 5–10°C as colorless crystals. X-ray crystallography established that the product was 2-iodo-(1-tert-butyldiphenylsilyloxy)]ethane **2a**, as shown in (Figure 1).

The structure of compound **2a** was confirmed by x-ray crystallography (Fig. 1). Bond length and bond angle analysis indicate that the two phenyl rings are almost perpendicular to each other. In both ring systems, the carbon atoms next to silicon show bond angles with the adjacent carbon which are smaller than expected for a benzene ring [bond angle $C_{(18)}$-$C_{(13)}$-$C_{(14)} = 115°$ and $C_{(12)}$-$C_{(7)}$-$C_{(8)} = 116°$]. This is probably due to the stereochemically hindered situation of the substituents around the silicon atom. This effect seem to be propagating through the aromatic ring,

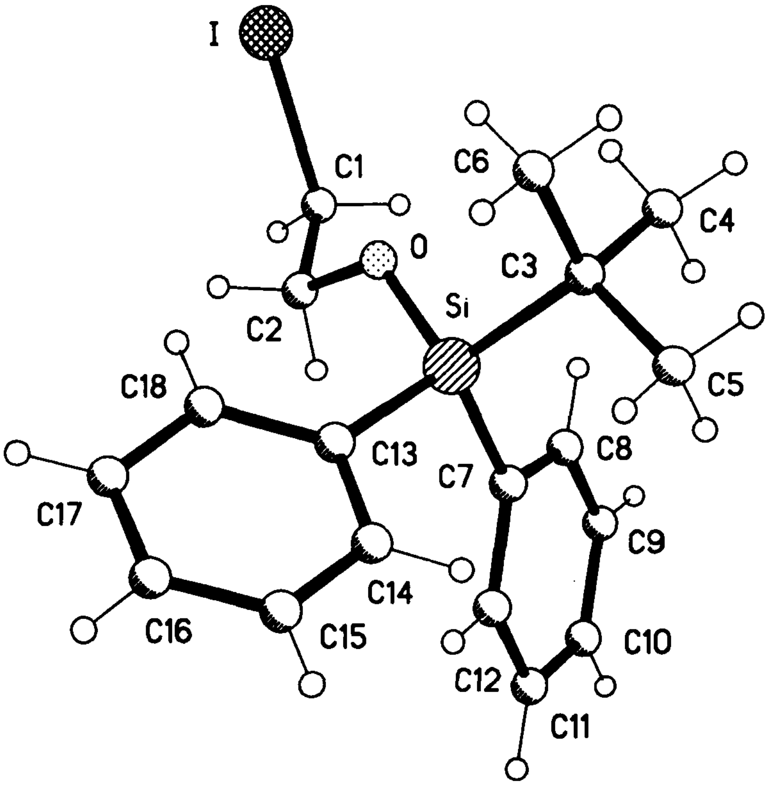


FIGURE 1 X-ray crystal structure of 2-Iodo-[(1-tert-butyldiphenylsilyloxy)]ethane **2a**

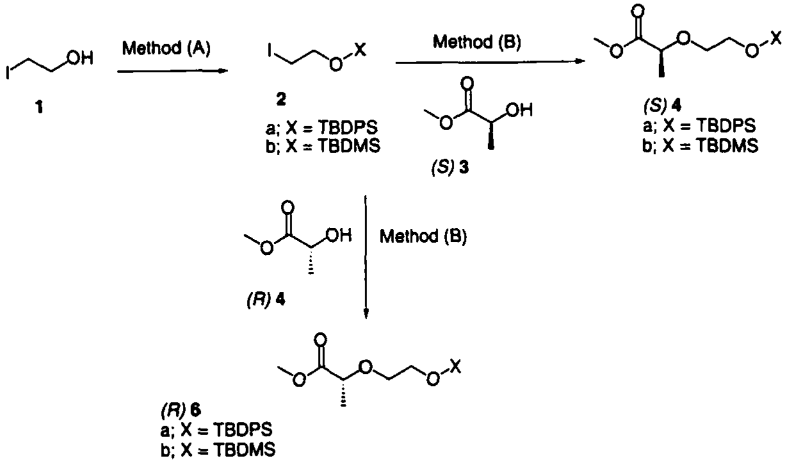
causing unexpected bond lengths [e.g. bond length $C_{(17)}$-$C_{(16)}$ = 1.361 Å and $C_{(16)}$-$C_{(15)}$ = 1.309 Å]. The bond length for the $C_{(1)}$-$C_{(2)}$ bond (1.493Å) in the $-OCH_2CH_2I$ unit is also smaller than expected for a single bond between sp^3 carbon atoms. Compound **2a** was also chracterized by ^1H and ^{13}C NMR spectroscopy. The data collected indicates that in chloroform solution, both phenyl rings are equivalent as only one set of signals is visible for the proton and carbon atoms in either ^1H or ^{13}C NMR. The ($Si-O-CH_2CH_2I$) protons can be seen as two triplets at δ 3.86 and 3.22 ppm and in ^{13}C NMR the corresponding carbon atoms are unequivocally identified by (DEPT 135) at 64.65 and 6.70 ppm. This unexpected result does not entirely compare with the ^{13}C NMR chemical shifts for the same functional group in compound **2b**, where the two phenyl groups were replaced by two methyl groups. This compound shows the (Si-O-CH_2CH_2I) protons at δ 3.75 and 3.44 ppm (both triplets) and the carbon atoms at 63.68 and 45.02 ppm by (DEPT 135). It is not possible to explain this apparently abnormal result, although it seems to be associated with the presence of the two aromatic substituents.

TABLE I Crystal data and details of refinement for compound **2a**

Compound No.	*2a*
Formula	$Cl_8H_{23}SiOI$
Mr	(410.35)
Crystal size/mm	0.60 × 0.30 × 0.30
Z	1874.72(6) Å
Dc/mg^{-3}	1.454 mg m^{-3}
F(000)	824

The etherification[7] reaction of **2a** and **2b** with commercially available (Aldrich Catalog) compound of (*S*)-(-)-methyl lactate **3** (1 equivalent) in the presence of (2.6 equivalents) of silver (I) oxide in dry ether to provide compounds (**4a**, **4b**) as a yellow liquid in 65% yield, after purification by flash chromatography using silica gel (ether/pentane; 1:10), Compounds **6a**, **6b** were also prepared following the previous method (B) where the the (*S*)-(-)-methyl lactate **3** was replaced with (*R*)-(+)-methyl lactate **4** to give a yellow liquid and which was purified by flash chromatography using silica gel (ether/pentane; 1:10) and provided the corresponding compound in 65% yield, as shown in (scheme 1).

The counpounds (**4a**, **6a**) and (**4b**, **6b**) were synthesized for the first time and in high overall yield. Compounds (*S*) **4a** and (*R*) **6a** was characterized by ^1H and ^{13}C NMR spectroscopy. The data collected indicates that in chloroform solution, both phenyl rings are equivalent as only one set of signals in visible for the proton and carbon atoms in either ^1H or ^{13}C NMR. Exhibited as multiplet signals for three non equivalent proton in benzene rings corresponding to 10 hydrogen at δ = 7.71–7.66 ppm. The (Si-O-CH_2CH_2O) protons can be seen as two triplets at δ 4.23 and 3.85–3.80 ppm for (-O-$C\underline{H}_2$-CH_2-O-Si) and (-$C\underline{H}_2$-O-Si) respectively, at the same coupling constant $^{13}J = 6.1$ Hz and in ^{13}C NMR the corresponding carbon atoms are unequivocally identified by (DEPT 135) at 71.34 and 63.40 ppm. This result was compared with the ^{13}C NMR chemical shifts



SCHEME 1

for the same functional group in compounds (*S*) **4b** and (*R*) **6b**, where the two phenyl groups were replaced by two methyl groups. This compound shows the (Si-O-CH_2CH_2I) protons at δ 3.83 and 3.52 ppm (both triplets) for (-O-$C\underline{H}_2$-CH_2-O-Si) and (-$C\underline{H}_2$-O-Si) respectively, at the same coupling constant $^{13}J = 6.2$ Hz. and the carbon atoms at 64.49 and 58.96 ppm by (DEPT 135).

EXPERIMENTAL SECTION

IR spectra were recorded on Perkin-Elmer 580, FT 1710 and Nicolet 320 FT-IR spectrometers. NMR spectra were recorded on Bruker AM 400 and DMX 600 spectrometers. All organometallic reactions were performed under nitrogen, and pure products were obtained after flash chromatography on Merck silica gel 60 (40–63mm). Additions were carried out by means of a syringe pump. Optical rotations were recorded with a Perkin Elmer 241 Polarimeter. Elemental analyses were performed by M-H-N Laboratories (Phoenix, AZ).

2-Iodo-[(1-tert-butyldiphenylsilyloxy)]ethane (2a); Method (A)

Into an oven dried round bottom flask (50 ml r. b.) were placed 2-iodoethanol **1** (1.72 gm, 10 mmole, 1 equiv.), tert-butyldiphenylsilylchloride

(TBDPSICl) (3.56 gm, 13 mmole, 1.3 equiv.), imidazole (1.77 gm, 26 mmole, 2.6 equiv.), and dry DMF (25 mL) was added. The reaction mixture was stirred for 48 hours at RT and then filtered through a short pad of silica gel and then the product purified via flash chromatography (pure pentane) which afforded the protected product **2a** (3.26 gm, 79.5% yield as colorless oil. Solidified at 5°C as colorless crystal and melt at 17°C to become colorless viscous liquid. TLC: R_f (pure pentane); 0.37; IR (film) υ *max* = 3065(w), 3031(w), 2965 (s), 2957(s), 2595(s), 2890(s), 2863(s), 1721(s), 1508(m), 1473(m), 1365(w), 1256(s), 1109(s), 840(s) cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) : $\delta = 7.68$–7.67 (dd, 2H, J = 1.9, 1.4 Hz, Ar-HO), 7.66 –7.65 (dd, 2H, J = 1.68, 1.06 Hz, Ar′-HO), 7.41 – 7.38 (m, 6H, H, Ar-H, Ar′-H], 3.86 (t, 2H, J = 6.90 Hz, I-CH$_2$-C$\underline{H}_2$O-Si-), 3.199 (t, 2H, J = 6.65 Hz, I-C$\underline{H}_2$-CH$_2$O-Si-), 1.07 (s, 9H, Si-^{t}Bu).; ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 135.56$, 133.31, 129.82, 127.75, 64.65, 26.79, 19.25, 6.75; Anal. Calcd for C$_{18}$H$_{23}$SiOI (410.37): C, 52.68; H, 5.64. Found: C, 52.42; H, 5.32. HRMS (EI) Calcd for C$_{18}$H$_{23}$SiOI (410.37), found 410.37.;

X-ray crystallography

Crystal data and refinement details for the compound **2a** is presented in table I. The crystal was mounted on glass fibre. All measurements were made on a difractometer, employing graphite monochromated Mo – Kα radiation, the data were collected at a temperature of 203(2) K using C^i w/2O scanning technique with a θ range for data collection of 2.03 to 28.28°. The structure was solved C^i by direct method using C^i (ref.) and refined using C^i (ref.).

2-Iodo-[(1-tert-butyldimethylsilyloxy)]ethane (2b); Method (A)

Into an oven dried a round bottom flask (50 ml r. b.) were placed 2-iodoethanol **1** (1.72 gm, 10 mmole), tert-butyldiphenylsilylchloride (TBDMSICl) (2.26 gm, 15 mmole, 1.5 equiv.), imidazole (2.04 gm, 30 mmole, 3 equiv.), and DMF (25 mL) was added. The reaction mixture was stirred for 48 hours at RT and then filtrate through a short pad of silica gel and then the organic layer extracts were washed with water, brine, dried over MgSO$_4$, and concentrated under reduce pressure to provide the crude product. The product purified via flash chromatography (ether/pentane 1:10) afforded the protected product **2b** (2.5 gm, 87% yield as colorless viscous liquid.

TLC: $R_f = 0.37$ in (ether/pentane 1:10); IR (film) υ *max* = 2960 (s), 2956(s), 2593(s), 2889(s), 2860(s), 1722(s), 1506(m), 1473(m), 1363(w), 1256(s), 1102(s), 837(s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) : δ = 3.76 –3.73 (t, 2H, J = 6.3 Hz, I-CH_2-$C\underline{H}_2$O-Si-), 3.45 –3.42 (t, 2H, J = 6.21 Hz, I-$C\underline{H}_2$-CH_2O-Si-), 0.08 (s, 9H, Si-^{t}Bu), –0.06 –0.01 (2s, 6H, Si-CH_3 and Si-CH_3′); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 63.68, 45.01, 25.82, 18.29, –5.31, –5.34; Anal. Calcd for $C_8H_{19}SiOI$ (286.23): C, 33.57; H, 6.69. Found: C, 33.34; H, 6.56.; HRMS (EI) Calcd for $C_8H_{19}SiOI$ (286.23), found 286.23.

Method (B)

A mixture of compounds **2a** or **2b** derivatives (1.1 eq, 11.1 mmol), 2.6 eq of silver (I) oxide (26 mmol, 6.08 gm), and 1 eq of methyl lactate (10 mmol, 1.04 gm). The reaction mixture was refluxed for 72 hours, filtered and then distilled at 36°C to remove the solven. Purification of the residue by flash chromatography using silica gel (ether/pentane; 1:10) gave yellow liquid of o-alkylated compound in 65 % yield.

(S) 2-methyl-3-oxa-5-(tert-butyldiphenylsilyloxyl)methylpentanoate (4a)

Compound **2a** was reacted with (*S*)-(-)-methyl lactate **3** follow in detial the procedure described in method (B). $[\alpha]^{20}_D = -13.7$ (c = 1.0, $CDCl_3$).; IR (film) υ *max* = 3085(w), 3035(w), 3033(w), 3031(w), 2965 (vs), 2957(s), 2595(s), 2890(s), 2863(vs), 1721(vs), 1508(m), 1473(m), 1365(w), 1256(s), 1109(s), 840(vs) cm^{-1};

^1H NMR (400 MHz, $CDCl_3$) : δ = 7.71–7.35 (m, 10 H, Ar-H, Ar-H′), 4.23 (t, 2H, J = 6.08 Hz, –O-$C\underline{H}_2$-CH_2-O-Si), 4.12–4.07 (q, 1H, J = 6.8 Hz, $CH_3C\underline{H}$-), 3.85 – 3.80 (t, 2H, J = 6.09 Hz, O-CH_2-$C\underline{H}_2$O-Si-), 3.70 (s, 3H, OCH_3), 1.05 (s, 9H, Si-^{t}Bu), 0.94 (d, 3H, J = 7.48 Hz, $C\underline{H}_3$CH).; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.55, 135.64, 133.52, 130.86, 128.68, 75.40, 71.34, 67.96, 63.40, 51.58, 38.69, 26.81; Anal. Calcd for $C_{22}H_{30}SiO4$ (386.56): C, 68.35; H, 7.8. Found: C, 68.40; H, 7.99. HRMS (EI) Calcd for $C_{22}H_{30}SiO4$ (386.56), found 386.56.;

(S) 2-methyl-3-oxa-5-(tert-butyldimethylsilyloxyl) methylpentanoate(4b)

Compound **2b** was reacted with (*S*)-(-) methyl lactate **3** follow in detial the procedure described in method (B). $[\alpha]^{20}_D = -10.2$ (c = 1.0, $CDCl_3$).; IR (film) υ max = 2961 (s), 2959(s), 2591(s), 2882(s), 2863(s), 1722(s), 1509(m), 1473(m), 1363(w), 1256(s), 1105(s), 837(s) cm^{-1}

^1H NMR (400 MHz, $CDCl_3$): $\delta = 4.22$–4.16 (q, 1H, J = 6.15 Hz, $CH_3C\underline{H}$-), 3.84–3.80 (t, 2H, J = 6.65 Hz, -O-$C\underline{H}_2$-CH_2-O-Si), 3.81 (s, 3H, OCH_3), 3.54–3.51 (t, 2H, J = 6.20 Hz, O-CH_2-$C\underline{H}_2$O-Si-), 1.46 (d, 3H, J = 7.56 Hz, $C\underline{H}_3CH$), 0.89 (s, 9H, Si-^{t}Bu). 0.069 [(s, 6H, – Osi$(CH_3)_2$]; ^{13}C NMR (100MHz, $CDCl_3$): $\delta = 166.90$, 74.25, 64.49, 61.02, 58.96, 51.55, 32.69, 23.81, 17.59, –5.16; Anal. Calcd for $C_{12}H_{26}SiO4$ (262.42): C, 54.92; H, 9.98. Found: C, 54.83; H, 9.99. HRMS (EI) Calcd for $C_{12}H_{26}SiO4$ (262.42), found 262.42.;

(R) 2-methyl-3-oxa-5-(tert-butyldiphenylsilyloxyl) methylpentanoate (6a)

Compound **2a** was reacted with (*R*)-(+)-methyl lactate **4** following in detial the procedure described in method (B) to yield a yellow liquid which was purified by flash chromatography using silica gel (ether/pentane; 1:10) to afford the corresponding compound in 65% yield. $[\alpha]^{20}_D = +15.5$ (c = 1.0, $CDCl_3$).; The spectral data corresponded to compound **4a** as the previously reported.

(R) 2-methyl-3-oxa-5-(tert-butyldimethylsilyloxyl) methylpentanoate (6b)

Compound **2b** was reacted with (*R*)-(+)-methyl lactate **4** follow in detial the procedure described in method (B) to yield a yellow liquid which was purified by flash chromatography using silica gel (ether/pentane; 1:10) afforded the corresponding compound in 65% yield. $[\alpha]^{20}_D = +11.2$ (c = 1.0, $CDCl_3$).; The spectral data corresponded to compound **4b** as the previously reported.

TABLE II Atomic coordinates [× 10^4] and equivalent isotropic displacement parameters [Å^2 × 10^3] for **2a**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij}tensor

	x	*y*	*z*	*U(eq)*
I	1154.2(6)	3177.4(7)	149.5(3)	80.6(2)
Si	3321.4(16)	503(2)	-1443.9(7)	46.8(4)
O	2715(6)	1315(6)	-856(2)	74.4(17)
C(1)	1847(14)	1045(9)	125(4)	103(4)
C(2)	3076(12)	942(12)	-170(3)	110(4)
C(3)	2165(6)	1066(8)	-2250(3)	52.4(15)
C(4)	727(10)	660(20)	-2261(7)	224(12)
C(5)	2559(16)	341(15)	-2827(4)	163(7)
C(6)	2215(13)	2640(11)	-2348(6)	125(5)
C(7)	3332(6)	-1493(7)	-1299(3)	49.4(14)
C(8)	2174(7)	-2176(11)	-1170(4)	76(2)
C(9)	2156(9)	-3635(12)	-1042(4)	86(3)
C(10)	3283(9)	-4474(10)	-1032(4)	73(2)
C(11)	4453(9)	-3849(8)	-1160(4)	72(2)
C(12)	4461(7)	-2379(8)	-1295(4)	59.6(17)
C(13)	5118(7)	1160(7)	-1397(4)	56.9(17)
C(14)	5903(7)	704(9)	-1850(5)	74(2)
C(15)	7234(8)	1164(10)	-1834(5)	82(2)
C(16)	7828(10)	2032(11)	-1356(5)	86(3)
C(17)	7173(8)	2582(8)	−898(4)	68(2)
C(18)	5766(9)	2143(8)	-912(4)	72(2)

TABLE III Bond lengths [Å] and angles [°] for **2a**

I-C(1)	2.107(9)	Si-O	1.649(4)
Si-C(3)	1.879(6)	Si-C(7)	1.880(7)
Si-C(13)	1.892(7)	O-C(2)	1.418(8)
C(1) -C(2)	1.493(14)	C(3) -C(6)	1.480(12)

C(3) -C(5)	1.488(11)	C(3) -C(4)	1.491(11)
C(7) -C(8)	1.402(9)	C(7) -C(12)	1.402(9)
C(8) -C(9)	1.383(13)	C(9) -C(10)	1.374(13)
C(10) -C(11)	1.389(11)	C(11) -C(12)	1.395(11)
C(13) -C(18)	1.403(9)	C(13) -C(14)	1.409(11)
C(14) -C(15)	1.401(10)	C(15) -C(16)	1.309(13)
C(16) -C(17)	1.361(13)	C(17) -C(18)	1.469(12)
O-Si-C(3)	105.0(3)	O-Si-C(7)	109.1(3)
C(3) -Si-C(7)	113.3(3)	O-Si-C(13)	108.4(3)
C(3) -Si-C(13)	111.0(3)	C(7) -Si-C(13)	109.8(3)
C(2) -O-Si	124.0(4)	C(2) -C(1) -I	112.2(6)
O-C(2) -C(1)	109.3(8)	C(6) -C(3) -C(5)	108.5(9)
C(6) -C(3) -C(4)	108.1(11)	C(5) -C(3)-C(4)	107.4(11)
C(6) -C(3) -Si	111.2(5)	C(5) -C(3) -Si	110.6(6)
C(4) -C(3) -Si	110.9(5)	C(8) -C(7) -C(12)	116.0(7)
C(8) -C(7) -Si	120.0(6)	C(12) -C(7) -Si	123.9(5)
C(9) -C(8) -C(7)	121.8(8)	C(10) -C(9) -C(8)	121.0(8)
C(9) -C(10) -C(11)	119.4(8)	C(10) -C(11) -C(12)	119.3(8)
C(11) -C(12) -C(7)	122.5(7)	C(18) -C(13) -C(14)	115.1(7)
C(18) -C(13) -Si	122.6(6)	C(14) -C(13) -Si	122.4(5)
C(15) -C(14) -C(13)	124.3(8)	C(16) -C(15) -C(14)	119.0(9)
C(15) -C(16) -C(17)	122.6(9)	C(16) -C(17) -C(18)	119.5(7)
C(13) -C(18) -C(17)	119.5(8)		

TABLE IV Anisotropic displacement parameters $Å^2 \times 10^3$] for **2a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[(ha^*)^2U_{11} + \ldots + 2hka^*b^*U_{12}]$

	U11	*U22*	*U33*	*U23*	*U13*	*U12*
I	79.1(4)	84.9(4)	75.4(4)	-21.0(3)	11.6(3)	33.9(3)
Si	40.2(8)	66.8(11)	32.4(7)	-13.2(7)	5.7(6)	11.8(7)
O	92(4)	102(4)	33(2)	7(2)	22(2)	60(3)

	U11	*U22*	*U33*	*U23*	*U13*	*U12*
C(1)	202(12)	54(5)	64(5)	8(4)	53(6)	-12(6)
C(2)	160(9)	139(9)	34(3)	15(4)	31(5)	103(8)
C(3)	47(3)	74(4)	35(3)	-1(3)	5(2)	-7(3)
C(4)	56(6)	420(30)	168(13)	192(17)	-46(7)	−65(10)
C(5)	270(18)	160(12)	41(5)	-23(6)	-6(7)	108(12)
C(6)	147(10)	74(6)	114(8)	-2(6)	-63(7)	22(6)
C(7)	42(3)	70(4)	36(3)	-9(3)	8(2)	–4(3)
C(8)	45(4)	112(7)	71(5)	31(5)	13(3)	2(4)
C(9)	59(5)	122(8)	74(5)	30(5)	4(4)	-31(5)
C(10)	94(6)	75(5)	53(4)	-10(4)	22(4)	-20(5)
C(11)	83(5)	59(4)	85(5)	-25(4)	41(4)	-2(4)
C(12)	59(4)	59(4)	69(4)	-25(3)	31(3)	-9(3)
C(13)	56(4)	35(3)	67(4)	–8(3)	-14(3)	0(3)
C(14)	45(4)	63(4)	118(7)	-10(4)	28(4)	-2(3)
C(15)	60(4)	73(5)	116(7)	11(5)	26(5)	-2(4)
C(16)	77(5)	87(6)	88(6)	33(5)	1(5)	0(5)
C(17)	73(5)	55(4)	59(4)	11(3)	-23(4)	-25(4)
C(18)	95(6)	49(4)	58(4)	6(3)	-15(4)	-7(4)

TABLE V Hydrogen coordinates (× 10^4) and isotropic displacement parameters ($Å^2$ × 10^3) for **2a**

	x	*y*	*z*	*U(eq)*
H(1A)	2065	659	580	124
H(1B)	1118	454	-139	124
H(2A)	3783	1596	66	131
H(2B)	3437	-40	-121	131
H(4A)	670	-370	-2197	269
H(4B)	154	928	-2687	269
H(4C)	422	1159	-1904	269

	x	*y*	*z*	*U(eq)*
H(5A)	2530	-694	-2769	196
H(5B)	3473	629	-2850	196
H(5C)	1930	614	-3236	196
H(6A)	1960	3128	-1976	150
H(6B)	1588	2904	-2760	150
H(6C)	3131	2920	-2373	150
H(8)	1389	-1628	-1171	91
H(9)	1360	-4059	-959	104
H(10)	3263	-5463	-939	88
H(11)	5231	-4411	-1157	87
H(12)	5254	-1966	-1386	72
H(14)	5507	48	-2185	89
H(15)	7695	855	-2161	98
H(16)	8743	2284	-1329	104
H(17)	7618	3238	-574	82
H(18)	5302	2518	-598	87

Acknowledgements

This work was supported by University of Otto-Von-Guerick University, Magdeburg, Germany. We deeply thank to Dr. Axel Fischer, for obtaining x-ray crystalography, Chemisches Institut der otto-von-Guericke-Universitat, Universitatsplatz 2D-39106 magdeburg, Germany. and to Professor Dr. M. Fernanda Proenca, Departamento de Química, Universidade do Minho, 4710 Braga, Portugal for her generous assistance

References

1. I. Fleming, R. Henning, D.C. Parker; H.E. Plaut and P.E.J. Sanderson, *J. Chem. Soc., Perkin trans. 1*, 317 (1995).
2. R. Angeland, Y. Landais and L. parra-Rapado, *Tetrahedron lett.*, ***38***, 8845 (1997).
3. Oxidation of C-Si bond into C-O bond: colvin, E. W. *In comprehansive organic synthesis, vol. 7*; Ley S.V.; Prost, B. M.; Fleming I. Eds.; Pergamon press; Oxford, (P641, 1991).
4. G. Hofle, N. Bedrof, H. Steinmetz, D. Schomburg, K. Gerth, H. Reichnbach *Angew. Chem.*, ***108***, 1671–1673, (1996).; *Angew. Chem. Int. Ed. Engl.*, ***35***, 1567–1569 (1996).

5. D. Schinzer, Epothilones – New promising Microtubule -Stabilizing Natural Products with Taxol – Like Biological Activity, *Eur. Chem. Chron.*, ***1***, 7–10 (1996).
6. Dieter Schinzer, Anja Limberg and Oliver M. Bohn *Chem. Eur. J.*, ***2***, No. 11, 1477–1482 (1996).
7. Guy. Solladie, Eva Arce, Claude. Bauder, and M. Curmen Carreno, *J. Org. Chem.* ***63***, No. 7, 2332–2337, (1998).