A New General Route to Acceptor-Substituted Vinyloxiranes via Siloxyoxiranes – Novel Promising Synthetic Building-Blocks

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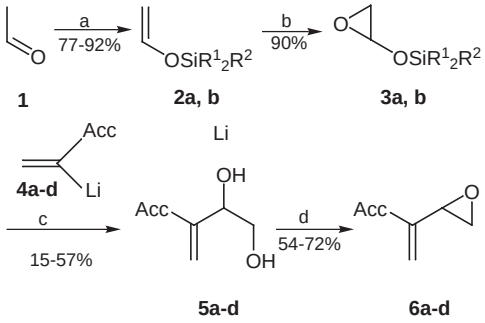
Abstract: Epoxidation of silyl enol ethers **2a**,**b** with dimethyldioxirane yields siloxyoxiranes **3a**,**b**. Anions **4a**–**d** lead to nucleophilic ring-opening in the acetal position C-1 of **3** to give diols **5a**–**d**. Monotosylation and cyclisation provide acceptor-substituted vinyloxiranes **6a**–**d**.

Key words: dimethyldioxirane, silyl enol ethers, siloxyoxiranes, vinyloxiranes, epoxide ring opening

Vinyloxiranes are very useful building blocks in organic synthesis. Their fully functionalised carbon backbone opens up a broad range of reaction possibilities.[1] Thus, the general synthetic utility of oxiranes is further enhanced and numerous uses of vinyloxiranes as intermediates in natural-product synthesis have been reported.[2]

Herein, we describe a conceptually new route to a novel type of vinyloxiranes **6** with a sulfide or silyl substituent in the internal olefinic position (Scheme). Vinyloxiranes with this substitution pattern are difficult to access by the usual oxidation routes starting from the corresponding butadienes[3] as these oxidation methods inevitably affect sulfide functions to give sulfoxides or even sulfones. Similarly, the presence of a silyl substituent on a butadiene directs the oxidation to the silicon-substituted double bond.[4] To avoid these problems, another strategy was required for the synthesis of acceptor-substituted vinyloxiranes **6**, i.e vinyloxiranes with a carbanion-stabilising heterosubstituent. The idea to employ a ring-closure reaction rather than an oxidation makes enediols **5** our crucial intermediates as they should readily provide the oxirane unit via monotosylation and base-controlled cyclisation. On the other hand, an obvious synthetic route to enediols **5** involves addition of a vinyl anion to glycolaldehyde, probably modified by a protective group for the alcohol function.

However, the need of laborious protective group chemistry is an obvious drawback of the starting material glycolaldehyde. Moreover, this aldehyde has an unfortunate tendency to polymerise. An attractive alternative would be the use of a siloxyoxirane **3** which may be looked upon as an equivalent of glycolaldehyde. Oxidation of silyl enol ethers should lead to oxiranes **3**. However, attempted epoxidation of trimethylsilyl enol ethers **2** using peracids usually yields α-hydroxy carbonyl compounds (Rubottom reaction).[5] Siloxyoxiranes **3** so far can only be isolated if they are ketone derivatives loaded with substituents in the α-position and under neutral conditions using sulfonyl oxaziridines.[6] It now turned out that simple aldehyde-derived siloxy epoxides can be isolated in the case of a bulky silyl residue and neutral reaction conditions employing dimethyldioxirane[7] (DMDO) as reagent. This is shown here for gylcolaldehyde equivalents **3a**,**b**, but the approach also works for equivalents of higher α-hydroxy aldehydes.[8]



Compound	R^1	R^2	Acc
2a	Me	Ph	—
2b	Ph	Ph	—
3a	Me	Ph	—
3b	Ph	Ph	—
4a, 5a, 6a	—	—	SPh
4b, 5b, 6b	—	—	$SiMe_3$
4c, 5c, 6c	—	—	$SiMe_2Ph$
4d, 5d, 6d	—	—	$SiPh_3$

Scheme *Reagents and conditions*: a) Et_3N, DMF, $ClSiR^1{}_2R^2$, r.t., 2 d; b) DMDO/acetone, CH_2Cl_2, –78 °C, 2 h; c) Et_2O, –78 °C, r.t., 12 h; d) i. Et_3N, *p*-TosCl, 4-DMAP, CH_2Cl_2, 0 °C, 12 h, ii. K_2CO_3, MeOH, r.t., 1 h

Siloxyoxiranes **3a**,**b** were prepared from silyl enol ethers **2a**,**b** by epoxidation with dimethyldioxirane at –78 °C in a high-yield reaction (Scheme). Especially product **3b** can be stored at –25 °C for weeks without appreciable deterioration. As to the formation of the present reaction partners, anion **4a**[9] was obtained by deprotonation of the

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corresponding vinyl sulfide at the α-position with BuLi/TMEDA, while metalation of the corresponding α-bromovinylsilanes with *t*-BuLi/TMEDA yielded anions **4b**–**d**.[10,11] Addition of freshly prepared **3** to **4** gave the expected diols **5a**–**d** in 15–57% yield. In all cases, in situ desilylation was observed. Steric hindrance to nucleophilic attack at the acetalic position and electronic reasons may account for the relatively low yields. Finally, monotosylation with *p*-TosCl, triethylamine and 4-DMAP in anhydrous dichloromethane and cyclisation with potassium carbonate in anhydrous methanol gave the desired acceptor-substituted vinyloxiranes **6a**–**d** in good yields.

Beyond the present synthetic use, siloxyoxiranes **3** deserve general interest as equivalents of glycolaldehyde. Moreover, multifunctional vinyloxiranes **6** are now in our hands and promise a rich chemistry.

All experiments were performed under dry N_2. THF was distilled from sodium benzophenone ketyl prior to use. CH_2Cl_2 was distilled from CaH_2. Column chromatography was carried out on Merck silica gel (70–230 mesh). Petroleum ether (PE) with the boiling range 60–70 °C was always used in the chromatographic separations. Analytical TLC was performed on Merck silica gel 60 PF_{254} plates (visualisation with UV light or 4-methoxybenzaldehyde spray reagent). Mps are uncorrected. IR spectra were recorded on a PYE Unicam SP 3-200 spectrometer and on a Bruker Vektor 22 instrument. NMR spectra were obtained on Bruker ARX 400 or DPX 200 spectrometers in $CDCl_3$ using TMS as an internal standard Assignments of ^{13}C NMR signals were supported by broadband decoupled DEPT.

α-Lithiophenylvinylsulfide (**4a**),[9] α-bromovinylsilanes[10] and the corresponding α-lithiovinylsilanes **4b**–**d**[10,11] were prepared according to literature procedures.

Silyl Enol Ethers 2a,b; General Procedure

A solution of chlorosilane (1.0 equiv) in DMF (1 mL/mmol) was treated with Et_3N (2.0 equiv) and freshly distilled **1** (1.0 equiv) at r.t. The reaction mixture was stirred for 48 h. The insoluble residue was removed by filtration over Celite. The organic phase was washed with aq sat. $NaHCO_3$ solution and brine, dried ($MgSO_4$) and concentrated in vacuo.

Dimethyl(phenyl)vinyloxysilane (2a)

Prepared from **1** (0.22 g, 5 mmol). Kugelrohr distillation (bp 60 °C/0.01 Torr) gave **2a** (0.684 g, 77%) as a colorless oil.

IR (film): 2963, 1632 (C=C), 1592 (C=C_{arom}), 1428, 1319, 1256, 1175, 1120, 1018, 987, 948, 827 ($SiMe_2Ph$), 792, 732, 641 cm^{-1}.

^1H NMR (200 MHz): δ = 0.32 [s, 6 H, $Si(CH_3)_2$], 4.00 (dd, ^2J = 1.0, ^3J = 6.0 Hz, 1 H, $=CH_2$), 4.33 (dd, ^2J = 1.0, ^3J = 13.6 Hz, 1 H, $=CH_2$), 6.25 (dd, ^3J = 6.0, ^3J = 13.6 Hz, 1 H, =CH), 7.20–7.49 (m, 5 H, C_6H_5).

^{13}C NMR (50 MHz): δ = 145.8 (+, =CH), 136.5 (0, C_{arom}), 133.4, 133.0, 127.9 (+, CH_{arom}), 95.2 (–, $=CH_2$), –1.8 [+, $Si(CH_3)_2$].

Anal. Calcd for $C_{10}H_{14}OSi$ (178.3): C, 67.38; H, 7.92; found, C, 67.41; H, 8.41.

Triphenyl(vinyloxy)silane (2b)

Prepared from **1** (2.203 g, 50 mmol). Flash chromatography (PE) gave **2b** (13.947 g, 92%) as colorless crystals; mp 82–84 °C.

IR (KBr): 3067, 3053, 1631 (C=C), 1589 (C=C_{arom}), 1428, 1313, 1171, 1154, 1130, 1106, 996, 951, 841 ($SiPh_3$), 766, 739, 715, 698 cm^{-1}.

^1H NMR (200 MHz): δ = 4.22 (dd, ^2J = 1.0, ^3J = 5.8 Hz, 1 H, H_2C=CH), 4.65 (dd, ^2J = 1.0, ^3J = 13.6 Hz, 1 H, H_2C=CH), 6.55 (dd, ^3J = 5.8, ^3J = 13.6 Hz, 1 H, H_2C=C*H*OSi), 7.36–7.71 [m, 15 H, $Si(C_6H_5)_3$].

^{13}C NMR (50 MHz): δ = 146.0 (+, C=*C*HOSi), 135.4, 130.4, 128.0 (+, CH_{arom}), 133.0 (0, C_{arom}), 95.8 (–, H_2C=CH).

Anal. Calcd for $C_{20}H_{18}OSi$ (302.4): C, 79.44, H; 6.00; found, C, 79.35; H, 6.01.

Epoxidation of Silyl Enol Ethers 2a,b; General Procedure

To a solution of silyl enol ether **2** (1.0 equiv) in CH_2Cl_2 (10 mL) was slowly (1–3 drops/sec) added dimethyldioxirane solution[7] (1.2 equiv) at –78 °C. The mixture was stirred for 1 h and then concentrated at 1 mbar first at –78 °C, and subsequently without a cooling bath. After CH_2Cl_2 and acetone had been removed, the residue was dissolved in either pentane or Et_2O, dried (Na_2SO_4), and concentrated again in vacuo at r.t. The crude product can be used without further purification and for **3b** storage at –25 °C is possible, but immediate use is recommended.

Dimethyl(oxiranyloxy)phenylsilane (3a)

Prepared from **2a** (1.78 g, 10 mmol); yield: ≈90% (determined by GC); colorless oil.

IR (film): 3070 (oxirane), 1591 (C=C_{arom}), 1428, 1397, 1288 (oxirane), 1119 (C–O), 1255 ($SiMe_2$), 996, 864, 832, 731, 701 cm^{-1}.

^1H NMR (400 MHz): δ = 0.35, 0.38 [s each, 3 H, $Si(CH_3)_2$], 2.05 (dd, ^3J = 2.4, ^2J = 4.6 Hz, 1 H, CH_2O), 2.48 (dd, ^3J = 1.2, ^2J = 4.6 Hz, 1 H, CH_2O), 4.50 (dd,, ^3J = 1.2, ^3J = 2.4 Hz, 1 H, CHO), 7.17–7.25 (m, 3 H, ArH), 7.54–7.60 (m, 2 H, ArH).

^{13}C NMR (100 MHz): δ = 137.7 (0, C_{arom}), 134.3, 130.6, 128.7 (+, CH_{arom}), 73.7 (+, CHO), 48.2 (–, CH_2O), –0.5, –0.7 [+, $Si(CH_3)_2$].

Oxiranyloxy(triphenyl)silane (3b)

Prepared from **2b** (3.025g, 10 mmol); yield: 3.142 g (≈90%, determined by GC); solid.

IR (film): 3067 (oxirane), 2855, 1589 (C=C_{arom}), 1428, 1388 (O–CO), 1282, 1118s (C–O), 1026 ($SiPh_3$), 1261, 872, 801 (oxirane), 740, 714, 699 cm^{-1}.

^1H NMR (400 MHz): δ = 2.07 (dd, ^3J = 2.0, ^2J = 4.6 Hz, 1 H, CH_2O), 2.63 (dd, ^3J = 1.0, ^2J = 4.6 Hz, 1 H, CH_2O), 4.76 (dd, ^3J = 1.0, ^3J = 2.0 Hz, 1 H, CHO), 7.15–7.25, (m, 9 H, ArH), 7.75–7.85 (m, 6 H, ArH).

^{13}C NMR (100 MHz): δ = 135.8, 130.6, 128.3 (+, CH_{arom}), 133.8 (0, C_{arom}), 73.8 (+, CHO), 48.0 (–, CH_2O).

Nucleophilic Oxirane-Opening of Epoxides 3 by Acceptor-Substituted α-Lithioethenes 4; General Procedure

An acceptor-substituted α-lithioethene **4** (1 equiv) in THF (2 mL/mmol) was treated dropwise at –60 °C (– 30 °C for **4a**) with **3a** or **3b** (1 equiv) dissolved in THF (3 mL/mmol). The reaction mixture was allowed to warm slowly to r.t. and stirred for 12 h. For workup, it was hydrolysed with a mixture of Et_2O–aq sat. NH_4Cl solution (1:1). The aqueous phase was separated and extracted twice with Et_2O and washed with brine. The combined organic layers were dried ($MgSO_4$) and concentrated in vacuo.

3-(Phenylsulfanyl)but-3-ene-1,2-diol (5a)

Prepared from **4a** and freshly prepared **3a**; flash chromatography (PE–EtOAc, 20:1 → 10:1 → 5:1 → 1:1) gave **5a** (448 mg, 30%) as a yellow oil. In an analogous reaction with **3b** (0.545 g, 4 mmol), the same work up gave **5a** (448 mg, 57%).

IR (film): 3383 (OH), 1608, 1583 (C=C), 749, 692 cm^{-1}.

^{1}H NMR (200 MHz): δ = 2.51 (s, 1 H, CH_2OH), 3.06 (s, 1 H, CHO*H*), 3.64 (dd, ^3J = 6.6, ^2J = 11.6 Hz, 1 H, CH_2OH), 3.76 (dd, ^3J = 3.2, ^2J = 11.6 Hz, 1 H, CH_2OH), 4.24 (dd, ^3J = 3.2, ^3J = 6.6 Hz, 1 H, C*H*OH), 5.09 (s, 1 H, =CH_2), 5.55 (d, ^4J = 1.0 Hz, 1 H, =CH_2), 7.19–7.42 (m, 5 H, ArH).

^{13}C NMR (50 MHz): δ = 144.4 (0, C_{olef}), 132.2 (0, C_{arom}), 132.7, 129.3, 128.0 (+, CH_{arom}), 115.3 (–, $CH_{2\ olef}$), 74.3 (+, CHOH), 65.7 (–, CH_2OH).

3-(Trimethylsilyl)but-3-ene-1,2-diol (5b)

Anion **4b** was generated from α-bromovinyltrimethylsilane[10] (1.79 g, 10 mmol), then $BF_3{\cdot}Et_2O$ (10 mmol) and freshly prepared **3a** were added. Flash chromatography (PE/EtOAc, 20:1 → 10:1 → 5:1 → 1:1) gave **5b** (528 mg, 33%) as a colorless oil.

IR (film): 3377 (OH), 1714, 1655 (C=C), 1409, 1250, 1077, 1030, 944, 841, 760, 694 cm^{-1}.

^{1}H NMR (200 MHz): δ = 0.12 [s, 9 H, $Si(CH_3)_3$], 3.42 (dd, ^3J = 8.4, ^2J = 11.4 Hz, 1 H, CH_2OH), 3.62 (dd, ^3J = 3.2, ^2J = 11.4 Hz, 1 H, CH_2OH), 4.42 (m, 1 H, C*H*OH), 5.51 (dd, ^2J = 1.2, ^4J = 1.6 Hz, 1 H, =CH_2), 5.89 (dd, ^2J = 1.2, ^4J = 1.6 Hz, 1 H, =CH_2).

^{13}C NMR (50 MHz): δ = 151.2 (0, C_{olef}), 125.5 (–, = CH_2), 75.8 (+, CHOH), 66.7 (–, CH_2OH), –0.2, –0.9 [+, $Si(CH_3)_3$].

3-[Dimethyl(phenyl)silyl]but-3-ene-1,2-diol (5c)

Prepared from α-bromovinyldimethylphenylsilane (2.412 g, 10 mmol) as precursor of **4c** and freshly prepared **3a**. Flash chromatography (PE–EtOAc, 20:1 → 10:1 → 5:1 → 1:1) gave **5c** (372 mg, 33%) as a colorless oil.

IR (film): 3383 (OH), 1688 (C=C), 1428, 1252 ($SiMe_2$), 1111 (C–O), 1073, 948, 836, 822, 779, 734, 701 cm^{-1}.

^{1}H NMR (200 MHz): δ = 0.42, 0.44 [s each, 3 H, $Si(CH_3)_2$], 2.27, 2.44 (s each, 1 H, OH), 3.30 (dd, ^3J = 8.0, ^2J = 11.2 Hz, 1 H, CH_2), 3.48 (m, 1 H, CH_2), 4.37 (m, 1 H, C*H*OH), 5.60 (dd, ^4J = 1.4, ^2J = 2.2 Hz, 1 H, =CH_2), 6.0 (dd, ^4J = 1.4, ^2J = 2.2 Hz, 1 H, =CH_2), 7.31–7.55 (m, 5 H, ArH).

^{13}C NMR (50 MHz): δ = 149.6 (0, C_{olef}), 137.7, 133.8, 129.2, 127.9 (+, CH_{arom}), 133.0 (0, C_{arom}), 127.4 (–, =CH_2), 75.7 (+, CHOH), 66.6 (–, CH_2OH), –2.3, –2.7 [+, $Si(CH_3)_2$].

3-(Triphenylsilyl)but-3-ene-1,2-diol (5d)

Prepared from α-bromovinyltriphenylsilane (2.375 g, 6.5 mmol) as precursor of **4d** and freshly prepared **3a.** Flash chromatography (PE–EtOAc 20:1 → 10:1 → 5:1 → 1:1) gave **5d** (345 mg, 15%) as colorless crystals; mp 143–144 °C. The analogous reaction with **3b** (3.653 g, 10 mmol) and the same workup gave **5d** (151 mg, 10%) as colorless crystals; mp 143–144 °C.

IR (film): 3285 (OH), 1426, 1107, 949, 743, 702 cm^{-1}.

^{1}H NMR (200 MHz): δ = 2.11 (s, 2 H, OH), 3.28 (dd, ^3J = 7.8, ^2J = 11.4 Hz, 1 H, CH_2OH), 3.45 (dd, ^3J = 3.2, ^2J = 11.4 Hz, 1 H, CH_2OH), 4.50 (m, 1 H, C*H*OH), 5.75 (dd, ^2J = 1.2, ^4J = 1.6 Hz, 1 H, =CH_2), 6.37 (dd, ^2J = 1.2, ^4J = 1.6 Hz, 1 H, =CH_2), 7.33–7.49 (m, 9 H, ArH), 7.55–7.63 (m, 6 H, ArH).

^{13}C NMR (50 MHz): δ = 146.0 (0, C_{olef}), 133.3 (0, C_{arom}), 136.2, 129.8 128.0 (+, CH_{arom}), 131.8 (–, = CH_2), 74.8 (+, CHOH), 66.6 (–, CH_2OH).

Anal. Calcd for $C_{22}H_{22}O_2Si$ (346.5): C, 76.27, H, 6.41; found, C, 76.32, H, 6.44.

Acceptor-Substituted Vinyloxiranes 6 from the Corresponding Diols 5 via the Corresponding Monotosylates; General Procedure

The monotosylates were prepared according to the literature procedure.[12] To the crude tosylate (1.0 equiv), dissolved in MeOH (5 mL/mmol), was added K_2CO_3 (1.1 equiv). The mixture was stirred for several min at r.t. and the reaction monitored by TLC. If tosylate could still be detected, more K_2CO_3 was added. For workup, Et_2O (45 mL/mmol) was added and the mixture was filtered. The organic phase was washed with aq sat. NH_4Cl solution, H_2O, brine, dried ($MgSO_4$) and concentrated in vacuo.

(1-Phenylsulfanylvinyl)oxirane (6a)

Prepared from **5a** (1.82 g, 5.2 mmol). Flash chromatography (PE–EtOAc, 40:1 → 5:1 → 1:1) gave **6a** (581 mg, 63%) as a yellow oil.

IR (film): 1605, 1583 (C=C), 1477, 1439, 1024, 916, 748, 691 cm^{-1}.

^{1}H NMR (400 MHz): δ = 2.69 (dd, ^3J = 2.6, ^2J = 5.6 Hz, 1 H, CH_2O), 2.78 (dd, ^3J = 4.0, ^2J = 5.6 Hz, 1 H, CH_2O), 3.42 (ddd, ^4J = 0.6, ^3J = 2.6, ^3J = 4.0 Hz, 1 H, CHO), 5.12 (s, 1 H, =CH_2), 5.53 (d, ^4J = 0.6 Hz, 1 H, =CH_2), 7.15–7.40 (m, 5 H, ArH).

^{13}C NMR (100 MHz): δ = 141.6 (0, C_{olef}), 132.4 (0, C_{arom}), 132.4, 129.2, 127.8 (+, CH_{arom}), 116.4 (–, =CH_2), 53.1 (+, CHO), 49.1 (–, CH_2O).

Trimethyl(1-oxiranylvinyl)silane (6b)

Prepared from **5b (**817 mg, 5.1 mmol) gave, after partial removal of the solvent, a solution of **6b** (392 mg, 54%) in Et_2O (2.62 g) (yield was determined based on integration of the ^{1}H NMR spectrum).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.03 [s, 9 H, $Si(CH_3)_3$], 2.35 (dd, ^3J = 2.8, ^2J = 6.0 Hz, 1 H, CH_2O), 2.79 (dd, ^3J = 4.4, ^2J = 6.0 Hz, 1 H, CH_2O), 3.30–3.40 (m, 1 H, CHO; overlaps with OCH_2), 5.31 (dd, ^4J = 0.8, ^2J = 3.0 Hz, 1 H, =CH_2), 5.74 (dd, ^4J = 1.2, ^3J = 3.0 Hz, 1 H, =CH_2).

^{13}C NMR (50 MHz): δ = 148.5 (0, C_{olef}), 124.5 (–, =CH_2), 54.2 (+, CHO), 49.4 (–, CH_2O), –1.7 [+, $Si(CH_3)_3$].

Dimethyl(1-oxiranylvinyl)phenylsilane (6c)

Prepared from **5c** (222 mg, 1.0 mmol). Flash chromatography (PE–EtOAc, 40:1 → 5:1) gave **6c** (147 mg, 72%) as a colorless oil.

IR (film): 1590 (C=C), 1428, 1251 ($SiMe_2$), 1112 (C–O), 938, 924, 835 ($SiMe_2$), 822, 776, 734, 701 cm^{-1}.

^{1}H NMR (200 MHz): δ = 0.44, 0.44 [s each, 3 H, $Si(CH_3)_2$], 2.37 (dd, ^3J = 2.8, ^2J = 5.6 Hz, 1 H, CH_2O), 2.82 (dd, ^3J = 4.4, ^2J = 5.6 Hz, 1 H, CH_2O), 3.46 (m, 1 H, CHO), 5.51 (d, ^2J = 2.4 Hz, 1 H, =CH_2), 5.98 (dd, ^4J = 1.2, ^2J = 2.4 Hz, 1 H, =CH_2), 7.33–7.59 (m, 5 H, ArH).

^{13}C NMR (50 MHz): δ = 146.9 (0, C_{olef}), 137.2 (0, C_{arom}), 133.9, 129.2, 127.8 (+, CH_{arom}), 126.6 (–, = CH_2), 54.4 (+, CHO), 49.8 (–, CH_2O), –2.9, –3.0 [+, $Si(CH_3)_2$].

(1-Oxiranylvinyl)triphenylsilane (6d)

Prepared from **5d** (540 mg, 1.56 mmol). Flash chromatography (PE–EtOAc, 40:1 → 10:1 → 5:1 → 1:1) gave **6d** (356 mg, 72%) as colorless crystals; mp 118–119 °C.

IR (film): 1586 (C=C), 1484, 1427, 1109 (C–O), 943, 847, 704 cm^{-1}.

^{1}H NMR (400 MHz): δ = 2.41 (dd, ^3J = 2.6, ^2J = 6.0 Hz, 1 H, CH_2O), 2.81 (dd, ^3J = 4.2, ^2J = 6.0 Hz, 1 H, CH_2O), 3.55 (ddd, ^4J = 1.2, ^3J = 2.8, ^3J = 4.2 Hz, 1 H, CHO), 5.58 (d, ^2J = 2.8 Hz, 1 H, =CH_2), 6.23 (dd, ^4J = 1.2, ^3J = 2.8 Hz, 1 H, =CH_2), 7.32–7.48 (m, 9 H, ArH), 7.53–7.61 (m, 6 H, ArH).

^{13}C NMR (100 MHz): δ = 143.2 (0, C_{olef}), 133.1 (0, C_{arom}), 136.1, 129.8, 127.9 (+, CH_{arom}), 130.2 (–, =CH_2), 53.8 (+, CHO), 51.2 (–, CH_2O).

Anal. Calcd for $C_{22}H_{20}OSi$ (328.5): C, 80.46; H, 6.14; found, C, 80.44; H, 6.10.

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