

Synthesis and reactions of *p*-vinylbenzyltris(trimethylsilyl)methane

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Abstract

Benzyl chloride was treated with $(\text{Me}_3\text{Si})_3\text{ClLi}$ to give $(\text{Me}_3\text{Si})_3\text{CCH}_2\text{Ph}$ (**1**). A new styrene derivative, $(\text{Me}_3\text{Si})_3\text{CCH}_2\text{C}_6\text{H}_4(\text{CH}=\text{CH}_2\text{-}p)$ (**2**), was synthesized by reaction of *p*-vinylbenzyl chloride with $(\text{Me}_3\text{Si})_3\text{ClLi}$ in the presence of CuCl. Addition and oxidation reactions on **2** gave a series of new compounds $(\text{Me}_3\text{Si})_3\text{CCH}_2\text{C}_6\text{H}_4\text{X-}p$ ($\text{X} = \text{CH}_2\text{CH}_3, \text{CHBrCH}_2\text{Br}, \text{CHClCH}_2\text{I}, \text{CHBrCH}_2\text{I}, \text{cyclo-C}_3\text{H}_3\text{Cl}_2, \text{CHOHCH}_2\text{OH}, \text{COOH}, \text{CH}_2\text{OH}$).

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1. Introduction

p-Vinylbenzyl chloride (VBC), or 4-chloromethylstyrene (CMS), is one of the most important monomers which is produced industrially in pure form. Many nucleophilic substitutions are possible at the benzylic chlorine, leaving the double bond unchanged and providing new functionalized monomers under appropriate conditions [1–5].

The tris(trimethylsilyl)methyl group, $\{(\text{Me}_3\text{Si})_3\text{C-}\}$, is a highly sterically hindered ligand in which three organosilyl groups are bound to the central carbon. It is often referred to as the ‘trisylyl’ ligand and commonly denoted by ‘Tsi’. This ligand has been used extensively as bulky alkyl substituent in main group, alkali metal, transition metal and lanthanide chemistry. A large number of metal compounds containing the bulky $(\text{Me}_3\text{Si})_3\text{C-}$ group have been studied [6–13], but there are few references in the literature about the attachment of the trisylyl group to carbon.

We now describe the preparation of a new organosilyl styrene derivative, bearing the Tsi ligand, and its reactions with various chemical reagents for the preparation of some new organosilicon compounds.

2. Results and discussion

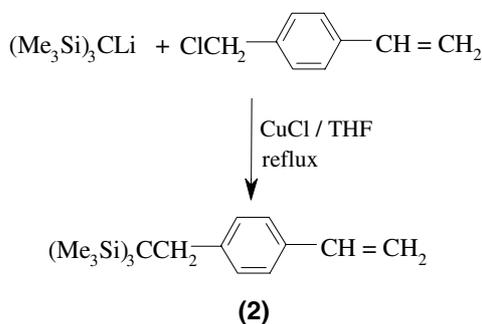
Because of the reactivity of benzylic chlorine, nucleophilic substitution reactions on VBC are generally easy and leave the carbon–carbon double bond unchanged when the experimental conditions are carefully chosen. A solvent is necessary, and the duration of the reaction must be as short as possible with a minimum heating and with polymerization inhibitor. Many substitution reactions on VBC have already been performed with various nucleophiles and new compounds with numerous applications have been obtained [14–16].

2.1. Synthesis of $\text{TsiCH}_2\text{C}_6\text{H}_4(\text{CH}=\text{CH}_2\text{-}p)$ (**2**)

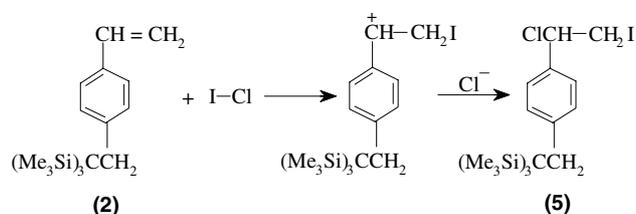
The yield of trisylyl substitution on VBC depends on the temperature and it is increased with increasing temperature. Reaction of VBC with TsiLi in the absence of an inhibitor under reflux in THF gave an insoluble

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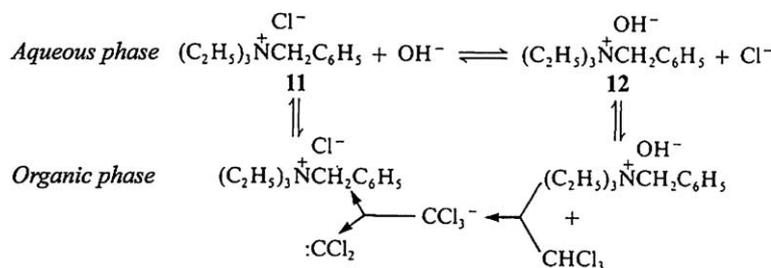
E-mail address: dsafa@tabrizu.ac.ir (K.D. Safa).



Scheme 1.



Scheme 2.



Scheme 3.

polymer. Therefore, as shown in Scheme 1, a small amount of CuCl was added as an inhibitor for double bond polymerization and after heating under reflux for about 3 h, the expected **2** was obtained in good yield.

2.2. Miscellaneous reactions of **2**

The new compound **2** is an unsymmetrical alkene and reacts with electrophilic and oxidizing reagents. The reaction of **2** with an excess of LiAlH₄ in THF gave the TsiCH₂C₆H₄(CH₂CH₃-*p*) (**3**). Treatment of **2** with electrophilic addition reagents such as Br₂, ICl and IBr gave addition products TsiCH₂C₆H₄(CHBrCH₂Br-*p*) (**4**), TsiCH₂C₆H₄(CHClCH₂I-*p*) (**5**) and TsiCH₂C₆H₄(CHBrCH₂I-*p*) (**6**), respectively. In the addition of ICl and IBr to the carbon–carbon double bond, the iodide atom with lower electronegativity is attached to the sp² carbon to give stable benzylic carbocation (Scheme 2), in which the positive charge is delocalized into the aromatic ring.

Compound **2** also reacted with dichlorocarbene generated from the reaction of chloroform with 50% aqueous NaOH in the presence of a catalytic amount of the quaternary ammonium salt [Et₃(PhCH₂)N]Cl to give TsiCH₂C₆H₄(*cyclo*-C₃H₃Cl₂-*p*) (**7**) as a cyclopropane derivative of **2**. As shown in Scheme 3, both benzyltriethylammonium chloride (**11**) and benzyltriethylammonium hydroxide (**12**) partition between the aqueous and organic phases. In the aqueous phase, **11** reacts with concentrated hydroxide to give **12**. In the organic phase,

12 reacts with chloroform to give the trichloromethyl anion, which eliminates chloride ion to give dichlorocarbene, :CCl₂, and **11**. This dichlorocarbene added to the carbon–carbon double bond of **2** to give addition product **7**.

A dilute solution of KMnO₄ reacted with **2** to give the 1,2-diol TsiCH₂C₆H₄(CHOHCH₂OH-*p*) (**8**). KMnO₄ is also the preferred reagent for the oxidative cleavage of carbon–carbon double bonds [17]. An alternative approach involves the use of phase transfer reagent to solubilize permanganate ion in organic solvents [18]. Tributylammonium iodide was used as the phase transfer agent because it is inexpensive and readily available. Treatment of **2** with KMnO₄ in the presence of the phase transfer agent in acidic medium led to oxidation and cleavage of the carbon–carbon double bond of **2** to give TsiCH₂C₆H₄(COOH-*p*) (**9**). The acidic medium is used to neutralize hydroxide ions formed during the reduction of permanganate. In the absence of acid the accumulation of base promotes side reactions and in-

Table 1

| (Me ₃ Si) ₃ CCH ₂ C ₆ H ₄ X- <i>p</i> | | | |
|--|---------------------------------|-----------|---|
| Compound | X | Compound | X |
| 1 | H | 6 | CHBrCH ₂ I |
| 2 | CH=CH ₂ | 7 | <i>cyclo</i> -C ₃ H ₃ Cl ₂ |
| 3 | CH ₂ CH ₃ | 8 | CHOHCH ₂ OH |
| 4 | CHBrCH ₂ Br | 9 | COOH |
| 5 | CHClCH ₂ I | 10 | CH ₂ OH |

crease the stickiness of the manganese (IV) oxides, which precipitate as the reaction proceeds. Compound **9** was reduced to the related alcohol $\text{TsiCH}_2\text{C}_6\text{H}_4(\text{CH}_2\text{OH}-p)$ (**10**) by LiAlH_4 in THF (see Table 1).

3. Experimental

Reactions involving lithium metal, organolithium reagents and LiAlH_4 were carried out under dry argon to exclude oxygen and moisture from the reaction systems. Solvents were dried by standard methods.

3.1. Spectra

The Infrared spectra were recorded on a Bruker Spectrometer Tensor 27 FTIR with KBr pellets, and ^1H NMR and ^{13}C NMR spectra were run on a Bruker 400 MHz spectrometer at room temperature using CDCl_3 as a solvent. Mass spectra were obtained by use of a Shimadzu Qp 100X spectrometer at 70 eV. Elemental analyses were carried out with a Heareus CHN-ORAPID instrument. Melting points were determined on a 9100 Electrothermal apparatus.

3.2. Preparation of $\text{TsiCH}_2\text{C}_6\text{H}_5$ (**1**)

A solution of TsiH (1.56 g, 6.8 mmol) in THF (15 ml) reacted with MeLi generated from MeI (1.25 g, 8.8 mmol) and Li (0.12 g, 17.6 mmol) in Et_2O (10 ml). After the lithiation of TsiH was complete [13], a solution of benzyl chloride (0.576 g, 4.5 mmol) in THF (25 ml) was added dropwise with stirring to solution of the flask at room temperature. The mixture was heated under reflux for about 2 h, poured into aqueous NH_4Cl and extracted with Et_2O . The extract was dried with anhydrous Na_2SO_4 , filtered and solvent evaporated. The residue was recrystallized from methanol to give **1** (78%); m.p. 81 °C. FTIR (KBr, cm^{-1}) 3060 (C–H aromatic), 2960, 2910 (C–H aliphatic), 1600, 1470 (C=C aromatic), 1250 (Si–C). ^1H NMR (CDCl_3) 0.11 (s, 27H, Tsi), 3.18 (s, 2H, CH_2 -Tsi), 7.18–7.31 (m, 5H, aryl-H). ^{13}C NMR (CDCl_3) 3.4 (9C, CH_3 -Si), 10.7 (1C, C-SiMe₃), 35.7 (1C, CH_2 -Tsi), 126.24, 127.95, 130.60, 142.56 (6C, aromatic carbons). *m/z* (EI): 323 (2%, M^+), 308 (10%, $[\text{M}-\text{Me}]^+$), 235 (25%, $[\text{M}-\text{Me}_4\text{Si}]^+$), 162 (50%, $[\text{M}-\text{Me}_3\text{Si}-\text{Me}_4\text{Si}]^+$), 135 (55%, Me_2PhSi^+), 91 (10%, $\text{C}_6\text{H}_5\text{CH}_2^+$), 73 (100%, Me_3Si^+). Anal. Calc. for $\text{C}_{17}\text{H}_{34}\text{Si}_3$: C, 63.3; H, 10.5. Found: C, 62.9; H, 10.6%.

3.3. Preparation of $\text{TsiCH}_2\text{C}_6\text{H}_4(\text{CH}=\text{CH}_2-p)$ (**2**)

A solution of TsiLi that had been made by the reaction of TsiH (4.6 g, 20 mmol) in THF (30 ml) with MeLi generated from MeI (3.54 g, 25 mmol) and Li (0.35 g, 50 mmol) in Et_2O (15 ml) was transferred into a dropping

funnel under dried argon. A mixture of VBC (1.7 g, 10 mmol) and CuCl (0.1 g, 0.99 mmol) in THF (20 ml) was stirred in an ice bath at 0 to –5 °C. The solution of TsiLi in THF was added dropwise over a period of 30 min and the reaction mixture was stirred for about 1 h, and then heated under reflux for 3 h. Then aqueous NH_4Cl was added and the organic layer extracted with Et_2O (50 ml). The ethereal layer was dried with anhydrous Na_2SO_4 and filtered. The solid, obtained by evaporation of Et_2O from the filtrate, was washed several times with cold ethanol to give **2** (60%); m.p. 139 °C. FT-IR (KBr, cm^{-1}) 3066, 3033 (=C–H), 2950, 2890 (C–H aliphatic), 1637 (C=C vinyl), 1605, 1470 (C=C aromatic), 1250 (C–Si). ^1H NMR (CDCl_3) 0.11 (s, 27H, Tsi), 3.16 (s, 2H, CH_2 -Tsi), 5.24 and 5.79 (d, 2H, = CH_2), 6.72 (q, 1H, =CH), 7.39–7.49 (q, 4H, aryl-H). ^{13}C NMR (CDCl_3) 3.35 (9C, CH_3 -Si), 9.88 (1C, C-SiMe₃), 34.52 (1C, CH_2 -Tsi), 112.75 (1C, = CH_2), 135.60 (1C, =CH), 125.56, 127.18, 135.90, 141.41 (6C, aromatic carbons). *m/z* (EI): 349 (2%, M^+), 334 (5%, $[\text{M}-\text{Me}]^+$), 117 (50%, $[\text{M}-\text{Tsi}]^+$), 91 (35%, $\text{C}_6\text{H}_5\text{CH}_2^+$), 73 (100%, Me_3Si^+). Anal. Calc. for $\text{C}_{19}\text{H}_{36}\text{Si}_3$ Calc.: C, 65.4; H, 10.3. Found: C, 65.3; H, 10.2%.

3.4. Preparation of $\text{TsiCH}_2\text{C}_6\text{H}_4(\text{C}_2\text{H}_5-p)$ (**3**)

LiAlH_4 (5 g, 0.13 mol) was gradually added to a stirred solution of **2** (2.0 g, 5.7 mmol) in dry THF (75 ml). The mixture was heated under reflux for 5 days. Aqueous saturated NH_4Cl solution was slowly added at 0 °C, and the mixture was extracted with Et_2O . The extract was dried (Na_2SO_4), and filtered and solvent was evaporated. The residue was then recrystallized from EtOH to give **3** (94%); m.p. 132 °C. ^1H NMR (CDCl_3) 0.11 (s, 27H, Tsi), 1.26 (t, 3H, CH_3), 2.55 (q, 2H, CH_2 -Me), 3.19 (s, 2H, CH_2 -Tsi), 7.33–7.40 (q, 4H, aryl-H). ^{13}C NMR (CDCl_3) 2.07 (9C, CH_3 -Si), 9.80 (1C, C-SiMe₃), 17.08 (1C, CH_3), 28.26 (1C, CH_2 -Me), 34.55 (1C, CH_2 -Tsi), 126.19, 128.08, 141.90, 149.94 (6C, aromatic carbons). *m/z* (EI): 350 (5%, M^+), 335 (63%, $[\text{M}-\text{Me}]^+$), 321 (18%, $[\text{M}-\text{Et}]^+$), 119 (16%, $[\text{M}-\text{Tsi}]^+$), 105 (60%), 91 (72%), 73 (100%). Anal. Calc. for $\text{C}_{19}\text{H}_{38}\text{Si}_3$: C, 65.0; H, 10.9. Found: C, 65.0; H, 10.7%.

3.5. Preparation of $\text{TsiCH}_2\text{C}_6\text{H}_4(\text{CHBrCH}_2\text{Br}-p)$ (**4**)

A solution of Br_2 (0.16 g, 1 mmol) in CCl_4 (15 ml) was added dropwise during a period of 30 min with stirring to a solution of **2** (0.2 g, 0.57 mmol) in CCl_4 (5 ml) at 0 °C. The mixture was stirred for 1 h at room temperature, then solvent was removed under reduced pressure and the residue recrystallized from EtOH to give **4** (91%); m.p. >152 °C. ^1H NMR (CDCl_3) 0.12 (s, 27H, Tsi), 3.18 (s, 2H, CH_2 -Tsi), 4.01 (m, 2H, CH_2Br), 5.11 (q, 1H, CHBr), 7.21–7.30 (q, 4H, aryl-H). ^{13}C NMR (CDCl_3) 2.06 (9C, CH_3 -Si), 10.06 (1C, C-SiMe₃),

33.52 (1C, CH₂-Tsi), 34.12 (1C, CH₂Br), 49.47 (1C, CHBr), 126.19, 127.08, 134.57, 148.57 (6C, aromatic carbons). *m/z* (EI): 508 (2%, M⁺), 493 (9%, [M-Me]⁺), 414 (19%, [M-Br-Me]⁺), 341 (15%, [M-Br-Me₄Si]⁺), 289 (47%), 277 (60%), 269 (35%), 198 (52%), 137 (67%), 91 (35%), 73 (100%). Anal. Calc. for C₁₉H₃₆Si₃Br₂: C, 44.8; H, 7.1. Found: C, 44.6; H, 7.0%.

3.6. Preparation of TsiCH₂C₆H₄(CHClCH₂I-p) (5)

A solution of ICl (0.16 g, 1 mmol) in CCl₄ (15 ml) was added dropwise to a stirred solution of **2** (0.2 g, 0.57 mmol) in CCl₄ (5 ml). The mixture was stirred for 1 h and the solvent removed under reduced pressure. The residue was recrystallized from EtOH to give **5** (92%); m.p. 162 °C. ¹H NMR (CDCl₃) 0.11 (s, 27H, Tsi), 3.16 (s, 2H, CH₂-Tsi), 3.95 (m, 2H, CH₂I), 5.19 (t, 1H, CHCl), 7.26–7.38 (q, 4H, aryl-H). ¹³C NMR (CDCl₃) 2.44 (9C, CH₃-Si), 10.01 (1C, C-SiMe₃), 14.06 (1C, CH₂I), 35.14 (1C, CH₂-Tsi), 61.93 (1C, CHCl), 124.88, 130.20, 135.01, 147.38 (6C, aromatic carbons). *m/z* (EI): 511 (3%, M⁺), 496 (6%, [M-Me]⁺), 384 (40%, [M-I]⁺), 369 (25%, [M-I-Me]⁺), 354 (12%, [M-I-Me₄Si]⁺), 280 (32%), 224 (41%), 153 (42%), 91 (15%), 73 (100%). Anal. Calc. for C₁₉H₃₆Si₃ICl: C, 44.6; H, 7.1. Found: C, 44.4; H, 7.0%.

3.7. Preparation of TsiCH₂C₆H₄(CHBrCH₂I-p) (6)

A solution of IBr (0.2 g, 1 mmol) in CCl₄ (15 ml) was added dropwise with stirring to a solution of **2** (0.2 g, 0.57 mmol) in CCl₄ (5 ml). The mixture was stirred for 1 h and the solvent removed under reduced pressure. The solid residue was recrystallized from EtOH to give **6** (87%); m.p. 170 °C. ¹H NMR (CDCl₃) 0.11 (s, 27H, Tsi), 3.18 (s, 2H, CH₂-Tsi), 3.86 (m, 2H, CH₂I), 4.92 (t, 1H, CHBr), 7.25–7.41 (q, 4H, aryl-H). ¹³C NMR (CDCl₃) 2.45 (9C, CH₃-Si), 9.88 (1C, C-SiMe₃), 17.77 (1C, CH₂I), 34.52 (1C, CH₂-Tsi), 55.95 (1C, CHBr), 124.76, 127.48, 135.55, 147.51 (6C, aromatic carbons). *m/z* (EI): 555 (2%, M⁺), 428 (2%, [M-I]⁺), 413 (15%, [M-I-Me]⁺), 340 (16%, [M-I-Me₄Si]⁺), 267 (30%), 197 (30%), 91 (15%), 73 (100%). Anal. Calc. for C₁₉H₃₆Si₃IBr: C, 41.0; H, 6.5. Found: C, 40.9; H, 6.6%.

3.8. Preparation of TsiCH₂C₆H₄(cyclo-C₃H₃Cl₂-p) (7)

To a mixture of **2** (2.0 g, 5.7 mmol), CHCl₃ (3.2 g, 27 mmol), 50% aqueous NaOH (20 ml) and CH₂Cl₂ (20 ml) was added [Et₃(CH₂Ph)N]Cl (0.2 g). The mixture was stirred vigorously to give a thick emulsion. The temperature was gradually raised to 40 °C and then kept between 40–45 °C by cooling with an ice bath. After the exothermic reaction was complete (about 1 h), the dark brown reaction mixture was heated to 55–60 °C for 1 h. Then allowed to cool to 30 °C and diluted with water (50

ml). The organic layer was separated and the aqueous phase extracted with Et₂O (25 ml). The organic fractions were combined and washed once with water (20 ml). The cloudy organic layer was dried with Na₂SO₄, filtered and solvent evaporated. The residue was purified by preparative TLC (silica gel, 1:1 cyclohexane:dichloromethane as eluent) to give **7** (75%); m.p. >124 °C. ¹H NMR (CDCl₃) 0.10 (s, 27H, Tsi), 1.96 (q, 2H, CH₂-CCl₂), 2.95 (t, 1H, CH-CCl₂), 3.18 (s, 2H, CH₂-Tsi), 7.46–7.69 (q, 4H, aryl-H). ¹³C NMR (CDCl₃) 2.44 (9C, CH₃-Si), 10.07 (1C, C-SiMe₃), 27.94 (1C, CH₂-cyclopropyl), 33.74 (1C, CH-cyclopropyl), 35.15 (1C, CH₂-Tsi), 64.34 (1C, CCl₂), 126.38, 130.20, 135.38, 148.45 (6C, aromatic carbons). *m/z* (EI): 432 (2%, M⁺), 417 (4%, [M-Me]⁺), 382 (36%, [M-Me-Cl]⁺), 346 (42%, [M-Me-Cl₂]⁺), 307 (61%, [M-Me-C₃H₃Cl₂]⁺), 234 (41%), 161 (22%), 105 (24%), 73 (100%). Anal. Calc. for C₂₀H₃₆Si₃Cl₂: C, 55.6; H, 8.4. Found: C, 55.4; H, 8.6%.

3.9. Preparation of TsiCH₂C₆H₄(CHOHCH₂OH-p) (8)

A solution of 1% KMnO₄ in acetone was added dropwise to a stirred solution of **2** (0.2 g, 0.57 mmol) in CH₂Cl₂ (15 ml) at 0 °C. The colour immediately became dark brown. The mixture was stirred at 0 °C for about 1 h, then water (25 ml) was added. The organic layer was extracted with Et₂O, and the extract was dried by anhydrous Na₂SO₄ and filtered and solvent evaporated. The residue was recrystallized from EtOH and purified by preparative TLC (silica gel, 1:2 *n*-hexane:dichloromethane as eluent) to give **8** (68%); m.p. 186 °C. FTIR (KBr, cm⁻¹) 3350 (O-H), 1250 (C-Si), 1100, 1050 (C-O). ¹H NMR (CDCl₃) 0.10 (s, 27H, Tsi), 3.22 (s, 2H, CH₂-Tsi), 3.52 (s, 2H, OH), 4.29 (m, 2H, CH₂-O), 4.46 (q, 1H, CH-O), 7.43–7.81 (q, 4H, aryl-H). ¹³C NMR (CDCl₃) 2.44 (9C, CH₃-Si), 9.95 (1C, C-SiMe₃), 35.15 (1C, CH₂-Tsi), 64.33 (1C, CH₂OH), 126.38, 130.20, 137.07, 148.22 (6C, aromatic carbons). *m/z* (EI): 382 (2%, M⁺), 381 (20%, [M-H]⁺), 350 (58%, [M-Me-OH]⁺), 277 (37%, [M-OH-Me₄Si]⁺), 260 (45%), 187 (54%), 145 (20%), 73 (100%). Anal. Calc. for C₁₉H₃₈Si₃O₂: C, 59.6; H, 10.1. Found: C, 59.4; H, 9.7%.

3.10. Preparation of TsiCH₂C₆H₄(COOH-p) (9)

KMnO₄ (5.0 g, 34 mmol) was added in small portions over 1 h to a rapidly stirred solution of distilled water (50 ml), 9 M sulfuric acid (10 ml), (*n*-Bu)₄NI (0.5 g), glacial acetic acid (5 ml), CH₂Cl₂ (50 ml) and **2** (3.0 g, 8.5 mmol) and stirring was continued for an additional 18 h at room temperature. The organic layer was separated and the aqueous layer extracted with two 50 ml portions of CH₂Cl₂. The organic extracts were combined, washed with two 50-ml portions of water, dried with anhydrous

Na₂SO₄ and filtered. After evaporation of CH₂Cl₂, the yellowish residue was recrystallized from a mixture of ethanol and water (8:2 v:v) to give **9** (83%); m.p. 159 °C. FTIR (KBr, cm⁻¹) 3328 (O–H), 1687 (C=O), 1290 (C–O), 1250 (C–Si). ¹H NMR (CDCl₃) 0.11 (s, 27H, Tsi), 3.16 (s, 2H, CH₂–Tsi), 7.39–7.49 (q, 4H, aryl-H), 11.2 (s, 1H, COOH). ¹³C NMR (CDCl₃) 2.44 (9C, CH₃–Si), 10.12 (1C, C–SiMe₃), 35.15 (1C, CH₂–Tsi), 126.38, 127.28, 130.21, 150.00 (6C, aromatic carbons), 166.83 (1C, COOH). *m/z* (EI): 367 (4%, M⁺), 352 (62%, [M–Me]⁺), 335 (83%, [M–Me–OH]⁺), 322 (20%, [M–COOH]⁺), 307 (19%, [M–Me–COOH]⁺), 278 (40%), 261 (38%), 189 (25%), 165 (35%), 91 (24%), 73 (100%). Anal. Calc. for C₁₈H₃₄Si₃O₂: C, 58.9; H, 9.3. Found: C, 59.0; H, 9.7%.

3.11. Preparation of TsiCH₂C₆H₄(CH₂OH-*p*) (**10**)

A mixture of **9** (0.5 g, 1.37 mmol) and LiAlH₄ (1.0 g, 26 mmol) in dry THF (50 ml) was stirred and heated under reflux for 24 h. The mixture was allowed to cool, then carefully treated with aqueous saturated NH₄Cl and extracted with Et₂O. The extract was dried (Na₂SO₄), filtered and solvent evaporated, and the residue was recrystallized from EtOH to give **10** (87%); m.p. 142 °C. ¹H NMR (CDCl₃) 0.10 (s, 27H, Tsi), 2.35 (s, 1H, O–H), 3.18 (s, 2H, CH₂–Tsi), 4.46 (s, 2H, CH₂O), 7.24–7.32 (q, 4H, aryl-H). ¹³C NMR (CDCl₃) 2.48 (9C, CH₃–Si), 10.02 (1C, C–SiMe₃), 35.15 (1C, CH₂–Tsi), 64.33 (1C, CH₂OH), 126.38, 130.22, 137.57, 146.17 (6C, aromatic carbons). *m/z* (EI): 353 (1%, M⁺), 338 (40%, [M–Me]⁺), 337 (28%, [M–Me–H]⁺), 321 (18%, [M–

Me–OH]⁺), 307 (19%, [M–Me–CH₂OH]⁺), 234 (20%), 161 (25%), 105 (27%), 91 (40%), 73 (100%). Anal. Calc. for C₁₈H₃₆OSi₃: C, 61.3; H, 10.3. Found: C, 60.8; H, 9.8%.

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