A Quantitative NMR Method for Silyllithium Analysis

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SUPPORTING INFORMATION
General experimental conditions.
Reagents and solvents were purchased from Aldrich Chemical Company, Fisher Scientific, Alfa Aesar or Acros Organics. Lithium (granular, 99% trace metals basis) was purchased from Aldrich (catalogue number of 499811). Most silicon reagents were purchased from Gelest Inc.

Reaction solvents were taken from a “Grubbs-style” Solvent Dispensing System purchased from Glass Contour or distilled as described in the literature.

Silica gel (60 Å, 170–400 mesh) or basic alumina (aluminum oxide, 50–200 micron, activated) was used for flash column chromatography. Analytical thin layer chromatography (TLC) was performed using Analtech Uniplate Silica Gel GF (250 micron) pre-coated glass plates. Spots were detected by UV, iodine and phosphomolybdic acid solution.

3-Methoxymethoxypropyl diphenylsilane 10. To a solution of diphenylsilane (5.41 g, 29.4 mmol) in heptane (25 mL) under argon was added 3-methoxymethoxypropene1 (1.5 g, 14.7 mmol), tert-dodecylmercaptan (0.35 mL, 0.30 g, 1.5 mmol) and AIBN (0.12 g, 0.73 mmol), and the resulting mixture was heated to 75 °C for 19h. After cooling and concentration in vacuo, purification by flash chromatography (1% to 4% ethyl acetate/hexanes) gave 10 as a colorless oil (3.6 g, 85%).

\[ R_f = 0.57 \] (4: 1 hexanes/ethyl acetate).

IR (neat) 3068, 2932, 2881, 2118 cm\(^{-1}\).

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.54-7.60 (m, 4H), 7.31-7.44 (m, 6H), 4.90 (t, \(J = 3.5\) Hz, 1H), 4.60 (s, 2H), 3.54 (t, \(J = 6.5\) Hz, 2H), 3.35 (s, 3H), 1.72-1.80 (m, 2H), 1.18-1.24 (dt, \(J = 3.5, 8.0\) Hz, 2H).

\(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 135.3, 134.3, 129.8, 128.1, 96.5, 70.1, 55.3, 24.8, 8.7.

1-(3-Methoxymethoxypropyl)-2,2,2-trimethyl-1,1-diphenyl-disilane 11. To a 0 °C suspension of lithium shot (0.1 g, 14 mmol) in THF (3 mL) was added chlorotrimethylsilane (50 µL). After 30 min the solution was removed by syringe and the lithium was washed with THF (3 x 1 mL). THF (3 mL) and 10 (261 mg, 0.91 mmol) were added and stirred at 0 °C. After 8 h the mixture was added to neat chlorotrimethylsilane (1.5 mL, 12 mmol) and then concentrated. Purification by flash chromatography (1% to 9% ethyl acetate/hexanes) gave 11 as a colorless oil (215 mg, 66%).

\[ R_f = 0.53 \] (4: 1 hexanes/ethyl acetate)

IR (neat) 3067, 2947, 2086, 1954, 1428 cm\(^{-1}\).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.45-7.50 (m, 4H), 7.32-7.37 (m, 6H), 4.60 (s, 2H), 3.50 (t, \(J = 6.6\) Hz, 2H), 3.34 (s, 3H), 1.64-1.73 (m, 2H), 1.17-1.24 (m, 2H), 0.17 (s, 9H).

\(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 136.3, 135.4, 128.9, 128.0, 96.5, 70.7, 55.3, 25.1, 9.1, -1.1.

Exact mass \(\text{C}_{20}\text{H}_{34}\text{NO}_2\text{Si}_2\) \([\text{M+NH}_4]^+\); calcd: 376.2123, found: 376.2123.

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Ph  Ph
Cl Si

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\[
\begin{align*}
\text{Ph}_2\text{Si} & \quad \text{Ph}_2\text{Si} \\
\text{F} & \quad \text{Cl-SiMe}_3
\end{align*}
\]

1. Li
2. Cl-SiMe\(_3\)
4 h
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Ph\_2SiO\_3 

1. Li, 0.5 h  
2. Cl–SiMe\_3

Ph\_2SiO\_3 

11.58

1.00

2.24

2.28

0.34

PPM