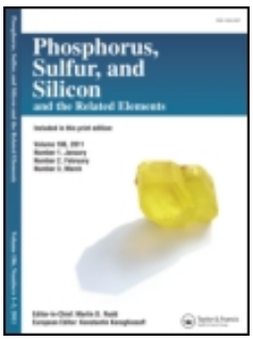

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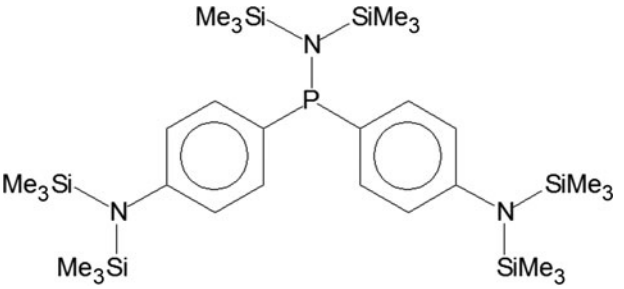
# SYNTHESIS AND CHARACTERIZATION OF (DISILYLANILINO)PHOSPHINES

**Pradeep Devulapalli, Bin Wang, and Robert H. Neilson**
*Department of Chemistry, Texas Christian University, Fort Worth, TX 76134, USA*

## GRAPHICAL ABSTRACT




*The disilyl(4-bromo)aniline $(Me_3Si)_2NC_6H_4Br$ (**A**) readily undergoes metal-halogen exchange to give the reactive organolithium derivative $(Me_3Si)_2NC_6H_4Li$ (**B**). Subsequent reactions with various chlorophosphines, R(R′)PCl, or chloro(disilylamino)phosphines, $(Me_3Si)_2NP(R)Cl$, were used to prepare three varieties of the title compounds: $(Me_3Si)_2NC_6H_4P(R')R$ (**1**: R = R′ = $NMe_2$; **2**: R = R′ = $OCH_2CF_3$; **3**: R = Ph, R′ = $OCH_2CF_3$; **4**: R = R′ = Ph; **5**: R = Ph, R′ = Me), $(Me_3Si)_2NC_6H_4P(R)N(SiMe_3)_2$ [**6**: R = Me; **7**: R = i-Pr; **8**: R = n-Bu, **9**: R = $OCH_2CF_3$; **10**: R = $C_6H_4N(SiMe_3)_2$; **11**: R = Ph], and $(Me_3Si)_2NC_6H_4P(Ph)R$ [**12**: R = n-Bu; **13**: R = $C_6H_4N(SiMe_3)_2$]. The new compounds **1–13** were generally obtained as colorless, distillable liquids that were fully characterized by NMR ($^1H$, $^{13}C$, and $^{31}P$) spectroscopy and elemental analysis.*

**Keywords** Silylaniline; anilinophosphine; phosphine; aminophosphine; silylamine

## INTRODUCTION

The derivative chemistry of silicon-nitrogen-phosphorus compounds is quite extensive and, in many cases, synthetically useful.[1] A wide variety of oxidation and substitution reactions at phosphorus combined with facile Si-N bond cleavage often leads to

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Dedicated to Professor Robert R. Holmes in honor of his many years of professionalism and high standards as Editor of this journal.

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intermolecular silyl group rearrangements[2] or elimination of small-molecule silane byproducts.[3] In particular, N-silylphosphoranimines, $Me_3SiN{=}P(R')(R)X$, readily undergo thermally or catalytically induced elimination of $Me_3SiX$ to afford either cyclic[4] or polymeric[5] phosphazenes, $(N{=}PRR')_n$, depending on the nature of the leaving group (X) and/or catalytic factors.

More recently, we have extended our studies of Si-N-P compounds to include systems in which the silicon-nitrogen and phosphorus-containing groups are not directly connected. In this context, we report here on the synthesis and characterization of a series of new (disilylanilino)phosphines, $(Me_3Si)_2N\text{-}C_6H_4\text{-}P(R')R$.[6] Pending future studies, some of these compounds are viewed as potential precursors to novel macrocyclic or polymeric organic-inorganic hybrid materials, $[\text{-}C_6H_4\text{-}N{=}P(R')R\text{-}]_n$.

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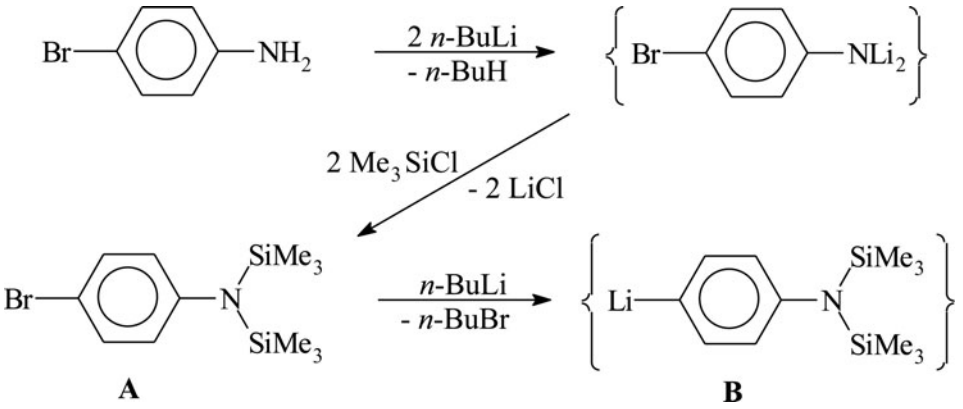
## RESULTS AND DISCUSSION

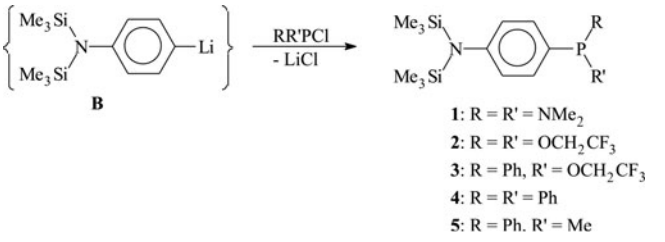
All of the synthetic chemistry reported here begins with deprotonation reactions of 4-bromoaniline (Equation (1)). Addition of one or two equivalents of *n*-BuLi readily affords the corresponding N-lithio reagents in solution. In a slight modification of the published procedure,[7] the dilithio ($\text{-}NLi_2$) intermediate was converted to the disilylaniline reagent **A** in good yield. While the $\text{-}NLi_2$ reagent reacted rapidly at 0°C with the first equivalent of $Me_3SiCl$, addition of the second required refluxing for several hours in hexane. Subsequent metal-halogen exchange (at 0°C in $Et_2O$ solution) was used to generate the N-silylated aryllithium reagent **B**.




**A** **B**

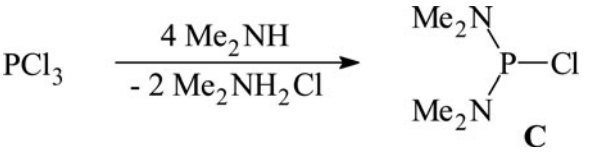
(1)

The new (disilylanilino)phosphines described here were obtained from the aryllithium reagent **B** by way of nucleophilic substitution reactions with three different types of P-Cl compounds. In the first variation, treatment of mono-chlorophosphines RR′PCl with reagent **B** at −78°C in $Et_2O$ resulted in the formation of (disilylanilino)phosphines **1**–**5** (Equation (2)). These compounds were obtained in moderate yields (ca. 60%) as colorless, distillable liquids (**1**–**3**, **5**) or a pale yellow solid (**4**) that were fully characterized by NMR ($^1H$, $^{13}C$, and $^{31}P$) spectroscopy and elemental analysis (see Experimental section).

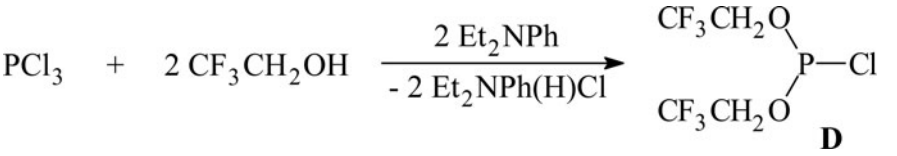


(2)

Although these new phosphines **1**–**5** were readily prepared, this synthetic pathway is limited by difficulties in obtaining many of the necessary mono-chlorophosphines. Other than $Ph_2PCl$ (used to prepare **4**), few such reagents are commercially available. The other chlorophosphines (**C**–**F**) were prepared in this work as summarized in Equations (3)–(6).



(3)



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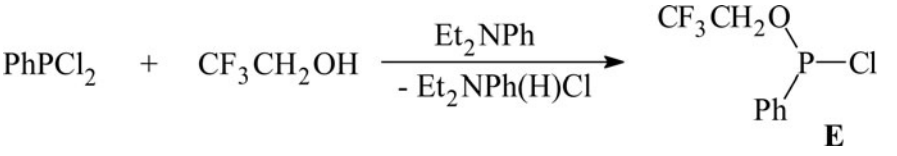
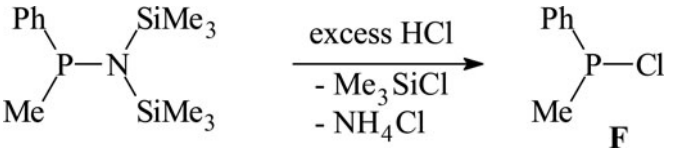


(5)



(6)

While the dehydrohalogenation reaction of $PCl_3$ with $Me_2NH$ (Equation (3)) was a relatively straightforward, published procedure,[8] those involving the P-trifluoroethoxy analogs **D** (Equation (4)) and **E** (Equation (5)) were more complicated.[9] Mixtures of products, such as **D** combined with smaller amounts of $(CF_3CH_2O)_3P$ and $CF_3CH_2OPCl_2$, were generally obtained due to multiple P-Cl replacements and/or disproportionation reactions of the mixed-substituent products.[9] Nonetheless, the impure reagents **D** and **E** were used successfully to prepare the corresponding anilinophosphines **2** and **3** (Equation (2)).

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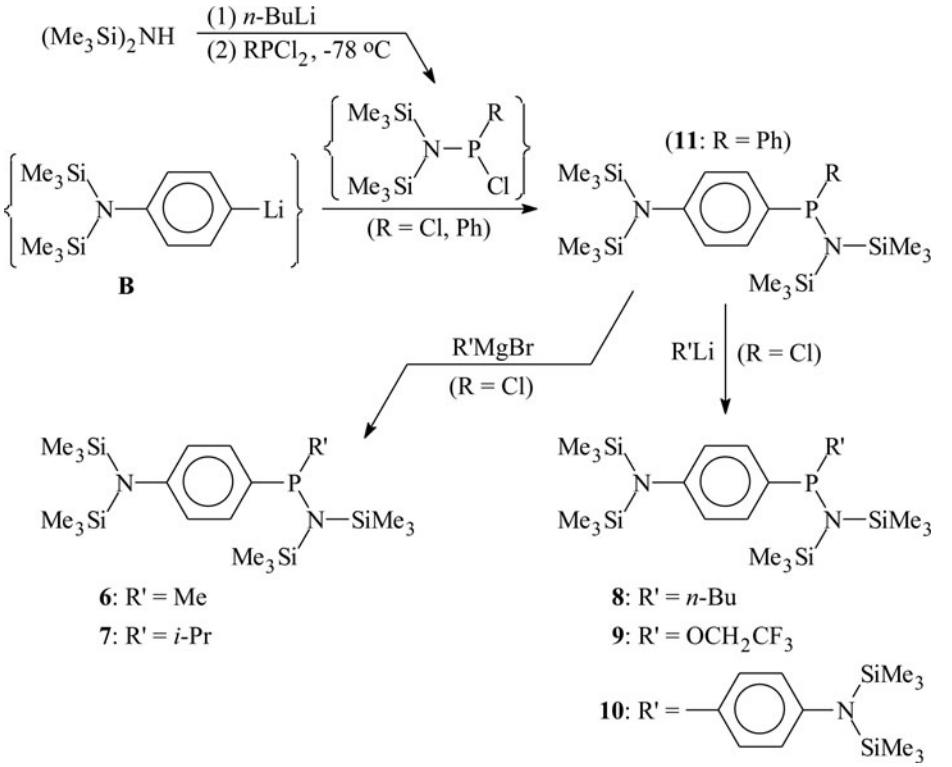
The alkyl/aryl(chloro)phosphine[10] (**F**) was prepared in this study by treatment of a (disilylamino)phosphine, $(Me_3Si)_2NP(Ph)Me$, with four equivalents of anhydrous HCl (Equation (6)). Although the yield of **F** was relatively low (ca. 40%), this new method holds promise for the preparation of other mixed-substituent chlorophosphines since the requisite (silylamino)-phosphines are readily available from a "one-pot" procedure known as the Wilburn[11] method. In this process, either $PCl_3$ or $PhPC_{l2}$ is treated first with one equivalent of $(Me_3Si)_2NLi$ and the remaining P-Cl groups are then replaced by addition of Grignard or organolithium reagents.

Our second synthetic approach to the title compounds generally made use of the Wilburn[11] method as summarized in **Scheme 1**. In this "one-pot" procedure, the dichlorophosphine intermediate, $(Me_3Si)_2NPCl_2$, was treated first with organolithium reagent **B**, followed by the appropriate Grignard or lithium reagent to afford compounds **6**–**10**. Alternatively, by starting with $PhPC_{l2}$ instead of $PCl_3$, the P-phenyl derivative **11** was easily prepared. Notably, all of these new phosphines (**6**–**11**) contain both disilyl*anilino* and disilyl*amino* groups on phosphorus (**10** actually incorporates two of the anilino groups). They were all obtained in moderate yields (ca. 50–60%) as colorless, distillable liquids that were fully characterized by NMR ($^1H$, $^{13}C$, and $^{31}P$) spectroscopy and elemental analysis.




**Scheme 1**

As is the case for all of the products reported here, the NMR spectral data for compounds **6**–**11** are completely consistent with the proposed structures. For example, the 1,4-substitution pattern of aryl ring is clearly indicated by the observation of four distinct

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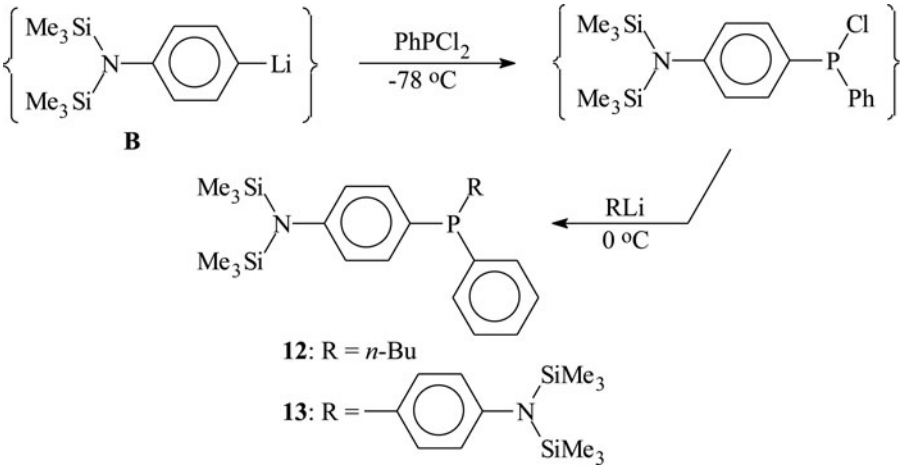
signals in the $^{13}C$ NMR spectra with three of the signals being doublets due to coupling to phosphorus. The $^{31}P$ chemical shifts generally reflect the expected electronic and steric effects of the substituents at the 3-coordinate phosphorus center.[12] It seems noteworthy that, in all cases, the $^{31}P$ chemical shifts are within 1 ppm of those observed for analogous structures containing a simple P-phenyl group instead of the P-$C_6H_4N(SiMe_3)_2$ substituent.

In the third synthetic route to the title compounds, $PhPCl_2$ was employed as a convenient starting material (**Scheme 2**). In one case, it was treated first with the organolithium reagent **B** and then with *n*-BuLi to yield the mixed-substituent phosphine **12**. Similarly, the direct reaction of $PhPCl_2$ with two equivalents of **B** afforded **13** that contains two silylanilino groups, similar to compound **10** (**Scheme 1**). Compounds **12** and **13** were obtained as colorless, distillable liquids, and were characterized as previously described.




**Scheme 2**

In summary, this work demonstrates that a significant series (i.e., **1**–**13**) of the title compounds are accessible by varied synthetic routes. Studies of the derivative chemistry of selected members of this series are ongoing and will be reported in due course.

## EXPERIMENTAL SECTION

### Materials and General Procedures

The following reagents were obtained from commercial sources and used without further purification: $BrC_6H_4NH_2$, $(Me_3Si)_2NH$, $Me_3SiCl$, $PCl_3$, $PhPCl_2$, $Ph_2PCl$, $CF_3CH_2OH$, $Me_2NH$, $Et_2NPh$, $CH_3MgBr$ (3.0 M in ether), *i*-PrMgBr (2.0 M in ether), *n*-BuLi (2.5 M in hexane), and anhydrous HCl (1.0 M in $Et_2O$). The disilylaniline reagent $(Me_3Si)_2NC_6H_4Br$ (**A**[7]) and the chlorophosphines RR′PCl (**C**[8]: R = R′ = $NMe_2$; **D**[9]: R = R′ = $OCH_2CF_3$; **E**[9]: R = Ph, R′ = $OCH_2CF_3$) were prepared by the referenced procedures, in some cases with modifications as detailed below. The chlorophosphine, Ph(Me)PCl (**F**[10]), was prepared by the reaction of the (disilylamino)phosphine $(Me_3Si)_2NP(Me)Ph$[11] with dry HCl as described below. Hexane and $Et_2O$ were distilled under $N_2$ from $CaH_2$ and either used immediately or stored over molecular sieves. Proton, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were obtained on a Varian XL-300 spectrometer using $CDC1_3$ or $C_6D_6$ as a lock solvent. Positive $^1H$ and

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$^{13}C$ NMR chemical shifts and $^{31}P$ NMR shifts are downfield from the external references Me4Si and $H_3PO_4$, respectively, with coupling constants ($J$) given in Hz. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY or E&R Microanalytical Laboratory, Corona, NY. All reactions and manipulations were carried out under a nitrogen atmosphere and/or by using standard vacuum line techniques.

### Preparation of the Disilylaniline, $(Me_3Si)_2NC_6H_4Br$ (A)

A three-neck (2000 mL) round-bottom flask, equipped with a mechanical stirrer, $N_2$ inlet, and an addition funnel was charged with $Et_2O$ (800 mL) and $BrC_6H_4NH_2$ (51.6 g, 300 mmol). The mixture was cooled to 0°C and *n*-BuLi (240 mL, 600 mmol) was added slowly from the addition funnel. The mixture was allowed to warm to room temperature and stirred for 1 h. The solution was cooled again to 0°C and $Me_3SiCl$ (32.6 g, 300 mmol) was added slowly. The mixture was then allowed to warm to room temperature and was stirred for 2 h. Most of the $Et_2O$ was then removed under reduced pressure and hexane (800 mL) was added, followed by additional $Me_3SiCl$ (39.0 g, 350 mmol). The mixture was then refluxed while stirring overnight to complete the reaction. The salt was removed by filtration and hexane was removed under reduced pressure. Fractional distillation afforded compound **A**[7] as a colorless liquid, bp: 57–59°C (0.01 mm Hg), generally in 65–70% yield.

### Preparation of the Chlorophosphine, $(CF_3CH_2O)_2PCl$ (D)

In a typical experiment, a three-neck (3000 mL) round-bottom flask, equipped with a mechanical stirrer, $N_2$ inlet, and an addition funnel was charged with $Et_2O$ (1500 mL) and $PCl_3$ (67.3 g, 490 mmol). The solution was cooled to 0°C and a mixture of $Et_2NPh$ (147.7 g, 990 mmol) and $CF_3CH_2OH$ (99.0 g, 990 mmol) was added from the addition funnel. The mixture was then allowed to warm to room temperature and was stirred for 3 h. Ether was removed under reduced pressure and the remaining volatile material was removed by distillation at ca. 70°C (5 mm Hg). By NMR spectroscopy, the distillate was determined to be a mixture consisting of **D**[9] ($^{31}P$ NMR: $\delta$ 166.0), $(CF_3CH_2O)_3P$, and $CF_3CH_2OPCl_2$. Repeated distillations increased the relative proportion of **C** to ca. 60–70%. The mixture containing **C** was subsequently used to prepare the (disilylanilino)phosphine **2**. In a similar procedure, the reaction of $PhPC_{l2}$ and $CF_3CH_2OH$ (mixed with $Et_2NPh$) afforded the chlorophosphine **E**, $Ph(CF_3CH_2O)PCl$ ($^{31}P$ NMR: $\delta$ 177.5), containing ca. 10–20% of $PhP(OCH_2CF_3)_2$. This product mixture was then used to prepare the (disilylanilino)phosphine **3**.

### Preparation of the Chlorophosphine, Ph(Me)PCl (F)

A three-neck (1000 mL) round-bottom flask, equipped with a mechanical stirrer, $N_2$ inlet, and an addition funnel was charged with $Et_2O$ (200 mL) and $(Me_3Si)_2NP(Ph)Me$[11] (14.2 g, 50.0 mmol). The mixture was cooled to 0°C and HCl (200 mL, 200 mmol, 1.0 M in $Et_2O$) was added slowly. The mixture was allowed to warm to room temperature and was stirred for ca. 4 h. Most of the ether was removed under reduced pressure and hexane (ca. 200 mL) was added to precipitate the salt. The salt was removed by filtration and hexane was removed under reduced pressure. Fractional distillation afforded the chlorophosphine **F**[10] ($^{31}P$ NMR: $\delta$ 87.0) as a colorless, very moisture-sensitive liquid, bp: 38–42°C (0.01 mm Hg), typically in ca. 40% yield.

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### Preparation of (Disilylanilino)phosphines, $(M_3Si)_2NC_6H_4P(R')R$ (1–5)

A typical experiment for the synthesis of **1 ($\mathbf{R = R' = NMe_2}$)** is described here. A three-neck (100 mL) round-bottom flask, equipped with a magnetic stirring bar, $N_2$ inlet, rubber septum, and an addition funnel was charged with $Et_2O$ (50 mL) and the disilylaniline **A** (15.8 g, 50.0 mmol). The mixture was cooled to 0°C and *n*-BuLi (20 mL, 50 mmol) was added slowly via syringe. The mixture was allowed to warm to room temperature and was stirred for 1 h, affording a solution of the organolithium reagent **B**. Separately, another three-neck (250 mL) round-bottom flask, equipped with a magnetic stirring bar, $N_2$ inlet, rubber septum, and an addition funnel was charged with $Et_2O$ (50 mL) and the chlorophosphine, $(Me_2N)_2PCl$ (7.70 g, 50.0 mmol). The solution of **B**, prepared above, was transferred via cannula to the addition funnel and added slowly to the solution of $(Me_2N)_2PCl$ with stirring at −78°C. The mixture was allowed to warm to room temperature and was stirred for ca. 2 h. Most of the ether was removed under reduced pressure and hexane (ca. 100 mL) was added to precipitate the salt. The salt was removed by filtration and hexane was removed under reduced pressure. Fractional distillation afforded **1** as a colorless liquid. **(1: $\mathbf{R = R' = NMe_2}$)** Yield: 63%. bp: 87–90°C (0.01 mm Hg). $^{31}$P NMR: $\delta$ 100.8. $^1$H NMR: $\delta$ 0.05 (s, $Me_3$SiN), 2.74 (d, $Me_2$N, $J_{PH} = 9.1$), 6.9–7.2 (m, $C_6H_4$). $^{13}$C NMR: $\delta$ 2.1 (s, $Me_3$SiN), 41.6 (d, $Me_2$N, $J_{PC} = 15.2$), 134.9 (d, $PC_6H_4$, $C_1$, $J_{PC} = 6.8$), 129.9 (d, $PC_6H_4$, $C_{2,6}$, $J_{PC} = 4.1$), 131.3 (d, $PC_6H_4$, $C_{3,5}$, JPC = 4.1), 147.5 (s, $PC_6H_4$, $C_4$). Anal. Calcd. for $C_{16}H_{34}N_3PSi_2$: C, 54.04; H, 9.64. Found: C, 53.91; H, 10.22.

The (disilylanilino)phosphines **2** and **3** were prepared in the same manner from the corresponding chloro(trifluoroethoxy)phosphine reagents **C** and **D**, respectively. Both were initially obtained by fractional distillation as colorless liquids containing ca. 3–5% impurities as indicated by NMR spectroscopy. Redistillation afforded the pure compounds that were characterized as follows. **(2: $\mathbf{R = R' = OCH_2CF_3}$)**. Yield: ca. 60%. bp: 61–61°C (0.01 mm Hg). $^{31}$P NMR: $\delta$ 168.4. $^1$H NMR: $\delta$ 0.07 (s, $Me_3$SiN), 3.9–4.2 (m, $OCH_2CF_3$), 6.9–7.2 (m, $C_6H_4$). $^{13}$C NMR: $\delta$ 2.0 (s, $Me_3$SiN), 63.5 (dq, $OCH_2CF_3$, $J_{PC} = 8.7$, $J_{FC} = 36.2$), 123.5 (dq, $J_{PC} = 6.2$, $J_{FC} = 277.8$), 131.8 (d, $PC_6H_4$, $C_1$, $J_{PC} = 18.5$), 130.3 (d, $PC_6H_4$, $C_{2,6}$, $J_{PC} = 6.2$), 130.1 (d, $PC_6H_4$, $C_{3,5}$, $J_{PC} = 21.8$), 152.0 (s, $PC_6H_4$, $C_4$). Anal. Calcd. for $C_{16}H_{26}F_6O_2NPSi_2$: C, 41.28; H, 5.63. Found: C, 41.73; H, 6.13. **(3: $\mathbf{R = Ph}$, $\mathbf{R' = OCH_2CF_3}$)**. Yield: ca. 60%. bp: 121–123°C (0.01 mm Hg). $^{31}$P NMR: $\delta$ 128.3. $^1$H NMR: $\delta$ 0.06 (s, $Me_3$SiN), 4.0–4.2 (m, $OCH_2CF_3$), 7.0–7.5 (m, $C_6H_4$), 7.3–7.4 (m, *Ph*). $^{13}$C NMR: $\delta$ 2.1 (s, $Me_3$SiN), 66.9 (dq, $OCH_2CF_3$, $J_{PC} = 21.2$, $J_{FC} = 35.2$), 123.7 (dq, $J_{PC} = 9.3$, $J_{FC} = 278.8$), 134.4 (d, $PC_6H_4$, $C_1$, $J_{PC} = 16.1$), 128.4 (d, $PC_6H_4$, $C_{2,6}$, $J_{PC} = 6.9$), 130.4 (d, $PC_6H_4$, $C_{3,5}$, $J_{PC} = 21.2$), 150.6 (s, $PC_6H_4$, $C_4$), 140.6 (d, PPh, $C_1$, $J_{PC} = 16.3$), 130.1 (d, PPh, $C_{2,6}$, $J_{PC} = 7.5$), 131.5 (d, PPh, $C_{3,5}$, $J_{PC} = 23.2$), 129.6 (s, PPh, $C_4$). Anal. Calcd. for $C_{20}H_{29}F_3ONPSi_2$: C, 54.15; H, 6.59. Found: C, 53.98; H, 6.47.

Similarly, the reaction of **B** with $Ph_2PCl$ afforded (disilylanilino)phosphine **4** as a pale yellow solid. **(4: $\mathbf{R = R' = Ph}$)**. Yield: ca. 60%. $^{31}$P NMR: $\delta$ −6.4. $^1$H NMR: $\delta$ 0.08 (s, $Me_3$SiN), 6.8–7.2 (m, $C_6H_4$), 7.2–7.4 (m, *Ph*). $^{13}$C NMR: $\delta$ 2.1 (s, $Me_3$SiN), 135.7 (d, $PC_6H_4$, $C_1$, $J_{PC} = 21.3$), 128.4 (d, $PC_6H_4$, $C_{2,6}$, $J_{PC} = 7.2$), 133.6 (d, $PC_6H_4$, $C_{3,5}$, $J_{PC} = 19.1$), 149.2 (s, $PC_6H_4$, $C_4$), 137.8 (d, PPh, $C_1$, $J_{PC} = 11.3$), 130.3 (d, PPh, $C_{2,6}$, $J_{PC} = 7.4$), 134.1 (d, PPh, $C_{3,5}$, $J_{PC} = 20.0$), 128.5 (s, PPh, $C_4$). Anal. Calcd. for $C_{24}H_32NPSi_2$: C, 68.36; H, 7.65. Found: C, 67.99; H, 8.02.

In the same manner, the reaction of **B** with Ph(Me)PCl (**E**), freshly prepared as described above, afforded (disilylanilino)phosphine **5** as a colorless liquid. **(5: $\mathbf{R = Ph}$, $\mathbf{R'}$ = Me).** Yield: 62%. bp: 135–139°C (0.03 mm Hg). $^{31}$P NMR: $\delta$ −27.1. $^1$H NMR: $\delta$ 0.00

(s, $Me_3$SiN), 1.54 (d, P$Me$, $J_{PH} = 3.6$), 6.8–7.2 (m, $C_6H_4$), 7.2–7.3 (m, $Ph$). $^{13}$C NMR: $\delta$ 0.0 (s, $Me_3$SiN), 10.8 (d, P$Me$, $J_{PH} = 13.3$), 126.1 (d, $PC_6H_4$, $C_1$, $J_{PC} = 22.2$), 131.5 (d, $PC_6H_4$, $C_{2,6}$, $J_{PC} = 9.5$), 130.5 (d, $PC_6H_4$, $C_{3,5}$, $J_{PC} = 19.6$), 146.7 (s, $PC_6H_4$, $C_4$), 139.1 (d, PPh, $C_1$, $J_{PC} = 12.4$), 128.1 (d, PPh, $C_{2,6}$, $J_{PC} = 7.2$), 129.7 (d, PPh, $C_{3,5}$, $J_{PC} = 18.1$), 126.2 (s, PPh, $C_4$). Anal. Calcd. for $C_{19}H_{30}NPSi_2$: C, 63.46; H, 8.41. Found: C, 63.25; H, 9.19.

### Preparation of (Disilylanilino)phosphines, $(M_3Si)_2NC_6H_4P(R)N(SiMe_3)_2$ (6–11)

A typical experiment for the synthesis of **6 (R = Me)** is described here. A three-neck (1000 mL) round-bottom flask, equipped with a mechanical stirrer, $N_2$ inlet, and an addition funnel was charged with $Et_2O$ (200 mL) and $(Me_3Si)_2NH$ (8.25 g, 51.1 mmol). The mixture was cooled to 0°C and *n*-BuLi (21.6 mL, 54.0 mmol) was added slowly. The mixture was allowed to warm to room temperature and was stirred for 1 h. The mixture was then cooled to −78°C and $PCl_3$ (7.08 g, 51.6 mmol) was added slowly. The mixture was allowed to warm to room temperature and was stirred for 2 h. The mixture was again cooled to 0°C and a previously prepared solution of the organolithium reagent **B** (51.2 mmol) was added slowly via cannula. The reaction mixture was allowed to warm to room temperature and was stirred for 2 h. To replace the remaining chlorine, the mixture was again cooled to 0°C and $CH_3MgBr$ (17.3 mL, 52 mmol) was added slowly from the addition funnel. After warming to room temperature, the mixture was stirred for ca. 3 h. Most of the solvents were removed under reduced pressure and hexane (300 mL) was added to precipitate the salt. After filtration and solvent removal under reduced pressure, fractional distillation afforded **6** as a colorless liquid. **(6: R = Me)**. Yield: 62%. bp: 75–80°C (0.10 mm Hg). $^{31}$P NMR: $\delta$ 38.5. $^1$H NMR: $\delta$ 0.01 (s, $Me_3$SiN), 0.08 (s, $Me_3$SiNP), 1.56 (d, P$Me$, $J_{PH} = 5.7$), 6.8–7.2 (m, $C_6H_4$). $^{13}$C NMR: $\delta$ 0.0 (s, $Me_3$SiN), 2.1 (s, $Me_3$SiNP), 14.9 (d, P$Me$, $J_{PC} = 25.0$), 139.2 (d, $PC_6H_4$, $C_1$, $J_{PC} = 18.3$), 126.9 (d, $PC_6H_4$, $C_{2,6}$, $J_{PC} = 15.8$), 127.7 (s, $PC_6H_4$, $C_{3,5}$), 144.8 (s, $PC_6H_4$, $C_4$). Anal. Calcd. for $C_{19}H_{43}N_2PSi_4$: C, 51.52; H, 9.78. Found: C, 51.93; H, 10.88.

Compounds **7–10** were prepared in the same manner using the appropriate Grignard (*i*-PrMgBr) or lithium reagent RLi [R = *n*-Bu, $OCH_2CF_3$, $C_6H_4N(SiMe_3)_2$], instead of MeMgBr. All were obtained as colorless liquids after fractional distillation. **(7: R = *i*-Pr)**. Yield: 50%. bp: 130–135°C (0.01 mm Hg). $^{31}$P NMR: $\delta$ 57.8. $^1$H NMR: $\delta$ 0.00 (s, $Me_3$SiN), 0.08 (s, $Me_3$SiNP), 1.07 (dd, PCH$Me_2$, $J_{PH} = 21.9$, $J$HH = 6.9), 1.15 (dd, PCH$Me_2$, $J_{PH} = 16.2$, $J$HH = 6.3), 2.35 (ds, P$CH$Me$_2$, $J_{PH} = 6.6$, $J$HH = 6.9), 6.7–7.3 (m, $C_6H_4$). $^{13}$C NMR: $\delta$ 0.1 (s, $Me_3$SiN), 2.5 (d, $Me_3$SiNP, $J_{PC} = 6.6$), 17.5 (d, PCH$Me_2$, $J_{PC} = 11.2$), 18.8 (d, PCH$Me_2$, $J_{PC} = 37.6$), 24.7 (d, P$CH$Me$_2$, $J_{PC} = 18.4$), 136.0 (d, $PC_6H_4$, $C_1$, $J_{PC} = 23.6$), 128.9 (d, $PC_6H_4$, $C_{2,6}$, $J_{PC} = 15.5$), 127.7 (s, $PC_6H_4$, $C_{3,5}$), 145.6 (s, $PC_6H_4$, $C_4$). Anal. Calcd. for $C^{21}H_{47}N_2PSi_4$: C, 53.56; H, 10.06. Found: C, 52.41; H, 10.26. **(8: R = *n*-Bu)**. Yield: 59%. bp: 128–133°C (0.10 mm Hg). $^{31}$P NMR: $\delta$ 47.6. $^1$H NMR: $\delta$ 0.01 (s, $Me_3$SiN), 0.09 (s, $Me_3$SiNP), 0.94 (t, $CH_2CH_3$, $J$HH = 6.6), 1.5–1.6 (m, $PCH_2CH_2$, $CH_2CH_3$), 1.9–2.0 (m, P$CH_2$) 6.8–7.2 (m, $C_6H_4$). $^{13}$C NMR: $\delta$ 0.0 (s, $Me_3$SiN), 2.3 (d, $Me_3$SiNP, $J_{PC} = 6.6$), 11.9 (s, $CH_2CH_3$), 22.4 (d, $CH_2CH_3$, $J_{PC} = 13.6$), 26.2 (d, $PCH_2CH_2$, $J_{PC} = 20.3$), 29.5 (d, P$CH_2$, $J_{PC} = 21.2$), 138.7 (d, $PC_6H_4$, $C_1$, $J_{PC} = 21.6$), 127.1 (d, $PC_6H_4$, $C_{2,6}$, $J_{PC} = 15.2$), 127.7 (s, $PC_6H_4$, $C_{3,5}$), 144.8 (s, $PC_6H_4$, $C_4$). Anal. Calcd. for $C_{22}H_{49}N_2PSi_4$: C, 54.49; H, 10.18. Found: C, 53.27; H, 10.87. **(9: R = $OCH_2CF_3$)**. Yield: ca. 60%.

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bp: 93–96°C (0.10 mm Hg). $^{31}$P NMR: $\delta$ 150.2. $^{1}$H NMR: $\delta$ 0.01 (s, *Me*$_3$SiN), 0.11 (s, *Me*$_3$SiNP), 4.0–4.2 (m, O*CH*$_2$CF$_3$), 6.8–7.2 (m, *C*$_6$*H*$_4$). $^{13}$C NMR: $\delta$ 0.0 (s, *Me*$_3$SiN), 1.9 (d, *Me*$_3$SiNP, $J_{PC} = 7.2$), 63.9 (dq, O*CH*$_2$CF$_3$, $J_{PC} = 27.5$, $J_{FC} = 35.2$), 123.5 (dq, $J_{PC} = 6.2$, $J_{FC} = 278.0$), 139.2 (d, PC$_6$H$_4$, *C*$_1$, $J_{PC} = 18.3$), 126.9 (d, PC$_6$H$_4$, *C*$_{2,6}$, $J_{PC} = 15.8$), 127.7 (s, PC$_6$H$_4$, *C*$_{3,5}$), 144.8 (s, PC$_6$H$_4$, *C*$_4$). Anal. Calcd. for $C_{20}H_{42}F_3ON_2PSi_4$: C, 45.59; H, 8.03. Found: C, 45.73; H, 7.84. **(10: R = C$_6$H$_4$N(SiMe$_3$)$_2$)**. Yield: 46%. bp: 170–180°C (0.01 mm Hg). $^{31}$P NMR: $\delta$ 48.9. $^{1}$H NMR: $\delta$ 0.02 (s, *Me*$_3$SiN), 0.08 (s, *Me*$_3$SiNP), 6.8–7.3 (m, *C*$_6$*H*$_4$). $^{13}$C NMR: $\delta$ 0.0 (s, *Me*$_3$SiN), 2.2 (d, *Me*$_3$SiNP, $J_{PC} = 7.2$), 133.1 (d, PC$_6$H$_4$, *C*$_1$, $J_{PC} = 21.0$), 128.9 (d, PC$_6$H$_4$, *C*$_{2,6}$, $J_{PC} = 19.6$), 127.4 (s, PC$_6$H$_4$, *C*$_{3,5}$), 146.7 (s, PC$_6$H$_4$, *C*$_4$). Anal. Calcd. for $C_{30}H_{62}N_3PSi_6$: C, 54.24; H, 9.41. Found: C, 54.50; H, 9.17.

Compound **11** was prepared in the same manner starting from PhPC$_{l2}$ instead of PCl$_3$. Fractional distillation afforded **11** as a colorless liquid. **(11: R = Ph).** Yield: 58%. bp: 149–152°C (0.10 mm Hg). $^{31}$P NMR: $\delta$ 48.9. $^{1}$H NMR: $\delta$ 0.00 (s, *Me*$_3$SiN), 0.02 (s, *Me*$_3$SiNP), 6.8–7.3 (m, *C*$_6$*H*$_4$), 7.3–7.5 (m, *Ph*). $^{13}$C NMR: $\delta$ 0.1 (s, *Me*$_3$SiN), 2.4 (d, *Me*$_3$SiNP, $J_{PC} = 7.0$), 138.8 (d, PC$_6$H$_4$, *C*$_1$, $J_{PC} = 23.4$), 129.3 (d, PC$_6$H$_4$, *C*$_{2,6}$, $J_{PC} = 19.6$), 129.3 (d, PC$_6$H$_4$, *C*$_{3,5}$, $J_{PC} = 19.0$), 146.7 (s, PC$_6$H$_4$, *C*$_4$), 133.2 (d, PPh, *C*$_1$, $J_{PC} = 21.2$), 127.6 (d, PPh, *C*$_{2,6}$, $J_{PC} = 5.4$), 128.8 (d, PPh, *C*$_{3,5}$, $J_{PC} = 5.0$), 125.4 (s, PPh, *C*$_4$). Anal. Calcd. for $C_{24}H_{45}N_2PSi_4$: C, 57.09; H, 8.98. Found: C, 56.93; H, 9.43.

### Preparation of (Disilylanilino)phosphines, (M$_3$Si)$_2$NC$_6$H$_4$P(R)Ph (12, 13)

A solution of the silylaniline reagent **B** (141 mmol) in Et$_2$O (300 mL) was prepared (as described above in the synthesis of **1**). The mixture was cooled to −78°C and PhPC$_{l2}$ (25.1 g, 140.0 mmol) was slowly added via syringe. The mixture was allowed to warm to 0°C and was stirred for 2 h before *n*-BuLi (56.0 mL, 140.0 mmol) was slowly added. The mixture was allowed to warm to room temperature and was stirred for 3 h. The ether was removed under reduced pressure and hexane was added to precipitate the salt. After filtration and solvent removal under reduced pressure, fractional distillation afforded **12** as a colorless liquid. **(12: R = Ph, R′ = *n*-Bu).** Yield: 50%. bp: 140–144°C (0.01 mm Hg). $^{31}$P NMR: $\delta$ −16.2. $^{1}$H NMR: $\delta$ 0.01 (s, *Me*$_3$SiN), 0.84 (t, CH$_2$*CH*$_3$, *J*HH = 6.3), 1.3–1.4 (m, PCH$_2$*CH*$_2$, *CH*$_2$CH$_3$), 1.9–2.0 (m, P*CH*$_2$), 6.8–7.2 (m, *C*$_6$*H*$_4$), 7.3–7.5 (m, P*Ph*). $^{13}$C NMR: $\delta$ 0.0 (s, *Me*$_3$SiN), 11.7 (s, CH$_2$*CH*$_3$), 22.2 (d, *CH*$_2$CH$_3$, $J_{PC} = 13.3$), 26.1 (d, PCH$_2$*CH*$_2$, $J_{PC} = 10.6$), 26.2 (d, P*CH*$_2$, $J_{PC} = 4.9$), 131.1 (d, PC$_6$H$_4$, *C*$_1$, $J_{PC} = 19.0$), 130.3 (d, PC$_6$H$_4$, *C*$_{2,6}$, $J_{PC} = 17.9$), 127.0 (s, PC$_6$H$_4$, *C*$_{3,5}$), 146.8 (s, PC$_6$H$_4$, *C*$_4$), 125–133 (m, P*Ph*). Anal. Calcd. for $C_{22}H_{36}NPSi_2$: C, 65.78; H, 9.03. Found: C, 65.51; H, 9.98.

Similarly, the one-step reaction of the silylaniline reagent **B** (100 mmol) with PhPC$_{l2}$ (50 mmol) afforded **13** as a colorless liquid. **(13: R = Ph, R′ = C$_6$H$_4$N(SiMe$_3$)$_2$).** Yield: 55%. bp: 180–186°C (0.01 mm Hg). $^{31}$P NMR: $\delta$ −7.0. $^{1}$H NMR: $\delta$ 0.00 (s, *Me*$_3$SiN), 6.8–7.2 (m, *C*$_6$*H*$_4$), 7.3–7.5 (m, P*Ph*). $^{13}$C NMR: $\delta$ 0.0 (s, *Me*$_3$SiN), 131.8 (d, PC$_6$H$_4$, *C*$_1$, $J_{PC} = 19.9$), 131.4 (d, PC$_6$H$_4$, *C*$_{2,6}$, $J_{PC} = 19.2$), 128.0 (s, PC$_6$H$_4$, *C*$_{3,5}$), 146.8 (s, PC$_6$H$_4$, *C*$_4$), 126–136 (m, P*Ph*). Anal. Calcd. for $C_{30}H_{49}N_2PSi_4$: C, 62.01; H, 8.50. Found: C, 62.20; H, 8.45.

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## REFERENCES


1. Neilson, R. H. Phosphorus-nitrogen compounds. In: R. B. King (Ed.), *Encyclopedia of Inorganic Chemistry*, Vol 6; John Wiley & Sons: Chichester, England, **1994,** pp. 3180-3199.
2. For example, see the following and references cited therein: (a) Scheide, G. M.; Neilson, R. H. *Organometallics* **1989,** 8, 1987-1991. (b) Morton, D. W.; Neilson, R. H. *Organometallics* **1982,** 1, 289-295. (c) Neilson, R. H.; Wisian-Neilson, P.; Wilburn, J. C. *Inorg. Chem*. **1980,** 19, 413-416. (d) Wilburn, J. C.; Neilson, R. H. *Inorg. Chem*. **1979,** 18, 347-351.
3. For early examples, see: (a) Wisian-Neilson, P.; Neilson, R. H.; Cowley, A. H. *Inorg. Chem*. **1977,** 16, 1460-1463. (b) Wisian-Neilson, P.; Neilson, R. H. *J. Am. Chem. Soc*. **1980,** 102, 2848-2849.
4. See, for example: (a) Neilson, R. H.; Klaehn, J. R. *J. Inorg. Organomet. Polym.* **2006,** 16, 319-326. (b) Wisian-Neilson, P.; Johnson, R. S.; Zhang, H.; Jung, J.-H.; Neilson, R. H.; Ji, J.; Watson, W. H.; Krawiec, M. *Inorg. Chem*. **2002,** 41, 4775-4779. (c) Jung, J.-H.; Pomeroy, J. C.; Zhang, H.; Wisian-Neilson, P. *J. Am. Chem. Soc*. **2003,** 125, 15537-15542.
5. See, for example: (a) Neilson, R. H.; Hani, R.; Wisian-Neilson, P.; Meister, J. J.; Roy, A. K.; Hagnauer, G. L. *Macromolecules* **1987,** 20, 910-916. (b) Neilson, R. H.; Wisian-Neilson, P. *Chem. Rev*. **1988,** 88, 541-562. (c) Wisian-Neilson, P.; Neilson, R. H. *Inorg. Synth*. **1989,** 25, 69-74. (d) Matyjaszewski, K.; Dauth, J.; Montague, R. A.; Reddick, C.; White, M. L. *J. Am. Chem. Soc*. **1990,** 112, 6721-6723. (e) White, M. L.; Matyjaszewski, K. *J. Polym. Science (A)* **1996,** 34, 277-289. (f) Honeyman, C. H.; Manners, I.; Morrissey, C. T.; Allcock, H. R. *J. Am. Chem. Soc*. **1995,** 117, 7035-7036. (g) Allcock, H. R.; Crane, C. A.; Morrissey, C. T.; Nelson, J. M.; Reeves, S. D.; Honeyman, C. H.; Manners, I. *Macromolecules* **1996,** 29, 7740-7747. (h) Allcock, H. R.; Nelson, J. M.; Reeves, S. D.; Honeyman, C. H.; Manners, I. *Macromolecules* **1997,** 30, 50-56. (i) Wang, B.; Rivard, E.; Manners, I. *Inorg. Chem*. **2002,** 41, 1690-1691. (j) Wang, B. *Macromolecules* **2005,** 38, 643-645.
6. Some preliminary aspects of this work were briefly reported in a conference proceedings but without experimental details. See: Neilson, R. H.; Devulapalli, P.; Jackson, B. K.; Neilson, A. R.; Parveen, S.; Wang, B. *ACS Sympos. Ser*. **2006,** 917, 325-334.
7. Broser, W.; Harrer, W. *Angew. Chem. Int. Ed. Engl.* **1965,** 4, 1081.
8. Nöth, H.; Vetter, H.-J. *Chem. Ber.* **1963,** 96, 1109.
9. Lenton, M. V.; Lewis, B. *Chem. Indus.* **1965**, 946-947.
10. For other syntheses and NMR data of Me(Ph)PCl, see: (a) Wolfsberger, W. *J. Organomet. Chem.* **1986,** 317, 167-173. (b) Lindner, E.; Merkle, R. D.; Mayer, H. A. *Chem. Ber*. **1986,** 119, 645-658.
11. (a) Wilburn, J. C.; Neilson, R. H. *Inorg. Chem*. **1979,** 18, 347-351. (b) Neilson, R. H.; Wisian-Neilson, P. *Inorg. Chem*. **1982,** 21, 3568-3569.
12. For comparative $^{31}$P NMR data, see: (a) Crutchfield, M. M.; Dungan, C. H.; Letcher, J. H.; Mark, V.; Van Wazer, J. R. P-31 nuclear magnetic resonance. In: M. Grayson; E. J. Griffith (Eds.), *Topics in Phosphorus Chemistry*, Vol. 5; John Wiley & Sons: New York, **1967**. (b) Verkade, J. G.; Quin, L. D. Phosphorus-31 NMR spectroscopy in stereochemical analysis. In: A. P. Marchand (Ed.), *Methods in Stereochemical Analysis*, Vol. 8; VCH Publishers: Dearfield Beach, FL, **1987**.


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