Free and Supported Phosphorus Ylides as Strong Neutral Brønsted Bases

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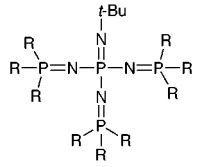
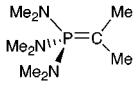
Introduction

In the early 1990s, Schwesinger reported that phosphazenes such as **1** (namely P_4-*t*-Bu) are nonnucleophilic very strong bases.[1] They have found numerous applications in organic synthesis,[2] but their high molecular weight and cost are drawbacks for their extensive use. Here, we report that simple ylides[3] such as *P*-tris(dimethylamino)-*C*-dimethylphosphonium ylide **2** can be conveniently used in place of P_4-*t*-Bu; moreover, a supported version **3** of this type of base is also presented.[4]



1 : R = NMe_2



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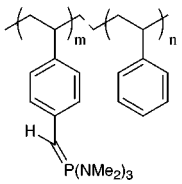

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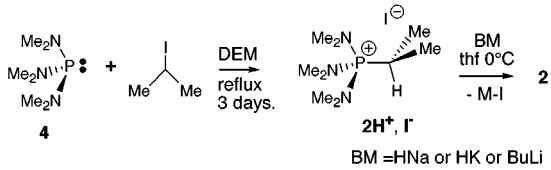
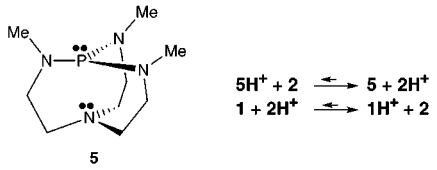
Results and Discussion

Synthesis of the Ylide 2. Alkylation of tris(dimethylamino)phosphine **4** with the 2-iodopropane leads to the phosphonium salt $\mathbf{2H^+I^-}$, which has been isolated in 91% yield as an air-stable white solid storable for months at room temperature. Treatment of this salt with a strong base, such as *n*-BuLi or alkaline hydrides in dry THF, followed by extraction with pentane, offers the salt-free[5] ylide **2** (no trace of alkali iodide was detected by elemental analysis) (Scheme 1).

Scheme 1



Scheme 2



Evaluation of the pK_a Value of $\mathbf{2H^+}$. The most common strong neutral bases used in organic synthesis are, by order of increasing power, tertiary amines, proton sponges,[6] guanidines[7] (mainly DBN and DBU), Verkade's phosphatrane **5**,[8] and the polyphosphazene **1**. ^{31}P NMR spectroscopy was used to evaluate the pK_a value of $\mathbf{2H^+}$. In THF-d_8, the ^{31}P NMR chemical shift of $\mathbf{2H^+}$ (+65 ppm) is not affected by addition of a stoichiometric amount of DBU or DBN. More interestingly, phosphatrane **5** was also unable to deprotonate $\mathbf{2H^+}$, while **1** quantitatively (according to ^{31}P NMR spectroscopy) reacted with $\mathbf{2H^+}$ affording $\mathbf{1H^+}$ and **2**. Therefore, we can assume that the pK_a value of $\mathbf{2H^+}$ is intermediate between those of $\mathbf{5H^+}$ and $\mathbf{1H^+}$ (26[8] and 28[1] in THF, respectively). Even though the pK_a values of $\mathbf{1H^+}$, $\mathbf{2H^+}$, and $\mathbf{5H^+}$ are very close, no equilibria were detected by ^{31}P NMR spectroscopy (Scheme 2). Note that the amino substituents at phosphorus play an important role on the pK_a value; for comparison, the pK_a value of $Ph_3PCH_3^+$ is only around 19.[3]

Synthetic Uses of the Ylide 2. We first tested N-functionalization reactions of lactam **6a** and benzodiazepine **7a**. Addition at −78 °C of a slight excess (5%) of a freshly prepared THF solution of the ylide **2** to THF solutions of **6a** and **7a**, followed by addition of the alkylating reagent (CH_3I, *t*-BuO_2CCH_2Br, $PhCH_2Br$), led to the expected products **6b**−**d** and **7b**−**d**, respectively (Scheme 3). According to NMR spectroscopy, the reactions were quantitative; the isolated yields obtained after purification on column chromatography were not optimized. Of particular interest, the phosphonium salt

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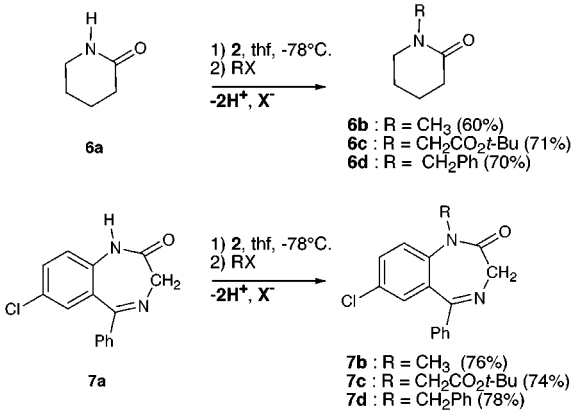
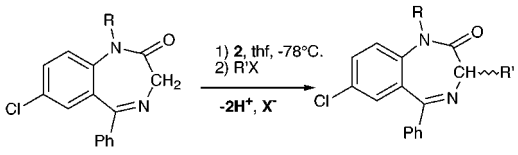
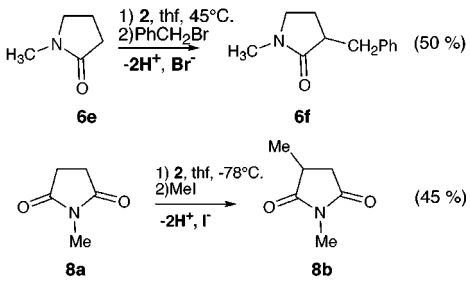
Scheme 3



Scheme 4



Reagents	R	R'	Products	Yield (%)
7b	$-CH_3$	$-CH_2Ph$	**7e**	55
7b	$-CH_3$	$-CH_2CO_2t$-Bu	**7f**	42
7b	$-CH_3$	$-CH_3$	**7g**	43
7c	$-CH_2CO_2t$-Bu	$-CH_2CO_2t$-Bu	**7h**	48
7c	$-CH_2CO_2t$-Bu	$-CH_2Ph$	**7i**	39
7c	$-CH_2CO_2t$-Bu	$-CH_3$	**7j**	54
7d	$-CH_2Ph$	$-CH_2Ph$	**7k**	38
7d	$-CH_2Ph$	$-CH_2CO_2t$-Bu	**7l**	42
7d	$-CH_2Ph$	$-CH_3$	**7m**	67



$\mathbf{2H}^+,\mathbf{X}^-$ (X = Br or I) can be precipitated from the reaction mixture by addition of ether, and, thus, easily eliminated by simple filtration.

We then investigated several C-functionalization reactions using **2** as a base (Scheme 4). With 1,4-benzodiazepines, the results are very similar to those obtained with LDA as the base.[9] It is known that all benzodiazepines are chiral by virtue of their nonplanarity.[10] The introduction of a substituent at C3 only occurred on the less sterically hindered face leading to only one diastereomer. This has been confirmed by a single-crystal X-ray diffraction study of **7k**.

C-Alkylation reactions of the lactam **6e** and succinimide **8a** have also been performed and led to the desired products **6f** and **8b**, respectively. However, in the case of **6f**, heating during the step of deprotonation was necessary to reach a reasonable yield (Scheme 4).

In all of the reactions mentioned above, no trace of adducts resulting from the nucleophilic behavior of **2** has been observed.

Supported Ylides. To make more attractive the use of ylides as strong nonnucleophilic bases, we investigated the possibility of immobilizing an ylide on resins. Interestingly, polymers of type **A** have been reported in the literature[11] and have been used as very efficient Wittig's reagents. Considering the relative acidity of the benzyl and methyl protons, thermodynamic considerations suggest that the ylide **B** should be preferred over **A**.[3] However, it has been clearly demonstrated that the polymers react in Wittig reactions as **A**, which strongly suggest that the ylide carbon in **B** is nonnucleophilic, because of the steric bulk of the polymer skeleton. Therefore, in the hope of preparing a strongly hindered nonnucleophilic supported base **3**, a suspension of Merryfield's resin and phosphine **4** in DCE was first stirred under reflux for 5 days. After treatment, an elemental analysis showed that 1.25 mequiv/g of phosphine was grafted on the polymer. Then, deprotonation of the phosphonium salt $\mathbf{3H}^+,\mathbf{Cl}^-$ with excess *n*-BuLi led to the desired supported ylide **3** (Scheme 5).

To check the reactivity of **3**, N-benzylation of **7a** was carried out, and the result was comparable to that obtained with **2**. Simple filtration of the solution afforded **7d**, while the resin **3** could be regenerated by washing with acetonitrile and simple deprotonation.

Conclusion

These results show that the ylide **2** is a nonnucleophilic strong base, comparable but cheaper than P_4-*t*-Bu. Applications of the resin **3** in combinatorial synthesis are currently being investigated.

Experimental Section

All experiments were performed under an atmosphere of dry argon or nitrogen. Conventional glassware was used. Compound **5** was prepared according to literature procedure.[8a,f]

$2H^+I^-$. To a diethoxymethane (DEM) solution (40 mL) of **4** (5 mL, 23 mmol) was added at room temperature an excess (4.69 g, 27.6 mmol) of 2-iodopropane. The solution was stirred under reflux for 72 h. A white precipitate was formed, and after filtration and recrystallization in acetonitrile, $\mathbf{2H}^+\mathbf{I}^-$ was obtained as a white solid (6.97 g, 91% yield): mp 309 °C dec; ^{31}P NMR (32 MHz, CD_3CN) δ 65.0; ^{1}H NMR (200 MHz, CD_3CN) δ 1.31 (dd, $^3J_{(HH)}$ = 7.1 Hz, $^3J_{(PH)}$ = 18.2 Hz, 6H), 2.81 (d, $^3J_{(PH)}$ = 9.4 Hz, 18H), 3.67 (sept d, $^2J_{(PH)}$ = 9.8 Hz, $^3J_{(HH)}$ = 7.1 Hz, 1H); ^{13}C NMR (200 MHz, CD_3CN) δ 15.13 (d, $^2J_{(PC)}$ = 3.4 Hz), 23.80 (d, $^1J_{(PC)}$ = 103.6 Hz), 36.43 (d, $^2J_{(PC)}$ = 2.6 Hz). Anal. Calcd for $C_9H_{25}IN_3P$: C, 32.44; H, 7.56; N, 12.61. Found: C, 32.22; H, 7.40; N, 12.41.

2. Potassium hydride (0.288 g, 7.2 mmol) was added at 0 °C to a suspension of $\mathbf{2H}^+\mathbf{I}^-$ (2 g, 6 mmol) in 40 mL of THF. The solution was stirred at room temperature until complete evolution of hydrogen (12 h). The solution was filtered, and after evaporation of the solvent under vacuum, the residue was twice extracted with 20 mL of pentane. Evaporation of pentane led to **2** as a colorless oil (0.92 g, 75% yield): ^{31}P NMR (32 MHz, C_6D_6) δ 60.6; ^{1}H NMR (200 MHz, C_6D_6) δ 1.78 (d, $^3J_{(PH)}$ = 15.7 Hz, 6H), 2.45 (d, $^3J_{(PH)}$ = 9.3 Hz, 18H); ^{13}C NMR (250 MHz, $CDCl_3$) δ 12.39 (d, $^1J_{(PC)}$ = 221.0 Hz), 19.49 (d, $^2J_{(PC)}$ = 15.9 Hz), 38.52 (d, $^2J_{(PC)}$ = 2.8 Hz). Anal. Calcd for $C_9H_{24}N_3P$: C, 52.66; H, 11.78; N, 20.47. Found: C, 52.30; H, 11.52; N, 20.31. If **2** was complexed with 1 equiv of LiI, the following values should be obtained: C, 31.88; H, 7.13; N, 12.39.

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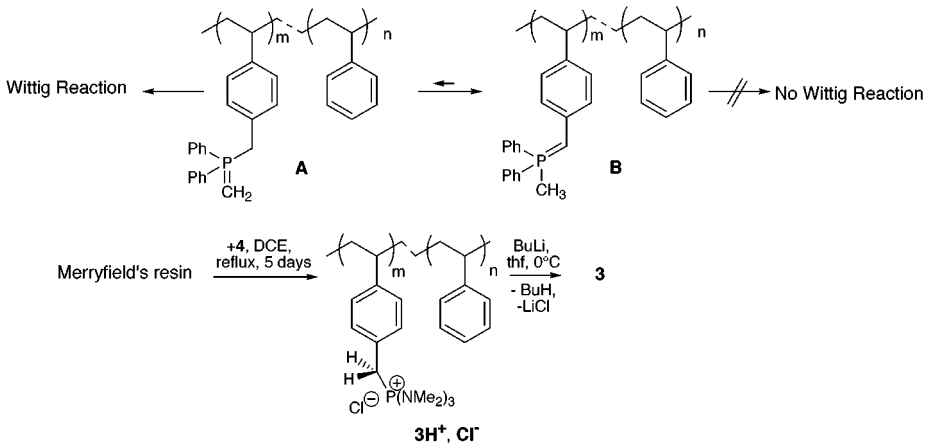
Scheme 5



Comparison of the Basicities of 1, 2, and 5. To a THF suspension (1 mL) of $\mathbf{2H}^+,\mathbf{I}^-$ (50 mg, 0.15 mmol) in an NMR tube was added 1 equiv of **1** in THF (150 μL, 1 M). The ^{31}P NMR spectrum was measured right after the addition and 1 h later. Both spectra were identical and show the signals due to $\mathbf{1H}^+$ (+13.4 and −22.9 ppm) and **2** (+60.6 ppm). The same spectrum was obtained by reacting a stoichiometric amount or an excess of **2** with $\mathbf{1H}^+$ under the same experimental conditions.

Similar experiments have been performed to compare the basicities of **2** and **5**. When a solution of **2** was added to an equimolar solution of $\mathbf{5H}^+$, after 1 h, the signals of **5** (+119.9 ppm) and $\mathbf{2H}^+$(+ 65.0 ppm) were observed.

Procedure for N-Functionalization of the Lactam 6a and Benzodiazepine 7a. A solution of **2** (3.15 mmol) in THF (17 mL) was added at −78 °C to a solution of **6a** or **7a** (3 mmol) in THF (14 mL). The solution was stirred for 1 h, and then 3.15 mmol of alkyl halide was added. The mixture was stirred for 3 h at room temperature. The solution was separated from the phosphonium salts by addition of ether (60 mL) and filtration. After evaporation of the solvent, the residue was purified by silica gel column chromatography to yield compounds **6b**−**d** and **7b**−**d**.

6b:[12a] eluent, ether/methanol 85/15; yellow oil; 0.20 g, 60% yield.

6c: eluent, ether; yellow oil; 0.45 g, 71% yield; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1,43 (s, 9H), 1.80 (m, 4H), 2.55 (m, 2H), 3.35 (m, 2H), 4.09 (s, 2H); ^{13}C NMR (250 MHz, $CDCl_3$) δ 20.44, 22.42 (s), 27.73 (s), 31.72 (s), 49.21, 49.90 (s), 82.49 (s), 168.59, 172.37 (s). Anal. Calcd for $C_{11}H_{19}NO_3$: C, 61.95; H, 8.98; N, 6.57. Found: C, 62.15; H, 8.71; N, 6.48.

6d:[12b] eluent, ether/methanol 30/70; yellow oil; 0.40 g, 70% yield.

7b:[9] eluent, ether; white solid; 0.65 g, 76% yield.

7c: eluent, THF/pentane 90/10; yellow solid; mp 181 °C; 0.85 g, 74% yield; IR ($CDCl_3$) 1688, 1740 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.41 (s, 9H), 3.80 (d, $^2J_{(HH)}$ = 10.7 Hz, 1H), 4.21 (d, $^2J_{(HH)}$ = 15.0 Hz, 1H), 4.45 (d, $^2J_{(HH)}$ = 15.0 Hz, 1H), 4.85 (d, $^2J_{(HH)}$ = 10.7 Hz, 1H), 7.21−7.60 (m, 8H); ^{13}C NMR (250 MHz, $CDCl_3$) δ 27.65 (s), 51.03 (s), 55.88 (s), 83.50 (s), 121.63−131.98 (s), 130.23, 130.64, 137.85, 140.56 (s), 168.30, 170.26, 170.58 (s). Anal. Calcd for $C_{21}H_{21}ClN_2O_3$: C, 65.54; H, 5.50; N, 7.28. Found: C, 65.41; H, 5.76; N, 7.09.

7d: eluent, ether; orange solid; mp 178 °C; 0.84 g, 78% yield; IR ($CDCl_3$) 1679 cm^{-1}; MS *m*/*z* 361 (M + 1); ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.80 (d, $^2J_{(HH)}$ = 10.5 Hz, 1H), 4.68 (d, $^2J_{(HH)}$ = 15.5 Hz, 1H), 4.96 (d, $^2J_{(HH)}$ = 10.5 Hz, 1H), 5.64 (d, $^2J_{(HH)}$ = 15.5 Hz, 1H), 7.30 (m, 13H); ^{13}C NMR (250 MHz, $CDCl_3$) δ 49.77 (s), 56.83 (s), 123.94−131.30 (s), 130.02, 131.93, 136.20, 138.04, 140.43 (s), 169.48, 169.50 (s). Anal. Calcd for $C_{22}H_{17}ClN_2O$: C, 73.23; H, 4.75; N, 7.76. Found: C, 73.50; H, 5.01; N, 7.52.

Procedure for the C-Functionalization of the Lactam 6e, Succinimide 8a, and Benzodiazepines 7b-d. A solution of **2** (1.23 g, 6 mmol) in THF (27 mL) was added at −78 °C to a THF solution (23 mL) of **6e**, **8a**, or **7b**−**d** (5 mmol). The solution was stirred at room temperature for 1 h (except for **6e**: 45 °C, 6 h), and then the alkyl halide (6 mmol) was added. The mixture was stirred for an additional hour. The solution was separated from the phosphonium salts by addition of ether (60 mL) and filtration. After evaporation of the solvent, the residue was purified by silica gel column chromatography.

6f: eluent, ether/methanol 95/5; yellow oil; 0.47 g, 50% yield; ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.00 (m, 2H), 2.63 (m, 2H), 2.79 (s, 3H), 3.10 (m, 3H), 7.19 (m, 5H); ^{13}C NMR (250 MHz, $CDCl_3$) δ 23.88 (s), 29.59 (s), 36.99 (s), 43.27 (s), 47.39 (s), 126.17, 128.28, 128.88 (s), 139.29 (s), 175.72 (s). Anal. Calcd for $C_{12}H_{15}NO$: C, 76.16; H, 7.99; N, 7.40. Found: C, 76.63; H, 8.15; N, 6.92.

8b: eluent, ether; yellow oil; 0.29 g, yield 45%; IR($CDCl_3$) 1696 cm^{-1}; ^{1}H NMR see ref 13; ^{13}C NMR (250 MHz, $CDCl_3$) δ 16.53 (s), 30.10 (s), 34.55 (s), 36.20 (s), 176.45, 180.55 (s). Anal. Calcd for $C_6H_9NO_2$: C, 56.68; H, 7.13; N, 11.02. Found: C, 56.81; H, 7.22; N, 10.84.

7e:[9] eluent, pentane/ether 50/50; orange solid; mp 115 °C; 1.03 g, yield 55%.

7f: eluent, ether; white solid; mp 141 °C; 0.84 g, 42% yield; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.45 (s, 9H), 3.40 (s, 3H), 3.11 (dd, $^2J_{(HH)}$ = 17.1 Hz, $^3J_{(HH)}$ = 7.0 Hz, 1H), 3.39 (dd, $^2J_{(HH)}$ = 17.1 Hz, $^3J_{(HH)}$ = 6.8 Hz, 1H), 4.07 (dd, $^3J_{(HH)}$ = 7.0 Hz, $^3J_{(HH)}$ = 6.8 Hz, 1H), 7.25−7.57 (m, 8H); ^{13}C NMR (250 MHz, $CDCl_3$) δ 28.12 (s), 35.21 (s), 37.91 (s), 60.56 (s), 80.59 (s), 122.83−130.36 (s), 131.52, 137.97, 139.40, 142.20 (s), 167.20, 169.70, 171.25 (s). Anal. Calcd for $C_{22}H_{23}ClN_2O_3$: C, 66.24; H, 5.81; N, 7.02. Found: C, 66.51; H, 5.62; N, 6.77.

7g:[9,10a] eluent, ether; orange solid; mp 103 °C; 0.64 g, 43% yield.

7h: eluent, pentane/ether 50/50; yellow solid; mp 128 °C; 1.20 g, 48% yield; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.40 (s, 9H), 1.44 (s, 9H), 3.14 (dd, $^2J_{(HH)}$ = 16.9 Hz, $^3J_{(HH)}$ = 6.8 Hz, 1H), 3.43 (dd, $^2J_{(HH)}$ = 16.9 Hz, $^3J_{(HH)}$ = 7.0 Hz, 1H), 4.15 (dd, $^3J_{(HH)}$ = 7.0 Hz, $^3J_{(HH)}$ = 6.8 Hz, 1H), 4.20 (d, $^2J_{(HH)}$ = 17.1 Hz, 1H), 4.48 (d, $^2J_{(HH)}$ = 17.1 Hz, 1H), 7.25−7.60 (m, 8H); ^{13}C NMR (250 MHz, $CDCl_3$) δ 27.90, 28.06 (s), 37.82 (s), 50.81 (s), 60.33 (s), 80.61, 82.43 (s), 123.02−131.64 (s), 129.89, 130.60, 130.98, 138.08 (s), 167.39, 167.76, 170.92 (s). Anal. Calcd for $C_{27}H_{31}ClN_2O_5$: C, 64.99; H, 6.26; N, 5.61. Found: C, 64.58; H, 5.92; N, 5.41.

7i: eluent: pentane/ether 50/50; yellow solid; mp 81 °C; 0.93 g, 39% yield; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.41 (s, 9H), 3.72 (m, 3H), 4.40 (d, $^2J_{(HH)}$ = 16.7 Hz, 1H), 4.52 (d, $^2J_{(HH)}$ = 16.7 Hz, 1H), 7.20−7.58 (m, 13H); ^{13}C NMR (250 MHz, $CDCl_3$) δ 27.79 (s), 37.69 (s), 50.77 (s), 64.72 (s), 82.33 (s), 122.69−131.45 (s), 130.68, 131.10, 138.10, 138.91, 141.08 (s), 167.30, 167.47, 169.49 (s). Anal. Calcd for $C_{28}H_{27}ClN_2O_3$: C, 70.80; H, 5.73; N, 5.90. Found: C, 71.22; H, 5.83; N, 5.49.

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7j: eluent, pentane/ether 50/50; white solid; mp 152 °C; 1.08 g, 54% yield; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.41 (s, 9H), 1.70 (d, $^3J_{(HH)}$ = 6.4 Hz, 3H), 3.77 (q, $^3J_{(HH)}$ = 6.4 Hz, 1H), 4.23 (d, $^2J_{(HH)}$ = 17.2 Hz, 1H), 4.51 (d, $^2J_{(HH)}$ = 17.2 Hz, 1H), 7.21−7.60 (m, 8H); ^{13}C NMR (250 MHz, $CDCl_3$) δ 17.16 (s), 27.81 (s), 50.65 (s), 58.46 (s), 82.25 (s), 122.29−131.37 (s), 129.41, 130.82, 138.04, 141.18 (s), 167.04, 167.59, 170.50 (s). Anal. Calcd for $C_{22}H_{23}ClN_2O_3$: C, 66.24; H, 5.81; N, 7.02. Found: C, 66.62; H, 5.58; N, 6.63.

7k: eluent, ether/pentane 90/10; yellow solid; mp 87 °C; 0.86 g, 38% yield; ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.65 (m, 2H), 3.87 (m, 1H), 4.68 (d, $^2J_{(HH)}$=15.3 Hz, 1H), 5.68 (d, $^2J_{(HH)}$ = 15.3 Hz, 1H), 6.95−7.50 (m, 18H); ^{13}C NMR (250 MHz, $CDCl_3$) δ 37.95 (s), 49.95 (s), 65.27 (s), 123.92−131.24 (s); 129.43, 131.99, 136.27, 137.94, 138.99, 140.05 (s), 167.43, 169.05 (s). Anal. Calcd for $C_{29}H_{23}ClN_2O$: C, 77.24; H, 5.14; N, 6.21. Found: C, 77.49; H, 5.48; N, 5.93.

7l: eluent. pentane/ether 50/50; yellow solid; mp 166 °C; 1.00 g, 42% yield; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.47 (s, 9H), 3,25 (dd, $^2J_{(HH)}$ = 16.9 Hz, $^3J_{(HH)}$ = 7.5 Hz, 1H), 3.43 (dd, $^2J_{(HH)}$ = 16.9 Hz, $^3J_{(HH)}$ = 6.5 Hz, 1H), 4.19 (dd, $^3J_{(HH)}$ = 7.6 Hz, $^3J_{(HH)}$ = 6.5 Hz, 1H), 4.75 (d, $^2J_{(HH)}$ = 15.5 Hz, 1H), 5.60 (d, $^2J_{(HH)}$ = 15.5 Hz, 1H), 6.97−7.43 (m, 13H); ^{13}C NMR (250 MHz, $CDCl_3$) δ 28.14 (s), 37.80 (s), 50.28 (s), 60.62 (s), 80.70 (s), 124.01−131.38 (s), 129.54, 132.11, 136.20, 137.90, 140.31 (s), 167.50, 169.02, 171.30 (s). Anal. Calcd for $C_{28}H_{27}ClN_2O_3$: C, 70.80; H, 5.73; N, 5.90. Found: C, 71.15; H, 6.02; N, 5.41.

7m: eluent, pentane/ether 50/50; pink solid; mp 164 °C; 1.26 g, 67% yield; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.77 (d, $^3J_{(HH)}$ = 6.4 Hz, 3H), 3.81 (q, $^3J_{(HH)}$ = 6.4 Hz, 1H), 4.68 (d, $^2J_{(HH)}$ = 15.5 Hz, 1H), 5.70 (d, $^2J_{(HH)}$ = 15.5 Hz, 1H), 6.99−7.42 (m, 13H); ^{13}C NMR (250 MHz, $CDCl_3$) δ 17.32 (s), 49.82 (s), 58.81 (s), 123.94−131.30 (s), 130.38, 131.07, 136.39, 137.93, 140.20 (s), 167.16, 170.35 (s). Anal. Calcd for $C_{23}H_{19}ClN_2O$: C, 73.69; H, 5.11; N, 7.47. Found: C, 73.19; H, 5.75; N, 7.13.

Procedure for the Preparation of the Supported Phosphonium Salt 3H$^+$. A DCE solution (100 mL) of Merrifield's resin (10 g, 2% cross linked; approximately 1 mequiv/g) and phosphine **4** (3.26 g, 20 mmol) was stirred under reflux for 5 days in order to optimize the functionalization of the resin. After being cooled to room temperature, the polymer was washed several times, first with dichloromethane and then with diethyl ether. The resin **3H**$^+$ was dried under vacuum at 60 °C until it reached a stationary weight. Elemental analyses were in good agreement with a total functionalization of the polymer. Anal. Found: P, 3.9; 1.25 mequiv/g.

Synthesis of 3. The deprotonation of **3H**$^+$ was performed using the procedure described in the literature for **A**[14] and the supported ylide **3** directly used.

Procedure for N-Benzylation of 7a Using 3. A THF solution (20 mL) of **7a** (0.27 g, 1 mmol) was added to a THF suspension of **3** (1.1 g), and the mixture was stirred at room temperature for 1 h. Then, benzylbromide (0.22 g, 1.3 mmol) was added to the suspension, which was stirred overnight. Filtration and evaporation of the solvent under vacuum led to **7d** in 97% yield.

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Supporting Information Available: Tables of crystal and intensity collection data, position and thermal parameters, and interatomic distances and angles for derivative **7k**. This material is available free of charge via the Internet at http://pubs.acs.org.

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