Preparation and Reactivity of Allyl *N*-[(Arylsulfonyl)oxy]carbamates, New Reagents for Electrophilic Transfer of an NHAlloc Group

C. Greck, L. Bischoff, F. Ferreira, and J. P. Genêt*

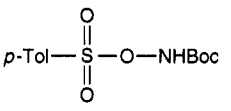
Laboratoire de synthèse organique (U.A. 1381), Ecole Nationale Supérieure de Chimie de Paris, 11 rue Pierre et Marie Curie, 75231 Paris Cédex 05, France

Received April 24, 1995

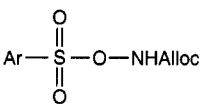
Carbon–nitrogen bonds are usually formed by attack of nucleophilic nitrogen on an electrophilic carbon bearing a leaving group, via an SN_2-type reaction. Since the discovery of the polarity reversal process by Sheverdina and Kocheskov,[1] in combination with the development of new metalation procedures, increased attention has been focused on the development of electrophilic reagents for the amination of carbon nucleophiles.[2] This type of "Umpolung" amination process has also been modified for the construction of chiral amines by the reaction of electrophilic aminating reagents with chiral enolates.[3] More recently, Oppolzer *et al.* have reported a chiral α-chloro-α-nitroso reagent which reacted with prochiral ketone enolates with high enantiofacial differentiation.[4]

N-Protected amines are also important as synthetic intermediates, and new aminating reagents that allow the one step transfer of an N-protected moiety would be of great interest. We recently reported that treatment of various organometallics with the electrophilic aminating agent, metalated *tert*-butyl *N*-(tosyloxy)carbamate, resulted in the formation of amines as their *tert*-butyl carbamates in good to moderate yields.[5] *N*-Boc-3-(4-cyanophenyl)oxaziridine, described by Collet *et al.*, has also been shown to be an effective electrophilic aminating agent.[6] Ricci *et al.* have developed *N,O*-bis(trimethylsilyl)hydroxylamine which upon reaction with high order aryl cuprates delivers the $NHSiMe_3$ moiety to produce, after hydrolysis, the corresponding free aromatic amines.[7] However, the use of acidic conditions for the removal of the *tert*-butyl carbamate (Boc) functionality renders it incompatible for some synthetic applications.[8] Thus, it was desirable to modify the *tert*-butyl *N*-(tosyloxy)-carbamate **1** by replacement of the Boc fragment with the (allyloxy)carbonyl (Alloc) moiety to give the corresponding (allyloxy)carbamate **2a** (Chart 1). The Alloc protecting group is complementary to the Boc protecting group in that it is removed under neutral conditions in the presence of a Pd(0) catalyst[9] and, hence, is compatible with a large variety of functional groups.

Chart 1



1



2a: Ar = *p*-tolyl ($ArSO_2$ = Ts)
2b: Ar = 2,4,6-trimethylphenyl (Mes)

The synthesis of **2a** and **2b** began by reaction of allylchloroformate with hydroxylamine under basic aqueous conditions giving the *N*-[(allyloxy)carbonyl]hydroxylamine **3** in 92% yield. The tosylation of **3** was run under standard conditions to provide **2a** in 81% yield (Scheme 1). The synthesis of **2b** was carried out following the same protocol except for the sulfonylation reaction in which 2-mesitylenesulfonyl chloride was substituted for tosyl chloride to give **2b** in quantitative yield.

Both **2a** and **2b** were isolated as white crystalline solids. Lithium allyl *N*-[(arylsulfonyl)oxy]carbamates **4a** and **4b** were obtained by treatment of **2a** and **2b** with 1 equiv of *n*-butyllithium in anhydrous THF at −78 °C and were used *in situ* for the electrophilic amination. Various organocopper species were tested in the electrophilic amination with both lithiated reagents **4a** and **4b** (Table 1). The reactions were run at −78 °C in the presence of 1.1 equiv of aminating reagent, and the Alloc N-protected amines were typically obtained in up to 68% yield after hydrolysis.

N-Alloc-arylamines **5–10** were produced from the corresponding aryl bromides by a one-pot process consisting of transmetalation of the aryllithium with copper(I) bromide/dimethyl sulfide and subsequent electrophilic amination. The best yields were obtained for arylcopper reagents bearing an electron-donating substituent such as *p*-tolyl or *p*-anisyl. In addition, the *N*-Alloc group could be efficiently transferred to the nucleophilic carbon of a phosphonic ester. Treatment of **4a** and **4b** with α-cupro phosphonate at −78 °C gave the corresponding *N*-Alloc-α-aminophosphonic ester **11**. Aromatic organolithium reagents showed lower reactivity toward electrophilic amination with only 10% of **5** formed upon reaction of **4a** with phenyllithium. No reaction was observed with α-lithio phosphonate. Lithium and copper enolates of acetophenone were also tested without result. Finally, electrophilic amination of N-nucleophiles was performed by treatment of N-methylaniline with 2 equiv of **4a** and **4b** at 80 °C for 18 h to give the *N*-Alloc-protected hydrazine **12** in 57 and 62% yields, respectively.

(1) Sheverdina, N. L.; Kocheskov, Z. *J. Gen. Chem. USSR* **1938**, *8*, 1825.

(2) Reviews: Erdik, E.; Ay, M. *Chem. Rev.* **1989**, *89*, 1947. Mulzer, J.; Altenbach, H. J.; Braun, M.; Krohn, K.; Reissig, H. U. *Organic Synthesis Highlights*; VCH Publishers: Weinheim, 1991; p 45. See also: Gmeiner, P.; Bollinger, B. *Liebigs Ann. Chem.* **1992**, 273. Andreae, S.; Schmitz, E. *Heterocycles* **1994**, *37*, 379. Mitchell, H.; Leblanc, Y. *J. Org. Chem.* **1994**, *59*, 682.

(3) Gennari, C.; Colombo, L.; Bertolini, G. *J. Am. Chem. Soc.* **1986**, *108*, 6394. Evans, D. A.; Britton, T. C.; Dorow, R. L.; Dellaria, J. F. *J. Am. Chem. Soc.* **1986**, *108*, 6395. Trimble, L. A.; Vederas, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 6397. Genêt, J. P.; Jugé, S.; Mallart, S. *Tetrahedron Lett.* **1988**, *29*, 6765. Guanti, G.; Banfi, L.; Narisano, E. *Tetrahedron* **1988**, *44*, 5553. Oppolzer, W.; Tamura, O. *Tetrahedron Lett.* **1990**, *31*, 991. Greck, C.; Bischoff, L.; Ferreira, F.; Pinel, C.; Piveteau, E.; Genêt, J. P. *Synlett* **1993**, 475.

(4) Oppolzer, W.; Tamura, O.; Sundarababu, G.; Signer, M. *J. Am. Chem. Soc.* **1992**, *114*, 5900.

(5) Genêt, J. P.; Mallart, S.; Greck, C.; Piveteau, E. *Tetrahedron Lett.* **1991**, *32*, 2359. Greck, C.; Bischoff, L.; Girard, A.; Hajicek, J.; Genêt, J. P. *Bull. Soc. Chim. Fr.* **1994**, *131*, 429. **1** also reacted with organoboranes to give *N*-Boc-protected primary amines. See: Genêt, J. P.; Hajicek, J.; Bischoff, L.; Greck, C. *Tetrahedron Lett.* **1992**, *33*, 2677.

(6) Vidal, J.; Guy, L.; Stérin, S.; Collet, A. *J. Org. Chem.* **1993**, *58*, 4791. Vidal, J.; Damestoy, S.; Collet, A. *Tetrahedron Lett.* **1995**, *36*, 1439.

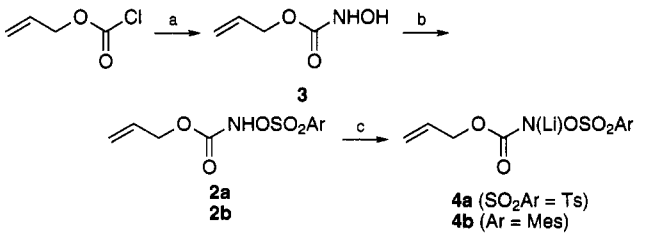
(7) Casarini, A.; Dembech, P.; Lazzari, D.; Marini, E.; Reginato, G.; Ricci, A.; Seconi, G. *J. Org. Chem.* **1993**, *58*, 5620.

(8) Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 2nd ed.; Wiley Interscience: New York, 1991; p 327.

(9) (a) Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 2nd ed.; Wiley Interscience: 1991; p 331. (b) Guibé, F.; Dangles, O.; Balavoine, G.; Loffet, A. *Tetrahedron Lett.* **1989**, *30*, 2641. (c) Hayakawa, Y.; Wakabayashi, S.; Kato, H.; Noyori, R. *J. Am. Chem. Soc.* **1990**, *112*, 1691. (d) Hiemstra, H.; Speckamp, W. N. *Tetrahedron Lett.* **1991**, *32*, 6629. (e) Genêt, J. P.; Blart, E.; Savignac, M.; Paris, J. M. *Tetrahedron Lett.* **1993**, *34*, 4189. (f) Genêt, J. P.; Blart, E.; Savignac, M.; Lemeune, S.; Lemaire-Audoire, S.; Bernard, J. M. *Synlett* **1993**, 680.

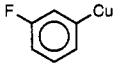
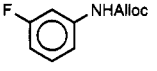
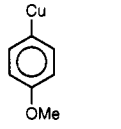
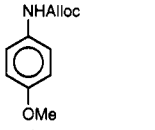
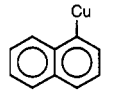
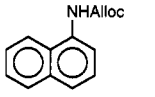
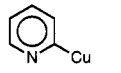
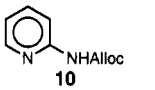
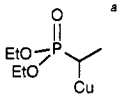
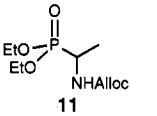
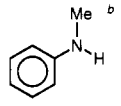
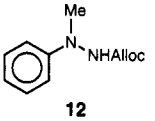
0022-3263/95/1960-7010$09.00/0

Scheme 1[a]



[a] Key: (a) H_2NOH (1 equiv), NaOH, H_2O, 0 °C, 1.5 h; (b) $ArSO_2Cl$ (1 equiv), Et_3N, CH_2Cl_2, 0 °C 15 min then rt; (c) *n*-BuLi, −78 °C, THF.

Table 1. Amination with Lithium Allyl *N*-[(Arylsulfonyl)oxy]carbamates at −78 °C

nucleophiles	time, (h)	% yield with **4a**	% yield with **4b**	carbamates
PhCu	1	51	51	PhNHAlloc (**5**)
p-TolCu	3	65	60	*p*-TolNHAlloc (**6**)
	3	44	36	 **7**
	3	68	52	 **8**
	4	57	37	 **9**
	3	26	10	 **10**
 [a]	4	55	58	 **11**
 [b]	18	57	62	 **12**

[a] Amination with 1.1 equiv of **4a** or **4b** from −78 °C to 0 °C. [b] Amination with 0.5 equiv of **2a** or **2b** at 80 °C.

To our knowledge, this is the first example of direct synthesis of an N_β-Alloc-protected hydrazine from the corresponding amine. A better reactivity was generally observed for the lithiated *N*-(tosyloxy)carbamate reagent **4a**.

Titrated solutions in THF of amination reagents **4a** and **4b** proved to be somewhat unstable upon storage at 5 °C. Production of *N*-Alloc-4-methoxyaniline (**8**) from *p*-anisylcopper and lithium allyl *N*-(tosyloxy)carbamate (**4a**) decreased rapidly from 68% (freshly prepared solution) to 8% after storage of a 0.5 M THF solution for 14 days at 5 °C. One M THF solutions of the corresponding lithium allyl *N*-(mesityloxy)carbamate (**4b**) increased stability with the yield of product **8** falling from an initial 52% to a level of 32% after 14 days of storage at 5 °C. Recently, lithium *tert*-butyl *N*-[(mesitylsulfonyl)oxy]carbamate has been crystallized and observed as its dimer by X-ray crystallography by Boche and co-workers.[10] The authors did not report the X-ray structure of lithium *tert*-butyl *N*-(tosyloxy)carbamate.

Finally, removal of the (allyloxy)carbonyl moiety from allylic carbamates was carried out via Pd(0)-catalyzed allyl transfer to a thiol derivative as an accepting nucleophile.[9f] Thus, treatment of allyl *p*-anisylcarbamate (**8**) and N_β-Alloc-hydrazino-*N*-methylaniline (**12**) with 5% of $Pd(dba)_2$, dppb,[11] and 2-mercaptobenzoic acid (1.1 equiv) at room temperature in anhydrous THF gave the corresponding amino derivatives in near quantitative yields.

In conclusion, we have developed two new reagents for electrophilic amination that are able to directly transfer the NHAlloc moiety to various substrates (C- and N-nucleophiles). The crystalline materials are easily handled, and the lithiated allyl *N*-[(mesitylsulfonyl)oxy]-carbamate **4b** can be stored in THF solutions at 0 °C for several days. Further exploration of the synthetic potential of these reagents is in progress.

Experimental Section

Allyl *N*-(Tosyloxy)carbamate (2a). To a stirred aqueous solution (50 mL) of hydroxylamine hydrochloride (6.95 g, 0.1 mol) and NaOH (6 g) at 0 °C was added dropwise allyl chloroformate (5.2 mL, 50 mmol). The solution was stirred for 1.5 h. The pH was adjusted to 1 with 12 N HCl, and the resulting mixture was extracted with Et_2O. The organic layer was dried over $MgSO_4$ and evaporated *in vacuo*. The residue was distilled under reduced pressure (bp 160 °C/1 mmHg) to afford *N*-[(allyloxy)-carbonyl]hydroxylamine (**3**) (5.4 g) as a colorless oil which was dissolved in benzene (100 mL) and CH_2Cl_2 (30 mL). Tosyl chloride (8.75 g, 46 mmol) was added in one portion, the solution was cooled at 0 °C, and Et_3N (6.35 mL, 46 mmol) was added dropwise. An instantaneous white precipitate of Et_3N−HCl was observed. The reaction mixture was stirred at rt for 3.5 h. Water (70 mL) was added. The aqueous layer was extracted with Et_2O. The organic layer was washed with brine, dried over $MgSO_4$, and evaporated *in vacuo* to an oily residue which was purified by column chromatography on silica gel (cyclohexane/ethyl acetate 1/1) to give **2a** as a white solid (10.1 g, 74%): mp 62 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.86 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.3 Hz, 2H), 5.72 (ddt, J = 16, 10.9, 5.7 Hz, 1H), 5.21 (d, J = 16 Hz, 1H), 5.19 (d, J = 10.9 Hz, 1H), 4.48 (d, J = 5.7 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 155.3, 146.1, 130.8, 130.1, 129.7, 129.4, 119, 67.3, 21.7; IR (CH_2Cl_2, cm^{-1}) 3338 (s), 3053 (s), 1774 (s), 1739 (s), 1595 (s), 1380 (s), 740 (s), 705 (s). Anal. Calcd for $C_{11}H_{13}O_5NS$: C, 48.71; H, 4.83; N, 5.16. Found: C, 48.88; H, 4.80; N, 5.21.

Allyl *N*-[(Mesitylsulfonyl)oxy]carbamate (2b). **2b** was prepared from hydroxylamine hydrochloride as described as above for the preparation of **2a**, using mesityl chloride (10 g, 46 mmol). After chromatography on silica gel, **2b** was isolated as a white solid (13.7 g, 92%): mp 100 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 8.23 (s, 1H), 6.97 (s, 2H), 5.73 (ddt, J = 17.2, 10.1, 5.8 Hz, 1H), 5.19 (ddd, J = 17.2, 1.3, 1.3 Hz, 1H), 5.18 (ddd, J = 10.1, 1.3, 1.3 Hz, 1H), 4.48 (ddd, J = 5.8, 1.3, 1.3 Hz, 2H), 2.65 (s, 6H), 2.31 (s, 3H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 155.4, 144.5, 141.8, 131.6, 130.8, 128.1, 119, 67.2, 22.8, 21; IR (CH_2Cl_2, cm^{-1}) 3280 (m), 3025 (s), 1775 (s), 1740 (s), 1600 (s), 854 (s), 705 (s). Anal. Calcd for $C_{13}H_{17}O_5NS$: C, 52.16; H, 5.72; N, 4.68. Found: C, 52.35; H, 5.79; N, 4.71.

General Procedure for Electrophilic Amination. Under an argon atmosphere, a solution of aryllithium was prepared at −78 °C by addition of a 2.5 M solution of *n*-BuLi (0.4 mL, 1 mmol) in hexane to a solution of the corresponding aryl bromide (1 mmol) in THF (5 mL). After 30 min, the solution was added to a suspension of CuBr·Me_2S (0.204 g, 1 mmol) in THF (2 mL) at −78 °C. The reaction mixture was stirred for 1 h between −78 °C and −60 °C and cooled at −78 °C. A solution of lithium allyl *N*-[(arylsulfonyl)oxy]carbamate (1 mmol) in THF was added dropwise, and the reaction mixture was stirred at −78 °C. The

(10) Boche, G.; Boie, C.; Bosold, F.; Harms, K.; Marsch, M. *Angew. Chem.* **1994**, *33*, 115.

(11) $Pd(dba)_2$: palladium(0) dibenzylideneacetone. dppb: 1,4-bis-(diphenylphosphino)butane.

reaction mixture was hydrolyzed with a saturated aqueous solution of NH_4Cl/NH_3 = 9/1 (5 mL). The aqueous phase was extracted with diethyl ether, and the combined organic layers were collected, washed with brine, dried over $MgSO_4$, and evaporated *in vacuo*. The residue was purified by flash chromatography (ethyl acetate/cyclohexane = 1/4) to afford *N*-Alloc aryl primary amines.

***N*-Phenyl allylcarbamate (5)**: IR ν_{max} 3419, 3326, 3053, 2983, 1717, 1600, 1526, 1218, 703 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.5–7.2 (m, 4H), 7.08 (tt, J = 7.1, 1.4 Hz, 1H), 6.88 (broad s, 1H), 5.99 (ddt, J = 17.2, 10.3, 5.7 Hz, 1H), 5.37 (ddt, J = 17.2, 1.4, 1.4 Hz, 1H), 5.28 (ddt, J = 10.3, 1.4, 1.2 Hz), 4.68 (ddd, J = 5.7, 1.4, 1.2 Hz, 2H). Anal. Calcd for $C_{10}H_{11}O_2N$: C, 67.78; H, 6.26; N, 7.90. Found: C, 67.71; H, 6.39; N, 7.78.

***N*-(4-Methylphenyl) allylcarbamate (6)**: IR ν_{max} 3423, 3330, 3052, 2984, 1727, 1592, 1523, 1264, 853 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.31 (d, J = 8.3 Hz, 2H), 7.11 (d, J = 8.3 Hz, 2H), 6.93 (broad s, 1H), 5.98 (ddt, J = 17.2, 10.4, 5.7 Hz, 1H), 5.37 (ddt, J = 17.2, 1.4, 1.4 Hz, 1H), 5.27 (ddt, J = 10.4, 1.4, 1.2 Hz, 1H), 4.68 (ddd, J = 5.7, 1.4, 1.2 Hz, 2H), 2.32 (s, 3H). Anal. Calcd for $C_{11}H_{13}O_2N$: C, 69.10; H, 6.85; N, 7.32. Found: C, 69.25; H, 6.93; N, 7.31.

***N*-(3-Fluorophenyl) allylcarbamate (7)**: IR ν_{max} 3319, 3089, 2951, 1707, 1643, 1604, 1544, 1266, 1220, 862, 769, 680 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.37–7 (m, 4H), 6.75 (tdd, J = 8.3, 2.5, 1 Hz, 1H), 5.96 (ddt, J = 17.2, 10.4, 5.7 Hz, 1H), 5.37 (ddt, J = 17.2, 1.4, 1.4 Hz, 1H), 5.28 (ddt, J = 10.4, 1.4, 1.2 Hz, 1H), 4.67 (ddd, J = 5.7, 1.4, 1.2 Hz, 2H). Anal. Calcd for $C_{10}H_{10}FO_2N$: C, 61.53; H, 5.16; N, 7.17. Found: C, 61.54; H, 5.32; N, 7.10.

***N*-(4-Methoxyphenyl) allylcarbamate (8)**: IR ν_{max} 3421, 3325, 3052, 2983, 2910, 1723, 1644, 1596, 1511, 1264, 1219, 828 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.29 (d, J = 9.2 Hz, 2H), 6.89 (broad s, 1H), 6.84 (d, J = 9.2 Hz, 2H), 5.96 (ddt, J = 17.2, 10.4, 5.6 Hz, 1H), 5.34 (ddt, J = 17.2, 1.5, 1.5 Hz, 1H), 5.24 (ddt, J = 10.4, 1.5, 1.4 Hz, 1H), 4.65 (ddd, J = 5.6, 1.5, 1.4 Hz, 2H), 3.77 (s, 3H). Anal. Calcd for $C_{11}H_{13}O_3N$: C, 63.76; H, 6.32; N, 6.76. Found: C, 64.24; H, 6.33; N, 6.74.

***N*-(2-Naphthyl) allylcarbamate (9)**: IR ν_{max} 3420, 3052, 2984, 1729, 1596, 1530, 1343, 1264 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.9–7.4 (m, 7H), 7.07 (broad s, 1H), 6.03 (ddt, J = 17.2, 10.4, 5.7 Hz, 1H), 5.4 (dd, J = 17.2, 1 Hz, 1H), 5.3 (dd, J = 10.4, 1.2 Hz, 1H), 4.74 (ddd, J = 5.7, 1.2, 1 Hz, 2H). Anal. Calcd for $C_{14}H_{13}O_2N$: C, 73.99; H, 5.76; N, 6.16. Found: C, 74.01; H, 5.85; N, 6.09.

***N*-(2-Pyridyl) Allylcarbamate (10)**: IR ν_{max} 3408, 3051, 2984, 1728, 1585, 1537, 1515, 1262, 856 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 9.32 (broad s, 1H), 8.33 (ddd, J = 5, 1.9, 1 Hz 1H), 8.11 (d, J = 8.5 Hz 1H), 7.7 (ddd, J = 8.5, 7.3, 1.9 Hz, 1H), 6.99 (ddd, J = 7.3, 5, 1 Hz, 1H), 6 (ddt, J = 17.2, 10.4, 5.7 Hz, 1H), 5.39 (ddt, J = 17.2, 1.4, 1.4 Hz, 1H), 5.29 (ddt, J = 10.4, 1.4, 1.3 Hz, 1H), 4.72 (ddd, J = 5.7, 1.4, 1.3 Hz, 2H). Anal. Calcd for $C_9H_{10}O_2N_2$: C, 60.66; H, 5.66; N, 15.72. Found: C, 60.63; H, 5.76; N, 15.66.

Diethyl [*N*-[(Allyloxy)carbonyl]-1-aminoethyl]phosphonate (11). *n*-Butyllithium (0.4 ml, 1 mmol, 2.5 M solution in hexane) was added dropwise to a solution of diethyl ethylphosphonate (0.162 g, 0.98 mmol) in THF (2 mL) at −78 °C. The solution was stirred for 30 min. Copper(I) iodide (0.186 g, 0.98 mmol) was added, and the reaction mixture warmed to −30 °C until the complete dissolution of the salt was observed. Lithium allyl *N*-[(arylsulfonyl)oxy]carbamate (1 mmol) in THF was added dropwise to the solution of α-cuprophosphonate at −78 °C. The reaction mixture was warmed to 0 °C and stirred for 4 h. The reaction mixture was hydrolyzed with a saturated aqueous solution of NH_4Cl/NH_3 = 9/1 (5 mL). The aqueous phase was extracted with diethyl ether. The combined organic layers were collected, washed with brine, dried over $MgSO_4$, and evaporated *in vacuo*. The residue was purified by flash chromatography (CH_2Cl_2/methanol 95/5) to afford **11** as an oil (0.155 g, 58%): IR ν_{max} 3430, 3250, 3050, 2985, 1730, 1645, 1540, 1250, 1230, 970 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.88 (ddt, J = 17.2, 10.4, 5.6 Hz, 1H), 5.25 (dd, J = 17.2, 1.5 Hz, 1H), 5.16 (dd, J = 10.4, 1.3 Hz, 1H), 4.53 (d, J = 5.6 Hz, 2H), 4.2–4 (m, 6H), 1.38 (d, J = 7.3 Hz, 3H), 1.28 (t, J = 7.1 Hz, 6H). Anal. Calcd for $C_{10}H_{20}O_5NP$: C, 45.28; H, 7.60; N, 5.28. Found: C 45.20; H, 7.61; N, 5.23.

[*N*-β-[(Alloxy)carbonyl]hydrazino]methylphenylamine (12). A solution of *N*-methylaniline (0.32 g, 3 mmol) and allyl *N*-[(arylsulfonyl)oxy]carbamate (1.5 mmol) in dry toluene (7.5 ml) was heated at 80 °C for 18 h. The reaction mixture was filtrated through Celite, and the solvent was evaporated *in vacuo*. The residue was purified by column chromatography on silica gel (cyclohexane/ethyl acetate 9/1) to give **12** as an oil (0.19 g, 62%): IR ν_{max} 3279, 3063, 2947, 2880, 1719, 1643, 1599, 1254, 1219, 750, 691 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.24 (t, J = 6.7 Hz, 2H), 6.9–6.8 (m, 3H), 6.6 (broad s, 1H), 5.92 (m, 1H), 5.4–5.25 (m, 2H); 4.65 (d, J = 5.6 Hz, 2H), 3.2 (s, 3H). Anal. Calcd for $C_{11}H_{14}O_2N_2$: C, 64.06; H, 6.84; N, 13.58. Found: C, 64.02; H, 6.87; N, 13.57.

JO9507606