the growing carbocation even when employed at a very high concentration. This finding accounts for the ineffectiveness of the monomer and polymer of IBVE in stabilizing the growing carbocations, although both ethereal compounds are inevitably and abundantly present in the polymerization solution. The pendant ether oxygens of poly(IBVE), on one hand, carry much bulkier substituents than that of iPr_2O does, and thereby cannot interact effectively with the cationic active site. IBVE monomer, on the other hand, would be less basic as an ether than iPr_2O, because the nonbonded electron pairs of its oxygen are conjugated with the adjacent carbon–carbon double bond. Thus there is a suitable basicity range of ethers for achieving living polymerization of vinyl ethers, which range would depend on both electric and steric factors.

Acknowledgment. We thank Dr. M. Sawamoto of this laboratory for his helpful discussions. We also thank the Ministry of Education, Science and Culture of Japan for financial support (Grant-in-Aid for Scientific Research, No. 63470099).

Registry No. 1, 114043-46-8; IBVE (homopolymer), 9003-44-5; EtOEt, 60-29-7; $EtAlCl_2$, 563-43-9; H_2O, 7732-18-5; CH_3CO_2H, 64-19-7; 1,4-dioxane, 123-91-1; tetrahydrofuran, 109-99-9.

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Blocked Amine Functional Initiator for Anionic Polymerization

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Received July 13, 1988; Revised Manuscript Received February 15, 1989

ABSTRACT: Preparation and utilization of a new blocked amine functional initiator for anionic polymerization is reported. This initiator is prepared from the quantitative reaction of *sec*-butyllithium with *p*-(*N*,*N*-bis(trimethylsilyl)amino)styrene under very specific, controlled conditions. The carbanion initiator formed, unlike most blocked functional anionic initiators, is soluble in nonpolar solvents. This nonpolar solubility opens up the possibility of preparing new well-defined, end-reactive polymers, such as polysiloxanes and high *cis*-1,4-polydienes. This new initiator was used to prepare novel semitelechelic and telechelic linear poly(dimethylsiloxane)s of controlled molecular weights, narrow molecular weight distributions, and theoretical functionalities. The end-functional polymers were characterized by gel permeation chromatography, infrared spectroscopy, vapor-phase osmometry, and nuclear magnetic resonance spectroscopy.

Introduction

The field of end-reactive polymer synthesis has been active for more than 20 years. Several methods have been used to prepare end-reactive polymers including anionic,[1-10] radical,[11-14] cationic,[15-21] and group-transfer polymerizations.[22] To date, use of "living" anionic polymerization has been the most generally successful method for the preparation of end-reactive polymers with theoretical functionalities, narrow molecular weight distributions, and controlled molecular weights.[8]

End-reactive polymers can be prepared via living anionic polymerization by two primary methods.[8] To prepare telechelic polymers, one can use multifunctional anionic initiators followed by functional termination[1-5,8] or one can utilize blocked functional anionic initiators followed by multifunctional termination.[6-10] The latter method, pioneered by Schulz, has a distinct advantage over the former method. Utilization of blocked functional anionic initiators alleviates the frequently encountered problem of gelation of multiple living ends found in anionic polymerizations with multifunctional initiators.[8] This gelation problem is particularly troublesome when performing polymerizations in nonpolar solvents; however, in many cases, nonpolar solvents are the solvents of choice to achieve well-defined polymer microstructure.

Presently available blocked functional anionic initiators have, with varied levels of success, been used to prepare well-defined polymers with hydroxyl, carboxylic acid, and amine end functionalities.[6-10] However, use of the blocked functional anionic initiator method has been limited due to the insolubility in nonpolar solvents of currently reported blocked functional anionic initiators.[8] This limited initiator solubility prevents their use in the preparation of high 1,4- and *cis*-1,4-polydienes and in the preparation of well-defined telechelic poly(dimethylsiloxane)s. Only a blocked hydroxyl functional anionic initiator has shown any solubility in benzene;[10] however, this initiator is not soluble in hexanes,[6] which limits its use to prepare polydienes with the highest cis-1,4 content.

This paper will outline the preparation and use of a new blocked amine functional anionic initiator that is soluble in nonpolar solvents. The preparation of well-defined, end-reactive, amine functional poly(dimethylsiloxane)s utilizing this new initiator will be reported.

Experimental Section

Materials. *p*-Aminostyrene (PAS, 1) was obtained from Polysciences and vacuum distilled from calcium hydride. Chlorotrimethylsilane and dichlorodimethylsilane were obtained from Aldrich, distilled, and titrated prior to use. *N*,*O*-Bis(trimethylsilyl)acetamide (BSA) was obtained from Sigma and used as

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received. *n*-Butyllithium and *sec*-butyllithium were obtained from Aldrich and standardized as described in the Measurements section. Ethylmagnesium bromide was obtained from Aldrich and used as received. Molecular sieves, 3 Å, were obtained from MCB, soaked and washed with tetrahydrofuran (THF) for 5 days, and vacuum dried for 2 days at 140 °C. Ionol, 2,6-di-*tert*-butyl-4-methylphenol, was obtained from Shell and recrystallized from Skelly F. Diphenylacetic acid was obtained from Aldrich and sublimed prior to use. Hexamethylcyclotrisiloxane (D_3) was obtained from Petrarch, sublimed into a flask containing activated molecular sieves, and dispensed as a solution in dry benzene. Methyl violet and perchloric acid (70%) were obtained from Eastman Kodak and used as received.

Hexane (HPLC grade) was obtained from Fisher and distilled from calcium hydride into a flask containing molecular sieves. Benzene and cyclohexane were obtained from Fisher (spectroscopic grade), stirred over sulfuric acid, washed and neutralized with aqueous sodium hydroxide and water, distilled from phosphorus pentoxide, refluxed over sodium and benzophenone, and distilled into a flask containing Molecular Sieves. THF was obtained from Fisher (spectroscopic grade), refluxed over sodium and benzophenone, and distilled into a flask containing molecular sieves. Hexamethylphosphoramide (HMPA) was obtained from Aldrich, stirred, fractionally vacuum distilled from calcium oxide into sodium, refluxed over sodium for 2 days, and vacuum distilled into a flask containing molecular sieves. Acetic acid was obtained from Fisher and distilled prior to use.

Preparation of *p*-(*N*,*N*-Bis(trimethylsilyl)amino)styrene (3). Into a 100-mL, round-bottom flask containing a small amount of Ionol was distilled 3.0 g (0.025 mol) of PAS. Under argon, to this flask was added 25 mL of THF and 10 mL (0.049 mol) of BSA. The reaction mixture was allowed to stir for 3 days at room temperature. The N-monosilylated PAS (2) was isolated by vacuum distillation (0.01 mmHg) at 59–63 °C (97% yield) after the THF, excess BSA, and the (trimethylsilyl)acetamide side product were removed under vacuum. The product, a clear, colorless oil, exhibited an ^{1}H NMR spectrum identical with that reported for *N*-(trimethylsilyl) PAS (2).[23] Introduction of the second trimethylsilyl group according to the method of Yamaguchi et al.[23] gave *N*,*N*-bis(trimethylsilyl) PAS (3) as a colorless oil in 81% overall yield from PAS. The ^{1}H NMR spectrum of the product was identical with that previously reported.[23]

Reactions of Alkyllithiums with *p*-(*N*,*N*-Bis(trimethylsilyl)amino)styrene (3). Generation of the Initiator. To a clean, dry, argon-filled flask at room temperature was added 7 mL of benzene, 9.3 mL of *sec*-butyllithium (0.00023 mol in cyclohexane), and then 3.7 mL of 3 (0.00023 mol in benzene). The reaction mixture slowly became colored until an orange/red color persisted. The reaction proceeded for 1.5 h, at which time it was terminated with dilute acetic acid. The termination with dilute acetic acid was a titration for living ends, which along with gas chromatography and NMR data indicated that the desired initiator species (DP = 1) was generated.

Polymerization of D_3 with the Blocked Amine Functional Anionic Initiator. To a clean, dry, argon-filled flask at room temperature was added 70 mL of benzene, 1.32 mL of *sec*-butyllithium (0.00186 mol in cyclohexane), and then 3.76 mL of 3 (0.00186 mol in benzene). After 1.2 h, the orange/red color indicated that the initiator was formed. Then 1.0 g of D_3 as a solution in benzene, 2 mL, was added, followed by 1.0 mL of HMPA. Only after addition of HMPA did the characteristic color of the initiator immediately fade to the colorless appearance of the propagating silanolate. After 1.5 h, 1.0 mL of the reaction was removed and terminated by 1.5 equiv of chlorotrimethylsilane for use in gel permeation chromatography analysis; at the same time, 0.46 mL (0.00095 mol in benzene) of dichlorodimethylsilane was added to form the blocked telechelic polymer. The coupling reaction was allowed to proceed for 2 days at room temperature under argon, at which time the polymer was ready for unblocking of the amine functionality.

Unblocking of the Telechelic Blocked Amine Functional Poly(dimethylsiloxane). After infrared spectroscopic analysis, 10 mL of 2 N aqueous HCl was added to the colorless solution containing the telechelic blocked amine functional poly(dimethylsiloxane). After 30 min, the now cloudy reaction mixture was investigated by infrared spectroscopy to ensure total unblocking had occurred. Then the colorless solution was transferred to a separatory funnel, neutralized and washed with dilute aqueous sodium hydroxide and water, and filtered into a round-bottom flask. Removal of the solvent via rotary evaporation left an oily polymer that was dried under vacuum 65 h at 65 °C, yielding 1.23 g (98%) of the product. The resulting polymer was investigated by gel permeation chromatography, NMR, qualitative and quantitative infrared spectroscopy, and vapor-phase osmometry to determine its polydispersity, molecular weight, and functionality.

Measurements. Titrations for living end concentration in the reactions of alkyllithiums with *p*-(*N*,*N*-bis(trimethylsilyl)-amino)styrene were performed with known amounts of dilute aqueous acetic acid in benzene and are based upon the disappearance of the characteristic styrene anion color.

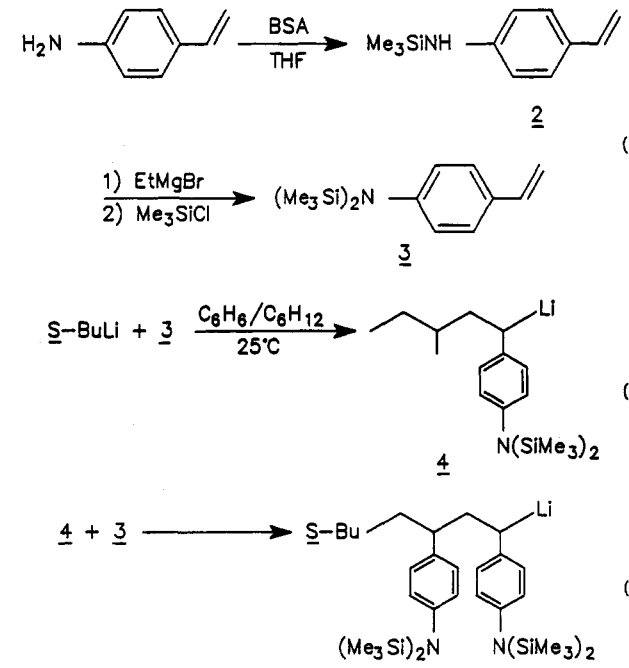
End-group analysis for the concentration of aromatic amine in the poly(dimethylsiloxane) polymers was performed by nonaqueous titrations as reported by Schulz[7] and by quantitative infrared analysis of chloroform solutions using the 1600-cm^{-1} phenyl ring breathing peak. Calibration was based on a Beer's law plot of *p*-*n*-butylaniline.

Gas chromatography was performed on a Hewlett-Packard 5790A with an OV101 column, flame ionization detector, and helium carrier gas. Infrared spectroscopy was performed on a Perkin-Elmer 1420 spectrophotometer. NMR was performed on a T60 or Varian EM-390 spectrometer. Vapor-phase osmometry was performed on a Knauer osmometer in chloroform at 37 °C with benzil as the standard. Gel permeation chromatography was performed on a Waters chromatograph in THF using a 50-, 10^3-, 10^4-, and 10^5-Å Styragel column set.

Alkyllithiums were standardized for total base and total alkyllithium by the method of Kofron[24] utilizing diphenylacetic acid in THF.

Results and Discussion

Synthesis of the blocked functional initiator is shown in eq 1 and 2. Initial attempts to prepare the mono(trimethylsilyl) PAS by reflux with hexamethyldisilazane in accordance with the previous report[23] failed due to the



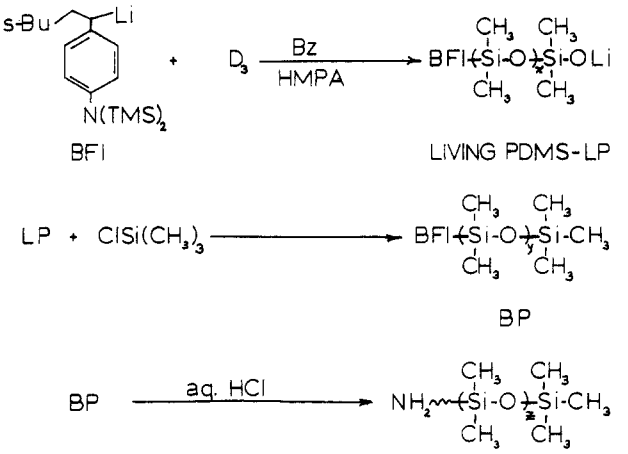
formation of polymeric species. Silylation of hydroxyl, amine, and carboxylic acid functions under mild conditions has been reported utilizing a number of silylating agents.[24-26] BSA was chosen to monosilylate the PAS due to a report that amines could be monosilylated by BSA in THF or dimethylacetamide at room temperature.[26] Product structure was verified by NMR and infrared spectroscopy,[23] and gas chromatography indicated the

Table I
Reaction Conditions and Results of the Reaction of *p*-(*N*,*N*-Bis(trimethylsilyl)amino)styrene with Alkyllithiums

reaction	alkyllithium	solvent	temp, °C	result[a]
1	*n*-BuLi	bz[b]	25	olig[j]
2	*n*-BuLi	bz/HMPA[c]	25	olig
3	*n*-BuLi	bz/THF[d]	25	olig
4	*n*-BuLi	bz/THF[d]	−78	olig[e]
5	*n*-BuLi	bz/THF[d]	5	olig[e]
6	*n*-BuLi	bz/THF[d]	25	olig[e]
7	*n*-BuLi	bz/THF[f]	25	olig[e]
8	*n*-BuLi	bz/THF[g]	25	olig[e]
9	*n*-BuLi	bz/THF[h]	25	olig[e]
10	*s*-BuLi	bz	25	DP = 1[i]
11	*s*-BuLi	bz/THF	25	olig[e]
12	*s*-BuLi	bz	25	DP = 1[i]

[a] The reported results are based on titration for living end concentration, gas chromatography, and NMR data. [b] bz is benzene. [c] HMPA was used at 2.5% by volume total solvent. [d] THF was used at 45% by volume total solvent. [e] Although mostly oligomer was formed, the reaction did take on a highly colored appearance indicative of styryl anion generation. [f] THF was used a 5% by volume total solvent. [g] THF was used at 14% by volume total solvent. [h] THF was used at 33% by volume total solvent. [i] The desired product was generated. [j] olig is oligomer.

Scheme I
Polymerization and Unblocking Scheme for the Preparation of Semitelechelic Poly(dimethylsiloxane) Utilizing the New Blocked Amine Functional Anionic Initiator[a]



[a] The living polymerization is commenced and terminated with chlorotrimethylsilane, and the amine functionality is unblocked to form the desired material.

product was pure. Transformation of this intermediate to (*N*,*N*-bis(trimethylsilyl))acetamide by the method of Yamaguchi et al.[23] gave an overall yield of 81% (eq 1).

The key step in the preparation of the new blocked amine functional anionic initiator (4) was the generation of the anion by a clean, quantitative addition of an alkyllithium reagent quantitatively to *p*-(*N*,*N*-bis(trimethylsilyl)amino)styrene, without subsequent reaction of the initiator with additional 3 (eq 2 and 3).

Table I shows the many conditions under which *p*-(*N*,*N*-bis(trimethylsilyl)amino)styrene was added to an equimolar amount of alkyllithium. As can be seen, only the addition of *p*-(*N*,*N*-bis(trimethylsilyl)amino)styrene to *sec*-butyllithium under totally nonpolar conditions resulted in the generation of the desired initiator. In no case was the desired 1-deg polymerization achieved with *n*-butyllithium or in the presence of any polar promoter. Gas chromatography clearly revealed the absence of the protonalysis product from 4. In most cases, no gas chromatography volatiles other than solvent were observed. Reactions 10 and 12 yielded, after acetic acid quench, a single gas chromatography fraction which exhibited a ^{1}H NMR spectrum in accord with that expected for 1-(*p*-(bis(trimethylsilyl)amino)phenyl)-4-methylhexane. Choice of the more reactive *sec*-butyllithium increases the rate of the desired reaction 2 without affecting that of side reaction 3. The effect of polar promoters may be to "activate" all alkyllithiums in solution and to decrease the rate ratio of eq 2 to eq 3.

The literature has stated mixed results in efforts to prepare nonpolar-solvent-soluble difunctional anionic initiators via the reaction of alkyllithiums with divinyl- and diisopropenylbenzenes. Rempp[29] has reported the successful generation of a difunctional initiator by the addition *m*-diisopropenylbenzene to 2 equiv of *sec*-butyllithium; however, Cameron[28] disputes this result. Cameron added the alkyllithium to the diisopropenylbenzene, which encourages the oligomerization of the diisopropenyl compounds that he observed. Cameron suggests that gel permeation chromatography be used in the analysis of any such reactions to observe whether any oligomerization has taken place.

Scheme I shows our strategy for the preparation of semitelechelic amine functional poly(dimethylsiloxane) polymers via living anionic polymerization. It has been shown over the last 15 years that low polydispersity, controlled molecular weight poly(dimethylsiloxane)s can be prepared without cyclic byproducts by using living anionic polymerization techniques.[30-32] This can only be accomplished in nonpolar reaction media and with traces of a promoter. HMPA was used in this case, although other promoters like THF and DMSO can also be used. In our reaction, addition of D_3 to the initiator solution does not cause the orange/red color of the reaction medium to change. Only upon addition of HMPA does the initiator color vanish and polymerization commence. By use of this method, several polymers of theoretical molecular weights of up to 6000 were prepared with polydispersities of 1.07–1.32. Under no circumstances were lower molecular weight oligimers or bimodal distributions encountered.

The end-blocked poly(dimethylsiloxane)s can be unblocked easily by treatment with dilute aqueous hydrochloric acid, as shown in Scheme I. This unblocking reaction is easily followed by observing changes in infrared spectra as shown in Figures 1 and 2. In addition to the expected peaks from the siloxane polymer at 2960, 1260, 1000–1100, and 800 cm^{-1}, the blocked polymer exhibits no N–H stretching absorption at 3350 and 3450 cm^{-1}; however, the silicon–nitrogen stretch appears at 931 cm^{-1}. In the unblocked polymer spectrum, the 931-cm^{-1} peak is absent, while the 3350- and 3450-cm^{-1} peaks indicative of free primary amine appear. Unblocking of the end function of the siloxane polymers does not degrade the polymer, as can be seen in Figure 3, showing gel permeation chromatography results for blocked and unblocked polymers.

Table II shows the results of the synthesis of end-reactive poly(dimethylsiloxane) materials. As can readily be seen, the results show that low polydispersity, controlled molecular weight poly(dimethylsiloxane)s of theoretical functionalities can be prepared by the methods outlined in this article. The preparations of telechelic star poly(dimethylsiloxane)s utilizing this new method are reported in the following paper in this issue.

This work has several significant implications. Due to the favorable solubility characteristics of this new blocked amine functional anionic initiator, the possibility of preparing amine telechelic high 1,4 and high cis-1,4 linear- and star-type polydienes now seems reasonable. Additionally,

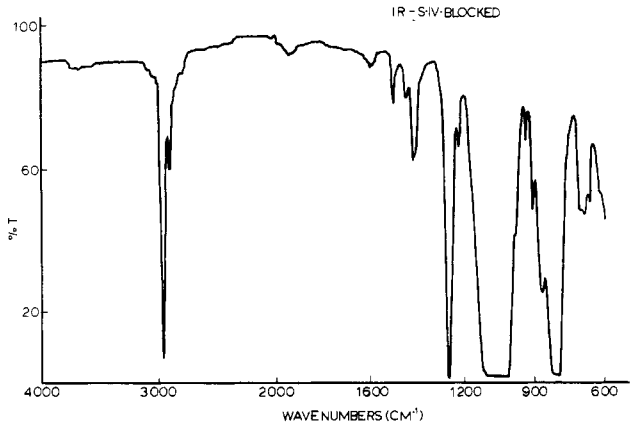


Figure 1. Infrared spectrum of a blocked poly(dimethylsiloxane) film. Typical siloxane absorptions appear at 2960, 1260, 1000–1100, and 800 cm^{-1} along with aromatic ring stretching of the blocked initiator at 1500 and 1600 cm^{-1}. The absence of primary amine absorptions and the presence of a sharp band for the Si–N stretch at 931 cm^{-1} indicates the presence of the blocking group.

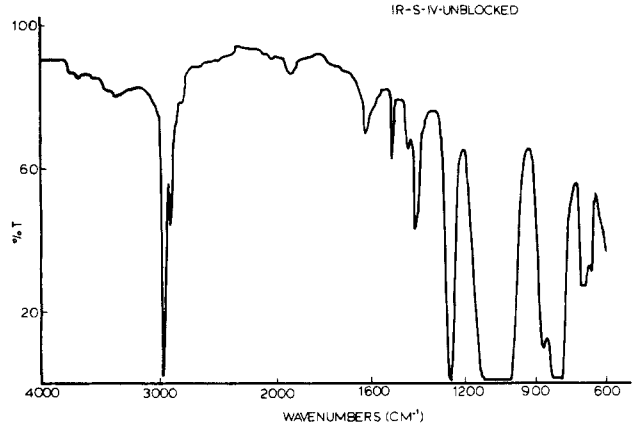


Figure 2. Infrared spectrum of an unblocked poly(dimethylsiloxane) film. Deblocking led to the appearance of free primary amine peaks at 3350 and 3450 cm^{-1} and the disappearance of the Si–N stretch formally at 931 cm^{-1}.

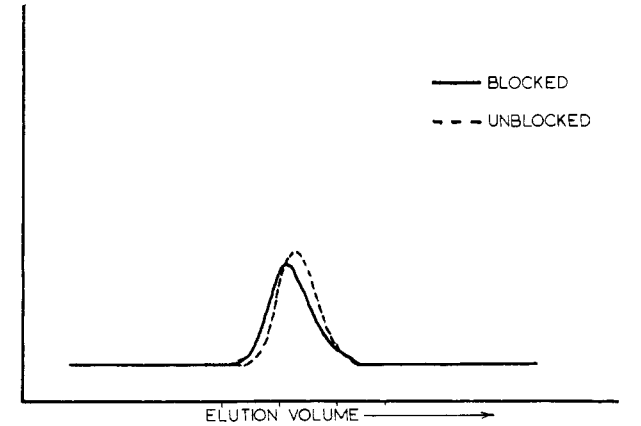


Figure 3. Gel permeation chromatography traces from a blocked poly(dimethylsiloxane) and its deblocked product. No degradation of the parent blocked polymer is observable. Additionally, the resulting polymers show a unimodal distribution, low polydispersity, and no evidence for the formation of lower molecular weight oligimers.

it should be possible to prepare hexane-soluble blocked hydroxyl functional anionic initiators by reacting silylated *p*-hydroxylstyrene with alkyllithiums. Furthermore, utilization of this work should assist in the expanding efforts of many groups to prepare increasingly well-defined polymeric materials.

Table II
Molecular Weights, Functionality, and Polydispersity of Telechelic Siloxanes

polymer	M_n(theo)[a]	M_n(found)[b]	functionality[c]	M_w/M_n[d]
II		6000	0.97	1.26
III		780	0.94	1.14
IV	1500	1600	1.9	1.32

[a] Theoretical M_n based on (monomer)/(initiator) ratio. [b] M_n found via vapor-phase osmometry, chloroform at 37 °C. [c] Functionality found via infrared spectroscopy of 1600-cm^{-1} phenyl ring vibration combined with M_n data. [d] M_w/M_n based on polystyrene calibrated GPC in THF with no correction for broadening.

Acknowledgment. This research was supported in part by a grant from the Materials Research Laboratory, University of Massachusetts.

Registry No. 2, 85968-77-0; 3, 85967-70-0; 4, 120496-28-8; *s*-BuLi, 598-30-1; $H_2NC_6H_4$-*p*-CH=CH_2, 1520-21-4.

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