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Oligomeric Benzylsulfonium Salts: Facile Benzylation via High-Load ROMP Reagents

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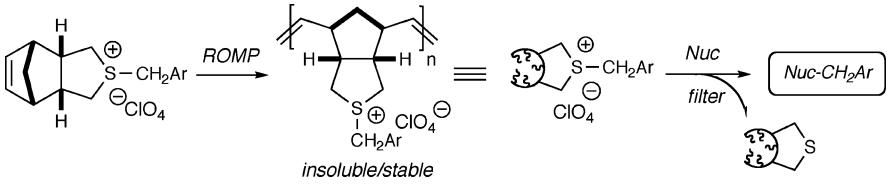
Received September 30, 2006



The development of high-load, oligomeric benzylsulfonium salts, generated via ring-opening metathesis polymerization, and their utility in facile benzylations of various nucleophiles is reported. These oligomeric sulfonium salts exist as free-flowing powders and are stable at room temperature. After the benzylation event, purification is attained via simple dry load/filtration, followed by solvent removal to deliver products in excellent yield and purity.

Introduction

The recent growth of high-throughput screening for biologically active agents has placed a huge demand on efficient generation of quality libraries comprised of novel structures. This presents several challenges: increasing the speed in which molecules can be made, ensuring the integrity of libraries produced, and optimizing novelty of chemical space mapped by each library. Traditional solid-phase organic synthesis (SPOS) is undoubtedly a primary tool that has been utilized to address this demand. While SPOS has its merits for offering a direct purification technique and is highly amenable to automation, it also presents limitations, such as low load levels of reactive functionality in traditional solid-phase resins (typically 1 mmol/g), poor reaction kinetics due to heterogeneity issues, and long validation times in converting solution-phase protocols to SPOS protocols.

One powerful approach to address these limitations is to ultimately place the scaffold in solution while immobilizing the reagent. In the context of this paradigm shift an array of polymer-bound reagents and scavengers[1] have appeared, effectively eliminating or circumventing the need for chromatographic purifications, which typically is a bottleneck in synthetic sequences.[2] Recent successes in multistep total synthesis, using exclusively immobilized reagents and scavengers, whereby filtration is the sole purification protocol, are a testament to the power of this approach that integrates synthesis and purification. Despite huge advances in this area, limitations in nonlinear reaction kinetics, low resin-load capacities, means of distributing reagents, and facile access to designer resins continue to warrant the development of new methods. One such method is the general use of ring-opening metathesis polymerization (ROMP) for generating high-load, immobilized reagents originally pioneered by Barrett and co-workers.[3,4] Overall, the ability to produce designer ROMP-derived polymers with tunable properties has now surfaced as a powerful technological advancement in the arena of facilitated synthesis.

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10.1021/jo0620260 CCC: $37.00
Published on Web 04/04/2007

Previously, we have used ROMP in the development of several high-load, soluble oligomeric sulfonate ester reagents, which effectively serve as facile benzylating agents for a series of cyclic secondary amines.[5] We now report a number of high-load, oligomeric sulfonium salts (^{2G}OBSPc$_n$)[6] that can be readily prepared and offer a wider versatility to the types of nucleophiles they can benzylate. These include secondary amines, phenols, benzenethiols and 2-mercapto-benzimidazoles.

Sulfonium salts have been widely employed in organic synthesis. Prominent among the uses of such salts are their conversion into sulfonium ylides for use in the Corey epoxidation procedure[7] and for alkylation of nucleophiles. Examples of the latter include reactions with azide ion,[8] carboxylates,[9] nucleosides,[10] phenols and thiophenols,[11] amines,[12] cyanides,[13] amides,[14] enolates,[15] and sulfenates.[16] Application in Pd-catalyzed carbon−carbon formations has also been reported.[17] With this versatility in mind, we set out to develop an oligomeric benzylsulfonium salt with applications in benzylation of a series of nucleophiles.

Results and Discussion

OBSPc (oligomeric benzylsulfonium perchlorate) can be synthesized using a simple 5-step process starting from commercially available anhydride **1** (Scheme 1). Reduction of **1** with lithium aluminum hydride in THF gave diol **2** in high yield (95%).[18] Diol **2** was subsequently treated with methanesulfonyl chloride to produce bismesylate **3** in high yield (83%). Norbornenyl-tagged sulfide **4**[19] was obtained from reaction of **3** with sodium sulfide in the presence of aliquate 336 in a mixed solvent of toluene and water. Benzylation[20] of sulfide **4** with various benzyl bromides in the presence of 1 equiv of sodium perchlorate afforded monomers **5** in good to excellent yield (75−96%). Subsequent ROM polymerization with $(IMesH_2)(PCy_3)(Cl)_2RuCHPh$ [cat-**6**][21] yielded ^{2G}OBSPc$_n$ of differing lengths (n) depending upon the mol % of the catalyst used. Quenching of ROM polymerization with ethyl vinyl ether, followed by filtration, provided various oligomeric variants of OBSPc in excellent yields (92−99%) (Table 1). All exist as free-flowing solids with theoretical load values of 2.4−2.9 mmol/g.[22] These oligomers can be isolated and stored at room temperatures for long periods of time.

SCHEME 1

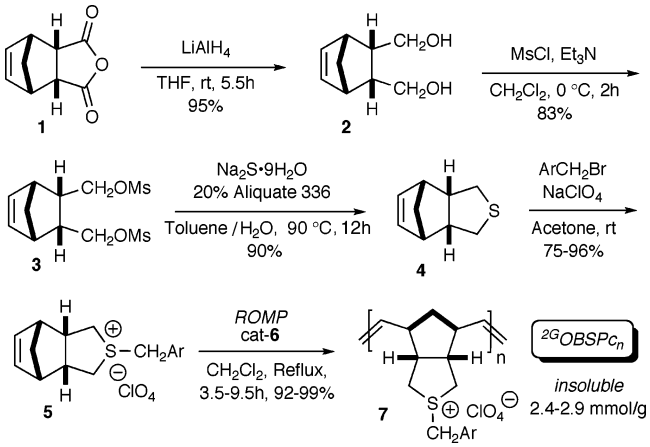

TABLE 1. Sulfonium Salt Monomers and Oligomers[23]

Ar	monomer **5**	ROM Polymer **7**	theoretical load (mmol/g)
Ph	**5a**, 96%	**7a** (n = 50), 97%	2.9
		(n = 10), 96%	2.8
		(n = 30), 98%	2.9
		(n = 100), 99%	2.9
3-Cl-Ph	**5b**, 90%	**7b** (n = 50), 94%	2.6
4-Cl-Ph	**5c**, 75%	**7c** (n = 50), 96%	2.6
3-Me-Ph	**5d**, 90%	**7d** (n = 50), 92%	2.8
4-CF_3-Ph	**5e**, 86%	**7e** (n = 50), 99%	2.4

We initially followed an approach developed by Matsuyma and co-workers,[15d,e] in which longer reaction times (3 days) were required. Test reactions of different lengths of oligomer **7a** with *N*-methylaniline revealed the 50-mer as the best benzylation oligomer. The use of ^{2G}OBSPc$_{50}$ (**7a**) in the benzylation of an

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(6) ^{2G}OBPSc$_n$ stands for oligomeric benzylsulfonium perchlorate of *n*-mer length (n = 10, 30, 50, 100) prepared by ROMP of monomer sulfonium salts **5** using the second generation Grubbs catalyst **6**.

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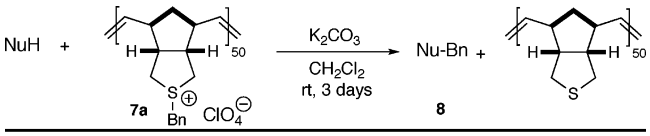
(22) The actual load of reagent **7a** (n = 50) was experimentally determined to be 2.7−2.8 mmol/g utilizing ^{1}H NMR to measure the product of benzylation of excess 1-phenylpiperazine with **7a** (n = 50) in DCM using DMF as an internal standard.

(23) We have previously found that there is a good correlation between the mol % of Grubbs catalyst added and the Gaussian distribution of oligomers formed, which is the case with OBSPc. We have made these reagents several times with good reproducibility and consistency. MALDI-TOF and/or GPC data is normally attained on all oligomers; however, both methods have failed to give good results for our previously published reactive oligomeric bis-acid chloride (OBAC) and sulfonyl chloride resin (OSC).

(24) (a) Purification of final compounds was carried out using a SiO_2 SPE (∼1 g) and eluting with 6 mL of EtOAc. (b) Purities were determined by GC and confirmed by ^{1}H NMR. (c) Yields were calculated from pure products after SPE purification.

TABLE 2. Benzylation of Nucleophiles with Reagent 7a in CH_2Cl_2 at Room Temperature[24]



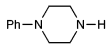
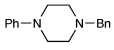
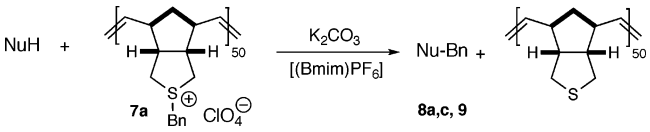
Entry	Nu-H	Nu-Bn	Yield (%)	Purity (%)
1	PhNHMe	PhN(Me)Bn **8a**	71	94
2	Bn_2NH	Bn_3N **8b**	93	95
3	Et_2NH	Et_2NBn **8c**	82	96
4		 **8d**	89	95
5	PhOH	PhOBn **8e**	85	90

TABLE 3. Benzylation of Nucleophiles with Reagent 7a in Ionic Liquid [(Bmim)PF_6][24]



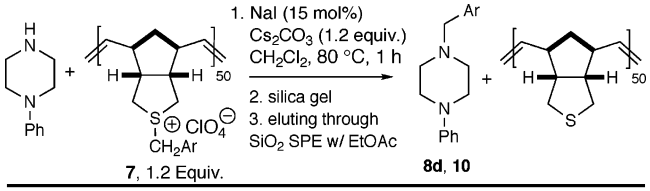
entry	Nu−H	Nu−Bn	temp (°C)	time (h)	yield (%)	purity (%)
1	PhNHMe	PhN(Me)Bn **8a**	25	72	80	95
2	PhNHMe	PhN(Me)Bn **8a**	50	2	93	95
3	Et_2NH	Et_2NBn **8c**	50	2	82	93
4	*p*-BrPhSH	*p*-BrPhSBn **9**	50	2	82	94

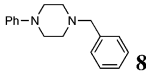
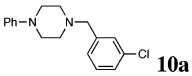
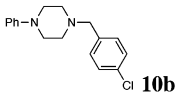
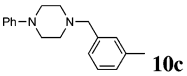
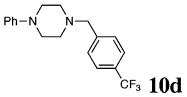
array of nucleophiles, such as secondary amines and phenol, produced promising results (Table 2), although the method required a large excess of reagent **7a** (8 equiv) in order to complete the reactions. Nonetheless, benzylated products **8** were obtained with high yield and purity using precipitation/filtration as the sole purification protocol.

In order to improve this protocol, we next studied the benzylation of secondary amines and benzenethiol with ^{2G}OBSPc$_{50}$ (**7a**) in an ionic liquid [(Bmim)PF_6]. After the benzylation event, the reaction mixture was partitioned between hexanes and the ionic liquid. Good yields and excellent purities were obtained after evaporation of the solvent (Table 3). The results show that the ionic liquid [(bmim)PF_6] facilitated the benzylating event (3 vs 8 equiv of **7a** used) and occurred with shortened reaction times when carried out at 50 °C. Although an improvement in some respects, the use of nonpolar solvents such as hexanes severely limited the ionic liquid variant of the method.

With this limitation in mind, we therefore developed an improved procedure for benzylation with OBSPc, employing CH_2Cl_2 as solvent, Cs_2CO_3 as base, NaI as an additive, and using higher temperatures (80 °C) in a sealed vial. 1-Phenylpiperazine was selected as a substrate and was subsequently treated with different benzyl variants of reagent **7**. Thus, a mixture of 1-phenylpiperazine (1 equiv), reagent **7** (1.2 equiv), Cs_2CO_3 (1.2 equiv), and NaI (15 mol %) in CH_2Cl_2 was heated to 80 °C in a sealed vial. After stirring for 1 h at 80 °C, silica gel was added to the reaction mixture and the solvent was removed. Simple loading of the residue on a SiO_2 SPE and elution with EtOAc afforded pure product. This method exploits inherent polarity of the oligomers produced via ROMP to yield pure products

TABLE 4. Benzylation of 1-Phenylpiperazine with Reagents 7 (1.2 Equiv) in CH_2Cl_2 at 80 °C in a Sealed Vial[24]



Entry	Reagent	Product	Yield (%)	Purity (%)
1	**7a**	 **8d**	98	99
2	**7b**	 **10a**	96	99
3	**7c**	 **10b**	93	99
4	**7d**	 **10c**	98	99
5	**7e**	 **10d**	89	98

with excellent yields (Table 4). It is noteworthy that only 1.2 equiv of reagent was required to carry out the reaction. Benzylations were equally effective with benzyl systems substituted with both electron-withdrawing (Table 4, entries 2, 3, and 5) and electron-donating groups (Table 4, entry 4).

We next examined the benzylation of other secondary amines using the simple benzylating agent **7a** ($n = 50$). Over the course of this study, it was found that cyclic secondary amines were easily benzylated in this process in comparison to acyclic secondary amines, which required a longer reaction time. The results of the benzylation of these scaffolds, using the identical procedure described as above, led to the corresponding tertiary amines **8a**−**c** and **11a**−**e** in good to excellent yields and purities as outlined below in Table 5.

Benzylation of phenols and thiophenol were similarly investigated. Variable phenols and benzenethiol were also benzylated with oligomer **7a** ($n = 50$) using the procedure described above to deliver the ethers (**8e**, **12a**−**f**) and thioether (**9**) in good to excellent yields and purities (Table 6, entries 1−8). Finally, various 2-mercaptobenzimidazoles were benzylated under the same condition using reagent **7a** ($n = 50$) (Table 6, entries 9−11) in good yields and purities.

In conclusion, we have demonstrated the first synthesis and utilization of ROMP-derived oligomeric sulfonium salts as benzylating agents. These entities proved extremely efficient in the benzylation of cyclic and acyclic secondary amines, phenols, thiophenols, and 2-mercaptobenzimidazoles. Benzylation of primary amines such as aniline gave a mixture of mono- and dibenzylated products. Purifications following the benzylation reaction were carried out via simple filtration, which exploits inherent polarity of oligomers produced via ROMP. Efforts to widen the scope of these reagents, preparation of more diversified reagents as well as extension into library synthesis are underway. The results of these endeavors will be reported in due course.

TABLE 5. Benzylation of Secondary Amines with Reagent 7a in CH_2Cl_2 at 80 °C in a Sealed Vial[24]

Entry	R^1R^2NH	Rxn time (h)	R^1R^2N-Bn	Yield (%)	Purity (%)
1		1	 **11a**	93	96
2		1	 **11b**	96	88
3		1	 **11c**	94	95
4	PhNHMe	3	PhN(Me)Bn **8a**	99	91
5	Bn_2NH	3	Bn_3N **8b**	97	94
6	Et_2NH	3	Et_2NBn **8c**	98	94
7	Diallyl amine	3	 **11d**	91	98
8		3	 **11e**	88	95

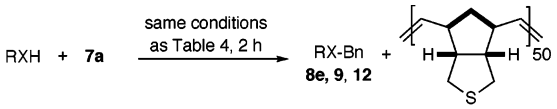
Experimental Section

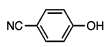
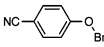
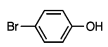
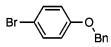
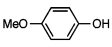
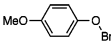
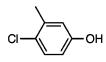
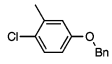
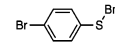
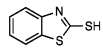
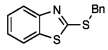
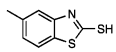
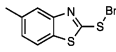
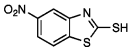
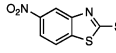
Reduction of *cis*-5-Norbornene-*endo*-2,3-dicarboxylic Anhydride 1.[25] Anhydride **1** (10.0 g, 61 mmol) was reduced with $LiAlH_4$ (4.32 g, 122 mmol) in THF (200 mL) at room temperature (RT) for 5.5 h. Nonaqueous workup and solvent removal gave *cis-endo*-2,3-bis(hydroxymethyl) bicyclo[2.2.1]hept-5-ene (**2**, 8.97 g, 95% yield); ^{1}H NMR 1.40 (t, J = 1.0 Hz, 2H), 6.02 (t, J = 1.8 Hz, 2H), 4.07 (br s, 2H), 3.61 (dd, J = 3.5, 11.2 Hz, 2H), 3.39−3.30 (m, 2H), 2.78 (t, J = 1.5 Hz, 2H), 2.55−2.47 (m, 2H), 1.42−1.35 (m, 2H); ^{13}C NMR 134.7, 63.4, 49.9, 46.5, 45.0.

Preparation of Bismesylate 3. To a solution of diol **2** (4.13 g, 26.78 mmol) and Et_3N (10.84 g, 107.13 mmol, 15 mL) in CH_2Cl_2 was added dropwise methanesulfonyl chloride (12.27 g, 107.13 mmol, 8.3 mL) at 0 °C under Ar over 10 min. The mixture was stirred at 0 °C under Ar for 2 h; H_2O (40 mL) was added dropwise at 0 °C to quench the reaction. The organic layer was separated, and the aqueous layer was extracted with $CHCl_3$ (2 × 30 mL). The combined organic layers were washed with H_2O (20 mL) and brine (20 mL) and dried ($MgSO_4$). The solvent was removed under reduced pressure, Et_2O was added to the residue, and a yellow solid was formed and washed with additional Et_2O to obtain pure bismesylate **3** (6.91 g, 83%). ^{1}H NMR 6.24 (d, J = 1.7 Hz, 2H), 4.04−4.00 (m, 2H), 3.95−3.88 (m, 2H), 3.04−2.96 (m, 8H), 2.73−2.64 (m, 2H), 1.60 (dd, J = 1.8, 7.0 Hz, 1H), 1.40 (d, J = 8.6 Hz, 1H); ^{13}C NMR 135.5, 69.6, 49.0, 45.5, 41.2, 37.3.

Synthesis of Norbornenyl-Tagged Cyclic Sulfide 4.[26] A mixture of bismesylate **3** (19.00 g, 61.2 mmol), $Na_2S{\cdot}9H_2O$ (19.11 g, 79.6 mmol), and Aliquate-336 (4.95 g, 12.2 mmol) in a mixed solvent of toluene (100 mL) and H_2O (100 mL) was stirred and heated to 90 °C overnight. The organic portion was separated and the aqueous layer was extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with water and brine, dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by column chromatograph (10% EtOAc in hexanes) to obtain 8.41 g of cyclic sulfide **4** (90%). ^{1}H NMR 6.18 (t, J = 1.8 Hz, 2H), 3.26−3.13 (m, 2H), 2.75 (br s, 2H), 2.71−2.62 (m, 2H), 2.41−2.32 (m, 2H), 1.78 (dt, J = 1.7, 8.2 Hz, 1H), 1.72 (dd, J = 0.4, 8.2 Hz, 1H); ^{13}C NMR 137.0, 55.1, 54.0, 45.5, 34.5.

TABLE 6. Benzylation of Phenols, Benzenethiols, and 2-Mercaptobenzimidazoles with Reagent 7a in Ch_2Cl_2 at 80 °C in a Sealed Vial[24]



Entry	RXH	RX-Bn	Yield (%)	Purity (%)
1		 **8e**	98	98
2		 **12a**	94	96
3		 **12b**	95	95
4		 **12c**	88	90
5		 **12d**	70	88
6		 **12e**	99	97
7		 **12f**	89	96
8		 **9**	99	90
9		 **12g**	93	94
10		 **12h**	90	88
11		 **12i**	98	81

General Procedure for Preparation of Norborene-Tagged Sulfonium Perchlorate Monomers 5.[27] Sulfide (1 equiv), benzyl bromide (1 equiv), and $NaClO_4{\cdot}H_2O$ (1 equiv) were stirred in a minimum amount of acetone at RT until no further sulfide remained. The salt (NaBr) was filtered off and washed with a minimum amount of acetone. The resulting filtrate was evaporated under reduced pressure and triturated with Et_2O to yield crude sulfonium salt monomer **5a**−**e**, which was further washed with Et_2O twice to afford sulfonium salts **5a**−**e** as mixtures of sulfur diastereoisomers with ratios varying between 1:1 and 6:1.

5a: sulfide **4** (1.470 g, 9.65 mmol), benzyl bromide (1.651 g, 9.65 mmol, 1.15 mL), and $NaClO_4{\cdot}H_2O$ (1.356 g, 9.65 mmol) were stirred in acetone (8 mL). 3.170 g (96%) of **5a** was obtained as white solid (∼1/1 mixture). ^{1}H NMR major: 7.52−7.33 (m, 5H), 6.35 (t, J = 1.9 Hz, 2H), 4.66 (s, 2H), 3.75−3.56 (m, 3H), 3.19−3.06 (m, 2H), 2.99 (br s, 2H), 1.77−1.60 (m, 3H); minor: 7.52−7.33 (m, 5H), 5.90 (t, J = 1.8 Hz, 2H), 4.73 (s, 2H), 3.75−3.56 (m, 3H), 3.19−3.06 (m, 2H), 2.90 (br s, 2H), 2.39 (dd, J = 11.8, 10.0 Hz, 2H), 1.77−1.60 (m, 1H); ^{13}C NMR 137.8, 136.9, 131.7, 130.34, 130.30, 130.0, 129.7, 129.4, 128.2, 125.8, 54.9, 53.2, 50.7,47.0, 46.9, 46.5, 46.3, 45.1, 44.2, 41.4; HRMS (EI) calcd for M^+ ($C_{16}H_{19}S$) required 243.1208, found 243.1197.

5b: sulfide **4** (200 mg, 1.31 mmol), 3-chloro-benzyl bromide (270 mg, 1.31 mmol, 172 μL), and $NaClO_4{\cdot}H_2O$ (185 mg, 1.31

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(26) Bloch, R.; Abecassis, J. *Tetrahedron Lett.* **1982**, *23*, 3277.

(27) Aggarwal, V. K.; Thompson, A.; Jones, R. V. H. *Tetrahedron Lett.* **1994**, *35*, 8659.

mmol) were stirred in acetone (1 mL). 443 mg (90%) of **5b** was obtained as white solid (~5/1 mixture). ^{1}H NMR major: 7.49−7.29 (m, 4H), 6.37 (t, J = 1.8 Hz, 2H), 4.66 (s, 2H), 3.80−3.58 (m, 3H), 3.23−3.09 (m, 2H), 3.01 (br s, 2H), 1.74−1.64 (m, 2H), 1.62 (br s, 1H); minor: 7.49−7.29 (m, 4H), 6.05 (t, J = 1.8 Hz, 2H), 4.75 (s, 2H), 3.80−3.58 (m, 3H), 3.23−3.09 (m, 2H), 2.96 (br s, 2H), 1.74−1.64 (m, 2H), 1.62 (br s, 1H); ^{13}C NMR (CD_3COCD_3) 138.6, 138.3, 135.6, 135.5, 132.7, 132.2, 132.1, 131.4, 131.1, 130.9, 130.7, 130.0, 129.99, 55.3, 54.4, 54.3, 51.59, 51.53, 48.6, 47.4, 47.3, 46.1, 45.8, 44.8, 44.1; HRMS (EI) calcd for M^+ ($C_{16}H_{18}ClS$) required 277.0818, found 277.0817.

5c: sulfide **4** (200 mg, 1.31 mmol), 4-chloro-benzyl bromide (270 mg, 1.31 mmol), and $NaClO_4 \cdot H_2O$ (185 mg, 1.31 mmol) were stirred in acetone (1 mL). 370 mg (75%) of **5c** was obtained as white solid (~2/1 mixture). ^{1}H NMR (CD_3COCD_3) major: 7.75−7.56 (m, 2H), 7.56−7.43 (m, 2H), 6.42 (br s, 2H), 4.79 (s, 2H), 3.93−3.76 (m, 2H), 3.70 (dd, J = 13.8, 7.5 Hz, 2H), 3.25 (dd, J = 13.4, 5.0 Hz, 2H), 3.13−2.88 (m, 2H), 1.84−1.61 (m, 2H); minor: 7.75−7.56 (m, 2H), 7.56−7.43 (m, 2H), 6.25 (br s, 2H), 4.91 (s, 2H), 3.93−3.76 (m, 2H), 3.70 (dd, J = 13.8, 7.5 Hz, 2H), 3.25 (dd, J = 13.4, 5.0 Hz, 2H), 3.13−2.88 (m, 2H), 1.84−1.61 (m, 2H); ^{13}C NMR (CD_3COCD_3) 138.5, 138.3, 136.5, 136.2, 133.9, 133.2, 130.5, 130.4, 129.2, 127.8, 55.3, 54.3, 51.5, 48.5, 47.4, 47.2, 44.6, 43.8; HRMS (EI) calcd for M^+ ($C_{16}H_{18}ClS$) required 277.0818, found 277.0817.

5d: sulfide **4** (200 mg, 1.31 mmol), 3-methy-benzyl bromide (242 mg, 1.31 mmol), and $NaClO_4 \cdot H_2O$ (185 mg, 1.31 mmol) were stirred in acetone (1 mL). 420 mg (90%) of **5d** was obtained as a white solid (~3/1 mixture). ^{1}H NMR (CD_3COCD_3) major: 7.51−7.21 (m, 4H), 6.41 (t, J = 1.8 Hz, 2H), 4.73 (s, 2H), 3.90−3.75 (m, 2H), 3.67 (dd, J = 14.2, 8.0 Hz, 2H), 3.21 (dd, J = 14.2, 6.0 Hz, 2H), 3.05 (br s, 2H), 2.34 (s, 3H), 1.74−1.64 (m, 2H); minor: 7.51−7.21 (m, 4H), 6.14 (t, J = 1.8 Hz, 2H), 4.83 (s, 2H), 3.90−3.75 (m, 2H), 3.36−3.26 (m, 2H), 3.00 (br s, 2H), 2.67 (m, 2H), 2.38 (s, 3H), 1.82−1.75 (m, 2H); ^{13}C NMR (CD_3COCD_3) 140.3, 140.2, 138.5, 138.1, 132.8, 131.8, 131.6, 131.4, 130.4, 130.2, 130.1, 129.4, 128.4, 128.3, 55.2, 54.4, 51.6, 48.4, 47.3, 47.2, 46.5, 46.4, 44.4, 43.3, 21.3; HRMS (EI) calcd for M^+ ($C_{17}H_{21}S$) required 257.1364, found 257.1358.

5e: sulfide **4** (152 mg, 1.00 mmol), 4-trifluoromethyl-benzyl bromide (239 mg, 1.00 mmol), and $NaClO_4 \cdot H_2O$ (140 mg, 1.00 mmol) were stirred in acetone (1 mL). 352 mg (86%) of **5e** was obtained as a white solid (~6/1 mixture). ^{1}H NMR major: 7.70−7.55 (m, 4H), 6.37 (t, J = 1.8 Hz, 2H), 4.76 (s, 2H), 3.80−3.60 (m, 4H), 3.16 (br d, J = 12.4 Hz, 2H), 3.01 (br s, 2H), 1.74−1.64 (m, 3H); minor: 7.70−7.55 (m, 4H), 6.07 (t, J = 1.8 Hz, 2H), 4.86 (s, 2H), 3.80−3.60 (m, 4H), 3.16 (br d, J = 12.4 Hz, 2H), 2.96 (br s, 2H), 1.74−1.64 (m, 3H); ^{13}C NMR (CD_3COCD_3) 138.6, 138.3, 135.1, 132.4, 132.3, 132.0, 127.3 (q, J = 4.1 Hz), 126.4, 123.7, 54.4, 51.7, 51.6, 48.6, 47.4, 47.3, 45.8, 45.0, CF_3 missed because of highly coupled; HRMS (EI) calcd for M^+ ($C_{17}H_{18}F_3S$) required 311.1081, found 311.1071.

ROMP Procedure for the Generation of the Oligomeric Benzylsulfonium Perchlorates 7 (^{2G}OBSPc$_n$). In a round-bottom flask, sulfonium perchlorate **5** was dissolved in degassed (argon) CH_2Cl_2. To this solution was added the second generation Grubbs metathesis catalyst **6** in one portion. The reaction was refluxed under argon and a precipitate was formed immediately. Once the polymerization was complete (3.5−9.5 h), the reaction was quenched by the addition of ethyl vinyl ether (EVE). The precipitate was filtrated and washed with copious amounts of CH_2Cl_2 to furnish ^{2G}OBSPc$_n$ as a light-tan-colored free-flowing solid.

7a (X=H, n = 50): **5a** (2.00 g, 5.83 mmol) and catalyst **6** (99 mg, 0.117 mmol) in CH_2Cl_2 (60 mL) was refluxed for 3.5 h to give 1.98 g of light-brown free-flowing solid (98%).

7a (X=H, n = 10): **5a** (100 mg, 0.29 mmol) and catalyst **6** (25 mg, 0.029 mmol) in CH_2Cl_2 (5 mL) was refluxed for 3.5 h to give 99 mg of a light-tan-colored free-flowing solid (96%).

7a (X = H, n = 30): **5a** (252 mg, 0.73 mmol) and catalyst **6** (21 mg, 0.024 mmol) in CH_2Cl_2 (7 mL) was refluxed for 3.5 h to give 248 mg of a light-tan-colored free-flowing solid (98%).

7a (X = H, n = 100): **5a** (228 mg, 0.665 mmol) and catalyst **6** (5.6 mg, 0.006 mmol) in CH_2Cl_2 (6 mL) was refluxed for 3.5 h to give 227 mg of a tan-colored free-flowing solid (99%).

7b (X = 3-Cl, n = 50): **5b** (443 mg, 1.17 mmol) and catalyst **6** (20 mg, 0.023 mmol) in CH_2Cl_2 (13 mL) was refluxed for 5 h to give 418 mg light-tan-colored free-flowing solid (94%).

7c (X = 4-Cl, n = 50): **5c** (369 mg, 0.98 mmol) and catalyst **6** (17 mg, 0.02 mmol) in CH_2Cl_2 (10 mL) was refluxed for 3.5 h to give 353 mg of a light-tan-colored free-flowing solid (96%).

7d (X = 3-Me, n = 50): **5d** (415 mg, 1.16 mmol) and catalyst **6** (20 mg, 0.023 mmol) in CH_2Cl_2 (12 mL) was refluxed for 3.5 h to give 380 mg of a light-tan-colored free-flowing solid (92%).

7e (X = 4-CF_3, n = 50): **5e** (350 mg, 0.85 mmol) and catalyst **6** (14 mg, 0.017 mmol) in CH_2Cl_2 (10 mL) was refluxed for 9.5 h to give 350 mg of a light-tan-colored free-flowing solid (99%).

General Procedure for Benzylation Using ^{2G}OBSPc$_n$ in CH_2Cl_2 at RT. A mixture of nucleophile (0.06 mmol), ^{2G}OBSPc$_n$ (8.0 equiv), and anhydrous K_2CO_3 (8 equiv) was stirred in dry CH_2Cl_2 (2 mL) at RT for 3 days. EtOAc (5 mL) was added to precipitate the oligomeric sulfide. After filtration of insoluble materials, the filtrate was concentrated to dryness. The residue was passed through a SiO_2 SPE to afford benzylated products **8a**−**e** in high yield and purities (see Tables 2).

General Procedure for Benzylation Using ^{2G}OBSPc$_{50}$ in An Ionic Liquid. A mixture of nucleophile (0.06 mmol), ^{2G}OBSPc$_n$ (2.4−3.0 equiv), and anhydrous K_2CO_3 (2.4−3.0 equiv) was stirred in (Bmim)PF_6 (1 mL) at RT for 3 days or heated at 50 °C for 2−4 h. Hexane (2 mL) was added to separate the required product from the oligomers, inorganic salts, and ionic liquid. The hexane layer was concentrated and the residue was passed through a SiO_2 SPE to afford benzylated products **8a**,**c** and **9** in high yield and purities (see Tables 3).

General Procedure for Benzylation Using ^{2G}OBSPc$_{50}$ in CH_2Cl_2 at 80 °C. A mixture of nucleophile (0.05 mmol), ^{2G}OBSPc$_n$ (1.2 equiv), anhydrous Cs_2CO_3 (1.2 equiv), and NaI (0.15 equiv) was stirred in CH_2Cl_2 (1 mL) and heated at 80 °C in a sealed vial for 1−3 h. Silica gel (150 mg) was added to the reaction mixture, and the solvent was removed under reduced pressure. The residue was then loaded on a SiO_2 SPE and eluted with EtOAc to afford pure benzylated products **8a**−**e**, **9, 10a**−**d**, **11a**−**e**, and **12a-i** in high yield and purities (see Tables 4−6).

Acknowledgment. This investigation was generously supported by partial funds provided the National Institutes of Health (KU Center of Excellence for Chemical Methodologies and Library Development, 1P50 GM069663) with additional funds from the State of Kansas and NIGMS P41 GM076302. The authors thank Materia, Inc., for supplying catalyst and helpful discussions.

Supporting Information Available: Tabulated ^{1}H NMR and mass data of crude products **8**−**12** obtained by the described successful benzylation method; ^{1}H NMR and ^{13}C NMR spectra of intermediates **2**−**5**, ^{1}H NMR spectra of **8**−**12**. This material is available free of charge via the Internet at http://acs.pubs.org.

JO0620260