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Effects of Electronics, Aromaticity, and Solvent Polarity on the Rate of Azaquinone–Methide-Mediated Depolymerization of Aromatic Carbamate Oligomers

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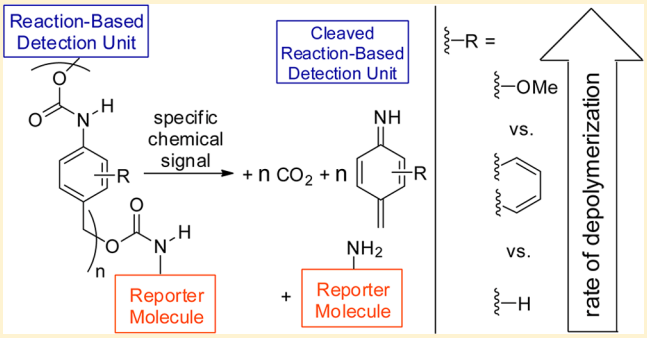
Supporting Information

ABSTRACT: This paper uses physical-organic studies on well-defined oligomers to establish design principles for creating aromatic poly(carbamates) that depolymerize from head-to-tail in low dielectric constant environments when exposed to specific applied signals. We show that either increasing electron density or decreasing the aromaticity of aromatic repeating units in poly(carbamates) increase the overall depolymerization rate. For example, a methoxybenzene-based repeating unit provides depolymerization rates that are 143× faster than oligomers that contain a benzene-based repeating unit. Furthermore, the rate of depolymerization in the methoxybenzene-based system is tolerant to low dielectric environments, whereas the benzene-based oligomers are not.



INTRODUCTION

An emerging strategy in polymer chemistry involves designing polymers and dendrimers that depolymerize continuously from head to tail in response to a single, specific chemical or physical signal (Figure 1).[1−4] Macromolecules with this capability have been demonstrated for signal amplification schemes[5−8] and have been configured to create responsive micelles and nanoparticles for drug delivery,[9−13] responsive capsules for self-healing applications,[14] autonomous analyte-responsive pumps,[15] and shape-shifting/reconfigurable plastic materials.[16]

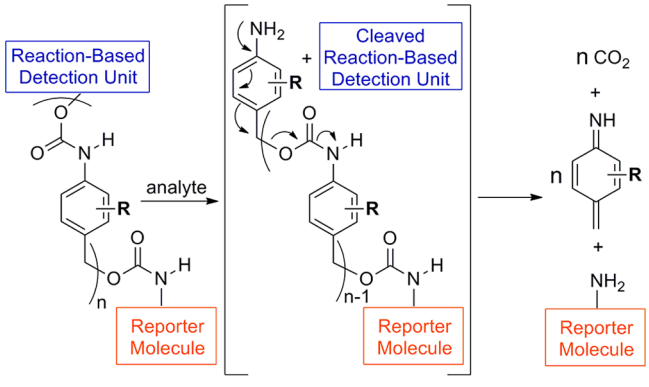


Figure 1. General mechanism of analyte-induced depolymerization in an aromatic poly(carbamate). Once the reaction-based detection unit is cleaved by reaction with a specific analyte, the repeating units of the polymer are released through successive azaquinone methide elimination reactions. Release of the reporter molecule is used to determine the kinetics of the depolymerization process.

Currently, there are four classes of these polymers that depolymerize from head-to-tail, including those that (i) depolymerize via formation of quinone or azaquinone methide,[5,9,14] (ii) depolymerize via cyclization reactions,[10] (iii) combine (i) and (ii) to depolymerize via alternating cyclization and quinone or azaquinone methide elimination reactions,[11,12,17] and (iv) depolymerize via acetal chemistry.[16]

This paper addresses a major limitation of the benzene-based depolymerizable polymers that proceed through azaquinone methide elimination pathways (Figure 1); these polymers exhibit slow rates of depolymerization (i.e., hours) in polar environments and exceedingly slow rates (i.e., days or even not at all) in environments that have relatively low dielectric constants compared with that of water (e.g., in plastics, films, or capsule shell walls).[14] In order for these polymers to be useful in applications that require rapid and tunable responses, we seek to develop methods both to increase the rate of depolymerization of this class of polymers and to tune the ability of the polymers to depolymerize in a variety of environments.

Depolymerizable aromatic poly(carbamates) contain two components (Figure 1): (i) a reaction-based detection unit and (ii) aromatic repeating units. In response to a specific chemical signal, the reaction-based detection unit is cleaved, revealing an aniline at the terminus of the polymer, which initiates release of the next aromatic repeating unit via a presumed azaquinone methide intermediate. This release process is continuous along the length of the polymer until the entire polymer

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depolymerizes. A reporter molecule (e.g, a chromophore, such as *p*-nitroaniline, Figure 1) often is tethered to the terminus opposite the reaction-based detection unit as a means to monitor the kinetics of depolymerization (e.g., by UV/vis spectroscopy).

The proposed mechanism of azaquinone methide elimination in these polymers suggests that the release of each repeating unit proceeds through a less aromatic transition state (i.e., azaquinone methide) than the aromatic repeating unit. Proceeding through this less aromatic transition state presumably results in a large energetic penalty for depolymerization and a slow rate for azaquinone methide-mediated depolymerization. We reasoned that tuning the electronics and aromaticity of the aromatic portion of the polymer backbone could offset the energy penalty associated with the depolymerization reaction. Specifically, we envisaged two different approaches (Figure 2) that would lower the activation energy

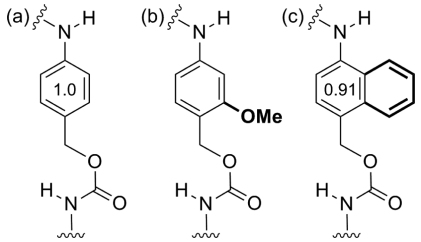

Figure 2. Three repeating units employed in the present study. The benzene-based repeating unit (a) serves as a reference point, while the *m*-methoxybenzene-based unit in (b) tests the effects of electron-donating groups on the rate of depolymerization.[18] The naphthalene-based unit in (c) tests the effects of aromaticity on the rate of depolymerization. Naphthalene is less aromatic than benzene as indicated by the relative aromaticity values of 0.91 and 1.0, respectively.[19]

for the depolymerization reaction either by (i) raising the HOMO of each repeating unit by addition of electron density into the aromatic ring (Figure 2b) or (ii) reducing the aromatic character of the repeating unit (Figure 2c).

Herein we describe a physical organic study to determine the effects of these hypotheses on the rate of depolymerization of aromatic poly(carbamates). We designed, synthesized, and studied several poly(carbamate) oligomers and determined the rate of release for a single repeating unit in each system. Furthermore, we studied the effect of environment polarity on the depolymerization rate of the altered polymer backbones to quantify the relationship between environment polarity and the rate of depolymerization. We anticipate that these studies will help guide future efforts to design poly(carbamate) polymers that depolymerize quickly in nearly any environment when exposed to a specific signal.

RESULTS AND DISCUSSION

Design of the Experiments. The oligomeric systems shown in Figure 3 were designed with the goal of determining the release time for a single repeating unit from the polymer backbone. Each oligomer consists of a reaction-based detection unit (blue), one or two repeating units, and a reporter (orange). An aryl boronate ester was used as the reaction-based detection unit. The anticipated mechanism of response is as follows: the boronate ester reacts selectively with hydrogen peroxide under mild conditions to reveal a phenol,[20] which

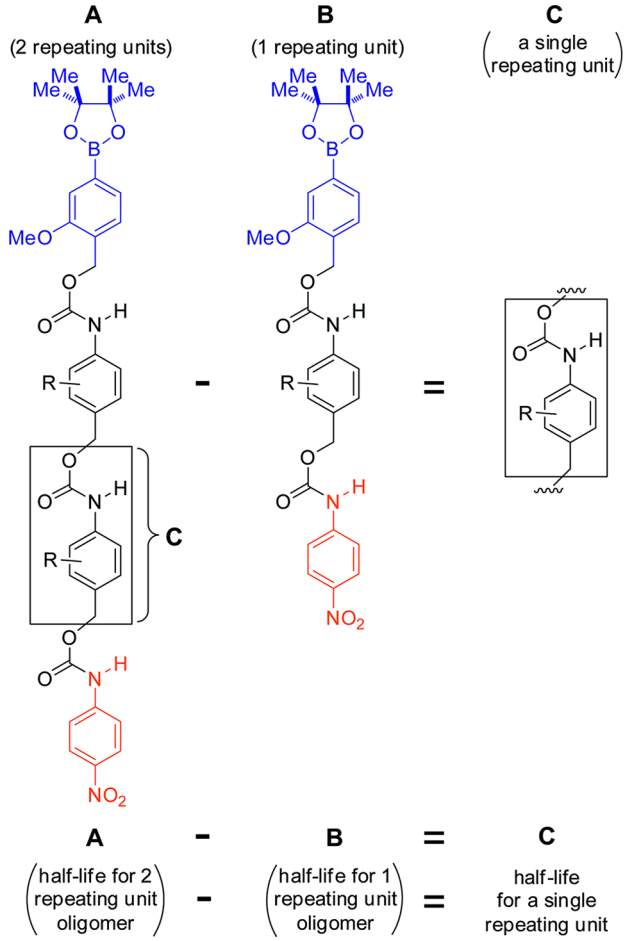

Figure 3. Two oligomeric systems consisting of an aryl boronate acting as a reaction-based detection unit, one or two repeating units, and a *p*-nitroaniline terminus, which when released, will serve as a reporter molecule. R represents −H, −OMe, or a second aromatic ring. The difference in half-life between an oligomer containing one repeating unit (**B**) and an oligomer containing two repeating units (**A**) gives the half-life for the release of a single repeating unit (**C**).

subsequently proceeds through a quinone methide intermediate to release the first repeating unit. The last repeating unit will release *p*-nitroaniline, which absorbs strongly at 385 nm and provides a spectroscopic signature of depolymerization that can be quantified easily using UV/vis spectroscopy.

Hydrogen peroxide was used in 20-fold excess so that the depolymerization reaction would operate under pseudo-first-order kinetics. To obtain the rate of release of a single repeating unit from the data, we measured the half-lives for oligomers containing one repeating unit (Figure 3, **B**) and two repeating units (Figure 3, **A**). The difference in the half-lives between these two oligomers provides the half-life for release of a single repeating unit (Figure 3, **C**) without complication from the rate of oxidative cleavage or the rate for release of *p*-nitroaniline.

Synthesis of the Oligomers. Scheme 1 depicts the synthetic route to the benzene-based oligomers. The reaction-based detection unit **2** was synthesized by Miyaura borylation of 4-bromo-2-methoxybenzyl alcohol. The resulting alcohol was linked through a trans-carbamation to compound **4**, which was synthesized in two steps from 4-aminobenzyl alcohol. Deprotection of the resulting carbamate gave **5**, which was linked with *p*-nitrophenyl isocyanate to afford oligomer **6**. To synthesize oligomer **7**, **5** was resubjected to the trans-

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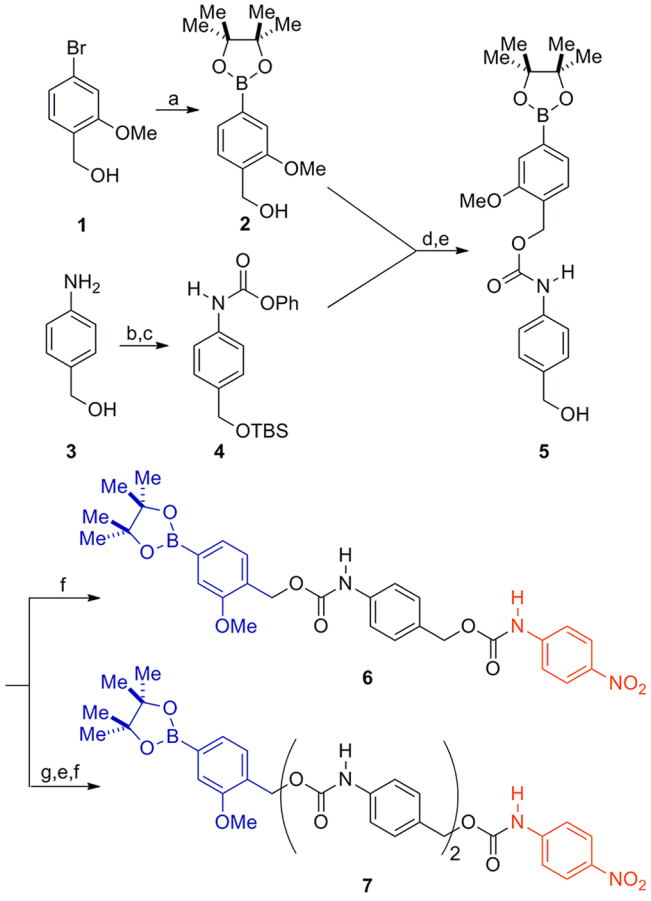
Scheme 1. Synthesis of Benzene-Based Carbamate Oligomers 6 and 7[a]



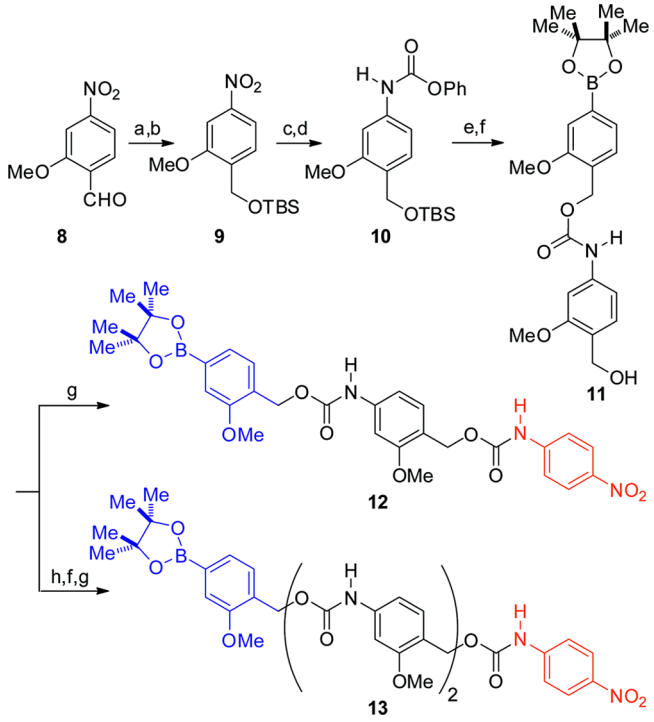
[a]Reagents and conditions: (a) bis(pinacolato)diboron, $PdCl_2dppf$, KOAc, 80 °C (85%); (b) PhOCOCl, $NaHCO_3$ (100%); (c) TBS-Cl, DMAP, imidazole (100%); (d) DBTL, toluene, 110 °C (96%); (e) TsOH, THF/H_2O (58% for **5**, 76% toward **7**); (f) 4-nitrophenyl isocyanate, 80 °C (58% for **6**, 98% for **7**); (g) **4**, DBTL, dioxanes, 110 °C (78%).

carbamation reaction, the product was deprotected, and the deprotected material was labeled with *p*-nitrophenyl isocyanate. Oligomer **6** could have been accessed in fewer steps by a tail-to-head approach, however, the synthesis would have required the development of two synthetic routes rather than one.

Scheme 2 depicts the synthetic route to the methoxybenzene-based oligomers **12** and **13**. Compound **10** was made in four steps from 2-methoxy-4-nitrobenzaldehyde and subjected to reaction conditions similar to those used to synthesize the benzene-based oligomers. The poor yields for the silyl ether deprotection steps were caused by hydrolysis of the pinacol boronate ester under the aqueous, acidic conditions. Fluoride could not be used in place of the acid in this step because it binds to boron and complicates purification steps. To circumvent these low-yielding steps, an alternative, but similar route to that depicted in Scheme 2 was carried out using 4-bromo-2-methoxybenzyl alcohol (compound **1**) instead of the boronate ester (compound **2**). Attempts to install the boronate ester through a Miyaura coupling as a final step, however, led to decomposition of the oligomers.

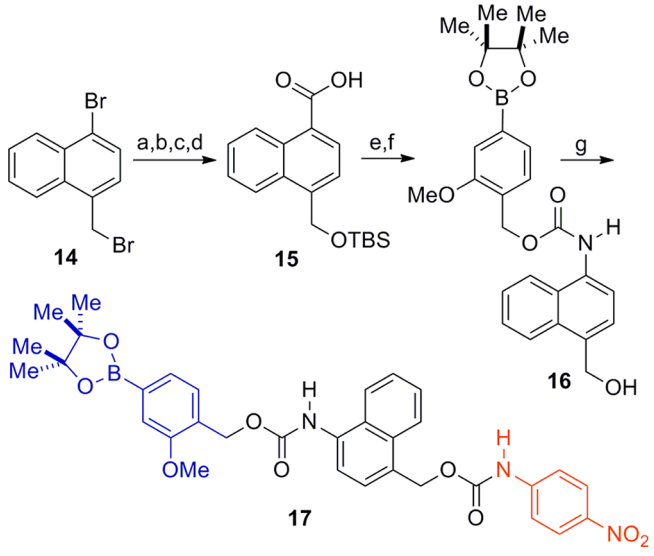
A better solution to the problem of boronate hydrolysis was employed in the synthesis of the naphthalene-based oligomers **17** and **20** (Schemes 3 and 4). After acid-mediated

Scheme 2. Synthesis of Methoxybenzene-Based Carbamate Oligomers 12 and 13[a]



[a]Reagents and conditions: (a) $NaBH_4$; (b) TBS-Cl, DMAP, imidazole (99% over two steps); (c) Pd/C, H_2 (93%); (d) PhOCOCl, $NaHCO_3$ (100%); (e) **2**, DBTL, toluene, 110 °C (81%); (f) TsOH, THF/H_2O (27% for **11**, 66% toward **13**); (g) 4-nitrophenyl isocyanate, 80 °C (77% for **12**, 63% for **13**); (h) **10**, DBTL, dioxanes, 100 °C (37%).

Scheme 3. Synthesis of Naphthalene-Based Carbamate Oligomer 17 with a Single Repeating Unit[a]



[a]Reagents and conditions: (a) $CaCO_3$, water, 110 °C; (b) TBS-Cl, imidazole (84% over two steps); (c) *n*-BuLi, DMF, −78 °C (97%); (d) $NaClO_2$, NaH_2PO_4, 2-methyl-2-butene; (e) DPPA, TEA, **2**, 90 °C (82% over two steps); (f) TsOH, THF−water (79%); (g) 4-nitrophenyl isocyanate, TEA (54%).

deprotection, the acid was neutralized with triethylamine, and an excess of pinacol was added. This mixture was stirred for 24

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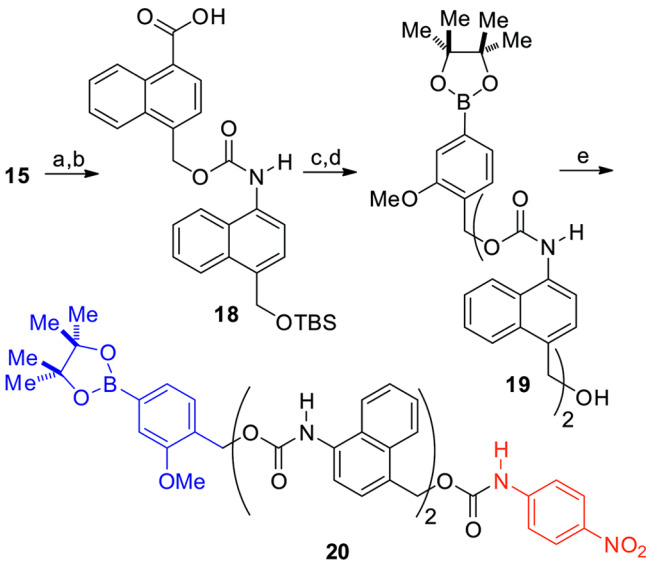
Scheme 4. Synthesis of Naphthalene-Based Carbamate Oligomer 20 with Two Repeating Units[a]



[a]Reagents and conditions: (a) DPPA, TEA, 4-(hydroxymethyl)-1-naphthalenecarboxaldehyde), 90 °C (79% over two steps from (d) in Scheme 3); (b) $NaClO_2$, NaH_2PO_4, 2-methyl-2-butene; (c) DPPA, TEA, **2**, 90 °C (55% over two steps); (d) TsOH, THF–water (91%); (e) 4-nitrophenyl isocyanate, TEA, DMF (40%)

h to convert the boronic acid back to the pinacol ester, providing yields of 79–91%. These oligomers were accessed by routes that differed from those of the benzene- and methoxybenzene-based oligomers because functionalized naphthalene starting materials (such as amino- or nitro-functionalized naphthalene) were not available commercially. Therefore, the carbamates were installed using Curtius rearrangements.

Demonstration that the Oligomers Depolymerize When Exposed to H_2O_2. Oligomer **12** was exposed to 20 equiv of hydrogen peroxide in a 200 μM solution of 5:4:1 *p*-dioxanes–DMSO–water (0.01 M phosphate buffer, pH 7.1). The absorbance values from 250–450 nm were monitored every 5 min for 1 h (Figure 4a); the λ_{max} for *p*-nitroaniline in this solvent composition is 385 nm. The two distinct isosbestic points in Figure 4a suggest clean conversion from the parent oligomer to the released *p*-nitroaniline.

The depolymerization reaction also was followed using LCMS (Figure 4b). Oligomer **13** was exposed to 20 equiv of hydrogen peroxide in a 1 mg/mL (1.27 M) solution of 9:1 acetonitrile–water (0.01 M phosphate buffer, pH 7.1). After 30 min, the oligomer had converted completely into the expected small molecules products 4-hydroxybenzyl alcohol, 4-aminobenzyl alcohol, and *p*-nitroaniline (see Figure S1 (Supporting Information) for representative mass spectra). The presence of these products suggests that the oligomer depolymerizes from head-to-tail upon exposure to hydrogen peroxide.

Analysis of the Depolymerization Kinetics of Aromatic Poly(carbamate) Oligomers. The rate of release of *p*-nitroaniline from oligomers **6**, **7**, **12**, **13**, **17**, and **20** was determined from UV/vis absorbance data acquired over time after exposure to hydrogen peroxide. A 200 μM solution of each oligomer in a 5:4:1 mixture of *p*-dioxanes–DMSO–water (0.01 M phosphate buffer, pH 7.1) was treated with excess of hydrogen peroxide (20 equiv) (Figure 5a). The release of *p*-

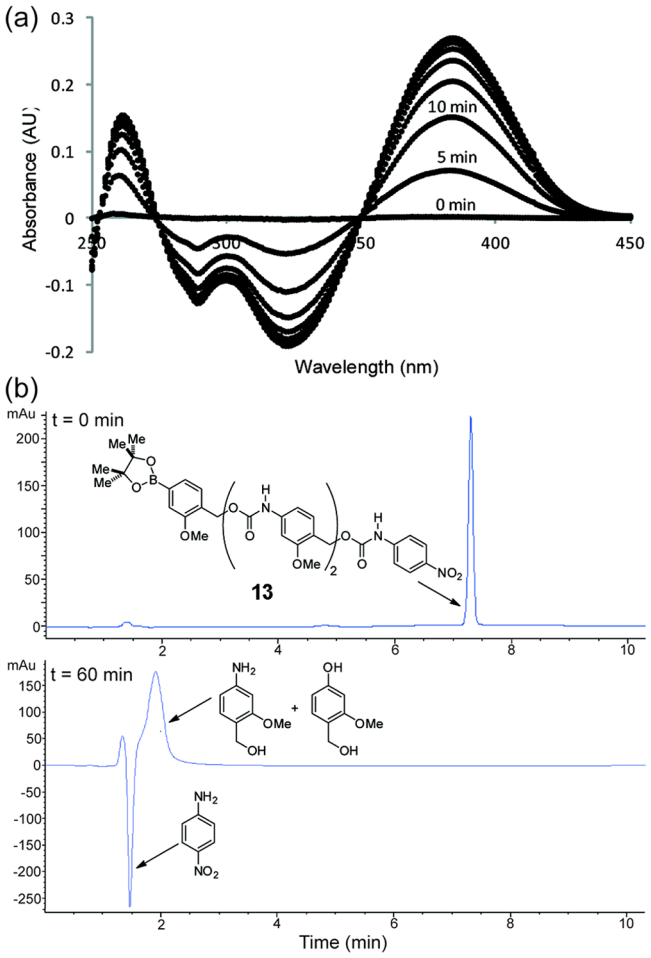


Figure 4. (a) Wavelength scans over time for oligomer **12** when treated with 20 equiv of hydrogen peroxide. (b) LCMS spectra at 254 nm for oligomer **13** before and 60 min after exposure to 20 equiv of hydrogen peroxide. The oligomer depolymerizes into 4-hydroxybenzyl alcohol, 4-aminobenzyl alcohol, and *p*-nitroaniline. See Figure S1 (Supporting Information) for representative mass spectra.

nitroaniline was monitored by UV/vis spectroscopy at 385 nm. The rate constants for release of *p*-nitroaniline were converted to half-lives for each oligomer and further comparisons (e.g., Figure 3) provided half-lives per repeating unit (Figure 5). For example, the half-lives for the benzene-based oligomers were found to be 39.5 ± 2.1 min for oligomer **6** (one repeating unit) and 639 ± 3.8 min for oligomer **7** (two repeating units). By subtracting the half-life for the one-unit oligomer (**6**) from the half-life of the two-unit oligomer (**7**), we obtained the half-life for release of a single repeating unit, which is 599.5 ± 4.3 min. Figure 5 reveals that the naphthalene-based repeating unit depolymerizes 113× faster than the benzene-based system, whereas the methoxybenzene-based system is 1.3× faster still. These results suggest that both hypotheses of (i) adding electron density into the benzene ring and (ii) decreasing the aromaticity of the ring improve the rate of depolymerization substantially over the parent benzene-based oligomer.

Adding electron density and/or decreasing the aromaticity of each repeating unit also increases the occurrence of background depolymerization due to hydrolysis reactions, but this increase is offset substantially by the rapid rate of depolymerization when exposed to the desired signal. For example, exposure of oligomers **7**, **13**, and **20** to the same solvent conditions as in

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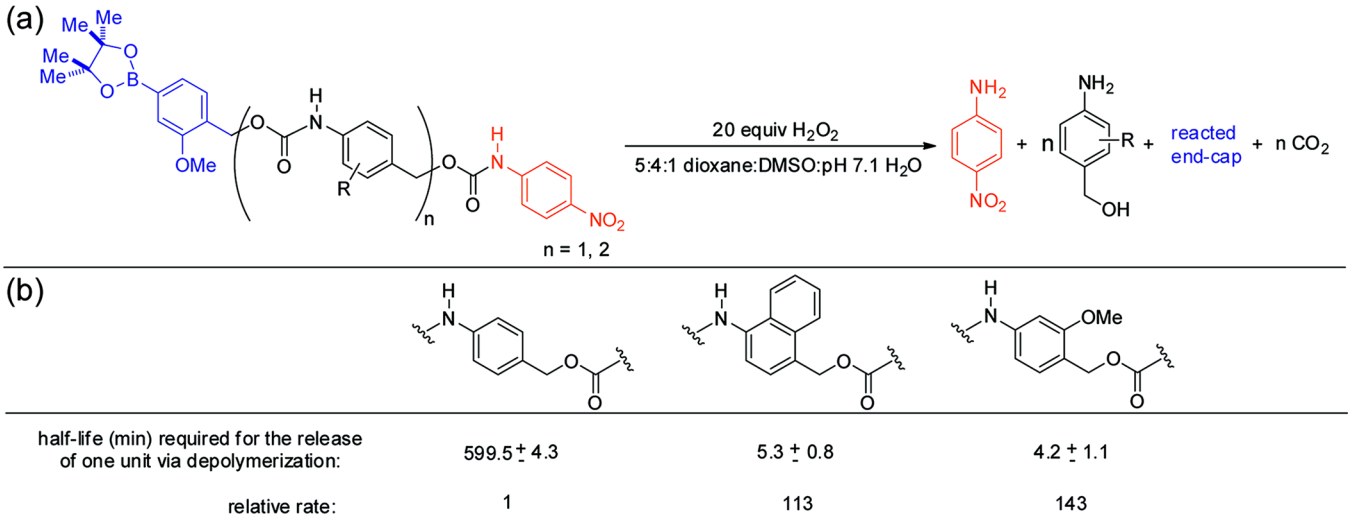

Figure 5. Half-lives for release of each repeating unit during a depolymerization reaction. (a) The release of *p*-nitroaniline from the oligomers via depolymerization in response to excess hydrogen peroxide was measured by UV/vis spectroscopy. (b) Comparison of the half-lives for the release of one repeating unit. The values are the average of three measurements and the error bars represent the standard deviations from these averages.

Figure 5a, but in the absence of hydrogen peroxide, over 10 h (a long exposure time given the depolymerization half-life of 4.2 ± 1.1 min and 5.3 ± 0.8 min for a single unit in **13** and **20**, respectively) revealed that the methoxybenzene- and naphthalene-based oligomers decomposed nonspecifically 4× and 14× more than the benzene-based oligomer (Figure S3, Supporting Information). The magnitude of nonspecific depolymerization under this long exposure time is equally telling: i.e., the benzene-based oligomer decomposed by 1.7% while the methoxybenzene- and naphthalene-based oligomers decomposed 7.5% and 24%, respectively. Consequently, the rate of background reaction must be taken into account when designing functional materials from these types of oligomers/polymers when the material will remain exposed to an aqueous environment for prolonged periods.

Solvent Effects on the Depolymerization Rate. The polarity of the environment in which the aromatic-based oligomers/polymers depolymerize should have a substantial effect on the rate of depolymerization.[18] To test this idea, we measured the half-life for release of a single repeating unit in solvent systems that varied in polarity (Figure 6).

The reaction conditions and subtraction procedure shown in Figure 5a were used in this experiment as well, with the exception that the solvent system was varied by altering the percentage of dioxanes in the *p*-dioxanes−DMSO−water (0.01 M phosphate buffer, pH 7.1) mixture. For example, the experiment corresponding to 30% dioxanes used a solvent system consisting of 30% dioxanes and 70% 4:1 DMSO−water. The ratio of DMSO to buffered H_2O was kept constant at 4:1 in all experiments.

For the benzene-based oligomers, the half-life is prohibitively long, even in the highest polarity solvents in which it is soluble, yet increases further as the polarity of the solvent decreases. The methoxybenzene- and naphthalene-based systems, in contrast, show slight increases in half-life as the polarity of the solvent decreases up to a solvent composition containing 50% dioxanes. Even in 70% dioxanes, the half-life for one repeating unit increases by only 22 min for the methoxybenzene-based system and 15 min for the naphthalene-based system relative to the half-lives in 10% dioxanes. These new oligomers not only depolymerize faster than the benzene-based system, they also depolymerize quickly in substantially more nonpolar environments than the benzene-based system.

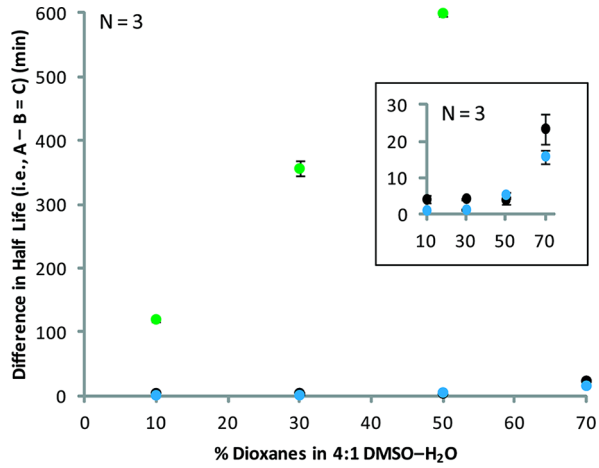

Figure 6. Solvent effects on the rate for releasing a single repeating unit using the general conditions described in Figure 3. The color of the data points reflects the composition of the repeating unit as follows: the benzene-based repeating unit is green, the methoxybenzene-based repeating unit is black, and the naphthalene-based repeating unit is blue. The inset shows the data for just the methoxybenzene- and naphthalene-based repeating units. The solvent polarity reflects the percentage of dioxanes in the solvent system. The half-lives are the average of three trials (N = 3); most of the error bars are smaller than the data points.

CONCLUSIONS

In conclusion, our fundamental studies show that the rate of depolymerization of stimuli-responsive poly(carbamates) can be increased both by altering the electron density and decreasing the overall aromatic character of the repeating units. Implementation of these strategies is especially useful in low polarity environments where the rate of depolymerization (i.e., formation of azaquinone methide) is slow. We expect that this work will provide guidance for modifying depolymerizable poly(carbamates) rationally, which will make this class of depolymerizable polymers more suitable to a diverse range of

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applications, including those involving responses in the solid state, such as in stimuli-responsive materials and smart coatings.

EXPERIMENTAL PROCEDURES

Materials. All reactions were performed in flame-dried glassware under a positive pressure of argon unless otherwise noted. Air- and moisture-sensitive liquids were transferred via syringe or stainless steel cannula. Organic solutions were concentrated by rotary evaporation (25−40 mmHg) at 30 °C. All reagents were purchased commercially and were used as received. Acetonitrile, benzene, dichloromethane, *N*,*N*-dimethylformamide, tetrahydrofuran, toluene, and triethylamine were purified by the method of Pangborn et al.[21] Flash column chromatography was performed as described by Still et al.,[22] employing silica gel (60 Å pore size, 32−63 μm, standard grade). Thin-layer chromatography was carried out on silica gel TLC plates (20 × 20 cm w/h, F-254, 250 μm). Deionized water was purified by filtration and irradiation with UV light.

Methods. Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded using either a 300, 360, or 400 MHz NMR spectrometer at 25 °C, as indicated. Proton chemical shifts are expressed in parts per million (ppm) and are referenced to residual protium in the NMR solvent ($CHCl_3$ δ 7.26 ppm or $CO(CH_3)_2$ δ 2.05 ppm).[23] Data are represented as follows: chemical shift, multiplicity (s = singlet, bs = broad singlet, d = doublet, dd = doublet of doublets, t = triplet, m = multiplet, and/or multiple resonances), integration, and coupling constant (*J*) in hertz. Carbon chemical shifts are expressed in parts per million and are referenced to the carbon resonances of the NMR solvent ($CDCl_3$ δ 77.0 ppm or $CO(CH_3)_2$ δ 29.8 and 206.3 ppm). UV/vis spectroscopic data were obtained using a six-cell spectrometer. LCMS data was obtained using an HPLC with a UV detector, a quadrupole mass spectrometer equipped with an atmospheric-pressure chemical ionization chamber, and a 150 mm ×2.1 mm Betasil diphenyl column. Preparative-scale HPLC was performed using an HPLC with a UV detector and a 150 mm × 30 mm preparative C18 column. Low- and high-resolution mass spectra were acquired using mobile phases containing 5 mM ammonium formate.

General Conditions for Measuring the Release Kinetics of Oligomers 6, 7, 12, 13, 17, and 20. *p*-Dioxanes (250 μL), dimethyl sulfoxide (190 μL), and phosphate-buffered water (40 μL, 0.01 M, pH 7.1) were added to a 2 mL vial and swirled to mix. Compound **6** (10 μL from a 0.01 M solution in DMSO) was added to the vial, and the vial was vortexed for 5 s. Hydrogen peroxide (10 μL from a 0.2 M solution in phosphate-buffered water, 0.01 M, pH 7.1) was added, and the combined solution was aspirated using a pipet. The solution was transferred to a quartz cuvette (500 μL, 0.1 cm path length), and the absorbance value at 385 nm was monitored continuously. (This example is for the "50% dioxanes" scenario referred to in Figures 5 and 6.)

Methodology for Determining Half-Lives. 3-Methoxyphenylboronic acid pinacol ester, compound **21** (Figure 7), was synthesized as a model of a reaction-based detection unit to measure the rate of oxidative cleavage of the boronic ester in the absence of a subsequent depolymerization. The oxidation of compound **21** to 3-methoxyphenol was monitored using UV/vis spectroscopy. The absorbance value at 288 nm was measured continuously under the solvent conditions shown in Figure 5. Figure 7a compares the rate of oxidative cleavage of **21** to the rate of release of *p*-nitroaniline for oligomer **13**. The oxidative cleavage reaction reaches 90% completion at approximately 20 min; thus, the first 20 min of the oligomer depolymerization kinetics will be affected by the kinetics of the oxidative cleavage reaction. Therefore, the first 20 min of the kinetics data for **13** and the other oligomers were excluded when determining half-lives for depolymerization.

Based on this caveat, the following method was used to calculate the half-lives for the depolymerization reactions based on the relative quantity of released *p*-nitroaniline. The natural log of the extent of the reaction was plotted against time (Figure 7b). The half-life was determined by dividing ln(2) by the slope of the line obtained from the first-order plot.

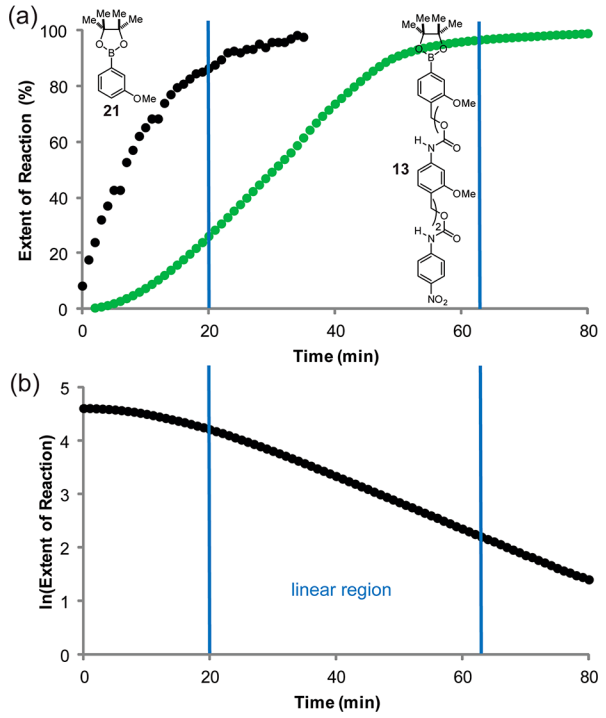

Figure 7. (a) Plot of "extent of reaction" vs "time" for oligomer **13** and compound **21**. For the oligomer, the extent of reaction refers to the complete release of *p*-nitroaniline, whereas for compound **21**, extent of reaction refers to complete oxidative cleavage to reveal 2-methoxyphenol. (b) A plot of "ln(extent of reaction)" vs "time" for oligomer **13**. The linear region, showing first-order kinetics, is bracketed with blue lines.

Preparation of Compound 4. Phenyl chloroformate (1.7 mL, 13 mmol, 1.1 equiv) was added dropwise over 5 min to a solution of 4-aminobenzyl alcohol (1.5 g, 12 mmol, 1.0 equiv) in a 2:2:1 mixture of tetrahydrofuran-saturated aqueous sodium bicarbonate−water (60 mL) under an atmosphere of air. The reaction mixture was stirred for 15 min at 23 °C. Dichloromethane (30 mL) was added in one portion, followed by saturated aqueous sodium bicarbonate (10 mL) in one portion, and the organic and aqueous layers were separated. The organic layer was washed with saturated aqueous sodium bicarbonate solution (1 × 50 mL) and was dried over sodium sulfate. The sodium sulfate was removed by filtration, the solvent was removed by rotary evaporation, and the residue was purified by silica gel flash column chromatography (10% ethyl acetate in hexanes, increasing to 70% ethyl acetate in hexanes) to afford compound **22** as a white solid (2.8 g, 12 mmol, 95%), which was identical by ^{1}H NMR with the known compound.[7]

tert-Butyldimethylsilyl chloride (0.75 g, 5.0 mmol, 1.2 equiv), imidazole (0.42 g, 6.2 mmol, 1.5 equiv), and dimethylaminopyridine (50 mg, 42 μmol, 0.01 equiv) were added to a solution of compound **22** (1.0 g, 4.2 mmol, 1.0 equiv) in dichloromethane (14 mL) at 23 °C. The reaction mixture was stirred for 1 h at 23 °C and then quenched by dropwise addition of methanol (5 mL). The solvent was removed by rotary evaporation, and the residue was purified by silica gel flash column chromatography (2% ethyl acetate in hexanes, increasing to 20% ethyl acetate in hexanes) to afford compound **4** as a white, amorphous solid (1.4 g, 4.0 mmol, 96%): IR (cm^{-1}) 3314, 2928, 2856, 1713, 1614, 1543; ^{1}H NMR δ (300 MHz, $CDCl_3$) 7.44−7.20 (m, 9H), 6.97 (bs, 1H), 4.73 (s, 2H), 0.96 (s, 9H), 0.12 (s, 6H); ^{13}C NMR δ (300 MHz, $CDCl_3$) 150.7, 136.3, 129.6, 127.1, 125.8, 121.8, 118.8, 64.7, 26.1, 18.6, −5.1 (There appear to be overlapping peaks in the aromatic region of the ^{13}C spectrum); MS (Q MS APCI+) 358.3 (M +

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H^+); HRMS (TOF MS AP+) calcd for $C_{20}H_{31}N_2O_3Si$ ($M + NH_4^+$) 375.2104, found 375.2125.

Preparation of Compound 2. 4-Bromo-2-methoxybenzyl alcohol (1.0 g, 4.6 mmol, 1 equiv), bis(pinacolato)diboron (1.4 g, 5.5 mmol, 1.2 equiv), $PdCl_2(dppf)\cdot CH_2Cl_2$ (0.19 g, 0.23 mmol, 0.05 equiv), 1,1′-bis(diphenylphosphino)ferrocene (0.13 g, 0.23 mmol, 0.05 equiv), and KOAc (1.4 g, 13.8 mmol, 3 equiv) were sealed in a two-neck round-bottom flask equipped with a coldfinger and placed under vacuum for 1 h. The flask was purged with argon, and *p*-dioxanes (35 mL) was added. The reaction mixture was heated to 80 °C and stirred for 48 h. The reaction mixture was cooled to 23 °C, diluted with ethyl acetate (35 mL), and filtered through a pad of alternating layers of Celite and silica gel (with silica gel as the bottom layer, 6 layers in total). The filtrate was concentrated by rotary evaporation, and the residue was purified using preparative, centrifugally accelerated radial thin-layer chromatography (10% ethyl acetate in hexanes on a 4 cm silica gel plate) to afford compound **2** as a white, amorphous solid (1.1 g, 3.9 mmol, 85%): IR (cm^{-1}) 3505, 2984; ^1H NMR δ (300 MHz, $CDCl_3$) 7.45 (d, 1H, J = 7.2 Hz), 7.32−7.30 (m, 2H), 4.71 (d, 2H, J = 5.1 Hz), 3.92 (s, 3H), 2.53 (bs, 1H), 1.37 (s, 12H); ^{13}C NMR δ (300 MHz, $CDCl_3$) 156.8, 132.2, 127.9, 127.5, 115.5, 83.8, 62.1, 55.3, 24.9 (there appear to be overlapping peaks in the aromatic region of the ^{13}C spectrum); MS (Q MS APCI+) 247.1 ($M - OH^-$); HRMS (TOF MS AP+) calcd for $C_{14}H_{20}O_3B$ ($M - OH^-$) 247.1506, found 247.1504.

Preparation of Oligomer 6. Dibutyltin dilaurate (25 μL, 43 μmol, 0.2 equiv) was added dropwise to a solution of compounds **2** (63 mg, 0.24 mmol, 1.1 equiv) and **4** (77 mg, 0.22 mmol, 1.0 equiv) in toluene (2.2 mL) at 110 °C. The reaction mixture was stirred for 2 h at 110 °C, then cooled to 23 °C. The solution was concentrated by rotary evaporation and the residue was purified by silica gel flash chromatography (5% ethyl acetate in hexanes, increasing to 15% ethyl acetate in hexanes) to afford **23** as a yellow oil (110 mg, 0.21 mmol, 96%): IR (cm^{-1}) 3318, 2923, 2852, 1724, 1532; ^1H NMR δ (300 MHz, $CDCl_3$) 7.47−7.27 (m, 7H), 6.98 (bs, 1H), 5.31 (s, 2H), 4.72 (s, 2H), 3.91 (s, 3H), 1.39 (s, 12H), 0.97 (s, 9H), 0.13 (s, 6H); ^{13}C NMR δ (300 MHz, $CDCl_3$) 159.9, 156.8, 136.7, 132.0, 128.9, 127.5, 127.2, 126.8, 118.5, 115.8, 83.9, 64.6, 62.4, 55.5, 25.9, 24.8, 18.3, −5.3 (There appear to be overlapping peaks in the aromatic region of the ^{13}C spectrum); MS (Q MS APCI−) 526.3 ($M - H^+$); HRMS (TOF MS AP−) calcd for $C_{28}H_{41}BNO_6Si$ ($M - H^+$) 526.2796, found 526.2811.

p-Toluenesulfonic acid monohydrate (32 mg, 0.17 mmol, 0.3 equiv) was added in one portion to a solution of compound **23** (0.30 g, 0.57 mmol, 1.0 equiv) in a 4:1 mixture of tetrahydrofuran−water (5.7 mL). The reaction mixture was stirred at 23 °C under an atmosphere of air for 3 h. Ethyl acetate (10 mL) was added in one portion, followed by saturated aqueous sodium bicarbonate (10 mL) in one portion, and the organic and aqueous layers were separated. The organic layer was washed with saturated aqueous sodium bicarbonate solution (1 × 10 mL) and was dried over sodium sulfate. The sodium sulfate was removed by filtration, the solvent was removed by rotary evaporation, and the residue was purified by silica gel flash column chromatography (100% hexanes increasing to 60% ethyl acetate in hexanes) to afford compound **5** as a white, amorphous solid (140 mg, 0.33 mmol, 58%): IR (cm^{-1}) 3493, 3278, 2968, 2918, 2860, 1713, 1604, 1545; ^1H NMR δ (400 MHz, $CO(CD_3)_2$) 8.72 (bs, 1H), 7.53 (d, 2H, J = 8.4 Hz), 7.40 (d, 1H, J = 7.4 Hz), 7.36 (d, 1H, J = 7.4 Hz), 7.29−2.27 (m, 3H), 5.21 (s, 2H), 4.56 (s, 2H), 4.08 (bs, 1H), 3.87 (s, 3H), 1.33 (s, 12H); ^{13}C NMR δ (400 MHz, $CO(CD_3)_2$) 157.3, 154.1, 138.7, 137.4, 128.9, 128.7, 127.9, 127.6, 118.7, 116.1, 84.4, 64.2, 61.9, 55.5, 25.0 (There appear to be overlapping peaks in the aromatic region of the ^{13}C spectrum); MS (Q MS APCI−) 412.1 ($M - H^+$); HRMS (TOF MS AP−) calcd for $C_{22}H_{27}BNO_6$ ($M - H^+$) 412.1937, found 412.1935.

A solution of compound **5** (0.14 g, 0.33 mmol, 1.0 equiv) and 4-nitrophenyl isocyanate (64 mg, 0.39 mmol, 1.2 equiv) in toluene (3.3 mL) was heated to 80 °C. The reaction mixture was stirred for 3 h at 80 °C and then cooled to 23 °C. The solvent was removed by rotary evaporation and the residue was purified by preparative scale HPLC (C18 column, 30% acetonitrile in water increasing to 90% over 10 min, maintaining 90% acetonitrile in water for 15 min) to afford oligomer **6** as an off-white, amorphous solid (0.11 g, 0.19 mmol, 58%): IR (cm^{-1}) 3308, 2976, 1708, 1598, 1534, 1508; ^1H NMR δ (300 MHz, $CO(CD_3)_2$) 9.31 (bs, 1H), 8.81 (bs, 1H), 8.16 (d, 2H, J = 5.0 Hz), 7.76 (d, 2H, J = 5.0 Hz), 7.56 (d, 2H, J = 8.6 Hz), 7.36−7.30 (m, 5H), 5.18 (s, 2H), 5.12 (s, 2H), 3.83 (s, 3H), 1.29 (s, 12H); ^{13}C NMR δ (300 MHz, $CO(CD_3)_2$) 157.3, 154.0, 153.8, 146.1, 143.1, 140.1, 131.0, 129.9, 128.7, 128.7, 127.5, 125.4, 118.8, 118.3, 118.2, 116.1, 84.3, 67.2, 62.0, 55.5, 24.9; MS (Q MS APCI−) 576.2 ($M - H^+$); HRMS (TOF MS AP−) calcd for $C_{29}H_{31}BN_3O_9$ ($M - H^+$) 576.2153, found 576.2130.

Preparation of Oligomer 7. Dibutyltin dilaurate (0.15 mL, 0.26 mmol, 0.2 equiv) was added dropwise to a solution of compounds **5** (0.53 g, 1.3 mmol, 1.0 equiv) and **4** (0.50 g, 1.4 mmol, 1.1 equiv) in toluene (6.4 mL) at 110 °C. The reaction mixture was stirred for 2 h at 110 °C and then cooled to 23 °C. The solution was concentrated by rotary evaporation, and the residue was purified by silica gel flash chromatography (10% ethyl acetate in hexanes increasing to 30% ethyl acetate in hexanes) to afford **24** as a yellow oil (0.68 g, 1.1 mmol, 78%): IR (cm^{-1}) 3314, 2929, 2856, 1709, 1600, 1528; ^1H NMR δ (400 MHz, $CO(CD_3)_2$) 8.84 (bs, 1H), 8.67 (bs, 1H), 7.62 (d, 2H, J = 8.3 Hz), 7.55 (d, 2H, J = 8.3 Hz), 7.42−7.36 (m, 4H), 7.30−7.26 (m, 3H), 5.22 (s, 2H), 5.11 (s, 2H), 4.71 (s, 2H), 3.89 (s, 3H), 1.34 (s, 12H), 0.93 (s, 9H), 0.10 (s, 6H); ^{13}C NMR δ (400 MHz, $CO(CD_3)_2$) 157.6, 154.4, 154.4, 140.2, 139.1, 136.7, 132.0, 130.0, 129.1, 129.0, 127.9, 127.7, 119.0, 116.5, 84.7, 66.7, 65.3, 62.3, 55.8, 26.4, 18.9, 17.5, −5.0 (there appear to be overlapping peaks in the aromatic region of the ^{13}C spectrum); MS (Q MS APCI−) 675.3 ($M - H^+$); HRMS (TOF MS AP−) calcd for $C_{36}H_{48}BN_2O_8Si$ ($M - H^+$) 675.3273, found 675.3254.

p-Toluenesulfonic acid monohydrate (57 mg, 0.30 mmol, 0.3 equiv) was added in one portion to a solution of compound **24** (0.68 g, 1.0 mmol, 1.0 equiv) in a 9:1 mixture of tetrahydrofuran−water (10 mL). The reaction mixture was stirred at 23 °C under an atmosphere of air for 5 h. Ethyl acetate (5 mL) was added in one portion, followed by saturated aqueous sodium bicarbonate (5 mL) in one portion, and the organic and aqueous layers were separated. The organic layer was washed with saturated aqueous sodium bicarbonate solution (1 × 10 mL) and was dried over sodium sulfate. The sodium sulfate was removed by filtration, the solvent was removed by rotary evaporation, and the residue was purified by silica gel flash column chromatography (30% ethyl acetate in hexanes increasing to 50% ethyl acetate in hexanes) to afford compound **25** as a white, amorphous solid (0.43 g, 0.76 mmol, 76%): IR (cm^{-1}) 3302, 2976, 1705, 1601, 1530; ^1H NMR δ (300 MHz, $CO(CD_3)_2$) 8.85 (bs, 1H), 8.66 (bs, 1H), 7.60 (d, 2H, J = 8.5 Hz), 7.52 (d, 2H, J = 8.3 Hz), 7.41−7.26 (m, 7H), 5.21 (s, 2H), 5.10 (s, 2H), 4.55 (s, 2H), 4.00 (bs, 1H), 3.88 (s, 3H), 1.33 (s, 12H); ^{13}C NMR δ (300 MHz, $CO(CD_3)_2$) 157.7, 154.5, 154.4, 140.3, 139.1, 137.8, 132.1, 130.1, 129.1, 128.2, 127.9, 119.1, 116.6, 84.8, 66.8, 64.5, 62.4, 55.9, 25.3 (there appear to be overlapping peaks in the aromatic region of the ^{13}C spectrum); MS (Q MS APCI−) 561.3 ($M - H^+$); HRMS (TOF MS AP−) calcd for $C_{30}H_{34}BN_2O_8$ ($M - H^+$) 561.2408, found 561.2406.

A solution of compound **25** (0.10 g, 0.18 mmol, 1.0 equiv) and 4-nitrophenyl isocyanate (35 mg, 0.21 mmol, 1.2 equiv) in toluene (1.8 mL) was heated to 80 °C. The reaction mixture was stirred for 2.5 h at 80 °C and then cooled to 23 °C. The solvent was removed by rotary evaporation, and the residue was purified by preparative scale HPLC (C18 column, 30% acetonitrile in water increasing to 90% over 10 min, maintaining 90% acetonitrile in water for 15 min) to afford oligomer **7** as an off-white, amorphous solid (130 mg, 0.17 mmol, 98%): IR (cm^{-1}) 3307, 2976, 2148, 1705, 1598, 1529, 1508; ^1H NMR δ (300 MHz, $CO(CD_3)_2$) 9.37 (bs, 1H), 8.85 (bs, 1H), 8.79 (bs, 1H), 8.22 (d, 2H, J = 9.3 Hz), 7.82 (d, 2H, J = 9.3 Hz), 7.60 (d, 4H, J = 8.3) 7.40−7.33 (m, 7H), 5.20 (s, 2H), 5.15 (s, 2H), 5.11 (s, 2H), 3.88 (s, 3H), 1.32 (s, 12H); ^{13}C NMR δ (360 MHz, $CO(CD_3)_2$) 157.5, 154.3, 154.3, 146.4, 143.4, 140.4, 140.2, 131.8, 131.2, 130.2, 130.0, 129.0, 128.9, 127.8, 125.7, 119.0, 118.6, 118.5, 116.4, 84.6, 67.4, 66.8, 62.2, 55.8, 25.1; MS (Q MS APCI−) 761.2 ($M - H^+ + 2H_2O$); HRMS (TOF MS AP−) calcd for $C_{37}H_{38}BN_4O_{11}$ ($M - H^+$) 725.2630, found 725.2632.

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Preparation of Compound 10. Sodium borohydride (0.69 g, 18 mmol, 1.1 equiv) was added in one portion to a solution of 2-methoxy-4-nitrobenzaldehyde (3.0 g, 17 mmol, 1.0 equiv) in a 1:1 mixture of dichloromethane−methanol (56 mL) at 0 °C. The reaction mixture was stirred for 15 min at 0 °C and then was slowly diluted by dropwise addition of saturated aqueous ammonium chloride solution (10 mL) and allowed to warm to 23 °C. Dichloromethane (50 mL) was added in one portion, followed by saturated aqueous ammonium chloride solution (50 mL) in one portion, and the organic and aqueous layers were separated. The organic layer was washed with saturated aqueous sodium chloride solution (1 × 50 mL) and was dried over sodium sulfate. The sodium sulfate was removed by filtration, and the solvent was removed by rotary evaporation to provide compound **26** as a pale yellow, amorphous solid, which was used without further purification.

tert-Butyldimethylsilyl chloride (3.0 g, 20 mmol, 1.2 equiv), imidazole (1.7 g, 25 mmol, 1.5 equiv), and dimethylaminopyridine (20 mg, 0.17 mmol, 0.01 equiv) were added in one portion to a solution of compound **26** (3.0 g, 17 mmol, 1.0 equiv) in dichloromethane at 23 °C. The reaction mixture was stirred for 1 h at 23 °C and then was quenched by dropwise addition of methanol (10 mL). The solvent was removed by rotary evaporation and the residue was purified by silica gel flash column chromatography (100% hexanes followed by 10% ethyl acetate in hexanes) to afford compound **9** as a light yellow, amorphous solid (4.9 g, 16 mmol, 99% over 2 steps): IR (cm^{-1}) 2926, 2855, 1516; ^1H NMR δ (300 MHz, $CDCl_3$) 7.89 (dd, 1H, J = 8.3 Hz, 2.0 Hz), 7.67−7.64 (m, 2H), 4.80 (s, 2H), 3.93 (s, 3H), 0.98 (s, 9H), 0.15 (s, 6H); ^{13}C NMR δ (300 MHz, $CDCl_3$) 156.0, 147.8, 138.1, 126.6, 116.1, 104.5, 60.1, 55.8, 26.1, 18.5, −5.3. Anal. Calcd for $C_{14}H_{23}NO_4Si$: C, 56.54; H, 7.79; N, 4.71. Found: C, 56.56; H, 7.88; N, 4.65.

Palladium (10% by weight on carbon powder) (0.30 g, 15% by weight of compound **9**) was added in one portion to a solution of compound **9** (2.0 g, 6.7 mmol, 1.0 equiv) in tetrahydrofuran (34 mL) under a N_2 atmosphere. The flask was evacuated and purged three times with H_2 gas. The reaction mixture was stirred vigorously for 1.5 h at 23 °C under an atmosphere of H_2. The flask was evacuated and purged with argon, and the reaction mixture was filtered through a pad of Celite. The solvent was removed by rotary evaporation, and the residue was purified by silica gel flash column chromatography (25% ethyl acetate in hexanes, increasing to 60% ethyl acetate in hexanes) to afford compound **27** as a brown, amorphous solid (1.7 g, 6.2 mmol, 93%): IR (cm^{-1}) 3364, 2928, 2855, 1616, 1511; ^1H NMR δ (400 MHz, $CDCl_3$) 7.21 (d, 1H, J = 8.0 Hz), 6.31 (dd, 1H, J = 8.0, 1.8 Hz), 6.23 (d, 1H, J = 1.6 Hz), 4.69 (s, 2H), 3.78 (s, 3H), 3.65 (bs, 2H), 0.96 (s, 9H), 0.12 (s, 6H); ^{13}C NMR δ (400 MHz, $CDCl_3$) 157.4, 146.7, 128.6, 120.1, 107.0, 98.2, 60.3, 55.2, 26.2, 18.6, −5.1; MS (Q MS APCI +) 268.2 (M + H^+); HRMS (TOF MS AP+) calcd for $C_{14}H_{26}NO_2Si$ (M + H^+) 268.1733, found 268.1723.

Phenyl chloroformate (0.85 mL, 6.8 mmol, 1.1 equiv) was added dropwise over 5 min to a solution of compound **27** (1.7 g, 6.2 mmol, 1.0 equiv) in a 2:2:1 mixture of tetrahydrofuran−saturated aqueous sodium bicarbonate−water (30 mL) under an atmosphere of air. The reaction mixture was stirred for 15 min at 23 °C. Ethyl acetate (30 mL) was added in one portion, followed by saturated aqueous sodium bicarbonate (10 mL) in one portion, and the organic and aqueous layers were separated. The organic layer was washed with saturated aqueous sodium bicarbonate solution (1 × 50 mL) and was dried over sodium sulfate. The sodium sulfate was removed by filtration, the solvent was removed by rotary evaporation, and the residue was purified by silica gel flash column chromatography (5% ethyl acetate in hexanes, increasing to 10% ethyl acetate in hexanes) to afford compound **10** as a white, amorphous solid (2.4 g, 6.2 mmol, 100%): IR (cm^{-1}) 3272, 2928, 2854, 1712, 1610, 1550; ^1H NMR δ (300 MHz, $CDCl_3$) 7.45−7.21 (m, 8H), 6.81 (d, 1H, J = 8.1 Hz), 4.78 (s, 2H), 3.81 (s, 3H), 1.02 (s, 9H), 0.17 (s, 6H); ^{13}C NMR δ (300 MHz, $CDCl_3$) 156.9, 151.9, 150.6, 137.3, 129.5, 127.3, 125.8, 125.4, 121.8, 110.3, 101.3, 60.1, 55.2, 26.1, 18.6, −5.2; MS (Q MS APCI+) 256.1 (M − $OTBS^-$); HRMS (TOF MS AP+) calcd for $C_{15}H_{14}NO_3$ (M - $OTBS^-$) 256.0974, found 256.0963.

Preparation of Oligomer 12. Dibutyltin dilaurate (0.10 mL, 0.18 mmol, 0.2 equiv) was added dropwise to a solution of compounds **2** (0.23 g, 0.89 mmol, 1.1 equiv) and **10** (0.31 g, 0.81 mmol, 1.0 equiv) in toluene (8 mL) at 110 °C. The reaction mixture was stirred for 0.5 h at 110 °C and then cooled to 23 °C. The solution was concentrated by rotary evaporation, and the residue was purified by silica gel flash chromatography (10% ethyl acetate in hexanes increasing to 15% ethyl acetate in hexanes) to afford **28** as a yellow oil (0.36 g, 0.65 mmol, 81%): IR (cm^{-1}) 3318, 2928, 2854, 2361, 1736, 1605, 1535, 1511; ^1H NMR δ (400 MHz, $CDCl_3$) 7.41−7.26 (m, 5H) 6.72−6.69 (m, 2H), 5.27 (s, 2H), 4.70 (s, 2H), 3.89 (s, 3H), 3.80 (s, 3H), 1.35 (s, 12H), 0.94 (s, 9H), 0.09 (s, 6H); ^{13}C NMR δ (300 MHz, $CDCl_3$) 156.8, 156.4, 153.5, 137.7, 128.8, 127.4, 127.1, 127.1, 125.0, 115.8, 109.9, 100.9, 83.9, 62.3, 59.9, 55.4, 55.1, 26.0, 24.8, 18.4, −5.4 (there appear to be overlapping peaks in the aromatic region of the ^{13}C spectrum); MS (Q MS APCI−) 556.3 (M − H^+). HRMS (TOF MS AP−) calcd for $C_{29}H_{43}BNO_7Si$ (M − H^+) 556.2902, found 556.2900.

p-Toluenesulfonic acid monohydrate (37 mg, 0.20 mmol, 0.3 equiv) was added in one portion to a solution of compound **28** (0.36 g, 0.65 mmol, 1.0 equiv) in a 4:1 mixture of tetrahydrofuran−water (6.5 mL). The reaction mixture was stirred at 23 °C under an atmosphere of air for 3.5 h. Ethyl acetate (5 mL) was added in one portion, followed by saturated aqueous sodium bicarbonate (5 mL) in one portion, and the organic and aqueous layers were separated. The organic layer was washed with saturated aqueous sodium bicarbonate solution (1 × 20 mL) and was dried over sodium sulfate. The sodium sulfate was removed by filtration, the solvent was removed by rotary evaporation, and the residue was purified by silica gel flash column chromatography (5% acetone in methylene chloride increasing to 10% acetone in methylene chloride) to afford compound **11** as a yellow, amorphous solid (79 mg, 0.18 mmol, 27%): IR (cm^{-1}) 3302, 2974, 2855, 1729, 1606, 1538, 1511; ^1H NMR δ (360 MHz, $CO(CD_3)_2$) 8.74 (bs, 1H), 7.40−7.27 (m, 5H), 7.06 (dd, 1H, J = 8.1 Hz, 1.8 Hz), 5.20 (s, 2H), 4.53 (s, 2H), 3.87 (s, 3H), 3.77 (s, 3H), 1.34 (s, 12H); ^{13}C NMR δ (360 MHz, $CO(CD_3)_2$) 157.7, 157.3, 154.0, 140.0, 128.9, 128.6, 128.4, 127.6, 125.3, 116.1, 110.3, 101.6, 84.4, 61.9, 59.5, 55.5, 55.2, 24.9 (There appear to be overlapping peaks in the aromatic and aliphatic regions of the ^{13}C spectrum); MS (Q MS APCI−) 442.1 (M − H^+); HRMS (TOF MS AP−) calcd for $C_{23}H_{29}BNO_7$ (M − H^+) 442.2037, found 442.2058.

A solution of compound **11** (0.10 g, 0.23 mmol, 1.0 equiv) and 4-nitrophenyl isocyanate (45 mg, 0.27 mmol, 1.2 equiv) in toluene (1.8 mL) was brought to 80 °C. The reaction mixture was stirred for 1 h at 80 °C, and then the solution was cooled to 23 °C. The solvent was removed by rotary evaporation and the residue was purified by preparative scale HPLC (C18 column, 30% acetonitrile in water increasing to 90% over 10 min, maintaining 90% acetonitrile in water for 15 min) to afford oligomer **12** as a yellow, amorphous solid (0.11 g, 0.18 mmol, 77%): IR (cm^{-1}) 3309, 2975, 1709, 1600, 1509; ^1H NMR δ (400 MHz $CO(CD_3)_2$) 9.31 (bs, 1H), 8.86 (bs, 1H), 8.19 (d, 2H, J = 9.2 Hz), 7.80 (d, 2H, J = 9.2 Hz), 7.41−7.29 (m, 5H), 7.10 (d, 1H, J = 8.1 Hz), 5.22 (s, 2H), 5.16 (s, 2H), 3.87 (s, 3H), 3.82 (s, 3H), 1.33 (s, 12H); ^{13}C NMR δ (400 MHz, $CO(CD_3)_2$) 158.9, 157.2, 154.0, 153.9, 146.2, 143.0, 141.7, 131.3, 128.6, 127.5, 125.4, 118.7, 118.2, 116.1, 110.3, 101.8, 84.3, 62.5, 62.0, 55.5, 24.9 (there appear to be overlapping peaks in the aromatic and aliphatic regions of the ^{13}C spectrum); MS (Q MS APCI−) 606.2 (M − H^+); HRMS (TOF MS AP−) calcd for $C_{30}H_{33}BN_3O_{10}$ (M − H^+) 606.2259, found 606.2267.

Preparation of Oligomer 13. Dibutyltin dilaurate (0.10 mL, 0.17 mmol, 0.2 equiv) was added dropwise to a solution of compounds **11** (0.39 g, 0.87 mmol, 1.0 equiv) and **10** (340 mg, 0.87 mmol, 1.0 equiv) in toluene (8.7 mL) at 110 °C. The reaction mixture was stirred for 2 h at 110 °C and then cooled to 23 °C. The solution was concentrated by rotary evaporation, and the residue was purified by silica gel flash chromatography (5% ethyl acetate in hexanes increasing to 10% ethyl acetate in hexanes) to afford **29** as a yellow, amorphous solid (0.39 g, 0.53 mmol, 61%): IR (cm^{-1}) 3315, 2928, 2853, 2360, 1710, 1604, 1513; ^1H NMR δ (300 MHz, $CO(CD_3)_2$) 8.83 (bs, 1H), 8.60 (bs, 1H), 7.41−7.28 (m, 7H), 7.12−7.09 (m, 2H), 5.22 (s, 2H), 5.11 (s, 2H), 4.68 (s, 2H), 3.89 (s, 3H), 3.83 (s, 3H), 3.77 (s, 3H), 1.33 (s,

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12H), 0.94 (s, 9H), 0.09 (s, 6H); ^{13}C NMR δ (300 MHz, $CO(CD_3)_2$) 158.8, 157.3, 157.2, 154.2, 154.0, 141.6, 140.1, 131.0, 128.8, 127.9, 127.6, 124.2, 119.5, 116.2, 110.4, 101.8, 101.5, 84.4, 67.8, 62.0, 61.9, 60.3, 55.6, 55.2, 26.1, 24.9, 18.7, −5.4 (there appear to be overlapping peaks in the aromatic region of the ^{13}C spectrum); MS (Q MS APCI−) 735.3 (M − H$^+$); HRMS (TOF MS AP−) calcd for $C_{40}H_{56}BN_2O_{12}Si$ (M + CH_3COO^-) 795.3721, found 795.3696.

p-Toluenesulfonic acid monohydrate (12 mg, 65 μmol, 0.2 equiv) was added in one portion to a solution of compound **29** (0.24 g, 0.32 mmol, 1.0 equiv) in a 4:1 mixture of tetrahydrofuran−water (3.3 mL). The reaction mixture was stirred at 23 °C under an atmosphere of air for 8 h. Ethyl acetate (5 mL) was added in one portion, followed by saturated aqueous sodium bicarbonate (5 mL) in one portion, and the organic and aqueous layers were separated. The organic layer was washed with saturated aqueous sodium bicarbonate solution (1 × 10 mL) and dried over sodium sulfate. The sodium sulfate was removed by filtration, the solvent was removed by rotary evaporation, and the residue was purified by silica gel flash column chromatography (50% ethyl acetate in hexanes increasing to 70% ethyl acetate in hexanes) to afford compound **30** as a yellow, amorphous solid (0.13 g, 0.32 mmol, 66%): IR (cm^{-1}) 3307, 2923, 2852, 1707, 1604, 1533; ^{1}H NMR δ (400 MHz, $CO(CD_3)_2$) 8.83 (bs, 1H), 8.59 (bs, 1H), 7.41−7.26 (m, 7H) 7.11−7.07 (m, 2H), 5.22 (s, 2H), 5.11 (s, 2H), 4.55 (s, 2H), 3.88 (s, 3H), 3.82 (s, 3H), 3.78 (s, 3H), 1.33 (s, 12H); ^{13}C NMR δ (400 MHz, $CO(CD_3)_2$) 158.8, 157.8, 157.3, 154.2, 154.0, 141.6, 140.1, 131.0, 128.8, 128.5, 127.6, 125.2, 119.5, 116.2, 110.4, 101.9, 84.4, 62.0, 61.9, 59.5, 55.6, 55.5, 55.3, 24.9 (There appear to be overlapping peaks in the aromatic region of the ^{13}C spectrum); MS (Q MS APCI−) 621.3 (M − H$^+$); HRMS (TOF MS AP−) calcd for $C_{32}H_{38}BN_2O_{10}$ (M − H$^+$) 621.2620, found 621.2620.

A solution of compound **30** (67 mg, 0.11 mmol, 1.0 equiv) and 4-nitrophenyl isocyanate (23 mg, 0.14 mmol, 1.3 equiv) in toluene (1.1 mL) was brought to 80 °C. The reaction mixture was stirred for 2 h at 80 °C, and then the solution was cooled to 23 °C. The solvent was removed by rotary evaporation, and the residue was purified by preparative-scale HPLC (C18 column, 30% acetonitrile in water increasing to 90% over 10 min, maintaining 90% acetonitrile in water for 15 min) to afford oligomer **13** as a yellow, amorphous solid (53 mg, 68 μmol, 63%): IR (cm^{-1}) 3311, 2974, 1706, 1600, 1509; ^{1}H NMR δ (400 MHz, $CO(CD_3)_2$) 9.31 (b, 1H), 8.84 (bs, 1H), 8.72 (bs, 1H), 8.19 (dd, 2H, J = 7.3 Hz, 2.0 Hz), 7.80 (dd, 2H, J = 7.2 Hz, 2.0 Hz) 7.40−7.28 (m, 7H) 7.11−7.10 (m, 2H), 5.22 (s, 2H), 5.16 (s, 2H), 5.13 (s, 2H), 3.87 (s, 3H), 3.82 (s, 6H), 1.33 (s, 12H); ^{13}C NMR δ (400 MHz, $CO(CD_3)_2$) 158.9, 158.8, 157.3, 154.2, 154.0, 153.9, 146.3, 143.0, 141.9, 141.6, 131.3, 131.0, 128.7, 127.5, 125.4, 119.3, 118.6, 118.2, 116.1, 110.3, 101.8, 84.4, 62.7, 62.1, 55.5, 24.9 (there appear to be overlapping peaks in the aromatic and aliphatic regions of the ^{13}C spectrum); MS (Q MS APCI−) 821.3 (M − H$^+$ + 2H$_2$O); HRMS (TOF MS AP−) calcd for $C_{39}H_{42}BN_4O_{13}$ (M − H$^+$) 785.2841, found 785.2844.

Preparation of Compound 15. 1-Bromo-4-(bromomethyl)-naphthalene (2.4 g, 8.0 mmol, 1 equiv) and calcium carbonate (8.0 g, 80 mmol, 10 equiv) were suspended in *p*-dioxanes (40 mL) and water (40 mL). The suspension was heated to 110 °C for 12 h and allowed to cool to 23 °C, and 1 M HCl was added until the pH of the solution was 7. The resulting solution was extracted with ethyl acetate (150 mL), and the combined organics were washed with saturated aqueous sodium chloride (1 × 150 mL). The organic and aqueous layers were separated, the organic layer was dried over sodium sulfate, and the sodium sulfate was removed by filtration. The solvent was removed by rotary evaporation to afford compound **31** as a white, amorphous solid, which was used without further purification.

tert-Butyldimethylsilyl chloride (1.4 g, 9.2 mmol, 1.3 equiv) was added in one portion to a solution of compound **31** (1.7 g, 7.1 mmol, 1 equiv) and imidazole (0.72 g, 10.6 mmol, 1.5 equiv) in dichloromethane (40 mL) at 23 °C and was stirred for 16 h. Methanol (3 mL) was added in one portion, and the solution was stirred for 15 min at 23 °C. Dichloromethane (60 mL) was added in one portion, and the solution was washed with saturated aqueous ammonium chloride (1 × 100 mL) followed by saturated aqueous sodium chloride solution (1 × 100 mL). The layers were separated, the organic layer was dried over sodium sulfate, and the sodium sulfate was removed by filtration. The solvent was removed by rotary evaporation, and the residue was purified by silica gel flash column chromatography (1% ethyl acetate in hexanes, increasing to 5% ethyl acetate in hexanes), yielding compound **32** as a white, amorphous solid (2.3 g, 6.7 mmol, 84% over two steps): IR (cm^{-1}) 2954, 2856; ^{1}H NMR δ (300 MHz, $CDCl_3$) 8.28 (d, 1H, J = 8.0 Hz), 7.97 (d, 1H, J = 8.1 Hz), 7.76 (d, 1H, J = 7.7 Hz), 7.61−7.52 (m, 2H), 7.43 (d, 1H, J = 7.7 Hz), 5.14 (s, 2H), 0.94 (s, 9H), 0.11 (s, 6H); ^{13}C NMR δ (360 MHz, $CDCl_3$) 136.8, 131.9, 131.7, 129.5, 127.8, 126.9, 126.6, 124.3, 123.6, 122.1, 63.0, 25.9, 18.4, −5.2; MS (TOF MS ES+, m/z) 351.1 (M + H$^+$); HRMS (TOF MS ES+) calcd for $C_{17}H_{22}OSiBr$ (M − H$^-$) 349.0623. Found: 349.0633.

n-Butyllithium (5.4 mL, 2.5 M in hexanes, 2.0 equiv) was added dropwise to a solution of compound **32** (2.3 g, 6.7 mmol, 1 equiv) in tetrahydrofuran (60 mL) at −78 °C, and the resulting mixture was stirred for 5 min. *N*,*N*-Dimethylformamide (2.6 mL, 34 mmol, 5 equiv) was added, the reaction mixture was stirred for 30 min at −78 °C, and then was allowed to warm to 23 °C. After stirring at 23 °C for 1 h, the solution was slowly diluted by dropwise addition of saturated ammonium chloride solution (5 mL), followed by ethyl acetate (200 mL) in one portion, and then saturated aqueous sodium bicarbonate solution (200 mL) in one portion. The layers were separated, and the organic layer was washed with saturated aqueous sodium chloride (1 × 200 mL). The organic layer was dried over sodium sulfate, and the sodium sulfate was removed by filtration. The solvent was removed by rotary evaporation, and the residue was purified by silica gel flash column chromatography (2.5% ethyl acetate in hexanes, increasing to 10% ethyl acetate in hexanes), yielding compound **33** as a waxy, white solid (2.0 g, 6.6 mmol, 97%): IR (cm^{-1}) 2931, 2865, 1687; ^{1}H NMR δ (300 MHz, $CDCl_3$) 10.34 (s, 1H), 9.32 (d, 1H, J = 8.5 Hz), 7.98−7.95 (m, 2H), 7.82 (d, 1H, J = 7.2), 7.69 (t, 1H, J = 7.5), 7.61 (t, 1H, J = 8.0), 5.26 (s, 2H), 0.96 (s, 9H), 0.15 (s, 6H); ^{13}C NMR δ (360 MHz, $CDCl_3$) 193.5, 144.6, 137.0, 130.7, 130.5, 130.4, 128.6, 127.0, 125.7, 122.9, 122.2, 63.0, 25.9, 18.4, −5.3; MS (TOF MS AP+, m/z) 301.1 (M + H$^+$); HRMS (TOF MS AP+) calcd for $C_{20}H_{28}O_2SiN$ (M + H$^+$ + MeCN) 342.1889, found 342.1857.

A solution of sodium dihydrogen phosphate monohydrate (2.8 g, 20 mmol, 6.0 equiv) and sodium chlorite (1.8 g, 20 mmol, 6.0 equiv) in water (30 mL) was added dropwise to a solution of compound **33** (1.0 g, 3.4 mmol, 1 equiv) and 2-methyl-2-butene (2.1 mL, 20 mmol, 6.0 equiv) in acetone (30 mL). The suspension was stirred vigorously for 30 min at 23 °C. Acetone was removed by rotary evaporation, and the aqueous solution was diluted with ethyl acetate (50 mL) in one portion. The organic and aqueous layers were separated, and the organic layer was washed sequentially with saturated aqueous ammonium chloride solution (1 × 30 mL), saturated aqueous sodium chloride (1 × 50 mL), saturated aqueous sodium thiosulfate (1 × 50 mL), and saturated aqueous sodium chloride (1 × 50 mL). The organic layer was dried over sodium sulfate, and the sodium sulfate was removed by filtration. The solvent was removed by rotary evaporation to afford compound **15** as a white, amorphous solid, which was used without further purification.

Preparation of Oligomer 17. Triethylamine (0.1 mL, 0.72 mmol, 1.2 equiv) and diphenylphosphoryl azide (0.16 mL, 0.72 mmol, 1.2 equiv) were added sequentially to a solution of compound **15** (0.19 g, 0.60 mmol, 1 equiv) in benzene (3 mL). The solution was heated to 85 °C for 1 h, and then compound **2** (0.17 g, 0.66 mmol, 1.1 equiv) was added in one portion to the hot solution. The solution was heated to 85 °C for 3 h, allowed to cool to 23 °C, and concentrated by rotary evaporation. The residue was purified by silica gel flash column chromatography (20% ethyl acetate in benzene, increasing to 30% ethyl acetate in benzene) to afford **34** as a white, amorphous solid (0.28 g, 0.49 mmol, 82% over two steps): IR (cm^{-1}) 3311, 2930, 2856, 1731, 1715; ^{1}H NMR δ (300 MHz, $CDCl_3$) 8.05−8.01 (m, 1H), 7.90−7.82 (m, 2H), 7.54−7.47 (m, 3H), 7.42−7.00 (m, 4H), 5.32 (s, 2H), 5.14 (s, 2H), 3.90 (s, 3H), 1.34 (s, 12H), 0.93 (s, 9H), 0.10 (s, 6H); ^{13}C NMR δ (360 MHz, $CDCl_3$) 156.9, 133.7, 131.4, 130.0, 128.9, 127.6, 127.2, 126.1, 125.9, 125.8, 124.2, 124.1, 121.2, 120.2,

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120.1, 115.8, 88.9, 63.4, 62.6, 55.5, 25.9, 24.8, 18.4, −5.2; MS (TOF MS AP−, *m*/*z*) 576.3 (M − H^+); HRMS (TOF MS AP+) calcd for $C_{32}H_{48}BN_2O_6Si$ (M + NH_4^+) 595.3375, found 595.3370.

A solution of *p*-toluenesulfonic acid monohydrate (24 mg, 0.13 mmol, 0.3 equiv) in water (0.2 mL) was added dropwise to a solution of compound **34** (0.25 g, 0.43 mmol, 1 equiv) in tetrahydrofuran (3.8 mL). The resulting solution was stirred at 23 °C for 14 h. Triethylamine (21 μL, 0.15 mmol, 0.35 equiv) was added dropwise to the reaction mixture, and the resulting solution was stirred at 23 °C for 15 min. Pinacol (0.25 g, 2.1 mmol, 5 equiv) was added in one portion, and the reaction mixture was stirred at 23 °C for 24 h. The solvent was removed by rotary evaporation and the residue was dissolved in ethyl acetate (20 mL). The solution was washed with saturated aqueous ammonium chloride solution (1 × 20 mL) followed by saturated aqueous sodium chloride (1 × 20 mL). The organic layer was dried over sodium sulfate, and the sodium sulfate was removed by filtration. The solvent was removed by rotary evaporation, and the residue was purified by silica gel flash column chromatography (20% ethyl acetate in benzene, increasing to 40% ethyl acetate in benzene), yielding compound **16** as a white, amorphous solid (0.16 g, 0.34 mmol, 79%): IR (cm^{-1}) 3389, 3312, 2977, 1724, 1714; ^1H NMR δ (300 MHz, $CDCl_3$) 8.12 (d, 1H, *J* = 6.7 Hz), 7.88 (d, 1H, *J* = 7.5), 7.78 (s, 1H), 7.54−7.45 (m, 2H), 7.41−7.34 (m, 3H), 7.29 (s, 1H), 7.12 (s, 1H), 5.30 (s, 2H), 5.03 (s, 2H), 3.87 (s, 3H), 2.09 (bs, 1H), 1.33 (s, 12H); ^{13}C NMR δ (360 MHz, $CDCl_3$) 157.3, 133.2, 132.5, 129.5, 128.8, 127.9, 127.6, 126.8, 126.5, 126.0, 125.0, 121.6, 116.3, 84.4, 63.9, 63.1, 56.0, 25.2 (there appear to be overlapping peaks in the aromatic region of the ^{13}C spectrum); MS (TOF MS AP−, *m*/*z*) 462.1 (M − H^+); HRMS (TOF MS AP+) calcd for $C_{26}H_{34}BN_2O_6$ (M + NH_4^+) 481.2510, found 481.2513.

Triethylamine (56 μL, 0.40 mmol, 1.5 equiv) was added dropwise to a solution of compound **16** (0.12 g, 0.27 mmol, 1 equiv) and 4-nitrophenyl isocyanate (48 mg, 0.29 mmol, 1.1 equiv) in tetrahydrofuran (2.5 mL). The reaction mixture was stirred at 23 °C for 1.5 h and the solvent was removed by rotary evaporation. The residue was purified by silica gel flash column chromatography (10% ethyl acetate in benzene, increasing to 30% ethyl acetate in benzene), yielding oligomer **17** as a pale yellow, amorphous solid (90 mg, 0.14 mmol, 53%): IR (cm^{-1}) 3312, 2978, 1737, 1714; ^1H NMR δ (300 MHz, $CDCl_3$) 8.13 (d, 2H, *J* = 9.0 Hz), 8.01 (d, 1H, *J* = 8.5 Hz), 7.70 (s, 2H), 7.55−7.34 (m, 7H), 7.26 (s, 1H), 5.57 (s, 2H), 5.25 (s, 2H), 3.84 (s, 3H), 1.32 (s, 12H); ^{13}C NMR δ (360 MHz, $CDCl_3$) 152.8, 142.8, 132.1, 128.5, 127.2, 127.1, 126.9, 126.4, 125.1, 117.8, 115.8, 84.0, 65.8, 62.9, 55.5, 24.8; MS (TOF MS AP−, *m*/*z*) 626.2 (M − H^+); HRMS (TOF MS AP+) calcd for $C_{33}H_{38}BN_4O_9$ (M + NH_4^+) 645.2732, found 645.2731.

Preparation of Oligomer 20. A solution of *p*-toluenesulfonic acid monohydrate (0.18 g, 1.0 mmol, 0.3 equiv) in water (4.3 mL) was added dropwise to a solution of compound **33** (0.95 g, 3.2 mmol, 1 equiv) in tetrahydrofuran (26 mL). The resulting solution was stirred at 23 °C for 14 h. Triethylamine (0.18 mL, 1.3 mmol, 0.4 equiv) was added dropwise to the reaction mixture, and the solvent was removed by rotary evaporation. The residue was dissolved in ethyl acetate (50 mL), and the solution was washed with saturated aqueous ammonium chloride solution (1 × 50 mL) followed by saturated aqueous sodium chloride (1 × 50 mL). The organic layer was dried over sodium sulfate, and the sodium sulfate was removed by filtration. The solvent was removed by rotary evaporation, and the residue was purified by silica gel flash column chromatography (20% ethyl acetate in hexanes, increasing to 60% ethyl acetate in hexanes), yielding compound **35** as a white, amorphous solid (0.58 g, 3.1 mmol, 98%): IR (cm^{-1}) 3391, 2860, 1683; ^1H NMR δ (300 MHz, $CDCl_3$) 10.25 (s, 1H), 9.23 (d, 1H, *J* = 8.4 Hz), 8.01 (d, 1H, *J* = 8.4 Hz), 7.86 (d, 1H, *J* = 7.3 Hz), 7.69−7.62 (m, 2H), 7.59 (t, 1H, *J* = 7.5) 5.17 (s, 2H), 2.54 (s, 1H); ^{13}C NMR δ (360 MHz, $CDCl_3$) 193.6, 144.0, 136.7, 131.0, 130.9, 130.6, 128.8, 127.2, 125.5, 123.4, 123.1, 63.0; MS (TOF MS AP+, *m*/*z*) 187.0 (M + H^+); HRMS (TOF MS AP−) calcd for $C_{12}H_9O_2$ (M − H^+) 185.0603, found 185.0604.

Triethylamine (0.25 mL, 1.8 mmol, 1.2 equiv) and diphenylphosphoryl azide (0.39 mL, 1.8 mmol, 1.2 equiv) were added sequentially to a solution of compound **33** (0.47 g, 1.5 mmol, 1 equiv) in benzene (7.5 mL). The solution was heated to 85 °C for 1 h, and then compound **35** (0.31 g, 1.7 mmol, 1.1 equiv) was added to the hot solution in one portion. The solution was heated to 85 °C for 3 h, allowed to cool to 23 °C, and concentrated by rotary evaporation. The residue was purified by silica gel flash column chromatography (10% ethyl acetate in hexanes, increasing to 30% ethyl acetate in hexanes) to afford **36** as a white, amorphous solid (0.59 g, 1.2 mmol, 79% over two steps): IR (cm^{-1}) 3309, 2928, 2855, 1725, 1693; ^1H NMR δ (300 MHz, $CDCl_3$) 10.36, (s, 1H), 9.32 (d, 1H, *J* = 8.5 Hz), 8.13 (s, 1H), 8.03 (d, 1H, *J* = 7.3 Hz), 7.96 (d, 1H, *J* = 6.2 Hz), 7.88 (d, 1H, 7.5 Hz), 7.83−7.60 (m, 4H) 7.55 (d, 1H, *J* = 7.7 Hz), 7.52−7.48 (m, 2H), 7.02 (s, 1H), 5.76 (s, 2H), 5.14 (s, 2H), 0.93 (s, 9H), 0.10 (s, 6H); ^{13}C NMR δ (360 MHz, $CDCl_3$) 193.3, 139.0, 136.1, 131.5, 131.4, 128.9, 127.5, 126.1, 125.6, 123.7, 64.9, 63.3, 25.9, 18.4, −5.2; MS (TOF MS AP+, *m*/*z*) 517.3 (M + NH_4^+); HRMS (TOF MS AP+) calcd for $C_{30}H_{37}N_2O_4Si$ (M + NH_4^+) 517.2523, found 517.2524.

A solution of sodium dihydrogen phosphate monohydrate (0.98 g, 7.2 mmol, 6.0 equiv) and sodium chlorite (0.64 g, 7.2 mmol, 6.0 equiv) in water (12 mL) was added to a solution of compound **36** (0.59 g, 1.2 mmol, 1 equiv) and 2-methyl-2-butene (0.75 mL, 7.2 mmol, 6.0 equiv) in acetone (12 mL). The suspension was stirred vigorously for 30 min at 23 °C. Acetone was removed by rotary evaporation, and the aqueous solution was diluted with ethyl acetate (50 mL) in one portion. The organic and aqueous layers were separated, and the organic layer was washed sequentially with saturated aqueous ammonium chloride solution (1 × 30 mL), saturated aqueous sodium chloride (1 × 50 mL), saturated aqueous sodium thiosulfate (1 × 50 mL), and saturated aqueous sodium chloride (1 × 50 mL). The organic layer was dried over sodium sulfate, and the sodium sulfate was removed by filtration. The solvent was removed by rotary evaporation to afford compound **18** as a white, amorphous solid, which was used without further purification.

Triethylamine (0.16 mL, 1.1 mmol, 1.2 equiv) and diphenylphosphoryl azide (0.25 mL, 1.1 mmol, 1.2 equiv) were added sequentially to a solution of compound **18** (0.49 g, 0.95 mmol, 1 equiv) in benzene (5 mL). The solution was heated to 85 °C for 1 h, and then compound **2** (0.28 g, 1.1 mmol, 1.1 equiv) was added to the hot solution in one portion. The solution was stirred at 85 °C for 3 h, allowed to cool to 23 °C, and concentrated by rotary evaporation. The residue was purified by silica gel flash column chromatography (5% ethyl acetate in benzene, increasing to 30% ethyl acetate in benzene) to afford **37** as a white, amorphous solid (0.51 g, 0.65 mmol, 65% over two steps): IR (cm^{-1}) 3309, 2930, 1713 (b); ^1H NMR δ (300 MHz, $CDCl_3/C_6D_6$) 8.09 (s, 1H), 8.02 (d, 1H, *J* = 8.2 Hz), 7.87−7.84 (m, 4H), 7.53−7.35, (m, 9H), 7.14, (s, 2H), 5.63 (s, 2H), 5.33 (s, 2H), 5.14 (s, 2H), 3.89 (S, 3H), 1.34 (s, 12H), 0.94 (s, 9H), 0.11 (s, 6H); ^{13}C NMR δ (360 MHz, $CDCl_3/C_6D_6$) 156.9, 154.2, 133.6, 132.2, 131.8, 131.4, 130.0, 129.0, 128.3, 128.1, 127.4, 127.2, 126.6, 126.1, 125.9, 125.8, 124.5, 124.1, 121.2, 121.1, 120.2, 120.1, 115.8, 83.9, 65.4, 63.3, 62.7, 55.5, 25.9, 24.8, 18.3, −5.2 (there appear to be overlapping peaks in the aromatic region of the ^{13}C spectrum); MS (TOF MS AP+, *m*/*z*) 794.2 (M + NH_4^+); HRMS (TOF MS AP+) calcd for $C_{44}H_{57}BN_3O_8Si$ (M + NH_4^+) 794.4008, found 794.4013.

A solution of *p*-toluenesulfonic acid monohydrate (17 mg, 98 μmol, 0.3 equiv) in water (150 μL) was added dropwise to a solution of compound **37** (0.26 g, 0.33 mmol, 1 equiv) in tetrahydrofuran (2.9 mL). The resulting solution was stirred at 23 °C for 14 h. Triethylamine (13 μL, 1.3 mmol, 0.4 equiv) was added dropwise to the reaction mixture, and the resulting solution was stirred at 23 °C for 15 min. Pinacol (0.18 g, 1.7 mmol, 5 equiv) was added in one portion, and the reaction mixture was stirred at 23 °C for 24 h. The solvent was removed by rotary evaporation and the residue was dissolved in ethyl acetate (20 mL). The solution was washed with saturated aqueous ammonium chloride solution (1 × 20 mL) followed by saturated aqueous sodium chloride (1 × 20 mL). The organic layer was dried over sodium sulfate and the sodium sulfate was removed by filtration. The solvent was removed by rotary evaporation and the residue was purified by silica gel flash column chromatography (20% ethyl acetate in benzene, increasing to 50% ethyl acetate in benzene), yielding

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compound **19** as an off-white, amorphous solid (0.2 g, 0.3 mmol, 91%): IR (cm^{-1}) 3430, 3254, 2977, 1707 (b); ^1H NMR δ (300 MHz, $CDCl_3$) 8.07 (d, 2H, J = 8.2 Hz), 7.83−7.63 (m, 4H), 7.52−7.36 (m, 8H), 7.29 (s, 1H), 7.16 (s, 2H), 5.58 (s, 2H), 5.30 (s, 2H), 5.00 (s, 2H), 3.87 (s, 3H), 1.34 (s, 12H); ^{13}C NMR δ (360 MHz, $CDCl_3$) 156.9, 154.2, 133.6, 132.2, 131.7, 128.0, 128.3, 128.1, 127.4, 127.2, 126.6, 126.3, 126.1, 126.0, 125.4, 124.4, 121.2, 115.9, 83.9, 65.4, 63.4, 62.7, 55.5, 24.8 (There appear to be overlapping peaks in the aromatic region of the ^{13}C spectrum); MS (TOF MS AP+, m/z) 680.3 (M + NH_4^+). HRMS (TOF MS AP+) calcd for $C_{38}H_{43}BN_3O_8$ (M + NH_4^+) 680.3143, found 680.3169.

Triethylamine (63 μL, 0.45 mmol, 1.5 equiv) was added dropwise to a solution of compound **19** (0.20 g, 0.30 mmol, 1 equiv) and 4-nitrophenyl isocyanate (60 mg, 0.36 mmol, 1.2 equiv) in tetrahydrofuran (3 mL). The reaction mixture was stirred at 23 °C for 1.5 h, and the solvent was removed by rotary evaporation. The residue was eluted through a short plug of silica (15% ethyl acetate in benzene, increasing to 20% ethyl acetate in benzene), and the solvent was removed by rotary evaporation. The residue was purified by preparative scale HPLC (C18 column, 40% acetonitrile in water increasing to 90% over 15 min, maintaining 90% acetonitrile in water for 10 min) yielding oligomer **20** (0.10 g, 0.12 mmol, 40%) as a pale yellow, amorphous solid: IR (cm^{-1}) 3300, 2977, 1737, 1713 (b); ^1H NMR δ (300 MHz, $CDCl_3/C_6D_6/ CO(CD_3)_2$) 8.87 (s, 1H), 8.04−7.92 (m, 9H), 7.70 (bs, 2H), 7.61 (d, 2H, J = 8.9 Hz), 7.47−7.34 (m, 8H), 5.52 (s, 2H), 5.50 (s, 2H), 5.23 (s, 2H), 3.82 (s, 3H), 1.28 (s, 12H); ^{13}C NMR δ (360 MHz, $CDCl_3/CO(CD_3)_2$) 156.3, 154.2, 152.8, 144.6, 142.1, 133.9, 133.7, 131.8, 128.1, 127.7, 127.4, 127.3, 126.7, 126.2, 125.6, 124.5, 123.7, 121.5, 117.4, 115.4, 83.5, 65.0, 64.9, 62.0, 55.0, 24.4 (there appear to be overlapping peaks in the aromatic region of the ^{13}C spectrum); MS (TOF MS AP+, m/z) 844.2 (M + NH_4^+); HRMS (TOF MS AP+) calcd for $C_{46}H_{48}BN_4O_{11}$ (M + NH_4^+) 844.3365, found 844.3345.

Preparation of Compound 21. Bis(pinacolato)diboron (0.61 g, 2.4 mmol, 1.2 equiv), $PdCl_2(dppf)\cdot CH_2Cl_2$ (0.081 g, 0.099 mmol, 0.05 equiv), and KOAc (0.58 g, 5.9 mmol, 3 equiv) were sealed in a two-neck round-bottom flask equipped with a coldfinger and placed under vacuum for 1 h. The flask was purged with argon, and *p*-dioxanes (15 mL) was added in one portion, followed by 3-bromoanisole (0.25 mL, 2.0 mmol, 1 equiv) in one portion. The reaction mixture was brought to 80 °C and stirred for 18 h. The reaction mixture was cooled to 23 °C, diluted with ethyl acetate (15 mL) in one portion, and filtered through a thin layer of silica gel covered by a pad of Celite. The filtrate was concentrated and the residue was purified by silica gel flash column chromatography (100% hexanes, followed by 2% ethyl acetate in hexanes) to afford compound **21** as a colorless oil (0.23 g, 0.96 mmol, 48%), which was identified by comparison of ^1H NMR data with literature values.[24]

■ ASSOCIATED CONTENT

Supporting Information

Tables of data as well as figures showing ^1H and ^{13}C NMR spectra for intermediates and final compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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