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One-Pot Oxidation and Bromination of 3,4-Diaryl-2,5-dihydrothiophenes Using Br_2: Synthesis and Application of 3,4-Diaryl-2,5-dibromothiophenes

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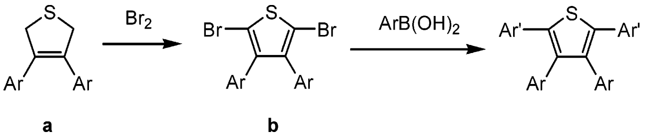

A class of 3,4-diaryl-2,5-dibromothiophenes (**1b**−**5b**) was synthesized by a one-pot reaction of 3,4-diaryl-2,5-dihydrothiophenes with Br_2 reagent in excellent yield (83−92%). It was found that Br_2 performed a double function (oxidation and bromination) during the conversion of 3,4-diaryl-2,5-dihydrothiophenes to 3,4-diaryl-2,5-dibromothiophenes. The application of 3,4-diaryl-2,5-dibromothiophenes used as building blocks was also investigated. Employing 3,4-diphenyl-2,5-dibromothiophene (**1b**) as a template, a class of 2,3,4,5-tetraarylthiophenes was prepared by the Suzuki coupling reaction. This provided a new and simple approach to the preparation of 2,3,4,5-tetraarylthiophenes.

Introduction

Aryl halides are important synthetic intermediates for a variety of transformations that range from formation of functionalized aromatic compounds to aryl organometallic reagents that are used in other reactions. Thiophenes are one of the most important class of heterocyclic compounds, not only as building blocks in synthesis of natural products or as key structure units[1,2] of compounds with interesting biological activities but also in the field of material chemistry.[3,4]

3,4-Disubstituted 2,5-dibromothiophenes are used widely as active components in the preparation of oligothiophenes or polythiophenes, which have proven to be one of the most promising functional materials as a result of their intrinsic electron-rich nature, thermal stabilities, and special optical and electrical properties.[5] Synthesis of 3,4-disubstituted 2,5-dibromothiophenes is challenging because the preferred sites for electrophilic substitution are C-2 and C-5 rather than C-3 and C-4. The preparation of 3,4-disubstituted-2,5-dibromothiophenes usually involves two steps: modification of 3,4-dibromothiophene and then bromination of 3,4-disubstituted thiophenes.[6] Some disadvantages to this approach include the use of expensive reagents, low yields, and strict reaction conditions. This is particularly true in the preparation of 3,4-diaryl-2,5-dibro-

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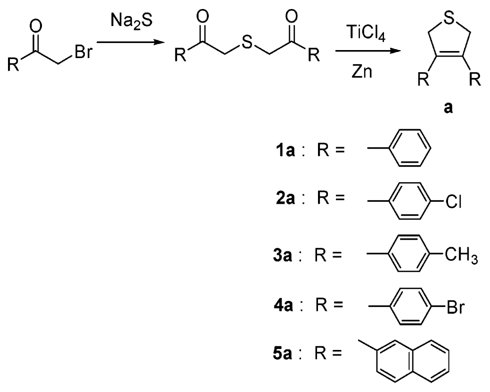
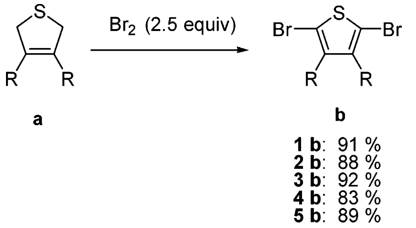
SCHEME 1



SCHEME 2



mothiophenes. Herein we present a new approach to the preparation of 3,4-diaryl-2,5-dibromothioiphenes. It is found that 3,4-diaryl-2,5-dihydrothiophenes, which were easily obtained from inexpensive starting materials, are converted to 3,4-diaryl-2,5-dibromothiophenes by one-pot reaction with Br$_2$ in excellent yields.

Results and Discussion

The starting materials 3,4-diaryl-2,5-dihydrothiophenes (Scheme 1) were prepared according to the literature[7] starting from acetophenone and its derivatives, which were brominated at the 2-position with Br$_2$ in CHCl$_3$. After sulfuration of bromoacetophenone and its derivatives with Na$_2$S in EtOH, the sulfides were coupled via the McMurry coupling reaction to afford **1a**−**5a** in good yields (70−83%).

3,4-Diaryl-2,5-dibromothiophenes (**1b**−**5b**) were obtained by treatment of 3,4-diaryl-2,5-dihydrothiophenes (**1a**−**5a**) with Br$_2$ in dichloromethane (DCM) as shown in Scheme 2. The reaction was simple and quick: the mixture was stirred at room temperature until no further starting material was detected by TLC plate (0.5−1 h). The solution was washed with water, NaHCO$_3$ (10%), and saturated NaCl solution, respectively, and extracted with DCM. The combined organic solution was dried over MgSO$_4$. After evaporation of the solvent, the target compounds (**1b**−**5b**) were obtained without further purification in excellent yields (83−92%).

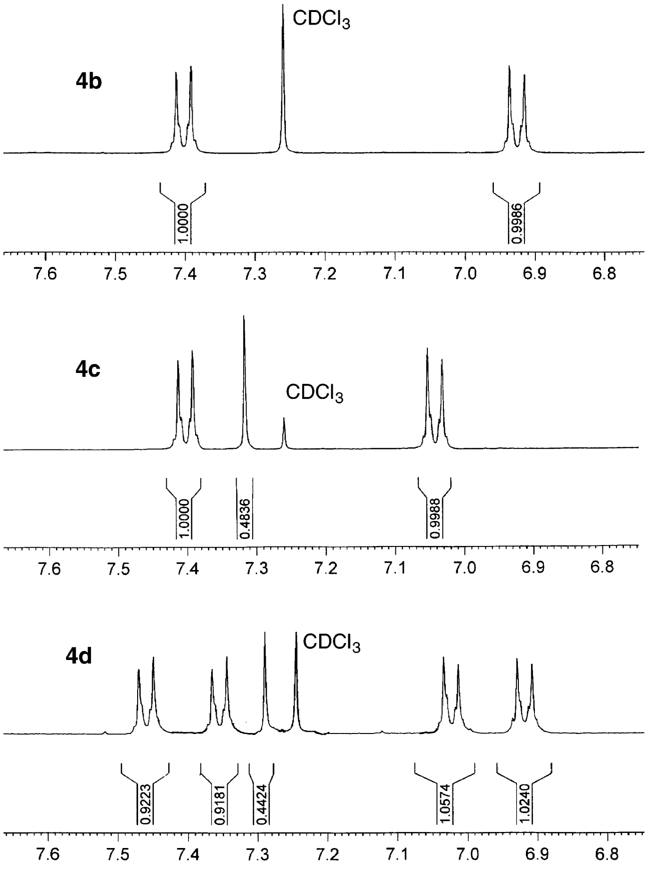


FIGURE 1. ^{1}H NMR spectral of **4b**−**d**.

Further investigation found that three main intermediates were detected by TLC plate during the conversion of **4a** to **4b**. Three products were isolated by flash column in yields of 25% (**4b**), 35% (**4c**), and 23% (**4d**), respectively, and their structures were identified by ^{1}H NMR (Figure 1) and MS spectrometry. As demonstrated in Figure 1, the single peak, whose chemical shift is around 7.30 ppm, attributes to the proton of thiophene ring. Comparing the intensity of chemical shifts around 7.30 ppm found that there are two protons for **4c**, one proton for **4d**, and no proton for **4b**. Moreover, the mass spectral analysis of **4b**, **4c**, and **4d** showed the relative abundance of the molecular ion (**4b**, m/z = 552; **4c**, m/z = 394, **4d**, m/z = 473) was 100%, respectively. Additionally, it was found that both **4c** and **4d** were quickly converted to **4b** during the reaction (Scheme 3). Also, neither **4c** nor **4d** be could obtained as a major product by the modification of the reaction such as decreasing the amount of Br$_2$ or the shortness of the reaction time. In these cases, the starting material was not completely consumed. It was worth noting that increasing the amount of Br$_2$ from 2.5 to 3.0 equiv or more could not raise markedly the yield of target compound but cut down the reaction time. Similar results were observed when other 3,4-diaryl-2,5-dihydrothiophenes converted into 3,4-diaryl-2,5-dibromothiophenes.

To extend the scope of the conversion, 1,3,4-triaryl-2,5-dihydropyrrole (**6a**), which was prepared according to the literature,[8] was employed as a model compound. It was found that 1,3,4-triaryl-2,5-dihydropyrrole **6a** could also be converted to 1,3,4-triaryl-2,5-dibromopyrrole **6b** in a good yield of 75%

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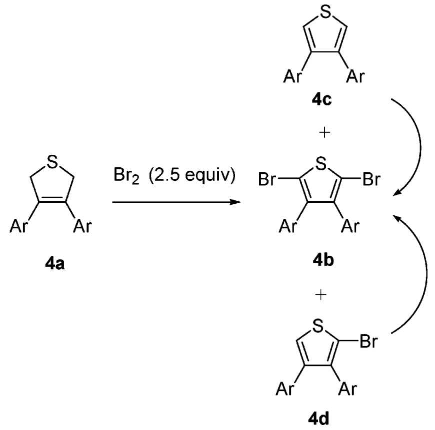
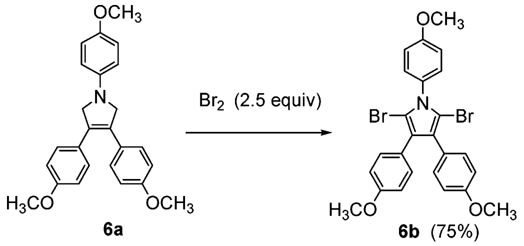
SCHEME 3



SCHEME 4



(Scheme 4). It suggested that Br$_2$ was also efficient for the preparation of 1,3,4-triaryl-2,5-dibromopyrroles.

It is known that the performance of a functional material is strongly dependent on its molecular organization and structure.[9] 2,3,4,5-Teterarylthiophenes possess interesting photophysical and electrochemical properties and are useful as the charge-transporting material in optoelectronic devices.[10] In this paper, 3,4-diphenyl-2,5-dibromothiophene **1b** was employed as template and the application of **1b** as building block to the synthesis of 2,3,4,5-tetrathiophenes was also investigated. As presented in Scheme 5, treatment of **1b** with various commercially available boronic acid reagents provided compounds **1c**−**h** in good yields (76−85%). Both electron-donating and electron-accepting of substituents of boronic acid reagents have no significant effect on the coupling reaction, suggesting that 3,4-diphenyl-2,5-dibromothiophene **1b** was efficient for the Suzuki coupling reaction.

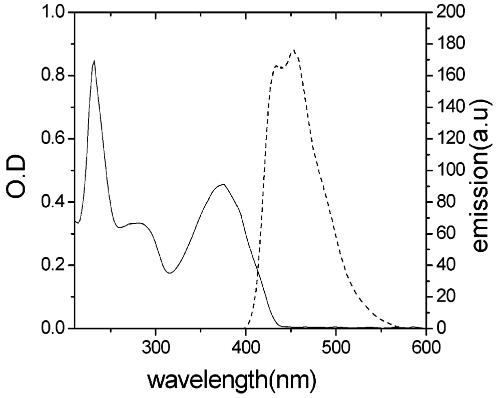
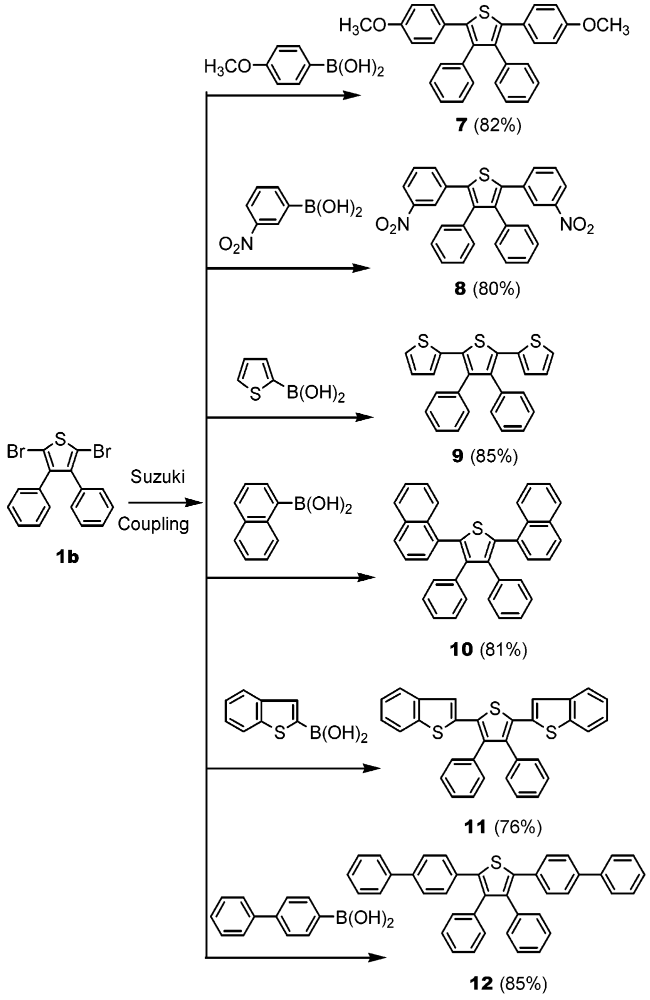


FIGURE 2. Absorption and fluorescence spectra of **1g** in DCM (1.5×10^{-5} M) ($\lambda_\mathrm{em} = 380$ nm).

SCHEME 5



The photophysical properties of **1c**−**h** were preliminarily investigated. Figure 2 represented the absorption and emission spectra of **1g** in CH$_2$Cl$_2$. It is found that the absorption and emission maxima located at 370 nm and 464 nm, respectively. A small fluorescence quantum yield ($\phi_\mathrm{f} = 0.081$, in CH$_2$Cl$_2$) was obtained by using coumarin 307 ($\phi_\mathrm{f} = 0.58$, in CH$_3$CN) as a reference. Similar results were obtained when other compounds were measured in solution except for **1d**, in which no emission was observed. The photophysical data of **1c**−**h** are listed in Table 1.

Conclusion

A new approach for the preparation of 3,4-diaryl-2,5-dibromothiophenes has been developed. The reaction has several advantages, such as inexpensive starting material, simple

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TABLE 1. Photophysical Data of Compounds 1c−h in DCM

compd	λ_{abs}^{max} (nm)	ϵ ($\times 10^4$)	λ_{em}^{max} (nm)	ϕ_f
1c	320	1.87	418	0.029
1d	310	1.75		
1e	350	1.77	446	0.021
1f	300	1.75	417	0.020
1g	370	3.01	464	0.081
1h	330	1.98	418	0.098

procedure, and excellent yield. With 3,4-diaryl-2,5-dibromothiophenes, a class of 2,4,5,6-tetraarylthiophenes has also been prepared in good yields. These may provide a useful synthetic route to the preparation of 3,4-diaryl-2,5-dibromothiophenes and 2,3,4,5-tetraarylthiophenes.

Experimental Section

General Procedure for the Preparation of Compounds 1b−6b. To the solution of **1a**−**6a** (1.0 mmol) in DCM (15 mL) was added Br_2 (2.5 mmol) in DCM (10 mL). The mixture was stirred at room temperature until no further starting material was detected by TLC. The solution was washed with water (50 mL), $NaHCO_3$ (10%, 50 mL), and saturated NaCl solution (50 mL), respectively, and extracted with DCM. The combined organic solution was dried over $MgSO_4$. After evaporation of the solvent, the target compounds were obtained without further purification. **1b.** Yield: 91%. Mp = 150−151 °C. ^{1}H NMR δ: 7.25−7.23 (m, 6H), 7.07−7.05 (m, 4H). ^{13}C NMR δ: 142.4, 134.6, 130.3, 128.1, 127.8, 109.7. HRMS *m/z*: calcd for $C_{16}H_{10}Br_2S$ 393.8849, found 393.8853 (100%). Anal. Calcd for $C_{16}H_{10}Br_2S$: C, 48.79; H, 2.56. Found: C, 48.81; H, 2.51. **2b.** Yield: 88%. Mp = 129−130 °C. ^{1}H NMR δ: 7.25 (d, J = 8.5 Hz, 4H), 6.99 (d, J = 8.4 Hz, 4H). ^{13}C NMR δ: 140.9, 134.1, 132.7, 131.6, 128.6, 110.4. HRMS *m/z*: calcd for $C_{16}H_8Br_2Cl_2S$ 461.8070, found 461.8071 (100%). Anal. Calcd for $C_{16}H_8Br_2Cl_2S$: C, 41.61; H, 1.75. Found: C, 41.58; H, 1.71. **3b.** Yield: 95%. Mp = 103−104 °C. ^{1}H NMR δ: 7.06 (d, J = 7.9 Hz, 4H), 6.96 (d, J = 8.0 Hz, 4H), 2.30 (s, 6H). ^{13}C NMR δ: 142.3, 137.5, 131.7, 130.1, 128.8, 109.4, 21.4. HRMS *m/z*: calcd for $C_{18}H_{14}Br_2S$ 421.9162, found 421.9160 (100%). Anal. Calcd for $C_{18}H_{14}Br_2S$: C, 51.24; H, 3.34. Found: C, 51.28; H, 3.29. **4b.** Yield: 80%. Mp = 132−134 °C. ^{1}H NMR δ: 7.41 (d, J = 8.5 Hz, 4H), 6.93 (d, J = 8.4 Hz, 4H). ^{13}C NMR δ: 140.8, 133.1, 131.9, 131.6, 122.4, 110.4. HRMS *m/z*: calcd for $C_{16}H_8Br_4S$ 551.7039, found 551.7040 (100%). Anal. Calcd for $C_{16}H_8Br_4S$: C, 34.83; H, 1.46. Found: C, 34.88; H, 1.42. **5b.** Yield: 89%. Mp = 78−79 °C. ^{1}H NMR δ: 7.75−7.73 (m, 6H), 7.62 (d, J = 8.6 Hz, 2H), 7.47−7.41 (m, 4H), 7.11 (dd, J_1 = 8.5 Hz, J_2 = 8.4 Hz, 2H). ^{13}C NMR δ: 142.3, 133.0, 132.6, 132.0, 129.8, 128.3, 127.8, 126.5, 126.2, 110.2. HRMS *m/z*: calcd for $C_{24}H_{14}Br_2S$ 493.9162, found 493.9164 (100%). Anal. Calcd for $C_{24}H_{14}Br_2S$: C, 58.36; H, 2.86. Found: C, 58.41; H, 2.82. **6b.** Yield: 75%. Mp = 216−218 °C. ^{1}H NMR δ: 7.55 (d, J = 11.7 Hz, 4H), 7.35 (d, J = 8.9 Hz, 2H), 7.01 (d, J = 8.9 Hz, 2H), 6.91 (d, J = 11.7 Hz, 4H), 3.84 (s, 9H). ^{13}C NMR δ: 170.5, 160.9, 159.0, 134.2, 131.7, 127.8, 124.8, 121.4, 114.5, 114.3, 55.6, 55.4. Anal. Calcd for $C_{25}H_{21}Br_2NO_3$: C, 55.27; H, 3.90. Found: C, 55.35; H, 3.85.

General Procedure for the Preparation of Compounds 1c−1h. To a solution of **1b** (0.5 mmol) in anhydrous THF (15 mL) were added $Pd(PPh_3)_4$ (3 mol %) and a solution of K_2CO_3 solution (2.5 M, 2 mL). The resulting solution was stirred for 10 min at ambient temperature. To the resulting solution was added the corresponding boronic acid reagent (1.5 mmol) under nitrogen, and the reaction was monitored by TLC. After no further starting material **1b** was detected by TLC, H_2O (20 mL) was added to the residue, and the product was extracted with Et_2O (3 × 20 mL). The combined organic phase was washed with H_2O (30 mL) and a saturation solution of NaCl (30 mL), respectively, and dried over $MgSO_4$. After evaporation of the solvent, the crude product was purified by flash column chromatography (PE-EtOAc). **1c.** Yield: 82%. Mp = 204−205 °C. ^{1}H NMR δ: 7.16−7.10 (m, 10H), 6.96−6.94 (m, 4H), 6.76−6.74 (d, J = 8.8 Hz, 4H), 3.77 (s, 6H). ^{13}C NMR δ: 158.9, 138.8, 137.8, 136.9, 131.0, 130.5, 127.9, 127.0, 126.6, 113.9, 55.3. HRMS *m/z*: calcd for $C_{30}H_{24}O_2S$ 448.1497, found 448.1495 (100%). Anal. Calcd for $C_{30}H_{24}O_2S$: C, 80.40; H, 5.39. Found: C, 80.38; H, 5.33. **1d.** Yield: 80%. Mp = 174−176 °C. ^{1}H NMR δ: 8.14 (t, 2H), 8.09 (d, J = 8.2 Hz, 2H), 7.51 (d, J = 7.9 Hz, 2H), 7.39 (t, 2H), 7.22−7.15 (m, 6H), 6.98 (d, J = 7.6 Hz, 4H). ^{13}C NMR δ: 148.4, 141.6, 136.8, 135.7, 135.2, 135.0, 130.6, 129.5, 128.5, 127.7, 124.0, 122.4. HRMS *m/z*: calcd for $C_{28}H_{18}N_2O_4S$ 478.0987, found 478.0985 (100%). Anal. Calcd for $C_{28}H_{18}N_2O_4S$: C, 70.34; H, 3.79. Found: C, 70.38; H, 3.73. **1e.** Yield: 85%. Mp = 155−156 °C. ^{1}H NMR δ: 7.22−7.19 (m, 6H), 7.12−7.09 (m, 6H), 6.97 (d, J = 3.6 Hz, 2H), 6.90 (dd, J_1 = 5.0 Hz, J_2 = 5.1 Hz, 2H). ^{13}C NMR δ: 140.1, 136.2, 136.0, 131.3, 130.9, 128.2, 127.5, 127.0, 126.0, 125.7. HRMS *m/z*: calcd for $C_{24}H_{16}S_3$ 400.0414, found 400.0405 (100%). Anal. Calcd for $C_{24}H_{16}S_3$: C, 72.06; H, 4.03. Found: C, 72.03; H, 3.98. **1f.** Yield: 81%. Mp = 203−205 °C. ^{1}H NMR δ: 8.02 (d, J = 7.8 Hz, 2H), 7.84−7.80 (m, 4H), 7.52 (d, J = 7.0 Hz, 2H), 7.46−7.38 (m, 6H), 6.96 − 6.91 (m, 10H). ^{13}C NMR δ: 140.7, 137.5, 136.5, 133.7, 132.9, 132.1, 130.5, 130.0, 128.6, 128.2, 127.6, 126.4, 126.4, 126.3, 126.0, 125.2. HRMS *m/z*: calcd for $C_{36}H_{24}S$ 488.1599, found 488.1602 (100%). Anal. Calcd for $C_{36}H_{24}S$: C, 88.58; H, 4.95. Found: C, 88.54; H, 4.93. **1g.** Yield: 76%. Mp = 269−271 °C. ^{1}H NMR δ: 7.66−7.64 (m, 4H), 7.31−7.20 (m, 12H), 7.17−7.14 (m, 4H). ^{13}C NMR δ: 141.5, 140.1, 139.6, 136.2, 135.6, 132.3, 130.9, 128.3, 127.8, 124.6, 123.6, 122.6, 122.1. HRMS *m/z*: calcd for $C_{32}H_{20}S_3$ 500.0727, found 500.0733 (100%). Anal. Calcd for $C_{32}H_{20}S_3$: C, 76.86; H, 4.03. Found: C, 76.81; H, 3.97. **1h.** Yield: 85%. Mp = 250−251 °C. ^{1}H NMR δ: 7.59 (d, J = 7.4 Hz, 2H), 7.48 (d, J = 8.3 Hz, 2H), 7.42 (t, 2H), 7.34−7.30 (m, 3H), 7.16−7.12 (m, 3H), 7.05 (m, 2H). ^{13}C NMR δ: 140.6, 139.9, 138.4, 136.7, 133.4, 131.0, 129.6, 128.9, 128.1, 127.5, 127.1, 127.0, 126.9. HRMS *m/z*: calcd for $C_{40}H_{28}S$ 540.1912, found 540.1908 (100%). Anal. Calcd for $C_{40}H_{28}S$: C, 88.94; H, 5.22. Found: C, 88.91; H, 5.18.

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Supporting Information Available: Synthetic procedures, characterization data, and ^{1}H NMR, ^{13}C NMR, and HRMS spectra of **1b**−**6b** and **1c**−**h**. This material is available free of charge via the Internet at http://pubs.acs.org.

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