Communications to the Editor

Poly(aryl ether)s Containing Pendent Benzoxazole and Benzothiazole Units

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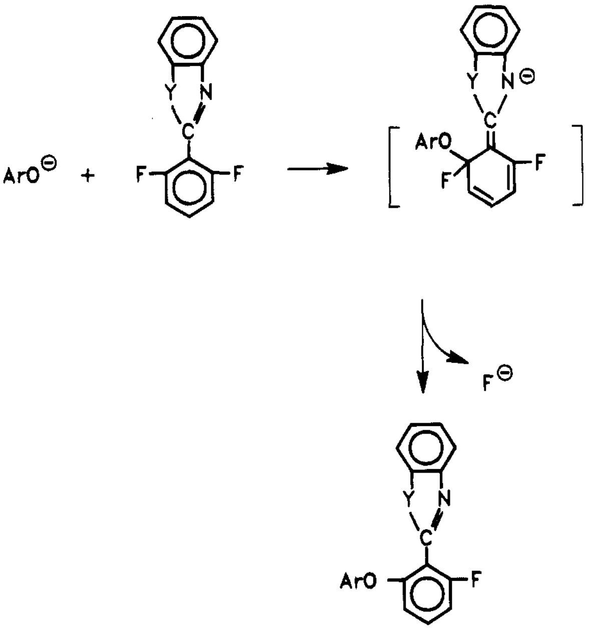
Poly(benzothiazole)s, PBT, and poly(benzoxazole)s, PBO, are among the most thermally stable polymers reported. High-modulus polymers containing a high degree of rigidity in the backbone can be formed for potential applications such as fibers and multilayer circuit boards.[1–3] PBT's and PBO's are generally synthesized by the polycondensation of a carboxylic acid derivative with either a bis(*o*-aminothiophenol) or bis(*o*-aminophenol) derivative, respectively, where the heterocycle ring formation is the polymer-forming reaction.[4] These polymerizations are generally carried out in poly(phosphoric acid) (PPA) since it solvates the starting materials and the final polymer and reacts with the water formed by the condensation to effectively dehydrate the system. The use of these rigid heterocycle-containing polymers has been limited since they are only soluble in strong acids and cannot be processed from organic solvents. It has recently been demonstrated that the incorporation of aryl ether linkages in the polymer backbone provides improved solubility in many common organic solvents as well as a lower T_g and subsequent lower melt processing temperatures.[5–14] Examples of high-temperature polymers which have been favorably modified by the incorporation of aryl ether linkages include polyimides,[5] poly(phenylquinoxaline)s,[6,7] poly(benzoxazole)s,[8,9] poly(benzothiazole)s,[10] poly(oxadiazole)s,[11,12] and poly(triazole)s.[13,14] The most efficient means of introducing an aryl ether linkage in such polymer systems is through a poly(ether) synthesis, where the heterocycle is preformed in either the bishalide or bisphenol monomer. Our interest has primarily focused on bis(halide) monomers where the electron-deficient heterocycle activates the aryl halide toward nucleophilic aromatic substitution. Further rationale for the heterocycle-activated displacement was the ability of the heterocycle to stabilize the negative charge developed in the transition state through the formation of a Meisenheimer complex, analogous to conventional activating groups for poly(aryl ether) synthesis (i.e., sulfone, ketone, etc.).[15,16] We have recently demonstrated that aryl fluorides para to a 2-phenylbenzoxazolyl group were readily displaced with bisphenoxides to prepare soluble poly(aryl ether benzoxazoles).[9] Likewise, it seemed plausible that aryl halides ortho to the azole ring would also be activated toward nucleophilic aromatic substitution, analogous to conventional halophenyl ketones and sulfones for which both the ortho and para positions are activated.[17] This will allow for the synthesis of poly(aryl ether)s containing pendent heterocycles.

Scheme 1



Facile nucleophilic aromatic substitution of *o*-aryl halides from an azole-substituted benzene ring should occur since the heterocycle is an electron-withdrawing group. In addition, a Meisenheimer complex would form as a stabilized intermediate during the transformation due to resonance of the negative charge into the azole ring analogous to a conventional activating group (e.g., ketone)[15,16] (Scheme 1). It has been shown that the electronic effect of the heterocycle both on the benzo aromatic ring and on the 2-phenyl group can be evaluated by ^{1}H NMR as the deshielding of the protons ortho to a substituent is indicative of an electron-withdrawing effect.[9] The ^{1}H NMR spectral assignments for 2-(4-fluorophenyl)benzoxazole show that the protons of the 2-phenyl ring ortho to the oxazole heterocycle (H_a) are at δ 8.3, further downfield than the ortho protons of the benzo ring, H_b and H_c, at δ 7.8 and 7.6, respectively (Figure 1b). This indicates that the oxazole has a greater electron-withdrawing effect on the 2-phenyl group than on the benzo ring of the benzoxazole. In addition, it also indicates that the 4-position of the 2-phenyl ring is activated toward displacement. Rationale for the possible displacement of halides ortho to the azole ring can be seen in the ^{1}H NMR of 2-(2,6-difluorophenyl)benzoxazole (**1a**) where the proton para to the oxazole (H_a) on the 2-phenyl ring is shifted downfield at δ 7.9 (Figure 1a). Comparison of these assignments with 4,4′-difluorobenzophenone, in which the protons ortho to the ketone group are shifted downfield to δ 7.9, shows the electron-withdrawing effect of the 2-benzoxazolyl group on a benzene ring in the ground state comparable to that of the ketone group (Figure 1c). However, it should be pointed out that comparison of para and ortho proton chemical shifts on different types of compounds may not necessarily be valid. Since ^{1}H NMR shielding can vary significantly

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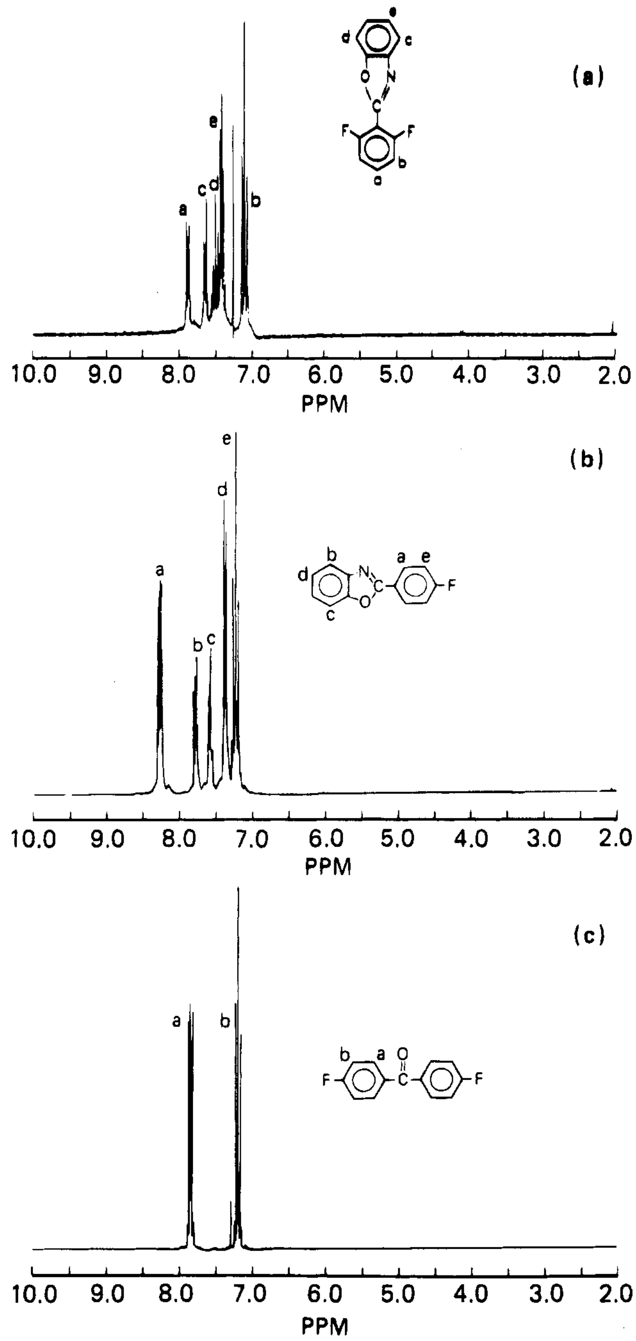


Figure 1. ^{1}H NMR spectra of (a) 2-(2,6-difluorophenyl)benzoxazole, (b) 2-(4-fluorophenyl)benzoxazole, and (c) 4,4′-difluorobenzophenone.

due to anisotropic and ring current effects, on alternative probe to the effectiveness of these displacement reactions was sought.

Table 1. ^{19}F NMR Substituent Chemical Shifts of Selected Fluorinated Compounds[a]

compound	chemical shift[b]	compound	chemical shift[b]
1a	−108.76	fluorobenzene	−112.77
1b	−110.06	4,4′-difluorodiphenyl sulfone	−104.08
1c	−110.94	4,4′-difluorobenzophenone	−106.01

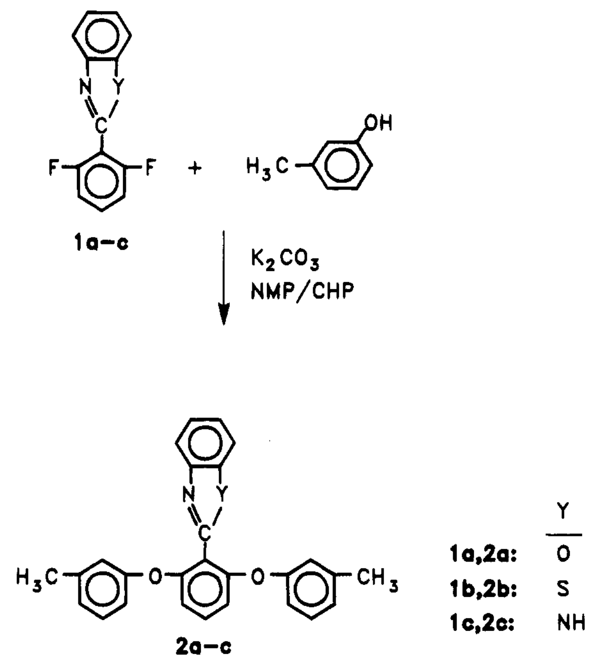
[a] NMR performed on dilute solutions in DMSO-d_6. [b] Chemical shifts are reported in ppm relative to CCl_3F = 0.0 ppm.

As a part of a larger study concerning the reactivity of activated fluorinated monomers, to be published in a forthcoming paper, we have been examining the ^{19}F NMR chemical shifts of various compounds. Fluorine is an excellent probe due to its high natural abundance and sensitivity to NMR detection. In addition, it is located at the reactive site in these reactions, and its chemical shift is very sensitive to any perturbations of the aromatic ring electron density by a substituent arising from both inductive and resonance effects.[18] The ^{19}F NMR chemical shifts of fluorines both para and ortho to electron-withdrawing groups are shifted downfield, and the magnitude of this shift can be directly related to the electron density at the carbon to which it is attached. Unlike ^{1}H NMR probes, ^{19}F is not greatly affected by ring current effects. Table 1 shows the ^{19}F chemical shifts of several fluorinated compounds including the 2-(2,6-difluorophenyl)benzazole monomers. Comparison of the chemical shifts of the benzazole monomers with conventional activated monomers such as 4,4′-difluorobenzophenone or 4,4′-difluorodiphenyl sulfone and the nonactivated fluorobenzene not only gives a good approximation of the benzazoles' overall reactivity, but also predicts the relative reactivity among the benzazoles. The most activated benzazole, **1a**, has a chemical shift of δ −108.76, followed by **1b** at δ −110.06. It has been our observation that monomers with $\delta > -110.00$ are sufficiently activated toward nucleophilic aromatic substitution, whereas those with $\delta < -110.00$ become so weakly activated that they require extended reaction times and higher reaction temperatures to affect the displacement reaction and in many cases competing side reactions, and monomer instability at higher temperatures precludes some monomers from undergoing quantitative displacement reactions. The chemical shifts of **1a** and **1b** indicate the possibility of nucleophilic aromatic substitution at the ortho positions of the 2-phenyl ring of the oxazole and thiazole monomers. Conversely, **1c** shows a chemical shift of δ −110.94 which is lower than the oxazole and thiazole analogs; therefore, the likelihood of the imidazole-activated displacement from the ortho position of the 2-phenyl ring of **1c** is marginal by ^{19}F NMR.

Poly(aryl ether)s containing pendent benzazole heterocycles required the preparation of the appropriately substituted difluoro monomers. The monomers, 2-(2,6-difluorophenyl)benzoxazole (**1a**), 2-(2,6-difluorophenyl)benzothiazole (**1b**), and 2-(2,6-difluorophenyl)benzimidazole (**1c**), were prepared by the reaction of 2,6′-difluorobenzoic acid with either 2-aminophenol, 2-aminothiophene, or 1,2-diaminobenzene, respectively, in poly(phosphoric acid)[19] according to a general literature procedure.[20] In each case, high conversion of the starting materials was observed with the formation of the desired product and a small unidentified side product. The monomers were purified by both flash liquid chromatography and recrystallization to afford the desired products (**1a**–**c**) with the expected spectral characteristics and chemical compositions, as determined by ^{1}H NMR and elemental analysis, respectively.[19]

As for the case of the ortho-substituted halophenyl ketones and sulfones, where the halogen reactivities are substantially lower than those of the para analogs due to steric hindrance, the rate of the nucleophilic aromatic displacement of aryl fluorides from the ortho position of an azole-substituted benzene ring was of some concern.[17] To demonstrate the feasibility of this approach to prepare poly(aryl ethers) containing pendent benzoxazole, benzothiazole, and benzimidazole units, model reactions between the appropriately substituted difluoro monomers, **1a**–**c**, and *m*-cresol in a *N*-methyl-2-pyrrolidinone (NMP)/*N*-cyclohexyl-2-pyrrolidinone

Scheme 2



(CHP) solvent mixture containing potassium carbonate, were investigated (Scheme 2).[21] For the case of the oxazole (**1a**) and thiazole (**1b**) activated displacements, quantitative conversion of the aryl fluorides with the formation of a single product was observed by thin layer chromatography (ethyl acetate/hexane (20/80)). As expected, there was a noticeable reactivity difference between the displacement from the para and ortho positions, with the latter taking approximately twice as long (24–35 h) for complete conversion. These model reactions demonstrated that the ortho fluorides were readily displaced by phenoxides as a result of activation by either the oxazole or thiazole heterocycles, affording aryl ethers **2a** and **2b**, respectively, with spectral data and chemical compositions consistent with the expected structure.[21]

In contrast to these results, the imidazole-activated fluoro displacement of **1c** with *m*-cresol in a NMP/CHP solvent mixture containing potassium carbonate was not as effective, as is evident by ^{19}F NMR results. Since the reaction took longer, presumably due to the poor reactivity as well as the difficulty in dehydrating the system in the presence of the imidazole, several unidentified side reactions were observed in the latter stages of the reaction. Hence, due to these side reactions, the imidazole-activated fluoro displacement was not judged suitable as a polymer-forming reaction.

The synthesis of poly(aryl ether)s is generally carried out in aprotic dipolar solvents such as NMP, CHP, or dimethyl sulfoxide (DMSO). These solvents effectively solvate the monomer, polar intermediates, and in most cases the subsequent polymer. Furthermore, the formation of the Meisenheimer complex is strongly influenced by the solvent, and polar solvents stabilize this complex assisting the displacement reaction. The choice of the solvent depends on the solubility of the polymer and the polymerization temperature required to produce high molecular weight. NMP and CHP allow the highest reaction temperatures, 200 and 260 °C, respectively, and these high polymerization temperatures are required in the preparation or rigid- or stiff-chain poly(aryl ether)s to maintain solubility. Furthermore, since CHP is not miscible with water at temperatures above 100 °C, nonpolar cosolvents used to azeotrope the water generated during the polymerization are not required. Mixtures of NMP and CHP also show a similar behavior with water, with CHP compositions as low as 20%. We have found that a CHP/NMP (50/50) solvent mixture is the preferred reaction medium for the polymerizations.

Scheme 3

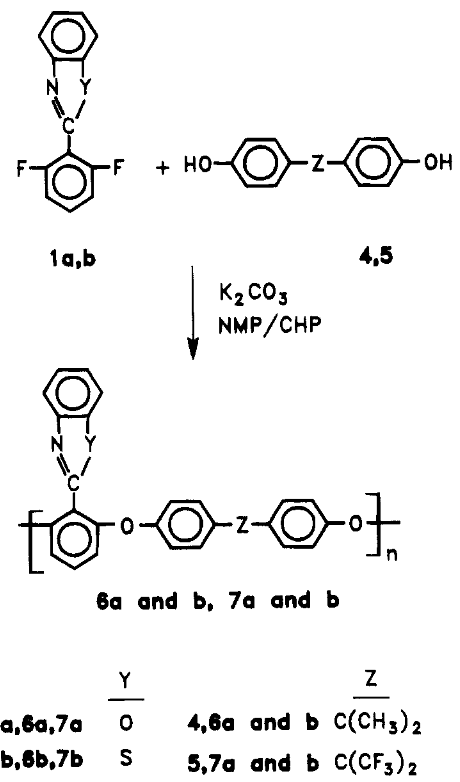


Table 2. Characteristics of Poly(aryl ethers) Containing Pendent Benzazoles

sample entry	$[\eta]^{25\,°C}_{NMP}$ (dL/g)	T_g (°C)
6a	0.36	165
6b	0.45	170
7a	0.44	165
7b	0.83	167

The polymerization of **1a** and **1b** with two bisphenols (**4** and **5**) in a CHP/NMP (50/50) solvent mixture containing K_2CO_3 was successful in preparing high molecular weight poly(aryl ethers) containing pendent benzoxazoles and benzothiazoles **6a** and **6b** and **7a** and **7b**, respectively (Scheme 3).[6,7] During the initial stage of the polymerizations, the reaction temperatures were maintained at approximately 150 °C and the water generated by phenoxide formation was removed through the Dean–Stark trap. Upon dehydration (4–6 h), the polymerization temperatures were increased to 185–195 °C to affect the displacement reactions. High molecular weight polymer was obtained after 24–30 h as judged by the increase in viscosity. The resulting polymers were isolated in an excess methanol/water mixture, subjected to the appropriate solvent rinses, and dried in a vacuum oven (80 °C) for 24 h.

Table 2 contains the results of the intrinsic viscosity and glass transition measurements. The viscosity values, measured in NMP (25 °C), ranged from 0.36 to 0.83 dL/g, typical values for high molecular weight poly(aryl ether)s. For comparison, the commercially available poly(aryl ether sulfone) (UDEL) has an intrinsic viscosity of 0.48 dL/g in NMP. The glass transition temperatures were somewhat lower than values typically observed for heterocycle-containing poly(aryl ethers) and are believed to result from the meta linkages in the polymer backbone.

The polymerization provides a general method for the preparation of poly(aryl ethers) containing pendent benzazole heterocycles. We have demonstrated that aryl fluorides ortho to a 2-benzoxazolyl group were readily displaced with phenoxides. A series of fluoro-substituted benzazole-containing monomers were prepared and polymerized with two bisphenols in a NMP/CHP solvent mixture containing potassium carbonate, yielding high molecular weight polymers. This investigation represents another example of a poly(aryl ether) synthesis based on the polymerization of aryl fluorides activated by a heterocycle ring.

References and Notes

(1) Arnold, F. E.; Van Deusen, R. L. *Macromolecules* **1969**, *2*, 497.

(2) Wolfe, J. E. *Encycl. Polym. Sci. Technol.* **1988**, *11*, 601.

(3) Helminiak, T. E.; Arnold, F. E.; Benner, C. L. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1975**, *16* (2), 659.

(4) Hergenrother, P. M.; Wrasidlo, W.; Levine, H. H. *J. Polym. Sci. A* **1965**, *3*, 1665.

(5) White, D. M.; Takekoshi, T.; Williams, F. J.; Relles, H. M.; Donahue, P. E.; Klopfer, H. J.; Loucks, G. R.; Manello, J. S.; Matthews, R. O.; Schluenz, R. W. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 1635.

(6) Hedrick, J. L.; Labadie, J. W. *Macromolecules* **1988**, *21*, 1883.

(7) Connell, J. W.; Hergenrother, P. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *29* (1), 172.

(8) Connell, J. W.; Hergenrother, P. M. *Polym. Mater. Sci. Eng. Proc.* **1989**, *60*, 527.

(9) Hilborn, J.; Labadie, J.; Hedrick, J. L. *Macromolecules* **1990**, *23*, 2854.

(10) Hedrick, J. L. *Macromolecules* **1991**, *24*, 6361.

(11) Hedrick, J. L.; Tweig, R. *Macromolecules* **1992**, *25*, 2021.

(12) Connell, J. W.; Hergenrother, P. M.; Wolf, P. *Polym. Mater. Sci. Eng. Proc.* **1990**, *63*, 366.

(13) Carter, K. R.; Jonsson, H.; Twieg, R.; Miller, R. D.; Hedrick, J. L. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33* (1), 338.

(14) Connell, J. W.; Hergenrother, P. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1989**, *29* (1), 172.

(15) Johnson, R. N.; Farnham, A. G.; Clendinning, R. A.; Hale, W. F. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *18*, 354.

(16) Attwood, T. E.; Davidson, P. C.; Freeman, J. C.; Hoy, J. C.; Rose, J. B.; Staniland, P. A. *Polymer* **1981**, *22*, 1076.

(17) Newton, A. B.; Rose, J. B. *Polymer* **1972**, *13*, 465.

(18) (a) Taft, R. W.; Price, E.; Fox, I. R.; Lewis, I. C.; Anderson, K. K.; Davis, G. T. *J. Am. Chem. Soc.* **1963**, *85*, 709. (b) Taft, R. W.; Price, E.; Fox, I. R.; Lewis, I. C.; Andersen, K. K.; Davis, G. T. *J. Am. Chem. Soc.* **1963**, *85*, 3146.

(19) The synthetic route used for the azole monomers is exemplified by the synthesis of 2-(2,6-difluorophenyl)benzoxazole (**1a**). 2,6-Difluorobenzoyl chloride (4.85 g, 0,0275 mol) and 2-aminophenol (3.00 g, 0.0275 mol) were mixed, and enough poly(phosphoric acid) was added to give a stirrable paste. The temperature was slowly increased to 250 °C where the reaction was carried out for 4 h under a nitrogen atmosphere. The solution was cooled to about 100 °C and then poured into a large volume of water. The resulting suspension was stirred with chloroform, and the organic phase was collected, subsequently washed with 10 wt % sodium carbonate solution, water, and brine, respectively, and dried over magnesium sulfate. The solution was filtered and concentrated under reduced pressure, and the resulting crude product was purified by column chromatography (silica gel, ethyl acetate/hexane (20/80) eluent) and recrystallized from ethanol/water (50/50) to yield 2.3 g (36%) of crystals. Mp: 80–82 °C ^{1}H NMR ($CDCl_3$, ppm): δ 7.07–7.14 (m, 2H), 7.39–7.50 (m, 3H), 7.62–7.66 (m, 1H), 7.86–7.90 (m, 1H). Anal. Calcd for $C_{13}H_7F_2NO$: C, 67.53; H, 3.03; N, 6.05. Found: C, 67.26; H, 3.03; N, 7.20.

(20) Hein, D. W.; Alheim, R. J.; Leavitt, J. J. *J. Am. Chem. Soc.* **1957**, *79*, 427.

(21) The synthetic route used to demonstrate the benzazole-activated fluoro displacement is exemplified by the synthesis of **2a**. To a solution of 2-(2,6-difluorophenyl)benzoxazole (1.00 g, 4.3 mmol) and *m*-cresol (1.04 g, 9.5 mmole) in 8 mL of NMP/CHP (50/50) was added potassium carbonate (2.50 g, 18.1 mmol). The mixture was heated to 160 °C and kept at this temperature for 24 h. Upon completion, the reaction mixture was cooled and diluted with chloroform, and the resulting solution was washed repeatedly with brine and dried over magnesium sulfate. The solution was filtered and concentrated under reduced pressure, and the crude product was purified by column chromatography (silica gel, ethyl acetate/hexane (10/90) eluent) to yield 1.5 g (83%) of product. ^{1}H NMR ($CDCl_3$, ppm): δ 2.31 (s, 6H), 6.66 (s, 1H), 6.69 (s, 1H), 6.88–6.94 (m, 6H), 7.17–7.23 (m, 2H), 7.28–7.35 (m, 3H), 7.52–7.56 (m, 1H), 7.77–7.83 (m, 1H).

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