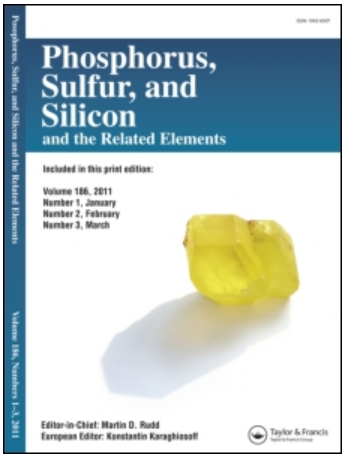

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SYNTHESIS OF ARYLCARBINOLS AND/OR ARYLKETONES END CAPPED THIOPHENE AND 2,2'-BITHIOPHENE

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SYNTHESIS OF ARYLCARBINOLS AND/OR ARYLKETONES END CAPPED THIOPHENE AND 2,2'-BITHIOPHENE

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Synthesis of arylmethanol of thiophene and 2,2'-bithiophene derivatives (**4, 5, 8, 9** and **13**) and the corresponding ketones (**6, 10, 11** and **14**) which were prepared by lithiation/addition exchange sequence on the arylbromides (**2, 3** and **12**) followed by trapping with thienyl-2-carbaldehyde (**1**) and/or 2,2'-bithienyl-5,5'-dicarbaldehyde (**7**).

Keywords: Thiophene; Oligomers; 2,2'-bithiophene; End-Capped

INTRODUCTION

It was reported that the bromine-lithium exchange on the treatment of bromoarenes with butyllithium generally proceeds smoothly and quantitatively.[1] Interest is increasing in the preparation of oligothienylenes which contain aromatic rings because of their potential biological activity[2] and use as electroconducting polymers.[3] These reports previously prompted our efforts towards the synthesis and isolation of several analogous of thiophene and 2,2'-bithiophene derivatives, starting from arylbromides (**2, 3,** and **12**) which were lithiated by n-BuLi and then trapped by thienyl-2-carboxaldehyde (**1**) and/or 2,2'-bithienyl-5,5'-dicarbaldehyde[4,5] (**7**).

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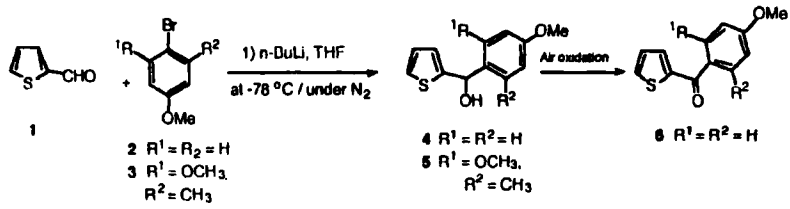
RESULT AND DISCUSSION

We report here the synthesis of arylmethanol thiophene and 2,2′-bithiophene derivatives and the corresponding ketones. Firstly, 2-bromo-3,5-dimethoxytoluene (**3**) was prepared following the literature reports.[6,7,8]

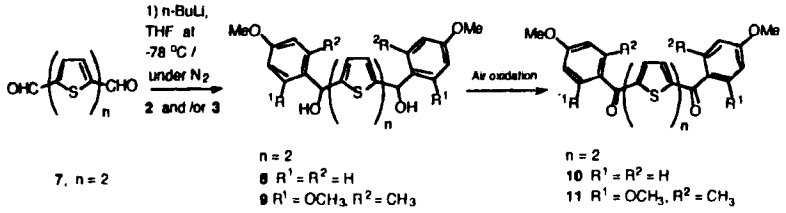
Thienylarylcarbinols(**4**) and (**5**) were prepared by lithiation of arylbromides (**2**) and (**3**) (THF, n-BuLi) and then trapped with 2-thienyl-2-carbaldehyde (**1**). Purification of compound (**4**) by flash chromatography using silica gel (hexane/EtOAc; 20:1) afforded a yellow oil in 73 % yield which was oxidized by air to give the corresponding thienylarylketone (**6**) in low yield (20 %). TLC was used to monitored the course of the reaction and GC/MS revealed two peaks with retention time of $t_R = 9.48$ and $t_R = 9.89$ respectively. The corresponding mass numbers (M^{+}+1) were (220) and (218) which is in agreement with the structures of compounds (**4**) and (**6**). Compound (**5**) was prepared following the same previous procedure method (A) but care was taken to protect it from air and light during the reaction condition. The product was then purified by flash chromatography using silica gel (hexane/EtOAc; 6:1) to provide a yellow oil in 78 % yield.



SCHEME 1

2,2′-Bithienyl-5,5′-dicarbaldehyde (**7**) was prepared[4,5] in good yield following the literature reports (**9**). α,α′-bis[(4″-methoxyphenyl)]-2,2′-bithienyl- 5,5′-dimethanol (**8**) and α,α′-bis[(4″-methoxyphenyl)]-2,2′-bithienyl-5,5′- diketone (**9**) were prepared by lithiation of arylbromide (**2**) following the same general procedure method (A) and reacted with 2,2′-bithienyl-5,5′-dicarbaldehyde (**7**). Purification by flash chromatography using silica gel (hexane/EtOAc,

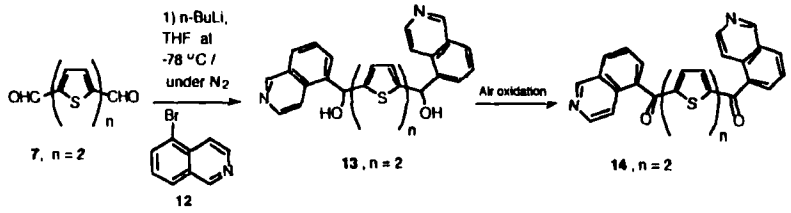
12:1) to provide a clear yellow oil, in 82 % yield, as shown in (Scheme 2). TLC and GC/MS were used to monitored the course of the reaction and two peaks in the gas chromatogram with retention times t_R = 10.89 and t_R = 11.56 corresponded to mass number (M^{+}+1) (438) and (434). This was in agreement with the structures of compounds (**8**) and (**9**) respectively. Similarly 2-bromo-3,5-dimethoxytoluene (**3**)[6] was lithiated with n-BuLi and then trapped with 2,2′-bithienyl-5,5′-dicarbaldehyde (**7**) to give dark yellow oil of 2,2′-bithienyl-5,5′-dicarbinol (**9**) and 2,2′-bithienyl-5,5′-diketone (**11**). Purification was attempted to isolate the product. Unfortunately the combined product was not isolated by flash chromatography (hexane/EtOAc, 90:7 with 3% methanol) but a clear yellow oil were obtained, TLC showed two close spots at $R_{f_1} = 0.42$ and $R_{f_1} = 0.41$ that suggested the structures of products (**9**) and (**11**) respectively. GC showed that the peak of diketone (**11**) increased as the peak of the dicarbinol (**9**) decreased.



SCHEME 2

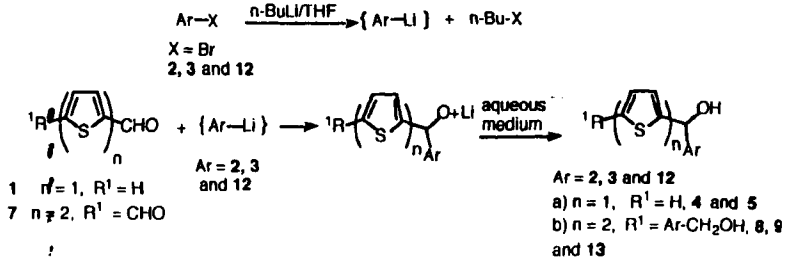
α,α′-Bis(5″-isoquinolinyl)-2,2′-bithienyl-5,5′-dimethanol (**13**) and α,α′-bis(5″-isoquinolinyl)-2,2′-bithienyl-5,5′-diketone (**14**), were prepared by reaction of 2,2′-bithienyl-5,5′-dicarbaldehyde (**7**), with 5-bromoisoquinoline[10] (**12**) after lithiation with n-Bu-Li following procedure method (A) to give a dark yellow oil. Purification was attempted to isolate the products (**13**) and (**14**) and unfortunately the combined product was not isolated by flash chromatography (hexane/EtOAc, 90:7: with 3% methanol) but it gave a clear yellow oil residue which were confirmed by GC/Ms and ^{1}H NMR spectra data were clear and easy to distinguish.

A probable reaction pathway for the formation of the coupling products is shown in (Scheme 4). It should be noted that Comins and Killpack[11] were able to use lithium N-methylpiperazine (LNMP) as a temporary pro-



SCHEME 3

tecting group for thienyl-2-carboxaldehyde. The arylbromide was lithiated by n-BuLi in THF under N_2 to give aryllithium as intermediate compound which was subsequently trapped with thienyl-2-carbaldehyde (**1**) and/or 2,2′-bithienyl-5,5′-dicarbaldehyde (**7**) to afford the desirable products.



SCHEME 4

Conclusions

The method described for obtaining α,α′-bis(5″-isoquinolinyl))-2,2′-bithienyl-5,5′-dimethanol (**13**) which was prepared by lithiation/addition exchange sequence on the 5-bromoisoquinoline (**12**) followed by trapping with 2,2′-bithienyl-5,5′-dicarbaldehyde (**7**) is advantageous as the only other method for preparing compounds of this type gives mixtures of products and low yields.

EXPERIMENTAL SECTION

M.P. (Thomas Hoover Capillary Melting Point Apparatus), were determined either in sealed capillaries on a Mel-Temp apparatus or on a Bristo-

line hot-stage microscope and are uncorrected. All reactions requiring anhydrous conditions were performed under an atmosphere of nitrogen or argon in oven dried glassware. Flash column chromatography was performed as described by Still[12] using E. Merck silica gel (230–400 mesh). The R_f value reported for TLC analysis was determined on Macherey-Nagel 0.25 mm layer fluorescent UV_{254} plates with the indicated solvent system. ^1H NMR spectra were obtained using an IBM NR-200, an Varian VXR-500 (500 MHz) spectrometer. Chemical shifts are reported relative to the TMS (tetramethylsilane, 0.00 ppm). The following format was used to report peaks: chemical shift in ppm (on the δ scale relative to TMS, 0.00 ppm and coupling constant(s) (J, in Hz), of protons and proton assignment. ^{13}C NMR spectra were obtained using an IBM NR-200(50 MHz) and Varian VXR-500(125 MHz) spectrometer. Chemical shifts of peaks were recorded relative to the deuterated solvent resonance as the internal standard(77.0), and are reported in ppm from TMS. Infrared IR spectra listed as recorded "neat" refer to a thin film of material on NaCl disks. Infrared spectra were recorded on a MIDAC Prospect spectrometer. Peaks of the IR spectrum are reported in $cm.^{-1}$ Elemental analyses were performed by M-H-W Laboratories (Phoenix, AZ). Tandem gas chromatography/low resolution mass spectrometry (GC/LRMS) using electron impact (EI) ionization was performed on a Hewlett-Packard 5890 series II gas chromatography and 5971A mass selective detector at 70 eV. Gas chromatography retention time is reported along with the capillary column configuration

General Procedure

Method (A)

Arylbromide (3.8 mmol) was dissolved in THF (10 mL), cooled to –78 °C, n-BuLi (4.2 mmol, 1.68 mL of a 2.5 M solution in hexane) was added and the reaction mixture which was stirred under N_2 for 15 min. Thienyl-2-carbaldehyde (**1**) and/or 2,2′-bithienyl-5,5′-dicarbaldehyde (**7**) (4 mmol) in THF (5 mL) was added with continued stirred at –78°C for 2 hrs and then at RT for one h. Finally the reaction mixture was quenched with aqueous $NaHCO_3$ and extracted with ether, the organic layers were washed with water, dried over Na_2SO_4 anhyd.), and then concentrated in a vacuum. Purification by flash chromatography using silica gel (hex-

ane/EtOAc;) to provide a yellow oil of thienyl-aryl-carbinols and/or α,α′-5′,5″-bis(aryl)-2′,2″-bithienyl-bicarbinols in 73–80 % yield) which were oxidized to give the corresponding thienylarylketones in low yield 20%.

α-[(4′-Methoxyphenyl)-2-thienylmethanol(4) and α-(4′-methoxyphenyl) -2-thienylketone (6)

4-Bromoanisole (**2**) was lithiated following the same general procedure method (A) and trapped by thiophene-2-carboxaldehyde (**1**). The product was purified by flash chromatography using silica gel (hexane/EtOAc; 15:1) to give compound (**4**) in 73 % yield which was oxidized by air to give compound (**6**) in low yield (15 %).

(**4**); TLC: R_f (hexane/EtOAc; 20:1): 0.26. LRMS (EI): m/z 220 (M^+, 35), 205 (5), 203 (28), 187 (14), 171 (4), 160 (5), 144 (<3), 135 (100), 115 (50, 109 (45), 94 (7), 77 (16), and 45 (5). GC: t_R = 9.489 min.; column: DB-5 6 m × 0.01 mm + 1m guard column: temp. prog: 50 °C / 2 min. / 20 °C min.$^{-1}$ / 250 °C / 5 min. ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.99 (d, J = 8.9 Hz, 2H, Ar-H), 7.77 (dd, J = 1.0 and 4.9 Hz, 1H, Th-H_5), 7.29 (dd, J = 1.0 and 3.8 Hz, 1H, Th-H_3), 7.25 (dd, J = 3.8 and 4.8 Hz, 1H, Th-H_4), 7.1 (d, J = 8.9 Hz, 2H, Ar-H), 5.68 (d, J = 2.8 Hz, 1H, Ar-CHO<u>H</u>), 4.82 (d, J = 2.8 Hz, 1H, Ar-C<u>H</u>OH), 3.85 (s, 3H, ArOC<u>H</u>$_3$) ppm.

(**6**); TLC: R_f (hexane/EtOAc; 15:1): 0.31. LRMS (EI): m/z 218 (M^+, 50), 203 (5), 175 (3), 147 (4), 135 (100), 111 (25), 92 (9), 77 (12), 64 (5), and 44 (12). GC: t_R = 9.89 min.; column: DB-5 6 m × 0.01 mm + 1 m guard column: temp. prog: 50 °C / 2 min. / 20 °C min.$^{-1}$/ 250 °C / 5 min. ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 8.01 (d, J = 8.9 Hz, 2H, Ar-H), 7.77 (dd, J = 1.0 and 4.9 Hz, 1H, Th-H_5), 7.29 (dd, J = 1.0 and 3.8 Hz, 1H, Th-H_3), 7.25 (dd, J = 3.8 and 4.8 Hz, 1H, Th-H_4), 7.12 (d, J = 8.9 Hz, 2H, Ar-H), 3.8 (s, 3H, ArOC<u>H</u>$_3$) ppm.

α-[(3′,5′-Dimethoxytolyl)]-2-thienylmethanol (5)

2-Bromo-3,5-dimethoxytoluene (**3**) was lithiated following the same general procedure method (A) and then trapped by thiophene-2-carboxaldehyde (**1**). Purification of the residue by flash chromatography using silica gel (6.1 hexane/EtOAc) gave a yellow oil compound (**5**) (205 mg, in 78% yield). TLC: R_f (hexane/EtOAc; 6:1): 0.42.

(**5**): LRMS (EI): m/z (relative intensity %) 264 (M^+, 35), 153 (5), 152 (100), 137 (<3), 123 (60), 109 (10), 107 (7), 91 (40), 77 (35), 66 (12), 53 (4), 51 (12), and 45 (<3). GC: t_R = 5.72 min.; column: DB-5 6 m × 0.01 mm + 1 m guard column: temp. prog: 50 °C / 2 min. / 20 °C $min.^{-1}$/ 250 °C / min. ^1H NMR ($CDCl_3$, 200 MHz): δ = 7.28–7.31 [dd, J = 5.7 and 1.2 Hz, 1H, Th-H(5)], 7.01–7.03 [dd, J = 3.9 and 1.2 Hz, 1H, Th-H(3)], 6.9 [dd, J = 3.9 and 5.7 Hz, 1H, Th-H(4)], 6.4 [bs, 1H, Ar-H(4′)], 6.34 [bs, 1H, Ar-H(6)], 4.97 (bs, 1H, Ar-CHOH), 4.82 (d, J = 2.8 Hz., 1H, Ar-C<u>H</u>-OH), 3.86 [s, 3H, ArOC<u>H</u>$_3$(3)], 3.83 [s, 3H, ArOC<u>H</u>$_3$(5)], 2.36 (s, 3H, Ar-CH3) ppm.; Anal. Calcd for $C_{14}H_{16}O_3S$: C, 63.63; H, 6.06. Found: C, 64.32; H, 6.59.

αα′-Bis[(4″-methoxyphenyl]-2,2′-bithienyl-5,5′-dimethanol (8) and αα′-bis[(4″-methoxyphenyl)]-2,2′-bithienyl-5,5′-diketone (10)

4-Bromoanisole (**2**) was lithiated following the same general procedure method (A) and then trapped by 2,2′-bithienyl-5,5-dicarbaldehyde (**7**). The combined product was purified by flash chromatography using silica gel (hexane/EtOAc; 12:1) to provide a colorless oil of compound (**8**) in 80 % yield and compound (**10**) in 12 % yield.

(**8**); TLC: Rf (hexane/EtOAc; 12:1): 0.34. LRMS (EI): m/z 438 (M+, 30), 434 (5), 407 (28), 376 (14), 327 (15), 171 (4), 156 (5), 144 (<3), 135 (100), 115 (50, 109 (45), 96 (7), and 68 (16). GC: t_R = 10.89 min.; column: DB-5 6 m × 0.01 mm + 1 m guard column: temp. prog: 50 °C / 2 min. / 20 °C $min.^{-1}$/ 250 °C / 5 min. ^1H NMR ($CDCl_3$, 200 MHz): δ = 7.05 [d, J = 3.8 Hz, 2H, of Th-H(3,3′)], 6.95 [d, J = 3.8 Hz, 2H, of Th-H(4,4′)], 7.11 (d, J = 8.9 Hz, 2H, Ar-Ho), 7.09 (d, J = 8.9 Hz, 2H, Ar-Hm), 5.70 (d, J = 2.8 Hz, 1H, Ar-CHO<u>H</u>), 4.88 (d, J = 2.8 Hz, 1H, Ar-C<u>H</u>OH), 3.88 (s, 3H, ArOC<u>H</u>$_3$) ppm. Anal. Calcd for $C_{24}H_{22}O_4S_2$: C, 65.75; H, 5.02. Found: C, 66.12; H, 5.79.

(**10**); TLC: R_f (hexane/EtOAc; 12:1): 0.38. LRMS (EI): m/z 434 (M^+, 30), 434 (5), 407 (28), 376 (10), 327 (11), 171 (<3), 156 (4), 144 (<3), 135 (100), 115 (45), 109 (45), 96 (5), and 68 (15). GC: t_R = 11.56 min.; column: DB-5 6 m × 0.01 mm + 1 m guard column: temp. prog: 50 °C / 2 min. / 20 °C $min.^{-1}$ / 250 °C / 5 min. ^1H NMR ($CDCl_3$, 200 MHz): δ = 7.05 [d, J = 3.8 Hz, 2H, of Th-H(3,3′)], 6.95 [d, J = 3.8 Hz, 2H, of Th-H(4,4′)], 7.11 (d, J = 8.9 Hz, 2H, Ar-Ho), 7.09 (d, J = 8.9 Hz, 2H,

Ar-Hm), 3.68 [(s, 6H, ($ArOCH_3$)$_2$] ppm. Anal. Calcd for $C_{24}H_{18}O_4S_2$: C, 66.35; H, 4.17. Found: C, 66.95; H, 5.79.

α,α′-Bis[2-(3″,5″-dimethoxytolyl)]-2,2′-bithienyl-5,5′-dimethanol (9) and α,α′-bis[2-(3″,5″-dimethoxytolyl)]-2,2′-bithienyl-5,5′-diketone (11)

2-Bromo 3,5-dimethoxytoluene (**3**) was lithiated following the same general procedure method (A) and then trapped by 2,2′-bithienyl-5,5′-dicarbaldehyde (**7**). Attempts were made to isolate and characterize products (**9**) and (**11**), unfortunately the product mixture was not resolvable by flash chromatography (hexane/ethylacetate 6:1 with 3% methanol), but it appears to be clear and easily identified by GC/MS and ^{1}H NMR spectra. TLC is shows two close spots at $R_{f_1} = 0.42$ and $R_{f_2} = 0.41$ after flash chromatography.

(**9**); LRMS (EI): m/z (relative intensity) 153 (5), 152 [M^+, $C_9H_{12}O_2$, (100)], 123 (60), 109 (10), 107 (10), 91 (35), 77 (30), 66 (12), 53 (5), and 44 (35). GC: t_R = 10.83 min.; column: DB-5 6 m × 0.01 mm + 1 m guard column: temp. prog: 50 °C / 2 min. / 20 °C min.$^{-1}$/ 270 °C / 5 min. ^{1}H NMR ($CDCl_3$, 200 MHz, from the mixture): δ = 7.03 [d, J = 3.8 Hz, 2H, of Th-H(3,3′)], 6.92 [d, J = 3.8 Hz, 2H, of Th-H(4,4′)], 6.4 [bs, 2H, Ar-H(4″)], 6.34 [bs, 2H, Ar-H(6″)], 5.32 (bs, 2H, Ar-CHOH), 4.82 (bs, 2H, Ar-CHOH), 3.92 [s, 6H, $ArOCH_3$(3″)], 3.83 [s, 6H, $ArOCH_3$(5″)], 2.36 [s, 6H, Ar-CH3(1")], in ppm.

(**11**); LRMS (EI): m/z (relative intensity) 180 (10), 153 (5), 152 [M^+, $C_9H_{12}O_2$, (100)], 123 (60), 109 (10), 107 (10), 91 (35), 77 (30), 66 (12), 53 (5), and 44 (35). GC: t_R = 11.9 min.; column: DB-5 6 m × 0.01 mm + 1 m guard column: temp. prog: 50 °C / 2 min. / 20 °C min.$^{-1}$ / 270 °C / 5 min. ^{1}H NMR ($CDCl_3$, 200 MHz, from the mixture): δ = 7.03 [d, J = 3.7 Hz, 2H, of Th-H(3,3′)], 6.92 [d, J = 3.7 Hz, 2H, of Th-H(4,4′)], 6.45 [bs, 2H, Ar-H(4″)], 6.34 [bs, 2H, Ar-H(6″)], 3.92 [s, 6H, $ArOCH_3$(3″)], 3.83 [s, 6H, $ArOCH_3$(5″)], 2.36 [s, 6H, Ar-CH3(1")], in ppm.

α,α′-Bis(5″-isoquinolinyl)-2,2′-bithienyl-5,5′-dimethanol (13) and αα′-bis(5″-isoquinolinyl)-2,2′-bithienyl-5,5′-diketone (14)

5-Bromoisoquinoline (**12**) was lithiated following the same general procedure method (A) and trapped with 2,2′-bithienyl-5,5′-dicarbaldehyde (**7**).

Attempts were made to isolate and characterize products (**13**) and (**14**), but the product was not resolvable by flash chromatography (hexane / ethylacetate 6:1 with 3% methanol), it was easy to distinguish by GC / MS and ^{1}H NMR spectral data.

(**13**); LRMS (EI): m/z (relative intensity) 480 (<2), 276 (<4), 186 (10), 177 (<3), 156 (100), 117 (5), 92 (100), 91 (30), 86 (70), and 42 (20). GC: t_R = 14.16 min.; column : DB-5 6 m × 0.01 mm + 1 m guard column: temp. prog: 50°C / 2 min. / 20°C min.$^{-1}$ / 270 °C/ 5 min. ^{1}H NMR (200 MHz, $CDCl_3$, from the mixture): δ = 9.33 [s, 2H, Ar-H(1″)], 8.65 [d, J = 6.08 Hz, 2H, Ar-H(3″)], 8.14 [d, J = 5.95 Hz, 2H, Ar-H(8″)], 7.98 [d, J = 6.1 Hz, 2H, Ar-H(6″)], 7.85 [d, J = 6.6 Hz, 2H, Ar-H(4″)], 7.67 [t, J = 7.59 and 7..99 Hz, 2H, Ar-H(7″)], 7.33 [d, J = 3.5 Hz, 2H, bith-H(3,3′)], 7.26 [d, J = 3.5 Hz, 2H bith-H(4,4′), 5.42 (bs, 2H, of Ar-CHO<u>H</u>), 4.86 (bs, 2H, of Ar-C<u>H</u>OH), ppm.

(**14**); LRMS (EI): m/z (relative intensity) 476 (<4), 278 (<4), 186 (10), 177 (<3), 156 (100), 117 (5), 92 (100), 91 (30), 86 (70), and 42 (20). GC: t_R = 16.16 min.; column : DB-5 6 m × 0.01 mm + 1 m guard column: temp. prog: 50 °C / 2 min. / 20 °C min.$^{-1}$ / 270 °C / 5 min. ^{1}H NMR (200 MHz, $CDCl_3$, from the mixture): δ = 9.32 [s, 2H, Ar-H(1″)], 8.60 [d, J = 6.08 Hz, 2H, Ar-H(3″)], 8.12 [d, J = 5.95 Hz, 2H, Ar-H(8″)], 7.99 [d, J = 6.1 Hz, 2H, Ar-H(6″)], 7.83 [d, J = 6.6 Hz, 2H, Ar-H(4″)], 7.66 [t, J = 7.59 and 7.99 Hz, 2H, Ar-H(7″)], 7.36 [d, J = 3.6 Hz, 2H, bith-H(3,3′)], 7.24 [d, J = 3.6 Hz, 2H bith-H(4,4′)] ppm.

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References

1. Lambert, Brandsma and Herman Verkruijsse, (preparative polar organometallic chemistry, 1987), Vol. 1, QD411. B67 pp. 186.
2. a) J. H. Uhlenbroek and J. D. Bijloo, *Rec. Trav. Chim. Pays-Bas*, **1960**, *79*, 1181.
   b) H. J. Kooreman and H. Wynberg, *ibid.*, **1967**, *86*, 37.
   c) C. M. Beaton, N. B. Chapman, and K. Clarke, *J. Chem. Soc., Perkin I*, **1976**, 2355.
3. T. Yamamoto, K. Sanechika, and A. Yamamoto, *J. Polym. Sci., Polym. Lett. Ed.*, **1980**, *18*, 9.
4. Juzo, Nakayama; Fujimori: *Sulfer Letters*. **1990**, *Vol. 11*, PP. 29–30.
5. Yen, Wei; Bin, Wang; Wei, wang; Tian. *Tetrahedron Letters.*, **1995**, *36*, 5, 665–668.
6. Hoye, T. R.; Chen, M. *J. Org. Chem.*, **1996**, *61*, 7940–7942.

7. Berthelot, J.; Guette, C.; Ouchefoune, M.; Desbene P.-L.; Basselier, J.-J. *J. Chem. Research*, **1986**, 381.
8. Kajigaeshi, S.; Kakinami, T.; Okamois, T.; Nakamura, H.; Fujikawa, M. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 4187.
9. B. L. Feringa, R. Hulst, R. Rikers, and L. Brandsma, *Synthesis*, **1988**, *316*.
10. Owen P. Priest, Ph. D. Thesis, university of Minnesota, **1996**.
11. Comins, D. L.; Killpack, M. O. *J. Org. Chem.* **1987**, *52*, 104.
12. W.C. Still, M. Kahn, and A. Mitra, *J. Org. Chem.*, **1978**, *43*, 2923.