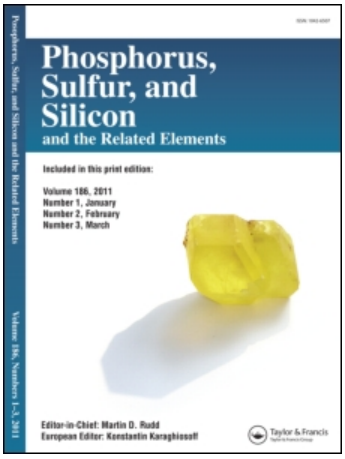

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SYNTHESIS OF THIOPHENE OLIGOMERS VIA ORGANOTIN COMPOUNDS

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SYNTHESIS OF THIOPHENE OLIGOMERS VIA ORGANOTIN COMPOUNDS

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A versatile synthetic route involving the use of organotin compounds has been applied for the preparation of functionalized oligothiophenes. Substituted bithiophenes have been synthesized via the coupling reaction of 2-bromothiophenes with 3-trimethylstannylthiophene. The latter reagent couples with bromoaromatics, bromoheteroaromatics and 2,5-dibromothiophenes to give the corresponding 3-arylthiophenes, 3-heteroarylthiophenes and terthiophenes, respectively. 2-Trimethylstannylthiophene couples with 2,5-dibromo-3-arylthi ophenes to give 3-aryl-α-terthiophenes.

The structures of the new compounds were confirmed by elemental analysis, mass spectrometry, ^{1}H- and ^{13}C- NMR spectral data.

Keywords: Functionalized bithiophene; 3'-aryl-α-terthiophene; synthesis; 3-trimethylstannylthiophene

INTRODUCTION

2,2': 5',2''-Terthiophene (**1**), 2,2'-bithiophene (**2**), and several of their derivatives are biologically active natural products[1–4]. 2,2':5',2''-Terthiophene, the best known of this series, was found in plants of the family *compositae (Asteraceae).* It shows nematicidal and fungicidal activity, which is enhanced by near ultraviolet radiation. It was found that thiophene and its higher α-oligomers are of interest as repeating units for the construction of electroconductive polymers. Much of the research has been focused on modification of the base monomer units, specifically the 3-alkyl derivatives which yield soluble polymers (**3**) with improved conductivity. Several drugs derived from 3-substituted thiophene[5] are in use,

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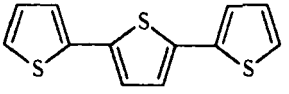
for example Cetiedil an efficient vaso-dilator, Ticarcilline, Semi-synthetic β-lactam antibiotic with thiophene-3-malonic acid unit. Various synthetic methods for the preparation of 3-substituted thiophenes have been reviewed[5]. The synthesis, functionalization and application of conjugated poly (thiophene) have been recently reviewed[6].



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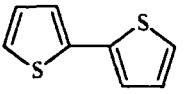

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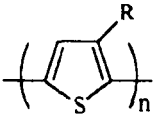

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Thiophene oligomers have been prepared by several methods. Historically, 2,2′:5′, 2″-terthiophene (**1**) was obtained via oxidative coupling of iodothiophene with copper bronze[7]. 2,2′:5′,2″-Terthiophene (**1**) has been prepared by cyclization of the corresponding 1,4-diketone[8]. α-Quaterthiophene and α-sexithiophene have been prepared by coupling of α-lithiated thiophenes in the presence of cupric chloride or organoboranes[9]. A convenient synthesis has been introduced by Kumada[10] in which α-terthiophene was prepared in 86% yield by coupling of 2-thienylmagnesium bromide with 2,5-dibromothiophene in the presence of nickel catalyst.

Oligothiophenes and 3-arylthiophenes bearing electrophilic soups (such as nitro, formyl and acetyl) are desirable for the exploration of the chemistry of oligothiophenes via functional group conversion. The present strategy involves an extension of the Stille[11] coupling method to prepare functionalized bithiophenes, functionalized 3-arylthiophenes, and terthiophenes using tin compounds. Herein, their synthesis and characterization are described.

SYNTHESIS

Lithium and magnesium organometallic compounds have been proven to be very useful intermediates in organic synthesis. However, their higl reactivity and the method used for their preparation precludes the presence of most functional groups in these compounds. In view of the known reactivity of electrophilic groups like nitro, acetyl and formyl towards organometallic reagents, tin was chosen as the activating metal. Organotin

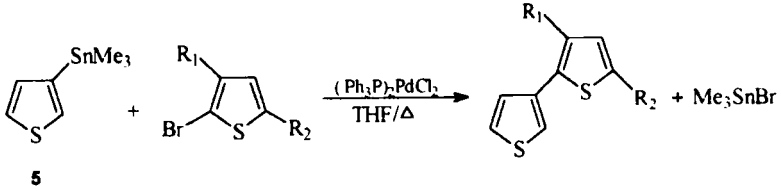
compounds have been used in organic synthesis due to the low ionicity of tin-carbon bond as compared with the magnesium or lithium carbon bonds. Such organotin compounds allow the direct transfer of the organic moiety from the tin metal to the organic substrate in the presence of catalytic amounts of $(Ph_3P)_2PdCl_2$, as shown in equation 1.

$$R_3Sn\text{-}R^1 + R^2\text{-}X \xrightarrow{[Pd]} R^1\text{-}R^2 + R_3SnX \qquad \text{...eq.(1)}$$

This coupling reaction is regio- and stereoselective; for example, 2-trimethylstannylthiophene (**4**) was reacted with ethyl (E)-3-iodoacrylate in the presence of $(Ph_3P)_2PdCl_2$ as a catalyst to give ethyl (E)-3-(2-thienyl)propanoate[12].

Versatile synthetic route has been recently reported[13] involving the use of organotin compounds to prepare functionalized oligothiophenes, for example, 5-trimethylstannyl-2,2′-bithiophene was reacted with 2-bromo-3,5-dinitrothiophene in the presence of $(Ph_3P)_2PdCl_2$ as a catalyst to give 3,5-dinitro-2,2′:5′,2″-terthiophene in good yield.

In the present study, 3-trimethylstannylthiophene (**5**) is found to react with a variety of substituted bromothiophenes bearing electron-withdrawing groups in the presence of catalytic amount of dichloro[bis(triphenylphosphin)]palladium(II) chloride, [Pd], give the corresponding bithiophene derivatives (6–10) in 50–60 % yield, as shown in scheme I.



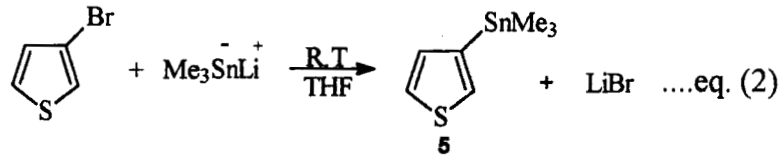
5

6 : $R^1 = H$, $R^2 = H$
7 : $R^1 = H$, $R^2 = NO_2$
8 : $R^1 = H$, $R^2 = CHO$
9 : $R^1 = H$, $R^2 = COCH_3$
10 : $R^1 = NO_2$, $R^2 = NO_2$

SCHEME I

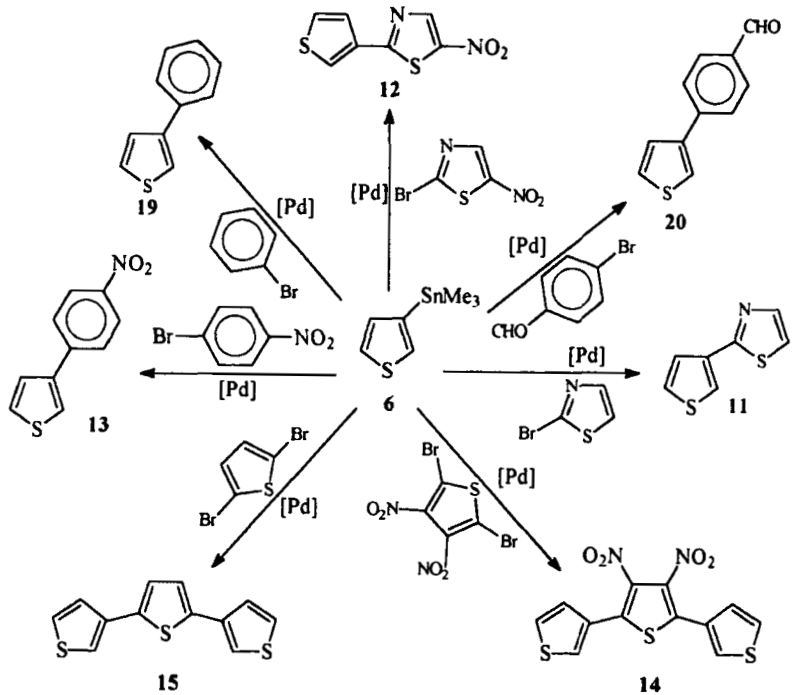
The required starting material 3-trimethylstannylthiophene (**5**) was prepared by the reaction of trimethylstannyl lithium with 3-bromothiophene

in 70% yield as shown in equation 2. It is worth mentioning that the synthesis reported here is quite suitable for obtaining isomerically pure nitro, acetyl and formyl derivatives of bithiophenes (**7–10**). Such derivatives are previously unknown.



5

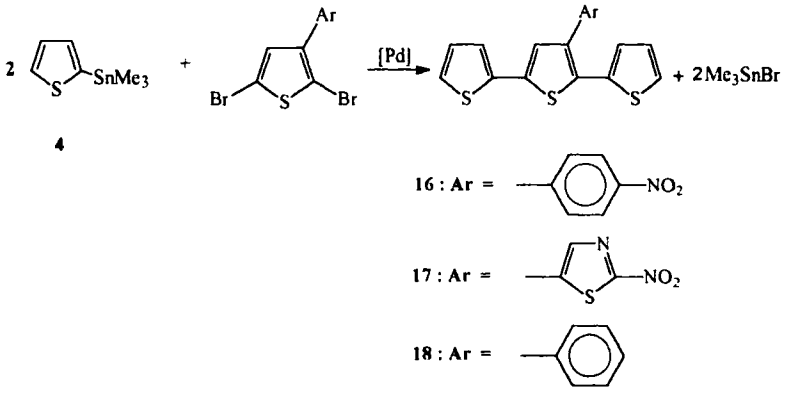
Under the same conditions, the reaction of 3-trimethylstannyl-thiophene (**5**) with 2-bromothiazole, 2-bromo-5-nitrothiazole, 4-bromonitrobenzene, 2,5-dibromo-3,4-dinitrothiophene and 2,5-dibromothiophene give 3-(2-thiazoyl)thiophene (**11**), 3-(5-nitro-2-thiazoyl)thiophene (**12**), 3-(4-nitrophenyl)thiophene (**13**), 3′,4′-dinitro-3,2′:5′,3″-terthiophene (**14**) and 3,2′:5′,3″-terthiophene (**15**), as shown in scheme (II).



SCHEME II

Also, this coupling method is a good method for preparing 3-arylthiophenes, in which the aryl group is substituted with an electrophilic group such nitro and formyl (12, 13, 14, 20). In contrast, 3-arylthiophenes have been prepared in the literature[14] via two-step synthesis, in which the aryl group is substituted with electron-releasing group only (like alkyl groups and methoxy group). This synthesis involves the reaction of 2,5-dichlorothiophene with aromatic compound in the presence of anhydrous $AlCl_3$ to give 4-aryl-2-chlorothiophene, followed with catalytic dechlorination with H_2 using Pd/C.

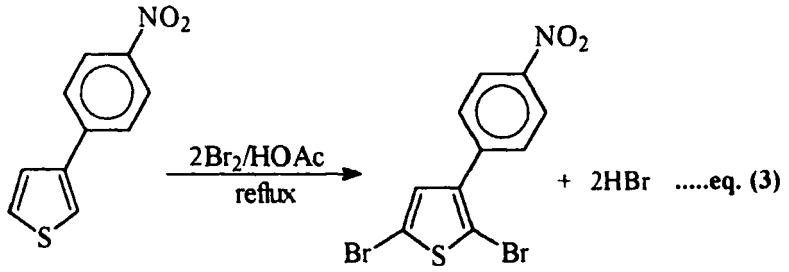
A novel 3′-(4-nitrophenyl)-2,2′:5′,2″-terthiophene (**16**) has been prepared from the reaction of 2 moles of 2-trimethylstannylthiophene (**4**) with one mole of 2,5-dibromo-3-(4-nitrophenyl)thiophene, in the presence of palladium catalyst, [Pd], as yellow solid, as shown in Scheme (III).



SCHEME III

In contrast, Kankare[15] reported a three-step synthesis of 3′-arylterthiophene derivatives via the ring closure of the suitable 1,4-butadione using Lawesson's reagent. The required starting material 2,5-dibromo-3-(4-nitrophenyl)thiophene was prepared by the bromination of 3-(4-nitrophenyl)thiophene (**13**) using Br_2 in acetic acid, as shown in equation 3.

Similarly, 3′-(5-nitro-2-thiazoyl)-2,2′:5′,2″-terthiophene (**17**), and 3′-phenyl-2,2′:5′,2″-terthiophene (**18**), have been prepared from the reaction of 2 moles of 2-trimethylstannylthiophene (**4**) with one mole of



13

2,5-dibromo-3-(5-nitro-2-thiazoyl)thiophene, and with one mole of 2,5-dibromo-3-phenylthiophene, respectively, in the presence of palladium catalyst [Pd], as shown in Scheme III.

The required starting materials, 2,5-dibromo-3-(-5-nitrothiazoyl)thiophene and 2,5-dibromo-3-arylthiophenes, were prepared via the bromination of 3-(5-nitro-2-thiazoyl) thiophene (**12**), and 3-phenylthiophene (**19**), respectively, with two moles of bromine in acetic acid under reflux.

Experimentals

2,5-Dibromothiophene, 2-bromothiazole, 5-bromo-2-thiophenecarboxaldehyde, and 2-bromo-5-nitrothiazole, purchased from Janseen Chemica. 2-Bromothiophene, 3-bromothiophene, dichloro[bis(triphenylphosphin)]palladium(II) $(ph_3p)_2PdCl_2$, trimethylstannyl chloride were purchased from Merck.

2-Acetyl-5-bromothiophene[16], 2-bromo-5-nitrothiophene[17], 2-bromo-3,5-dinitrothiophene[18], 2,5-dibromo-3,4-dinitrothiophene[19], 2-trimethylstannylthiophene[20], were prepared according to literature procedures.

Solvents were dried by using standard procedures. NMR spectra were obtained with Brucker AC-200 and Brucker AVANCY DPX – 300 spectrometers, for solutions in $CDCl_3$. The ^{1}H-NMR spectra were calibrated by using signals from the solvent referenced to $(Me)_4$ Si. The elemental analysis was determined by M.H.W. Laboratories Arizona, U.S.A. Mass spectra were determined by using a Finnigan MAT 731 spectrometer at 70 eV and VG – 70S spectrometer.

3-Trimethylstannylthiophene (5) [20]

A solution of trimethylstannyllithium [21] in THF, prepared from trimethylstannyl chloride (2.14 g, 0.011 mol) and lithium metal (0.3 g, 0.043 mol) in dry THF (30 ml) at 0 °C under nitrogen atmosphere was added dropwise at 0°C to a solution of 3-bromothiophene (1.6 g, 0.01 mol) in dry THF (20 ml), stirring was continued overnight at room temperature. THF was evaporated in vacuum, and the residue was extracted with n-hexane (3×30 ml). Hexane was evaporated to leave an oily residue which was purified by vacuum distillation (b.p.60 / 2mm Hg), yield = 67 %. ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.48 (dd, J = 3 Hz, J = 4 Hz, 1H), 7.38 (dd, J= 3 Hz, J = 1 Hz, 1H), 7.19 (dd, J = 4 Hz, J = 1 Hz, 1H), 0.44 (s, 9H). MS (EI) exact mass calcd. for $C_7H_{12}SnS$-CH_3 m/e 232.9447; found; m/e 232.9455. MS (EI) [m/e (intensity)]: 248 (6,M for $C_7H_{12}SnS$), 233 (100, M^+-CH3).

General procedures

A three-neck round bottomed flask (100 ml), equipped with condenser, magnetic stirrer and N_2-inlet, was charged with a particular bromothiophene, bromoaromatics, or bromoheteroaromatics. bis(triphenylphosphine) palladium (II) chloride (0.1 mmol) and dry DMF (20 ml). 3-Trimethylstannylthiophene was added, and the reaction mixture was then refluxed for 20 hours with vigorous stirring under N_2-atmosphere. After being cooled to room temperature, the reaction mixture was poured into water, the product was isolated either by extraction with ether (3×30 ml) or by filtration, the product purified by TLC using silica gel as adsorbent and chloroform-hexane (2:8 v/v) as the eluent.

Yields, and melting points of the bithiophenes, 3-arylthiophenes and terthiophenes prepared by the above procedures are listed below:

5-Formyl-2,3′-bithiophene (8)

This compound was prepared from the reaction of one mole of 5-bromo-2-thiophenecarboxaldehyde and one mole of 3-trimethylstannylthiophene. Yield 60%, m.p. 136 °C. ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 9.85 (s, 1H), 7.69 (d, J=4 Hz, 1H), 7.58 (s, 1H), 7.37 (m, 2H), 7.25 (dd, J= 4 Hz, J=3 Hz, 1H). Anal. Calcd. for $C_9H_6S_2O$: C, 55.64; H, 3.44. Found: C, 55.50; H, 3.36. MS (EI) [m/e (intensity)]: 194 (100, M^+), 167 (8), 121 (60).

5-Acetyl-2,3'-bithiophene (9)

This compound was prepared from the reaction of one mole of 2-acetyl-5-bromothiophene and one mole of 3-trimethylstannylthiophene. Yield 60%, m.p. 125 °C. ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.60 (d, J = 4 Hz, 1H), 7.52 (dd, J = 4 Hz, J = 1 Hz, 1H), 7.34 (m, 2 H), 7.18 (d, J = 4 Hz, 1H), 2.55 (s, 3H). Anal. Calcd. for $C_{10}H_8S_2O$: C, 57.87; H, 4.00. Found: C, 57.69; H, 3.88. MS (EI) [m/e (intensity)]: 208 (67), 193 (100), 121 (47).

5-Nitro-2,3'-bithiophene (7)

This compound was prepared from the reaction of one mole of 2-bromo-5-nitrothiophene and one mole of 3-trimethylstannylthiophene. Yield 60%, m.p. 86°C. ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.86 (dd, J = 4 Hz, J = 1 Hz, 1H), 7.59 (dd, J = 4 Hz, J = 1 Hz, 1H), 7.41 (m, 1H), 7.31 (dd, J = 4 Hz, J = 1 Hz, 1H), 7.10 (dd, J = 4 Hz, J = 1 Hz, 1H). Anal. Calcd. for $C_8H_5S_2NO_2$: C, 45.48; H, 2.39. Found: C, 45.29; H, 2.85. MS (EI) [m/e (intensity)]: 211(100, M^+), 121 (88).

3,5-Dinitro-2, 3'-bithiophene (10)

This compound was prepared from the reaction of one mole of 2-bromo-3,5-dinitrothiophene and one mole of 3-trimethylstannylthiophene. Yield 60%, m.p. 165 °C. ^{1}H-NMR (DMSO-d_6, 200 MHz) 6 8.73 (s, 1H), 8.38 (dd, J = 3 Hz, J = 1 Hz, 1H), 7.89 (dd, J = 5 Hz, J = 3 Hz, 1H), 7.60 (dd, J= 5 Hz, J = 1 Hz, 1H), ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 8.39 (s, 1H), 7.86 (dd, J= 4 Hz, J = 1 Hz), 7.47 (dd, J = 6 Hz, J = 5 Hz, 1H), 7.35 (dd, J= 5 Hz, J=1 Hz, 1H). Anal. Calcd. for $C_8H_4S_2N_2O_4$: C, 37.50; H, 1.57. Found: C, 37.44; H, 1.70. MS (EI) [m/e (intensity)]: 256 (63, M^+), 164 (50), 120 (100), 45 (84).

2,3'-Bithiophene (6)

This compound was prepared from the reaction of 2-bromothiophene and one mole of 3-trimethylstannylthiophene. Yield 53%, m.p.73°C, ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.00 – 7.40 (m, 6 H). Anal. Calcd. for $C_8H_6S_2$: C, 57.79; H, 3.65. Found: C, 57.65; H, 3.70. MS (EI) [m/e (intensity)]: 166 (100, M^+), 121 (30).

3,2':5',3''-Terthiophene (15)

This compound was prepared from the reaction of one mole of 2,5-dibromothiophene and two moles of 3-trimethylstannylthiophene. Yield 44%,

m.p.185°C. ^{1}H-NMR (DMSO-d_6, 200 MHz) δ 7.83 (dd, J=6 Hz, J=3 Hz, 1H), 7.75 (dd, J=10 Hz, J=8 Hz, 1H), 7.50 (dd, J=10 Hz, J=3 Hz, 1H), 7.48 (s, 1H). In ($CDCl_3$, 200 MHz)δ 7.29–7.40 (m, 3H), 7.12 (s, 1H). Anal. Calcd. for $C_{12}H_8S_3$: C, 58.03; H, 3.25. Found: C, 57.37; H, 3.52. MS (EI) [m/e (intensity)]: 248 (100, M^+), 203 (8).

3'-(4-Nitrophenyl)-2,2': 5',2''-terthiophene (16)

This compound was prepared from the reaction of one mole of 2,5-dibromo-3-(4-nitrophenyl)thiophene and two moles of 2-trimethylstannylthiophene. Yield 66%, m.p.155°C. ^{1}H-NMR (DMSO-d_6, 200 MHz) δ 8.23 (d, J= 9 Hz, 2H), 7.67 (d, J=9 Hz, 2H) 7.75 (dd, J=5 Hz, J=1 Hz 1H), 7.55 (dd, J=5 Hz, J=1Hz, 1H) 7.46 (s,1H), 7.42 (dd, J=3 Hz, J=1 Hz 1H), 7.13 (dd, J=3 Hz, J=3 Hz, 1H), 7.16(dd, J= 4 Hz), 7.05 (dd,J=5 Hz, J=3 Hz, 1H). Anal. Calcd. for $C_{18}H_{11}S_3NO_2$: C, 58.52; H, 3.00. Found: C, 58.64; H, 2.79. MS (EI) [m/e (intensity)]: 369 (100, M^+). UV (CH_3CN)[$\lambda_{max, nm}$ (ε)]: 332 (17000).

3',4'-Dinitro-3,2':5',3''-terthiophene (14)

This compound was prepared from the reaction of one mol of 2,5-dibromo-3,4-dinitrothiophene with two moles of 3-trimethylstannylthiophene. Yield 25%, m.p. 118°C, ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.75 (dd, J = 3 Hz, J = 2 Hz, 1H), 7.46 (dd, J=5 Hz, J=3, 1H), 7.28 (dd, J=2 Hz, J=2 Hz, 1H). Anal. Calcd for $C_{12}H_6S_3N_2O_4$: C, 42.60; H,1.97. Found: C, 42.46; H, 1.92. MS (EI) [m/e (intensity)]: 338 (100, M^+).

3-(5-Nitro-2-thiazoyl)thiophene (12)

This compound was prepared from the reaction of one mole of 2-bromo-5-nitrothiazole and one mol of 3-trimethylstannylthiophene. Yield 48%, m.p. 148°C. ^{1}H-NMR ($CDCl_3$. 200 MHz) δ 8.50 (s, 1H), 8.05 (dd, J=3 Hz, J=1 Hz, 1H), 7.55 (dd, J=2 Hz, J=5 Hz, 1H), 7.44 (dd, J=4 Hz, J=3 Hz, 1H) Anal. Calcd for $C_7H_4S_2N_2O_2$: C, 39.61; H, 1.90. Found: C, 39.73; H, 2.04. MS (EI) [m/e (intensity)]: 212 (80, M^+), 166 (100), 122 (32), 57 (80).

3-(4-Formylphenyl)thiophene (20)

This compound was prepared from the reaction of one mole of 4-bromobenzaldehyde with one mole of 3-trimethylstannylthiophene. Yield 37%, m.p. 100°C. ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 10.00 (s, 1H), 7.90 (d,

J= 4Hz, 2H), 7.75 (d, J= 4 Hz, 2H), 7.6 (dd, J=1 Hz, J=1 Hz, 1H), 7.44 (d, J=1Hz, 2H). Anal. Calcd. for $C_{11}H_8SO$: C, 70.20; H,4.29 Found: C, 70.42; H, 4.52. MS (EI) [m/e (intensity)]: 188 (100, M^+), 167(22), 115 (50).

3-(4-Nitrophenyl)thiophene (13)

This compound was prepared from the reaction of one mole of 4-bromonitrobenzene with one mole of 3-trimethylstannylthiophene. Yield 68% m.p. 68°C. ^{1}H-NMR ($CDCl_3$, 200 MHz) 6 8.25 (d, J= 8 Hz, 2H), 7.72 (d, J= 8 Hz, 2H), 7.63 (m, 1H), 7.43 (m, 2H). Anal. Calcd. for $C_{10}H_7SNO_2$ C, 58.53; H, 3.42. Found: C, 58.34; H, 3.60. MS (EI) [m/e (intensity)]: 205 (100, M^+), 115 (53).

3-(2-Thiazoyl)thiophene (11)

This compound was prepared from the reaction of one mole of 2-bromothiazole with one mole of 3-trimethylstannylthiophene. Yield 51%, oil. ^{1}H-NMR ($CDCl_3$ 200 MHz) δ 7.85 (d,J= 3 Hz, 1H), 7.77 (d, J= 3 Hz, 1H), 7.55 (d, J= 5 Hz, 1H), 7.36 (dd, J= 5 Hz, J= 2 Hz, 1H), 7.25 (d, J=3 Hz, 1H). Anal. Calcd. for $C_7H_5S_2N$: C, 50.30; H, 3.02. Found: C, 50.61; H, 2.96. MS (EI) [m/e (intensity)]: 167 (50, M^+), 85 (100).

3-Phenylthiophene (19)[14]

This compound was prepared from the reaction of one mole of bromobenzene with one mole of 3-trimethylstannylthiophene. Yield 62%, m.p. 90°C. (Lit[14]. m.p 93–94 °C).

2,5-Dibromo-3-Phenylthiophene

A solution of (0.6 g, 3.75 mmol) of bromine in acetic acid (15ml) was added dropwise to a stirred solution of 3-phenylthiophene (0.20 g, 1.25 mmol) in acetic acid (15 ml). The mixture was refluxed for 12 hours, after being cooled to room temperature. The mixture was poured into water, precipitate was collected and recrystallized from methanol. Yield 67%, oil. ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.00 (s, 1H), 7.20 – 7.60 (m, 5H). MS (EI) [m/e (intensity)]: 318 (100, M^+), 158 (98).

2,5-Dibromo-3-(4-nitrophenyl)thiophene

A solution of bromine (0.6 g, 3.75 mmol) in acetic acid (15ml) was added dropwise to a stirred solution of 3-(4-nitrophenyl)thiophene (0.27 g, 1.33 mmol) in acetic acid (15 ml). The mixture was refluxed for 12 hours,

after being cooled to room temperature. The mixture was poured into water, precipitate was collected and recrystallized from methanol. Yield 60%, m.p. 155 °C, ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 8.27 (d, J= 9 Hz, 2H), 7.65 (d, J= 9 Hz, 2H), 7.04 (s, 1H). MS (EI) [m/e (intensity)]: 363 (100, M^+), 238 (47).

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