# PREPARATION AND CHARACTERIZATION OF NEW SUBSTITUTED PHENYLTHIENYLACETYLENES: COMPARISON OF THREE POSSIBLE PATHWAYS.

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**Abstract:**

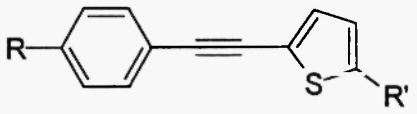
The synthesis of new substituted phenylthienylacetylenes is studied starting from selenadiazole rings, β-chloro acroleines and substituted phenyl or thienyl acetylenes.

**Introduction:**

In the last twenty years, much scientific attention was focused on acetylenic building blocks (1) for many purpose like molecular scale wires (2), carbon rich or graphite like systems (3), acetylenic bridged ligands (4), phenylacetylene dendrimers (5). On the other hand, small molecules like diphenyl acetylenes showed second order nonlinear optical activity (6). More recently Neidlein (7) reported the preparation of poly-phenyl or -trimethylsilyl ethynyl bithiophenes as photodynamic tumor therapy agents. In the course of our interest in the synthesis of new thiophenic structures (8), we describe here the preparation of some new substituted phenylthienylacetylenes.

Some phenylthienylacetylenes have already been synthezised mostly by palladium or copper catalysed cross coupling reactions. Scheme 1 outlines some of the more representative compounds actually prepared.

Scheme 1



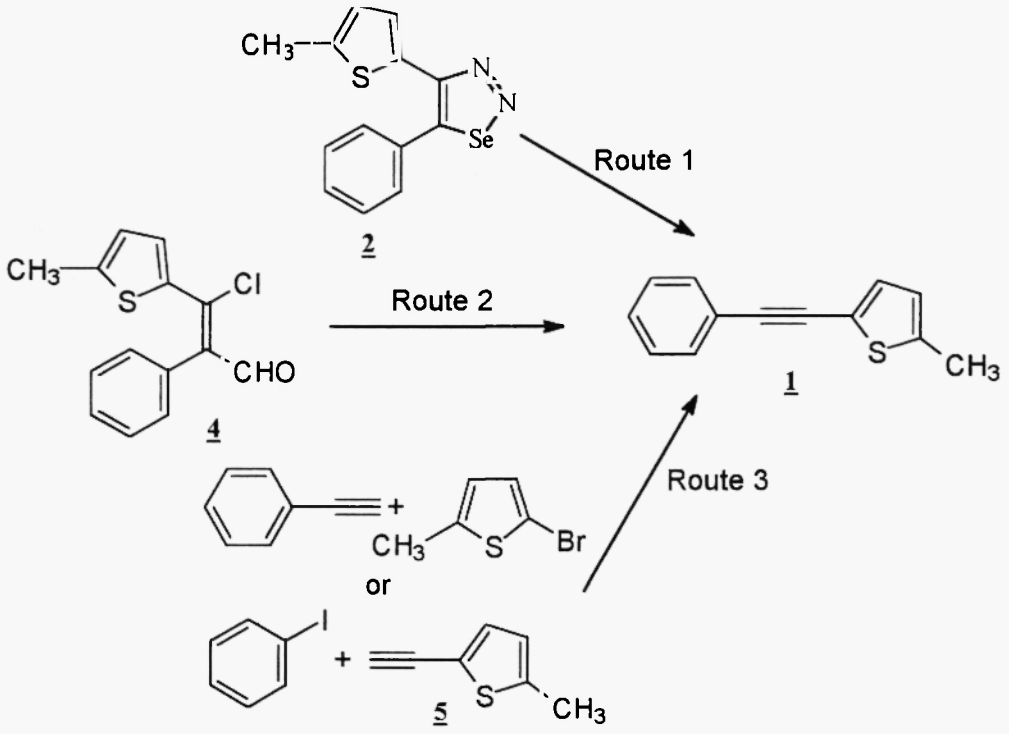

R = R' = H; ref. (9)
R = H; R' = $CH_3$; ref. (10)
R = $CH_3$; R' = H; ref. (11)
R = H; R' = CHO; ref. (12, 13)
R = H; R' = $CHOHCH_3$; ref. (13)
R = H; R' = $CO_2CH_3$; ref. (12)
R = H; R' = $NO_2$; ref. (14)
R = H; R' = $CH{=}CH_2$; ref. (13)
R = H; R' = phenyl; ref. (15)
R = H; R' = 5-bromothienyl; ref. (9)
R = H; R' = phenylethynyl; ref. (16)
R = H; R' = methylethynyl; ref. (16)
R = $CH_3$; R' = p-tolylethynyl; ref. (17)
R = p-nitrophenyl; R' = H; ref. (18)

We propose in the first part of this paper, an investigation of three different strategies for the preparation of phenylthienylacetylene 1 and the determination of the best experimental conditions (scheme 2). In a second part, we describe the synthesis of new substituted phenyl and phenylthienyl acetylenes (Scheme 7).

**Results and discussion:**

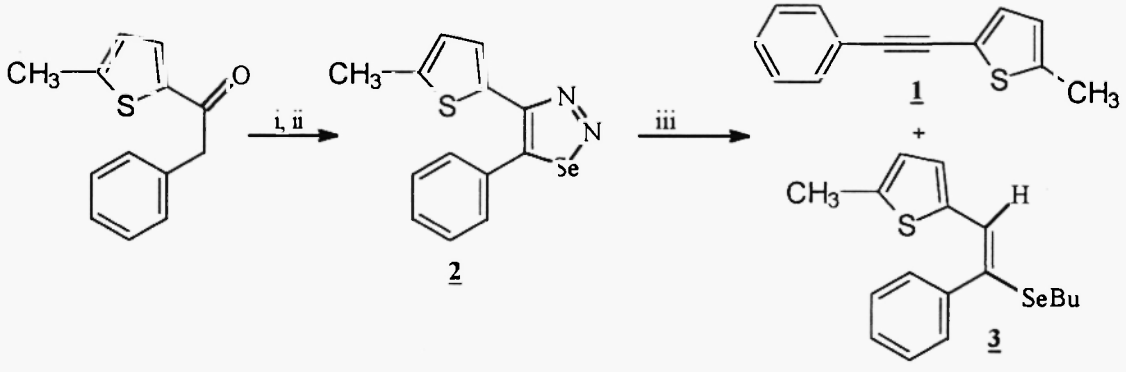
Acetylenic compounds can be obtained by decomposition of selenadiazoles (19) (route 1), by basic treatment of β-chloro acroleines (20) (route 2) or by palladium mediated cross coupling reactions between an aryl alkyne and an aryl haloderivative (21) (route 3).

Scheme 2




In route 1, semicarbazone, obtained classically from benzylthienylketone and semicarbazide hydrochloride in ethanol (22), is refluxed with selenium dioxide in acetic acid to afford 5-methylthienylphenyl selenadiazole 2 (scheme 3).

Scheme 3

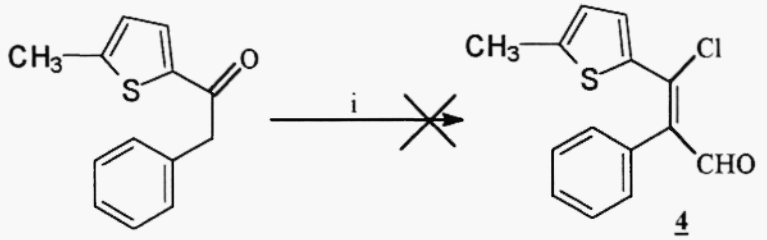



Reagents and conditions: i: $H_2NHNCO_2Et$, EtOH, $Na_2CO_3$; ii: $SeO_2$, AcOH; iii: BuLi, THF, -78°C.

As thermal or photochemical degradation of selenadiazole rings to triple bond often leads to formation of undesired products (19), we choose the base promoted reaction described by MEIER (23). At low temperature (-78°C), nucleophilic attack of butyllithium at the selenium atom of the heterocyclic ring, as suggested by ANDO (24), allows an access to alkyne 1 in low yield (10%), the intermediate vinylselenide 3 being isolated as the major product (55%).

The second pathway has been proposed by BODENDORF (20), who described an access to acetylenic bond by treatment of β-chloro acroleines in strongly basic media. Unfortunately the desired β-chloro acroleine 4 could not be obtained using N,N-dimethyl or N-methyl-N-phenyl formaldehyde and phosphorus oxychloride at 60°C (scheme 4) (25).

Scheme 4

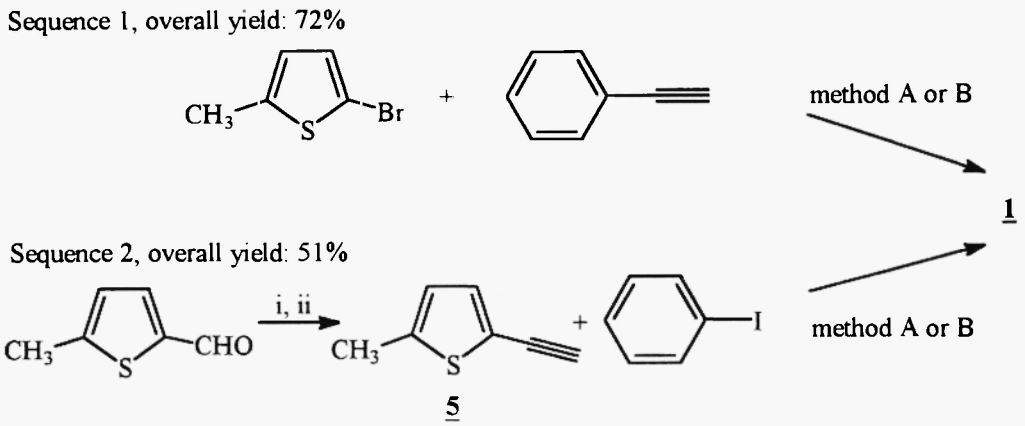



4

Reagents and conditions: i: DMF-$POCl_3$ or MPhF- $POCl_3$.

The third route investigated, was the coupling reaction between arylacetylenes and halothiophenes (or thienylacetylenes and arylhalides).
The coupling reactions were made through the Heck procedure using palladium acetate or tetrakistriphenylphosphine palladium as a catalyst (Scheme 5).

Scheme 5




Reagents and conditions: i: $CBr_4$, $PPh_3$, $CH_2Cl_2$; ii: nBuLi, $Et_2O$, -78°C; Method A: $Pd(OAc)_2$, $PPh_3$, piperidine; Method B: $Pd(TPP)_4$, CuI, $Et_3N$, $CH_3CN$.

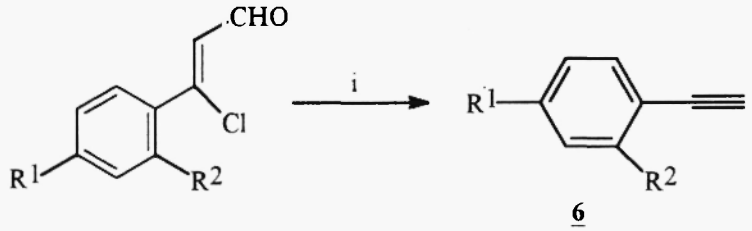
So, the best way for the preparation of compounds 1 was sequence 1. The yields higher by coupling arylacetylenes with halothiophenes. Moreover, thienylacetylenes show low stability on standing at room temperature.

In conclusion, Heck cross coupling reactions starting from phenylacetylene derivatives is the most appropriate pathway to synthesize phenylthienyl acetylenes.

We decide therefore to prepare polysubstituted phenyl thienylacetylenes 7 to 12 by coupling reaction between a substituted phenylacetylene and a bromo or iodo thiophene derivatives.

Alkynes 6 were prepared by BODENDORF's method starting from β-chloro acroleine synthesized as described elsewhere (25) (Scheme 6, Table 1).

Scheme 6



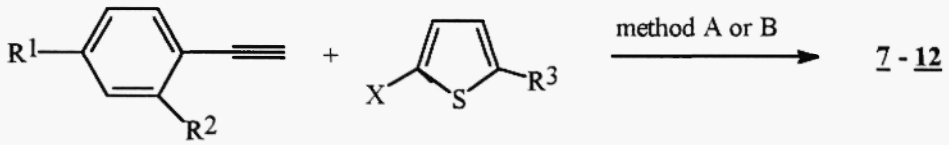

Reagents and conditions: i: NaOH, Dioxane reflux.

Table 1: preparation of phenylacetylenes 6

| compound | $R^1$ | $R^2$ | yield(%) |
|---|---|---|---|
| 6b | MeO | H | 60 |
| 6c | $NO_2$ | H | 71 |
| 6d | MeO | MeO | 79 |

Coupling reaction between phenyl alkynes 6and halothiophenes yielded the polysubstituted phenylthienylacetylenes 7 to 12 as shown in table 2 (scheme 7).

Scheme 7




6a-d

Table 2: substituted phenylthienyl acetylenes 7 to 12

| Compound | $R^1$ | $R^2$ | $R^3$ | X | Method | Yield(%) |
|---|---|---|---|---|---|---|
| 7 | H | H | H | Br | A | 72 |
| 8 | MeO | H | CHO | Br | B | 67 |
| 9 | $NO_2$ | H | $CH_3$ | I | B | 50 |
| 10 | MeO | H | $NO_2Ph$ | Br | B | 40 |
| 11 | MeO | H | $NO_2$ | I | B | 55 |
| 12 | MeO | MeO | $NO_2$ | I | B | 45 |

All new compounds were characterized by $^1H$, $^{13}C$ NMR, IR and microanalysis.

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The authors thanks gratefully Dr. N. Jarkas for running the elemental analysis

## Experimental section

### General

Melting points were determined on a KOFLER bench and are uncorrected. $^{1}H$ and $^{13}C$ NMR spectra were recorded on a BRUKER AC 250 Mhz instrument. Infrared spectra (IR) were measured on a PERKIN-ELMER 881 spectrometer and are reported in wavenumbers ($cm^{-1}$). UV-vis absorbances were measured on a SHIMADZU UV 1205 apparatus and are reported in nanometers (nm). Elemental analyses were performed on a Carlo Erba elemental analyser. β-Aryl-β-chloroacroleines were prepared as described in ref. 25. THF and dioxane were distilled over sodium. $CH_3CN$ was distilled over potassium hydroxyde. Phenylacetylene was commercialy available from ALDRICH. Solvents used in coupling reactions were deaerated.

**5-Phenyl-4-[2'-(5'-methylthienyl)]-[1,2,3]selenadiazole 2**:

A mixture of benzyl-2-(5-methylthienyl)ketone (2.16g, 0.01mol), semicarbazide hydrochloride (0.82g, 0.01mol), and sodium carbonate (1.1g, 0.01mol) in ethanol (50ml) was heated at reflux for 15h. The mixture was poured into ice/water and the precipitate filtered off. Recristallization from methanol yielded 80% of the semicarbazone.

m.p. 198°C; $^{1}H$ NMR ($CDCl_3$): $\delta_H$: 2.4(s, 3H, $CH_3$), 4.37(s, 2H, $CH_2$), 6.6(d, 1H, Har, J = 3.4 Hz), 7.1(d, 1H, Har, J = 3.3 Hz), 7.16(s, 2H, $NH_2$), 7.2(sl, 5H, Har), 7.3(s, 1H, NH); $^{13}C$ NMR ($CDCl_3$): δc: 15.8, 34.7, 125, 126, 128.4, 128.9, 137, 141, 144.4, 160; IR(KBr): 3510, 3435, 2922, 1685, 1571, 739.

The above obtained semicarbazone (1.36g, 5mmol) was dissolved in hot acetic acid (20ml). Powdered selenium dioxide (0.55g, 5mmol) was added, and the mixture was gently heated for 30min and then filtered trhough a celite pad which was washed with acetic acid (30ml). The filtrate was diluted with water (150ml) and the precipitate filtered off and dried. The solid was purified by recristallization in methanol. Yield :50%.

m.p. 89°C; $^{1}H$ NMR ($CDCl_3$): $\delta_H$: 2.47(s, 3H, $CH_3$), 6.6(d, 1H, Har, J = 3.6 Hz), 6.9(d, 1H, Har, J = 3.5 Hz), 7.4(sl, 5H, Har); $^{13}C$ NMR ($CDCl_3$): δc: 14, 125, 127, 129, 129.2, 129.4, 130, 131, 141, 152, 154; IR(KBr): 2910, 1596. Anal. calcd for $C_{13}H_{10}N_2SSe$: C, 51.15; H, 3.30; N, 9.18. Found: C, 51.08; H, 3.21; N, 9.32.

**Phenyl-2-(5methylthienyl)acetylene 5 by degradation of selenadiazole 1:**

nButyllithium (0.34 ml of 2.5M in hexanes, $5.39.10^{-4}$mol) was added dropwise, at -78°C, to selenadiazole **2** (0.15 g, $4.9.10^{-4}$mol) in 10 ml anhydrous THF. After $N_2$ evolution ceased, 4 ml of ethanol and 4ml of water were added. The reaction mixture was stirred at 0-5°C for 5 to 10 min. The mixture was poured into 50 ml ice/water and extracted with ethyl acetate. The organic layer was washed with 3x30ml water, dried and evaporated. The residue was purified by chromatography on silica gel (Et.Pet. /AcOEt: 95/5). Yield: 10%.
m.p. 56°C(litt. (28):57-58°C); $^1$H NMR ($CDCl_3$): $\delta_H$: 2.49(s, 3H, $CH_3$), 6.6(d, 1H, HAr, J = 2.5 Hz), 7(d, 1H, HAr, J = 3.3 Hz), 7.4(m, 5H, HAr); $^{13}$C NMR ($CDCl_3$): δc: 15.3, 83, 92.2, 120.7, 123, 125.4, 128.2, 128.3, 131.3, 132, 142.1; IR(KBr): 2919, 2200; UV-Vis $\lambda_{max}$: 309.
Anal. calcd for $C_{13}H_{10}S$: C, 78.75; H, 5.08. Found: C, 78.58; H, 7.94.

**1-Phenyl-1-butylselanyl-2-[2'(5'-methylthienyl)]ethylene 3**:

Yield: 62%; $^1$H NMR ($CDCl_3$): $\delta_H$: 0.9(t, 3H, $CH_2CH_3$), 1.4(m, 2H, $CH_2CH_2CH_3$), 1.7(m, 2H, $SeCH_2CH_2CH_2$), 2.49(s, 3H, $CH_3$), 2.93(t, 2H, $SeCH_2CH_2$) 6.6(s, 1H), 7.1(d, 1H, HAr, J = 3.5 Hz), 7.3(sl, 5H, HAr), 7.5(d, 1H, HAr, J = 3.4 Hz).

**Synthesis of 2-(5-methylthienyl)acetylene 5:**

5-Methyl thiophene-2-carboxaldehyde (2g, 0.016mol) was added at 0°C to triphenylphosphine (10.5g, 0.04mol) and carbon tetrabromide ( 6.64g, 0.02mol) in diclhoromethane (60ml) and the mixture was stirred 1h at room temperature. The suspension was then filtered and the filtrate evaporated. The solid obtained was purified by recristallization in petroleum ether.
2-(2',2'-Dibromoethenyl)-5-methylthiophene: Yield: 85%; m.p. 63°C(litt. (26):65°C); $^1$H NMR ($CDCl_3$): $\delta_H$: 2.47(s, 3H, $CH_3$), 6.7(d, 1H, HAr, J = 3.2 Hz), 7.03(d, 1H, HAr, J = 3.4 Hz), 7.5(s, 1H, CH); $^{13}$C NMR ($CDCl_3$): δc: 15.4, 85.1, 124.8, 130.4, 131.13, 135.8, 142.2.

nButyllithium (20.4ml of 2.5M in hexanes, 0.051mol) was added dropwise, at -78°C, to 2-(2',2'-dibromoethenyl)-5-methylthiophene (5g, 0.017mol) dissolved in anhydrous ether (200ml). The mixture was stirred 1h at -78°C, then 1h at room temperature, hydrolysed with

water (500ml) and extracted with ethyl acetate. The organic layer was washed with 3x 50ml water, dried and evaporated. The residue was purified by distillation. Yield: 85%.
eb. $p_{.5.3}$: 30°C(litt. (26): eb. $p_{.66.5}$:103°C); $^1$H NMR ($CDCl_3$): $\delta_H$: 2.4(s, 3H, $CH_3$), 3.3(s, 1H, CH), 6.6(d, 1H, HAr, J = 3.6 Hz), 7.09(d, 1H, HAr, J = 3.5 Hz); $^{13}$C NMR ($CDCl_3$): δc: 15.2, 80.3, 119.4, 125.1, 133.2, 142.3. Anal. calcd for $C_7H_6S$: C, 68.81; H, 4.95. Found: C, 68.97; H, 5.03.

**Preparation of phenylacetylenes 5 by BODENDORF: general procedure**

β-Aryl-β-chloroacroleins (0.01mol) in dioxane (60ml) were added to sodium hydroxyde ( 0.024mol) in hot water (30ml). The reaction mixture was refluxed 1h and then allowed to cool at room temperature. The mixture was poured in water (200ml) and extracted with 3x 50ml ethyl acetate. The combined organic layer were dried and evaporated. The crude product was purified by flash chromatography ($CH_2Cl_2$).
**4-Methoxyphenylacetylene 6b**: Yield: 60%; oil; $^1$H NMR ($CDCl_3$): $\delta_H$: 3.02(s, 1H, CH), 3.8(s, 3H, $OCH_3$), 6.8(d, 2H, HAr, J = 8.7 Hz), 7.4(d, 2H, HAr, J = 8.7 Hz); $^{13}$C NMR($CDCl_3$): δc: 55, 76, 83, 113, 114, 133, 159. IR($CCl_4$): 3305. Anal. calcd for $C_9H_8O$: C, 81.18; H, 6.10. Found: C, 81.16; H, 6.21.

**4-Nitrophenylacetylene 6c** : Yield: 70%; m.p. 149°C(Litt. (28):150°C); $^1$H NMR ($CDCl_3$): $\delta_H$: 3.3 (s, 1H, CH), 7.6(d, 2H, HAr, J = 8.6 Hz), 8.1(d, 2H, HAr, J = 8.6 Hz); $^{13}$C NMR ($CDCl_3$): δc: 58, 81, 82, 123.7, 128.8, 132.6, 147.3. IR(KBr): 3300, 1625, 1296. Anal. calcd for $C_8H_5NO_2$: C, 65.31; H, 3.42; N, 9.52. Found: C, 65.28; H, 3.39; N, 9.64.

**2,4-Dimethoxyphenylacetylene 6d**: Yield: 81%; oil; $^1$H NMR ($CDCl_3$): $\delta_H$: 3.1(s, 1H, CH), 3.78 (s, 3H, $OCH_3$), 3.85 (s, 3H, $OCH_3$), 6.4(m, 2H, HAr), 7.35(d, 1H, HAr, J = 9.1 Hz); $^{13}$C NMR ($CDCl_3$): δc: 54, 56, 79.5, 97, 103.4, 105.8, 134.6, 134.8, 161.35, 161.65. IR($CCl_4$): 3310. Anal. calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21. Found: C, 73.92; H, 6.17.

**Preparation of 2-bromo-5-(p-nitrophenyl)thiophene:**

2-Bromo-5-tributylstannyl thiophene:

nButyllithium (30ml of 2.5M in hexanes, 0.06mol) was added dropwise, at -20°C, to diisopropylamine (6.06g, 0.06mol) dissolved in anhydrous THF (50ml). The reaction mixture was then stirred 1h at room temperature. 2-Bromothiophene (9.78g, 0.06mol) dissolved in anhydrous THF (10ml) was added dropwise at -20°C. After 30min at -20°C, tributylstannyl chloride ( 19.53g, 0.06mol) was added, and the reaction mixture was allowed to stand 1h at room temperature. The mixture was poured in water (200ml) and extracted with 3x 50ml ethyl acetate. The combined organic layer were dried and evaporated. The crude product was purified by distillation. Yield: 81%; oil; eb.p.$_{0.08}$: 100°C; $^1$H NMR ($CDCl_3$): $\delta_H$: 0.9(t, 9H, $CH_2\underline{CH_3}$), 1.1(m, 6H, $\underline{CH_2}CH_3$), 1.3(m, 6H, $\underline{CH_2}CH_2CH_3$), 1.5(t, 6H, $Sn\underline{CH_2}CH_2$), 6.9(d, 1H, HAr, J = 3.5 Hz), 7.1(d, 1H, HAr, J = 3.5 Hz).

2-Bromo-5-tributylstannyl thiophene (2.25g, $5.10^{-3}$mol), 4-nitroiodobenzene (1.24g, $5.10^{-3}$mol), tetrakistriphenylphosphine (0.288g, $2.5.10^{-4}$mol) were refluxed 12h in toluene (50ml) under $N_2$ atmosphere. The reaction mixture was poured into a KF saturated solution (50ml) and extracted with 3x 50ml ethyl acetate. The combined organic layer were dried and evaporated. The residue was purified by chromatography on silica gel (petroleum ether). Yield: 31%; m.p. 124-125°C; $^1$H NMR ($CDCl_3$): $\delta_H$: 7.11(d, 1H, HAr, J =4.1 Hz), 7.2(d, 1H, HAr, J = 4.1 Hz), 7.6(d, 2H, HAr, J = 8.9 Hz), 8.2(d, 2H, HAr, J = 8.9 Hz); $^{13}$C NMR ($CDCl_3$): δc: 114.8, 124.45, 125.7, 125.8, 131.5, 139.55, 142.8, 146.75. Anal. calcd for $C_{10}H_6BrNO_2S$: C, 42.27; H, 2.13; N, 4.93. Found: C, 42.38; H, 2.28; N, 5.02.

**Synthesis of thienylarylacetylenes by HECK coupling reaction**

**Sequence 1:**

At room temperature and under $N_2$ atmosphere, palladium acetate (0.031g, 0.14mmol), triphenylphosphine (0.074g, 0.28mmol) and the halothiophene derivative (14mmol) were added to phenylacetylene (1.43g, 14mmol) and piperidine (16.7g, 0.2mol). The reaction mixture was heated 2h at 80°C, allowed to cool at room temperature and poured into 100ml anhydrous ether. The ethereal layer was washed with 3x20ml water, dried and evaporated.

**Sequence 2:**

At room temperature and under $N_2$ atmosphere, tetrakistriphenylphosphine palladium (0.07g, $6.05.10^{-5}$mol), copper iodide (0.015g, $7.8.10^{-5}$ mol), were added to substituted phenyl acetylene (1mmol) and the thienyl derivative (1mmol) in acetonitrile (20ml) and triethylamine (6ml). The reaction mixture was heated at reflux until no starting material appeared in TLC and allowed to cool to room temperature.The solvent was then evaporated and the residue taken with water (100ml) and ethyl acetate. The organic layer was washed with 3x50ml water, dried and evaporated.

**Phenyl-2-thienylacetylene** 7 ( method A): purification by chromatography on silica gel (petroleum ether). yield 72%; m.p. 48°C(litt. (22):48-49°C); $^1$H NMR ($CDCl_3$): $\delta_H$: 7(t, 1H, HAr), 7.3(m. 5H, HAr), 7.4(d, 1H, HAr, J = 3.4 Hz), 7.5(d, 1H, HAr, J = 3.5 Hz); $^{13}$C NMR ($CDCl_3$): δc: 82.6, 93, 122.9, 123.3, 127, 128.4, 129.2, 131.4, 132, 132.5; IR(KBr): 2187; UV-Vis $\lambda_{max}$: 303. Anal. calcd for $C_{12}H_8S$: C, 78.22; H, 4.37. Found: C, 78.29; H, 4.48.

**4-Methoxyphenyl-[2-(5-formylthienyl)]acetylene** 8 (method B): purification by chromatography on silica gel ($CH_2Cl_2$). yield 67%; m.p. 70°C; $^1$H NMR ($CDCl_3$): $\delta_H$: 3.8(s, 3H, $OCH_3$), 6.9(d, 2H, HAr, J = 8.9 Hz), 7.2(d, 1H, HAr, J = 4.2 Hz), 7.4(d, 2H, HAr, J = 8.9 Hz), 7.6(d, 1H, HAr, J = 4.1 Hz), 9.8(s, 1H, CHO); $^{13}$C NMR ($CDCl_3$): δc: 55.3, 81, 98.3, 113.8, 114.2, 132, 133.2, 133.4, 136.2, 143.4, 160.4, 182.4; IR(KBr): 2194, 1658; UV-Vis, $\lambda_{max}$: 357. Anal. calcd for $C_{14}H_{10}O_2S$: C, 69.40; H, 4.16. Found: C, 69.31; H, 4.12.

**4-Nitrophenyl-[2-(5-methylthienyl)]acetylene** 9 (method B): purification by chromatography on silica gel ($CH_2Cl_2$). yield 50%; m.p. 117°C; $^1$H NMR ($CDCl_3$): $\delta_H$: 2.5(s, 3H, $CH_3$), 6.7(d, 1H, HAr, J = 3.6 Hz), 7.1(d, 1H, HAr, J = 3.5 Hz), 7.6(d, 2H, HAr, J = 8.9 Hz), 8.2(d, 2H, HAr, J = 8.9 Hz); $^{13}$C NMR ($CDCl_3$): δc: 15.5, 88.7, 90.7, 119.4, 123.6, 125.7, 130.1, 131.7, 133.6, 144, 146.7; IR(KBr): 2919, 2194, 1337; UV-Vis, $\lambda_{max}$: 364. Anal. calcd for $C_{13}H_9NO_2S$: C, 64.18; H, 3.73; N, 5.76. Found: C, 64.22; H, 3.81; N, 5.77.

**4-Methoxyphenyl-[2-(5-(p-nitrophenyl))thienyl]acetylene** 10 ( method B): purification by chromatography on silica gel ($CH_2Cl_2$). yield 40%; m.p. 115°C; $^1$H NMR ($CDCl_3$): $\delta_H$: 3.8(s, 3H, $OCH_3$), 6.8(d, 2H, HAr, J = 8.9 Hz), 7.2(d, 1H, HAr, J = 3.7 Hz), 7.3(d, 1H, HAr, J =

3.7Hz), 7.5(d, 2H, HAr, J = 8.9 Hz), 7.7(d, 2H, HAr, J = 8.8 Hz), 8.2(d, 2H, HAr, J = 8.8 Hz); $^{13}C$ NMR ($CDCl_3$): δc: 21.8, 31, 55.3, 81, 95.5, 114.1, 114.4, 124.5, 125.6, 125.8, 126, 132.7, 133, 140, 142, 147, 160; IR(KBr): 2197, 1338; UV-Vis, $\lambda_{max}$: 392. Anal. calcd for $C_{19}H_{13}NO_3S$: C, 68.04; H, 3.90; N, 4.18. Found: C, 67.92; H, 3.81; N, 4.17.

**4-Methoxyphenyl-[2-(5-nitrothienyl)]acetylene** 11 ( method B): purification by chromatography on silica gel ($CH_2Cl_2$). yield 55%; m.p. 127°C; $^1H$ NMR ($CDCl_3$): $\delta_H$: 3.8(s, 3H, $OCH_3$), 6.8(d, 2H, HAr, J = 8.7 Hz), 7.1(d, 1H, HAr, J = 4.1 Hz), 7.4(d, 2H, HAr, J = 8.6 Hz), 7.8(d, 1H, HAr, J = 4.2 Hz); $^{13}C$ NMR ($CDCl_3$): δc: 55.3, 80.2, 98.7, 113.2, 114.2, 128.6, 130.2, 131.6, 133.4, 150.2, 160.7; IR(KBr): 2200, 1321; UV-Vis, $\lambda_{max}$: 399. Anal. calcd for $C_{13}H_9NO_3S$: C, 60.22; H, 3.50; N, 5.40. Found: C, 60.17; H, 3.42; N, 5.51.

**4,2-Dimethoxyphenyl-[2-(5-nitrothienyl)]acetylene** 12 ( method B): purification by chromatography on silica gel ($CH_2Cl_2$). yield 45%; m.p. 84°C; $^1H$ NMR ($CDCl_3$): $\delta_H$: 3.85(s, 3H, $OCH_3$), 3.89(s, 3H, $OCH_3$), 6.49(m, 2H, HAr), 7.1(d, 1H, HAr, J = 4.3 Hz), 7.4(d, 1H, HAr, J = 8.4 Hz), 7.8(d, 1H, HAr, J = 4.3 Hz); $^{13}C$ NMR ($CDCl_3$): δc: 55.6, 56.05, 83.95, 95.7, 98.7, 102.95, 105.05, 128.6, 132.05, 132.1, 135.1, 135.2, 161.6, 162.45; IR(KBr): 2318, 1184; UV-Vis, $\lambda_{max}$: 415. Anal. calcd for $C_{14}H_{11}NO_4S$: C, 58.12; H, 3.83; N, 4.84. Found: C, 58.01; H, 3.88; N, 4.71.

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