A Facile and Convenient Synthesis of some Novel Hydrazones, Schiff’s Base and Pyrazoles Incorporating Thieno[2,3-b]thiophenes


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Abstract: A facile and convenient synthesis of some novel hydrazones, schiff’s base and pyrazoles from thieno[2,3-b]thiophene derivatives 1 have been achieved in high yields assisted by microwave and classical methods. The structures of all the title compounds have been elucidated by elemental analysis, IR, MS, $^1$H-NMR and $^{13}$C-NMR. Generally, these findings represent a new class of sulfur and nitrogen moieties that should also be of interest as new materials.

Keywords: bicyclic compounds; hydrazone; thieno[2,3-b]thiophenes; heterocycles; schiff’s base

1. Introduction

obtainable building blocks possessing multiple electrophilic and nucleophilic moieties. We decided to take advantage of our recent results in the synthesis of bis-heterocycles thieno[2,3-\(b\)]thiophenes derivatives \[21,22\], to extend the synthesis of a variety of schiff’s base and hydrazones bis-heterocycles systems for biological and pharmacological evaluation.

2. Results and Discussion

We chose to combine the \(N\)-terminal and central portions of analogues first. Construction of the substituted thienothiophenes \(2a,b\) proceeded from initial condensation of the [2,3-\(b\)]thienothiophene central constraints with hydrazine derivatives. An example of our initial synthetic approach is outlined in Scheme 1.

Scheme 1. Synthesis of hydrazones derivatives \(2a,b\) from thienothiophene 1.

\[
\text{HNMR (DMSO-\(d_6\)) of compound } 2a \text{ revealing two singlet signal at } \delta 2.19 \text{ and } 2.05 \text{ ppm which were readily assigned to the } 12\text{H attached at CH}_3, \text{ and a singlet at } \delta 4.55 (4\text{H, s}) \text{ assigned to the } –\text{NH}_2. \text{ The IR spectra of compound } 2a \text{ indicated a characteristic adsorption band at } 3340–3217 \text{ cm}^{-1} \text{ for the } \text{NH}_2 \text{ group.}
\]

Nevertheless, Phenylhydrazones \(2b\) were then synthesized in almost quantitative yields by the reaction between phenylhydrazine and 1. The structure of phenylhydrazone derivatives was established on the basis of their elemental analysis and spectral data.

Microwave (MW) irradiation has been widely exploited in recent decades to carry out a striking number of organic syntheses, benefiting from dielectric heating in terms of reduced reaction times and increased yields, especially when coupled with solvent-free techniques. One of the most fertile applications in this field, also known as Microwave Assisted Organic Syntheses (MAOS) technique is heterocyclic chemistry, as reported in a recent review \[23\]. In particular, the synthetic pathways of
pyrazole derivatives represent an interesting topic since these compounds have numerous applications in the pharmaceutical and agrochemical industry [24]. Some of the most widespread synthetic strategies to obtain these heterocyclic structures are the reactions between hydrazines with β-difunctional compounds [25] and 1,3-dipolar cycloaddition of diazo compounds onto multiple bonds [26].

Another approach which has been investigated would afford the pyrazole after an elimination/aromatization of the cycloadduct intermediate. On the basis of these studies in the present work, we utilized simple and mild solvent-free microwave mediated methodologies for the synthesis of pyrazoles derivatives from α,β-unsaturated carbonyl compounds. α,β-unsaturated carbonyl compounds 3a–c were obtained starting from thieno[2,3-b] thiophene 1 coupled with corresponding aldehyde under microwave activation in the presence of ZnCl$_2$. Pyrazoles derivatives 4a–f were prepared following the classical procedure (ketone plus hydrazine derivatives in ethanol at reflux in very good yield as depicted in Scheme 2. The novel bis pyrazoles 4a–f were assumed to be formed via a stepwise formation of hydrazone followed by a Michael 1,4-addition of the nucleophile nitrogen atom. We then decided to investigate the generality of this strategy and focused on the preparation of thieno[2,3-b]thiophenes pyrazole derivatives 4a–f.

**Scheme 2.** Synthesis of pyrazole derivatives 4a–f from thienothiophene 1.

The utility of thieno[2,3-b]thiophenes 1 in the synthesis of schiff’s base bis-heterocycles 5a,b was further explored via its reaction with aniline derivatives under microwave activation in the presence of ZnCl$_2$. It is assumed that the product 5a,b was formed via initial formation of nonisolable phenylamino ethanol derivatives followed by elimination of water molecules to give the desired product 5a,b as drawn in Scheme 3. Spectral data (IR, NMR, MS) and elemental analysis was consistent with isolated product 5a,b.
On the other hand, the study was extended to investigate the behavior of thieno[2,3-b]thiophenes derivatives 1 with different N-nucleophile like 1H-benzo[d]imidazol-2-amine and 1H-1,2,4-triazol-5-amine with a view to synthesizing various Schiff’s base bis-heterocycles ring system. Thus, the reaction of 1 with these compounds in refluxing ethanol, in the presence of catalytic amount of ZnCl₂, furnished the corresponding products 6 and 7 in very good to excellent yields Scheme 4.
3. Experimental Section

All melting points were measured on a Gallenkamp melting point apparatus in open glass capillaries and are uncorrected. IR spectra were measured as KBr pellets on a PerkinElmer FT 1000 spectrophotometer. The NMR spectra were recorded on a Varian Mercury Jeol-400 NMR spectrometer. $^1$H-NMR (400 MHz) and $^{13}$C-NMR (100 MHz) were run in deuterated dimethylsulphoxide (DMSO-$d_6$). Chemical shifts ($\delta$) are referred in terms of ppm and $J$ -coupling constants are given in Hz. Abbreviations for multiplicity are as follows: s (singulet), d (doublet), t (triplet), q (quadruplet), m (multiplet). Mass spectra were recorded on a Shimadzu GCMS-QP 1000 EX mass spectrometer at 70 eV (EI). Elemental analysis was carried out on an Elementar Vario EL analyzer.

3.1. General Method for Preparation of Compounds Derivatives 2a,b (GP1)

A mixture of Compound 1 (0.25 g, 1 mmol) with hydrazine derivatives (2 mmol) in absolute ethanol (20 mL, 99.9%) was refluxed for 4 h in the presence of TEA (triethyl amine). The reaction mixture was left to cool to RT. The formed solid product was filtered off and recrystallized from EtOH/DMF to afforded the corresponding hydrazones 2a,b.

(3,4-dimethylthieno[2,3-b]thiophene-2,5-diyl)bis(ethan-1-yl-1-ylidene) bis (hydrazine) (2a). Compound 2a was prepared from hydrazine followed GP1 as yellow light scales crystals; Yield (95%); m.p.: 181 °C; IR (KBr) $\nu$ max 3340–3217 (NH$_2$), 1625 (C=N) cm$^{-1}$; $^1$H-NMR: $\delta$ 2.19, 2.05 (s, 12H, CH$_3$), 4.55 (s, 4H, NH$_2$); $^{13}$C-NMR: $\delta$ 15.0, 16.1, 126.8, 132.6, 140.1, 141.7, 157.5; MS m/z (%): 282 (M$^+$, 46), 280 (M$^+$, 87), 266 (18), 248 (51); Anal. for C$_{12}$H$_{16}$N$_4$S$_2$ (280.41) calcd: C, 51.40; H, 5.75; N, 19.98; S, 22.87. Found: C, 51.10; H, 5.45; N, 19.68; S, 22.57.

(3,4-dimethylthieno[2,3-b]thiophene-2,5-diyl)bis(ethan-1-yl-1-ylidene)bis(1-phenylhydrazine) (2b). Compound 2b was prepared from phenylhydrazine followed GP1 as yellow powder crystals; Yield (75%); m.p.: 194 °C; IR (KBr) $\nu$ max 3202 (NH), 1580 (C=N) cm$^{-1}$; $^1$H-NMR: $\delta$ 2.28, 2.19 (s, 12H, CH$_3$), 6.91–7.35 (m, 10H, ArH’s), 12.2 (br, 2H, NH); $^{13}$C-NMR: $\delta$ 14.8, 17.2, 113.2, 122.4, 123.2, 123.9, 127.2, 135.8, 140.7, 142.5, 157.5; MS m/z (%): 434 (M$^+$, 17), 432 (M$^+$, 35), 418 (56), 404 (25); Anal. for C$_{24}$H$_{24}$N$_4$S$_2$ (432.60) calcd; C, 66.33; H, 5.89; N, 12.65; S, 14.52. Found: C, 66.33; H, 5.89; N, 12.65; S, 14.52.

3.2. General Method for Preparation of Compounds Derivatives 3a–c (GP2)

A mixture of Compound 1 (0.25 g, 1 mmol) and aromatic aldehyde (2 mmol) with the addition of zinc chloride as a catalyst, was exposed to microwave irradiation at for 3–5 min. The formed solid product was filtered off and recrystallized from ethanol afforded the corresponding derivatives 3a–c.

1,1’-(3,4-dimethylthieno[2,3-b]thiophene-2,5-diyldi)bis(3-phenylprop-2-en-1-one) (3a). Compound 3a was prepared from benzaldehyde followed GP2 as dark yellow powder crystals; Yield (75%); m.p.: 210 °C; IR (KBr) $\nu$ max: 1651 (C=O), 1573 (C=C) cm$^{-1}$; $^1$H-NMR: $\delta$ 2.26 (s, 6H, CH$_3$), 8.24 (d, 2H, $J$ = 12.6 Hz, ethylene), 8.81 (d, 2H, $J$ = 12.6 Hz, ethylene), 7.46–7.50 (m, 12H, ArH’s); $^{13}$C-NMR: $\delta$ 15.6, 113.3, 145.0, 126.2, 129.8, 129.9, 133.7, 138.6, 141.5, 147.7, 148.2, 186.6; MS m/z (%): 428
1,1'-(3,4-dimethylthieno[2,3-b]thiophene-2,5-diyi)bis(3-(4-chlorophenyl)prop-2-en-1-one) (3b).

Compound 3b was prepared from p-chlorobenzaldehyde followed GP2 as greenish yellow cubes crystals; Yield (88%); m.p.: 265 °C; IR (KBr) ν max: 1721 (C=O), 1580 (C=C) cm\(^{-1}\); \(^1\)H-NMR: δ 2.33 (s, 6H, CH\(_3\)), 7.70 (d, 2H, \(J = 12.4\) Hz, ethylene), 8.47 (d, 2H, \(J = 12.6\) Hz, ethylene), 7.93 (d, 2H, \(J = 8.8\) Hz, ArH’s); \(^13\)C-NMR: δ 14.8, 112.6, 145.4, 125.8, 129.2, 131.1, 134.8, 137.1, 142.3, 148.3, 185.8; MS m/z (%): 498 (M\(^+\), 14), 496 (M\(^+\), 26), 495 (58), 426 (8); Anal. for C\(_{26}\)H\(_{20}\)O\(_2\)S\(_2\) (428.57) calcd; C, 72.87; H, 4.70; O, 7.47; S, 14.96. Found: C, 72.57; H, 4.40; O, 7.77; S, 14.66.

1,1'-(3,4-dimethylthieno[2,3-b]thiophene-2,5-diyi)bis(3-(4-methoxyphenyl)prop-2-en-1-one) (3c).

Compound 3c was prepared from p-methoxybenzaldehyde followed GP2 as willowish white needles crystals; Yield (65%); m.p.: 239 °C; IR (KBr) ν max: 1732 (C=O), 1596 (C=C) cm\(^{-1}\); \(^1\)H-NMR: δ 2.29 (s, 6H, CH\(_3\)), 3.49 (s, 6H, OCH\(_3\)), 8.16 (d, 2H, \(J = 12.2\) Hz, ethylene), 8.80 (d, 2H, \(J = 12.8\) Hz, ethylene), 7.55 (d, 2H, \(J = 8.8\) Hz, ArH’s), 7.97 (d, 2H, \(J = 8.8\) Hz, ArH’s); \(^13\)C-NMR: δ 16.2, 113.9, 145.6, 126.5, 128.8, 128.9, 136.0, 138.7, 140.7, 147.1, 147.8, 186.1; MS m/z (%): 488 (M\(^+\), 37), 487 (M\(^+\), 18), 474 (7), 457 (86); Anal. for C\(_{28}\)H\(_{24}\)O\(_4\)S\(_2\) (488.62) calcd; C, 68.83; H, 4.95; S, 13.12 Found: C, 68.83; H, 4.65; S, 13.42.

3.3. General Method for Preparation of Compounds Derivatives 4a–f (GP3).

To a mixture of 1,1'-(3,4-dimethylthieno[2,3-b]thiophene-2,5-diyi)bis(3-arylprop-2-en-1-one) derivatives (3a–c) (1 mmol) with hydrazine or phenylhydrazine (2 mmol) in mixture absolute ethanol (20 mL, 99.9%) and DMF (2–3 mL) was refluxed for 4–6 h. the reaction mixture was left to cool to RT. The formed solid product was filtered off and recrystallized from EtOH/DMF to afford the corresponding derivatives 4a–f.

3,3'-(3,4-dimethylthieno[2,3-b]thiophene-2,5-diyi)bis(5-phenyl-4,5-dihydro-1H-pyrazole) (4a).

Compound 4a was prepared according to GP3 as yellow needles crystals; Yield (74%); m.p.: 270 °C; IR (KBr) v max: 3250 (NH), 1624 (C=N) cm\(^{-1}\); \(^1\)H-NMR: δ 2.30 (s, 6H, CH\(_3\)), 3.04 (dd, 4H, \(J = 10.5\) Hz, \(J = 14.6\) Hz, Methylene), 3.77 (dd, 4H, \(J = 10.5\) Hz, \(J = 16.4\) Hz, Methylene), 4.85 (dd, 4H, \(J = 10.2\) Hz, \(J = 16.6\) Hz, Methine), 7.27–7.39 (m, 12H, ArH’s), 8.84 (br, 2H, NH); \(^13\)C-NMR: δ 14.8, 51.3, 64.0, 121.9, 125.8, 126.0, 127.3, 138.4, 141.5, 147.8, 148.4, 162.0; MS m/z (%): 456 (M\(^+\), 6), 454 (M\(^+\), 11), 441 (22), 240 (31); Anal. for C\(_{26}\)H\(_{24}\)N\(_4\)S\(_2\) (456.63) calcd; C, 68.39; H, 5.30; N, 12.27; S, 14.04 Found: C, 68.09; H, 5.60; N, 11.97; S, 13.74.

3,3'-(3,4-dimethylthieno[2,3-b]thiophene-2,5-diyi)bis(1,5-diphenyl-4,5-dihydro-1H-pyrazole) (4b).

Compound 4b was prepared according to GP3 as light brown powder; Yield (65%); m.p.: 300 °C; IR (KBr) v max: 1585 (C=N) cm\(^{-1}\); \(^1\)H-NMR: δ 2.32 (s, 6H, CH\(_3\)), 3.13 (dd, 4H, \(J = 10.6\) Hz, \(J = 14.1\) Hz, Methylene), 3.76 (dd, 4H, \(J = 10.2\) Hz, \(J = 16.1\) Hz, Methylene), 4.88 (dd, 4H, \(J = 10.6\) Hz, \(J = 16.2\) Hz, Methine), 7.22–7.50 (m, 24H, ArH’s); \(^13\)C-NMR: δ 14.8, 51.6, 65.2, 121.8, 122.2, 124.7, 125.8, 126.8, 128.2, 129.3, 131.8, 137.3, 140.5, 142.2, 144.7, 161.2; MS m/z (%): 608 (M\(^+\), 17), 606...
3,3’-(3,4-dimethylthieno[2,3-b]thiophene-2,5-diyl)bis(5-(4-chlorophenyl)-4,5-dihydro-1H-pyrazole) (4c). Compound 4c was prepared according to GP3 as yellowish white powder; Yield (75%); m.p.: 320 °C; IR (KBr) νmax: 3298 (NH), 1620 (C=N) cm⁻¹; ¹H-NMR: δ 2.35 (s, 6H, CH₃), 3.04 (dd, 4H, J = 10.6 Hz, J = 14.1 Hz, Methylene), 3.77 (dd, 4H, J = 10.2 Hz, J = 16.1 Hz, Methylene), 4.81 (dd, 4H, J = 10.66 Hz, J = 16.22 Hz, Methine), 7.90 (d, 2H, J = 8.8 Hz, ArH’s), 8.30 (d, 2H, J = 8.8 Hz, ArH’s), 8.87 (br, 2H, NH); ¹³C-NMR: δ 15.4, 52.2, 64.3, 126.6 128.7, 131.1, 132.4, 136.6, 142.0, 142.9, 146.6, 158.8; MS m/z (%): 526 (M⁺, 61), 524 (M⁺, 82), 522 (17), 509(26); Anal. for C₂₆H₂₂Cl₂N₄S₂ (525.52) calcd; C, 59.42; H, 4.22; Cl, 13.49; N, 10.66; S, 12.20. Found: C, 59.12; H, 4.52; Cl, 13.19; N, 10.36; S, 12.50.

3,3’-(3,4-dimethylthieno[2,3-b]thiophene-2,5-diyl)bis(5-(4-chlorophenyl)-1-phenyl-4,5-dihydro-1H-pyrazole) (4d). Compound 4d was prepared according to GP3 as brown cubes Crystals; Yield (67%); m.p.: 320 °C; IR (KBr) νmax: 1584 (C=N) cm⁻¹; ¹H-NMR: δ 2.31 (s, 6H, CH₃), 3.23 (dd, 4H, J = 10.6 Hz, J = 14.1 Hz, Methylene), 3.79 (dd, 4H, J = 10.2 Hz, J = 16.1 Hz, Methylene), 4.83 (dd, 4H, J = 10.5 Hz, J = 16.2 Hz, Methine), 7.24–7.29 (m, 10H, phenyl), 7.92 (d, 2H, J = 8.8 Hz, ArH’s), 8.00 (d, 2H, J = 8.8 Hz, ArH’s); ¹³C-NMR: δ 15.6, 50.8, 63.8, 120.3, 122.6, 124.8, 125.4, 125.9, 127.1, 130.6, 133.5, 135.6, 143.3, 143.9, 145.2, 158.8; MS m/z (%): 678 (M⁺, 13), 676 (M⁺, 78), 661 (9), 641 (84); Anal. for C₃₈H₃₂Cl₂N₄S₂ (777.71) calcd; C, 67.35; H, 4.46; Cl, 10.46; N, 8.27; S, 9.46. Found: C, 67.05; H, 4.16; Cl, 10.16; N, 8.57; S, 9.16.

3,3’-(3,4-dimethylthieno[2,3-b]thiophene-2,5-diyl)bis(5-(4-methoxyphenyl)-4,5-dihydro-1H-pyrazole)(4e). Compound 4e was prepared according to GP3 as yellow powder crystals; Yield (77%); m.p.: 295 °C; IR (KBr) νmax: 3272 (NH), 1582 (C=N) cm⁻¹; ¹H-NMR: δ 2.34 (s, 6H, CH₃), 3.48 (s, 6H, Methoxy), 3.75 (dd, 4H, J = 10.6 Hz, J = 14.1 Hz, Methylene), 3.80 (dd, 4H, J = 10.5 Hz, J = 16.4 Hz, Methine), 4.85 (dd, 4H, J = 10.5 Hz, J = 16.2 Hz, Methine), 7.56 (d, 2H, J = 8.8 Hz, ArH’s), 7.95 (d, 2H, J = 8.8 Hz, ArH’s), 8.90 (br, 2H, NH); ¹³C-NMR: δ 14.7, 41.6, 53.1, 65.6, 126.1, 127.9, 131.4, 134.2, 134.5, 146.0, 148.2, 148.6, 161.9; MS m/z (%): 516 (M⁺, 88), 514 (M⁺, 56), 501 (62), 485 (9); Anal. for C₂₈H₂₀N₂O₅S₂ (516.68) calcd; C, 65.09; H, 5.46; N, 10.84; S, 12.41. Found: C, 64.79; H, 5.16; N, 10.54; S, 12.11.

3,3’-(3,4-dimethylthieno[2,3-b]thiophene-2,5-diyl)bis(5-(4-methoxyphenyl)-1-phenyl-4,5-dihydro-1H-pyrazole)(4f). Compound 4f was prepared according to GP3 as dark yellow powder crystals; Yield (85%); m.p.: 300 °C; IR (KBr) νmax: 1622 (C=N) cm⁻¹; ¹H-NMR: δ 2.28 (s, 6H, CH₃), 3.47(s, 6H, Methoxy), 3.02 (dd, 4H, J = 10.6 Hz, J = 14.6 Hz, Methylene), 3.76 (dd, 4H, J = 10.5 Hz, J = 16.4 Hz, Methylene), 4.87 (dd, 4H, J = 10.5 Hz, J = 16.2 Hz, Methine), 7.22–7.28 (m, 10H, phenyl), 7.58 (d, 2H, J = 8.8 Hz, ArH’s), 7.96 (d, 2H, J = 8.8 Hz, ArH’s); ¹³C-NMR: δ 14.6, 42.6, 55.1, 66.0, 119.86, 122.74, 124.3, 126.1, 126.2, 128.1, 131.1, 133.6, 135.9, 145.7, 147.2, 148.4, 162.3; MS m/z (%):668 (M⁺, 88), 666 (M⁺, 16), 653 (38), 638 (58); Anal. for C₄₀H₃₆N₂O₅S₂ (516.68) calcd; C, 71.83; H, 5.42; N, 8.38; S, 9.59. Found: C, 71.53; H, 5.22; N, 8.08; S, 9.89.
3.4. General Method for Preparation of Compounds Derivatives 5a,b (GP4)

A mixture of Compound 1 (0.25 g, 1 mmol) with aniline derivatives (2 mmol) with the addition of zinc chloride as a catalyst, was exposed to microwave irradiation at for 5–6 min. The formed solid product was filtered off and recrystallized from ethanol afforded the corresponding derivatives 3a–c.

(3,4-dimethylthieno[2,3-b]thiophene-2,5-diyl)bis(ethan-1-yl-1-ylidene) aniline derivatives (5a). Compound 5a was prepared from aniline followed GP4 as white scales crystals; Yield (75%); m.p.: 260 °C; IR (KBr) νmax: 1600 (C=N) cm⁻¹; ¹H-NMR: δ 2.33, 2.05 (s, 12H, CH₃), 6.48–6.99 (m, 10H, aromatic); ¹³C-NMR: δ 15.6, 24.07, 122.0, 126.0, 126.9, 127.6, 138.5, 141.8, 148.0, 148.3, 166.0; MS m/z (%): 402 (M⁺, 98), 400 (M⁺, 42), 387 (76), 248 (58); Anal. for C₂₄H₂₂N₂S₂ (402.57) calcd; C, 71.60; H, 5.51; N, 6.96; S, 15.93. Found: C, 71.30; H, 5.21; N, 6.66; S, 15.63.

(3,4-dimethylthieno[2,3-b]thiophene-2,5-diyl)bis(ethan-1-yl-1-ylidene)bis(4-chloroaniline)(5b). Compound 5b was prepared from p-chloroaniline followed GP4 as yellowish white powder Crystals; Yield (66%); m.p.: 230 °C; IR (KBr) νmax: 1575 (C=N) cm⁻¹; ¹H-NMR: δ 2.25, 2.12 (s, 12H, CH₃), 6.50 (d, J = 7.2 Hz, 2H, ArH’s), 6.72 (d, J =7.2 Hz, 2H, ArH’s); ¹³C-NMR: δ 14.8, 23.8, 125.3, 127.4, 128.2, 131.1, 137.2, 139.1, 146.4, 147.8, 164.5; MS m/z (%): 472 (M⁺, 56), 470 (M⁺, 48), 468 (9), 435 (18); Anal. for C₂₄H₂₀Cl₂N₂S₂ (471.46) calcd; C, 61.14; H, 4.28; Cl, 15.04; N, 5.94; S, 13.60. Found: C, 61.44; H, 3.98; Cl, 14.74; N, 5.64; S, 13.30.

(3,4-dimethylthieno[2,3-b]thiophene-2,5-diyl)bis(ethan-1-yl-1-ylidene)bis(1H-1,2,4-triazol-5-amine) (6). A mixture of Compound 1 (0.25 g, 1 mmol) with amino triazole (0.16 mL, 2 mmol) in absolute ethanol (20 mL, 99.9%) with addition a little of DMF (2 mL) was refluxed for 7–8 h. then left to cool. The formed solid product was filtered off and recrystallized from EtOH/DMF to afforded the corresponding compound 6 as dark yellow powder Crystals; Yield (78%); m.p.: 256 °C; IR (KBr) νmax 3332 (NH), 1620 (C=N) cm⁻¹; ¹H-NMR: δ 2.10, 2.64 (s, 12H, CH₃), 7.86 (s, 2H, triazole), 13.02 (s, 2H, NH); ¹³C-NMR: δ 14.2, 20.2, 145.0, 155.2, 135.9, 141.5, 147.8, 148.2, 162.3; MS m/z (%): 384 (M⁺, 83), 382 (M⁺, 15), 369 (26), 275 (46); Anal. for C₁₆H₁₆N₈S₂ (384.48) calcd; C, 49.98; H, 4.19; N, 29.14; S, 16.68 Found: C, 49.68; H, 4.49; N, 28.84; S, 16.38.

(3,4-dimethylthieno[2,3-b]thiophene-2,5-diyl)bis(ethan-1-yl-1-ylidene)bis(1H-benzo[d]imidazol-2-amine) (7). A mixture of Compound 1 (0.25 g, 1 mmol) with amino benzoimidazol (0.26 mL, 2 mmol) in absolute ethanol (20 mL, 99.9%) with addition a little of DMF (2 mL) was refluxed for 7–8 h. then left to cool. The formed solid product was filtered off and recrystallized from EtOH/DMF to afforded the corresponding compound 7 as greenish yellow powder Crystals; Yield (92%); m.p.: 320 °C; IR (KBr) νmax 3332 (NH), 1620 (C=N) cm⁻¹; ¹H-NMR: δ 1.23, 2.82 (s, 12H, CH₃), 7.15–7.35 (m, 8H, Benzoimidazol), 7.74 (s, 2H, NH); ¹³C-NMR: δ 14.9, 19.0, 102.3, 120.5, 123.1, 126.9, 128.9, 134.1, 135.9, 144.5, 148.2, 160.0; MS m/z (%): 482 (M⁺, 42), 480 (M⁺, 78), 467 (100), 451 (24); Anal. for C₂₆H₂₂N₈S₂ (384.48) calcd; C, 64.70; H, 4.59; N, 17.41; S, 13.29 Found C, 64.40; H, 4.29; N, 17.11; S, 13.59.
4. Conclusions

In summary, we have successfully prepared various polylsubstituted thieno[2,3-b]thiophenes based on the reaction of carbonyl compounds with appropriate N-nucleophile assisted by microwave or classical methods. The simple procedure, mild conditions, high yields and especially environmental friendliness make this protocol very attractive, and may possess interesting biological properties or applications in material sciences.

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