合成新穎之取代基4-芳基-3-氰基-2-胺基-噻吩衍生物

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摘　要

本研究以具取代基之芳基甲基酮化合物 **1a-f** 與丙二腈 2 進行克諾芬納吉耳縮合反應(Knoevenagel condensation)得到含有甲基之巴豆腈衍生物 **3a-f**。將含有甲基之巴豆腈衍生物 **3a-f** 在四氯化碳溶劑下與溴進行反應可得溴化巴豆腈衍生物 **4a-f**。最後，將合成之溴化巴豆腈衍生物 **4a-f** 與硫氫化鈉進行環化縮合反應得到目標化合物取代基 4-芳基-3-氰基-2-胺基-噻吩新衍生物 **7a-f**。

關鍵詞：胺基-噻吩，溴化巴豆腈，克諾芬納吉耳縮合反應，取代基胺基-噻吩

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SYNTHESIS OF SOME NOVEL SUBSTITUTED 4-ARYL-3-CYANO-2- AMINO-THIOPHENE DERIVATIVES

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Abstract

Knoevenagel condensation of aryl methyl ketones 1a-f with malononitrile 2 gave the corresponding crotonitriles **3a-f.** Methyl groups of the crotonitriles 3a-f were then efficiently brominated by refluxing and lightening the reaction media to give bromocrotonitriles **4a-f.** On the other hand, the 4-substituted-2-amino-3-cyano-thiophene derivatives **7a-f** were obtained by the cyclocondensation reaction bromocrotonitriles **4a-f** with NaSH.

Key Word: Aminothiophenes, bromocrotonitriles, Knoevenagel condensation, substituted aminothiophenes.

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1. INTRODUCTION

Sulphur containing heterocycles paved way for the active research in the pharmaceutical Chemistry. Nowadays thiophene derivatives in combination with other ring systems have been used extensively in pharmaceutical applications such as antiallergic, analgesic, anti-inflammatory and ocular hypotensive activities [1-4]. Thiophene derivatives have also been reported to possess broad spectrum of biological properties including anti-inflammatory, analgesic, antidepressant, antimicrobial and anticonvulsant activities [5-8]. They are often used as novel conducting polymers [9] and as isosteric replacements for phenyl groups in medicinal chemistry [10]. The electronic and optical properties of polythiophene and its derivatives have been the subject of many papers [11-13]. On the other hand, some azo thiophene derivatives obtained from the coupling moieties of 2-aminothiophenes and 2-aminothiazoles were distinguished by their high colour strength and brilliant shades [14-17]. In this report, we describe the synthesis of a series of highly functionalized 3,4-disubstituted-2-aminothiophenes derivatives by a stepwise Gewald reaction.

2. RESULTS AND DISCUSSION

The synthetic route used is shown in Scheme 1. The required compounds crotonitriles **3a-f** were prepared by the condensation of acetophenone derivatives **1a-f** with malononitrile **2** and ammonium acetate [18]. Allylic bromination of crotonitriles was reported to result in low yields [19]. Crotonitriles may be efficiently brominated in allylic position by treatment with potassium tert-butoxide and then molecular Br_2. However, when the crotonitriles **3a-f** were subjected to bromination under a project lamp (500 W mercury) at reflux temperature bromocrotonitrile derivatives **4a-f** were obtained in high yields (80-88%) (Scheme 1). The bromocrotonitrile derivatives **4a-f** were used as a key intermediate for the synthesis of novel aminothiophene derivatives **7a-f**. The structures of bromocrotonitriles **4a-f** were established on the basis of their elemental analysis and spectral data. The IR spectral of bromocrotonitriles **4a-f** showed the characteristic absorption bands at 2221-2236 cm^{-1} for the C≡N group. The ^1H NMR spectra ($CDCl_3$) of bromocrotonitriles **4a-f** showed a singlet at δ 4.53-4.71 (2H, s) assigned to the CH_2Br protons. On the other hand, cyclocondensation of

bromocrotonitriles **4a-f** with anhydrous NaHS in ethanol to afford the corresponding 4-substituted-2-amino-3-cyano-thiophenes **7a-f** (Scheme 1). The structures of compounds **7a-f** were established on the basis of their elemental analysis and spectral data. The IR spectra of compounds **7a-f** showed the characteristic absorption bands at 3306-3449 and 3202-3326 cm^{-1} for the NH_2 group and at 2201-2221 cm^{-1} for the C≡N. Moreover, in the ^1H NMR spectra of compounds **7a-f**, the characteristic downfield signal at δ 4.53-4.71 (2H, s) attributed to the CH_2Br protons in compound **4a-f** are absent, and revealed a singlet at δ 6.23-6.55 (1H, s), which were assigned to the 5-H of the thiophene moiety. On the other hand, the ^1H NMR spectra of compounds **7a-f** also revealed a singlet at δ 4.86-5.24 (2H, bs), which were assigned to NH_2 group, was also confirmed by the mass spectra.

It is noteworthy that all the bromocrotonitriles **4a-f** were completely cyclised to aminothiophene in high yields ranging from 74% to 85%. Importantly, HS− reacts with bromocrotonitriles **4a-f** to afford unstable intermediates **5a-f,** and then **6a-f,** which are converted to compounds **7a-f** under the experimental conditions (Scheme 1). In conclusion, the present work provides a facile synthesis of substituted- 2-aminothiophenes via a stepwise Gewald reaction.

3. EXPERIMENTAL SECTION

3.1 General.

All melting points are uncorrected and in ℃. IR spectra were recorded on a JASCO FTIR-3 spectrometer (KBr); ^1H and ^{13}C NMR spectra were obtained on a Bruker AM-300 WB FI-NMR spectrometer, and chemical shifts are expressed in δ ppm using TMS as an internal standard. Electron impact mass spectra were obtained at 70 eV using a Finingan Mat TSQ-46C spectrometer. Microanalyses for C, H, and N were performed on a Perkin-Elmer 240 elemental Analyzer. Column chromatography was performed on silica gel (60-200 mesh) and activated alumina (70-230 mesh) from Merck Co. TLC was carried out on Merck 0.2 mm silica gel 60 F254 analytical aluminium plates.

3.2 The preparation n of crotonitriles 3a-f; typical procedure

To a stirred solution of acetophenone (**1a**) (5.8 g, 0.048 mol) in 50 ml of dry and freshly distilled benzene were added ammonium acetate (6.96 g, 0.090 mol) and malononitrile **2** (3.2 g, 0.048 mol). The reaction mixture was refluxed for 6 h (**1b**, **1c, 1e** and **1f**: 12 h, **1d:** 8 h), and then cooled to room temperature. After the solvent was removed, the residue was diluted with water. The organic phase was extracted with ether (3 x 50 ml). The combined solutions were washed with water (2 x 10 ml) and dried over $MgSO_4$. After removal of the solvent, the residue was recrystallised from $CHCl_3$ to give 2-(1-Phenyl-ethylidene)-malononitrile (**3a**) (6.4 g, 79%).

3.2.1 2-(1-Phenyl-ethylidene)-malononitrile (3a): (79%; from $CHCl_3$/Hexane, colourless crystals, mp 92 ℃). ^{13}C NMR ($CDCl_3$): 177.39, 137.94, 134.25, 131.12, 129.34, 114.77, 114.71, 86.80, 26.27. IR (KBr): 3052, 3019, 2225, 1578, 1503, 1429, 1369, 1258, 1187, 1025 cm^{-1}. EIMS *m*=*z* (%): 168 (M^+, 100), 203(44), 190(72), 176(31), 152(20), 128(30). Anal. calc. For $C_{11}H_8N_2$: C, 78.57; H, 4.76; N, 16.66. Found C, 78.99; H, 4.65; N, 16.64.

3.2.2 2-(1-Naphthalen-1-yl-ethylidene)-malononitrile (3b): (82%; from $CHCl_3$/Hexane, colourless crystals, mp 72-73 ℃). ^1H NMR ($CDCl_3$): 7.95 (m, 2H, ArH), 7.42-7.35 (m, 5H, ArH), 2.74 (s, 3H, CH_3) ^{13}C NMR ($CDCl_3$): 179.97, 136.56, 135.74, 133.18, 131.11, 130.74, 129.69, 128.96, 127.13, 126.71, 125.79, 114.03, 113.71, 91.10, 27.87. IR (KBr): 3062, 3021, 2235, 1588, 1513, 1429, 1371, 1260, 1177, 1025 cm^{-1}. EIMS *m*=*z* (%): 218 (M^+, 100), 203(64), 190(82), 176(21), 152(20), 128(19). Anal. calc. For $C_{15}H_{10}N_2$: C, 82.55; H, 4.62; N, 12.84. Found C, 82.67; H, 4.65; N, 12.64.

3.2.3 2-(1-Naphthalen-2-yl-ethylidene)-malononitrile (3c): (85%; yellow crystals, mp 106-107 ℃). ^1H NMR ($CDCl_3$): 8.09 (bs, 1H, ArH), 7.98-7.55 (m, 6H, ArH), 2.74 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): 177.21, 136.74, 135.19, 134.50, 131.06, 130.66, 130.35, 129.86, 129.45, 129.25, 125.44, 115.01, 114.89, 86.68, 26.29. IR (KBr): 3050, 2225, 1630, 1562, 1500, 1465, 1373, 1288, 1176, 1014 cm^{-1}. EIMS *m*=*z* (%):218 (M^+, 100), 203(10), 190(40), 153(12), 128(20). Anal. calc. For $C_{15}H_{10}N_2$: C, 82.55; H, 4.62; N, 12.84. Found C, 82.43; H, 4.68; N, 13.03.

3.2.4 2-[1-(4-Methoxy-phenyl)-ethylidene]-malononitrile (3d): (82%; from $CHCl_3$/Hexane, colourless crystals mp 76-77 ℃), ^1H NMR ($CDCl_3$): 7.62 (d, A part of AB system, J = 9.0 Hz, 2H, ArH), 6.99 (d, B part of AB system, J = 9.0 Hz, 2H, ArH),

3.87 (s, 3H, OCH_3), 2.61 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): 175.88, 165.12, 131.79, 129.92, 116.48, 115.62, 115.36, 84.03, 57.58, 25.78. IR (KBr): 3025, 2844, 2221, 1601, 1547, 1431, 1266, 1189, 1023, 842 cm^{-1}. EIMS *m*=*z* (%): 197 (M^+, 100), 183(10), 155(18), 128(30). Anal. calc. For $C_{12}H_{10}ON_2$: C, 73.09; H, 5.07; N, 14.21. Found C, 73.19; H, 4.95; N, 14.34.

3.2.5 2-(1-Biphenyl-4-yl-ethylidene)-malononitrile (3e): (70%; from $CHCl_3$/Hexane, light yellow crystals, mp 160-161 ℃). ^1H NMR ($CDCl_3$): 7.76−7.63 (m, 5H, ArH), 7.61-7.41 (m, 4H ArH), 2.68 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): 176.62, 147.29, 141.31, 136.53, 131.08, 130.52, 130.10, 129.65, 129.19, 115.06, 114.92, 85.90, 26.10. IR (KBr): 3068, 2970, 2220, 1574, 1485, 1412, 1374, 1312, 1197, 1131, 1081, 1004, 965 cm^{-1}. EIMS *m*=*z* (%): 244 (M^+, 100), 229(32), 189(10), 179(12), 152(20). Anal. calc. For $C_{17}H_{12}N_2$: C, 83.60; H, 4.91; N, 11.47. Found C, 83.71; H, 4.95; N, 11.34.

3.2.6 2-(1-Phenanthren-3-yl-ethylidene)-malononitrile (3f): (78%; from $CHCl_3$/Hexane, yellow crystals mp 164-165 ℃). ^1H NMR ($CDCl_3$): 8.97 (s, 1H, ArH), 8.69 (d, J = 7.9 Hz, 1H, ArH), 7.97-7.67 (m, 7H, ArH), 2.79 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): 177.19, 136.29, 135.47, 134.33, 132.10, 132.04, 131.96, 131.47, 130.97, 129.60, 129.62, 128.03, 126.58, 124.89, 124.57, 115.29, 115.01, 86.54, 26.37. IR (KBr): 3056, 2952, 2228, 1566, 1428, 1285, 1239, 1181, 1150, 1035, 965 cm^{-1}. EIMS *m*=*z* (%): 268 (M^+, 100), 253(54), 240(40), 202(20), 178(18), 120(14), 106(30). Anal. calc. For $C_{19}H_{12}N_2$: C, 85.05; H, 4.51; N, 10.44. Found C, 84.97; H, 4.63; N, 10.58

3.3 The preparation of bromocrotonitriles 4a-f; typical procedure

To a stirred solution of crotonitriles **3a** (1.1 g, 6.55 mmol) in 25 ml of CCl_4 was added dropwise a solution of bromine (0.53 g, 3.313 mmol) in 5 ml of CCl_4 at room temperature over 20 min. The reaction flask was irradiated with a 500-W sunlamp for 2 h (**3e** and **3f**: 2 h; **3b**: 6 h; **3c** and **3d**: 4 h). After evaporation of the solvent, the residue was filtered over silica gel (10 g) after eluting with hexane/chloroform (9:1). Removal of the solvent and recrystallisation from hexane/chloroform (4:1) gave **4a** (1.41 g, 88%).

3.3.1 2-(2-Bromo-1-phenyl-ethylidene)-malononitrile (4a): (88%; colourless crystals, mp 111-112 ℃). ^1H NMR ($CDCl_3$): 7.65-7.50 (m, 5H, ArH), 4.56 (s, 2H, CH_2Br). ^{13}C NMR ($CDCl_3$): 173.45, 134.90, 131.39, 130.95, 129.86, 113.56, 112.79,

88.65, 30.73. IR (KBr): 3039, 2981, 2233, 1585, 1573, 1488, 1438, 1315, 1284, 1207, 1195, 1083, 998 cm^{-1}. EIMS *m*=*z* (%): 246/248 (M^+, 14), 166/168(42), 140/142(100). Anal. calc. For $C_{11}H_8BrN_2$: C, 53.65; H, 3.25; N, 11.38. Found C, 53.74; H, 3.35; N, 11.64.

3.3.2 2-(2-Bromo-1-napthalen-1-yl-ethylidene)-malononitrile (4b): (85%; from $CHCl_3$/Hexane, yellow crystals, mp 103-104 ℃). ^1H NMR ($CDCl_3$): 8.05-8.02 (m, 2H, ArH), 7.99-7.48 (m, 5H, ArH), 4.86 (s, 2H, CH_2Br). ^{13}C NMR ($CDCl_3$): 174.73, 135.69, 134.02, 132.68, 131.26, 129.99, 129.09, 128.98, 128.88, 125.55, 113.18, 112.89, 93.25, 31.87. IR (KBr): 3056, 2968, 2236, 1582, 1516, 1447, 1335, 1258, 1220, 1170, 1023, 912 cm^{-1}. EIMS *m*=*z* (%): 296/298 (M^+, 24), 216/218(66), 188/190(100). Anal. calc. For $C_{15}H_9BrN_2$: C, 60.63; H, 3.05; N, 9.43. Found C, 60.54; H, 3.12; N, 9.37

3.3.3 2-(2-Bromo-1-napthalen-2-yl-ethylidene)-malononitrile (4c): (82%; from $CHCl_3$, light yellow crystals, mp 152-153 ℃). ^1H NMR ($CDCl_3$): 8.18 (m, 1H, ArH), 8.01-7.90 (m, 3H, ArH), 7.69-7.61 (m, 3H, ArH), 4.62 (s, 2H, CH_2Br). ^{13}C NMR ($CDCl_3$): 172.61, 136.99, 134.52, 132.19, 131.48, 131.32, 131.23, 131.02, 129.96, 129.83, 125.39, 114.23, 113.54, 88.77, 30.57. IR (KBr): 3031, 2981, 2233, 1627, 1585, 1500, 1438, 1365, 1211, 1168, 1126 cm^{-1}. EIMS *m*=*z* (%): 296/298 (M^+, 60), 216/218(64), 188/190(100). Anal. calc. For $C_{15}H_9BrN_2$: C, 60.63; H, 3.05; N, 9.43. Found C, 60.81; H, 3.02; N, 9.30

3.3.4 2-[2-Bromo-1-(4-methoxy-phenyl)-ethylidene]-malononitrile (4d): (87%; from $CHCl_3$/Hexane, colourless crystals, mp 104-105 ℃). ^1H NMR ($CDCl_3$): 7.39 (d, A part of AB system J = 9.0 Hz, 2H, ArH), 7.02 (d, B part of AB system J = 9.0 Hz, 2H, ArH), 4.53 (s, 2H, CH_2Br), 3.88 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$): 172.16, 165.74, 132.41, 126.91, 116.90, 115.24, 114.35, 85.57, 57.45, 30.69. IR (KBr): 3056, 2968, 2844, 2236, 1605, 1516, 1451, 1312, 1266, 1181, 1023, 958 cm^{-1}. EIMS *m*=*z* (%): 276/278 (M^+, 64), 196/198(58), 180/182(100). Anal. calc. For $C_{12}H_9OBrN_2$: C, 52.17; H, 3.26; N, 10.14. Found C, 52.22; H, 3.33; N, 10.34.

3.3.5 2-(1-Biphenyl-4-yl-2-bromo-ethylidene)-malononitrile (4e): (83%; from $CHCl_3$, light yellow crystals, mp 163-164 ℃). ^1H NMR ($CDCl_3$): 7.75-7.62 (m, 5H, ArH), 7.53-7.43 (m, 4H, ArH), 4.60 (s, 2H, CH_2Br). ^{13}C NMR ($CDCl_3$): 172.75, 147.98, 141.09, 133.56, 131.15, 130.73, 130.61, 129.93, 129.25, 114.75, 113.81, 88.05, 30.61. IR (KBr): 3037, 2979, 2875, 2228, 1582s, 1485, 1447, 1324, 1216, 1189, 1079, 946

cm^{-1}. EIMS *m*=*z*(%): 322/324 (M^+, 32), 242/244(68), 214/216(100). Anal. calc. For $C_{17}H_{11}BrN_2$: C, 63.18; H, 3.43; N, 8.67. Found C, 63.21; H, 3.55; N, 8.80.

3.3.6 2-(2-Bromo-1-phenanthren-3-yl-ethylidene)-malononitrile (4f): (80% ; from $CHCl_3$/Hexane, light red crystals, mp 164-165 ℃). ^1H NMR ($CDCl_3$): 9.07 (d, J = 1.8 Hz, 1H, ArH), 8.68 (d, J = 7.8 Hz, 1H, ArH), 8.01 (d, J = 8.4 Hz, 1H, ArH), 7.94 (d, J = 7.4 Hz, 1H, ArH), 7.89 (d, J = 8.9 Hz, 1H, ArH), 7.79-7.64 (m, 4H, ArH), 4.71 (s, 2H, CH_2Br). ^{13}C NMR ($CDCl_3$): 173.23, 136.74, 134.38, 132.59, 132.52, 132.03, 131.79, 131.02, 131.00, 129.82, 129.79, 128.01, 129.59, 125.76, 124.62, 113.86, 104.05, 88.32, 30.76. IR (KBr): 3048, 2991, 2883, 2221, 1612, 1547, 1408, 1354, 1293, 1247, 1200, 1123, 1035, 969 cm^{-1}. EIMS *m*=*z* (%): 346/348 (M^+, 38), 266/268(100), 252/254(68), 240/242(98). Anal. calc. For $C_{19}H_{11}BrN_2$: C, 65.73; H, 3.19; N, 8.07. Found C, 65.79; H, 3.35; N, 8.18.

3.4 The preparation of aminothiophenes 7a-f; typical procedure

Bromocrotonitrile **4a** (0.94 g, 3.84 mmol) was dissolved in a solution of dioxane (5 mL) and absolute ethanol (20 ml). The stirred solution was cooled to 0 ℃, and then a suspension of NaSH (0.24 g, 4.29 mmol) in absolute ethanol (10 ml) was added dropwise over 30 min. The resulting reaction mixture was stirred for an additional 1 h at room temperature. After removal of the solvent, the residue was dissolved in hexane/ethylacetate (7:3) and the solution filtered over of 20 g neutral Al_2O_3 (activity-IV). After removing the solvent, the residue was crystallised from chloroform to yield **7a** (655 mg, 85%).

3.4.1 2-Amino-4-phenyl-thiophene-3-carbonitrile (7a): (85%; colourless crystals, mp101-102 ℃). ^1H NMR ($CDCl_3$): 7.61-7.31 (m, 5H, ArH), 6.35 (s, 1H, H5), 5.24 (bs, 2H, NH_2); ^{13}C NMR ($CDCl_3$): 165.65, 142.01, 136.23, 130.78, 130.22, 129.19, 117.83, 107.97, 90.63. IR (KBr): 3421, 3309, 3101, 2210, 1631, 1504, 1442, 1396, 1195, 941 cm^{-1}. EIMS *m*=*z* (%): 200 (M^+, 100), 172(18), 155(36), 128(10). Anal. calc. For $C_{11}H_8N_2S$: C, 65.97; H, 4.03; N, 13.99. Found C, 66.10; H, 4.33; N, 13.79.

3.4.2 2-Amino-4-naphthalen-1-yl-thiophene-3-carbonitrile (7b): (76%; from $CHCl_3$, colourless crystals, mp 152-153 ℃). ^1H NMR ($CDCl_3$): 7.98-7.48 (m, 7H, ArH), 6.37 (s, 1H, H_5), 4.92 (bs, 2H, NH_2); ^{13}C NMR ($CDCl_3$): 164.43, 140.72, 135.79, 134.09, 133.73, 130.86, 130.39, 129.30, 128.43, 128.06, 127.43, 127.20, 117.14,

110.49, 93.47. IR (KBr): 3415, 3300, 3092, 2215, 1638, 1515, 1415, 1384, 1207, 784 cm^{-1}. EIMS *m*=*z* (%): 250 (M^+, 100), 233(10), 216(15), 207(24), 190(20), 163(14). Anal. calc. For $C_{15}H_{10}N_2S$: C, 71.97; H, 4.03; N, 11.19. Found C, 72.01; H, 4.01; N, 11.32.

3.4.3 2-Amino-4-naphthalen-2-yl-thiophene-3-carbonitrile (7c): (74%; from $CHCl_3$/Hexane, colourless crystals, mp 129-130 ℃). ^1H NMR ($CDCl_3$): _ 8.09 (s, 1H, ArH), 7.92-7.48(m, 6H, ArH), 6.47 (s, 1H, H_5), 4.94 (bs, 2H, NH_2); ^{13}C NMR ($CDCl_3$): 165.55, 141.98, 135.39, 134.99, 133.52, 130.52, 130.31, 129.67, 128.49, 128.38, 128.09, 127.15, 117.83, 108.38, 90.84. IR (KBr): 3428, 3326, 3122, 3054, 2204, 1640, 1619, 1514, 1402, 1198 cm^{-1}. EIMS *m*=*z* (%): 250 (M^+, 100), 223(10), 216(10), 207(30), 190(12), 151(10), 125(10). Anal. calc. For $C_{15}H_{10}N_2S$: C, 71.97; H, 4.03; N, 11.19. Found C, 71.79; H, 4.30; N, 11.48.

3.4.4 2-Amino-4-(4-methoxy-phenyl)-thiophene-3-carbonitrile (7d): (81%; from $CHCl_3$/Hexane, white crystals, mp 154-155 ℃). ^1H NMR ($CDCl_3$): 7.52 (d, A part of AB system, J = 8.9 Hz, 2H, ArH), 6.94 (d, B part of AB system, J = 8.9 Hz, 2H, ArH), 6.23 (s, 1H, H_5), 4.86 (bs, 2H, NH_2). ^{13}C NMR ($CDCl_3$): 165.22, 121.68, 141.78, 130.31, 128.88, 117.83, 116.23, 106.82, 90.98, 57.33. IR (KBr): 3449, 3326, 3210, 3114, 2201, 1624, 1508, 1393, 1254, 1157, 1023, 946 cm^{-1}. EIMS *m*=*z* (%): 230 (M^+, 100), 215(42), 187(26), 143(10), 115(12). Anal. calc. For $C_{12}H_{10}N_2OS$: C, 62.60; H, 4.34; N, 12.17. Found C, 62.69; H, 4.33; N, 12.23.

3.4.5 2-Amino-4-biphenyl-4-yl-thiophene-3-carbonitrile (7e): (82%; from $CHCl_3$, light yellow crystals, mp 192-193 ℃). ^1H NMR (DMSO-d_6): 7.78-7.64 (m, 5H, ArH), 7.54-7.39 (m, 4H, ArH), 7.32 (bs, 2H, NH_2), 6.63 (s, 1H, H_5). ^{13}C NMR (DMSO-d_6): 168.29, 141.29, 139.69, 135.27, 130.76, 129.36, 129.15, 128.66, 128.34, 118.47, 106.93, 106.89, 84.89. IR (KBr): 3372, 3314, 3210, 2209, 1651, 1509, 1408, 1293, 1200, 1123, 1081, 1004, 939 cm^{-1}. EIMS *m*=*z* (%): 276 (M^+, 100), 248(10), 231(22), 216(10), 189(8), 152(8), 138(12), 110(20). Anal. calc. For $C_{17}H_{12}N_2S$: C, 73.88; H, 4.38; N, 10.14. Found C, 73.62; H, 4.40; N, 9.86.

3.4.6 2-Amino-4-phenanthren-3-yl-thiophene-3-carbonitrile (7f): (76%; from $CHCl_3$; brown crystals, mp 155-156 ℃). ^1H NMR ($CDCl_3$): 8.97 (bs, 1H, ArH), 8.74 (d, J = 7.5 Hz, 1H, ArH), 7.96-7.76 (m, 2H, ArH), 7.74-7.58 (m, 5H, ArH), 6.55 (s, 1H, H_5), 4.92 (bs, 2H, NH_2). ^{13}C NMR ($CDCl_3$): 165.67, 142.21, 134.30, 134.12, 133.73,

132.44, 132.33, 131.05, 130.62, 129.49, 128.87, 128.41, 127.84, 127.52, 124.84, 123.26, 118.03, 108.37, 90.79. IR (KBr): 3306, 3202, 3048, 2221, 1651, 1516, 1420, 1381, 1285, 1200, 1035, 958 cm^{-1}. EIMS *m*=*z* (%): 300 (M^+, 100), 275(10), 260(16), 178(12), 125(15). Anal. calc. For $C_{19}H_{12}N_2S$: C, 75.97; H, 4.03; N, 9.33. Found C, 76.15; H, 4.06; N, 9.50.

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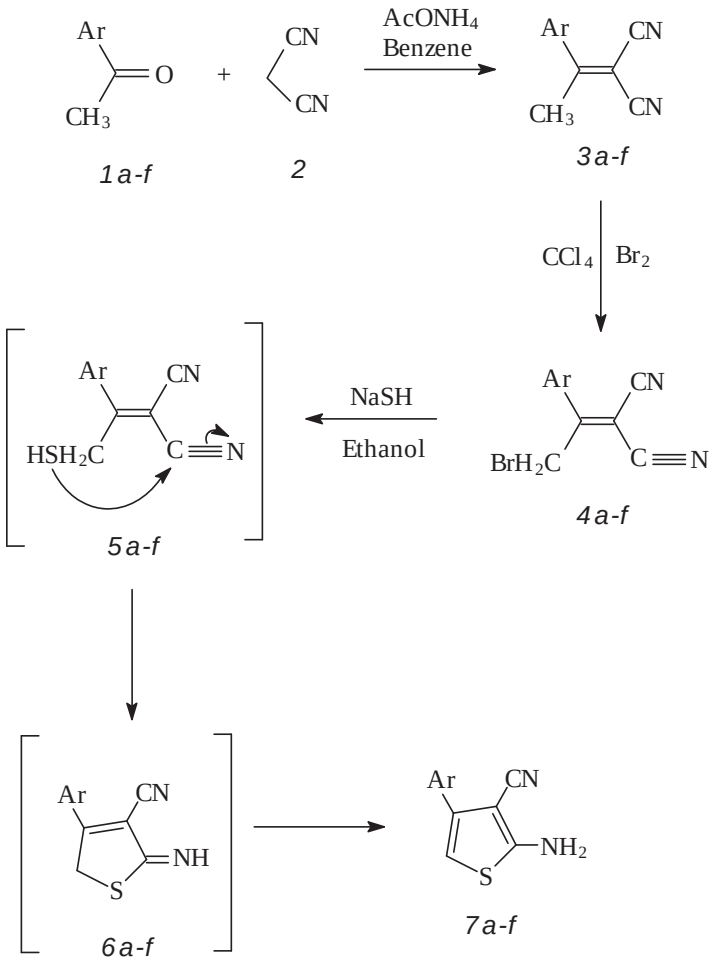
Scheme 1



a: Ar = phenyl
b: Ar = 1-naphthyl
c: Ar = 2-naphthyl
d: Ar = 4-methoxy phenyl
e: Ar = biphenyl-4-yl
f: Ar = phenanthren-3-yl