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Review

Synthesis and characterization of some novel polyfunctionally substituted indeno[2,1-*b*]thiophene compounds derived from indanones

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Abstract

Condensation of 3-dicyanovinylindan-1-one **3** with arylamines **5a–5c** afforded 2-[3-(substituted-amino)-inden-1-ylidene]-malononitriles **7a–7c**, which were converted to 2-amino-indeno[2,1-*b*]thiophene **8a–8c** using the Gewald reaction. Cyclization of ethyl(1-indanylidene)-cyanoacetate **4** with elemental sulfur gave 2-amino-8*H*-indeno[2,1-*b*]thiophene-3-carboxylic acid ethyl ester **9**. Acetylation of **9** with acetic anhydride afforded the 2-acetyl compound **11**, which was condensed with arylaldehydes **12a–12c** to yield the corresponding 2-amino-indeno[2,1-*b*]thiophene moiety **13a–13c** containing a methine chromophore located at the 8-position using the Knoevenagel reaction. Compound **9** was condensed with *N*,*N*-dimethylaminobenzaldehyde **12d** in piperidine to afford the corresponding 2-amino-indeno[2,1-*b*]thiophene compound **13d**. Electronic absorption spectra of these compounds were discussed.

Keywords: Indandione; Indanone; Indeno[2,1-*b*]thiophene; Gewald reaction

1. Introduction

In contrast to intensive studies on azo dyes based on simple aminothiophene derivatives [1–4], considerable interest tends to the use of the strong electron-withdrawing ability of 1,3-indandione **1** and 1-indanone **2** (Scheme 1) as precursors for the preparation of polyfunctionally substituted indeno[2,1-*b*]thiophene compounds. While thiophene-containing azo dyes display effective bathochromic shifts compared to the corresponding benzenoid compounds, there are few synthetic procedures for the preparation of polyfunctionally substituted indeno[2,1-*b*]thiophene compounds. Previously, we reported azo dyes prepared using 2-amino-indeno[2,1-*b*]thiophene compounds as diazo component [5]. In this paper, we report the synthesis and spectral characterization of polyfunctionally substituted, indeno[2,1-*b*]thiophene compounds derived from 3-dicyanovinylindan-1-one **3** and ethyl(1-indanylidene)-cyanoacetate **4**. These compounds were usually obtained via the Gewald reaction in ethanol in the presence of secondary amine as catalyst [6–12]. The substituent effects of these compounds on electronic absorption spectra in acetone were also evaluated.

2. Results and discussion

2.1. Synthesis and characteristic spectra

2.1.1. Synthesis of 2-amino-8-[(*Z*)-4-substituted-phenylimino]-8H-indeno[2,1-b]thiophene-3-carbonitriles (*8a–8c*)

The synthetic routes used for the preparation of the intermediates 2-[3-(4-substituted-phenylamino)-inden-1-ylidene]-malononitriles **7a–7c** and the compounds 2-amino-8-[(*Z*)-4-substituted-phenylimino]-8*H*-indeno[2,1-*b*]thiophene-3-carbonitriles **8a–8c** are outlined in Scheme 2.

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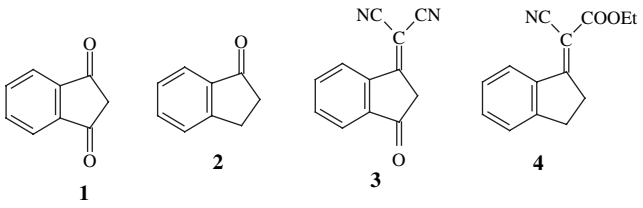


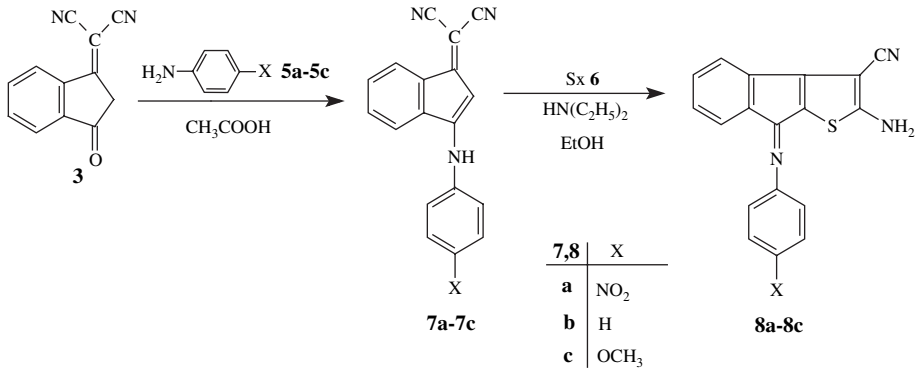
Scheme 1.

Condensation of 3-dicyanovinylindan-1-one **3** with various arylamines **5a–5c** in refluxing acetic acid for 3 h led to the formation of 2-[3-(4-substituted-phenylamino)-inden-1-ylidene]-malononitriles **7a–7c** as red solids in excellent yield (90–94%). These compounds were then refluxed with elemental sulfur in the presence of a catalytic amount of diethylamine in ethanol through the Gewald cyclization to afford 2-amino-8-[(*Z*)-4-substituted-phenylimino]-8*H*-indeno[2,1-*b*]thiophene-3-carbonitriles **8a–8c** as yellow to orange solids in high yield (82–85%). The structures of **7a–7c** and **8a–8c** were confirmed on the basis of elemental analysis and spectral data. The IR spectra of compounds **7a–7c** showed the strong absorption bands of the cyano group in the range 2221–2210 cm^{-1} and the presence of the NH group stretching absorption at 3346–3267 cm^{-1}. Additionally, the ^1H NMR spectra of **7a–7c** displayed a broad singlet for the NH proton at ca. $\delta = 10.9$ ppm and the indene ring proton appeared as a singlet in the range $\delta = 6.1–5.6$ ppm. Compound **7c** showed a singlet at $\delta = 3.81$ ppm attributed to the three protons of the methoxy group in the phenyl ring. Based on spectral data, **7a–7c** exist in the enamine form. The IR spectra of **8a–8c** showed two, well-defined, characteristic absorption bands in the range 3411–3275 cm^{-1} due to the amino group. A sharp absorption band appeared at 2216–2205 cm^{-1} which can be attributed to the cyano group. The ^1H NMR spectra of **8a–8c** showed a 2H singlet at $\delta = 8.31–8.13$ ppm due to the amino group; **8c** showed a 3H singlet at $\delta = 3.77$ ppm, attributable to the protons of the methoxy group at the *p*-position of the phenyl ring. The physical and UV–vis absorption spectral data are summarized in Table 1 and their spectral characterization are shown in Section 3.

*2.1.2. Synthesis of 2-amino-8-[1-(p-substituted-phenyl)-meth-(E)-ylidene]-8H-indeno[2,1-b]thiophene-3-carboxylic acid ethyl ester (**13a–13d**)*

The compounds **13a–13c** were prepared via a three-stage reaction as shown in Scheme 3.

In the first stage, 2-amino-8*H*-indeno[2,1-*b*]thiophene-3-carboxylic acid ethyl ester **9** was obtained by cyclization of ethyl(1-indanylidene)-cyanoacetate **4** with elemental sulfur in the presence of a catalytic amount of diethylamine in ethanol in moderate yield (70%). Then, 2-acetylamino-8*H*-indeno[2,1-*b*]thiophene-3-carboxylic acid ethyl ester **11** was obtained by acetylation of compound **9** with acetic anhydride under reflux for 8 h in high yield (85%). Finally, the condensation of compound **11** with various *p*-substituted arylaldehydes **12a–12c** in the presence of piperidine in absolute ethanol afforded, by elimination of a acetyl group, the yellow-orange to orange-red 2-amino-8-[1-(*p*-substituted-phenyl)-meth-(*E*)-ylidene]-8*H*-indeno[2,1-*b*]thiophene-3-carboxylic acid ethyl ester **13a–13c**. In contrast, when compound **9** was condensed with *N*,*N*-dimethylaminobenzaldehyde **12d**, 2-amino-8-[1-(4-dimethylamino-phenyl)-meth-(*E*)-ylidene]-8*H*-indeno [2,1-*b*]thiophene-3-carboxylic acid ethyl ester **13d** was obtained in the presence of a catalytic amount of piperidine in refluxing ethanol (Scheme 3). The structures of compounds **9**, **11** and **13a–13d** were confirmed by elemental analysis and spectral data. The IR spectra of compound **9** showed a strong absorption band at 1649 cm^{-1} assignable to the ester C=O group and the absorption bands of the NH_2 group appeared at 3403–3300 cm^{-1}. The cyano group was not observed in the IR spectra of compound **9**. The ^1H NMR spectra of compound **9** revealed a 3H triplet at $\delta = 1.52$ ppm and a 2H quartet at $\delta = 4.48$ ppm attributed to the $-CH_2-CH_3$ of ethyl ester group, and a 2H singlet at $\delta = 3.65$ ppm was attributed to the methylene group at the C-8 position of indeno[2,1-*b*]thiophene ring and a 4H multiplet at $\delta = 8.22–7.17$ ppm due to the aromatic ring protons. The ^1H NMR spectra of compound **11** showed a 3H singlet at $\delta = 2.30$ ppm which was attributed to protons of the acetyl group. A broad 1H singlet at $\delta = 11.44$ ppm for NH group was observed; a signal due to the NH_2 group was not present in the ^1H NMR spectra of compound **11**. It was observed that a 2H singlet appeared at $\delta = 6.35–6.33$ ppm for the NH_2 group and a 1H singlet at



Scheme 2.

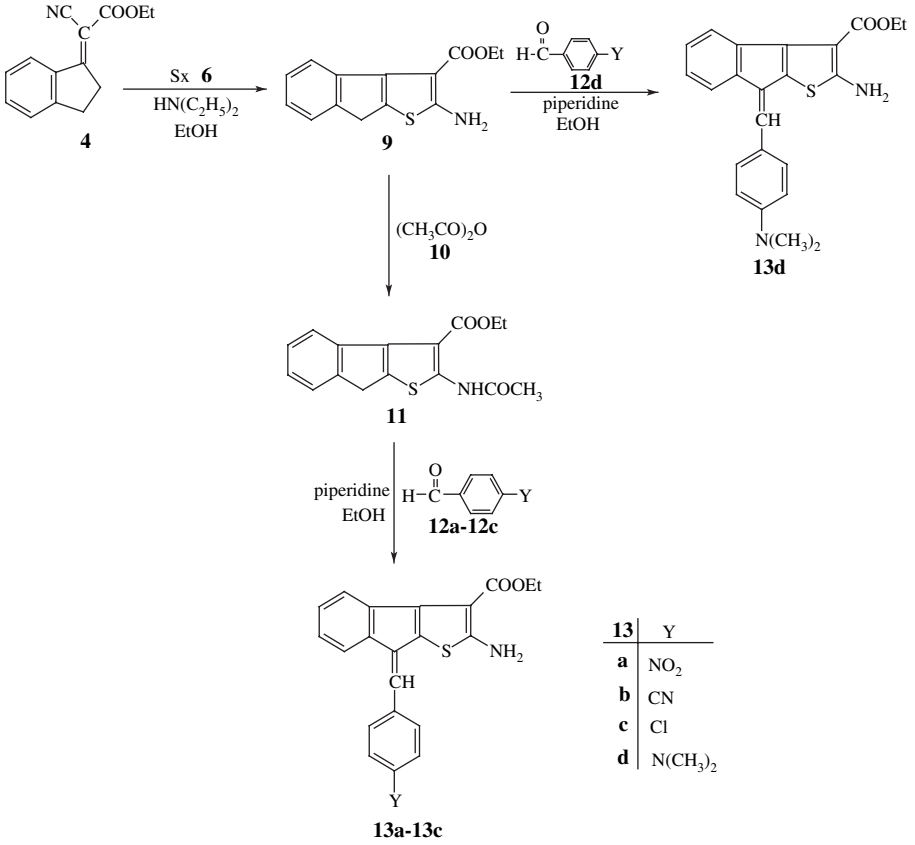
Table 1
Physical and UV–vis absorption spectral data of compounds **7–9**, **11** and **13**

Compounds	Mol. formula	M.p. (°C)	UV–vis λ_{max} (log ε) in acetone	Yield (%)	Appearance
7a	$C_{18}H_{10}N_4O_2$	296–298	529 (4.06)	90	Red
7b	$C_{18}H_{11}N_3$	255–257	510 (4.35)	94	Red
7c	$C_{19}H_{13}N_3O$	260–263	524 (4.19)	92	Red
8a	$C_{18}H_{10}N_4O_2S$	338–340	464 (3.60)	82	Orange
8b	$C_{18}H_{11}N_3S$	258–260	445 (3.77)	80	Yellow
8c	$C_{19}H_{13}N_3OS$	282–284	472 (3.72)	85	Orange
9	$C_{14}H_{13}NO_2S$	130–132	330 (3.56)	70	Off-white
11	$C_{16}H_{15}NO_3S$	194–196	332 (3.75)	85	Off-white
13a	$C_{21}H_{16}N_2O_4S$	228–231	492 (3.60)	66	Orange-red
13b	$C_{22}H_{16}N_2O_2S$	220–222	466 (4.00)	69	Orange
13c	$C_{21}H_{16}ClNO_2S$	160–162	453 (4.25)	48	Yellow-orange
13d	$C_{23}H_{22}N_2O_2S$	198–201	421 (4.27)	30	Yellow

$\delta = 7.30–7.20$ ppm for the =CH group at the C-8 position on the indeno[2,1-*b*]thiophene ring in the ^{1}H NMR spectra of compounds **13a–13d**. The ^{1}H NMR spectra of **13d** showed a 6H singlet at $\delta = 3.07$ ppm that was attributed to the protons of the dimethyl group at the *p*-position on the phenylmethylidene residue. The physical and UV–vis absorption spectral data are summarized in Table 1 and their spectral characterization are shown in Section 3.

2.2. Electronic absorption spectra

The absorption spectra of the prepared compounds were recorded in acetone at a concentration of 3×10^{-5} M (Table 1). It was observed that the introduction of the electron-withdrawing nitro group in the *p*-position of the phenyl ring caused a significant bathochromic shift. Compared to the UV–vis absorption at 510 nm in compound **7b**, the absorption of compound **7a** with electron withdrawing nitro group shifts to 529 nm. The introduction of an electron-donating methoxy group also resulted in a bathochromic shift in the same solvent. It was noticed that **8c**, which contained an electron-donating OCH_3 group in the *p*-position of the phenyl ring, showed a bathochromic shift of +27 nm relative to **8b**. Surprisingly, the absorption maximum of **8a** which contained an electron-withdrawing NO_2 group had a longer wavelength than **8b**. The bathochromic shift imparted by substituents at the *p*-position of the phenyl ring was in the following order: *p*-OCH_3-Ph > *p*-NO_2-Ph > Ph.



Scheme 3.

The λ_{max} of **13a**–**13d** ranged from 421 to 492 nm (Table 1). It was found that the **13a** which contained a strong electron-withdrawing NO_2 group at the *p*-position of the phenyl ring absorbed at longer wavelength (492 nm) and had a much lower log ε value (3.60) than that of **13b**–**13d**. In contrast to **13a**, the introduction of an electron-donating group such as *N*,*N*-dimethylamino at the same position caused a large hypsochromic shift. Compound **13d** which contained a *N*,*N*-dimethylamino group on the phenyl ring absorbed at low wavelength (421 nm) but had a higher log ε value (4.27) than **13a**–**13c**. The introduction of an electron-donating group such as chloro (**13c**) and cyano (**13b**) at the same position, resulted in bathochromic shifts of +32 nm and +45 nm relative to **13d**, respectively. The bathochromic effect of the substituents was of the order: $NO_2 > CN > Cl > N(CH_3)_2$ on the phenyl ring.

3. Experimental

3.1. Apparatus and starting materials

Chemicals were obtained from Aldrich and used without purification. All melting points were determined on an electrothermal apparatus and are uncorrected. Infrared spectra were recorded as KBr pellets on a JASCO *FTIR-3* spectrometer. ^{1}H NMR spectra were obtained on a Joel-*EX-400* MHz NMR spectrometer; chemical shifts are expressed in δ ppm using TMS as internal standard. The mass spectra were obtained using a *Finnigan TSQ-700* GC/LC/MS spectrometer. Microanalytical data for C, H, N and S were performed on a Perkin–Elmer *2400* elemental analyzer; UV–vis absorption spectra were recorded on a Heliosa *UV1* in acetone. All solvents were of spectroscopic grade. 3-Dicyanovinylindan-1-one **3**, as starting material was prepared in good yield by the Knovenagel reaction of 1,3-indandione **1** with malononitrile; ethyl(1-indanylidene)-cyanoacetate **4** was prepared in good yield also using the Knoevenagel reaction of 1-indanone **2** with ethylcyanoacetate based on the published literature [13,14].

*3.2. Synthesis of 2-[3-(4-substituted-phenylamino)-inden-1-ylidene]-malononitrile (**7a**–**7c**)*

The synthesis of **7a**–**7c** followed the same procedure as described below for the preparation of **7a**.

*3.2.1. 2-[3-(4-Nitro-phenylamino)-inden-1-ylidene]-malononitrile (**7a**)*

p-Nitroaniline **5a** (1.38 g, 0.01 mol) was added to a solution of 3-dicyanovinylindan-1-one **3** (1.94 g, 0.01 mol) in acetic acid (50 ml) at room temperature. The reaction mixture was heated under reflux for 3 h and then cooled to room temperature. The precipitated product was filtered, washed with ethanol (2 × 10 ml), dried and recrystallized from ethanol as red needles (2.83 g, yield 90%). M.p. 296–298 °C; FT-IR (KBr, cm^{-1}): 3346 ν (N–H), 2221 ν (C≡N), 1538, 1335 ν (NO_2); MS: *m/z* (rel. int. %), 314 (M^+, 12), 284 (100), 256 (10), 69 (11), 57 (13); ^{1}H NMR (DMSO-d_6, δ): 10.92 (1H, s, NH), 8.38–7.54 (8H, m, Ar–H), 6.05 (1H, s, CH). Anal. Calcd. for $C_{18}H_{10}N_4O_2$: C, 68.79; H, 3.18; N, 17.83. Found: C, 68.99; H, 3.22; N, 17.75%.

*3.2.2. 2-[3-Phenylamino-inden-1-ylidene]-malononitrile (**7b**)*

Compound **7b** was recrystallized from ethanol to give red needles (2.53 g, yield 94%). M.p. 255–257 °C; FT-IR (KBr, cm^{-1}): 3267 ν (N–H), 2210 ν (C≡N); MS: *m/z* (rel. int. %), 269 (M^+, 100), 242 (10), 204 (11), 77 (10); ^{1}H NMR (DMSO-d_6, δ): 10.88 (1H, s, NH), 7.99–7.32 (9H, m, Ar–H), 5.74 (1H, s, CH). Anal. Calcd. for $C_{18}H_{11}N_3$: C, 80.30; H, 4.09; N, 15.61. Found: C, 80.18; H, 4.02; N, 15.76%.

*3.2.3. 2-[3-(4-Methoxy-phenylamino)-inden-1-ylidene]-malononitrile (**7c**)*

Compound **7c** was recrystallized from ethanol to give red needles (2.75 g, yield 92%). M.p. 260–263 °C; FT-IR (KBr, cm^{-1}): 3277 ν (N–H), 2212 ν (C≡N); MS: *m/z* (rel. int. %), 299 (M^+, 100), 284 (21), 257 (37), 229 (14), 77 (5); ^{1}H NMR (DMSO-d_6, δ): 10.90 (1H, s, NH), 7.98–7.09 (8H, m, Ar–H), 5.63 (1H, s, CH), 3.81 (3H, s, OCH_3). Anal. Calcd. for $C_{19}H_{13}N_3O$: C, 76.25; H, 4.35; N, 14.05. Found: C, 76.31; H, 4.38; N, 14.11%.

*3.3. Synthesis of 2-amino-8-[(Z)-4-substituted-phenylimino]-8H-indeno[2,1-b] thiophene-3-carbonitrile (**8a**–**8c**)*

The synthesis of **8a**–**8c** followed the same procedure as described below for the preparation of **8a**.

*3.3.1. 2-Amino-8-[(Z)-4-nitro-phenylimino]-8H-indeno[2,1-b]thiophene-3-carbonitrile (**8a**)*

Compound **7a** (3.14 g, 0.01 mol) was added to a solution of elemental sulfur (0.32 g, 0.01 mol) and diethylamine (5 ml) in 50 ml absolute ethanol at room temperature. The reaction mixture was refluxed for 3 h and then cooled. The precipitated product was filtered, washed with ethanol, dried and recrystallized from ethanol as orange needles (2.84 g, yield 82%). M.p. 338–340 °C; FT-IR (KBr, cm^{-1}): 3411, 3312 ν (NH_2), 2212 ν (C≡N), 1543, 1337 ν (NO_2); MS: *m/z* (rel. int. %), 346 (M^+, 100), 316 (52), 273 (22), 273 (22), 183 (35), 138 (23), 63 (34); ^{1}H NMR (DMSO-d_6, δ): 8.31 (2H, s, NH_2), 7.65–7.23 (8H, m, Ar–H). Anal. Calcd. for $C_{18}H_{10}N_4O_2S$: C, 62.43; H, 2.89; N, 16.18; S, 9.25. Found: C, 62.22; H, 2.94; N, 16.25; S, 9.30%.

*3.3.2. 2-Amino-8-[(Z)-phenylimino]-8H-indeno[2,1-b] thiophene-3-carbonitrile (**8b**)*

Compound **8b** was recrystallized from ethanol to give yellow needles (2.41 g, yield 80%). M.p. 258–260 °C; FT-IR (KBr, cm^{-1}): 3439, 3333 ν (NH_2), 2216 ν (C≡N); MS: *m/z* (rel. int. %), 301 (M^+, 100), 242 (12), 198 (27), 270 (11), 77 (22); ^{1}H NMR (DMSO-d_6, δ): 8.15 (2H, s, NH_2), 7.67–6.70 (9H, m, Ar–H). Anal. Calcd. for $C_{18}H_{11}N_3S$: C, 71.76;

H, 3.65; N, 13.95; S, 10.63. Found: C, 71.89; H, 3.68; N, 13.99; S, 10.77%.

3.3.3. 2-Amino-8-[(Z)-4-methoxy-phenylimino]-8H-indeno[2,1-b]thiophene-3-carbonitrile (**8c**)

Compound **8c** was recrystallized from ethanol to give orange needles (2.81 g, yield 85%). M.p. 282–284 °C; FT-IR (KBr, cm^{-1}): 3388, 3275 ν (NH_2), 2205 ν (C≡N); MS: *m/z* (rel. int. %), 331 (M^+, 74), 316 (100), 254 (12), 228 (12), 165 (18), 153 (12), 63 (11); ^1H NMR (DMSO-d_6, δ): 8.13 (2H, s, NH_2), 7.65–6.94 (8H, m, Ar–H), 3.77 (3H, s, OCH_3). Anal. Calcd. for $C_{19}H_{13}N_3OS$: C, 68.88; H, 3.93; N, 12.69; S, 9.67. Found: C, 68.66; H, 3.84; N, 12.80; S, 9.53%.

3.4. Synthesis of 2-amino-8H-indeno[2,1-b]thiophene-3-carboxylic acid ethyl ester (**9**)

Ethyl(1-indanylidene)-cyanoacetate **4** (2.27 g, 0.01 mol) was added to a solution of elemental sulfur (0.32 g, 0.01 mol) and diethylamine (5 ml) in absolute ethanol (50 ml) at room temperature. The reaction mixture was heated under reflux for 3 h and then cooled to room temperature. The precipitated product was filtered, washed with ethanol (2 × 10 ml), dried and recrystallized from ethanol as off-white needles (2.59 g, yield 70%). M.p. 130–132 °C; FT-IR (KBr, cm^{-1}): 3403, 3300 ν (N–H), 1649 ν (C=O); MS: *m/z* (rel. int. %), 259 (M^+, 50), 213 (100), 185 (29), 153 (21), 140 (16), 115 (10); ^1H NMR (DMSO-d_6, δ): 8.22–7.17 (4H, m, Ar–H), 6.16 (2H, s, NH_2), 4.48 (2H, q, CH_2), 3.65 (2H, s, CH_2), 1.52 (3H, t, CH_3). Anal. Calcd. for $C_{14}H_{13}NO_2S$: C, 64.86; H, 5.02; N, 5.41; S, 12.36. Found: C, 64.72; H, 5.08; N, 5.49; S, 12.31%.

3.5. Synthesis of 2-acetylamino-8H-indeno[2,1-b]thiophene-3-carboxylic acid ethyl ester (**11**)

Compound **9** (2.27 g, 0.01 mol) was dissolved in 50 ml acetic anhydride and heated under reflux for 8 h, and then cooled to room temperature. The precipitated product was filtered, washed with ethanol (2 × 10 ml), dried and recrystallized from ethanol as off-white needles (2.56 g, yield 85%). M.p. 194–196 °C; FT-IR (KBr, cm^{-1}): 3240 ν (N–H), 1688, 1659 ν (C=O); MS: *m/z* (rel. int. %), 301 (M^+, 71), 259 (40), 255 (16), 213 (100), 185 (28), 140 (15), 115 (10); ^1H NMR (DMSO-d_6, δ): 11.44 (1H, s, NH), 8.14–7.21 (4H, m, Ar–H), 4.53 (2H, q, CH_2), 3.72 (2H, s, CH_2), 2.30 (2H, s, CH_3), 1.56 (3H, t, CH_3). Anal. Calcd. for $C_{16}H_{15}NO_3S$: C, 63.79; H, 4.98; N, 4.65; S, 10.63. Found: C, 63.81; H, 4.96; N, 4.51; S, 10.65%.

3.6. Synthesis of 2-amino-8-[1-(p-substituted-phenyl)-meth-(E)-ylidene]-8H-indeno[2,1-b]thiophene-3-carboxylic acid ethyl esters (**13a–13d**)

The synthesis of **13a–13c** followed the same procedure, as described below for the preparation of **13a**.

3.6.1. 2-Amino-8-[1-(4-nitro-phenyl)-meth-(E)-ylidene]-8H-indeno[2,1-b]thiophene-3-carboxylic acid ethyl ester (**13a**)

To a solution of compound **11** (3.01 g, 0.01 mol) and piperidine (2 ml) in 50 ml absolute ethanol, 4-nitro-benzaldehyde **12a** (2.26 g, 0.01 mol) was added. The reaction mixture was heated under reflux for 6 h until the solution changed to dark orange-red, and then cooled to room temperature. The precipitated solid was filtered, washed with ethanol (2 × 10 ml), dried and recrystallized from ethanol to give orange-red needles (2.59 g, yield 66%). M.p. 228–231 °C; FT-IR (KBr, cm^{-1}): 3446, 3313 ν (N–H), 1657 ν (C=O), 1563, 1350 ν (NO_2); MS: *m/z* (rel. int. %), 392 (M^+, 94), 346 (100), 271 (39), 245 (16), 227 (9), 57 (5); ^1H NMR (DMSO-d_6, δ): 8.30–7.21 (8H, m, Ar–H), 7.22 (1H, s, =CH–), 6.35 (2H, s, NH_2), 4.48 (2H, q, CH_2), 1.51 (3H, t, CH_3). Anal. Calcd. for $C_{21}H_{16}N_2O_4S$: C, 64.29; H, 4.08; N, 7.14; S, 8.16. Found: C, 64.23; H, 4.13; N, 7.26; S, 8.14%.

3.6.2. 2-Amino-8-[1-(4-cyano-phenyl)-meth-(E)-ylidene]-8H-indeno[2,1-b]thiophene-3-carboxylic acid ethyl ester (**13b**)

Compound **13b** was recrystallized from ethanol to give orange needles (2.57 g, yield 69%). M.p. 220–222 °C; FT-IR (KBr, cm^{-1}): 3419, 3306 ν (N–H), 2230 ν (C≡N) 1649 ν (C=O); MS: *m/z* (rel. int. %), 372 (M^+, 78), 326 (100), 297 (62), 270 (23), 227 (12), 57 (5); ^1H NMR (DMSO-d_6, δ): 8.14–7.19 (8H, m, Ar–H), 7.20 (1H, s, =CH–), 6.33 (2H, s, NH_2), 4.47 (2H, q, CH_2), 1.50 (3H, t, CH_3). Anal. Calcd. for $C_{22}H_{16}N_2O_2S$: C, 70.97; H, 4.30; N, 7.53; S, 8.60. Found: C, 70.82; H, 4.33; N, 7.48; S, 8.62%.

3.6.3. 2-Amino-8-[1-(4-chloro-phenyl)-meth-(E)-ylidene]-8H-indeno[2,1-b]thiophene-3-carboxylic acid ethyl ester (**13c**)

Compound **13c** was recrystallized from ethanol to give yellow-orange needles (1.83 g, yield 48%). M.p. 160–162 °C; FT-IR (KBr, cm^{-1}): 3442, 3332 ν (N–H), 1653 ν (C=O); MS: *m/z* (rel. int. %), 381 (M^+, 72), 335 (100), 306 (22), 272 (61), 213 (16), 136 (18), 57 (5); ^1H NMR (DMSO-d_6, δ): 8.17–6.54 (8H, m, Ar–H), 7.20 (1H, s, =CH–), 6.33 (2H, s, NH_2), 4.48 (2H, q, CH_2), 1.52 (3H, t, CH_3). Anal. Calcd. for $C_{21}H_{16}ClNO_2S$: C, 66.06; H, 4.19; N, 3.67; S, 8.39. Found: C, 66.18; H, 4.23; N, 3.52; S, 8.62%.

3.6.4. 2-Amino-8-[1-(4-dimethylamino-phenyl)-meth-(E)-ylidene]-8H-indeno[2,1-b]thiophene-3-carboxylic acid ethyl ester (**13d**)

A mixture of compound **9** (2.59 g, 0.01 mol), *N*,*N*-dimethylaminobenzaldehyde **12d** (1.49 g, 0.01 mol) and piperidine (2 ml) in 50 ml absolute ethanol was gradually heated under reflux for 8 h. The separated solid was filtered, washed with ethanol (2 × 10 ml), dried and recrystallized from ethanol to give yellow needles (1.17 g, yield 30%). M.p. 198–201 °C; FT-IR (KBr, cm^{-1}): 3383, 3275 ν (N–H), 1667 ν (C=O); MS: *m/z* (rel. int. %), 390 (M^+, 100), 344 (84), 315 (55), 272 (61), 172 (38), 157 (16), 137 (12); ^1H NMR (DMSO-d_6,

δ): 8.17–7.17 (8H, m, Ar–H), 7.30 (1H, s, =CH–), 6.35 (2H, s, NH_2), 4.48 (2H, q, CH_2), 3.07 (6H, s, $N(CH_3)_2$, 1.51 (3H, t, CH_3). Anal. Calcd. for $C_{23}H_{22}N_2O_2S$: C, 70.77; H, 5.64; N, 7.18; S, 8.21. Found: C, 70.70; H, 5.59; N, 7.22 S, 8.23%.

4. Conclusions

Condensation of 3-dicyanovinylindan-1-one **3** with arylamines **5a–5c** afforded 2-[3-(substituted-amino)-inden-1-ylidene]-malononitriles **7a–7c**, which were converted to 2-amino-indeno[2,1-*b*]thiophene **8a–8c** using the Gewald reaction. Cyclization of ethyl(1-indanylidene)-cyanoacetate **4** with elemental sulfur gave 2-amino-8*H*-indeno[2,1-*b*]thiophene-3-carboxylic acid ethyl ester **9**. Compound **11** was synthesized through acetylation of compound **9**. The subsequent condensation of compound **11** and arylaldehydes **12a–12c** yields the corresponding 2-amino-indeno[2,1-*b*]thiophene moiety **13a–13c** containing a methine chromophore located at the 8-position using the Knoevenagel reaction. Compound **9** was condensed with *N*,*N*-dimethylaminobenzaldehyde **12d** in piperidine to afford the corresponding 2-amino-indeno[2,1-*b*]thiophene compound **13d**.

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